SYSTEM OF NOMENCLATURE FOR TERPENE HYDROCARBONS

Acyclics, Monocyclics, Bicyclics

A report of the Nomenclature Committee of the Division of Organic Chemistry, American Chemical Society



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FOREWORD

Wide agreement as to a clear and useful nomenclature is of great benefit in any field of science. The nomenclature here presented merits wide acceptance among terpene and other interested chemists because of the thorough way in which the careful work was done. Many versed in the chemistry of terpenes and many others experienced in naming chemical compounds were consulted. Full opportunity for criticism was offered. The proposed system of nomenclature for terpene hydrocarbons has been accepted by the Nomenclature Committee of the American Chemical Society's Division of Organic Chemistry (Committee A) and approved by the American Chemical Society (ACS) on recommendation of its general Nomenclature, Spelling, and Pronunciation Committee. Furthermore the Commission on the Nomenclature of Organic Compounds of the International Union of Pure and Applied Chemistry (IUPAC) has agreed to accept these nomenclature recommendations and has expressed intention to recommend them for acceptance by IUPAC on the customary tentative basis.

In working up the rules much information was brought together which should be of real help in the reading of terpene literature. Accordingly, the essential portion of this information is given in this monograph in addition to the officially approved nomenclature rules, examples, and discussion. The index by common terpene names will guide readers to structural formulas and recommended names.

The traditional nomenclature used in the terpene field is at best an exacting exercise in memory. Most of the terpene names are derived from the genus or family names of plants or from the essential oils from which the products were first isolated or in which they occur most abundantly. Many terpene names used in the past, both for fundamental structures and for derivatives, especially the latter, give no clue as to the nature of the specific compounds or as to the structural relationships which exist among several terpenes or between terpenes and similar organic compounds. The close chemical and biogenetical interrelationships of the terpenes justify treatment as a special field, and the necessity for introducing some systematization into the nomenclature had become more and more evident as knowledge of the field continued to expand.

Terpenes can be named systematically by the general nomenclature rules of IUPAC and recognized extensions of those rules, but the resulting names are frequently unmanageably long and complicated, are difficult in speech, and conceal the terpene nature of the compounds. Therefore, in 1946 Committee A (then led by Howard S. Nutting, later by Mary Alexander) set up a Subcommittee on Nomenclature of Terpenes under the chairmanship of Mildred W. Grafflin to explore the possibility of developing an alternative, consistent, unambiguous, and workable scheme for naming terpenes. The chairman of this subcommittee was its sole official member; she did an enormous amount of careful work. Leonard T. Capell, Charles D. Hurd, Howard S. Nutting, Austin M. Patterson, and Louis Schmerling, all members of Committee A, served as consultants continuously during the development of this project to its present stage. In addition, more than 50 terpene chemists, organic chemists, and nomenclaturists, both American and European, criticized various drafts of proposals and offered constructive suggestions and stimulating ideas that aided immeasurably in resolving controversial points, revising initial proposals, and directing necessary decisions. They all now have indicated their approval of the final recommendations here reported.

The official ACS report is limited to the naming of the simple acyclic, monocyclic, and bicyclic terpene hydrocarbons because official action has been taken only on the recommendations relating to these three classes of terpenes. The term "terpene hydrocarbons" is intended to include not only the numerous $C_{10}H_{16}$ hydrocarbons but also their hydrogenated derivatives and other hydrocarbons possessing similar fundamental structures; they may be of natural or synthetic origin.

During the developing work which has led to the mature report here given, there have been three long typescript versions of the terpene nomenclature report (April, 1949, June, 1950, and June, 1952, respectively) and one condensed typescript version (September, 1953). In addition the work was presented briefly by Miss Grafflin under the title "Nomenclature of Terpene Hydrocarbons and Related Compounds" at a Symposium on Nomenclature of Hydrocarbons held in 1949 by the ACS Division of Petroleum Chemistry and preprinted along with the other papers of this symposium. Furthermore, Austin M. Patterson presented a preview of this nomenclature in his column in *Chemical and Engineering News (Chem. Eng. News* 30, 930-5(1952)). It should be noted that the present report differs in some respects from the proposals in these earlier, more or less widely circulated versions.

The nomenclature rules, as recommended by a joint meeting of the National Research Council Subcommittee on Organic Nomenclature and Committee A at Buffalo, N. Y., March 23, 1952, have been revised slightly in this published version in order to limit "nor" to its traditional meaning in the terpene field, that is, to denote a ring system devoid of methyl groups. The parent saturated ring structure of thujane is designated by the name bicyclo[3.1.0] hexane instead of by northujane. This action was taken by Committee A at its meeting in Chicago, Illinois, September 5, 1953.

For a task well done with exceptional thoroughness Miss Mildred W. Grafflin deserves the gratitude of all chemists who will have an opportunity to benefit by this full nomenclature report. She has mine.

> E. J. Crane, Chairman Committee on Nomenclature, Spelling, and Pronunciation American Chemical Society

Nomenclature Rules for Terpene Hydrocarbons Approved by the Council, American Chemical Society^a

The general principles underlying the recommended scheme for systematizing the nomenclature of acyclic, monocyclic, and bicyclic terpene hydrocarbons are:

1. Application of IUPAC and recognized rules to the naming and numbering of the acyclic and the dimethylcyclohexane-type (Type B) monocyclic compounds. In each of these classes of hydrocarbons there exists no outstanding common terpene name or structure to serve as the basis for developing a logical series of simple terpene-like names.

2. Reduction of the chemical structures of the remaining simple monocyclic and bicyclic hydrocarbons to five fundamental types.

3. Assignment of fixed numberings to the five typical carbon skeletons which are larger than the ring-carbon skeletons.

4. Well known terpene names are retained for the parent compounds of four of these fundamental types and a new terpene-like name, bornane, is recommended for the fifth, to replace camphane and bornylane.

5. The nor- type of name (nor- in the traditional terpene sense of complete stripping of methyl groups from the ring) is used for ring-carbon skeletons where convenient.

6. Development, on the basis of the names of the larger parent compounds and the nor-structures and with the aid of established nomenclature rules, of logical series of simple names which are sufficiently definitive to show immediately the relations among compounds of a single series and which are exceedingly useful in the spoken language.

7. The following structures, numberings, and names are used:

^a March 27, 1954, 125th national meeting. Kansas City, Mo.



Nor- structures:



The nomenclature system outlined in this report follows many customary terpene practices but also conforms to established nomenclature rules and practices. The resulting terpene-like names are much simpler than the strict systematic names formed according to IUPAC rules. Replacement of the currently used common terpene names by the recommended terpene-like pseudosystematic names will facilitate ready recognition of the terpene hydrocarbon structures and will aid in integrating terpene chemistry with the entire field of organic chemistry. Extension of the hydrocarbon rules to the naming of functional derivatives will simplify and unify nomenclature within the terpene field.

Stereoisomers and Their Nomenclature

Stereoisomers among the terpenes are abundant and exceedingly important to the chemistry of the field. Stereochemical nomenclature therefore cannot be ignored in any complete scheme for systematizing terpene nomenclature. The recommendations in this report provide only structural names for the acyclic, monocyclic, and bicyclic terpene hydrocarbons. Studies in various fields (e.g., steroids) on preferred methods of designating isomeric configurations are being made.

Recommendations

The specific recommendations made by the American nomenclature committees for naming each class of the simple terpene hydrocarbons are:

Acyclics:

The acyclic terpene hydrocarbons will be named in a manner similar to other unsaturated aliphatic hydrocarbons (IUPAC rules) when pure compounds are involved. Example: 7-methyl-3-methylene-1.6-octadiene.

Monocyclics:

Menthane Type: For this type of monocyclic terpene hydrocarbon (para, ortho, and meta isomers of menthane) the menthane, menthene, and menthadiene names and the well-established fixed numbering of menthane (Formula I above) will be used.



Dimethylcyclohexane Type: This type of monocyclic terpene hydrocarbon will be named systematically as derivatives of cyclohexane, cyclohexene, and cyclohexadiene (IUPAC rules).





Bicyclics:

Thujane Group (Bicyclo[3.1.0]hexane Type): The thujane-type bicyclic terpene hydrocarbons will be named as thujanes, thujenes, and thujadienes, and these names will be based on the recommended fixed numbering of the thujane carbon skeleton (see Formula II). For those derivatives which contain (1) fewer carbon atoms than thujane, (2) the same number as, or more carbon atoms than, thujane but do not have a carbon skeleton identical with that of thujane, or (3) more carbon atoms than thujane and a carbon skeleton identical with that of thujane but contain substituents such that the principle of like treatment of like things will be violated by using the thujane, thujene, and thujadiene the bicyclo[3.1.0]hexane-type names, names based on systematic bicyclo numbering will be used. Examples: 4(10)thuiene. 5-isopropylbicyclo[3.1.0]hex-2ene.

Carane Group (Bicyclo[4.1.0]heptane Type): The carane-type bicyclic terpene hydrocarbons will be named as caranes, carenes, and caradienes, and these names will be based on the recommended fixed numbering of the carane carbon skeleton (see Formula III). For those derivatives which contain (1) fewer carbon atoms than carane, (2) the same number as, or more carbon atoms than, carane but do not have a carbon skeleton identical with that of carane, or (3) more carbon atoms than carane and a carbon skeleton identical with that of carane but contain substituents such that the principle of like treatment of like things will be violated by using the carane, carene, and caradiene names, the nor- type of terpene names based on systematic bicyclo numbering will be used (see Formula VI). Examples: 2,4-norcaradiene, 3,4,7,7-tetramethylnorcarane.

Pinane Group (Bicyclo[3.1.1]heptane Type): The pinane-type bicyclic terpene hydrocarbons will be named as pinanes, pinenes, and pinadienes, and these names will be based on the recommended fixed numberings of the pinane carbon skeleton (see Formula IV). For those derivatives which contain (1) fewer carbon atoms than pinane, (2) the same number as, or more carbon atoms than, pinane but do not have a carbon skeleton identical with that of pinane, or (3) more carbon atoms than pinane and a carbon skeleton identical with that of pinane but contain substituents such that the principle of like treatment of like things will be violated by using the pinane, pinene, and pinadiene names, the nor- type of terpene names based on systematic bicyclo numbering will be used (see Formula VII). Examples: 2(10),3-4-methylenepinane, 6.6-dipinadiene. methyl-2-vinyl-2-norpinene.

Group (Bicyclo[2.2.1]hep-Bornane tane Type): The new name bornane is recommended to replace "camphane." The bornane-type bicyclic terpene hydrocarbons will be named as bornanes, bornenes, and bornadienes, and these names will be based on the recommended fixed numbering of the bornane carbon skeleton (Formula V above). For those derivatives which contain (1) fewer carbon atoms than bornane, (2) the same number as, or more carbon atoms than, bornane but do not have a carbon skeleton identical with that of bornane or (3) more carbon atoms than bornane and a carbon skeleton identical with that of bornane but contain substituents such that the principle of like treatment of like things will be violated by using the bornane, bornene, and bornadiene names, the nor- type of terpene names based on systematic bicyclo numbering will be used (see Formula VIII). Camphene will be preferred to 2,2-dimethyl-3-methylenenorbornane for the unsubstituted compound. Examples: 7,7-2,7,7-trimethyl-2dimethylnorbornane, norbornene.

System of Nomenclature For Terpene Hydrocarbons Acyclics, Monocyclics, Bicyclics

Prepared by Mildred W. Grafflin, chairman (1946–53) of Subcommittee on Nomenclature of Terpenes of the Nomenclature Committee of the Division of Organic Chemistry, American Chemical Society

Introduction

The necessity for introducing some systematization into the nomenclature of terpenes has become more and more evident as knowledge of the field continues to expand. The close chemical and biogenetical interrelationships of terpenes justify treatment as a special field. In any proposed systematic scheme of naming series of related compounds and their derivatives, the nomenclature of hydrocarbons is the logical starting point. The report presented herewith is limited to the naming of the simple acyclic, monocyclic, and bicyclic terpene hydrocarbons because official ACS action has been taken only on the recommendations relating to these three classes of terpenes. The general sources used for information on terpenes and their nomenclature are listed (5, 6, 23, 30, 31, 40, 41, 45, 47, 51) in "Literature Cited."

Historical and Current Nomenclature

The traditional nomenclature used in the terpene field is at best an exacting exercise in memory. Most of the terpene names are derived from the genus or family names of the plants or from the essential oils from which the products were first isolated or in which they occur most abundantly. Many terpene names currently used, both for fundamental structures and especially for derivatives, give no clue as to the nature of the specific compounds or to the structural relationships which exist among several terpenes or between terpenes and similar organic compounds.

The earlier investigators considered their products homogeneous; later, a number of these were found to be mixtures not merely of isomers but in some cases mixtures of entirely different structures. Some of these compounds were then distinguished from each other by prefixing Greek letters to established terpene names – e.g., α , β -, and γ -terpene and α , β -, and δ -pinene. Prefixes such as allo-, apo-, epi-, homo-, iso-, neo-, and nor-, or combinations of these as isoallo- and neoiso-, were also attached to the common terpene names to indicate real or assumed relationships of a new product to one already known – e.g., ocimene, allo-ocimene: terpinolene, isoterpinolene; camphane, isocamphane, apocamphane, and norcamphane; fenchene, isofenchene, isoallofenchene, and apoisofenchene. Other prefixes such as fencho- and pino- were introduced – e.g., fenchocamphorane and pinocamphane. When later investigations proved that some of the relationships originally assumed were incorrect, usage of many of these names persisted.

The practice of (a) naming hydrogenated derivatives as hydro compounds of more unsaturated structures - e.g., dihydrodipentene and hydrodicamphene - and (b) assigning similar names such as terpinene, terpinolene, and terpin to compounds, either closely related as the first two are or widely different as the last compound is from the other two, has added to the confusion in the existing nomenclature of terpenes and related compounds. Simple names such as camphane and camphene do not apply, respectively, to a saturated and unsaturated single basic structure as the modern chemist would assume. The unsaturated structure corresponding to camphane has been called bornylene consistently, whereas the saturated structure corresponding to camphene has been called isocamphane or dihydrocamphene. As would be expected from the historical development of terpene nomenclature, products of the same composition but isolated from different sources by different investigators were, in some cases, given different names - e.g., d-limonene has also been called hesperidene, citrene, carvene, cinene, di-isoprene, isoterebenthene, and cautchene. A specific form of one compound was frequently designated by a new name rather than by adding recognized prefixes to an established name - e.g., the dl- form of limonene was named dipentene. Later, when some products were found to differ only in name and not in structure, unanimity of opinion as to which name should be retained was often difficult to attain and hence several of the synonym names have been used interchangeably – e.g., thujane and sabinane, β -pinene and nopinene. This lack of decision on a preferred name is reflected in the traditional names of a series of related derivatives - e.g., camphane rather than bornylane has been used almost invariably for the saturated structure but many of the derivative names contain the root born- rather than camph-. Many similar terpenes contain identical substituents and differ only in the positions of double bonds, which may be in the ring, outside the ring, or both; others differ only in the number or type of substituents. These similarities are not evident from the common terpene names which are often even misleading.

Sufficient information has been given to indicate the desirability and necessity for attempting to introduce some systematization into terpene nomenclature so that structural relationships and differences among terpenes can be readily recognized from the names of the compounds. A complete and satisfactory systematic nomenclature for terpenes already exists - they can be named according to the general nomenclature rules of the International Union of Pure and Applied Chemistry (IUPAC) and recognized extensions of these rules. For example, by recognized rules and Chemical Abstracts alphabetical order of prefixes, a terpinene can be named systematically as 1-isopropyl-4-methyl-1,3-cyclohexadiene; β -fenchene as 2,2-dimethyl-5-methylenebicyclo 2.2.1 heptane. However, these systematic names are unmanageably long and complicated, are difficult to speak, and conceal the terpene nature of the compounds. This approach to systematization is neither practical nor desirable, and is definitely contrary to the spirit of Rule 1 of the Definitive Report (41) which states: "As few changes as possible will be made in terminology universally adopted." The recommendations in this report offer an alternative scheme for naming terpenes. The resulting names are more concise and conform more closely to current terpene literature. The underlying principles of this scheme, which in this report are applied only to the simple acyclic, monocyclic, and bicyclic terpene hydrocarbons but can be applied generally to the entire terpene field, will be summarized later.

Classification of Terpenes

The term terpenes originally was applied to cyclic hydrocarbon structures with the empirical formula C₁₀H₁₆ or to their derivatives which occur in the essential oils of plants. These compounds have often been referred to as the "true" or "proper" terpenes. As knowledge of the chemistry of the terpene field developed, compounds related both chemically and biogenetically to the C10H16 hydrocarbons have been identified. Some natural products have been synthesized; other synthetic compounds resemble known terpene structures. Consequently, today the term terpenes is broader in scope than its original meaning. The term terpene bydrocarbons, to which this report is limited, includes not only the numerous C10H16 hydrocarbons but also their hydrogenated derivatives and other hydrocarbons possessing similar fundamental chemical structures. They may be acyclic or cyclic, simple or complex, and of natural or synthetic origin. Many of their carbon skeletons have been shown to consist of multiples of the isoprene nucleus, C5H8, which led Wallach (56) to suggest the name hemiterpene for isoprene. The cyclic terpene hydrocarbons may be further classified as monocyclic, bicyclic, or tricyclic. The few known structures of the sesquiterpenes, $C_{15}H_{24}$, and of the polyterpenes, $(C_5H_8)_x$, indicate that these hydrocarbons may eventually be classified similarly to the simpler terpenes. Formulas for typical examples of these general classes of terpene hydrocarbons are shown in Chart 1. Add to the above hydrocarbons their oxygenated and hydrogenated derivatives as well as other types of derivatives; include the interconversion, rearrangement, and degradation products of these hydrocarbons and their many derivatives; do not ignore the synthetic terpenes for which no natural counterparts have as yet been found; recognize the existence of stereoisomers among which, in general, no one form predominates — that is modern terpene chemistry.

Stereoisomers and Their Nomenclature

Stereoisomers among the terpenes are abundant and exceedingly important to the chemistry of the field. Stereochemical nomenclature therefore cannot be ignored in any complete scheme for systematizing terpene nomenclature; for the present, however, the recommendations in this report provide only structural names for the simple acyclic, monocyclic, and bicyclic terpene hydrocarbons. Studies in various fields – e.g., steroids – on preferred methods of designating isomeric configurations are being made by other committees (1, 21, 25).

The scope of this problem can be indicated by a brief consideration of the stereochemical nomenclature of hydroxy derivatives of the bicyclic terpenes. For the parent bicyclic hydrocarbon compound known in the literature at present as camphane, the name "bornane" is recommended in this report. (Reasons for choosing "bornane" are discussed later under "The Bornane Hydrocarbons".) A mono-hydroxy derivative of bornane, on the basis of IUPAC rules (41), would be named as a bornanol. Two such derivatives have the common terpene names, borneol and isoborneol; these names, on the basis of recommendations in this report would both become 2-bornanol. Obviously, this is inadequate and additional designations are necessary to distinguish between the two stereoisomers.

In the steroid field, a similar problem has been solved successfully (19, 26, 29) by using the Greek letters a and β , immediately after (with no comma intervening) the position number of the substituted carbon atom, to indicate a configuration which is either *trans* or *cis* to a standard reference point in the molecular structure.



Since the adoption of this method of nomenclature for the steroids, the same method has been used with other classes of compounds – for example, the triterpenes (4).

This method can be extended to the bornane-type bicyclic terpenes by choosing the gem-dimethyl bridge carbon as a reference point; then borneol could be named 2α -bornanol (the *a* indicating a hydroxyl group which is *trans* to the gem-dimethyl bridge carbon) and isoborneol could be named 2β -bornanol (the β indicating a hydroxyl group which is *cis* to the gem-dimethyl bridge carbon). Thus:



An argument which can be offered against this suggested use of a and β in terpene nomenclature to designate stereoisomers is that confusion may result because of the extensive use of Greek letter prefixes in the common terpene names in the literature. In those names, however, the Greek letters are used alone -e.g., y-terpinene, β -pinene - in the a,β scheme of stereochemical nomenclature a Greek letter is always combined with a number, and the combination -e.g., 2a, 4β - is considered as a single prefix. Furthermore, the scheme of nomenclature for terpenes recommended in this report eliminates the use of Greek letters in structural names.

An alternative to the a,β method for designating the type of stereoisomerism that occurs with borneol and isoborneol is the *endo*, *exo* method. The prefixes *endo*and *exo*- have been used to some extent in the past to indicate, respectively, for example, a borneol configuration and an isoborneol configuration (34). If these prefixes are used with the new bornanol names, then borneol would be named 2-*endo*bornanol and isoborneol would be named 2-*exo*-bornanol. An argument which can be offered against the continuation of *endo*- and *exo*- in stereochemical nomenclature is the current confusion that already exists in the literature because of other uses of these same prefixes – for example, the use of *endo*- in naming valence and atomic bridges; the use of *exo*- to denote "outside of" in a very general sense and to denote specifically an attachment to a side chain of a ring structure. Preliminary testing of the two schemes for configurational names indicates strong preference for the α,β method. Although this method was applied above only to bornane-type bicyclics, it can be applied equally as well to configurational names for the other fundamental bicyclic structures – that is, the thujane, carane, and pinane types. The reference point of these structures could be the same as in the case of bornane – that is, the most substituted bridge carbon atom. For example:



Structural Relationships Among Terpene Hydrocarbons

The chemical interrelationships among these seemingly widely different types of compounds justify the recognized segregation of the terpenes from other fields of organic chemistry. The structural significance of the isoprene residue (CC-C-C) to the different types of terpene carbon skeletons has already been indicated. The simplest type of terpene is an open-chain olefinic structure formed by the union of two isoprene units. Such compounds are called the *acyclic terpenes*. From two units of isoprene or from the simple acyclic structures, under proper conditions, simple cyclic compounds are formed. Many of these are derivatives of p-cymene (1-isopropyl-4-methylbenzene) or much less frequently of o- or m-cymene; others are derivatives of dimethylcyclohexane. These cymene and dimethylcyclohexane derivatives are designated, respectively, as Type A and Type B monocyclic terpenes in this report. The monocyclics, by splitting of the ring, may be reconverted to the acyclics. The monocyclics may be formed also from the bicyclic terpenes; the reverse reaction, however, with only a few exceptions, is more difficult. The few known tricyclic terpenes have all been prepared synthetically and none have as yet been detected in essential oils. From the acyclic to the tricyclic terpenes having the $C_{10}H_{16}$ composition, there is a progressive decrease in unsaturation which can also form the basis for a limited type of classification: the acyclics contain three double bonds, the monocyclics two, the bicyclics one, and the tricyclics none; these $C_{10}H_{16}$ terpenes therefore can add on, respectively, six, four, two, or zero univalent atoms or groups.

The sesquiterpenes, diterpenes, and polyterpenes can be considered most simply from a structural point of view as products composed of multiple units of isoprene. Structures currently assigned to some of the sesquiterpenes may have to be revised as the study of terpene chemistry advances, since many of these have been based on the validity of the "isoprene rule" for terpene structures and exceptions to this rule are becoming known (37).

