Klyne and Buckingham Atlas of Stereochemistry

Atlas of Stereochemistry

Absolute Configurations of Organic Molecules

Second Edition

Volume One

W. Klyne and
J. Buckingham

Chapman and Hall

The first edition of the *Atlas of Stereochemistry* was the only extensive compilation of absolute configurations to appear in print. Over 3000 compounds were represented by their stereochemical formulae and portrayed in a diagrammatic form showing at a glance the evidence on which the accepted absolute configuration of a given compound was based and allowing the interrelationships of a chiral centre in a natural product to be readily traced.

Since the first edition went to press, the absolute configurations of many new natural products and other chiral compounds have been determined for the first time and, in addition, the generally accepted absolute configurations of a significant number of important compounds have been reversed or otherwise changed. The second edition of the *Atlas* is therefore a major revision and a considerable enlargement of the work and now appears in two volumes. The literature coverage has been extended to mid-1976 thus incorporating approximately 50% more compounds.

Volume One covers mainly the literature up to the end of 1971, as did the first edition, with the difference that sections have been enlarged and rewritten as a result of new work. The compounds covered include the most important dissymmetric compounds of low molecular weight and the various classes of natural product: amino acids, terpenes (including steroids), carbohydrates, alkaloids, antibiotics, vitamins and others. Special sections deal with dissymmetry due to the presence of chiral axes and planes; metallocene stereochemistry; chirality due to isotopic substitution, and chirality of atoms other than carbon (for instance, phosphorus and sulphur).

Volume Two covers the literature to mid-1976 and includes sections previously in Volume One dealing with compounds whose absolute configurations have been reversed since 1971, or on which a great deal of important work has been done. The scope has been enlarged to incorporate more compounds of pharmaceutical interest and the sections on compounds with chirality due to isotopic substitution and with chirality at atoms other than carbon have been particularly strengthened.

All the material is fully referenced and a cumulative index is given at the end of Volume Two.

The *Atlas of Stereochemistry* has already proved an essential reference work for all research workers in the fields of organic and biological chemistry and an invaluable aid in the teaching of stereochemistry.

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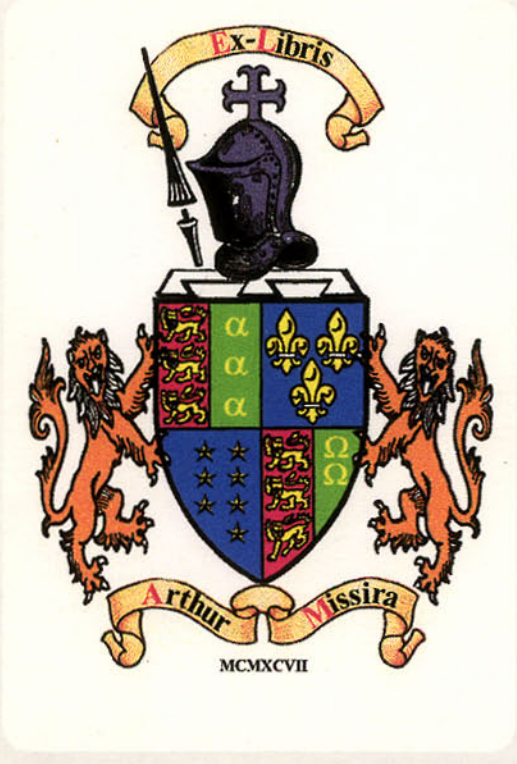

Atlas of Stereochemistry

VOLUME ONE

William Klyne

1913–1977

The death of Bill Klyne on 11 November 1977 is regretfully recorded. He was born near London in 1913 and graduated from Oxford University. In 1936 he became assistant in medical chemistry at Edinburgh; further posts at Edinburgh and at the Postgraduate Medical School, Hammersmith, London, eventually led to his appointment in 1960 to the first Chair of Chemistry at Westfield College, University of London.

During the 1940s and 1950s he became interested in the use of optical rotation methods and this remained his primary research interest, together with steroid chemistry. As equipment for ORD measurements became available in the late 1950s he built up a relatively small but very active research group which exploited the technique in an extensive range of measurements. These resulted in numerous research papers, which made valuable contributions to absolute configuration determinations and other stereochemical problems by the exploitation of the empirical or semi-empirical approach. He was extremely active on international chemical bodies such as IUPAC and had numerous friends among chemists throughout the world.

In addition to the *Atlas of Stereochemistry*, his longer publications included *The Chemistry of the Steroids, Practical Chemistry for Medical Students* and several review articles on ORD/CD. A full-length book on the latter subject was in course of preparation at the time of his death. He was also a member of the Editorial Advisory Committee of *Heilbron's Dictionary of Organic Compounds.*

J.B.

ATLAS OF STEREOCHEMISTRY

Absolute Configurations of Organic Molecules

Second Edition

Volume One

W. Klyne and J. Buckingham

Westfield College, University of London

LONDON

CHAPMAN AND HALL

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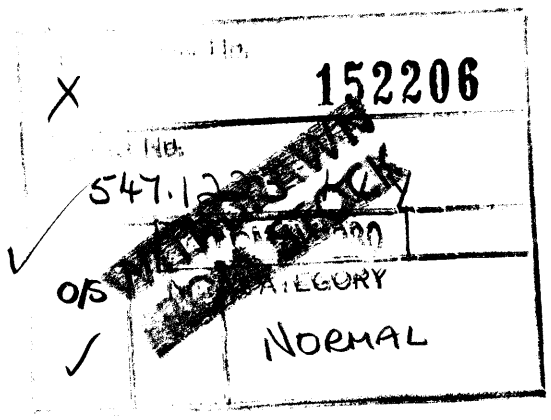

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Preface to the Second Edition

The favourable reaction which greeted the first edition of the *'Atlas'*, combined with the high rate at which new work in the field of absolute configurations has continued to appear since its publication, persuaded us that its updating and revision would be worthwhile. The result is a new and completely revised edition in two volumes.

Together, the two new volumes cover the literature up to the middle of 1976, thus extending the literature coverage of the first edition by about 4½ years. During this period much new work on absolute configurations has appeared. Whilst it is true that by 1971 the majority of the biologically important compounds and types of natural products likely to be encountered by the average chemist (for example, the commoner terpene skeletons) had been fairly firmly 'anchored' stereochemically, the last five years has been a period of considerable consolidation and enlargement of the field. Many new and unusual types of natural product have been characterized and the determination of the absolute configuration is now often undertaken rightly as a matter of routine and not as a side-line which was often the case in the past. Many more small chiral molecules have had their absolute configurations determined for the first time, and several significant groups of compounds have had their accepted absolute configurations reversed, resulting in the need for the complete revision of certain sections. Examples are the abscisic acid group of sesquiterpenes, a number of compounds related to the santalenes, the cryptostylines, cularine and the *Iboga* alkaloids.

We wish to express our gratitude to those reviewers and other correspondents whose helpful and detailed comments on the first edition were most welcome. A few errors which were drawn to our attention have been corrected in this new edition, and in accordance with our stated policy of basing the *'Atlas'* on the most up-to-date and reliable correlations available, a few older correlations which appeared in the first edition have been deleted. In addition, the new edition contains a number of compounds from the older literature which have come to our attention since the first edition went to press.

April 1977

W Klyne
J Buckingham

Introduction

A striking feature in the development of Organic Chemistry over the last twenty years has been a steady growth in the study of steric factors—that is, of three-dimensional relationships within and between molecules. One such aspect of this work lies in stereochemical correlations, the determination of relationships between the absolute and relative configurations of optically active compounds. Until recently, the absolute configuration was considered all too often as a sideline, to be determined when the detailed structure of the compound in all other respects was known, but as a result of the growing interest in biological chemistry, knowledge of the absolute configuration is now considered an essential part of any structure determination.

The study of absolute configurations has its greatest importance in connection with biochemical problems, because all living organisms are composed largely of chiral substances. (The term 'chiral' is preferred to 'optically active', since 'chiral' reflects the fundamental nature of the compounds with which we are concerned, whilst 'optically active' refers to only one physical property, albeit an important one.) No biochemical study of any kind can be complete without three-dimensional knowledge of the relationships between the molecules concerned, and this cannot be achieved until the absolute configurations of all the compounds are known or at any rate all have been referred to one arbitrary standard.

We may refer here to Sir Frederick Gowland Hopkins's classical definition of biochemistry as 'an adequate and acceptable description of molecular dynamics in cells and tissues' and repeat that this definition must include three-dimensional knowledge. As a striking example of an area where three-dimensional knowledge was lacking until recently the following may be cited. Many discussions are found in biochemical literature on the role of biotin in intermediary metabolism, and formulae are drawn showing the way in which biotin is linked with various other biologically active molecules, but until the absolute configuration of biotin was determined in 1966, these formulae were inadequate in that they could not represent the three-dimensional relationships of the substances involved.

A full description of the mode of action of an enzyme must entail detailed knowledge of the relative stereochemistry of the enzyme and its substrate. Each year more precise knowledge of the fit between enzyme and substrate appears in the literature.

Knowledge of absolute configurations is also needed in the pharmaceutical industry, both for compounds which are the organic chemist's attempts to improve on nature, for example, analogues of oestrone, morphine or oxytocin, and for totally artificial structures. The suggestion might be seriously considered that no chiral pharmaceutical product should be used without (a) resolution of a racemate into its components, and (b) determination of the absolute configuration of the active enantiomer.

To stress this importance of chirality in biological problems is not to minimize its significance and usefulness in many problems of pure chemistry, such as the study of reaction mechanism, and of the relationship of optical activity to structure.

The purpose of this book is to bring together in a readily accessible form a proportion of the vast mass of data which exists in the literature concerning the absolute configurations of chiral molecules.

Previous surveys of absolute configurations of organic compounds are few in number, including two reviews from this Department (Mills & Klyne, Klyne & Scopes in *Progress in Stereochemistry*); a chapter in Eliel's book *Stereochemistry of Carbon Compounds*; and parts of the excellent two-volume work entitled *Molecular Asymmetry in Biology* by Bentley.

The connection of one of us with Heilbron's *Dictionary of Organic Compounds*, which provides a bird's-eye view of the whole range of organic compounds at a price accessible to the small library, suggested the use of the configurational data in that book as the basis for this 'Atlas'. We have been encouraged in this work by the comments of colleagues on the editorial board of Heilbron's *Dictionary*, and by other stereochemical friends, notably Professors D. H. R. Barton and V. Prelog.

The approximately 3000 compounds listed in the 'Atlas' still represent only an outline of the field, since to cover all chiral compounds would be to re-write about one tenth of Beilstein's *Handbuch*. We have concentrated first on compounds containing one or two centres of chirality. Secondly, we give a selection of the main groups of natural products; among the latter we list key compounds only for each group, since the links between individual members within a group are readily available in well-known reference books and reviews. Finally, special sections of the 'Atlas' deal with configuration around chiral axes and chiral planes, chiral centres other than carbon atoms, and chirality due to isotopic substitution.

Methods of correlation

These have been dealt with in some detail in the review articles mentioned above, and here we discuss only their relative importance.

The Bijvoet method for determination of absolute configuration by X-ray crystallography is the only sound and widely applicable direct method of determination. (For the past four years, Professor D. Rogers (Imperial College) and his colleagues have produced lists of compounds to which the Bijvoet method has been applied; we are grateful to Professor Rogers for supplying us with copies of these lists before publication.) The compounds to which the Bijvoet method has been applied are all marked specially in the 'Atlas'; they are so to speak the fundamental 'triangulation points' of the survey on which all others must in one way or another depend.

The linking of other compounds with these fundamental ones, the configurations of which have been established by the Bijvoet method, is most reliably carried out by chemical interconversion *not* involving the centre of chirality concerned. With certain simple precautions, this procedure is entirely safe. Much classical structure determination indirectly provides links of this kind.

The remaining methods are all of varying reliability, and all depend on argument by analogy. These methods include chemical interconversions involving the chiral centre(s) accompanied by mechanistic interpretation of the reaction pathway, asymmetric synthesis, chiroptical methods (ORD and CD) and the method of quasi-racemates, etc. In all of these the reliability depends directly on care in the choice of analogies. For example, in the case of asymmetric syntheses, the following quotation by Mislow and his co-workers (*J. Amer. Chem. Soc.*, 1965, 87, 1958) is relevant: 'Thus, in the assignment of configurations, a heavy burden of proof rests on the credibility of the transition state proposed in asymmetric syntheses, or in the initial analysis which underlies the weighting of conformational populations in mobile equilibria, whichever applies.' Similar cautions could be made to cover correlations involving the quasi-racemate method and the chiroptical methods.

We indicate by means of broken arrows that a somewhat lesser reliability is considered to be attached to *all* correlations involving asymmetric syntheses or comparison of monochromatic rotations; the same symbolism is used in a few other cases where the correlation is clearly not fully reliable, either as a result of comments made by the original authors, where subsequent work has cast doubt on the original correlation, or where there is a clear possibility of amibiguity or inconclusiveness.

The correlations given in the 'Atlas' are in general the most recent and reliable available. Where a chemical correlation between substances has been carried out, this is given preference over correlation by chiroptical methods, asymmetric synthesis, quasi-racemate formation, etc., and these in turn are given precedence over any older work involving comparison of monochromatic rotations. The latter is included only in a few cases where no more recent information is available and where the correlation is of considerable interest.

Absolute configurations of metal complexes

In general, the 'Atlas' covers the field of organic and organometallic (e.g. metallocene) stereochemistry. Metal complexes are not included; they have been comprehensively covered by a recent monograph (C. J. Hawkins, *Absolute Configuration of Metal Complexes* (Interscience Monographs on Chemistry), Wiley-Interscience, 1971.)

Note to the Second Edition on the assignment of absolute configurations by the Bijvoet method

During 1972-3 great concern was felt regarding the correctness of results based on the Bijvoet method of anomalous dispersion of X-rays. Calculations by Tanaka and his co-workers (*Chimia,* 1972, **26**, 271; *Chem. Comm.*, 1973, **21**, 22) appeared to indicate a contradiction between Bijvoet determinations for some compounds and *ab initio* calculations of the absolute configurations of the same compounds based on chiroptical measurements. This was taken as an indication that the Bijvoet treatment was giving the 'wrong' answer.

Careful analysis by other experts in the chiroptical techniques, however (S. F. Mason, *Chem. Comm.*, 1973, 239; A. M. F. Hezemans and M. P. Groenewege, *Tetrahedron,* 1973, **29**, 1223) and by X-ray crystallographers, now indicates that the error lay in the method used for the calculation of the absolute configurations from the spectroscopic data, and that the Bijvoet method is indeed *correct.* This interlude did show, however, how slender is the thread of argument, albeit correct, on which the Bijvoet assignments are made, and also how few chemists are truly competent to pass judgement on these matters.

Lists of Bijvoet X-rays

The lists of compounds to which the Bijvoet method has been applied, produced by Professor Rogers and his co-workers, which were referred to above, have been discontinued owing to the publication of 'Molecular Structure and Dimensions' beginning in 1973. This is a comprehensive listing of *all* X-ray determinations (relative and absolute) and for cross-checking the completeness of our Bijvoet listings we have relied on the published data in this book together with a computer-search program kindly run for us by Dr Kennard to cover the period subsequent to the appearance of the most recent volume.

Key

Scope

The 'Atlas' is intended to cover the most important simple chiral compounds and the main structural types of natural products.

Correlations within a 'stereochemically homogeneous' series of compounds, such as monosaccharides and steroids, which are well documented elsewhere in the literature, are considered in outline only. Series of compounds which are essentially dimeric or polymeric types built up from chiral monomeric units are not covered in detail, since their configurations follow readily from those of the monomeric unit. Examples of such polymeric-type compounds are di-, oligo- and polysaccharides; bis (benzylisoquinoline) and other dimeric alkaloids; biflavonoids and polypeptides. Series of natural products having essentially the same carbon skeleton but known in a variety of stereochemical types due to epimerism at one or more chiral centres are frequently covered by general notes rather than by large numbers of examples. This treatment is given, for example, to the labdane-type diterpenes and the yohimbane-type alkaloids.

If a chiral compound which does not fall into one of these categories cannot be found in the 'Atlas', the most likely explanations are (a) its absolute configuration has not been determined, or rests only on inconclusive data such as biogenetic analogy or specific rotation comparisons, or (b) it has been related by a fairly simple sequence to a compound which does appear. (We would, of course, be grateful to hear of any compounds of sufficient importance which we have not included.)

Literature coverage

The literature has been scanned to the end of 1971, and a few important references from 1972 have been incorporated.

We acknowledge the invaluable help rendered in the compilation of the 'Atlas' by the following standard works:

Dictionary of Organic Compounds, 2nd edition and supplements, Eyre & Spottiswoode, 1965-71.

Rodd's Chemistry of Carbon Compounds (2nd edition, S. Coffey, Ed.), Elsevier (1967-)

Molecular Asymmetry in Biology, by R. Bentley, 2 vols., Academic Press, 1970.

Other more specialized books and reviews pertaining to individual series of compounds are noted at the beginning of the appropriate sections.

Arrangement of material

The 'Atlas' is divided into the following chapters:

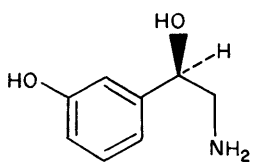
A – fundamental chiral compounds mostly containing one or two chiral carbon atoms (but also including the cyclitols, for convenience of presentation).
C – carbohydrates.
T – terpenoids, including steroids.
K – alkaloids.
Y – other classes of natural products.
D – chirality due to deuterium or other isotopes.
X – compounds containing chiral axes, planes, etc.
Z – chirality at atoms other than carbon (especially sulphur, phosphorus and silicon).

Some compounds may appear out of place because they have been correlated with compounds in another chapter; while others, for example alkaloids which contain only one chiral centre, belong strictly speaking in two different sections (in this case A and K). No hard-and-fast rules have been used to cover these situations and such compounds have been placed where it seemed most convenient, usually with notes at the other possible point of placement to assist the reader. Notes on the arrangement of material within each chapter appear at the head of the chapter.

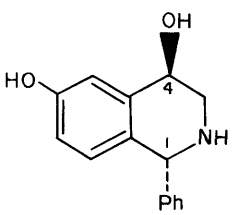
References

References are given for each correlation between substances against the arrow joining their formulae and for each determination of structure by X-ray analysis, etc. Extra references to the clarification of some point of stereochemistry are given in some cases beneath the structural formula of a compound and immediately after its name.

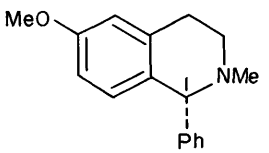
In general, however, *references are not given to work establishing the relative configuration of individual centres within a molecule*. This point is sufficiently important to justify further explanation by means of an example. The cyclization of (*R*)–(+) 2-amino-1-(3-hydroxyphenyl)-ethanol (A), studied by Kametani and his co-workers, was shown to produce two tetrahydroisoquinoline derivatives epimeric at the newly-created C_1 chiral centre. One of these, assigned the configuration (1*R*, 4*R*) (B) was then converted, by removal of the original chiral centre, into (*R*)–(+) 1,2,3,4-tetrahydro-6-methoxy-2-methyl-1-phenylisoquinoline (C).



A



B



C

Clearly the absolute configuration assigned to the new substance (C) depends as much on correct establishment of the *relative* configuration between the two chiral centres in (B) (in this case, principally by n.m.r. spectroscopy) as on a correct assignment of absolute configuration to the starting material (A). The details of how this relative configuration is determined lie outside the scope of the 'Atlas'.

Numbering of formulae and cross-references

At the first appearance of a given compound in the 'Atlas' it is given a unique reference number consisting of the page number followed by a number showing its position on the page, e.g. **A46.11**, the 11th formula on Page **A46**. On subsequent appearances the original reference number is given. Immediately after the compound name at the point of first mention, all subsequent appearances of the compound are listed, indexed by page number. Thus to trace all entries for a given compound it is necessary to find the original entry, and thence turn forward to all subsequent entries.

Combination of formulae

Derivatives such as esters of acids, acetates of alcohols, ring-substituted derivatives of aromatic compounds, etc. are usually listed under the parent compound. Similarly the formulae of closely related natural products are often combined, e.g. where one is a dihydro-derivative of the other. In such cases, a direct unequivocal correlation between the substances thus combined may be assumed to exist in the literature.

Nomenclature

No attempt has been made to systematize nomenclature throughout. The 'Atlas' covers a very wide range of simple and complex skeletal systems; for many of the latter the nomenclature has not been

formalized. In general the nomenclature of natural products follows that in the Heilbron *Dictionary* and the original publications.

In naming compounds containing two or more chiral centres, attempts have been made to avoid partially systematic forms, frequently encountered in the literature, such as '(2*S*,3*S*)-(-) hydroxycitric acid'. In the absence of further information, this can be misleading since it implies a numbering system for a non-systematically named compound (citric acid). We have preferred forms such as either (a) the systematic (2*S*,3*S*)-(-) 3-carboxy-2,3-dihydroxyadipic acid or (b) the trivial (-)-hydroxycitric acid.

Designation of configurations; The Sequence Rule

Absolute configurations are generally described by the Sequence Rule of R. S. Cahn, C. K. Ingold and V. Prelog, commonly called the (*R*,*S*)-system, which is the only completely general and unambiguous form of designation. (R. S. Cahn, C. K. Ingold & V. Prelog, *J. Chem. Soc.*, 1951, 612; *Experientia*, 1956, **12**, 81; *Angew. Chem. Internat. Edn.*, 1966, **5**, 385.) No attempt will be made to describe the system in detail here, since to attempt explanation without reproducing a large part of the original papers would tend to give rise to over-simplification.

For convenience, however, the following list of common substituents in order of fiducial precedence is presented:

$-I > -Br > -Cl > -SO_2R > -SOR > -SR > -SH > -F > -OCOR > -OR > -OH > -NO_2 > -NHCOR > -NR_2 > -NHR > -NH_2 > -CH_2Br > -CCl_3 > -CHCl_2 > -COCl > -CH_2Cl > -COOR > -COOH > -CONH_2 > -COR > -CH_2OH > -CN > -CH_2NH_2 >$ α–naphthyl > β-naphthyl > Ph > $-CMe_3 > -CH{=}CH_2 >$ cyclohexyl > $-CHMe_2 > -CH_2COOH > -CH_2{-}CH{=}CH_2 > -CH_2CH_2CH_3 > -C_2H_5 > -CH_3 > -D > -H >$ lone-pair.

In cases where (*R*,*S*) nomenclature is applied to complex chiral structures (especially in Chapter X), brief notes on its application in particular cases are appended where appropriate, but for a fuller description the user is again referred to the Cahn-Ingold-Prelog papers.

D,L *nomenclature*

The configuration of a few key compounds in Section A are also given according to the older D,L system, following the glyceraldehyde or serine conventions as appropriate. (This juxtaposition of the (*R*,*S*) and (D,L) conventions is contrary to normal practice and would not be accepted by journal editors; it is justified here purely on grounds of convenience to the user.)

The D,L system is now redundant for all compounds except carbohydrates, amino acids and closely related substances, but its limited inclusion here may assist those who have to consult the older literature. For a helpful discussion of the present state of the D,L system and its ambiguities, see D. W. Slocum, D. Sugarmann and S. P. Tucker, *J. Chem. Educ.*, 1971, **48**, 597.

Formulae

(a) General

The purpose of the 'Atlas' is to depict *absolute configurations* at chiral carbon atoms or other features of dissymmetry. It is not concerned with *conformations, bond-lengths* or *bond angles*. Even where 'perspective' type drawings have been included to improve the representation of a particular compound, distortions such as alteration of bond angles and flattening of rings may have been incorporated in order to improve general clarity and the depiction of configurations at individual centres of chirality.

(b) Fischer-type projections

These are used throughout Chapters A, C, D and Z.

The projections used in the 'Atlas' do not in general obey the Fischer convention that the principal

carbon chain of the molecule should be vertical with the lowest-numbered carbon atom at the top. To follow this convention in the 'Atlas' would have meant that a complex and confusing series of substituent interchanges would have been necessary on most pages.

Interconversion of Fischer-type formulae Interchanging any one pair of substituents in a Fischer-type drawing of compound (+)X produces the enantiomer, (−)X. Interchanging two pairs of substituents reverts to the original enantiomer (+)X. Special cases of this are (i) interchange of a with e then e with b, which has the effect of a cyclic interchange of a, b and e (Fig. 1), and (ii) interchange of a with d and of b with e, which has the effect of a 180° rotation in the *xy* plane. (Fig. 2).

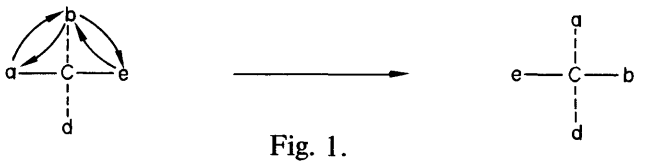
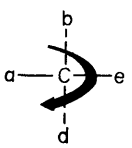


Fig. 1.

Fig. 2.

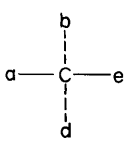
Assignment of (R,S) symbols to Fischer-type formulae If d is the group of lowest precedence, then examination of Fig. 3 shows that (*R*) or (*S*) chirality may be readily assigned by inspection.



(*R*)-chirality with precedence
a > b > e > d.

Fig. 3.

If d is not the group of lowest precedence, with a little practice it is again possible to assign chirality directly by inspection; the following table (Fig. 4) demonstrates the twelve ways of writing the formula having (*R*)-chirality.



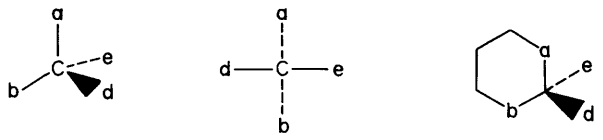
behind	*above and clockwise*		
d	abe	bea	eab
a	ebd	bde	deb
b	aed	eda	dae
e	adb	dba	bad

Fig. 4.

(c) Cyclic structures

Substituents lying above and below the *xy* plane in more complex structures are indicated by the use of wedges and dashed bonds respectively, in accordance with usual practice.

Interconversion of Fischer and cyclic formulae (Fig. 5) Consider the tetrahedral molecule (A). Rotation produces the Fischer formula (B). Substituents a and b can clearly be portions of a cyclic residue as well as acyclic groups; for example when a and b become incorporated into a six-membered ring, (C) results.



(A) (B) (C)

Fig. 5.

(d) More complex structures

In the depiction of complex structures, as much care as possible has been taken to give unambiguous representation of the correct configurations at all chiral centres. Deviations from the true bond angles are inevitable in any attempt to represent three-dimensional structures in two dimensions, and further distortions result from various conventions in common use, for example the representation of cyclohexane rings as planar hexagons with 120° valency angles. These distortions cannot be eliminated fully, but the aim has been to present drawings in which the amount of deviation from the drawing required to produce the 'correct' configuration at a given chiral centre, is always considerably smaller than that required to produce the opposite, 'incorrect' configuration. It should be reiterated that in complex structures containing several chiral centres, the aim has been to show the correct absolute configuration at each chiral centre considered individually, and in cases where there is any possibility of ambiguity, *each chiral centre should be inspected independently of other chiral centres in the molecule.*

Symbols and abbreviations

Abs. X-ray. Substance for which the Bijvoet method for determination of absolute configuration by the anomalous dispersion method has been applied.
Recent publications have pointed out some possible sources of error in methods of assigning absolute configurations by the anomalous dispersion method, and have indicated that *some* of the previous determinations are conceivably in error (see for example D. Rogers, A. Quick and M. Ul-Haque, *Acta Cryst.*, 1974, *B30*, 552)

Rel X-ray. X-ray determination of structure without application of anomalous dispersion. This determines the configurations of all chiral centres in the molecule relative to each other but does not place them on an absolute basis.
Conversion of compounds to derivatives, often those containing a heavy atom, for use in X-ray structure determination, is a very common procedure. No special mention has been made of such procedure unless it causes a significant change in configuration.

$A \xrightarrow{C(n)} B.$ Chemical conversion (C) of A to B in approximately *n* steps, i.e. A→K→L→M→N→B

$A \xrightarrow{C(n)} B.$ Chemical conversion of both A and B to a common intermediate, or of a common intermediate to both A and B, in a total of approximately *n* steps, i.e. A→K→L→M←N←P←B or A←K←L←M→N→P→B

ORD Optical rotatory dispersion

CD Circular dichroism

AS Asymmetric synthesis. The two most frequently encountered types of asymmetric synthesis are further distinguished as follows.

AS(H) Asymmetric synthesis by the method of Horeau (*Tetrahedron Letters*, 1961, 506). This involves reaction of the chiral alcohol with racemic 2-phenylbutyric anhydride.

The absolute configuration at the hydroxyl-bearing chiral centre is determined by measurement of the specific rotation of the recovered unreacted 2-phenylbutyric acid. The method has also been applied to amines, but correlations of this kind are of disputed validity.

AS(P) Asymmetric synthesis by the methods of Prelog (*Helv. Chim. Acta*, 1953, **36**, 308), Cram (D. J. Cram and F. A. A. Elhafez., *J. Amer. Chem. Soc.*, 1952, **74**, 5828), and related methods. A chiral alcohol is converted to its α-ketoester and this is allowed to react with a Grignard reagent. Hydrolysis of the product produces a chiral α-hydroxy acid. The method may be used to compare the absolute configuration of an unknown alcohol with that of a known α-hydroxy acid (usually atrolactic), or that of a known alcohol (e.g. menthol) with that of an unknown α-hydroxy acid.

Where an asymmetric synthesis is of neither of these two types, the original reference should be consulted for details of the precise method employed and the reasoning used to interpret the observed stereoselectivity.

AC Absolute configuration

—O→ Chemical conversion with inversion at a chiral centre

------→ Dashed arrow indicating a correlation which is considered to be of lower reliability (see Introduction)

—8— 'Enantiomer of' sign. For example A $\xrightarrow{C(n)}$ B means 'conversion of A to the *enantiomer* of B'

* Denotes natural products both enantiomers of which are known by us to occur naturally. This symbol is used only in the sections dealing predominantly with natural products, namely T (terpenoids), K (alkaloids) and Y (other natural products).

§ Indicates that the absolute configuration shown in the 'Atlas' differs from that appearing in one or more of the original references quoted. This may be due to one of several factors.

(a) a misprint or error in the paper.

(b) a relatively recent change in the generally accepted configuration due to further work by other or the same authors.

(c) personal correspondence between the authors and ourselves.

(d) in a few cases in Chapter X, changes in the accepted (*R,S*) convention since the date of the original publications have led to a change in (*R,S*) assignment although there has been no change in the accepted absolute configuration.

In all cases the absolute configuration given here is correct according to the best available information (June 1976); other sources showing a different configuration are believed to be in error.

ΔM_D Comparison by the Freudenberg method of molecular rotation shifts.

QR Comparison by the quasi-racemate method.

> Has precedence over, according to the Cahn, Ingold, Prelog system.

Other abbreviations have their usual chemical significance.

Choice of enantiomer depicted.

(a) As a general rule, *the enantiomer shown in the 'Atlas' may not be the one on which the correlations shown were originally carried out*. No special indication is given where this is the case. This is for convenience in fitting large numbers of formulae together, and to minimize use of the '—8—' sign.

(b) In the *chapters which deal with natural products*, namely T, K and Y, the enantiomer shown is the naturally occurring one unless otherwise stated.

When both enantiomers are known to occur as natural products, this is shown by the sign * after the name of the compound. Refer to the original publications to ascertain which enantiomer is obtained from which natural source.

(c) In the other chapters (A, C, D, X and Z) no distinction is made between natural and synthetic compounds. Check with the literature to determine which enantiomer, if either, is a natural product.

Rotations

The sign of rotation given for each compound is that shown in the Heilbron 'Dictionary' or in the original publication. Rotations are normally at the sodium D line but other wavelengths are often used for red or yellow compounds, e.g. carotenoids. In case of doubt, consult the original reference. An empty bracket ( ), means that the specific rotation has not been determined, or cannot be found.

In most cases, changes in sign of rotation with solvent or pH are noted where known, but the absence of such indication cannot of course be taken to mean that no such anomalous behaviour occurs under any circumstances. It is necessary to consult the original publication for details of solvent and temperature.

Some of the signs of rotation given have been interpolated from published ORD curves.

Supplementary Key to the Second Edition

Scope and Literature Coverage

The second edition covers the literature to mid-1976. Some correlations from the older (pre-1971) literature which came to light during the preparation of the second edition are also included, and the coverage of compounds of principally pharmaceutical significance has been enlarged.

Arrangement of material

Volume 1 covers mainly the literature up to the end of 1971, which was the scope of the first edition. Volume 2 is mostly based on the literature from 1972-6. There are, however, exceptions to this generalization; in particular, some sections which appeared in the First Edition have been enlarged and rewritten as a result of new work and most of these have been transferred to Volume 2.

Volume 2 is compatible for the most part with the single volume of the First Edition provided allowance is made for the fact that some of the assignments of absolute configuration given in the first edition have since been shown to be incorrect (see list on page xi, Volume 2).

Where space permitted, additional formulae have been added to existing pages in Volume 1 to minimize the number of cross-references between the two volumes. The arrangement and content of chapters is the same as in the first edition.

Numbering of formulae and cross-references

In general, this follows the same plan as in the first edition, with page numbers in Volume 2 distinguished by the addition of a prime, i.e., **A32′.2**, the second formula on page **A32** of Volume 2.

On a few pages in Volume 1, addition or deletion of formulae has meant that the order of formulae on the page is no longer strictly numerical, or else one or more formulae numbers are missing.

Symbols and abbreviations

The sign §, in addition to the meanings ascribed to it in the first edition, is used wherever a formula or absolute configuration given in the second edition differs for whatever reason from that given in the first edition for the same compound, except where the only difference is the correction of a trivial error.

-A-

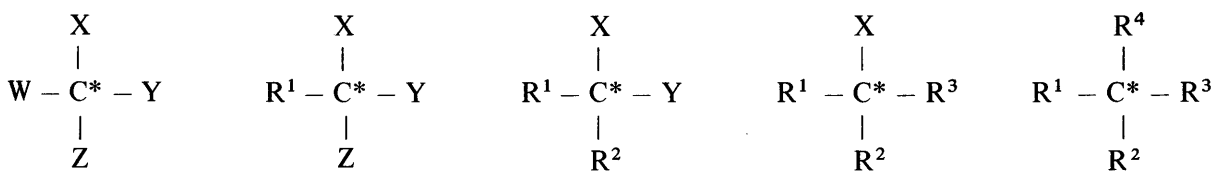
Fundamental Chiral Compounds

Introductory Notes to Chapter A

Chapter A contains a wide selection of the most important fundamental chiral molecules. The great majority contain one or two chiral centres, but a number (notably cyclitols, decalins and norbornanes) contain three or more.

Sub-classification of compounds in Chapter A

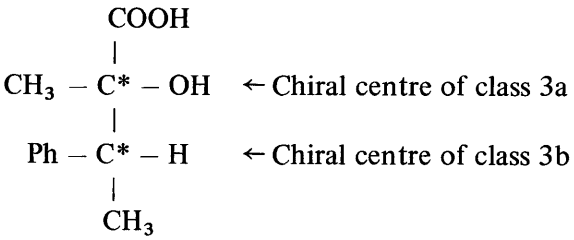
To facilitate the finding of a particular compound, the contents of Chapter A are subdivided according to the nature of the chiral carbon atom(s).
Classes 0, 1, 2, 3, 4 are designated according to the number of other *carbon* atoms directly attached to the chiral centre C* under consideration.
R^1, R^2, R^3, R^4 are groups of all kinds bonded by *carbon* atoms, including oxidised groups such as –COOH; W, X, Y, Z are groups bonded to the chiral centre by *non-carbon* atoms. (H, O, N, S, Halogen, etc.)



Class 0 Class 1 Class 2 Class 3 Class 4

The classes are further divided as follows: 1a, 2a, 3a, 4a; all R groups aliphatic. 1b, 2b, 3b, 4b; at least *one* R group aromatic or heteroaromatic.

Compounds containing two or more chiral centres, are indexed under the highest applicable number, with subgroup b taking precedence over subgroup a. For example:



is indexed under 3b.

Location of compounds by class

Class 0; no compounds belonging to this class are of known absolute configuration.
Classes 1a, 1b; See Volume 2 (and also chapter D).

Class 2a; Pages **A1-A26** and **A58**
Class 2b; Pages **A19-A25** and **A58**
Class 3a; Pages **A26-A47** and **A59-A61**
Class 3b; Pages **A40-A52** and **A61**
Class 4a; Pages **A53-A56**
Class 4b; Pages **A55-A56**

Simple compounds found in other chapters

The following is a list of simple compounds containing one or two chiral centres which would normally be considered to belong in Chapter A, but which because of difficulties of arrangement, appear in other chapters.

Class 2a

2,5-dioxo-5-methylhexanoic acid **T17.6**
2-hydroxymethyl-1-methylcyclohex-1-en-4-ol **T40.6**
2-(5-hydroxy-2-methylenecyclohexylidene) ethanol **T48.11**
cyclodopa **K17.9**
2-(dimethylamino)heptane **K19.3**
nonan-2-ol **K19.5**
2,6-dimethylpiperidine **K19.6**
6-methoxycarbonylpiperidine-2-acetic acid, methyl ester **K20.12**
3,4-dihydroxy-4-methylpentanoic acid lactone **Y1.6**
5-hydroxyhexanoic acid lactone **Y14.11**
3-aminoproline **Y22.7**
2,2-dimethylthiazolidine-4-carboxylic acid **Y29.7**
5,5-dimethyl-Δ^2-thiazoline-4-carboxylic acid **Y29.9**
3-hydroxycyclopentanone ethylene ketal **D2.9**
cyclooct-1-en-3-ol **X2.5**
3-acetoxycylooctyne **X2.6**
hexane-3,4-diol **X11.8**

Class 2b

3-methylphthalide **Y14.5**
3-butylphthalide **Y14.6**
2-mercapto-4-phenylimidazoline **Y30.6**
3-bromo-4-phenylcrotonolactones **X3.4**

Class 3a

2,6-dimethylheptanoic acid **T1.7**
4-hydroxy-4-methylhexanoic acid lactone **T3.9**
cinenic acid **T3.10**
3-carboxy-2,2-dimethylglutaric acid **T8.9**
pinononic acid **T8.14**
3-isopropenylcyclopentanone **T9.1**
3-isopropenylcyclopentanols **T9.2, T9.3**
paraconic acid **T15.14**
2,5-dimethyl-3-ethylhexan-2-ol **T17.7**
dihydrohaematinic acid **T22.7**
4,8-dimethylnonanal **T46.1**
5-ethyl-6-methylheptan-2-one **T48.3**
4-methylcyclohexane-1,2-dione **T58.4**
3-ethylglutaric acid mononitrile **T58.7**
4-methyl-2-pyrrolidone **K35.9**

2-hydroxy-3-methylsuccinic acid **Y5.4**
4,8-dimethyl-4-hydroxynonanoic acid lactone **Y9.6**
1-hydroxymethylcyclohexane-1,2-diol **Y19.11**
5-hydroxy-3-methylhexanoic acid lactone **Y21.5, Y21.10**
2,4-dimethylcyclohexanone **Y21.8,**
3-methylheptanedioic acid **Y27.4**

Class 3b

2-(*p*-methoxyphenyl)-propionic acid **Y5.7**
(*p*-methoxyphenyl)-succinic acid **Y6.8**
2,4-bis(*p*-methoxyphenyl)-butyric acid **Y9.4**
2-(3,5-dimethoxy-2-methylphenyl)-butane **Y13.10**
3-bromo-4-alkyl-4-phenylcrotonolactone **X3.4**

Class 4a

3,4-di(methoxymethyl)-4-methylcyclohexanone **T40.2**
4-carbethoxy-2-pyrrolidone-4-acetic acid **X4.5**

Chapters T, K and Y contain many natural products with one or two chiral centres, and the user scanning the 'Atlas' for a compound of a particular stereochemical type should search these chapters as well as Chapter A. In order to find any individual compound, the Index should be used.

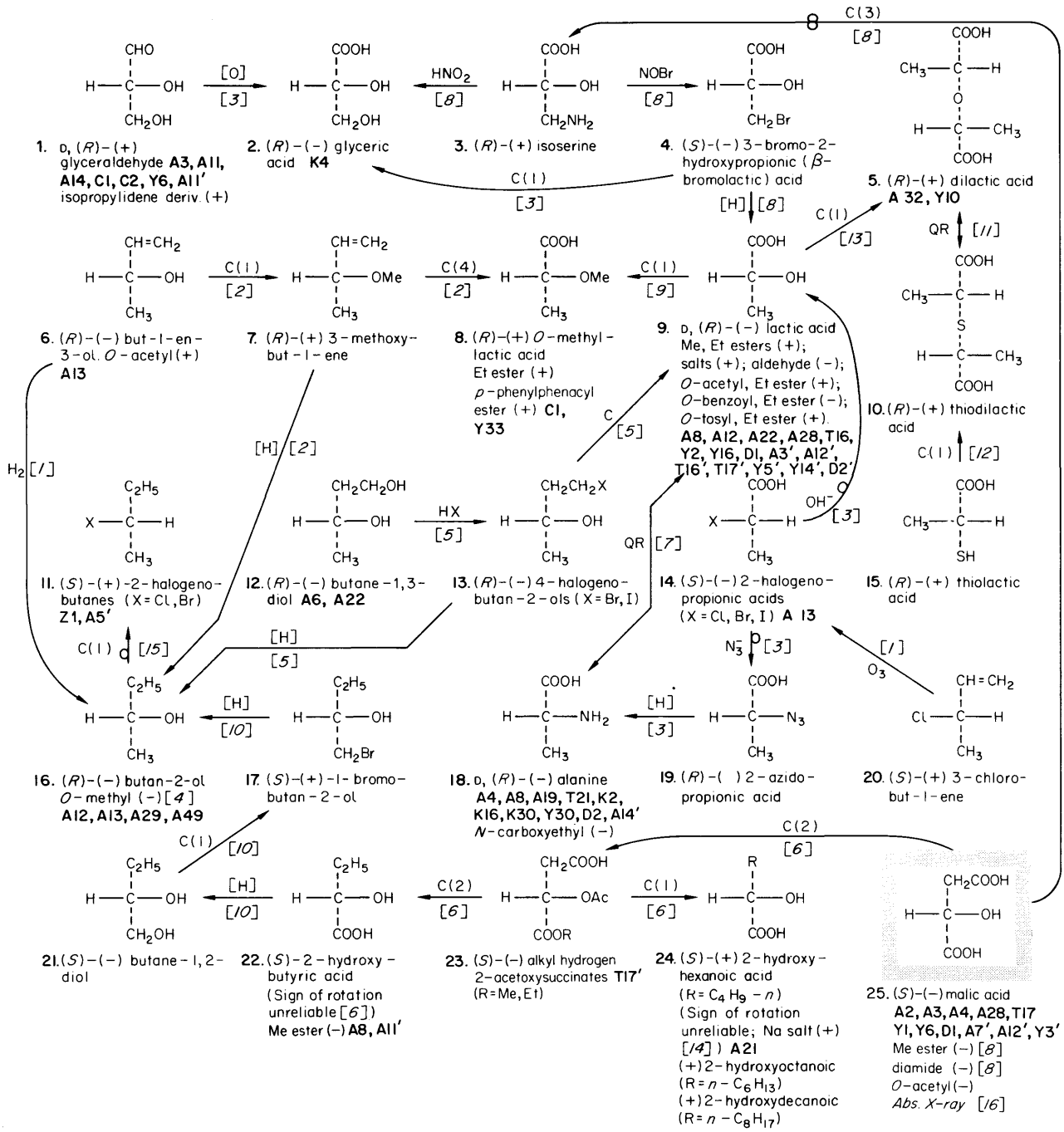
Amino acids

All the common amino acids have been chemically correlated with other chiral substances, and are included in the 'Atlas', as are many rarer amino acids. A large number of other less common amino acids have been isolated from natural sources (for a review, see L. Fowden, *Progr. Phytochem.*, 1970, 2, 203); the absolute configurations of many of these have been assigned indirectly, by one of the following methods.

(1) Enzymatic methods

(2) Molecular rotation shift methods. The most frequently used is the Clough-Lutz-Jirgenson rule which states that acids of the L series (which corresponds to (*S*) in most but not all cases) show a positive shift in molecular rotation on passing from neutral to acid solution. Studies of chiroptical properties at various pHs (P. M. Scopes and co-workers, *J. Chem. Soc., (C)*, 1971, 833) are a development of this method. These procedures rely on the availability as reference substances of amino acids which have been chemically correlated and which appear in Chapter A. Exceptions to the Clough-Lutz-Jirgenson rule have been noted (see for example J. H. Poupaert, R. Cavalier, M. H. Claesen and P. A. Dumont, *J. Medicin. Pharmaceut. Chem.*, 1975, 18, 1268).

See J. P. Greenstein and M. Winitz, *Chemistry of the Amino Acids*, Wiley, 1961, for descriptions of the enzymatic and molecular rotation shift methods.



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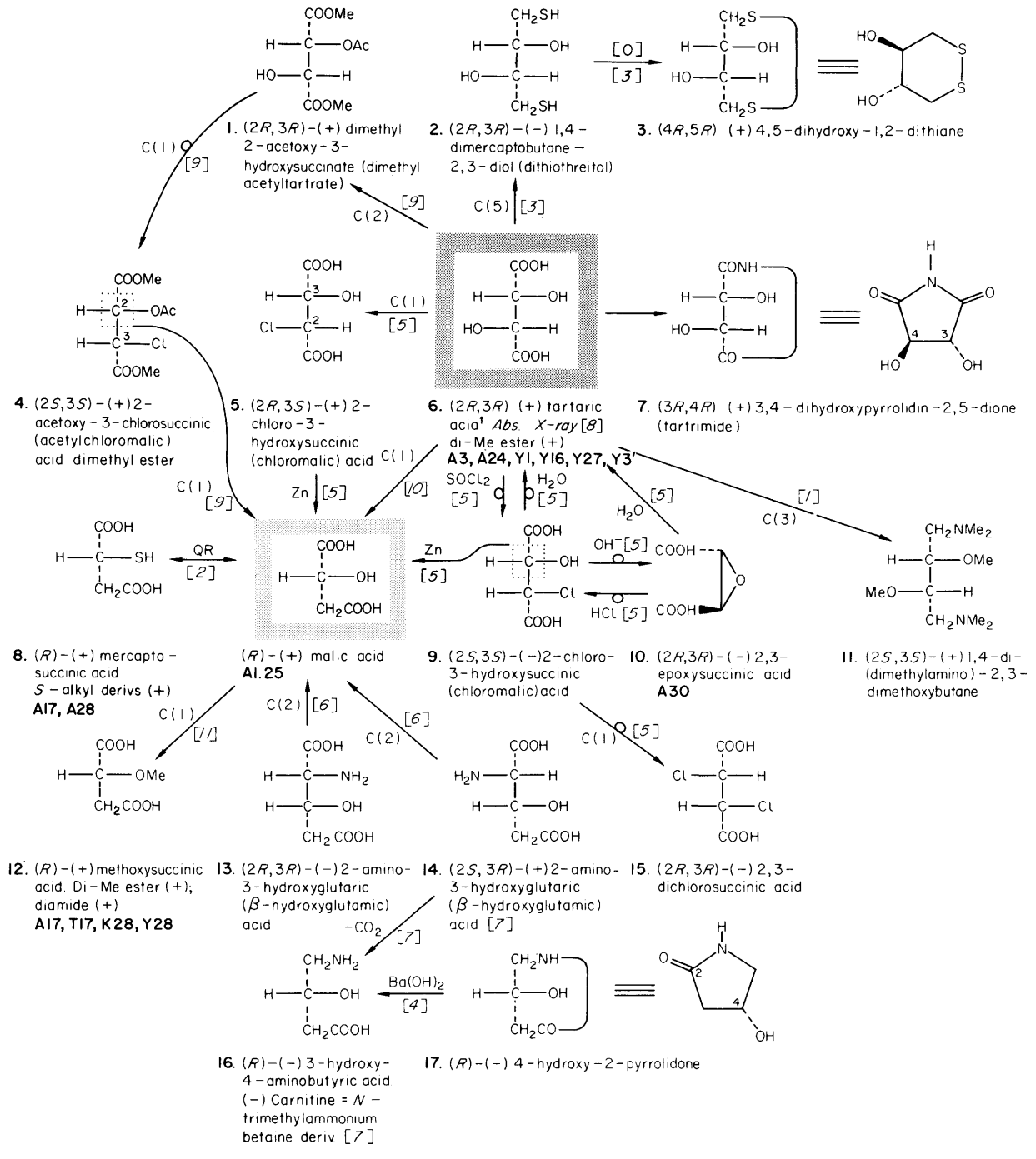
Mainly two-centre compounds related to tartaric acid



† For a discussion of the ambiguity of D,L-nomenclature as applied to tartaric acid, see [12]

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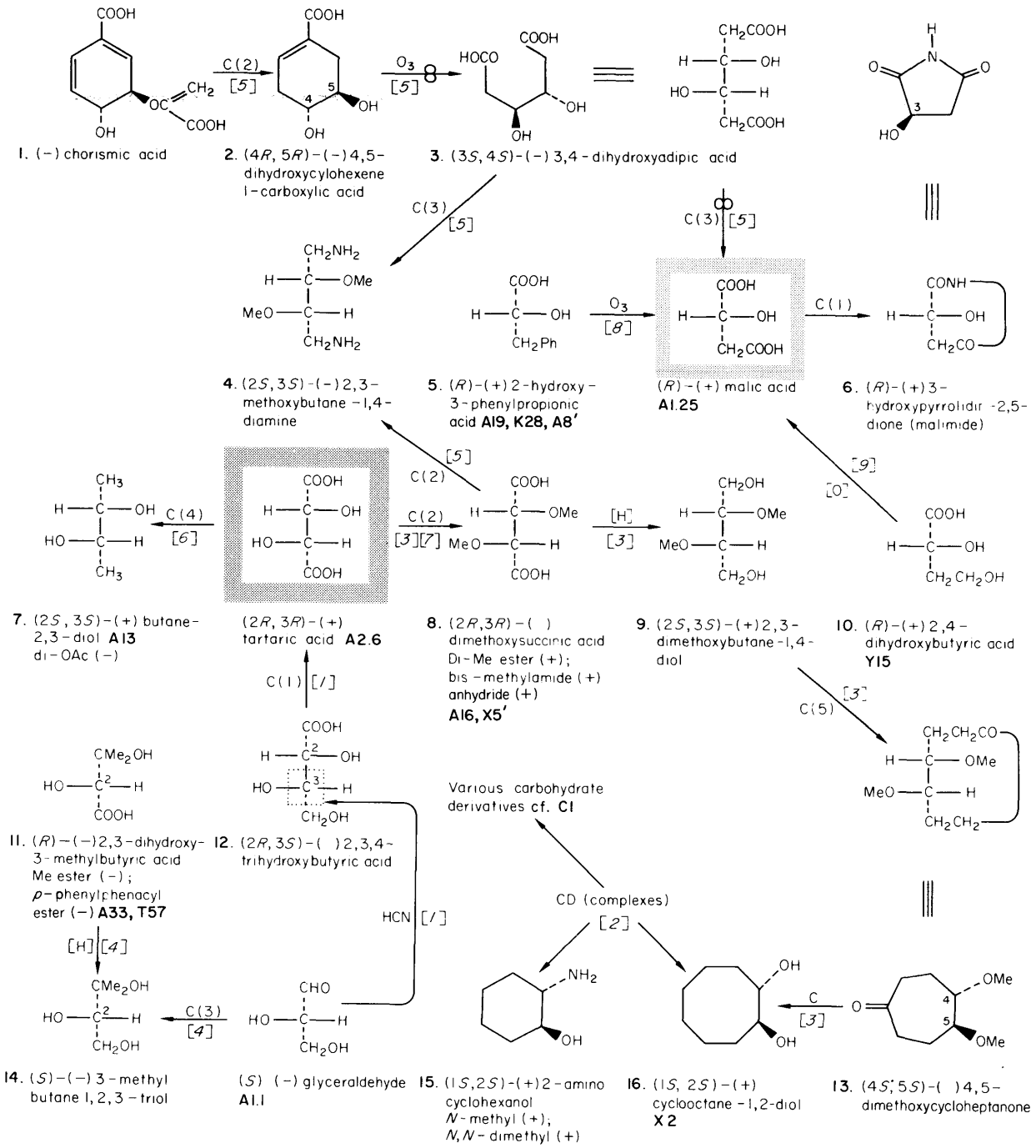

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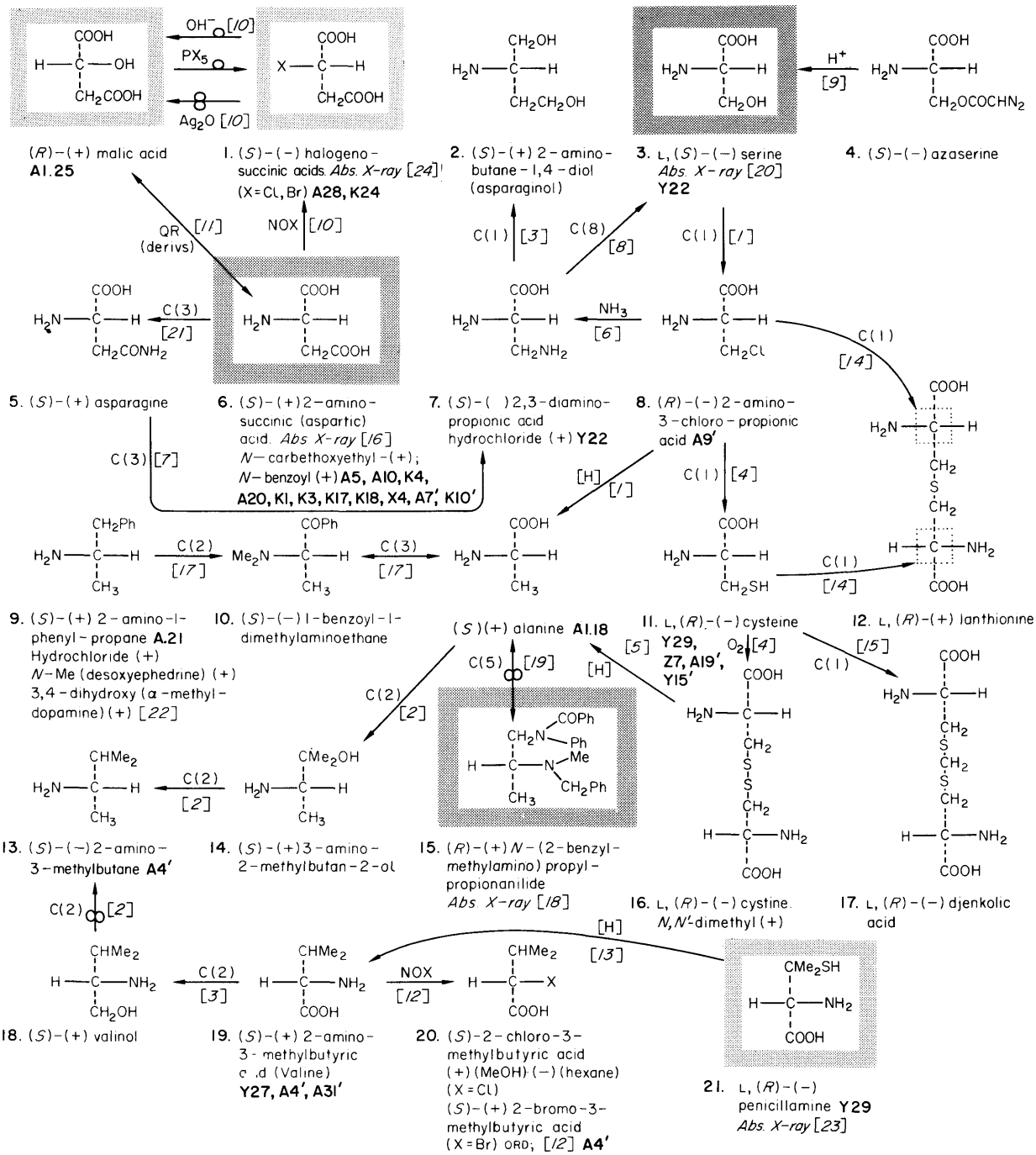

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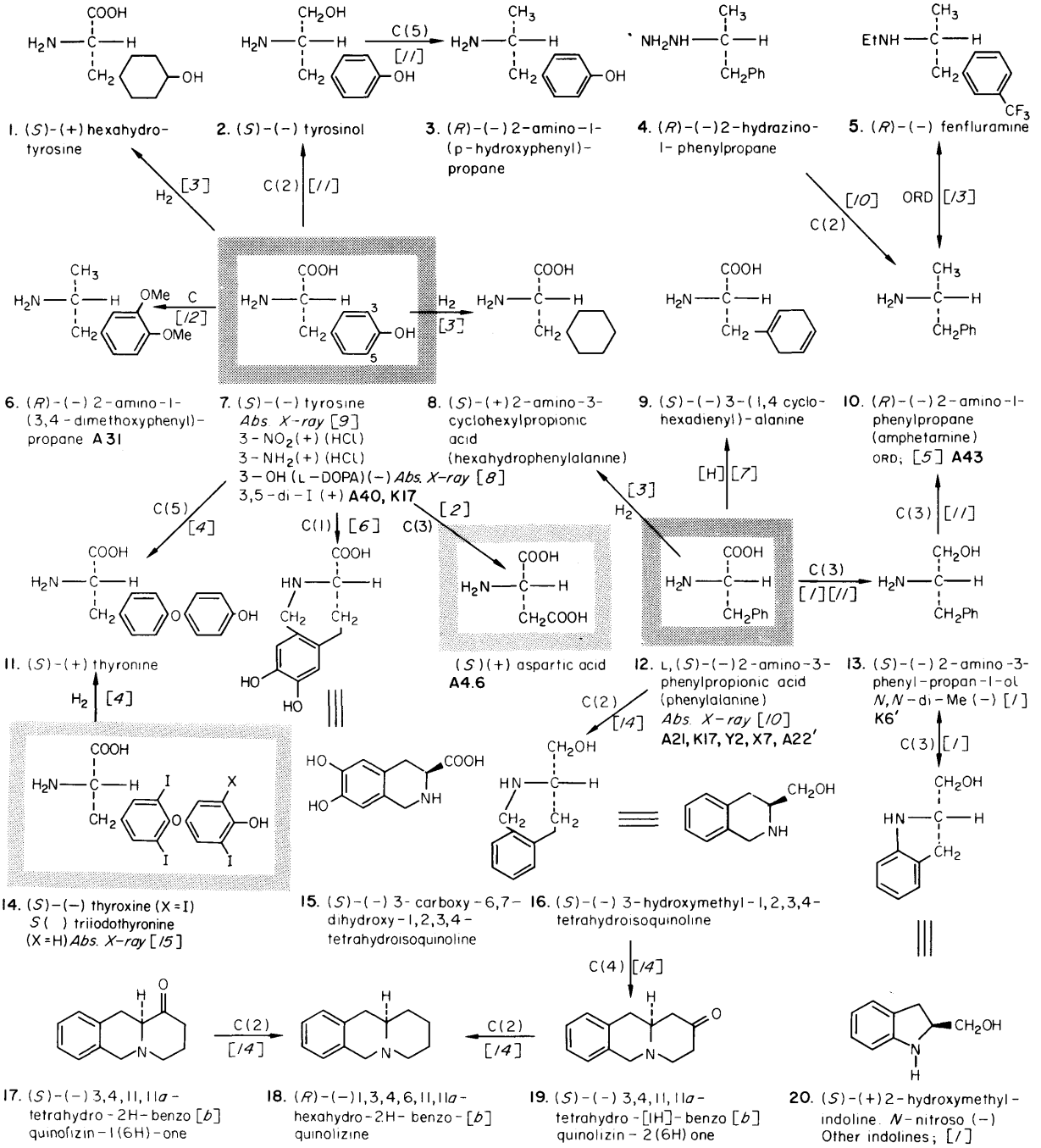

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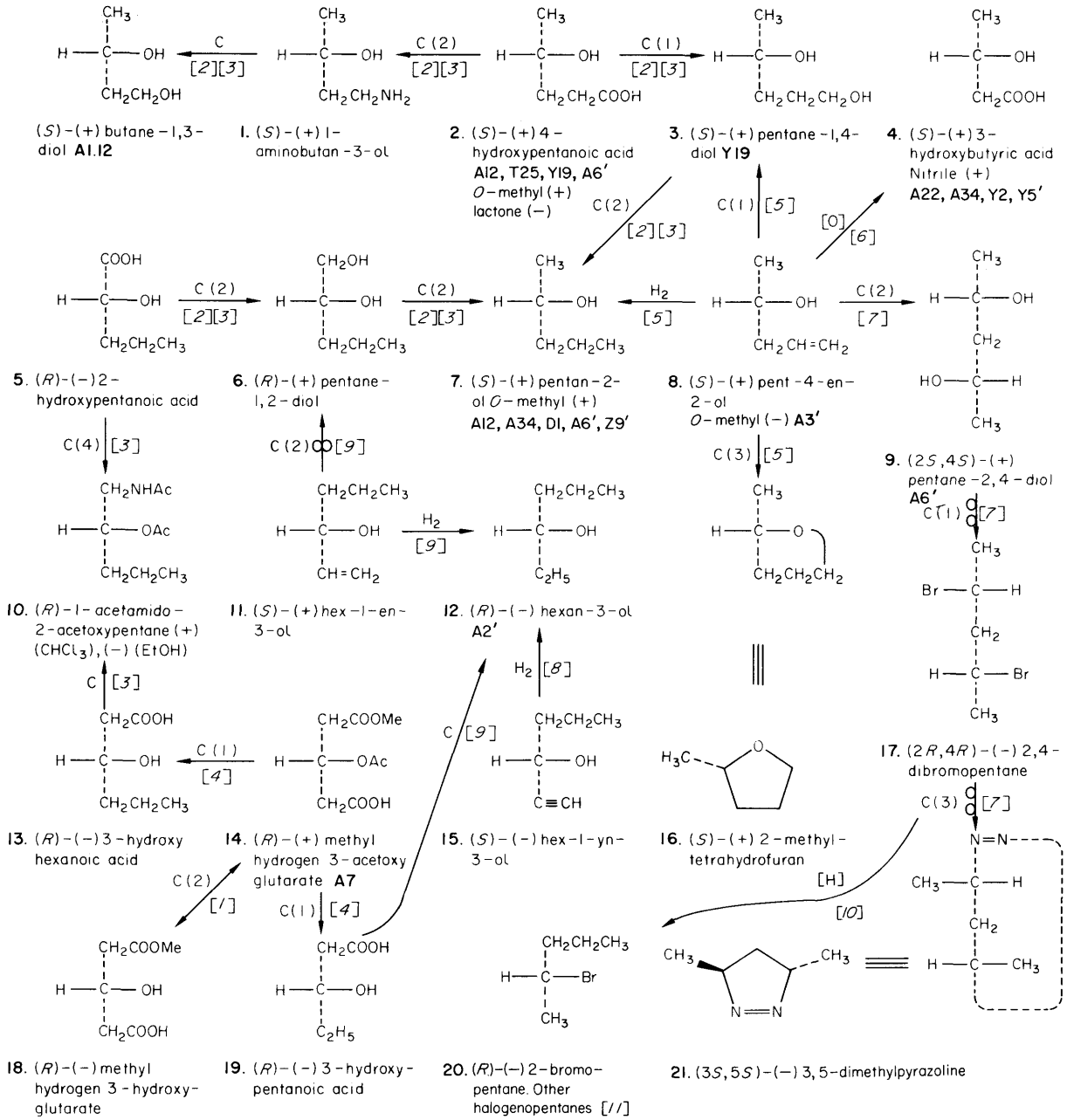

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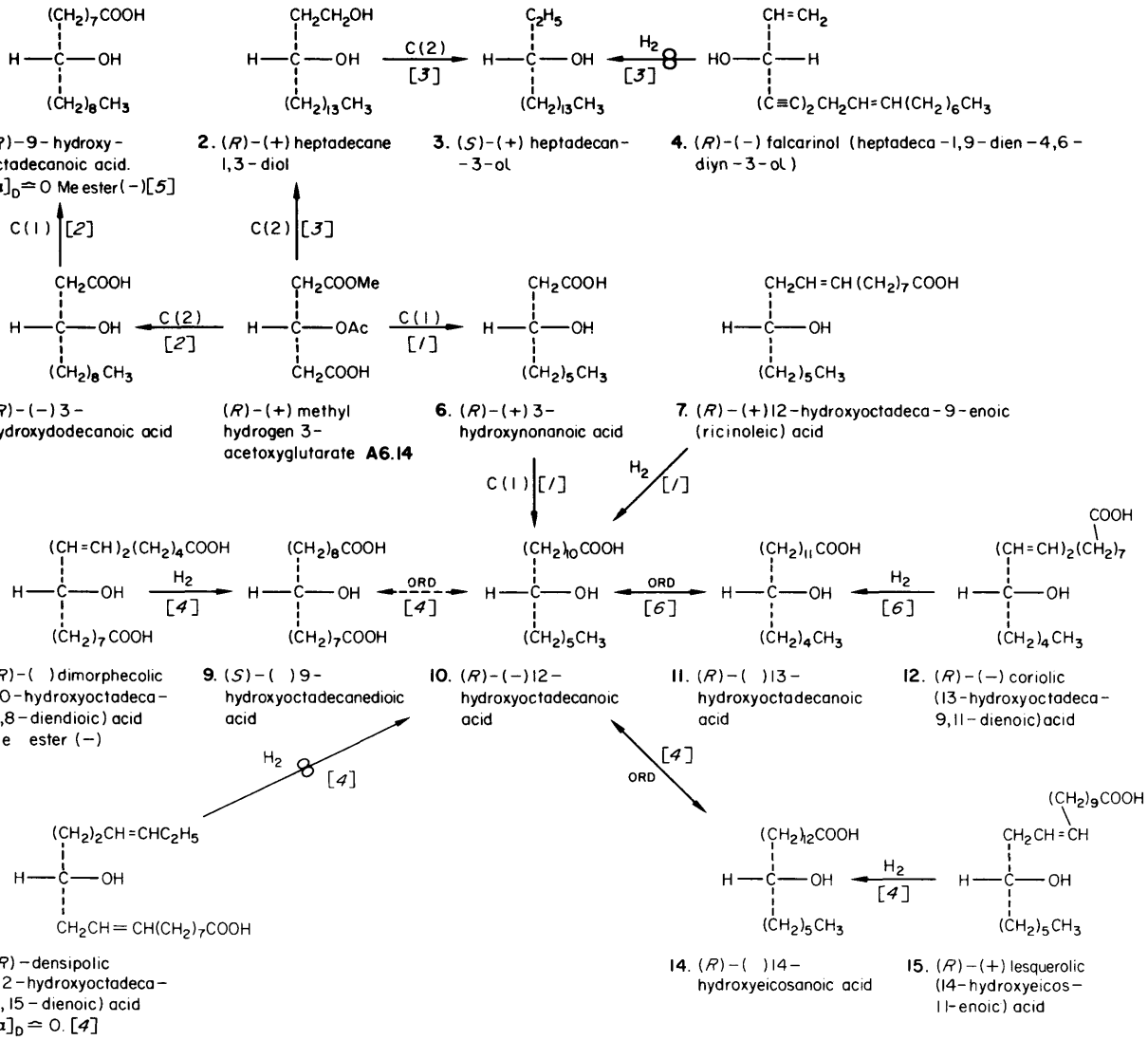

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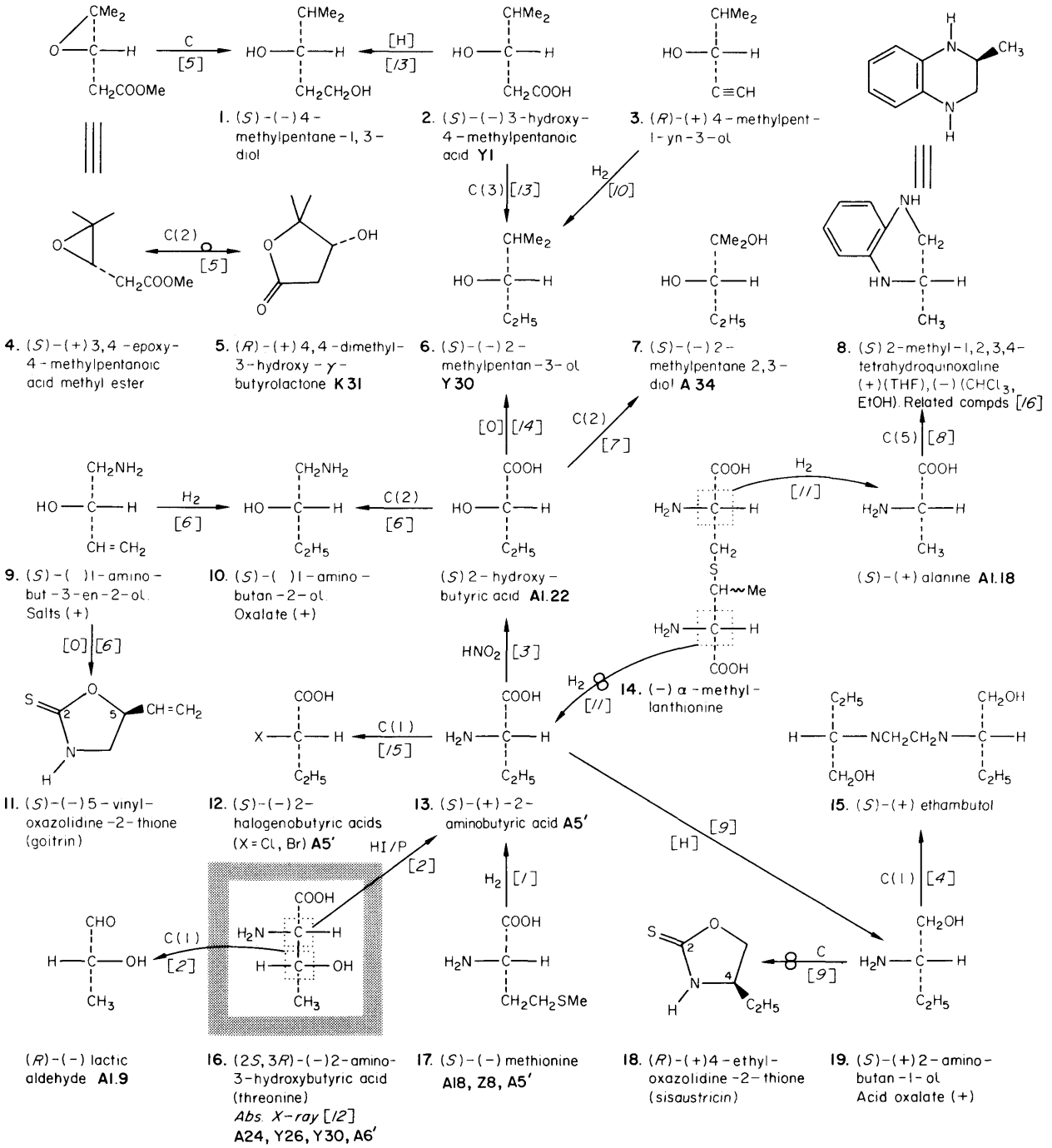

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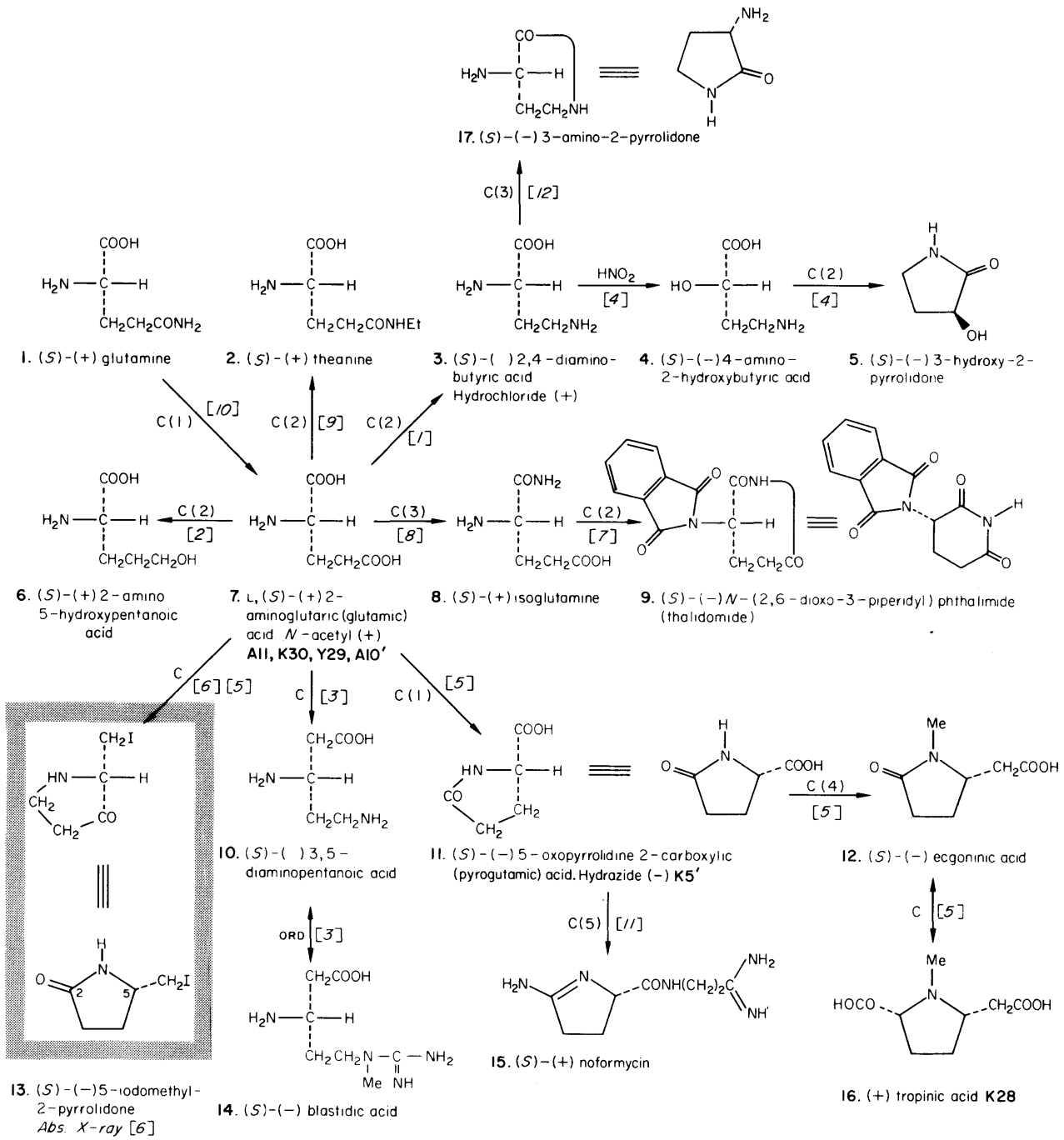

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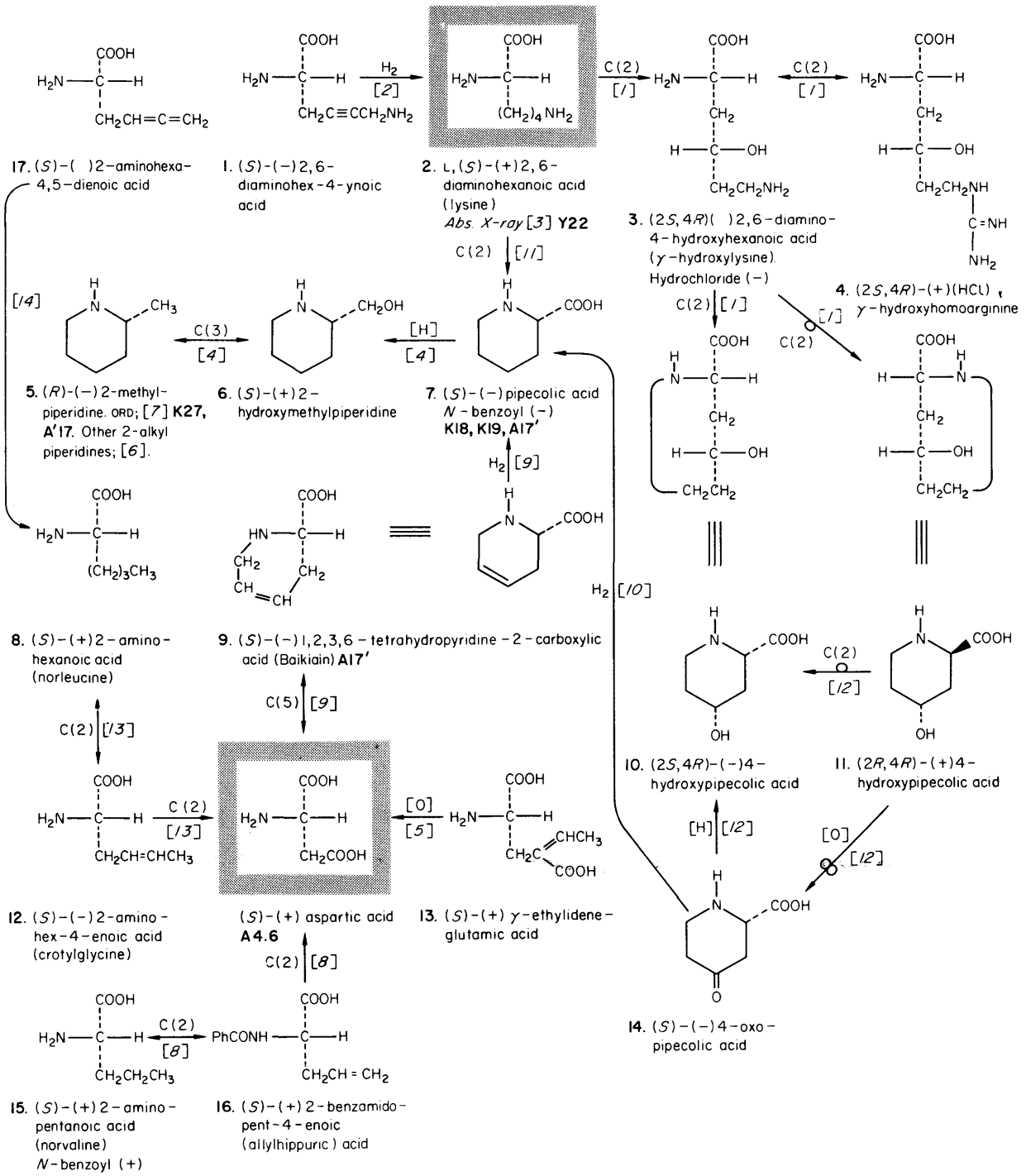

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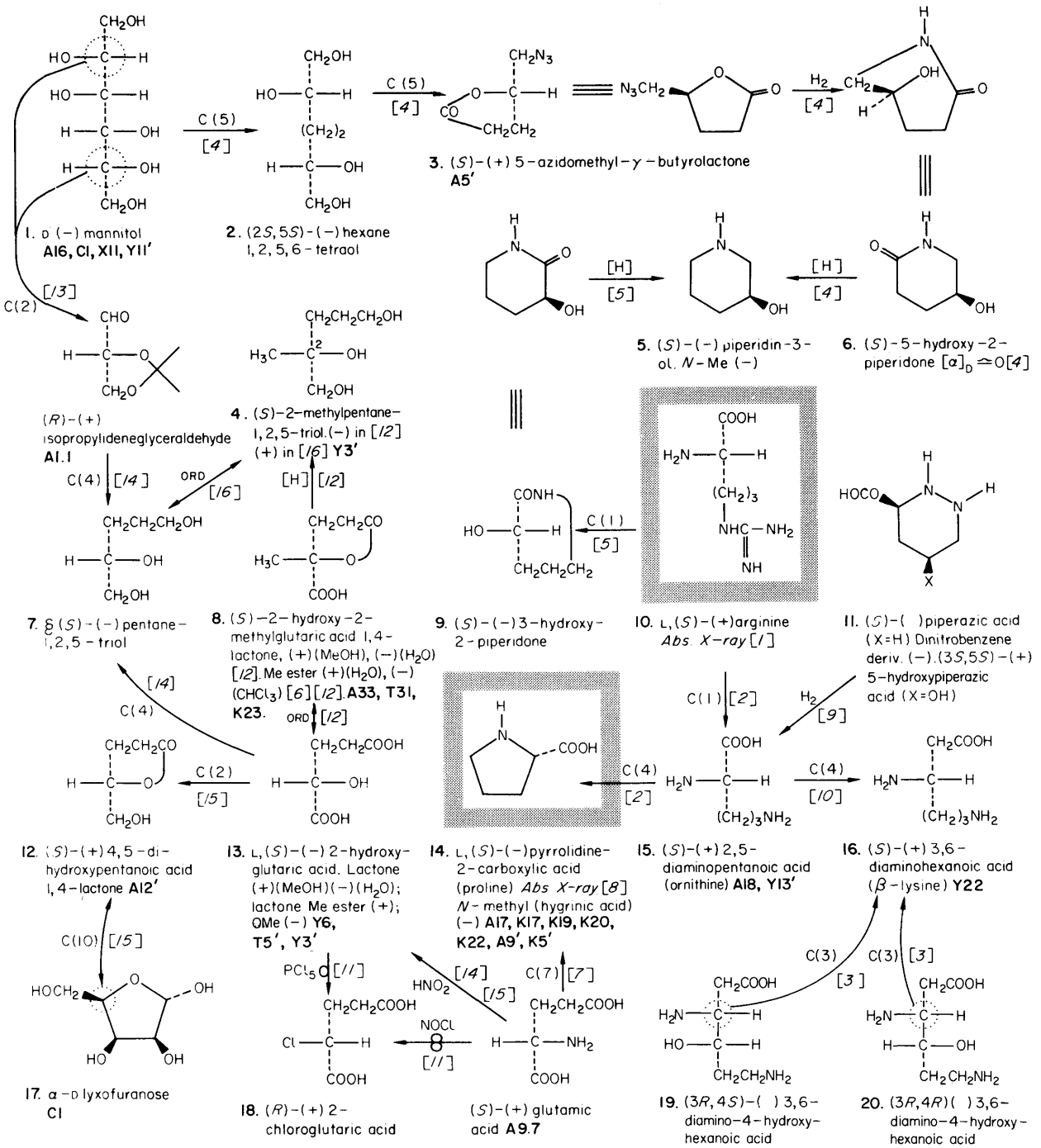

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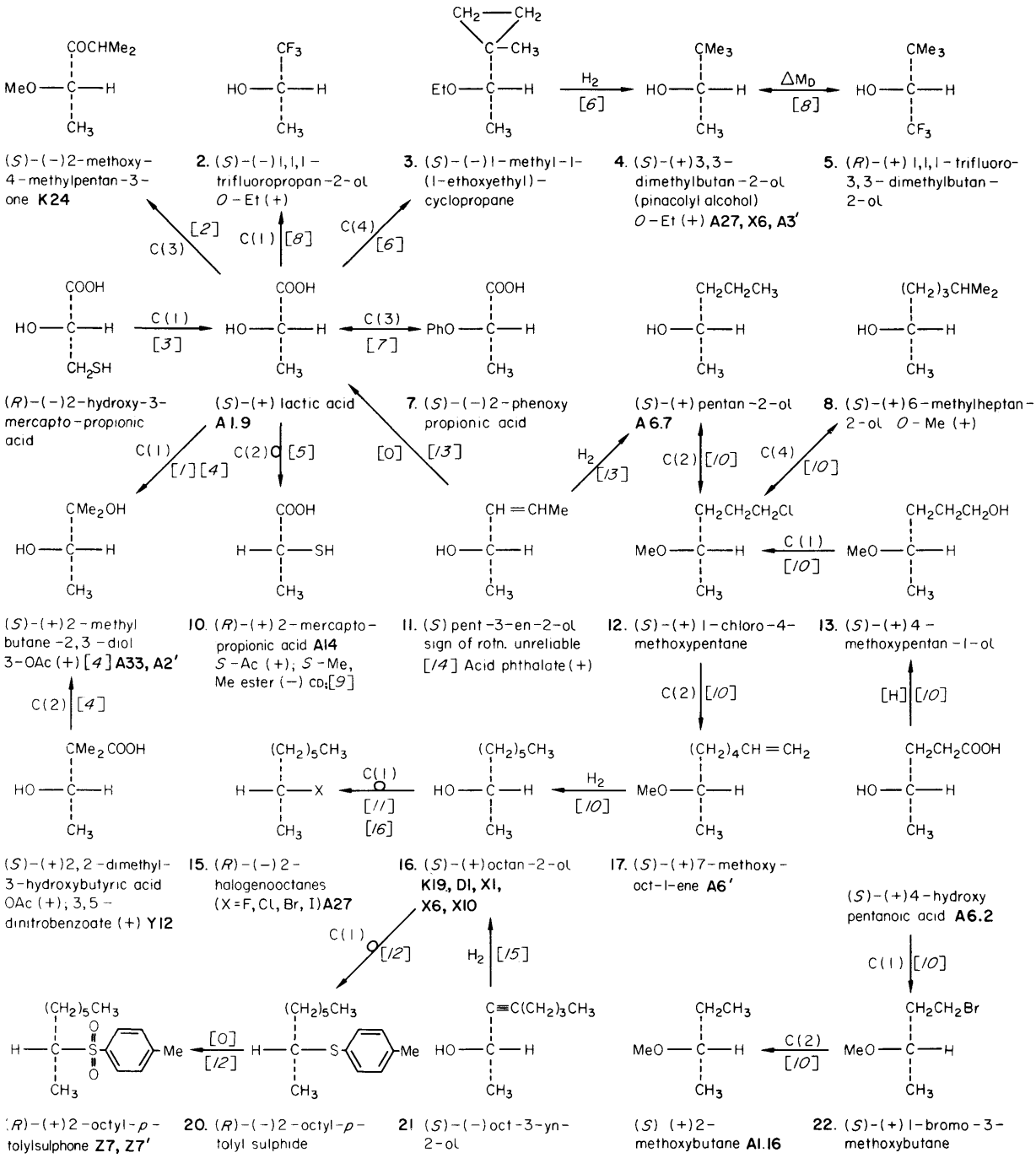
Lactic acid, octan-2-ol and related compounds



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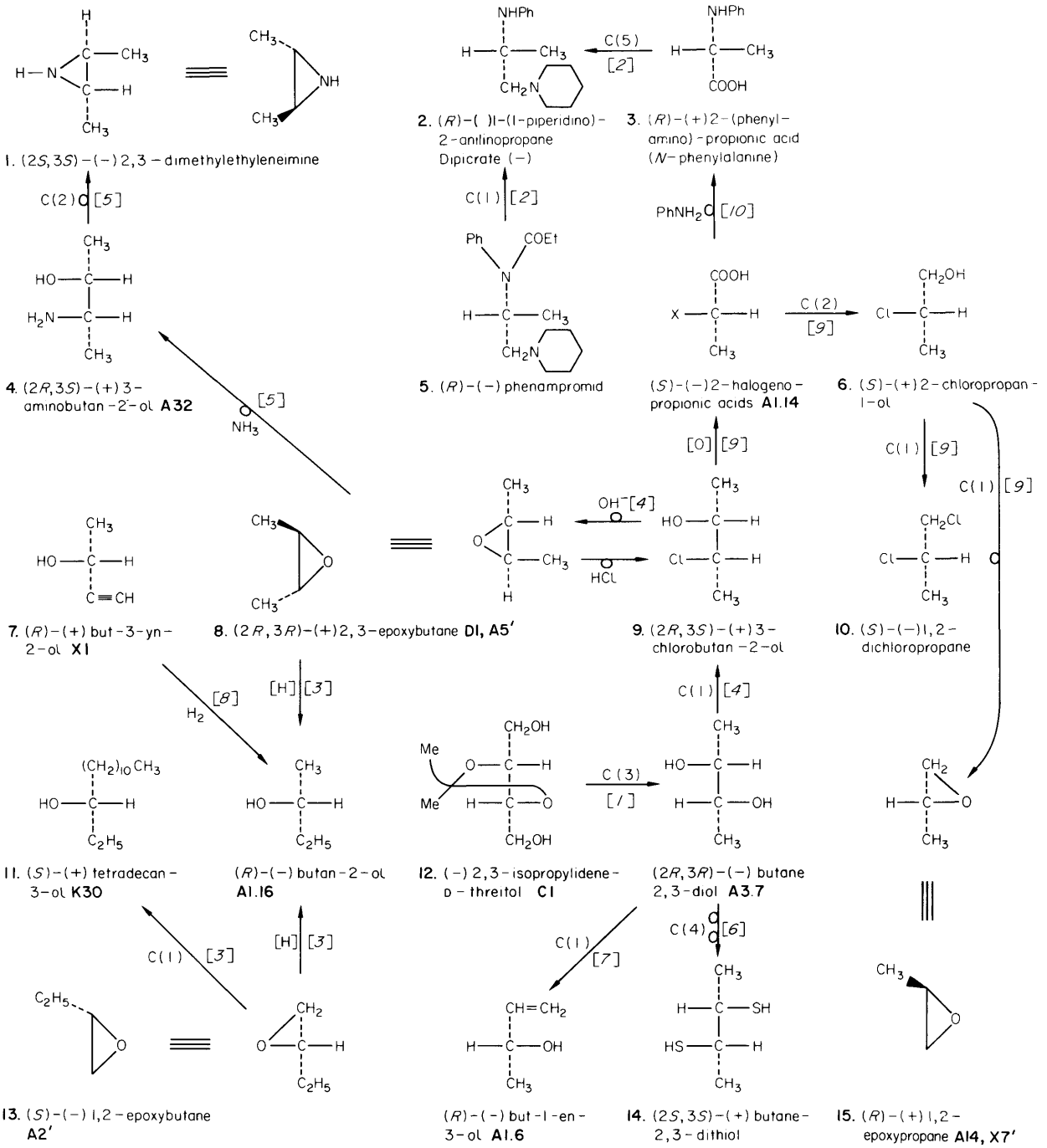

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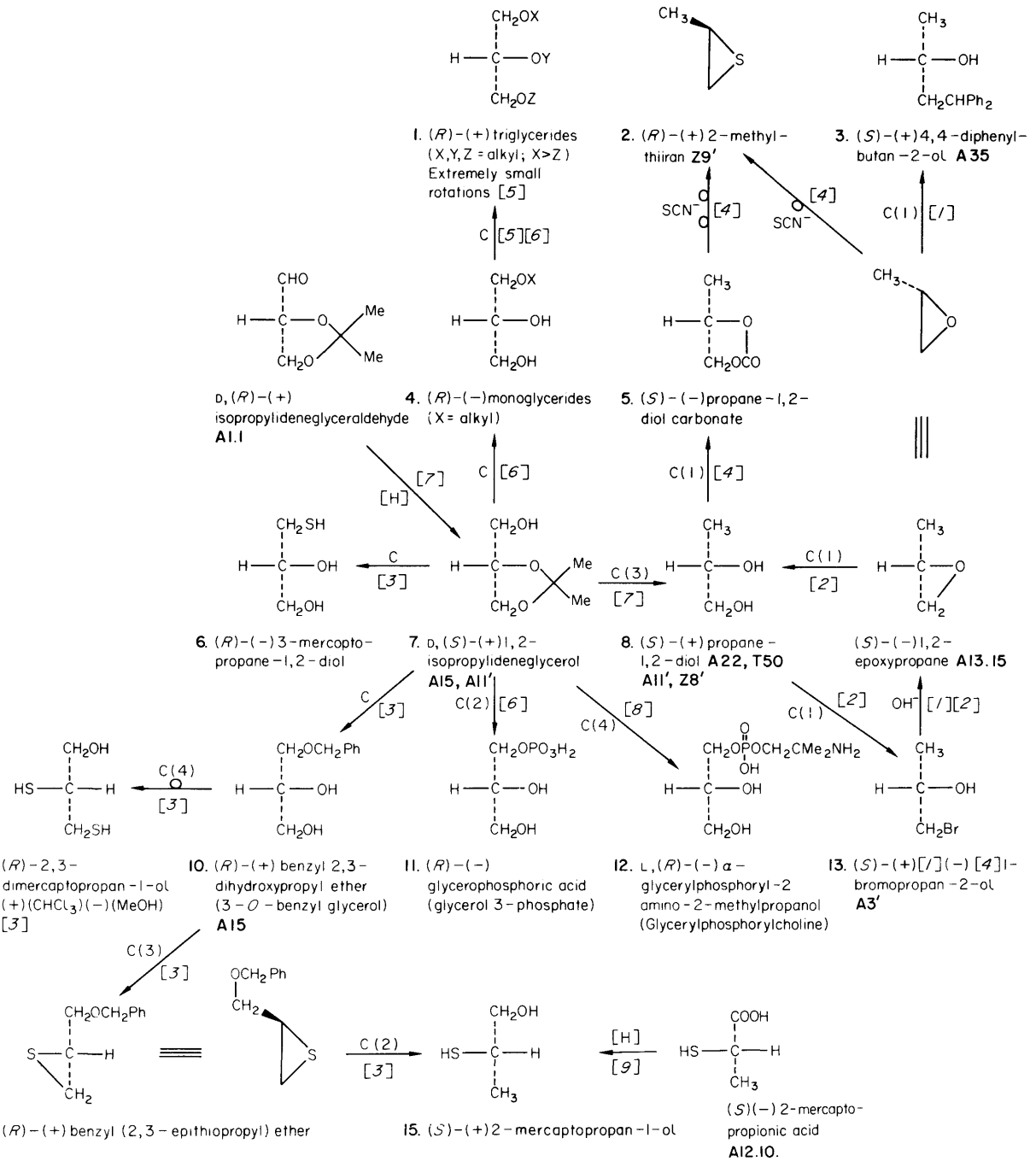

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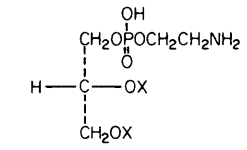
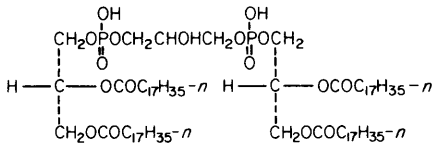
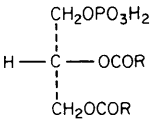


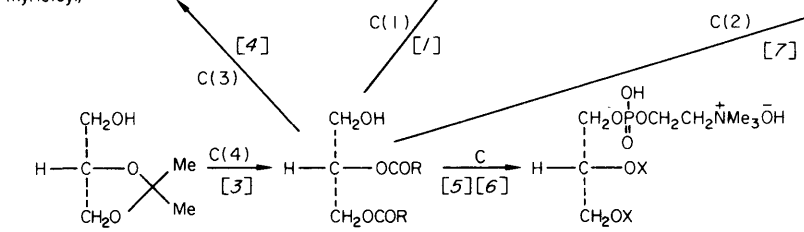
1. L,(*R*)-(+)α-cephalins (X=stearoyl, palmitoyl, myristoyl)



2. (+) cardiolipin (diphosphatidylglycerol)



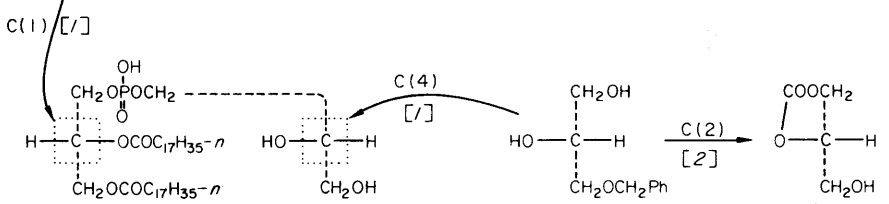
3. L,(*R*)-(+) phosphatidic acids (R=various alkyl groups [7])



D,(*S*)-(+)1,2-isopropylidene-glycerol **A14.7**

4. D,(*S*)-α,β-diglycerides [3]

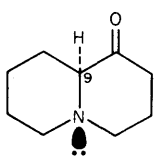
5. L,(*R*)-(+)α-lecithins (X = stearoyl, palmitoyl, myristoyl[5]; X = palmitoleyl[6])



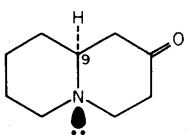
6. (+) phosphatidylglycerol

(*R*)-(+)3-*O* benzyl-glycerol **A14.10**

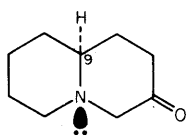
7. (*S*)-(−)glycerol-1,2-carbonate



8. (9*S*)-(−)1-oxo-quinolizidine. By CD [8] (octant rule)



9. (9*S*)-(+)2-oxo-quinolizidine. By CD [8] (octant rule)



10. (9*S*)-(+)3-oxo-quinolizidine. By CD [8] (octant rule)

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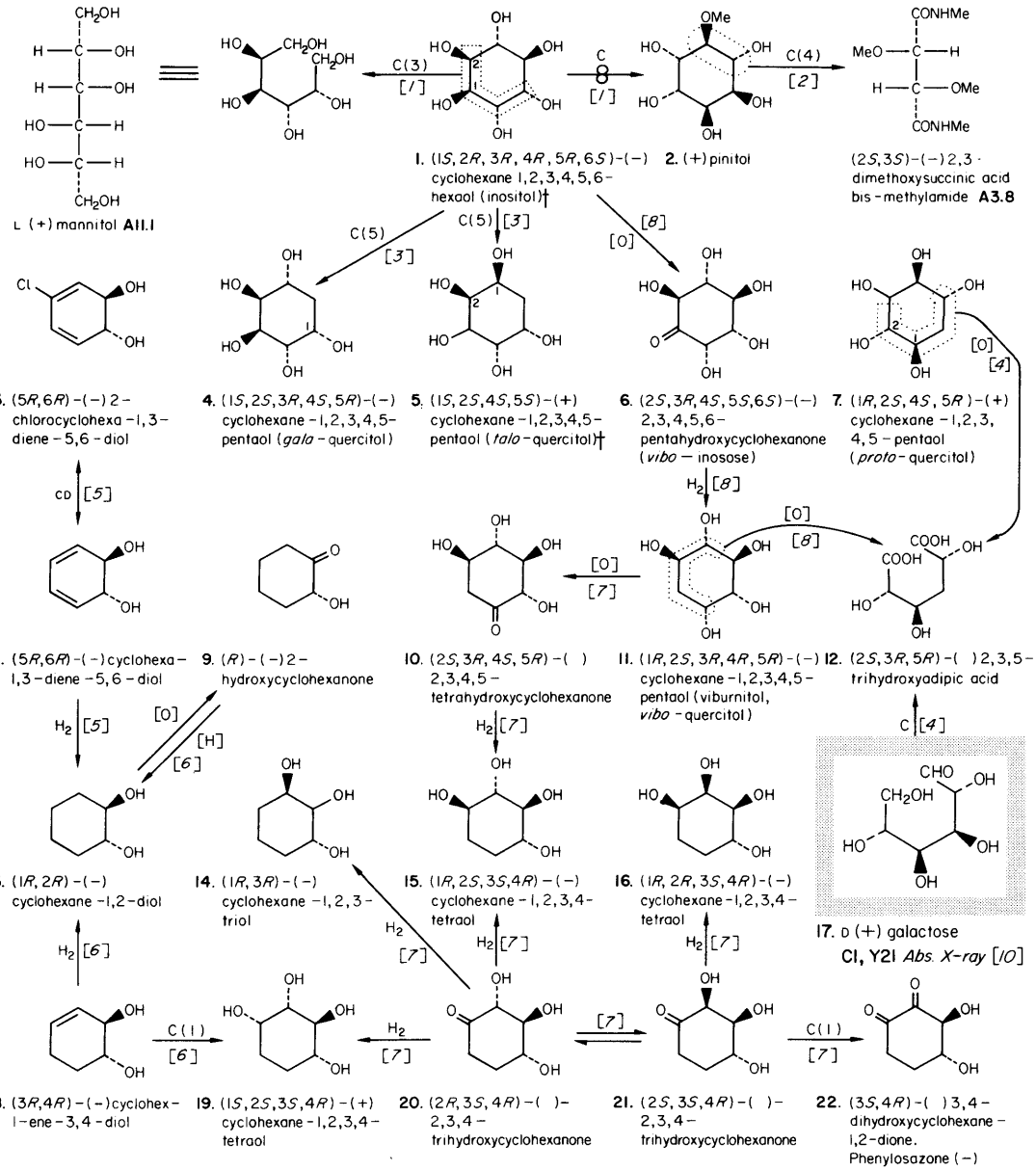
Reviews [9] (see also page A 26)



† For application of (*R,S*) nomenclature to these compounds see R. S. Cahn, C. K. Ingold and V. Prelog, *Angew. Chem. Internat. Edn.*, 1966, **5**, 385. The 'fractional' system of stereochemical nomenclature is frequently used in naming cyclitols, and is often more convenient than (*R,S*) nomenclature; the latter has been used here for consistency. For a description of the fractional system, see [9].

The following series of compounds closely related to the cyclitols, have also been studied in detail.

Cycloses (ketones derived from cyclitols by oxidation).

Amino analogues (M. Hichens & K. L. Rinehart, *J. Amer. Chem. Soc.*, 1963, **85**, 1547).

Halogeno derivatives (G. E. McCasland, S. Furuta and V. Bartuska, *J. Org. Chem.*, 1963, **28**, 2096).

Ethers (S. J. Angyal & L. Anderson, *Adv. Carbohydrate Chem.*, 1959, **14**, 135).

Many other cyclitols and derived compounds are themselves achiral, but are capable of giving rise to chiral derivatives when suitably substituted. One of the best studied examples is deoxystreptamine, which occurs as substitution products in antibiotics of the Kanamycin-neomycin type. See p. C3 and also M. Hichens and K. L. Rinehart, *J. Amer. Chem. Soc.*, 1963, **85**, 1547.

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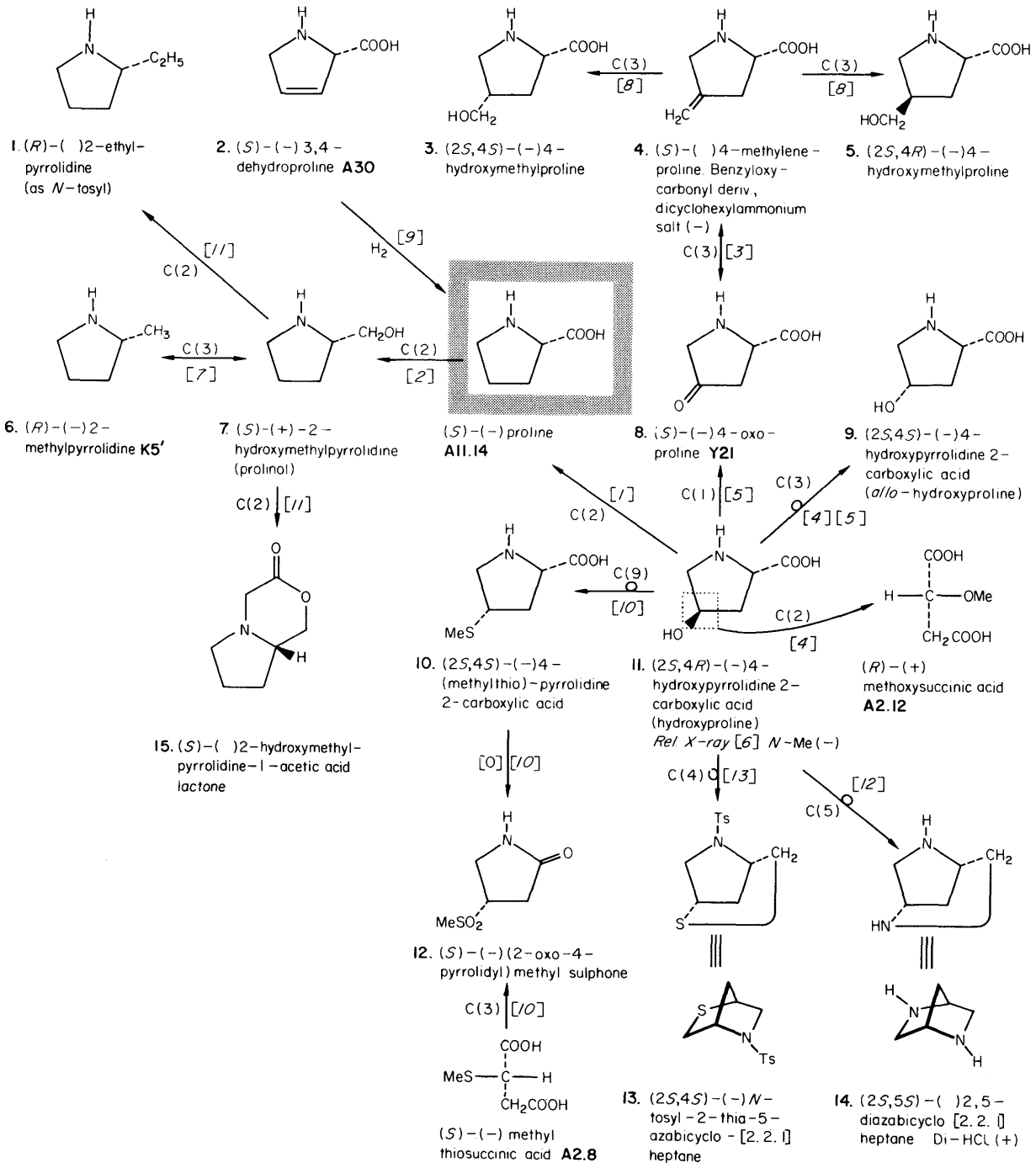

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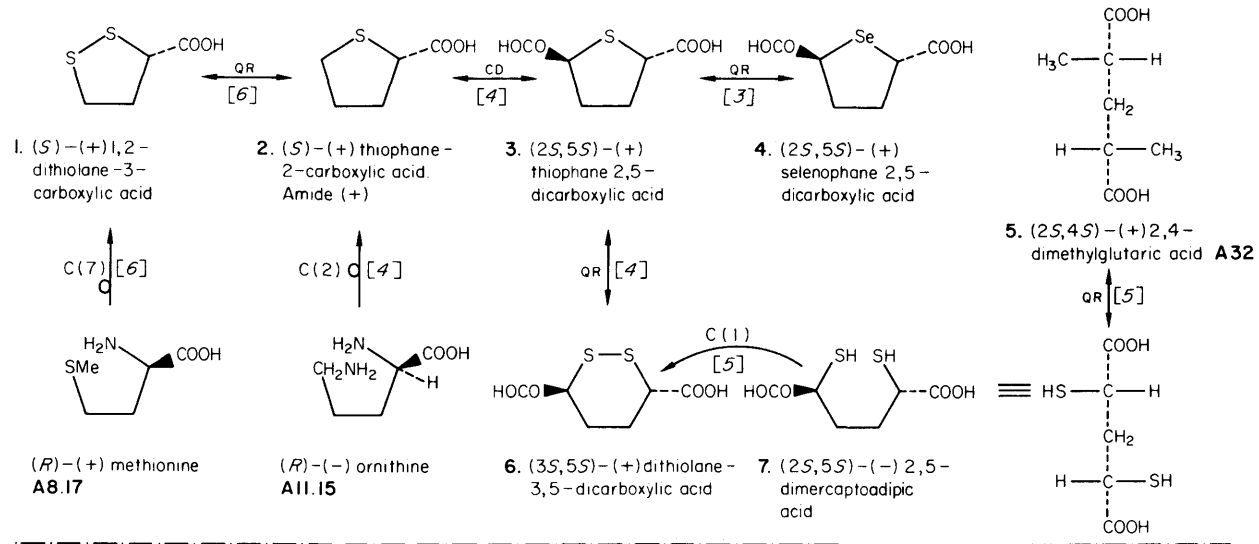
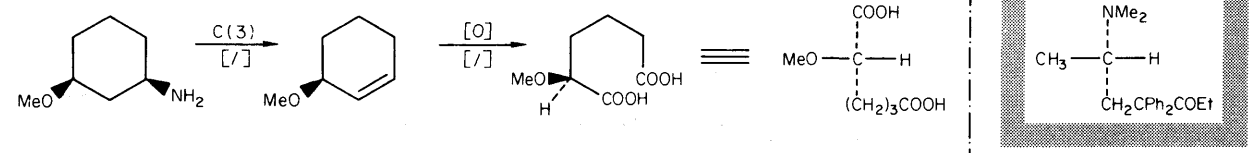


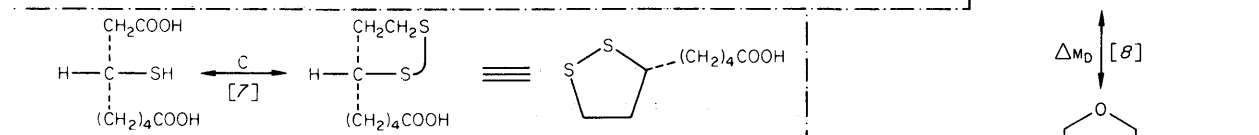
1. (*S*)-(+)1,2-dithiolane-3-carboxylic acid
2. (*S*)-(+) thiophane-2-carboxylic acid. Amide (+)
3. (2*S*,5*S*)-(+) thiophane 2,5-dicarboxylic acid
4. (2*S*,5*S*)-(+) selenophane 2,5-dicarboxylic acid
5. (2*S*,4*S*)-(+)2,4-dimethylglutaric acid **A32**
6. (3*S*,5*S*)-(+)dithiolane-3,5-dicarboxylic acid
7. (2*S*,5*S*)-(−) 2,5-dimercaptoadipic acid

(*R*)-(+) methionine **A8.17**

(*R*)-(−) ornithine **A11.15**

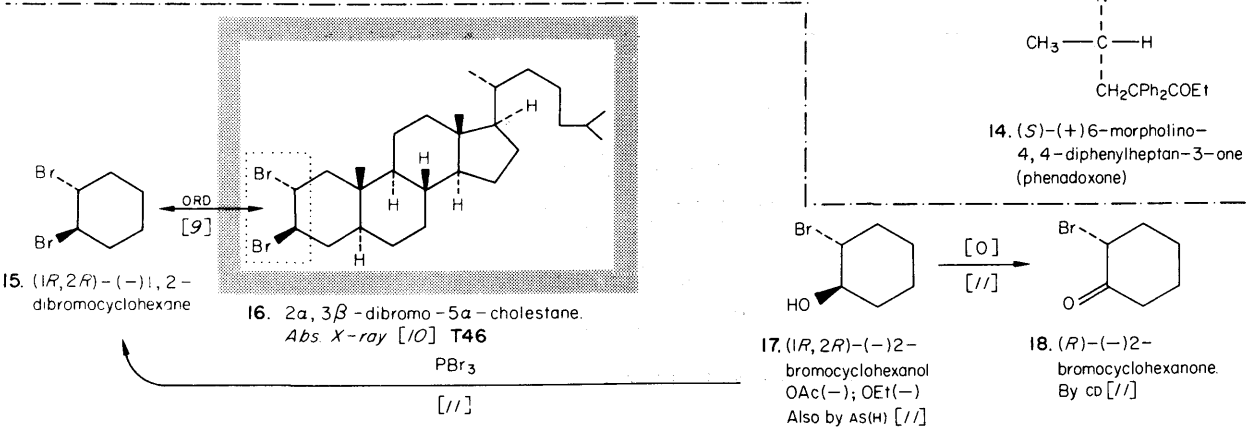


8. (1*R*,3*S*)-(−)3-methoxycyclohexylamine **A38**
9. (*S*)-(−)3-methoxycyclohexene
10. (*S*)-(−) 2-methoxyadipic acid
11. (*S*)-(+)6-dimethylamino-4,4-diphenylheptan-3-one (methadone) *Abs. X-ray*[2]



12. (*R*)-(−)3-mercapto-octanedioic acid **A32**
13. (*R*)-(+)α-lipoic acid

14. (*S*)-(+)6-morpholino-4,4-diphenylheptan-3-one (phenadoxone)



15. (1*R*,2*R*)-(−)1,2-dibromocyclohexane
16. 2α,3β-dibromo-5α-cholestane. *Abs. X-ray* [10] **T46**
17. (1*R*,2*R*)-(−)2-bromocyclohexanol OAc(−); OEt(−) Also by AS(H) [11]
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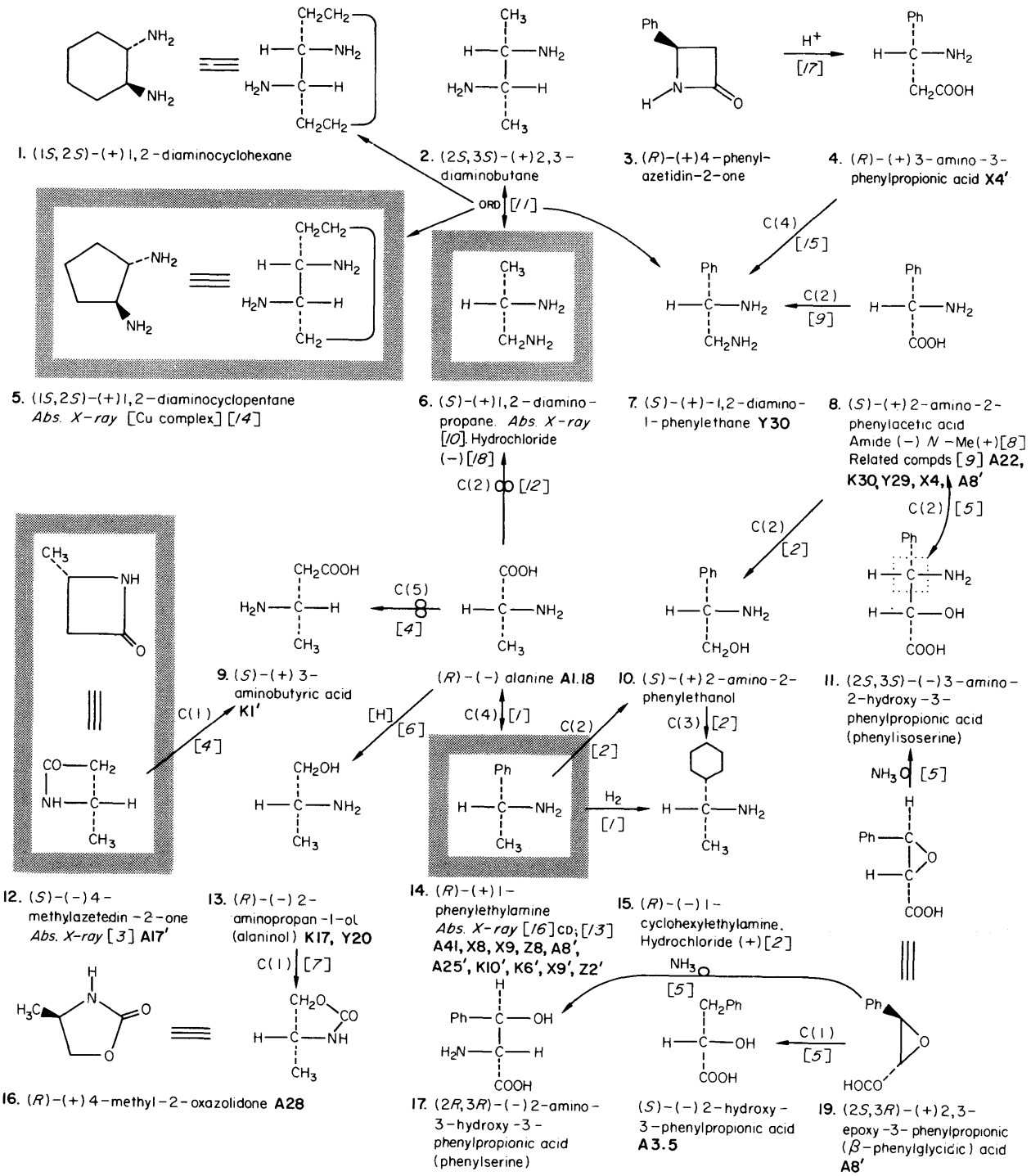

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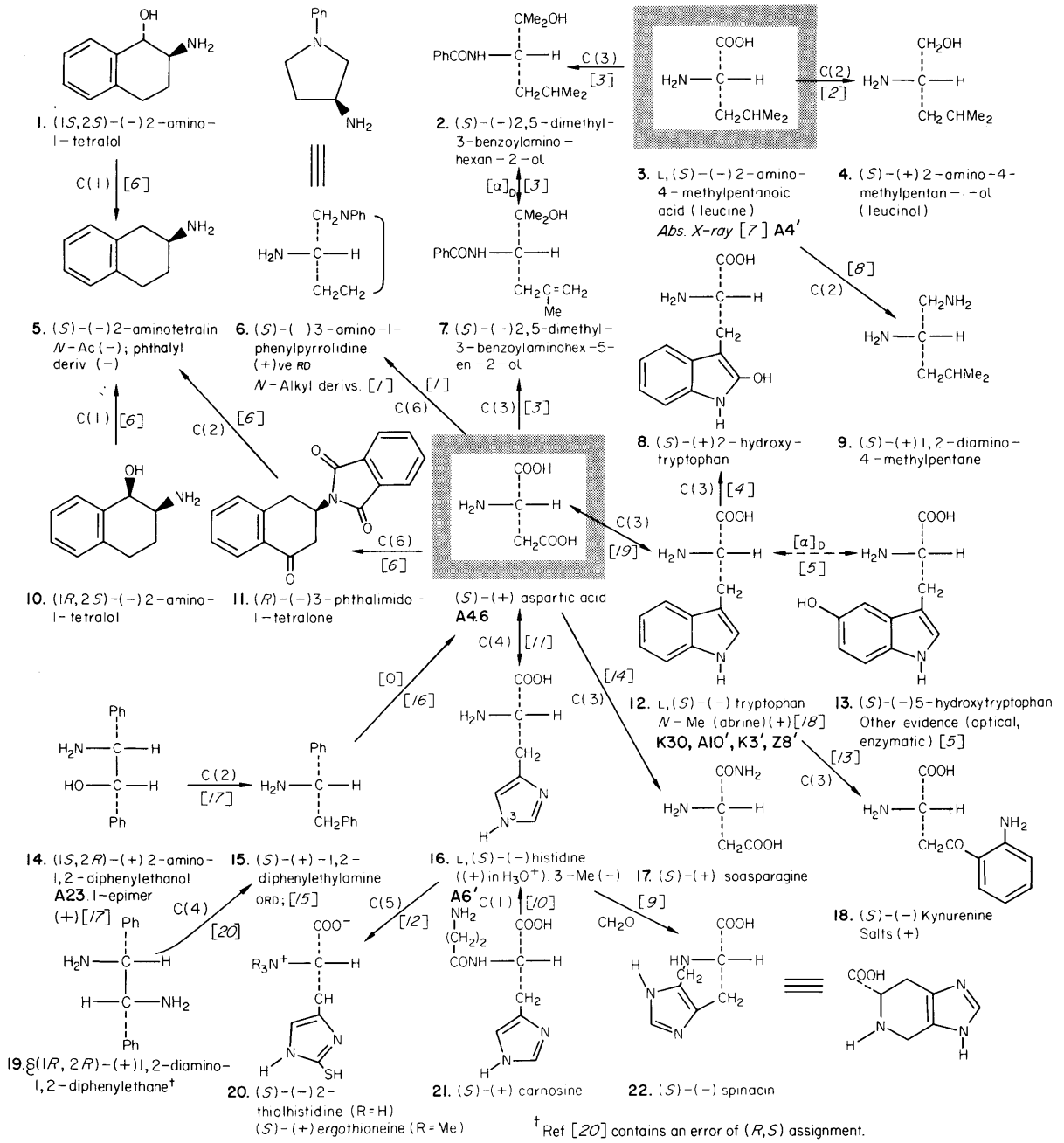

† Ref [20] contains an error of (R,S) assignment.

