BIOGENETICS IN THE TERPENE SERIES

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INTRODUCTION

Attempts to explain the biogenesis of the terpenes on the basis of occurrence side by side in one or more species of plants have not been wanting, but no scheme that is wholly satisfactory has appeared. The following explanation, which is based upon the chemical composition of all known terpene-containing volatile oils that occur naturally in the plant kingdom, departs somewhat from the usual conception. In consequence, many exceptions to the tentative rules that it advances will doubtless be found, especially since the study deals with general tendencies in the plant kingdom rather than with general laws.

Robinson (6) has developed a concept—state of oxidation (S.O.)—which, when applied to plant products, should serve as an important guide in biogenetic reasoning. State of oxidation is defined as the "number of hydroxyl groups present in the saturated open-chain formula of the substance, the saturation and ring fission being brought about by the addition of water."

As early as 1906 Semmler (7) suggested that the volatile oils were necessarily regressive products of metabolism and that the processes of dehydration, oxidation, and reduction as the plant applies them to sugars can explain the formation of the volatile oils.

Assuming that the formation of the volatile oils, as well as the genetically related phenols, methylated phenols, and those of their derivatives that do not happen to be volatile with steam, is

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by the condensation of simpler units produced in sugar metabolism in the plant, it is evident that the state of oxidation of the resultant compounds may then depend upon the degree to which the sugars are reduced or oxidized in metabolism. The resultant compounds, such as terpenes and allyl- and propenyl-phenols, may be formed from the same source material, although by slightly different routes that are unlike principally in the degree of oxidation of the simpler units from which they are finally formed.

In consequence, the application of logical reasoning to the biogenesis of volatile compounds will probably be more successful if it is limited to compounds in the same state of oxidation, unless there is excellent reason to think that a compound in a higher state of oxidation is derived in the plant directly from one in a lower state of oxidation, as piperitone is derived from piperitol. This discussion will therefore be confined to the biogenetic derivation of substances referable directly to the terpenes, $C_{10}H_{16}$, S.O.3.

The possible derivation of terpenes and their relatives by the aldol and true condensation of acetaldehyde and acetone has been taught by Edward Kremers for probably forty years, but he does not believe the idea originated with him. Smedley (11) suggested that citral was formed in the plant from two molecules of acetone and two of acetaldehyde. R. E. Kremers (4) amplified this theory in applying it to the mints. He indicated the derivation of the terpenes by way of citral, the latter being reduced at a double bond to form the precursor of the menthol series, citronellal. Astengo (1) regards isovaleraldehyde as the common progenitor of the entire group of compounds. The ideas of Kremers and Astengo were amplified by Francesconi (2).

Read (5) presents a most interesting theory relating many terpenes and terpene alcohols to geraniol. Taking his clue from the occurrence of geraniol in many eucalyptus oils, he is able to show the derivation in somewhat logical fashion of piperitol, piperitone, phellandrene, terpinenol-4, the carenes, α-terpineol, cineole, and pinene. His reasoning is based partly upon the occurrence of related compounds in the same oils.

Read's theory is recorded by Simonsen (9), with a tabulation placing piperitol, piperitone, 1,3-dihydroxymenthane and the phellandrenes in one group, terpinenol-4, terpinolene, 1,4-cineole, and sabinene in a second, and the Δ^4-carene in a third. Simonsen indicates that all these are derived in the plant from geraniol by simple means.

The derivation of all the terpenes from geraniol requires a shifting of double bonds and the formation of inner rings by successive hydrations and dehydrations in the plant analogous to similar processes performed *in vitro.* The straightforward cyclization of geraniol gives rise only to terpinolene, and considerable rearrangement must take place to arrive at the other members of the terpene group. Assuming that phytochemical processes are rather direct in their aim, it seems more logical to attempt to refer all known terpene configurations to underlying fully hydroxylated compounds. The simple dehydration of such compounds in a single stage, that is, without supposing any rehydration, should give groups of hydrocarbons of related biogenetic characteristics. The relationships found in such a derivation should persist in a more or less consistent fashion throughout all known volatile oils.

Corollaries to the preceding deductions are the assumptions that the terpenes as they occur in the plant represent true end products of metabolism, that is, are not mutually transformable in the plant except in certain restricted instances, and that, even in such instances, the transformation probably proceeds in one direction only. The configurations of the final products, the terpenes, are established by the configurations of their acyclic progenitors. In turn, the configurations of these perhaps transitory substances are established by the manner in which the simple metabolic products of the sugars are condensed in the plant. The state of oxidation of these simple products will determine to a large degree the state of oxidation of the resultant compounds.