In this report the simple acyclic, monocyclic, and bicyclic terpene hydrocarbons will be dealt with on the basis of these structural relationships and not on their natural or synthetic origin.

Underlying Principles of Recommended Nomenclature Scheme

The chief purpose of the recommended scheme of naming terpenes is to introduce more system into the current nomenclature of the field by providing terpenelike names which conform to systematic rules but are much simpler than the strict systematic names. The recommended names are sufficiently definitive to designate clearly the correct structures but are sufficiently simple to be exceedingly useful in the spoken language. They will facilitate ready recognition of the terpenes and allied structures and will aid in integrating terpene chemistry with the entire field of organic chemistry. The scheme has been developed in detail only for the hydrocarbons at present although considerable testing of its applicability to naming oxygenated and other derivatives has been carried out.

The general principles underlying the recommended scheme for systematizing the nomenclature of acyclic, monocyclic, and bicyclic terpene hydrocarbons are:

1. Applying IUP AC and recognized rules to the naming and numbering of the *acyclic* and the *dimethylcyclobexane-type* (Type B) monocyclic compounds. In each of these classes of hydrocarbons there exists no outstanding common terpene name or structure to serve as the basis for developing a logical series of simple terpene-like names.

2. Reducing the chemical structures of the remaining simple monocyclic and bicyclic hydrocarbons to five fundamental types.

3. Assigning fixed numberings to the five typical carbon skeletons which are larger than the ring-carbon skeletons.

4. Retaining a well-known terpene name for the parent compounds of four of these fundamental types and recommending a new terpene-like name (bornane to replace camphane) for the fifth.

5. Using the nor- type of names (nor- in the traditional terpene sense of complete stripping of methyl groups from the ring) for ring-carbon skeletons where convenient.

6. Developing, on the basis of the names of the larger parent compounds and the nor-structures and with the aid of established nomenclature rules, logical series of simple names which are sufficiently definitive to show immediately the relations among compounds of a single series and which are exceedingly useful in the spoken language.

7. Memorizing only the following structures, numberings, and names:

Fundamental Terpene Type.



The nomenclature system outlined in this report follows many customary terpene practices but also conforms to established nomenclature rules and practices. The

resulting terpenelike names are much simpler than the strict systematic names formed according to IUPAC rules. Replacement of the currently used common terpene names by the recommended terpenelike pseudosystematic names will facilitate ready recognition of the terpene hydrocarbon structures and will aid in integrating terpene chemistry with the entire field of organic chemistry. Extension of the hydrocarbon rules to the naming of functional derivatives will simplify and unify nomenclature within the terpene field.

Forms Used In Report

All of the acyclic, monocyclic, and bicyclic terpene hydrocarbons for which formulas are given are numbered, and for a single structure the same number is used throughout the report in both the text and the charts. For each hydrocarbon, the following information is given in the charts: the formula; the common terpene name, if one exists, for recognition; the recommended name for systematization of the nomenclature; and one type of systematic name for comparison. For the acyclics and the Type B monocyclics the systematic name is the recommended name. The convenient Baeyer-type names have been chosen as the systematic-type names for the bicyclic compounds; hence, no discussion of systematic names based on the radical scheme (for example, the endo-type and methano-type names) (49) is included. For uniformity among the systematic and recommended names used in this report, the Chemical Abstracts alphabetical order of names of substituent groups, and not the London Chemical Society alphabetical order or the complexity order, has been followed. Position numbers for double bonds have, in general, been placed as near the beginning of names as possible rather than immediately preceding the -ene or -diene endings - for example, 2,4-p-menthadiene; 1,5,5,6-tetramethyl-1,3-cyclohexadiene; 2(10),3-pinadiene; 2,5,5-trimethyl-2-norbornene. In bicyclo names for unsaturated structures, however, the new (1953) policy of Chemical Abstracts has been followed; this is, when a bracket breaks a name, the position numbers designating double bonds no longer follow the bracket immediately but are placed directly before the suffixes to which they apply – for example, 1-isopropyl-4-methylbicyclo[3.1.0] hex-2-ene; bicyclo 4.1.0 hepta-2,4-diene. These restrictions have been adopted because the purpose of this report is not to discuss the merits of various types of systematic names now in use, but to recommend simple and rational names for terpene hydrocarbons. To avoid any misunderstanding as to whether the name of a compound in a chart, too long to be placed on a single line, should contain a hyphen or be a solid word, the printer's link-over sign (C) has been added at the end of the line to indicate that the word is solid. A hyphen appearing at the end of a line in the name columns of the charts belongs in the name of the hydrocarbon.

In the majority of the charts, the skeletal monocyclic and bicyclic formulas familiar to the terpene chemist are used because they are convenient and practicable for the purposes of this report. According to usual practice, the methylene groups attached to a monocyclic ring are indicated only by the two bonds, whereas for the bicyclic formulas the CH₂ has been included. Many of these skeletal formulas, however, have been oriented to show structural relationships among members of one group, and to conform more nearly to currently accepted rules for ring structures and to the proposed fixed numberings of certain basic terpene carbon skeletons. Those formulas for which no numbering of the carbons is given are oriented so that the top ring carbon is No. 1 and the numbering runs clockwise. The recommended fixed numberings, and in a few cases the terpene numberings, are shown on the outside of the rings. The numbers which must be used for the strict systematic names are shown in general on the inside of the rings. The exceptions to this general form are obvious. Arrows have been placed on the circles enclosing many of these numbers to indicate whether the numbering runs clockwise or counterclockwise on the specific orientations shown; this eliminates numbering all carbons in a formula.

Complete fundamental cyclic formulas showing all carbons and hydrocarbons are given only in Charts 1, 2, 4, 8, and 9; in the other charts, the conventional terpene skeletal formulas have been used. For those not familiar with these common terpene formulas of the monocyclic and bicyclic structures, Chart 2 is included to show the different forms of identical structures which appear in current chemical literature. Only saturated structures are given. The three-dimensional type of skeletal formulas shown for the bicyclic structures is being used currently more and more because they often permit much more to be expressed concerning the properties of a compound and its relations to a fundamental type than do the classical structural formulas.

Chart 2. Various Forms of Structural Formulas of Fundamental Types of Monocyclic and Bicyclic Terpene Hydrocarbons



In SYSTEM OF NOMENCLATURE FOR TERPENE HYDROCARBONS; Advances in Chemistry; American Chemical Society: Washington, DC, 1955.

Acyclic Terpenes

Structural Features

The acyclic terpene bydrocarbons are not numerous, but are of wide interest, both scientifically and technically, because earlier investigations on these products established many of the fundamental structural relationships which exist among the various classes of terpenes. Many of those investigated are oils which are probably mixtures of isomeric forms rather than pure compounds. Structurally, however, the acyclics have been shown to be open-chain unsaturated compounds belonging to the general class of ethylenic hydrocarbons. One double bond is normally between the first and second or between the second and third of at least one of the terminal threecarbon atom groups, thus forming the end group $(a) \operatorname{CH}_2 = \operatorname{C}(\operatorname{CH}_3) - \operatorname{or} (b) (\operatorname{CH}_3)_2 \operatorname{C}=$. These identifying end groups were originally designated (50), respectively, as (a)the limonene or dipentene form and (b) the terpinolene form; now the accepted radical names for these two groups are, respectively, isopropenyl and isopropylidene (30). Most of the terpenes classed as simple acyclics can be considered as derivatives of a dimethyloctane.

Current Nomenclature

The common terpene names of a few acyclic hydrocarbons indicate the need for more precise names. For example, the name geraniolene, because of the "ol," suggests the presence of an OH group and some relation to the geraniols. From the name dihydromyrcene and a knowledge of the structure of myrcene, one cannot be sure where the two hydrogens have been added. The prefix allo- in allo-ocimene implies the more stable isomer, but knowledge of the structure of ocimene is insufficient to enable one to draw the correct formula for allo-ocimene.

The nomenclature of the acyclic hydrocarbons can be readily systematized by naming them in the same manner as other unsaturated aliphatic hydrocarbons (7,42). Hydro derivatives as well as methyl or other alkylated derivatives of the acyclics can be named systematically similarly to the hydrocarbons, and the system can be applied readily to derivatives containing functional groups.

Recommendation

Name the acyclic terpene bydrocarbons in a manner similar to other unsaturated aliphatic bydrocarbons (IUPAC rules) when pure compounds are involved.

See Chart 3 for the structures and recommended names of the better known simple acyclics. For completeness, the prefixes *cis*- and *trans*- must be added to the systematic names to designate specific stereoisomers.

Rules for Forming Systematic Acyclic Names

Names of branched-chain unsaturated aliphatic hydrocarbons (IUPAC rules) are formed from the name of the longest fundamental chain present in a formula and the names of the side chains with proper position designations. The resulting names

No.	Terpene Name	Formula	Recommended Systematic Name Lowest Numbers to Double Bonds
1A	Geraniolene	$ \begin{pmatrix} 1 & 2 & 3 & 4 & 5 & 67 \\ CH_2 = C - CH_2 CH_2 CH_2 CH_3 \\ & \\ CH_3 & CH_3 \end{pmatrix} $	2,6-Dimethyl- 1,5-heptadiene
1B	(C ₉ H ₁₆)	$\begin{cases} 1 & 2 & 3 & 4 & 5 & 6 & 7 \\ CH_2 = C - CH_2 & CH_2 & CH_2 - C = CH_2 \\ CH_3 & CH_3 & CH_3 \end{cases}$	2,6-Dimethyl- 1,6-heptadiene
2	Myrcene (C ₁₀ H ₁₆)	$CH_2 = CH_2CH_2CH_2CH_2CH_2CH_3$	7-Methyl-3-methylene- 1,6-octadiene
3	Dihydromyrcen e (or Linaloolene) (C ₁₀ H ₁₈)	$CH_{3}^{2} = CHCH_{2}^{3} CH_{2}^{4} CH_{2}^{5} = CHCH_{3}^{6} CH_{3}^{7} CH_{3}^{8}$	2,6-Dimethyl- 2,6-octadiene
4	Ocimene (C ₁₀ H ₁₆)	$ \begin{array}{c} 1 & 2 & 3 & 4 & 5 & 6 & 7 & 8 \\ CH_2 = CHC = CHCH_2CH_2CH_2C = CH_2 \\ CH_3 & CH_3 \end{array} $	3,7-Dimethyl- 1,3,7-octatriene
5	Allo-ocimene (C ₁₀ H ₁₆)	$\begin{bmatrix} 1 & 2 & 3 & 4 & 5 & 6 & 7 & 8 \\ CH_3C=CHCH=CHC=CHCH_3 \\ CH_3 & CH_3 \end{bmatrix}$	2,6-Dimethyl- 2,4,6-octatriene



are written as single words. Rules which will serve as guides to forming the systematic names for the acyclic terpene hydrocarbons when pure compounds are involved are:

Rule 1. Choose as the fundamental chain of a formula the longest chain containing the maximum number of double bonds — for example, choose the eight-carbon rather than the seven-carbon chain for myrcene (No. 2, Chart 3). The longest chain chosen by this rule may not necessarily be the longest chain in the molecule.

Rule 2. Arrange the chosen fundamental chain so that the positions of the double bonds in it are given the lowest numbers possible – for example, number the formula for ocimene (No. 4, Chart 3) so that the double bonds can be designated by the numbers 1,3,7- rather than by 1,5,7-. IUPAC rules do not provide for numbering carbons in side chains.

Rule 3. If two double bonds are present, the ending of the name will be *diene*; if three double bonds are present, the ending will be *triene*. These endings replace the ending *ane* in the name of the saturated fundamental chain; for euphony, the letter "a" sometimes precedes these endings — for example, the name octane for the eight-carbon fundamental chain becomes octa*diene* for dihydromyrcene (No. 3, Chart 3) and octa*triene* for allo-ocimene (No. 5, Chart 3).

Rule 4. Name the side chains by approved radical names and precede these with the correct position numbers. For the acyclics, the complexity order and the alphabetical order of prefixes will be identical, since only methyl and methylene side chains are involved – for example, 2,6-dimethyl in geraniolene (Nos. 1A and 1B, Chart 3) and 7-methyl-3-methylene in myrcene (No. 2, Chart 3).

Rule 5. The systematic names for acyclic compounds are single words and not two-part names – for example, the isomeric geraniolenes (Nos. 1A and 1B, Chart 3) are dimethylheptadienes; allo-ocimene is 2,6-dimethyl-2,4,6-octatriene.

Common Terpene Names

The common terpene names for acyclic terpene hydrocarbons are not sufficiently precise to indicate their structures or relationships among derivatives. It is recommended therefore that use of these names be discouraged, although the names alloocimene and myrcene will still be convenient for limited usage for commercial products.

Monocyclic Terpenes

Classification. Type A and Type B

The monocyclic terpene bydrocarbons, many of which are formed readily from the acyclic terpenes by ring closure or from the bicyclic terpenes by ring fission, contain a six-carbon ring and may all be considered as derivatives of either cyclohexane or benzene. They may also be classified, on the basis of common larger fundamental structures, into two distinct types of substituted six-carbon ring structures:

Type A. Those which contain as ring substituents an iso three-carbon group and a one-carbon group, usually in para position; for a few hydrocarbons of this type, these groups are in meta or ortho position. Thus, Type A monocyclics may be considered as derivatives of menthane (isopropylmethylcyclohexane) or of cymene (isopropylmethylbenzene).

Type B. Those which contain no iso three-carbon group. Most of the hydrocarbons of this type, for which structures have been proved, contain two one-carbon groups in gem configuration and one or two additional isolated one-carbon or twocarbon groups, one of which is usually in meta position. These structures could be further divided into those that contain the gem-dimethyl configuration and those that do not, but their similar chemical reactivity warrants classification as a single group of compounds. Thus, Type B monocyclics may be considered as derivatives of dimethylcyclohexane, for which no trivial name has been well established.

These structural relationships are evident from the typical formulas shown in Chart 4. Although in this chart *a*-pyronene is numbered as 1,5,5,6-tetramethyl, the numberings 1,1,2,3- and 1,2,3,3- appear frequently in the literature.

Nomenclature Problems

Nomenclature rules and practices are well established for forming the systematic cyclohexane-type names for both Type A and Type B monocyclic hydrocarbons (13, 43). Simpler names than these systematic names will result by applying the principle of largest parent compound because fewer substituents have to be named (8). However, operating against the blanket application of this principle to the naming of all monocyclic terpenes is the principle of treating like things alike (9). The latter principle, as currently interpreted by the London Chemical Society and Chemical Abstracts, does not affect formulating simpler names for the Type A structures since the ring substituents (a one-carbon and an iso three-carbon group) are unlike, and the unsaturation of the structures differs only in position and number of double bonds. Violation of this principle is encountered, however, in naming the Type B structures on the basis of larger parents because the ring substituents in gem con-

Chart 4. Structural Relation of Monocyclic Terpene Hydrocarbons to Aromatic and Saturated Cyclic Hydrocarbons

Numbers within the Rings Indicate the Systematic Numbering Based on Chemical Abstracts Order of Prefixes; Numbers outside the Rings Indicate the Usual Terpene Numbering. These Numberings Are Those in Current Usage and Are Not Necessarily the Recommended Numberings.



figuration common to most of the structures and the additional isolated groups at various ring positions are frequently identical — that is, all may be methyl groups. In addition, a trivial name, menthane, for the parent compound of Type A monocyclics is well established but none is established for the parent compound of Type B monocyclics. Coining a new trivial name for this latter parent compound may not be the soundest approach to systematizing the nomenclature. Therefore, recommendations for naming the Type A and Type B monocyclic terpene hydrocarbons will be discussed separately.

Monocyclics. Type A. Derivatives of Menthane

Structural Features

Emphasis will be placed on the *para-substituted Type A monocyclic terpene bydrocarbons* in this discussion, but by analogy the material may be applied equally to the few known meta and ortho derivatives. The fundamental largest carbon skeleton common to the para-substituted monocyclics, as has been pointed out previously, is identical to that of the saturated hydrocarbon *p*-menthane. (For *p*menthane, the systematic name based on *Chemical Abstracts* order of prefixes is 1-isopropyl-4-methylcyclohexane; Chart 4). These Type A monocyclic compounds may contain saturated or unsaturated rings. They may contain one or two double bonds; for the latter type, both bonds may be inside or outside the ring, or one bond may be in each position. The one-carbon group substituent may be methyl or methylene; the iso three-carbon group may be isopropyl, isopropenyl, or isopropylidene (structural formulas of known Type A monocyclics are given in Chart 5).

Early Attempts at Systematizing Nomenclature

Attempts at systematizing the nomenclature of monocyclic terpenes (classed in this report as Type A) were made by Baeyer and by Wagner over 50 years ago. Baeyer (2), by applying the Geneva system, suggested that the dihydro-*p*-cymenes ($C_{10}H_{16}$) be called terpadienes; the tetrahydro-*p*-cymenes ($C_{10}H_{18}$), the terpenes; and hexahydro-*p*-cymene ($C_{10}H_{20}$), terpane. There is no evidence in the literature, however, that such names were used by other investigators. Wagner (54), in addition to proposing the name *p*-menthane for the completely saturated *p*-cymene ($C_{10}H_{20}$), proposed *p*-menthenes for the tetrahydrocymene derivatives ($C_{10}H_{18}$), and *p*-menthadienes for the dihydrocymene derivatives ($C_{10}H_{16}$). *p*-Cymene on this scheme could be named 1,3,5-menthatriene. The fixed numbering of the *p*-menthane carbon skeleton - that is, the methyl group attached to the No. 1 ring carbon and the isopropyl group to No. 4; Chart 5 – was suggested by Wallach (55). These menthane-type names and Wallach's fixed numbering of the carbon skeleton of menthane were received favorably and began to appear occasionally in the literature before the end of the nineteenth century.

Current Nomenclature

The menthane-type names have been generally recognized for some time as good names for Type A monocyclics (15). The use of the prefixes p-, o-, and m- in names of this type to designate the positions of substituents conforms to recognized usage of these prefixes with trivial names. Many of the common monocyclic terpene names appear in current literature with no mention of the corresponding menthane-type names. However, the latter have been used almost invariably for recently identified monocyclic terpene derivatives and for those having no familiar common terpene names. The historical fixed numbering of the p-menthane carbon skeleton has been used consistently for over 50 years and hence is well established in the literature. The systematic cyclohexane names have also been used, but only infrequently, for some of these monocyclics. Both types of names and the corresponding formulas are given in Chart 5.

Recommendation

For the Type A monocyclic terpene hydrocarbons (para, ortho, and meta derivatives of menthane) use the menthane, menthene, and menthadiene names and the well-established fixed numbering of menthane.

See Chart 5 for the para structures and the recommended names. The familiar terpene skeletal formulas and a consistent orientation of these formulas were chosen for Chart 5 merely for convenience. The recommendation of the American committees concerns only the names and fixed numbering of the menthane skeleton – it carries no stated preference for orientation or for the form in which formulas are drawn.

Rules for Forming the Menthane-Type Names

Rule 1. Use the name menthane with the prefix p-, m-, or o- for the three fundamental saturated Type A monocyclic hydrocarbons.

Rule 2. Retain the well-established fixed numbering for the menthane carbon skeletons. (The familiar orientation of the menthane structures is used in these rules merely as an aid to memory.)



Draw unsaturated formulas so that the ring double bonds have as low numbers as are consistent with this fixed numbering – for example, in the para series:

Draw This

And Not This



Chart 5. Names and Formulas of Type A (Menthane-Type) Monocyclic Terpene Hydrocarbons

Recommended Names of Para Derivatives Are Based on Fixed Numbering of p-Menthane Carbon Skeleton



Vo.	Common Terpene Name	Systematic Name — Chemical Abstracts Order of Prefixes Low Numbers to Double Bonds and Substituents	Recommended Name Fixed Numbering
6	p+Menthane	1-Isopropyl-4-methylcyclohexane	p-Menthane
7	Carvomenthene $(d$ -Form =	4-Isopropyl-1-methylcyclohexene	1-p-Menthene
	8,9-Dihydrolimonene)		-
8		3-Isopropyl-6-methylcyclohexene	2-p-Menthene
9	Menthene	1-Isopropyl-4-methylcyclohexene	3-p-Menthene
	(Menthomenthene)		•
10		1-Isopropyl-4-methylenecyclohexane	1(7)-p-Menthene
11	Dihydroterpinolene	1-Isopropylidene-4-methylcyclohexane	4(8)-p-Menthene
12	Dihydrodipentene	1-Isopropenyl-4-methylcyclohexane	8-p-Menthene
	$(\beta$ -Dihydrolimonene)		
13	a-Terpinene	1-Isopropyl-4-methyl-1,3-cyclohexadiene	1,3-p-Menthadiene
14	y-Terpinene	1-Isopropyl-4-methyl-1,4-cyclohexadiene	1,4-p-Menthadiene
15	a-Phellandrene	5-Isopropyl-2-methyl-1,3-cyclohexadiene	1,5-p-Menthadiene
16		2-Isopropyl-5-methyl-1,3-cyclohexadiene	2,4-p-Menthadiene
17		3-Isopropyl-6-methyl-1,4-cyclohexadiene	2,5-p-Menthadiene
18	Pseudolimonene	1-Isopropenyl-4-methylenecyclohexane	1(7),8-p-Menthadiene
19		1-Isopropylidene-4-methylenecyclohexane	1(7),4(8)-p-Menthadiene
20	Limonene (dl-Form =	4-Isopropenyl-1-methylcyclohexene	1,8-p-Menthadiene
	Dipentene)		
21	Isolimonene	3-Isopropenyl-6-methylcyclohexene	2,8-p-Menthadiene
22		1-Isopropenyl-4-methylcyclohexene	3,8-p-Menthadiene
23	Terpinolene	4-Isopropylidene-1-methylcyclohexene	1,4(8)-p-Menthadiene
24	Isoterpinolene	3-Isopropylidene-6-methylcyclohexene	2,4(8)-p-Menthadiene
25	β -Phellandrene	3-Isopropyl-6-methylenecyclohexene	1(7),2-p-Menthadiene
26	β-Terpinene	1-Isopropyl-4-methylenecyclohexene	1(7),3-p-Menthadiene



Rule 3. For unsaturated hydrocarbons, replace the *-ane* ending of menthane, the name of the saturated hydrocarbon parent compound, by *-ene* to denote one double bond - i.e., menthene - and by *-diene* to denote two double bonds; for the latter, add the connective ''a'' to the root menth- for euphony - i.e., menthadiene.