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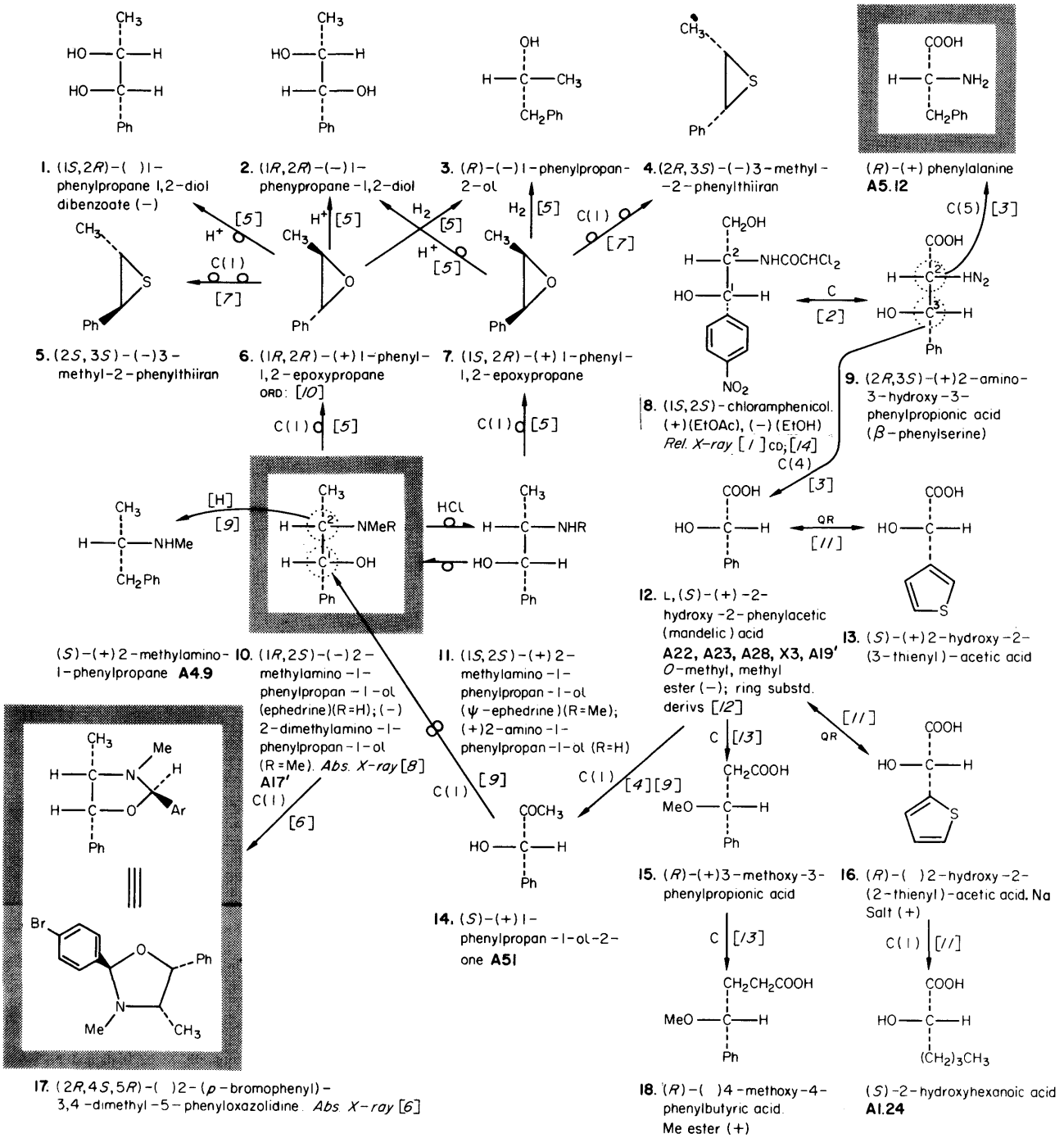

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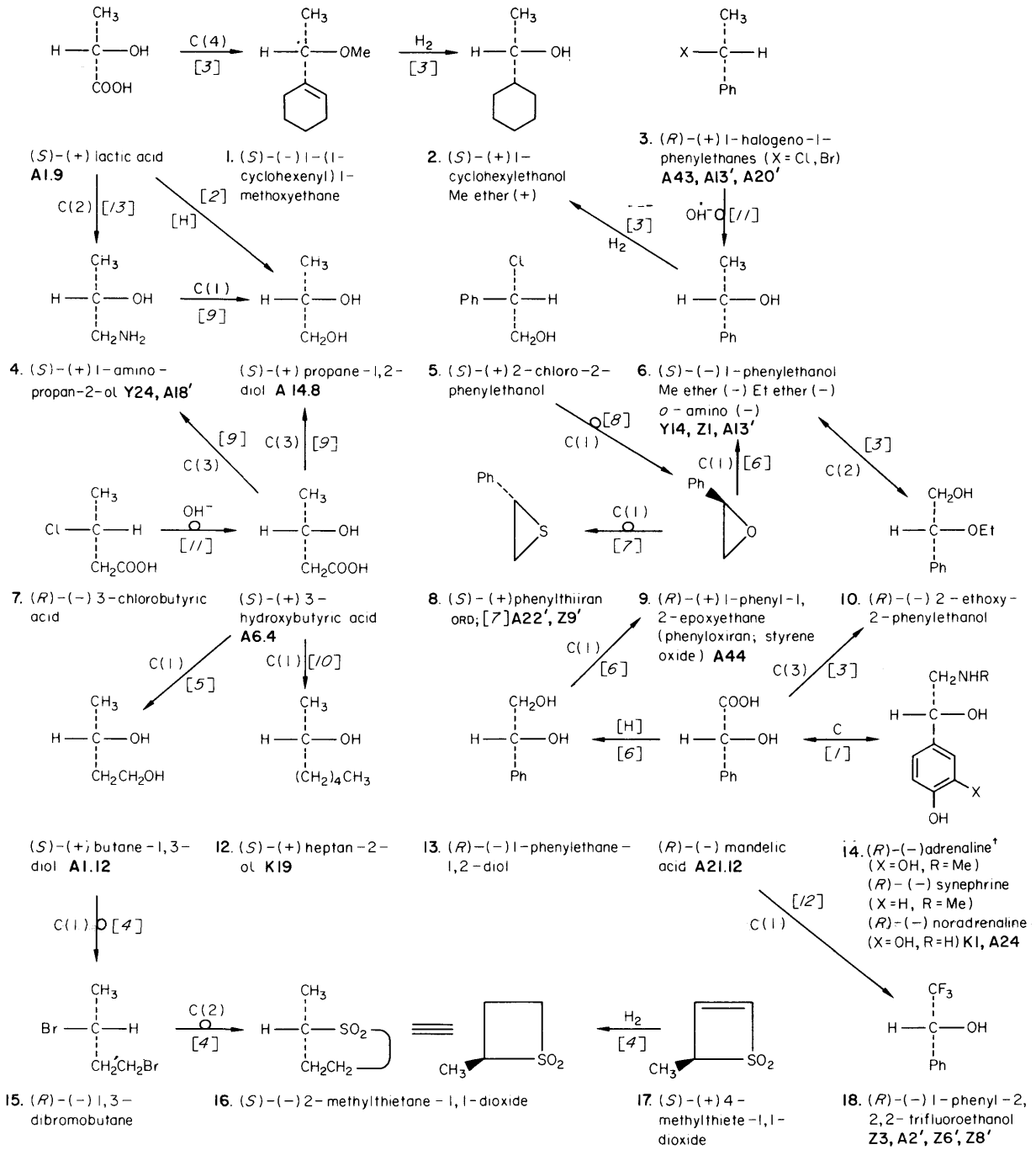

†Ambiguity of D,L-nomenclature; [14]

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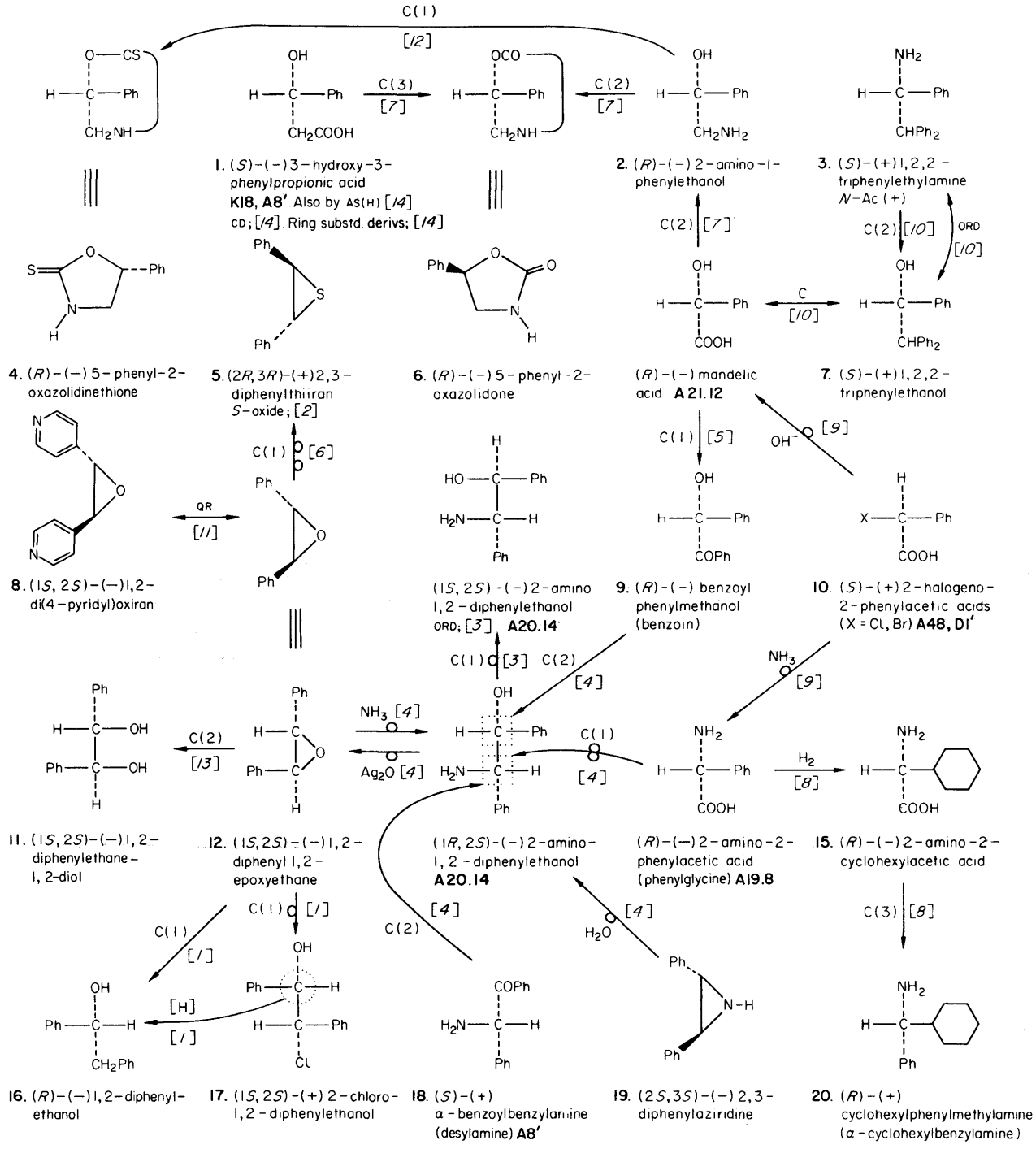

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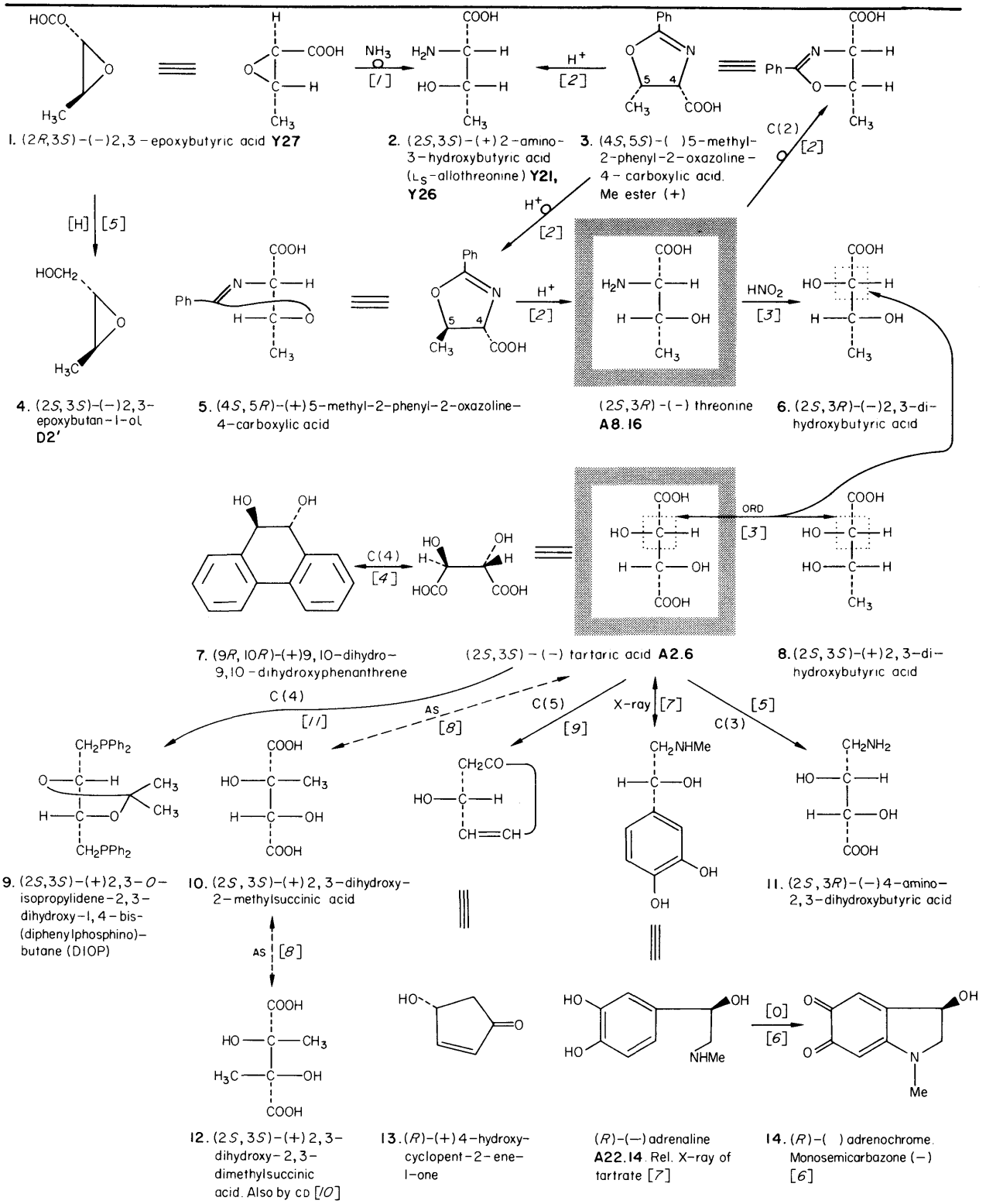

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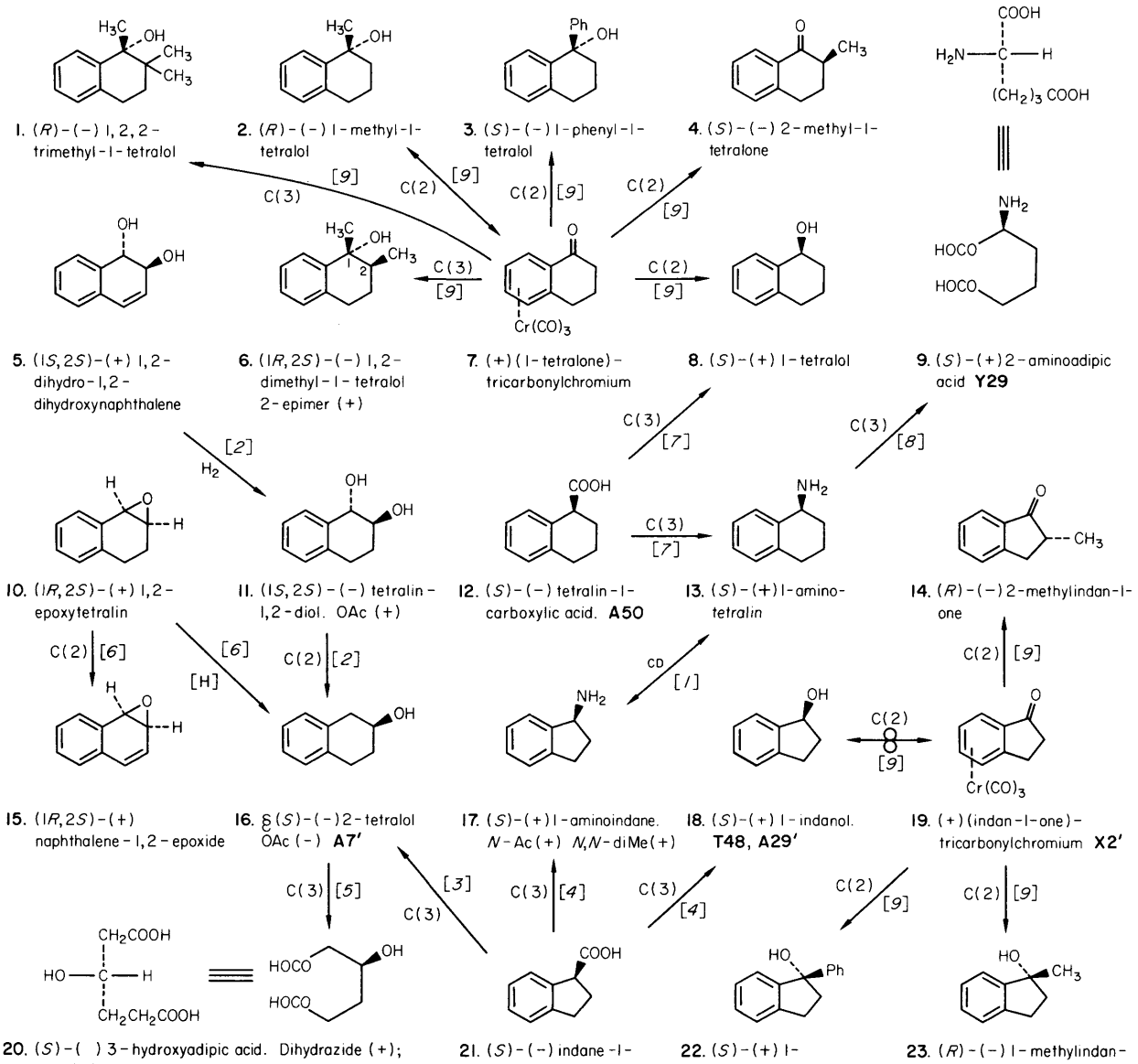

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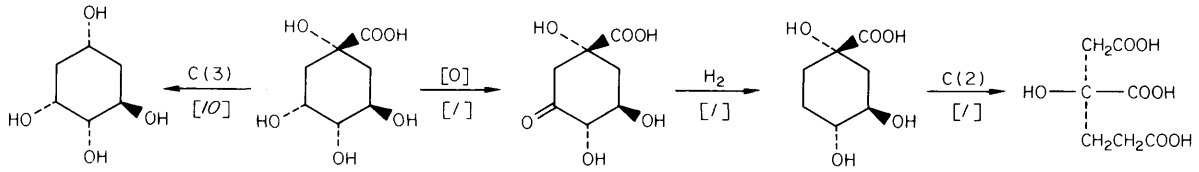


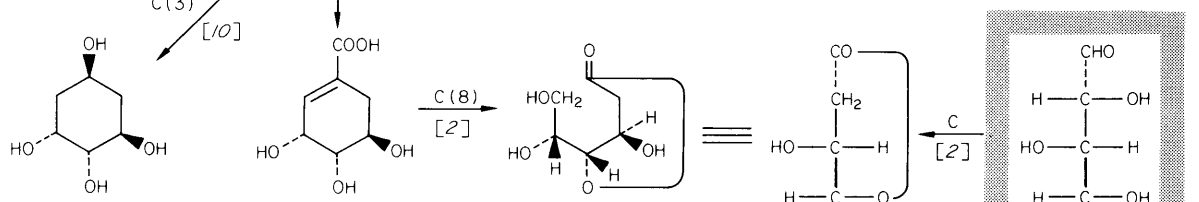
1. (1*R*,2*S*,3*R*,5*R*)-(−) cyclohexane-1,2,3,5-tetraol†

2. (−) Quinic acid **A33, A40.** Stereoisomers; [7]

3. (−) 5-dehydroquinic acid

4. (1*S*,3*R*,4*R*)-(−)1,3,4-trihydroxycyclohexane-carboxylic acid (5-deoxyquinic acid)

5. (*S*)-( )2-hydroxybutane-1,2,4-tricarboxylic (homocitric) acid. Lactone (+)

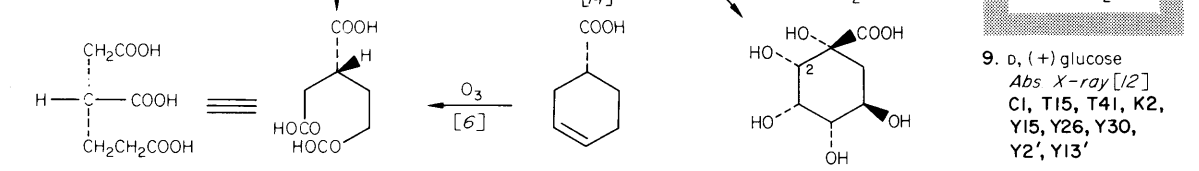


6. (1*R*,2*S*,3*R*,5*S*)-(−) cyclohexane-1,2,3,5-tetraol†

7. (−) Shikimic acid

8. (+) 2-deoxy-D-gluconolactone

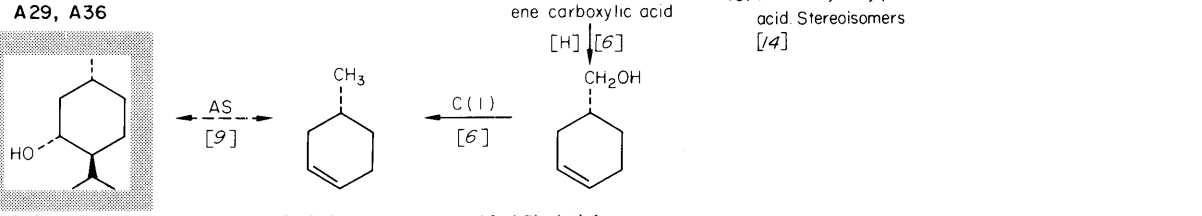
9. D, (+) glucose
Abs. X-ray [12]
C1, T15, T41, K2, Y15, Y26, Y30, Y2′, Y13′



10. (*R*)-(+) butane-1,2,4-tricarboxylic acid
A29, A36

11. (*R*)-(+) cyclohex-3-ene carboxylic acid

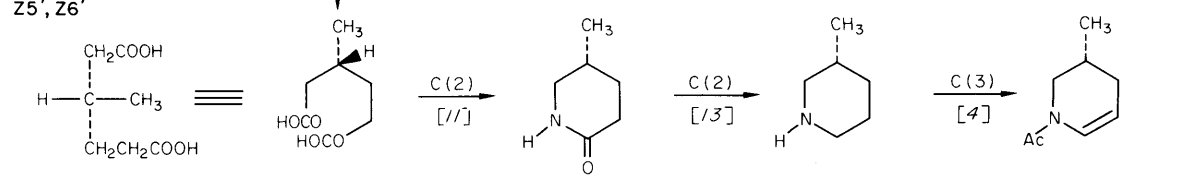
19. (−)-2-hydroxyquinic acid. Stereoisomers [14]



12. (−) menthol
Abs. X-ray [5]
A35, A54, T3, T4, X1, Z4, A44, Z2′, Z5′, Z6′

13. (*R*)-(+)4-methylcyclohexene
Z3, A24′

14. (*R*)-(+)4-hydroxymethylcyclohexene



15. (*R*)-(+) 3-methyladipic acid
A27, A32, A39, T1, Y17, Y27

16. (*R*)-(+) 5-methyl-2-piperidone
N-Me (+) **T49, K35**

17. (*R*)-(−) 3-methyl-piperidine
N-Me (+) **K35**

18. (*R*)-(−) 1-acetyl-3-methyl-1,2,3,4-tetrahydropyridine

† Application of (*R,S*) nomenclature to these compounds; see R. S. Cahn, C. K. Ingold and V. Prelog, *Angew. Chem. Internat. Edn.*, 1966, **5**, 385.

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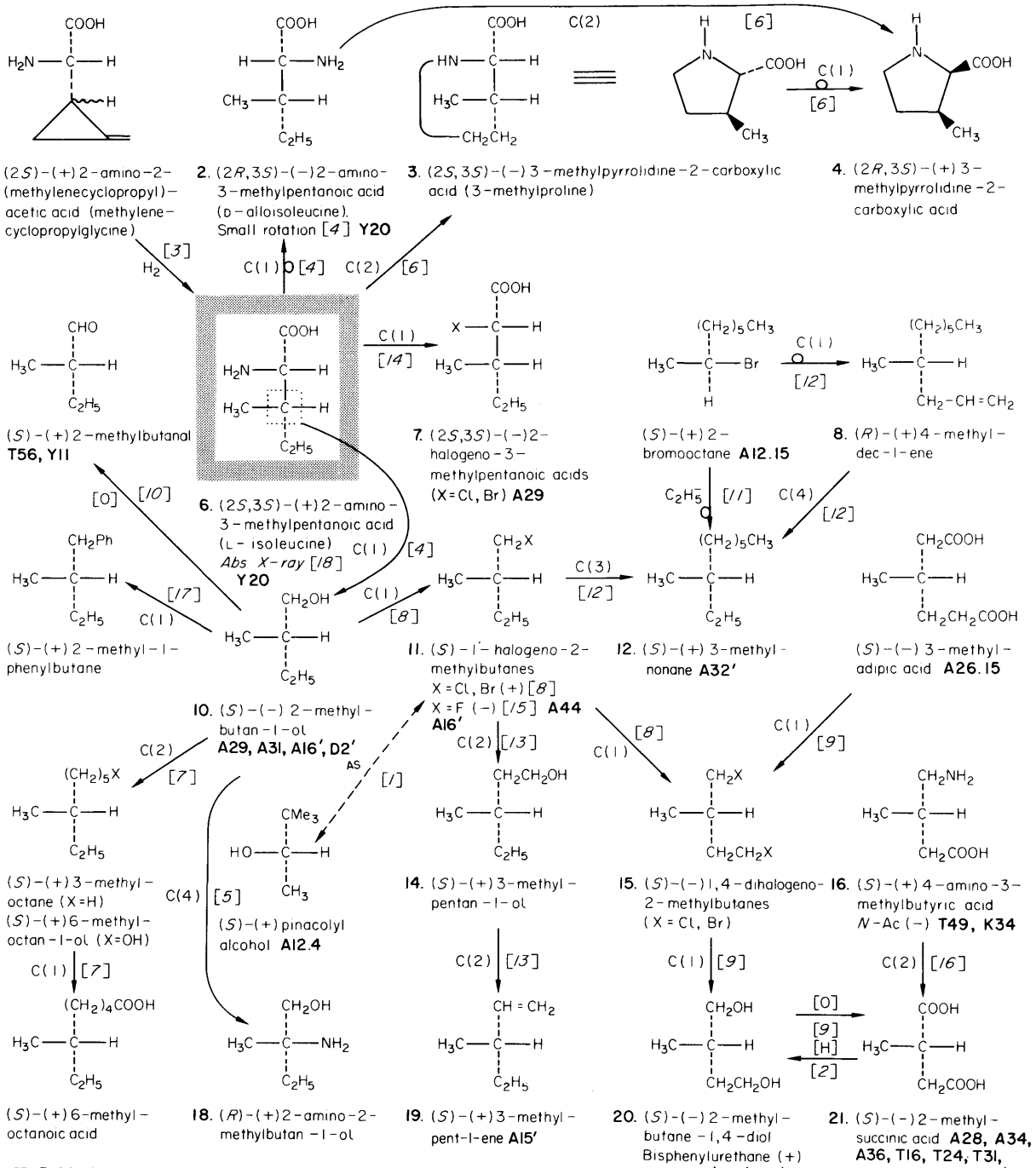

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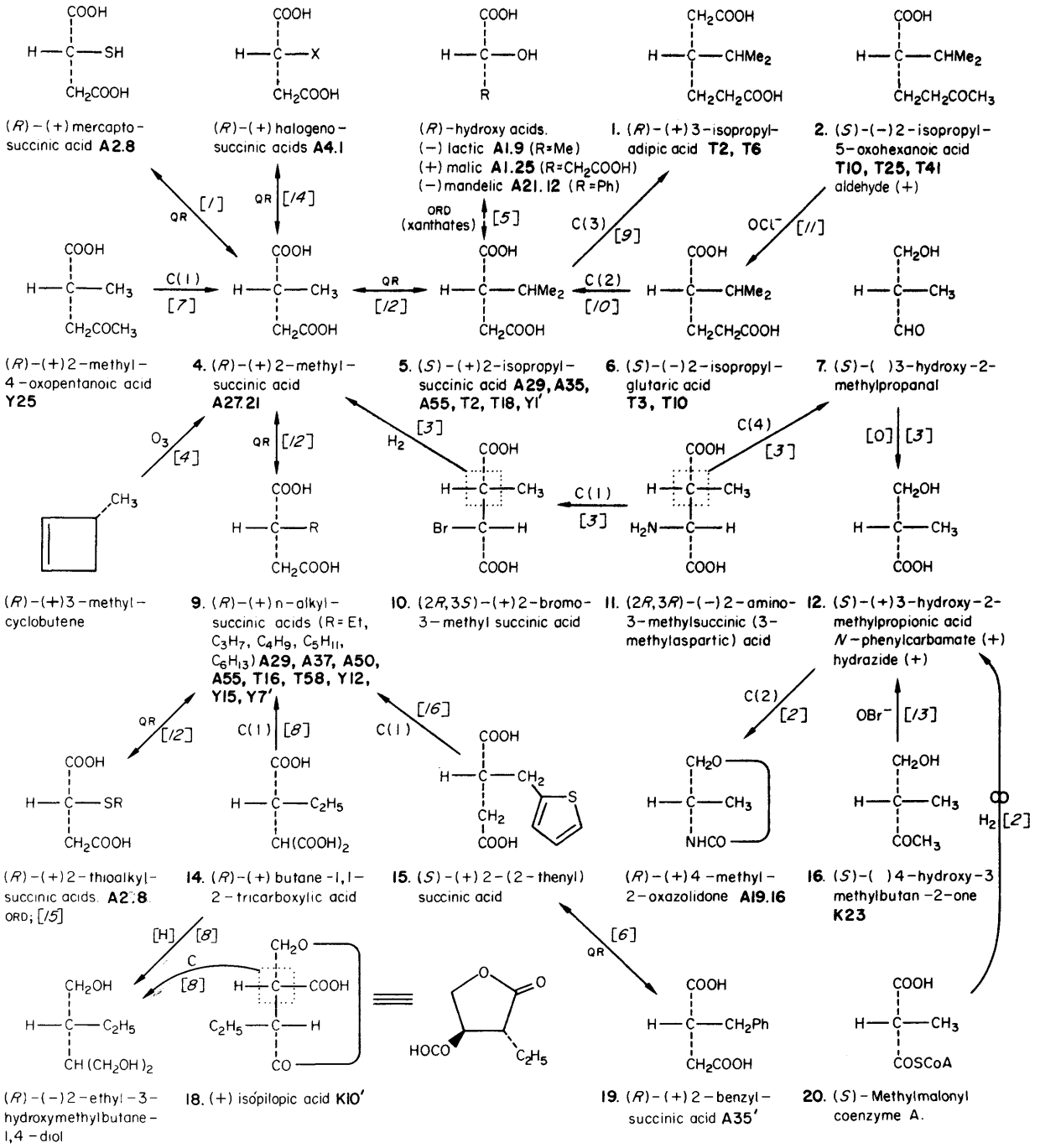

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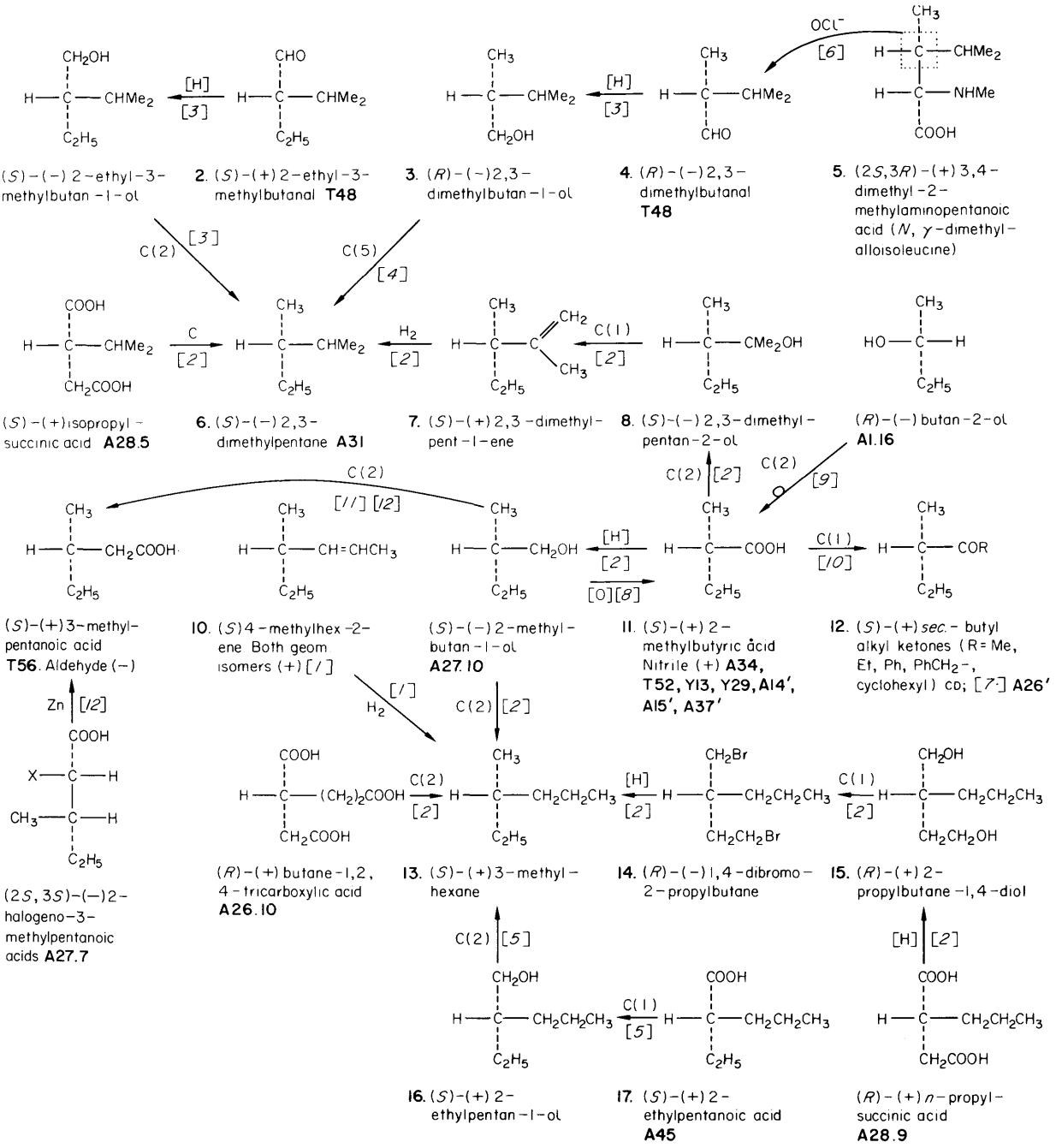

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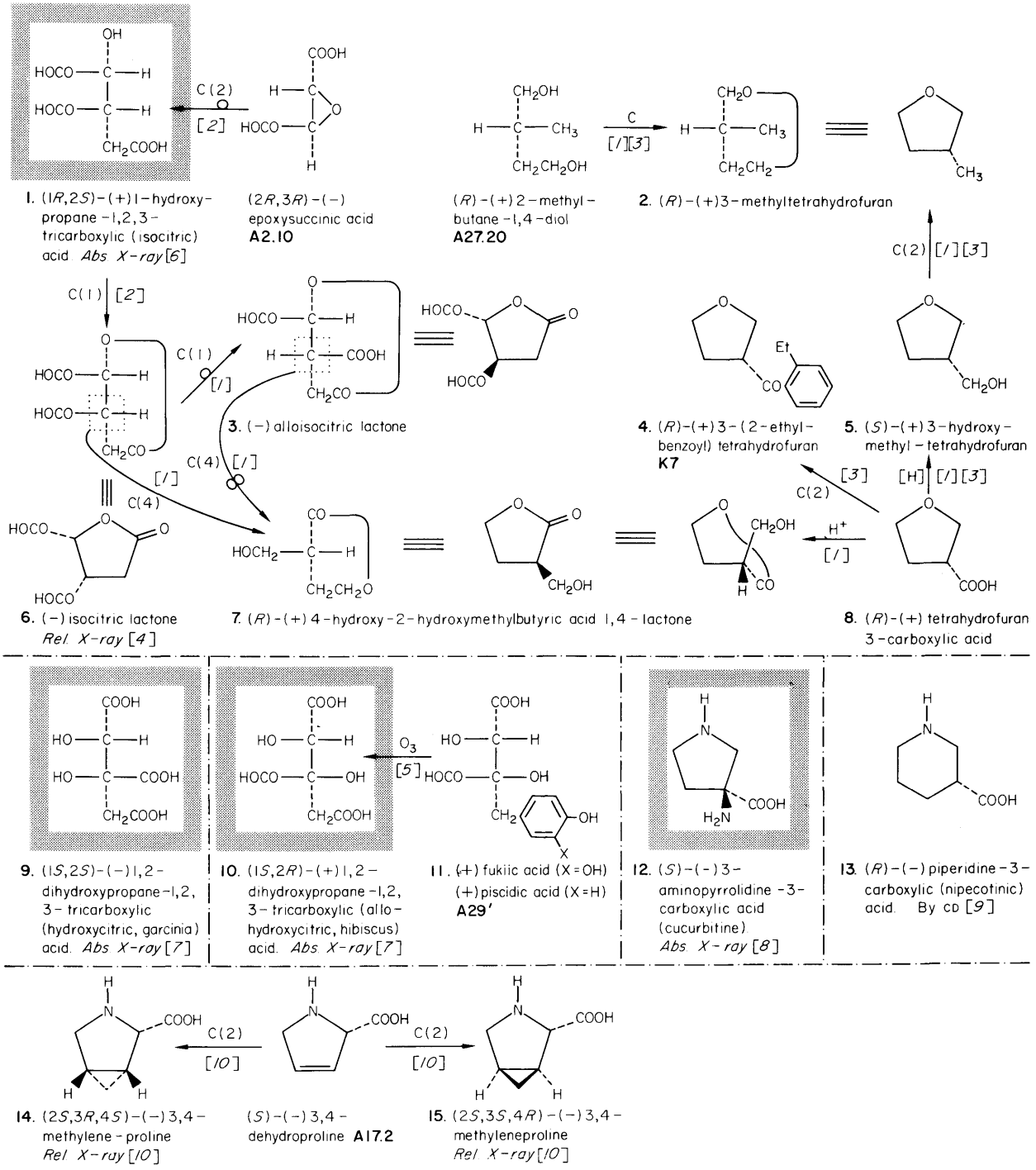

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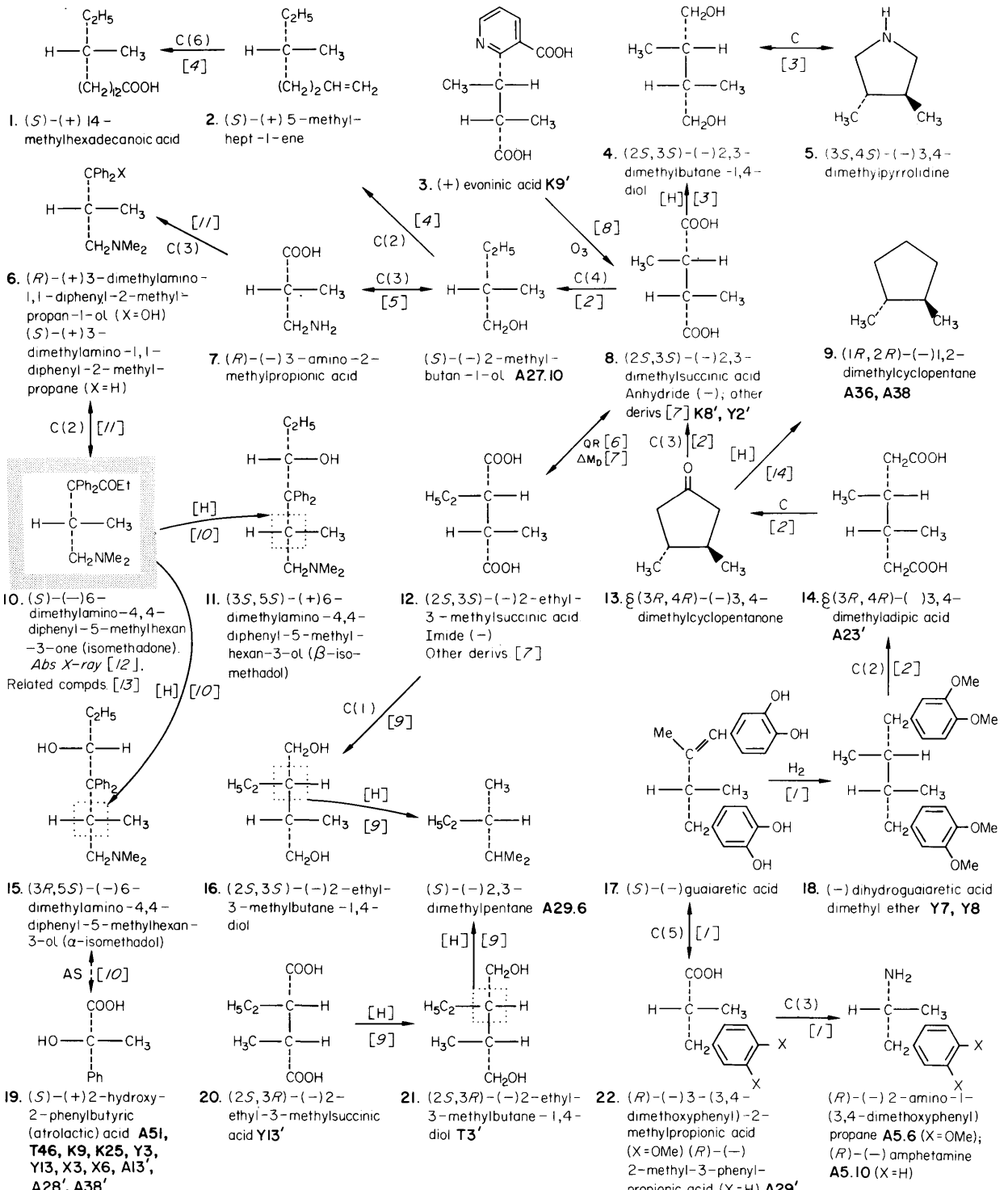

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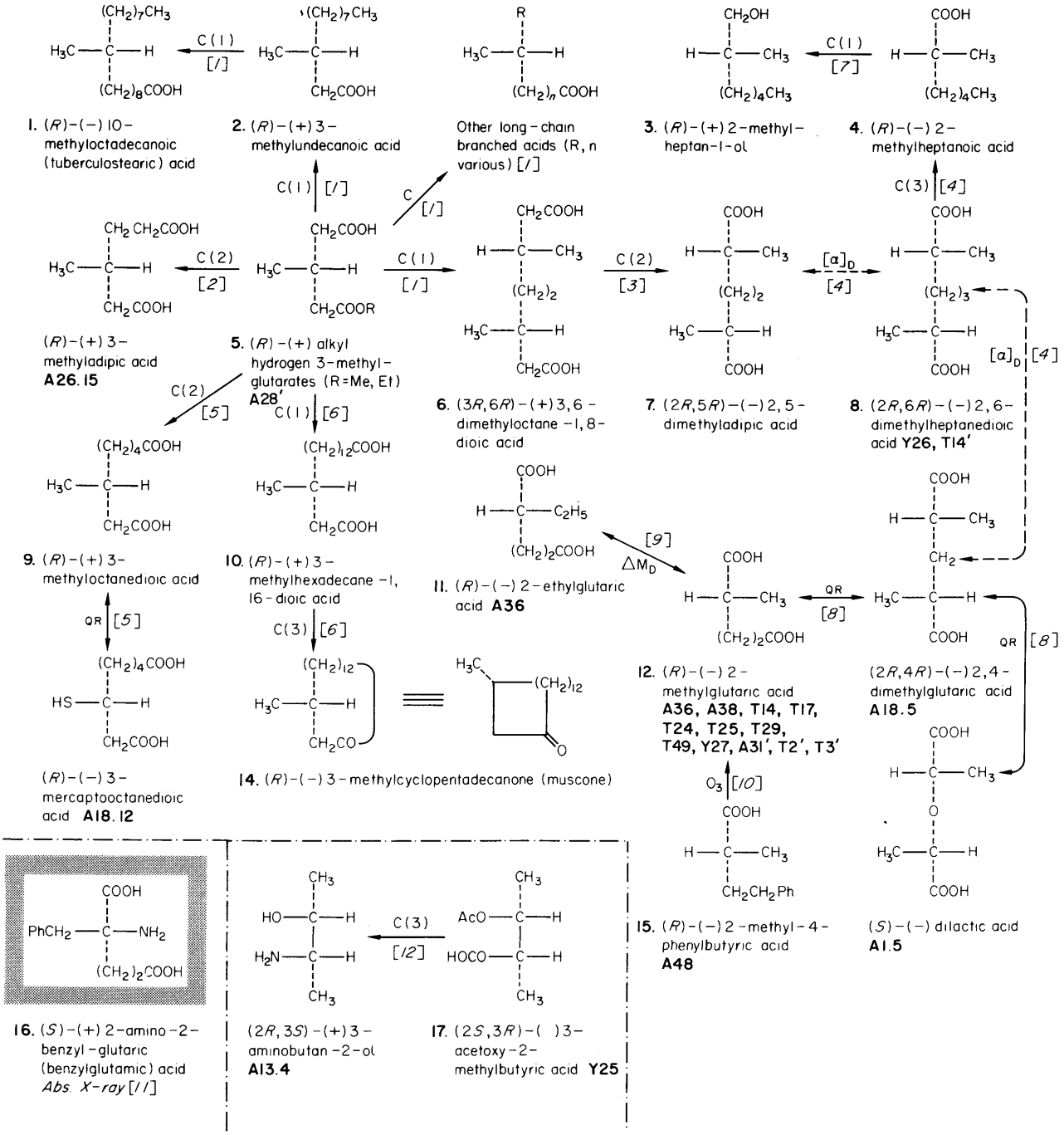

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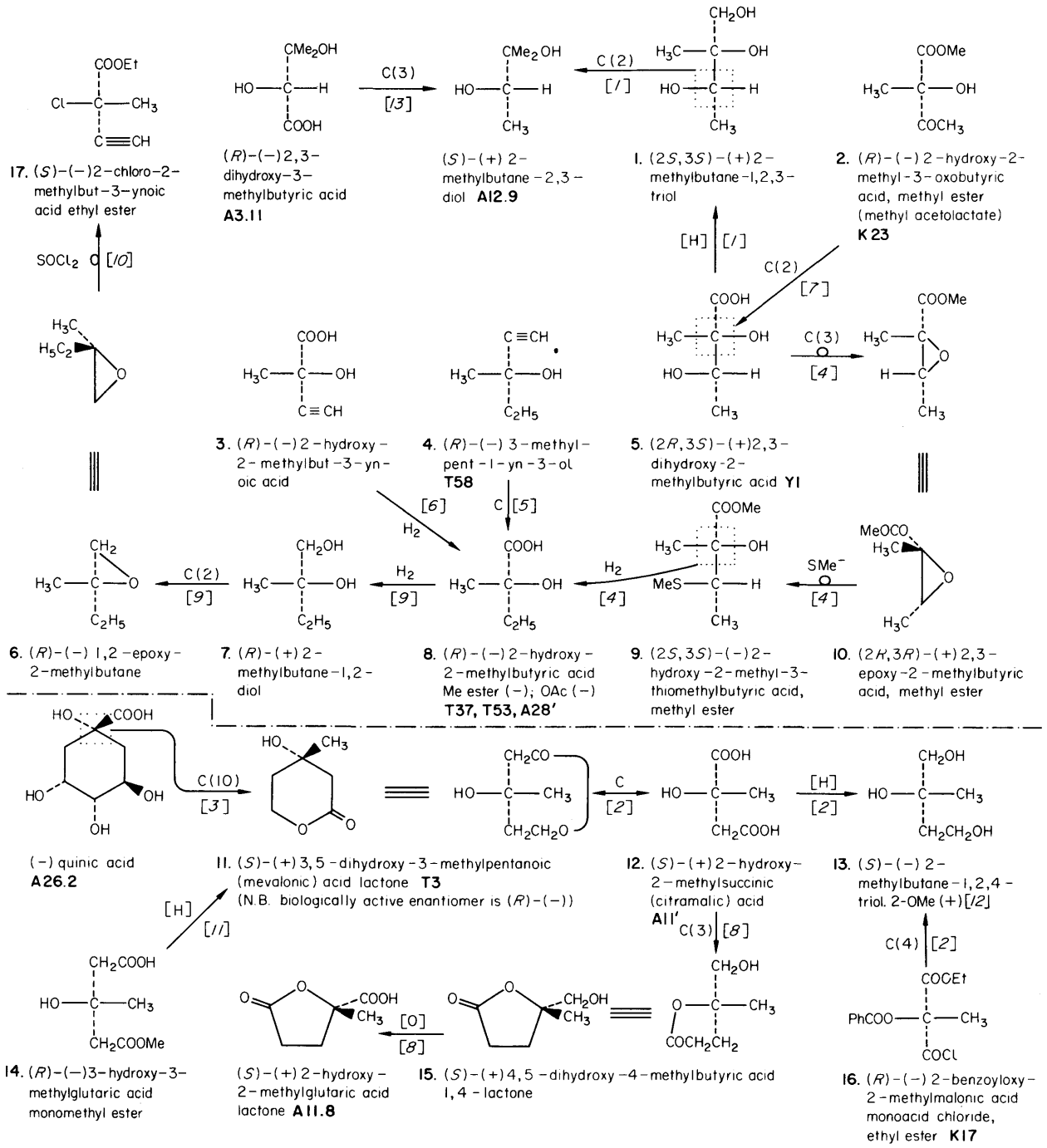

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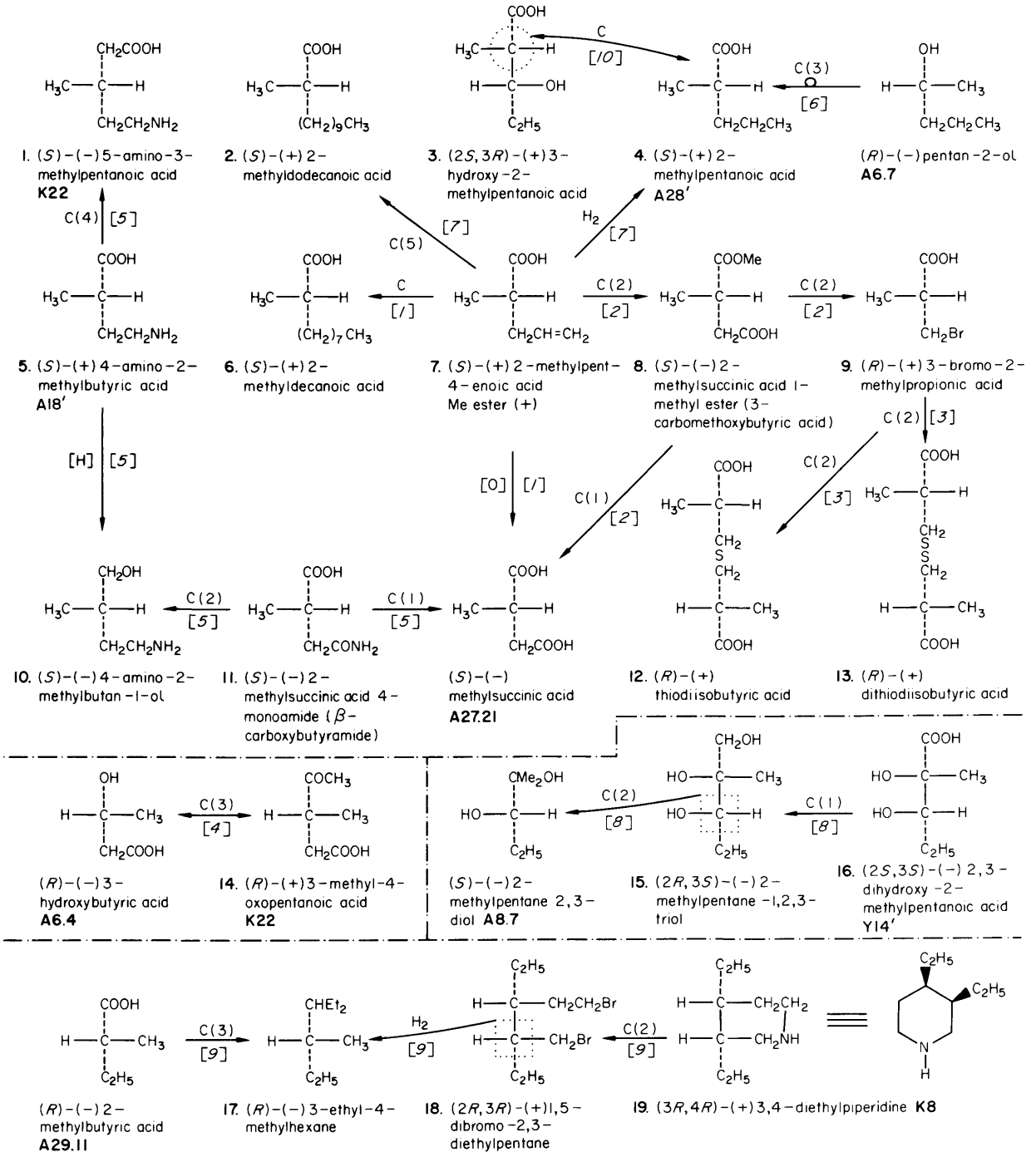

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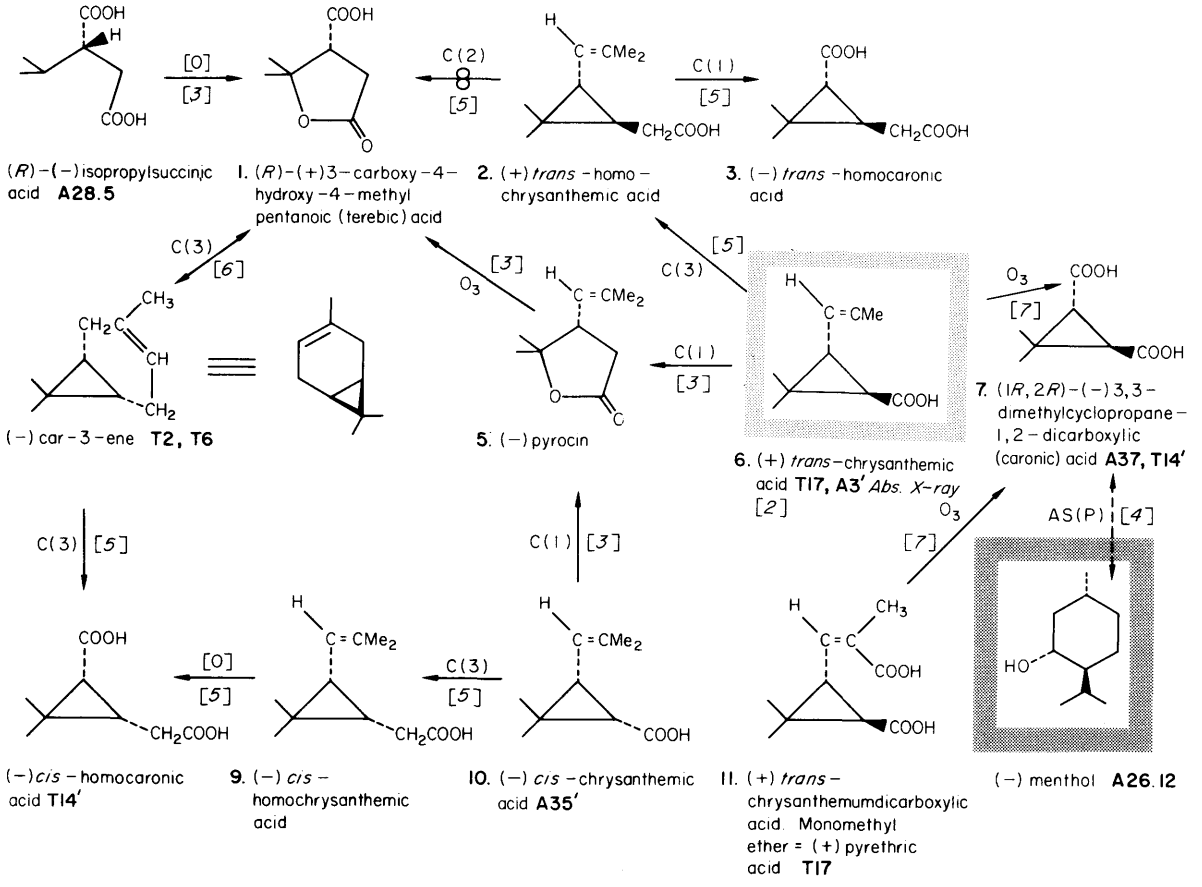


(*R*)-(−)isopropylsuccinic acid **A28.5**

1. (*R*)-(+)3-carboxy-4-hydroxy-4-methyl pentanoic (terebic) acid

2. (+) *trans*-homo-chrysanthemic acid

3. (−) *trans*-homocaronic acid

4. (−) car-3-ene **T2, T6**

5. (−) pyrocin

6. (+) *trans*-chrysanthemic acid **T17, A3′** *Abs. X-ray* [2]

7. (1*R*, 2*R*)-(−) 3,3-dimethylcyclopropane-1,2-dicarboxylic (caronic) acid **A37, T14′**

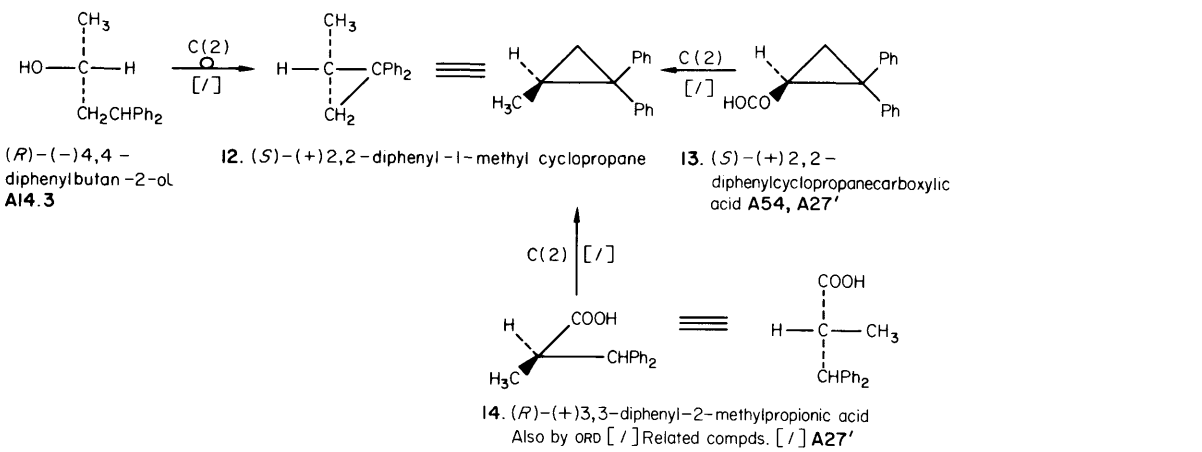
8. (−) *cis*-homocaronic acid **T14′**

9. (−) *cis*-homochrysanthemic acid

10. (−) *cis*-chrysanthemic acid **A35′**

11. (+) *trans*-chrysanthemumdicarboxylic acid. Monomethyl ether = (+) pyrethric acid **T17**

(−) menthol **A26.12**



(*R*)-(−)4,4-diphenylbutan-2-ol **A14.3**

12. (*S*)-(+)2,2-diphenyl-1-methyl cyclopropane

13. (*S*)-(+)2,2-diphenylcyclopropanecarboxylic acid **A54, A27′**

14. (*R*)-(+)3,3-diphenyl-2-methylpropionic acid
Also by ORD [/] Related compds. [/] **A27′**

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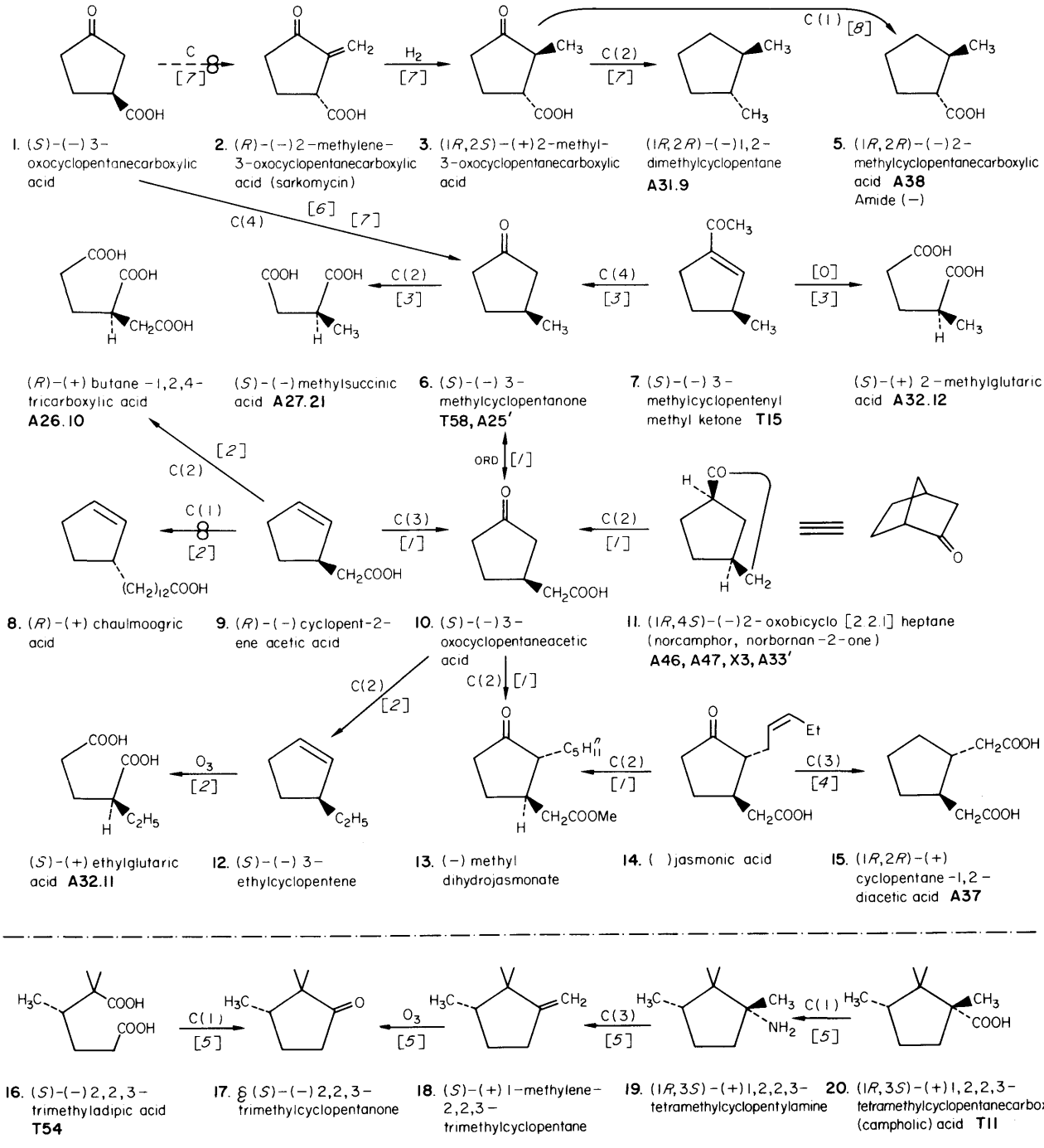

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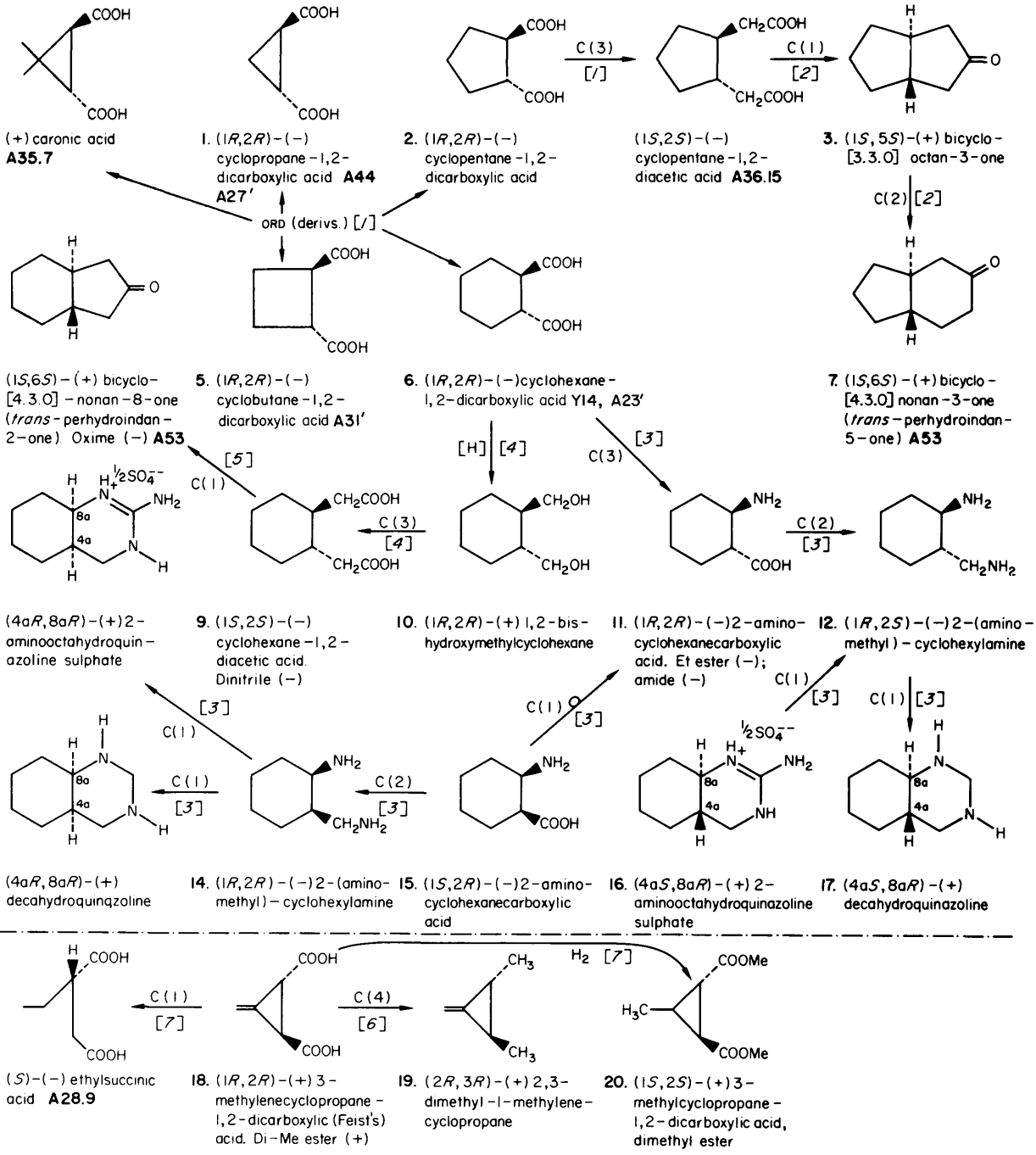

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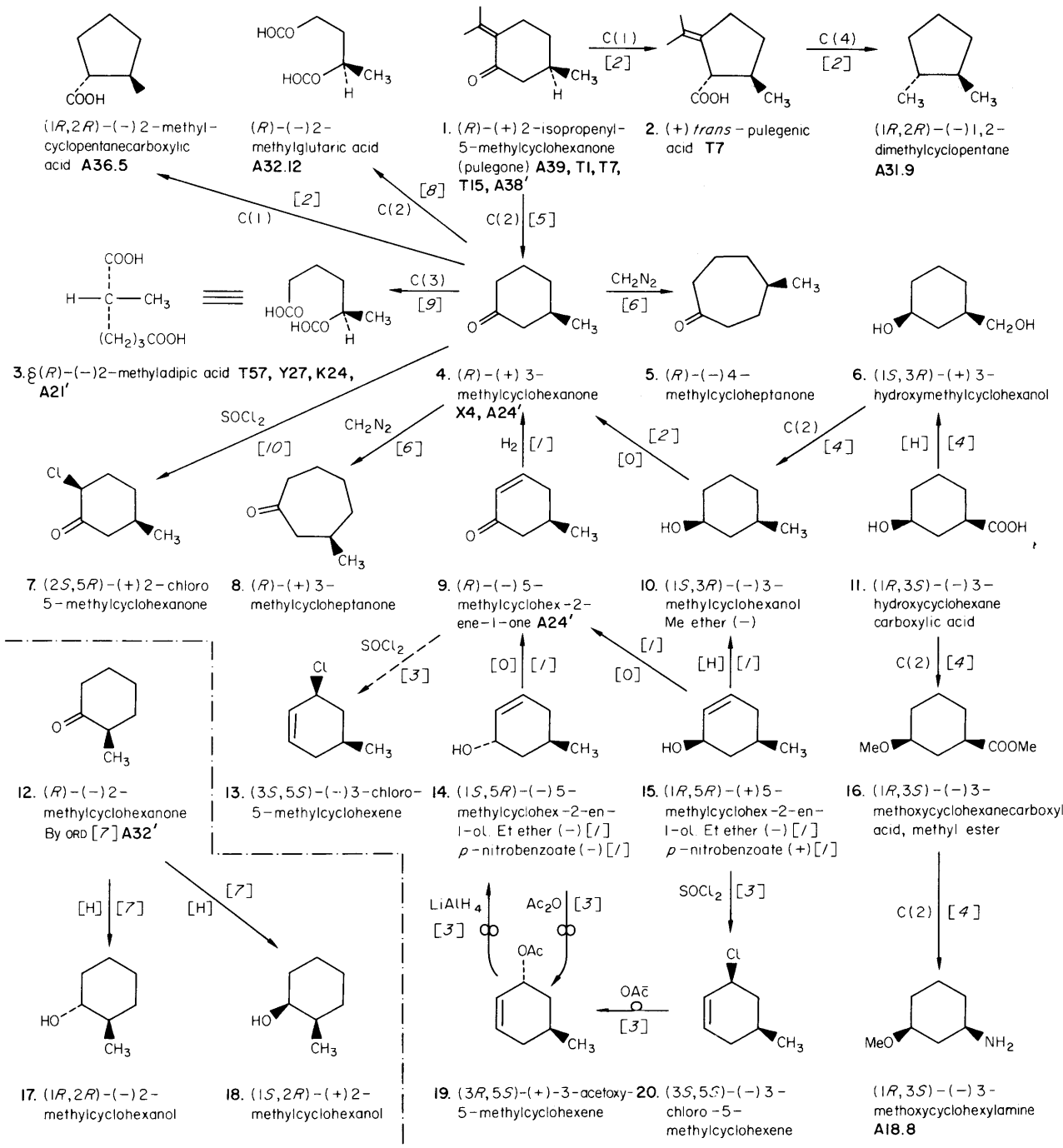

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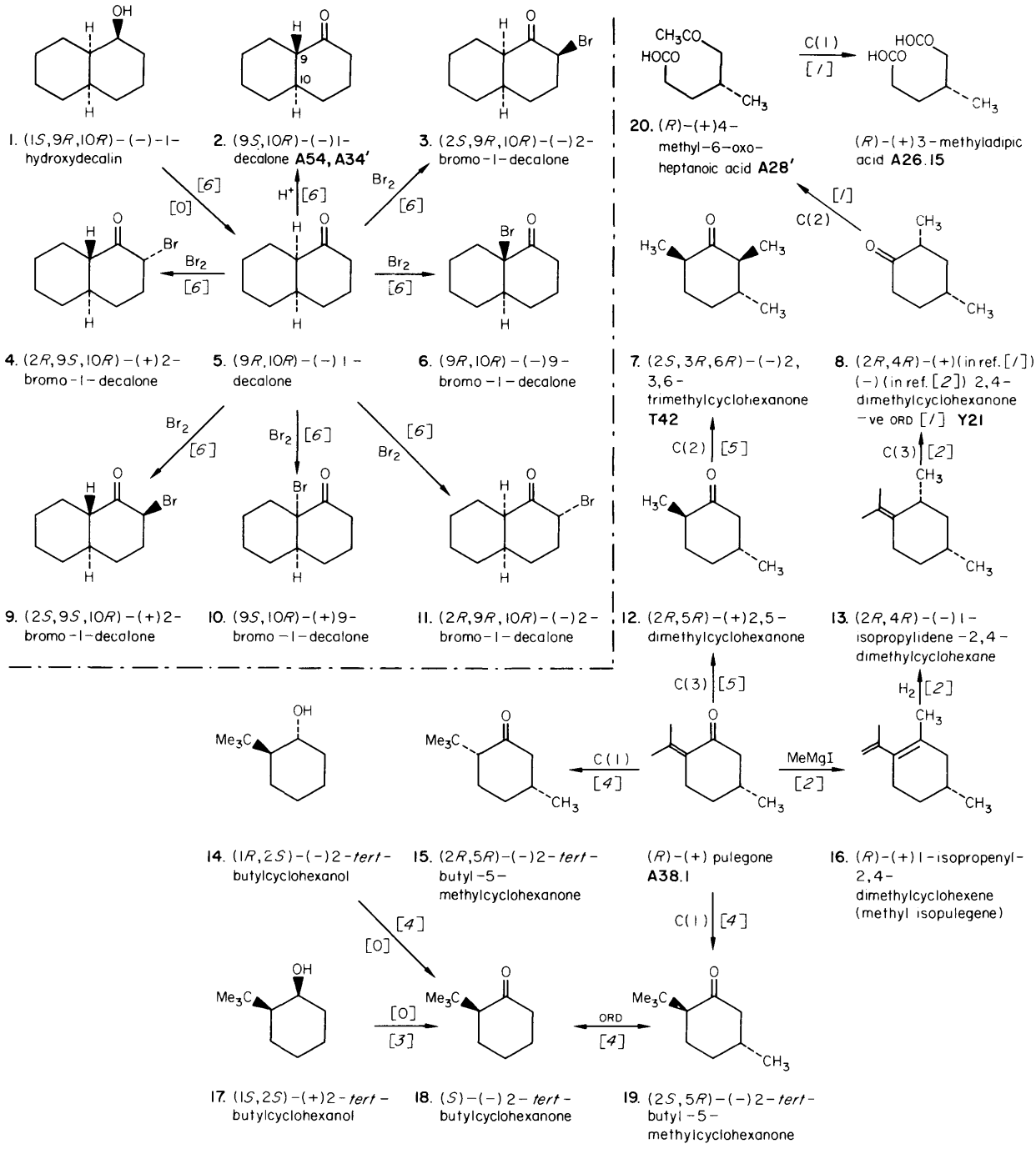

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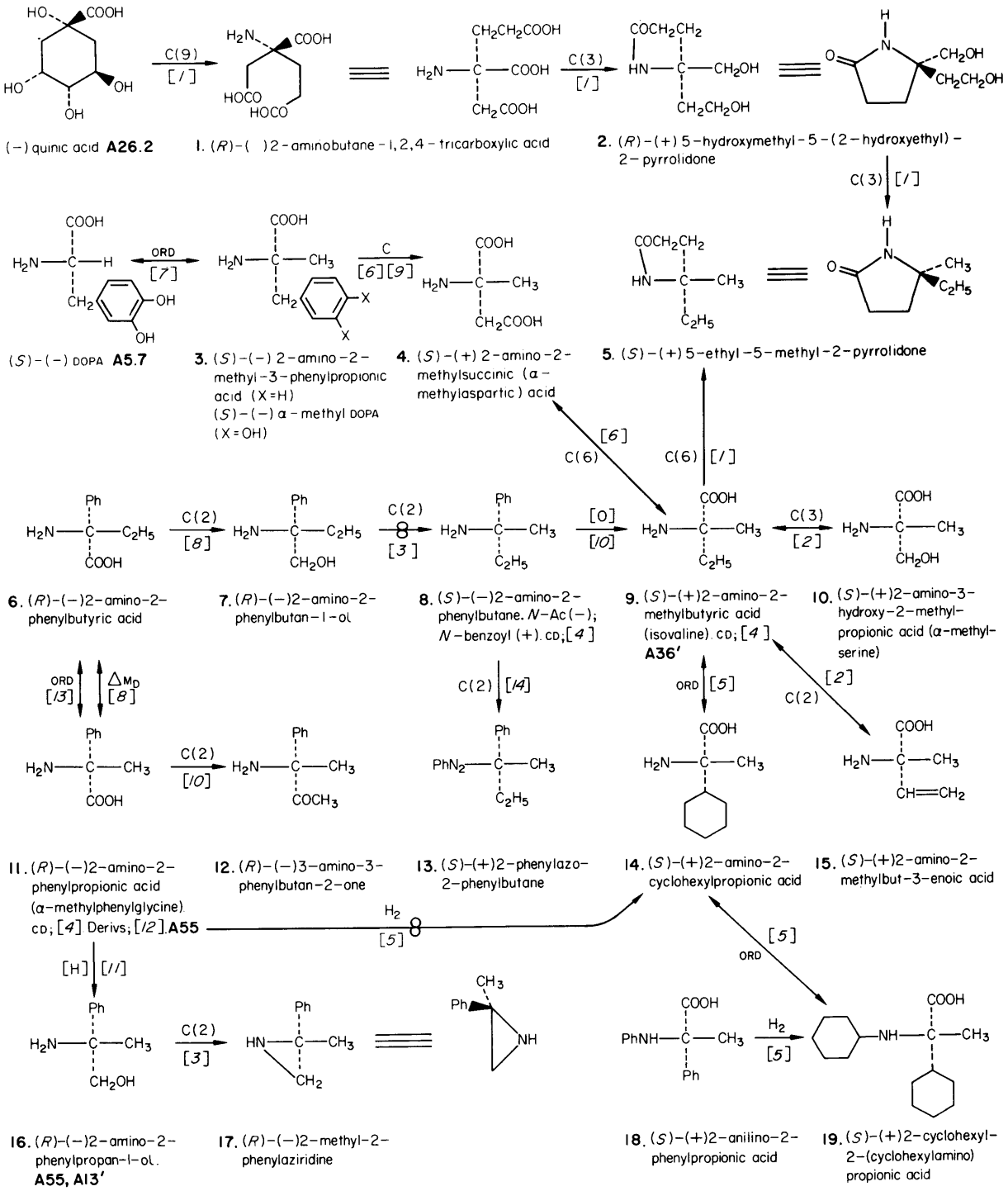

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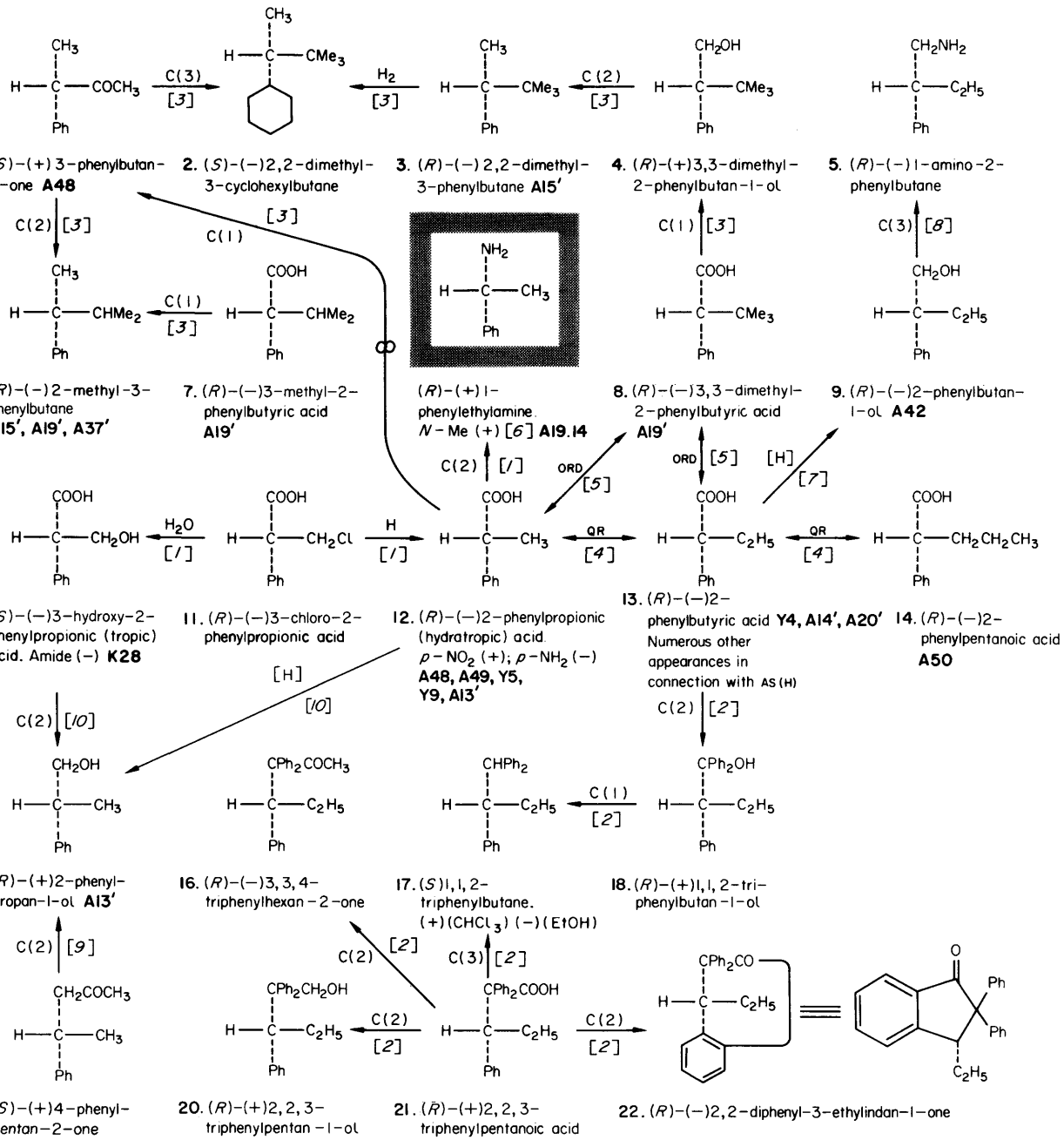

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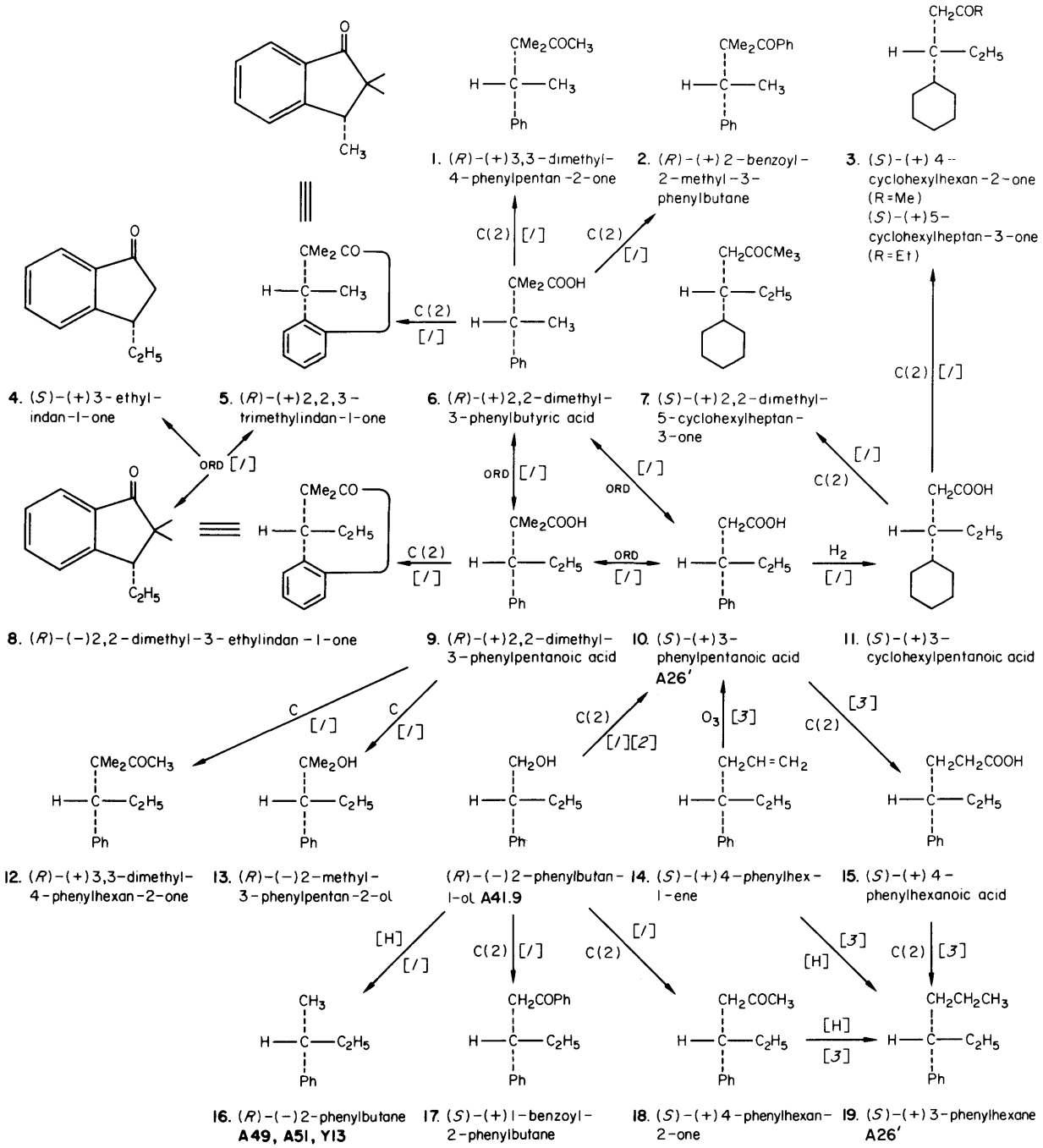

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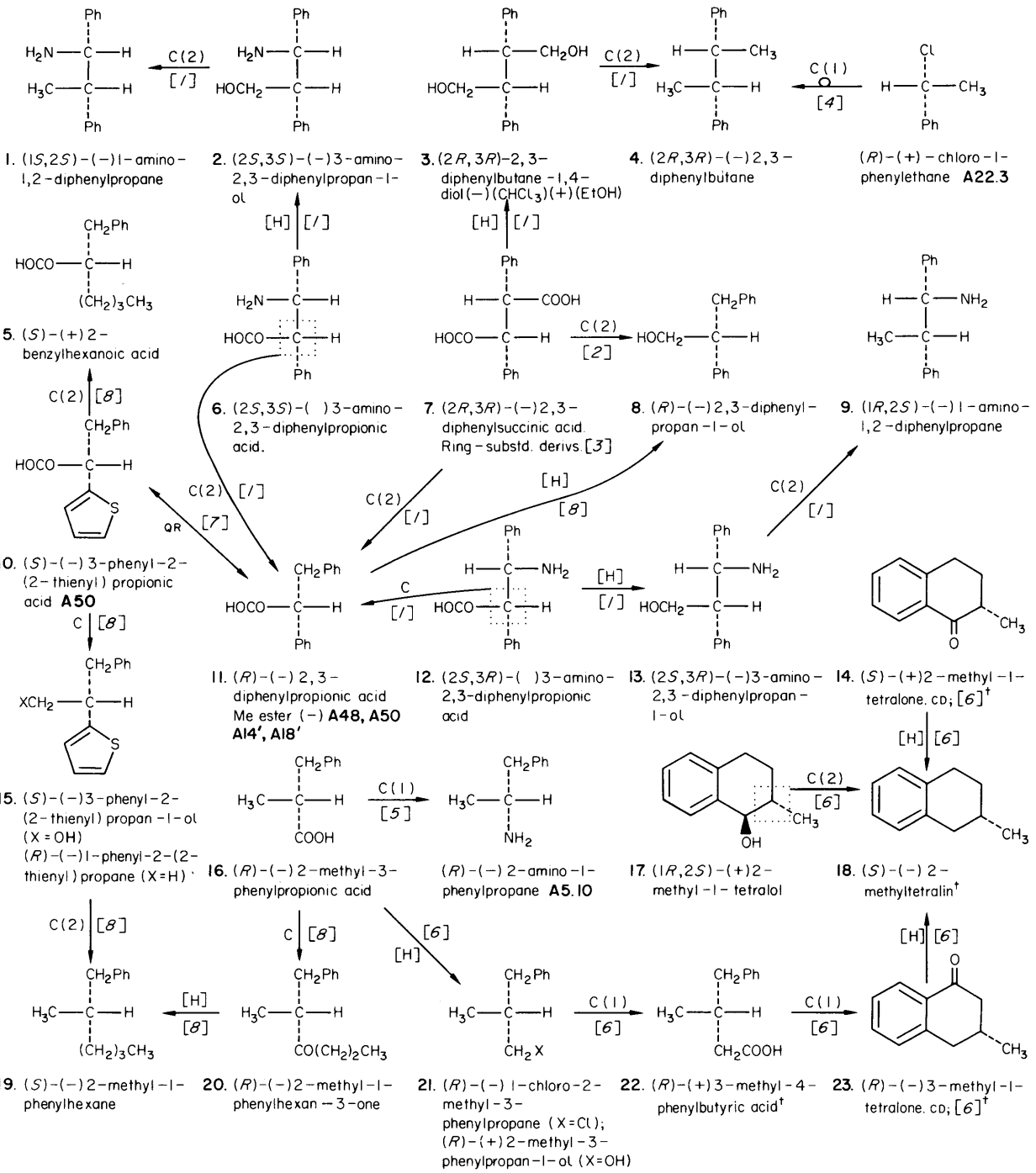

†The AC given here for **A43.14** contradicts that given at **A25.4** and the latter is probably correct (G. Jaouen and A. Meyer, personal communication; see also A. Schooes, J. P. Guette and A. Horeau, *Bull. Soc. chim. France*, 1973, 1215). This throws doubt on the ACs shown here for the formulae **21**, **22**, **23** and **18** and to a lesser extent on other formulae on this page.

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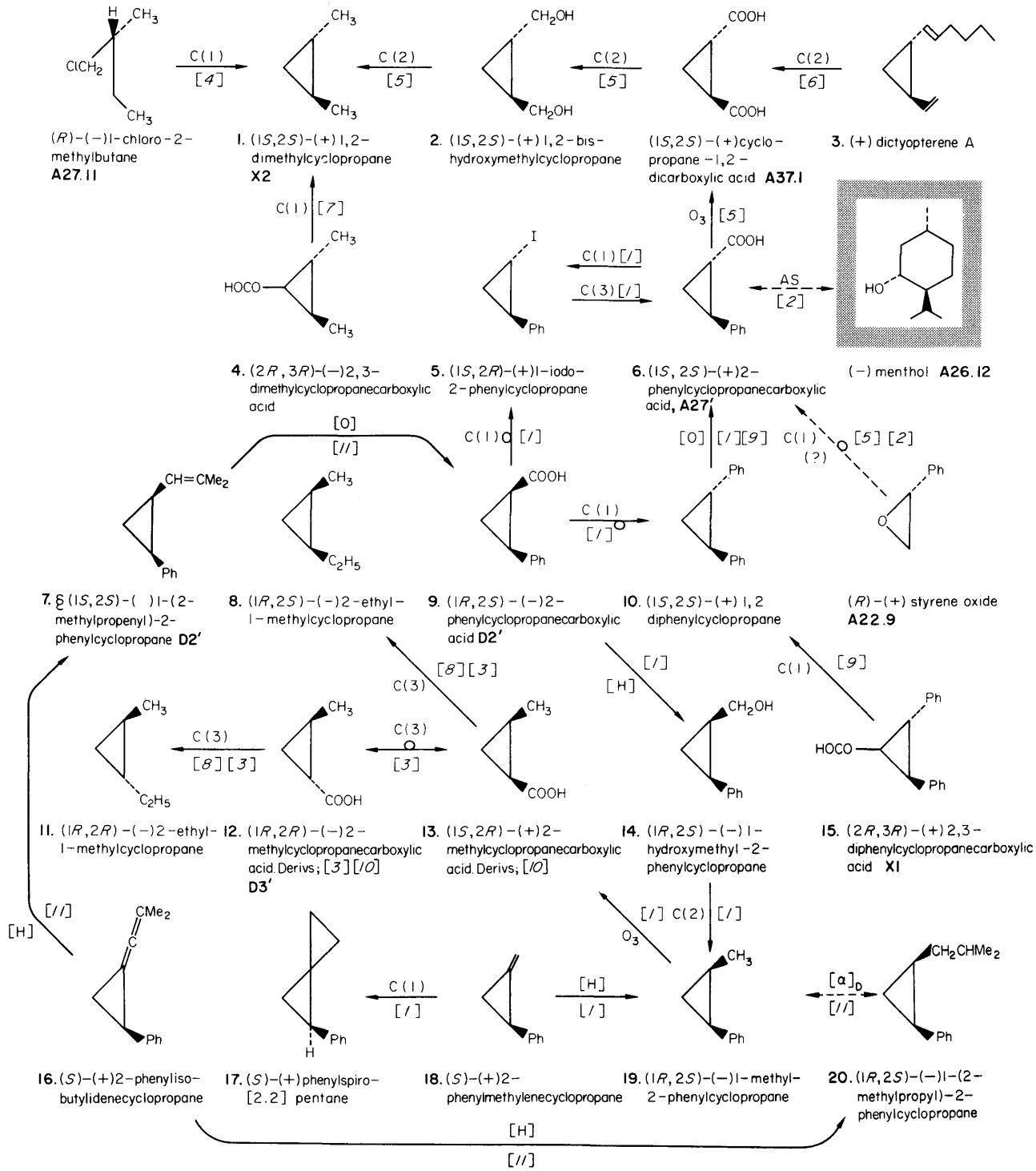

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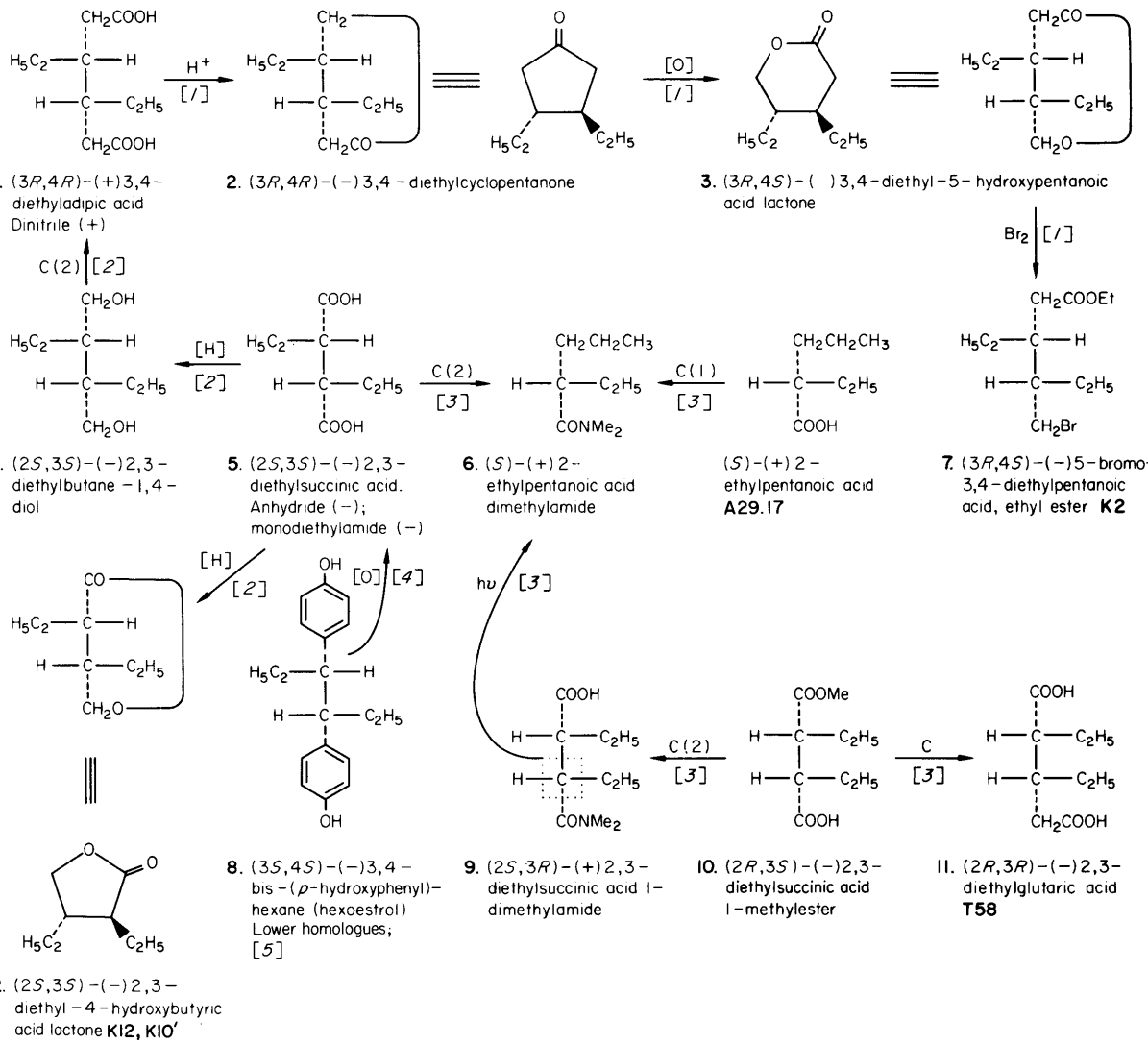

1. (3*R*,4*R*)-(+)3,4-diethyladipic acid Dinitrile (+)
2. (3*R*,4*R*)-(−)3,4-diethylcyclopentanone
3. (3*R*,4*S*)-( )3,4-diethyl-5-hydroxypentanoic acid lactone
4. (2*S*,3*S*)-(−)2,3-diethylbutane-1,4-diol
5. (2*S*,3*S*)-(−)2,3-diethylsuccinic acid. Anhydride (−); monodiethylamide (−)
6. (*S*)-(+)2-ethylpentanoic acid dimethylamide
   (*S*)-(+)2-ethylpentanoic acid **A29.17**
7. (3*R*,4*S*)-(−)5-bromo-3,4-diethylpentanoic acid, ethyl ester **K2**
8. (3*S*,4*S*)-(−)3,4-bis-(*p*-hydroxyphenyl)-hexane (hexoestrol) Lower homologues; [5]
9. (2*S*,3*R*)-(+)2,3-diethylsuccinic acid 1-dimethylamide
10. (2*R*,3*S*)-(−)2,3-diethylsuccinic acid 1-methylester
11. (2*R*,3*R*)-(−)2,3-diethylglutaric acid **T58**
12. (2*S*,3*S*)-(−)2,3-diethyl-4-hydroxybutyric acid lactone **K12, K10′**

1. A. R. Battersby, S. W. Breuer and S. Garratt, *J. Chem. Soc. (C)*, 1968, 2467.
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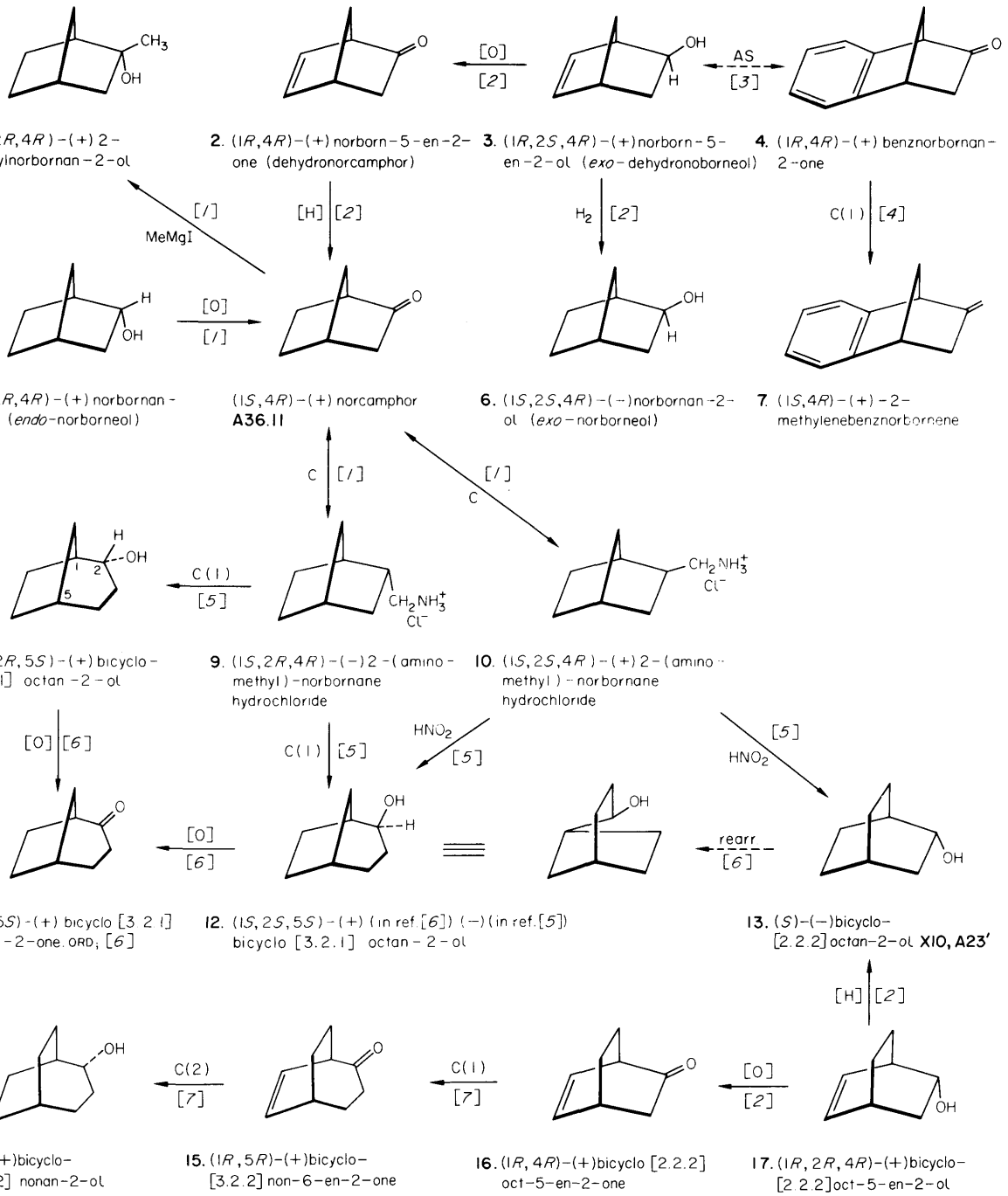

1. (1*S*,2*R*,4*R*)-(+)2-methylnorbornan-2-ol
2. (1*R*,4*R*)-(+)norborn-5-en-2-one (dehydronorcamphor)
3. (1*R*,2*S*,4*R*)-(+)norborn-5-en-2-ol (*exo*-dehydronoborneol)
4. (1*R*,4*R*)-(+)benznorbornan-2-one
5. (1*S*,2*R*,4*R*)-(+)norbornan-2-ol (*endo*-norborneol)
(1*S*,4*R*)-(+)norcamphor **A36.11**
6. (1*S*,2*S*,4*R*)-(−)norbornan-2-ol (*exo*-norborneol)
7. (1*S*,4*R*)-(+)-2-methylenebenznorbornene
8. (1*S*,2*R*,5*S*)-(+)bicyclo-[3.2.1]octan-2-ol
9. (1*S*,2*R*,4*R*)-(−)2-(amino-methyl)-norbornane hydrochloride
10. (1*S*,2*S*,4*R*)-(+)2-(amino-methyl)-norbornane hydrochloride
11. (1*S*,5*S*)-(+)bicyclo[3.2.1]octan-2-one. ORD; [6]
12. (1*S*,2*S*,5*S*)-(+) (in ref.[6]) (−) (in ref.[5]) bicyclo[3.2.1]octan-2-ol
13. (*S*)-(−)bicyclo-[2.2.2]octan-2-ol **X10, A23'**
14. (*R*)-(+)bicyclo-[3.2.2]nonan-2-ol
15. (1*R*,5*R*)-(+)bicyclo-[3.2.2]non-6-en-2-one
16. (1*R*,4*R*)-(+)bicyclo[2.2.2]oct-5-en-2-one
17. (1*R*,2*R*,4*R*)-(+)bicyclo-[2.2.2]oct-5-en-2-ol

1. J. A. Berson, J. S. Walia, A. Remanick, S. Suzuki, P. Reynolds-Warnhoff and D. Willner, *J. Amer. Chem. Soc.*, 1961, **83**, 3986. and references therein.
2. K. Mislow and J. G. Berger, *J. Amer. Chem. Soc.*, 1962, **84**, 1956.
3. D. J. Sandman, K. Mislow, W. P. Giddings, J. Dirlam and G. C. Hanson, *J. Amer. Chem. Soc.*, 1968, **90**, 4877.
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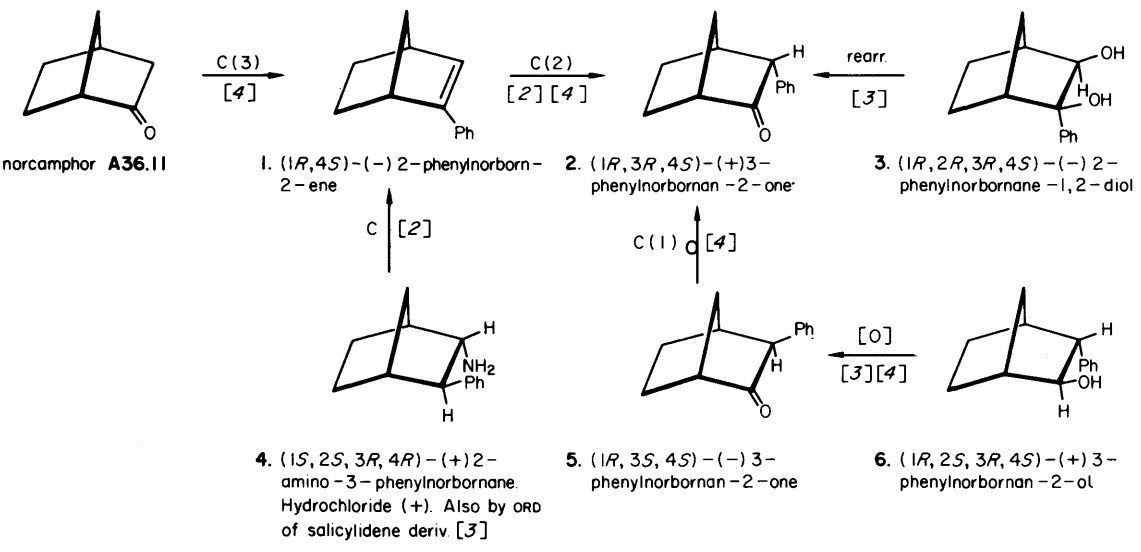


(−)norcamphor **A36.11**

1. (1*R*,4*S*)-(−)2-phenylnorborn-2-ene

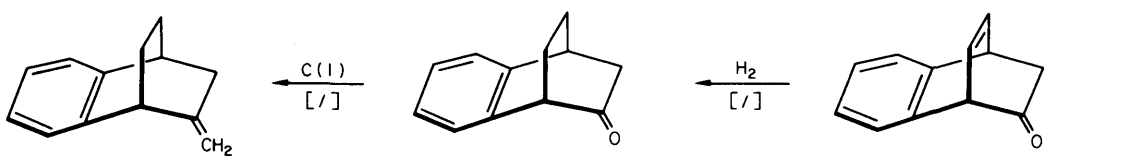
2. (1*R*,3*R*,4*S*)-(+)3-phenylnorbornan-2-one

3. (1*R*,2*R*,3*R*,4*S*)-(−)2-phenylnorbornane-1,2-diol

4. (1*S*,2*S*,3*R*,4*R*)-(+)2-amino-3-phenylnorbornane. Hydrochloride (+). Also by ORD of salicylidene deriv. [3]

5. (1*R*,3*S*,4*S*)-(−)3-phenylnorbornan-2-one

6. (1*R*,2*S*,3*R*,4*S*)-(+)3-phenylnorbornan-2-ol

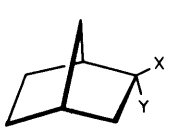


7. (1*R*,4*S*)-(−)2-methylene-5,6-benzobicyclo[2.2.2] octane

8. (1*S*,4*S*)-(−)5,6-benzobicyclo [2.2.2] octan-2-one. By CD [1]

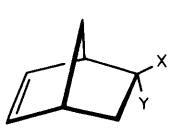
9. (1*S*,4*S*)-(+)7,8-benzobicyclo [2.2.2] oct-2-ene-5-one

The following class 3a norbornanes have also been correlated with those on page A46; [5]



10.