Any phytochemical generalizations limited to data obtained from a species, a genus, or even a family are questionable. The coëxistence of compounds in a few instances out of many, for example, may indicate nothing as to their biogenetic relationship; their coëxistence in a large percentage of their occurrences may indicate, not so much their mutual transformation one into the other, as their derivation from a common source.

DERIVATION OF GROUPS

In order to arrive at the possible precursors of the terpenes, it is convenient to deal with geraniol, which occurs in nature with

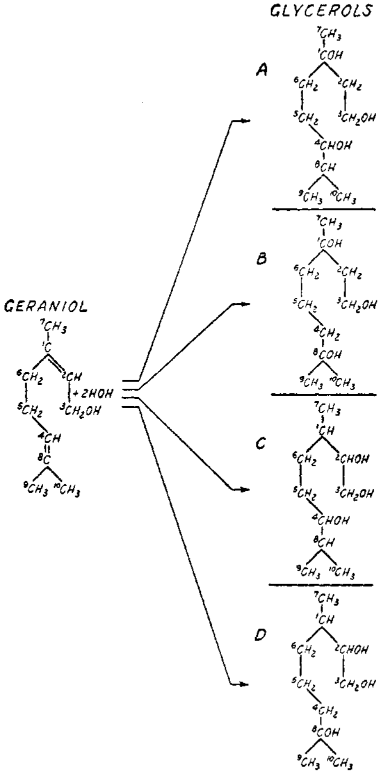

FIG. 1. THE DERIVATION OF FOUR GLYCEROLS FROM GERANIOL

all known types of the terpenes. For convenience geraniol is written in figure 1 in a form for cyclization, and the carbon atoms are numbered in cyclic manner. The addition of the elements of two molecules of water in simple fashion indicates that geraniol may have arisen in nature by the dehydration of four different glycerols,—A, B, C, and D. If geraniol had been written in the "limonene" manner, that is, Δ^8, it would have arisen from only the second and fourth of the glycerols, omitting the important first glycerol. These glycerols can be cyclized by the elimination of one molecule of water, as in figure 2. From each of the six cyclic glycols or menthanediols obtained in this fashion, the derivation of the terpenes, related alcohols, and the oxides may be started by simply eliminating one or two molecules of water in logically conceivable ways, as indicated in figures 3 to 8, inclusive. In these diagrams the compounds found in nature are underscored.

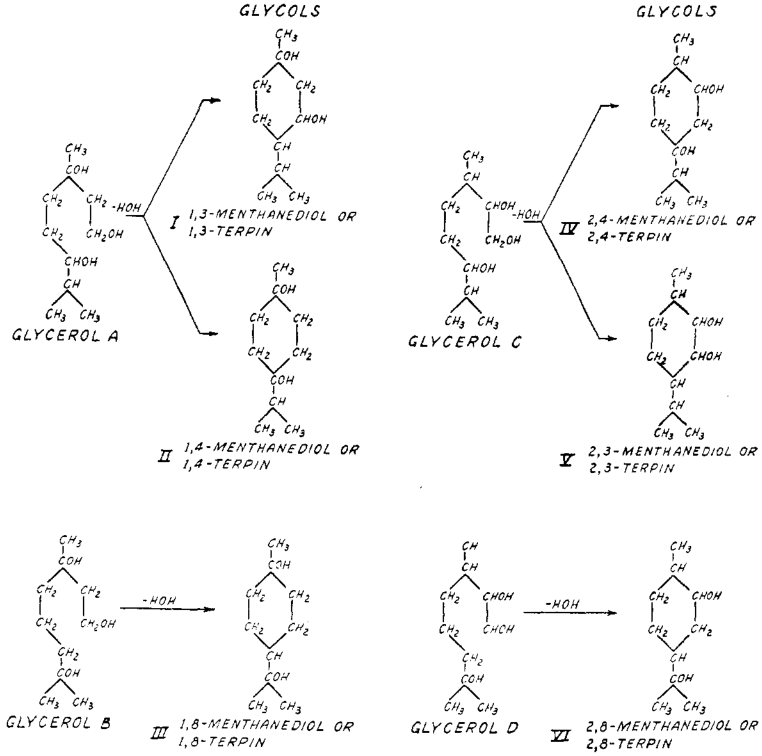

FIG. 2. THE CYCLIZATION OF FOUR GLYCEROLS

The compounds arranged under the respective glycols exhibit certain characteristics of association that furnish a working basis for testing the entire hypothesis. It seems logical that, if the development indicated is in line with the development actually transpiring in the plant, the same associations observed in the groups outlined should persist in the plant kingdom. Oils consisting entirely of representatives of one group, however, might be expected to be very rare. Thus, piperitol, piperitone, and the phellandrenes are found only under glycol I. Glycol II produces sabinene, which occurs in no other series. Glycol III has 1,8-cineole and β-pinene exclusively. Glycol IV shows thujyl alcohol. Glycol V furnishes no special arrangement. Glycol VI gives dihydrocarveol and borneol.