Rule 4. (a) Indicate the position of each double bond, if the bond is formed with the next-higher-numbered carbon atom and regardless of whether it is inside or outside the ring, only by the lower-numbered carbon to which it is attached – for example, in the para series:



1-p-Menthene [not 1(2)-p-menthene]



8-p-Menthene [not 8(9)-p-menthene]





2,4-p-Menthadiene [not 2,4(5)-p-menthadiene]

1,8-p-Menthadiene [not 1,8(9)-p-menthadiene]

On the basis of this portion of Rule 4, the hydrocarbon name 6-p-menthene (designating a bond between ring carbons 6 and 1) cannot arise, because there is nothing to prevent the formula being drawn with the bond between ring carbons 1 and 2 (Rule 2 above). The correct name for the hydrocarbon, therefore, would be 1-p-menthene. (b) If a double bond beginning at a specific carbon atom is not formed with the next-higher-numbered carbon atom but with a different adjacent carbon, indicate this by putting in parentheses, after the number designating the carbon from which the double bond begins, the number of the carbon atom to which the double bond is joined – for example, in the para series:



1(7)-p-Menthene 1(7),4(8)-p-Menthadiene 2,4(8)-p-Menthadiene

Those who advocate that double bonds designated as 1(7)- in two of the examples above can be designated by the single number 7- without ambiguity (59) violate the principle of lowest-numbered carbon atom for indicating the position of a double bond (12).

The above rules for naming the menthane-type (Type A) monocyclic terpene hydrocarbons differ from the strict nomenclature rules for cyclohexene and cyclohexadiene hydrocarbons (11, 43, 48) in that (1) the double bonds are not necessarily assigned the lowest numbers because of the established fixed numbering of the carbon skeleton (Rule 2 above), and (2) the method of designating positions of double bonds in rings has been extended to include bonds outside the rings (Rule 4 above). However, the series of rational names developed on the basis of these rules can be considered as conforming to current good nomenclature practice. Furthermore, the recommended names are simple to form; are concise, unambiguous, and practical; and are easy to grasp when spoken. The structure of a specific compound or the structural relationships among several compounds of the Type A monocyclics become immediately evident from these menthane-type names.

Common Terpene Names

A few of the trivial terpene names of the monocyclic hydrocarbons, especially for those products which have been produced commercially for some time, may continue in usage. These are dipentene, limonene, terpinene, and terpinolene. The latter two should be discouraged, however, because of the confusion caused by the roots terp- and terpin- and by the historical use of both Greek letters and the prefix iso- with these trivial names to designate structural isomers; the "ol" in terpinolene is also misleading because the compound is not alcoholic. The "commercial dipentene" is chemically so far from reasonably pure dipentene that the use of this trivial name for the commercial product is quite misleading and should also be discouraged. The natural question then is, why encourage continued usage of limonene?

Monocyclics. Type B. Derivatives of Dimethylcyclohexane

Structural Features

The unique carbon skeleton common to the compounds classed in this report as Type B monocyclic terpene bydrocarbons and larger than the six-carbon ring, as mentioned previously, is dimethylcyclohexane. The few unsubstituted cyclogeraniolenes (C9H16) and pyronenes (C10H16) contain a gem-dimethyl configuration. Most of the known isomers in these two series also have a one-carbon group (methyl or methylene) in the meta position. The pyronenes have in addition a one-carbon group (methyl or methylene) in the ortho position. The terpenes currently named as cyclogeraniolenes contain only one double bond which may be inside or outside the ring; those named as pyronenes contain two double bonds, both inside the ring or one inside and one outside. Compounds like 1,1,2-trimethylcyclohexane and 1,1,3,5tetramethylcyclohexane also contain gem-dimethyls and chemically resemble closely the respective parent compounds, 1,1,3-trimethylcyclohexane and 1,1,2,3-tetramethylcyclohexane, of the cyclogeraniolenes and of the pyronenes. There are numerous allied simple structures that occur widely in crude petroleum and other natural products - for example, 1,2,4-trimethylcyclohexane and ethylcyclohexane (58). Other well-known related structures include 1,3,5-trimethylcyclohexane and 1,6,6-trimethylcyclohexene. Typical terpene reactions such as the pyrolysis of allo-ocimene (38) yield two types of cyclohexane derivatives: some with a gem-dimethyl configuration as 1-ethyl-5,5-dimethyl(and 2-ethyl-6,6-dimethyl)-1,3-cyclohexadiene; some without the gem-dimethyls as 1,2,4,6(and 1,2,3,5)-tetramethyl-1,3-cyclohexadiene. These hydrocarbons can all be considered as derivatives of dimethylcyclohexane, but the common parent compound larger than the ring-carbon skeleton cannot be limited to the gem-dimethyl derivative of cyclohexane (see Chart 6).

Nomenclature Problems

Proposals for simplifying and coordinating the nomenclature of the Type B monocyclic terpene bydrocarbons should be sufficiently flexible to be applicable not only to the few known cyclogeraniolenes and pyronenes but also to the more numerous related structures. Names simpler than the systematic cyclohexane type and resembling more closely the menthane-type names recommended for the Type A monocyclics would fit nicely into the proposed scheme for systematizing the nomenclature of all terpene hydrocarbons. One practical drawback to devising for the Type B monocyclics such a simple logical series of names based on the largest parent compound is that no common name, such as menthane, has been established for dimethylcyclohexane. A compelling reason for not now coining a name for this parent compound is that the majority of Type B hydrocarbons, unlike the Type A hydrocarbons, are currently named systematically as cyclohexane derivatives by universally accepted rules and do not have trivial names.

The importance of these Type B compounds has only recently been recognized because of chemical developments in fields such as the irones, carotenoids, and petroleum cracking. The existence of the *gem*-dimethyl configuration in the irone and carotenoid structures and the growing importance of these compounds are responsible for serious consideration of limiting the Type B monocyclics to those having in common the carbon skeleton of *gem*-dimethylcyclohexane. In fact, several different nomenclature schemes based on coined names for this parent compound and aimed at simpler names have been tested. These proposals and others based on coined names for the still larger trimethylcyclohexane skeleton are summarized in Appendix A. All contain inherent elements that violate generally accepted nomenclature practices and each excludes too many chemically related compounds. Therefore, the American committees recommend that the Type B monocyclics not be limited to those hydrocarbons which contain the *gem*-dimethyl configuration.

On the basis of these considerations, the size of the parent compound for Type B monocyclics seems to be of only minor importance to the problem of systematizing their nomenclature. The systematic cyclohexane-type names are therefore recommended.

Recommendation

Name the Type B monocyclic terpene hydrocarbons (derivatives of dimethylcyclobexane) systematically as derivatives of cyclobexane, cyclobexene, and cyclobexadiene (IUPAC rules).

See Chart 6 for the structures and recommended names. In these names, the *Chemical Abstracts* order of prefixes has been followed. Compounds Nos. 30-32 and 34-38 are those which up to now have usually been included in treatises on terpenes. Many of the other structures, however, surely warrant inclusion in the future.

Rules for Forming the Cyclohexane-Type Names

The systematic cyclohexane-type names are formed according to IUPAC rules (11, 43, 48). For the Type B monocyclic terpene hydrocarbons, these rules may be stated as follows:

Rule 1. Name all Type B monocyclic terpene hydrocarbons (derivatives of dimethylcyclohexane) as derivatives of cyclobexane, cyclobexene, or cyclobexadiene; the name chosen depends on whether the ring structure is saturated, contains one double bond, or contains two double bonds.

Rule 2. For saturated ring structures, assign lowest numbers to the position of the substituents – for example, number Formula 28 so that the methyl groups are at 1,1,3- and not at 1,3,3-; in Formula 29 use 1,1,2,3- and not 1,2,3,3-.

Rule 3. For unsaturated ring structures containing only one double bond, the carbon at one end of this bond is always No. 1. If two double bonds are present, assign lowest possible numbers to their positions in the ring. After double bonds are numbered, then assign as low individual numbers as possible to the positions of the substituents.

IUPAC Rule 64 (41) states: "The expression 'lowest numbers' signifies those that include the lowest individual number or numbers". Thus, 1,3 is lower than 2,4; 1,1,3 lower than 1,3,3; 1,5,5 lower than 2,2,6; 1,2,3,5 lower than 1,3,4,5. At one time *Chemical Abstracts* interpreted "lowest numbers" to mean those which yielded the lowest sum – for example, 2,2,6 (which adds up to 10) was considered lower numbering than 1,5,5 (which adds up to 11). Now, however, this practice has been abandoned, and the lowest individual numbers are the determining factor (10, 44). If two sets of lowest numbers for double bonds and substituents are equally possible according to IUPAC Rule 64, then the chosen order of prefixes – that is, alphabetical or complexity – becomes the determining factor. Examples of this numbering rule from formulas and names shown in Chart 6 are: The substituents in No. 30 are at 1,5,5 and not at

Chart 6. Names and Formulas of Type B (Dimethylcyclohexane-Type) Monocyclic Terpene Hydrocarbons and Allied Compounds

Recommended Systematic Names Are Based on IUPAC Rules and Chemical Abstracts Order of Prefixes. Formulas Are Oriented So That No. 1 Carbon Is at Top, and the Numbering Runs Clockwise



No.	Common Terpene Name	Recommended Systematic Name – Chemical Abstracts Order of Prefixes Low Numbers to Double Bonds and Substituents
27		1,1-Dimethylcyclohexane
28	(Cyclogeraniolane)	1,1,3-Trimethylcyclohexane
28A.		1,1,2-Trimethylcyclohexane
28B.		1,1,4-Trimethylcyclohexane
28C.		1,2,3-Trimethylcyclohexane
28D.		1,2,4-Trimethylcyclohexane
28E.		1,3,5-Trimethylcyclohexane
29	(Pyronane)	1,1,2,3-Tetramethylcyclohexane
294.		1,1,2,4-Tetramethylcyclohexane
29B.		1,1,2,5-Tetramethylcyclohexane
29C.		1,1,3,5-Tetramethylcyclohexane
29D.		1,1,2,6-Tetramethylcyclohexane
29E.		1,1,3,4-Tetramethylcyclohexane
29F.		1,2,3,4-Tetramethylcyclohexane
29G.		1,2,3,5-Tetramethylcyclohexane
29H.		1,2,4,5-Tetramethylcyclohexane
30	a-Cyclogeraniolene	1,5,5-Trimethylcyclohexene
31	β -Cyclogeraniolene	1,3,3-Trimethylcyclohexene
32	y-Cyclogeraniolene	1,1-Dimethyl-3-methylenecyclohexane
33	·	1,6,6-Trimethylcyclohexene
34	Methyl-y-cyclogeraniolene	1,1,2-Trimethyl-3-methylenecyclohexane
35	Cyclodihydromyrcene	1,5,5,6-Tetramethylcyclohexene
36	a-Pyronene	1,5,5,6-Tetramethyl-1,3-cyclohexadiene
37	B-Pyronene	1,2,6,6-Tetramethyl-1,3-cyclohexadiene
38	y-Pyronene	1,5,5-Trimethyl-6-methylenecyclohexene
39		1,2,3,5-Tetramethyl-1,3-cyclohexadiene
40		1,2,4,6-Tetramethyl-1,3-cyclohexadiene
41		1-Ethyl-5,5-dimethyl-1,3-cyclohexadiene
42		2-Ethyl-6,6-dimethyl-1,3-cyclohexadiene

2,4,4 as they would be if the other end of the double bond had been assigned the position No. 1. In No. 36, the lowest numbers that can be assigned to the two double bonds are 1,3; since a substituent is attached to the ring at the end of one double bond, this ring carbon is assigned No. 1; then the lowest numbers possible for the substituents are 1,5,5,6.

Rule 4. Formulas of alicyclic hydrocarbons, of which cyclohexane is an example, are usually oriented so that the numbering runs clockwise. This orientation has been used for all formulas in Chart 6.

Rule 5. Name all side chains by approved radical names and precede these with correct position numbers – for example, 1,1-dimethyl-3-methylene as in Formula No. 32 (Chart 6); 1,2,6,6-tetramethyl as in Formula No. 37.

Rule 6. To form the complete name of a compound, arrange the names of the substituents in the alphabetical or complexity order (in Chart 6 the *Chemical Abstracts* alphabetical order has been followed); then prefix this part of the name to the correct cyclo part of the name. Such a systematic cyclohexane-type name forms a single word. For example: β -cyclogeraniolene (Formula 31, Chart 6) is named 1,3,3-trimethylcyclohexene; methyl- γ -cyclogeraniolene (Formula 34) is 1,1,2-trimethyl-3-methylenecyclohexane; *a*-pyronene (Formula 36) is 1,5,5,6-tetramethyl-1,3-cyclohexadiene.

Common Terpene Names

The first few Type B (derivatives of dimethylcyclohexane) terpene monocyclic hydrocarbons that were discovered had the empirical formula C_9H_{16} and were named as cyclogeraniolenes (53, 57). Much more recently the allied hydrocarbons with the empirical formula $C_{10}H_{16}$ were named as pyronenes (22). Both names were chosen to indicate the origin of the products – for example, *a*-cyclogeraniolene was obtained by isomerization of the acyclic hydrocarbon geraniolene; pyronene by the pyrolysis of pinene. These historical names have persisted in the literature. With current developments in the field, no attempts have been made to extend the use of the common names to new products; the systematic cyclohexane-type names have been used. This is probably because many of the newer Type B monocyclics do not contain a larger parent compound – that is, gem-dimethylcyclohexane – in common with the cyclogeraniolene and pyronene structures. In addition, the name pyronene causes confusion because of its similarity to terms (such as pyranone, pyrane, pyrone, pyrene) now in use for different types of structures. It is recommended therefore that the use of cyclogeraniolene and pyronene be discouraged.

Bicyclic Terpenes

Fundamental Bicyclic Groups and Structural Relationships to the Menthane—Type (Type A) Monocyclics

The bicyclic terpene hydrocarbons differ in fundamental structure from the monocyclic terpene hydrocarbons as any bicyclic compound differs from any monocyclic compound. The fundamental chemical structures and reactions of these bicyclics and their hydrogenated and other derivatives are currently classified in the terpene literature as belonging to one of four groups - the thujane (or sabinane) group, the carane group, the pinane group, and the campbane group. The names "thujane group" and "bornane group" are recommended to designate, respectively, the first and fourth type of bicyclic structures. Reasons for the choice of thujane over sabinane, and for the replacement of the historical name camphane by the newly coined name "bornane" will be discussed in the specific sections of this report dealing with the nomenclature of these two groups of bicyclic terpene hydrocarbons. All of the fundamental bicyclic types contain bridges; in two types the bridge is a "valence bridge" - that is, contains no carbon atom; in the other two types the bridge is an "atomic bridge" - that is, contains one carbon. The bridge carbon may have only hydrogens attached or may have methyl groups attached. Some bicyclics are completely saturated compounds; these all contain a gem-dimethyl configuration and an additional isolated methyl group. Others are unsaturated. Those which contain one double bond may have this bond inside or outside the ring structure. Practically all of those which contain two double bonds have only one double bond within the ring, the other being outside.

The bicyclic terpene structures are related much more closely to the menthanetype (Type A) monocyclics than to the dimethylcyclohexane-type (Type B) monocyclics. These structural relationships are shown in Chart 7. In this chart the recommended established fixed numbering of p-menthane and the familiar conventional terpene formulas are used. It is immediately evident that all of the structures contain a gem-dimethyl configuration; furthermore, from the viewpoint of chemical structure of the bicyclics, the ring carbon No. 4 and the isopropyl tertiary carbon No. 8 in the p-menthane are the two significant carbons. Each of the four types of bicyclics contains carbon No. 4 as the carbon at one end of the bridge. In the thujane type, the other end of the bridge can be carbon No. 2 (as shown in Chart 7) or carbon No. 6; the isopropyl group containing carbon No. 8 is intact as a ring substituent. For the other three bicyclic types, the tertiary carbon No. 8 is involved either as a carbon in the second ring (as in carane) or as a carbon in the bridge (as in pinane and bornane); hence, these three types do not contain an isopropyl group. The other end of the bridge in the carane, pinane, and bornane type, as shown in Chart 7, can be respectively carbon No. 5, No. 6, and No. 1. For carane and pinane, these bridge ends could also be, respectively, carbon No. 3 and No. 2.

Therefore, on the basis of their carbon skeletons, the bicyclic terpenes belong to the following condensed ring structures: *thujane type* to bicyclo[3.1.0]hexane; *carane type* to bicyclo [4.1.0]heptane; *pinane type* to bicyclo [3.1.1]heptane; and Chart 7: Structural Relation of Bicyclic to Menthane-Type (Type A) Monocyclic Terpene Hydrocarbons

The Recommended Fixed Numbering of p-Menthane is Shown. Corresponding Carbons in the Bicyclic Structures Carry Identical Numbers Merely to Demonstrate Relationships. In No Case Does the Bicyclic Numbering Coincide with the Recommended Fixed Numberings, Which Are Shown in Chart 8. The Name "Bornane" for Type IV Is the New Name Recommended in This Report to Replace the Historical Name "Camphane".



p-Menthane



bornane type to bicyclo [2.2.1] heptane. It should not be inferred from the structural relationships pointed out above that the bicyclics are readily formed from the menthane-type monocyclics; actually, with only a few exceptions, the reverse reaction is the usual one in terpene chemistry. However, this report is concerned with nomenclature problems and not with the chemical reactions.

Nomenclature

Current Status

Despite the early recognition of the four fundamental bicyclic structures and the agreement on their class names, no attempts seem to have been made to replace the many historical terpene names for the bicyclic terpene hydrocarbons and their derivatives by simple, logical series of names for each type. The terpene chemist's attitude in the thirties on nomenclature of the bicyclic terpenes has been summarized by Lipp (32) as follows:

"In general, the names used are derived from those of the species of plants in which some of the more important compounds occur. Only in certain cases is a systematic nomenclature of value; in these cases, reference is made to the completely demethylated hydrocarbons of the three main groups; these are called norcarane, norpinane, and norcamphane."

In contrast to this viewpoint, the current nomenclature practice followed in indexing bicyclic terpene bydrocarbons by Chemical Abstracts (14, 15) is:

"Bicyclic terpenes and their derivatives are in general named and numbered in the same manner as other bicyclo compounds.

"The IUPAC rules make no mention of bridged systems. In indexing such compounds *Chemical Abstracts* follows the Baeyer plan (3), using names beginning "bicyclo" - e.g., bicyclo 3.1.0 hexane... In the bicyclo names the three numbers in the brackets denote, respectively, the number of members in the right bridge, the left bridge, and the middle bridge...double bonds are given as low positions as is consistent with the numbering imposed by the bridges......."

A check of recent *Chemical Abstracts* indexes reveals, however, that many of the subject entries for bicyclic terpene hydrocarbons are listed under the common terpene names, and frequently the corresponding bicyclo names are not used either as synonym names or cross references.

Problems in Systematizing Naming of Bicyclics

Somewhere between these two extremes there must be a practical compromise system of nomenclature which will be acceptable to both the terpene chemist and the indexer. Naming the bicyclic terpene hydrocarbons is, however, not nearly so simple as naming Type A monocyclics for which the name of a single largest parent compound (menthane) suffices for forming names for the entire series. In addition to those bicyclics which contain the complete carbon skeleton of one of the four fundamental structures (Chart 7), there are a number of compounds, especially in the pinane and bornane groups, which contain in common only the complete ringcarbon skeleton or a carbon skeleton intermediate between the two. Size, unsaturation, and the principle of like treatment of like things are the determining factors in choosing the most useful largest bicyclic parent hydrocarbons with side chains. Often these factors are in conflict and the problem must be resolved on a compromise basis.

Prefixes Apo-, Homo-, and Demethyl

The prefixes apo- and homo- have been used with consistent specific meanings in historical terpene nomenclature. Apo- has denoted a parent ring system minus one methyl group, and this is always the isolated methyl group, and not one of the gem-dimethyl groups. Homo- has denoted the next higher homolog of a compound, and this homolog differs in formula from the latter by an increase in CH_2 . In other fields, apo- and homo- have been used with less specific or different meanings (16); also, other prefixes have been used with an established terpene meaning for different prefixes – e.g., nor- instead of apo- in the steroid field. Neither apo- nor homo- is needed in the recommended scheme for systematizing the nomenclature of the terpene bicyclics. The American committees recommend, therefore, that apo- and homocease to be recognized as useful prefixes for terpene names.

The prefix "demetbyl" as a replacement for apo- in naming terpenes has been proposed (see Appendix B) and is more precise. However, for such names as "demethylpinane" and "demethylbornane" to be definitive, knowledge of the structure of the compound from which the isolated methyl group has been removed is necessary. An alternative would be to attach to the name a prefix number to denote the ring position to which the original methyl group was attached - e.g., "2-demethylpinane," "1-demethylbornane." To form a consistent series of names for one type of bicyclics, a structure such as a-fenchane would then be named "1-demethyl-2methylbornane."

It is a temptation to extend the use of "demethyl" by attaching the prefixes dior tri- to denote removal of two or three methyl groups from their normal positions in the fundamental bicyclic structures larger than the ring structures. This would result in such illogical names as "7,7-didemethyl-3,3-dimethylbornane" (for fenchane) and "1,7,7-tridemethyl-2,2,3-trimethylbornane" (for isocamphane). Further extension would introduce the prefix "demethylene" and other variations.

Other complications become evident by applying "demethyl" nomenclature to the bornane group of bicyclics. The American committees recommend, therefore, that neither the prefix "demethyl" or the related prefix "demethylene" be introduced into terpene nomenclature.

Numbering and Orientation of The Four Fundamental Bicyclic Structures

Recommended Fixed Numberings

The four fundamental bicyclic structures, larger than the ring structures, provide an excellent starting point for systematization of the nomenclature of the bicyclic terpene hydrocarbons by applying the principles on which the recommendations in this report are based. Standardization of the conventional forms for depicting the skeletal formulas, adoption of fixed numberings for these formulas, retention of wellestablished terpene names or roots of these names, and agreement to apply only good nomenclature rules are obvious tools.

Various numberings and orientations of the four typical saturated bicyclic types are summarized in Chart 8. The familiar terpene skeletal formulas are used in some of the columns merely for convenience. The fixed numberings recommended by the American committees for adoption are given in column 3. These numberings have
Chart 8. Fundamental Structures of Bicyclic Terpene Hydrocarbons and Recommended Fixed Numberings

Identification Numbers for Formulas Correspond to Those Used in Later Charts.

Uniform Orientation of the Recommended Formulas in Column 3 Is Only for Numbering Purposes and Rapid Recognition.



(a) A second numbering of pinane used frequently assigns No. 1 to the ring carbon to which the lone methyl group is attached, and runs clockwise. In this numbering, No. 1 is not a bridge-end carbon and the bridge ends are Nos. 4 and 6.

- (b) The formulas in this column are based on the forms of the unsubstituted ring systems given in the ring index.
- (c) New name recommended to replace camphane.

been proposed as a feasible compromise which may be acceptable to the majority. This recommendation contains no connotation as to a preference for orientation or form of formula.

The formulas in column 3 are oriented with the lone methyl group at the top for purposes of numbering, for ready recognition in the terpene literature, and for simplifying the memory work throughout the four different series of bicyclic terpenes. The skeletal formulas showing the recommended fixed numberings for thujane and carane are mirror images of the familiar terpene forms. These orientations differ from those specified by the rules for ring systems (40, 46), according to which they would be oriented so that the two rings are in a horizontal row, with the larger ring on the right and the No. 1 bridge-end carbon at the top of the formula (cf. Baeyertype formulas, Chart 8). The orientation of the skeletal formula for pinane (column 3) is admittedly a compromise on the position of the bridge in order to retain the familiar terpene form. In the case of bornane, the orientation of the skeletal formula is identical with both the Baeyer-type and the familiar terpene form.