X	*Y*	*sign of rotn* [5]
H	COOH	+
H	COOMe	+
H	CH_2OH	−
H	CH_2OTs	+
H	OAc	+
H	NH_2	−
COOH	H	+
COOMe	H	+



11.

X10′

X	*Y*	*sign of rotn* [5]
H	COOH	+
H	COOMe	+
H	CH_2OH	+
H	CH_3	+
COOH	H	+
COOMe	H	+
CH_2OH	H	+

See [5] for many further norbornanes including methyl derivatives providing links with the monoterpenes.

1. K. Takeda, S. Hagishita, M. Sugiura, K. Kitahonoki, I. Ban, S. Miyazaki and K. Kuriyama, *Tetrahedron*, 1970, **26**, 1435.
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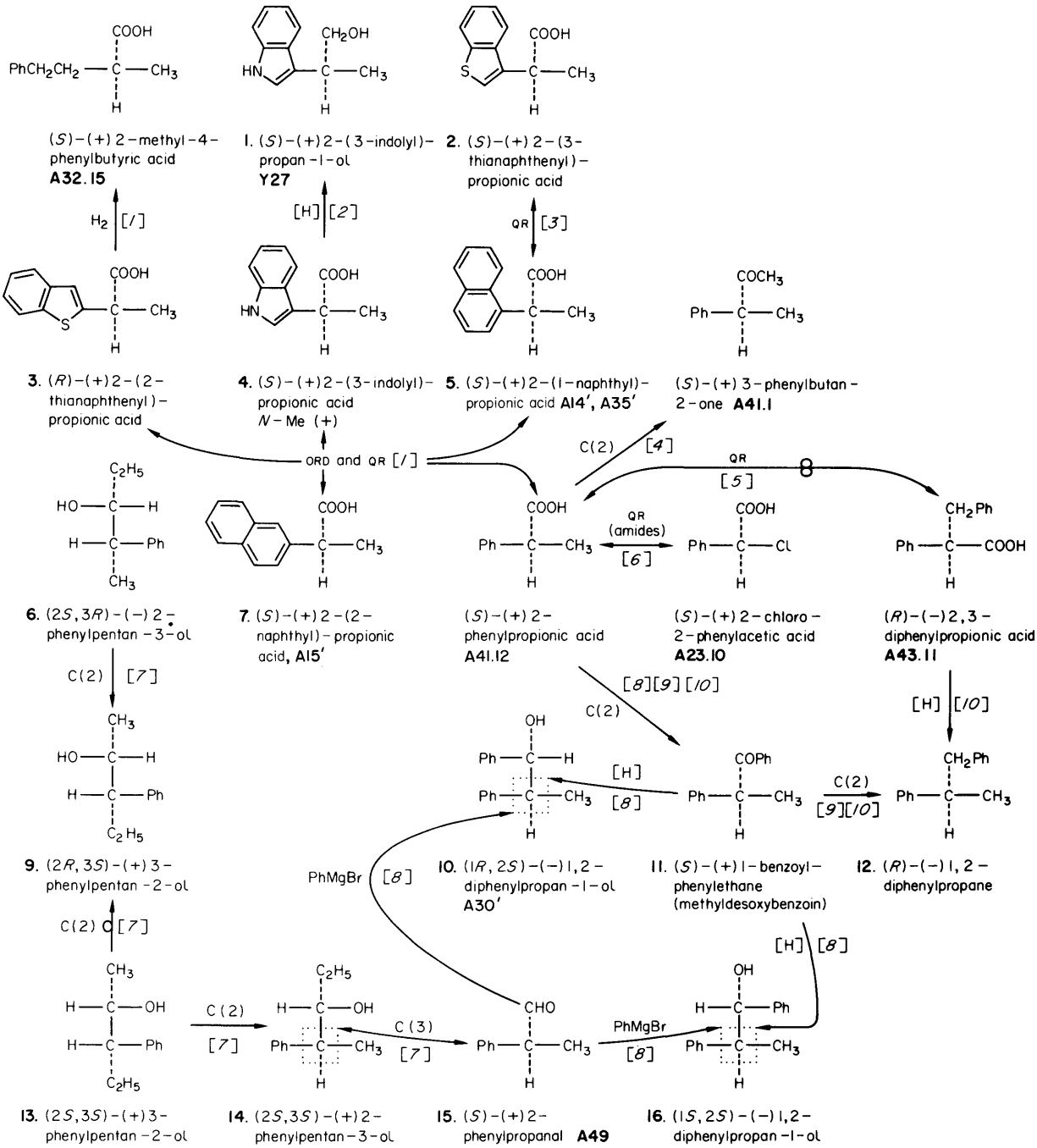

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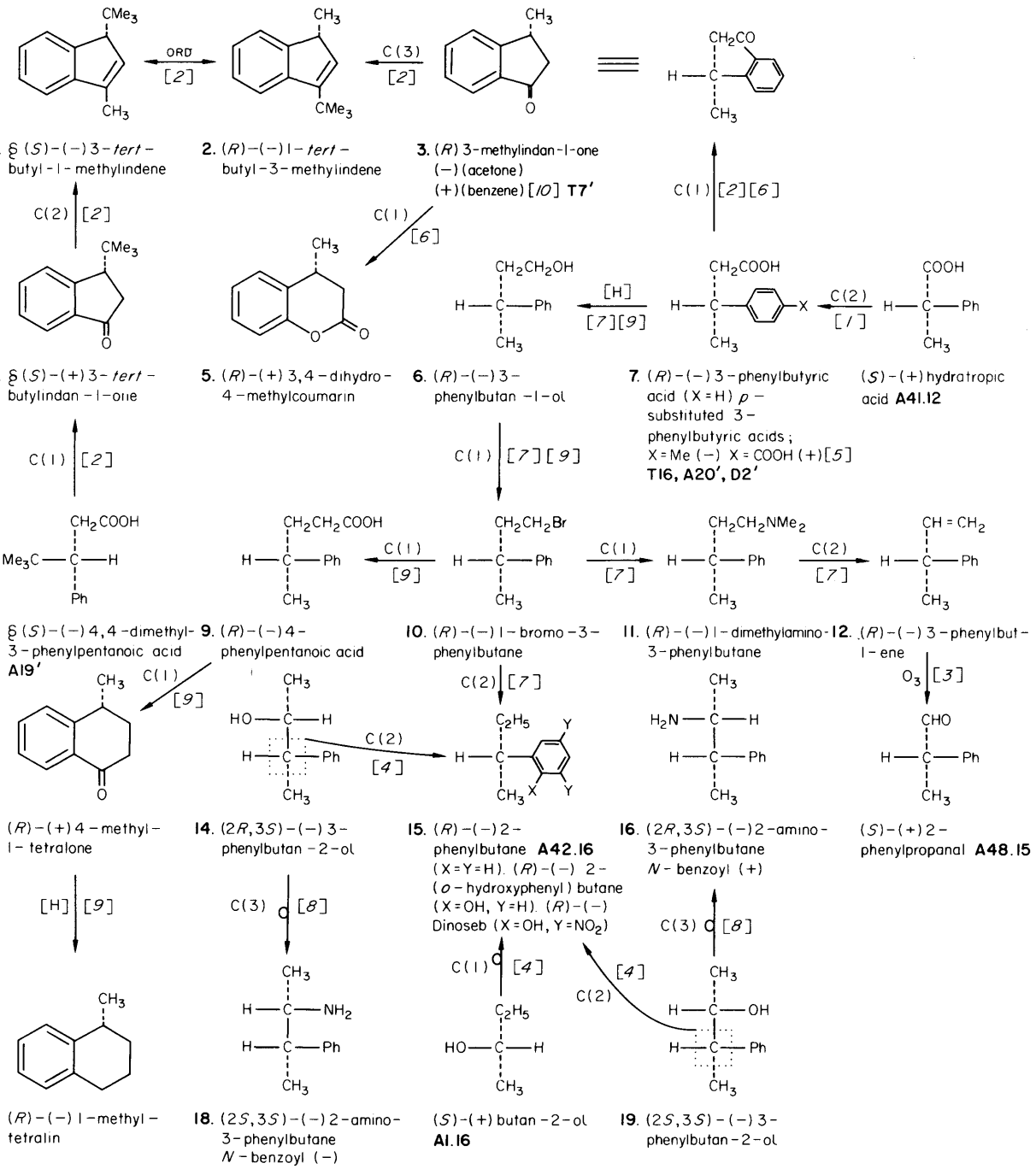

1. § (*S*)-(−)3-*tert*-butyl-1-methylindene
2. (*R*)-(−)1-*tert*-butyl-3-methylindene
3. (*R*)3-methylindan-1-one (−)(acetone) (+)(benzene) [*10*] **T7′**
4. § (*S*)-(+)3-*tert*-butylindan-1-one
5. (*R*)-(+)3,4-dihydro-4-methylcoumarin
6. (*R*)-(−)3-phenylbutan-1-ol
7. (*R*)-(−)3-phenylbutyric acid (X=H) *p*-substituted 3-phenylbutyric acids; X=Me (−) X=COOH (+)[*5*] **T16, A20′, D2′**
   (*S*)-(+)hydratropic acid **A41.12**
8. § (*S*)-(−)4,4-dimethyl-3-phenylpentanoic acid **A19′**
9. (*R*)-(−)4-phenylpentanoic acid
10. (*R*)-(−)1-bromo-3-phenylbutane
11. (*R*)-(−)1-dimethylamino-3-phenylbutane
12. (*R*)-(−)3-phenylbut-1-ene
13. (*R*)-(+)4-methyl-1-tetralone
14. (2*R*,3*S*)-(−)3-phenylbutan-2-ol
15. (*R*)-(−)2-phenylbutane **A42.16** (X=Y=H). (*R*)-(−)2-(*o*-hydroxyphenyl)butane (X=OH, Y=H). (*R*)-(−) Dinoseb (X=OH, Y=NO_2)
16. (2*R*,3*S*)-(−)2-amino-3-phenylbutane *N*-benzoyl (+)
    (*S*)-(+)2-phenylpropanal **A48.15**
17. (*R*)-(−)1-methyltetralin
18. (2*S*,3*S*)-(−)2-amino-3-phenylbutane *N*-benzoyl (−)
    (*S*)-(+)butan-2-ol **A1.16**
19. (2*S*,3*S*)-(−)3-phenylbutan-2-ol

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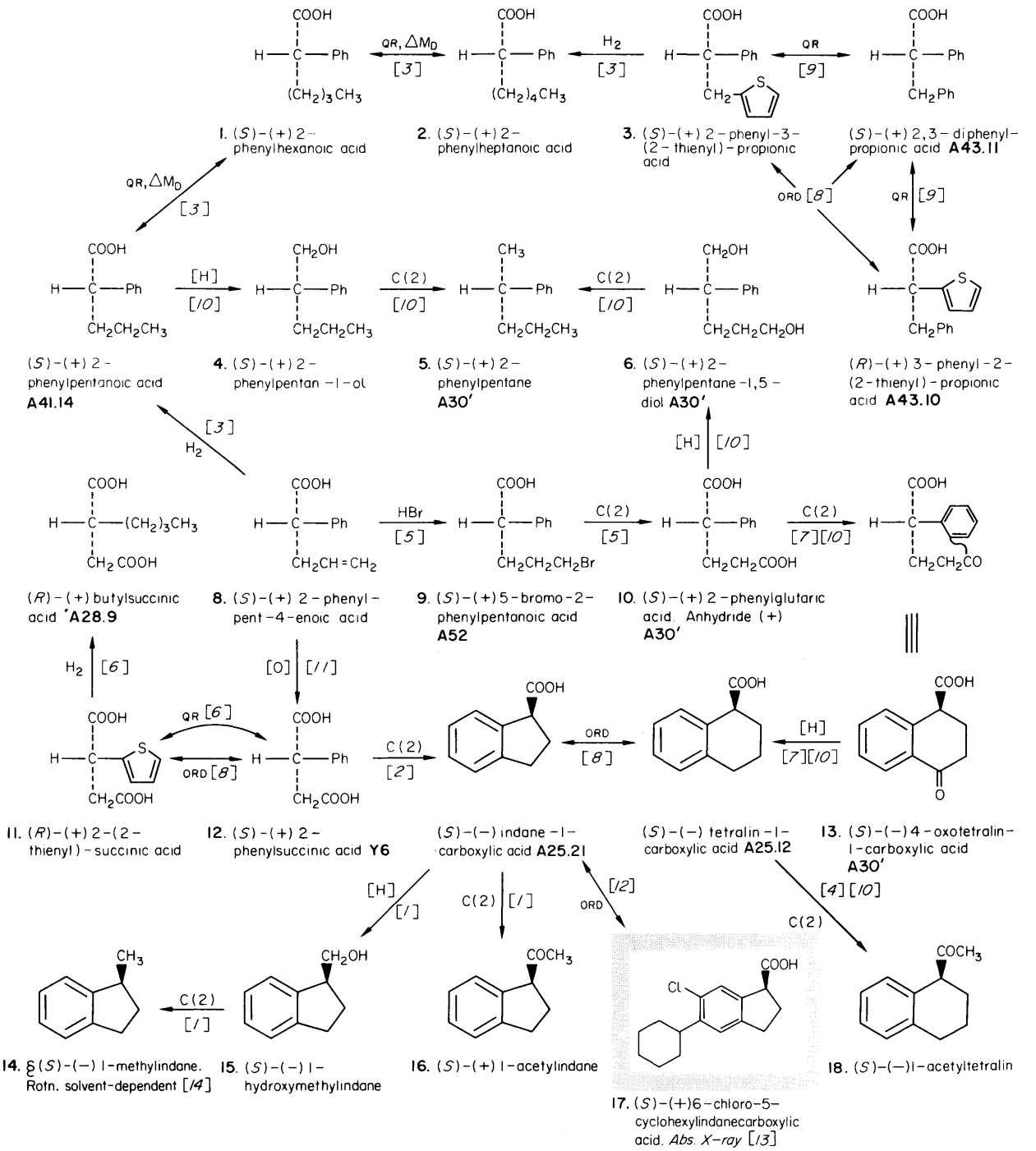
10. H. E. Smith, personal communication.



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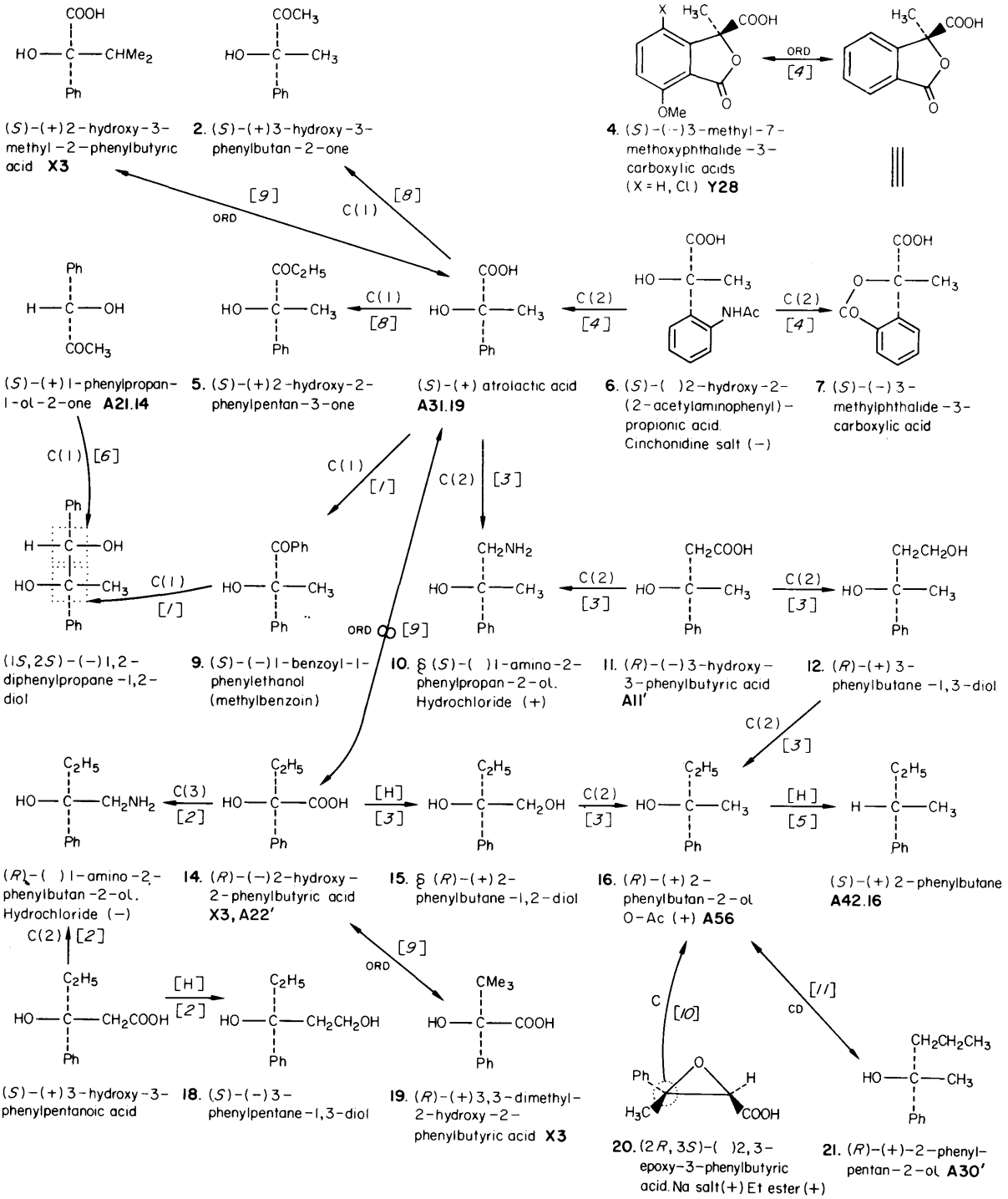

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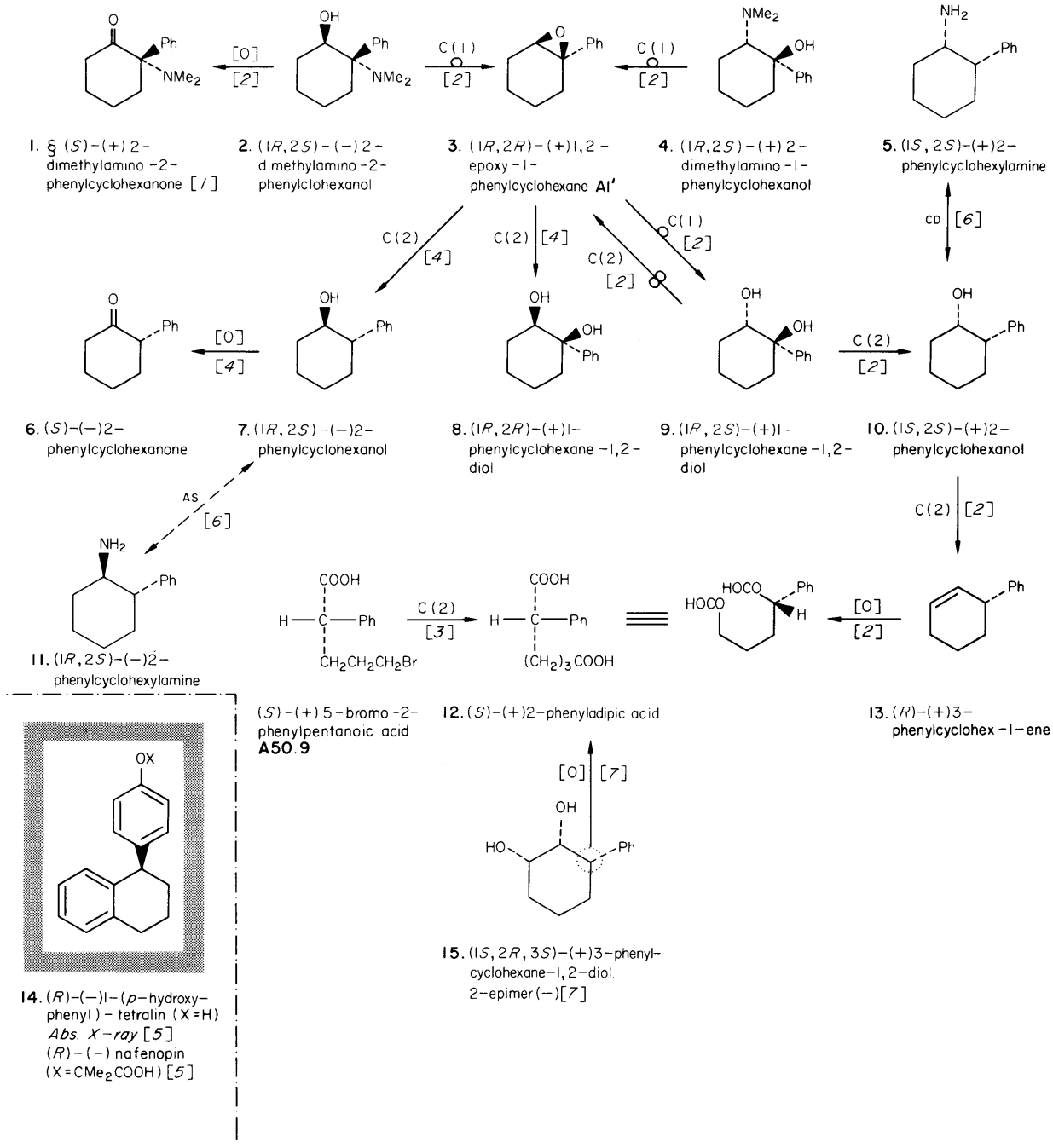

1. § (*S*)-(+)2-dimethylamino-2-phenylcyclohexanone [*1*]
2. (1*R*,2*S*)-(−)2-dimethylamino-2-phenylcyclohexanol
3. (1*R*,2*R*)-(+)1,2-epoxy-1-phenylcyclohexane **AI′**
4. (1*R*,2*S*)-(+)2-dimethylamino-1-phenylcyclohexanol
5. (1*S*,2*S*)-(+)2-phenylcyclohexylamine
6. (*S*)-(−)2-phenylcyclohexanone
7. (1*R*,2*S*)-(−)2-phenylcyclohexanol
8. (1*R*,2*R*)-(+)1-phenylcyclohexane-1,2-diol
9. (1*R*,2*S*)-(+)1-phenylcyclohexane-1,2-diol
10. (1*S*,2*S*)-(+)2-phenylcyclohexanol
11. (1*R*,2*S*)-(−)2-phenylcyclohexylamine
12. (*S*)-(+)2-phenyladipic acid
13. (*R*)-(+)3-phenylcyclohex-1-ene
14. (*R*)-(−)1-(*p*-hydroxyphenyl)-tetralin (X=H) *Abs. X-ray* [*5*] (*R*)-(−) nafenopin (X=CMe_2COOH) [*5*]
15. (1*S*,2*R*,3*S*)-(+)3-phenylcyclohexane-1,2-diol. 2-epimer (−)[*7*]

(*S*)-(+)5-bromo-2-phenylpentanoic acid **A50.9**

1. G. Berti, personal communication.
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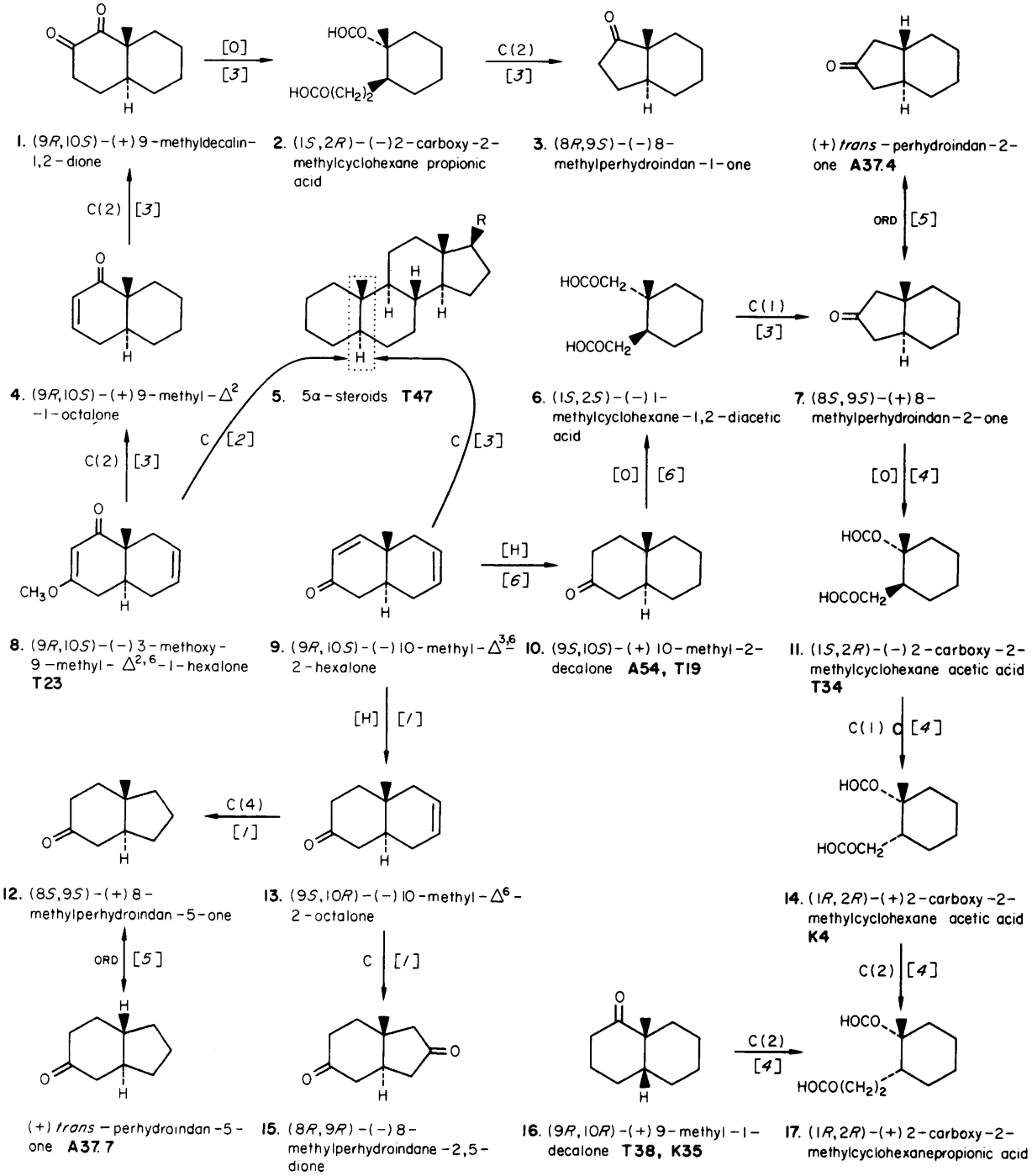

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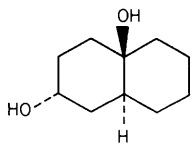
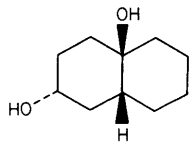
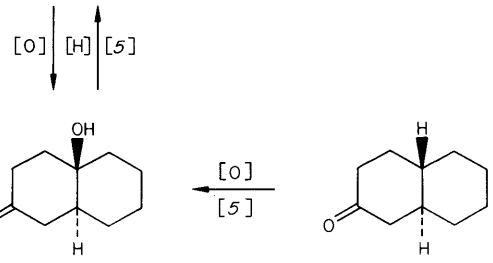


1. (2*R*,9*S*,10*R*)-(+)decalin-2,10-diol



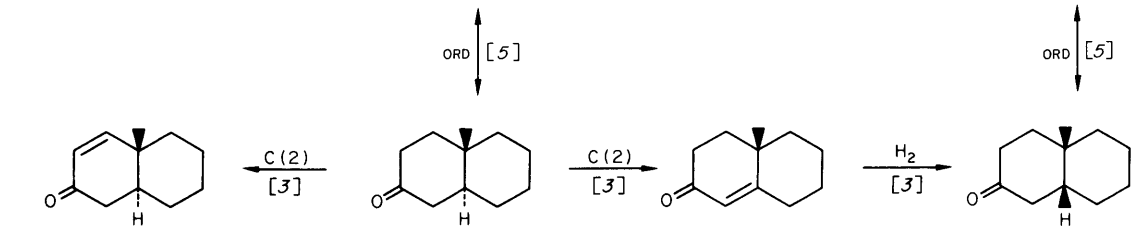
2. (2*R*,9*R*,10*R*)-(+)decalin-2,10-diol



3. (9*S*,10*R*)-(+)10-hydroxy-2-decalone

4. (9*S*,10*S*)-(+)2-decalone

5. (9*R*,10*R*)-(+)10-hydroxy-2-decalone

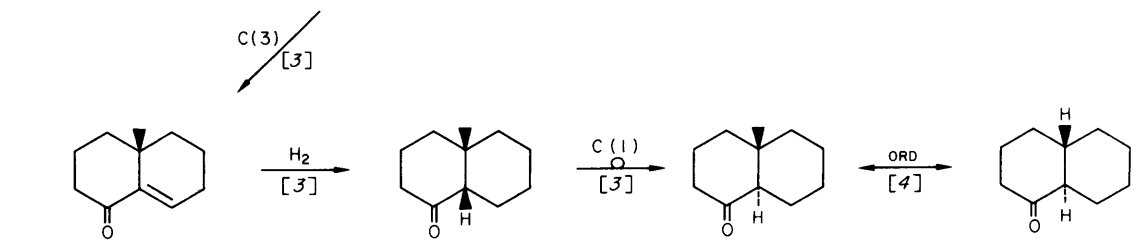


6. (9*S*,10*R*)-(−)10-methyl-Δ^3-2-octalone

(9*S*,10*S*)-(+)10-methyl-2-decalone **A53.10**

7. (*S*)-(+)9-methyl-Δ^4-3-octalone

8. (9*R*,10*S*)-(+)10-methyl-2-decalone

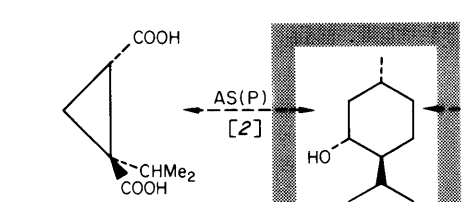


9. (*S*)-(−)10-methyl-Δ^8-1-octalone

10. (9*S*,10*S*)-(+)10-methyl-1-decalone

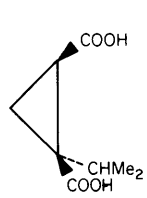
11. (9*R*,10*S*)-(+)10-methyl-1-decalone

(9*R*,10*S*)-(+)1-decalone **A39.2**

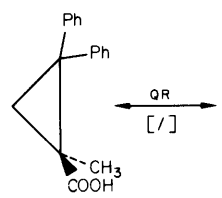


12. (1*R*,2*S*)-(−)1-isopropylcyclopropane-1,2-dicarboxylic (*trans*-umbellularic) acid

(−)menthol **A26.12**



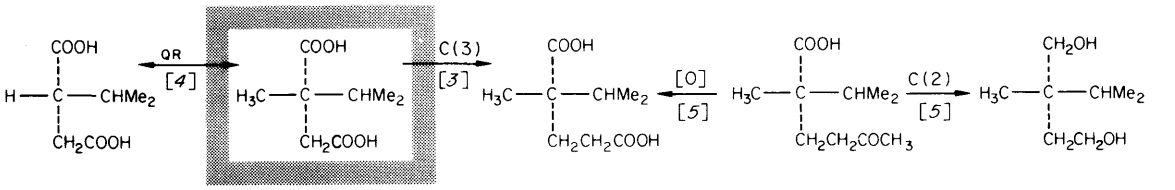
13. (1*R*,2*R*)-(−)1-isopropylcyclopropane-1,2-dicarboxylic (*cis*-umbellularic) acid **T7**



14. ξ(*S*)-(−)1-methyl-2,2-diphenylcyclopropanecarboxylic acid

ξ(*S*)-(+)2,2-diphenylcyclopropanecarboxylic acid **A35.13**

1. H. M. Walborsky, L. Barash, A. E. Young and F. J. Impastato, *J. Amer. Chem. Soc.*, 1961, **83**, 2517.
2. H. M. Walborsky, T. Sugita, M. Ohno and Y. Inouye, *J. Amer. Chem. Soc.*, 1960, **82**, 5255.
3. C. Djerassi and D. Marshall, *J. Amer. Chem. Soc.*, 1958, **80**, 3986, and references therein.
4. C. Djerassi and J. Staunton, *J. Amer. Chem. Soc.*, 1961, **83**, 736.
5. V. Prelog and H. E. Smith, *Helv. Chim. Acta*, 1959, **42**, 2624.



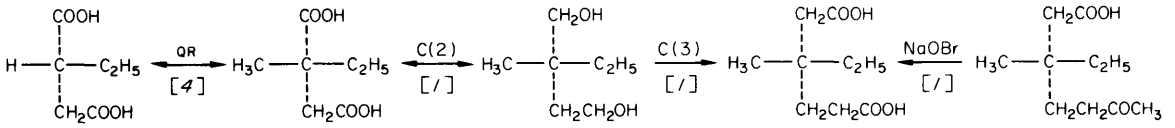
(*S*)-(+) isopropylsuccinic acid **A28.5**

1. (*S*)-(+) 2-isopropyl-2-methylsuccinic acid *Abs. X-ray* [3] **T7, A36', A39'**

2. §(*S*)-(+) 2-isopropyl-2-methylglutaric acid

3. §(*S*)-(+) 2-isopropyl-2-methyl-5-oxo-hexanoic acid **T7, A38'**

4. §(*S*)-(−) 2-isopropyl-2-methylbutane-1,4-diol (small rotation)

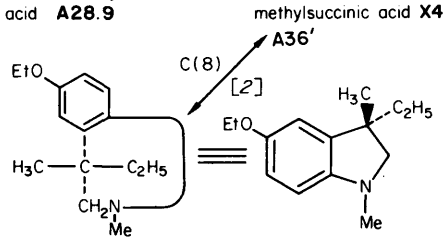


(*R*)-(+) ethylsuccinic acid **A28.9**

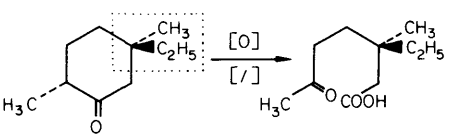
5. (*R*)-(+) 2-ethyl-2-methylsuccinic acid **X4**

6. (*R*)-(−) 2-ethyl-2-methylbutane-1,4-diol

7. (*R*)-(+) 3-ethyl-3-methyladipic acid

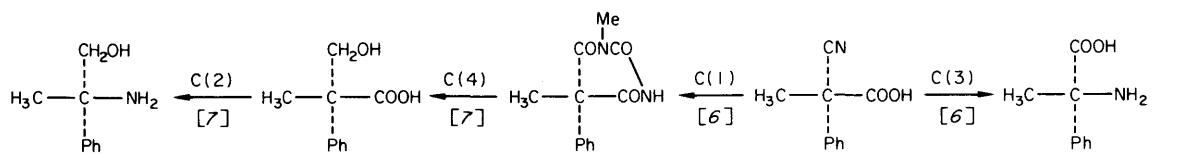


8. (*S*)-( )1,3-dimethyl-5-ethoxy-3-ethyl-2,3-dihydroindole **K30**



9. (2*R*,5*R*)-(+)2,5-dimethyl-5-ethyl-cyclohexanone [8] **T34**

10. (*R*)-(+) 3-ethyl-3-methyl-6-oxoheptanoic acid

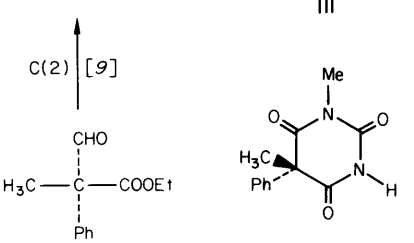


(*R*)-(−) 2-amino-2-phenylpropan-1-ol **A40.16**

11. (*R*)-(+) 3-hydroxy-2-methyl-2-phenylpropionic (α-methyltropic) acid.

12. (*R*)-(−) 2-cyano-2-phenylpropionic acid **A39'**

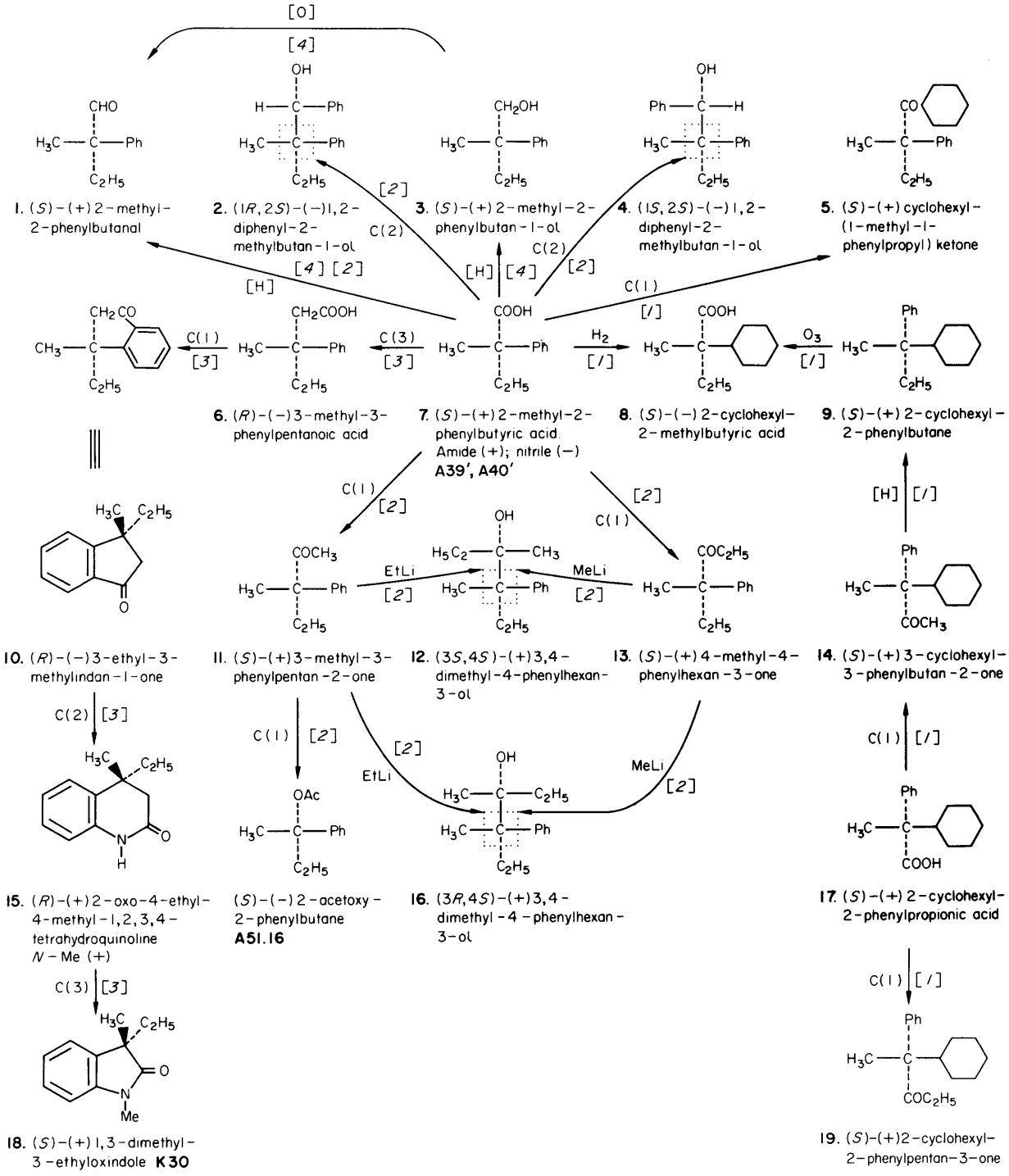
(*R*)-(−) 2-amino-2-phenylpropionic acid **A40.11**



13. (*R*)-(+)2-formyl-2-phenylpropionic acid ethyl ester

14. (*S*)-(+)*N*-methyleudan. Other barbiturates [6]

1. M. R. Cox, G. A. Ellestad, A. J. Hannaford, I. R. Wallwork, W. B. Whalley and B. Sjöberg, *J. Chem. Soc.*, 1965, 7257.
2. R. B. Longmore and B. Robinson, *Chem. & Ind.*, 1969, 622.
3. M. R. Cox, H. P. Koch, W. B. Whalley, M. B. Hursthouse and D. Rogers, *Chem. Comm.*, 1967, 212.
4. J. Porath, *Arkiv Kemi*, 1949, **1**, 385; 1951, **3**, 163.
5. E. J. Eisenbraun, F. Burian, J. Osiecki and C. Djerassi, *J. Amer. Chem. Soc.*, 1960, **82**, 3476.
6. J. Knabe and C. Urbahn, *Annalen*, 1971, **750**, 21.
7. J. Knabe, H. Junginger and W. Geismar, *Arch. Pharm.*, 1971, **304**, 1.
8. C. Djerassi, B. Green, W. B. Whalley and C. G. De Grazia, *J. Chem. Soc. (C)*, 1966, 624.
9. J. M. Domagala, R. D. Bach and J. Wemple, *J. Amer. Chem. Soc.*, 1976, **98**, 1975.



1. (*S*)-(+)2-methyl-2-phenylbutanal
2. (1*R*,2*S*)-(−)1,2-diphenyl-2-methylbutan-1-ol
3. (*S*)-(+)2-methyl-2-phenylbutan-1-ol
4. (1*S*,2*S*)-(−)1,2-diphenyl-2-methylbutan-1-ol
5. (*S*)-(+)cyclohexyl-(1-methyl-1-phenylpropyl) ketone
6. (*R*)-(−)3-methyl-3-phenylpentanoic acid
7. (*S*)-(+)2-methyl-2-phenylbutyric acid. Amide (+); nitrile (−) **A39′, A40′**
8. (*S*)-(−)2-cyclohexyl-2-methylbutyric acid
9. (*S*)-(+)2-cyclohexyl-2-phenylbutane
10. (*R*)-(−)3-ethyl-3-methylindan-1-one
11. (*S*)-(+)3-methyl-3-phenylpentan-2-one
12. (3*S*,4*S*)-(+)3,4-dimethyl-4-phenylhexan-3-ol
13. (*S*)-(+)4-methyl-4-phenylhexan-3-one
14. (*S*)-(+)3-cyclohexyl-3-phenylbutan-2-one
15. (*R*)-(+)2-oxo-4-ethyl-4-methyl-1,2,3,4-tetrahydroquinoline *N*-Me (+)
16. (3*R*,4*S*)-(+)3,4-dimethyl-4-phenylhexan-3-ol
17. (*S*)-(+)2-cyclohexyl-2-phenylpropionic acid
18. (*S*)-(+)1,3-dimethyl-3-ethyloxindole **K30**
19. (*S*)-(+)2-cyclohexyl-2-phenylpentan-3-one

(*S*)-(−)2-acetoxy-2-phenylbutane **A51.16**

1. B. Calas and L. Giral, *Bull. Soc. chim. France*, 1971, 2629.
2. D. J. Cram and J. Allinger, *J. Amer. Chem. Soc.*, 1954, **76**, 4516, and references therein.
3. R. K. Hill and G. R. Newkome, *Tetrahedron*, 1969, **25**, 1249.
4. H. M. Walborsky and L. E. Allen, *J. Amer. Chem. Soc.*, 1971, **93**, 5465.
5. B. Calas and L. Giral, *Bull. Soc. chim. France*, 1972, 2895.

Supplementary tables of one-centre compounds

Mills and Klyne [1] have made a number of generalizations relating the absolute configurations of certain classes of one-centre compounds to their signs of molecular rotation at the sodium D line. P. A. Levene and his co-workers [2], [3], [4], [5] interrelated a large number of 1-centre compounds by chemical reactions not involving the asymmetric centre. Some of these correlations have been incorporated in the main body of Section A, and the results of many others are tabulated here. Where the same compounds have been prepared by Levene *et al.* and by other workers the agreement is good, but caution should be exercised in taking absolute configurations determined in this work, and not elsewhere, completely without reservation, due to the following factors:

(1) One or two cases of sign contradiction between different papers in the Levene series have been noted.

(2) Many of the reactions were carried out with material of low optical rotation and/or low optical purity.

A non-standard form of Fischer projection was used by Levene, in common with several other authors at about this time [6]. Bonds which should be interpreted as lying above the plane of the paper are shown as dotted lines, i.e. the configurations shown, if interpreted literally, are the converse of the Fischer convention prevailing at the time.

Projection formula as used by Levene *et al.*

Usual Fischer projection.

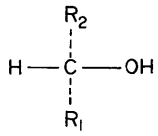
Note; In the second edition, these tables have been shortened so as to include only compounds which do not appear elsewhere.

References for pages 61–67

1. J. A. Mills and W. Klyne, *Progr. Stereochem.*, 1954, **1**, 177.
2. P. A. Levene and A. Rothen, *J. Org. Chem.*, 1936, **1**, 76.
3. P. A. Levene and R. E. Marker, *J. Biol. Chem.*, 1931, **91**, 405.
4. P. A. Levene and R. E. Marker, *J. Biol. Chem.*, 1931, **91**, 77.
5. P. A. Levene and M. Kuna, *J. Biol. Chem.*, 1941, **140**, 255.
6. A. Fredga and J. K. Miettinen, *Acta Chem. Scand.*, 1947, **1**, 371.

Class 2a

Secondary alcohols



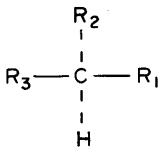
($R_1 > R_2$; (*S*) chirality); these are normally dextrorotatory when R_1 and R_2 are *n*-alkyl groups [*1*]

	R_1	R_2	Name	$[\alpha]_D$	ref.
1.	C_6H_{11}	C_3H_7–*n*	1-cyclohexylbutan-1-ol	–	[*2*]
2.	C_6H_{11}	CH_3	1-cyclohexylethanol	+	[*2*]
3.	$(CH_2)_2C_6H_{11}$	C_2H_5	6-cyclohexylhexan-3-ol	+	[*2*]
4.	C_6H_{11}	C_4H_9–*n*	1-cyclohexylpentan-1-ol	–	[*2*]
5.	CH_2–C_6H_{11}	C_2H_5	1-cyclohexylpentan-3-ol	+	[*2*]
6.	C_6H_{11}	C_2H_5	1-cyclohexylpropan-1-ol	–	[*2*]
7.	C_7H_{15}–*n*	C_2H_5	decan-3-ol	+	[*2*]
8.	C_6H_{13}–*n*	C_3H_7–*n*	decan-4-ol	+	[*2*]
9.	C_5H_{11}–*n*	C_4H_9–*n*	decan-5-ol	+	[*2*]
10.	C_4H_9–*n*	C_2H_5	heptan-3-ol	+	[*2*]
11.	–CH=CH_2	C_4H_9–*n*	hept-1-en-3-ol	+	[*2*]
12.	C_4H_9–*n*	CH_3	hexan-2-ol	+	[*2*]
13.	C_3H_7–*i*	C_4H_9–*n*	2-methylheptan-3-ol **Y'5**	–	[*2*]
14.	CH_2–C_3H_7–*i*	C_3H_7–*n*	2-methylheptan-4-ol	+	[*2*]
15.	C_3H_7–*i*	C_3H_7–*n*	2-methylhexan-3-ol	–	[*2*]
16.	CH_2–C_3H_7–*i*	C_5H_{11}–*n*	2-methylnonan-5-ol	+	[*2*]
17.	C_3H_7–*i*	C_5H_{11}–*n*	2-methyloctan-3-ol	–	[*2*]
18.	CH_2–C_3H_7–*i*	C_4H_9–*n*	2-methyloctan-4-ol	+	[*2*]
19.	CH_2–C_3H_7–*i*	CH_3	4-methylpentan-2-ol	+	[*2*]
20.	C_6H_{13}–*n*	C_2H_5	nonan-3-ol	+	[*2*]
21.	C_5H_{11}–*n*	C_3H_7–*n*	nonan-4-ol	+	[*2*]
22.	C_4H_9–*n*	C_3H_7–*n*	octan-4-ol	+	[*2*]
23.	–CH=$CHCH_3$	C_4H_9–*n*	oct 2-en-4-ol	+	[*2*]
24.	$(CH_2)_2$Ph	C_2H_5	6-phenylhexan-3-ol	+	[*2*]
25.	CH_2Ph	C_2H_5	1-phenylpentan-3-ol	+	[*2*]
26.	C_8H_{17}–*n*	C_2H_5	undecan-3-ol	+	[*2*]

References on page 61

Class 3a

Hydrocarbons



($R_1 > R_2 > R_3$; (*S*) chirality); these are normally dextrorotatory when R_1, R_2, R_3 are *n*-alkyl groups [*1*].

All of these examples have R_3=CH_3

	R_1	R_2	Name	$[\alpha]_D$	ref.
1.	C_6H_{11}	C_2H_5	2-cyclohexylbutane	–	[*2*]
2.	$CH_2C_6H_{11}$	C_2H_5	1-cyclohexyl-2-methylbutane	+	[*2*]
3.	$(CH_2)_2C_6H_{11}$	C_2H_5	1-cyclohexyl-3-methylpentane	+	[*2*]
4.	$CH_2C_3H_7$–*i*	C_2H_5	2,4-dimethylhexane	+	[*3*]
5.	$(CH_2)_2C_3H_7$ –*i*	C_2H_5	2,5-dimethylheptane	+	[*4*]
6.	C_7H_{15} –*n*	C_2H_5	3-methyldecane	+	[*2*]
7.	C_5H_{11}–*n*	C_4H_9–*n*	5-methyldecane	+	[*2*]
8.	C_4H_9–*n*	C_2H_5	3-methylheptane **K22**	+	[*2*]
9.	C_5H_{11}–*n*	C_3H_7–*n*	4-methylnonane **K21**, **K5′**	+	[*2*]
10.	C_4H_9–*n*	C_3H_7–*n*	4-methyloctane	+	[*2*]
11.	$(CH_2)_2Ph$	C_2H_5	3-methyl-1-phenylpentane	+	[*2*]

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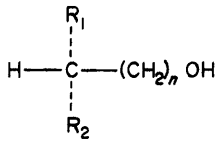
Class 3a

Alcohols

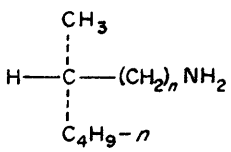
(*S*) chirality



	R_1	R_2	n	Name	$[\alpha]_D$	ref.
1.	CH_3	C_3H_7–*i*	1	3,4-dimethylpentan-1-ol	–	[4]
2.	CH_3	C_4H_9–*n*	2	3-methylheptan-1-ol	–	[2]
3.	CH_3	C_3H_7–*n*	3	4-methylheptan-1-ol	±0	[2]
4.	CH_3	C_2H_5	4	5-methylheptan-1-ol	+	[2]
5.	CH_3	C_4H_9–*n*	1	2-methylhexan-1-ol	–	[2]
6.	CH_3	C_3H_7–*n*	2	3-methylhexan-1-ol	–	[2]
7.	CH_3	C_2H_5	3	4-methylhexan-1-ol	+	[2]
8.	CH_3	C_5H_{11}–*n*	3	4-methylnonan-1-ol	–	[2]
9.	CH_3	C_4H_9–*n*	4	5-methylnonan-1-ol	±0	[2]
10.	CH_3	C_5H_{11}–*n*	2	3-methyloctan-1-ol	–	[2]
11.	CH_3	C_4H_9–*n*	3	4-methyloctan-1-ol	–	[2]
12.	CH_3	C_3H_7–*n*	4	5-methyloctan-1-ol	+	[2]

Class 3a

Amines



	n	Name	$[\alpha]_D$	ref.
13.	5	1-amino-6-methyldecane	+	[2]
14.	2	1-amino-3-methylheptane	–	[2]
15.	1	1-amino-2-methylhexane	–	[2]
16.	4	1-amino-5-methylnonane	+	[2]
17.	3	1-amino-4-methyloctane	–	[2]

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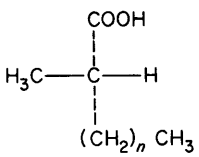
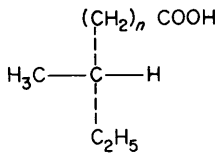
Class 3a

Carboxylic acids

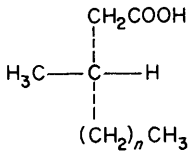
The following generalizations have been made: [*1*]



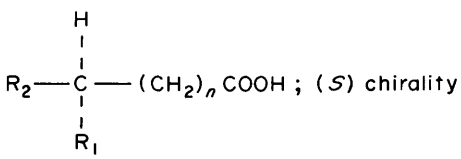
($n > 1$)
(*S*) chirality
dextrorotatory [*1*]



($n > 0$)
(*S*) chirality
dextrorotatory [*1*]



($n > 1$)
(*S*) chirality
laevorotatory [*1*]



	R_1	R_2	n	name	$[\alpha]_D$	ref.
1.	C_2H_5	C_6H_{13}–*n*	0	2-ethyloctanoic	+	[*2*]
2.	CH_3	C_5H_{11}–*n*	3	5-methyldecanoic	+	[*2*]
3.	CH_3	C_4H_9–*n*	1	3-methylheptanoic	–	[*2*]
4.	CH_3	C_3H_7–*n*	2	4-methylheptanoic	+	[*2*]
5.	CH_3	C_2H_5	3	5-methylheptanoic	+	[*2*]
6.	CH_3	C_4H_9–*n*	0	2-methylhexanoic	+	[*2*]
7.	CH_3	C_7H_{15}–*n*	0	2-methylnonanoic	+	[*2*]
8.	CH_3	C_5H_{11}–*n*	2	4-methylnonanoic	+	[*2*]
9.	CH_3	C_4H_9–*n*	3	5-methylnonanoic	+	[*2*]
10.	CH_3	C_6H_{13}–*n*	0	2-methyloctanoic	+	[*2*]
11.	CH_3	C_4H_9–*n*	2	4-methyloctanoic	+	[*2*]
12.	CH_3	C_3H_7–*n*	3	5-methyloctanoic	+	[*2*]
13.	$(CH_2)_2Ph$	CH_3	3	5-methyl-7-phenylheptanoic	+	[*2*]
14.	CH_3	$(CH_2)_2Ph$	1	4-methyl-6-phenylhexanoic	–	[*2*]
15.	CH_3	$(CH_2)_2Ph$	1	3-methyl-5-phenylpentanoic	–	[*2*]

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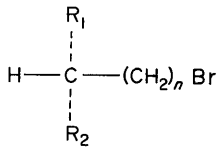
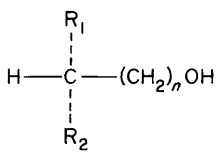
Class 3a
Bromoalkanes
(*S*) chirality



	R_1	R_2	*n*	name	$[\alpha]_D$	ref.
1.	CH_3	C_3H_7–*i*	1	1-bromo-2,3-dimethylbutane	+	[*4*]
2.	C_3H_7–*i*	CH_3	2	1-bromo-2,3-dimethylpentane	–	[*4*]
3.	CH_3	C_5H_{11}–*n*	4	1-bromo-5-methyldecane	+	[*2*]
4.	CH_3	C_5H_{11}–*n*	1	1-bromo-2-methylheptane	+	[*2*]
5.	CH_3	C_4H_9–*n*	2	1-bromo-3-methylheptane	+	[*2*]
6.	CH_3	C_3H_7–*n*	3	1-bromo-4-methylheptane	+	[*2*]
7.	CH_3	C_4H_9–*n*	1	1-bromo-2-methylhexane	+	[*2*]
8.	CH_3	C_3H_7–*n*	2	1-bromo-3-methylhexane	+	[*2*]
9.	CH_3	C_2H_5	3	1-bromo-4-methylhexane	+	[*2*]
10.	CH_3	C_2H_5	4	1-bromo-5-methylhexane	+	[*2*]
11.	CH_3	C_5H_{11}–*n*	3	1-bromo-4-methylnonane	+	[*2*]
12.	CH_3	C_4H_9–*n*	4	1-bromo-5-methylnonane	+	[*2*]
13.	CH_3	C_5H_{11}–*n*	2	1-bromo-3-methyloctane	+	[*2*]
14.	CH_3	C_4H_9–*n*	3	1-bromo-4-methyloctane	+	[*2*]
15.	CH_3	C_3H_7–*n*	4	1-bromo-5-methyloctane	+	[*2*]
16.	CH_3	C_2H_5	5	1-bromo-6-methyloctane	+	[*2*]
17.	CH_3	C_3H_7–*n*	1	1-bromo-2-methylpentane	+	[*2*]
18.	CH_3	C_2H_5	2	1-bromo-3-methylpentane	+	[*2*]

Class 3b
Alcohols

(*S*) chirality



	R_1	R_2	*n*	name	$[\alpha]_D$	ref.
19.	Ph	C_2H_5	4	5-phenylheptan-1-ol	+	[*2*]
20.	Ph	C_2H_5	3	4-phenylhexan-1-ol	–	[*2*]
21.	Ph	CH_3	4	5-phenylhexan-1-ol	+	[*2*]
22.	Ph	C_2H_5	2	3-phenylpentan-1-ol	+	[*2*]
23.	Ph	CH_3	3	4-phenylpentan-1-ol	+	[*2*]

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-C-

Carbohydrates

The treatment of carbohydrate stereoisomerism given here is very much an outline, and standard texts [1] [2] [20] should be consulted for detailed accounts of intraseries correlations. Carbohydrates shown in other sections of the 'Atlas' and not specifically included in this section have been chemically correlated by unambiguous methods with one or more compounds included here.

Scope†

(1) The parent trioses, tetroses, pentoses and hexoses which are fundamental to carbohydrate stereochemical nomenclature are shown. Derivatives of these, such as deoxy-, aminodeoxy- etc. derivatives are not included.
(2) All carbohydrates for which Bijvoet X-rays are available are included.
(3) Di- and polysaccharides are not included as their stereochemistry follows fairly readily from that of monosaccharides.
(4) Nucleosides likewise may be considered as simple substitution products of the sugars and require no further description within the context of the 'Atlas'.

Tetroses, Pentoses and Hexoses

Nomenclature

According to the traditional system of carbohydrate nomenclature, the configuration of any monosaccharide having up to six carbon atoms is completely defined by a prefix D or L followed by a syllable 'gluc-', 'mann-' etc. This latter specifies both the number of carbon atoms in the sugar and the relative stereochemistry of all chiral centres, while the D or L prefix designates the enantiomeric series to which the compound belongs.

Sugars having the D prefix are considered to be derived from D (*R*−) glyceraldehyde by the chain-lengthening process represented on p. **C1**, in which the asymmetric carbon atom of the glyceraldehyde becomes the penultimate carbon atom (ultimate chiral carbon atom) of the chain, i.e. C_3 of a tetrose, C_4 of a pentose and C_5 of a hexose. Sugars derived in this way from L (*S*−) glyceraldehyde belong to the antipodal series.

In many cases the homologation steps represented by arrows on page **C1** have been realised in practice, by sequences such as R–CHO → RCH(OH)CN → RCH(OH)CHO (Fischer-Kiliani reaction) but even in cases where they have not, the configurations of the individual monosaccharides are supported by a wealth of other evidence [1] [2].

For a table of compounds to which the homologation reaction has been applied, see reference [2], p. 144.

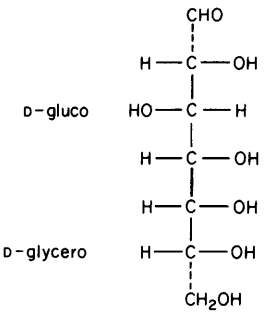
Specification of chirality by the (*R,S*) system is superfluous for carbohydrates and their simple derivatives to which the traditional system is applicable, but it may be invoked to specify the chirality at additional centres not covered by the carbohydrate 'local' convention [3].

† We thank Dr. R. D. Guthrie for helpful discussion.
References on page 72

Aldoheptoses, -octoses and higher sugars

Nomenclature

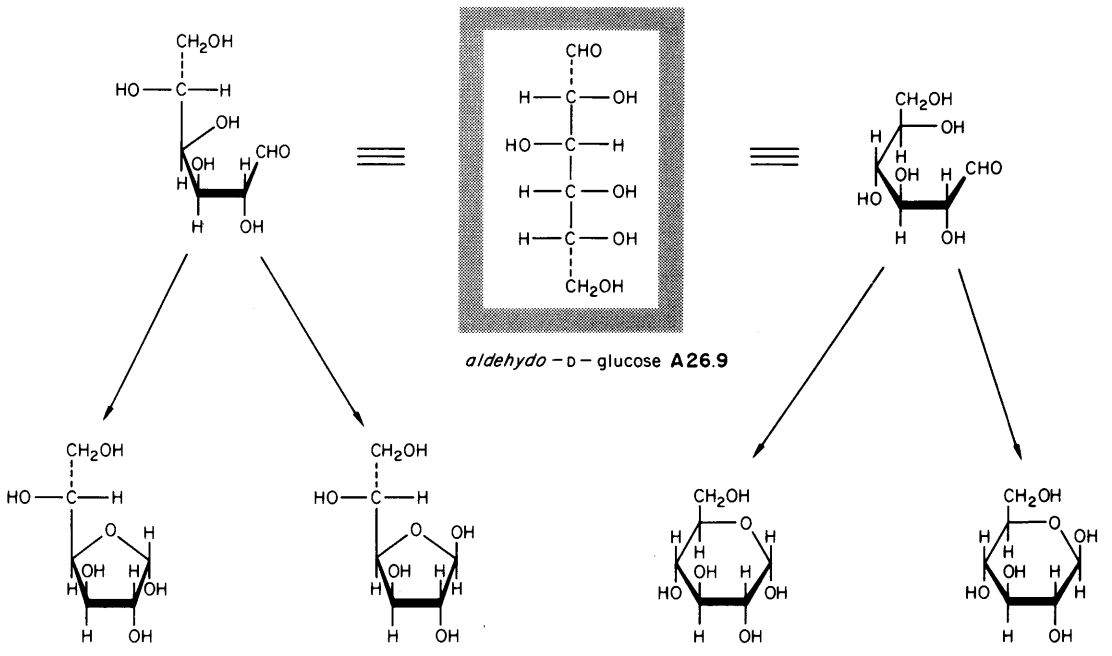
Definition of the stereochemistry of heptoses, octoses and nonoses requires two prefixes, one defining the configuration at C_2–C_5 as in a hexose, and the other, which appears first in the name, defining the configuration at the remaining chiral centre(s). The known aldoheptoses, aldoöctoses, octuloses and nonuloses are tabulated in Reference [1], pp. 245-50.



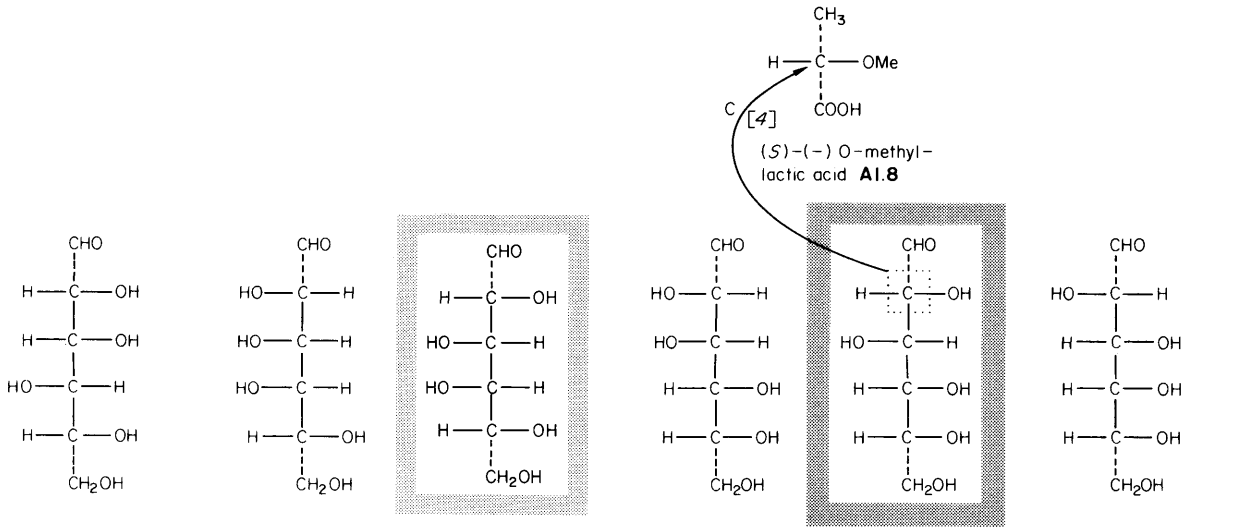
D – glycero – D – glucoheptose.

Anomerism of monosaccharides

The formation of five- and six-membered rings by sugars is denoted by the insertion of 'furano-' and 'pyrano-' respectively into the name. The configuration at the new C_1 chiral centre thus formed is described by the additional symbol α or β [1] [2].



1. α – D – glucofuranose
2. β – D – glucofuranose
3. α – D – glucopyranose
4. β – D – glucopyranose



1. D (−) gulose. Hexitol; D gulitol (≡ L glucitol q.v.)

2. D (+) talose. Hexitol; D (+) talitol

D (+) galactose. A16.17 Hexitol; galactitol (*meso*−)

3. D mannose. α form (+) β form (−)→(+) Hexitol; D (−) mannitol A11.1, Y5′

D (+) glucose A26.9 Hexitol; D-glucitol, (−)(H_2O)(+)(borax).

4. D altrose, (−)→(+) Hexitol; D (+) altritol (≡ D (+) talitol)

5. D (+) idose. Hexitol; D (+) iditol

6. D (+) xylose. Pentitol; xylitol

D lyxose. α form (+)→(−) β form (−)→(+). Pentitol; D (+)(borax) lyxitol A11.17

7. D (−) arabinose Pentitol; D Arabinitol (≡ D-lyxitol, q.v.) Y20

8. D(−) ribose. Y4, Y24 Y14′ Pentitol; ribitol

9. D (+) allose. Hexitol; allitol (*meso*−)

10. D (+) threose. Tetrol; D-threitol (+)(H_2O) (−)(EtOH) (c.f. A13.12)

11. D(−)erythrose. Tetrol; erythritol (*meso*−) Y8′

D (*R*)−(+) glyceraldehyde A1.1 Triol: glycerol

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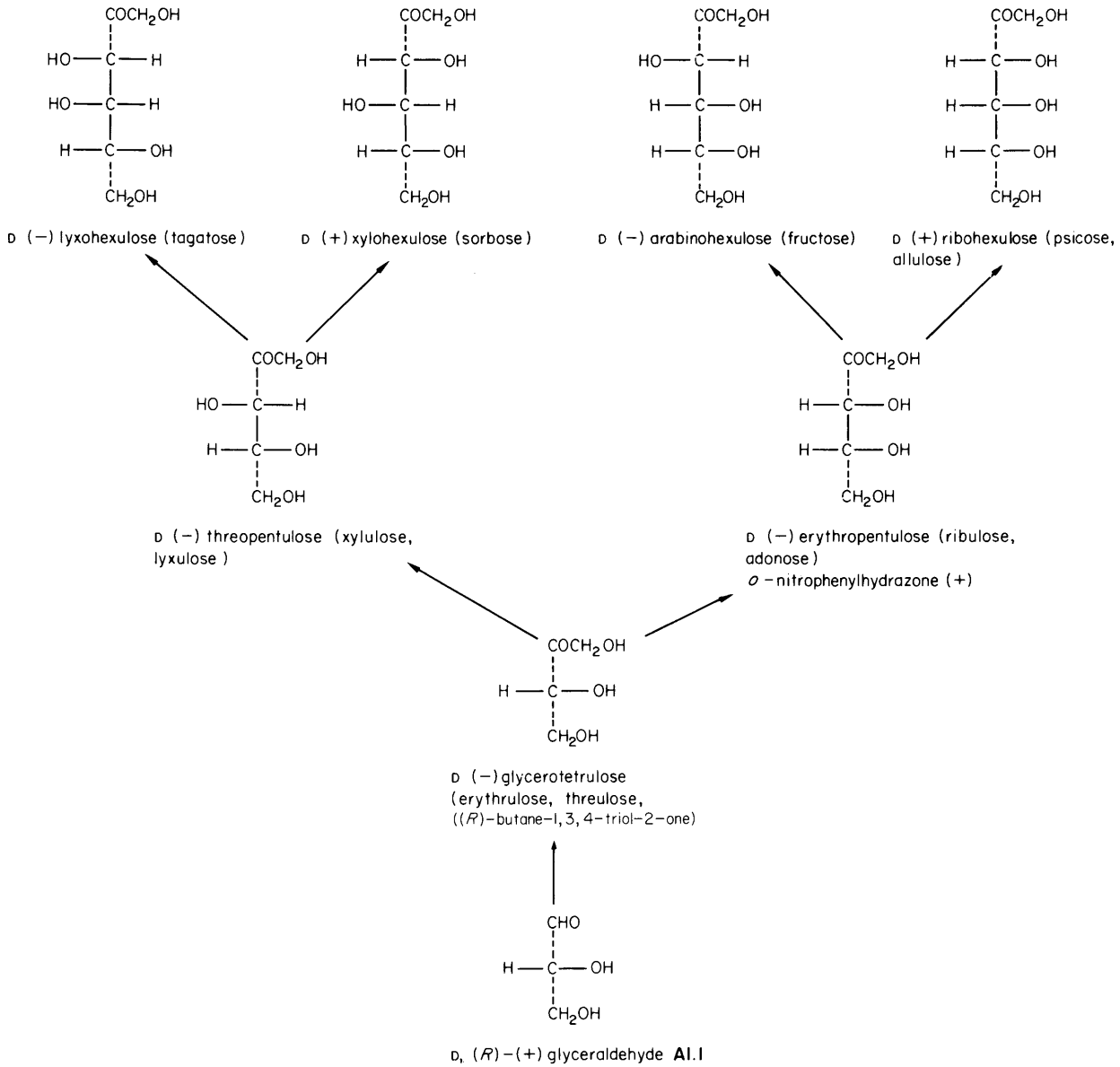

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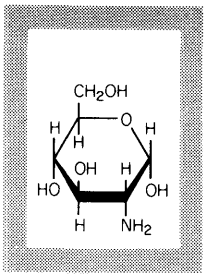
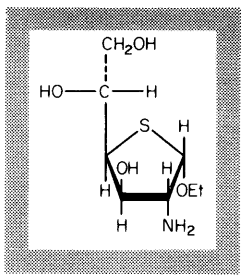
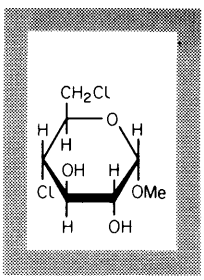


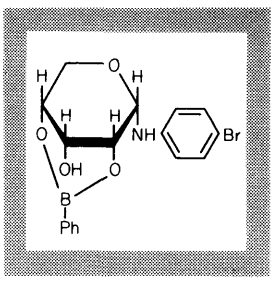
1. (+) 2-amino-2-deoxy-α-D-glucopyranose. *Abs. X-ray [5]*



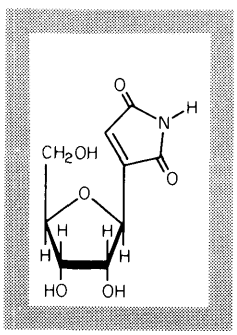
2. (+) ethyl 1-thio α-D glucofuranoside. *Abs. X-ray [6]*



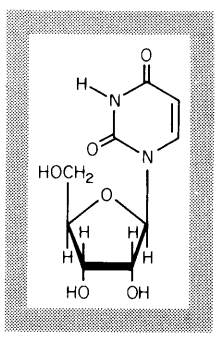
3. Methyl 4,6-dichloro-4,6-dideoxy α-D-glucopyranoside. *Abs. X-ray [7]*



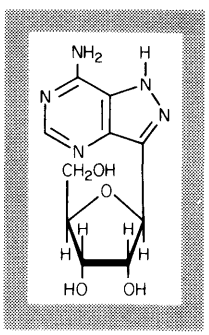
4. *N*-(*p*-bromophenyl) α-D ribopyranosylamine 2,4-phenylboronate. *Abs. X-ray [8]*



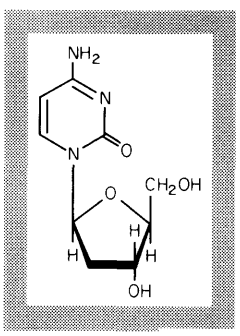
5. Showdomycin (3-β-D-ribofuranosyl maleimide) *Abs. X-ray [9]*



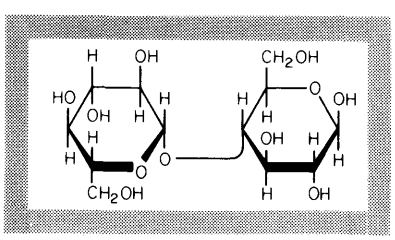
6. Uridine. *Abs. X-ray [10]*



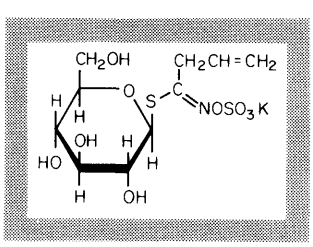
7. Formycin. *Abs. X-ray [11]*



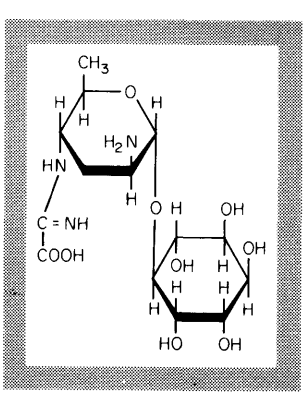
8. 2'-deoxycytidine. *Abs. X-ray [12]*



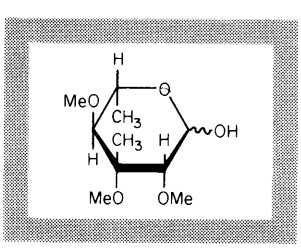
9. Cellobiose. *Abs. X-ray [13]*



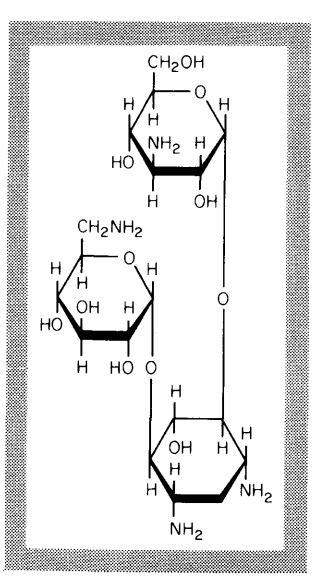
10. Sinigrin. *Abs. X-ray [14]*

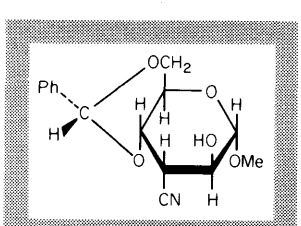


11. Kasugamycin. *Abs. X-ray [16]*



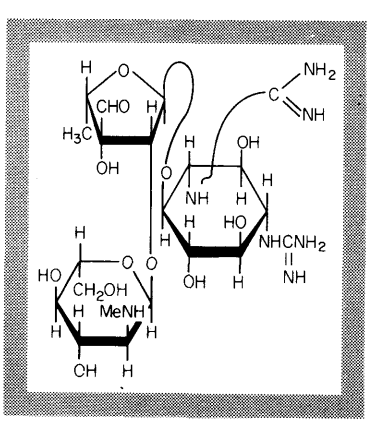
12. L-nogalose (3-*C*-methyl-2,3,4,-tri-*O*-methyl-6-deoxy-L-mannopyranose) *Abs. X-ray [15]*





13. Methyl 4,6-*O*-benzylidene-3-cyano-3-deoxy α-D-altropyranoside. *Abs. X-ray [17]*

14. Kanamycin A. *Abs. X-ray [18]*



15. Streptomycin. *Abs. X-ray [19]*

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-T-

Terpenes (including Steroids)

Introductory Notes to Chapter T

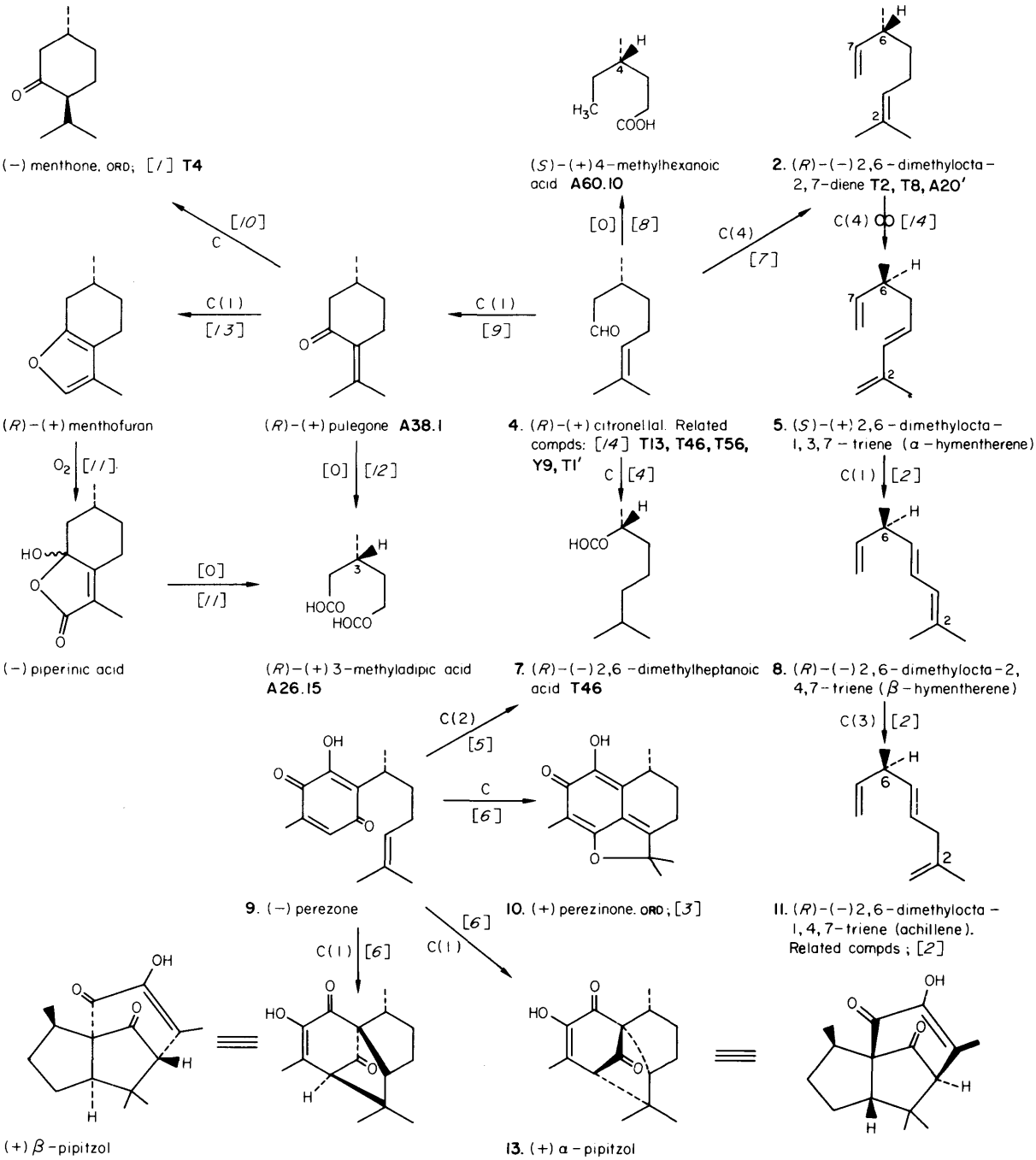
Scope

The term 'terpene' has been given its widest interpretation here, and modified terpene types such as furanoterpenes and norterpenes (including steroids) are included. The arrangement of material is basically in order of increasing molecular weight, i.e. from mono- to tetra-terpenes, and within each subdivision the simple types, as far as practicable, precede the more complex.

Arrangement

Monoterpenes	**T1–T17**
Sesquiterpenes	**T1–3, T6, T11–12, T16–32**
Diterpenes	**T32–T41**
Sesterterpenes	**T41**
Triterpenes	**T42–T51**
Steroids	**T46–T51**
Nortriterpenoids (Limonoids, etc.)	**T52–T53**
Tetraterpenes (including ionone group)	**T54–T55**
Phytol-tocopherol-phylloquinone group	**T56**
Miscellaneous modified terpenes	**T57–T58**

The section on steroids is considerably shorter than would be justified on the basis of their importance as natural products, but they fall into the category of a 'stereochemically homogenous' series of compounds (see Introduction), for which extensive further description in the 'Atlas' would be superfluous.



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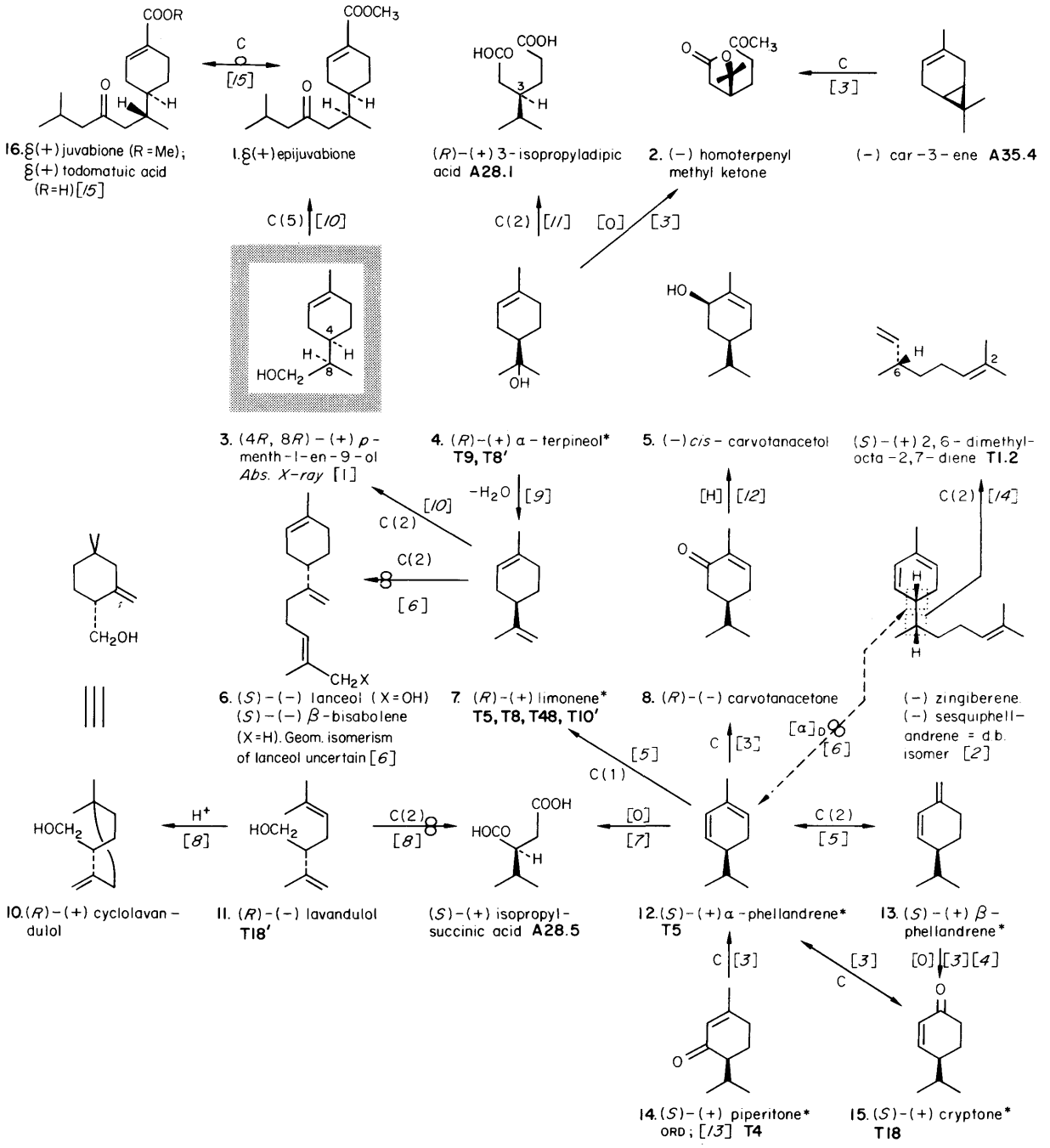

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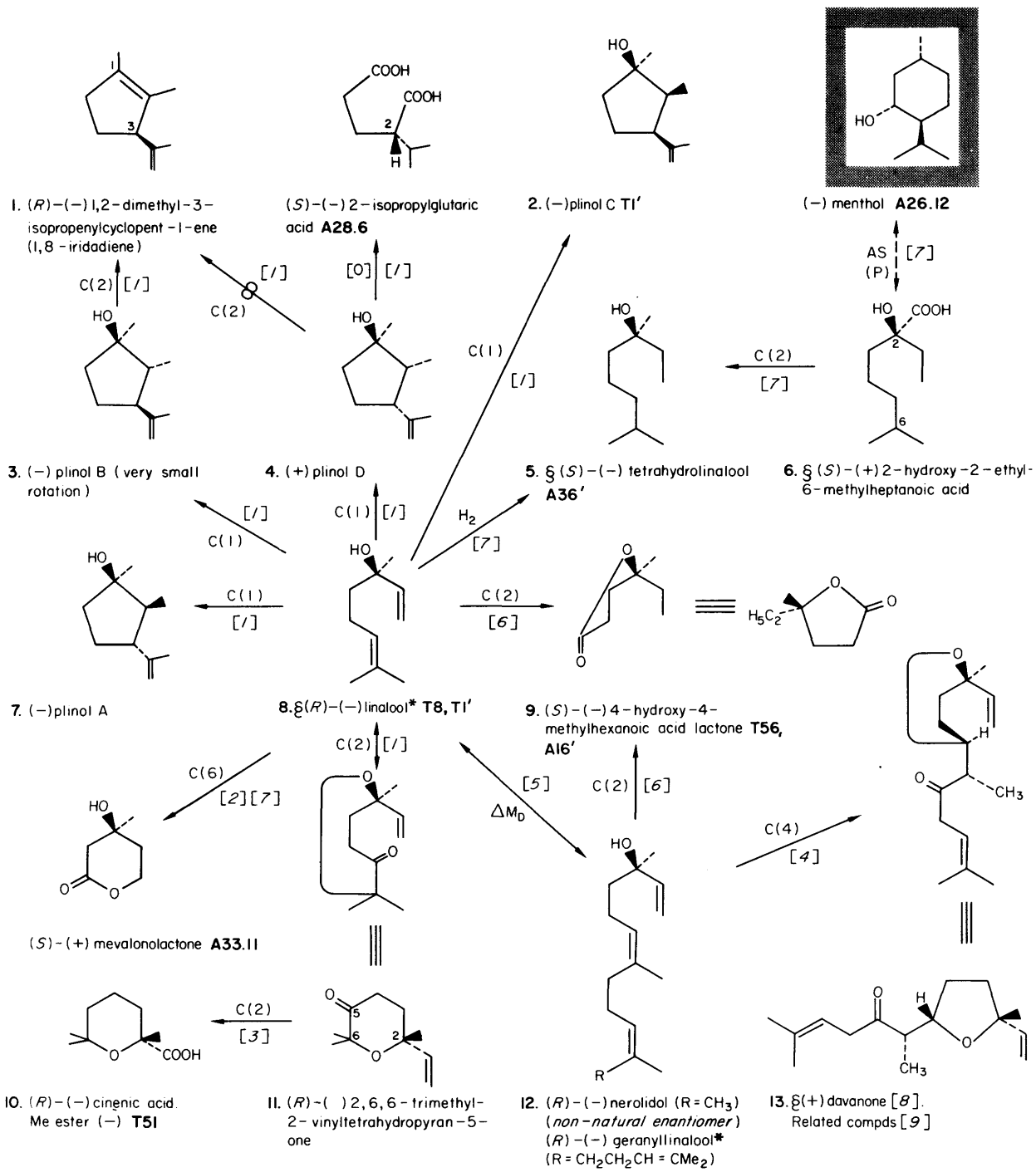

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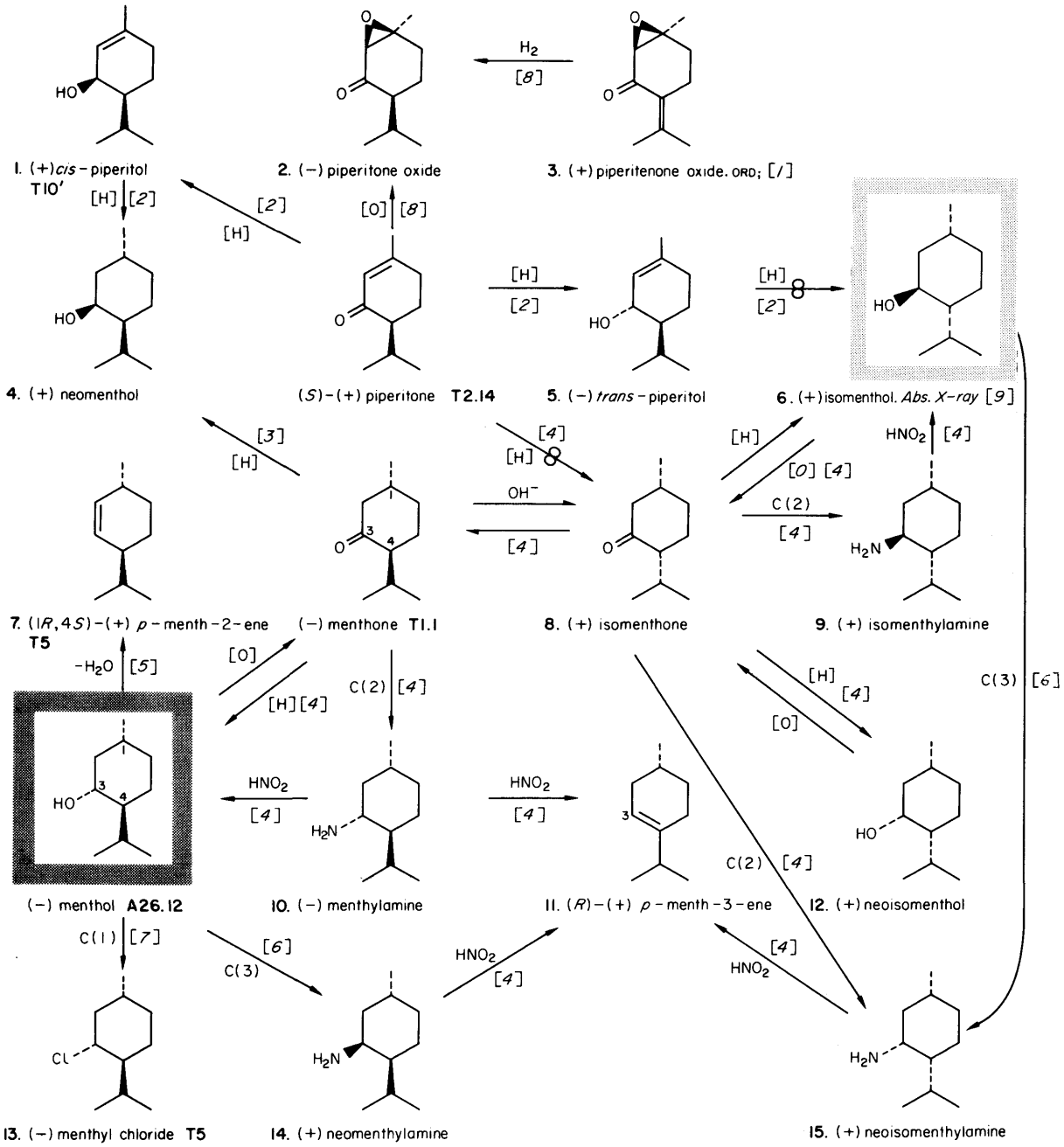

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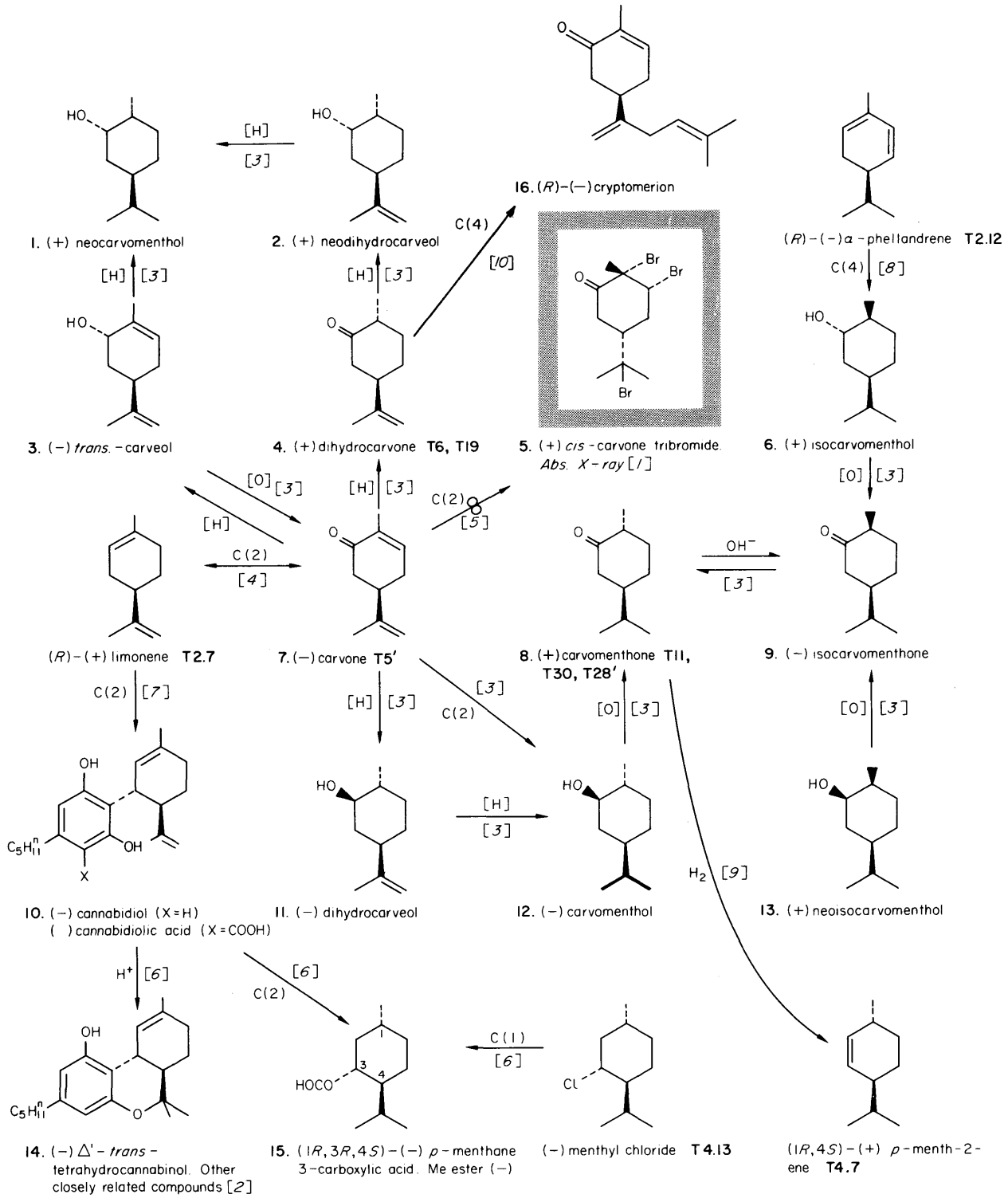

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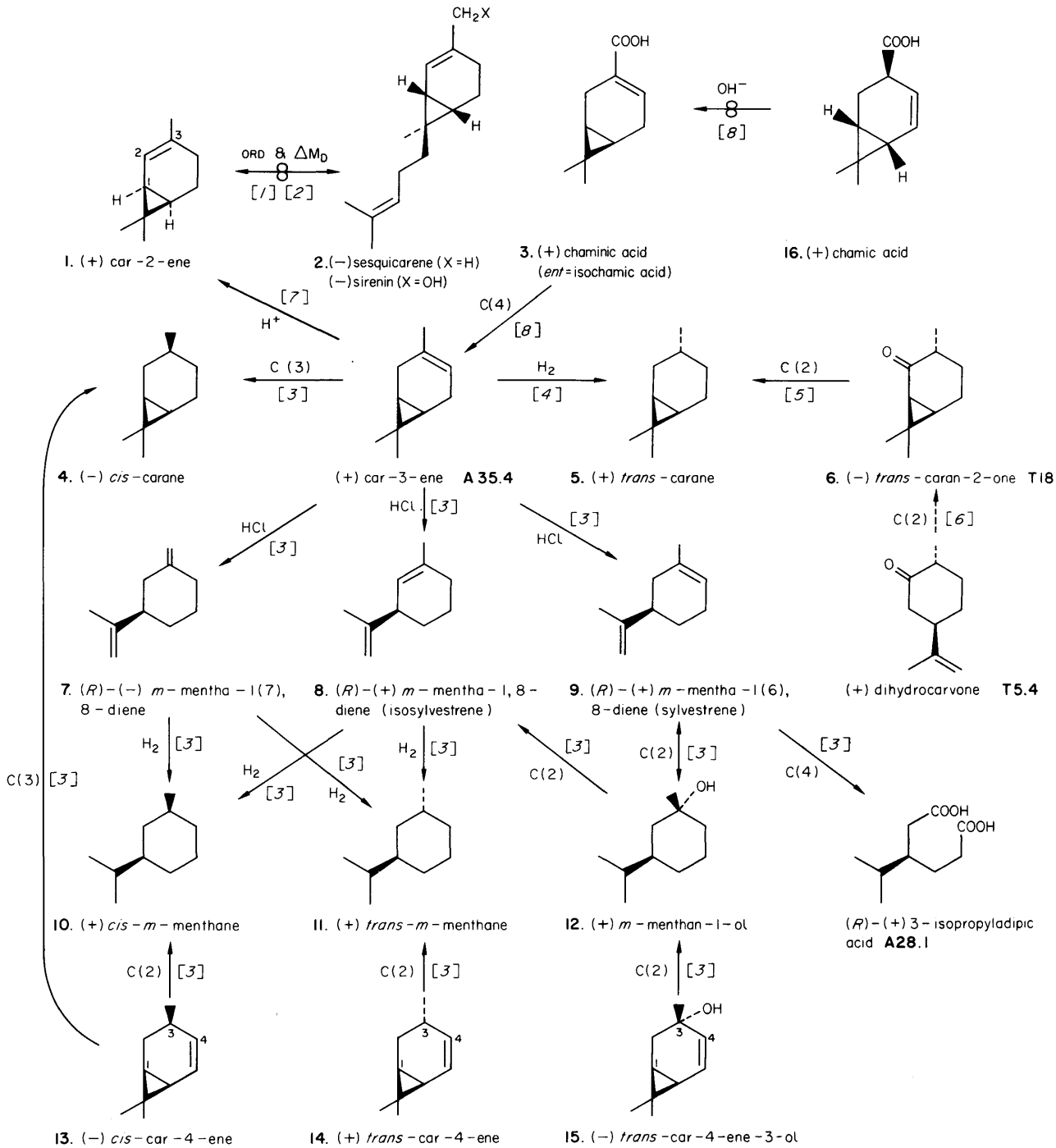

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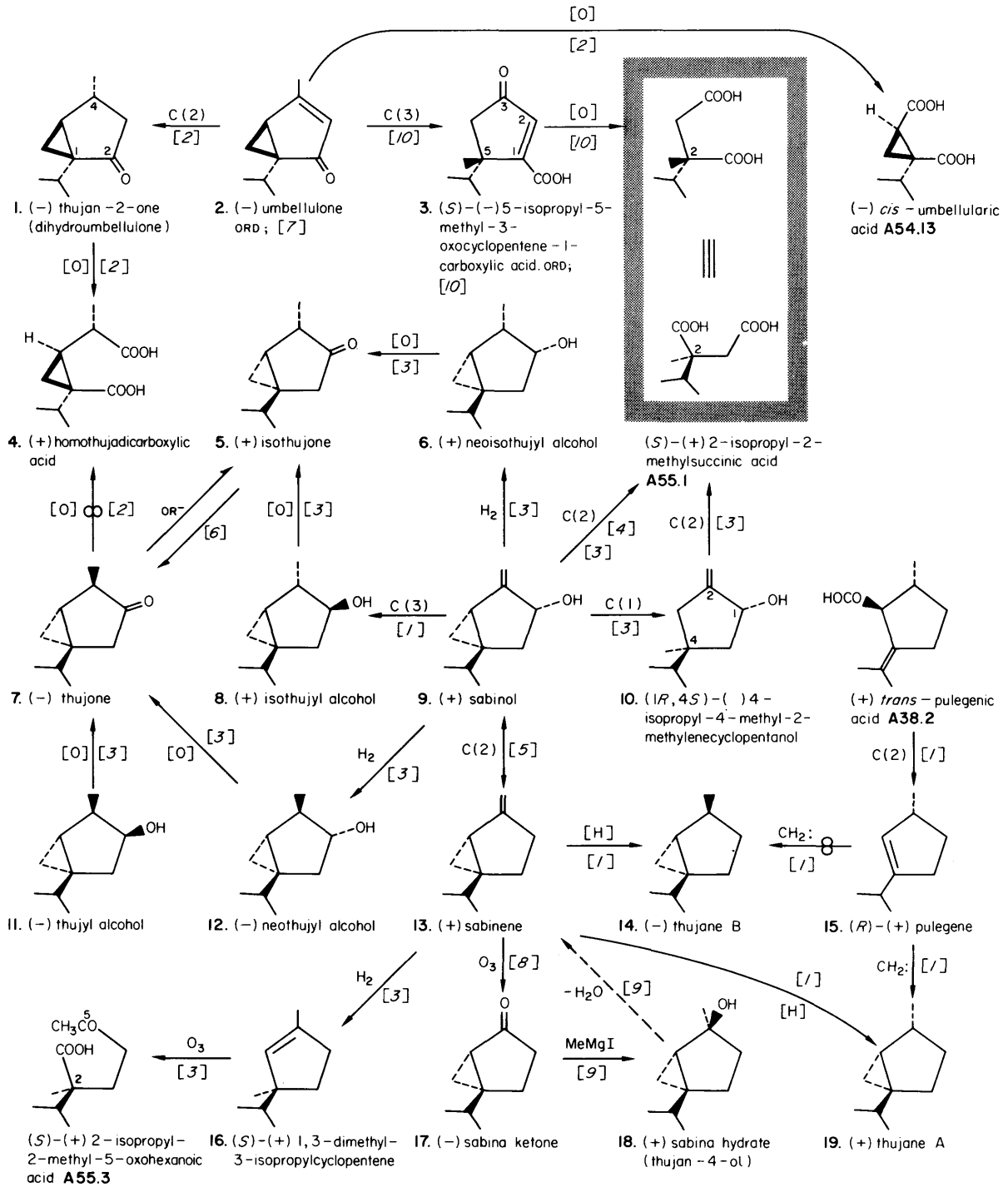
Review; [11]



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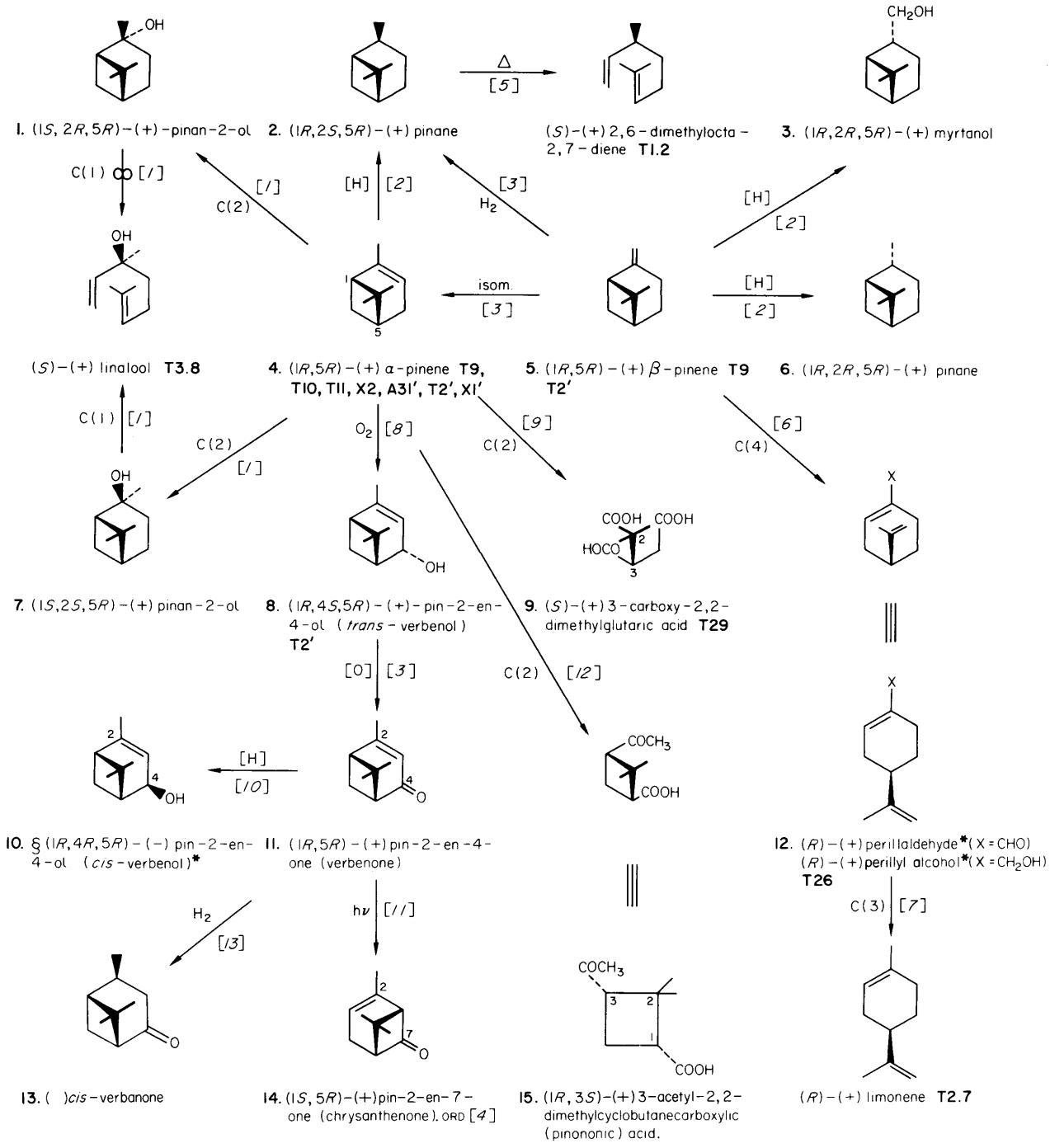
Pinane (bicyclo(3.1.1)heptane) group.