An examination of all recorded occurrences of these substances should give some indication of the validity of the scheme, although, of course, any conclusions drawn can be no more valid than the data upon which they are based. In the following compilations, therefore, care has been taken to eliminate from consideration instances of doubtful occurrence. Where distinct oils were reported from separate parts of a plant, as, for example, an oleoresin and a leaf oil, each oil was recorded separately. Liberal use has been made of the new edition of Wehmer (12), of Gildemeister and Hoffman (3), and of the recent issues of the annual reports of Schimmel and Company. Reference to the original was made when a doubtful point of importance arose.

Glycol I

Read (5) has noted and discussed the association of piperitol, piperitone, and the phellandrenes in the plant kingdom. Generally, in reporting the occurrence of a phellandrene, authors do not say which modification is present, but, for the present purpose, this really makes no difference because phellandrenes, piperitol, and piperitone do not occur in any other series.

Piperitol has been reported in five species of *Eucalyptus*. In four of these, either phellandrene, piperitone, or both, accompany it. In three of these it is accompanied by phellandrene, in three by piperitone, and in two by both. Simonsen (8) reports it in a species of *Andropogon* associated with d-Δ^4-carene, the formation of which from piperitol or glycol I requires elimination of water between carbon atoms 3 and 8 (figure 3). Or, carrying it back to the underlying glycerol, we can dehydrate first between carbon atoms 3 and 8, forming a seven-membered ring, and then between 3 and 4, forming the six-membered ring (figure 4).

In short, whether we start from piperitol, the glycol, or the glycerol, the carenes can be derived from the same parent substance as the phellandrenes, although they must take a little different route. The carenes occur again under glycols III and VI, and the Δ^4 variety under glycol V.

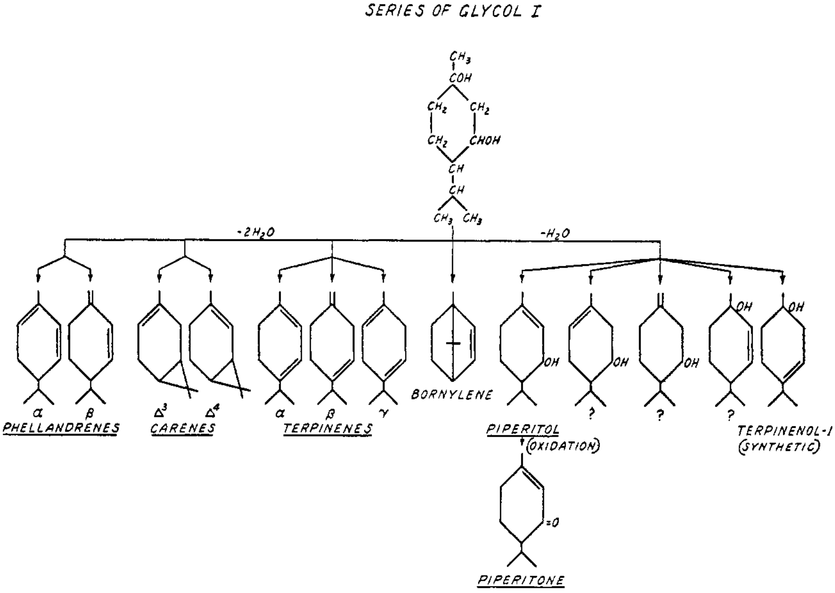

FIG. 3. THE SERIES OF COMPOUNDS POSSIBLY FORMED FROM GLYCOL I BY ELIMINATING WATER

We may consider piperitone a direct oxidation product of piperitol and, as such, it should occur in conjunction with phellandrenes as well. As a matter of fact, it is reported twenty-three times, eighteen of which are in the *Eucalyptus* genus. Of these eighteen eucalyptus oils containing piperitone, sixteen contain also phellandrene. Of the other five oils, *Cymbopogon schoenanthus* also contains piperitone and phellandrene. The fact of their joint occurrence in oil of *Mentha piperita* grown at Madison, Wisconsin, is not definitely established. One oil, that of *Mentha arvensis*, is not reported as containing compounds accompanying piperitone. *Andropogon iwarancusa* contains Δ^3-carene, to which the same reasoning applies as to the *Andropogon* already discussed. The remaining oil, *Mentha pulegium*, contains pulegone, the formula of which does not fit into the present scheme.