The recommended *fixed numberings* of the *ring carbons* in the four fundamental structures run clockwise according to the established rules for orienting bicyclic structures (40, 46), and all conform to the bicyclo plan rules (3, 14). The rules applied for establishing these terpene fixed numberings are:

Rule 1. The formula is oriented for uniformity and convenience so that the lone methyl is at the top.

Rule 2. One bridge-end carbon is No. 1, and the numbering proceeds clockwise around the entire ring skeleton, *first by the longer route* to the other bridge-end carbon and *then by the shorter route* back to carbon No. 1. Hence, in thujane and pinane, the bridge ends are 1-5 instead of 1-3; in carane, 1-6 instead of 1-3; in bornane, 1-4.

Rule 3. When a valence bridge – i.e., contains no carbon – is present, the ring carbon skeleton is completely numbered by Rule 2. This is the case for thujane and carane.

Rule 4. When an atomic bridge – i.e., contains one carbon – is present, the carbon in the bridge is numbered after the carbons in the complete ring skeleton have been numbered. This rule applies to pinane and bornane, in which the bridge carbon thus becomes No. 7.

Rule 5. When substituents are attached to the ring skeleton and a choice in numbering of the ring carbons is possible on the basis of Rule 2, the ring carbons are numbered so that the substituents are attached to the lower-numbered ring positions. Hence, in thujane the substituent groups are at 1,4 rather than at 2,5; in carane the lone methyl group is attached to No. 3 carbon rather than to No. 4. There is no choice in numbering the ring skeletons of pinane and bornane on the basis of Rule 2; therefore, according to Rule 5, the methyl groups are respectively at 2,6,6 and at 1,7,7.

Numbers are assigned to carbons in *substituent groups* only after all ring and bridge carbons have been numbered. There are no specific rules, however, on this type of numbering. In all of the fundamental bicyclic terpene formulas except thujane, the No. 7 carbon must be a ring carbon according to the bicyclo plan. In carane and bornane, two methyl groups are attached to this No. 7 carbon; it is logical therefore to number those methyl-group carbons with the two next higher numbers, 8 and 9, and to assign No. 10 to the carbon of the third methyl group. This numbering also has been used consistently in the terpene literature. In pinane, the carbons in the two methyl groups attached to a single carbon have been numbered consistently in the terpene literature as No. 8 and No. 9 and the carbon of the third methyl group as No. 10. Therefore, for uniformity of numbering among the four fundamental types of bicyclics, No. 10 has been chosen for the carbon of the isolated methyl group attached to a ring carbon in all four fundamental structures.

The rule governing the recommended *fixed numbering* of the carbons in substituent groups of the bicyclics is therefore:

Rule 6. Assign No. 8 and No. 9 to the carbons of the gem-dimethyl groups, and No. 10 to the carbon of the isolated methyl group in all four fundamental bicyclic structures. (See column 3 of Chart 8 for the numbering recommended for adoption.)

Importance of Orientation

Uniform orientation of the fundamental bicyclic parent structures (column 3, Chart 8) showing the recommended fixed numberings of their carbon skeletons has the advantages of: (1) ready recognition of structural similarities, and (2) aiding the remembering of the numberings of the different types of structures. Later charts showing formulas of derivatives of these fundamental bicyclic structures and recommended logical series of names for these derivatives emphasize the advantages of uniform orientation, especially in the terpene field. However, once the numberings of the ring systems and the carbons in the substituent groups have been determined, formulas may be oriented in any direction without violating the rules for numbering the carbon skeletons.

Differences in Recommended Fixed Numberings For Bicyclics and for Menthane-Type Monocyclics

The recommended fixed numberings for p-menthane (Formula 6, Chart 5) and for the four bicyclic terpene types (column 3, Chart 8) differ in (a) the numbers of the ring carbons to which the substituent groups are attached - for example, the isolated methyl group is attached to ring carbon No. 1 in p-menthane and to ring carbon No. 4, No. 3, No. 2, and No. 1, respectively, in thujane, carane, pinane, and bornane; and (b) the numbers assigned to the carbons in substituent groups attached to the rings - for example, the carbon of the isolated methyl group is No. 7 in p-menthane and No. 10 in the bicyclics. These numberings recommended by the American committees were arrived at, as discussed earlier, for the monocyclics, by retaining the well-established fixed numbering of the menthane carbon skeleton; and for the bicyclics, by choosing the recognized bicyclo plan of numbering as the guiding principle and by evaluating consistency in numbering as of prime importance for systematizing the nomenclature of any one class of compounds. The differences in numberings that have resulted are not unique for these two classes of terpene hydrocarbon structures; in other fields of chemistry there are similar numbering differences between chemically interrelated monocyclic and bicyclic compounds because of their fundamental structural differences and the universally recognized rules and principles that determine the numberings of their carbon skeletons.

The close structural relationships between the bicyclic and the menthane-type

monocyclic terpenes shown in Chart 7 have prompted several reviewers of earlier versions of this report to urge the adoption of an identical numbering scheme for the two classes of compounds. Specific proposals made and the schemes tested in an attempt to attain this consistency in numbering are summarized in Appendix C. They all center around the idea that preserving the numbering in going from bicyclics to monocyclics offers more advantages in the terpene field than conforming strictly to established principles and rules for allied structural types. The dominant change in numbering that has been promoted is for *p*-menthane; this is to replace the well-established numbering shown in Formula I by that shown in Formula II:



The various numberings proposed for the bicyclics to harmonize their numbering with that of the monocyclics violate, in general, the recognized bicyclo plan. All of these proposals contain limiting phrases such as "in so far as possible" and "with mild concessions to systematic numbering," indicating foreseen discrepancies in over-all applicability.

On evidence such as is presented in this paragraph, the American committees concluded that a consistent numbering for monocyclics and bicyclics is not feasible and that established nomenclature rules and practices should supercede structural relationships in determining the recommended fixed numberings of p-menthane (No. 6, Chart 5) and of the four fundamental bicyclic structures (Nos. 46, 55, 66, 75; column 3, Chart 8). An obvious advantage of a consistent numbering scheme is that a substituent attached to carbon No. 10 in a bicyclic terpene would still be attached to carbon No. 10 when a bicyclic is converted to a monocyclic terpene. For example:



a-Pinene

Dipentene

In SYSTEM OF NOMENCLATURE FOR TERPENE HYDROCARBONS; Advances in Chemistry; American Chemical Society: Washington, DC, 1955.

For purposes of systematizing nomenclature and fitting this into the over-all nomenclature of organic compounds, a test of the proposed consistent numbering scheme more significant than the above example of conversion of one structural type (bicyclic) to another structural type (monocyclic) is the conversion of one structural type – e.g., bicyclic – to other compounds belonging to the same structural type. For an example of the latter type, the commercial conversion of a-pinene to camphene has been chosen. The numbers assigned to the carbons in the a-pinene formulas are those which have been used most frequently in the terpene literature. To designate identity of carbons this same numbering has been carried through to the formulas of the products formed in the reaction. Thus:



The structural transformations shown are so drastic as to disrupt the logical sequence of numbering around the carbon skeletons of the fundamental bicyclo rings. This type of inconsistency in numbering structures belonging to a single class of terpenes violates recognized practices; also it necessitates a thorough knowledge of their chemical reactions and the memorizing of numberings which frequently conform to neither the historical terpene or the bicyclo plan numbering. The majority opinion of the American committees is that these disadvantages of the consistent numbering proposals far outweigh advantages such as having carbon No. 10 identical in monocyclics and bicyclics or having the actual or potential isopropyl group always attached to ring carbon No. 1.

Nor- Structures of Bicyclics

Parent Bicyclic Ring Systems and Nor-Names

For systematizing the nomenclature of bicyclic terpene hydrocarbons, a consideration of only the fundamental parent carbon skeletons larger than the unsubstituted ring systems (Chart 8) is not adequate. The fundamental unsubstituted *parent ring*

systems must also be considered to provide a basis for naming those bicyclics which do not contain carbon skeletons identical to the larger parent systems. In the terpene field, the prefix nor-, denoting replacement of all methyl groups in the larger parent structures by hydrogen, has been used with the common terpene names of the larger saturated parent structures to form names for the parent ring systems (20, 32) - for example, norpinane has been preferred to the systematic name bicyclo[3.1.1]heptane. This usage of nor- in the sense of "complete stripping" is closely akin to the original meaning - that is, as an abbreviation for "normal" proposed in 1868 for the prefix (35). The more recent use of nor- with different meanings in other fields (see Appendix D) does not justify discarding from terpene nomenclature a well-established prefix that is extremely useful in systematizing the naming of the bicyclics, especially those belonging to the bornane group. Therefore, the names recommended for the three fundamental saturated parent bicyclic ring systems to which the historical definition of nor-applies are: norcarane, norpinane, and norbornane. These names are written as solid words. The names recommended for the corresponding unsaturated parent rings containing one double bond are: norcarene, norpinene, and norbornene. If need arises for names of the unsaturated parent ring systems containing two double bonds, the -ene endings can be replaced by -diene - e.g., norcaradiene, norbornadiene.

The conciseness of the nor- names and their usefulness in the spoken language are obvious. They differ from the systematic bicyclo names only in that a simple nor- name – e.g., norpinane – replaces a more complex systematic name – e.g., bicyclo [3.1.1] heptane. The position numbers and names of the substituents are identical in the two types of names. The nor- names are easier to grasp when spoken, and they also retain familiar terpene names.

Since thujane contains as ring substituents an isopropyl group as well as a methyl group, the name "northujane" (see Appendix D) does not conform to the terpene traditional definition of nor-. The bicyclo plan name, that is bicyclo[3.1.0] hexane, is therefore recommended for the name of the parent ring structure of thujane, the fourth fundamental type of bicyclic terpenes.

Recommended Numberings for Parent Bicyclic Ring Structures

The formulas of the fundamental unsubstituted ring structures of the bicyclic terpene hydrocarbons, variously oriented and with two different numbering systems, are shown in Chart 9.

Both saturated bicyclo rings and unsaturated bicyclo rings containing one double bond are included. Unsaturated rings containing two double bonds are also possible in the norcarane and the norbornane series, but these are not shown. A comparison of Chart 9 with Chart 8 reveals that the different numberings and orientations of the unsubstituted ring structures and of the ring structures containing substituents are identical.

The recommended numberings of the ring structures shown in column 1 of Chart 9 conform to the bicyclo plan rules (3, 14). The numberings of the saturated formulas are determined by Rules 2 to 4 given earlier for the numbering of the ring carbons of the four fundamental bicyclic structures larger than these ring structures. The numberings of the unsaturated ring structures conform to the established practice of assigning to the double bond (or bonds if more than one double bond is present) as low a position number as is consistent with the numbering imposed by the bridges (14). For example, on the basis of this principle, there is no "3- ene" ring structure

Chart 9. Ring Carbon Parent Compounds of Bicyclic Terpene Hydrocarbons

The Prefix Nor- Is Used to Denote a Ring System Devoid of Methyl Groups. The Identification Numbers for the Formulas Correspond to Those Used in Later Charts. The Orientations Shown in Column 1 are Only for Ready Recognition of the Corresponding Larger Bicyclic Carbon Skeletons Recommended in Chart 8.



(a) This structure is called norcamphene by Simonsen (51) and Chemical Abstracts. Elsevier (24) and Heilbron (28) use the name norcamphene for the saturated ring structure with a methylene group at position 2; this nomenclature is not recommended.

in the thujane or pinane series; the following pairs of formulas are identical and always would be numbered as "2- enes":



Bicyclo[3.1.0]hex-2-ene

2-Norpinene

For the numbering to run clockwise in IB and IIB, the formulas can be reoriented. Thus:



In the norcarane and norbornane series, structures with two double bonds are possible; these bonds would be numbered, on the basis of the above principle, as 2,4- for both structures.

Principle of "Like Treatment of Like Things"

The principle of "like treatment of like things" is adhered to by both the British (36) and the American (9) nomenclaturists in formulating preferred systematic names for chemical compounds. A discussion of this principle is included here rather than earlier in this report because it applies more pertinently to decisions on recommended names for some of the bicyclic terpene hydrocarbons than it does to those for the acyclic and monocyclic terpene hydrocarbons.

The principle of "like treatment of like things," as applied to the naming of bicyclic terpene hydrocarbons, may be stated as follows:

A compound possessing a carbon skeleton with certain side chains is not named as a derivative of another compound possessing a carbon skeleton with fewer side chains when the "added" one or more side chains in the first compound are *identi*cal to side chains present in the second compound. When the "added" side chains are not identical, the first compound, other things being equal, is named as a derivative of the second.

According to current British and American practice, *like* is interpreted to mean *identical* – for example, the $-CH_3$ group is considered to be *unlike* the $=CH_2$ and $-C_2H_5$ groups. Therefore, to take pinane names merely as an example, this prin-

ciple allows such names as methylenepinane and ethylpinane. It does not allow such a name as methylpinane because the "added" side chain is the methyl group, and the pinane carbon skeleton already contains methyl groups. A methyl-substituted pinane would therefore have to be named as a derivative of the basic ring structure – for example, as tetramethylbicyclo[3.1.1]heptane or tetramethylnorpinane. For the names used as examples above to be specific, the names of the hydrocarbon side chains should be preceded by proper position numbers.

Although a name such as methylpinane violates the principle of "like treatment of like things," it is unambiguous, convenient, and simpler than tetramethylnorpinane. Also, relations among substituted derivatives of a fundamental bicyclic such as pinane are more readily seen from a series of names such as methylpinane, methylenepinane, and ethylpinane than from a series in which methylpinane is replaced by tetramethylnorpinane. If the principle is violated to the above extent, then the question arises as to how many "added" side chains and how many carbons in an added side chain will be allowed before the terpene-type nomenclature ceases to be applicable. Considerations such as these and the compelling desire of both the European and American reviewers of earlier drafts of this report to recommend consistent series of terpene names which conform without exceptions to a sound principle led to proposed modifications of the principle of 'like treatment of like things' (see Appendix E). Despite the fact that the names of only a few terpene hydrocarbons are involved, members of the American nomenclature committees could not reach a clear-cut decision on a preferred modification of the principle. Therefore in this report, the bicyclic names designated as recommended on the charts conform to the established British and American interpretation of the principle of like treatment of like things. This principle also governs the names recommended for the other classes of terpene hydrocarbons.

General Recommendations for Naming Bicyclics

The parent compounds, the terpene names, and the fixed numberings recommended by the American committees for the four fundamental bicyclic terpene structures are:



The parent structures, the terpene names, and the systematic bicyclo numberings recommended for the unsubstituted saturated ring carbon skeletons of these four fundamental bicyclic types are:



In forming names of derivatives based on the larger parent compounds – that is, on thujane, carane, pinane, or bornane – the recommended fixed numbering governs the position numbers assigned to double bonds; the position numbers of the side chains do not change. Nor- type names and the bicyclo names, however, are formed systematically, and double bonds are assigned position numbers as low as is consistent with the bridge numbering; these double bond numbers then govern the low numbers assigned to the side chains.

All of the bicyclic terpene hydrocarbon structures related to carane, pinane, and bornane can be named, on the basis of recommendations in this report, as derivatives of the nor- compounds. Since the name "northujane" has not been recognized, the corresponding names for the structures related to thujane would be based on bicyclo-[3.1.0] hexane. The American committees recommend, however, that names based on the complete larger carbon skeletons of the four fundamental types of bicyclics, when they apply, be given preference over the nor- and bicyclo names. This results in simpler names for many of the hydrocarbons - e.g., 2-thujene is preferred to 1isopropyl-4-methylbicyclo[3.1.0]hex-2-ene; 3-pinene is preferred to 4,6,6-trimethyl-2-norpinene. The nor- and bicyclo names are extremely useful, however, in systematizing the nomenclature of the bicyclic structures which contain carbon skeletons similar to but not identical to those of the larger parent compounds. These structures may contain: (1) the same number of methyl groups but in different ring positions e.g., the fenchanes; (2) an additional methyl or methylene group - e.g., homopinene or homoverbanene, the names of some of which may be governed by the principle of treating like things alike; (3) fewer methyl groups -e.g., apocamphane and santene; (4) a methylene group instead of the isolated methyl group - e.g., verbenene. For the entire series of hydrocarbons classed as the bornane group, the only single series of names which can be formulated to conform to the general principles developed in this report is that based on these nor- names. The nor- names can of course always be replaced with the systematic bicyclo names if the latter are more convenient. Adoption of the nor- and bicyclo names and of names based on the terpene names of the four fundamental larger bicyclic structures eliminates the prefixes apo- and homofrom terpene nomenclature.

Recommended systematization of the nomenclature of the bicyclic terpene hydrocarbons will now be discussed for each of the four fundamental types. The thujane, carane, and pinane groups present very few and similar nomenclature problems. Some drastic steps are indicated, however, to resolve some of the difficulties encountered in naming the bornane-group compounds. For this reason, one set of rules is formulated below for the first three groups, and the rules for naming the bornane-group bicyclics will be discussed separately.

The Thujane, Carane, and Pinane Hydrocarbons

Rules for Naming

The recommended systematic names of the thujane, carane, and pinane bicyclic hydrocarbons are formed from the common terpene names of the saturated fundamental structures larger than the unsubstituted ring systems. Where these do not apply, the nor- forms of these terpene names are recommended for the carane and pinane types of structures, and the bicyclo names for the thujane type. For purposes of uniformity and convenience, skeletal formulas resembling the familiar terpene formulas are used; they are oriented so that the isolated methyl group is at the top and the numbering runs clockwise. The general rules for forming the names are:

Rule 1. Conform to the principle of like treatment of like things.

Rule 2. Retain the names thujane, carane, and pinane for the fundamental saturated structures larger than the unsubstituted ring systems, and form series of names based on these common terpene names.

Rule 3. Adopt a fixed numbering (which for the ring systems conforms to the Baeyer enumeration) for the complete carbon skeleton of each type (column 3, Chart 8). These are:



To number the positions if double bonds are present, draw unsaturated formulas so that the ring double bonds have as low numbers as are consistent with this fixed numbering. For example:

Draw This

And Not This



In SYSTEM OF NOMENCLATURE FOR TERPENE HYDROCARBONS; Advances in Chemistry; American Chemical Society: Washington, DC, 1955.



Rule 4. Replace the *-ane* ending of the names of the saturated parent compounds by *-ene* to denote one double bond – i.e., thujene, carene, and pinene. Replace the *-ane* ending by *-diene* to denote two double bonds; add the connective "a" to the root for euphony – i.e., thujadiene, caradiene, and pinadiene.

Rule 5. Indicate the position of each double bond, regardless of whether it is inside or outside the ring, by the proper prefix numbers as determined by Rule 3 above.

For a double bond within the ring, only one prefix number is necessary – that of the lower-numbered carbon to which the double bond is attached – e.g., 3-thujene (Formula 48, Chart 10); 2-pinene (Formula 67, Chart 12).

For a double bond outside the ring, two prefix numbers are necessary – that of the ring carbon to which the double bond is attached, and following this in parentheses that of the substituent carbon to which the double bond is attached – e.g., 3(10)-carene (Formula 58, Chart 11); 2(10), 3-pinadiene (Formula 70, Chart 12). If the number of the substituent carbon in such a double bond were the next higher-numbered carbon to the ring carbon, which is impossible on the basis of the fixed numberings of the thujane, carane, and pinane structures (see Rule 2), then only one prefix number would be necessary.

Rule 6. When Rules 1-5 do not apply, use the systematic bicyclo name, that is, bicyclo[3.1.0] hexane, for the saturated bicyclic ring system of thujane, and the nor-names – that is, norcarane and norpinane – for the other two fundamental saturated bicyclic ring systems, and form series of names based on these parent names.

Rule 7. Adopt the Baeyer enumeration for the complete carbon skeleton of each bicyclo structure. These are:



Bicyclo[3.1.0]hexane

Norcarane

Norpinane

To number the positions if double bonds are present, follow the bicyclo plan of assigning to double bonds as low positions as are consistent with the numbering imposed by the bridges. For structures containing one double bond, this means that only 2- ene structures can exist in the thujane and pinane groups but both the 2- and 3- ene structures can exist in the carane group. Thus:



Bicyclo[3.1.0]hex-2-ene



To number the positions if substituents are present, also follow the bicyclo plan. For saturated structures, this means that substituents are given as low numbers as are consistent with the limitations imposed by the bridges. For unsaturated structures, the position numbers assigned to substituents are governed by the low numbers assigned to the double bonds. Thus, the correct systematic numberings for typical structures that will be named as derivatives of the fundamental saturated ring systems, rather than as derivatives of the larger parent compounds, are:



In SYSTEM OF NOMENCLATURE FOR TERPENE HYDROCARBONS; Advances in Chemistry; American Chemical Society: Washington, DC, 1955.

Rule 8. Form -ene (one double bond) and -diene (two double bonds) names according to Rule 4 above, and write the bicyclo and nor- names as solid words – e.g., bicyclo[3.1.0]hex-2-ene, norcarene, and norpinadiene.

Rule 9. Indicate the position of each double bond within the ring structure by only the number of the lower-numbered carbon to which the double bond is attached - e.g., bicyclo[3.1.0]hex-2-ene, 2,4-norcaradiene, 3-norpinene. If double bonds attach substituents to the rings or are present in the substituent groups, their presence is denoted in the names of the substituent groups - e.g., the systematic name for sabinene (Formula 49, Chart 10) is 1-isopropyl-4-methylenebicyclo[3.1.0]hexane; the nor- name, which is the recommended name, for nopadiene (Formula 64, Chart 12) is 6,6-dimethyl-2-vinyl-2-norpinene.

Recommendation

Thujane Group (Bicyclo[3.1.0]hexane Type). Name the thujane-type bicyclic terpene bydrocarbons (bicyclo[3.1.0] bexane type) as thujanes, thujenes, and thujadienes, and base these names on the recommended fixed numbering of the thujane carbon skeleton. (Formula 46, Chart 10). For those derivatives which contain (1) fewer carbon atoms than thujane, (2) the same number as, or more carbon atoms than thujane but do not have a carbon skeleton identical to that of thujane, or (3) more carbon atoms than thujane and a carbon skeleton identical to that of thujane but contain substituents such that the principle of like treatment of like things will be violated by using the thujane, thujene, and thujadiene names, use the bicyclo[3.1.0]bexane-type names based on systematic bicyclo numbering (Formula 43, Chart 10). See Chart 10.

Thujane group rather than sabinane group is chosen as the preferred name for this group of bicyclics because (a) the common terpene names of more compounds in this series are based on thujane than on sabinane -e.g., thujone, thujyl alcohol and (b) the combining form thuj- has the advantage of being shorter than sabin. At one time, this group was also known as the tanacetane group.

Structures, the recommended numberings and names, and the bicyclo names of compounds belonging to the *thujane group* are shown in Chart 10. Reasons for the recommended fixed numbering of the thujane structure (Formula 46, Chart 10) and for the orientation shown in Chart 10 were discussed in connection with Chart 8. The recommended bicyclo numbering of the ring carbon skeleton (Formula 43, Chart 10) was discussed in connection with Chart 9.