Review; [3]



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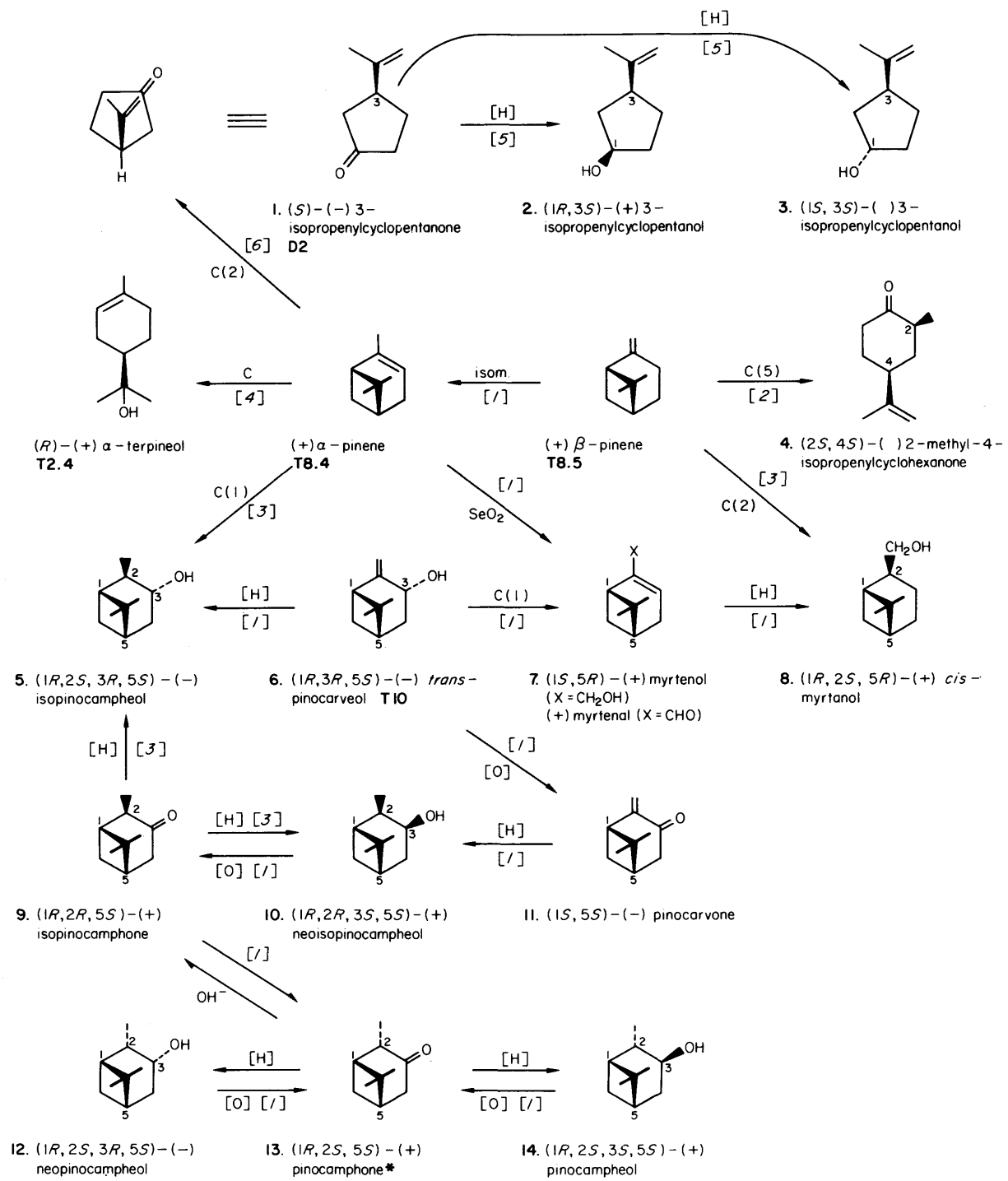

1. I. (*S*)-(−) 3-isopropenylcyclopentanone
2. (1*R*,3*S*)-(+)3-isopropenylcyclopentanol
3. (1*S*, 3*S*)-( )3-isopropenylcyclopentanol
4. (2*S*, 4*S*)-( )2-methyl-4-isopropenylcyclohexanone
5. (1*R*,2*S*, 3*R*, 5*S*)-(−) isopinocampheol
6. (1*R*,3*R*, 5*S*)-(−) *trans*-pinocarveol **T10**
7. (1*S*,5*R*)-(+) myrtenol (X = CH_2OH) (+) myrtenal (X = CHO)
8. (1*R*, 2*S*, 5*R*)-(+) *cis*-myrtanol
9. (1*R*,2*R*, 5*S*)-(+) isopinocamphone
10. (1*R*,2*R*, 3*S*, 5*S*)-(+) neoisopinocampheol
11. (1*S*, 5*S*)-(−) pinocarvone
12. (1*R*, 2*S*, 3*R*, 5*S*)-(−) neopinocampheol
13. (1*R*, 2*S*, 5*S*)-(+) pinocamphone*
14. (1*R*, 2*S*, 3*S*, 5*S*)-(+) pinocampheol

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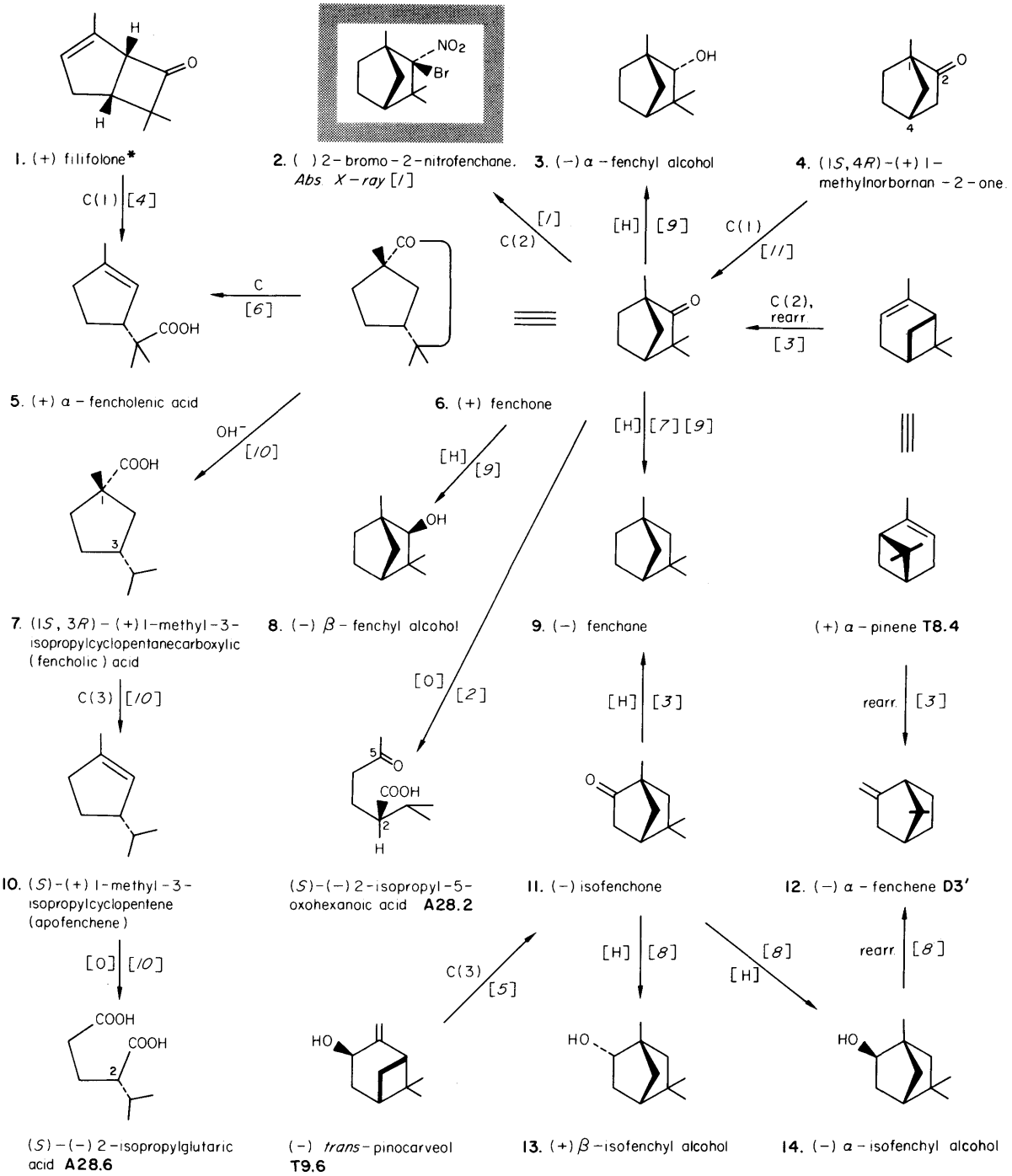
Bicyclo(2.2.1)heptane types; camphor and related terpenes.



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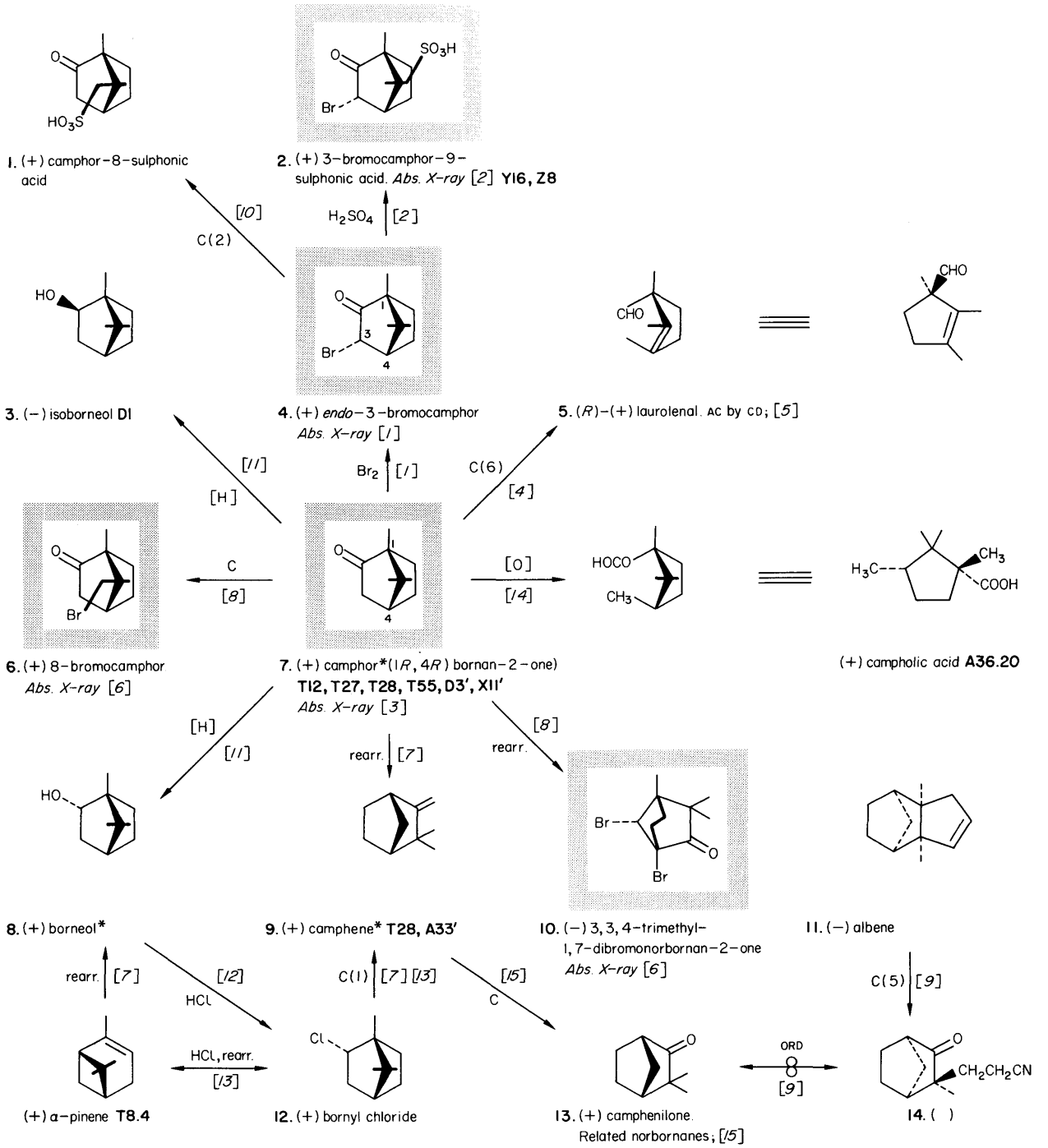

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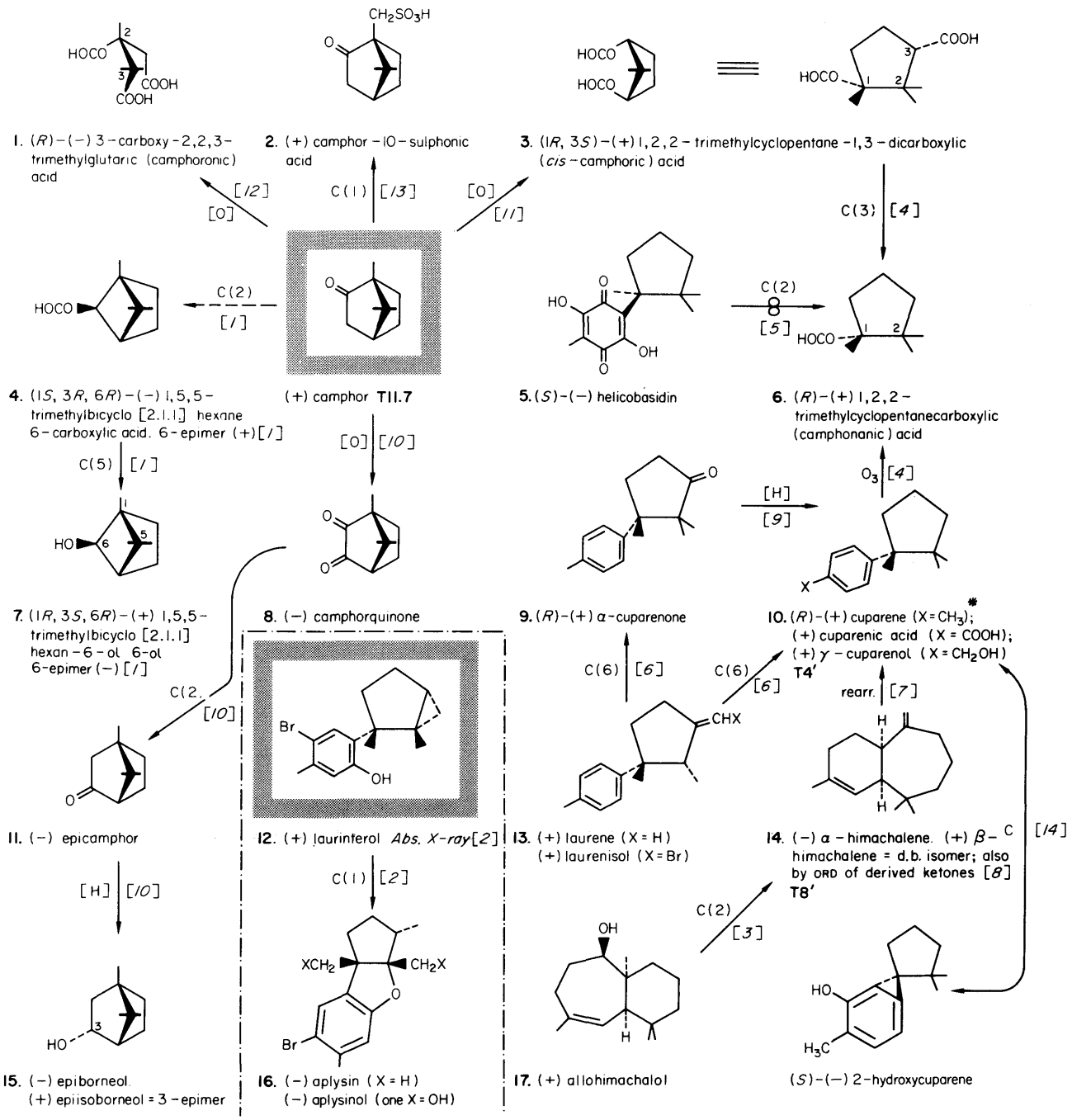
Further mono- and sesquiterpenes related to camphor.



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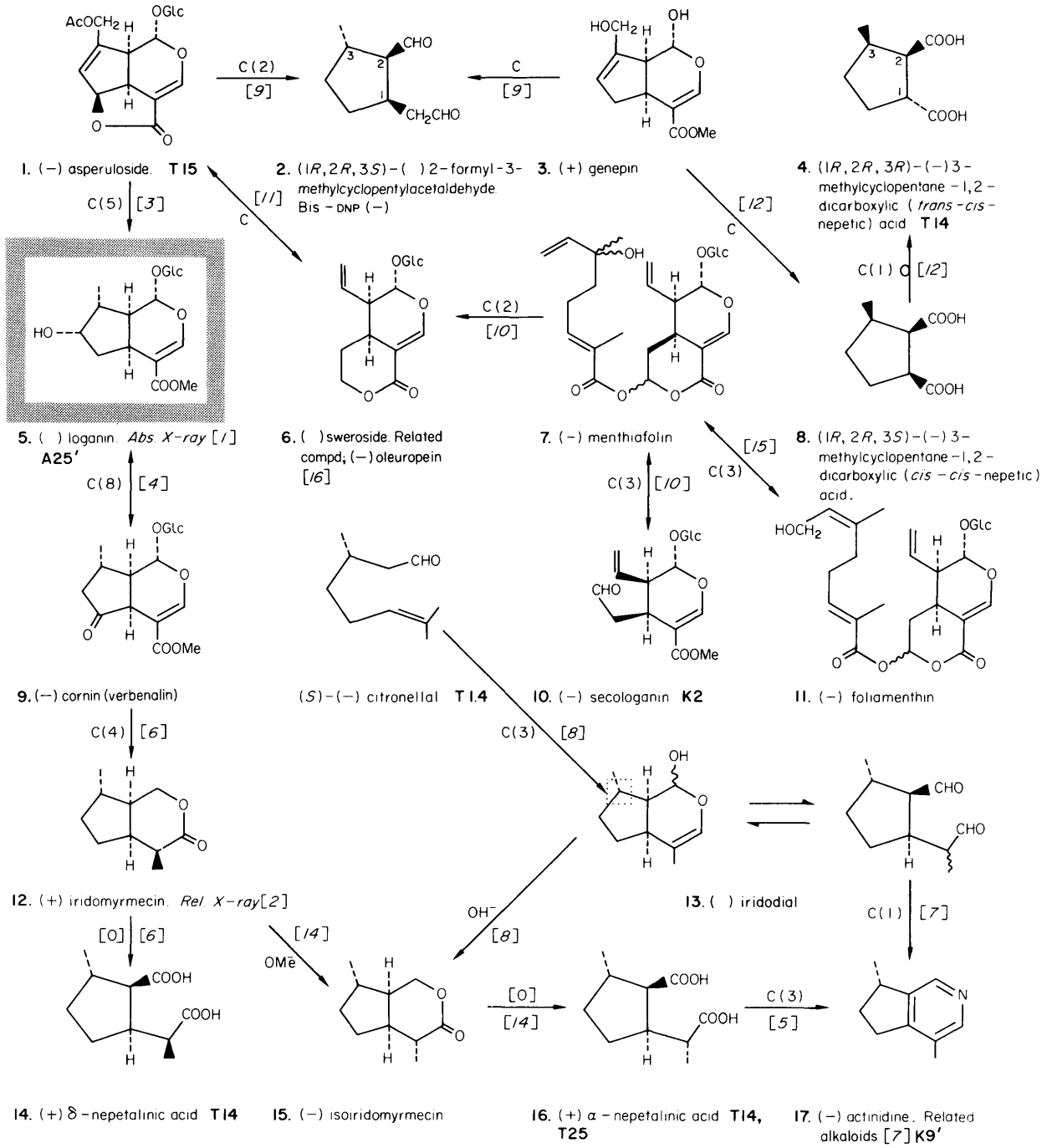
Cyclopentanoid monoterpenes. Iridanes and secoiridanes; loganin.

Review; [13].



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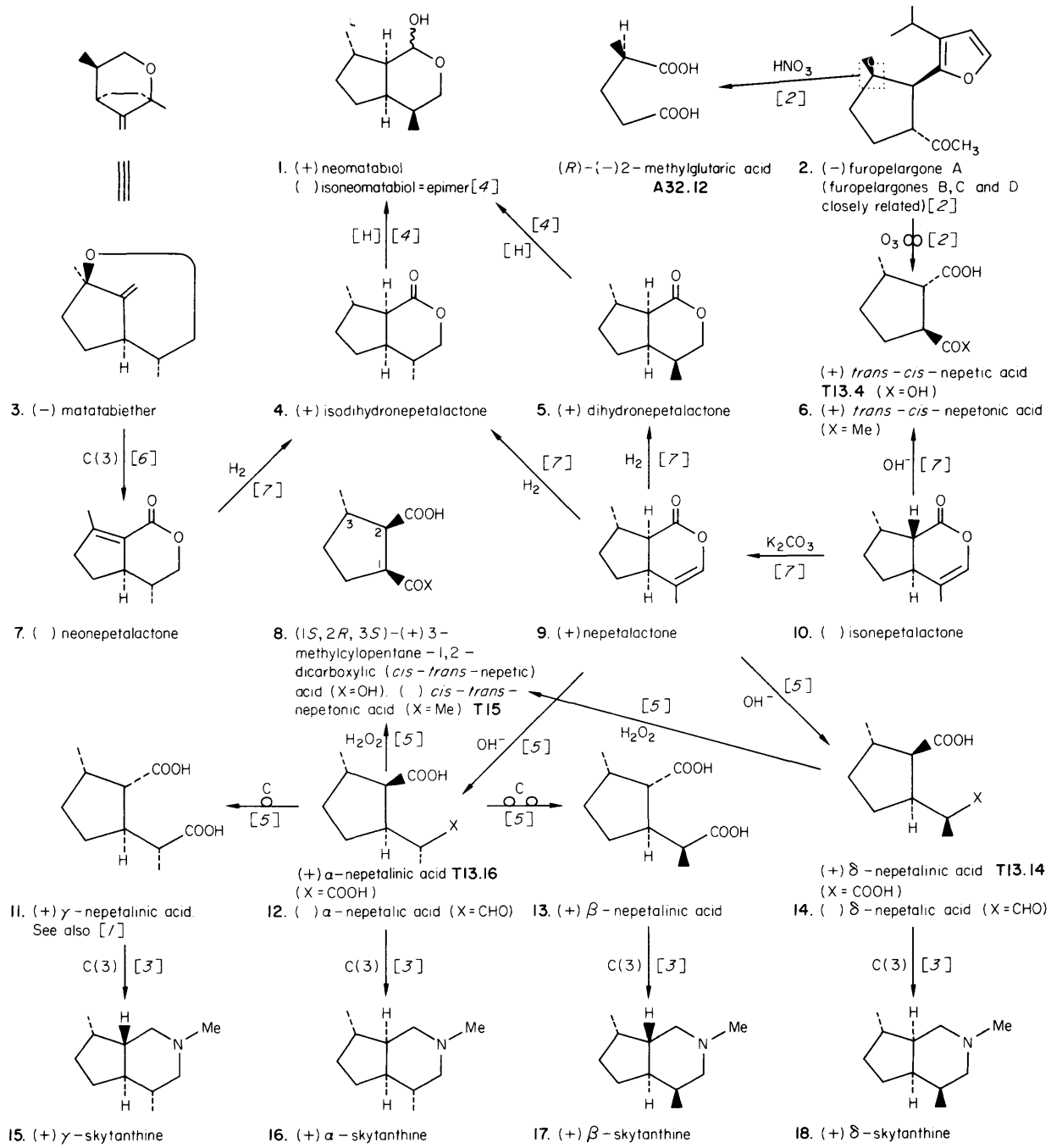
Cyclopentanoid monoterpenes (contd.); nepetic and nepetalinic acids.



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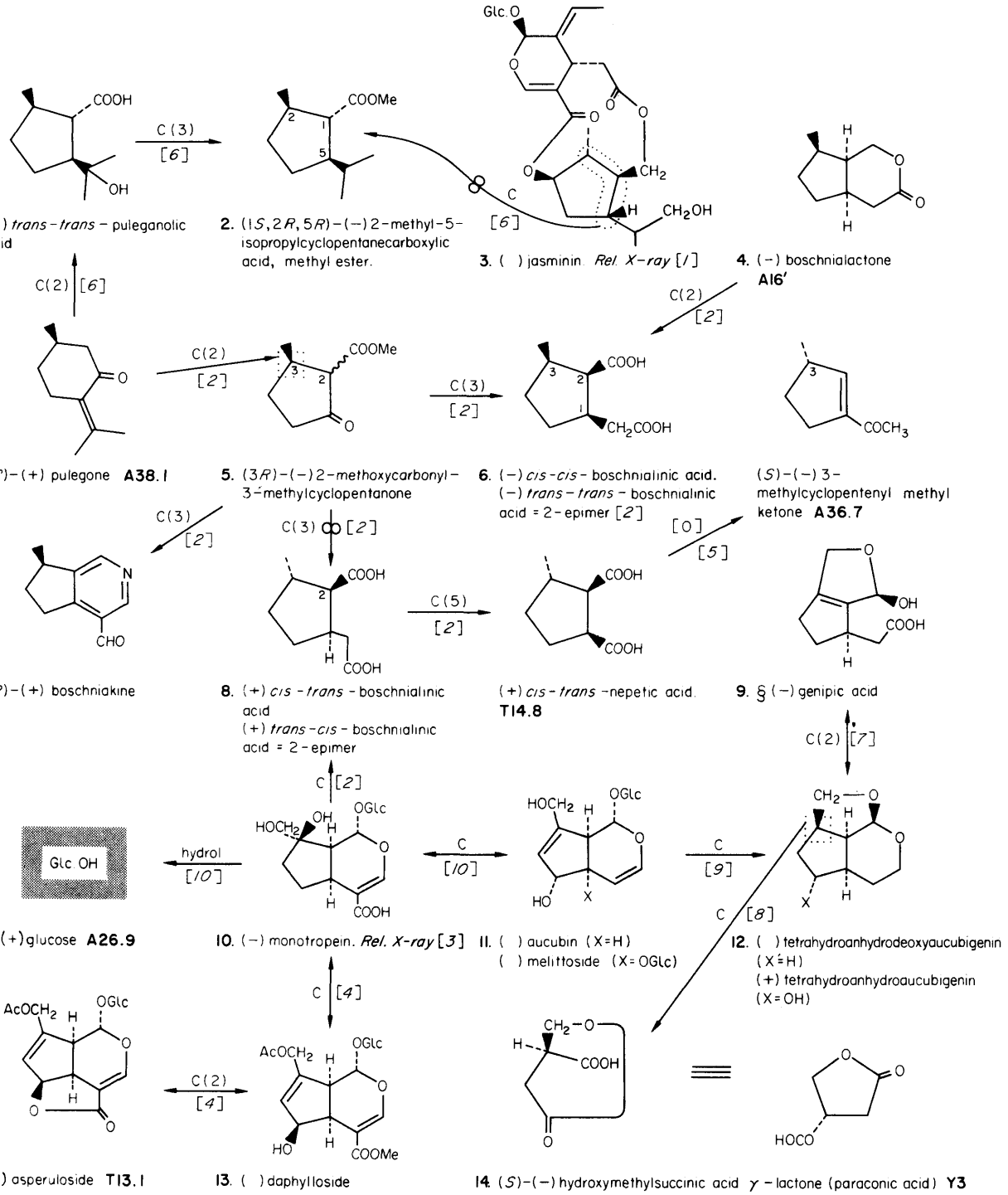

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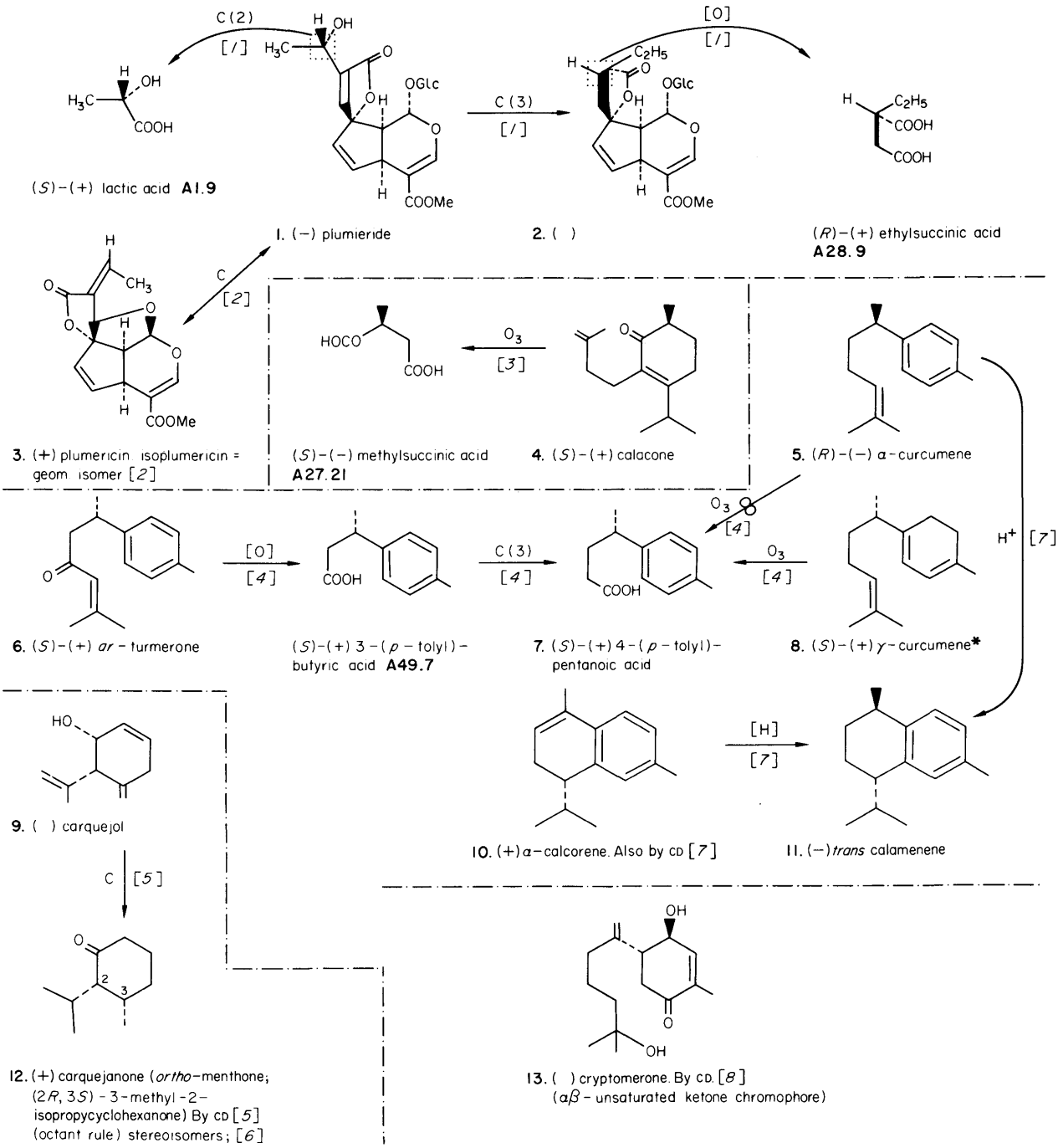

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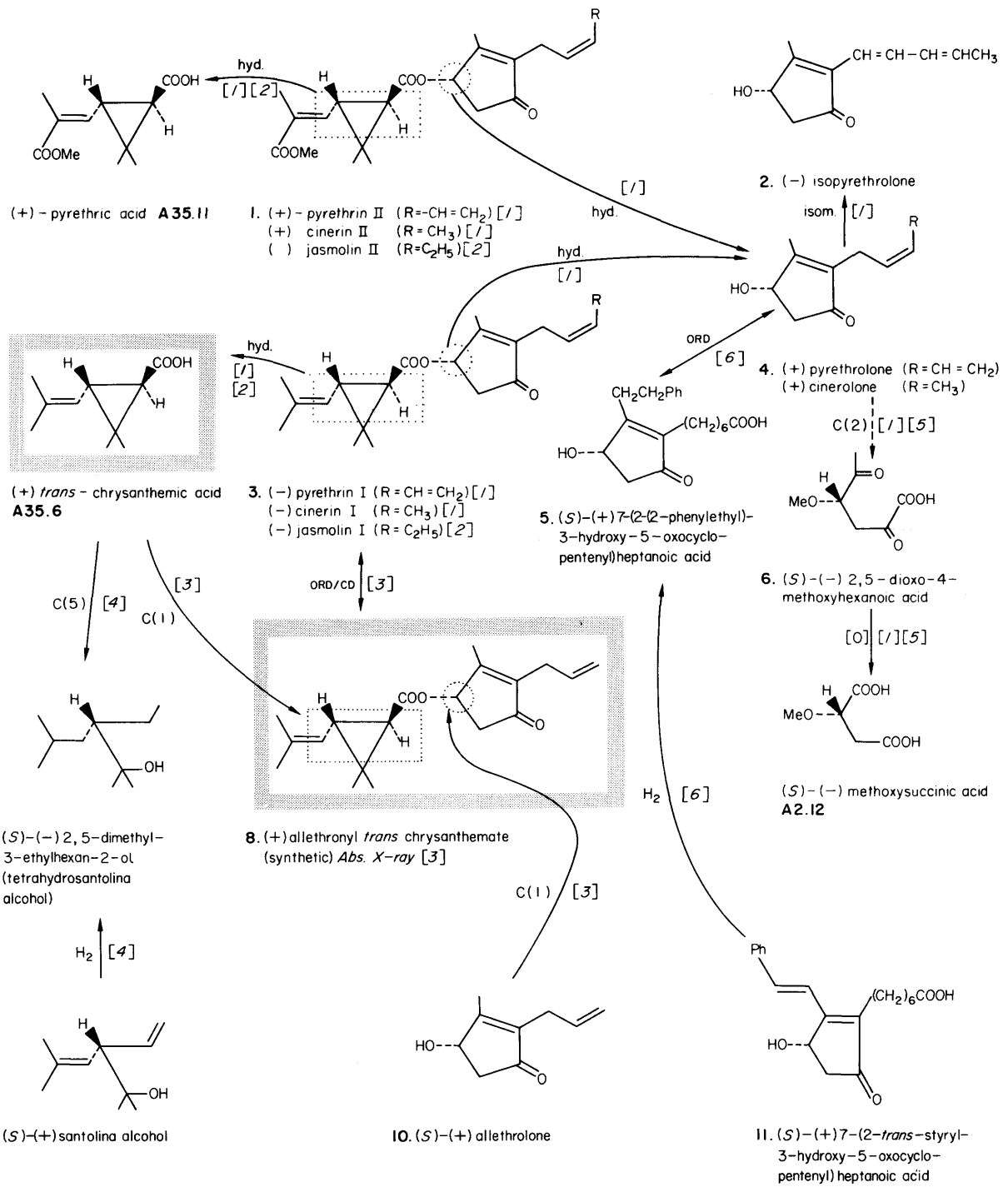

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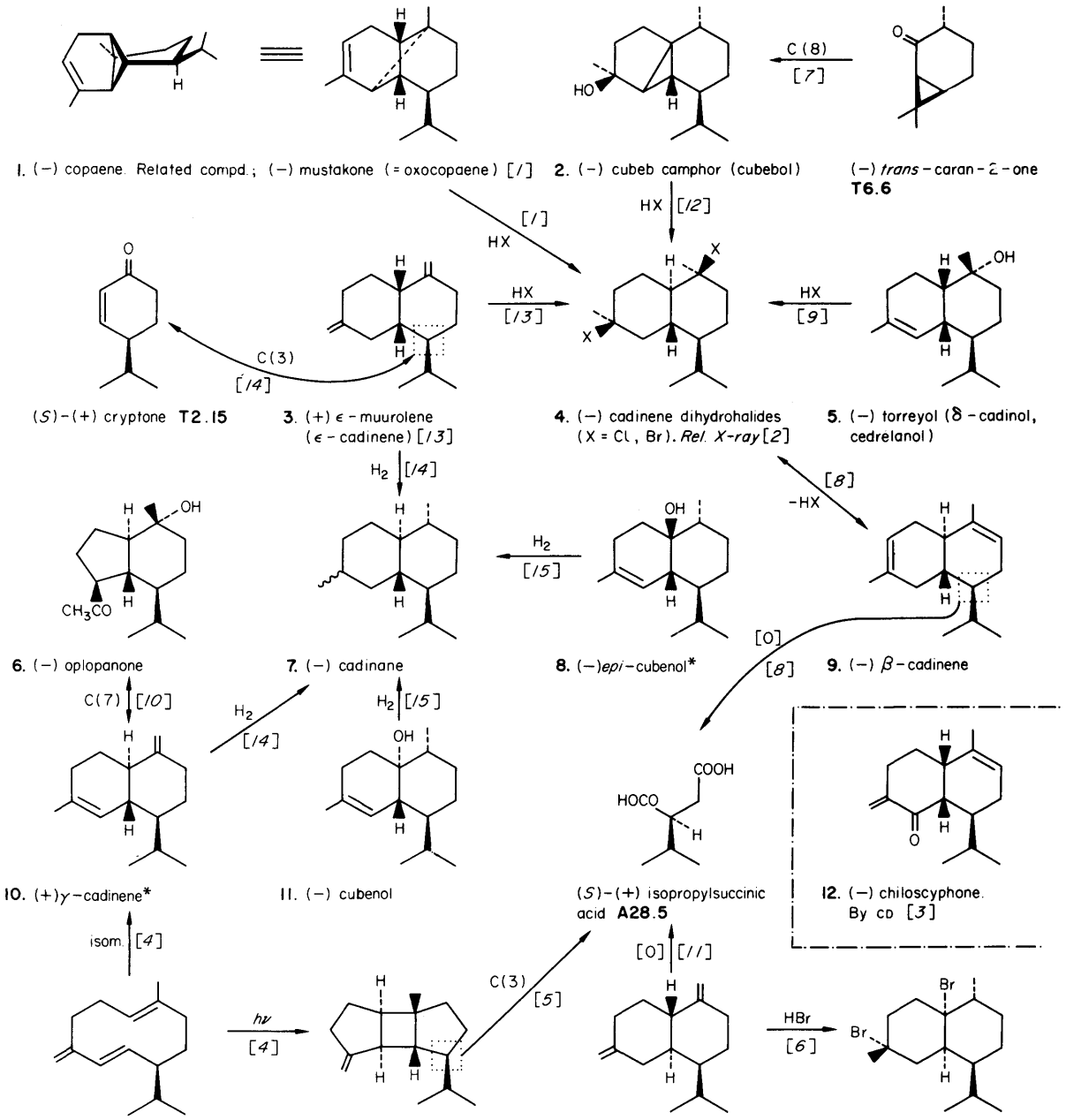
Cadinane group and related compounds.

Discussion of nomenclature and stereochemistry: [11]



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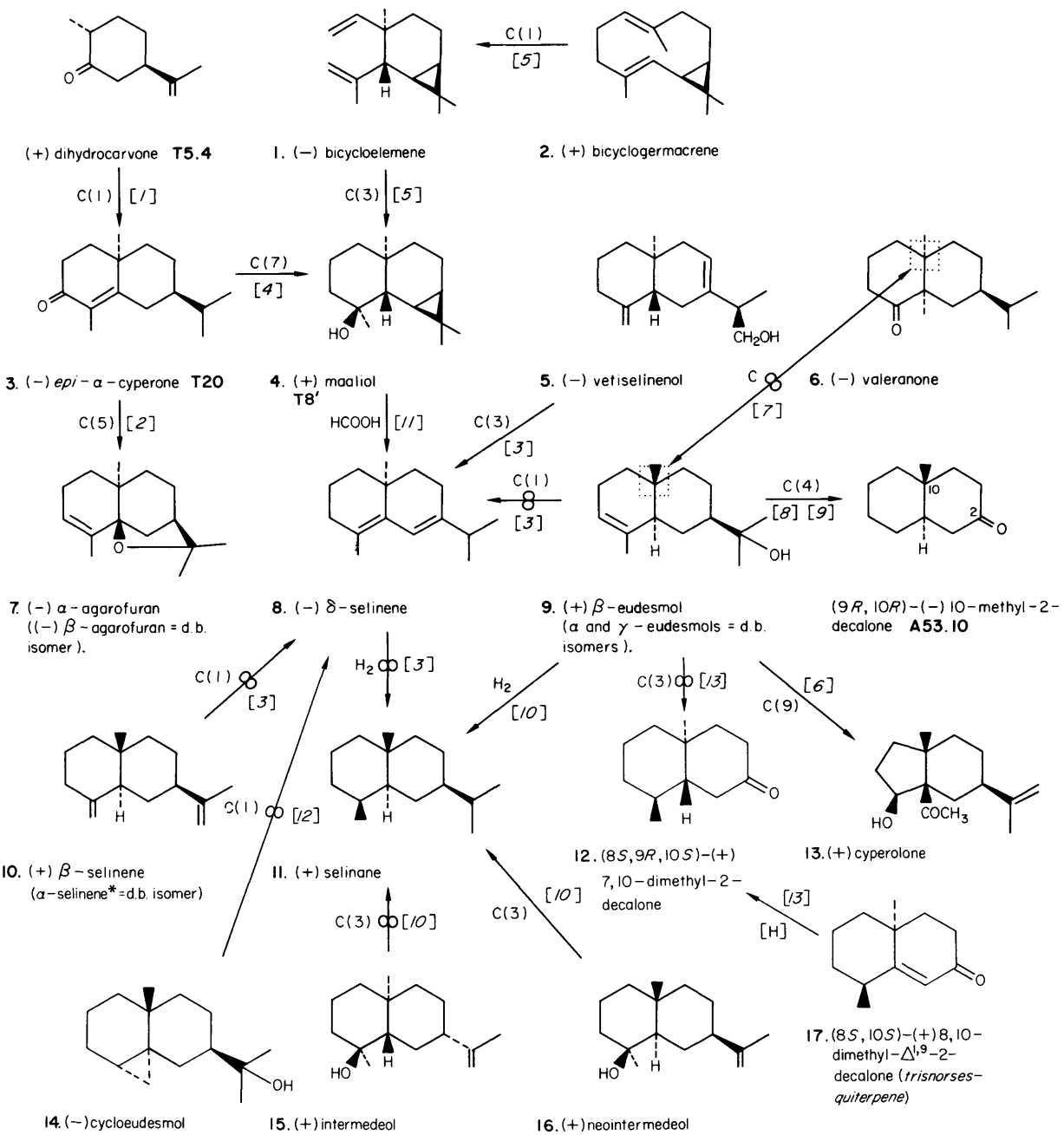

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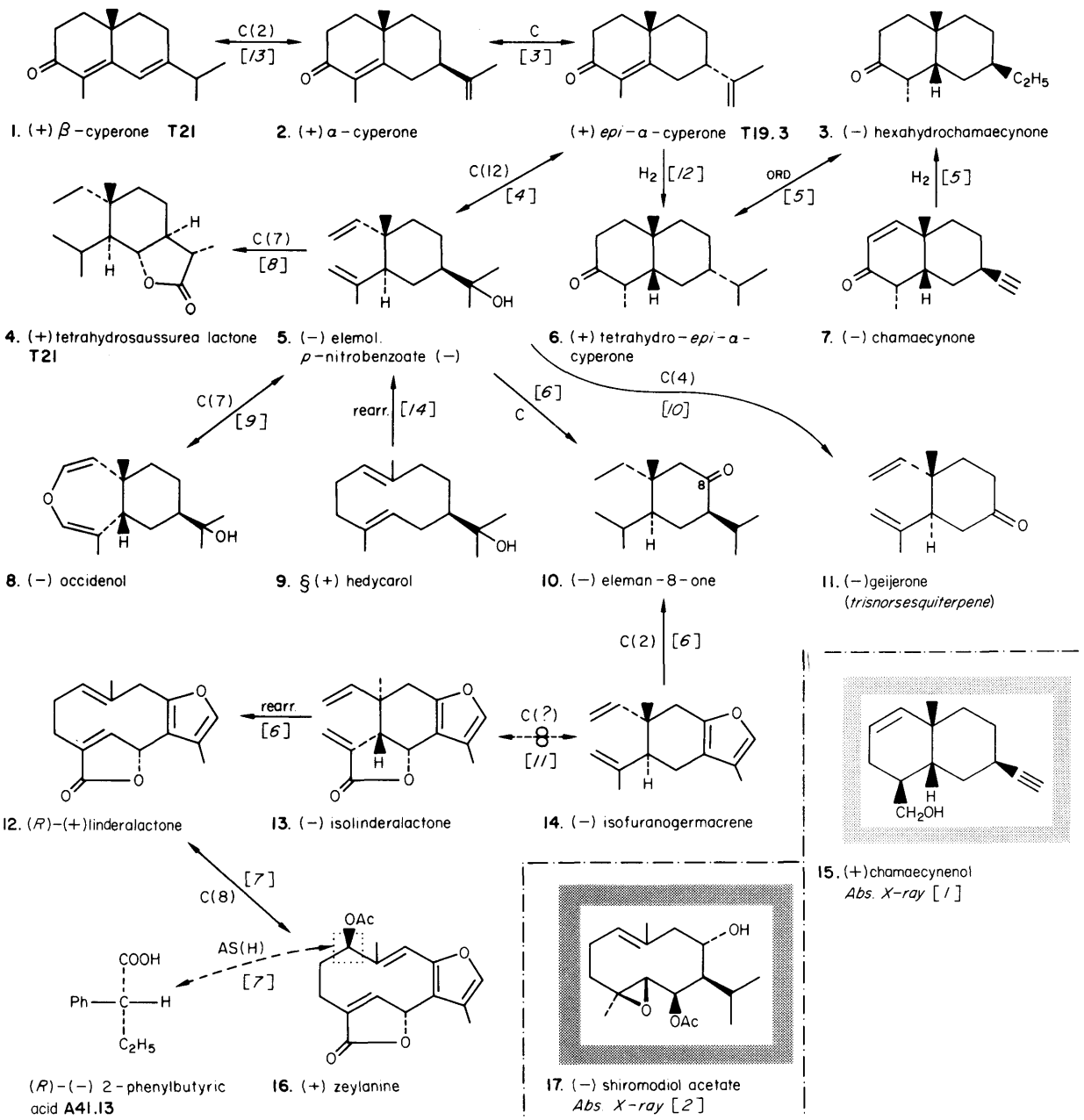
Elemane group and related sesquiterpenes.



1. (+) β-cyperone **T21**
2. (+) α-cyperone
3. (+) *epi*-α-cyperone **T19.3**
4. (+) tetrahydrosaussurea lactone **T21**
5. (−) elemol *p*-nitrobenzoate (−)
6. (+) tetrahydro-*epi*-α-cyperone
7. (−) chamaecynone
8. (−) occidenol
9. § (+) hedycarol
10. (−) eleman-8-one
11. (−) geijerone (*trisnorsesquiterpene*)
12. (*R*)-(+) linderalactone
13. (−) isolinderalactone
14. (−) isofuranogermacrene
15. (+) chamaecynenol *Abs. X-ray* [1]
16. (+) zeylanine
17. (−) shiromodiol acetate *Abs. X-ray* [2]

(*R*)-(−) 2-phenylbutyric acid **A41.13**

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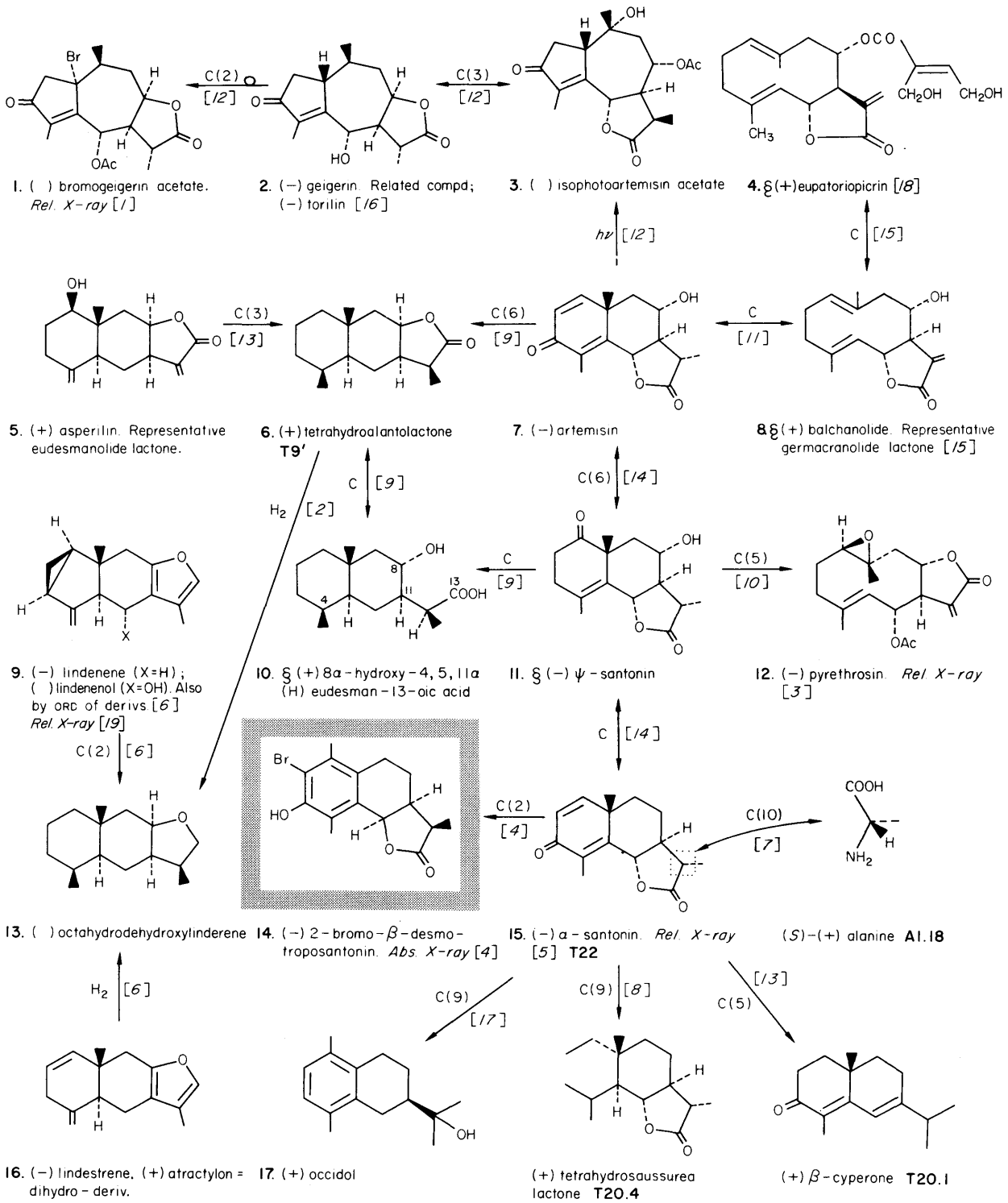

1. ( ) bromogeigerin acetate. *Rel. X-ray* [1]
2. (−) geigerin. Related compd; (−) torilin [16]
3. ( ) isophotoartemisin acetate
4. §(+)eupatoriopicrin [18]
5. (+) asperilin. Representative eudesmanolide lactone.
6. (+) tetrahydroalantolactone T9′
7. (−) artemisin
8. §(+) balchanolide. Representative germacranolide lactone [15]
9. (−) lindenene (X=H); ( ) lindenenol (X=OH). Also by ORD of derivs. [6] *Rel. X-ray* [19]
10. § (+) 8α-hydroxy-4, 5, 11α (H) eudesman-13-oic acid
11. § (−) ψ-santonin
12. (−) pyrethrosin. *Rel. X-ray* [3]
13. ( ) octahydrodehydroxylinderene
14. (−) 2-bromo-β-desmotroposantonin. *Abs. X-ray* [4]
15. (−) α-santonin. *Rel. X-ray* [5] T22
16. (−) lindestrene, (+) atractylon = dihydro-deriv.
17. (+) occidol

(S)-(+) alanine A1.18

(+) tetrahydrosaussurea lactone T20.4

(+) β-cyperone T20.1

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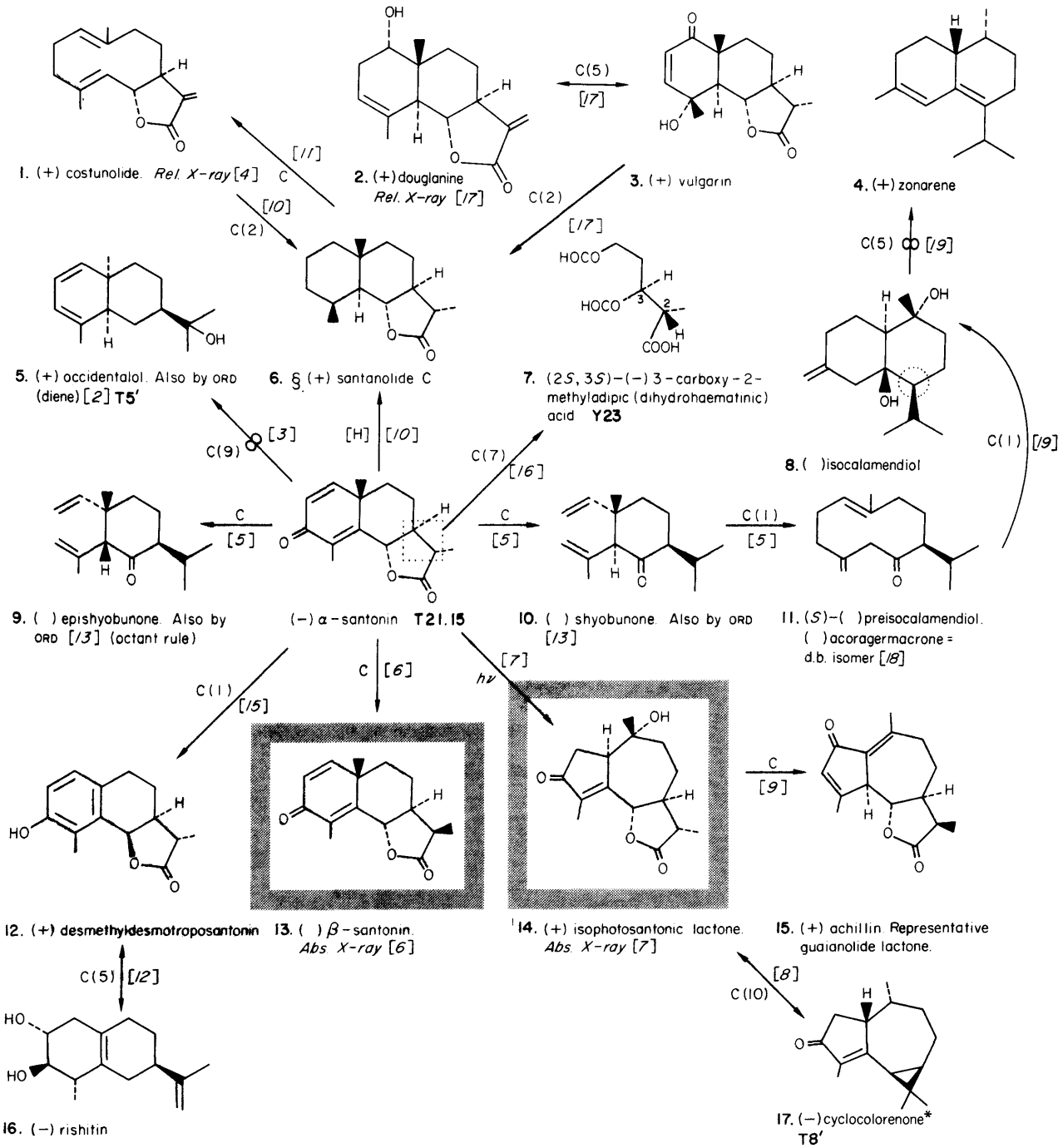
ORD/CD of santanolides and guaianolides: [14]



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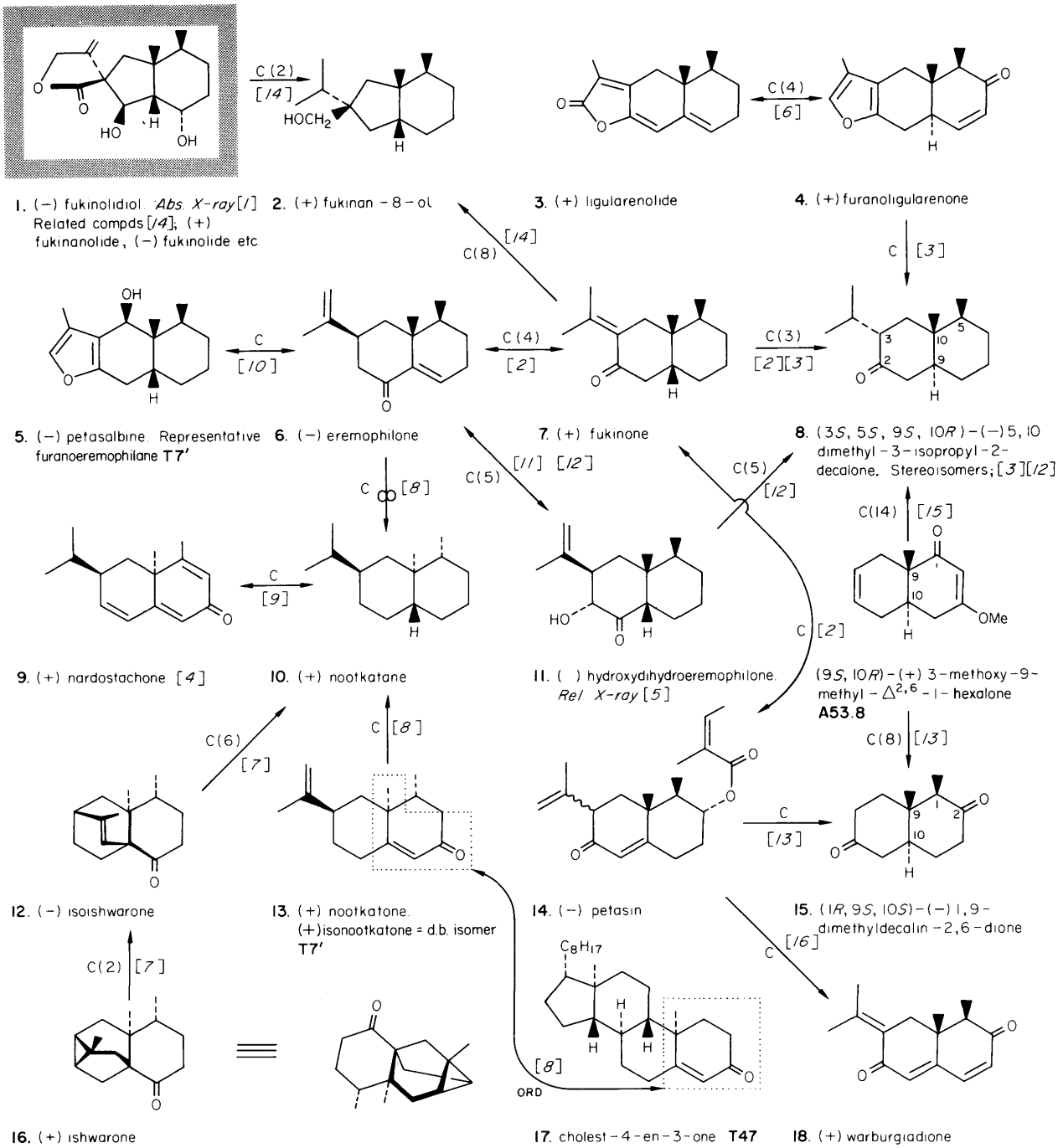

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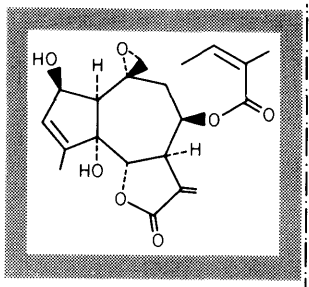
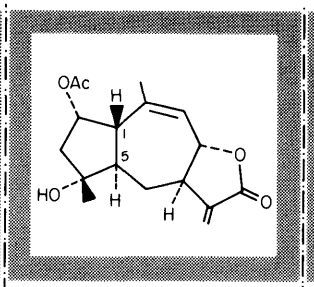
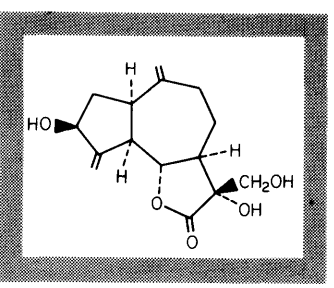
Pseudoguaianolide and xanthanolide lactones.



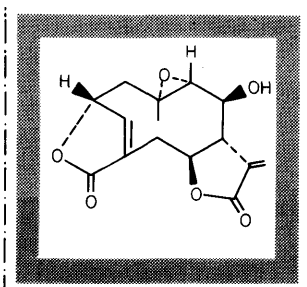
1. (−) euparotin. *Abs. X-ray* [1] Related compds; [2]



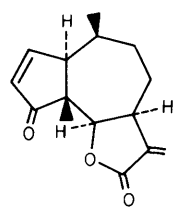
2. (−) gaillardin.† *Abs. X-ray* [3]



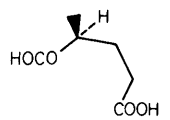
3. ( ) solsitalin. *Abs. X-ray* [4]



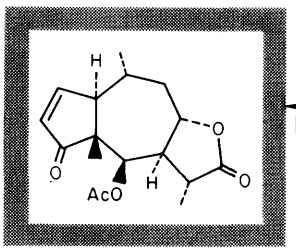
4. (+) elephantol. *Abs. X-ray* [5]



5. (−) ambrosin. *Rel. X-ray* [6]

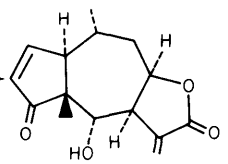


(*S*)-(+) 2-methylglutaric acid A32.12



6. (+) isotenulin. *Abs. X-ray* [7]

C [12]

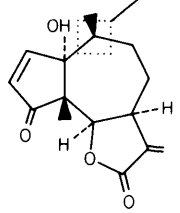


7. (−) helenalin. *Rel. X-ray* [8]

C [14]

[O]

[14]



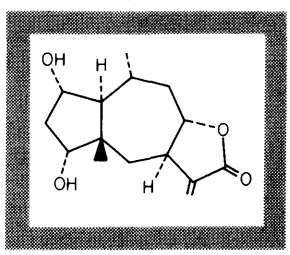
8. (+) parthenin.

Many other lactones of the psuedoguaianolide [12] and xanthanolide series have been chemically correlated with the few examples given here. ORD of pseudoguaianolides and xanthanolides; [10]

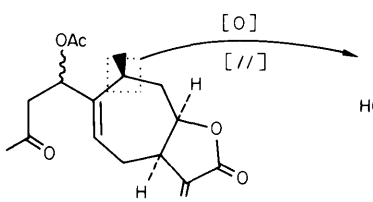
[12]

C

C [12]



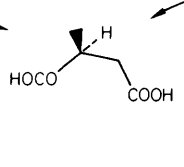
9. (−) pulchellin A. *Abs. X-ray* [9]



10. (−) xanthumin.

[O]

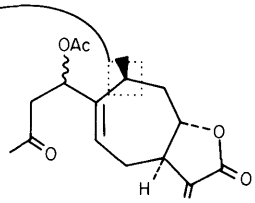
[11]



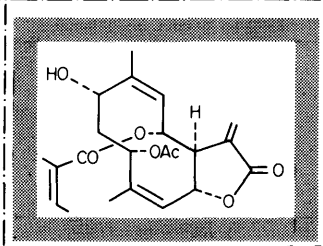
(*S*)-(−) methylsuccinic acid A27.21

[O]

[11]



11. ( ) xanthinin. Related compds; (−) xanthanol, ( ) ivalbin etc. [11]



12. (+) eupacunin. *Abs. X-ray* [13]

†Gaillardin is the only known fully characterised guaianolide with C_1C_5 *trans* stereochemistry [15]

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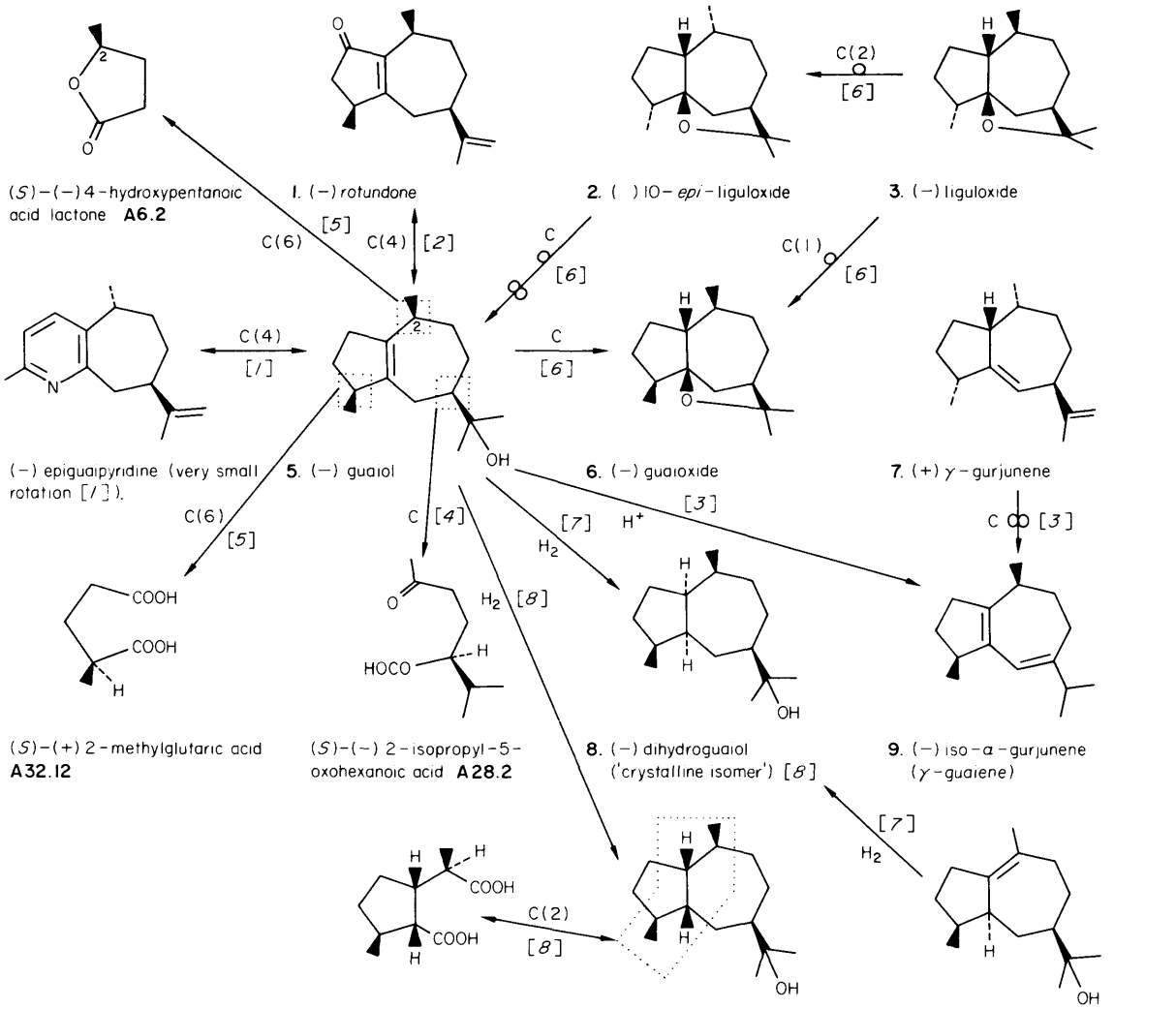
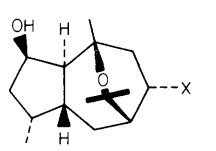
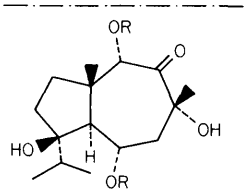
Bicyclo [5.3.0]-decane types: guaiol and related sesquiterpenes.





12. (−) α-kessyl alcohol (X=H) (−) α-kessyl glycol (X=OH) By ORD (benzoate chirality rule) [9]



13. ( ) laserol. (R=H) (+) laserpitine (R = COC(CH$_3$)=CHCH$_3$) *Rel. X-ray* [11] AC by ΔM_D of dinitrobenzoate formation [10]

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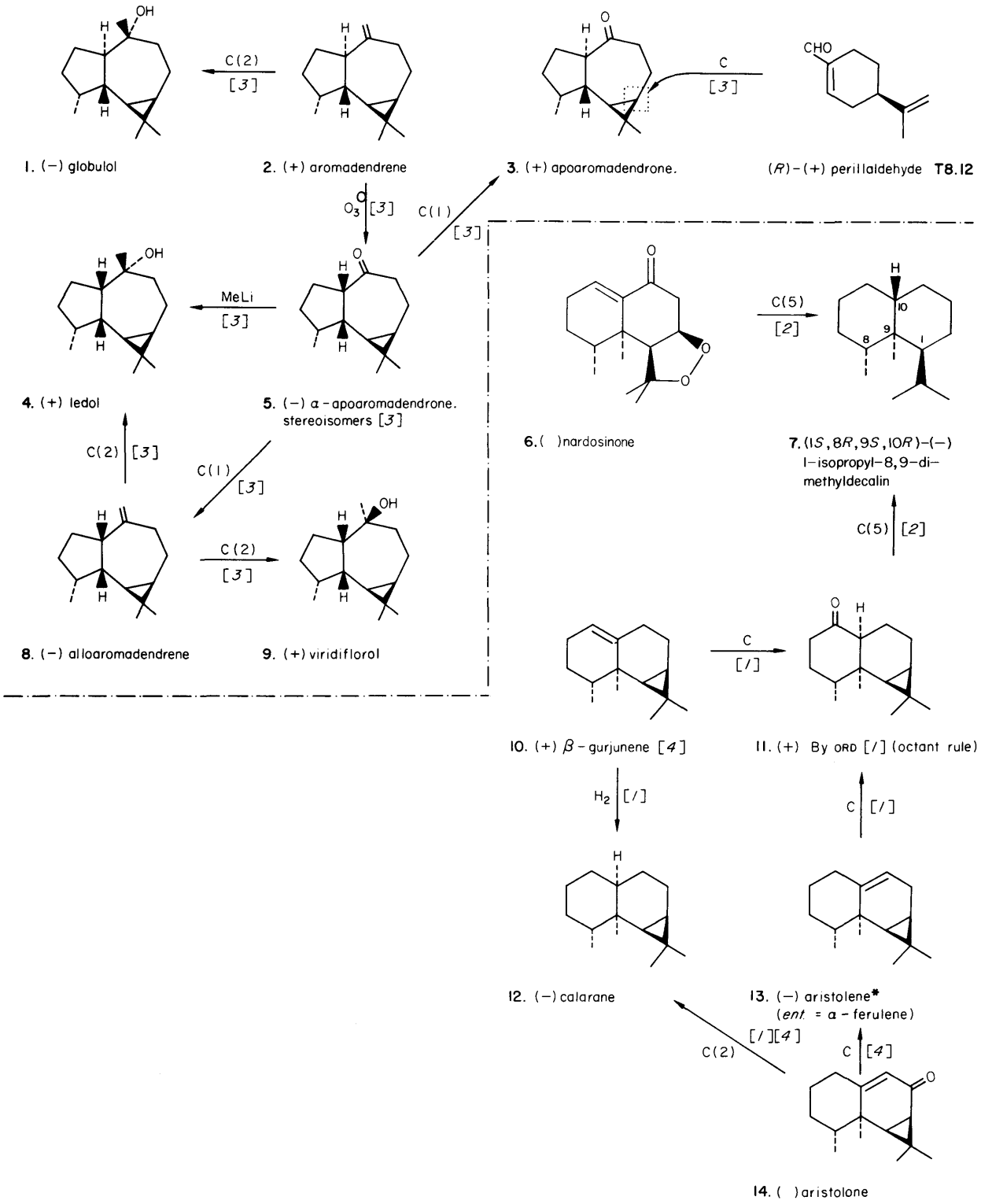
Further bicyclo[5.3.0] decanes; decalins, especially cyclopropyl types



1. (−) globulol
2. (+) aromadendrene
3. (+) apoaromadendrone.
(*R*)-(+) perillaldehyde **T8.12**
4. (+) ledol
5. (−) α-apoaromadendrone. stereoisomers [3]
6. ( )nardosinone
7. (1*S*,8*R*,9*S*,10*R*)-(−) 1-isopropyl-8,9-dimethyldecalin
8. (−) alloaromadendrene
9. (+) viridiflorol
10. (+) β-gurjunene [4]
11. (+) By ORD [1] (octant rule)
12. (−) calarane
13. (−) aristolene* (*ent.* = α-ferulene)
14. ( )aristolone

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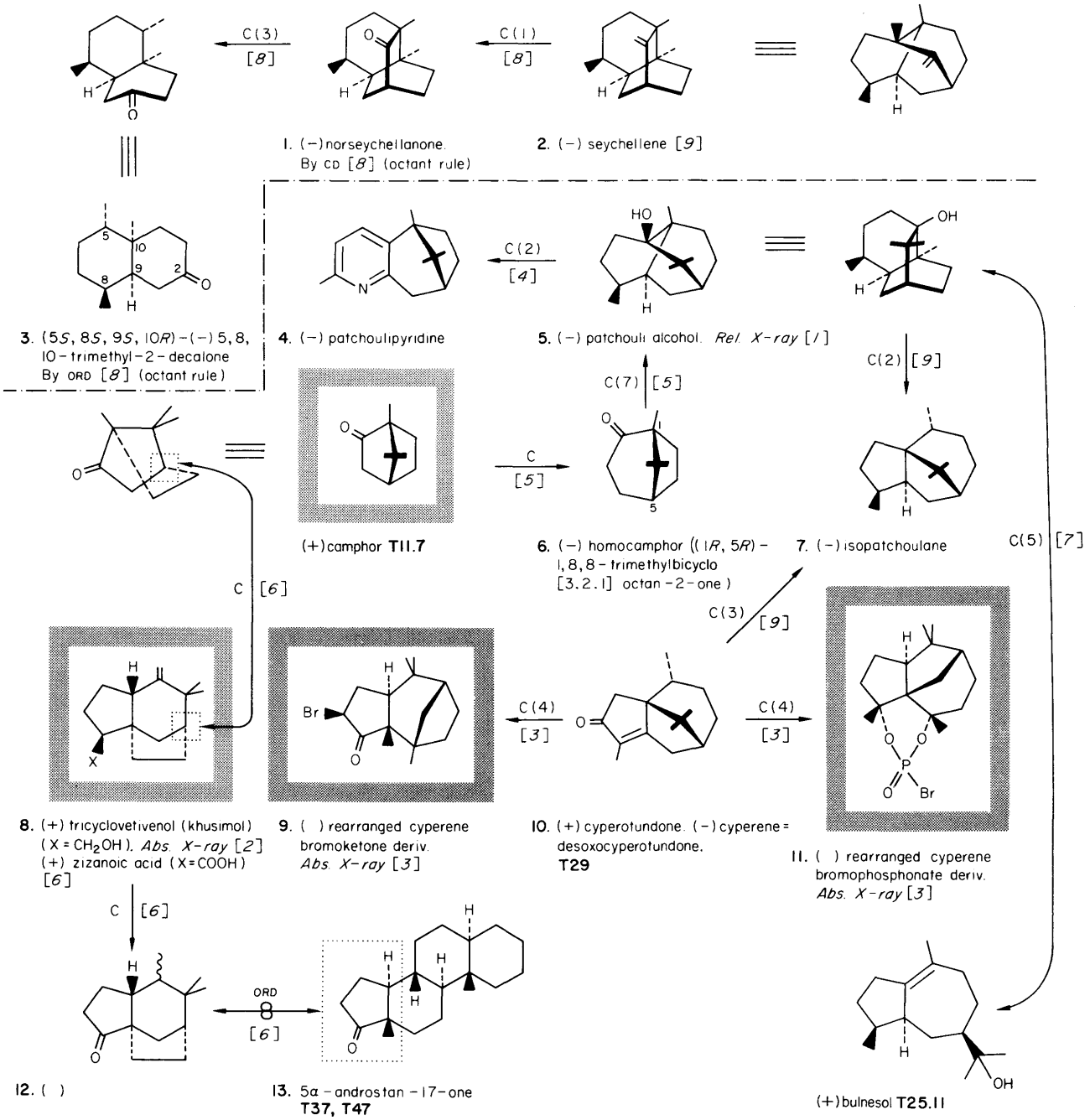

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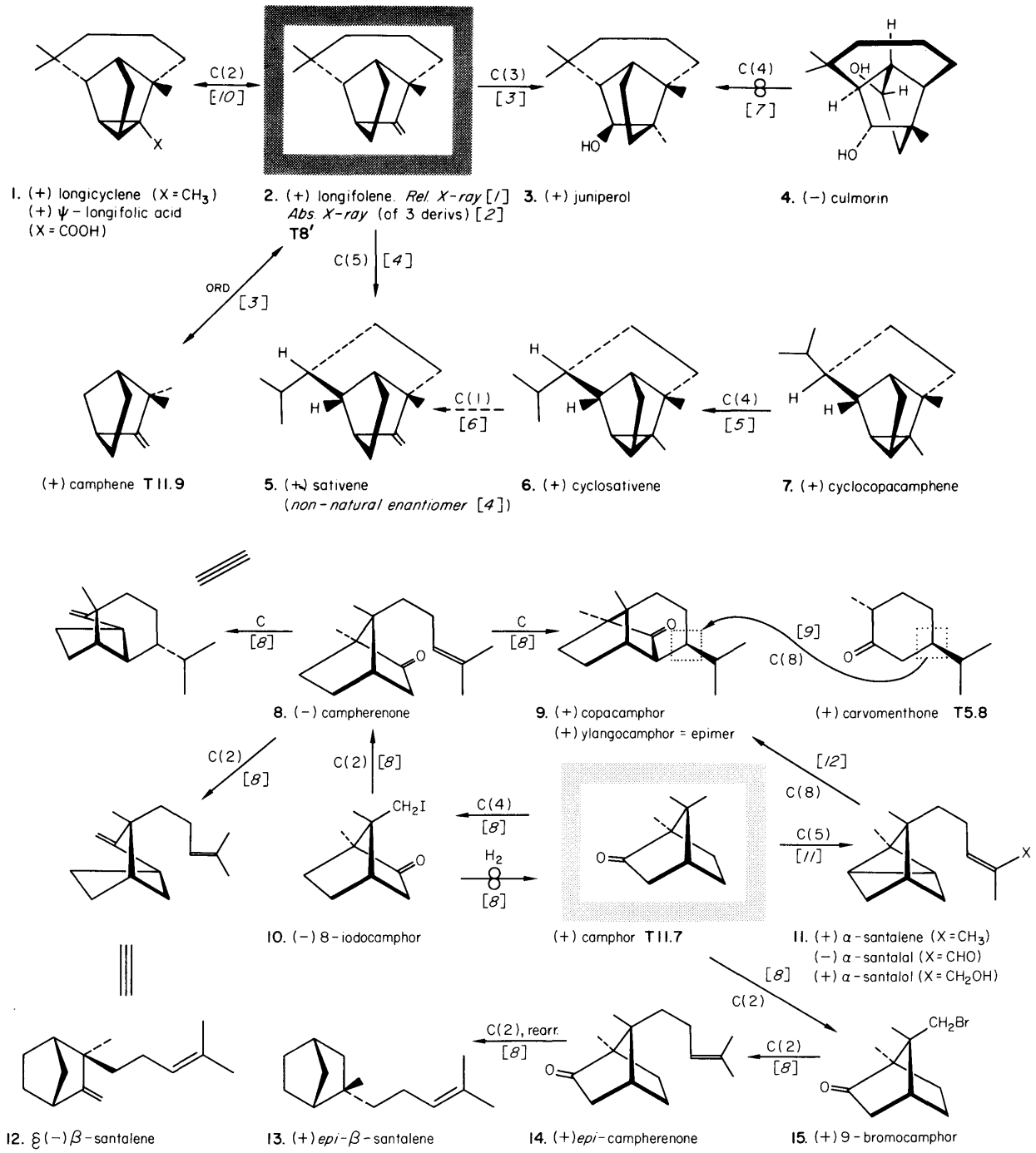
Longifolene group; santalenes.



1. (+) longicyclene (X = CH_3)
   (+) ψ - longifolic acid
   (X = COOH)
2. (+) longifolene. *Rel. X-ray* [1]
   Abs. X-ray (of 3 derivs) [2]
   T8′
3. (+) juniperol
4. (−) culmorin
5. (+) sativene
   (*non-natural enantiomer* [4])
6. (+) cyclosativene
7. (+) cyclocopacamphene
8. (−) campherenone
9. (+) copacamphor
   (+) ylangocamphor = epimer
10. (−) 8-iodocamphor
11. (+) α-santalene (X = CH_3)
    (−) α-santalal (X = CHO)
    (+) α-santalol (X = CH_2OH)
12. § (−) β-santalene
13. (+) *epi*-β-santalene
14. (+) *epi*-campherenone
15. (+) 9-bromocamphor

(+) camphene T11.9

(+) carvomenthone T5.8

(+) camphor T11.7

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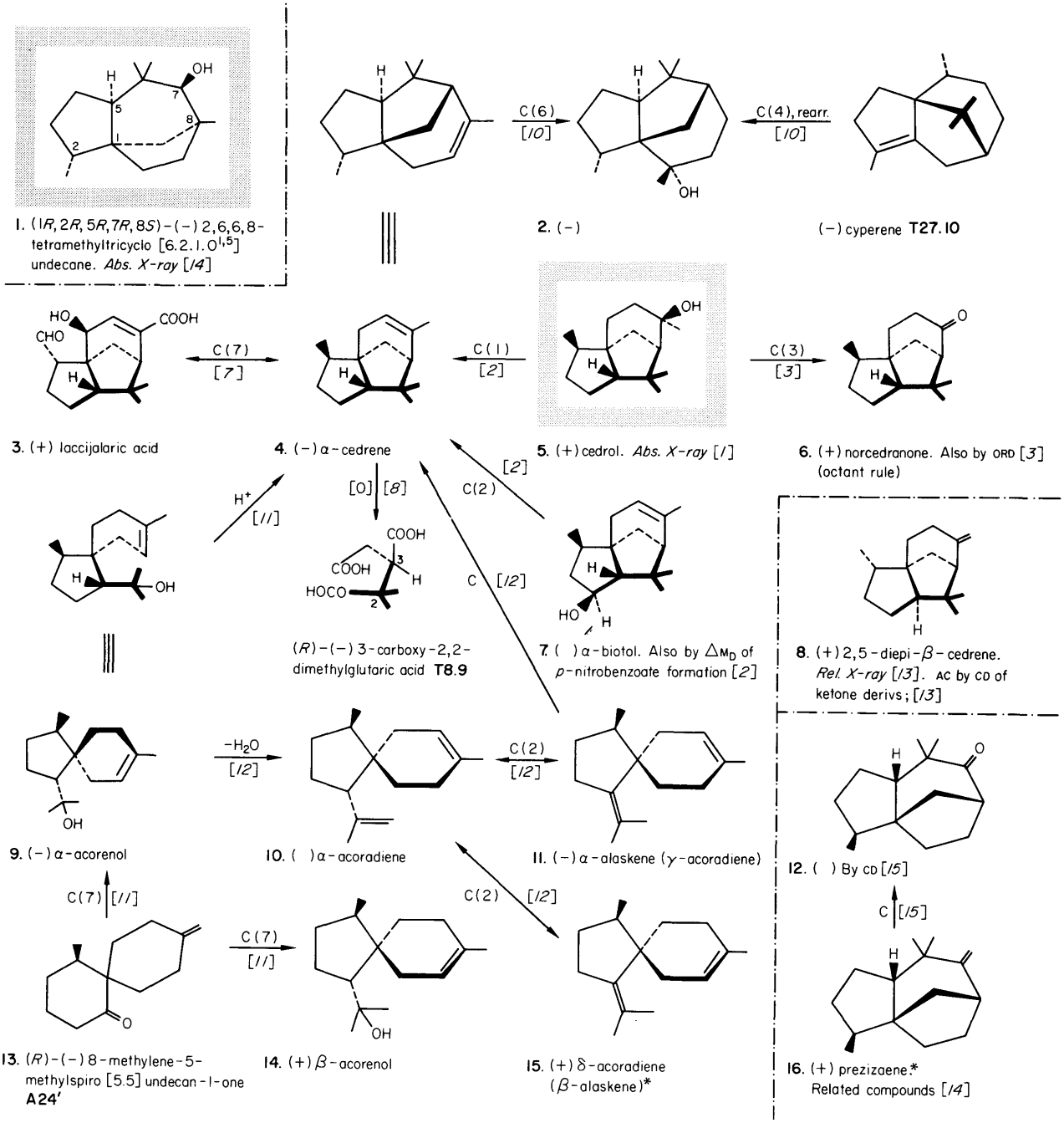
Cedrene and acorane (spiro-[5,6]-decane) groups.



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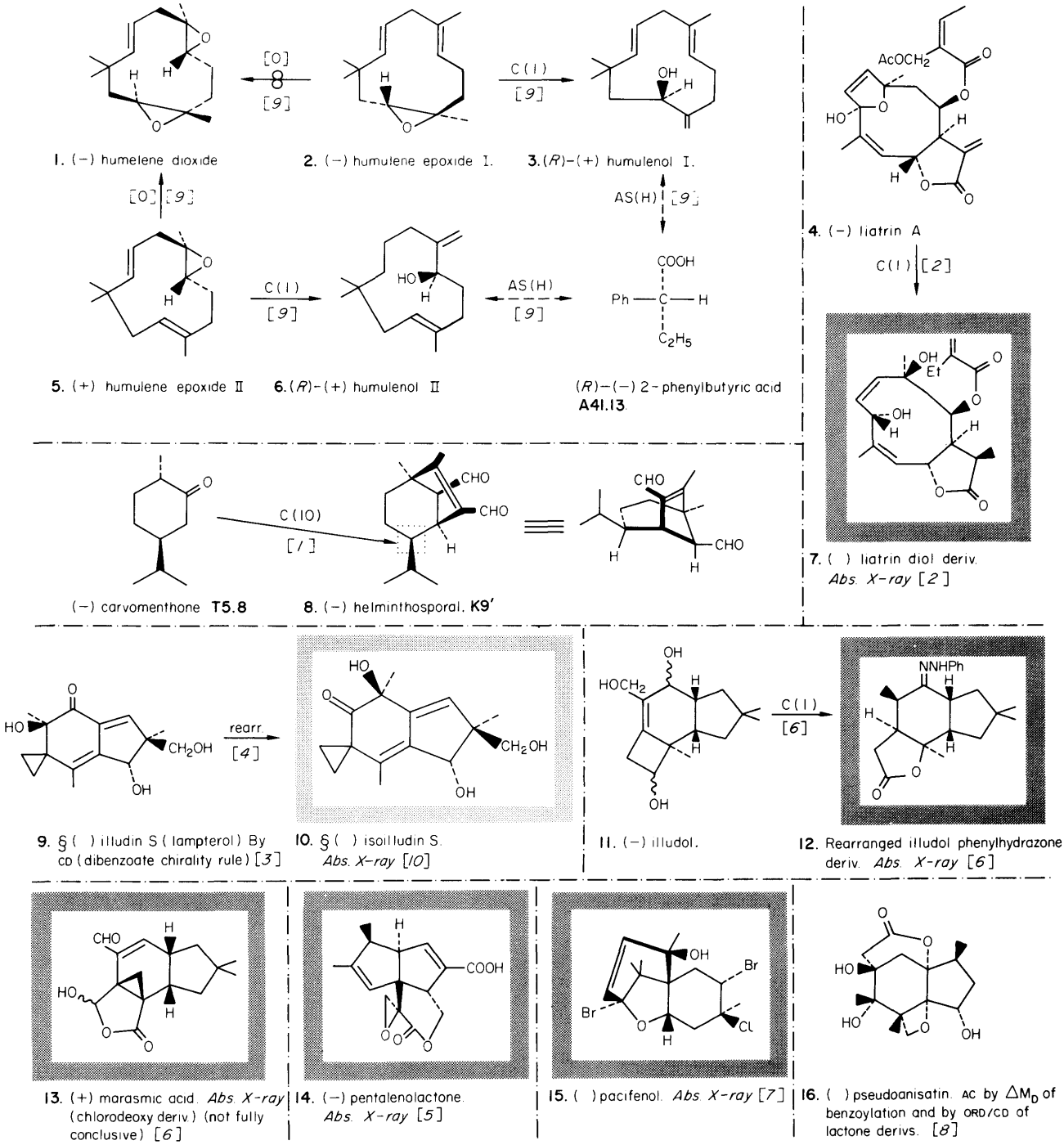
T 30 Humulene (cycloundecane) type; helminthosporal; illudin and miscellaneous types.



1. (−) humelene dioxide
2. (−) humulene epoxide I.
3. (*R*)-(+) humulenol I.
4. (−) liatrin A
5. (+) humulene epoxide II
6. (*R*)-(+) humulenol II
(*R*)-(−) 2-phenylbutyric acid **A41.13**
7. ( ) liatrin diol deriv. *Abs. X-ray* [2]
(−) carvomenthone **T5.8**
8. (−) helminthosporal. **K9'**
9. § ( ) illudin S (lampterol) By CD (dibenzoate chirality rule) [3]
10. § ( ) isoilludin S. *Abs. X-ray* [10]
11. (−) illudol.
12. Rearranged illudol phenylhydrazone deriv. *Abs. X-ray* [6]
13. (+) marasmic acid. *Abs. X-ray* (chlorodeoxy deriv) (not fully conclusive) [6]
14. (−) pentalenolactone. *Abs. X-ray* [5]
15. ( ) pacifenol. *Abs. X-ray* [7]
16. ( ) pseudoanisatin. AC by ΔM_D of benzoylation and by ORD/CD of lactone derivs. [8]

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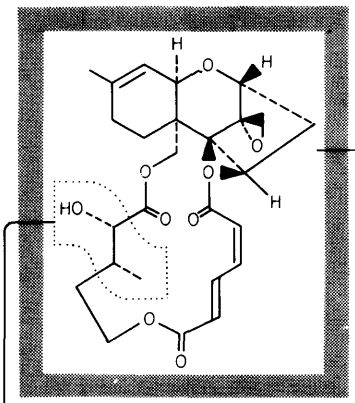
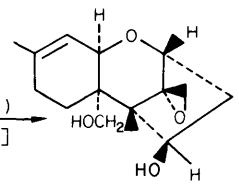
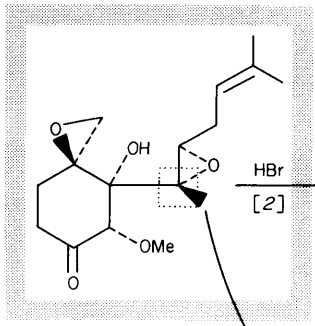


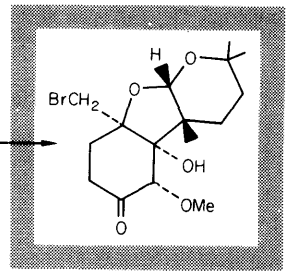
1. ( ) verrucarin A. *Abs. X-ray* [1]



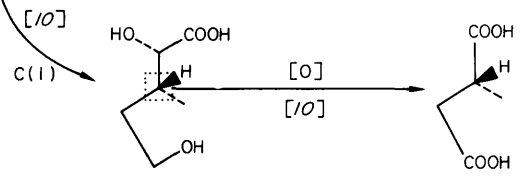
2. ( ) verrucarol. Related compds; trichothecin, crotocin, diacetoxyscirpenol etc. [11] T6'



3. §(−) ovalicine. *Abs. X-ray* [12]

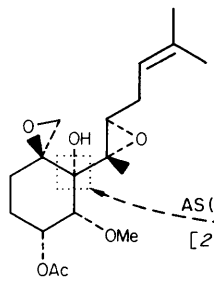


4. ( ) rearranged ovalicine deriv. *Abs X-ray* [2]

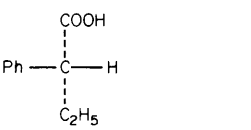


5. (2*S*, 3*R*)-( ) 2,5-dihydroxy-3-methylpentanoic (verrucarinic) acid.

(*R*)-(+) methylsuccinic acid. A27.21

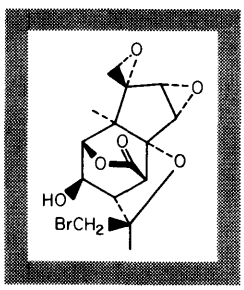


6. § ( ) acetyl dihydroovalicine

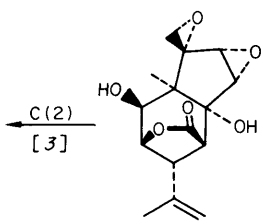


(*S*)-(+) 2-hydroxy-2-methylglutaric acid lactone methyl ester A11.8

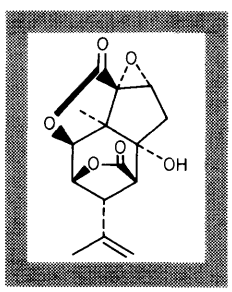
(*R*)-(−)2-phenylbutyric acid A41.13 Preferentially reacting enantiomer



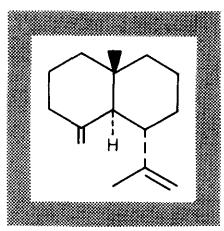
7. ( ) α-bromoisotutin. *Abs. X-ray* [3] K9'



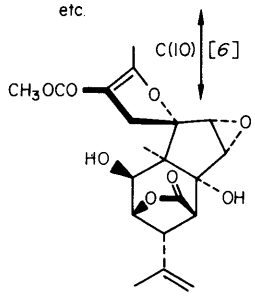
8. ( ) tutin. Related compds. ( ) coryamyrtin (+) mellitoxin etc.



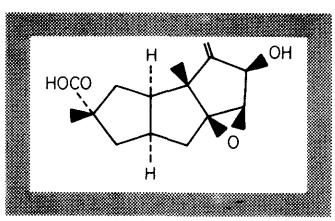
9. ( ) picrotoxinin. *Abs. X-ray* [4]



10. (+) β-gorgonene. *Abs. X-ray* [9]



11. (+) capenicin. Related compds [5]; pretoxin, lambicin



12. (+) hirsutic acid. *Abs. X-ray* [8]

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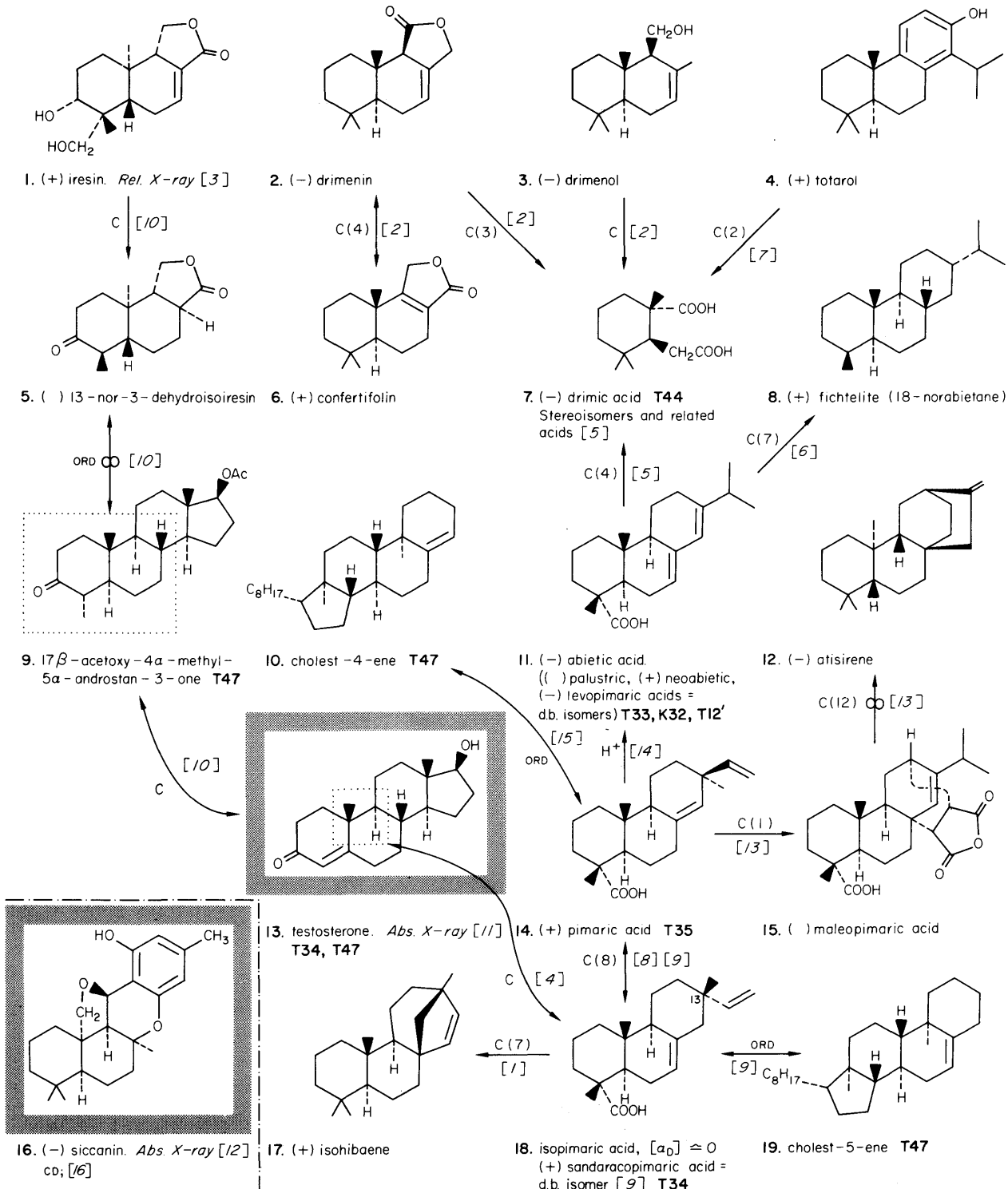
Drimane-type sesquiterpenes; abietane type diterpenes.



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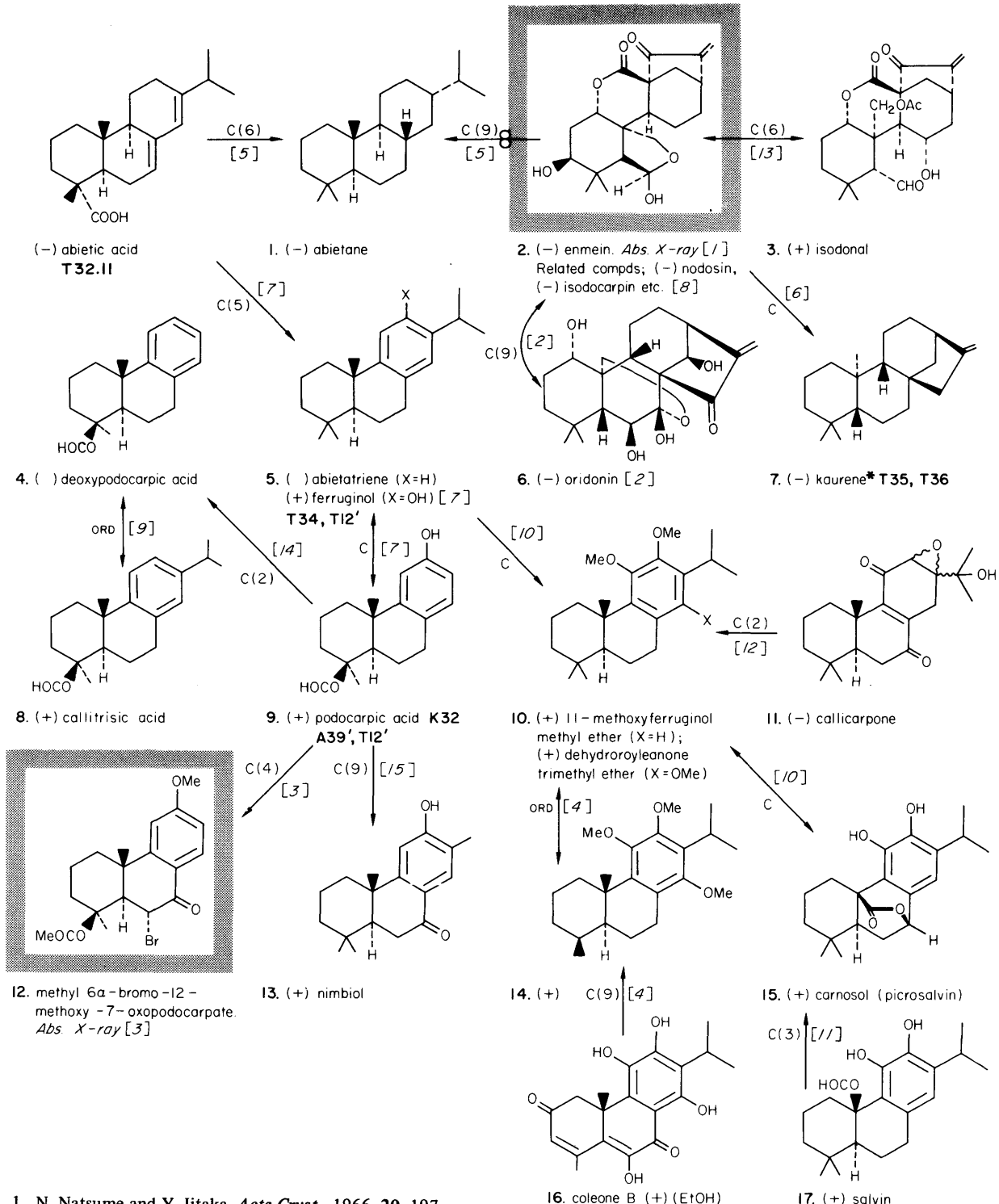

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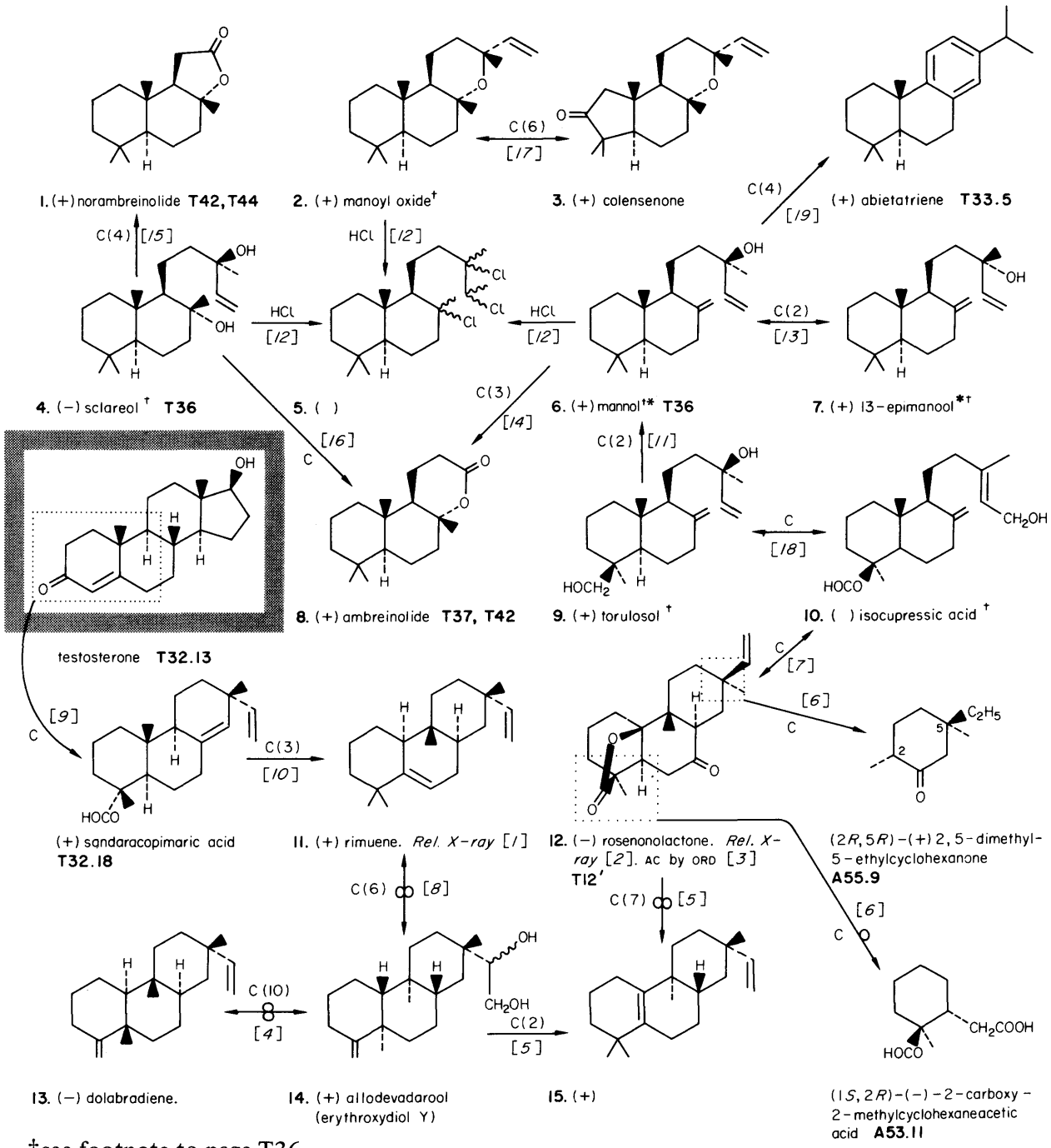

†see footnote to page T36

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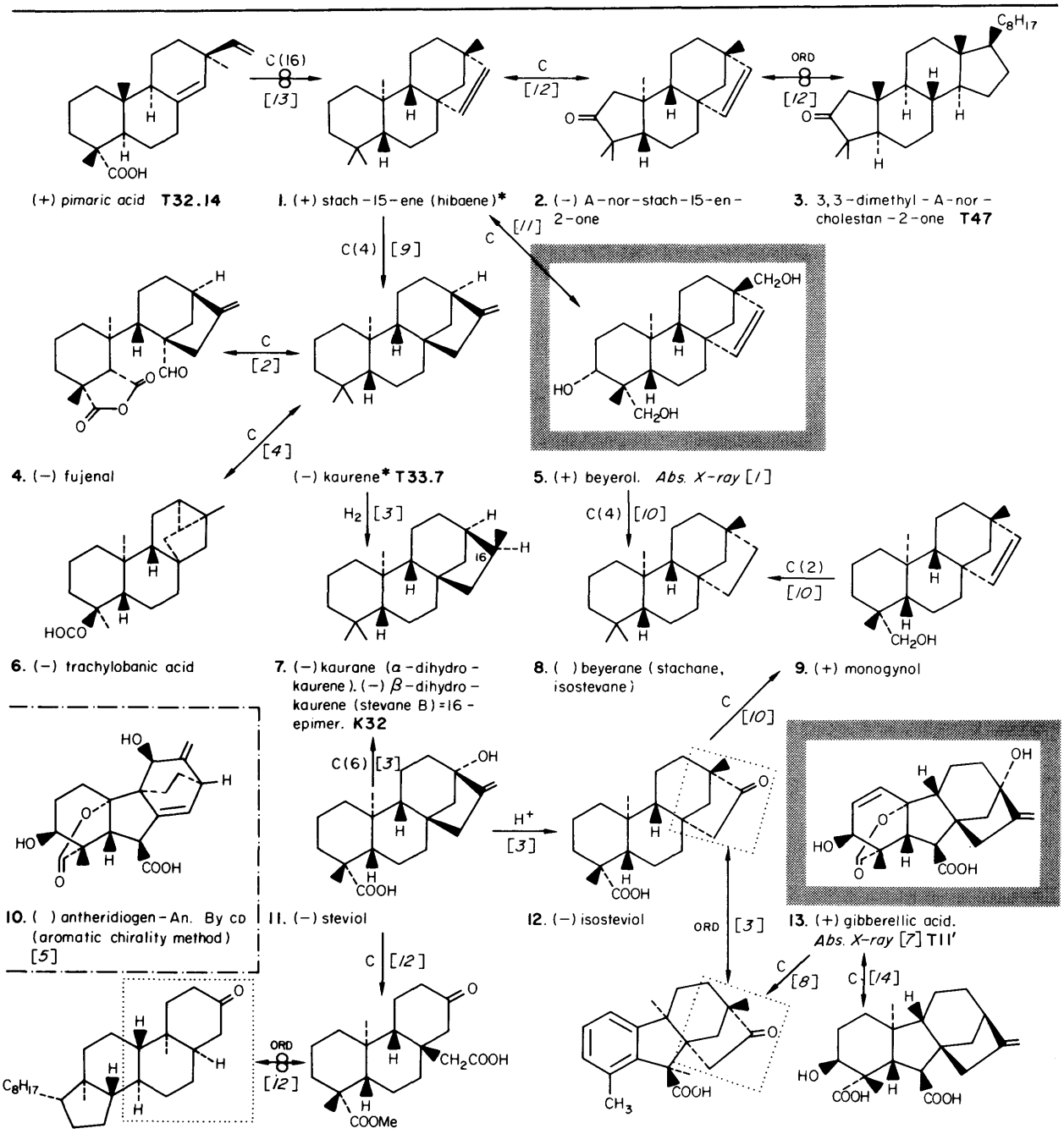

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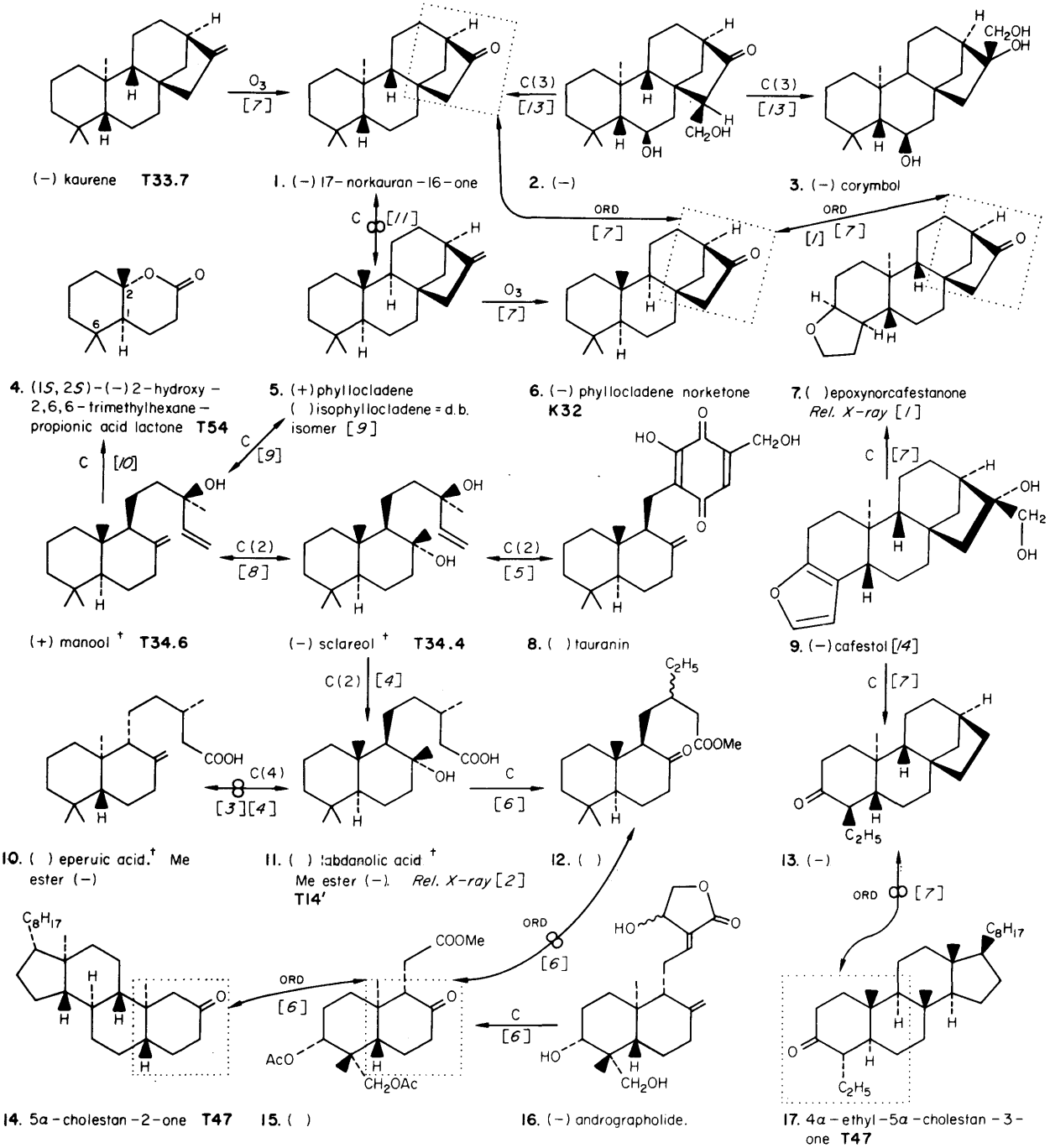
Labdane group; cafestol, phyllocladene and related compounds.



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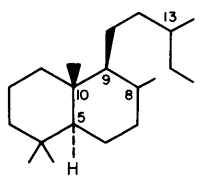
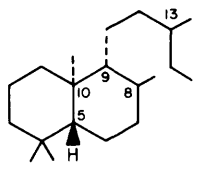
†*Note on the stereochemistry of the labdane group of diterpenoids* (Examples: manool, **T34.6**, sclareol **T34.4**, 13-epimanool **T34.7**, eperuic acid **T36.10**, labdanolic acid **T36.11**).

Diterpenes of this series, of which many are known, are derived from both antipodal series, i.e. from (5*S*, 9*S*, 10*R*)labdane and from (5*R*, 9*R*, 10*S*)labdane (eperuane, *ent.*-labdane).