The close association in occurrence between piperitol, piperitone, phellandrenes, and, in a small way, the carenes, leads to the thought that they may be derived in the plant from a common progenitor. The specificity of this association in the series of glycol I (see figure 3) lends weight to the assumption of such a progenitor substance.

The phellandrenes, α or β, or both, are reported as occurring one hundred and twenty-six times, fifty-five in the eucalypts and seventy-one in non-eucalypts. Thirty-eight of these oils may be considered as typically phellandrene oils, that is, the phellandrenes, piperitol, or piperitone form the major portion of the oil. Twenty-eight of these thirty-eight instances, however, are eucalypts, leaving only ten predominantly phellandrene oils out of eighty-eight, exclusive of the eucalypts.

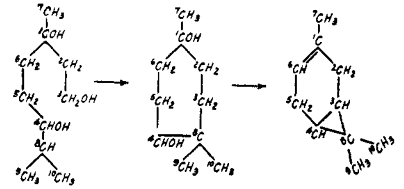

Fig. 4. The Derivation of the Carenes

Table 1 shows the occurrences of the phellandrenes with other substances.

Peculiar to the genus *Eucalyptus* seems to be the formation of phellandrene oils with a wide association of pinene and cineole, but containing neither limonene nor terpinenes. Outside of this genus, however, the association of pinene and limonene with phellandrene is especially wide.

Glycol II

The series of glycol II (see figure 5), derived from the same glycerol as the glycol I yielding the phellandrene series, contains all the terpinenes, although in association with terpinenol-4 and sabinene. To follow the occurrences of terpinenol-4 and especially sabinene, which incidentally is specific to the series, should be of interest.

TABLE 1

The reported occurrence of the phellandrenes in association with other substances

ACCOMPANYING COMPOUND	EUCALYPTS	NON-EUCALYPTS	TOTAL IN 126 OILS CONTAINING PHELLANDRENE
Pinene $\left.\begin{matrix}\alpha\\\beta\end{matrix}\right\}$	31	35	66
Cineole	49	16	65
Limonene or dipentene	0	27	27
Piperitone or piperitol	16	4	20
Terpinenes	0	5	5

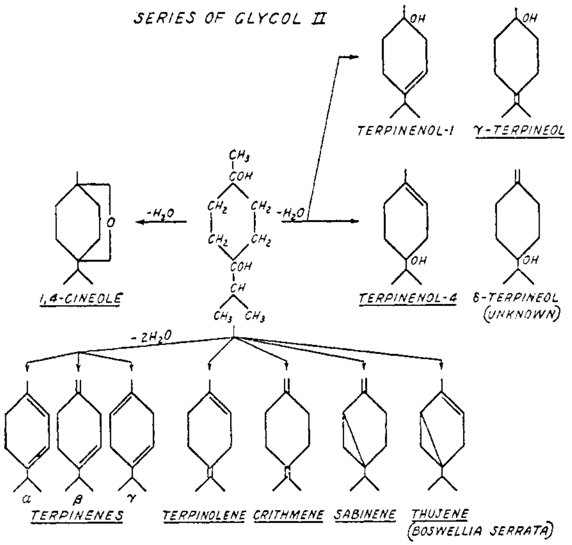

FIG. 5. THE SERIES OF COMPOUNDS POSSIBLY FORMED FROM GLYCOL II BY ELIMINATING WATER

Sabinene is reported as definitely established in sixteen oils, and of doubtful occurrence in seven others. Those in which it may be considered as established are *Juniperus communis*, *Juni-*

perus sabina, Cupressus torulosa, Thuja plicata, Thuja occidentalis, Elettaria cardamomum var. major, Piper cubeba, Pilea (species unknown), *Cinnamomum kanahirai, Xanthoxylum rhetsa, Xanthoxylum budrunga, Murraya koenigii, Origanum majorana, Thujopsis dolabrata, Mosla japonica,* and *Chamaecyparis obtusa.* In these oils we find terpinenol-4, terpinene, or both, accompanying sabinene in ten instances. One other, *Xanthoxylum rhetsa,* is reported as being more than 90 per cent sabinene. Of the seven oils in which the occurrence of sabinene is doubtful, *Melaleuca linariifolia* contains terpinenol-4 and α- and γ-terpinenes; it seems highly probable that this oil may contain sabinene. The oil of *Piper cubeba* is unique in that it is the only instance in which the isolation of 1,4-cineole has been reported; the cineole is accompanied, among others, by sabinene, terpinenol-4, and Δ^4-carene.