The recommended thujane-type names are simple and practical. The naming of functional derivatives of the thujane group of bicyclics on a consistent scheme, in which the functional groups are indicated in the endings of the names, will be readily solved on the basis of the above recommendations. Furthermore, many of the derivative names now in the literature will be retained on such a scheme. Although the recommended thujane-type names will present a minor problem to the indexer, adequate cross references can identify these names with names of nonterpene compounds possessing related structures. The American committees recommend that the name thujane and names derived from it replace all common terpene names of structures belonging to the thujane group of bicyclic terpenes.

Recommendation

Carane Group (Bicyclo 4.1.0 heptane Type). Name the carane-type bicyclic

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Chart 10. Thujane Group of Bicyclic Terpene Hydrocarbons – Bicyclo[3.1.0] hexane Type

Numbers Outside Rings in Formulas Indicate the Recommended Numberings for the

Ring Structures and Larger Parent Carbon Skeletons of the Thujane and Carane Types; Numbers inside Rings in Formulas Indicate the Systematic Numbering for Bicyclo Names; Arrows on Circles Enclosing Numbers Indicate whether Numbering Runs Clockwise or Counterclockwise on Orientation Shown.

		Recom. Numbering	Bicyclo Name	Recom. Name
No.	Terpene Name	Bicyclo for Parent Ring Names	Lowest Numbers for Double Bonds and Substituents	Bicyclo-Type Bicyclo Numbering
43.			Bicyclo[3.1.0]hexane	Bicyclo [3.1.0]hexane
44.			Bicyclo[3.1.0]hex-2-ene	Bicyclo [3.1.0]her- 2-ene
45.			5-Isopropyl bicyclo[3.1.0]hex-2-ene	5-Isopropyl bicyclo [3.1.0]hex- Z-ene
		Fixed For Thujane-Type Names		Thujane-Type Fixed Numbering
46.	Thujane Sabinane Tanacetane		1-Isopropyl-4-methyl bicyclo 3.1.0 hexane	Thujan e
47.	β-Thujene		1-Isopropyl-4-methyl bicyclo[3.1.0]hex-2-ene	2-Thujene
48.	a-Thujene		5-Isopropyl-2-methyl bicyclo[3.1.0]hex-2-ene	3-Thujene
49.	Sabinene		1-Isopropy1-4-methylene bicyclo[3.1.0]hexane	4(10)-Thujene
50.			5-Isopropenyl-2-methyl bicyclo [3.1.0]hex-2-ene	3, 7-Thujadiene

terpene bydrocarbons (bicyclo[4.1.0] beptane type) as caranes, carenes, and caradienes, and base these names on the recommended fixed numbering of the carane carbon skeleton. (Formula 55, Chart 11). For those derivatives which contain (1) fewer carbon atoms than carane, (2) the same number as, or more carbon atoms than, carane but do not have a carbon skeleton identical to that of carane, or (3) more carbon atoms than carane and a carbon skeleton identical to that of carane but contain substituents such that the principle of like treatment of like things will be violated by using the carane, carene, and caradiene names, use the nor-type of terpene names based on systematic bicyclo numbering (Formula 51, Chart 11). See Chart 11.

Structures, the recommended numberings and names, and the bicyclo names of compounds belonging to the *carane group* of bicyclic terpene hydrocarbons are shown in Chart 11.

Reasons for the recommended fixed numbering of the carane structure (Formula 55, Chart 11) and for the orientation shown in Chart 11 were discussed in connection with Chart 8. The recommended bicyclo numbering of the norcarane carbon skeleton (Formula 51, Chart 11) was discussed in connection with Chart 9.

The significant departure from the numbering established in the terpene literature is that recommended for the two carene structures, each containing one double bond in the ring (Formulas 56 and 57, Chart 11). These two compounds have been designated consistently as Δ^4 -carene and Δ^3 -carene, respectively. On the basis of the numbering recommendations in this report, Δ^4 -carene is named 2-carene, and Δ^3 carene is 3-carene. The elimination of Δ conforms to current nomenclature practices. The American committees recommend that the name carane and names derived from it replace all common terpene names of structures belonging to the carane group of bicyclic terpenes.

Recommendation

Pinane Group (Bicyclo 3.1.1 heptane Type). Name the pinane-type bicyclic terpene bydrocarbons (bicyclo 3.1.1 beptane type) as pinanes, pinenes, and pinadienes, and base these names on the recommended fixed numberings of the pinane carbon skeleton (Formula 66, Chart 12). For those derivatives which contain (1) fewer carbon atoms than pinane, (2) the same number as, or more carbon atoms than, pinane but do not bave a carbon skeleton identical to that of pinane, or (3) more carbon atoms than pinane and a carbon skeleton identical to that of pinane but contain substituents such that the principle of like treatment of like things will be violated by using the pinane, pinene, and pinadiene names, use the nor- type of terpene names based on systematic bicyclo numbering (Formula 59, Chart 12). See Chart 12.

To the *pinane group* of bicyclic terpene hydrocarbons belong a-pinene and β pinene (frequently called nopinene), chief constituents of turpentine oil and among the most widely chemically investigated terpene hydrocarbons. The name pinene is firmly established in chemical language, and it is neither desirable nor practical to attempt to discourage continued usage. The recommended scheme of systematizing the nomenclature of pinane-type bicyclics recognizes this fact.

Structures, the recommended numberings and names, and the bicyclo names of compounds belonging to the *pinane group of bicyclic terpene bydrocarbons* are shown in Chart 12. Reasons for the recommended fixed numbering of the pinane structure with the three methyl groups at 2,6,6- and not at 2,7,7- or other positions (Formula 66, Chart 12) and for the orientation shown were discussed in connection with Chart 8.

Chart 11. Carane Group of Bicyclic Terpene Hydrocarbons – Bicyclo[4.1.0] heptane Type

Numbers outside Rings in Formulas Indicate the Recommended Numberings for the

Ring Structures and Larger Parent Carbon Skeletons of the Thujane and Carane Types; Numbers inside Rings in Formulas Indicate the Systematic Numbering for Bicyclo Names; Arrows on Circles Enclosing Numbers Indicate whether Numbering Runs Clockwise or Counterclockwise on Orientation Shown.

				N
	Terpene Name	Recom. Numbering	Bicyclo Name	Recom. Name
No.		Bicyclo for Nor-Names	Lowest Numbers for Double Bonds and Substituents	Norcarane-Type Bicyclo Numbering
51.	Norcarane	A CONTRACTOR	Bicyclo[4.1.0]heptane	Norcarane
52.		No.	Bicyclo[4.1.0]hept-2-ene	2-Norcarene
53.			Bicyclo[4.1.0]hept-3-ene	3-Norcarene
54.		200	Bicyclo[4.1.0]hepta- 2,4 diene	2,4-Norcaradiene
		Fixed For Carane-type Names		Carane-Type Fixed Numbering
55.	Carane		3,7,7-Trimethyl bicyclo[4.1.0]heptane	Carane
56.	Δ ⁴ -Carene (d-Form = Pinonene)		3,7,7-Trimethyl bicyclo[4.1.0]hept-2-ene	2-Carene
57.	Δ ³ -Carene (d-Form = Isodiprene)	60	3,7,7-Trimethyl bicyclo[4.1.0]hept-3-ene	3-Carene
58.	ψ-Carene β-Carene	6	7, 7-Dimethyl-3-methylene bicyclo[4.1.0]heptane	3(10)-Carene

The recommended bicyclo numbering of the norpinane carbon skeleton (Formula 59, Chart 12) was discussed in connection with Chart 9.

Examination of the pinane-type formulas in Chart 12 shows that the unsaturated derivatives contain one double bond in two different positions in the ring – e.g., Formulas 67 and 68; one double bond outside the ring – e.g., Formula 69; or two double bonds, one inside and one outside the ring – e.g., Formula 70. Some of the structures contain a methyl – e.g., Formula 69 – or a methylene – e.g., Formula 71 – group as a substituent additional to the three methyl groups present in pinane. One – i.e., Formula 63 – contains three methyl groups as does the pinane carbon skeleton, but the isolated methyl group is tentatively believed to be attached to carbon No. 3 instead of to carbon No. 2. Another – i.e., Formula 64 – contains a vinyl group instead of the isolated methyl group. Two possess a carbon skeleton intermediate between that of pinane and that of norpinane – i.e., Formulas 61 and 62. In the norpinane structure, three pairs of position numbers are identical: 1 and 5; 2 and 4; 6 and 7. Thus, in the pinane group of bicyclics, more variety in structural features exists than in the thujane and carane groups. This would be expected because structures of more pinane-type compounds are known.

The common terpene names of the hydrocarbons belonging to the pinane group illustrate the historical use of Greek letter prefixes to designate structural isomers, of the prefixes apo- and homo- tc show structural relationships to the pinane carbon skeleton, and of various other names which in themselves indicate no similarity to pinane. With the number of structures already proved for hydrocarbons belonging to this terpene group, considerable memory work is required to identify readily the correct structures from these names. The numerous known functional derivatives whose terpene names are similarly derived but not necessarily from the names of the corresponding pinane-type hydrocarbons further complicates the memory problem. The proposed nor- names (based on systematic bicyclo numbering) and pinane-type names (based on a fixed numbering of the pinane carbon skeleton) and adherence to the recognized principle of treating like things alike obviously introduce system into the nomenclature of this group of bicyclic terpene hydrocarbons. All can be given nor-names, as pointed out earlier - e.g., pinane could be named as 2,6,6-trimethylnorpinane. However, the simpler pinane, pinene, and pinadiene names when they apply are given preference. The American committees recommend that the name pinane and names derived from it replace all common terpene names of structures belonging to the pinane group of bicyclic terpenes.

The Bornane Hydrocarbons

The bicyclic terpene hydrocarbons classified in this report as the bornane group (bicyclo[2.2.1] heptane type), but currently called the camphane group in terpene literature, are more numerous and have many more important derivatives (especially the camphors) than the other three fundamental bicyclic types – the thujane, carane, and pinane groups – already discussed. As would be expected, a greater variety in the arrangement of substituents and double bonds and in the number of substituents is found.

The Name Bornane

Georges Dupont of the University of Paris commented in the early stages (1949) of the development of this report: "In the case of the bicyclics.....could we not decide to call the skeleton which corresponds to bornylene by the name bornylane?.....Elimination of the term 'camphane' would do away with every cause of

Chart 12. Pinane Group of Bicyclic Terpene Hydrocarbons -Bicyclo[3.1.1] heptane Type

Numbers outside Rings in Formulas Indicate the *Recommended Numberings* for the Norpinane and Pinane Types of Carbon Skeletons: Numbers inside Indicate the Systematic Numbering for Bicyclo Names; Arrows on Circles Enclosing Numbers Indicate whether Numbering Runs Clockwise or

Counterclockwise on the Orientations Shown. The Names Recommended Conform to the Principle of Like Treatment of Like Things (as Interpreted by Chemical Abstracts and the London Chemical Society) and the 1953 Chemical Abstracts Form for Names of Unsaturated Structures.

No.	Structures for Which Nor- Names Are Recommended						
	Terpene Recommended		Bicyclo Name	Recommended Name			
	Name	Bicyclo	Lowest Numbers to Double Bonds and Substituents	Based on Bicyclo Numbering			
59.	Norpinane		Bicyclo[3.1.1]heptane	Norpinane			
60.			Bicyclo[3,1,1]hept-2-ene	2-Norpinene			
61.	Apopinane	2 2 3 5 4	6,6-Dimethyl bicyclo [3.1.1]heptane	6,6-Dimethyl norpinane			
62.	Apopinene	1 0 3 6 5 4	6,6-Dimethyl bicyclo 3.1.1_hept-2-ene	6,6-Dimethyl- 2-norpinene			
63.	Orthodene	5	3,6,6-Trimethyl bicyclo [3.1.1]hept-2-ene	3,6,6-Trimethyl- 2-norpinene			
64.	Nopadiene	2 2 2 4 3 4 5	6,6-Dimethyl-2-vinyl bicyclo [3.1.1]hept-2-ene	6,6-Dimethyl- 2-vinyl- 2-norpinene			
65.	Homopinene	5	2,4,6,6 Tetramethyl bicyclo [3,1.1]hept-2-ene	2,4,6,6-Tetramethy 2-norpinene †			

¹ This nor- name based on bicyclo numbering rather than the pinane-type name, 4-methyl-3-pinene, based on a fixed numbering is recommended to avoid violation of the established principle of like treatment of like things.

Chart 12. Pinane Group of Bicyclic Terpene Hydrocarbons – Bicyclo_[3.1.1_]heptane Type

(Continued)

	Structures for Which Pinane-Type Names Are Recommended						
No.	Terpene Name	Recommended Numbering	Bicyclo Name	Recommended Name			
		Fixed ††	Lowest Numbers to Double Bonds and Substituents	Based on Fixed Numbering			
66.	Pinane Dihydropinene	2 2 2 2 2 5 5	2,6,6-Trimethyl bicyclo 3.1.1]heptane	Pinane			
67.	æPinene	Q Q Q Q Q Q Q Q Q Q Q Q Q Q Q Q Q Q Q	2,6,6-Trimethyl — bicyclo [3.1.1]hept-2-ene	2-Pinene			
68.	δ-Pinene	20-2 -2 -2 -2 -2 -2 -2 -2 -2 -2 -2 -2 -2 -	4,6,6-Trimethyl bicyclo 3.1.1 hept-2-ene	3-Pinene			
69.	Nopinene β-Pinene Terebenthene		6,6-Dimethyl- 2-methylene bicyclo [3.1.1]heptane	2(10)-Pinene			
70.	Verbenene	8 9 6 3 7 3 4 3 3 4 3 5 4	6,6-Dimethyl- 4-methylene bicyclo [3,1.1]hept-2-ene	2(10),3-Pinadiene			
71.	Homoverbanene	10 10 10 7 4 7 4 7 4 7 4 5 4 4 4 5 4 5 4 5 4 5 4 5 4 5 4 5 5 5 5 5 5 5 5 5 5 5 5 5	2,6,6-Trimethyl- 4-methylene — bicyclo — 3.1.1]heptane	4-Methylenepinane			
72.		и 1 1 1 1 1 1 1 1 1 1 1 1 1	2,6,6-Trimethyl- 4-methylene — bicyclo — 3.1.1]hept-2-ene	4-Methylene-2-pinene			

^{††} The recommended fixed numbering of the ring systems in the pinane-type structures shown is in the majority of cases identical to the systematic bicyclo numbering.

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confusion." From this suggestion of a "master terpene chemist" and a consideration of the chaotic nomenclature of the camphane group of bicyclics (discussed below under "Common Terpene Names"), it was a natural for Miss Grafflin to remove the "yl" and propose the name "bornane". Thus, a modern terpene name is born!

The name bornane retains a distinct terpene flavor, is simpler than bornylane, and resembles more closely the names of the other fundamental groups of bicyclic terpene hydrocarbons. A series of names formed from bornane will be similar to bornylane-type names now in the literature but will be sufficiently different to avoid any confusion or ambiguity – for example; by applying universally recognized nomenclature rules, the *borneols* become *bornanols* and the corresponding unsaturated alcohols become *bornenols* instead of the currently used *bornylenols*. The saturated radical name *bornyl* remains unchanged, and the unsaturated radicals become *bornenyl* and *bornadienyl*. By replacing camphane with bornane, the root campb- can be reserved exclusively for names of camphor-type compounds, and the trivial name camphene will cause no ambiguity. Memory work is practically eliminated.

From its inception, the coined name *bornane* has been received quite favorably by both terpene chemists and nomenclaturists, European as well as American.

Structural Formulas, Numberings, and Orientations

Structural formulas of the bornane group of bicyclics, oriented and numbered according to three widely used reference works(6, 23, 51), are given in Chart 13. Those with saturated ring structures (Formulas 73 to 86) precede those with unsaturated ring structures (Formulas 87 to 96). The bicyclo numbering for norbornane (Formula 73) and the recommended fixed numbering for bornane (Formula 75) are shown. The numberings of the ring-cafbon skeletons of the other formulas as oriented are identical to these; there are no rules for numbering side-chain carbons.

Examination of the formulas in any one column of Chart 13 reveals that all possess in common two condensed five-membered rings, specifically the bicyclo [2.2.1]heptane carbon skeleton of norbornane (Formula 73). Certain formulas have additional structural features in common. About two-thirds of them, some saturated and others unsaturated, contain a gem-dimethyl configuration. Some have the two methyl groups attached to the bridge carbon (Formulas 74 to 77, 88 to 90); hence, in this respect, they resemble bornane (Formula 75). Others have the two methyl groups attached to a single ring carbon and only hydrogens attached to the carbon in the bridge (Formulas 80 to 85, 91 to 94); they, therefore, resemble camphenilane (Formula 80). Three formulas (Nos. 79, 95, 96) contain two methyl groups attached to adjacent ring carbons instead of to the same one; these resemble santane (Formula 79). The formula for santenane (No. 78) resembles none of these. The unsaturated structures containing a single double bond have this bond either inside the ring (Formulas 87 to 93, 95, 96) or between a ring carbon and a methylene group (Formulas 77, 84 to 86). The one unsaturated structure containing two double bonds (Formula 94) has one bond in each position. Despite the structural similarities noted above, the hydrocarbons belonging to the bornane group of bicyclics, unlike those of the thujane, carane, and pinane groups, do not have a single carbon skeleton larger than the ring carbon skeleton - i.e., of norbornane; Formula 73 - that is common to a majority of the known structures. This fact is pertinent to the problem of selecting a parent compound for the bornane group.

Differences in numberings and orientations of the bornane-type bicyclic formulas

Chart 13. Structural Formulas and Common Terpene Names of Bornane Group of Bicyclic Terpene Hydrocarbons – Bicyclo[2.2.1]heptane Type

No. 1 Carbon Is the Top Ring Carbon of Each Formula, and the Numbering Runs Clockwise. No. 7 Carbon Is the Carbon in the Bridge.

No.	Terpene Name	From Simonsen ^(a)	From Elsevier ^(b)	By Bicyclo Plan ^(c)
73.	Norcamphane ("Norbornane") Norbornylane		5 ()	s (2)3
74.	Apocamphane <i>a</i> -Fenchocamphorane Apobomylane	Ð	\oplus	\oplus
75.	Camphane ("Bornane") Bornylane Dihydrobornylene	, () ,	, 1	5 1 1 1 1 1 1 1 1 1 1
76.	a-Fenchane Isobornylane	Ð.	÷	(
77.	a-Fenchene (dl-Form = Isopinene)	<u>(</u> =с н ₂	(H= (H2	<u>(۳</u> 2
78.	Santenane		Ð	\bigcirc
79.	Santane	¢		\bigcirc
80.	Camphenilane β-Apofenchane	\bigcirc	\oplus	\bigcirc
81.	Fenchane &Fenchane	\bigcirc	Φ	¢
82.	Isocamphane Dihydrocamphene	\bigoplus	€¥	\oplus
83.	eta-Fenchane	\oplus	\Diamond	-\$
84.	Camphene	Ф [±] сн ₂	фт ^{си} г	() Ecn2
85.	β-Fenchene	4 ,c=€) [×]	× = «»2	<i>m_c=</i>
86.	Norcamphene. Name not recommended (Elsevier; Heilbron)		(M2	()=CM2
87.	Norbornylene Norcamphene (Chem. Abst.; Simonsen)	\bigcirc	\oplus	\bigcirc
88.	Apobornylene	\oplus	(\overline{T})	\bigcirc
89.	Bornylene		Ð	\bigcirc
90.	ζ-Fenchene	\bigoplus		$\overline{}$
91.	Camphenilene Apoisofenchene	$\overleftarrow{\mathbb{D}}$	Ð	\bigoplus
92.	δ-Fenchene; Fenchylene; Isofenchene; Isofenchylene	\mathbf{r}	Φ	Φ
93.	y-Fe nchene	-OX	Φ	Φ
94.	Isocamphodiene Camphenene	U CH2	€ CM2	*
95.	Santene	() L		() L
96.	1-Methylsantene €-Fenchene	\bigcirc		

(a) Simonsen, J.L., "The Terpenes", Vol. II, 2d Ed. Rev., Cambridge Univ. Press, England, 1949.
(b) "Elsevier's Encyclopaedia of Organic Chemistry", Vol. 12A, Elsevier Publishing Co.,

(b) "Elsevier's Encyclopaedia of Organic Chemistry", Vol. 12A, Elsevier Publishing Co., N.Y. and Amsterdam, 1948.

(c) This is according to IUPAC Rules whereby the double bond in the ring is given the low number.

preferred by three recognized authorities (6, 23, 51) are also shown in Chart 13. Excluding the nor- and the apo- structures (Formulas 73 and 87, and 74 and 88, respectively), only the following are identical in numbering and orientation in the three columns: bornane (Formula 75); bornylene (Formula 89); and the santane derivatives (Formulas 79, 95, 96). The preferred formula in one column differs from that in each of the other two columns for: δ -fenchane (Formula 81); δ -fenchene (Formula 92); camphenilene (Formula 91); and isocamphodiene (Formula 94). Among the remainder of the structures, some in the first column of formulas (Nos. 79, 80, 82 to 85) and others in the second column (Nos. 76 to 78, 86, 92, 93) are identical to the bicyclo orientations and numberings. In the formulas which contain the methylene group as a substituent (Formulas 77, 84 to 86, 94), this group is consistently attached to the No. 2 ring carbon by Elsevier (second column of formulas in Chart 13) and the methyl substituents are thus assigned higher numbers. Simonsen (first column of formulas in Chart 13), on the other hand, assigns the lower-numbered position (ring carbon No. 2) to the two methyl groups attached to a single ring carbon which coincides with the bicyclo numbering; and the methylene group thus receives a higher number. Even in a-fenchene (Formula 77) in which two methyl groups are attached to the bridge carbon (No. 7), Simonsen places the methylene group on ring carbon No. 3 rather than on No. 2. According to both Simonsen's and Elsevier's schemes for unsaturated ring structures, low numbers for substituents, as required by the original Geneva system, are usually but not always preferred to low numbers for double bonds (compare Formulas 91, 93, 94 in columns 1 and 2). This is exactly the opposite of the bicyclo plan of numbering, recognized by current IUPAC rules, in which the lower number is assigned to the double bond. Other similarities and differences among the three sets of orientations and numberings of the camphane-group hydrocarbons may be deduced by a study of Chart 13. Sufficient dissimilarity has been pointed out to indicate the scope of this part of the problem of systematizing the nomenclature of the bornane group of bicyclics.