(5*S*, 9*S*, 10*R*)

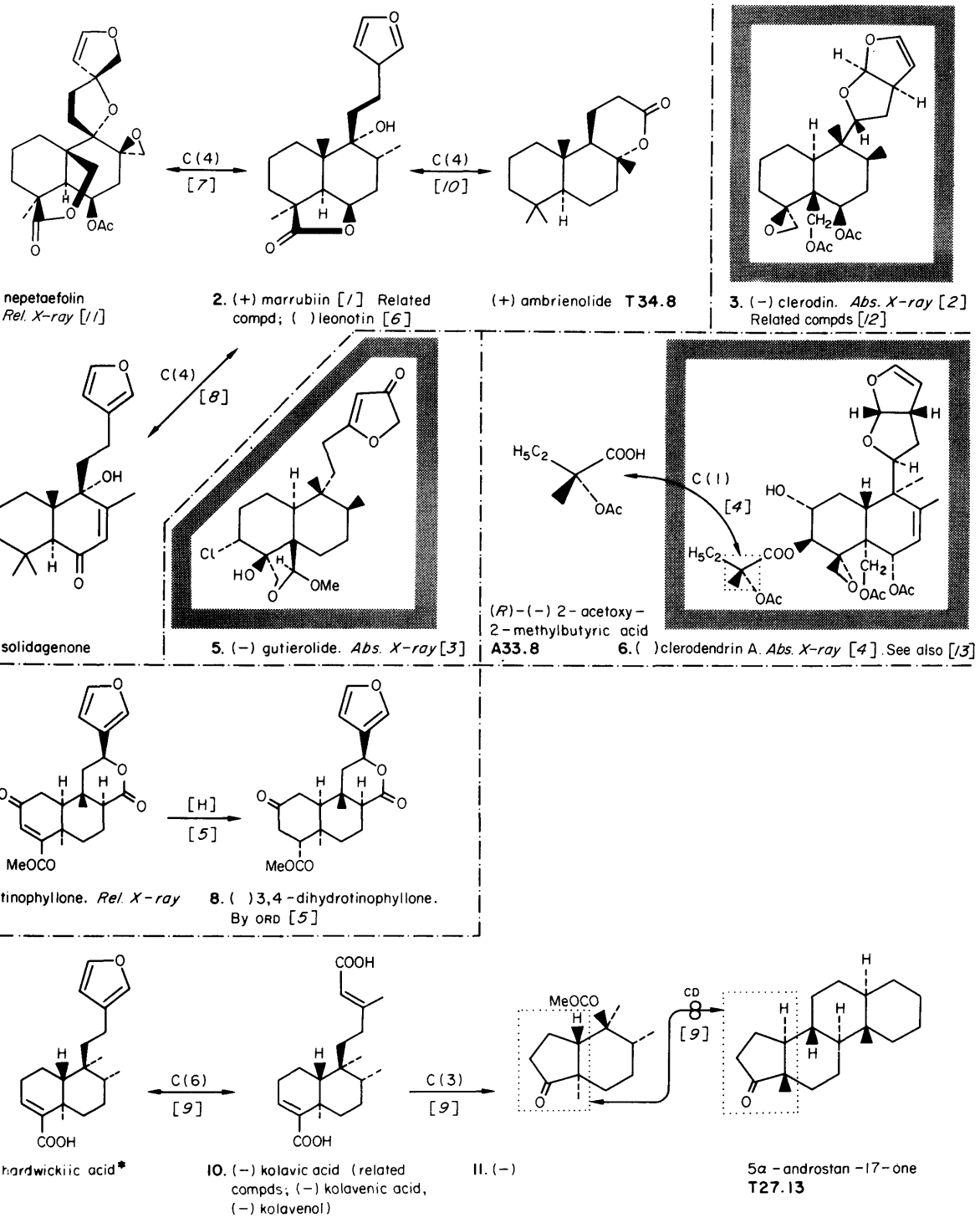


(5*R*, 9*R*, 10*S*)

Since all known natural products have the *trans-anti* stereochemistry at C_5, C_{10} and C_9, specification of the configuration at C_{10} fixes those at C_5 and C_9, and the two series are frequently referred to as 10β and 10α respectively. The configurations at C_8 and C_{13} are, however, variable. (Cf. manool and 13-epimanool.)

For a note on the configuration at C_{13}, see [*12*].

Marrubiin and clerodin types.



1. (−) nepetaefolin *Rel. X-ray* [11]

2. (+) marrubiin [1] Related compd; ( )leonotin [6]

(+) ambrienolide **T34.8**

3. (−) clerodin. *Abs. X-ray* [2] Related compds [12]

4. (−) solidagenone

5. (−) gutierolide. *Abs. X-ray* [3]

(*R*)-(−) 2-acetoxy-2-methylbutyric acid **A33.8**

6. ( )clerodendrin A. *Abs. X-ray* [4]. See also [13]

7. (−) tinophyllone. *Rel. X-ray* [5]

8. ( )3,4-dihydrotinophyllone. By ORD [5]

9. (−) hardwickiic acid*

10. (−) kolavic acid (related compds; (−) kolavenic acid, (−) kolavenol)

11. (−)

5α-androstan-17-one **T27.13**

1. I. Mangoni and M. Adinolfi, *Tetrahedron Letters*, 1968, 269.
2. I. C. Paul, G. A. Sim, T. A. Hamor and J. M. Robertson, *J. Chem. Soc.*, 1962, 4133.
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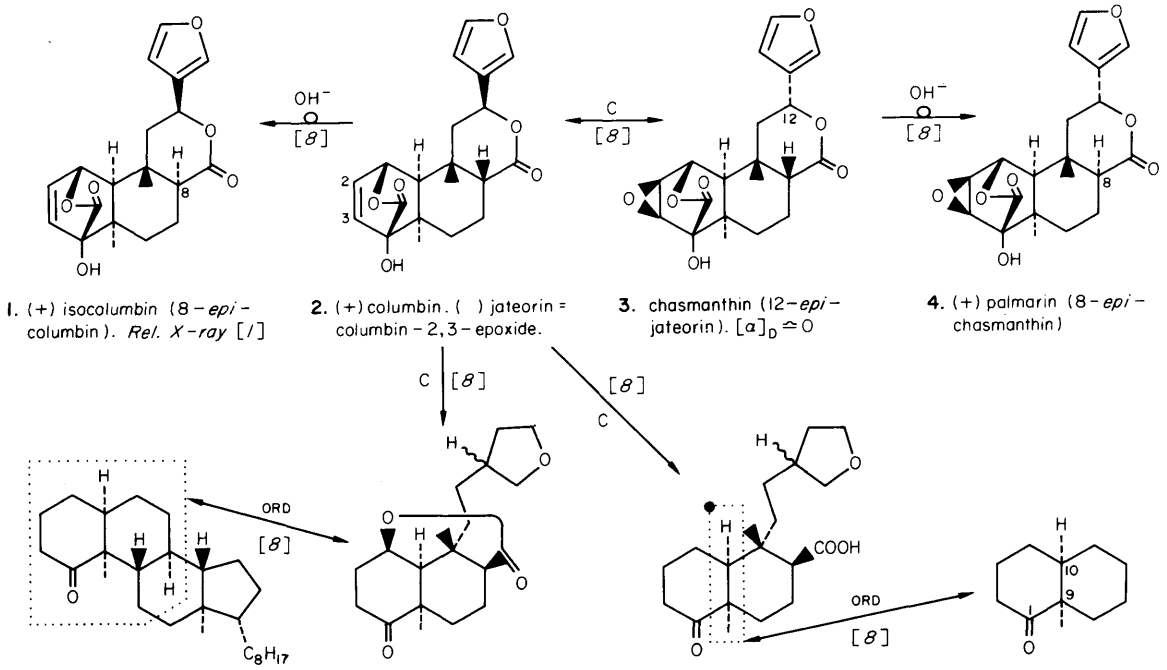
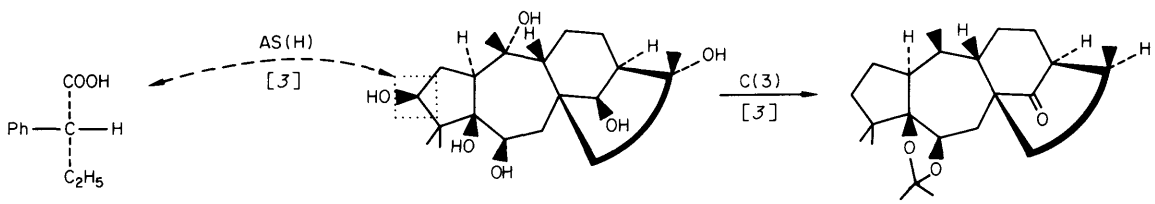


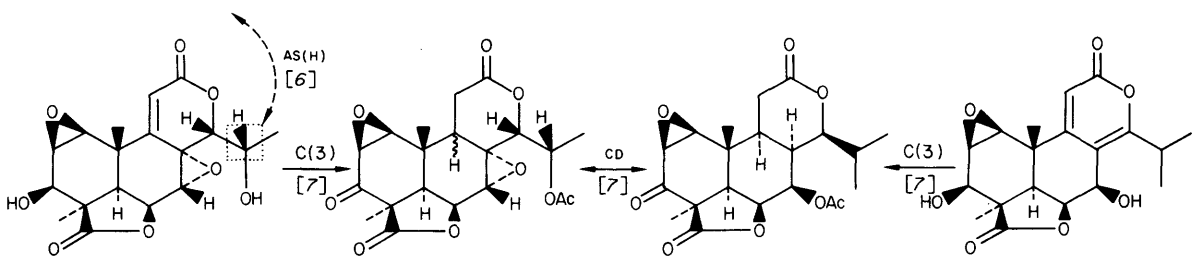
1. (+) isocolumbin (8-*epi*-columbin). *Rel. X-ray* [1]
2. (+) columbin. ( ) jateorin = columbin-2,3-epoxide.
3. chasmanthin (12-*epi*-jateorin). $[\alpha]_D \simeq 0$
4. (+) palmarin (8-*epi*-chasmanthin)
5. 5β-cholestan-1-one **T47**
6. ( )
7. ( )
(9*R*,10*R*)-(+)9-methyl-1-decalone **A53.16**



(*R*)-(−) 2-phenylbutyric acid **A41.13**

8. ( ) grayanotoxin III. *Rel. X-ray* [4]. Related compds; [2] TII'

9. (−) 'isopropylidene norketone'. By ORD [3]



10. § inumakilactone, $[\alpha]_D \simeq 0$. By ORD. of derivs. [6] Related compds; podolactones [5] *Rel. X-ray* [9]
11. §( )3-oxodihydroinumakilactone 15-acetate [9]
12. §( ) [9]
13. §(+)nagilactone C [9]

1. K. K. Cheung, D. Melville, K. H. Overton, J. M. Robertson and G. A. Sim, *J. Chem. Soc. (B)*, 1966, 853.
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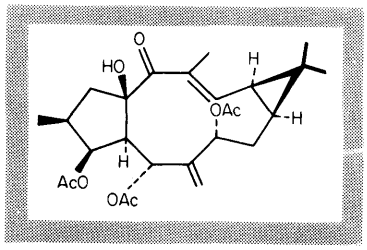
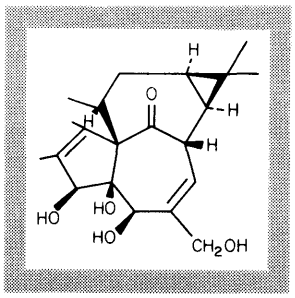
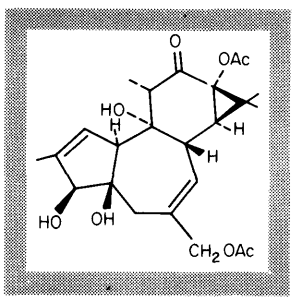


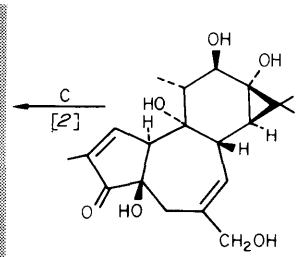
1. ( ) 7-hydroxylathyrol-3,5,7-triacetate. *Abs. X-ray* [4]



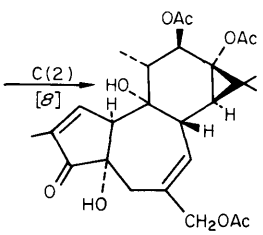
2. ( ) ingenol. *Abs. X-ray* [1]
Related compounds; milliamines [5]



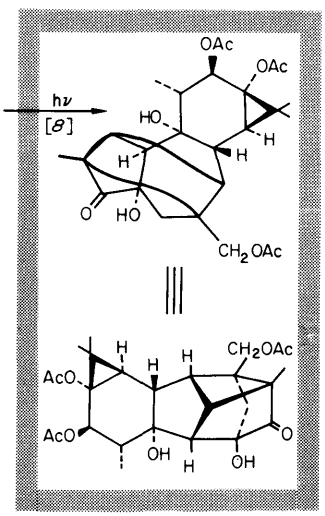
3. ( ) neophorbol 13,20-diacetate. *Abs. X-ray* [2]



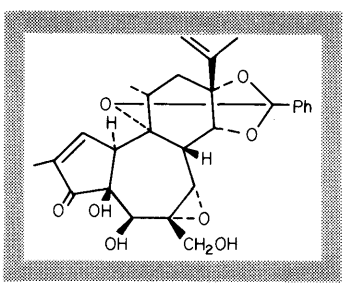
4. (+) phorbol. *Rel. X-rays* [6][7]
Related compounds; co-carcinogens (phorbol diesters).[6]



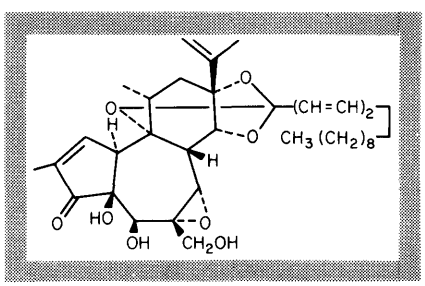
5. ( ) isophorbol triacetate



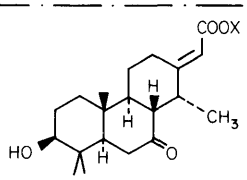
8. ( ) lumiphorbol triacetate
Abs. X-ray [8]



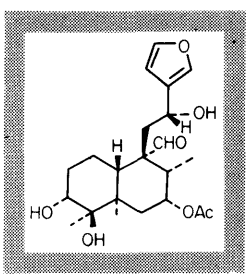
6. (+) daphnetoxin. *Abs. X-ray* [9]



7. (+) huratoxin *Abs. X-ray* [11]



9. (−) cassaine ($X = CH_2CH_2NMe_2$)
(−) cassaic acid ($X = H$). By ORD and ΔM_D
[3] See also [12]



10. ( ) cascarillin. *Abs. X-ray* [10]

1. K. Zechmeister, F. Brandl, W. Hoppe, E. Hecker, H. J. Opferkuch & W. Adolf, *Tetrahedron Letters*, 1970, 4075
2. W. Hoppe, F. Brandl, I. Strell, M. Röhrl, I. Gassman, E. Hecker, H. Bartsch, G. Krebich & C. v. Szczepanski, *Angew. Chem. (Internat. Edn.)*, 1967, 6, 809.
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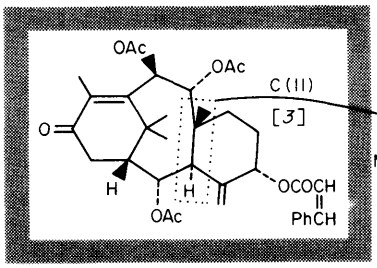
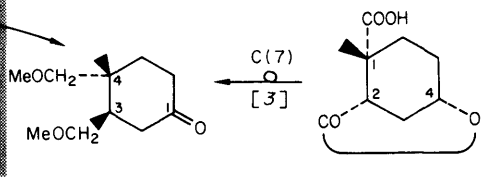
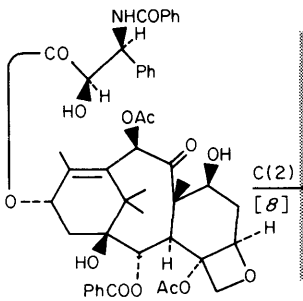


1. (+) taxinine. *Abs. X-ray* [2] Related compds; taxicins

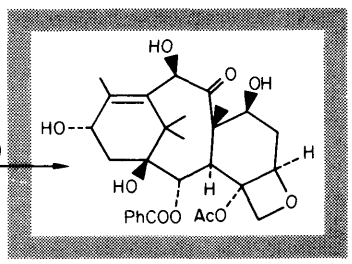


2. (3*R*, 4*R*)-(—) 3,4-di-(methoxymethyl)-4-methylcyclohexanone

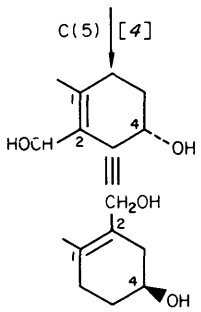
3. (1*R*, 2*S*, 4*S*)-(+) 4-hydroxy-1-methylcyclohexane-1,2-dicarboxylic acid lactone **A38'**



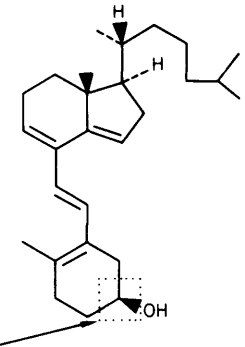
4. ( ) taxol



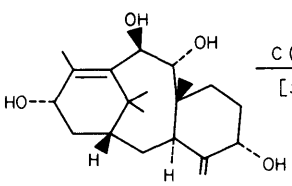
5. ( ) taxol derivative *Abs. X-ray* [8]



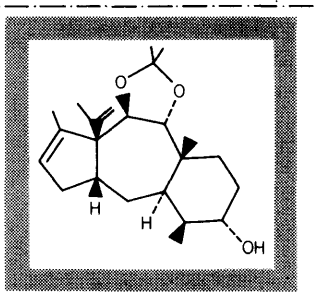
6. (*S*)-( ) 2-hydroxymethyl-1-methylcyclohex-1-en-4-ol



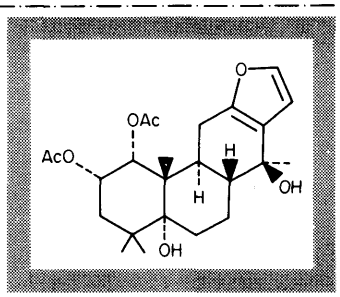
C(1) [4] 7. tachysterol III **T47**



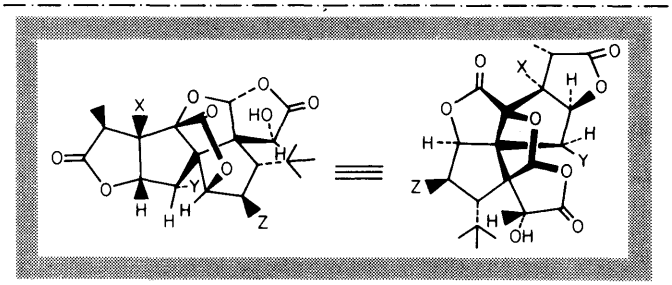
8. ( ) taxa-4(16), 11-diene-5α, 9α, 10β, 13α-tetraol



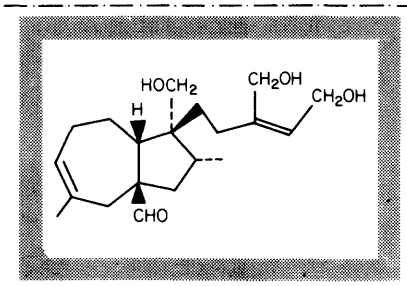
9. ( )dihydroanhydroacetonide deriv. *Abs. X-ray* [9]



10. (+) ε-caesalpin. *Abs. X-ray* [5]. Other caesalpins; [6]



11. (—) ginkgolide A (X = OH, Y = Z = H). *Abs. X-ray* [1]
(—) ginkgolide B (X = Y = OH, Z = H)
(—) ginkgolide C (X = Y = Z = OH)
(—) ginkgolide D (X = H, Y = Z = OH)



12. (—) portulal. *Abs. X-ray* [7]

1. N. Sakabe, S. Takada and K. Okabe, *Chem. Comm.*, 1967, 259.
2. M. Shiro and H. Koyama, *J. Chem. Soc. (B)*, 1971, 1342.
3. M. Dukes, H. Eyre, J. W. Harrison and B. Lythgoe, *Tetrahedron Letters*, 1965, 4765.
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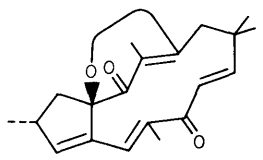
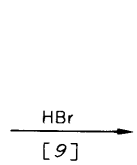
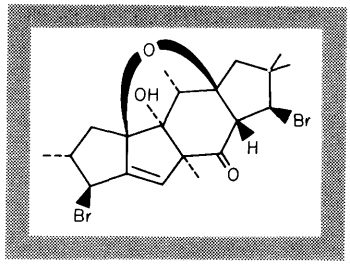
9. K. Bjamer, G. Ferguson and J. M. Robertson, *J. Chem. Soc. (B)*, 1967, 1272.

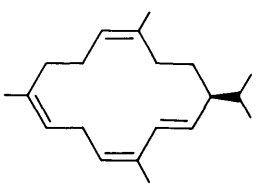


1. (+) jatrophone

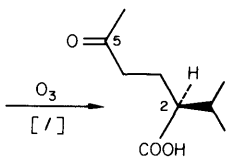




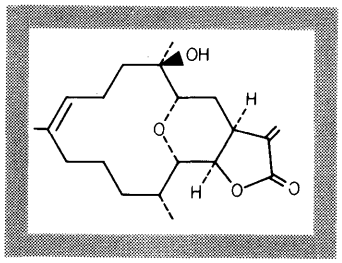
2. ( ) jatrophone dihydrobromide. *Abs. X-ray* [9]



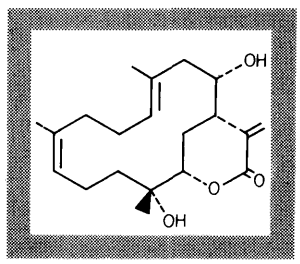
3. (+) cembrene



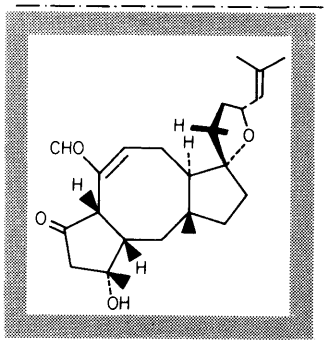
(*S*)-(−)2-isopropyl-5-oxohexanoic acid **A28.2**



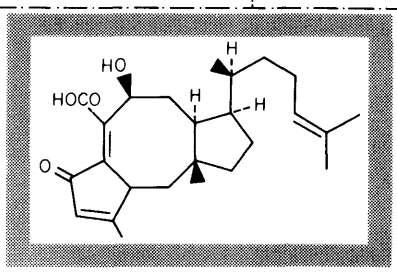
4. (−) eunicin. *Abs. X-ray* [2]



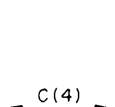
5. ( ) crassin. *Abs. X-ray* [3]

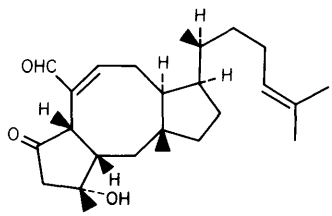


6. (+) ophiobolin A. *Abs. X-ray* [4]

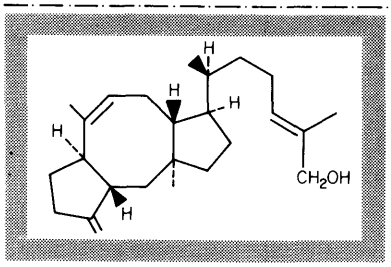


7. (+) cephalonic acid (ophiobolin D). *Abs. X-ray* [5]

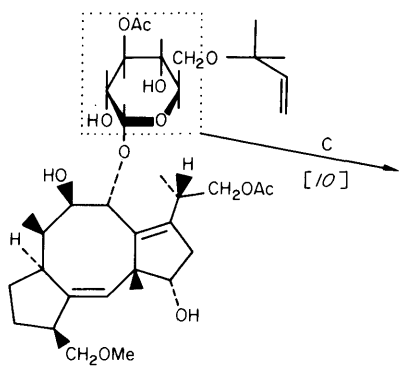




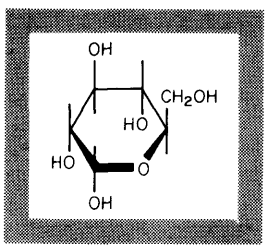
8. (+) ophiobolin C (zizanin A)



9. (+) ceroplastol I. *Abs. X-ray* [6]
Related compds; ceroplasteric acid, (+) albolic acid [7]



10. (+) fusicoccin A. *Rel. X-ray* [8]



α-D-glucopyranose **A26.9**

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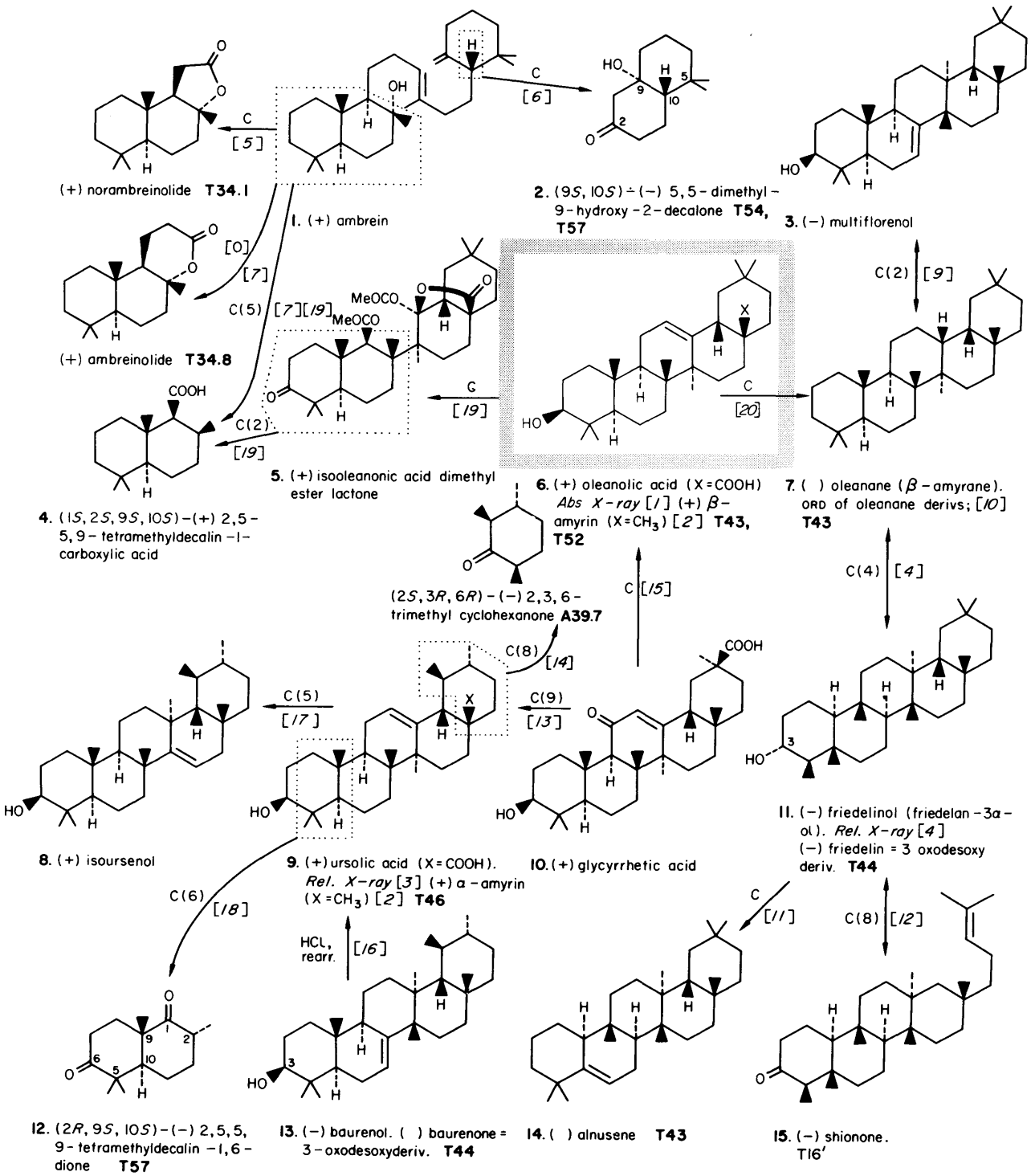

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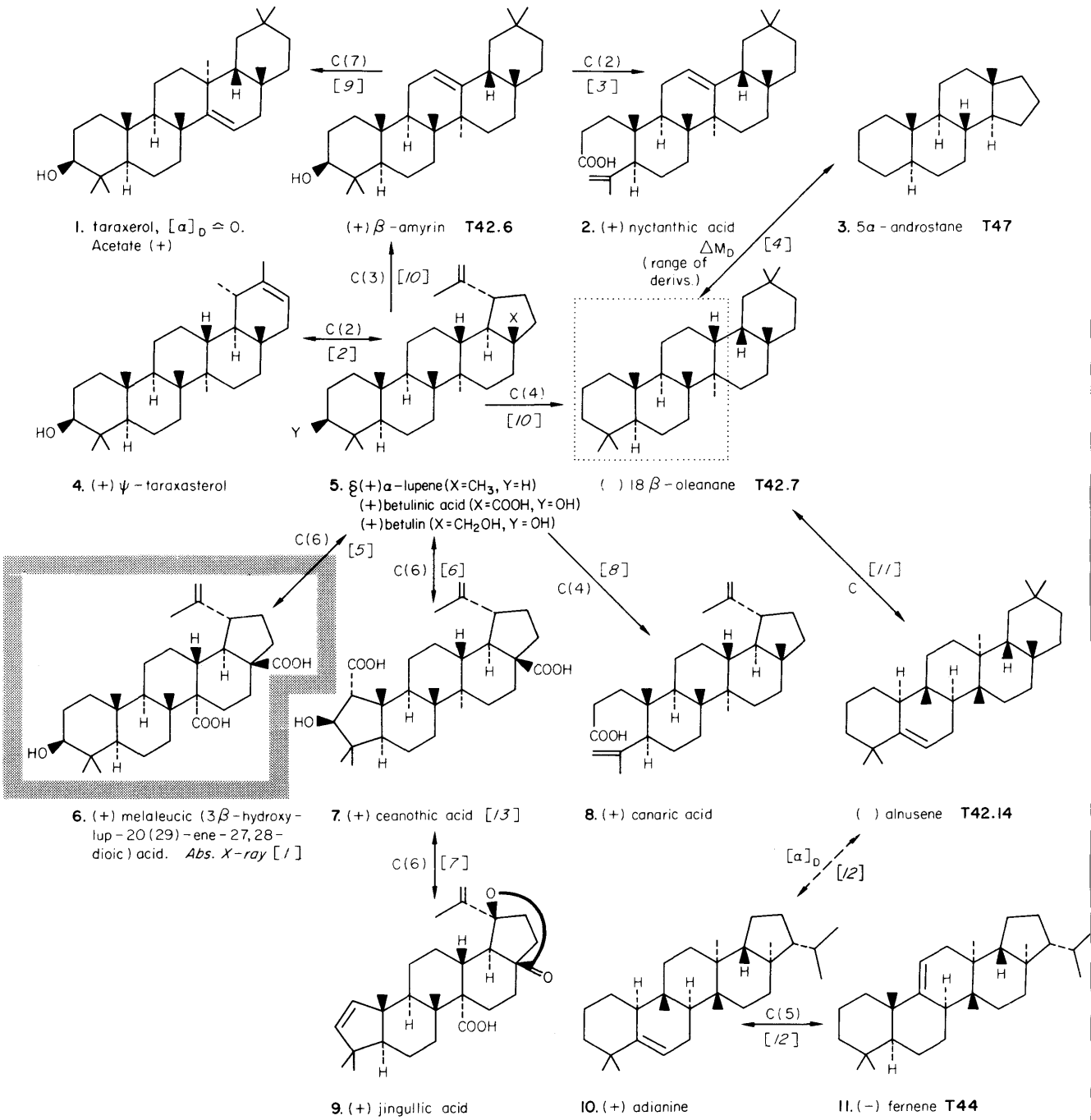

1. taraxerol, $[\alpha]_D \simeq 0$. Acetate (+)
(+) β-amyrin **T42.6**
2. (+) nyctanthic acid
3. 5α-androstane **T47**
4. (+) ψ-taraxasterol
5. ξ(+)α-lupene (X=CH_3, Y=H)
(+)betulinic acid (X=COOH, Y=OH)
(+)betulin (X=CH_2OH, Y=OH)
( ) 18β-oleanane **T42.7**
6. (+) melaleucic (3β-hydroxy-lup-20(29)-ene-27,28-dioic) acid. *Abs. X-ray* [1]
7. (+) ceanothic acid [13]
8. (+) canaric acid
( ) alnusene **T42.14**
9. (+) jingullic acid
10. (+) adianine
11. (−) fernene **T44**

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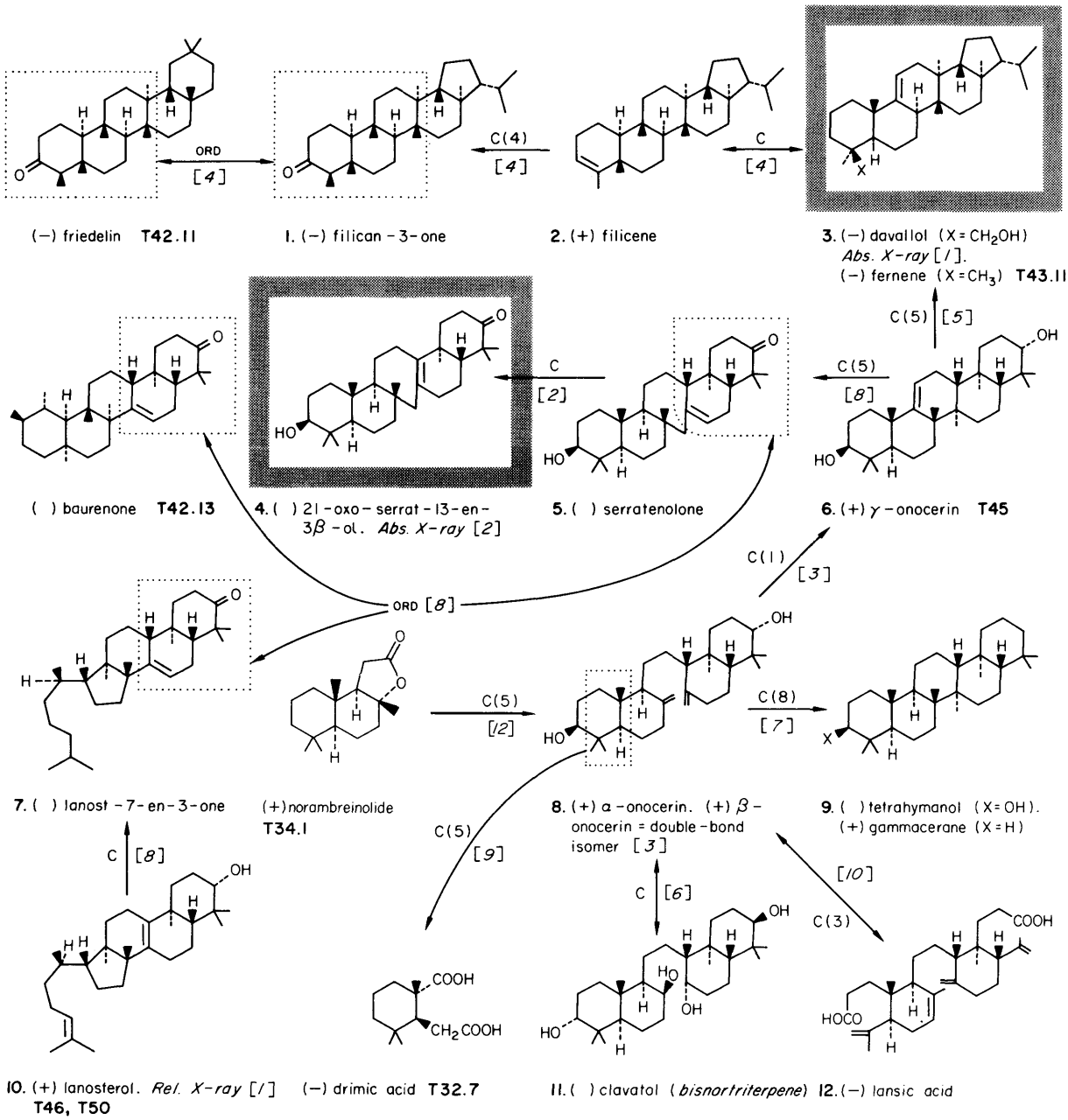

(−) friedelin **T42.11** — 1. (−) filican-3-one — 2. (+) filicene — 3. (−) davallol (X = CH_2OH) *Abs. X-ray* [1]. (−) fernene (X = CH_3) **T43.11**

( ) baurenone **T42.13** — 4. ( ) 21-oxo-serrat-13-en-3β-ol. *Abs. X-ray* [2] — 5. ( ) serratenolone — 6. (+) γ-onocerin **T45**

7. ( ) lanost-7-en-3-one — (+)norambreinolide **T34.1** — 8. (+) α-onocerin. (+) β-onocerin = double-bond isomer [3] — 9. ( ) tetrahymanol (X = OH). (+) gammacerane (X = H)

10. (+) lanosterol. *Rel. X-ray* [1] **T46, T50** — (−) drimic acid **T32.7** — 11. ( ) clavatol (*bisnortriterpene*) — 12. (−) lansic acid

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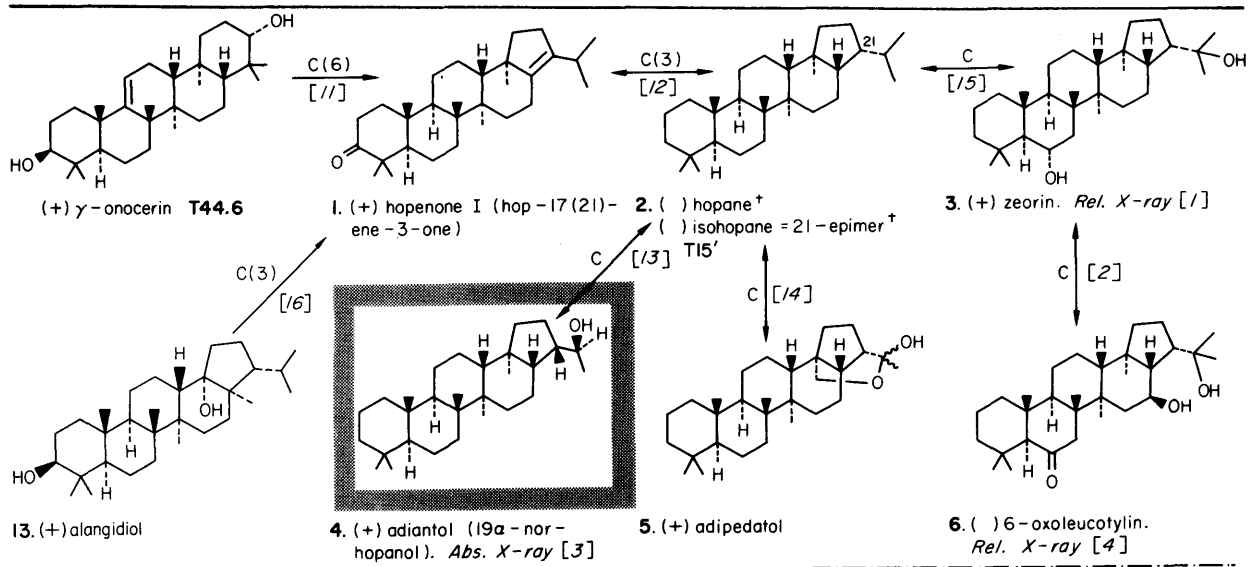
Onocerane group; miscellaneous pentacyclic triterpenes.



(+) γ-onocerin **T44.6**

1. (+) hopenone I (hop-17(21)-ene-3-one)

2. ( ) hopane† ( ) isohopane = 21-epimer† T15'

3. (+) zeorin. *Rel. X-ray* [1]

13. (+) alangidiol

4. (+) adiantol (19α-norhopanol). *Abs. X-ray* [3]

5. (+) adipedatol

6. ( ) 6-oxoleucotylin. *Rel. X-ray* [4]

7. (+) arborinol. *Rel. X-ray* [8] AC by ORD [9]

8. (+) ketohakonanol (*nor-triterpene*)

9. (+) platicodigenin. *Abs. X-ray* [5]

10. (+) eupteleogenin. *Rel. X-ray* [6] AC by ORD of derivs. [7]

11. ( ) pristimerin. Related compds; [17]

12. ( ) pristimerol. *Abs. X-ray* [10]

1. T. Nakanishi, H. Yamauchi, T. Fujiwara and K. Tomita, *Tetrahedron Letters*, 1971, 1157.
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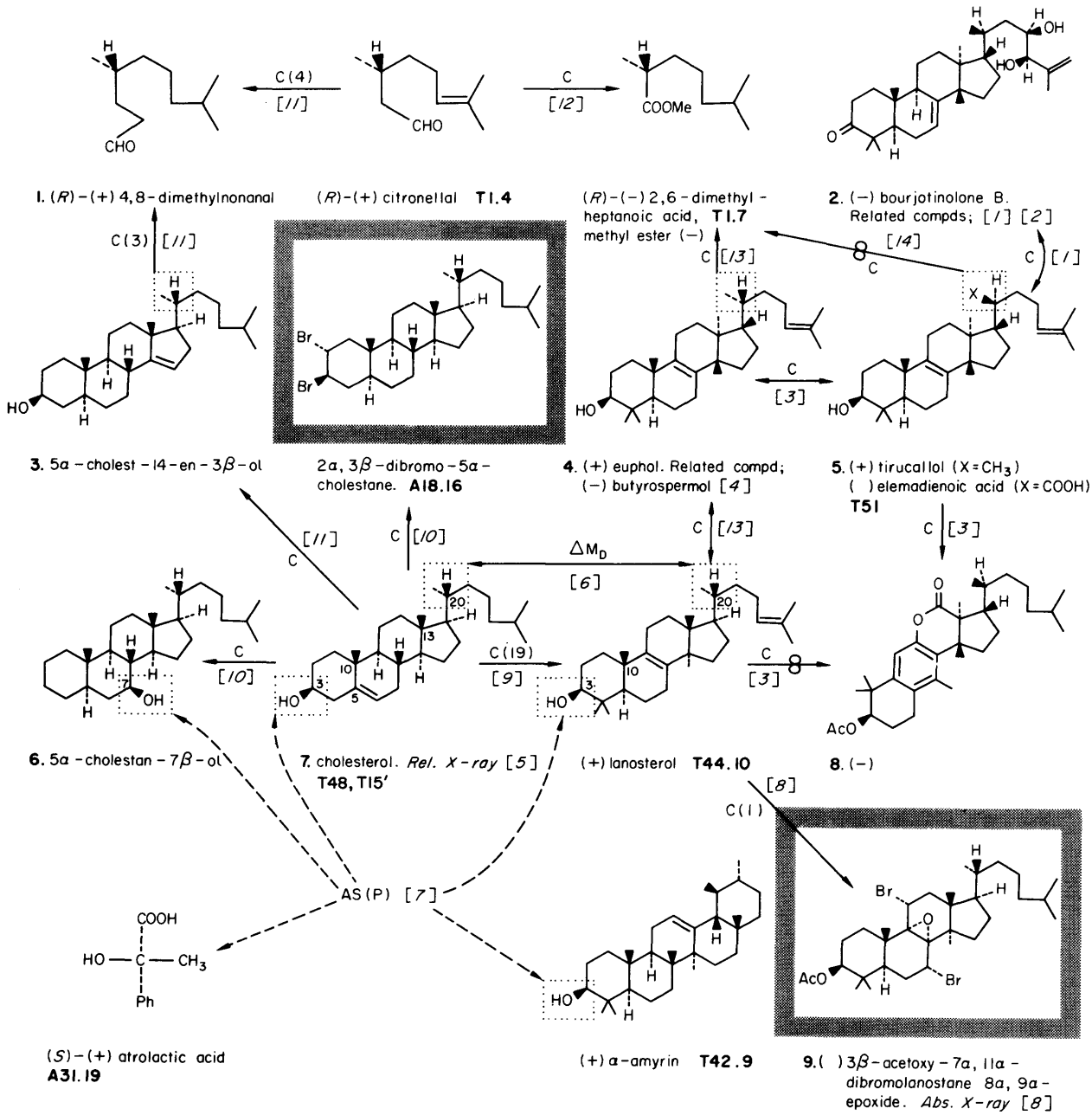
† Derivatives of both hopane and 21-epihopane (isohopane) occur naturally, frequently in the same plant. The situation regarding C_{21} stereochemistry in these compounds has been confused in the past. The latest work [2] indicates that hopane has the (21*R*) or 21β-H configuration shown, and this is corroborated by the X-ray structure determination of adipedatol [3].



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The following Bijvoet X-ray determinations have been carried out on steroids and other higher terpenes in addition to those shown explicitly;

17β-hydroxy-9β,10α-androst-4-en-3-one [*1*]; 17aβ-hydroxy-17α-methyl-19-nor-9β,10α-D-homo-androst-4-en-3-one [*2*]; 4α-bromo-5α-androst-2-ene-1,17-dione [*3*]; 5α-bromo-6β,19-oxidopregnan-3β-ol-20-one [*4*]; 6β-bromoprogesterone [*5*]; 12α-bromo-11β-hydroxyprogesterone [*6*]; pancuronium bromide (3α,17β-diacetoxy-2β,16β-dipiperidino-5α-androstane dimethobromide) [*7*]; 3β-bromoacetoxy-16α-ethyl-16²-cyano-16²,21-cyclo-5α-pregna-17,21-diene [*8*]; 2α, 3α-epithio-5α-androstan-17β-ol [*10*]; 3β-acetoxy-6,7-epidithio-19-norlanosta-5,7,9,11-tetrene [*11*]; pachysandiol (friedelane group) [*12*]; estro-*p*-quinol methyl ester [*13*]; beyeran-3-ol [*14*]; 7β-hydroxykanienolide [*14*]; cyproterone acetate [*15*].

A comprehensive compilation of steroid X-ray determinations (absolute and relative) is to appear in *Atlas of Steroid Structure* (D. A. Norton, Editor-in-Chief), in preparation (1971).

Unequivocal chemical correlations exist [*9*] between cholesterol and related steroids on page **T46** and other steroids which appear elsewhere in the 'Atlas' **A53.5, T20.18, T23.17, T26.19, T27.13, T32.9, T32.10, T32.19, T35.3, T35.14, T36.14, T36.17, T38.5, T40.7, T43.3, T53.11, T57.7, K34.2, K34.3, K34.4, Y21.7.**

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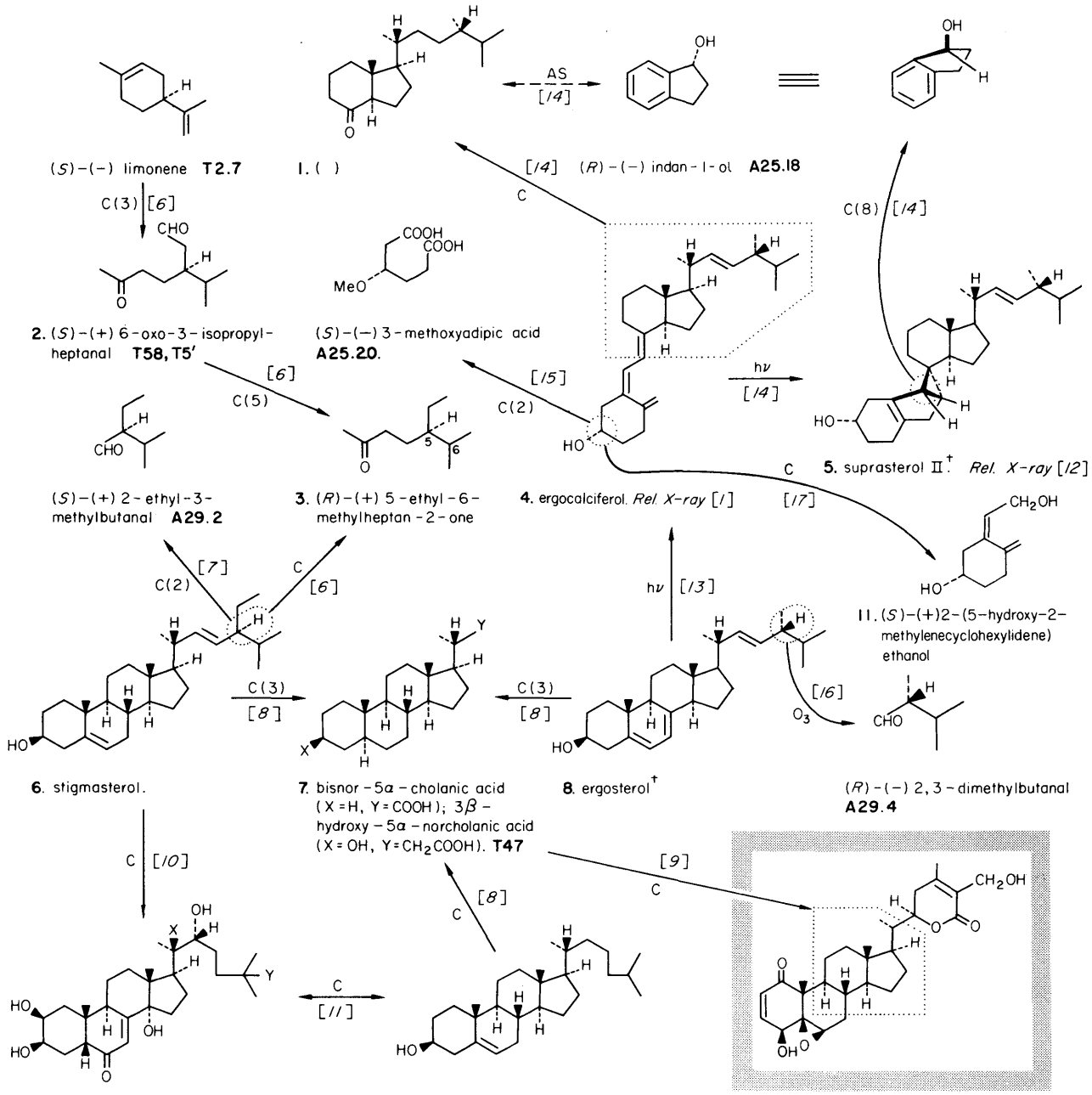
† For other D vitamins and their precursors and for further interrelationships between these and mono- and bicyclic intermediates, see T. M. Dawson, P. S. Littlewood, B. Lythgoe and A. K. Saksena, *J. Chem. Soc. (C)*, 1971, 2960 and references therein.



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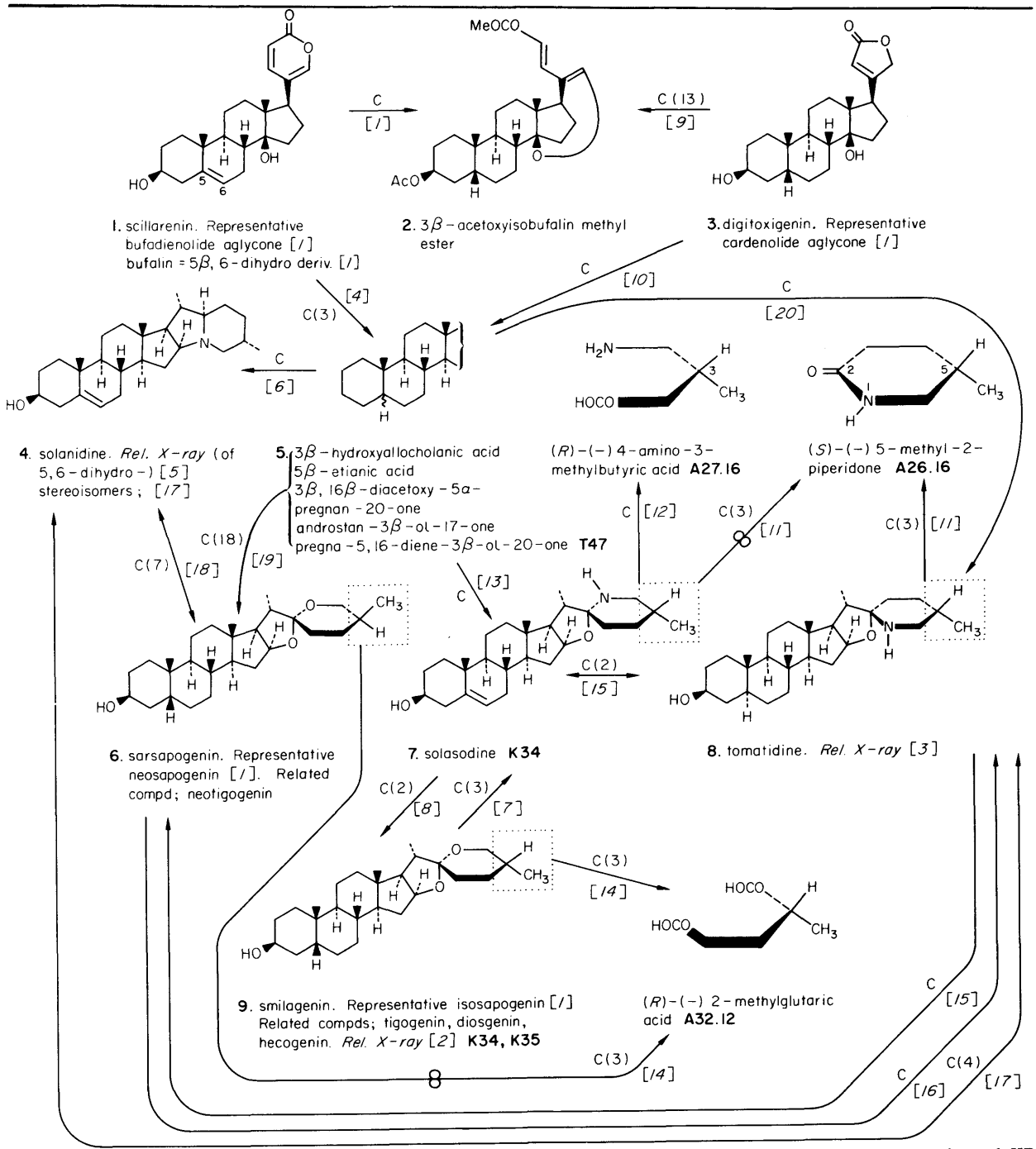

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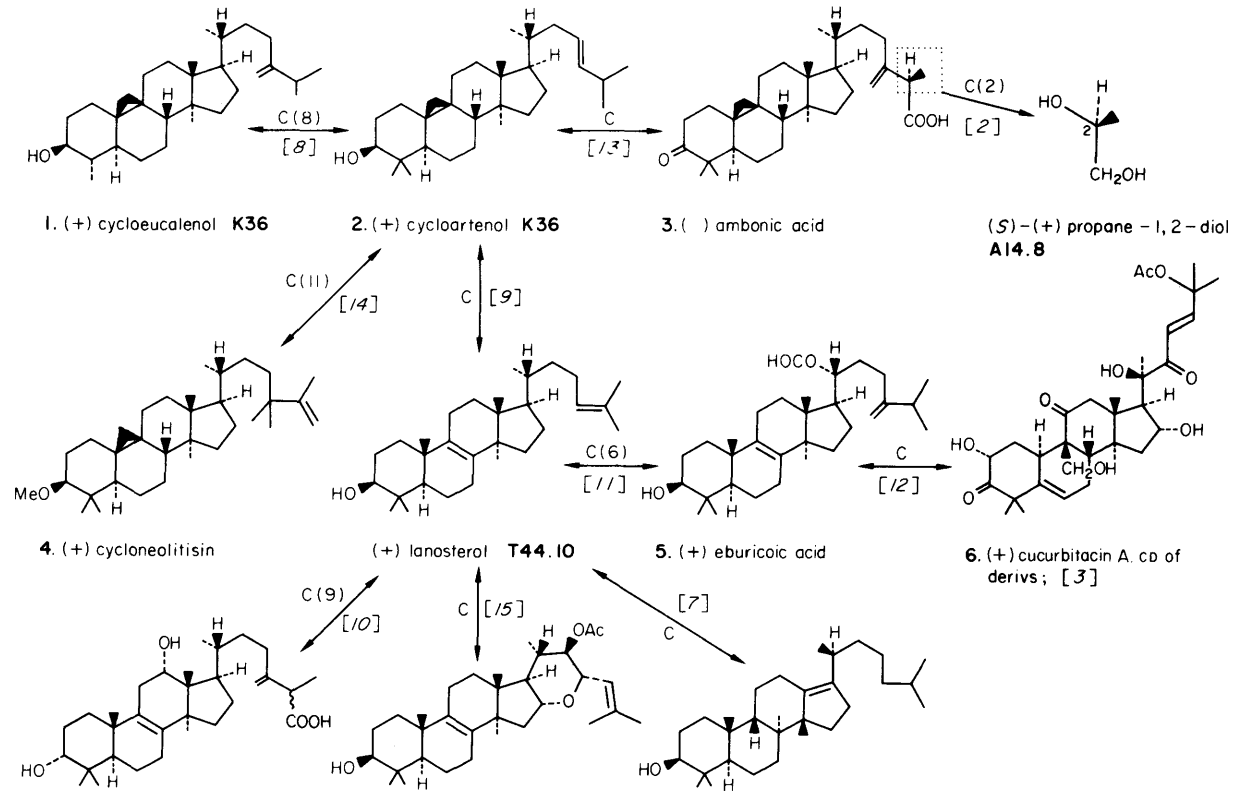
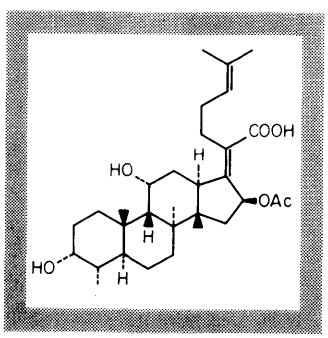


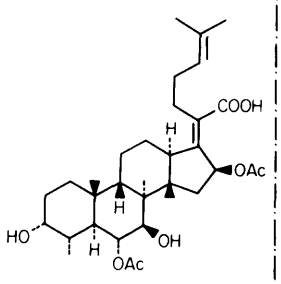
1. (+) cycloeucalenol **K36**
2. (+) cycloartenol **K36**
3. ( ) ambonic acid
4. (+) cycloneolitisin
5. (+) eburicoic acid
6. (+) cucurbitacin A. CD of derivs; [3]
7. (+) polyporenic acid A
8. (+) echinodol
9. 3β-hydroxyprotost-13(17)-ene

(+) lanosterol **T44.10**

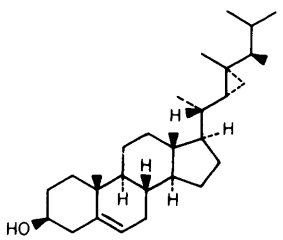
(S)-(+) propane-1,2-diol **A14.8**



10. (−) fusidic acid.
Abs. X-ray [4]
Related compd;
(−) helvolic acid [5]



11. (+) cephalosporin P_1.
By ORD of derivs. [6]



12. ( ) gorgosterol.
Rel. X-ray [1]
AC by ORD of 3-ketone
(octant rule) [1]

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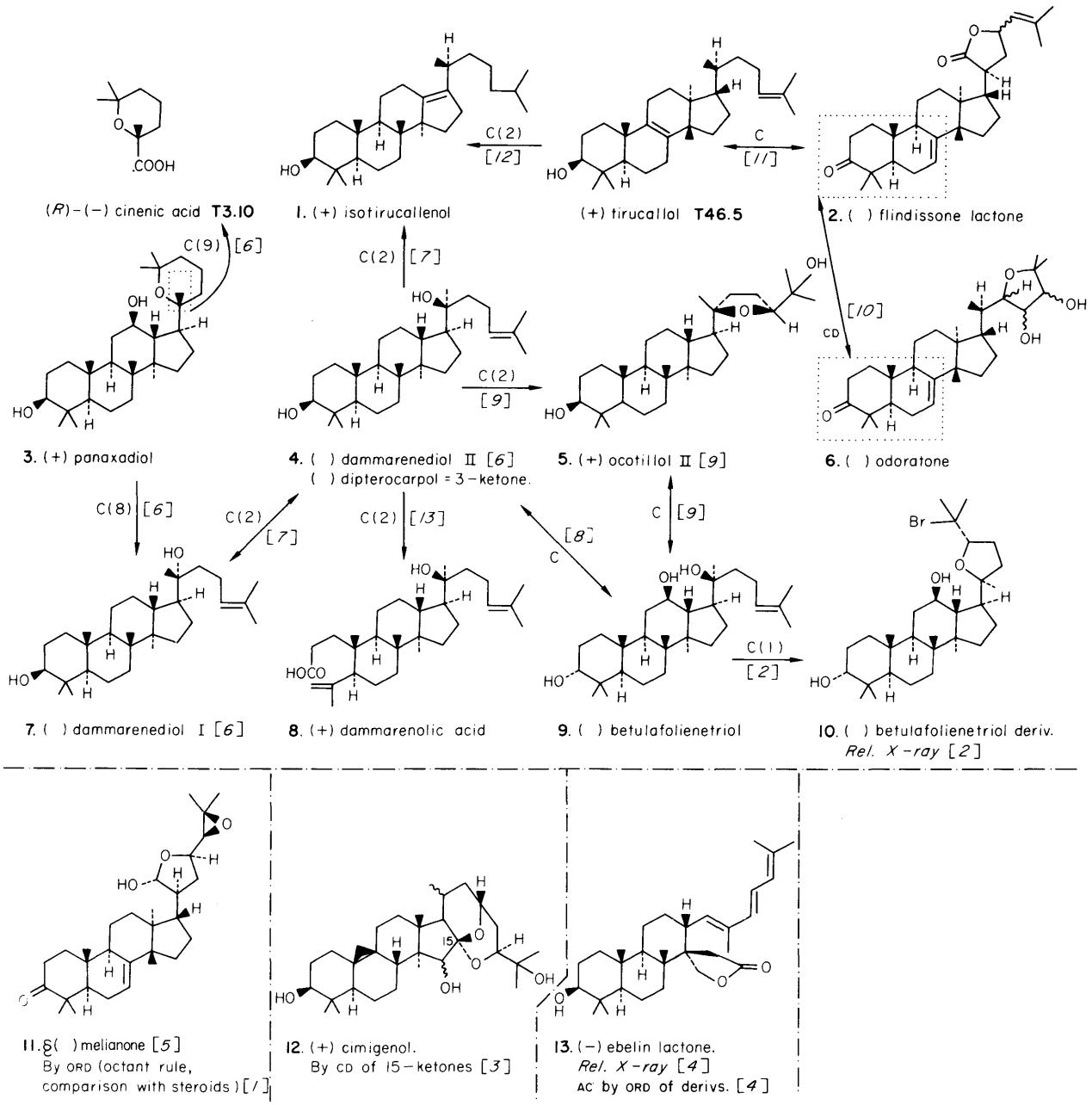
Steroids (contd.).



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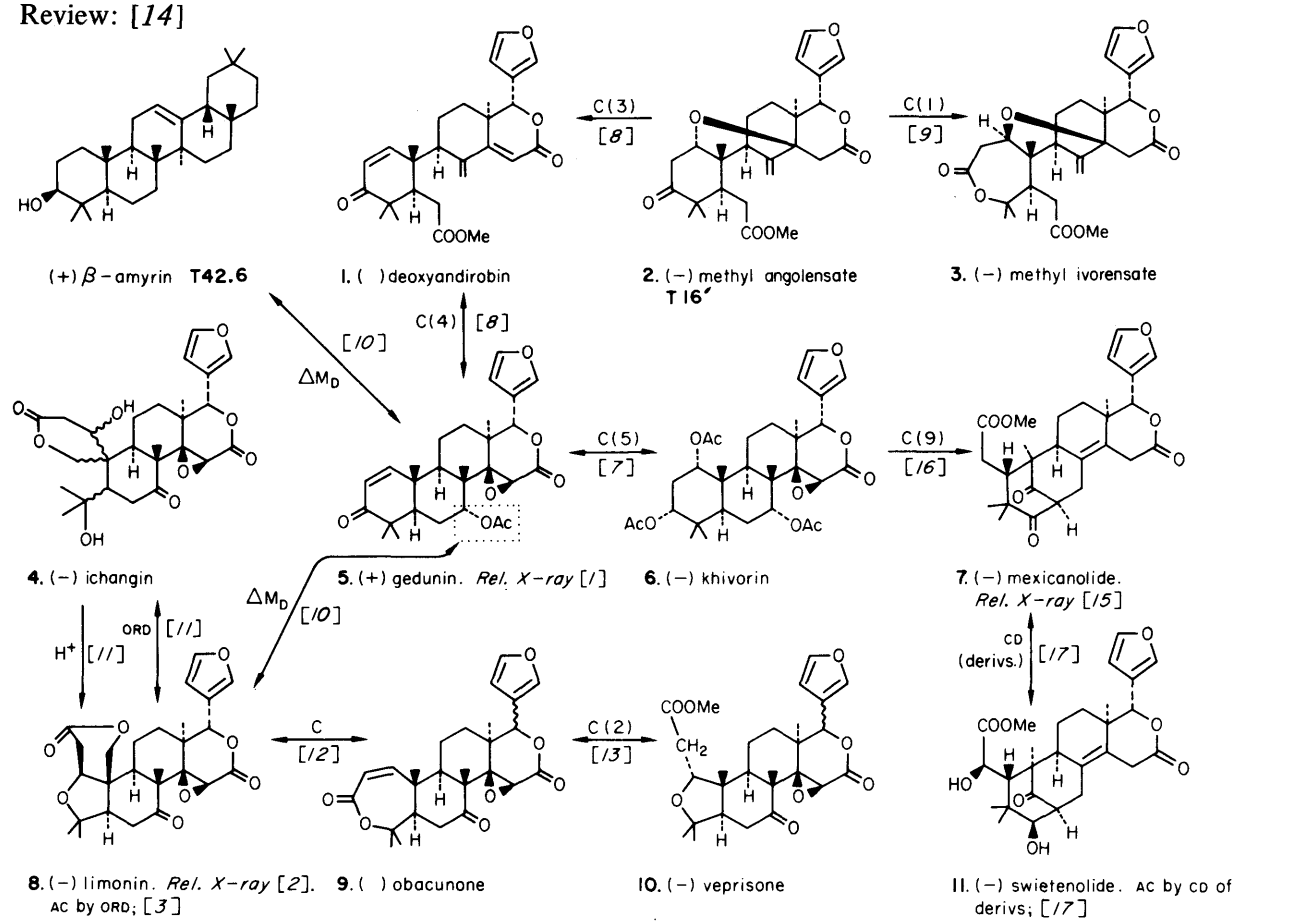
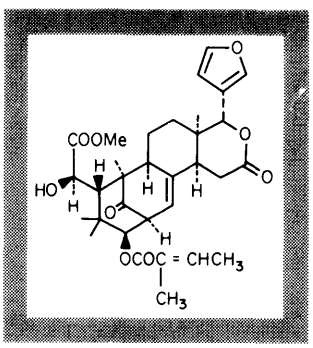
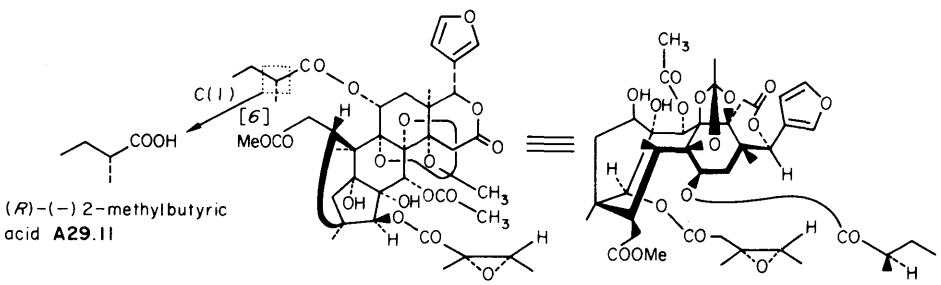
Limonoid bitter principles.

Review: [14]





12. (−) swietenine. Abs. X-ray [4]



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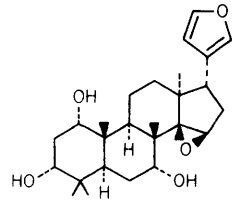
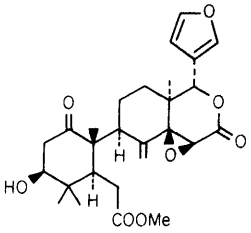
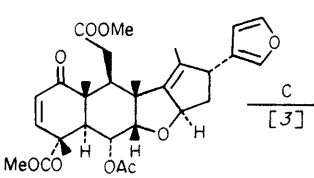
Further nortriterpenes; quassinoids.



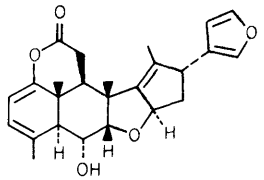
1. ( ) havanensin.
By CD of derivs. [1]



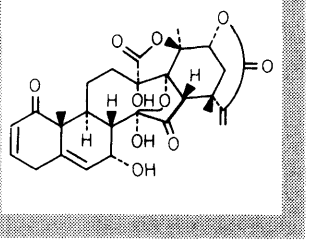
2. (−) mahoganin.
By ORD [2] (octant rule) (?)



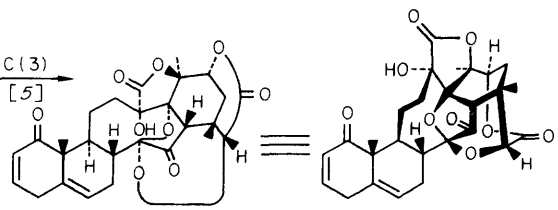
3. ( ) nimbin



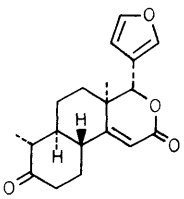
4. ( ) pyronimbic acid.
By ORD (cisoid diene) (?) [3]



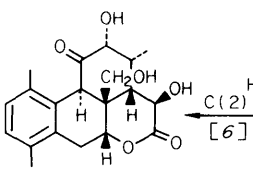
5. ( ) physalin A.
Abs. X-ray [4]



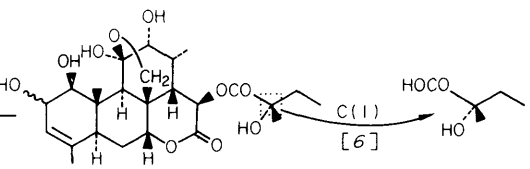
6. ( ) physalin B.



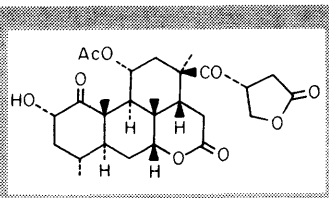
7. (+) odoratin. By CD [10]



8. (+) glaucanol

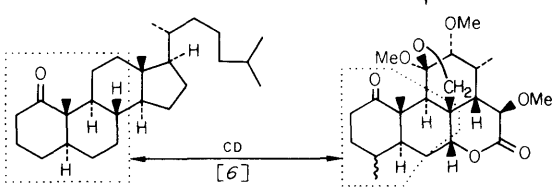


9. (+) glaucarubin



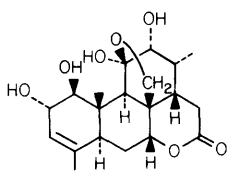
10. (+) simarolide. *Abs. X-ray* [9]
Related compd; picrasin A [7]

(*S*)−(+) 2-hydroxy-2-methylbutyric acid **A33.8**

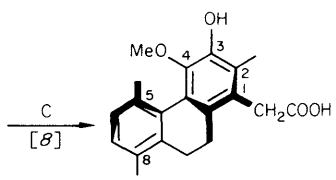


11. 5α-cholestan-1-one **T47**

12. (+)



13. (−) chapparin.
Also by ORD [8]



14. (*S*)−(+) 9,10-dihydro-3-hydroxy-4-methoxy-2,5,8-trimethylphenanthrene-1-acetic acid **X5**

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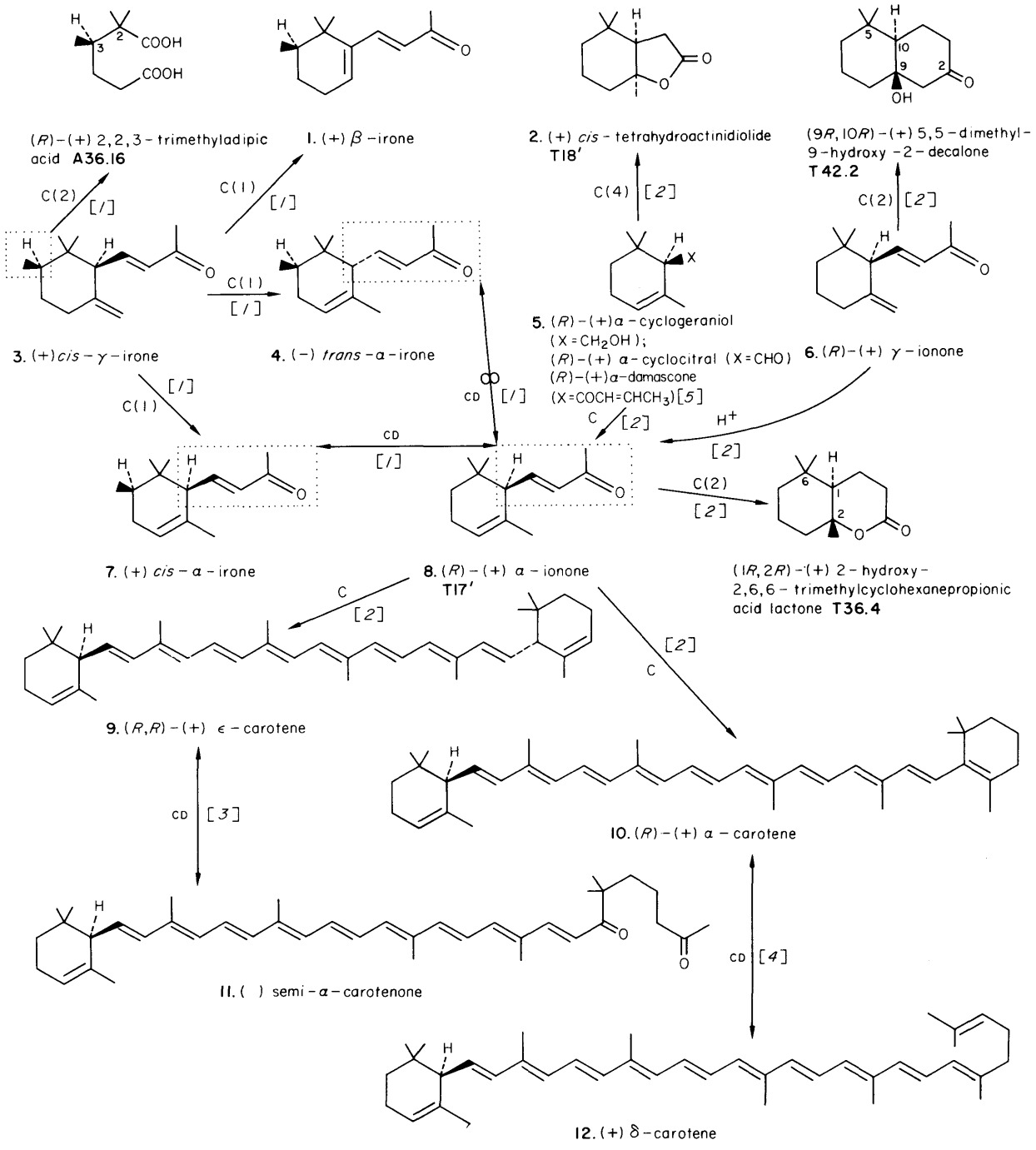
Carotenoids; ionone C_{13} group.



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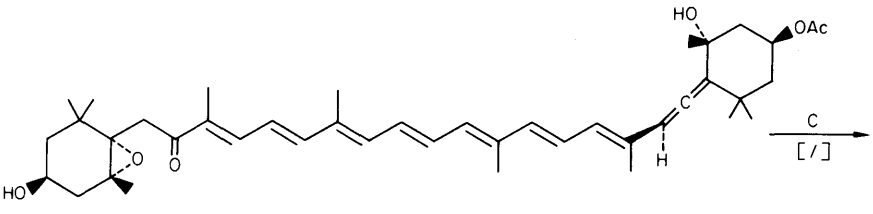
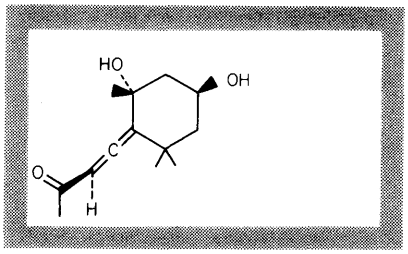
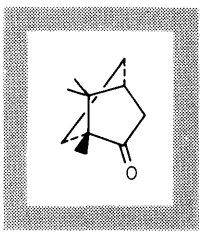


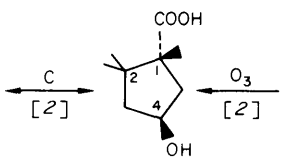
1. ( ) fucoxanthin [5]



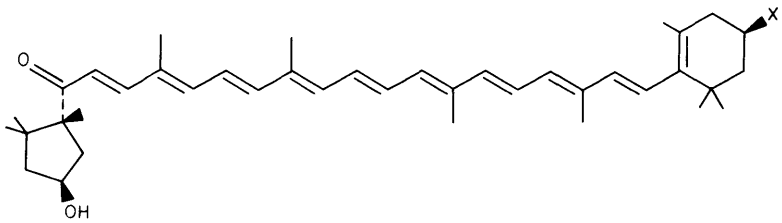
2. ( ) apo-9'-fucoxanthinone (grasshopper ketone) *Abs. X-ray* [1] T18'



(+) camphor
T11.7



3. (1*R*,4*S*)-( ) 4-hydroxy-1,2,2-trimethylcyclopentane-1-carboxylic acid



4. (+) capsanthin (X = OH)
( ) kryptocapsin (X = H)

The following natural carotenoids have also been correlated with fucoxanthin or capsanthin by chemical or chiroptical means; neoxanthin, violaxanthin, zeaxanthin, β-cryptoxanthin, α-cryptoxanthin, rubixanthin, gazaniaxanthin, β-citraurin, reticulatoxanthin, alloxanthin, diatoxanthin [*1*]; lutein [*3*] and many others [*4*].

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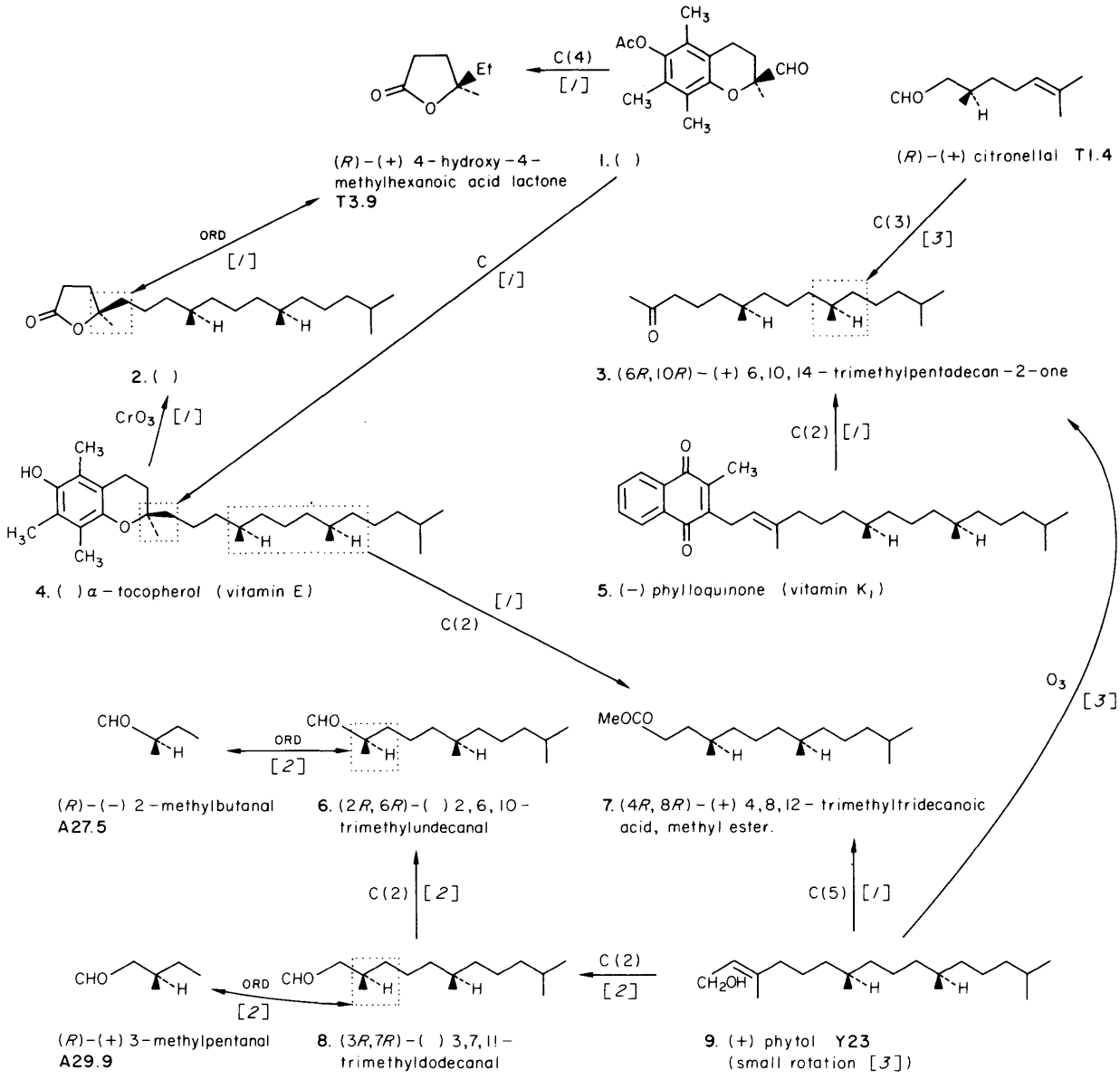

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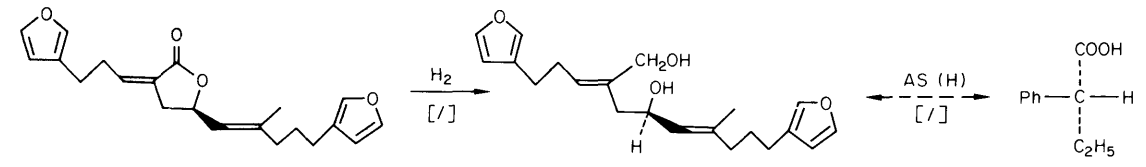
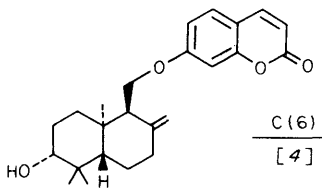
Miscellaneous terpenoids and norterpenoid derivatives.



1. (−) nitenin

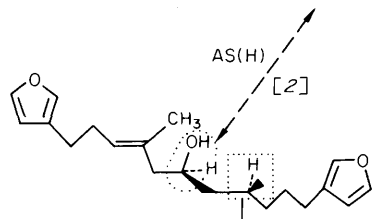
2. (+)

(*R*)−(−) 2-phenylbutyric acid **A41.13**



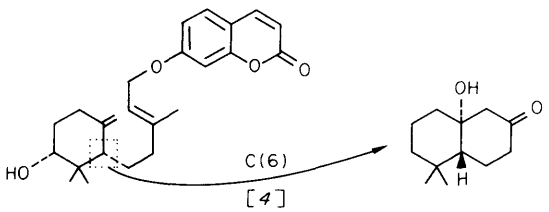
3. (−) farnesiferol A

(2*S*,9*R*, 10*R*)−(+) 2, 5, 5, 9-tetramethyldecalin −1,6-dione **T42.12**



4. ( ) § furospongin 1

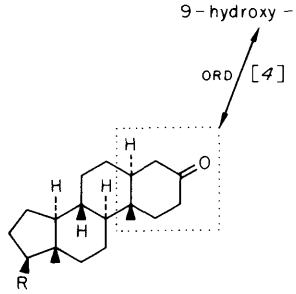
C(2) [2][3]



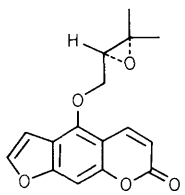
5. (+) farnesiferol B

(9*R*,10*R*)−(+) 5,5-dimethyl-9-hydroxy-2-decalone **T42.2**

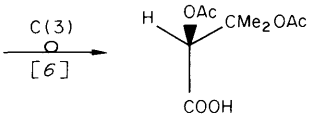
§(*S*)−(+) 2-methyladipic acid **A 38.3**



6. 3-oxo-5α-steroids **T47**



7. (−) oxypeucedanin
Related compd;
( ) ostruthol.
See also [5]



(*S*)−(+) 2,3-diacetoxy-3-methylbutyric acid **A3.11**

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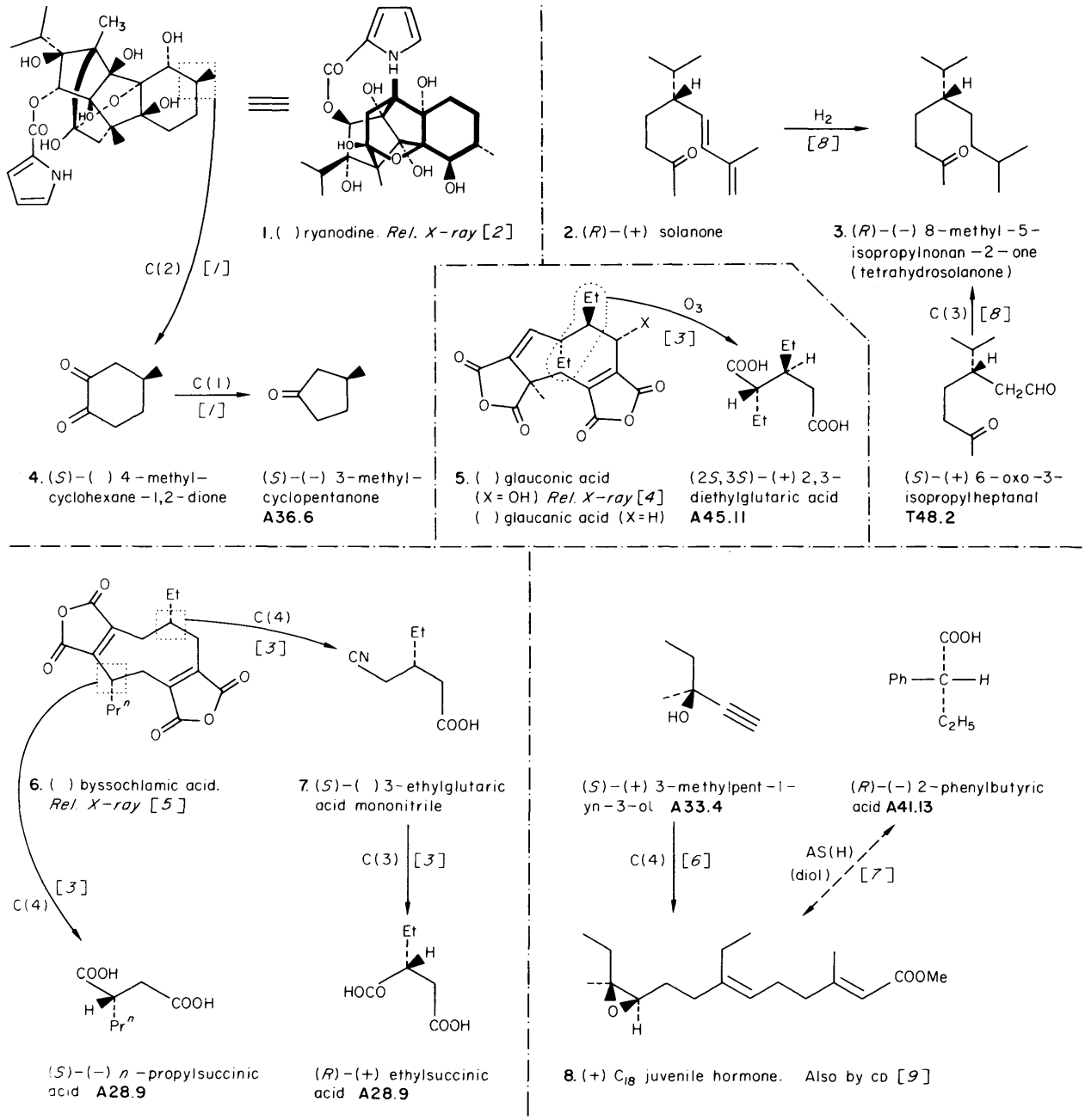

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-K-

Alkaloids

Introductory Notes to Chapter K

Sources

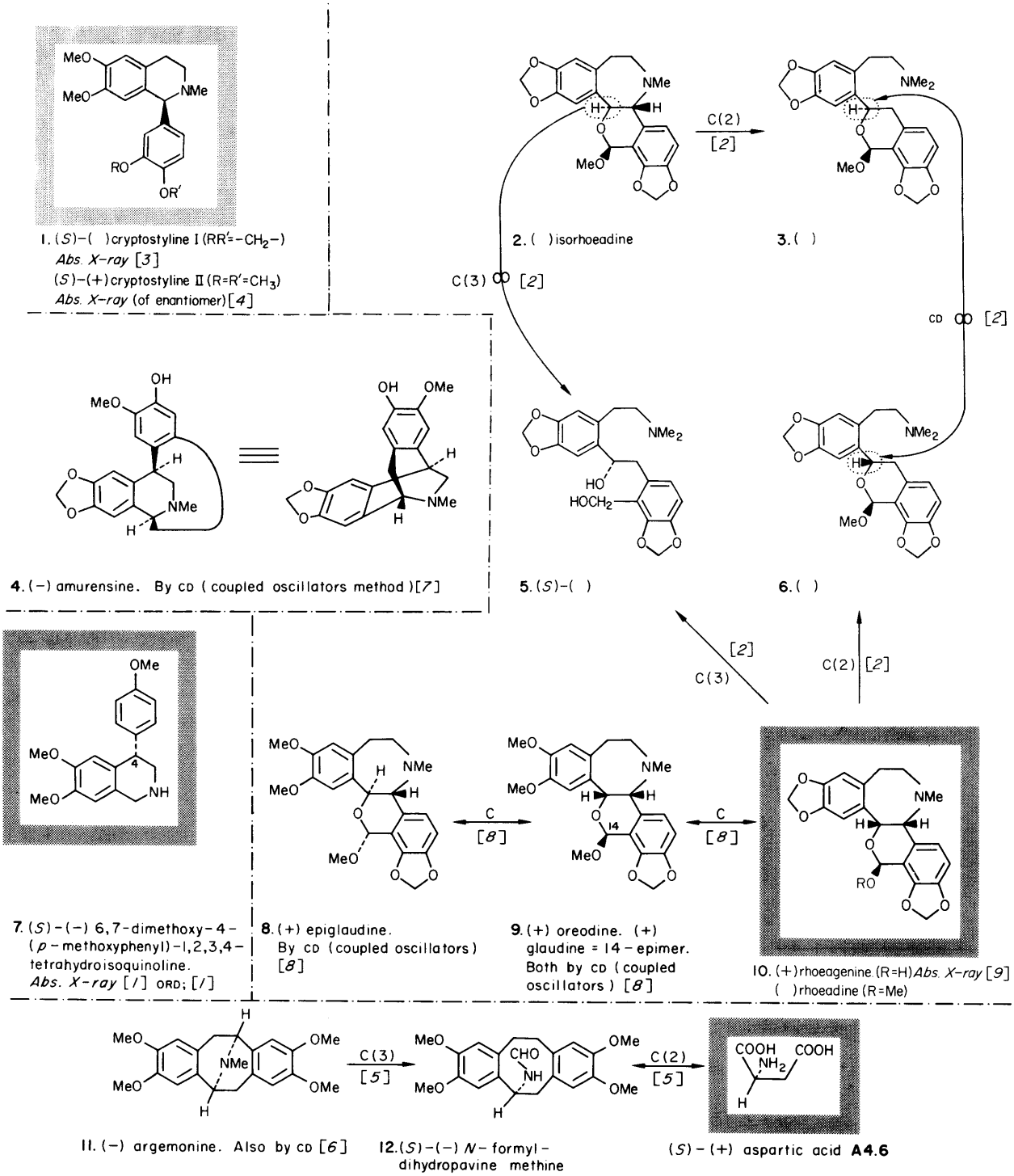
The major reference work dealing with alkaloid chemistry is *The Alkaloids* (R. H. F. Manske and H. L. Holmes, Eds., Academic Press, 1950-1970), in 13 volumes. A recent one-volume text (*Chemistry of the Alkaloids*, S. W. Pelletier, Ed., Van Nostrand, 1970), was also consulted extensively in preparing this chapter, and the arrangement of material largely follows the latter book.

See also R. F. Raffauf, *A Handbook of Alkaloids and Alkaloid-Containing Plants* (Wiley, New York, 1970).

Alkaloids found in other chapters

Some alkaloids, for reasons of convenience, appear elsewhere in the 'Atlas'. In addition, the term 'Alkaloid' is subject to varying interpretation, and there are a few nitrogenous substances listed elsewhere which may be considered as alkaloids in the widest sense but not according to the narrower definitions. The following is a list, in alphabetical order, of compounds falling into these two categories.

Actinidine **T13.17**
Adrenaline **A22.14**
Amphetamine **A5.10**
Boschniakine **T15.7**
Cassaine **T39.9**
Ephedrine **A21.10**
Epiguiapyridine **T25.4**
Evoninic acid **A31.9**
Julocrotine **Y29.9**
2-Methylpiperidine **A10.5**
Milliamines **T39.2**
Muscarine **Y20.8**
Patchoulipyridine **T27.4**
Ryanodine **T58.1**
Skytanthines **T14.15-T14.18**
Solanidine **T49.4**
Solasodine **T49.7**
Tomatidine **T49.8**



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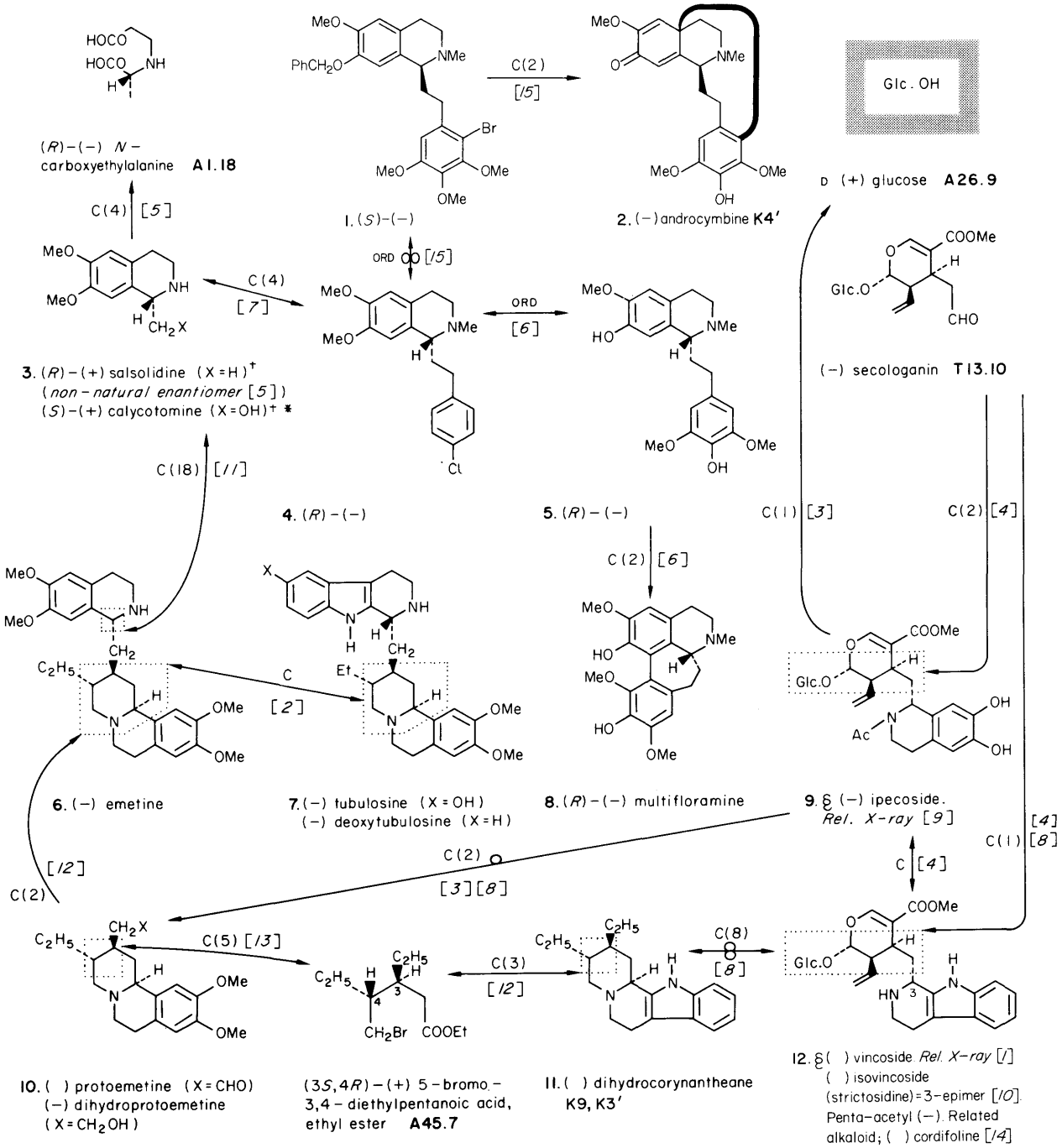

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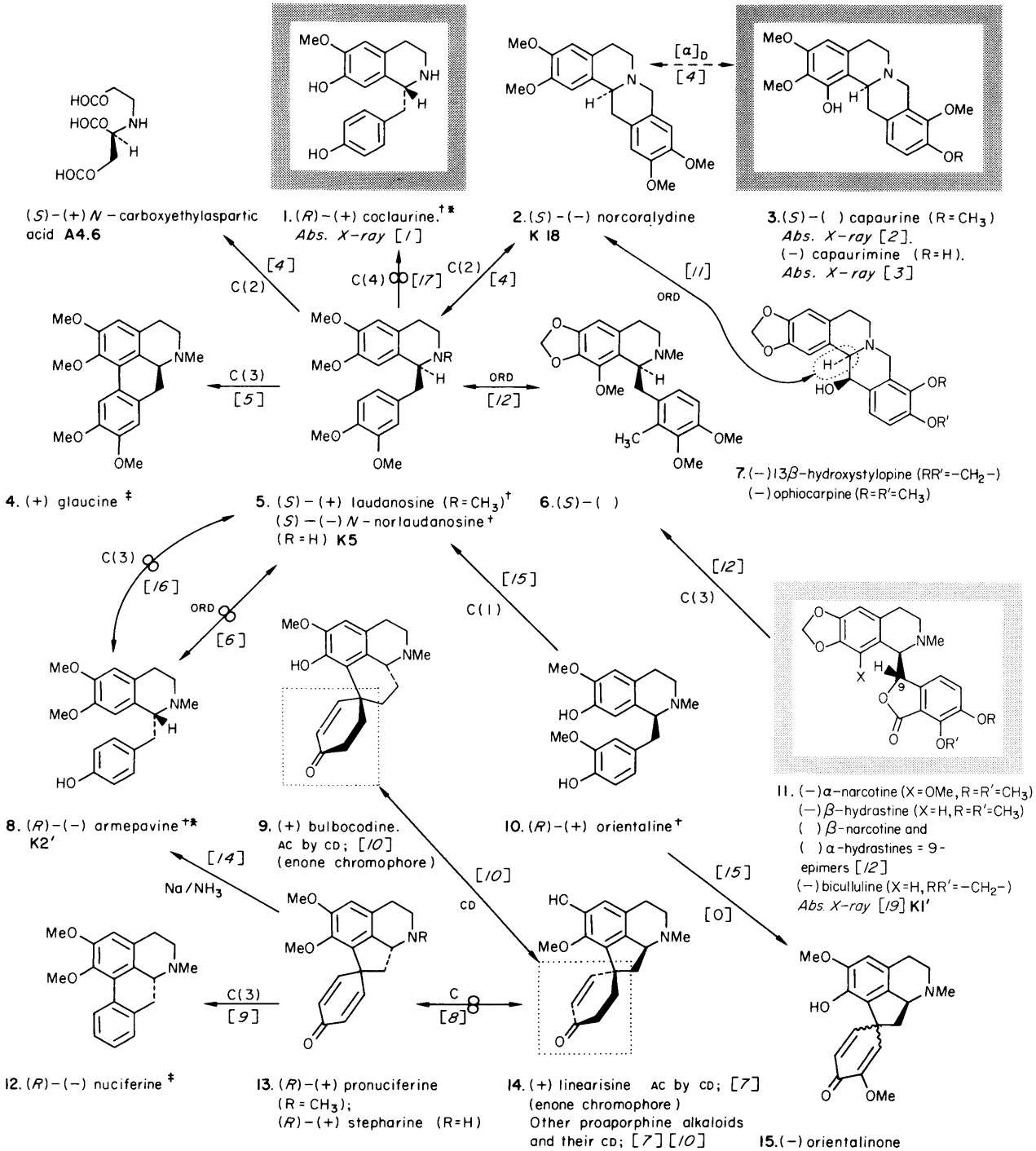
†Naturally occurring tetrahydroisoquinoline alkaloids may be of either enantiomeric type or may be racemic [5] [6].



†Naturally occurring benzylisoquinoline alkaloids may be of either enantiomeric series or may be racemic. Alkaloids homochirally analogous with (*R*)-(+) coclaurine, and their quaternary derivatives, have +veORD and vice-versa [6].

Bisbenzylisoquinoline alkaloids. At least 6 types of alkaloid are known in which one benzylisoquinoline moiety is joined to another by one or more ether linkages. Structural determination of these compounds is usually by fission followed by identification of the benzylisoquinoline components, and they are not therefore specifically treated here.
ORD of bisbenzylisoquinoline types; [13].

‡ see footnote on page **140**

References at top of page 140

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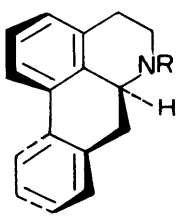
†Morphine bases of both enantiomeric types, derived from morphinan (e.g. (-) morphine, **K4.5**, (-) thebaine **K4.6**) and from *enantio* morphinan (e.g. sinomenine **K4.2**) occur naturally. One or two alkaloids are known to occur naturally as both enantiomers, e.g. (+) salutaridine **K4.4** (morphane type) and (-) sinoacutine (*enantio*-salutaridine) (*enantio*-morphane type).

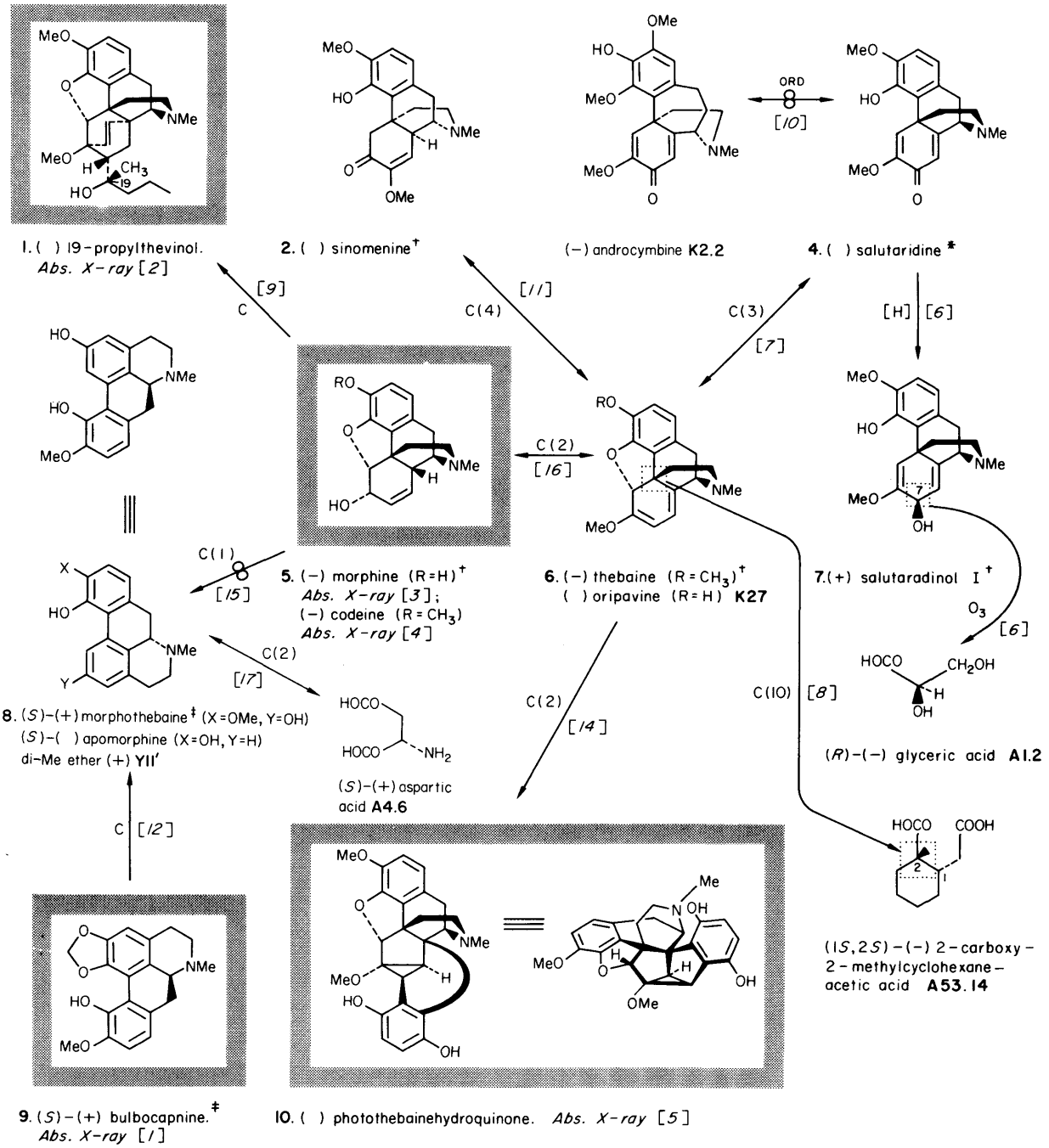
‡The ORD of aporphine alkaloids has been discussed [*12*] [*13*]. The overriding factor in determining the sign is the chirality of the biphenyl chromophore, which is in turn uniquely determined by the configuration at the asymmetric carbon atom.



biphenyl system (*S*)
asymmetric C atom (*S*)

The exact form of the ORD curve is, however, strongly determined by the 1,2,10,11-substitution pattern and it is therefore necessary to choose as a model compound for an alkaloid of unknown configuration one having a similar substitution pattern [*12*].

Chiroptical properties of morphinan derivs; [18]



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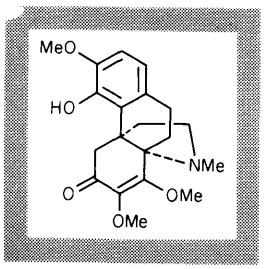
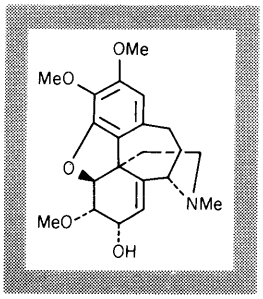
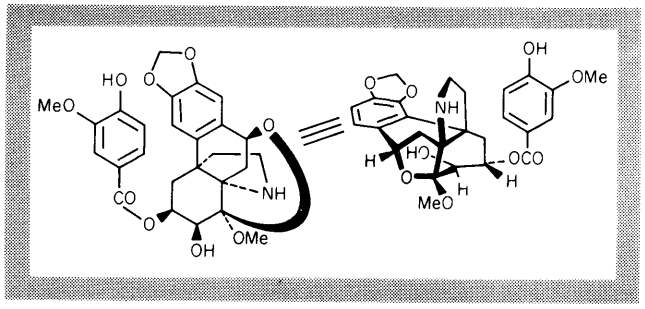


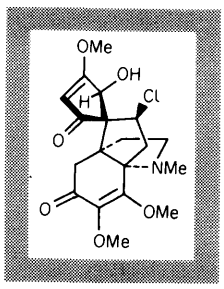
1. (−) 4 − demethylhasubanonine. *Abs. X-ray [1]*



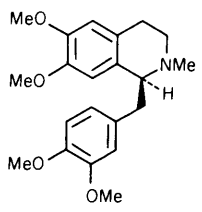
2. (+) kreysiginine. *Abs. X-ray [2]*



3. (+) stephavanine. *Abs. X-ray [3]*

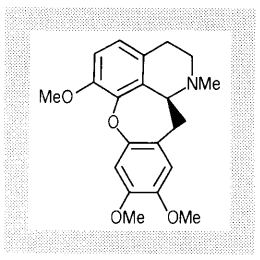


4. (−) acutumine. *Abs. X-ray [4]*



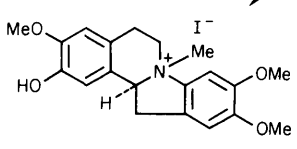
(*S*)−(+) laudanosine **K3.5**

C [6]

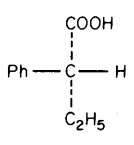


5. (+) cularine. *Abs. X-ray [8]*

C(3) [5]

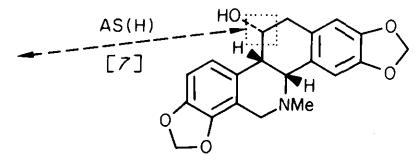


6. (−) cryptaustoline iodide



(*R*)−(−) 2-phenylbutyric acid **A41.13**

AS(H) [7]



7. (+) chelidonine. AC by CD; [7]

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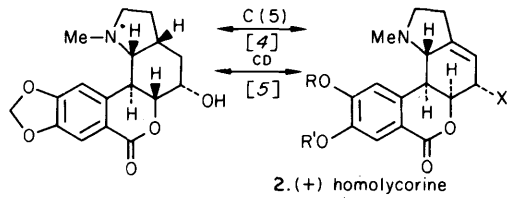
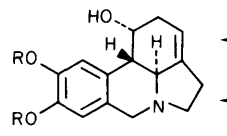
ORD/CD ; [7] Nomenclature; [4]

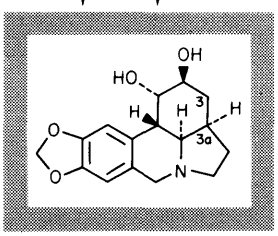


1. (+) clivonine. Related alkaloids [1]

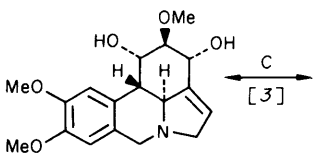
2. (+) homolycorine (R=R'=CH_3, X=H) (+) hippeastrine (RR'=CH_2, X=OH). *Rel. X-ray* of lycorenine (dihydrohomolycorine) [20]



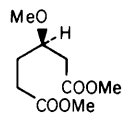
3. (−) pluviine (R=R'=CH_3); ( ) caranine (RR'=$-CH_2-$) CD; [18] X7



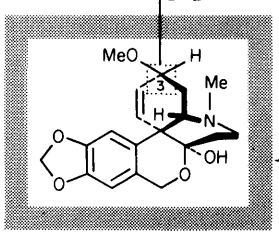
5. ( ) dihydrolycorine. *Abs. X-ray* [2] CD; [18] ( ) lycorine = 3, 3a-didehydro-deriv.



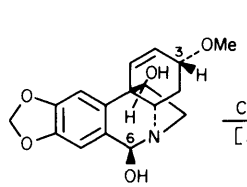
4. (−) narcissidine. *Rel. X-ray* [3]



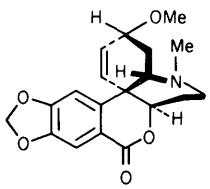
(*R*)-(+) dimethyl 3-methoxyadipate A25.20



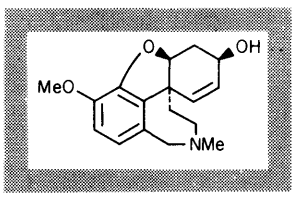
6. (+) tazettine. *Abs. X-ray* [9]. (+) criwelline = 3-epimer.



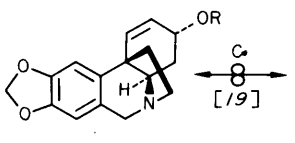
7. (+) 6-hydroxycrinamine. *Rel. X-ray* [10]. ( ) haemanthidine = 3-epimer. These compounds exist as mixtures of 6-epimers in solution [11]



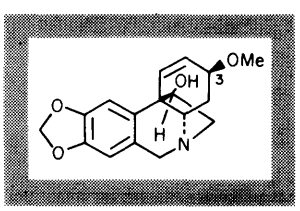
8. (+) macronine



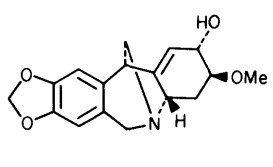
9. (−) galanthamine. *Abs. X-ray* [16]. See also [7] (−) lycoramine = dihydroderiv.