Considering now the occurrence of terpinenol-4, or Δ^1-menthenol-4, we find the fact definitely established in ten instances: *Piper cubeba, Juniperus communis, Cinnamomum kanahirae, Melaleuca alternifolia, Eucalyptus dives, Thymus zygis floribundis, Origanum majoram, Elettaria cardamomum major,* and *Chamaecyparis obtusa.* All these, except *Eucalyptus dives,* contain either sabinene or the terpinenes. In one doubtful instance, *Cupressus torulosa,* terpinene and sabinene are reported. Nine of the ten oils examined contain substances derivable from glycol III, that is, pinene, limonene, and so forth. Only one, *Eucalyptus dives,* contains compounds derivable from glycol I, the phellandrene compounds.

These facts point very strongly to the biogenetic association of sabinene with the terpinenes and terpinenol-4 on the one hand. On the other, terpinenol-4 is predominantly associated with terpinenes and sabinene.

The compounds of the glycol II group are accompanied by compounds derivable from glycol III to the exclusion of those from glycol I. Referring again to the glycol I group, we find that in one hundred and twenty-six oils the phellandrenes were accompanied ninety-seven times by substances derivable from glycol III (1,8-cineole, α-pinene, β-pinene, and limonene or dipentene), but only seven times by those from glycol II (terpinenes, terpinenols, and sabinene). The inference is plain that, since glycols I and II come from glycerol A, the further elaboration of glycerol A in the plant takes predominantly one or the other of the available routes, but not both in the same plant to any great degree. If the fact were otherwise, the derivatives of glycols I and II would be found mixed more often than in seven out of the one hundred and twenty-six instances in which it was possible under the phellandrenes, or in one out of ten possibilities in the terpinenol-4 group.

Since the 1,8-terpin series, glycol III, is derivable only from glycerol B, its members should appear in both the preceding groups (I and II). This is so in nine out of ten oils referable to glycol II, and ninety-seven out of one hundred and twenty-six phellandrene oils referable to glycol I.

The following conclusion seems warranted. In most instances, glycerol A is accompanied in the plant by glycerol B. Glycol III may be accompanied by either glycol I or II but not often by both. The practical significance of this conclusion is simply that in an oil found to contain derivatives of glycol II, finding phellandrene, piperitol, or piperitone, is unlikely, and the converse is also true. The carenes are derivable from glycols I, III, V, and VI, and may be expected in any oil. Fortunately, they are rare.

Glycol III

The derivatives of glycol III (see figure 6), from glycerol B, are the most widely distributed in nature of the terpene group. As just pointed out, they occur indiscriminately with compounds of the two preceding series, and often in predominant quantity. In short, nature shows a great preference for this group in both distribution and quantity. Now, the only difference between glycerols A and B is in the position of a hydroxyl group. In A, position 4 is occupied and in B, position 8. Whatever simpler units we may postulate as the source of these glycerols, we must explain nature's preference for a hydroxyl group in position 8.

The compounds under glycol III that are specific to this series are 1,8-cineole and β-pinene. The carenes occur also under glycols I, V, and VI, while crithmene and terpinolene occur under glycol II. The 1,8-cineole is reported definitely as occurring two hundred and sixty times, two hundred and twenty-three of which are recorded as having accompanying compounds of interest in this classification. Of these two hundred and twenty-three oils, one hundred and ninety-two contain other substances in this series, that is, α-pinene, β-pinene, terpineol, dipentene, or limonene. Sixty-three oils contain phellandrenes, piperitone, or piperitol. Seven contain terpinenol-4, terpinenes, or sabinene.

Table 2 is of interest in showing some characteristics of the distribution in eucalypts and other genera; one hundred and thirty-three oils containing 1,8-cineole are eucalypts, and one hundred and twenty-seven are not.