Common Terpene Names

The historically developed nomenclature of the compounds classified as the bornane group in this report contributes much more confusion to the terpene literature than the common terpene names of the compounds belonging to the thujane, carane, and pinane groups. Campbane (Formula 75, Chart 13) is a logical name for the saturated parent hydrocarbon of camphor, which differs from this parent only in that it has an oxo group instead of two hydrogens attached to ring carbon No. 2. The name campbene, from a nomenclature point of view, immediately suggests a bicyclic hydrocarbon similar to camphane but containing one double bond in the ring. That particular formula, however, has been called exclusively bornylene (Formula 89, Chart 13) in the terpene literature. The well-known campbene (Formula 84, Chart 13) has a saturated bicyclo 2.2.1 heptane ring structure, and the double bond implied by the -ene ending of the name is not in the ring but joins a methylene group to the ring; furthermore, the gem-dimethyl groups are attached to a ring carbon instead of to the bridge carbon as a camphane. The only bornane-group hydrocarbons which resemble camphane by containing two methyl groups attached to the bridge carbon and an additional methyl or methylene group attached to the ring are a-fenchane or isobornylane (Formula 76), a-fenchene (Formula 77), bornylene (Formula 89), and ξ -fenchene (Formula 90); of these, bornylene is the only one which has the isolated methyl group attached to a bridge end as in camphane. The common terpene names disguise well the relationships and dissimilarities that exist among the bornane-type

Names of *functional derivatives* of the bornane-group hydrocarbons do not form consistent series of names either. For example, the saturated alcohols derived from the saturated camphane are named consistently as the borneols, but names containing the born- root would be expected to be derived from a compound, such as the unsaturated hydrocarbon bornylene, whose name also begins with born-. Undoubtedly, this is one reason the rarely used name bornylane was introduced as an alternate name for camphane. The ketones derived from camphane are all named as camphor derivatives, but the aldehyde corresponding to camphor is called camphanaldehyde. Names of many of the functional derivatives of fenchane contain the root fench-, while those of camphene are named as derivatives of camphene. Campbenilane (Formula 80) suggests some resemblance to camphane or camphene or both, but it cannot be named as a derivative of either. The *-en-* in the middle of the name and the *-ane* ending also suggest unsaturation - saturation which does not exist. The compound camphenilane is also called β -apofenchane to indicate relationship to the fenchane structure.

Synonym names – for example, isocamphane and dihydrocamphene, α -fenchane and isobornylane – are frequently both given for a compound because the preferred name is not sufficiently well established. Derivative names based on a pair of synonym names also exist – for example, apoborneol and α -fenchocamphorol are used about equally for one of the monoalcohols derived from apocamphane and often without mention of the alternate name. In contrast to synonym names is current usage by standard reference works of one name, norcamphene, to denote two different structures – the 2,3-didehydro form of norcamphane (18) and 2-methylenenorcamphane (24, 28). Confusion is increased by use of the synonym name norbornylene for the former structure (28, 52).

Furthermore, the use of special subgroup names such as *fenchenes*, which applies to a series of synthetic compounds to indicate their derivation from fenchyl and isofenchyl derivatives and reportedly (33) to distinguish them from closely related naturally occurring terpenes, obviously complicates the problem of systematizing nomenclature. Names such as cyclofenchene and β -difenchene are two additional memory exercises. Such irregularities in nomenclature have, of course, been carried over into the nomenclature of derivatives of these bicyclic hydrocarbons.

Radical names beginning with the roots camph-, born-, and fench- are well enough established that they are included in lists of names of organic radicals (17). The use of prefixes such as iso- with different meanings (cf. Formulas 82 and 92) does not simplify the nomenclature problem. There are also compounds named as *endocamphene* and derivatives of *homoisocamphene* which have been omitted since they belong to the bicyclo[3.2.1] octane system rather than to the bicyclo[2.2.1] heptane system to which the designation bornane group has been limited in this report.

The common terpene names of this fundamental group of bicyclics obviously offer little from the viewpoint of systematic nomenclature except a strenuous memory exercise. The prime justification for retaining the name *camphane* as the group name for the bicyclo [2.2.1] heptane series of terpene hydrocarbons is the name of its important derivative, camphor. However, camphor is a trivial name which will have to be recognized as such, regardless of proposals for systematizing the naming of this group of bicyclics. The use of logically derived camphane-type names would change bornylene to 2-camphene, but confusion already exists between camphane and camphene, and among the names of many terpene derivatives containing the root camph-. Furthermore, usage of the trivial name camphene will undoubtedly persist. Other common names of hydrocarbons belonging to this group of bicyclics contain the roots born-, fench-, and sant-. Of these three types of names, the born- type is the most consist-

ently used in bicyclic terpene nomenclature and is the most significant from the viewpoint of chemical importance of the compounds so named; in fact, bornylane and dihydrobornylene are synonym names for camphane. In comparison to the born- and camph- names, the fench- and sant- type of names now in the literature are few. Furthermore, within each series of the latter types of names, there is no clear-cut and definitive pattern; consequently, these series of names would have to be systematized before they could be extended to naming other compounds.

These and other considerations led directly to the recommended name bornane group for the group of bicyclic terpene hydrocarbons currently called the camphane group. Specific recommendations on continued usage of the common terpene names of bornane-type bicyclics are being withheld until a more thorough study has been made of the nomenclature of their derivatives.

General Recommendations for Naming Bicyclo[2.2.1]heptane-Type Hydrocarbons

To create a basic framework for a single series of rational and terpenelike names for the fundamental bicyclo [2.2.1] heptane type of terpene hydrocarbons, the American committees make the following recommendations:

1. Adopt the names:

Bornane to replace Camphane and Bornylane. Bornane Group to replace Camphane Group. Norbornane to replace Norbornylane and Norcamphane. Bornene, Bornadiene, Norbornene, and Norbornadiene for the unsaturated structures.

2. Adopt the numberings:

Fixed for bornane (Formula 75, Chart 8) - that is,



The structure of bornane is such that the recommended fixed numbering for this larger parent is identical to the bicyclo numbering.

Bicyclo for norbornane (Formula 73, Chart 9) - that is,



In the discussion of structural similarities and differences among the compounds belonging to the bornane group (Chart 13), it was pointed out that only the norbornane ring carbon skeleton is common to all, and that only one compound in this group – i.e., bornylene, Formula 89, Chart 13 – possesses a carbon skeleton identical to that of bornane. In the recommendations for systematizing the nomenclature of the carane and pinane groups, use of nor-names and the names of the larger parent compounds proved adequate, without resorting to the use of the indefinite apo- and homonames for structures intermediate between the larger parent compounds and those containing in common only the stripped ring carbon skeletons. The same combination of the nor-name and the name of the larger parent compound and similar rules suffice for systematizing the nomenclature of the bornane group. On this scheme, however, practically all of the bornane-type bicyclics receive nor-names whereas for the other three fundamental types the majority of recommended names are based on the names of the larger parent compounds.

Rules for Naming the Bornane Hydrocarbons

The systematic names recommended by the American committees for the bornane bicyclic hydrocarbons are the nor- names based on the bicyclo plan rules (14, 15) with the exception that the bornane-type names based on a fixed numbering are recommended for the few structures that may possess the carbon skeleton of the larger parent compound. The prefix nor- is used in the "complete stripping" sense as defined earlier. In forming names for the *known structures* now classified as the bornane group, there is no need to consider the principle of treating like things alike which was necessary for naming the pinane group. However, the principle may apply to structures not yet known. The rules for forming the recommended names of the bornane-group bicyclics are:

Rule 1. Use the name norbornane for the fundamental saturated ring system, which is bicyclo 2.2.1 heptane. Use the name bornane for the saturated larger parent compound, which is 1,7,7-trimethylbicyclo 2.2.1 heptane. Form a series of names based on these two new terpene names.

Rule 2. Adopt bicyclo plan enumeration for the complete ring carbon skeleton (Chart 9) and for the structures named as norbornane derivatives. Adopt a fixed numbering for the complete carbon skeleton of the larger parent compound (Chart 8). Thus:



The numberings of the ring carbons in each saturated structure happen to be identical. However, this is not always the case for corresponding pairs of unsaturated structures because of the differences in the bicyclo and the fixed numbering schemes for naming compounds.

Rule 3. To number positions in the structures named as norbornane derivatives:

(a) If double bonds are present in the fundamental ring structure, follow the bicyclo plan of assigning to double bonds as low positions as are consistent with the numbering imposed by the bridges.

(b) If substituents are present, also follow the bicyclo plan. For saturated structures, this means that substituents are given as low numbers as are consistent with the limitations imposed by the bridges. For unsaturated structures, the position numbers assigned to substituents are governed by the low numbers assigned to double bonds. Thus, the correct systematic bicyclo numberings for typical structures to be named as norbornane derivatives would be:



and not:



Rule 4. To number positions in unsaturated structures named as bornane derivatives, assign the double bond as low a number as is consistent with the fixed numbering of the saturated carbon skeleton. Thus:



In SYSTEM OF NOMENCLATURE FOR TERPENE HYDROCARBONS; Advances in Chemistry; American Chemical Society: Washington, DC, 1955.

Rule 5. Replace the *-ane* ending of the names of the saturated parent compounds by *-ene* to denote one double bond – i.e., norbornene, bornene. Replace the *-ane* ending by *-diene* to denote two double bonds; add the connective "a" to the root for euphony – i.e., norbornadiene, bornadiene.

Rule 6. For a double bond within the ring, only one prefix number is necessary – that is, the lower-numbered carbon to which the double bond is attached – e.g., 2-norbornene, 2-bornene.

Rule 7. If a double bond attaches a substituent to the nor-ring, its presence is denoted by the name of the substituent group preceded by the proper ring position number, and the structure is named as a norbornane derivative -e.g., 2-methylene-norbornane.

Recommendation

Bornane Group (Bicyclo 2.2.1] heptane Type). Name the bornane-type bicyclic terpene bydrocarbons (bicyclo 2.2.1] beptane type) as norbornanes, norbornenes, and norbornadienes and base these names on systematic bicyclo numbering and rules (Formula 73, Chart 9). For those derivatives which have a carbon skeleton identical to bornane, use the bornane, bornene, and bornadiene names, and base these names on the recommended fixed numbering of the bornane carbon skeleton (Formula 75, Chart 8). See Chart 14.

Structures and the recommended names of compounds belonging to the bornane group of bicyclic terpene hydrocarbons are given in Chart 14. Reasons for coining the name bornane and for the necessity of using the norbornane-type names to systematize the nomenclature of the bicyclo [2.2.1] heptane bicyclics have been presented earlier. Examination of the names in Chart 14 reveals that in the systematic bicyclo [2.2.1] heptane names and the recommended norbornane names the prefix numbers for substituents and double bonds and the order of names of substituents are identical.

Several schemes of dividing this group of bicyclics into subgroups according to structural types - e.g., those with gem-dimethyls attached to the bridge carbon or to a ring carbon and those containing no gem-dimethyl configuration - were included in earlier versions of this report. They were tested exhaustively as potential bases for systematizing their nomenclature. Difficulties in attaining a solution along these lines included (1) determining which fundamental structures larger than the ring carbon skeleton were useful - a fair number have to be related to the nor- structures; (2) assigning fixed numberings to the carbon skeletons of the subgroup parent compounds - too many violations of accepted practices were encountered and, thus, memory work was increased; and (3) selecting the common terpene names to be retained - the logical choices added confusion to the already confused terpene nomenclature. Valid and, in some cases, unresolvable objections were made to all such schemes. By this path, the norbornane-bornane proposal was arrived at. The initial favorable reception of this proposal by reviewers of preliminary drafts of this report changed later to active urging that the norbornane and bornane names be those recommended for universal adoption.

Gradual replacement of the currently used common terpene names for this group of bicyclic hydrocarbons by the recommended new norbornane-bornane names should not be difficult, and may well be accomplished much more speedily than now antici-

Chart 14. Bornane Group of Bicyclic Terpene Hydrocarbons -Bicyclo 2.2.1 heptane Type

All Formulas Are Oriented According to the Bicyclo Plan; No. 1 Carbon Is at Top of Ring and the Numbering Runs Clockwise. Substitution of Bicyclo [2.2.1]heptane for Norbornane and of Bicyclo [2.1.1] hept-2-ene for 2-Norbornene in the Recommended Names Will Give the Systematic Bicyclo [2.2.1] heptane Type of Names.

	SATURATED RINGS			UNSATURATED RINGS			
No.	Substituents Assigned Lowest Numbers as Consistent with Bridge Numbers			No.	Double Bonds Assigned Lowest Numbers as Consistent with Bridge Numbers		
	Terpene Name	Formula	Recom. Name		Terpene Name	Formula	Recom. Name
73.	Norcamphane Norbornylane Norfenchane Norsantane		Norbornane	87.	Norbornylene Norcamphene Norfenchene Norsantene		2-Norbornene
74.	Apocamphane <i>a</i> -Fencho- camphorane Apobornylane	\oplus	7, 7-Dimethyl norbornane	88.	Apo bornyle ne	\bigoplus	7, 7-Dimethyl- 2-norbornene
75.	Camphane Bornylane Dihydrobornylene		Bornane (1,7,7-Tri methyl norbornane)	89.	Bomylene		2-Bornene (1,7,7-trimethyl- 2-norbornene)
76.	a-Fenchane Isobornylane	\bigoplus	2,7,7-Tri methyl norbornane	90.	ζ-Fenchene	\bigoplus	2, 7, 7-Trimethyl- 2-norbornene
77.	<i>a</i> -Fenchene (<i>dl</i> -Form = Isopinene)		7,7-Dimethyl- 2-methylene norbornane				
78.	Santenane	\bigcirc	1,7-Dimethyl norbornane				
79.	Santane	\bigcirc	2,3-Dimethyl norbornane	95.	Santene		2,3-Dimethyl- 2-norbornene
				96.	1-Methyl⊂ santene €-Fenchene		1,2,3-Trimethyl- 2-norbornene
86.	Norcamphene (Elsevier; Heilbron)	() C	2-Methylene norbornane				
80.	Camphenilane β -Apofenchane	\bigcirc	2,2-Dimethyl norbornane	91.	Camphenilene Apoisofenchene	\square	5,5-Dimethyl- 2-norbornene
81.	Fenchane δ-Fenchane	\bigcirc	1,3,3-Tri methyl norbornane	92.	ô-Fenchene Isofenchene Fenchylene Isofenchylene	\bigcirc	1,5,5-Trimethyl- 2-norbornene
82.	Isocamphane Dihydro- camphene	Œ	2,2,3-Tri methyl norbornane				
83.	eta-Fenchane	\bigcirc	2,2,5-Tri methyl norbornane	93	γ-Fenchene	(\square)	2,5,5-Trimethyl- 2-norbornene
84.	Camphene ^(a)	() Lenz	2,2-Dimethyle 3-methylene norbornane] ^a	94.	Isocamphodiene Camphene	***	5,5-Dimethyl- 6-methylene- 2-norbo:nene
85.	eta-Fenchene	4.c=	2,2-Dimethyl- 5-methylene norbornane				

(a) The name camphene is so firmly established in the literature that it is recommended that this common terpene name be designated as preferred to the systematic norbornane name for the unsubstituted compound.

pated. Only one – camphene – is likely to persist in the literature. It is recommended therefore that the name camphene be designated as an exception to the rules for naming the bornane-type bicyclic hydrocarbons, and thus as preferred to the name 2,2-dimethyl-3-methylenenorbornane for the unsubstituted compound only. For a period, chemical indexes will have to carry numerous cross references at the common terpene names; for example, norcamphane, norfenchane, and norsantane will all have to be recognized temporarily as synonym names for norbornane. The new generation of terpene chemists now in the making probably will look on names like camphane, fenchane, isocamphodiene, apobornylene, and camphenilane as of only historical interest. Drastic simplification and needed unification in the nomenclature of functional derivatives of the bicyclo[2.2.1] heptane type of terpenes can be attained by extending the recommended rules for naming the hydrocarbons of this group.

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Appendix A

Proposed Coined Names for Parent Compounds of Type B (Dimethylcyclohexane-Type) Monocyclic Hydrocarbons

The cyclogeraniolenes and pyronenes are the historical Type B monocyclic terpene hydrocarbons. Both series contain a gem-dimethyl configuration and no iso three-carbon group. In the report proper, the class of monocyclics designated as Type B has been defined to include derivatives of dimethylcyclohexane other than the gem-dimethyl derivatives. During the years since 1946 in which the recommended system of terpene nomenclature has been developing, several types of names have been coined for parent compounds of the Type B monocyclics. For record purposes, these proposed names will be mentioned briefly.

Gerane-Pyronane and Gerapymane Names (June 1950 Terpene Report of Organic Division's Nomenclature Committee):

Gerane was proposed by Miss Grafflin for 1,1,3-trimethylcyclohexane, and pyronane for 1,1,2,3-tetramethylcyclohexane. An alternate offered for pyronane was methylgerane, which violates the principle of like treatment of like things. Vigorous objections to these names eliminated them. A later suggested contraction – gerapymane – as a single parent (1,1,3-trimethylcyclohexane) for Type B monocyclics died almost before it was born.

2. Mecane Names (A. M. Patterson):

In his preview of terpene nomenclature proposals (39), Dr. Patterson proposed the dimecane-trimecane-tetramecane series of names (contractions of dimethyl-, trimethyl-, and tetramethyl-cyclohexane). These were received more favorably than the gerane-pyronane names, and mecane was considered seriously as a name for dimethylcyclohexane. Objections proved sufficiently valid, however, that these names were rejected by the American nomenclature committees at the Buffalo meeting in April 1952.

3. Objections to Gerane and Mecane Names:

Georges Dupont (letter of March 5, 1952) summarized the chief objections to the above names. The three proposals for naming basic Type B monocyclic hydrocarbons are:

C ₈ gem-Dimethyl cyclohexane	C9 1,1,3-Trimethyl cyclohexane	C ₁₀ 1,1,2,3-Tetramethyl cyclohexane
Norgerane	m-Gerane	Pyronane
Dimecane	<i>m</i> -Trimecane	o, <i>m</i> -Tetramecane
Apogerapymane	Gerapymane	o, m-Methylgerapymane

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Gerane, pyronane. (a) Two new root words are proposed for one type of terpenes which contains only a few representatives – it would be as well to preserve the original names. (b) The word gerane leads to confusion – geraniol and the geranyl radical are C_{10} types, geranol and geryl would be C_9 . (c) The prefixes o-, m-, and pare necessary in order to differentiate among the isomers.

Dimecane, trimecane, and tetramecane. These three names, because of their origin, are more specifically significant but present some objections: (a) The use of indices: one for trimecane and two for tetramecane are misleading, since the compounds contain three and four methyl groups; the forms o, m- are more satisfactory from this point of view. (b) Pronunciation presents some difficulties: should one say trimecene or trimekene? trimecyl or trimekyl? Furthermore, confusion with other hydrocarbons is possible - e.g., tridecane, tridecene.

Gerapymane. This name corresponds to a 3-methyl-gem-dimethylcyclohexane. (a) The name by itself is long and complicated and corresponds only very indirectly to what it signifies and to the number of carbons which it indicates. (b) For the isomers, for example, the 2-methyl, it leads to names such as 2-methylapogerapymane, which appears to be somewhat illogical.

4. Gemane (Georges Dupont).

In his letter of March 5, 1952, Professor Dupont proposed a solution for naming Type B monocyclics based on the following remarks:

(a) The hydrocarbons considered and their various isomers are derived from a simple, unique type, gem-dimethylcyclohexane, whose structure and numbering offer no ambiguity. (b) The gem-dimethylcyclohexane is found in the structure of a large number of natural derivatives — i.e., terpenes, polyterpenes, and others. Therefore, it seems suitable to give to this hydrocarbon and the corresponding radicals a simple name which corresponds to its structure unambiguously and to the number of carbon atoms which it contains, and which can be used for naming an adequate number of derivatives.

I propose the name gemane, a condensation of gem-dimethylcyclohexane:



This name is simpler and more characteristic than dimecane and apogerapymane. *m*-Trimecane would become *m*-methylgemane. *o,m*-Tetramecane would become *o,m*dimethylgemane. The derivatives, gemene, gemadiene, gemanol, etc., and the radicals, gemyl, gemylidene, etc., should not present any difficulty in usage. (The proposed methyl- and dimethyl-gemane names do, however, violate the principle of like treatment of like things. MWG)

5. Komppane (C. D. Hurd).

In his letter of February 22, 1952, Dr. Hurd commented on earlier proposed names and suggested another:

The dimecane, trimecane, and tetramecane names seem better than the gerane names. An objection to trivial names which are abridgments of systematic names is that they lead to things like besyl and mesyl just because somebody began advocating tosyl. Why not honor a great terpene chemist, one whose synthesis of camphor is a classic – namely, Gustav Komppa. We could use the name komppane for the gem-dimethyl structure. Then I for one would prefer to use methylkomppane than to coin a new trivial name for the homolog, and designate it as an exception to the principle of like treatment of like things. No ambiguity would result from names such as methylkomppane and dimethylkomppane, as long as the methyl prefixes are suitably numbered.
Appendix B

The Prefix Demethyl

The use of the prefix *apo*- with terpene names is sufficiently objectionable to some that the suggestion was made to replace *apo*- with *demethyl*. Since demethyl signifies the replacement of CH_3 by H, the initial suggestion led also to a consideration of using the prefix "demethylene" to signify the removal of CH_2 . These prefixes, to be specific in a name, would have to be preceded by a number to designate the position from which a group has been eliminated.

A test of the demethyl nomenclature was made on structures belonging to the bornane group of bicyclics (Chart 14 in the report proper).

No.	Terpene Name	Demetbyl Name
74	Apocamphane	1-Demethylbornane
76	<i>a</i> -Fenchane	1-Demethyl-2-methylbornane
78	Santenane	7-Demethylbornane

These are simple, but this pattern is short-lived as more bornane-type structures are named. For example:

No.	Terpene Name	Demetbyl Name
80	Camphenilane	1,7,7-Tridemethyl-2,2-dimethylbomane
81	Fenchane	7,7-Demethyl-3,3-dimethylbornane
84	Camphene	1,7,7-Tridemethyl-2,2-dimethyl- 3-methylenebornane

These names are confusing and misleading – for example, a fenchane (No. 81) contains a third methyl at position No. 1 which is concealed in the name bornane. The correct formula for camphene (No. 84) can be written more readily from the systematic and simpler name (2,2-dimethyl-3-methylenenorbornane) than from the demethyl name.

In SYSTEM OF NOMENCLATURE FOR TERPENE HYDROCARBONS; Advances in Chemistry; American Chemical Society: Washington, DC, 1955.

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Appendix C

Proposals on Consistent Numbering of Bicyclics and Menthane-Type Monocyclics

Several reviewers of the June 1950 version of this report suggested, in the interest of homogeneity, that: (1) the bicyclic fundamental parent structures should be numbered so that a return to the monocyclic forms would not change that numbering; (2) the actual or potential isopropyl group should always be attached to the No. 1 ring carbon in both the bicyclic structures and the menthane-type monocyclic structures. The American committees decided this was not feasible (see report proper). A summary of the specific proposals made by reviewers follows.