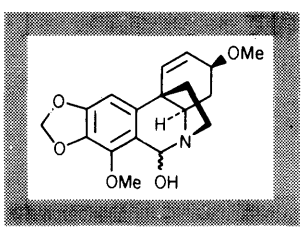
10. (−) crinine (R=H) * (−) buphanisine (R=CH_3) Other related alkaloids; [19]



11. ( ) haemanthamine. *Abs. X-ray* [14] ( ) crinamine = 3-epimer. Other related alkaloids; [19]



12. (−) isohaemanthamine. Related compds; (−) montanine, (−) coccinine, (−) manthine [15]



13. ( ) 6-hydroxybuphanidrine *Abs. X-ray* [14]

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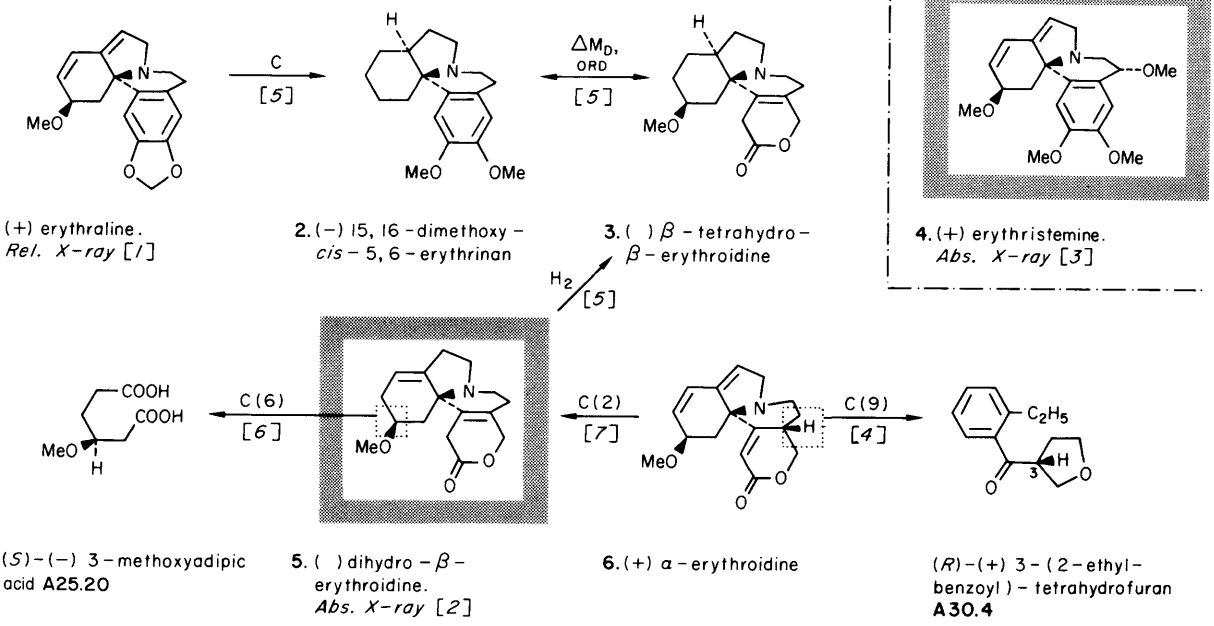


1. (+) erythraline. *Rel. X-ray [1]*

2. (−) 15, 16-dimethoxy-*cis*-5, 6-erythrinan

3. ( ) β-tetrahydro-β-erythroidine

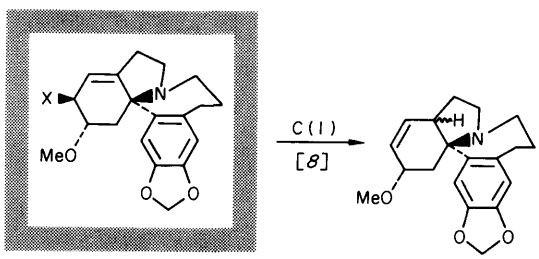
4. (+) erythristemine. *Abs. X-ray [3]*

(*S*)-(−) 3-methoxyadipic acid **A25.20**

5. ( ) dihydro-β-erythroidine. *Abs. X-ray [2]*

6. (+) α-erythroidine

(*R*)-(+) 3-(2-ethylbenzoyl)-tetrahydrofuran **A30.4**



7. (+) schellhammerine (X=OH) *Abs. X-ray [8]*. (+) schellhammericine (X=H) **X7**

8. (+) schellhammeridine

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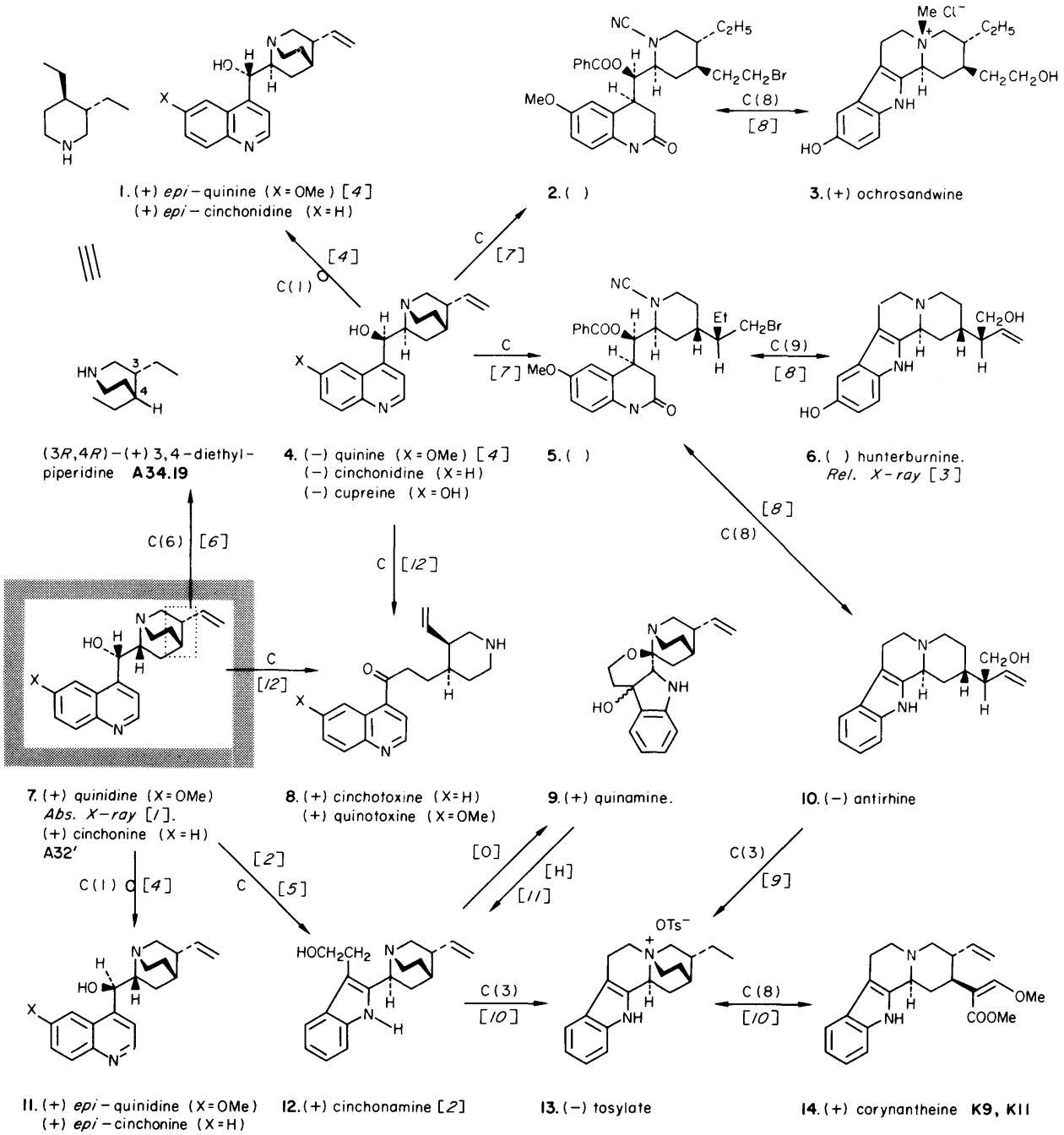

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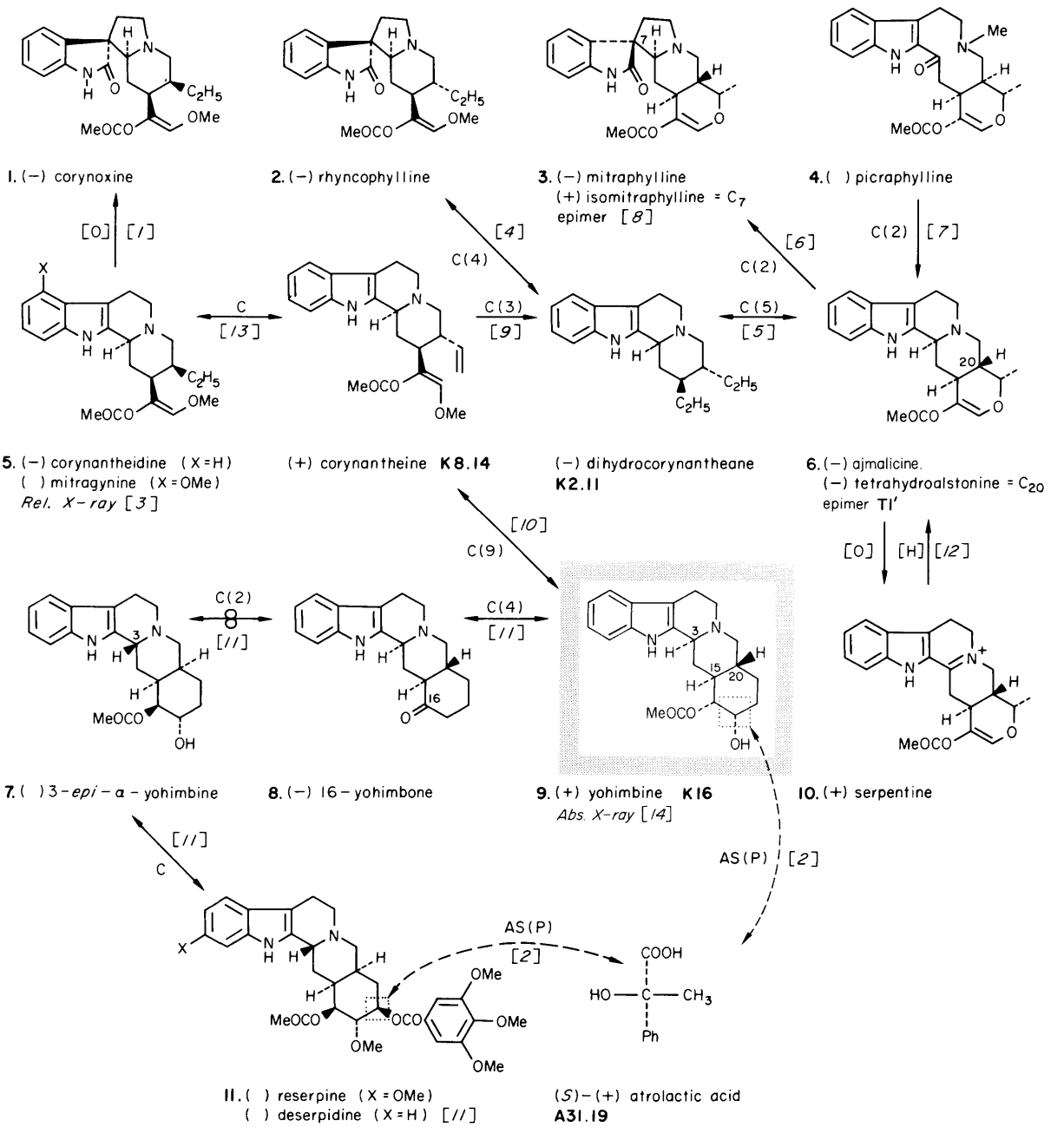

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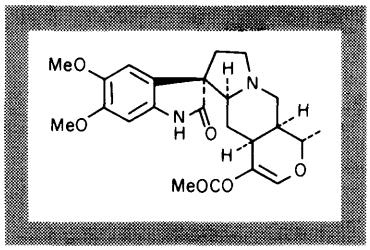
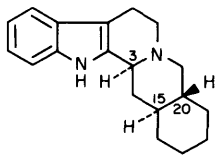


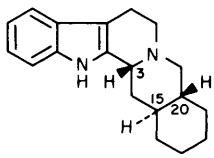
I. (+) rauvoxinine. *Abs. X-ray* [5]

Configurations of yohimbane, corynantheane and heteroyohimbane derivatives

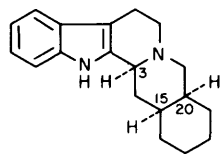
Only a few of the known configurational types of these alkaloids are represented on pp. **K8-K9**. The yohimbane skeleton contains 3 asymmetric centres. All known yohimbane derivatives are homochirally analogous at $C_{(15)}$, having the $C_{(15)}$ configuration corresponding to (15*S*) in yohimbane. There are thus 4 stereoisomeric types derived from the following 4 parent compounds:



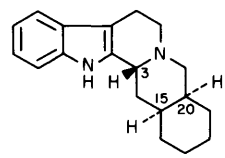
(−) yohimbane (3*S*, 15*S*, 20*S*)
Example;
(+) yohimbine **K9.10**



( ) pseudoyohimbane
(3*R*, 15*S*, 20*S*)



(−) alloyohimbane
(3*S*, 15*S*, 20*R*)



( ) epialloyohimbane
(3*R*, 15*S*, 20*R*)
Example;
(−) reserpine **K9.12**

The known yohimbane alkaloids have been correlated with the key compounds on p. **K9** by chemical and chiroptical means [*1*]. ORD/CD of the four yohimbane types; [*3*].

The situation with alkaloids containing the dihydro-corynantheane skeleton is similar; there are four stereoisomeric types, normal (e.g. corynantheine **K8.14**), *pseudo, allo* (e.g. corynantheidine **K9.5**) and *epiallo*. Their stereochemistry has been fully discussed [*2*]. On the basis of this work a corynantheine type alkaloid can be allotted to one of the four classes by spectroscopic measurement, making the same assumption about $C_{(15)}$ configuration [*2*].

The stereochemistry of the heteroyohimbine types resembles that of the yohimbines but with an additional chiral centre at C_{19}. It is again probable that only (15*S*) type compounds occur naturally and there are thus again 4 basic skeletal types, normal (e.g. ajmalicine **K9.6**), *pseudo, allo* and *epiallo*, each of which may in addition have the (19*R*) or (19*S*) configuration [*4*]. ORD of heteroyohimbine alkaloids; [*8*].

Oxindole group

There are 16 possible stereochemical types arising from the 4 asymmetric centres at C_3, C_7, C_{19} and C_{20} (cf. mitraphylline **K9.3**) although some of the isomers are sterically unfavourable [*7*]. As with the previous types of indole alkaloid, the C_{15} configuration is assumed to be always as shown for mitraphylline.

Other correlations by rearrangement of yohimbane-type alkaloids to oxidinole alkaloids in addition to these shown on p. **K9** have been carried out.

CD of oxindole alkaloids; [*6*].

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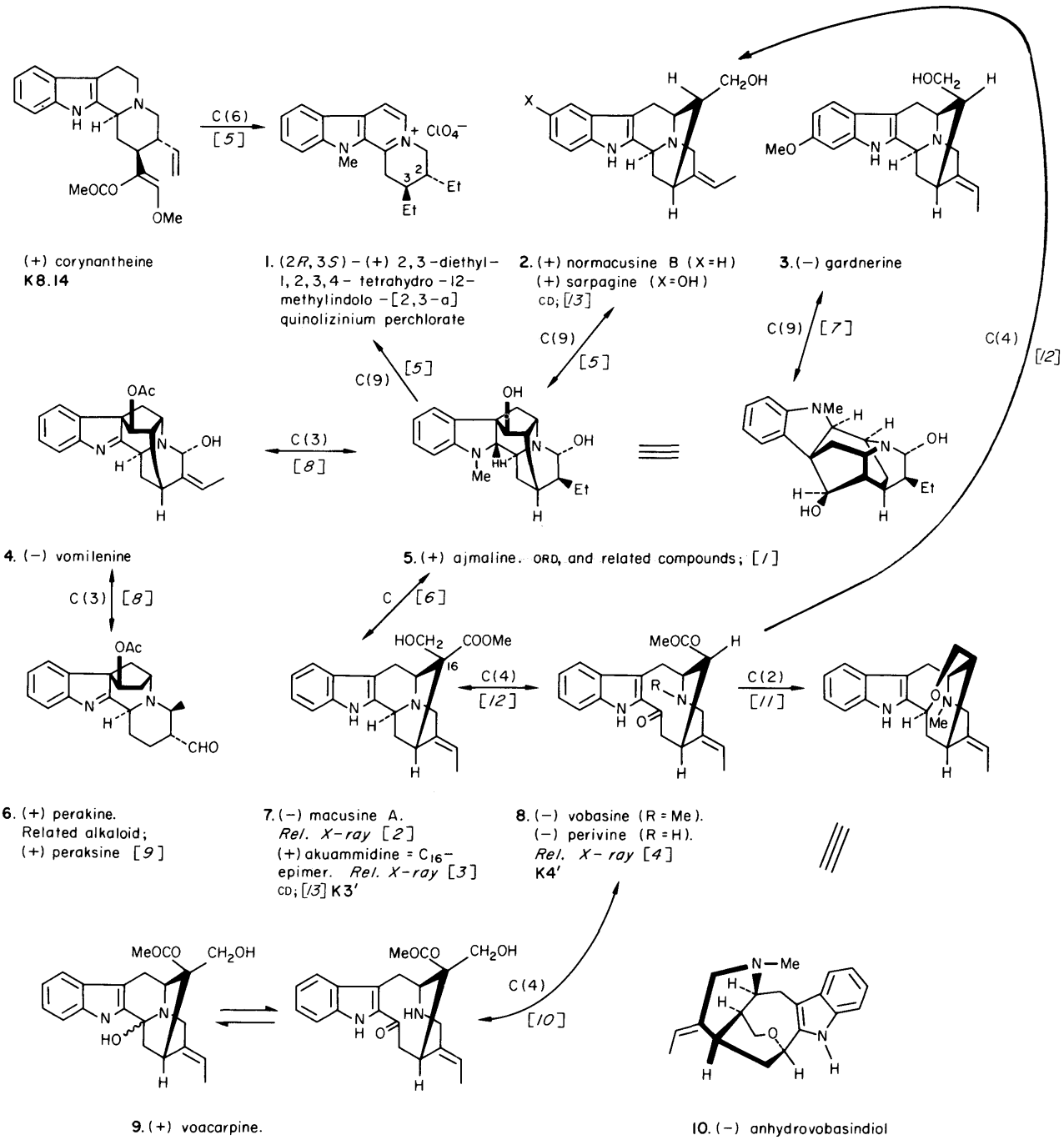

(+) corynantheine
K8.14

1. (2*R*,3*S*) – (+) 2,3-diethyl-1,2,3,4-tetrahydro-12-methylindolo-[2,3-a] quinolizinium perchlorate

2. (+) normacusine B (X=H)
(+) sarpagine (X=OH)
CD; [13]

3. (–) gardnerine

4. (–) vomilenine

5. (+) ajmaline. ORD, and related compounds; [1]

6. (+) perakine.
Related alkaloid;
(+) peraksine [9]

7. (–) macusine A.
Rel. X-ray [2]
(+) akuammidine = C_{16}–epimer. *Rel. X-ray* [3]
CD; [13] K3′

8. (–) vobasine (R = Me).
(–) perivine (R = H).
Rel. X-ray [4]
K4′

9. (+) voacarpine.

10. (–) anhydrovobasindiol

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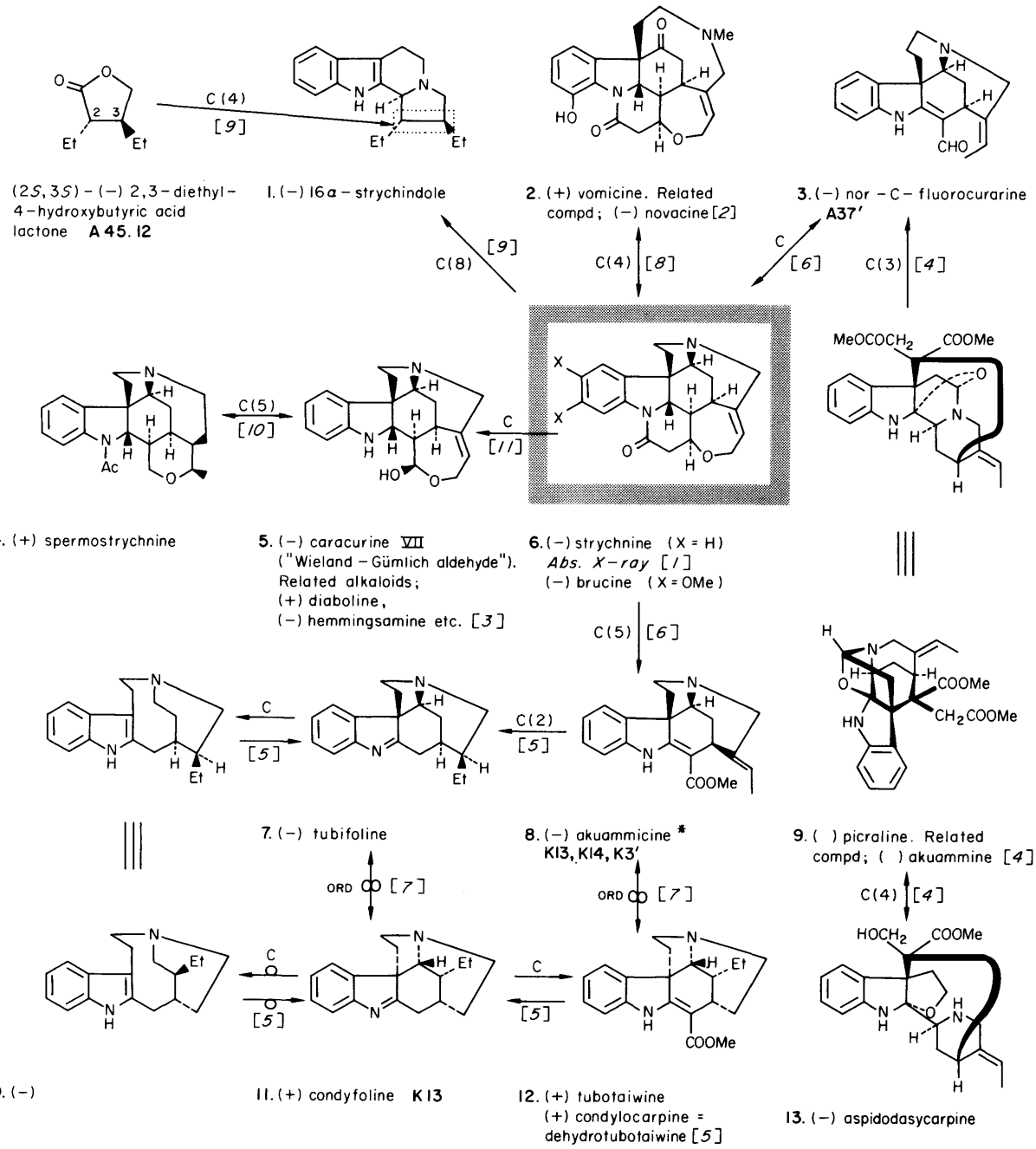
ORD/CD ; [7]



(2S,3S) - (−) 2,3-diethyl-4-hydroxybutyric acid lactone **A 45. 12**

1. (−) 16α - strychindole

2. (+) vomicine. Related compd; (−) novacine [2]

3. (−) nor - C - fluorocurarine **A37'**

4. (+) spermostrychnine

5. (−) caracurine VII ("Wieland - Gümlich aldehyde"). Related alkaloids; (+) diaboline, (−) hemmingsamine etc. [3]

6. (−) strychnine (X = H) *Abs. X-ray* [1] (−) brucine (X = OMe)

7. (−) tubifoline

8. (−) akuammicine * **K13, K14, K3'**

9. ( ) picraline. Related compd; ( ) akuammine [4]

10. (−)

11. (+) condyfoline **K13**

12. (+) tubotaiwine (+) condylocarpine = dehydrotubotaiwine [5]

13. (−) aspidodasycarpine

1. A. F. Peerdeman, *Acta Cryst.*, 1956, **9**, 824.
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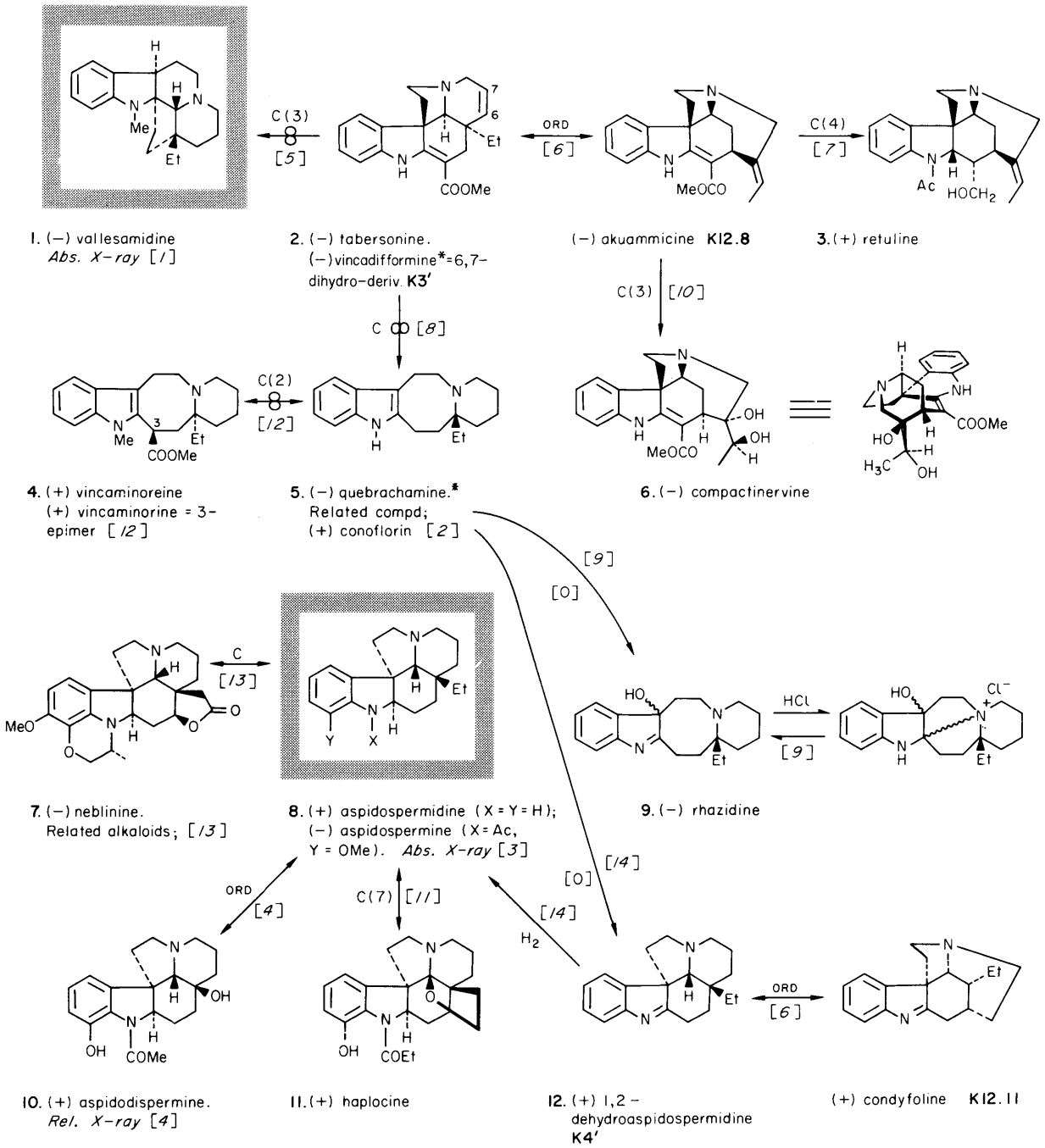

1. (−) vallesamidine
Abs. X-ray [1]

2. (−) tabersonine.
(−)vincadifformine*=6,7-dihydro-deriv. **K3'**

(−) akuammicine **K12.8**

3. (+) retuline

4. (+) vincaminoreine
(+) vincaminorine = 3-epimer [12]

5. (−) quebrachamine.*
Related compd;
(+) conoflorin [2]

6. (−) compactinervine

7. (−) neblinine.
Related alkaloids; [13]

8. (+) aspidospermidine (X = Y = H);
(−) aspidospermine (X = Ac, Y = OMe). *Abs. X-ray* [3]

9. (−) rhazidine

10. (+) aspidodispermine.
Rel. X-ray [4]

11. (+) haplocine

12. (+) 1,2-dehydroaspidospermidine
K4'

(+) condyfoline **K12.11**

1. S. H. Brown, C. Djerassi, and P. G. Simpson, *J. Amer. Chem. Soc.*, 1969, **90**, 2445.
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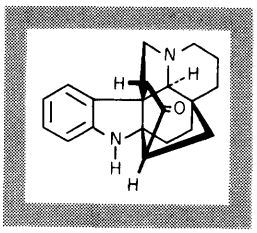
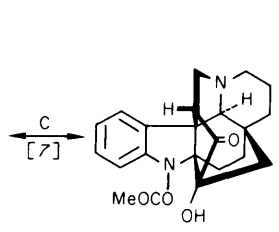
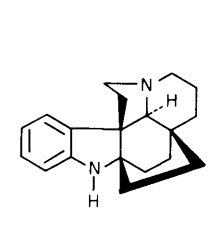


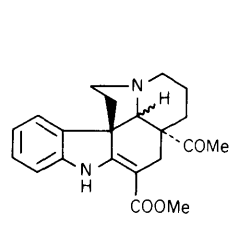
1. (−) kopsanone. *Abs. X-ray* [1]



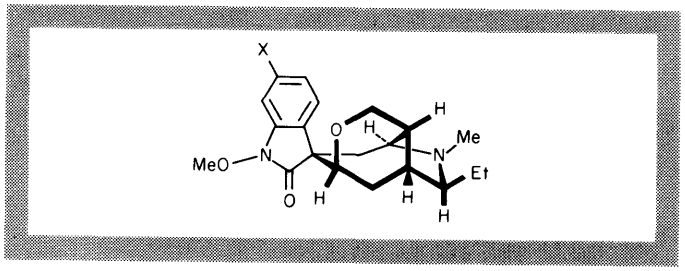
2. (−) kopsine



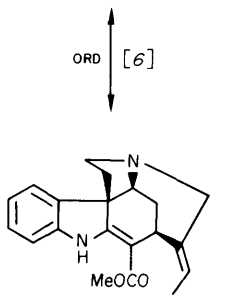
3. (−) aspidofractinine



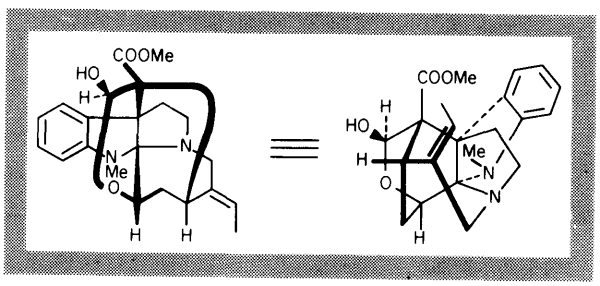
4. (−) minovincine



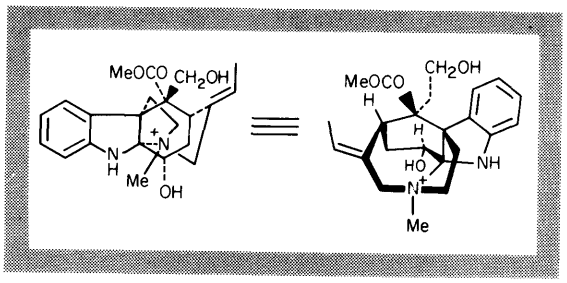
5. (−) gelsemicine (X = OMe). *Abs. X-ray* [2] (−) gelsedine (X = H)



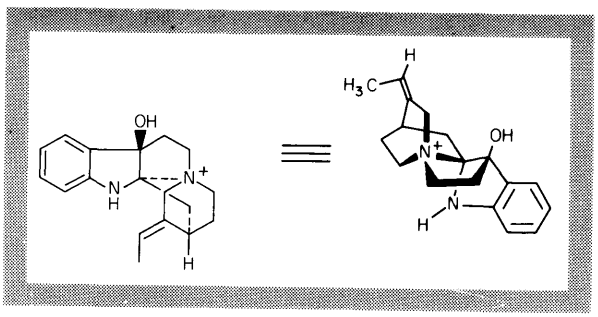
(−) akuammicine **K12.8**



6. (+) corymine. *Abs. X-ray* [3]



7. ( ) echitamine. *Abs. X-ray* [4]



8. (−) hunteracine. *Abs. X-ray* [5]

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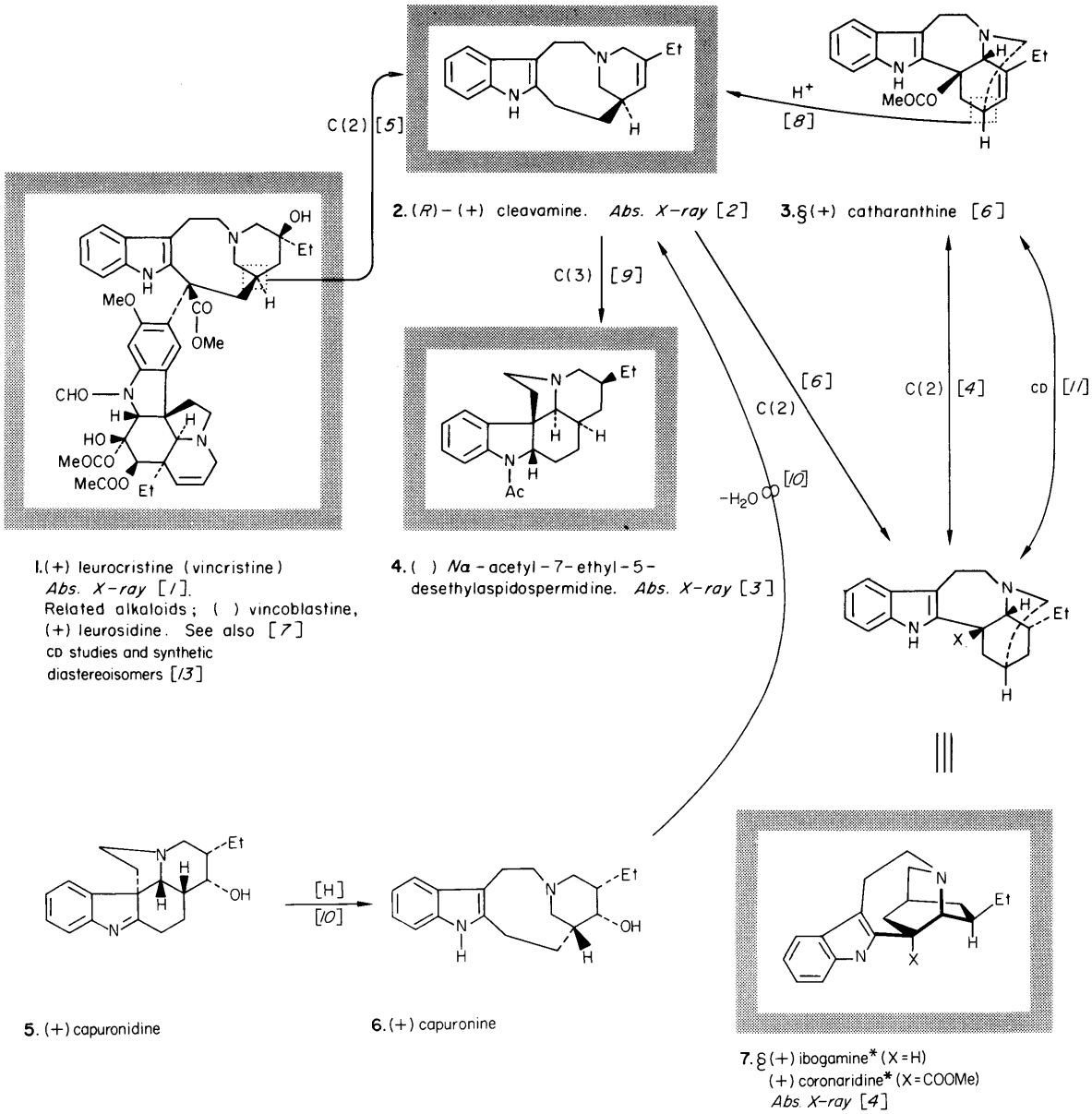

Other dimeric indole alkaloids. Some of these have been identified only by mass spectrometry and their absolute configurations are at present therefore unknown; others have been identified by fission followed by correlation of the constituent halves with other known indole alkaloids [5].

Iboga group. It is now clear [4] [12] that naturally occurring iboga alkaloids belong to both enantiomeric series. This fact resolves earlier contradictions in the literature (see for example [11]).

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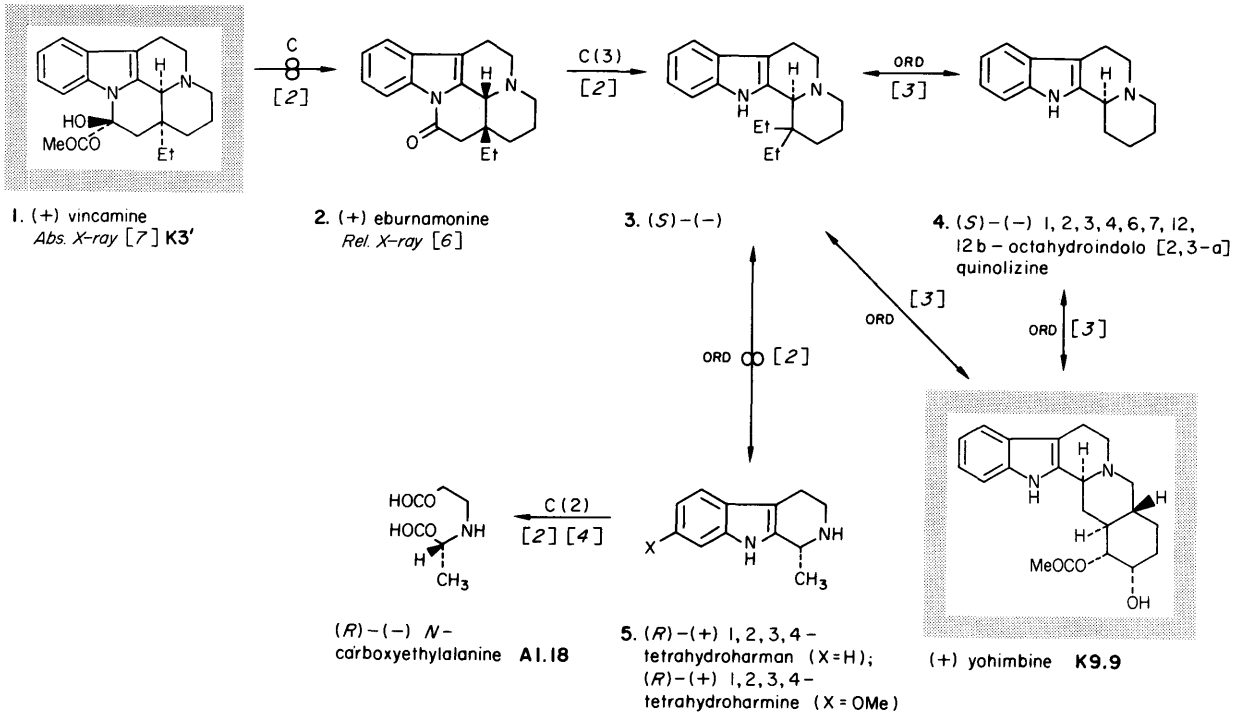
Other eburnamine alkaloids and their ORD; [1]



1. (+) vincamine
Abs. X-ray [7] **K3'**

2. (+) eburnamonine
Rel. X-ray [6]

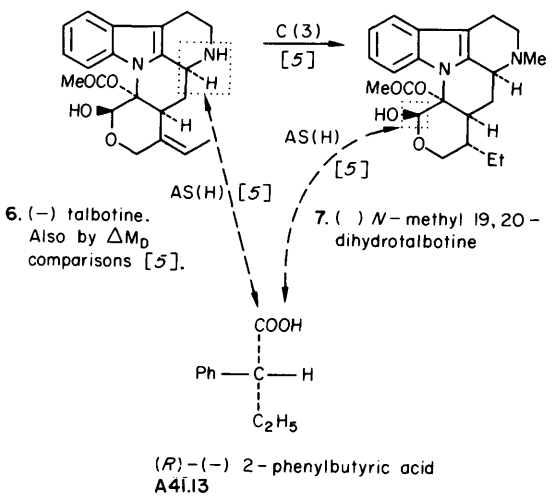
3. (*S*)-(−)

4. (*S*)-(−) 1, 2, 3, 4, 6, 7, 12, 12b-octahydroindolo [2,3-a] quinolizine

(*R*)-(−) *N*-carboxyethylalanine **A1.18**

5. (*R*)-(+) 1, 2, 3, 4-tetrahydroharman (X=H); (*R*)-(+) 1, 2, 3, 4-tetrahydroharmine (X = OMe)

(+) yohimbine **K9.9**



6. (−) talbotine.
Also by ΔM_D comparisons [5].

7. ( ) *N*-methyl 19, 20-dihydrotalbotine

(*R*)-(−) 2-phenylbutyric acid
A41.13

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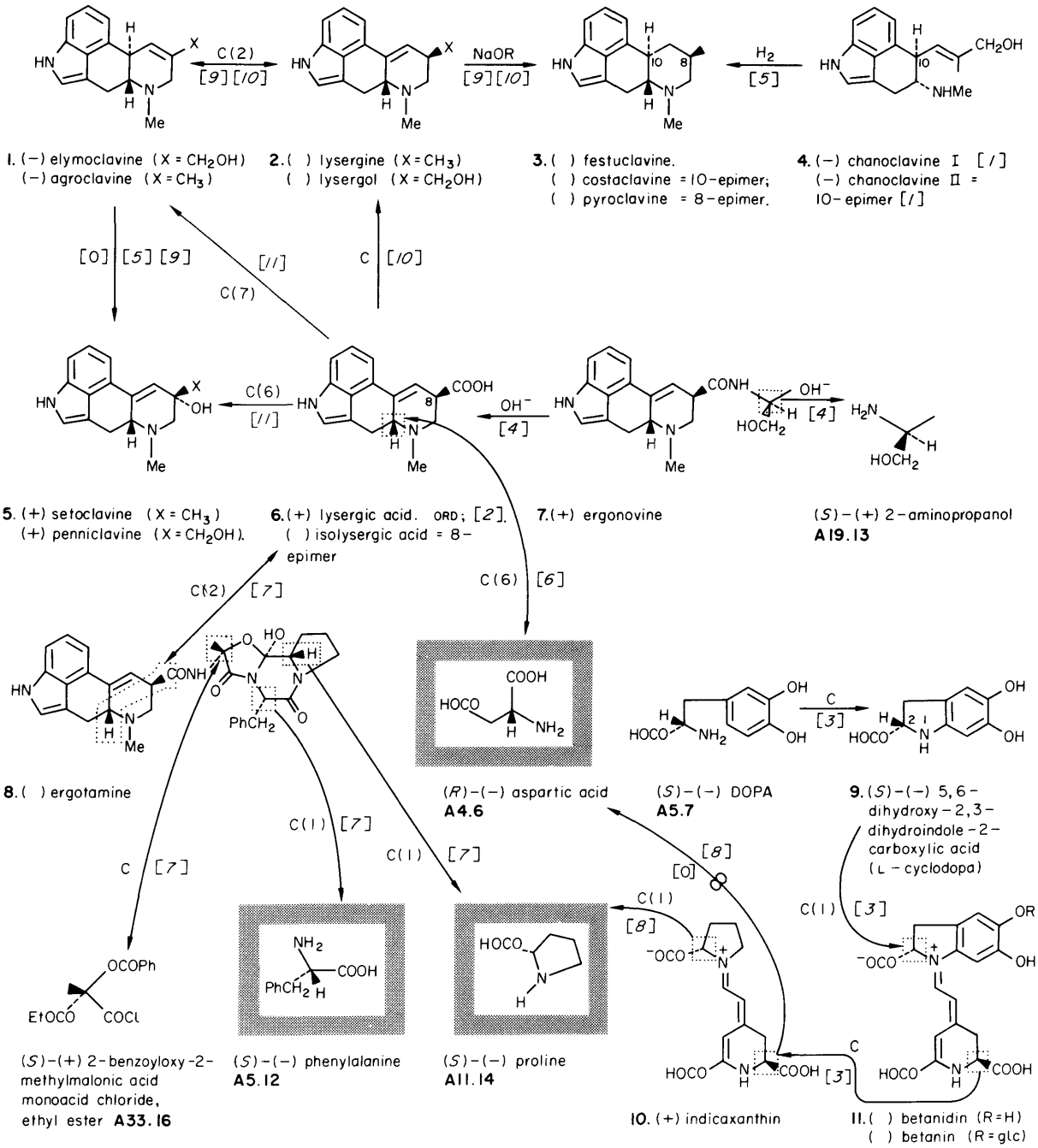
Ergot alkaloids; betanin, indicaxanthin.

For further ergot alkaloids, see [10]



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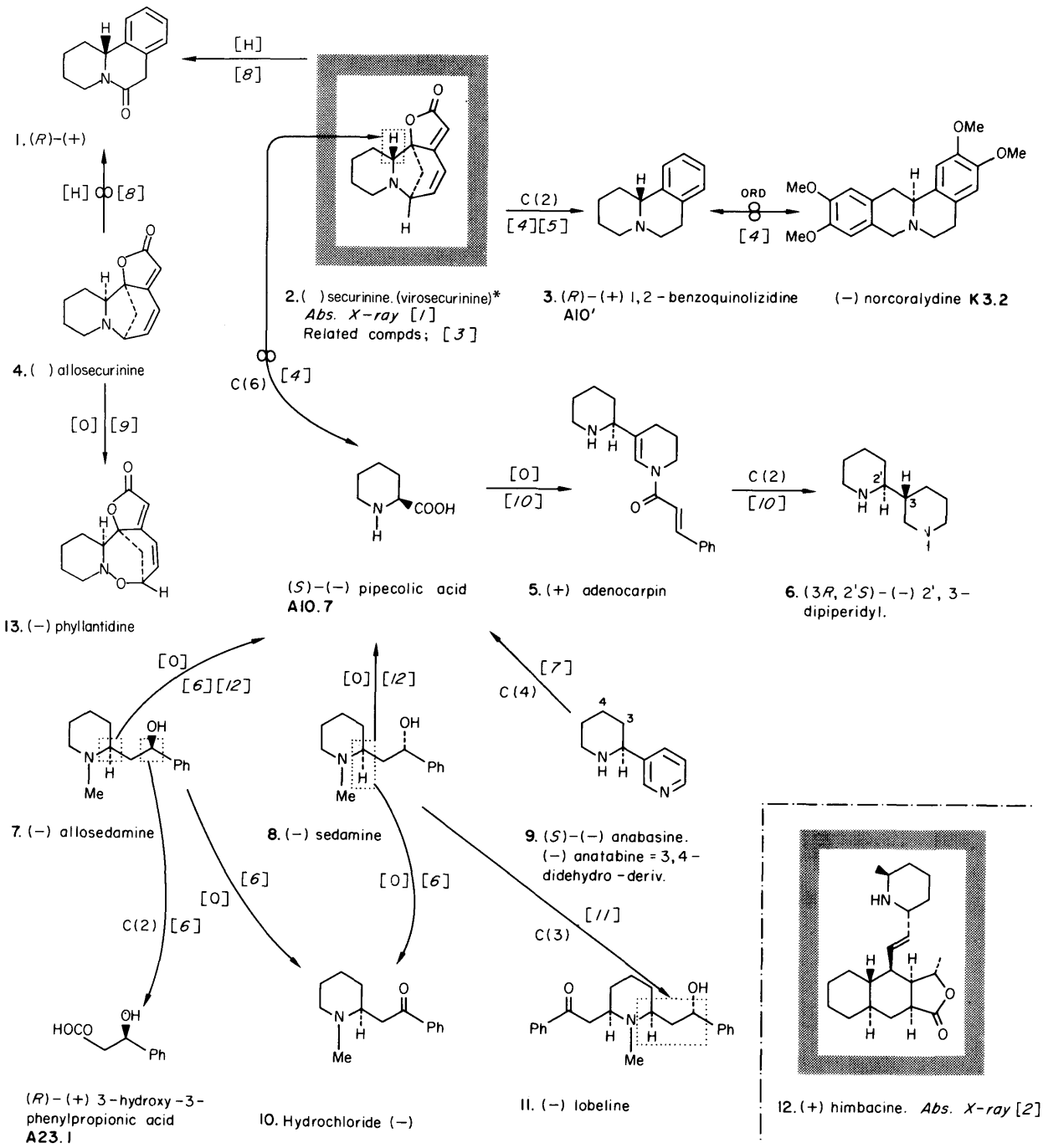

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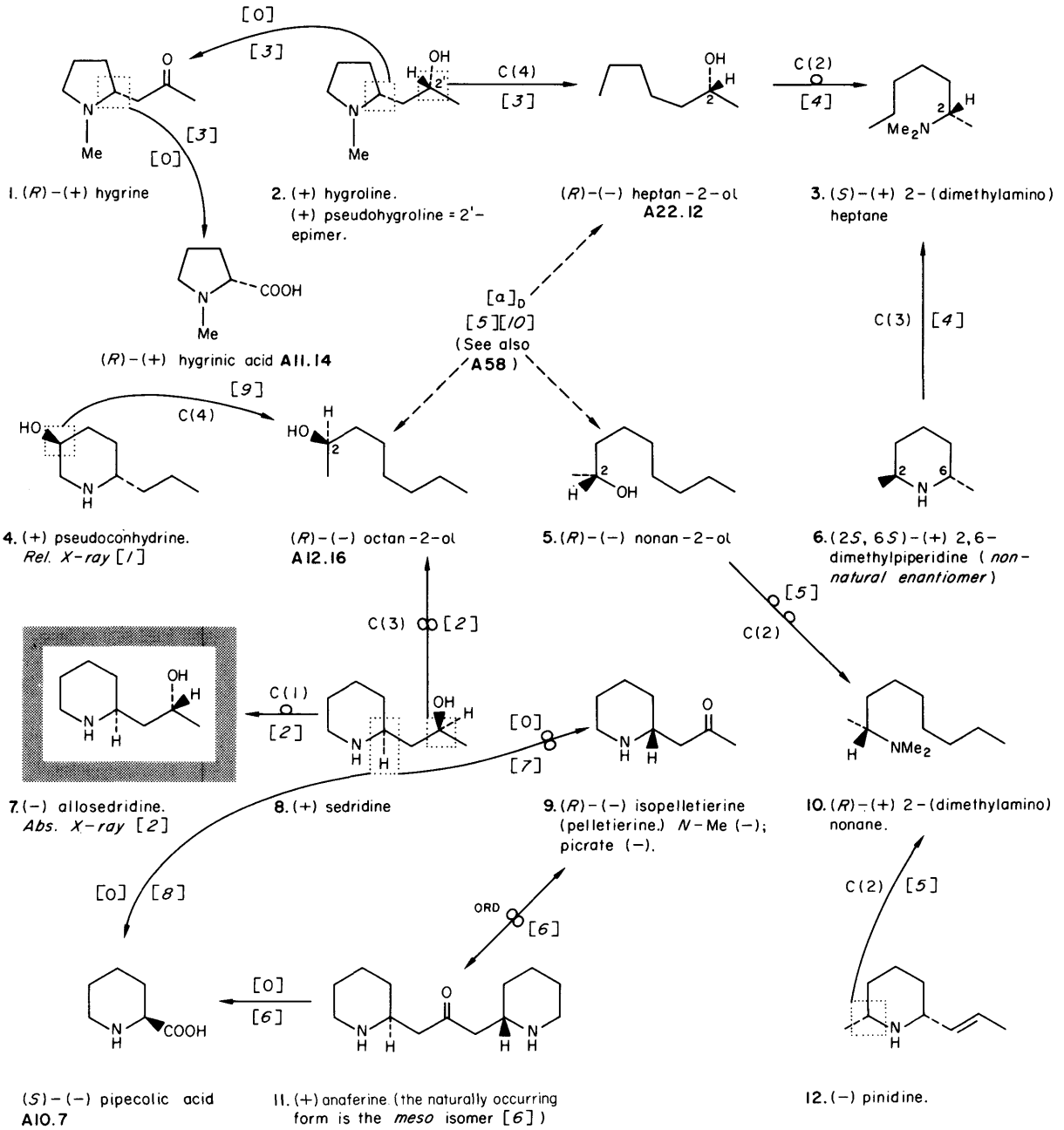

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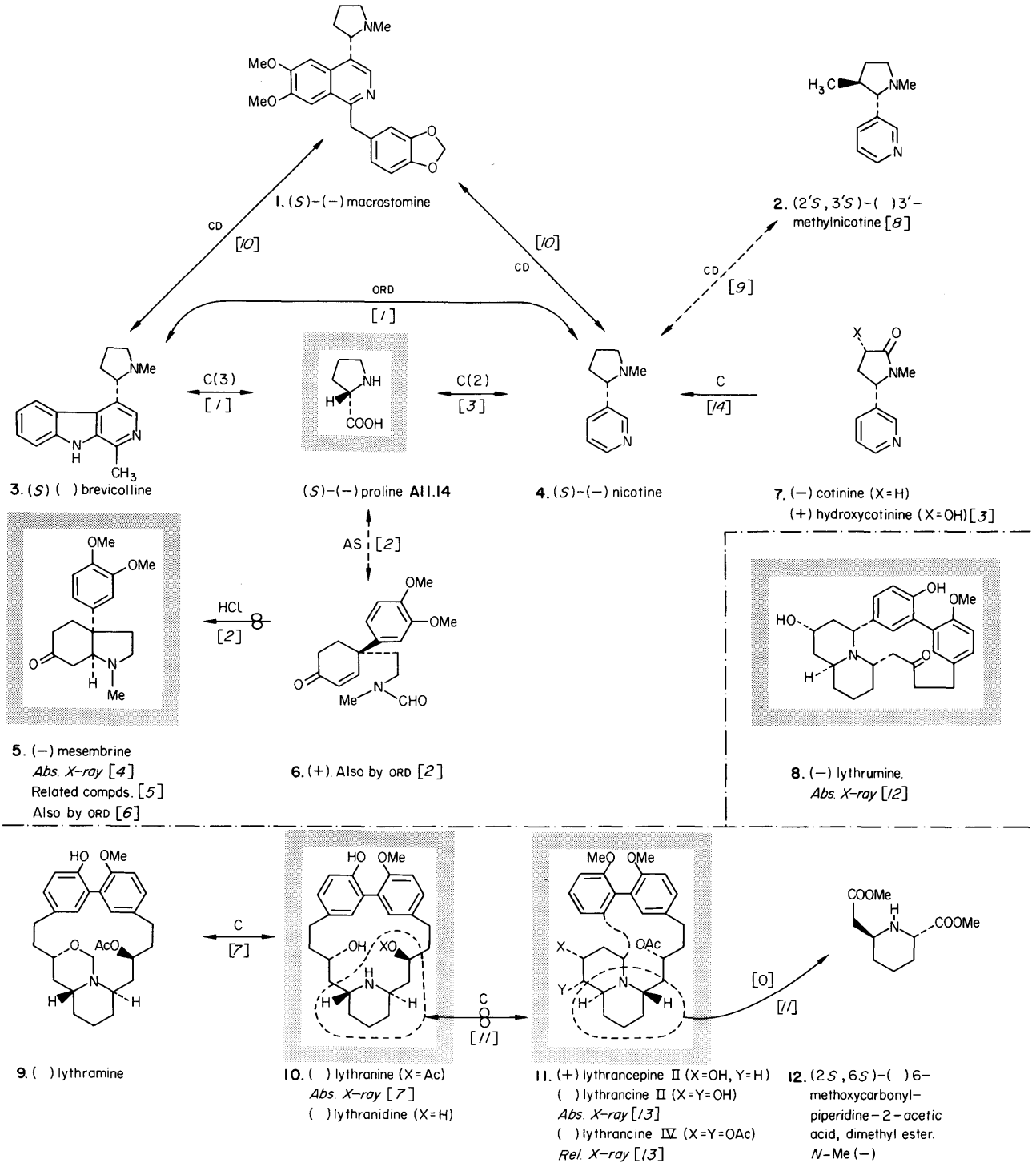

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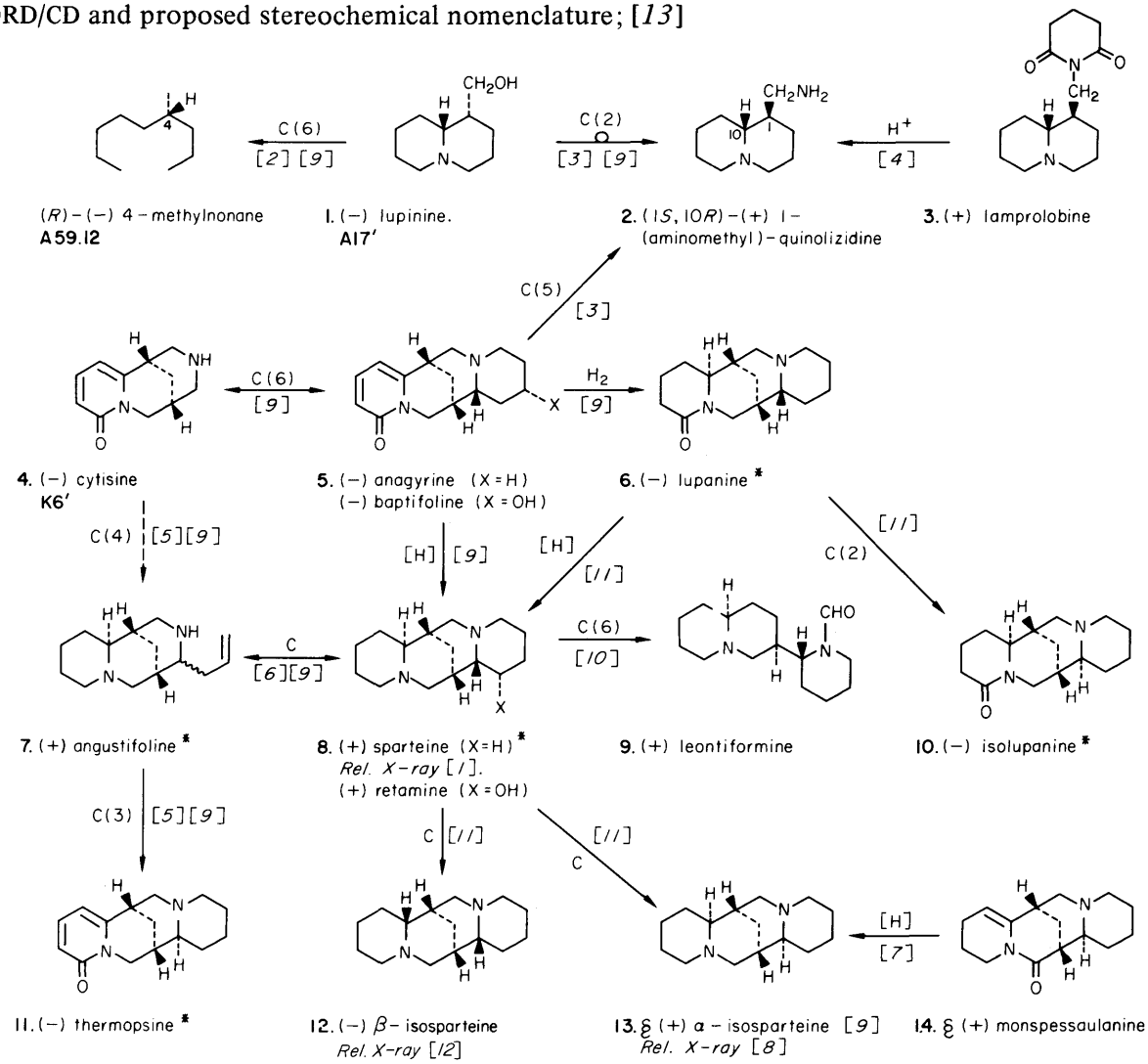
For a tabulation of others not shown here, see [9]
ORD/CD and proposed stereochemical nomenclature; [13]



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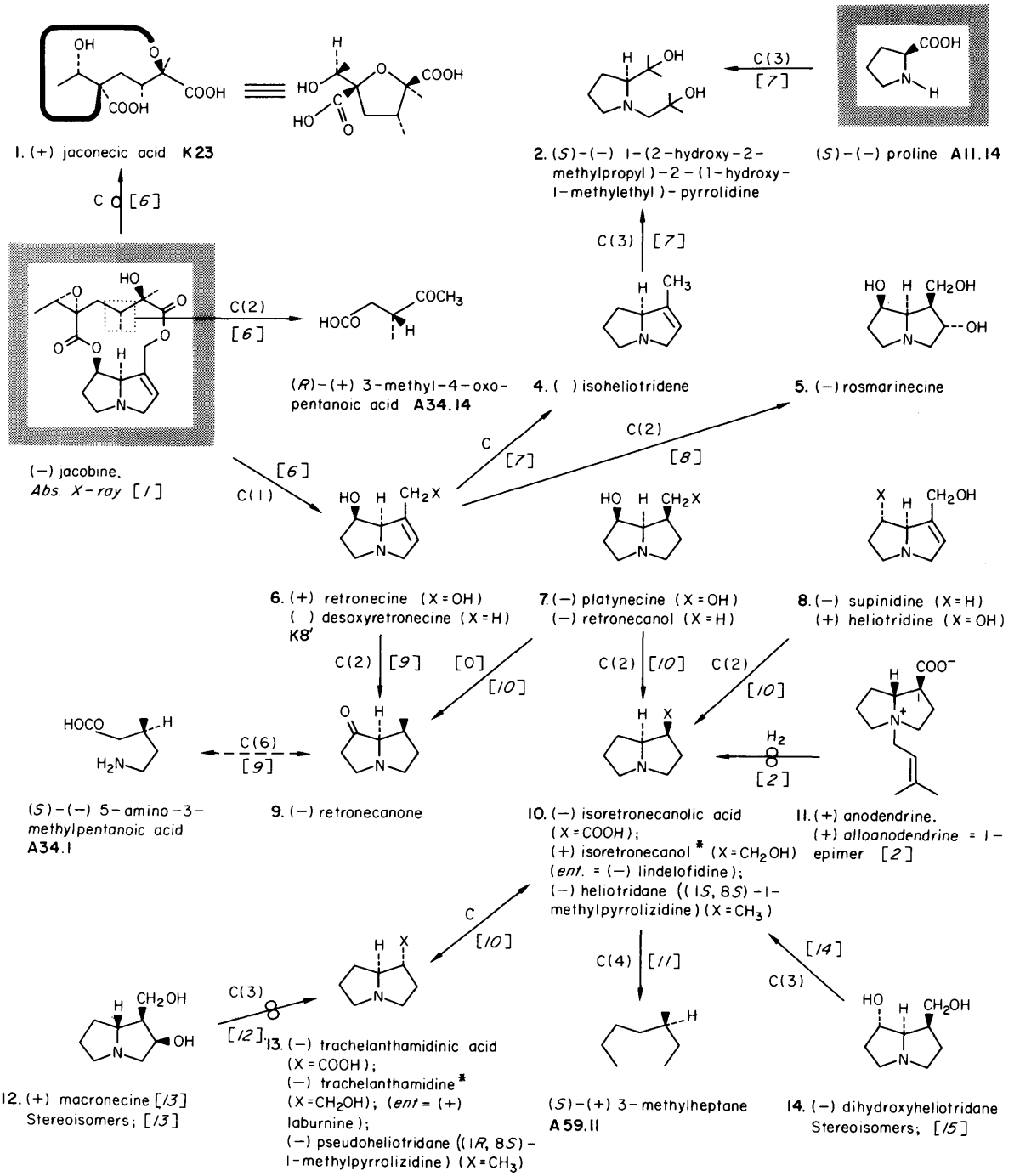
Pyrrolizidine alkaloids

These are usually mono- or diesters of a pyrrolizidine component (the necine) with a variety of carboxylic acids (the necic acids), some of which are achiral. The chiral necic acids appear on pp. K23-K24.

Reviews of necine stereochemistry; [3][4]. ORD/CD and tabulations of pyrrolizidine alkaloids; [5]



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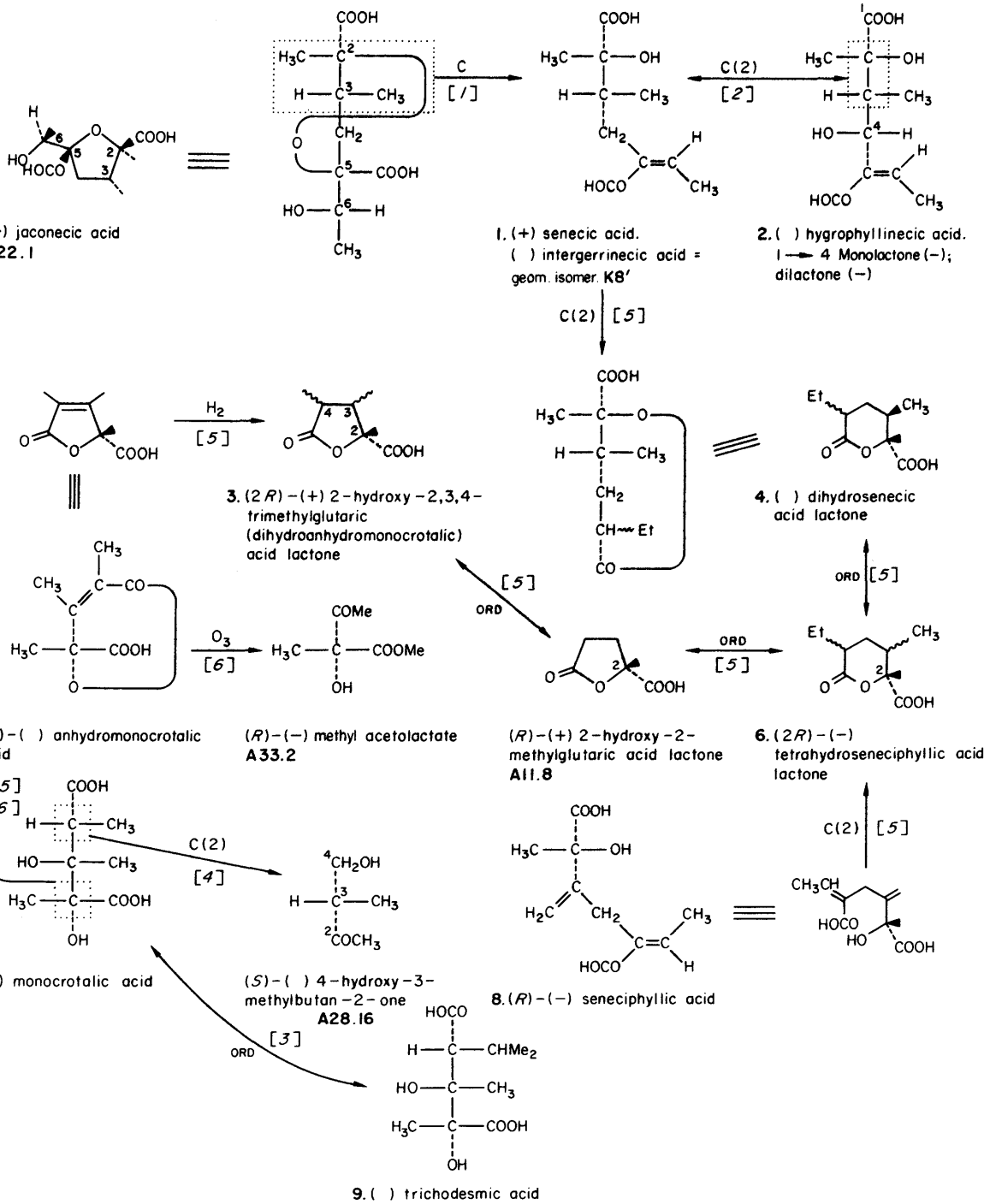
For others not given here, see [3]



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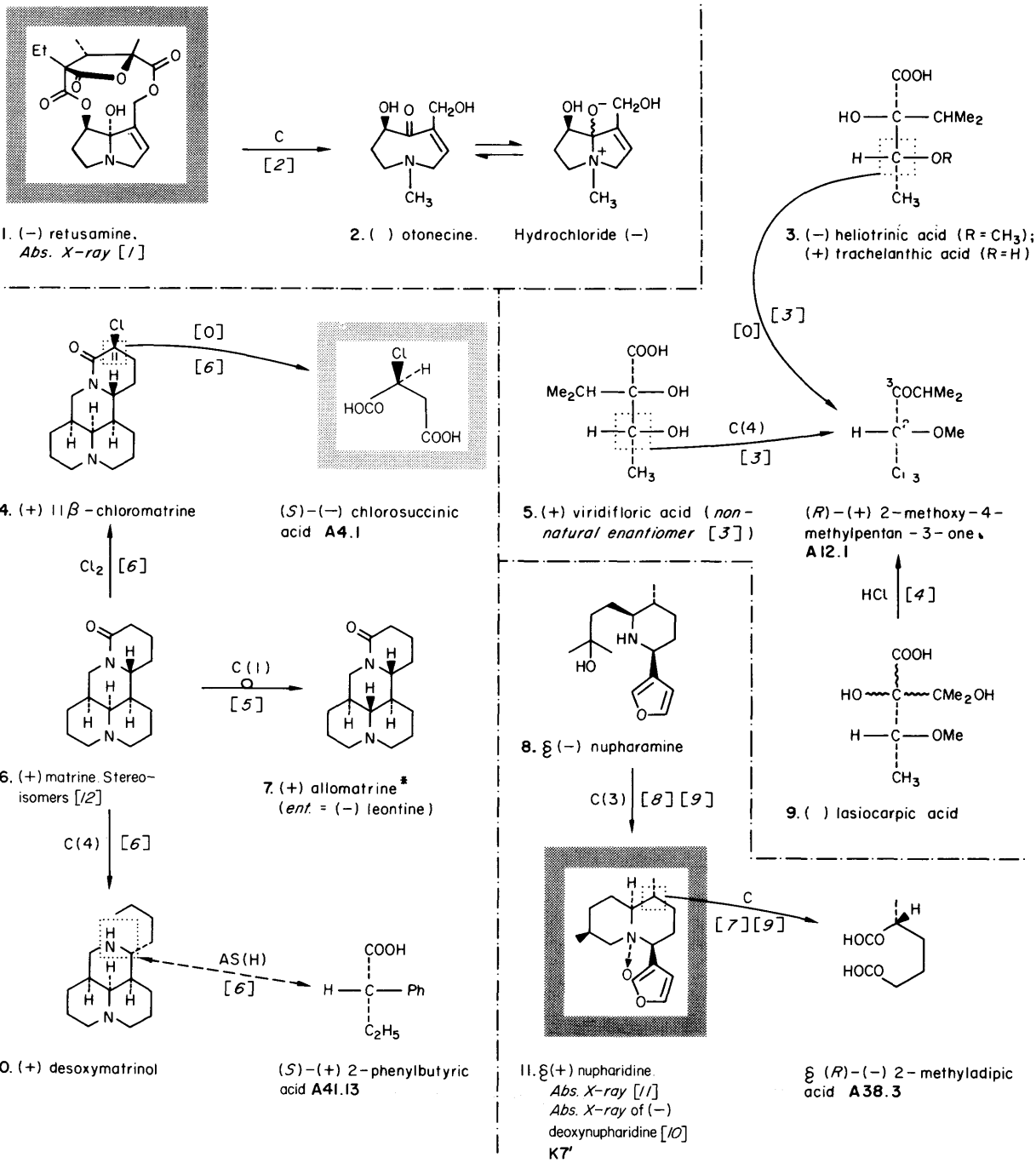

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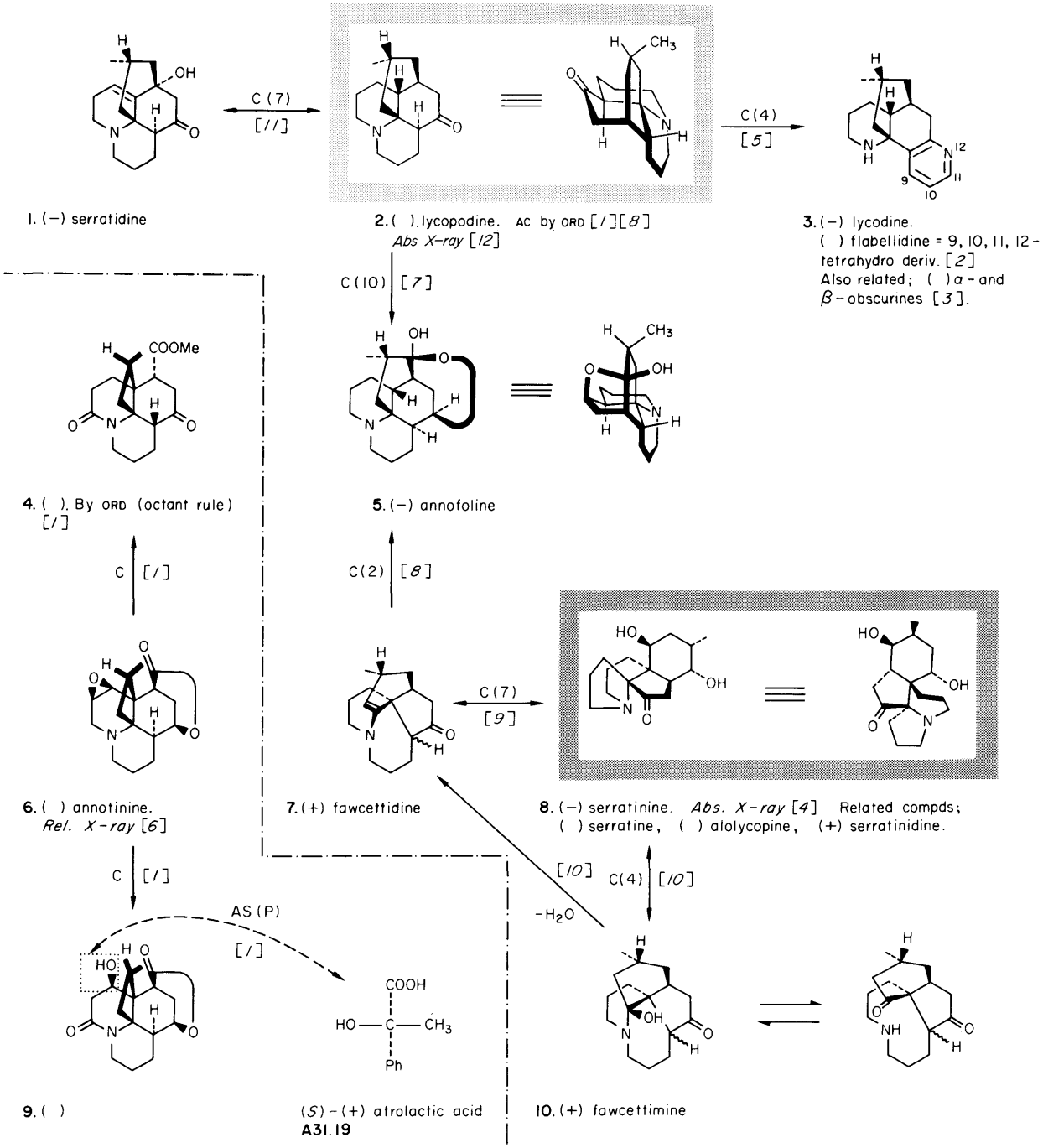

1. (−) serratidine

2. ( ) lycopodine. AC by ORD [1][8] *Abs. X-ray* [12]

3. (−) lycodine. ( ) flabellidine = 9, 10, 11, 12-tetrahydro deriv. [2] Also related; ( ) α- and β-obscurines [3].

4. ( ). By ORD (octant rule) [1]

5. (−) annofoline

6. ( ) annotinine. *Rel. X-ray* [6]

7. (+) fawcettidine

8. (−) serratinine. *Abs. X-ray* [4] Related compds; ( ) serratine, ( ) alolycopine, (+) serratinidine.

9. ( )

(*S*)-(+) atrolactic acid
A31.19

10. (+) fawcettimine

1. K. Wiesner, J. E. Francis, J. A. Findlay, and Z. Valenta, *Tetrahedron Letters*, 1961, 187.
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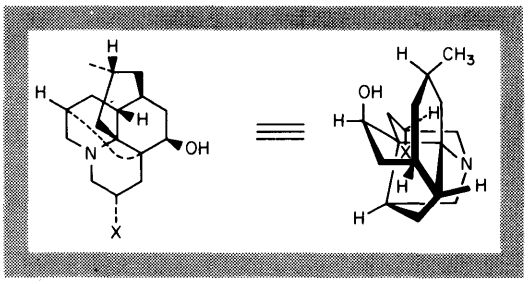
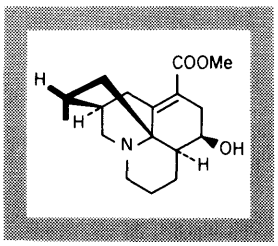
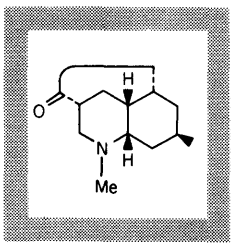


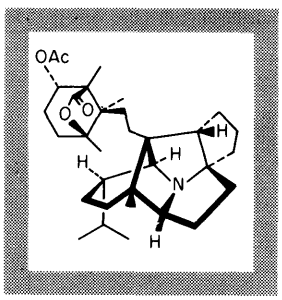
1. (−) alopecurine (X = OCOPh). *Abs. X-ray [1]*
( ) lycopecurine (X = H). *Abs. X-ray [2]*



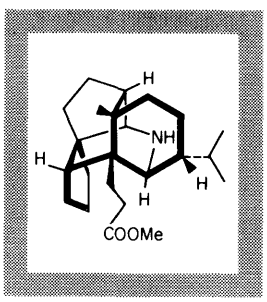
2. ( ) annopodine.
Abs. X-ray [3]



3. (+) luciduline.
Abs. X-ray [4]

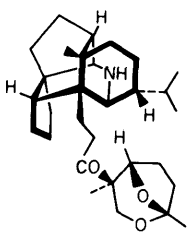


4. (+) daphmacrine.
Abs. X-ray [5]



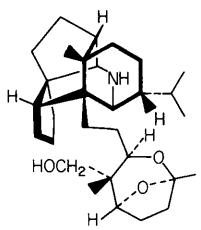
5. ( ) methyl homosecodaphniphyllate.
Abs. X-ray [6]

C(3) [6]



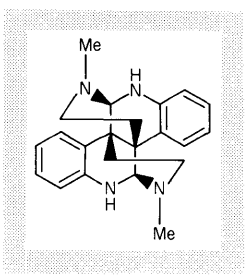
6. ( ) secodaphniphylline

C(5) [13]



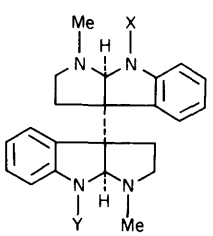
10. ( ) daphniteijsmanine

Most of the other known daphniphyllum alkaloids do not yet appear to have been rigorously correlated with daphmacrine or methyl homosecodaphniphyllate [7].

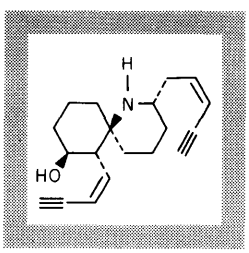


7. (+) calycanthine.
Abs. X-ray [8]
AC by CD (coupled oscillator method) [9]

C(1) [11]



8. (−) chimonanthine (X = Y = H). *Rel. X-ray [10]*
(−) folicanthine (X = Y = Me)
(−) calycanthidine (X = Me, Y = H)



9. ( ) histrionicotoxin.
Abs. X-ray [12]
Related alkaloids [14]

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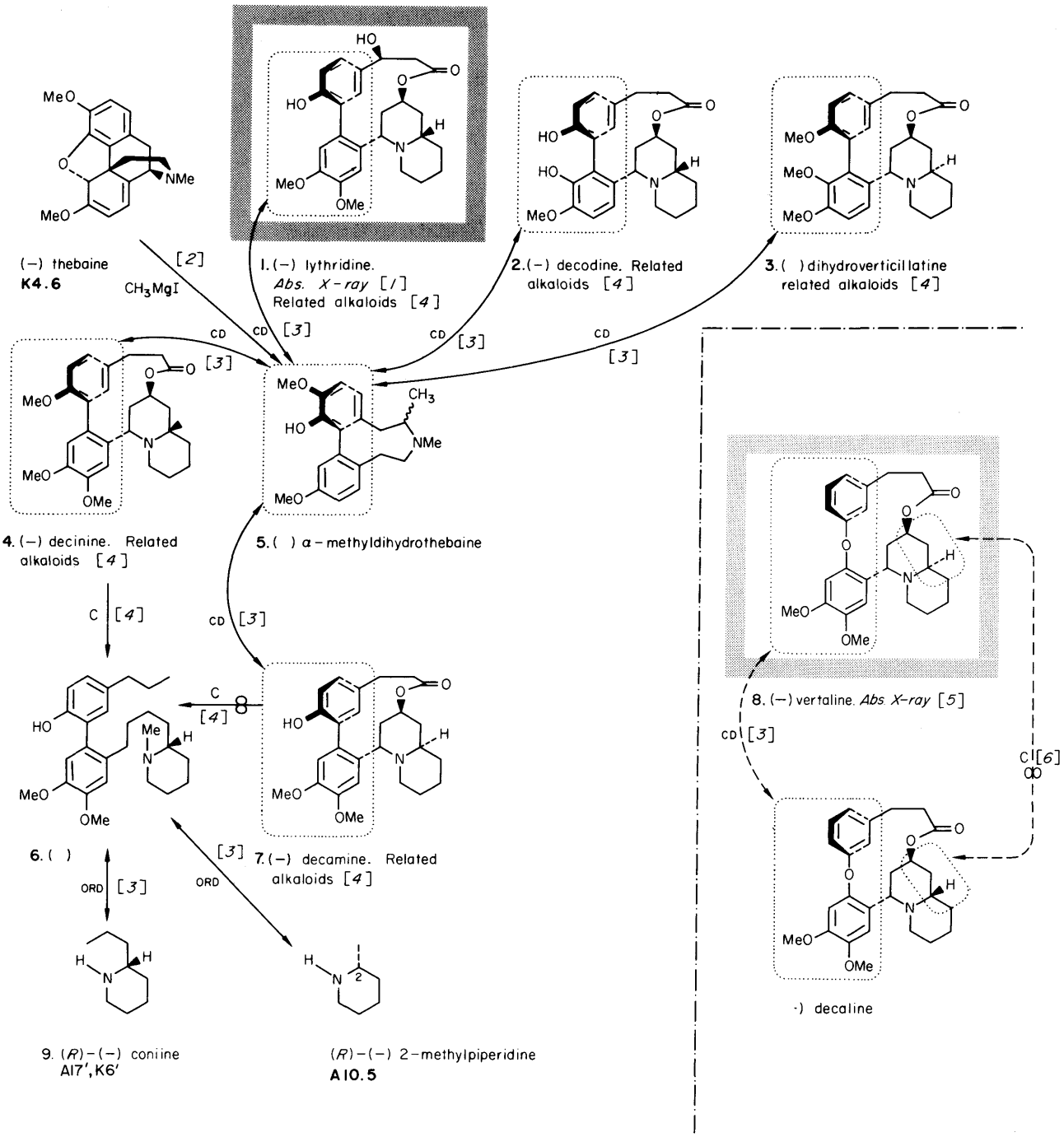

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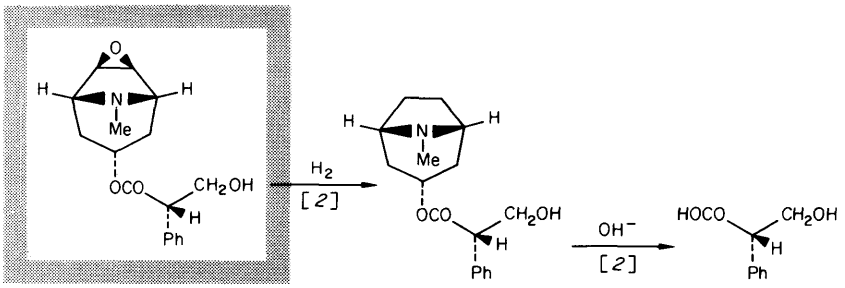
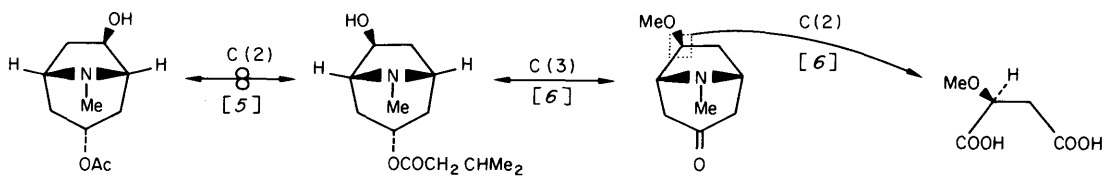
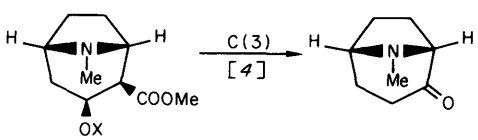


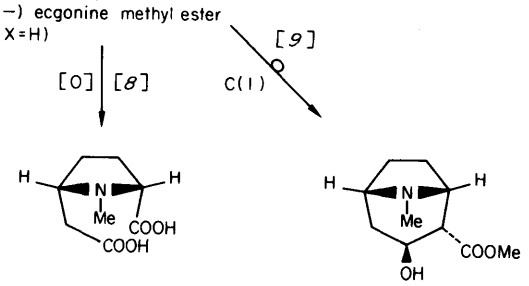
1. (−) hyoscine (scopolamine) *Abs. X-ray* [1]
2. (−) hyoscyamine
(*S*)-(−) tropic acid **A41.10**



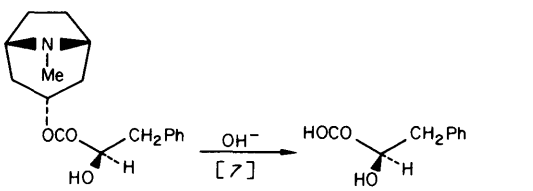
3. (3*R*, 6*R*)-(+) 3-acetoxy-6-hydroxytropane
4. (−) valeroidine *
5. (+) 6-methoxytropinone
(*S*)-(−) methoxysuccinic acid **A2.12**



6. (−) cocaine (X = COPh) *Rel. X-ray* [3]
(−) ecgonine methyl ester (X = H)
7. (+) 2-tropinone



(+) tropinic acid **A9.16**
9. (+) pseudoecgonine methyl ester



8. (−) littorine
(*R*)-(+) 2-hydroxy-3-phenylpropionic acid **A3.5**

1. C. S. Huber, G. Fodor, and N. Mandava, *Canad. J. Chem.*, 1971, **49**, 3258.
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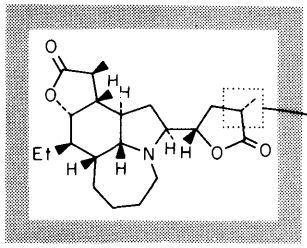
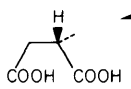


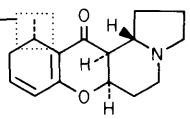
1. (−) tuberostemonine. *Abs. X-ray* [1]

[O] [4]



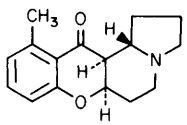
(*S*)-(−) methylsuccinic acid A27.21

[O] [3]



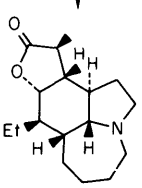
2. (−) isoelaecarpiline stereoisomers; [3]

C(1) [3]

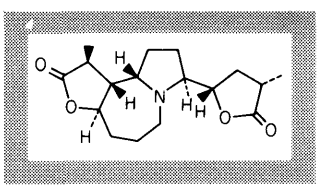


3. (−)isoelaeocarpine (+)elaeocarpine=bis-epimer [3]

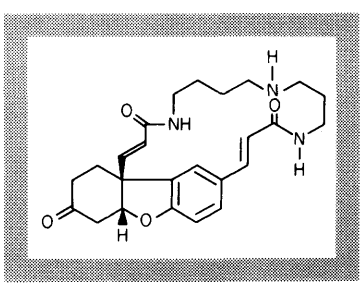
C [1]



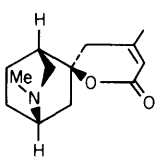
4. (−) stenine



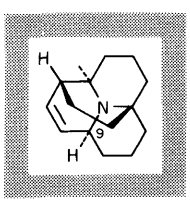
5. (+) stemonine. *Abs. X-ray* [2] Related compd; ( )protostemonine [13]



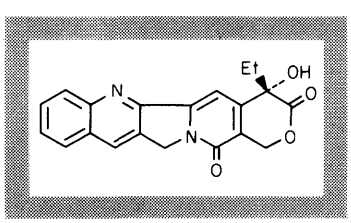
8. (+) lunarine. *Abs. X-rays* [8][9] Related compds; (+) alkaloid LBX, lunarinols [12]; (+) lunaridine [14]



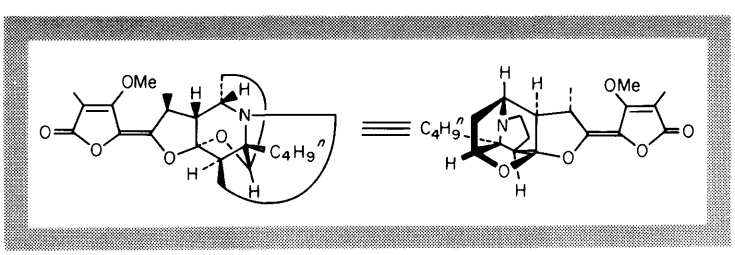
6. (−) dioscorine. By cd (lactone chromophore) [5]



7. §(+) porantherine.† *Abs. X-ray* [11]



9. (*S*)-(+) camptothecin. *Abs. X-rays* [6][7]



10. (+) stemofoline. *Abs. X-ray* [10]

†Various papers are contradictory on the configuration of porantherine at Cg. The (*S*) configuration given here is based on a careful reading of the X-ray drawings given in [11].

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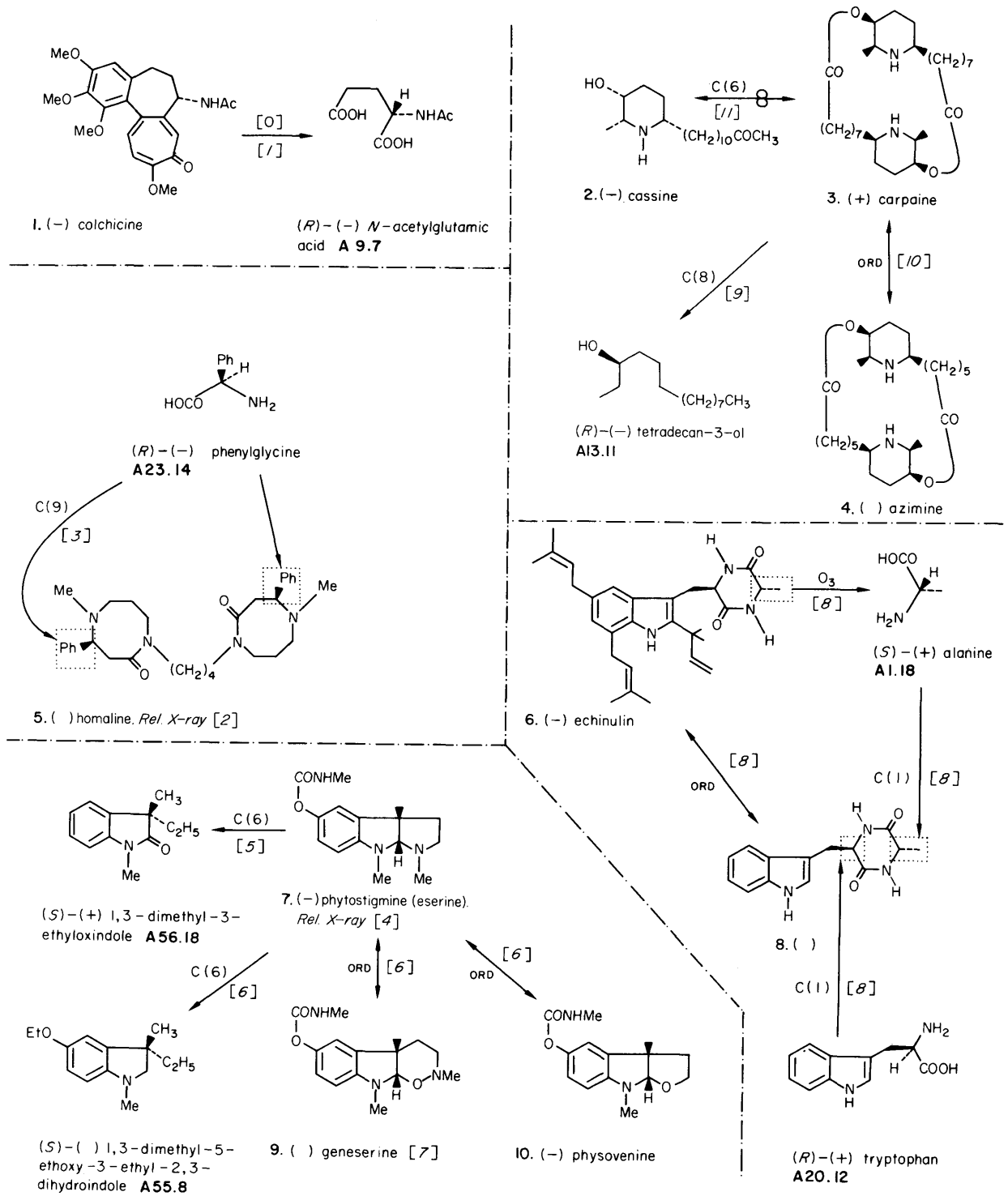
12. R. W. Doskotch, E. H. Fairchild and W. Kubelka, *Experientia*, 1972, **28**, 382.
13. H. Irie, K. Ohno, K. Osaki, T. Taga and S. Uyeo, *Chem. Pharm. Bull. Japan*, 1973, **21**, 451.
14. C. Poupat, H-P. Husson, B. C. Das, P. Bladon and P. Potier, *Tetrahdron*, 1972, **28**, 3103.



1. H. Corrodi and E. Hardegger, *Helv. Chim. Acta*, 1955, **38**, 2030.
2. O. Lefebre-Soubeyran, *Acta. Cryst.*, 1976, **B32**, 1305.
3. M. Païs, R. Sarfati, F. Jarreau, and R. Goutarel, *Comptes Rend. (C)*, 1971, **272**, 1728.
4. P. Pauling and T. J. Petcher, *J. Chem. Soc., Perkin II*, 1973, 1342.
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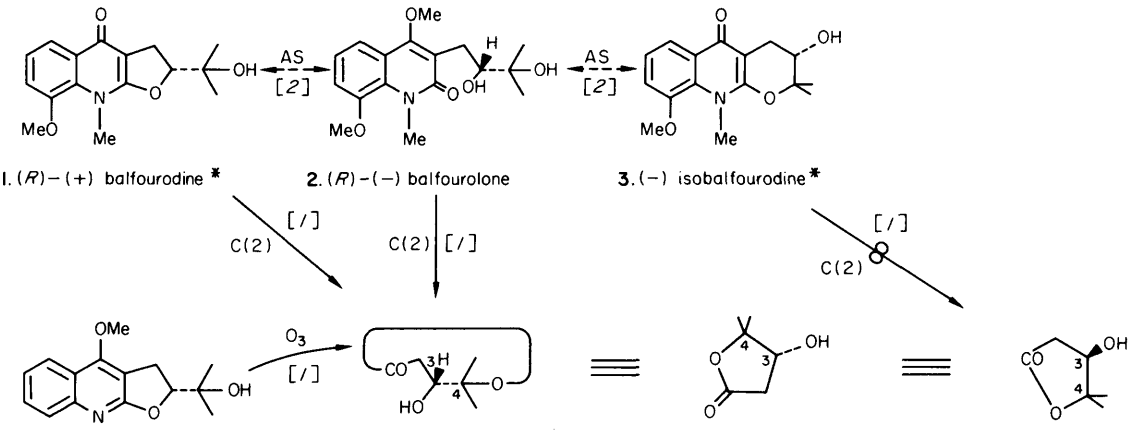
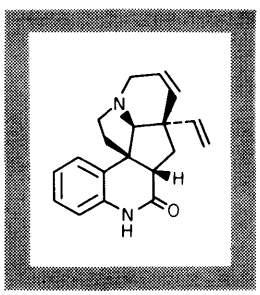
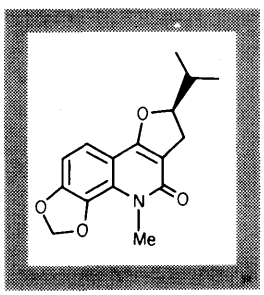


1. (*R*)-(+) balfourodine *
2. (*R*)-(−) balfourolone
3. (−) isobalfourodine *
4. (*R*)-(+) platydesmine

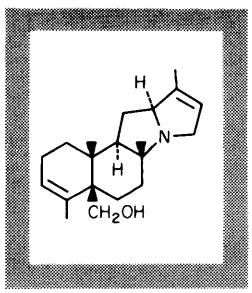
(*R*)-(+) 4, 4 − dimethyl − 3 − hydroxy − γ − butyrolactone **A8.5**



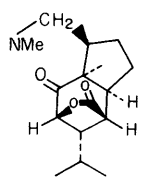
5. (+) meloscine.
Abs. X-ray [3]



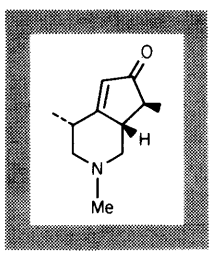
6. (*R*)-( ) isolunine
Abs. X-ray [4]



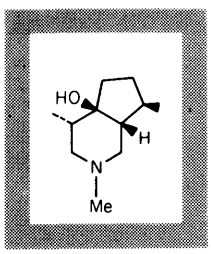
7. ( ) thelepogine.
Abs. X-ray [5]



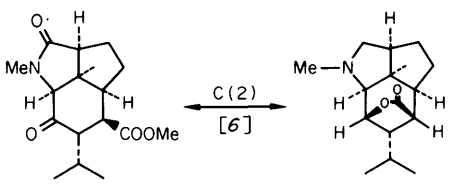
8. ( )nobilonine
K9'



9. (−) tecomanine.
Abs. X-ray [8]



10. ( ) "alkaloid C".
Abs. X-ray [8]



11. ( )
AC by CD (octant rule) [6]

12. (−) dendrobine (X = H)
(−) dendrine ($X = CH_2COOMe$)

For other alkaloids of this (the skytanthine) group, see p. T14

For corresponding compounds lacking nitrogen (sesquiterpenes of the picrotoxin − tutin group) see T31.7, T31.8, T31.9, T31.11

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2. R. M. Bowman, J. F. Collins, and M. F. Grundon, *Chem. Comm.*, 1967, 1131.
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4. M. F. Mackay and A. McL. Mathieson, *Acta Cryst.*, 1969, **B25**, 1925.
5. J. Fridrichsons and A. McL. Mathieson, *Acta Cryst.*, 1963, **16**, 206.
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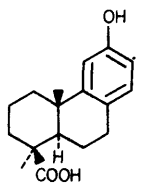
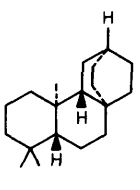
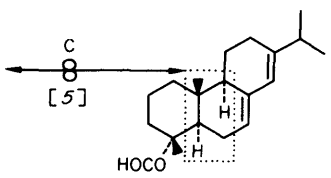


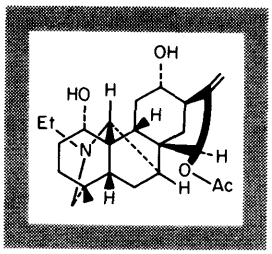
(+) podocarpic acid
T33.9



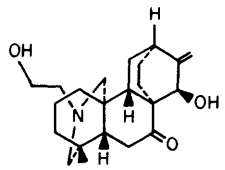
1.(−)



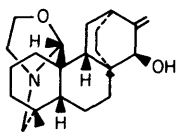
(−) abietic acid
T32.11

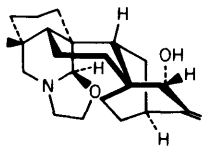


2. (−) lucidusculine.
Abs. X-ray [1]
Related alkaloids;
(−) songorine, (−) luciculine [1]

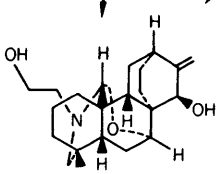


3. (−) atidine

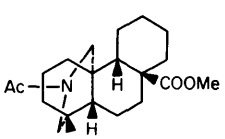




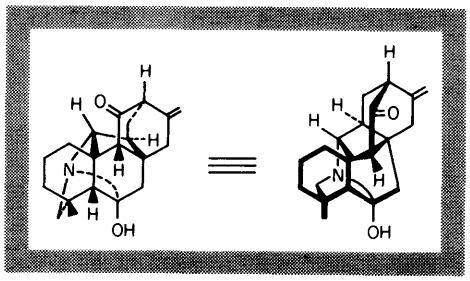
4. ( ) atisine. (+) hydrochloride



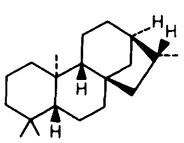
5. (−) ajaconine



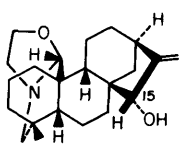
6.(−)



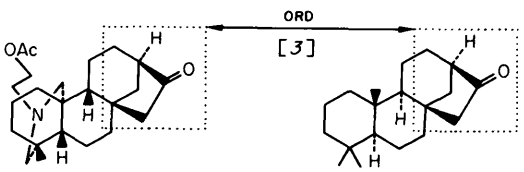
7.( ) spiradine A. *Abs. X-ray* [2]



(−) β-dihydrokaurene
T35.7



8. ( ) veatchine.
(−) garryfoline = 15-epimer.
[3]



9. ( )

(−) phyllocladene norketone
T36.6

1. A. Yoshino and Y. Iitaka, *Acta Cryst.*, 1966, **21**, 57.
2. G. Goto, K. Sasaki, and N. Sakabe, *Tetrahedron Letters*, 1968, 1369.
3. H. Vorbrueggen and C. Djerassi, *J. Amer. Chem. Soc.*, 1962, **84**, 2990.
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5. W. A. Ayer, C. E. McDonald, and G. G. Iverach, *Tetrahedron Letters*, 1963, 1095.
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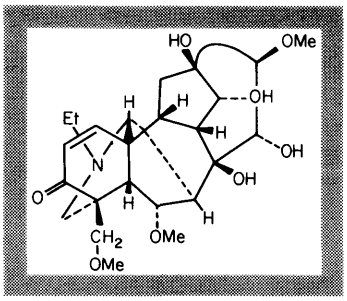
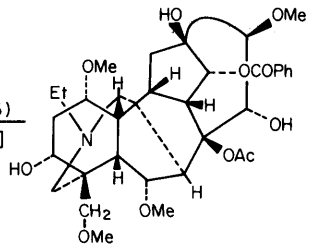
8. D. Dvornik and O. E. Edwards, *Chem. and Ind.*, 1957, 952.

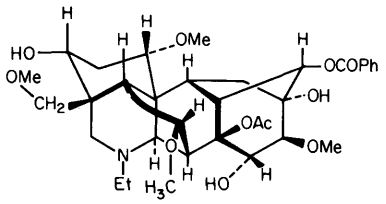


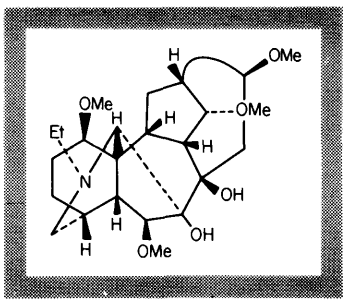
1. (+) demethanolaconinone *Abs. X-ray* [1][3]

C(3) [1]



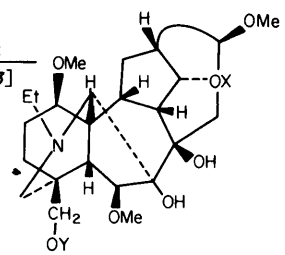
2. (+) aconitine [2]



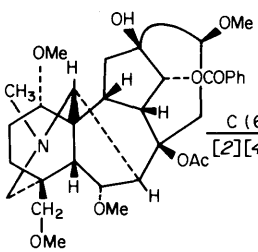


3. ( ) des(oxymethylene)-lycoctonine. *Abs. X-ray* [3]

C [3]



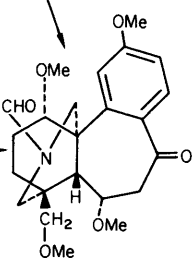
4. (+) lycoctonine (X=CH_3, Y=H) (+) browniine (X=H, Y=CH_3)



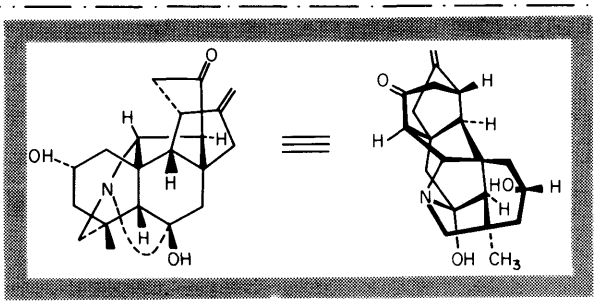
5. (+) delphinine *Rel. X-ray* [2]

C [2][4]

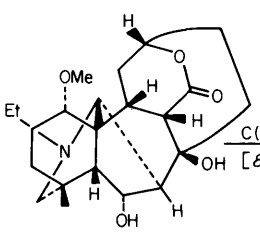
C (6) [2][4]



6. ( )

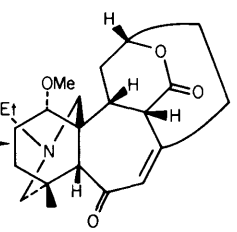


7. ( ) delnudine *Abs. X-ray* [5]

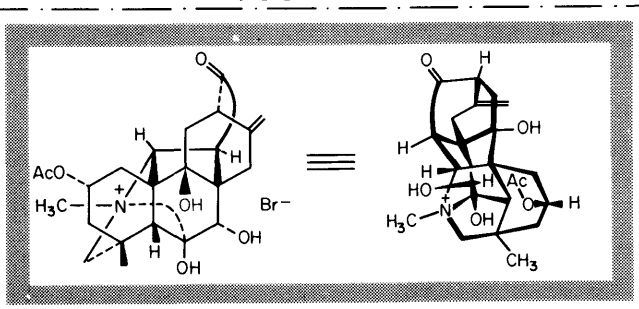


8. (+) heteratisine. *Rel X-ray* [9]

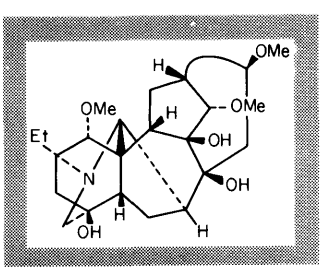
C(2) [8]



9. ( ) pyroheteratisine. By ORD (enone chromophore) [8]



10. ( ) miyaconitine hydrobromide *Abs. X-ray* [6]



11. (+) lappaconine. *Abs. X-ray* [7]

1. M. Przybylska, *Acta Cryst.*, 1961, **14**, 429.
2. K. B. Birnbaum, K. Weisner, E. W. K. Jay, and L. Jay, *Tetrahedron Letters*, 1971, 867.
3. M. Przybylska and L. Marion, *Canad. J. Chem.*, 1959, **37**, 1843.
4. K. Weisner, D. L. Simmons & L. R. Fowler, *Tetrahedron Letters*, 1959, no. 18, 1.
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6. H. Shimanouchi, Y. Sasada, and T. Takeda, *Tetrahedron Letters*, 1970, 2327.
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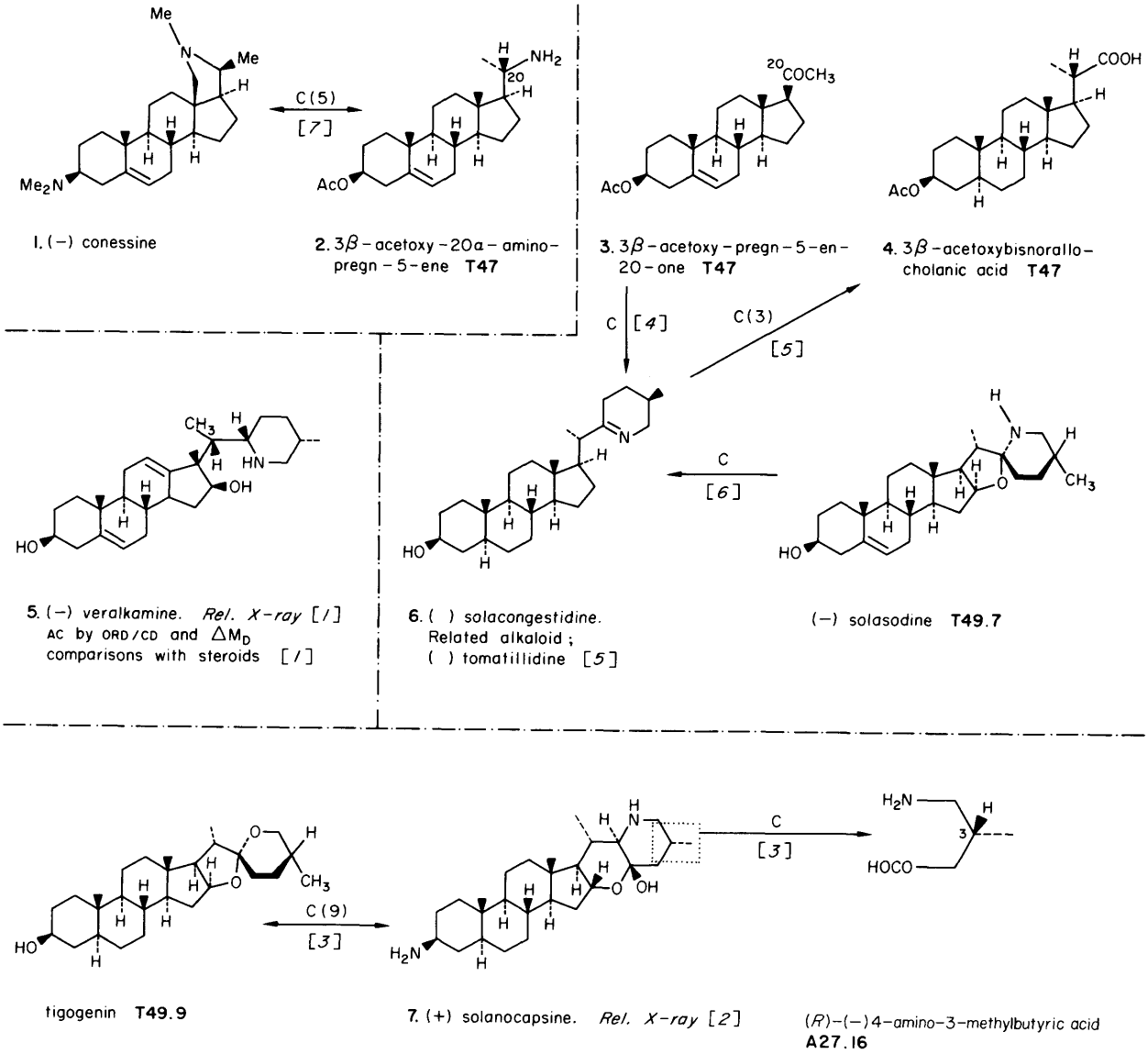
8. R. Aneja and S. W. Pelletier, *Tetrahedron Letters*, 1965, 215.
9. M. Przybylska, *Canad. J. Chem.*, 1963, **41**, 2911.

Steroidal alkaloids

See also **T49.4, T49.7, T49.8.**

A number of alkaloids are known which are best described as simple amino- or alkylamino steroids. Examples are funtumine (3α-amino-tα-pregnan-20-one) and paravallarine (3β-dimethylaminopregn-5-en-20-ol-18-oic acid 18→20 lactone). The structures of these have been proved by simple chemical conversion to or from nitrogen-free steroids. Only the more complex type of steroidal alkaloid is included here.