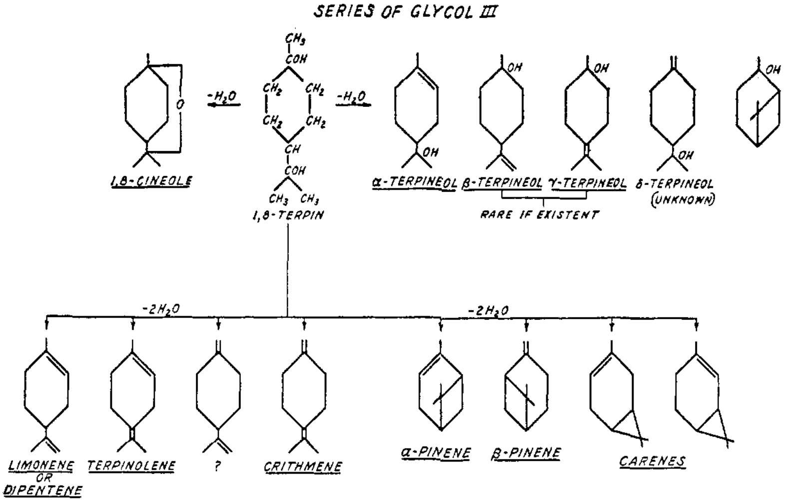

FIG. 6. THE SERIES OF COMPOUNDS POSSIBLY FORMED FROM GLYCOL III BY ELIMINATING WATER

α-Terpineol occurs in sixty-five oils. Of these oils, sixty-two contain α- or β-pinene, limonene (or dipentene), cineole, or mixtures of these substances. The phellandrene, piperitone, and piperitol compounds occur certainly in nine of these oils and are doubtfully reported in three. In all twelve instances, however, they are mixed with representatives of the glycol III series other than α-terpineol. Representatives of the series of glycol II, the terpinenol-4 series, occur in ten oils and are doubtful in one. Six of these contain substances of the glycol III series other than α-terpineol.

The association of α-terpineol with the other members of the glycol III series may be thought established.

In considering the occurrence of limonene, dipentene was called its equivalent unless the dipentene was to be taken as a pyrogenetic product. Limonene or dipentene occurs one hundred and fifty-eight times. These two compounds are associated with α-pinene, β-pinene, or both, ninety-three times; with α-terpineol twenty-four times; with 1,8-cineole thirty times; with phellandrene twenty-seven times; and with the terpinenes, including sabinene and terpinolene, eight times. Forty of these oils are not reported as containing substances considered in this classification, other than limonene or dipentene. One hundred and ten of them contain substances, the pinenes, cineole, and α-terpineol, of the series of glycol III. Hence only eight of the possibilities out of one hundred and fifty-eight are missing.

TABLE 2

The reported occurrence of 1,8-cineole

ACCOMPANYING COMPOUND	IN EUCALYPTS	IN OTHER SPECIES	TOTAL IN 223 OILS
Pinene α β	108	63	171
Limonene or dipentene	1	29	30
α-Terpineol	5	26	31
Phellandrene β	49	16	65
Piperitone or piperitol	14	2	16
Terpinenol-4 Terpinenes Sabinene	1	6	7

The genus *Cymbopogon* is noteworthy in that eight species contain limonene, while only one, *C. caesius*, contains another member of the series, α-terpineol. Phellandrene is found in *C. martini var. Sofia*, and piperitone in *C. sennaarensis*.

The *Rutoideae* are also noteworthy. Only one species, *Ruta graveolens*, produces an oil that conforms to the series, containing limonene, pinene, cineole, and so forth. *Xanthoxylum acanthopodum* has phellandrene. The oils in the family containing limonene, six in all, consist generally of olefinic alcohols, ketones, and so forth, diosphenol, and menthone.

α-Pinene, the most widely spread of the terpenes, has been reported as occurring in three hundred and seventy-four oils at the latest count (1931). In seventy-seven of these it was not reported as accompanied by any other substances used in this classification. Thus two hundred and ninety-seven oils are available for comparative data. In two hundred and sixty-nine of these oils it is accompanied by other members of its series, glycol III. One hundred and seven of these are eucalypts in which the accompanying compound is cineole; this compound, derived from glycol III, accompanies pinene in only thirty-four of the remaining oils, one hundred and sixty-two in number. Limonene, however, is found in one hundred and four of these oils outside of the genus *Eucalyptus*, which is contrary to the statement of Singleton (11) that cineole invariably accompanies pinene. Seventeen of the one hundred and sixty-two non-eucalyptus oils contain substances of the phellandrene series from glycol I, while twenty-seven of the eucalypts contain them. As usual the eucalypts tend more strongly toward the phellandrene type of compound than does the rest of the plant world.