1. By Georges Dupont

Professor Dupont, in a letter of March 5, 1952, expressed the opinion that the numbering in going from bicyclics to monocyclics should be preserved as much as possible – for example, for the transformation pinene \longrightarrow limonene, it would be useful to preserve the numbering. This would be obtained if *a*-pinene retained its classical formula (I) and if for limonene (II) the numbering corresponded to that required for menthene on the basis of the *Chemical Abstracts* alphabetic order of precedence of the names of the substituents – i.e., isopropyl methyl – thus:



(Chemical Abstracts, however, abandons its alphabetic order for menthane-type formulas and has always used the established fixed numbering in which the carbon of the isolated methyl group is No. 7, and the isopropyl group is attached to ring carbon No. 4. The numbering proposed above corresponds to the British alphabetic order because *iso* is italicized and *iso*propyl is alphabeted at "p". MWG) The recommendations on numberings by Professor Dupont is therefore:



67 In SYSTEM OF NOMENCLATURE FOR TERPENE HYDROCARBONS; Advances in Chemistry; American Chemical Society: Washington, DC, 1955.



(This recommendation means that the *gem*-dimethyls in pinane are attached to carbon No. 7 instead of No. 6; it will also be necessary to call the two carenes 3and 4- instead of 2- and 3-. Also, confusion in the literature will certainly result if the established fixed numbering of menthane is changed. MWG)

Earlier comments from Professor Dupont (letter of November 7, 1950) on the numbering of monocyclics and bicyclics included: According to Baeyer, the number 1 is assigned to the bridgehead carbon which is most heavily substituted. This is logical and should be accepted. But would it not then be advisable to revise the numbering of the terpenes of menthane type and assign the number 1 to the carbon atom bearing the isopropyl group? This would also be in agreement with the 1,1,3- and 1,1,2,3numbering of the other type of monocyclics – i.e., No. 1 assigned to the most heavily substituted carbon atom. A further advantage: Bicyclic terpenes open readily to yield monocyclic terpenes; in the majority of cases, the numbering of the atoms of the nucleus would remain the same. (The "most heavily substituted" principle applies to gem-dimethyl groups since they have separate numbers – e.g., 1,1- – but not to an isopropyl group which has but one number. MWG)

An objection to the recommended numbering of pinene. You select as the base nucleus that carrying the two methyl substituents on carbon No. 6 in contrast to the usual numbering. I see in this two drawbacks: (1) Lack of homogeneity with the numbering of the other three types (thujane, carane, and camphane), where the two methyl groups are borne by the No. 7 carbon atom; (2) the bridge in pinane is evidently the one bearing the two methyl radicals; it opens exactly between 1 and 7 (conventional numbering) to yield monocyclic terpenes but preserves the base ring of the conventional formula.

To resume: I would prefer to number pinane



in order to preserve so far as possible the numbering (proposed above) for the monocyclic terpenes resulting from the opening of the bridge. This last proposition would have the drawback of no longer necessarily corresponding to Baeyer's numbering.

2. By C.D. Hurd

Dr. Hurd, in a letter of February 22, 1952, expressed the opinion that if better correlation of numbering between the bicyclics and monocyclics could be achieved, this might be the time for a clean break from historical numbering patterns. For example, we could gain uniformity if we had the following sequence.



Since we are talking about the numbering of trivial names and not systematic names, it is questionable whether we need be bound by restrictions imposed on systematic names. If regularization can be achieved by use of mild concessions, the systematic "bicyclo" numbering need be no concern for these trivial names. The uniform numbering of steroid ring systems makes for easy transitions from cholesterol to estrone to cholic acid, etc. Unless something like this can be recommended and accepted generally, it may be well to retain the currently used numberings.

3. By Several Teachers of Organic Chemistry

Several teachers expressed the opinion that they would like to see the numbering assigned to menthane (whether it is the historical numbering or a new numbering) retained for bicyclics and other terpene derivatives to simplify the following through a series of terpene transformation reactions.

Some results of changing the menthane numbering have been given under Professor Dupont's comments above. An alternative is to retain the historical numbering of menthane and apply it to the bicyclics; thus:





(In this scheme, the numberings that result for three of the bicyclic structures violate the fundamental rule for numbering bicyclo structures; that is, the No. 1 carbon should be a bridge end. MWG)

4. By a Group of Terpene Chemists

Initially, it was felt by some terpene chemists that a prime consideration in any attempt to systematize terpene nomenclature should be a consistent numbering system which would carry through the various ring systems. Such a system is that suggested above by Professor Dupont. It was felt that this consistency would be highly advantageous for discussion purposes, even though accepted nomenclature practice was violated in many instances. The beauty of the system would be that a substituent attached to carbon 10 - for example in a-pinene - is still attached to carbon 10 if the bicyclic terpene is converted to a monocyclic terpene. The fault of this scheme is that transformations of the a-pinene to camphene or the fenchene type are so drastic as to disrupt the logical sequence of numbering around a ring (see pp. 32-34). Since the numbering cannot be made identical for the various ring systems, the American committees concluded that each ring system should be numbered by accepted rules (see Chart 8). An exception to this rule is the well-established numbering for p-menthane. The volume of literature in which the tertiary ring carbon bearing an isopropyl group is numbered 1 and the carbon of the methyl group is numbered 7 makes it inadvisable to effect a change which produces no simplification.

5. By G. M. Dyson and N. E. Wolff

Two entirely different approaches to systematizing the numberings of the basic monocyclic and bicyclic terpene structures were suggested in 1952 by G. M. Dyson of England and N. E. Wolff of Princeton University. It was the opinion of the American committees that these proposals needed considerable developmental work by their proponents before they could be properly evaluated.

Appendix D

The Prefix Nor-

The prefix nor- is being used in chemical nomenclature with several meanings, and for that reason is a rather ambiguous term. The *Chemical Abstracts* booklet (6, pp. 5953-54) defines nor- as follows:

nor- from normal; (a) indicating the parent from which another compound may be theoretically derived, usually by the removal of one or more carbon atoms (and attached hydrogen); as, norcamphane (of which camphane is a trimethyl derivative); (b) designating a compound of normal structure isomeric with the one to the name of which it is prefixed; as, norleucine.

Meaning (a) – that is, stripping to a parent ring skeleton by the replacement of methyl groups by hydrogen – has been the one generally used by terpene chemists. The American committees agreed that the use of nor- in meaning (b) should be discouraged.

Although there is nothing in the name "nor" to suggest the replacement of a CH_3 by H or the elimination of CH_2 adjacent to COOH, this definition states correctly the current steroid usage. The most common use of nor- in nonsteroid chemistry occurs in the names of alkaloids; here the prefix indicates the replacement of one CH_3 group by H in an NCH₃ group.

In the June 1952 version of the terpene nomenclature report, the recommendation was made to modernize the traditional terpene definition of the prefix nor- so that in a name it would denote a ring system devoid of all side chains rather than of only methyl groups. On this basis, the name "northujane" would be valid and fit in logically with the bicyclic series of names: norcarane, norpinane, and norbornane. Evidence from the chemical literature for the occasional use of nor- to denote stripping of an isopropyl group as well as a methyl group is: norsabinane (a synonym for northujane) in Richter's organic text(31, pp. 53, 240); northujane in Berichte (27); northujonedicarboxylic acid (with an asterisk) in the Third Decennial Index of Chemical Abstracts; and normenthane (a synonym for cyclohexane) in Mitchell's book (36, pp. 39, 120). However, majority opinion ruled out the recommended modernization of the definition of nor-, and thus the name northujane, at the meeting of the Nomenclature Committee, Division of Organic Chemistry, in Chicago, Ill., September 5, 1953. In the final report, therefore, the name bicyclo[3.1.0] hexane rather than northujane is recommended for the bicyclo ring structure of thujane.

Appendix E

Principle of "Like Treatment of Like Things"

Committee discussions on the principle of "like treatment of like things" as it affected recommendations for naming terpene hydrocarbons centered chiefly around three proposals. These apply to all series of names based on the approved terpene names for the parent compounds having carbon skeletons larger than the ring carbon skeletons. To simplify the interpretations of these proposals, pinane names are used throughout as the examples. However, the proposals were intended to be applicable to the entire proposed scheme for systematizing terpene hydrocarbon nomenclature. The three proposals, the types of names allowed by each, and some of the advantages and disadvantages of each are:

Proposal |

"Treating like things alike" as applied by Chemical Abstracts and the London Chemical Society. They interpret "like" to mean "identical." Thus, the -CH₃ group is considered to be unlike =CH₂, -CH₂Cl, and -C₂H₅. Therefore, this principle allows such names as methylenepinane, (chloromethyl)pinane, and ethylpinane, but does not allow such a name as methylpinane. The latter compound must be named as a tetramethylnorpinane because the substituent group is -CH₃ which is like (or identical to) the three -CH₃ groups present in the parent compound pinane.

This principle represents both British and American practice, and has been followed for some years. Although a name such as methylpinane violates this principle, it is unambiguous and simpler than tetramethylnorpinane. Also, relations among substituted pinane derivatives are more readily seen from a series of names such as methylpinane, (chloromethyl)pinane, and methylenepinane than from a series in which methylpinane is replaced by tetramethylnorpinane. The names of only a few terpene compounds are involved, however, in this problem and a compromise may be the best solution. For the sake of consistent nomenclature between terpenes and related compounds, sticking to a recognized principle is an important consideration.

Proposal II

"Not naming a compound as the derivative of a parent baving side chains if this means adding to the carbon skeleton of that parent" (proposed by A. M. Patterson). This principle is not intended to exclude the addition of such functional groups as -COOH and -CHO. It does exclude all hydrocarbon substituent groups or derivatives thereof. On the basis of this principle, the -CH₃, =CH₂, -CH₂Cl, and -C₂H₅ groups are considered to be like groups. Therefore, this principle does not allow such names as methylpinane, methylenepinane, (chloromethyl)pinane, and ethylpinane. These compounds must be named, respectively, as tetramethylnorpinane, trimethylmethylenepinane, (chloromethyl)trimethylnorpinane, and ethyltrimethylnorpinane.

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Proposal II can be considered as a particular case of "treating like things alike." In addition to forbidding a name such a methylpinane, it also forbids such names as methylenepinane, (chloromethyl)pinane, and ethylpinane, which are convenient and allowed by Proposal I. However, application of Proposal II automatically serves to limit the extent of compounds to which terpene-type names are given except as such a field may be extended by the adoption of additional trivial names.

Proposal III

"Allowing the addition of one carbon atom, or at most only two, to a terpene parent compound carbon skeleton for naming compounds as derivatives of that parent" (proposed by L. A. Goldblatt). This principle does not depend on a distinction between like and unlike groups, but is based merely on the number of carbon atoms in the substituents. Therefore, it allows such names as methylpinane, methylenepinane, (cbloromethyl)pinane, and (if two additional carbons are allowed) ethylpinane. The first of these four types of names are not allowed by either Proposal I or Proposal II. The other three types are allowed by I but not by II.

Proposal III violates the principle of "treating like things alike" (Proposal I), and therefore also Proposal II, because it allows such a name as methylpinane. It was proposed admittedly as a compromise suggestion which might be acceptable to both the nomenclaturists and the terpene chemists. To avoid indefinite extension of terpene-type names to allied compounds no longer classed as terpenes, which is undesirable from the overall nomenclature viewpoint, and in an attempt to resolve the troublesome problem of where to cut off the use of the names based on trivial names and substitute the systematic names, the arbitrary addition of only one or two carbon atoms to a parent carbon skeleton was proposed. Such practice is not usual procedure in organic nomenclature.

The difficulty in obtaining a preponderant vote of committee members for one of these proposals was due chiefly to the fact that any decision would affect nomenclature in its entirety and not be limited to systematizing terpene nomenclature.

In addition to comments of the official committee members, opinions were obtained from some research terpene chemists. They would not vote for any of the three proposals because none allowed a name such as methylpinane. They feel that names of this type are too useful and convenient to attempt to exclude them from the literature. The positions of the three methyl groups are fixed in the pinane structure and this structure is immediately visualized on mention of the name pinane. The structure of a compound named 4-methylpinane is then readily grasped from the name. To insist on a name such as 2,4,6,6-tetramethylnorpinane for a pinane hydrocarbon containing one additional methyl group seems illogical to them. Their first reaction to the "nor" in the name and the prefix position numbers - e.g., 2,4,6,6-tetramethylnorpinane - is that at least some of the methyl groups must be in positions other than the fixed positions of the pinane structure. Then they find by drawing the bicyclic ring structure and adding the methyls to the positions 2,4,6,6- that they come out with pinane which contains a methyl substituent in the 4 position. These simpler names have been used and the terpene chemists predict they will continue in usage in the terpene field regardless of nomenclature principles. They feel that the adoption of a name like pinane should imply the right to name all derivatives (even methyl derivatives) as pinanes.

Some general comments of C. D. Hurd (letter of May 24, 1952) bring out other inherent difficulties in nomenclature decisions. He pointed out that the principle of

treating like things alike has two aspects which have never been brought to the fore:

- 1. Names which reveal the groups in question.
- 2. Names which have groups concealed within a trivial name.

There is no doubt but that the first of these two is basically sound and generally adhered to. The second is the one causing trouble. The principle came into being long after such names as toluene, xylene, and mesitylene were in use. Although one may say that we never say methyltoluene for xylene or dimethyltoluene for mesitylene, the real reason probably is that the names xylene and mesitylene were entrenched before the principle was enunciated and that the principle had nothing to do with it.

Those who would invoke the principle in not calling xylene as methyltoluene . would probably be embarrassed in finding an appropriate simple synonym for methylcholestane or methyllycopene. Hence, in applying this principle we should regard it for what it is, namely, something that is usually helpful and that usually leads to better names; but not something that must be adhered to without exception.

Proposal II is artificial and would be inconsistent at once with so much of accepted usage. The name methylcholestane is an obvious exception to it. The purpose of the principle is to show a guiding preference for a name such as 2-methyl-4-phenylhexane over any "phenylisoheptane" but it runs afoul of names which would certainly be useful.

Proposal III is one of those arbitrary conceptions that makes nomenclature practice so difficult for those who are not in the expert bracket. Adherence to a few simple rules may lead to synonyms, but creation of arbitrary little "principles" is objectionable because of the arbitrariness involved.

Appendix F

System of Nomenclature for Hydrocarbon Terpene Radicals Acyclics, Monocyclics, Bicyclics

No official action on the names of *bydrocarbon terpene radicals* was taken by the Nomenclature Committee of the ACS Organic Division at its meeting in New York City, September 1954, but general recommendations were discussed. It was agreed that the earlier acceptance of the system of nomenclature for the simple acyclic, monocyclic, and bicyclic terpene hydrocarbons implied the systematization of the hydrocarbon terpene radicals derived from these compounds. Therefore this Appendix F has been added here, but it has no official status.

Recommendation

By adhering to the general underlying principles of the recommended system of nomenclature for the terpene hydrocarbons and applying IUPAC rules and established good nomenclature practices for forming names of radicals, series of unique, unambiguous, and simple names for the different types of *bydrocarbon terpene radicals* can be derived. The general recommendation is:

Form the names of simple acyclic, monocyclic, and bicyclic bydrocarbon terpene radicals systematically from the recommended names of the terpene bydrocarbons. For cyclic compounds, radicals may be formed with points of attachment in side chains which have a fixed numbering as well as in rings. Preference in numbering is given to the point of attachment over double bonds when there is a choice.

The general names which result are shown in Table 1. Two exceptions to the above recommendation are evident: (1) a few acyclic radicals; (2) the saturated radicals of the pinane group.

Trivial names for four unsubstituted acyclic hydrocarbon terpene radicals were sanctioned as permissible and exceptions to IUPAC Rule 55.1 by the Commission on Organic Chemistry at its meeting in Amsterdam in 1949 (30). These are:

geranyl (preferred to 3,7-dimethyl-trans-2,6(or 7)-octadienyl); $C_{10}H_{17}$ linalyl (preferred to 1,5-dimethyl-1-vinyl-4-hexenyl); $C_{10}H_{17}$ neryl (preferred to 3,7-dimethyl-cis-2,6(or 7)-octadienyl); $C_{10}H_{17}$ pbytyl (replaces 3,7,11,15-tetramethyl-2-hexadecenyl); $C_{20}H_{39}$ -

Table 1. Recommended General Names of Hydrocarbon Terpene Radicals for Acyclics, Monocyclics, and Bicyclics

Position designations must be added to identify completely the radicals. Names apply whether point of attachment is on the ring or on a numbered substituent.

Type of Terpene	See Chart	Recommended	l Radical Name
Acyclic	3, p.13	Use Systematic Names (IUPAC Rules). Exceptions: Four Unsubstituted Radicals Recognized by IUPAC (See Text)	
Monocyclic: Type A Menthane Type	5, p.19	Menthyl Menthenyl Menthadienyl	Menthylidene Menthylene
Monocyclic: Type B Dimethylcyclohexane Type	6, p.24	Use Systematic Names (IUPAC Rules	
		Based on Parent Structure Larger Than Ring Fixed Numbering	Based on Ring Carbon Structure Bicyclo Numbering
Bicyclic: Tbujane Group Bicyclo[3.1.0]hexane Type	10, p.44	Thujyl Thujenyl Thujadienyl Thujylidene Thujylene	Use Bicyclo Plan Names
Bicyclic: Carane Group Bicyclo[4.1.0]heptane Type	11, p.46	Caryl Carenyl Caradienyl Carylidene Carylene	Norcaryl Norcarenyl Norcaradienyl Norcarylidene Norcarylene
Bicyclic: Pinane Group Bicyclo[3.1.1]heptane Type	12, pp.48- 49	Pinanyl (not Pinyl) (See Text) Pinenyl Pinadienyl Pinanylidene Pinanylene	Norpinyl (See Text) Norpinenyl Norpinadienyl Norpinylidene Norpinylene
Bicyclic: Bornane Group Bicyclo[2.2.1]heptane Type	14, p.58	Bornyl Bornenyl Bornadienyl Bornylidene Bornylene	Norbornyl Norbornenyl Norbornadienyl Norbornylidene Norbornylene

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The four names are actually derived not from the common terpene names of hydrocarbons but from those of the corresponding alcohols, that is, geraniol, linalool, nerol, and phytol.

The name *pinanyl* is recommended for the univalent saturated radical $(C_{10}H_{17})$ derived from pinane because in the terpene literature the name pinyl (which would be the name formed by replacing the ending *ane* of pinane by *yl*) has been used exclusively and frequently for a $C_{10}H_{15}$ - radical (with point of attachment at position 3) derived from β -pinene. Since *pinanyl* must be an exception to the general rules, the names of the other two saturated radicals in the pinane-group series, that is, *pinanylidene* and *pinanylene*, should also be exceptions for consistency. In the series of nor-names, however, it does not seem necessary to insert the "an" syllable because the radical names norpinyl and the like have not been used in the literature.

Rules for Forming Names of Acyclic and Dimethylcyclohexane-Type (Type B) Monocyclic Hydrocarbon Terpene Radicals

Rules for forming names of radicals derived from the acyclic and dimethylcyclobexane-type (Type B) monocyclic terpene hydrocarbons need be stated only generally since it is recommended that these names conform to IUPAC rules. According to these rules, one point of attachment, whether the structure is saturated or unsaturated, is always numbered 1.

Acyclics: Name the acyclic hydrocarbon terpene radicals systematically in a manner similar to that for other unsaturated aliphatic hydrocarbon radicals (IUPAC rules) when pure compounds are involved. Examples:



For complete identification of an isomer, *cis*- or *trans*- must be added to the names of the acyclic radicals.

Dimethylcyclobexane-Type (Type B) Monocyclics: Name the dimethylcyclohexane-type (Type B) monocyclic hydrocarbon terpene radicals systematically

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in a manner similar to that for other hydrocarbon radicals derived from cyclohexane, cyclohexene, and cyclohexadiene (IUPAC rules). Examples:



2,2,6-Trimethylcyclohexylidene

(From Cyclogeraniolane; Formula 28, Chart 6, p. 24)



3,3,4,5-Tetramethylcyclohexyl

(From Pyronane; Formula 29, Chart 6, p. 24)



2,6,6-Trimethyl-2-cyclohexen-1-yl

(From *a*-Cyclogeraniolene; Formula 30, Chart 6, p. 24)



3,3-Dimethyl-1-cyclohexen-1-ylmethyl

(From β -Cyclogeraniolene; Formula 31, Chart 6, p. 24)



2,3,4,4-Tetramethyl-1,5-cyclohexadien-1-yl

(From *a*-Pyronene; Formula 36, Chart 6, p. 24)

Rules for Forming Names of Menthane-Type (Type A) Monocyclic Hydrocarbon Terpene Radicals

For the parent compound of the menthane-type (Type A) monocyclic terpene hydrocarbons, the name *menthane*, its well-established fixed numbering of the carbon skeleton, and extension of nomenclature rules to apply to double bonds outside the ring have been recommended (for the *p*-form, see Formula 6, Chart 5, p. 19). These recommendations and the extension of nomenclature practices to apply to points of attachment outside the ring are basic to the rules for forming the names of menthane-type monocyclic radicals. Since the enumeration of the parent compound is fixed, the position number of a point of attachment in radicals derived from it is predetermined and will not always be numbered as 1.

The rules for naming menthane-type monocyclic radicals are:

Rule 1: Form the names of univalent radicals derived from menthane (the saturated parent hydrocarbon of menthane-type monocyclic terpenes) by replacing the "ane" ending of the hydrocarbon name with "yl". That is: menthyl.

Rule 2: Form the names of univalent radicals derived from the unsaturated mentbane-type monocyclic terpene hydrocarbons containing one double bond, which may be either in the ring or outside the ring, by replacing the final "e" of the hydrocarbon name (menthene) with "yl". That is: menthenyl.

Rule 3: End the names of univalent radicals derived from the unsaturated menthanetype monocyclic terpene hydrocarbons containing two double bonds, regardless of their positions in the structure, with "dienyl". The root of the name of the saturated parent hydrocarbons plus the letter "a" for euphony precede this ending. That is: menthadienyl.

Rule 4: Form the names of bivalent radicals derived from menthane and baving two points of attachment on the same carbon atom by adding "idene" to the names of the saturated univalent radicals. That is: menthylidene.

If the bivalent radicals derived from menthane have the two points of attachment on different carbon atoms, add "ene" to the names of the saturated univalent radical names. That is: menthylene.

Rule 5: Form the above types of names for all hydrocarbon terpene radicals derived from menthane-type monocyclic hydrocarbons regardless of the position of the point or points of attachment; that is, the H or H's may be removed from carbons in the ring or from carbons in the numbered side chains. Use position numbers to designate the position of the point or points of attachment in the radicals.

In saturated radical names, the position number or numbers for the point or points of attachment will precede the name. Examples: 2-p-menthyl; 8-m-menthyl; 3-o-menthyl; 7-p-menthylidene; 1,4-p-menthylene.

In unsaturated radical names, the position number or numbers for the point or points of attachment will precede the distinguishing ending of the radical name since the position number or numbers designating the position of unsaturation will precede the radical name. Examples: 3-p-menthen-2-yl; 1-m-menthen-8-yl; 4(8)-p-menthen-2-yl; 1,3-p-menthadien-2-yl.