1. (−) conessine
2. 3β-acetoxy-20α-amino-pregn-5-ene **T47**
3. 3β-acetoxy-pregn-5-en-20-one **T47**
4. 3β-acetoxybisnorallocholanic acid **T47**
5. (−) veralkamine. *Rel. X-ray* [1] AC by ORD/CD and ΔM_D comparisons with steroids [1]
6. ( ) solacongestidine. Related alkaloid; ( ) tomatillidine [5]
7. (+) solanocapsine. *Rel. X-ray* [2]

(−) solasodine **T49.7**

tigogenin **T49.9**

(*R*)-(−)4-amino-3-methylbutyric acid **A27.16**

1. J. Tomko, A. Vassova, G. Adam, K. Schreiber, and E. Höhne, *Tetrahedron Letters*, 1967, 3907.
2. E. Höhne, H. Ripperger and K. Schreiber, *Tetrahedron*, 1970, **26**, 3569.
3. K. Schreiber and H. Ripperger, *Annalen*, 1962, **655**, 114.
4. K. Schreiber and G. Adam, *Tetrahedron*, 1964, **20**, 1707.
5. E. Bianchi, C. Djerassi, H. Budzikiewitz, and Y. Sato, *J. Org. Chem.*, 1965, **30**, 754.
6. G. Kusano, N. Aimi, and Y. Sato, *J. Org. Chem.*, 1970, **35**, 2624.
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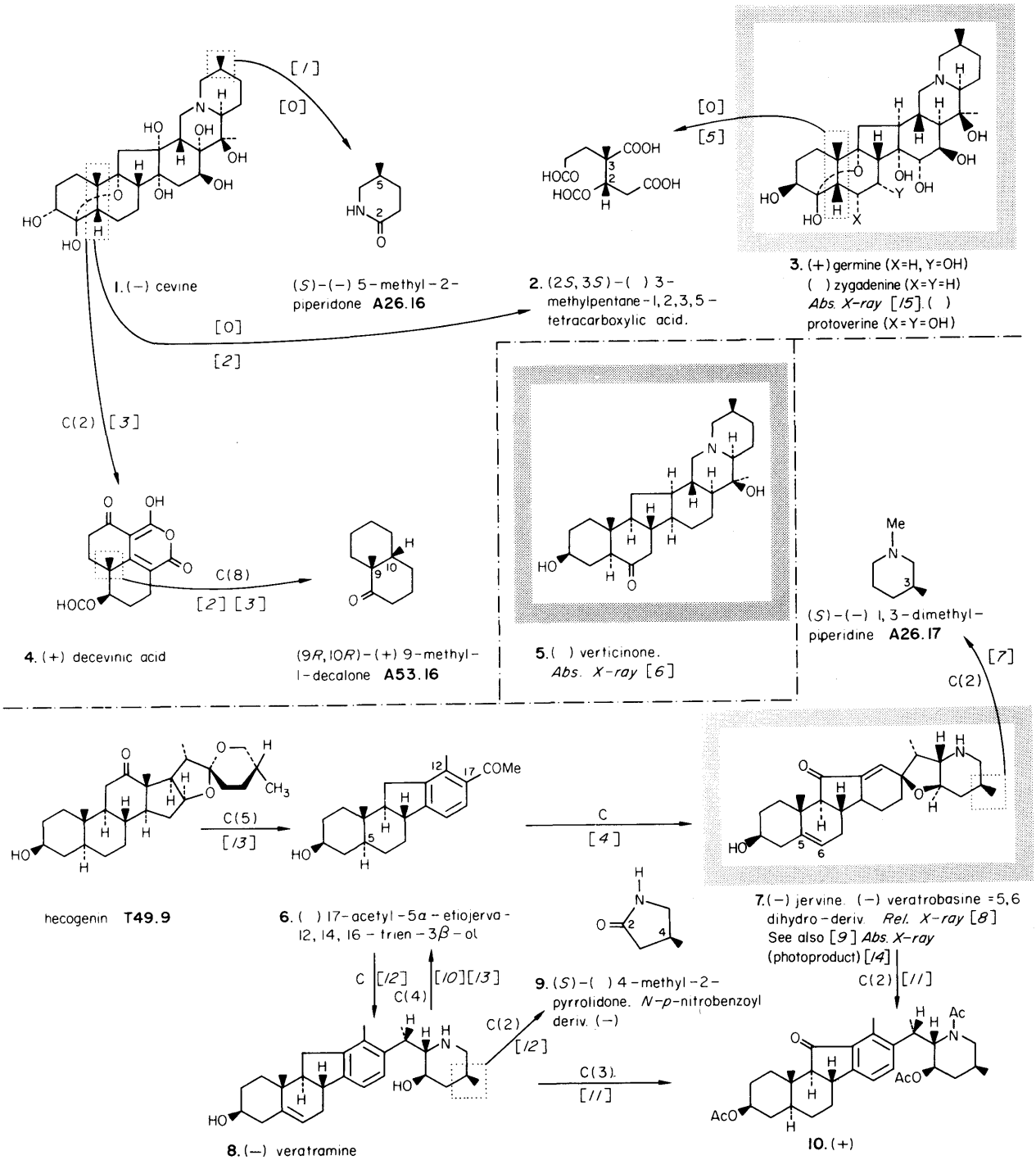
Steroidal alkaloids (contd.); Cevine and jervine groups.



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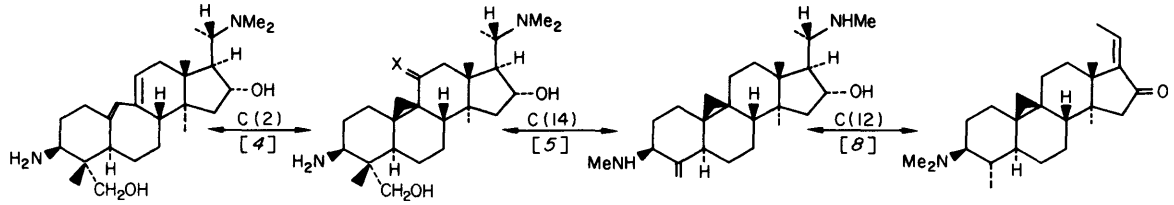
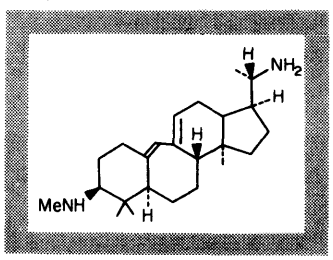
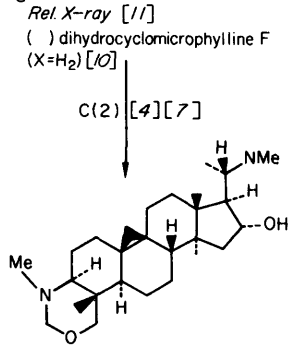


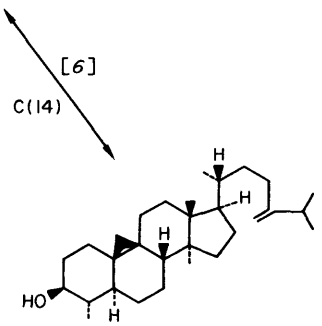
1. §( ) buxidienine F [10]
2. §( ) cyclobuxidine F (X=O) *Rel. X-ray* [11]
   ( ) dihydrocyclomicrophylline F (X=H_2) [10]
3. ( ) cyclobuxine D
4. (−) cyclobuxosuffrine



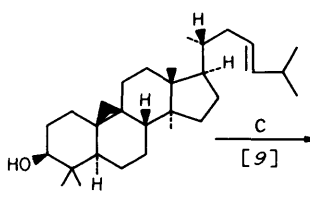
5. ( ) buxenine G. *Abs. X-ray* [1]



6. §(+) cyclobuxoxazine A [10]

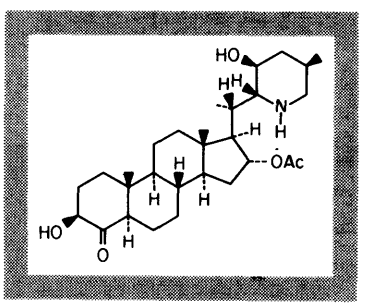


(+) cycloeucalenol **T50.1**

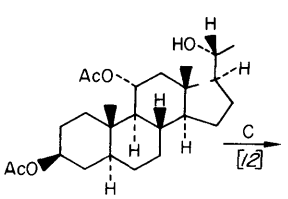


(+) cycloartenol **T50.2**

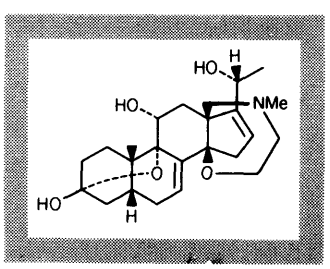
7. ( ) cycloprotobuxine C



8. (−) solaphyllidine. *Abs. X-ray* [2]



9. 3β,11α-diacetoxy-20-hydroxy-5α-pregnane **T47**



10. ( ) batrachotoxinin A *Abs. X-ray* [3]

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- Y -

Miscellaneous Natural Products

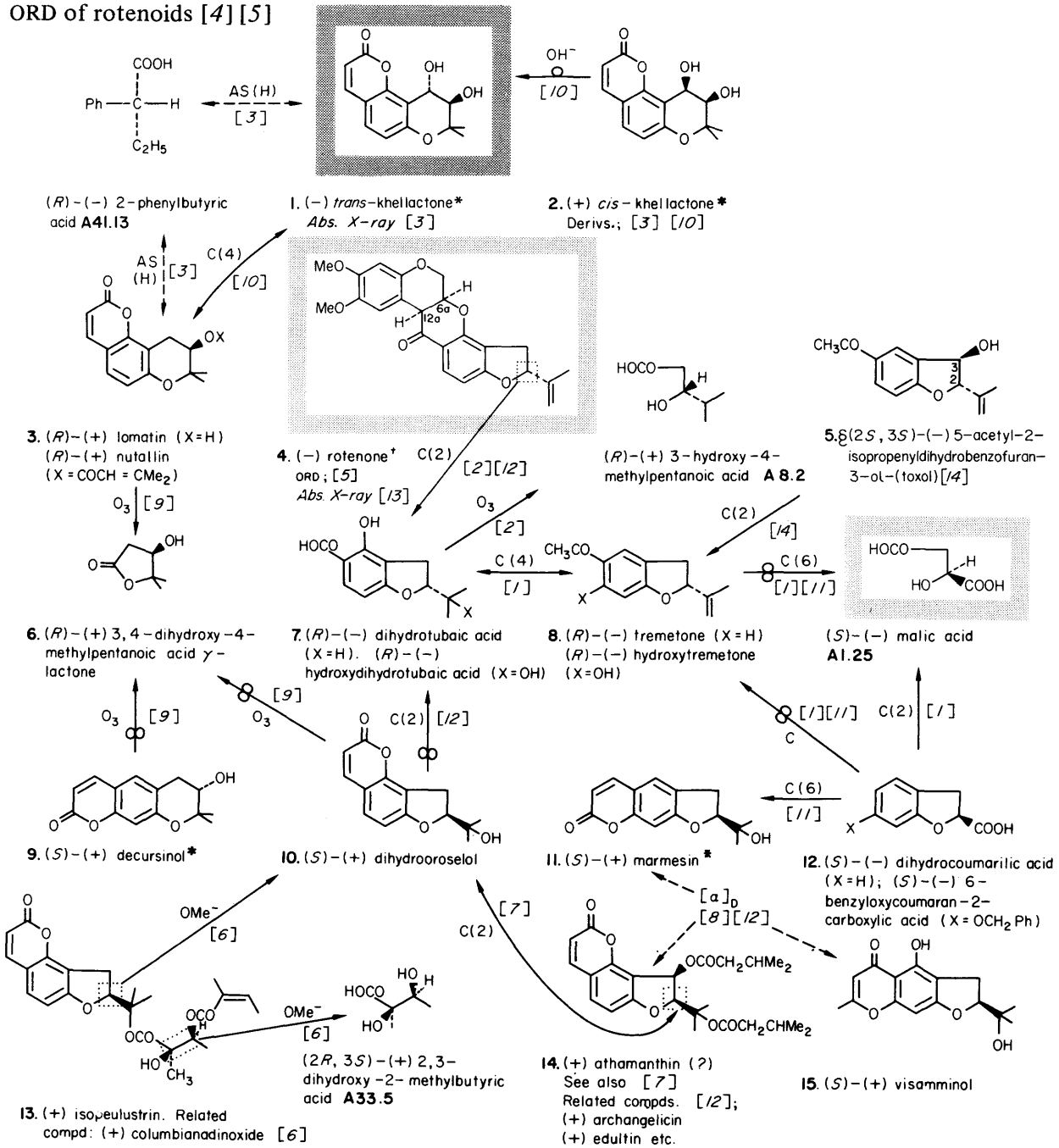
Introductory Notes to Chapter Y

Chapter Y contains natural products not covered by Chapters T or K. The material is divided into the following main categories:

1. *Compounds containing C,H,O and halogens only*
   (a) Open-chain† and O-heterocyclic compounds pp. **Y1-Y15.**
   (b) Carbocyclic compounds pp. **Y15-Y19.**
2. *Compounds containing N, S and P.* pp. **Y20-Y30**

†'Open-chain' here means that the *chiral centres* of the molecule are in an open-chain portion, and not necessarily that the molecule is completely acyclic.

ORD of rotenoids [4] [5]



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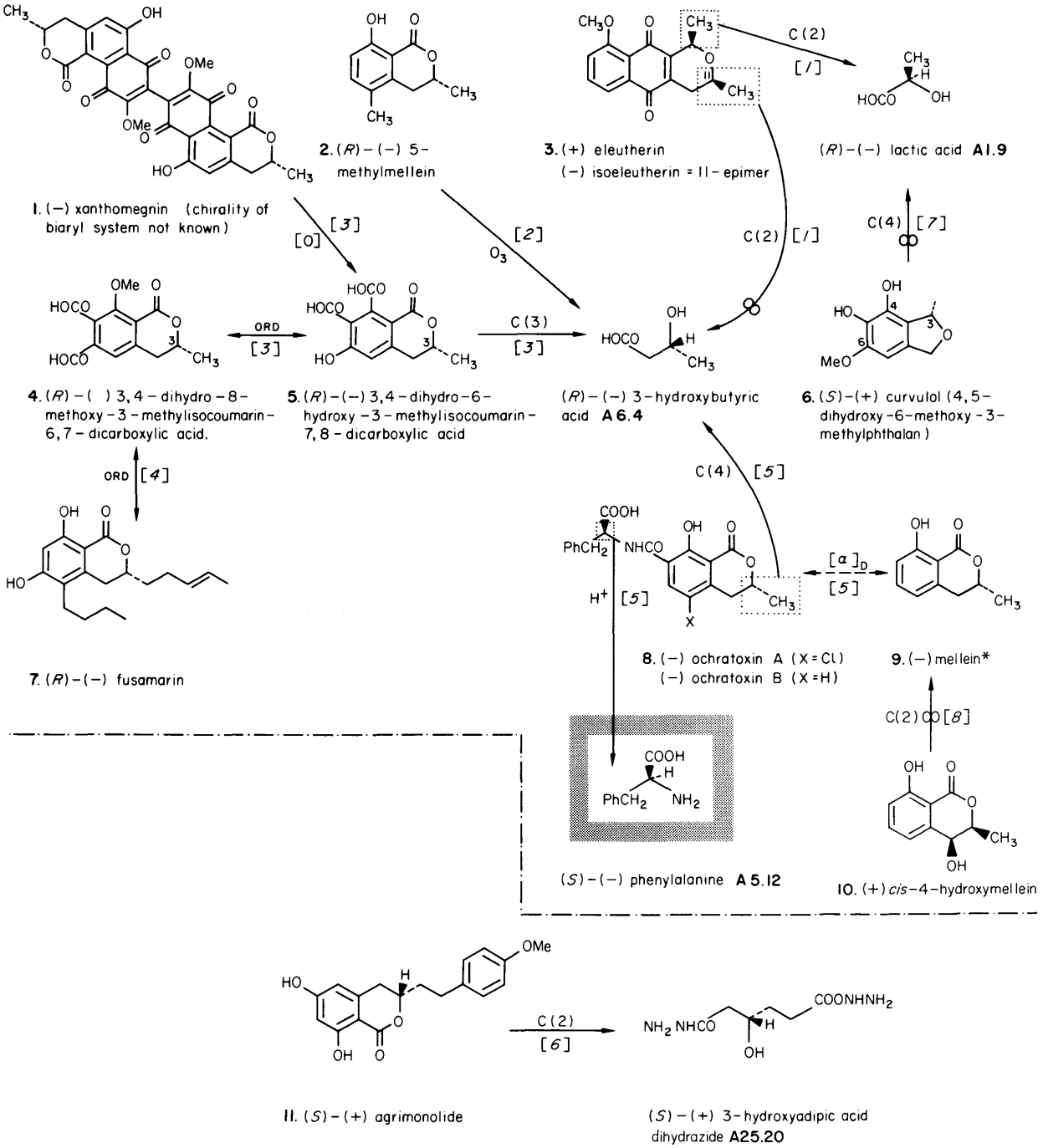
†Other natural rotenoids have been compared with (−) rotenone by ORD [4] [5]. All natural rotenoids examined appear to have the same configuration as rotenone at C6a and C12a. This configuration is characterised by +ve RD at long wavelengths and −ve RD at shorter wavelengths [5].



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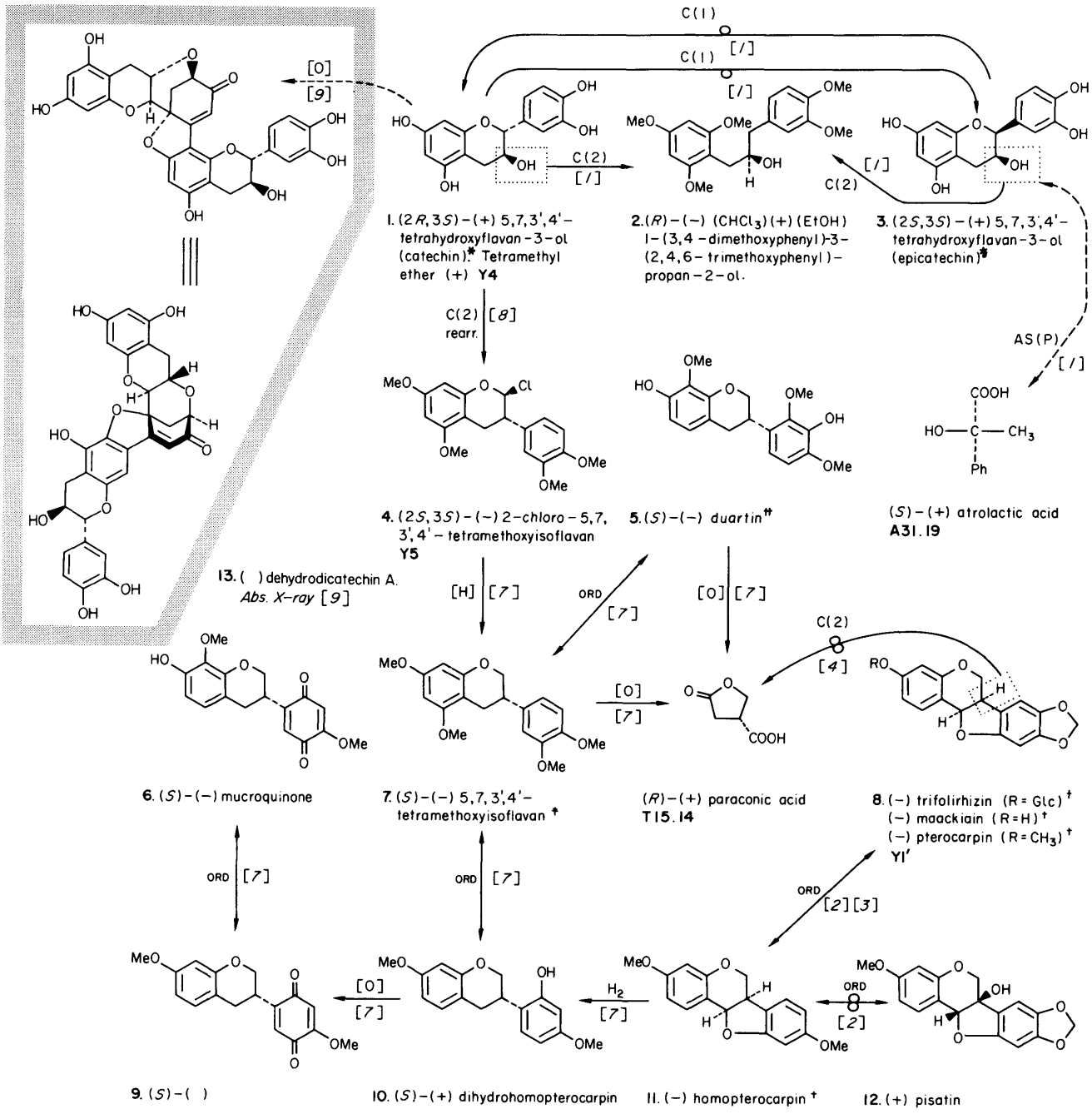

ORD/CD of flavonoids and their glycosides; [5]
A number of dimeric flavonoid types also occur in nature [6]

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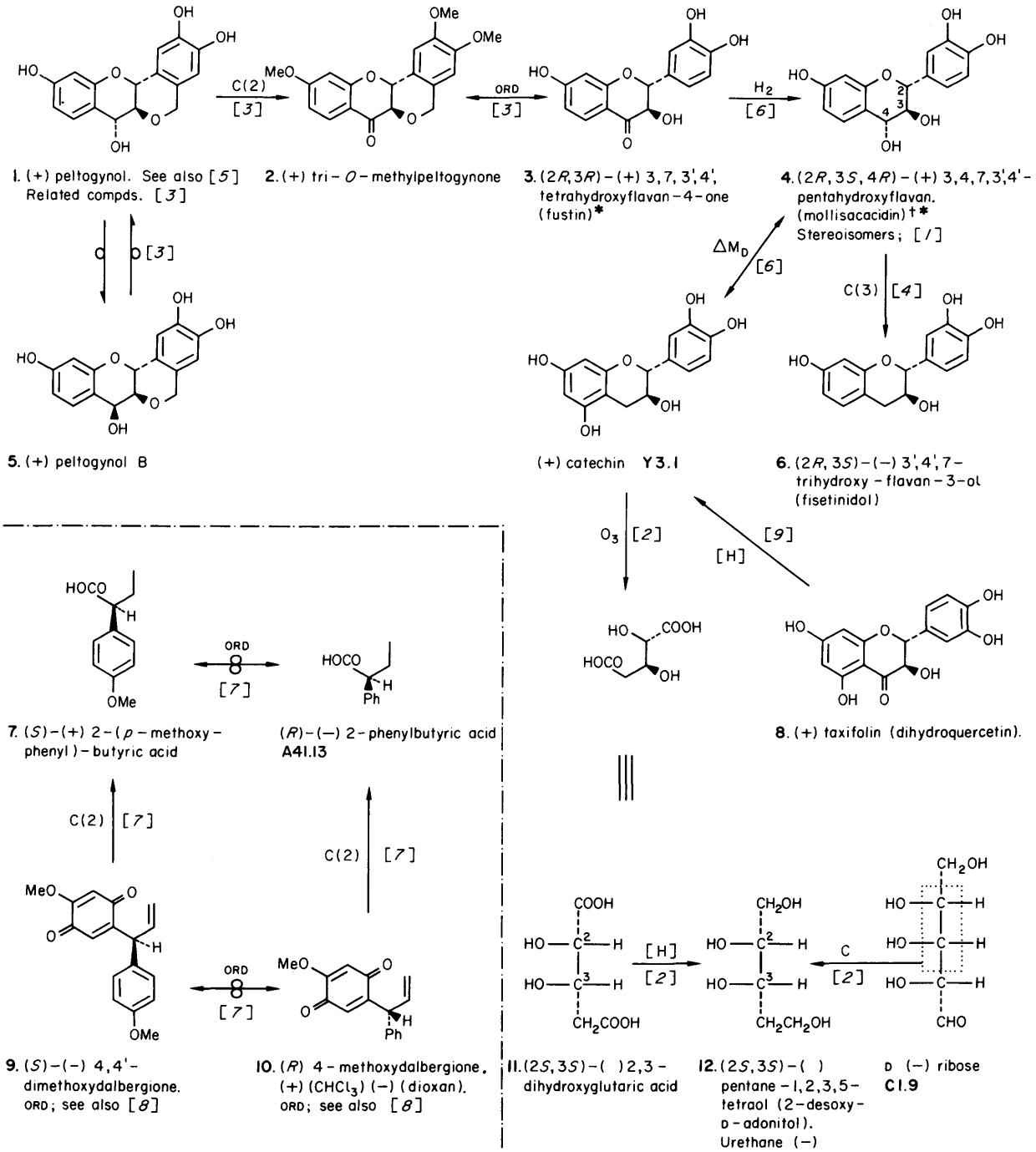
†Other pterocarpinoids have been compared with those shown by chiroptical methods [2] [3]. It has been suggested [4] that all laevorotatory pterocarpinoids have the (3*R*, 4*R*) configuration, and vice-versa.

††Other isoflavans have been compared with those shown by chiroptical methods. Care is necessary, however, in the interpretation of the spectra [7].



1. (+) peltogynol. See also [5] Related compds. [3]

2. (+) tri-O-methylpeltogynone

3. (2R,3R)-(+) 3,7,3',4', tetrahydroxyflavan-4-one (fustin)*

4. (2R,3S,4R)-(+) 3,4,7,3',4'-pentahydroxyflavan. (mollisacacidin)†* Stereoisomers; [1]

5. (+) peltogynol B

(+) catechin Y3.1

6. (2R,3S)-(−) 3',4',7-trihydroxy-flavan-3-ol (fisetinidol)

7. (S)-(+) 2-(p-methoxy-phenyl)-butyric acid

(R)-(−) 2-phenylbutyric acid A41.13

8. (+) taxifolin (dihydroquercetin).

9. (S)-(−) 4,4'-dimethoxydalbergione. ORD; see also [8]

10. (R) 4-methoxydalbergione. (+) ($CHCl_3$) (−) (dioxan). ORD; see also [8]

11. (2S,3S)-( )2,3-dihydroxyglutaric acid

12. (2S,3S)-( ) pentane-1,2,3,5-tetraol (2-desoxy-D-adonitol). Urethane (−)

D (−) ribose C1.9

1. S. E. Drewes and D. G. Roux, *Biochem. J.*, 1965, **96**, 68.
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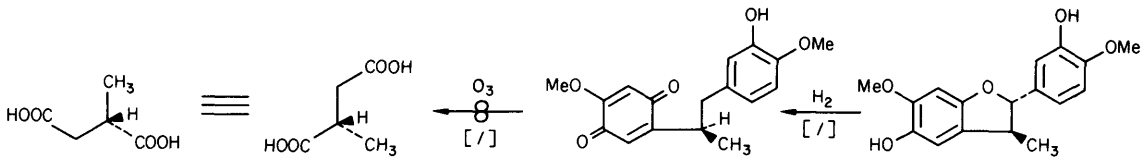
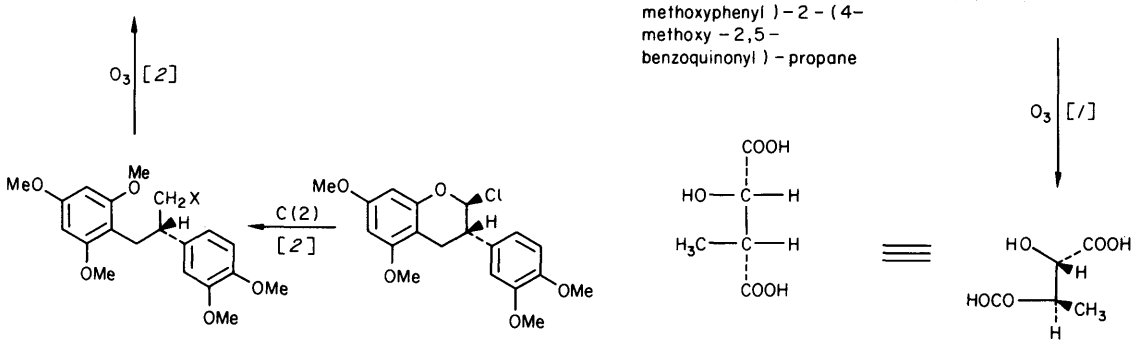
†A similar series of correlations has been carried out in the melacacidin (3',4',7,8-tetrahydroxyflavan-3,4-diol) series [4]. For a tabulation of other flavandiols, see [5]. For the ORD/CD of flavanones and 3-hydroxyflavones, see [6].



(*S*)-(−) methylsuccinic acid **A27.21**

1. (*R*)-(+) 1-(3-hydroxy-4-methoxyphenyl)-2-(4-methoxy-2,5-benzoquinonyl)-propane

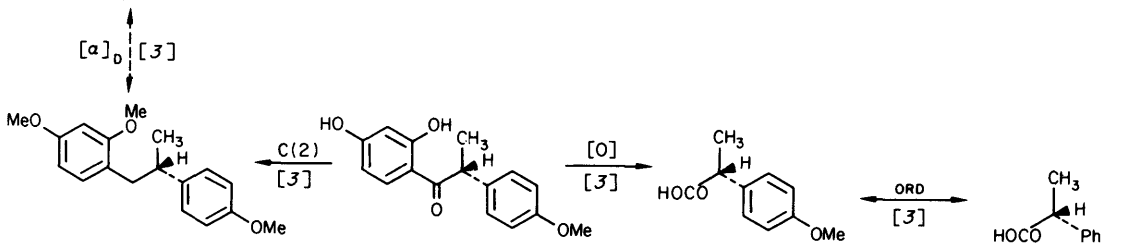
2. (−)melanoxin†



3. (*S*)-(+) 2-(3,4-dimethoxyphenyl)-1-(2,4,6-trimethoxyphenyl)-propane (X=H); (*S*)-(+) 2-(3,4-dimethoxyphenyl)-3-(2,4,6-trimethoxyphenyl)-propan-1-ol (X=OH)

(2*S*,3*S*)-(−) 2-chloro-5,7,3',4'-tetramethoxyisoflavan **Y3.3**

4. (2*S*,3*R*)-(−) 2-hydroxy-3-methylsuccinic (*β*-methylmalic) acid



5. (*S*)-(+) 1-(2,4-dimethoxyphenyl)-2-(*p*-methoxyphenyl)-propane

6. (*R*)-(−) angolensin

7. (*R*)-(−) 2-(*p*-methoxy-phenyl)-propionic acid

(*R*)-(−) 2-phenylpropionic acid **A41.12**

†enantiomeric compounds of the melanoxin type occur naturally, e.g. (+) obtusafuran [*4*].

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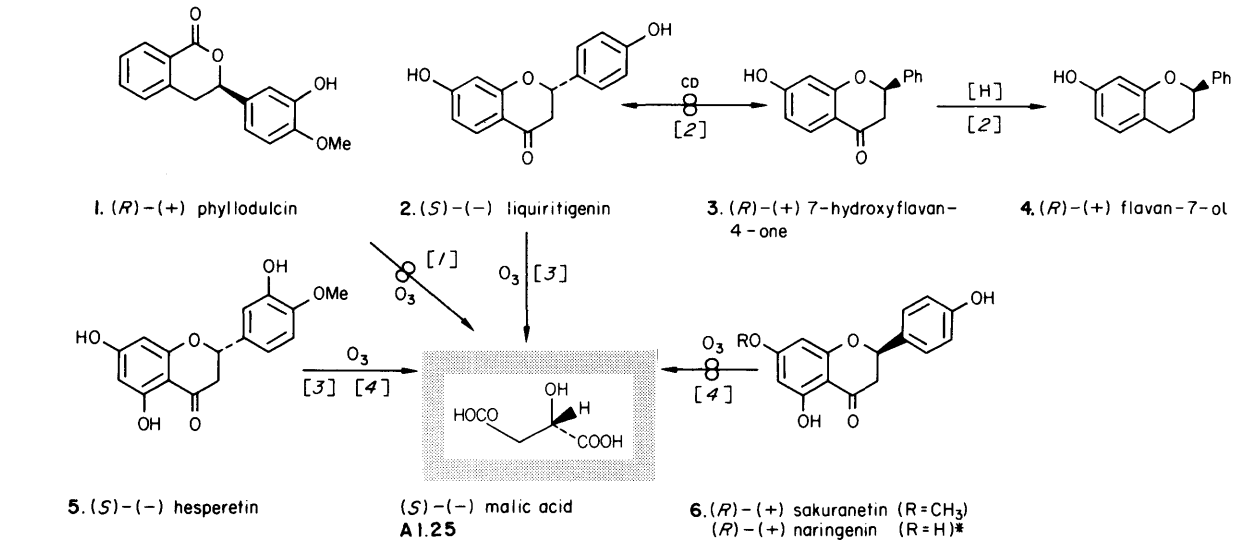
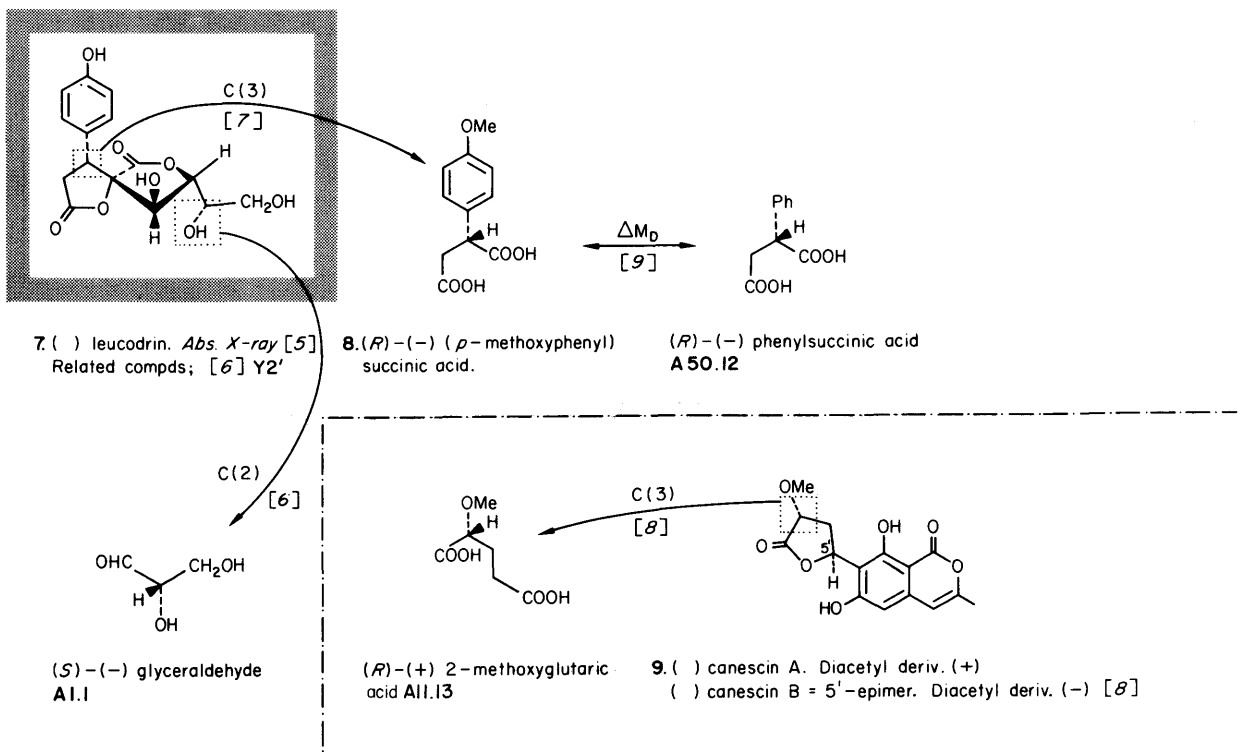


1. (*R*)-(+) phyllodulcin
2. (*S*)-(−) liquiritigenin
3. (*R*)-(+) 7-hydroxyflavan-4-one
4. (*R*)-(+) flavan-7-ol
5. (*S*)-(−) hesperetin
6. (*R*)-(+) sakuranetin (R=CH_3)
   (*R*)-(+) naringenin (R=H)*

(*S*)-(−) malic acid
A1.25



7. ( ) leucodrin. *Abs. X-ray* [5]
   Related compds; [6] Y2'
8. (*R*)-(−) (*p*-methoxyphenyl) succinic acid.

(*R*)-(−) phenylsuccinic acid
A50.12

(*S*)-(−) glyceraldehyde
A1.1

(*R*)-(+) 2-methoxyglutaric acid A11.13

9. ( ) canescin A. Diacetyl deriv. (+)
   ( ) canescin B = 5'-epimer. Diacetyl deriv. (−) [8]

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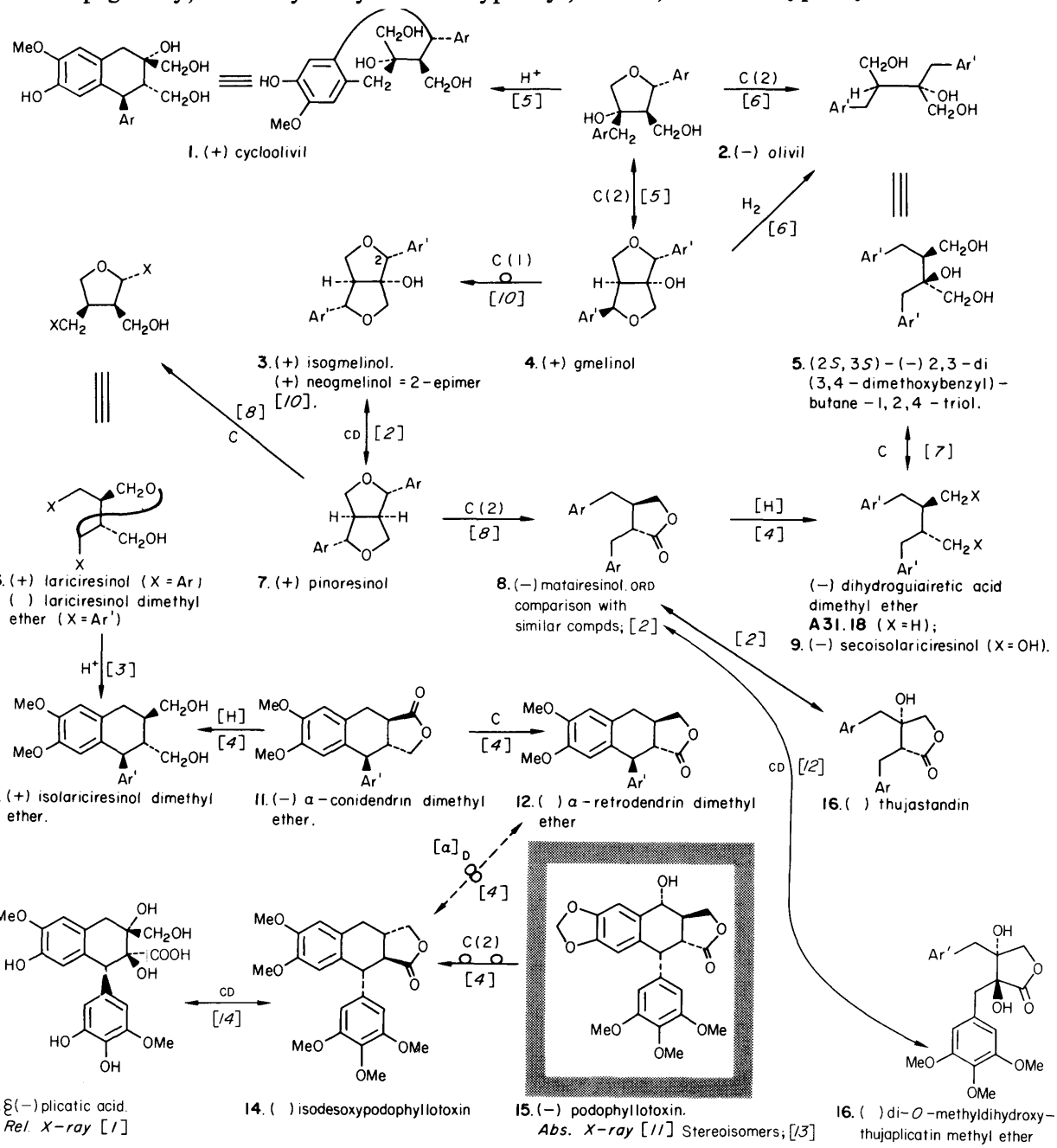
Lignans

Review; [9]

On this page only, Ar = 4-hydroxy-3-methoxyphenyl; Ar′ = 3,4-dimethoxyphenyl.



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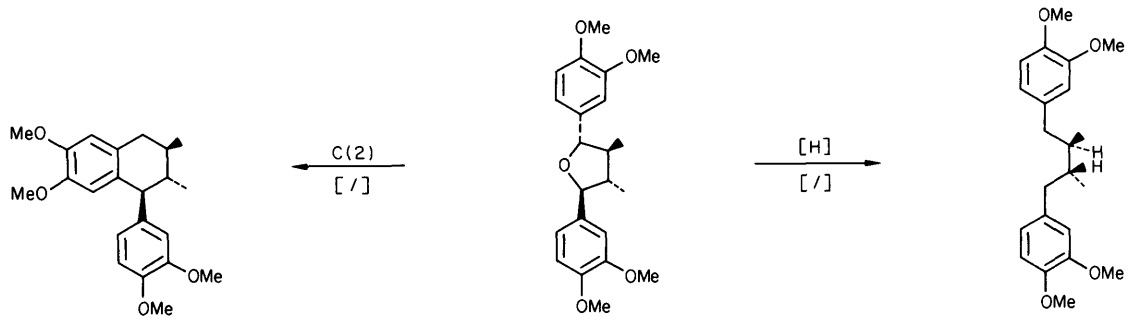
13. V. N. Aiyar and F. C. Chang, *J. Org. Chem.*, 1975, **40**, 2384.
14. R. J. Swan, W. Klyne and H. MacLean, *Canad. J. Chem.*, 1967, **45**, 319.



1. (−) galbulin

2. (−) galbegin. *Meso* − compounds of this type have also been characterized [/]

(−) dihydroguiaretic acid dimethyl ether A31.18

Notes on lignan stereochemistry†

The evidence on which the absolute configuration of a given lignan is assigned frequently consists of a combination of chemical interconversions within and between classes of compound and optical comparisons. The four main classes of lignan are:

(1) Open-chain types (diarylbutanes), e.g. dihydroguiaretic acid **A31.8**, secoisolariciresinol **Y7.10**; these have the general formula $ArCH_2CH(CH_2X)CH(CH_2X)CH_2Ar$. All have the *threo* configuration, leading to optical activity.

(2) Furanoid lignans ('monoepoxylignans'). Cyclization of diarylbutane lignans can occur in two ways, to give types exemplified by lariciresinol **Y7.9** and galbegin **Y8.2**. One or two new chiral centres, respectively, are created, and their configurations may be determined relative to the two pre-existing centres by spectroscopic methods, equilibration experiments, etc.

(3) Cyclolignans (phenyltetralins). The parent of the cyclolignans is 2,3-dimethyl-1-phenyltetralin, for which 8 stereoformulae can be written

(1a) (1*S*, 2*S*, 3*R*) (1b) (1*R*, 2*R*, 3*S*) (2a) (1*S*, 2*R*, 3*S*) (2b) (1*R*, 2*S*, 3*R*)

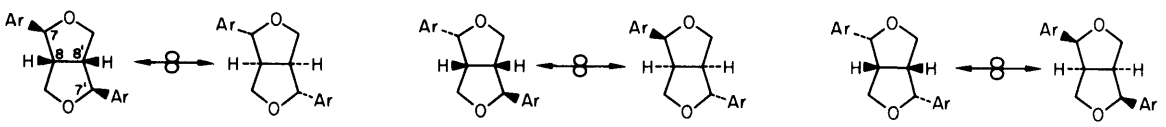
1. A. J. Birch, B. Milligan, E. Smith, and R. N. Speake, *J. Chem. Soc.*, 1958, 4471.
2. D. C. Ayres, personal communication.
3. V. N. Aiyar and F. C. Chang, *J. Org. Chem.*, 1975, **40**, 2384; E. Schreier, *Helv. Chim. Acta.*, 1963, **46**, 75.

†The help of Dr. D. C. Ayres in the preparation of these notes is gratefully acknowledged.

(3a) (1*S*, 2*S*, 3*S*) (3b) (1*R*, 2*R*, 3*R*) (4a) (1*S*, 2*R*, 3*R*) (4b) (1*R*, 2*S*, 3*S*)

Lignans derived from (1a), (1b), (2b), (3a), (3b), and (4b) are known to occur naturally. Assignment of chirality at the 1-position may be carried out by ORD/CD [*1*], from which the complete stereochemistry may be adduced by methods such as nmr. Alternatively evidence from cyclisation reactions such as lariciresinol → isolariciresinol can be used, but caution is necessary in the interpretation of this type of cyclisation because epimerisation at C_2 may occur [*2*].

(4) *Bisepoxylignans* (furanofurans), e.g. pinoresinol **Y7.7**. The bisepoxylignan skeleton contains four asymmetric centres, but since steric restrictions demand a *cis*-8,8′ fusion and since almost all natural bisepoxylignans have both aryl groups identical, only six stereochemical types are possible.



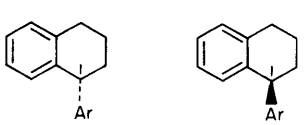
(1a) (1b) (2a) (2b) (3a) (3b)

Normal series *epi* series *dia* series

Structure determination in this class is generally by ring opening to a furanoid lignan, as shown for pinoresinol → lariciresinol **Y7.7** → **Y7.6.**

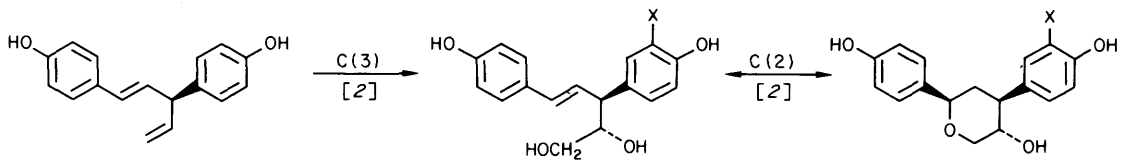
Stereochemical nomenclature

The application of the (*R*,*S*) system to aryltetralin lignans such as podophyllotoxin gives irregular results, because trivial variations of the aryl substitution pattern cause notational inversion. A proposed 'local' convention [*3*] used D and L to designate the C_1 configurations shown below.



L D

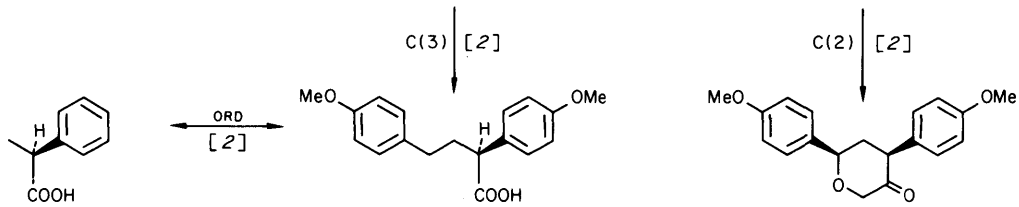
All known natural products belong to the L series.



1. (*S*)-( ) hinokiresinol. Dimethyl ether (+)

2. (−) agatharesinol (X = H)
( ) sequirin C (X = OH) [1]

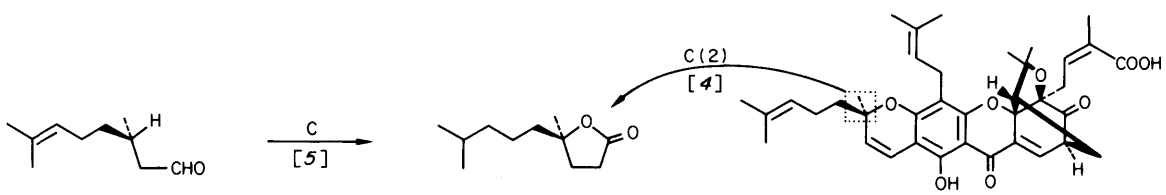
3. ( ) sugiresinol (X = H) (dimethyl ether (−))
( ) sequirin B (X = OH) [1]



(*S*)-(+) 2-phenylpropionic acid
A41.12

4. (*S*)-( ) 2,4-bis (*p*-methoxyphenyl)-butyric acid

5. ( ) sugiresinone dimethyl ether.
AC by ORD [2]



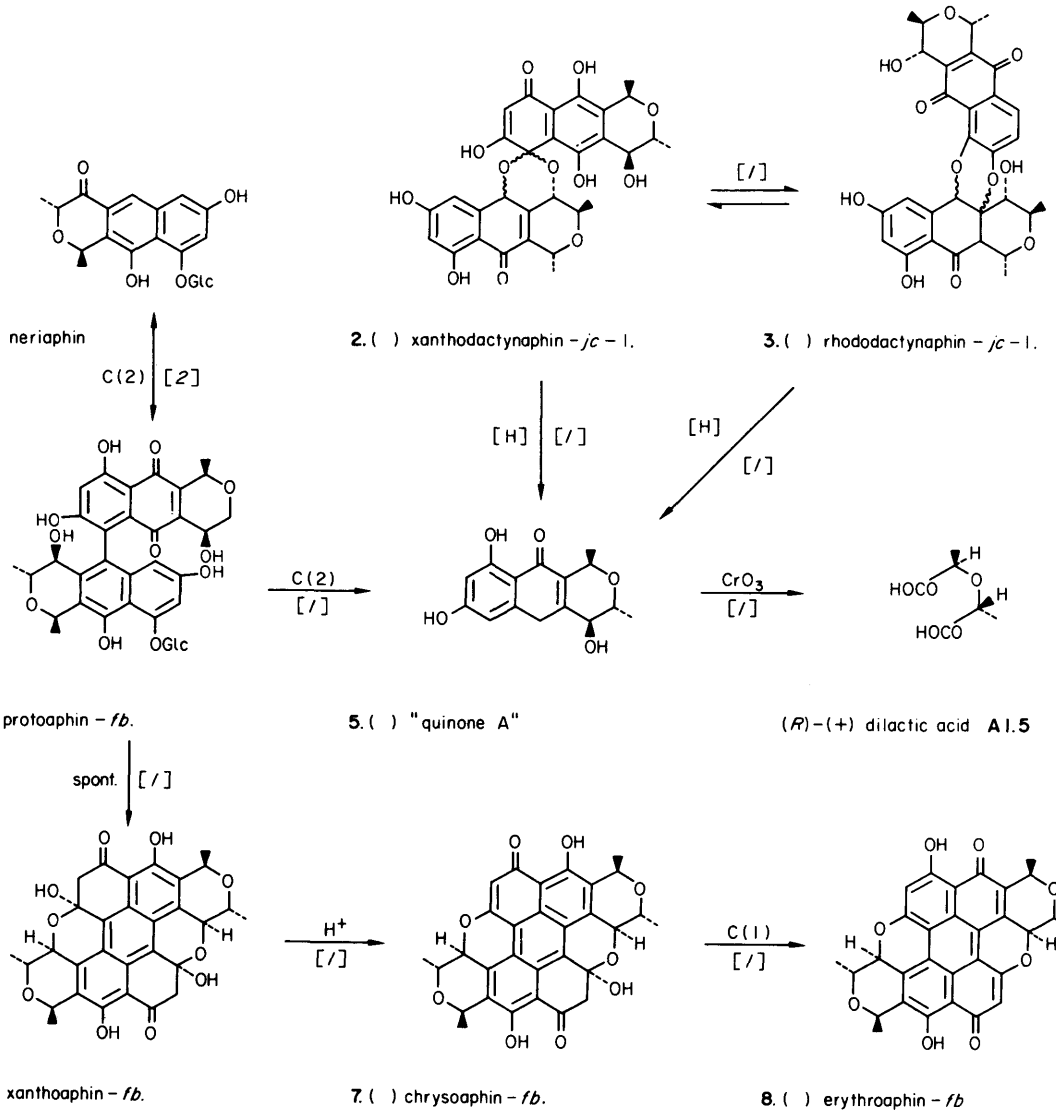
(*R*)-(+) citronellal
T1.4

6. (*R*)-(+) 4,8-dimethyl-4-hydroxynonanoic acid lactone

7. (−) gambogic acid. *Rel. X-ray* of (−) morellin (a similar natural product which does not appear to have been correlated with gambogic acid) [3]

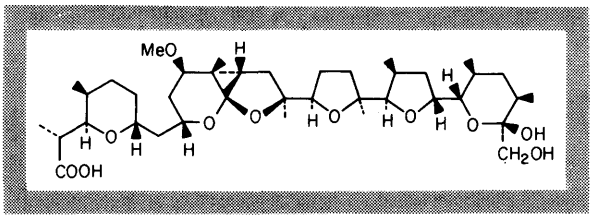
1. N. A. R. Hatam and D. A. Whiting, *J. Chem. Soc. (C)*, 1969, 1921.
2. C. R. Enzell, Y. Hirose, and B. R. Thomas, *Tetrahedron Letters*, 1967, 793.
3. G. Kartha, G. N. Ramachandran, H. B. Bhat, P. M. Nair, V. K. V. Raghavan, and K. Venkataraman, *Tetrahedron Letters*, 1963, 459.
4. G. Cardillo and L. Merlini, *Tetrahedron Letters*, 1967, 2529.
5. I. Orban, K. Schaffner, and O. Jeger, *J. Amer. Chem. Soc.*, 1963, **85**, 3033.

Review; [4]

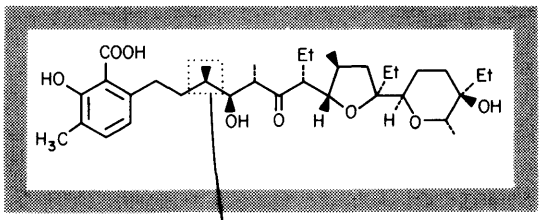


Pigments of the *-jc-2, -sl* and *-tt* series are epimeric with those shown [*1*] [*3*].
N.B. the protoaphin molecule contains a biaryl system of axial chirality, but its configuration is unknown [*1*].
The suffixes *-fb, -jc, -sl* and *-tt* refer to the aphid species from which the relevant pigments are obtained, e.g. *-fb* pigments from *Aphis fabae* [*1*].

1. A. J. Banks, D. W. Cameron, and J. C. A. Craik, *J. Chem. Soc. (C)*, 1969, 627 and references therein.
2. K. S. Brown, D. W. Cameron, and U. Weiss, *Tetrahedron Letters*, 1969, 471.
3. J. C. Bowie and D. W. Cameron, *J. Chem. Soc. (C)*, 1967, 712.
4. K. S. Brown, *Chem. Soc. Revs.*, 1975, 4, 263.

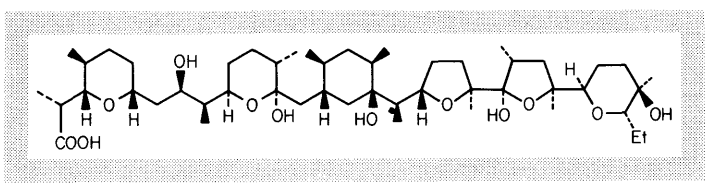


1. §( ) nigericin (antibiotic X-464) [1] *Abs. X-ray* [2]

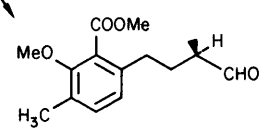


2. ( ) antibiotic X-537A. *Abs. X-ray* [4]. *Rel. X-ray* [7]

C(2) [8]

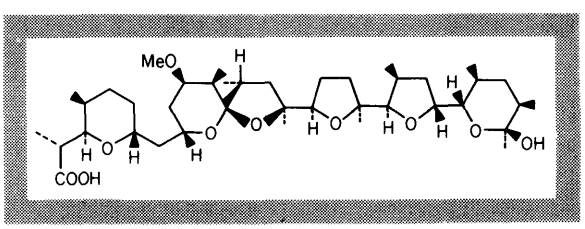


3. §( ) antibiotic X-206. *Abs. X-ray* [3]

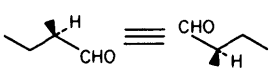


4. (*R*)-(−) 6-(3-formylbutyl)-2-methoxy-3-methylbenzoic acid, methyl ester

ORD [8]

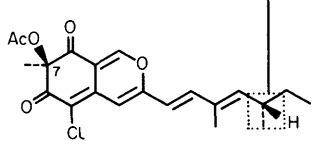


5. § ( ) grisorixin *Abs. X-ray* [6]



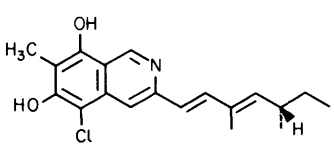
(*R*)-(−) 2-methyl-butanal **A27.5**

O_3 [9]



7. (+) sclerotiorin.
(−) sclerotiorin = 7-epimer
(*not* enantiomer) [9]
Other related compds. [10][5]

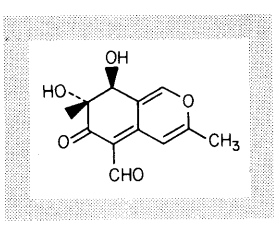
C(2) [9]



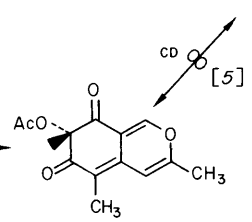
6. (*S*)-( ) aposclerotioramine
Related compds. [10]

CD [5]

C(4) [5]

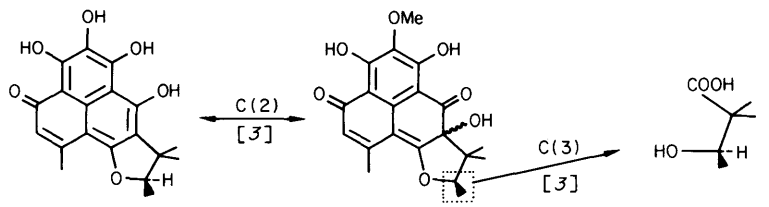


8. ( ) austdiol. *Abs. X-ray* [5]



9. (*S*)-(+)

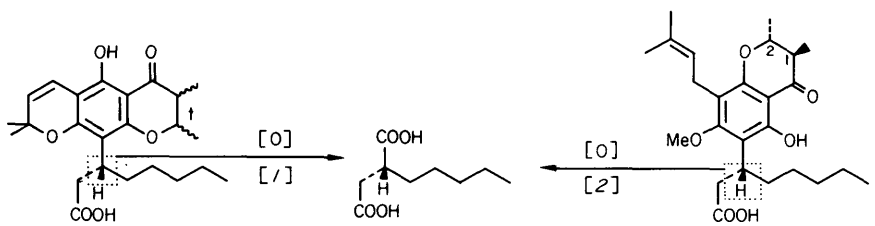
1. J. F. Blount and J. W. Westley, personal communication.
2. M. Shiro and H. Koyama, *J. Chem. Soc. (B)*, 1970, 243.
3. J. F. Blount and J. W. Westley, *Chem. Comm.*, 1975, 533.
4. S. M. Johnson, J. Herrin, S. J. Liu, and I. C. Paul, *J. Amer. Chem. Soc.*, 1970, **92**, 4428.
5. P. S. Steyn and R. Vleggaar, *J. Chem. Soc., Perkin I*, 1976, 204.
6. M. Alleaume and D. Hickel, *Chem. Comm.*, 1972, 175.
7. S. M. Johnson, J. Herrin, S. J. Liu, and I. C. Paul, *Chem. Comm.*, 1970, 72.
8. J. W. Westley, R. H. Evans, T. Williams, and A. Stempel, *Chem. Comm.*, 1970, 71.
9. G. A. Ellestad and W. B. Whalley, *J. Chem. Soc.*, 1965, 7260.
10. F. C. Chen, P. S. Manchand, and W. B. Whalley, *J. Chem. Soc. (C)*, 1971, 3577.



1. (*R*)-(−) atrovenetin

2. (+) herqueinone

(*R*)-(−) 2,2-dimethyl-3-hydroxybutyric acid **A12.14**

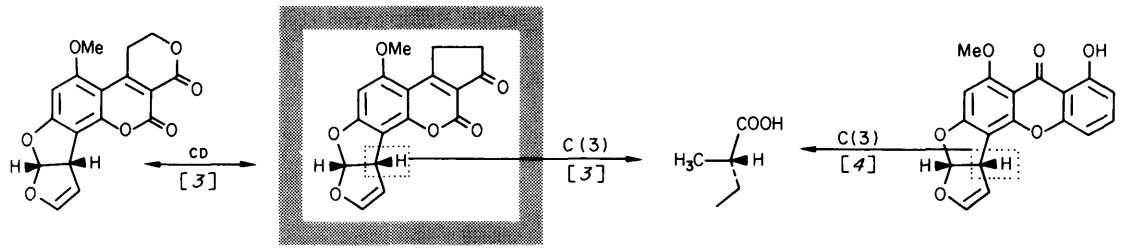


3. ( ) blancoic acid

(*R*)-(+) pentylsuccinic acid **A 28.9**

4. (+) papuanic acid
(−) isopapuanic acid = 2-epimer [2]
Rel. X-ray [2]

1. G. H. Stout and K. D. Sears, *J. Org. Chem.*, 1968, 33, 4185.
2. G. H. Stout, G. K. Hickernell, and K. D. Sears, *J. Org. Chem.*, 1968, 33, 4191.
3. J. S. Brooks and G. A. Morrison, *Chem. Comm.*, 1971, 1359.

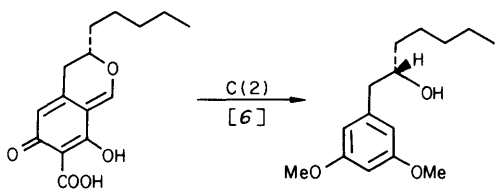


1. (−) aflatoxin G1. *Rel. X-ray* [1]

2. (−) aflatoxin B1. *Abs. X-ray* [2]

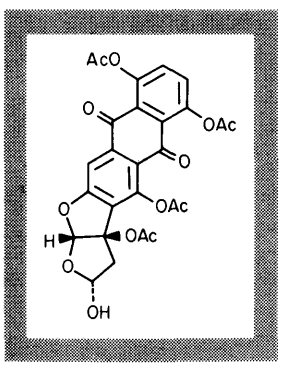
(*S*)-(+) 2-methylbutyric acid **A29.11**

3. (−) sterigmatocystin Y1'

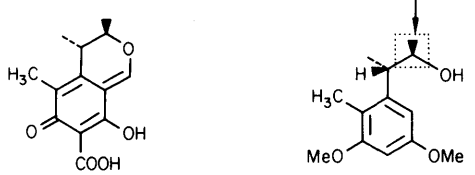


4. (+) pulvilloric acid

5. (*S*)-(−) 1-(3,5-dimethoxyphenyl)-heptan-2-ol

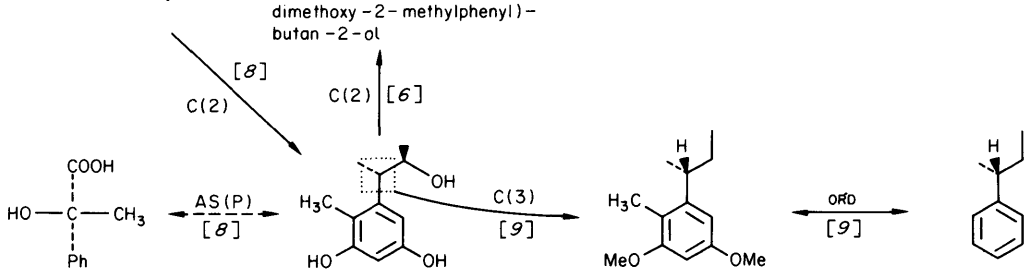


6. ( ) tetraacetoxydothistromin *Abs. X-ray* [5]



7. (−) citrinin. *Rel. X-ray* [7]

8. (2*R*,3*S*)-(−) 3-(3,5-dimethoxy-2-methylphenyl)-butan-2-ol



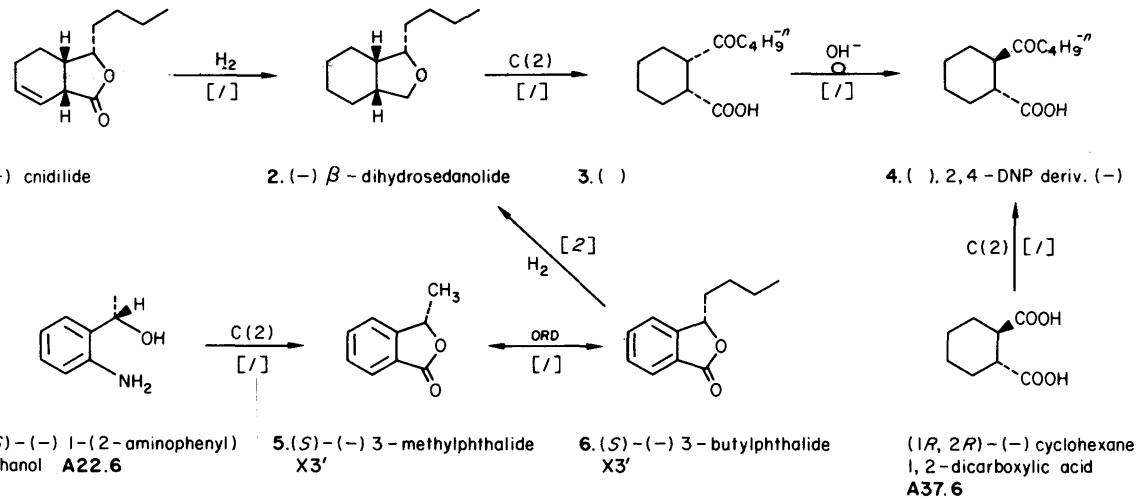
(*S*)-(+) atrolactic acid **A31.19**

9. (2*R*,3*S*)-(−) 3-(3,5-dihydroxy-2-methylpheny)-butan-2-ol

10. (*R*)-(−) 2-(3,5-dimethoxy-2-methylphenyl)-butane

(*R*)-(−) 2-phenylbutane **A49.15**

1. K. K. Cheung and G. A. Sim, *Nature*, 1967, **201**, 1185.
2. T. E. van Soest and A. F. Peerdeman, *Acta Cryst.*, 1970, **B26**, 1940.
3. S. Brechbühler, G. Büchi, and G. Milne, *J. Org. Chem.*, 1967, **32**, 2641.
4. J. S. E. Holker and J. Mulheirn, *Chem. Comm.*, 1968, 1576.
5. C. A. Bear, J. M. Waters, T. N. Waters, R. T. Gallagher, and R. Hodges, *Chem. Comm.*, 1970, 1705.
6. G. C. Barrett, J. F. W. McOmie, S. Nakajima, and S. W. Tanenbaum, *J. Chem. Soc. (C)*, 1969, 1068.
7. O. R. Rodig, M. Shiro, and Q. Fernando, *Chem. Comm.*, 1971, 1553.
8. P. P. Mehta and W. B. Whalley, *J. Chem. Soc.*, 1963, 3777.
9. R. K. Hill and L. A. Gardella, *J. Org. Chem.*, 1964, **29**, 766.



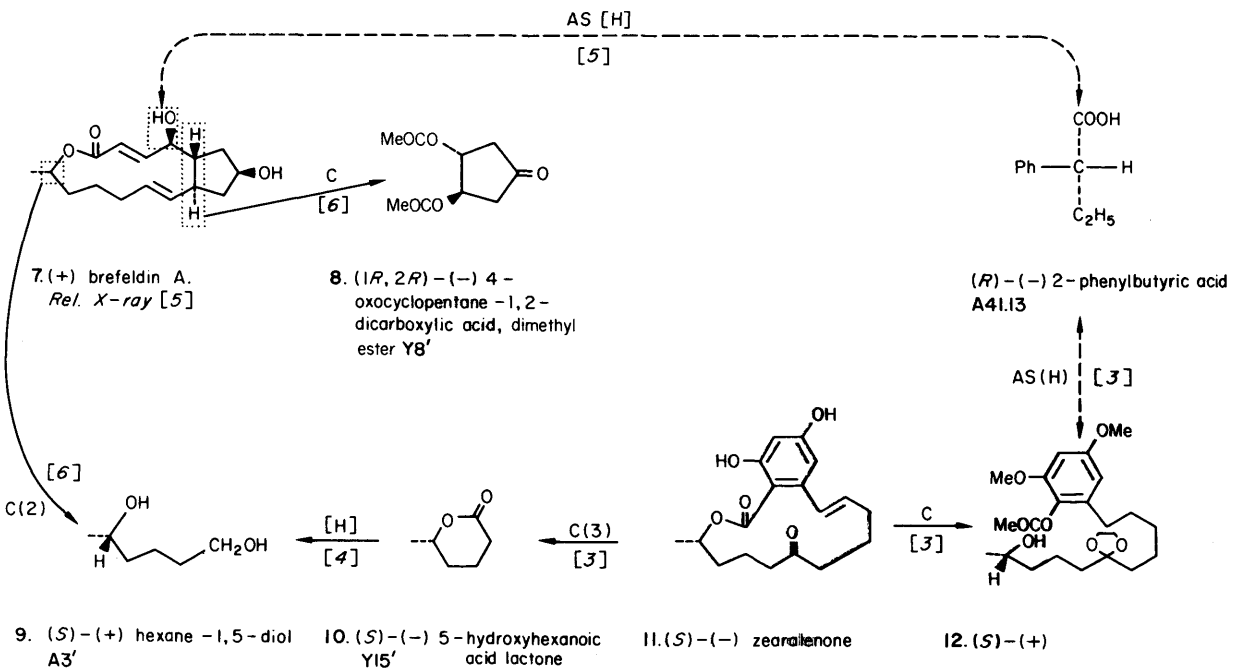
1. (−) cnidilide
2. (−) β-dihydrosedanolide
3. ( )
4. ( ). 2,4-DNP deriv. (−)

(S)-(−) 1-(2-aminophenyl) ethanol **A22.6**

5. (S)-(−) 3-methylphthalide **X3′**

6. (S)-(−) 3-butylphthalide **X3′**

(1R, 2R)-(−) cyclohexane-1, 2-dicarboxylic acid **A37.6**



7. (+) brefeldin A. *Rel. X-ray* [5]

8. (1R, 2R)-(−) 4-oxocyclopentane-1, 2-dicarboxylic acid, dimethyl ester **Y8′**

(R)-(−) 2-phenylbutyric acid **A41.13**

9. (S)-(+) hexane-1, 5-diol **A3′**

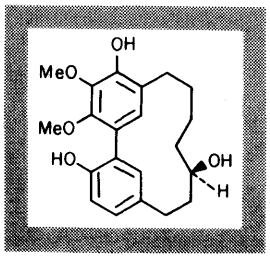
10. (S)-(−) 5-hydroxyhexanoic acid lactone **Y15′**

11. (S)-(−) zearalenone

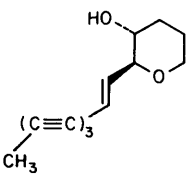
12. (S)-(+)

1. U. Nagai, T. Shishido, R. Chiba, and H. Mitsuhashi, *Tetrahedron*, 1965, **21**, 1701, and references therein.
2. D. H. R. Barton and J. X. de Vries, *J. Chem. Soc.*, 1963, 1916.
3. C. H. Kuo, D. Taub, R. D. Hoffsommer, N. L. Wendler, W. H. Urry, and G. Mullenbach, *Chem. Comm.*, 1967, 761.
4. R. Kuhn and K. Kum, *Chem. Ber.*, 1962, **95**, 2009.
5. H. P. Weber, D. Hauser, and H. P. Sigg, *Helv. Chim. Acta*, 1971, **54**, 2763.
6. H. P. Sigg, *Helv. Chim. Acta*, 1964, **47**, 1401.

Miscellaneous natural products containing C, H, O, halogens only.

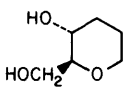


1. (−) myricanol.
Abs. X-ray [1]



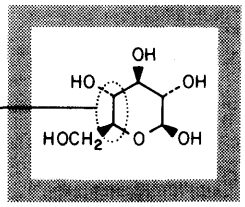
2. (−) ichthyothereol

C(3) [2]

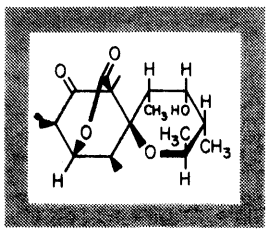


3. (2*S*, 3*R*)-( ) 2-hydroxymethyl-3-hydroxytetrahydropyran. Bis-3,5-dinitrobenzoyl deriv (−)

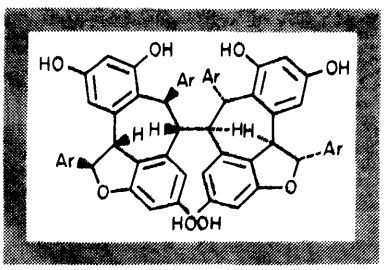
C(6) [2]



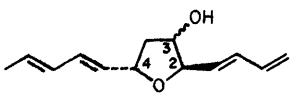
( ) β-L-glucopyranose **A26.9**



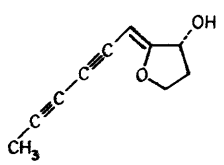
4. (+) portentol
Abs. X-ray [4]



5. (−) hopeaphenol (Ar = *p* C_6H_4OH)
Abs. X-ray [3]



6. (2*R*, 4*S*)-( ) 2-(buta-1,3-dienyl)-3-hydroxy-4-(penta-1,3-dienyl)-tetrahydrofuran
By calculation from CD (coupled oscillator method) [6]



7. (*R*)-(+) 1-(3-hydroxy-2-tetrahydrofurylidene)-hexa-2,4-diyne

O_3 [5]

(*R*)-(+) 2,4-dihydroxybutyric acid lactone **A3.10**

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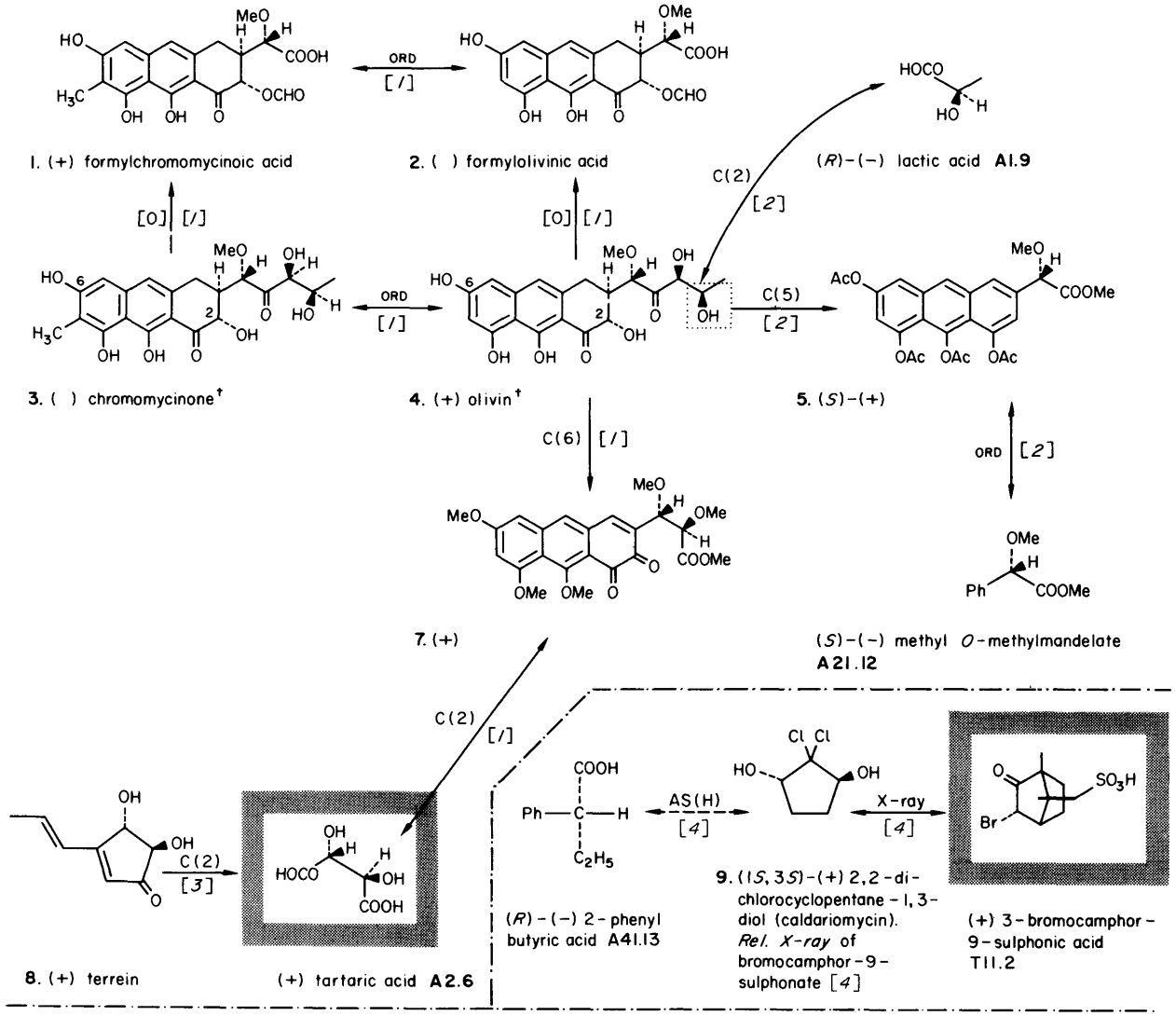

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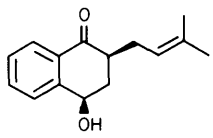
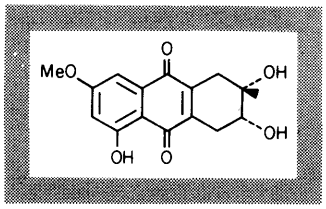
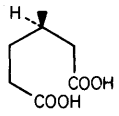
†The antibiotics of the aureolic acid group (chromomycins, olivomycins etc.) are *O*-glycosides of olivin and chromomycinone at C_2 and C_6.



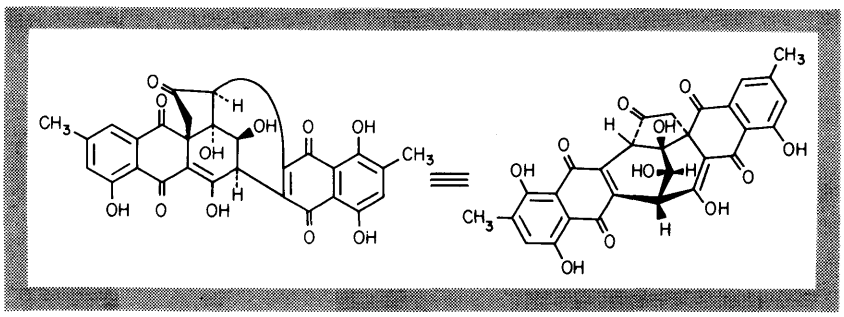
1. (+) catalponol. By CD (aromatic chirality rule) [1]



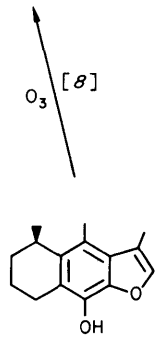
2. ( ) bostrychin. *Abs. X-ray* [2]



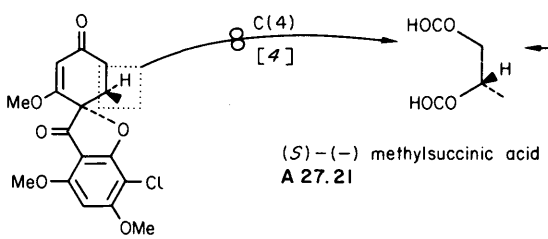
(*R*)-(+) 3-methyladipic acid
A 26.15



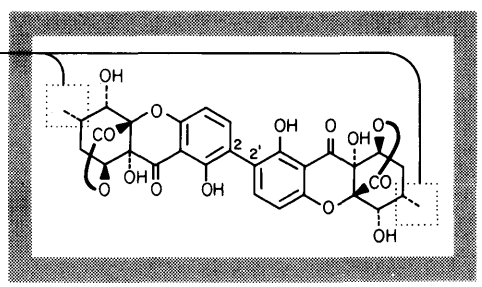
3. ( ) purpurogenone. *Abs. X-ray* [9]



4. (*R*)-(+) cacalol [7]. ORD: [7]



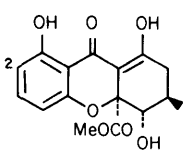
(*S*)-(−) methylsuccinic acid
A 27.21



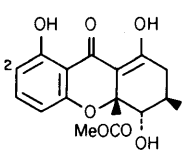
5. (+) griseofulvin. *Rel. X-ray* [3]

6. (+) ergoflavin (ergochrome CC) *Abs. X-ray* [6]

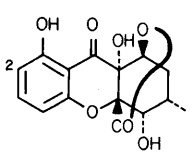
The ergot pigments (also called secalonic acids [11]) are derived from the following four structural units **Y17A-D** and others closely related by dimerisation and cross-dimerisation at the 2-positions [10]. Several of the pigments other than ergoflavin have been degraded to (*R*) or (*S*) methylsuccinic acid and the full stereochemistry worked out by a combination of spectroscopic methods and rotational arguments [5] [10]. Both enantiomers of some compounds are natural products, e.g. (-) secalonic acid E = enantiomer of (+) secalonic acid B[11].



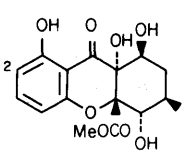
A



B



C



D

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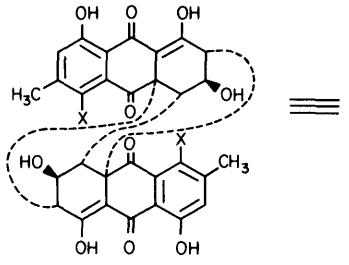
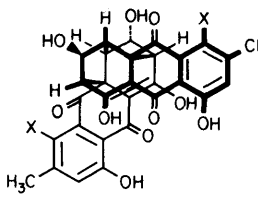
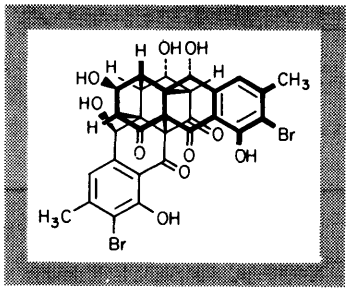




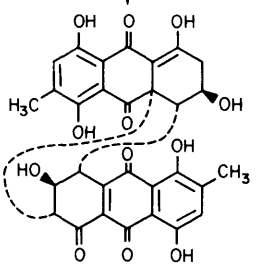
C(2) [1]



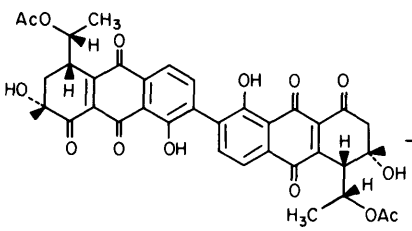
1. (+) rugulosin (X=H)
(+) luteoskyrin (X=OH)
(*non-natural enantiomer*)
YIO'

2. (+) dibromodehydrotetrahydrorugulosin.
Abs. X-ray [1]

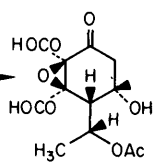
C [2]



3. (+) rubroskin
(*non-natural enantiomer*)



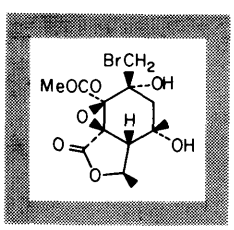
H_2O_2 [3]



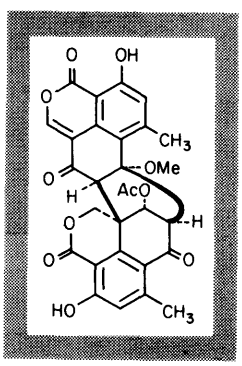
4. (−) julimycin-B II

5. ( )

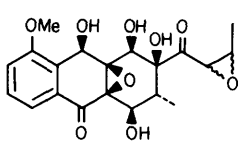
C(4) [3]



7. ( ) 6β-bromo-7β, 7aβ-epoxy-4a, 6α-dihydroxy-7a methoxycarbonyl-3β, 4β-dimethyl-3aβ, 7aβ-octahydrobeno [c] furan-1-one
Abs. X-ray [3]

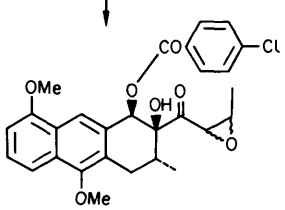


8. (+) duclauxin. *Abs. X-ray* [5]
Related compds. [6]



6. (−) cervicarcin

C [4]



9. ( ) By CD (aromatic chirality method) [4]

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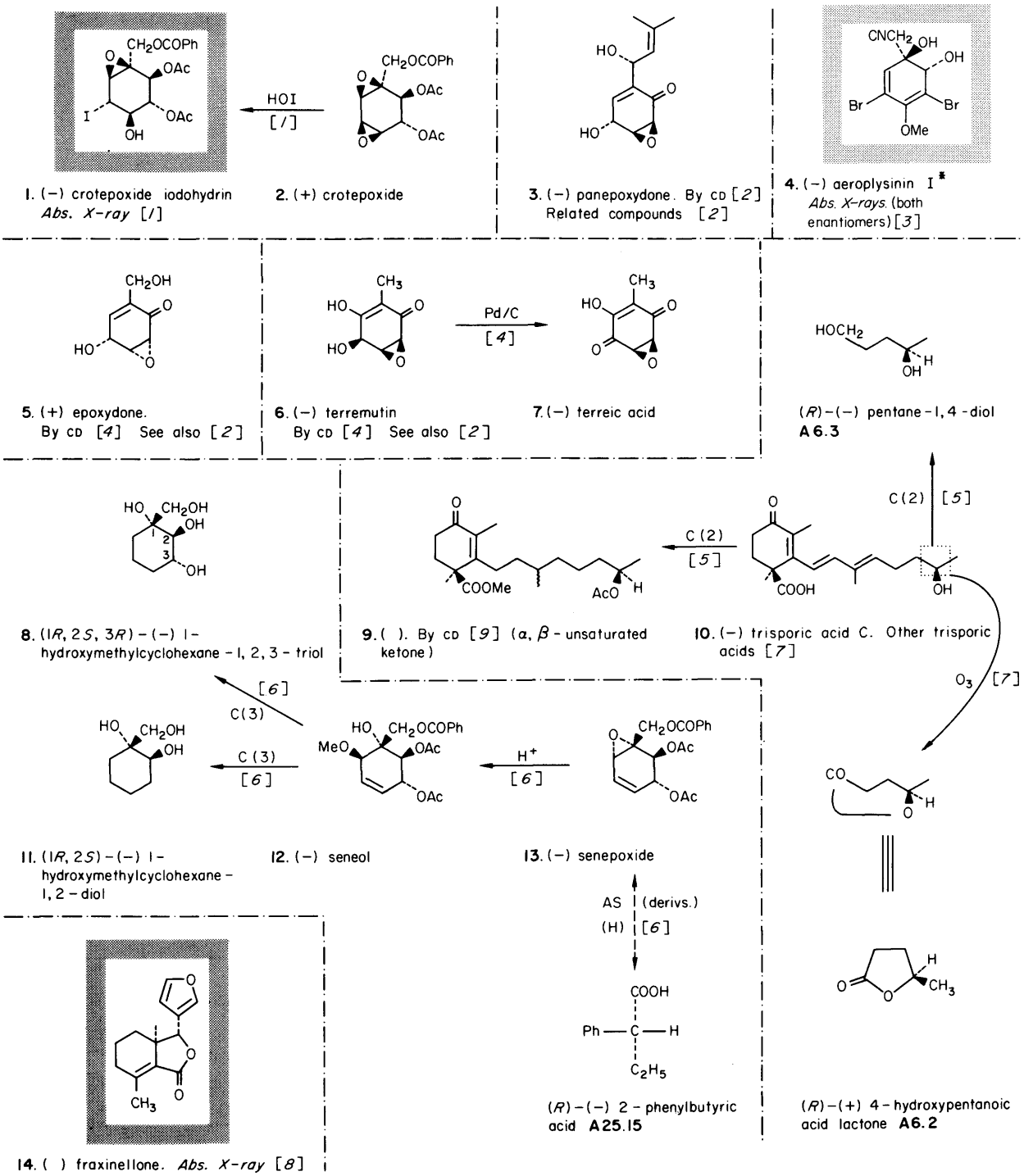

1. (−) crotepoxide iodohydrin *Abs. X-ray* [1]
2. (+) crotepoxide
3. (−) panepoxydone. By CD [2] Related compounds [2]
4. (−) aeroplysinin I* *Abs. X-rays.* (both enantiomers) [3]
5. (+) epoxydone. By CD [4] See also [2]
6. (−) terremutin By CD [4] See also [2]
7. (−) terreic acid
(*R*)-(−) pentane-1,4-diol **A6.3**
8. (1*R*, 2*S*, 3*R*)-(−) 1-hydroxymethylcyclohexane-1, 2, 3-triol
9. ( ). By CD [9] (α, β-unsaturated ketone)
10. (−) trisporic acid C. Other trisporic acids [7]
11. (1*R*, 2*S*)-(−) 1-hydroxymethylcyclohexane-1, 2-diol
12. (−) seneol
13. (−) senepoxide
(*R*)-(−) 2-phenylbutyric acid **A25.15**
(*R*)-(+) 4-hydroxypentanoic acid lactone **A6.2**
14. ( ) fraxinellone. *Abs. X-ray* [8]

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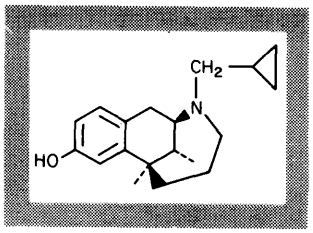
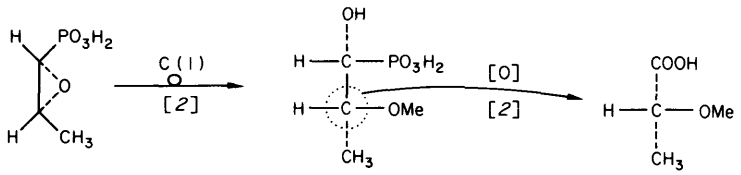


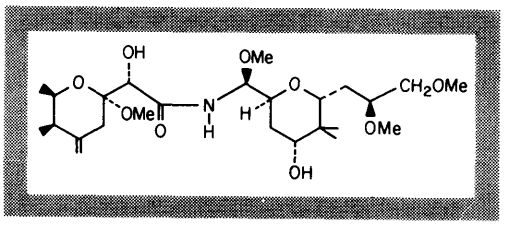
1. (−) cyclazocine (*synthetic compound*) *Abs. X-ray* [1]



2. (−) phosphonomycin ((1*R*, 2*S*) - 1, 2 - epoxypropylphosphonic acid)

3. (1*R*, 2*R*) - (−) 1 - hydroxy - 2 - methoxypropylphosphonic acid

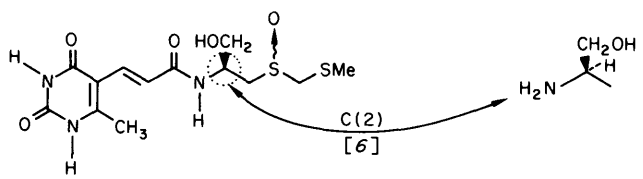
(*R*) - (+) *O* - methyllactic acid **A 1.8**



4. ( ) pederin. *Abs. X-rays* [3] [4]

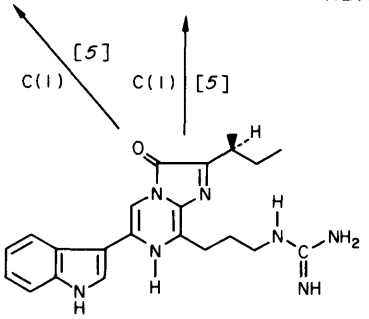
(+) isoleucine **A 27.6**

(−) alloisoleucine **A 27.2**

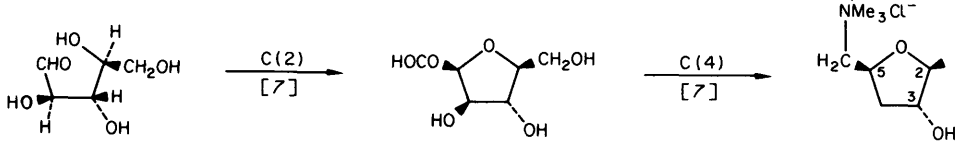


5. ( ) sparsomycin

(*R*) - (−) 2 - aminopropan - 1 - ol **A 19.13**



6. (*S*) - ( ) *Cypridina* luciferin



L (+) arabinose **C1.7**

7. L ( ) chitaric acid

8. (+) muscarine. *Rel. X-ray* [8] stereoisomers; [9]

1. I. L. Karle, R. D. Gilardi, A. V. Fratini, and J. Karle, *Acta Cryst.*, 1969, **B25**, 1469.
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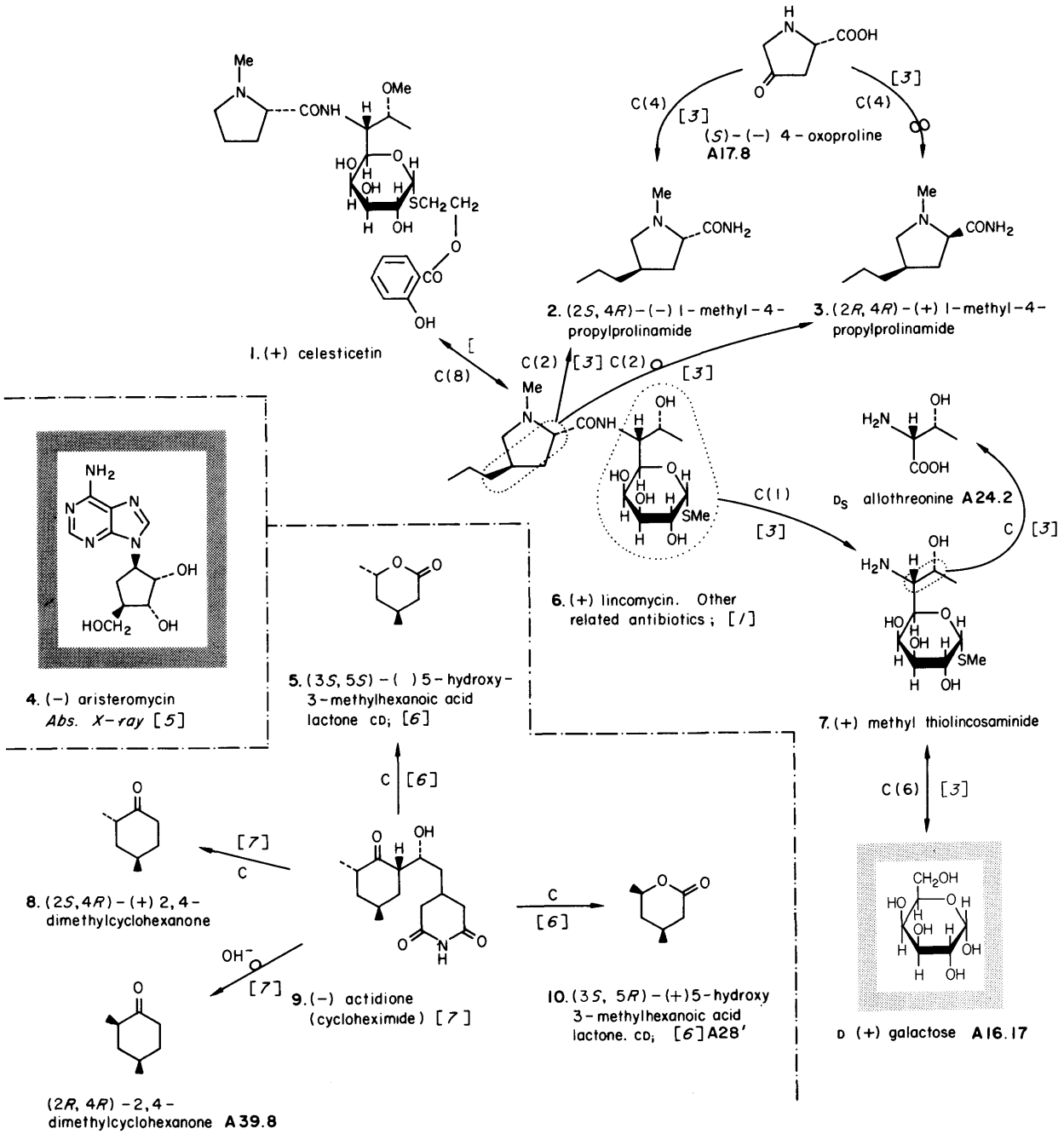

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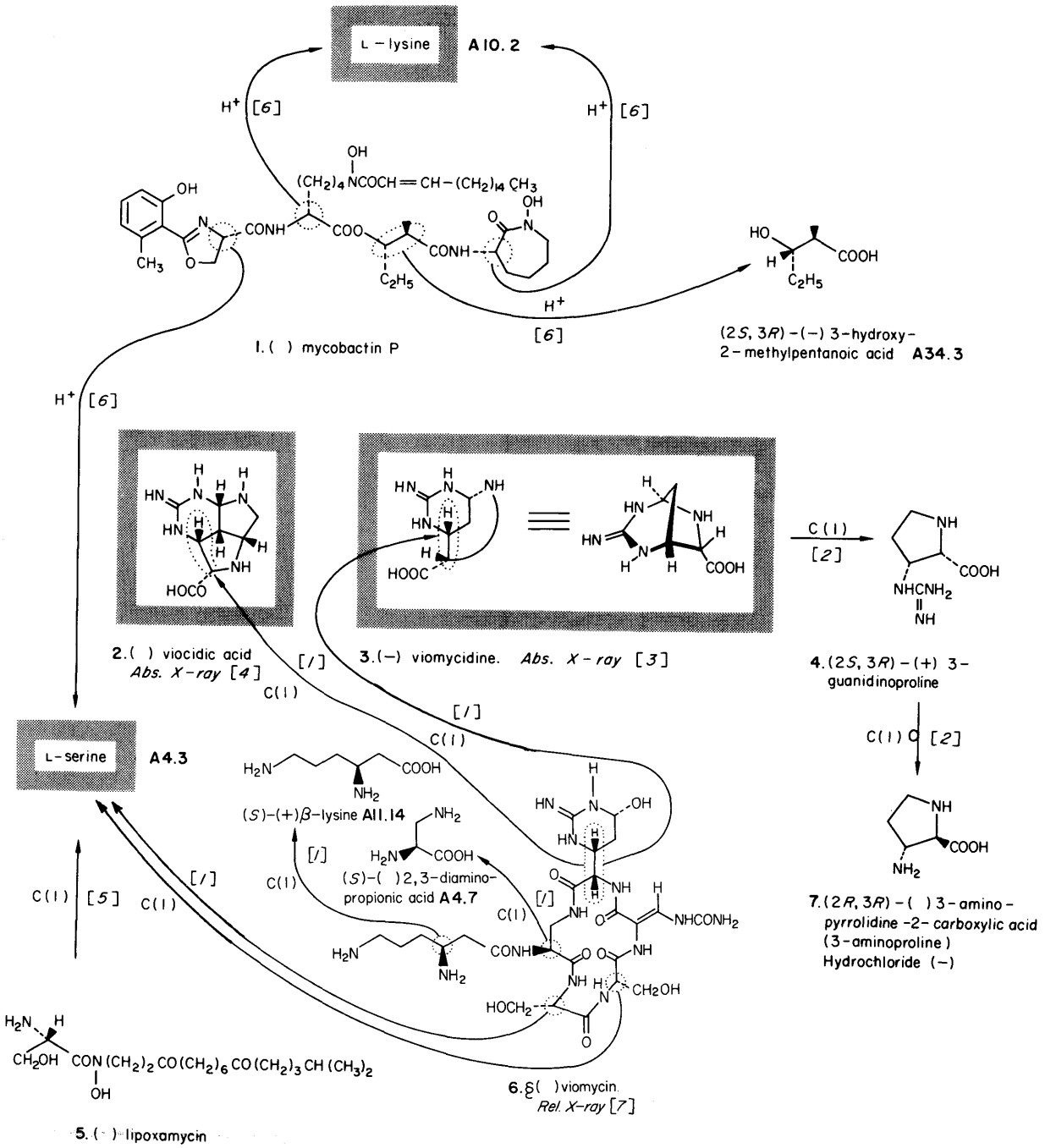

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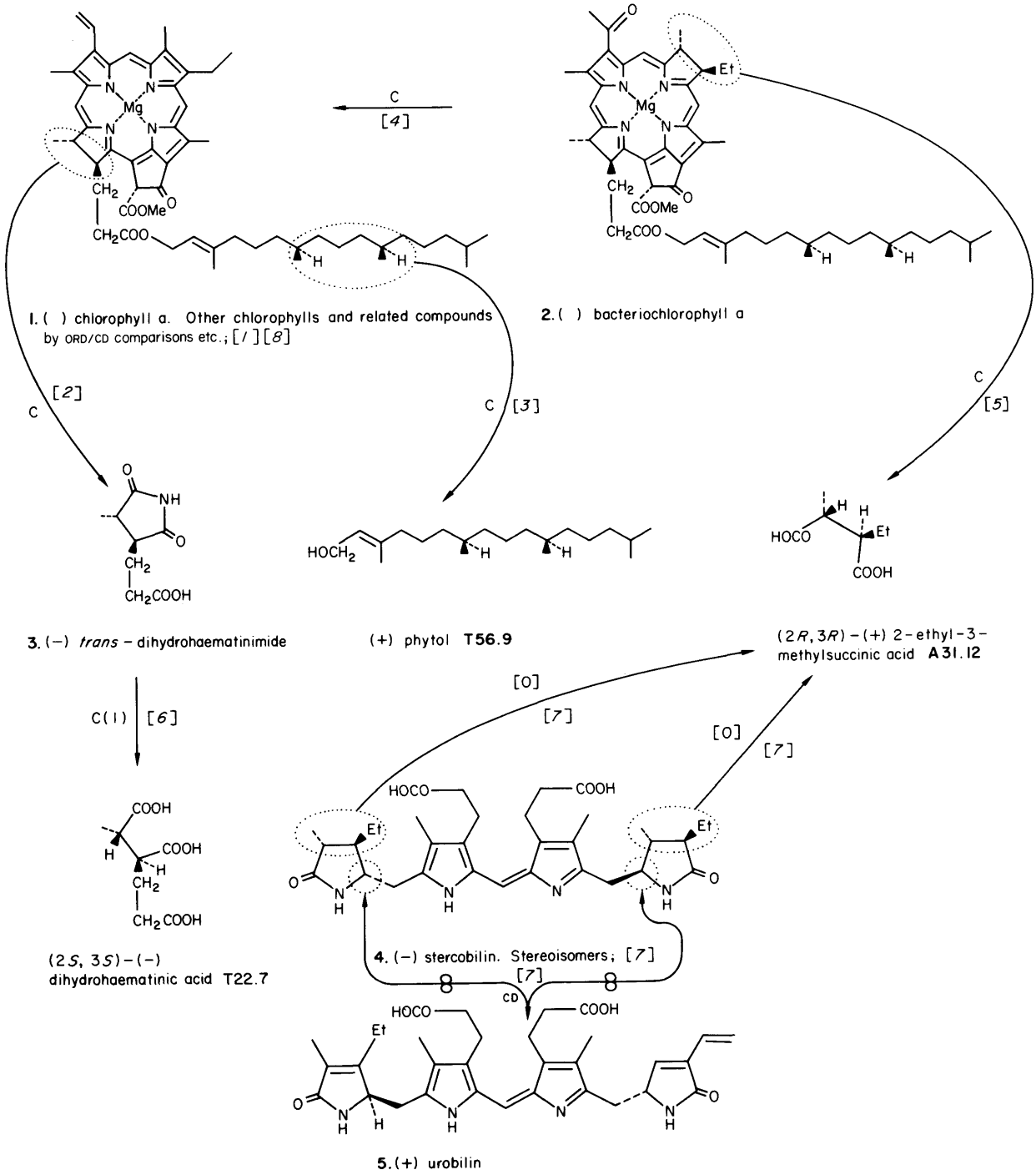

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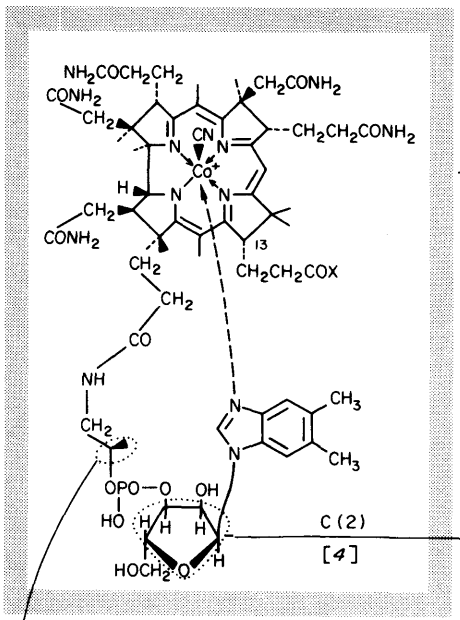
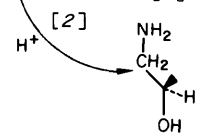
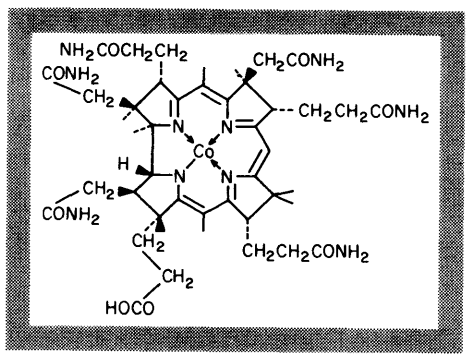


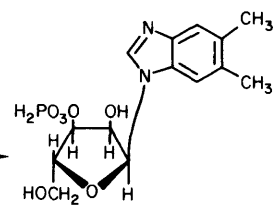
2. (−) vitamin B_{12} (X = NH_2)
( ) vitamin B_{12} monocarboxylic acid (X = OH). *Rel. X-ray* [ ]. CD [14]
Abs. X-ray of neovitamin B_{12} (13-epimer) [15]



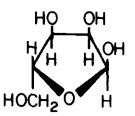
(*R*)-(−) 1-aminopropan-2-ol **A22.4**



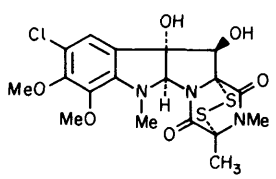
1. ( ) factor V-Ia (Cobyric acid)
Abs. X-ray [3]



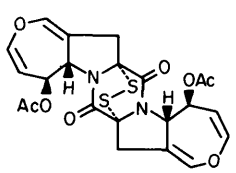
3. ( ) 1α-D-ribofuranosyl-5,6-dimethylbenzimidazole-3-phosphate



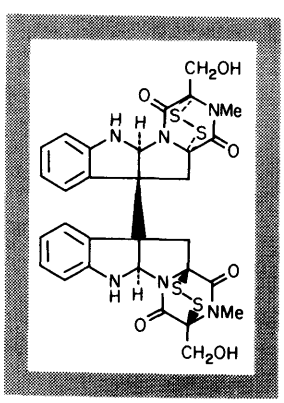
D-ribofuranose **C1.9**



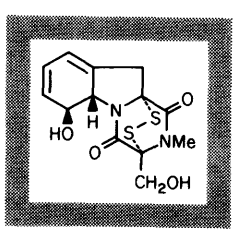
4. (−) sporidesmin. *Rel. X-ray* [6]



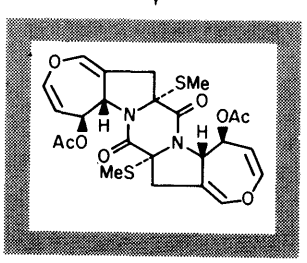
5. ( ) acetylaranotin



6. §(+) chaetocin. *Abs. X-ray* [11]



7. (−) gliotoxin. *Abs. X-ray* [8]. CD; [9]



8. (−) bisdethiodi(methylthio) acetylaranotin. *Abs. X-ray* [7]

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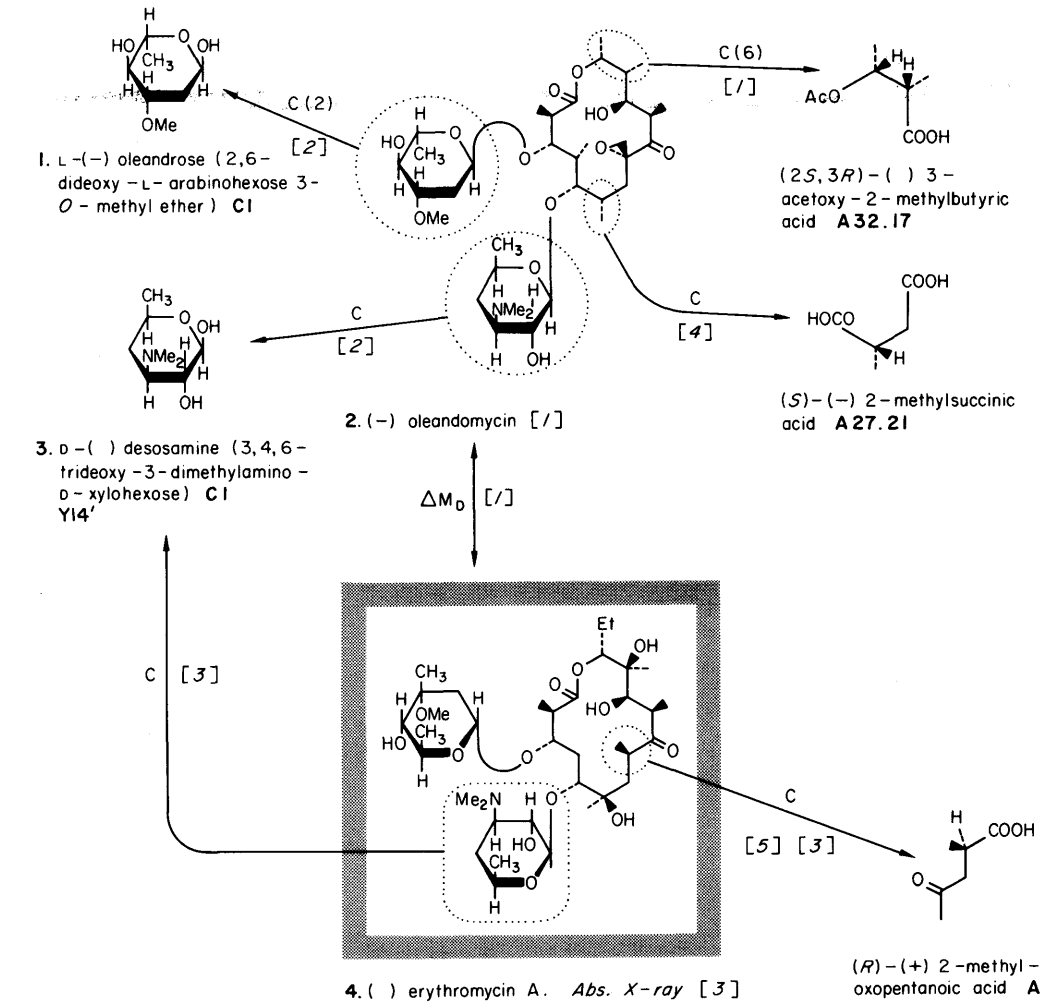


1. L-(−) oleandrose (2,6-dideoxy-L-arabinohexose 3-*O*-methyl ether) **C1**

(2*S*,3*R*)-( ) 3-acetoxy-2-methylbutyric acid **A32.17**

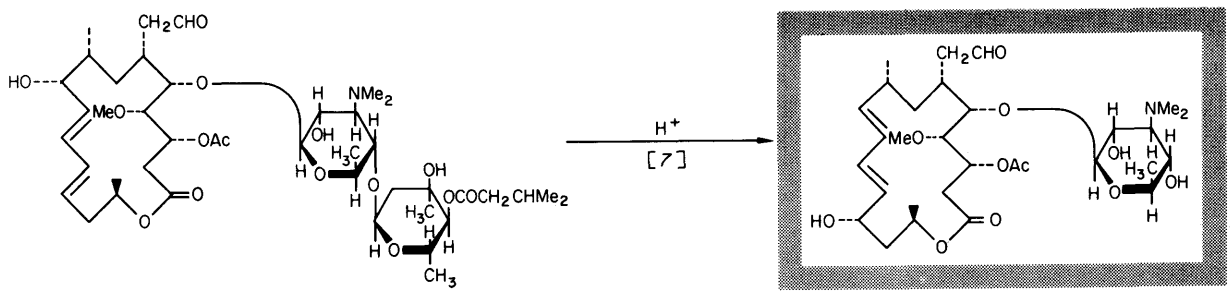
2. (−) oleandomycin [1]

3. D-( ) desosamine (3,4,6-trideoxy-3-dimethylamino-D-xylohexose) **C1** Yl4'

(*S*)-(−) 2-methylsuccinic acid **A27.21**

4. ( ) erythromycin A. *Abs. X-ray* [3]

(*R*)-(+) 2-methyl-4-oxopentanoic acid **A28.3**



5. §(−) leucomycin A_3 [7]

6. ( ) demycarosyl-leucomycin A. *Abs. X-ray* [8]

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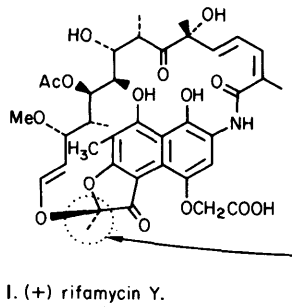
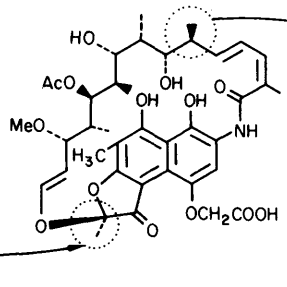
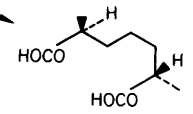


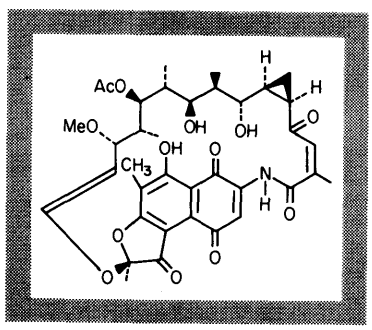
1. (+) rifamycin Y.
Rel. X-ray [1]



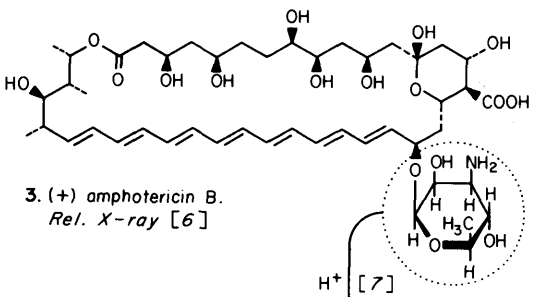
2. (−) rifamycin B.
Rel. X-ray [2]



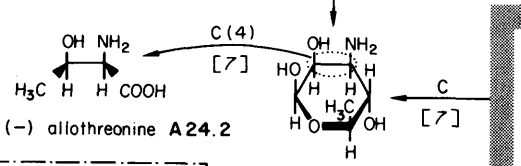
(2S, 6S)-(+) 2,6-dimethylheptanedioic acid **A32.8**



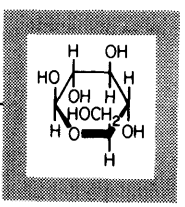
4. (+) tolpomycinone. *Abs. X-ray* [5]



3. (+) amphotericin B.
Rel. X-ray [6]

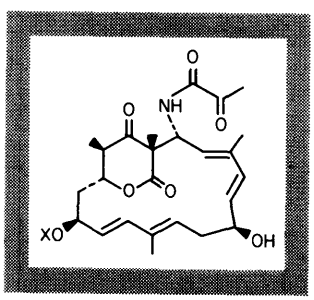


(−) allothreonine **A24.2**

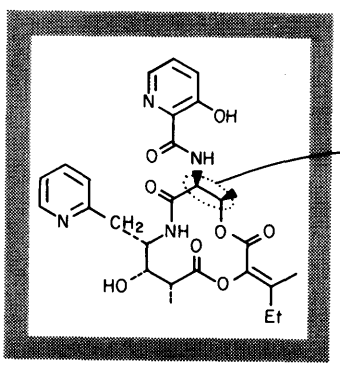


5. ( ) mycosamine (3-amino-3,6-dideoxy-β-D-mannopyranoside).