Pinene is accompanied fourteen times by derivatives of glycol II,—the terpinenol-4, sabinene, terpinene series.

β-Pinene, the closest relative of α-pinene, accompanies this terpene in fifty-five instances and is rarely found unassociated with it. The difficulty of isolation and identification of β-pinene when present only in small quantity renders it probable that the occurrence of this terpene is broader than is here indicated. Thirty-two of its occurrences are recorded under the *Abietineae.*

Glycol IV

Dehydration of the glycol, 2,4-menthanediol, in the usual manner gives rise to what appears to be another terpinenol-4, terpinene series (see figure 7). However, a difficulty arises from the absence of sabinene, which is predominantly associated with these compounds. Eliminating glycol IV from consideration would therefore be justified, but for one fact. Here we find thujyl alcohol for the first time; the ketone, thujone, which occurs more often, may be derived from it by oxidation. Thujene also occurs in this series, and in the first terpinenol-4 series under glycol II as well. Inspection will show, however, that thujyl alcohol and thujone are not derivable in the glycol II series without reverse hydration of thujene, which is not permitted in the present analysis. Thujene has been reported only in *Boswellia serrata,* which does not contain thujyl alcohol or thujone. Hence we are forced to assume that thujene is probably not genetically related to thujyl alcohol and thujone.

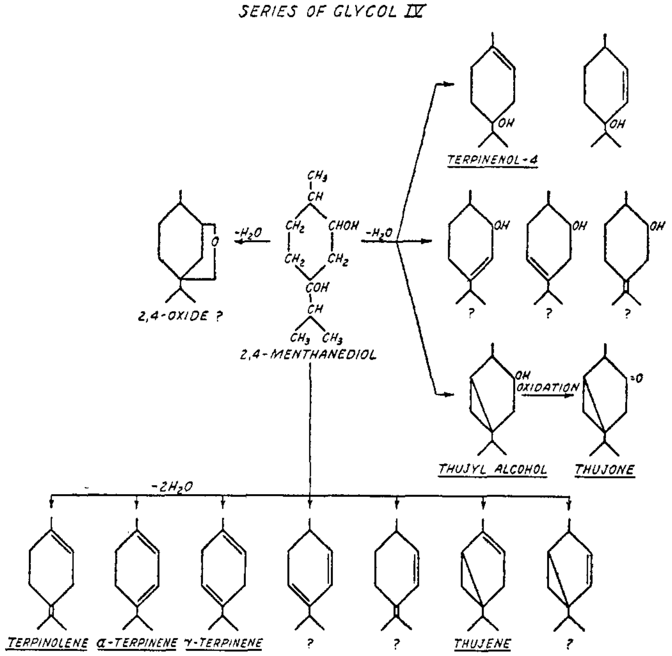

FIG. 7. THE SERIES OF COMPOUNDS POSSIBLY FORMED FROM GLYCOL IV BY ELIMINATING WATER

The ketone, thujone, is reported in fifteen oils, eleven of which contain also compounds of the glycol III series, that is, the pinene family. In none of these oils do any other members of the glycol

IV series occur. The structure of thujone accepted at present, therefore, does not fit well into the present scheme.

Glycol V

Glycol V, which gives rise only to the known compounds α-terpinene and Δ⁴-carene (see figure 8), may be dismissed for the present without further consideration.

Glycol VI

Glycol VI offers some aspects that require consideration (see figure 9). Here we find another pinene series, with 1,8-cineole and β-pinene missing. These facts would automatically exclude this glycol from consideration as existing in the *Abietineae* or the *Eucalypti*, but the occurrence of two new compounds in the series, dihydrocarveol and borneol, makes it worthy of consideration. Dihydrocarveol is reported as occurring in the oil of *Carum carvi* (caraway). It is accompanied by limonene, which is in accord with the theory presented here. Also present are carvone, carveol, and dihydrocarvone (figure 10).