The menthane-type radicals given below are based on the p-form of menthane. Names of the radicals derived from the few known o- and m-menthane-type monocyclics would be analogous. The established fixed numbering for p-menthane is shown on the formula for p-menthyl; the position numbers in all of the recommended radical names are based on this numbering. The names in parentheses shown below some of the recommended names are the common terpene radical names. Examples:



2-p-Menthyl (Carvomenthyl, Menthyl)

(From *p*-Menthane; Formula 6, Chart 5, p. 19)



8-p-Menthyl

(From *p*-Menthane; Formula 6, Chart 5, p. 19)



1,4-p-Menthylene

(From p-Menthane; Formula 6, Chart 5, p. 19)



7-p-Menthylidene





1-p-Menthen-8-yl (Terpinyl)

(From Carvomenthene; Formula 7, Chart 5, p. 19)



5-p-Menthen-2-yl

(From Menthene; Formula 9, Chart 5, p. 19)



4(8)-p-Menthen-2-yl (Terpenyl)

(From Dihydroterpinolene; Formula 11, Chart 5, p. 19)

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1,3-p-Menthadien-2-yl

(From a-Terpinene; Formula 13, Chart 5, p. 19)

Rules for Forming Names of Bicyclic Hydrocarbon Terpene Radicals

For parent compounds of the bicyclic terpene hydrocarbons, the names *thujane* (Formula 46, Chart 10, p. 44), *carane* (Formula 55, Chart 11, p. 46), *pinane* (Formula 66, Chart 12, p. 49), and *bornane* (Formula 75, Chart 14, p. 58) and fixed numberings of their carbon skeletons, which are larger than their ring carbon skeletons, have been recommended. In addition, the names *norcarane* (Formula 51, Chart 11, p. 46), *norpinane* (Formula 59, Chart 12, p. 48), and *norbornane* (Formula 73, Chart 14, p. 58) and the bicyclo plan numberings of their ring carbon skeletons have been recommended. The prefix *nor*- is limited to its traditional meaning in the terpene field, that is, to denote a ring system devoid of methyl groups. This definition excludes recognition of the name northujane (originally proposed for the fourth bicyclic ring carbon skeleton) since the larger parent compound thujane contains an isopropyl group. Hence, for this structure the name bicyclo[3.1.0]hexane was recommended (Formula 43, Chart 10, p. 44).

These recommendations and extension of nomenclature practices to apply to points of attachment outside the ring are basic to the rules for forming the names of the bicyclic radicals. Since the enumeration of the four parent compounds larger than the ring carbon skeletons is fixed, the position number of a point of attachment on radicals derived from them is predetermined and will not always be numbered as 1. For radicals derived from the nor- structures numbered according to the bicyclo plan, preference in assigning low numbers according to accepted practice is in the order: point or points of attachment, double bonds, substituents. In the nor- names the position number of a point of attachment also will not always be numbered as 1.

The rules for naming bicyclic hydrocarbon terpene radicals are:

Rule 1: Form the names of univalent radicals derived from the saturated parent bydrocarbon of each bicyclic fundamental structure type larger than the ring carbon skeletons (that is, thujane, carane, pinane, bornane) by replacing the "ane" ending of the hydrocarbon name with "yl". One exception is the name of the univalent radical derived from pinane. This name is to be pinanyl and not pinyl because by usage the latter designates a different radical. The resulting names are: thujyl, caryl, pinanyl, bornyl.

Rule 2: Form the names of univalent radicals derived from the four fundamental

types of unsaturated bicyclic terpene bydrocarbons containing one double bond, which may be either in the ring or outside the ring, by replacing the final "e" of the hydrocarbon names with "yl". The resulting names are: thujenyl, carenyl, pinenyl, bornenyl.

Rule 3: End the names of univalent radicals derived from the four fundamental types of unsaturated bicyclic terpene hydrocarbons containing two double bonds, regardless of their position in the structure, with "dienyl". The roots of the names of the saturated parent hydrocarbons plus the letter "a" for euphony precede this ending. The resulting names are: thujadienyl, caradienyl, pinadienyl, bornadienyl.

Rule 4: Form the names of bivalent radicals derived from the four fundamental types of saturated bicyclic terpene bydrocarbons and baving the two points of attachment on the same carbon by adding "idene" to the names of the saturated univalent radicals. The resulting names are: thujylidene, carylidene, pinanylidene, bornylidene. If the bivalent radicals derived from the saturated structures have the two points of attachment on different carbon atoms, add "ene" to the names of the saturated univalent radical names. The resulting names are: thujylene, carylene, pinanylene, bornylene.

Rule 5: Form the names of radicals derived from the saturated bicyclic compounds whose names begin with nor- in the regular way by substituting for "ane" the ending "yl", "ylidene", or "ylene". Form the radical names from nor- names of the unsaturated compounds according to Rules 2 and 3. Preference in numbering is given to the point of attachment over double bonds when there is a choice. Examples: norbornyl, norpinyl, 4-norcaren-2-yl.

The position numbers for point or points of attachment, double bonds, and substituents in the nor- names will be identical to those in the corresponding systematic bicyclo names. Examples: 4-norcaren-2-yl is synonomous to bicyclo [4.1.0]hept-4-en-2-yl; 1,3,3-trimethyl-2-norbornyl to 1,3,3-trimethylbicyclo [2.2.1]hept-2-yl; 3,3-dimethyl-2-norbornylidenemethyl to 3,3-dimethylbicyclo [2.2.1]hept-2-ylidenemethyl.

Rule 6: Form the names of radicals derived from bicyclo[3.1.0]hexane names regularly according to established practices for naming radicals derived from bicyclic structures. Examples: bicyclo[3.1.0]hex-2-yl, bicyclo[3.1.0]hex-3-en-2-yl, 5-isopropylbicyclo[3.1.0]hex-2-en-2-yl.

Rule 7: Form the above types of terpene-like names for all hydrocarbon terpene radicals derived from the four fundamental types of bicyclic hydrocarbons regardless of the position of the point or points of attachment; that is, the H or H's may be removed from carbons in the ring or from carbons in the numbered side chains. Use position numbers to designate the position of the point or points of attachment in the radicals.

In saturated radical names, the position number or numbers for the point or points

of attachment will precede the name, except in bicyclo[3.1.0]hexane names, in which the numbers precede the distinguishing ending of the radical name. Examples: 4-caryl, 3-thujylidene, 2-norbornyl, 2,3-pinanylene; but 1-isopropyl-4-methylbicyclo[3.1.0]hex-3-yl.

In unsaturated radical names, the position number or numbers designating the point or points of attachment will precede the distinguishing ending of the radical name. Examples: 3-thujen-7-yl, 3(10)-caren-2-yl, 4-norcaren-2-yl, 2-pinen-10-yl, 2(10),3-pinadien-3-yl, 2,5-bornadien-2-yl, 5-norbornen-2-yl; 1-isopropenyl-4-methylbicyclo[3.1.0]hex-3-en-2-yl.

Rule 8: Designate the names of substituents in radicals according to current good nomenclature rules and practices. Examples: 3-chloro-3,7-thujadien-2-yl, 4-methylene-2-caryl, 4-ethyl-3-pinen-3-yl, 2,4,6,6-tetramethyl-2-norpinen-3-yl, 3,3-dimethyl-2-norbornylidene, 5-bromo-2,5-bornadien-2-yl.

Examples of radicals derived from the largest parent compounds of the four types of bicyclics and the recommended names are given below. The recommended fixed numberings for these structures are shown on 3-thujyl, 2-caryl, 3-pinanyl, and 2-bornyl. Names in parentheses under some of the recommended radical names are the common terpene radical names.



(From Thujane; Formula 46, Chart 10, p. 44)



3-Thujylidene (β -Thujylidene)

(From Thujane; Formula 46, Chart 10, p. 44)



3-Thujen-7-yl





4(10)-Thujen-10-yl

(From Sabinene; Formula 49, Chart 10, p. 44)



3,7-Thujadien-2-yl

(From 3,7-Thujadiene; Formula 50, Chart 10, p. 44)



2-Caryl (Caryl)

(From Carane; Formula 55, Chart 11, p. 46)



3-Caren-4-yl

(From Δ ³-Carene; Formula 57, Chart 11, p. 46)



2-Caren-10-yl

(From Δ^4 -Carene; Formula 56, Chart 11, p. 46)



3(10)-Caren-2-yl

(From ψ -Carene; Formula 58, Chart 11, p. 46)



3-Pinanyl

(From Pinane; Formula 66, Chart 12, p. 49)



2-Pinen-4-yl (Verbenyl)

(From *a*-Pinene; Formula 67, Chart 12, p. 49)



2-Pinen-10-yl (Myrtenyl)

(From a-Pinene; Formula 67, Chart 12, p. 49)



2(10)-Pinen-3-yl (Pinyl)

(From β -Pinene; Formula 69, Chart 12, p. 49)



2-Pinen-10-ylidene (Myrtenylidene)

(From a-Pinene; Formula 67, Chart 12, p. 49)



2(10),3-Pinadien-3-yl

(From Verbenene; Formula 70, Chart 12, p. 49)



2-Bornyl (Bornyl, Isobornyl, Camphanyl)

(From Bornane; Formula 75, Chart 14, p. 58)



10-Bornyl

(From Bornane; Formula 75, Chart 14, p. 58)



3-Bornylidene

(From Bornane; Formula 75, Chart 14, p. 58)



(From Bornylene; Formula 89, Chart 14, p. 58)

Examples of radicals derived from the ring carbon skeletons of the four types of bicyclics and their recommended names are given below. The numberings of the structures are based on bicyclo plan numbering for radicals, which assigns low numbers in the order: (a) point of attachment; (b) double bonds; (c) substituents. The No. 1 carbon of a ring skeleton is always a bridge end, and the carbon atom so designated in the formulas below will be evident from the position numbers in the recommended names.



Bicyclo[3.1.0]hex-2-yl

(Ring Carbon Skeleton of Thujane; Formula 46, Chart 10, p. 44)



Bicyclo[3.1.0]hex-3-en-2-yl

(Ring Carbon Skeleton of 2-Thujene; Formula 47, Chart 10, p. 44)



3-Norcaryl

(From Norcarane; Formula 51, Chart 11, p. 46)



4-Norcaren-2-yl

(From 2-Norcarene; Formula 52, Chart 11, p. 46)



2,4-Norcaradien-3-yl

(From 2-Norcaradiene; Formula 54, Chart 11, p. 46)



2-Norpinyl

(From Norpinane; Formula 59, Chart 12, p. 48)



2,4,6,6-Tetramethyl-2-norpinen-3-yl

(From δ-Pinene; Formula 68, Chart 12, p. 49)



2-Norbornyl (Norcamphanyl, Norbornyl)

(From Norbornane; Formula 73, Chart 14, p. 58)



1,7-Dimethyl-2-norbornyl (Santenyl)

(From Santane; Formula 79, Chart 14, p. 58)



7,7-Dimethyl-2-norbornyl (Apobornyl)

(From Apocamphane; Formula 74, Chart 14, p. 58)



1,3,3-Trimethyl-2-norbornyl (Fenchyl, Fenchanyl)

(From Fenchane; Formula 81, Chart 14, p. 58)



3,3-Dimethyl-2-norbornyl (Camphenilyl)

(From Camphenilane; Formula 80, Chart 14, p. 58)



2,3,3-Trimethyl-2-norbornyl (Isocamphanyl)

(From Isocamphane; Formula 82, Chart 14, p. 58)



1,5,5-Trimethyl-2-norbornyl (Isofenchyl)

(From Fenchane; Formula 81, Chart 14, p. 58)



3,3-Dimethyl-2-methylene-1-norbornyl (1-Camphenyl, for unsubstituted radical only)

(From Camphene; Formula 84, Chart 14, p. 58)



3,3-Dimethyl-2-norbornylmethyl (Isocamphyl)

(From Isocamphane; Formula 82, Chart 14, p. 58)



3,3-Dimethyl-2-norbornylidenemethyl (8-Camphenyl, for unsubstituted radical only)

(From Camphene; Formula 84, Chart 14, p. 58)



3,3-Dimethyl-2-norbornylidene (Camphenilylidene)

(From Camphenilane; Formula 80, Chart 14, p. 58)



5-Norbornen-2-yl

(From Norbornylene; Formula 87, Chart 14, p. 58)



7,7-Dimethyl-5-norbornen-2-yl

(From Apobornylene; Formula 88, Chart 14, p. 58)



4,5,6-Trimethyl-5-norbornen-2-yl

(From ε-Fenchene; Formula 96, Chart 14, p. 58)



1,3,3-Trimethyl-5-norbornen-2-yl

(From δ-Fenchene; Formula 92, Chart 14, p. 58)



3-Methyl-2-norbornen-2-ylmethylene

(From Santene; Formula 95, Chart 14, p. 58)

Common Terpene Names for Radicals

The common terpene radical names shown in parentheses under the recommended names in many of the above examples were originally derived largely from the common terpene names of the corresponding alcohols; for example, bornyl from borneol; camphenilyl from camphenilol; carvomenthyl from carvomenthol; fenchyl from fenchyl alcohol; pinyl from pinyl alcohol; terpinyl from terpineol; verbenyl from verbenol. A few of the radical names were derived from the names of the corresponding ketones; for example, carylidene from carone; β -thujylidene from thujone. Still others were derived from hydrocarbon names; for example, camphyl from camphane; camphenyl from camphene. As such, these common terpene radical names have very specific meanings in the literature and are limited to designated points of attachment to the ring, even though position numbers or Greek letters are seldom used to show that specificity.

The advancement in naming terpene radicals exemplified by the rules recommended in this Appendix F is based on the general principles: (1) terpene radicals should be considered as derived from the corresponding hydrocarbons; (2) the radicals should be formed regularly with the exception of pinanyl, pinanylidene, and pinanylene; (3) position numbers should always be used to show the point or points of attachment which may be on a ring carbon or on a carbon in a numbered substituent.

Index to Recommended Names of Terpene Hydrocarbons by Alphabetical Arrangement of Common Terpene Names

Only seven of the fourteen charts included in the report are referred to in this index. These charts and the pages on which they appear are:

No. 3, p. 13	No. 11, p. 46
No. 5, p. 19	No. 12, pp. 48-49
No. 6, p. 24	No. 14, p. 58
No. 10, p. 44	

Information on many of the common terpene names will be found in the text, usually in connection with the discussion of a specific chart or in the sections on common terpene names.

Common Terpene Name	Recommended Name	Chart No.	Compound No.
allo-ocimene	2,6-dimethyl-2,4,6-octatriene (cis- or		
	trans-)	3	5
apobornylane	7,7-dimethylnorbornane	14	74
apobornylene	7,7-dimethyl-2-norbornene	14	88
apocamphane	7,7-dimethylnorbornane	14	74
β -apofenchane	2,2-dimethylnorbornane	14	80
apoisofenchene	5,5-dimethyl-2-norbornene	14	91
apopinane	6,6-dimethylnorpinane	12	61
apopinene	6,6-dimethyl-2-norpinene	12	62
bornylane	bornane	14	75
bornylene	2-bornene	14	89
camphane	bornane	14	75
camphene	camphene (systematic name is:		
	2,2-dimethyl-3-methylenenorbornane)	14	84
camphenene	5,5-dimethyl-6-methylene-2-norbornene	14	94
camphenilane	2,2-dimethylnorbornane	14	80
camphenilene	5,5-dimethyl-2-norbornene	14	91
carane	carane	11	55
Δ^3 -carene	3-carene	11	57
Δ^4 -carene	2-carene	11	56
β-carene	3(10)-carene	11	58
ψ -carene	3(10)-carene	11	58
carvomenthene	1-p-menthene	5	7
cyclodihydromyrcene	1,5,5,6-tetramethylcyclohexene	6	35

Index to Recommended Names of Terpene Hydrocarbons	by			
Alphabetical Arrangement of Common Terpene Names	;			
(Continued)				

Common	Recommended Name	Chart	Compound
I erpene Name		No.	NO.
cyclogeraniolane	1,1,3-trimethylcyclohexane	6	28
a-cyclogeraniolene	1,5,5-trimethylcyclohexene	6	30
β -cyclogeraniolene	1,3,3-trimethylcyclohexene	6	31
y-cyclogeraniolene	1,1-dimethyl-3-methylenecyclohexane	6	32
dihydrobornylene	bornane	14	75
d ihydrocamphene	2,2,3-trimethylnorbornane	14	82
dihydrodipentene	8-p-menthene	5	12
β -dihydrolimonene	8-p-menthene	5	12
8,9-dihydrolimonene	1-p-menthene (d-form)	5	7
dihydromyrcene	2,6-dimethyl-2,6-octadiene (cis- or		
	trans-)	3	3
d ihydropinene	pinane	12	66
dihydroterpinolene	4(8)-p-menthene	5	11
dipentene	1,8-p-menthadiene (dl-form)	5	20
fenchane	1,3,3-trimethylnorbornane	14	81
a-fenchane	2,7,7-trimethylnorbornane	14	76
β -fenchane	2,2,>-trimethylnorbornane	14	83
δ -fenchane	1,3,3-trimethylnorbornane	14	81
a-fenchene	7,7-dimethyl-2-methylenenorbornane	14	77
β -fenchene	2,2-dimethyl-5-methylenenorbornane	14	85
y-fenchene	2,5,5-trimethyl-2-norbornene	14	93
δ -fenchene	1,5,5-trimethyl-2-norbornene	14	92
<i>ϵ</i> -fenchene	1,2,3-trimethyl-2-norbornene	14	96
ζ-fenchene	2,7,7-trimethyl-2-norbornene	14	90
a-fenchocamphorane	7,7-dimethylnorbornane	14	74
fenchylene	1,5,5-trimethyl-2-norbornene	14	92
geraniolene	2,6-dimethyl-1,5 (and 1,6)-heptadiene (cis- or trans-)	3	1 A ,1B
homopinene	2,4,6,6-tetramethyl-2-norpinene	12	65
homoverbanene	4-methylenepinane	12	71
isobornylane	2,7,7-trimethylnorbornane	14	76
isocamph ane	2,2,3-trimethylnorbornane	14	82
isocamphodiene	5,5-dimethyl-6-methylene-2-norbornene	14	94
i sodiprene	3-carene (d-form)	11	57
isofenchene	1,5,5-trimethyl-2-norbornene	14	92

Index to Recommended Names of Terpene Hydrocarbons by Alphabetical Arrangement of Common Terpene Names (Continued)

Common Terpene Name	Recommended Name	Chart No.	Compound No.
isofenchylene	1.5.5-trimethyl-2-norbornene	14	92
isolimonene	2.8-p-menthadiene	5	21
isopinene	7,7-dimethyl-2-methylenenorbornane (<i>dl</i> -form)	14	77
isoterpinolene	2,4(8)-p-menthadiene	5	24
limonene	1,8-p-menthadiene	5	20
ψ -limonene	1(7),8-p-menthadiene	5	18
p-menthane (o- and m-menthane are analogous)	<i>p</i> -menthane (systematic name is: 1-isopropyl-4-methylcyclobexane)	5	6
menthene	3-p-menthene	5	9
menthomenthene	3-p-menthene	5	9
methyl- y-cyclogeraniolene	1,1,2-trimethyl-3-methylenecyclohexane	6	34
1-methylsantene	1,2,3-trimethyl-2-norbornene	14	96
myrcene	7-methyl-3-methylene-1,6-octadiene (cis- or trans-)	3	2
nopadiene	6,6-dimethyl-2-vinyl-2-norpinene	12	64
nopinene	2(10)-pinene	12	69
norbornylane	norbornane	14	73
norbornylene	2-norbornene	14	87
norcamphane	norbornane	14	73
norcamphene (Chem. Abstracts; Simonsen)	2-norbornene	14	87
norcamphene (Elseiver; Heilbron)	2-methylenenorbornane	14	86
norcarane	norcarane	11	51
norcarene	2(and 3)-norcarene	11	52,53
norfenchane	norbornane	14	73
norfenchene	2-norbornene	14	87
norpinane	norpinane	12	59
norpinene	2-norpinene	12	60
norsabinane	bicyclo [3.1.0] hexane	10	43
norsantane	norbornane	14	73
norsantene	2-norbornene	14	87
northujane	bicyclo [3.1.0] hexane	10	43
northujene	bicyclo [3.1.0] hex-2-ene	10	44

Common Terpene Name	Recommended Name	Chart No.	Compo und No.
ocimene	3,7-dimethyl-1,3,7-octatriene (cis- or trans-)	3	4
orthodene	3,6,6-trimethyl-2-norpinene	12	63
a-phellandrene	1,5-p-menthadiene	5	15
β -phellandrene	1(7),2-p-menthadiene	5	25
pinane	pinane	12	66
a-pinene	2-pinene	12	67
β -pinene	2(10)-pinene	12	69
δ-pinene	3-pinene	12	68
pinonene	2-carene (d-form)	11	56
pseudocarene	3(10)-carene	11	58
pseudolimonene	1(7),8-p-menthadiene	5	18
pyronane	1,1,2,3-tetramethylcyclohexane	6	29
a-pyronene	1,5,5,6-tetramethyl-1,3-cyclohexadiene	6	36
β-pyronene	1,2,6,6-tetramethyl-1,3-cyclohexadiene	6	37
y-pyronene	1,5,5-trimethyl-6-methylenecyclohexene	6	38
sabinane	thujane	10	46
sabinene	4(10)-thujene	10	49
santane	2,3-dimethylnorbornane	14	79
santenane	7,7-dimethylnorbornane	14	78
santene	2,3-dimethyl-2-norbornene	14	95
tanacetane	thujane	10	46
terebenthene	2(10)-pinene	12	69
a-terpinene	1,3-p-menthadiene	5	13
β -terpinene	1(7),3-p-menthadiene	5	26
y-terpinene	1,4-p-menthadiene	5	14
terpinolene	1,4(8)-p-menthadiene	5	23
thujane	thujane	10	46
a-thujene	3-thujene	10	48
β -thujene	2-thujene	10	47
verbenene	2(10),3-pinadiene	12	70
	bicyclo [3.1.0] hexane	10	43
	bicyclo [3.1.0] hex-2-ene	10	44
	1-ethyl-5,5-dimethyl-1,3-cyclohexadiene	6	41
	2-ethyl-6,6-dimethyl-1,3-cyclohexadiene	6	42

Index to Recommended Names of Terpene Hydrocarbons by Alphabetical Arrangement of Common Terpene Names (Continued)

Common Terpene Name	Recommended Name	Chart No.	Compound No.
	5-isopropylbicyclo[3.1.0]hex-2-ene	10	45
	2-p-menthene	5	8
	1(7)-p-menthene	5	10
	2,4-p-menthadiene	5	16
	2,5-p-menthadiene	5	17
	1(7),4(8)-p-menthadiene	5	19
	3,8-p-menthadiene	5	22
	4-methylene-2-pinene	12	72
	2,4-norcaradiene	11	54
	2-norcarene	11	52
······	3-norcarene	11	53
	2-norpinene	12	60
	1,2,3,5-tetramethyl-1,3-cyclohexadiene	6	39
	1,2,4,6-tetramethyl-1,3-cyclohexadiene	6	40
	1,6,6-trimethylcyclohexene	6	33
	3,7-thujadiene	10	50
		1	1

Index to Recommended Names of Terpene Hydrocarbons by Alphabetical Arrangement of Common Terpene Names (Continued)