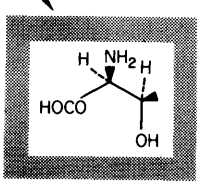
β-D-glucopyranose **A26.9**



6. (−) bundlin A (X=H).
Abs. X-ray [9]
(−) bundlin B (X=Ac)
Abs. X-ray [10]



7. ( ) pyridomycin. *Abs. X-ray* [11]



(−) threonine **A8.16**

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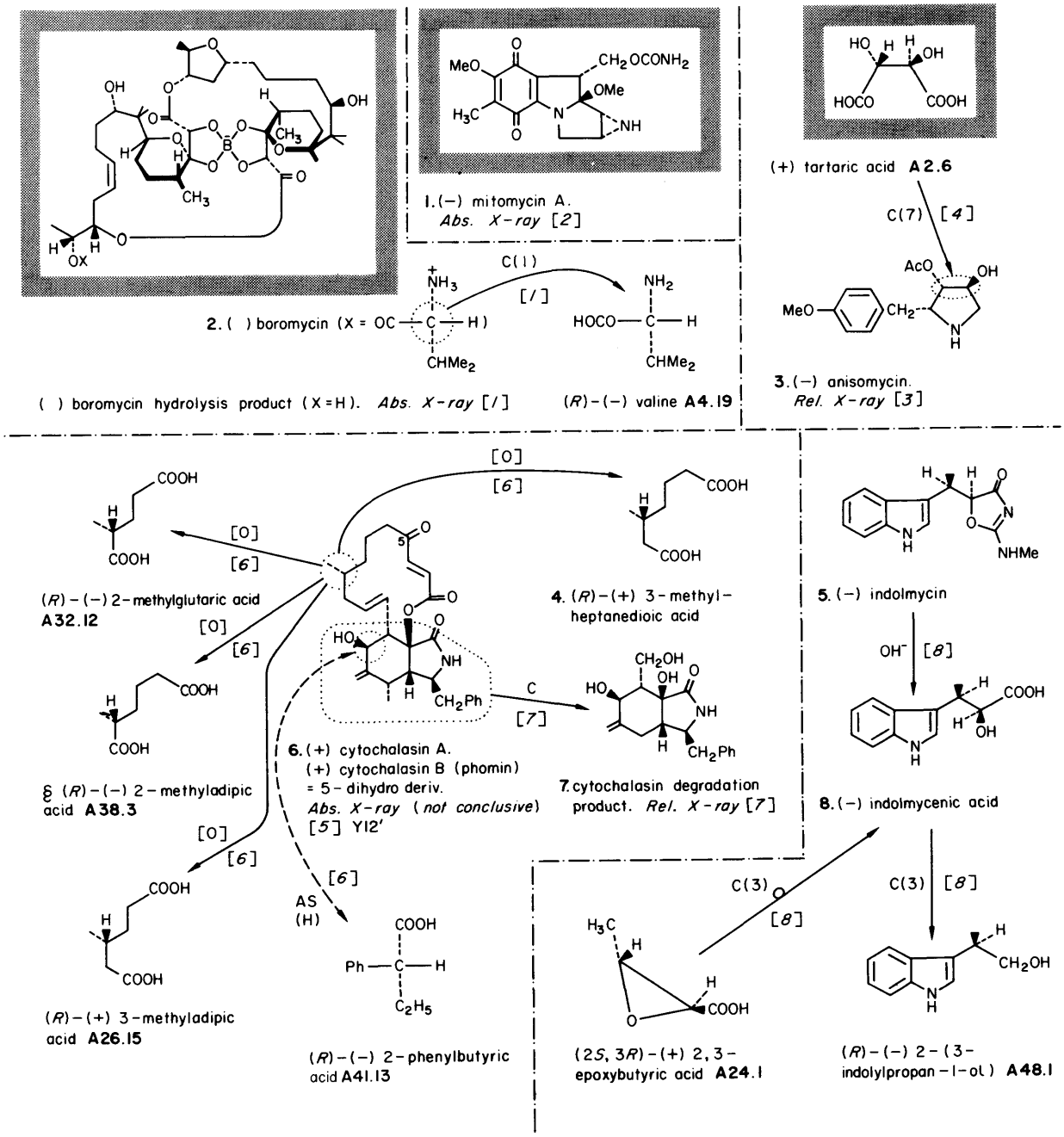

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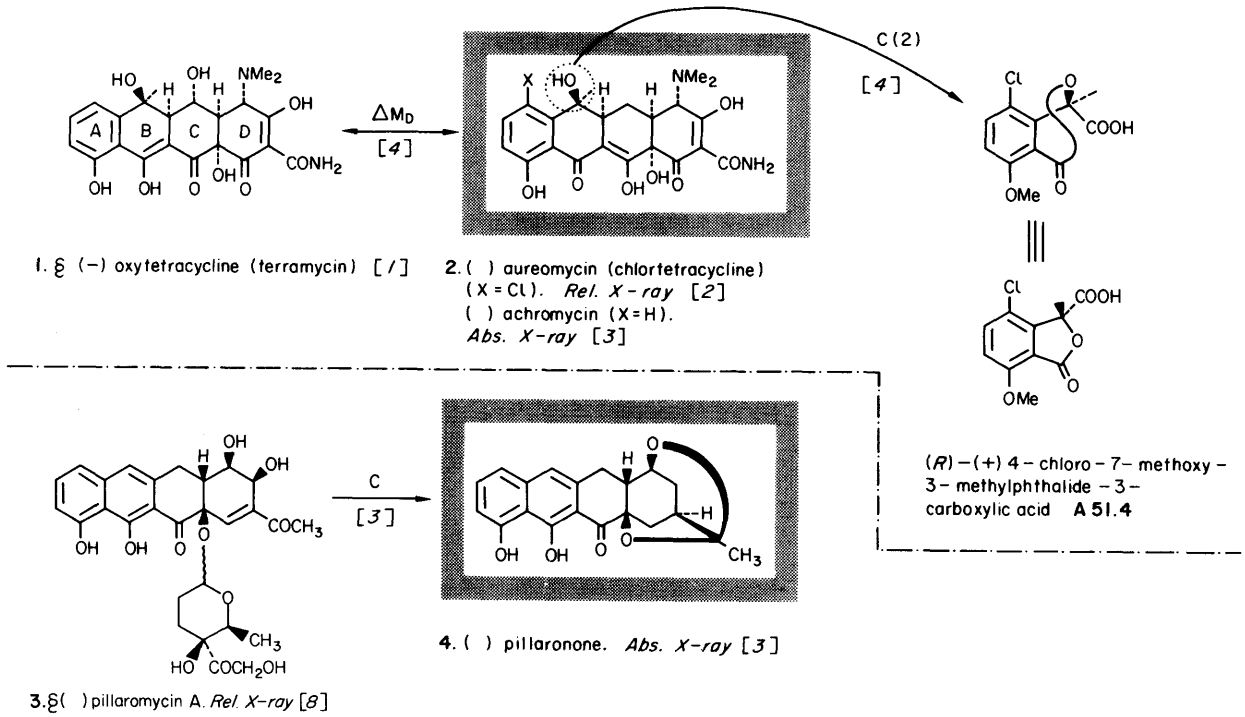


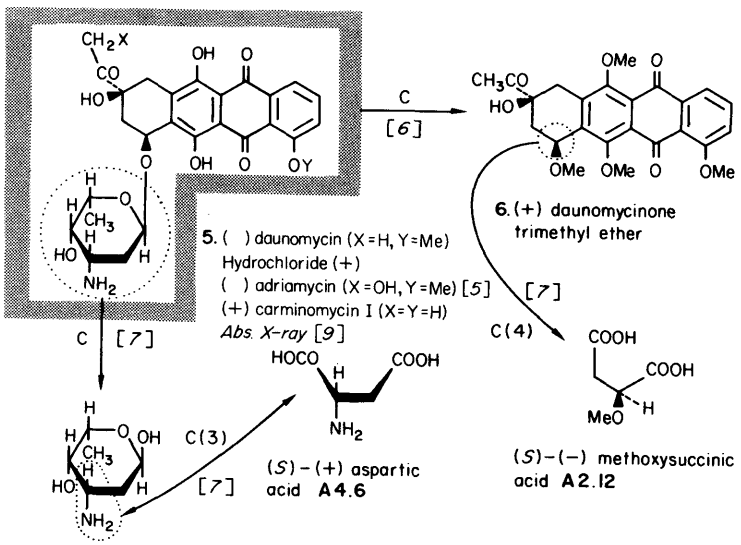
1. § (−) oxytetracycline (terramycin) [1]

2. ( ) aureomycin (chlortetracycline) (X = Cl). *Rel. X-ray* [2]
( ) achromycin (X = H). *Abs. X-ray* [3]

3. §( ) pillaromycin A. *Rel. X-ray* [8]

4. ( ) pillaronone. *Abs. X-ray* [3]

N.B. pillaromycin is the only known example of a tetracycline antibiotic having the antipodal-type configuration at the C/D ring junction relative to the other members of the group [3].



5. ( ) daunomycin (X = H, Y = Me) Hydrochloride (+)
( ) adriamycin (X = OH, Y = Me) [5]
(+) carminomycin I (X = Y = H)
Abs. X-ray [9]

6. (+) daunomycinone trimethyl ether

7. (−) daunosamine (3-amino-2,3,6-trideoxy-L-*lyxo*hexose)

Other antibiotics of the anthracyclinone group are derived from aglycones of the daunomycinone type by glycoside formation with various sugars [6]. The available evidence for their absolute configurations has been summarized [6].

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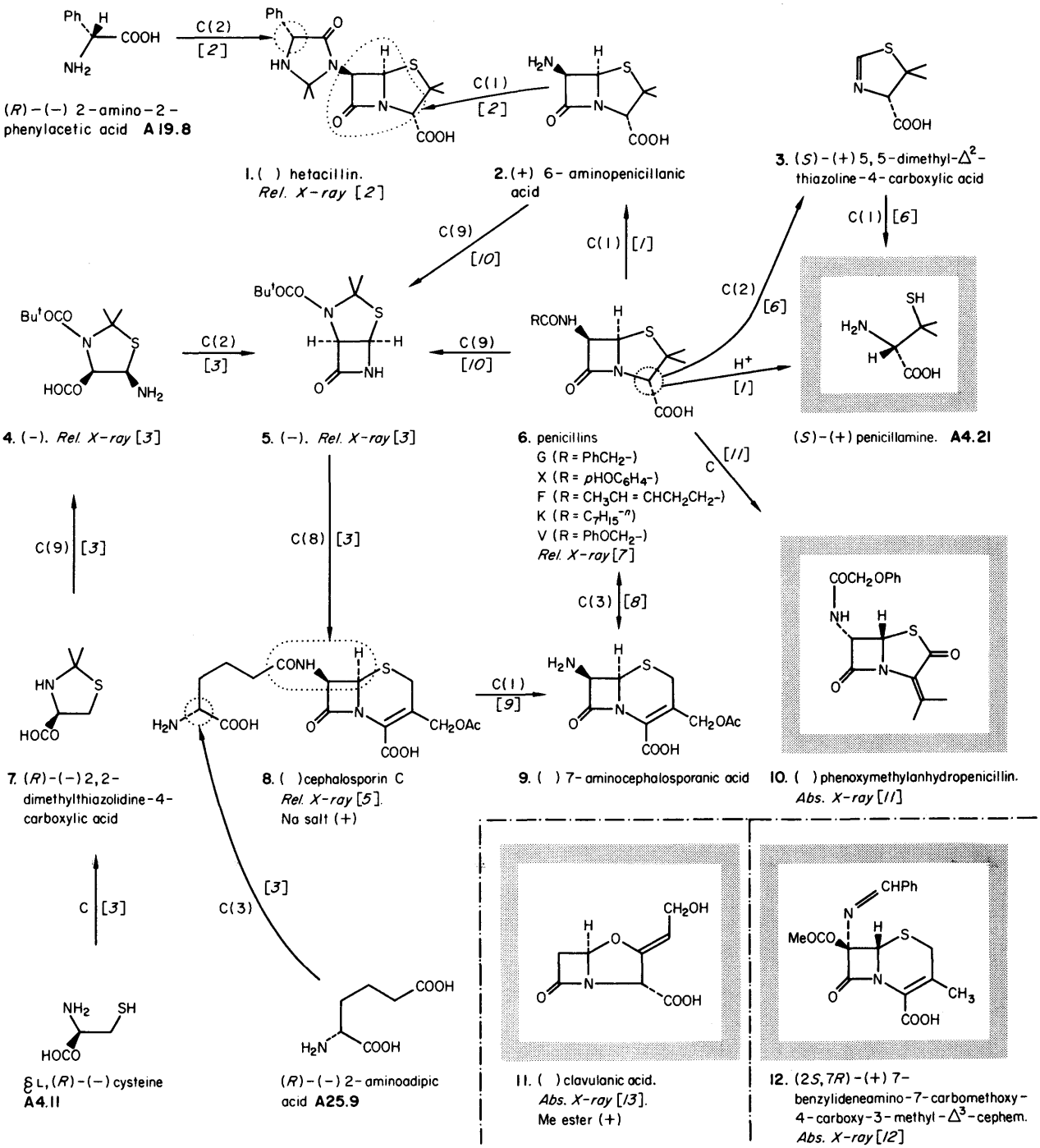

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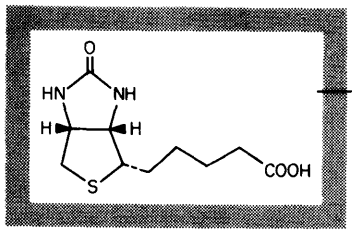
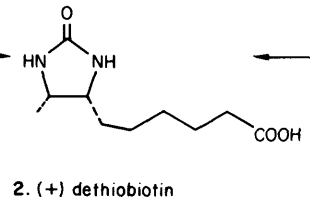
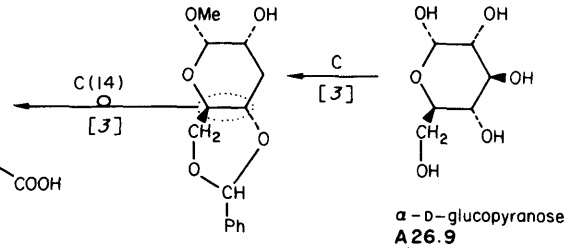
Biotin; miscellaneous antibiotics.



1. (+) biotin.
Abs. X-ray [1] ORD/CD; [4]
A9'

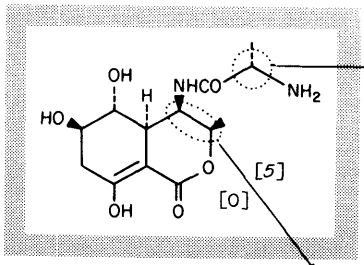


2. (+) dethiobiotin

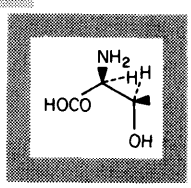


3. ( ) 4, 6 - *O* - benzylidene - 3 - deoxy - α - D - *ribo* - hexopyranoside

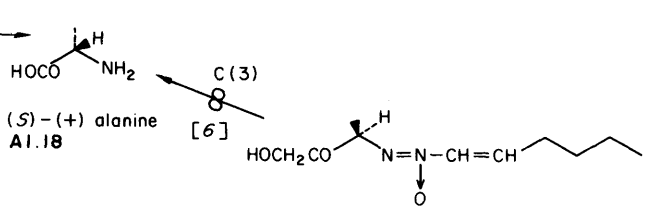
α - D - glucopyranose
A26.9



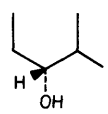
4. ( ) actinobolin.
Abs. X-ray [10]
Sulphate (+)



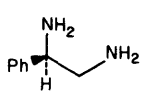
(−) threonine A8.16



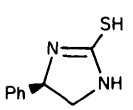
5. (*R*) - (+) 3 - (1 - hexenylazoxy) - 1 - hydroxybutan - 2 - one
(antibiotic LL-BH-872α)



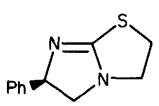
(*R*) - (+) 2 - methylpentan - 3 - ol A8.6



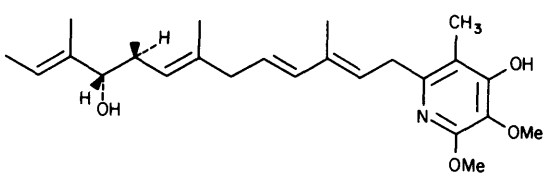
(*R*) - (−) phenylethylenediamine
A19.7



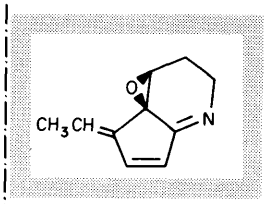
6. (*R*) - (−) 2 - mercapto - 4 - phenylimidazoline



7. (*R*) - (+) tetramisole



8. (−) piericidin A (small rotation)



9. (+) abikoviromycin
(latumcidin)
Abs. X-ray [9]

1. J. Trotter and J. A. Hamilton, *Biochemistry*, 1966, **5**, 713.
2. V. du Vigneaud, D. B. Melville, K. Folkers, D. E. Wolf, R. Mozingo, J. C. Keresztesy, and S. A. Harris, *J. Biol. Chem.*, 1942, **146**, 475.
3. H. Kuzuhara, H. Ohrui, and S. Emoto, *Tetrahedron Letters*, 1970, 1185.
4. N. M. Green, W. P. Mose, and P. M. Scopes, *J. Chem. Soc. (C)*, 1970, 1330.
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9. Y. Kono, S. Takeuchi, H. Yonehara, P. Marumo and Y. Saito, *Acta Cryst.*, 1971, **B27**, 2341.
10. J. B. Wetherington and J. W. Moncrief, *Acta Cryst.*, 1975, **B31**, 501.

-D-

Compounds with Chirality due to Isotopic substitution

Introductory Notes to Chapter D

Scope

Chapter D consists of compounds where the chirality is due solely to substitution of a hydrogen atom by deuterium or tritium (or, in one case, by substitution of ^{16}O by ^{18}O). Compounds containing stereospecifically incorporated deuterium or tritium in addition to other centres of chirality, of which many are known, are not specifically treated.

Application of (R,S) nomenclature

A sub-rule of the Cahn-Ingold-Prelog rules states that heavier isotopes take precedence over lighter. The order of priority of hydrogen isotopes is thus $^{3}H > {}^{2}H > {}^{1}H$.

Nomenclature

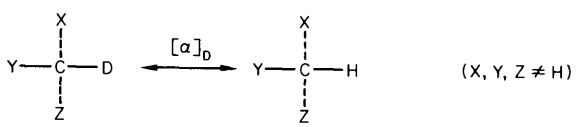
The IUPAC system of denoting isotopic substitution has been used in preference to the Chemical Abstracts system. Thus CH_3CHDOH is [1-^{2}H] ethanol rather than ethanol-1-*d*.

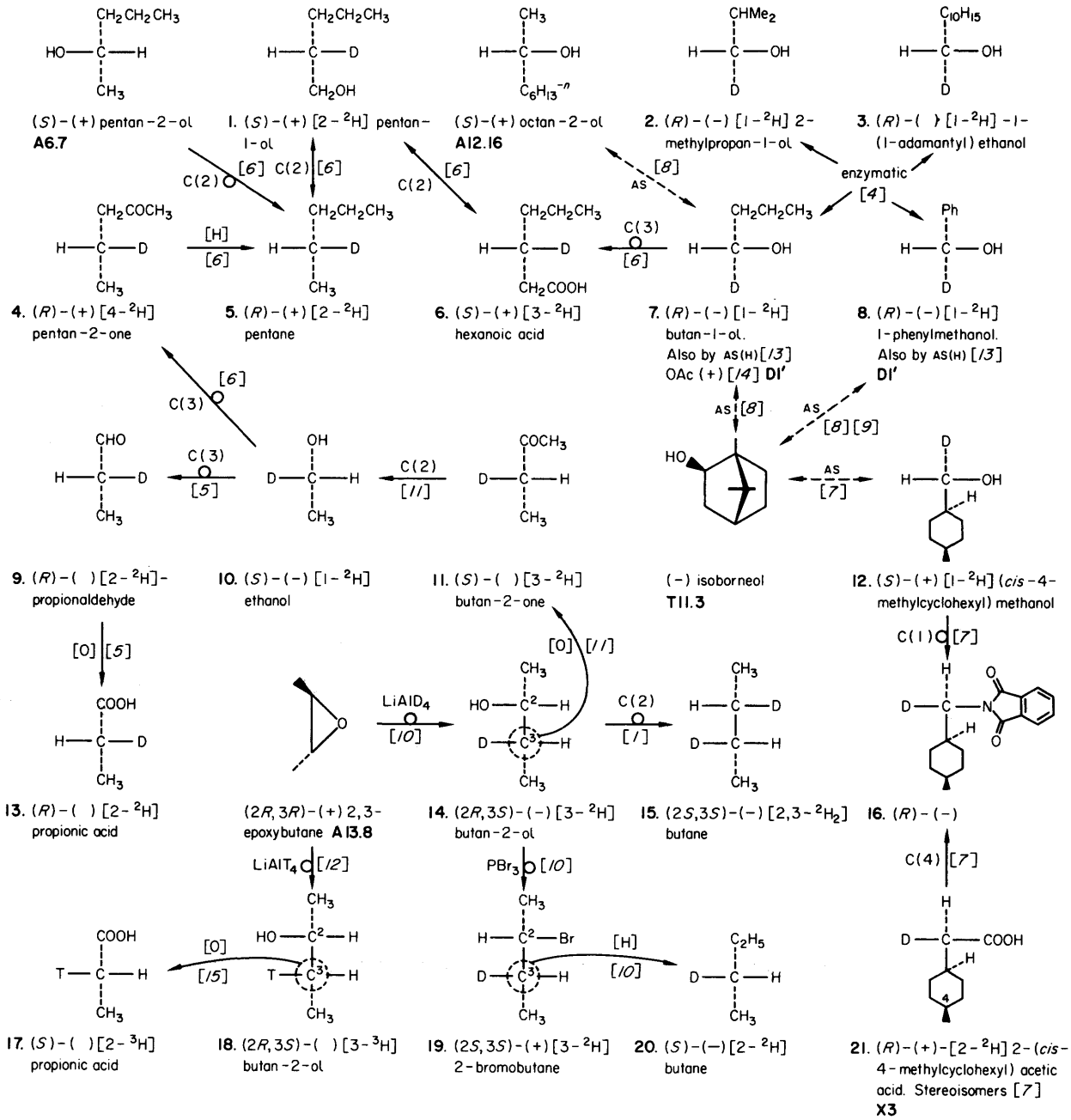
Brewster's rules

Brewster's rules (J. H. Brewster, *J.A.C.S.*, 1959, **81**, 5475) are a set of semi-empirical rules relating molecular chirality to sign of molecular rotation. For a molecule containing a chiral centre Cabde, the sign of rotation is predicted from the polarizabilities of the four groups abde. This rule has been used to predict the absolute configurations of a number of deutero-compounds where d = ^{2}H and e = ^{1}H.

Tertiary deuterium

The AC of compounds where the chirality is due to a tertiary deuterium atom can normally be readily and safely determined by $[\alpha]_D$ comparison with the corresponding protium compound.





1. G. K. Helmkamp and B. F. Rickborn, *J. Org. Chem.*, 1957, **22**, 479.
2. L. Verbit, *Progr. Phys. Org. Chem.*, 1970, **7**, 51.
3. D. Arigoni and E. L. Eliel, *Topics Stereochem.*, 1969, **4**, 107.
4. H. S. Mosher, *Tetrahedron*, 1974, **30**, 1733.
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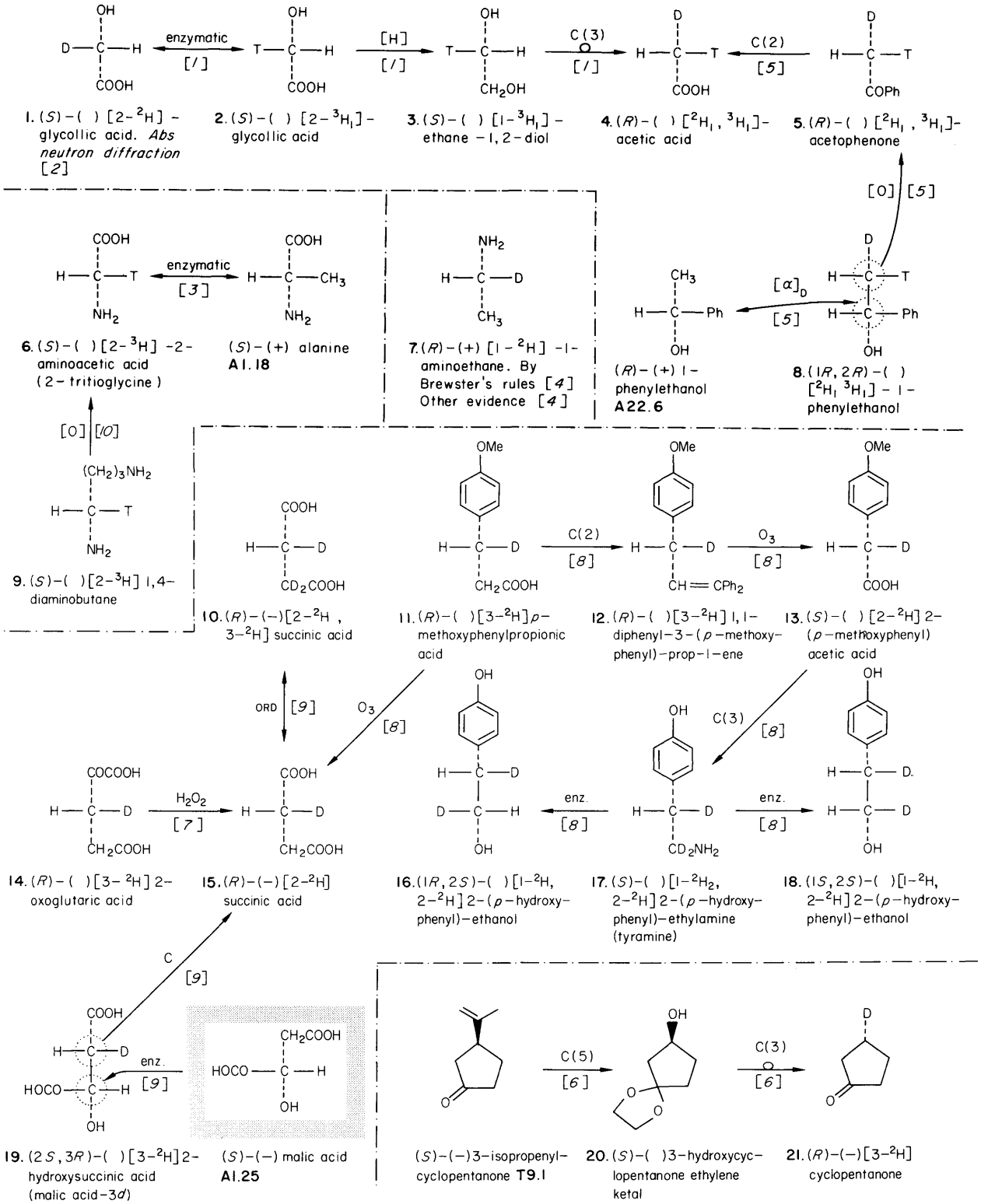
8. A. Streitweiser, J. R. Wolfe and W. D. Schaeffer, *Tetrahedron*, 1959, **6**, 338.
9. D. Nasipuri, C. K. Ghosh and R. J. L. Martin, *J. Org. Chem.*, 1970, **35**, 657.
10. G. K. Helmkamp, C. D. Joel and H. Sharman, *J. Org. Chem.*, 1956, **21**, 844.
11. H. Weber, J. Seibl and D. Arigoni, *Helv. Chim. Acta*, 1966, **49**, 741.
12. J. Retey and F. Lynen, *Biochem. Z.*, 1965, **342**, 256.
13. A. Horeau and A. Nouaille, *Tetrahedron Letters*, 1966, 3953.
14. L. Verbit, *J. Amer. Chem. Soc.*, 1967, **89**, 167.

D²



1. J. Lüthy, J. Rétey, and D. Arigoni, *Nature*, 1969, **221**, 1213.
2. C. K. Johnson, E. J. Gabe, M. R. Taylor, and I. A. Rose, *J. Amer. Chem. Soc.*, 1965, **87**, 1802.
3. M. Akhtar and P. M. Jordan, *Tetrahedron Letters*, 1969, 875.
4. W. Meister, R. D. Guthrie, J. L. Maxwell, D. A. Jaeger, and D. J. Cram, *J. Amer. Chem. Soc.*, 1969, **91**, 4452.
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6. J. W. Simek, D. L. Mattern and C. Djerassi, *Tetrahedron Letters*, 1975, 3671.
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8. C. Fuganti, D. Ghiringhelli, P. Grasselli and A. Santopietro-Amisano, *Chem. Comm.*, 1973, 862, and references therein.
9. G. Popják and J. W. Cornforth, *Biochem. J.*, 1966, **101**, 553.
10. E. Leistner and I. D. Spenser, *Chem. Comm.*, 1975, 378.

-X-

Compounds containing Chiral Axes, Planes, etc.

Introductory Notes to Chapter X

Scope

Chapter X contains compounds having axes and planes of chirality, and other synthetic compounds of purely stereochemical interest.

Establishment of the absolute configuration of compounds having axial or planar chirality by comparison with a compound containing a chiral centre is a problem of some difficulty. A number of different approaches have been employed; many of these entail a form of asymmetric synthesis. A recent review is by G. Krow in *Topics stereochem.*, 1970, 5, 31. In the 'Atlas' it is not possible to portray these various types of asymmetric synthesis in detail, but the user should have no difficulty in consulting the original publications.

Arrangement

Axes of chirality

Allenes, alkylidenecycloalkanes and related compounds **X1-X4**
Spiro compounds **X4-X5**

Axes of chirality; compounds showing atropisomerism

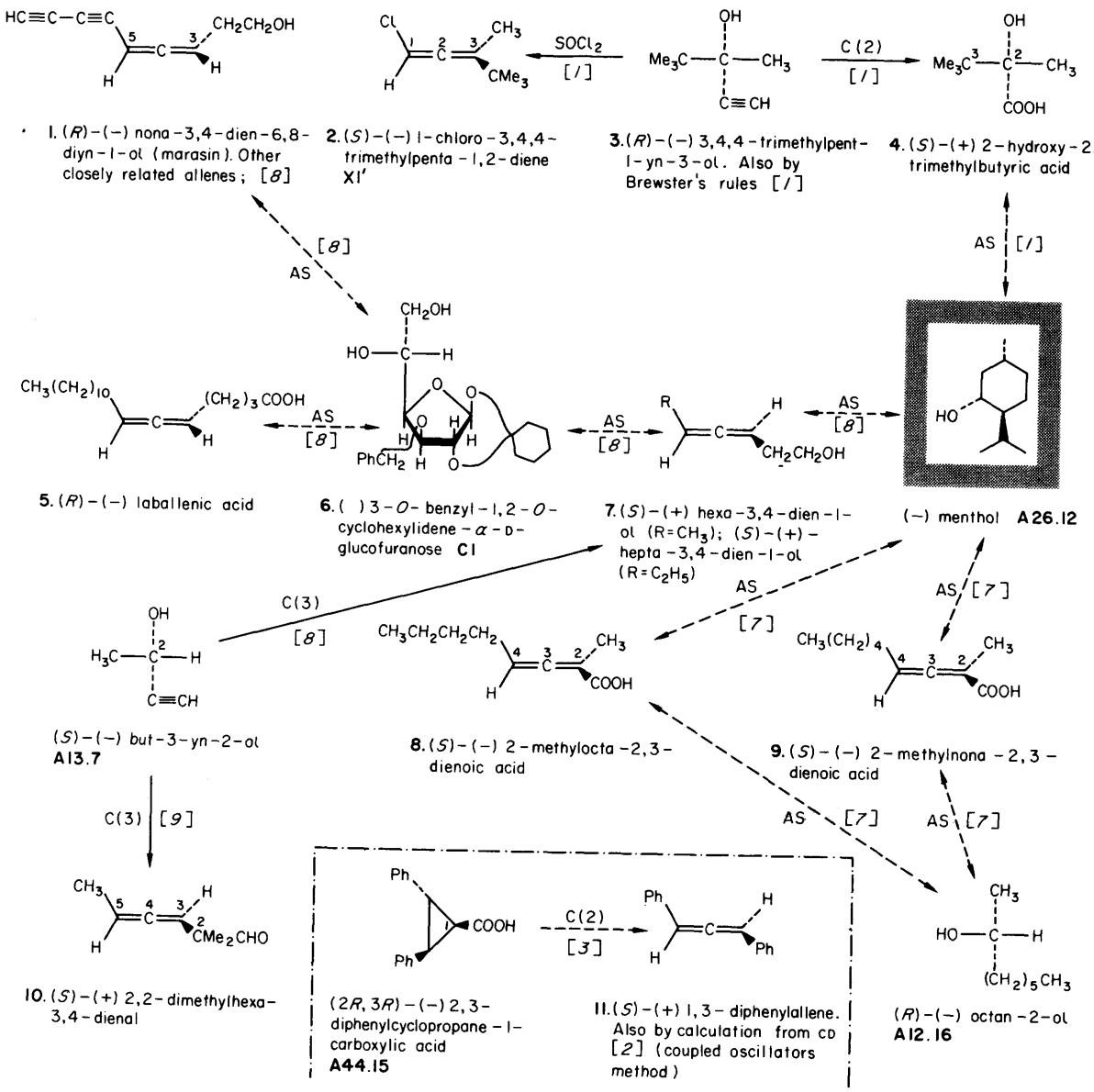
Biaryls **X5-X7**
Helicenes and related compounds **X7**

Planes of chirality

Cyclophanes **X8**
Metallocenes **X8-X9**

Miscellaneous compounds of C_2, C_3, D_2, and D_3 symmetry **X10-X11**

Lowe's rule for allenes. 'An allene is viewed along its orthogonal axis with the more polarizable substituent in the vertical axis uppermost. If the more polarizable substituent in the horizontal axis is to the right, then this enantiomer will be dextrorotatory and vice-versa' [4] [5] [6]. (This rule is not obeyed by cycloocta-1,2-diene X2.2.)



1. R. J. D. Evans and S. R. Landor, *J. Chem. Soc.*, 1965, 2553.
2. S. F. Mason and G. W. Vane, *Tetrahedron Letters*, 1965, 1593.
3. W. M. Jones and J. W. Wilson, *Tetrahedron Letters*, 1965, 1587.
4. G. Lowe, *Chem. Comm.*, 1965, 411.
5. G. Krow, *Topics Stereochem.*, 1970, 5, 31.
6. P. Crabbé, E. Velarde, H. W. Anderson, S. D. Clark, W. R. Moore, A. F. Drake, and S. F. Mason, *Chem. Comm.*, 1971, 1261.
7. I. Tömösközi and H. J. Bestmann, *Tetrahedron Letters*, 1964, 1293.
8. R. J. D. Evans, S. R. Landor, and J. P. Regan, *Chem. Comm.*, 1965, 397; S. R. Landor, B. J. Miller, J. P. Regan, and A. R. Tatchell, ibid., 1966, 585.
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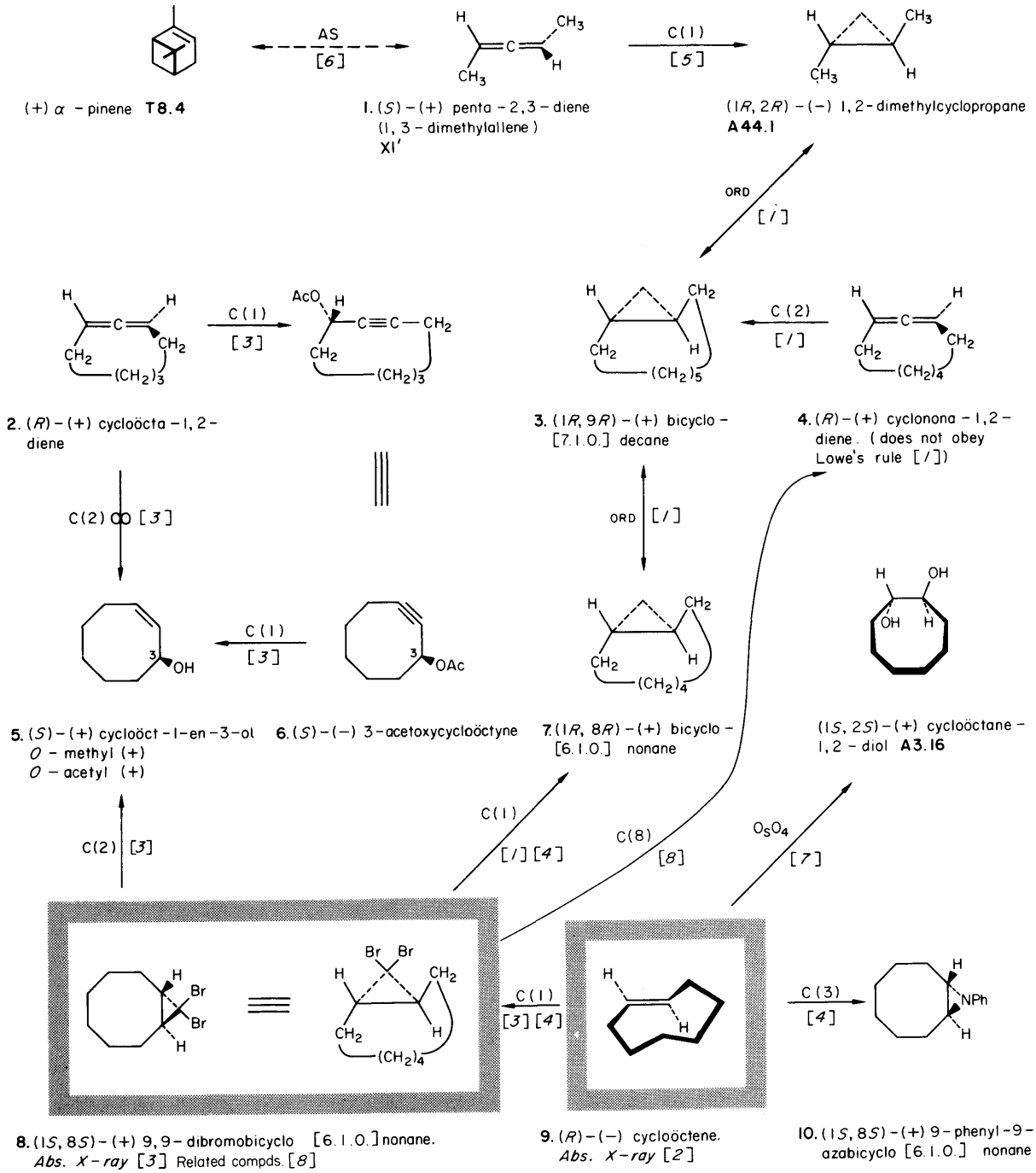

1. W. R. Moore, *J. Amer. Chem. Soc.*, 1971, **93**, 4932.
2. P. C. Manor, D. P. Shoemaker, and A. S. Parkes, *J. Amer. Chem. Soc.*, 1970, **92**, 5261.
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4. T. Aratani, Y. Nakanishi, and H. Nozaki, *Tetrahedron*, 1970, **26**, 4339.
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6. W. L. Waters and M. C. Caserio, *Tetrahedron Letters*, 1968, 5233.
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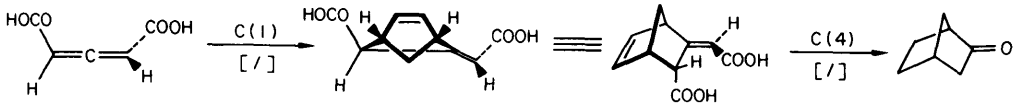
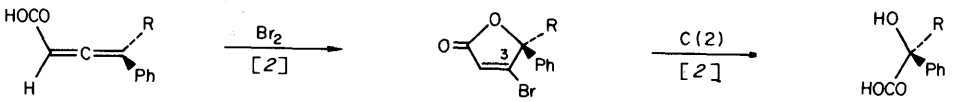
8. W. R. Moore and R. D. Bach, *J. Amer. Chem. Soc.*, 1972, **94**, 3148.

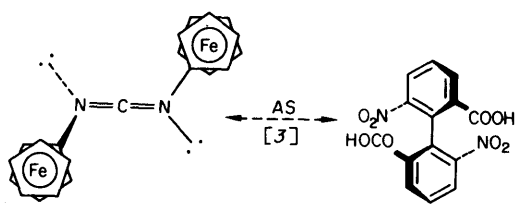


1. (*R*)-(−) pentadiendioic (glutinic) acid
2. (+) glutinic acid cyclopentadiene adduct
(+) norcamphor **A36.11**

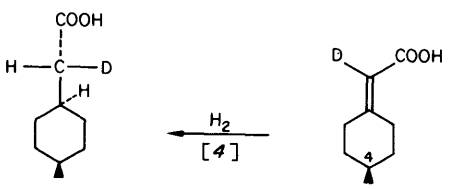


3. (*S*)-(+) phenyl alkyl allenic acids (R=H, CH_3, C_2H_5, $CHMe_2$, CMe_3)
4. (*S*)-(+) 3-bromo-4-alkyl-4-phenylcrotonolactones (R=H, CH_3, C_2H_5, $CHMe_2$, CMe_3)

(*S*)-(+) mandelic acid (R=H) **A21.12**
(*S*)-alkylmandelic acids **A31.19, A51.14, A51.1, A51.19** (R = CH_3, C_2H_5, $CHMe_2$, CMe_3)

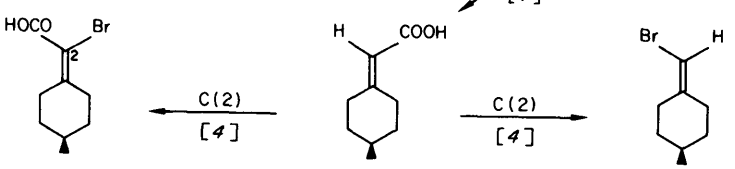


5. (*R*)-(−) *N, N'*-diferrocenyl-carbodiimide
6. (*S*)-(−) 6, 6'-dinitro-2, 2'-diphenic acid **X5, X6**



(*R*)-(+)[2-^{2}H]-2-(*cis*-4-methylcyclohexyl)-acetic acid **D1.21**

7. (*S*)-(+) 4-methylcyclohexylideneacetic acid -α-*d*



8. (*S*)-(+) 2-bromo-2-(4-methylcyclohexylidene) acetic acid
9. (*S*)-(+) 4-methylcyclohexylideneacetic acid
10. (*R*)-(−) (4-methylcyclohexylidene) bromomethane XI′

1. W. C. Agosta, *J. Amer. Chem. Soc.*, 1964, **86**, 2638.
2. K. Shingu, S. Hagishita, and M. Nakagawa, *Tetrahedron Letters*, 1967, 4371.
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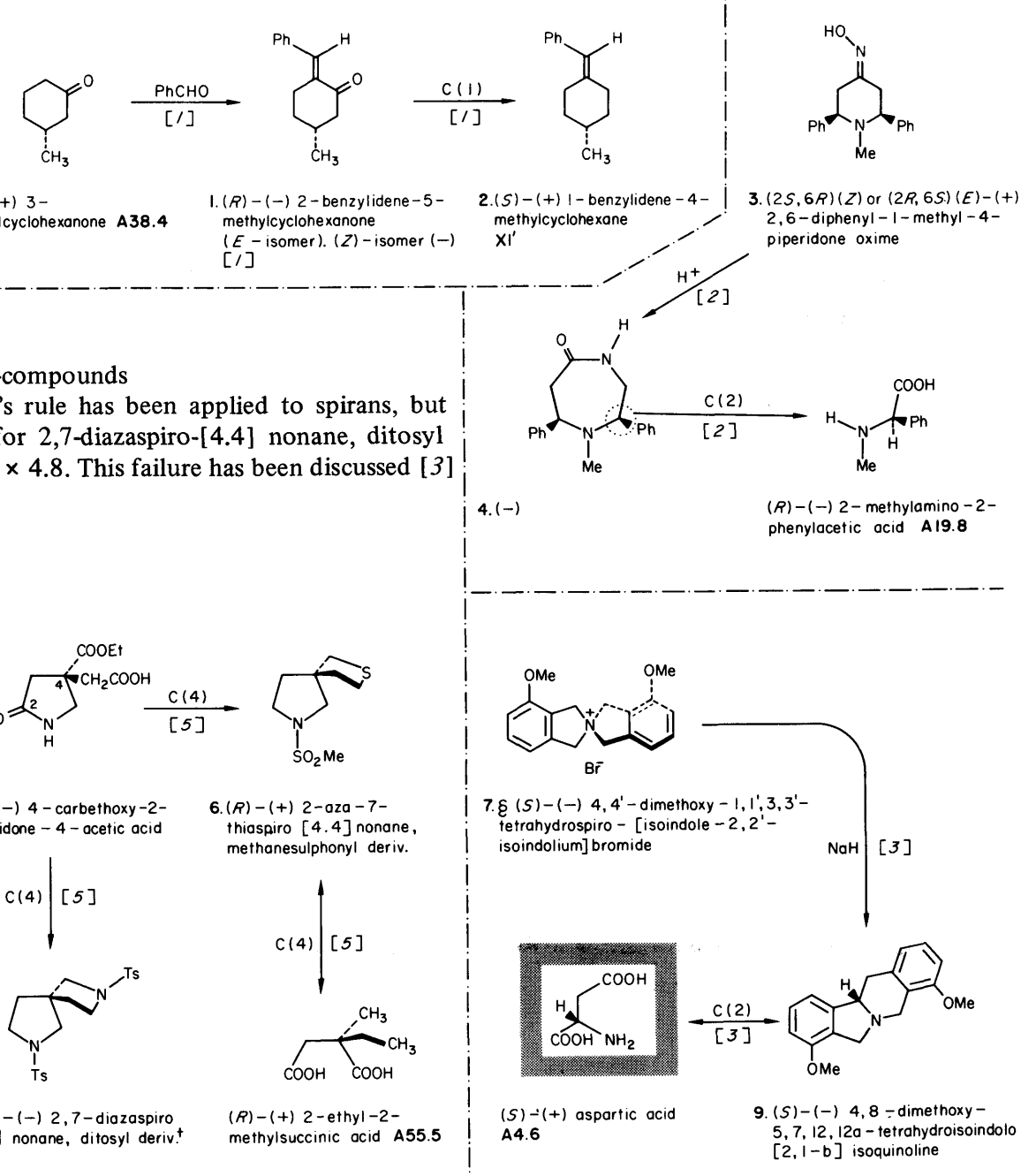

Spiro-compounds

Lowe's rule has been applied to spirans, but fails for 2,7-diazaspiro-[4.4] nonane, ditosyl deriv × 4.8. This failure has been discussed [3] [4].

1. J. H. Brewster and J. E. Privett, *J. Amer. Chem. Soc.*, 1966, **88**, 1419.
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4. H. Wynberg and J. P. M. Houbiers, *J. Org. Chem.*, 1971, **36**, 834.
5. G. Krow and R. K. Hill, *Chem. Comm.*, 1968, 430.
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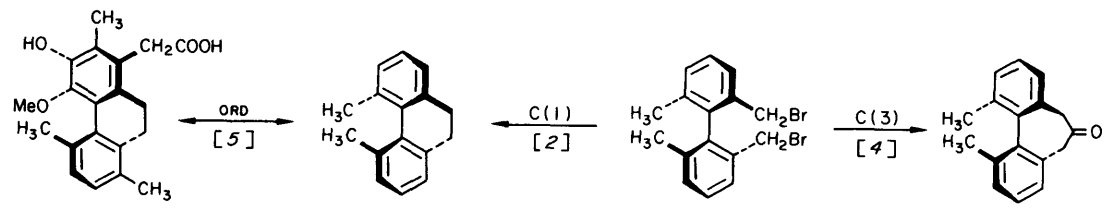
†Redesignated here as centrally chiral molecules with consequent reversal of the original (*R*,*S*) assignment [6].

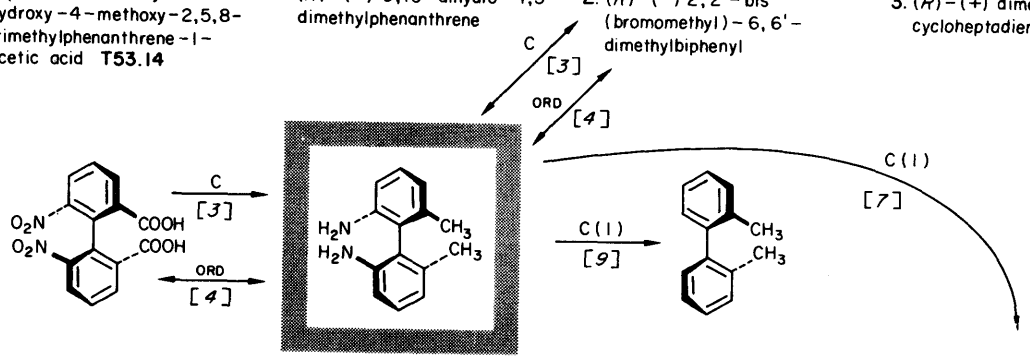


(S)-(+) 9,10-dihydro-3-hydroxy-4-methoxy-2,5,8-trimethylphenanthrene-1-acetic acid **T53.14**

1. (R)-(−) 9,10-dihydro-4,5-dimethylphenanthrene

2. (R)-(−) 2,2'-bis (bromomethyl)-6,6'-dimethylbiphenyl

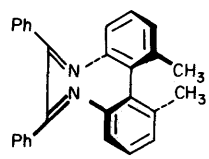
3. (R)-(+) dimethyldibenz-1,3-cycloheptadiene-6-one



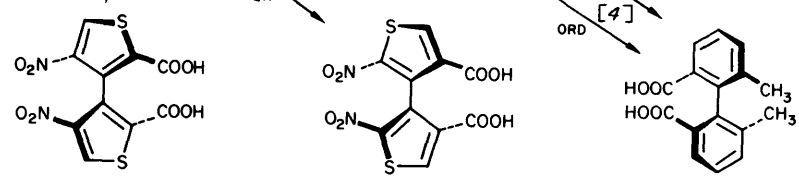
(R)-(+) 6,6'-dinitro-2,2'-diphenic acid **X3.6**

4. (R)-(+) 2,2'-diamino-6,6'-dimethylbiphenyl.
Abs. X-ray [6] D3'

5. (R)-(−) 2,2'-dimethylbiphenyl



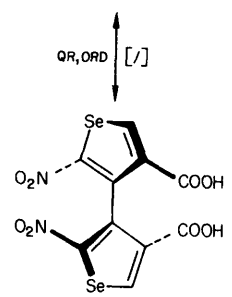
9. (R)-(−) 1,2-dimethyl-6,7-diphenyldibenzo [e,g] [1,4] diazocine.
Other related heterocylic 2,2' bridged biaryls; [3][7]



6. (R)-(+) 4,4'-dinitro-3,3'-bithienyl-2,2'-dicarboxylic acid

7. (R)-(+) 2,2'-dinitro-3,3'-bithienyl-4,4'-dicarboxylic acid

8. (R)-(−) 6,6'-dimethyl-2,2'-diphenic acid **X6, X10, X4'**



10. (R)-(+)2,2'-dinitro-3,3'-biselenienyl-4,4'-dicarboxylic acid

1. C. Dell'Erba, D. Spinelli, G. Garbarino and G. Leandri, *J. Heterocyclic Chem.*, 1968, **5**, 45.
2. K. Mislow and H. B. Hopps, *J. Amer. Chem. Soc.*, 1962, **84**, 3018.
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5. T. R. Hollands, P. de Mayo, M. Nisbet, and P. Crabbé, *Canad. J. Chem.*, 1965, **43**, 3008.
6. L. H. Pignolet, R. P. Taylor, and W. De W. Horrocks, *Chem. Comm.*, 1968, 1443.
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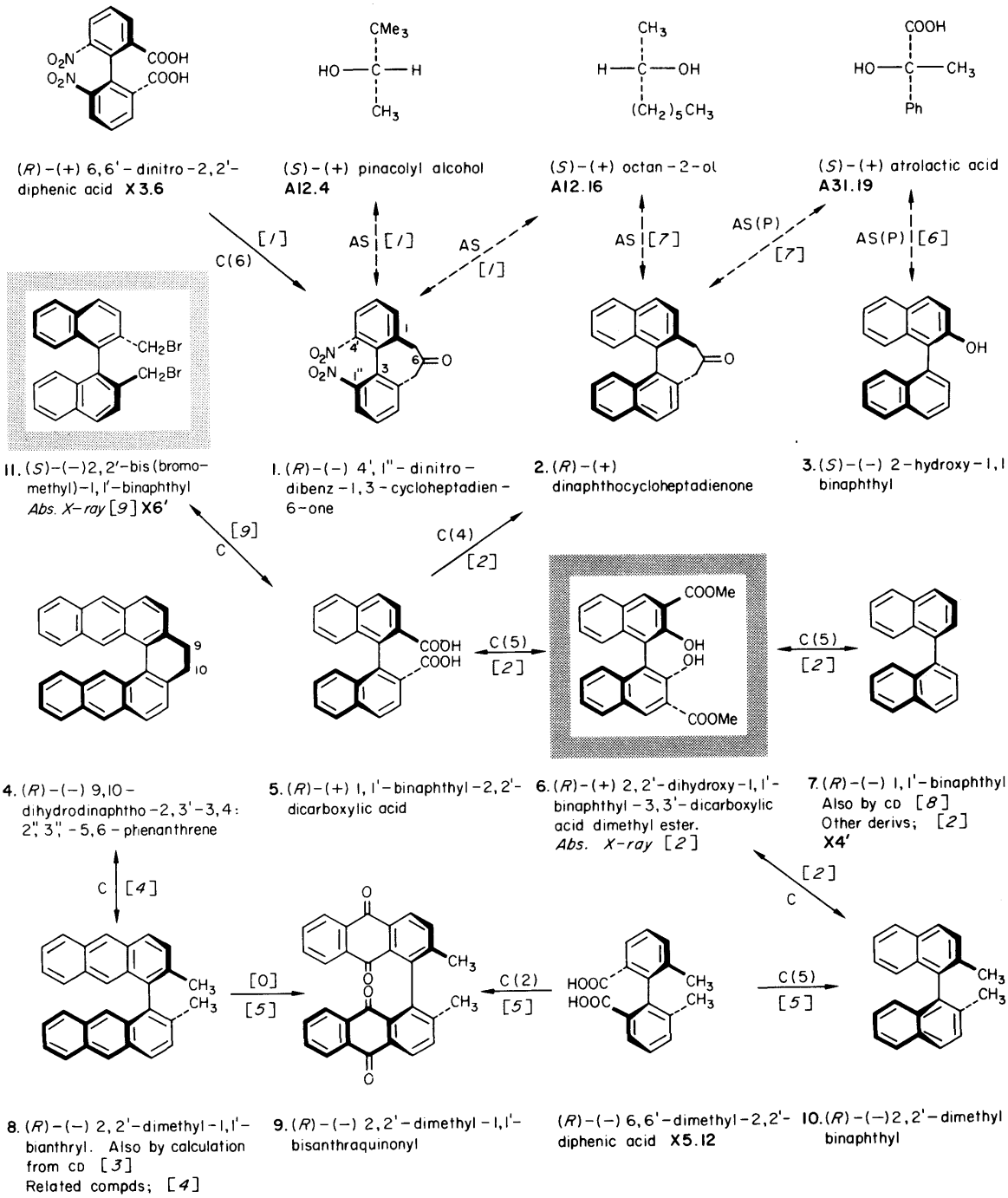
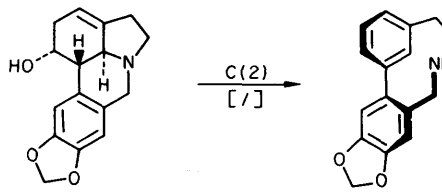
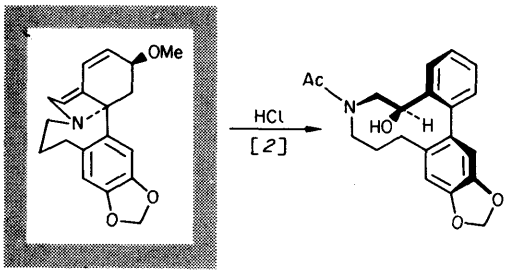


1. P. Newman, P. Rutkin, and K. Mislow, *J. Amer. Chem. Soc.*, 1958, **80**, 465.
2. H. Akimoto, T. Shioiri, Y. Iitaka, and S. Yamada, *Tetrahedron Letters*, 1968, 97.
3. R. Grinter and S. F. Mason, *Trans. Faraday Soc.*, 1964, **60**, 274.
4. G. M. Badger, R. J. Drewer, and G. E. Lewis, *J. Chem. Soc.*, 1962, 4268.
5. S. Yamada and H. Akimoto, *Tetrahedron Letters*, 1968, 3967.
6. J. A. Berson and M. A. Greenbaum, *J. Amer. Chem. Soc.*, 1958, **80**, 653.
7. K. Mislow, V. Prelog, and H. Scherrer, *Helv. Chim. Acta*, 1958, **41**, 1410; K. Mislow and F. A. McGinn, *J. Amer. Chem. Soc.*, 1958, **80**, 6036.
8. P. A. Browne, M. M. Harris, R. Z. Mazengo, and S. Singh, *J. Chem. Soc. (C)*, 1971, 3990.
9. K. Harata and J. Tanaka, *Bull. Chem. Soc. Japan.*, 1973, **46**, 2747.



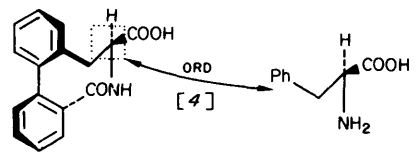
( ) caranine **K6.3**

1. (*S*)-(−) caranine anhydromethine ORD/CD; [*1*]

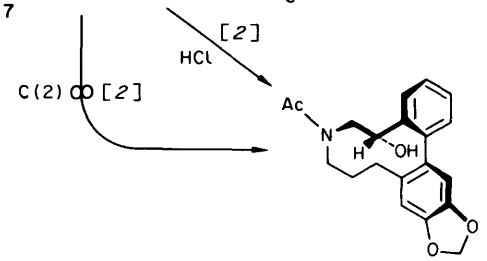


(+) schellhammeridine **K7.7**

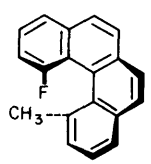
2. § (*aS*,*7R*)-(+)†



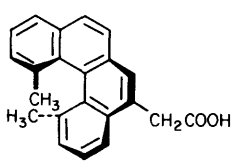
3. ( ) By ORD [*4*] (*S*)-( ) phenylalanine **A5.12**



4. § (*aS*, *7S*)-(+)†



5. (*S*)-(or *P*)-(+) 1-fluoro-12-methylbenzo [c] phenanthrene. By calculation from CD [*3*] ‡



6. (*S*)-(or *P*)-(+) 1, 12-dimethylbenzo [c] phenanthrene-5-acetic acid. By calculation from CD [*3*] ‡

1. E. W. Warnhoff and S. V. Lopez, *Tetrahedron Letters*, 1967, 2723.
2. S. R. Johns, J. A. Lamberton, A. A. Sioumis, and H. Suares, *Chem. Comm.*, 1969, 646.
3. C. M. Kemp and S. F. Mason, *Chem. Comm.*, 1965, 559.
4. B. Belleau and R. Chevalier, *J. Amer. Chem. Soc.*, 1968, **90**, 6864.

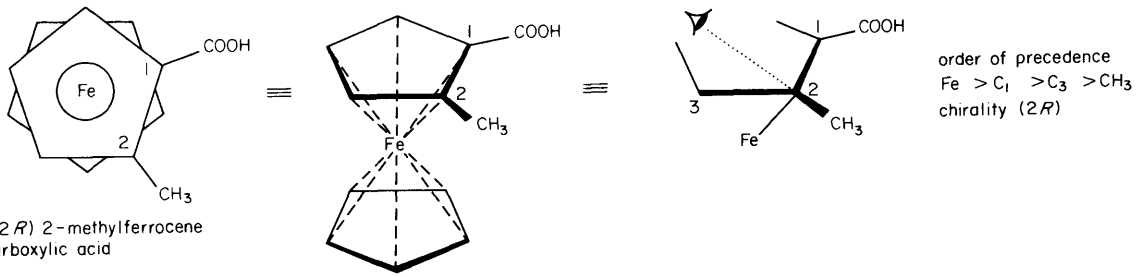
†Chirality specified according to the revised (1966) Cahn-Ingold-Prelog rules (*Angew. Chem. Internat. Edn.*, 1966, **5**, 385).

‡The recent X-ray determination of the absolute configuration of [6]-helicene has validated the method used [*1*] for calculation of the absolute configurations of other helicene systems.

Metallocenes (Review; [*1*])

Application of the (R,S) system to metallocenes

The most widely employed system for specification of metallocene chirality was put forward by Schlögl in consultation with Cahn and Prelog [*1*]. The bond from the central metal atom to the ring carbon atom under consideration is treated as a formal single bond. The carbon atom is then considered as a chiral centre and (*R,S*) nomenclature is applied in the usual way.



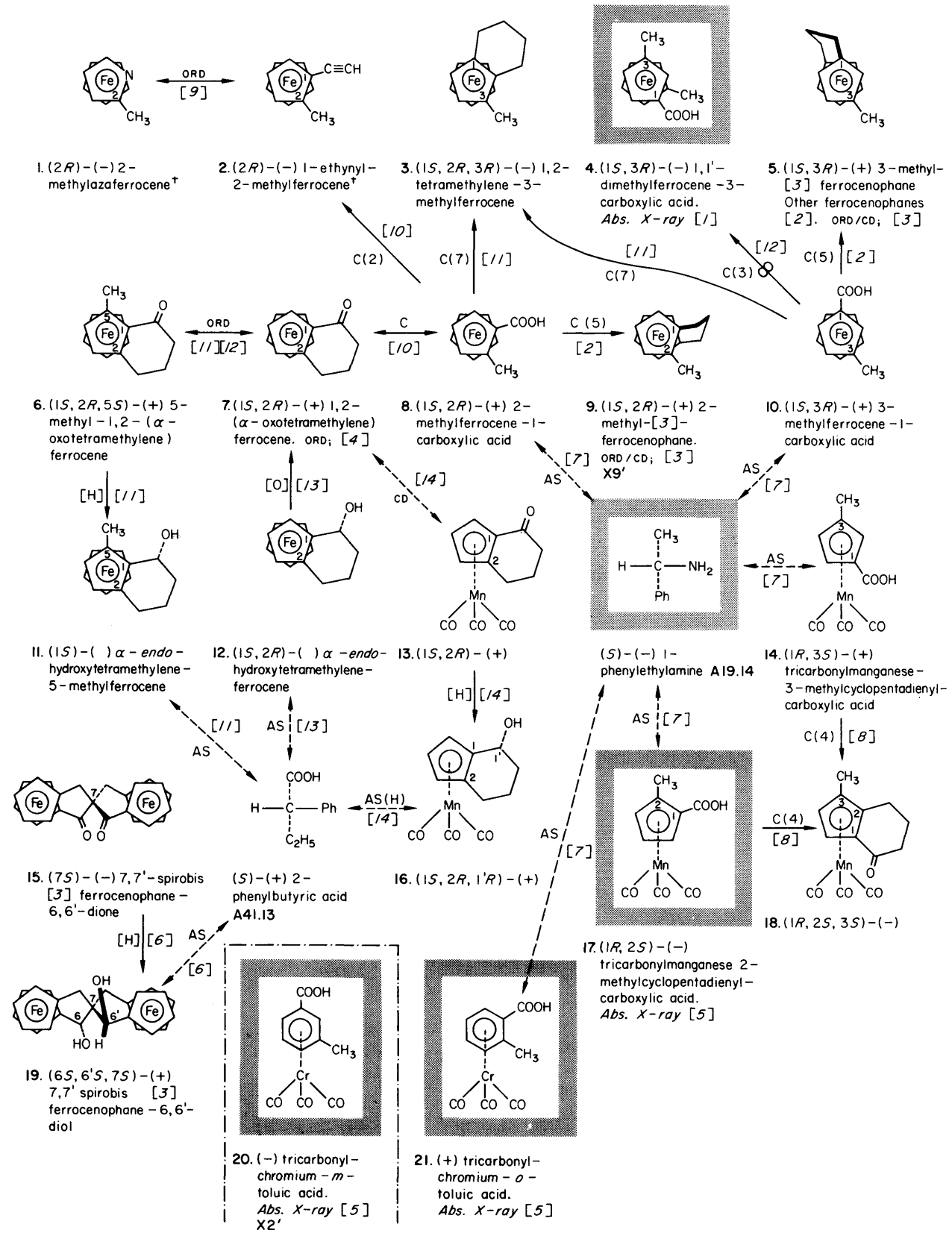
(1*S*, 2*R*) 2-methylferrocene 1-carboxylic acid

A recent publication [*2*] has suggested the readoption of an earlier proposal [*1*] according to which the molecule is treated overall as a case of planar chirality (cf. cyclophanes). In view of its widespread use, however, the Schlögl-Cahn-Prelog system is employed here [*3*].

1. K. Schlögl, *Topics Stereochem.*, 1967, 39.
2. D. Marquarding, H. Klusacek, G. Gokel, P. Hoffmann, and I. Ugi, *J. Amer. Chem. Soc.*, 1970, **92**, 5389.
3. K. Schlögl, Personal communication.

8. H. Gowal and K. Schlögl, *Monatsh*, 1968, **99**, 267.
9. K. Bauer, H. Falk, and K. Schlögl, *Angew. Chem. Internat. Edn.*, 1969, **8**, 135.
10. H. Falk and K. Schlögl, *Tetrahedron*, 1966, **22**, 3047 and references therein.
11. G. Haller and K. Schlögl, *Monatsh*, 1967, **98**, 2044.
12. H. Falk and K. Schlögl, *Monatsh*, 1971, **102**, 33 and references therein.
13. H. Falk and K. Schlögl, *Monatsh*, 1965, **96**, 266.
14. S. G. Cottis, H. Falk, and K. Schlögl, *Tetrahedron Letters*, 1965, 2857.

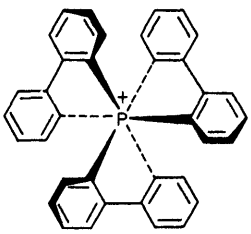
†Compounds **X9.1** and **X9.2** are examples of compounds having pure planar chirality independently of any conformation contribution from substituents [*10*]. A correlation, analogous to Brewster's Rules, between absolute configuration and rotation sign, has been put forward for this type of compound [*10*].



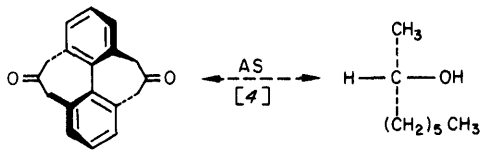
1. O. L. Carter, A. T. McPhail, and G. A. Sim, *J. Chem. Soc. (A)*, 1967, 365.
2. H. Falk, O. Hofer, and K. Schlögl, *Monatsh*, 1969, **100**, 624.
3. H. Falk and O. Hofer, *Monatsh*, 1969, **100**, 1540.
4. H. Falk and K. Schlögl, *Monatsh*, 1968, **99**, 279.
5. M. A. Bush, T. A. Dullforce, and G. A. Sim, *Chem. Comm.*, 1969, 1491.
6. H. Falk, W. Fröstl, and K. Schlögl, *Monatsh*, 1971, **102**, 1270.
7. H. Falk and K. Schlögl, *Monatsh*, 1968, **99**, 578.

References continued on page 222

Review; [2]

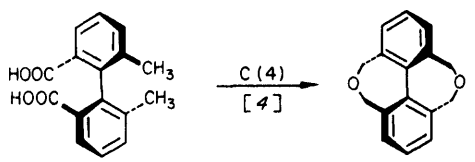


1. (*M*)-(−) tris-2,2'-bisphenylenephosphorus (V) ion (*C_3 symmetry*) By calculation from CD [1]



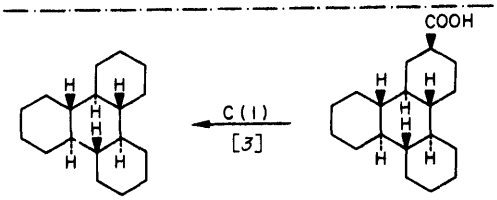
5. (*R*)-(+) 4,5,6,10,11,12-hexahydrodibenzo-[ef, kl]-heptalene-5,11-dione (*D_2 symmetry*)

(*S*)-(+) octan-2-ol A12.16



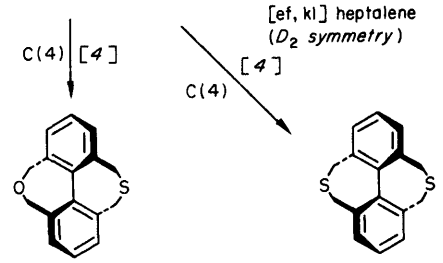
(*R*)-(−) 6,6'-dimethyl-2,2'-diphenic acid X5.12

7. (*R*)-(+) 10,12-dihydro-4H,6H-5,11-dioxadibenzo [ef, kl] heptalene (*D_2 symmetry*)



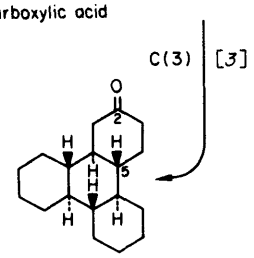
8. (*S*)-(+) perhydrotriphenylene (*D_3 symmetry*)

9. (2*S*)-(+) perhydrotriphenylene-2-carboxylic acid



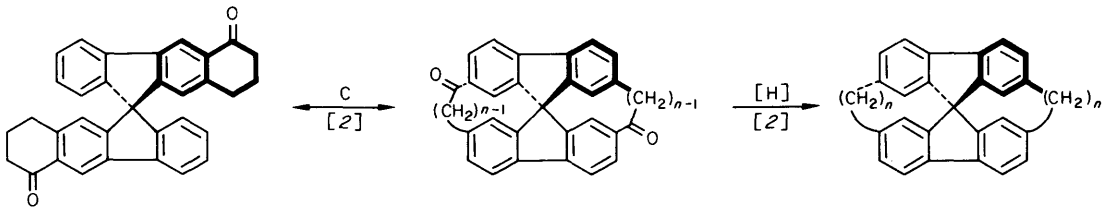
10. (*R*)-(+) 10,12-dihydro-4H,6H-5,11-oxathiadibenzo-[ef, kl] heptalene (*C_2 symmetry*)

11. (*R*)-(+) 10,12-dihydro-4H,6H-5,11-dithiadibenzo-[ef, kl] heptalene (*D_2 symmetry*)



12. (5*R*)-(+) perhydrotriphenylene-2-one. By ORD [3] (octant rule)

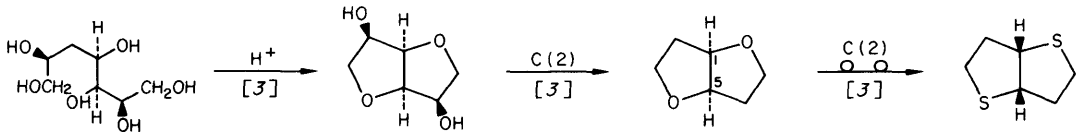
1. D. Hellwinkel and S. F. Mason, *J. Chem. Soc. (B)*, 1970, 640.
2. M. Farina and C. Morandi, *Tetrahedron*, 1974, **30**, 1819.
3. M. Farina and G. Audisio, *Tetrahedron*, 1970, **26**, 1839.
4. K. Mislow, M. A. W. Glass, H. B. Hopps, E. Simon, and G. H. Wahl, *J. Amer. Chem. Soc.*, 1964, **86**, 1710.



1. (*R*)-(+) 2,3,2',3'-bis (α-oxo-tetramethylene)-9,9'-spirobifluorene. By CD [1] Related compds. [1] [2]

2. (*R*)-(−) [6, 6] - vespirone (*n* = 6)
(*R*)-(−) [7, 7] - vespirone (*n* = 7)
(*R*)-(−) [8, 8] - vespirone (*n* = 8)
By CD [1]
Related compds. [1] [2]

3. (*R*)-(−) [6,6]-vespirene (*n* = 6)
(*R*)-(−) [7,7]-vespirene (*n* = 7)
(*R*)-(−) [8,8]-vespirene (*n* = 8)
(*D*$_2$ *symmetry*) By CD [1]
Related compds. [1] [2]

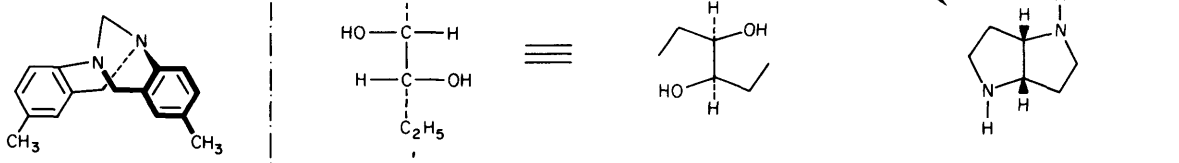


D (−) mannitol AII.1

4. D (+) isomannide

5. (1*R*, 5*R*)-(+)2,6-dioxabicyclo-[3.3.0] octane

6. (1*S*,5*S*)-(−) 2,6-dithiabicyclo-[3.3.0] octane



7. (+) Tröger's base. By calculation from CD [4] (coupled oscillators)

8. (3*R*, 4*R*)-(+) hexane-3,4-diol

9. (1*S*,5*S*)-(−) 2,6-diazabicyclo-[3.3.0] octane

1. G. Haas, P. B. Hulbert, W. Klyne, V. Prelog, and G. Snatzke, *Helv. Chim. Acta*, 1971, **54**, 491.
2. G. Haas and V. Prelog, *Helv. Chim. Acta*, 1969, **52**, 1202.
3. A. C. Cope and T. Y. Shen, *J. Amer. Chem. Soc.*, 1956, **78**, 5916.
4. S. F. Mason, G. W. Vane, K. Schofield, R. J. Wells, and J. S. Whitehurst, *J. Chem. Soc. (B)*, 1967, 553.

-Z-

Compounds containing Chiral Atoms other than Carbon

Introductory Notes to Chapter Z

Chapter Z deals with chiral compounds containing silicon, germanium, tin, lead, nitrogen, phosphorus, arsenic, and sulphur.

Arrangement

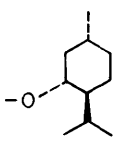
(1) Compounds containing a silicon, germanium, tin, or lead atom directly attached to a chiral carbon atom—page **Z1**.
(2) Compounds containing a chiral silicon or germanium atom—pages **Z1-Z2**.
(3) Compounds containing a chiral nitrogen, phosphorus or arsenic atom—pages **Z3-Z6**.
(4) Compounds containing a chiral sulphur atom—pages **Z7-Z8**.

For compounds containing a nitrogen or sulphur atom directly attached to a chiral carbon atom, see Chapter *A*.

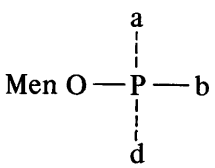
Abbreviations

For clarity, the following abbreviations are used throughout section Z.

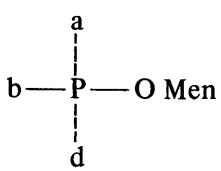
Men = (-) menthyl,



Note that since the menthyl group contains three chiral centres, forms such as



and



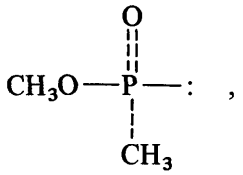
are diastereoisomers and not enantiomers.

Np = naphthyl, $C_{10}H_7$.

Specification of chirality at phosphorus and sulphur

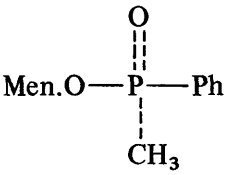
The Cahn-Ingold-Prelog rules contain a sub-rule which states that d orbital expansion is disregarded in assigning chirality. Hence, the SO bond in sulphoxides and the PO, PS etc. bond in P(V)

compounds is regarded as a formal single bond. For example in the compound



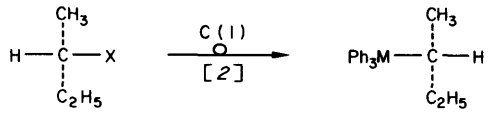
the order of precedence of the four substituents is $OCH_3 > = O > CH_3 >$ lone pair and the chirality is (*S*).

In dealing with compounds containing chiral P,S or other hetero-atoms, a recent development has been the introduction of P S, etc. as a subscript to denote the chirality at the hetero-atom as distinct from that at other chiral centres in the molecule, for example



= (*R*)P - menthyl methylphenyl phosphinate

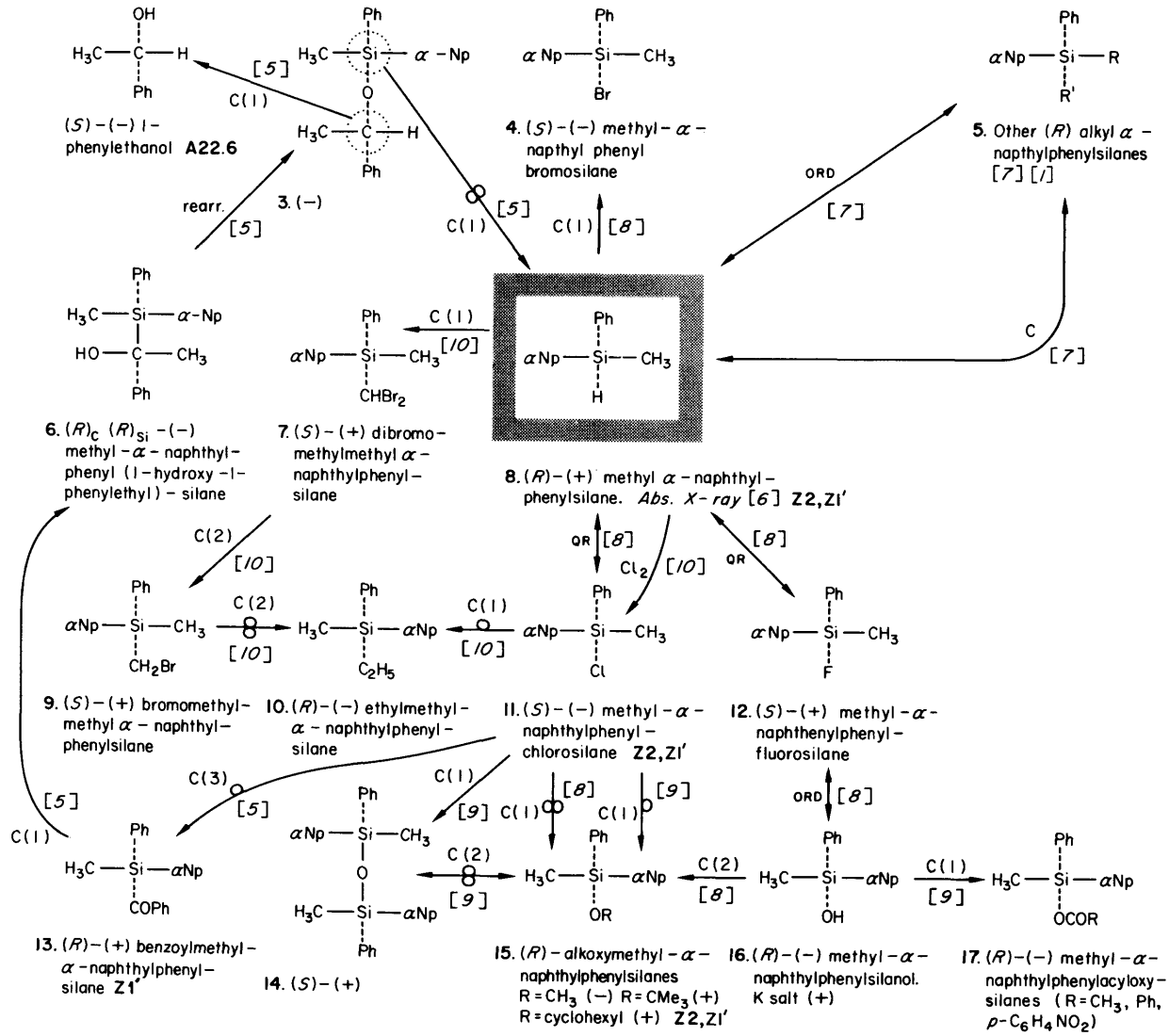
(a) Compounds containing a silicon, germanium, tin or lead atom directly attached to a chiral carbon atom.



(*S*)-(+) 2-halogenobutanes (X = Cl, Br) A1.11

2. (*R*)-(−) (1-methylpropyl)-triphenyl silane, germane, stannane, plumbane (M = Si, Ge, Sn, Pb)

(b) Compounds containing a chiral silicon or germanium atom. (Reviews; [3] [4].) See [3] for further compounds not given here.



(*S*)-(−) 1-phenylethanol A22.6

3. (−)

4. (*S*)-(−) methyl-α-napthyl phenyl bromosilane

5. Other (*R*) alkyl α-napthylphenylsilanes [7] [7]

6. $(R)_C$ $(R)_{Si}$ -(−) methyl-α-naphthyl-phenyl (1-hydroxy-1-phenylethyl)-silane

7. (*S*)-(+) dibromo-methylmethyl α-naphthylphenyl-silane

8. (*R*)-(+) methyl α-naphthyl-phenylsilane. *Abs. X-ray* [6] Z2,Z1'

9. (*S*)-(+) bromomethyl-methyl α-naphthyl-phenylsilane

10. (*R*)-(−) ethylmethyl-α-naphthylphenyl-silane

11. (*S*)-(−) methyl-α-naphthylphenyl-chlorosilane Z2,Z1'

12. (*S*)-(+) methyl-α-naphthenylphenyl-fluorosilane

13. (*R*)-(+) benzoylmethyl-α-naphthylphenyl-silane Z1'

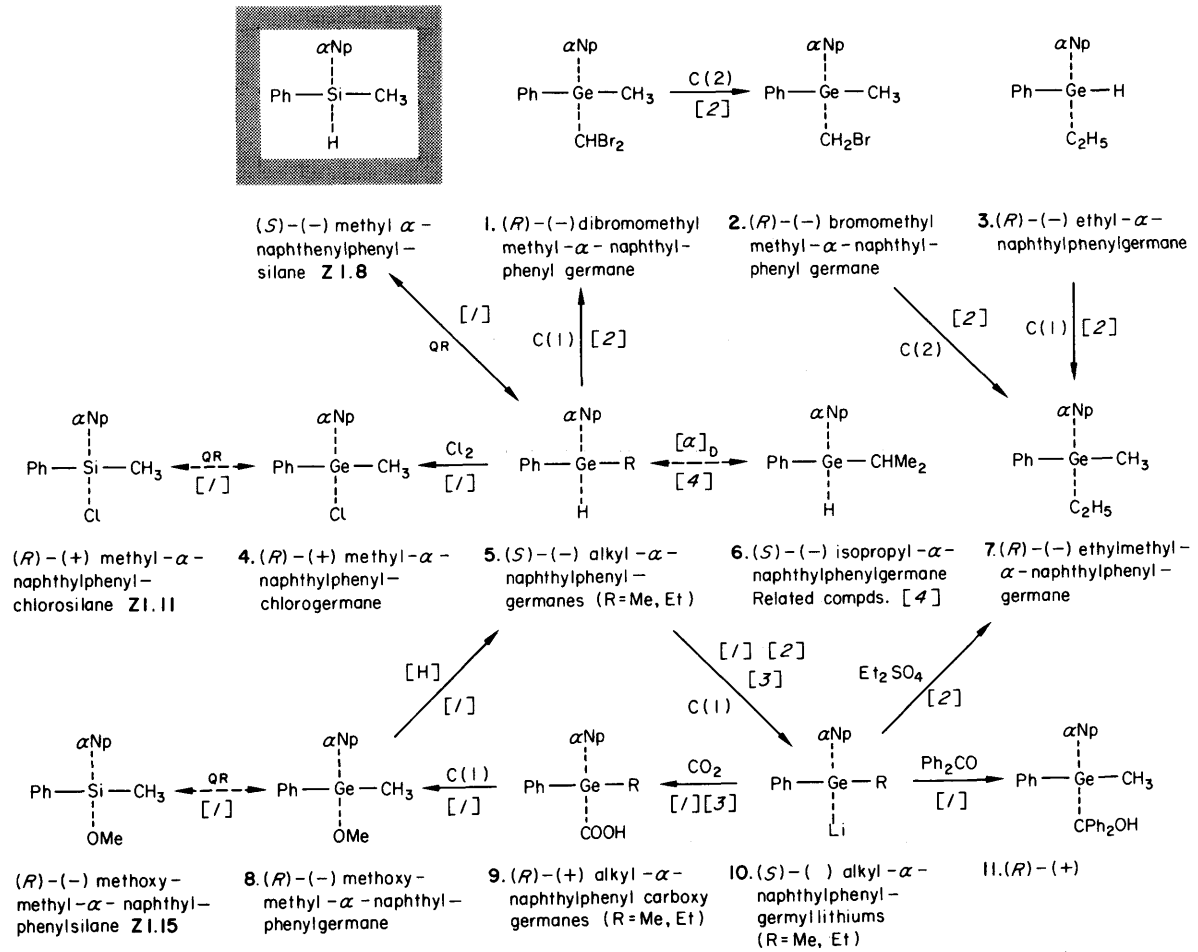
14. (*S*)-(+)

15. (*R*)-alkoxymethyl-α-naphthylphenylsilanes R = CH_3 (−) R = CMe_3 (+) R = cyclohexyl (+) Z2,Z1'

16. (*R*)-(−) methyl-α-naphthylphenylsilanol. K salt (+)

17. (*R*)-(−) methyl-α-naphthylphenylacyloxy-silanes (R = CH_3, Ph, p-$C_6H_4NO_2$)

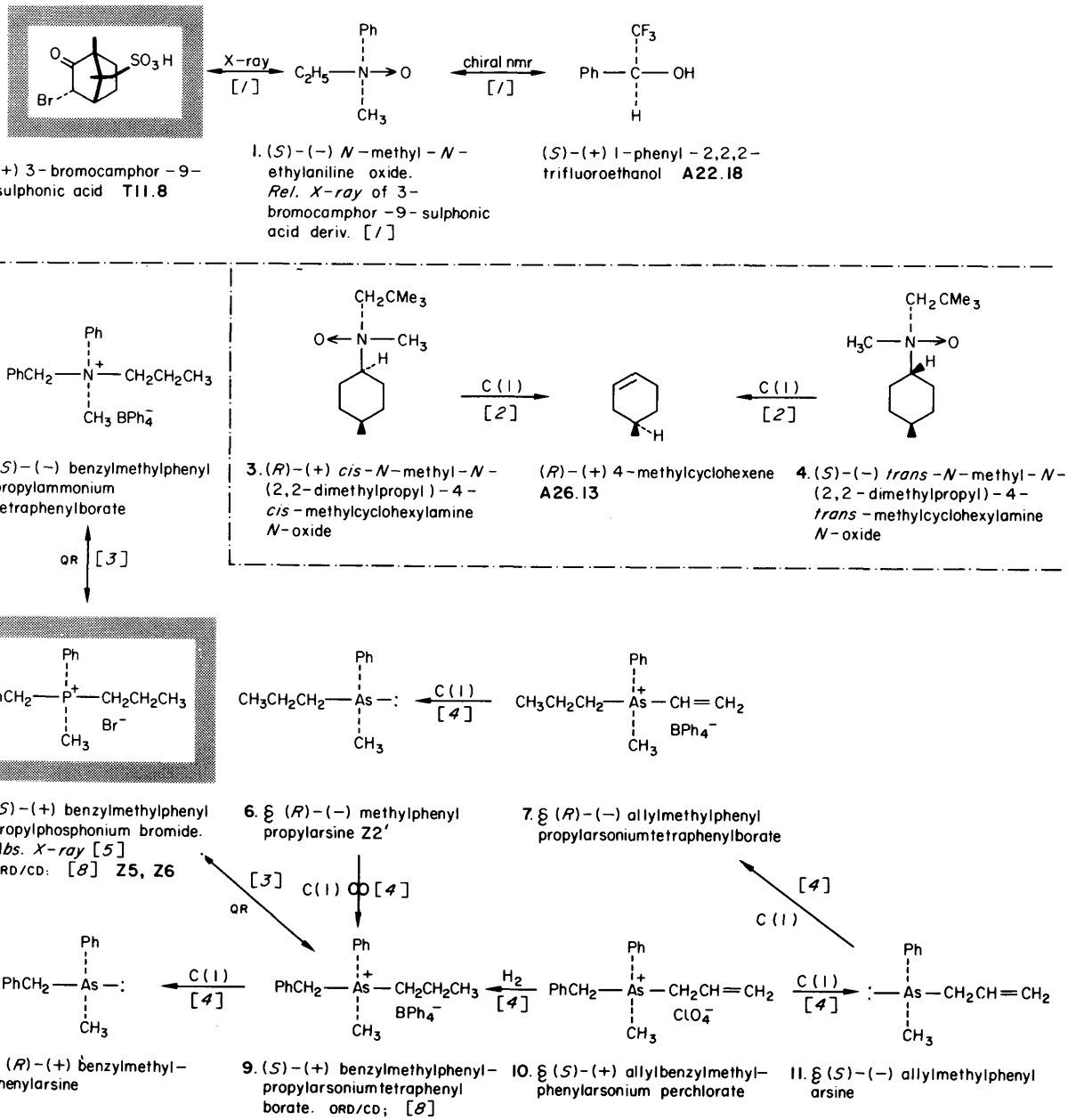
1. L. H. Sommer, W. D. Korte, and P. G. Rodewald, *J. Amer. Chem. Soc.*, 1967, **89**, 862; L. H. Sommer, K. W. Michael, and W. D. Korte, ibid., 868.
2. F. R. Jensen and D. D. Davis, *J. Amer. Chem. Soc.*, 1971, **93**, 4047.
3. L. H. Sommer, 'Stereochemistry, Mechanism and Silicon', McGraw-Hill, 1965.
4. B. J. Aylett, *Progr. Stereochem.*, 1969, **4**, 213.
5. A. G. Brook and W. W. Limburg, *J. Amer. Chem. Soc.*, 1963, **85**, 833.
6. T. Ashida, R. Pepinsky and Y. Okaya, *Acta Cryst.*, 1963, **16** (suppl.), A48, abstr. 5.8.
7. R. J. P. Corriu, G. F. Lanneau, and M. Leard, *Chem. Comm.*, 1971, 1365.
8. L. H. Sommer, C. L. Frye, G. A. Parker, and K. W. Michael, *J. Amer. Chem. Soc.*, 1964, **86**, 3271.
9. L. H. Sommer, C. L. Frye, and G. A. Parker, *J. Amer. Chem. Soc.*, 1964, **86**, 3276, 3280.
10. A. G. Brook, J. M. Duff, and D. G. Anderson, *J. Amer. Chem. Soc.*, 1970, **92**, 7567.



1. A. G. Brook and G. J. D. Peddle, *J. Amer. Chem. Soc.*, 1963, **85**, 1869, 2338.
2. A. G. Brook, J. M. Duff, and D. G. Anderson, *J. Amer. Chem. Soc.*, 1970, **92**, 7567.
3. C. Eaborn, R. E. E. Hill, and P. Simpson, *J. Organometall. Chem.*, 1968, **15**, P1.
4. F. Carré and R. Corriu, *J. Organometall. Chem.*, 1970, **25**, 395.

Reviews of phosphorus chirality; [6] [7]

(See also N,N′-diferrocenylcarbodiimide, **X3.5**, Tröger's base **X11.7** and tris-2,2′-bisphenylene-phosphorus (V) ion **X10.1**)



(+) 3-bromocamphor-9-sulphonic acid **T11.8**

1. (*S*)-(−) *N*-methyl-*N*-ethylaniline oxide. *Rel. X-ray* of 3-bromocamphor-9-sulphonic acid deriv. [1]

(*S*)-(+) 1-phenyl-2,2,2-trifluoroethanol **A22.18**

2. (*S*)-(−) benzylmethylphenyl propylammonium tetraphenylborate

3. (*R*)-(+) *cis*-*N*-methyl-*N*-(2,2-dimethylpropyl)-4-*cis*-methylcyclohexylamine *N*-oxide

(*R*)-(+) 4-methylcyclohexene **A26.13**

4. (*S*)-(−) *trans*-*N*-methyl-*N*-(2,2-dimethylpropyl)-4-*trans*-methylcyclohexylamine *N*-oxide

5. (*S*)-(+) benzylmethylphenyl propylphosphonium bromide. *Abs. X-ray* [5] ORD/CD: [8] **Z5, Z6**

6. § (*R*)-(−) methylphenyl propylarsine **Z2′**

7. § (*R*)-(−) allylmethylphenyl propylarsoniumtetraphenylborate

8. § (*R*)-(+) benzylmethyl-phenylarsine

9. (*S*)-(+) benzylmethylphenyl-propylarsoniumtetraphenyl borate. ORD/CD; [8]

10. § (*S*)-(+) allylbenzylmethyl-phenylarsonium perchlorate

11. § (*S*)-(−) allylmethylphenyl arsine

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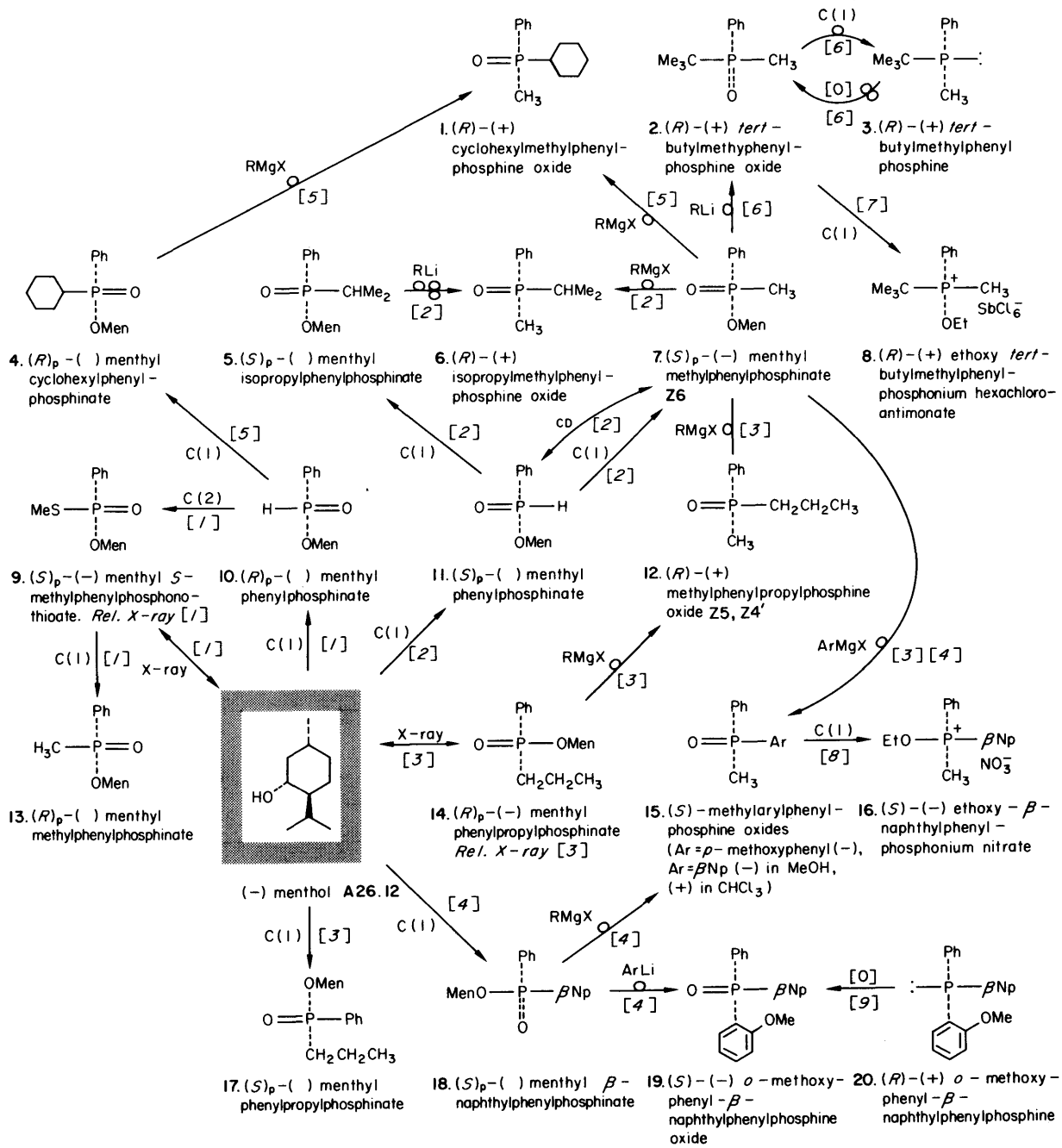

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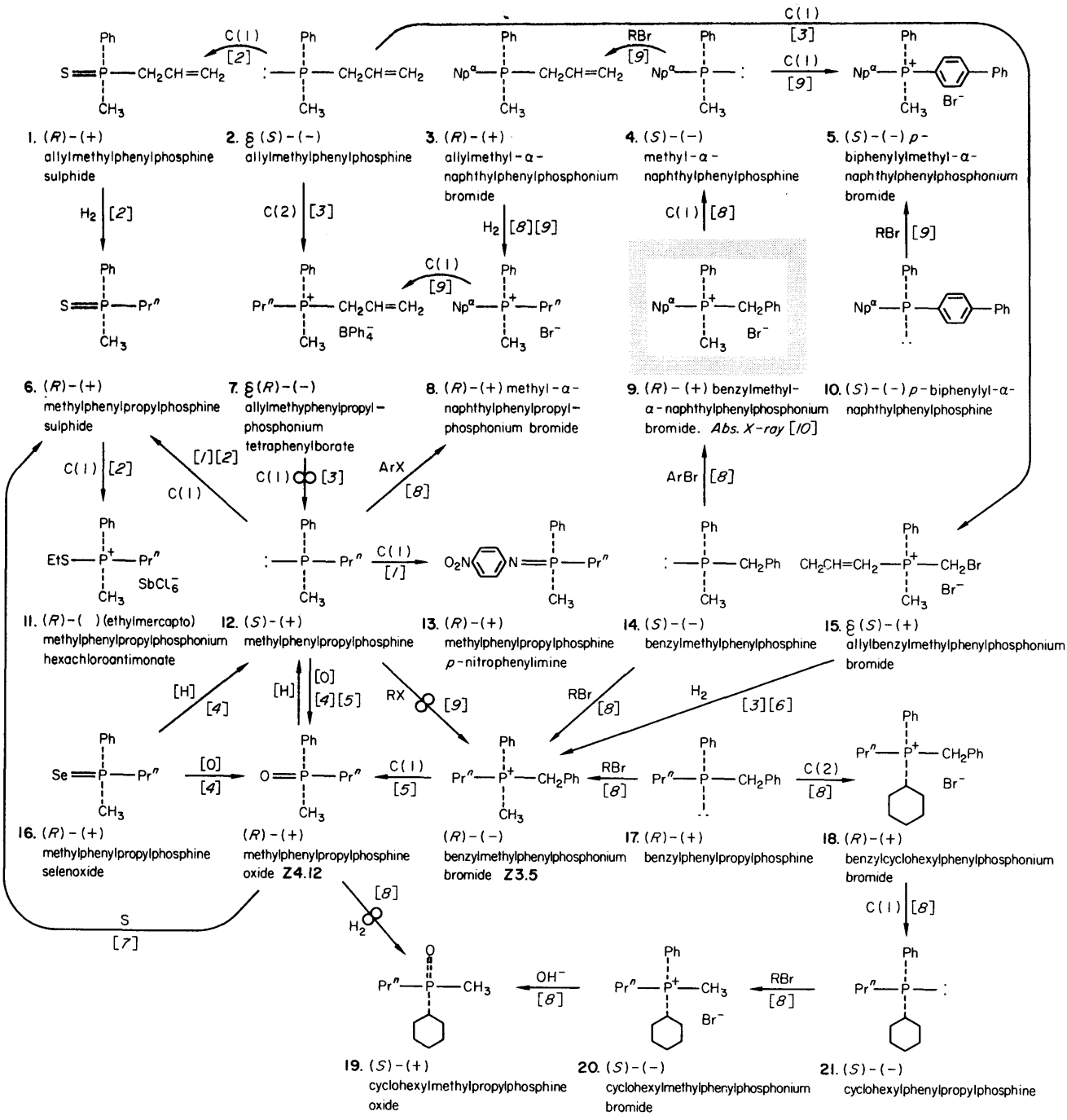

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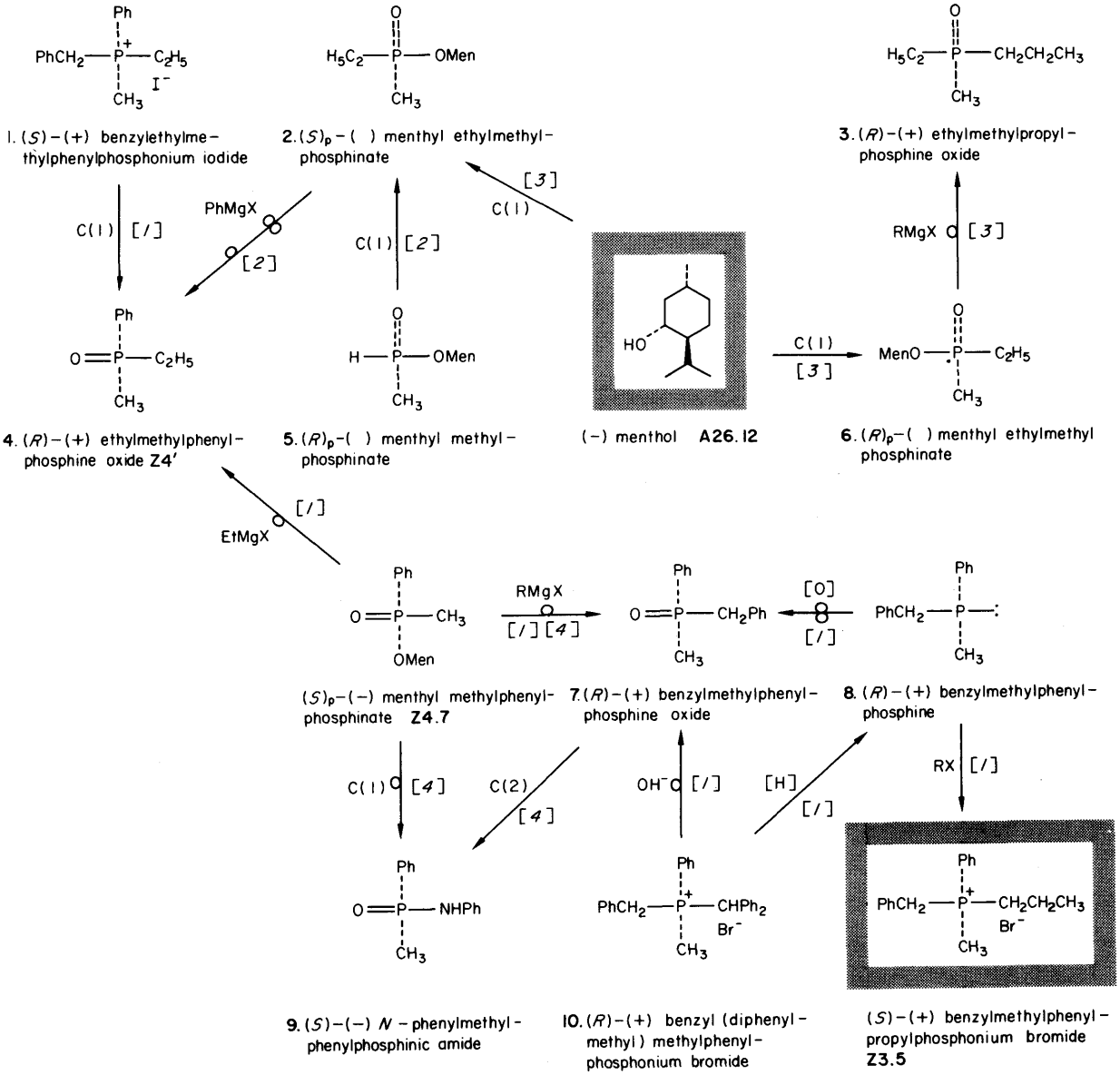

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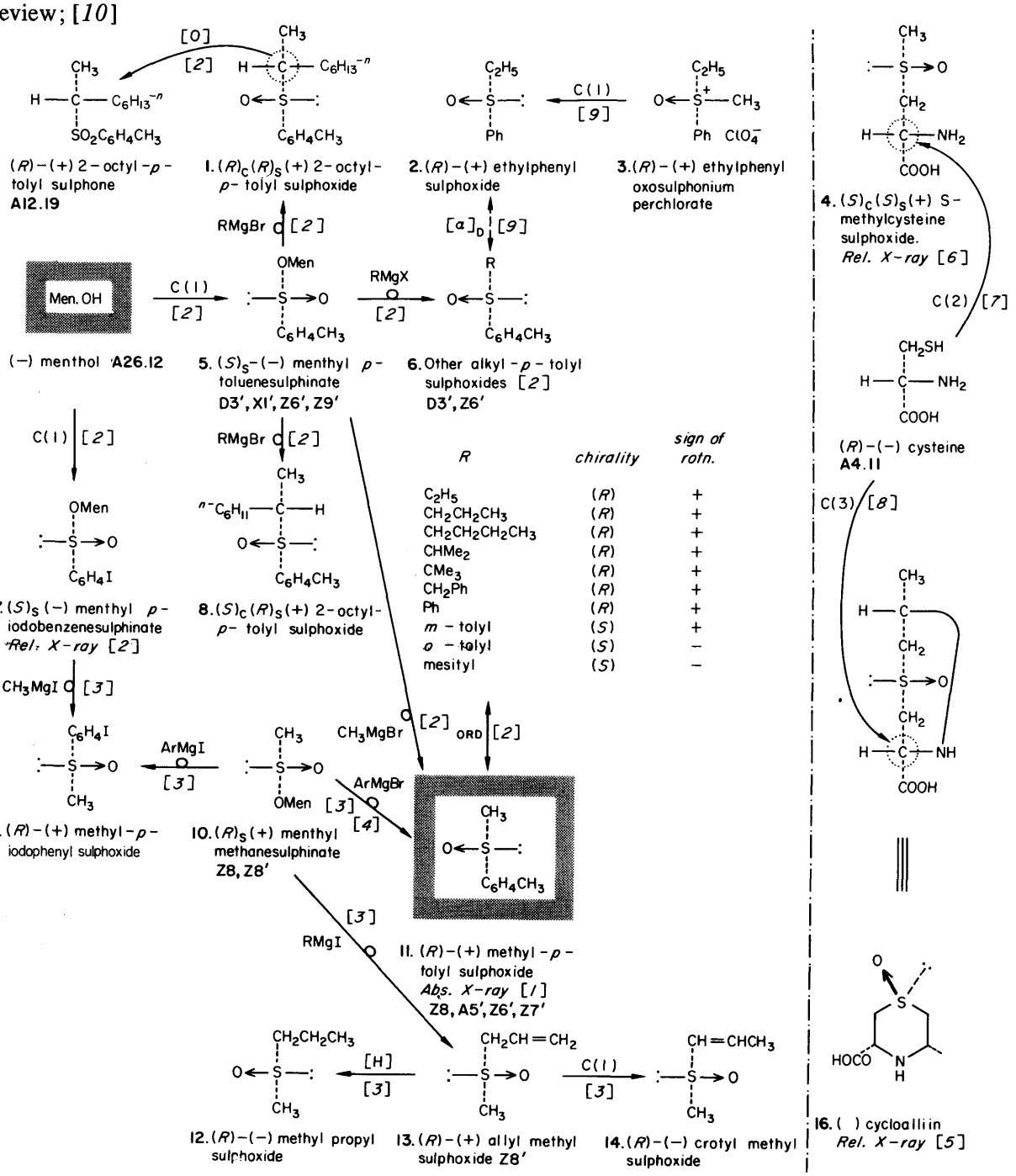

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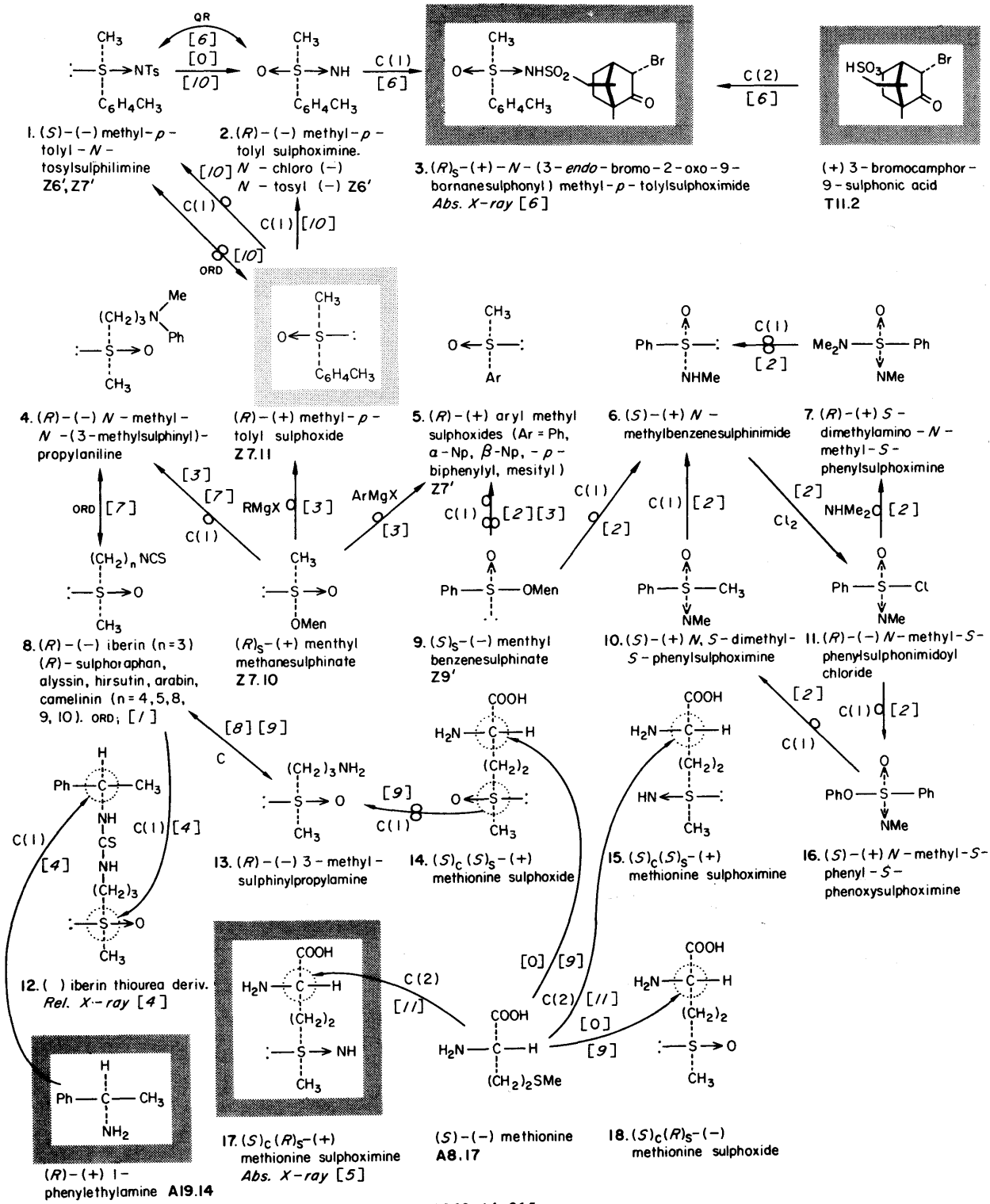

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