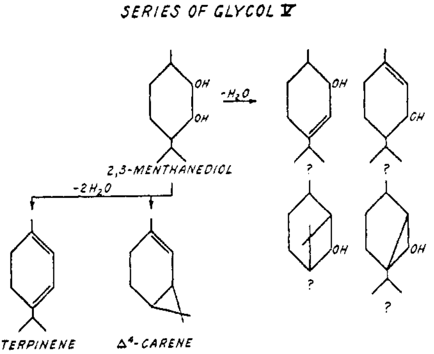

FIG. 8. THE SERIES OF COMPOUNDS POSSIBLY FORMED FROM GLYCOL V BY ELIMINATING WATER

The fitting of carvone and carveol, which are of a higher state of oxidation than the compounds under consideration, into a genetic scheme is another matter, which must be reserved for later treatment. For the time being, dihydrocarvone may be taken as related to dihydrocarveol in the way that piperitone is to piperitol.

The occurrence of borneol is confined to the series of glycol VI. It is reported authentically in one hundred and six oils, and in eighty-three instances as accompanied by compounds in this classification, distributed as follows: α-pinene, 68; β-pinene, 15; limonene or dipentene, 46; cineole, 22; phellandrenes and piperitone, 11; terpinenes, sabinene, and terpinenol-4, 3.

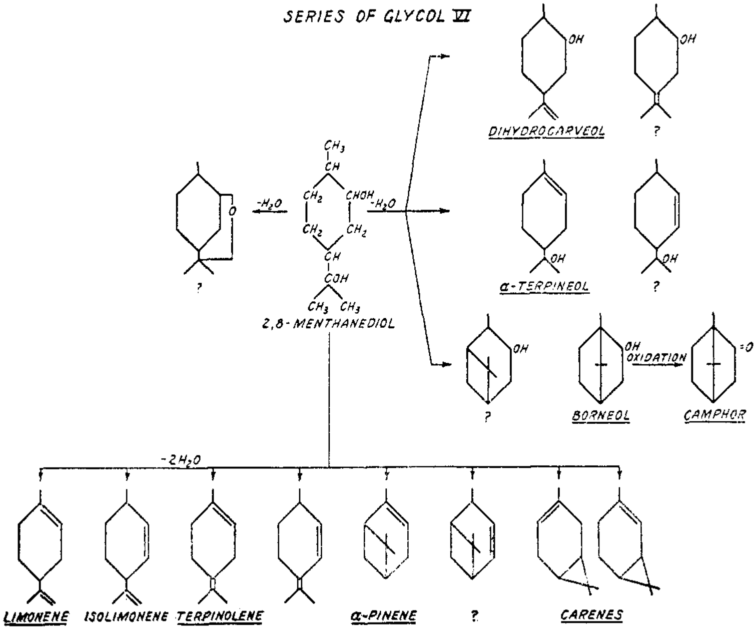

Fig. 9. The Series of Compounds Possibly Formed from Glycol VI by Eliminating Water

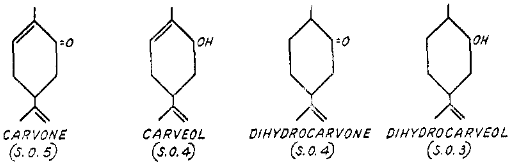

Fig. 10. Carvone, Carveol and Dihydrocarvone

Seventy-four oils out of the eighty-three contain α-pinene, limonene, or both, which is a sufficiently good check. With β-pinene, which occurs in the first pinene series under glycol III but not under glycol VI, its proportionate occurrence with borneol is about the same as with α-pinene. Cineole, however, shows a notable differentiation. Referable to glycol III but not to glycol VI, it occurs with α-pinene in one hundred and seventy-one out of two hundred and twenty-three possibilities, although with borneol the occurrence is only twenty-two out of sixty-eight. The cineole-rich genera, *Melaleuca* and *Eucalyptus*, together can produce only two instances of borneol, both in eucalypts from the Caucasus.

Another striking feature about borneol is its apparent association with the leaf. Of its one hundred and six reported occurrences, sixty are in leaf and twig oils and twenty-two more are in oils from herbs in which the whole plant is distilled. Thus eighty-two oils may be considered as derived wholly or in part from leaves. Further, there are five root oils. Only six oils from oleoresins contain borneol; the remainder are largely cone or fruit oils, with one from a bark and one from a wood.

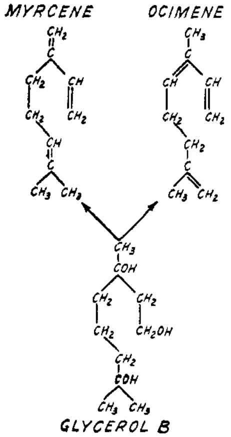

FIG. 11. THE DERIVATION OF THE OLEFIN TERPENES

The low association of cineole with borneol, contrasted with its high association with pinene, which occurs in both series, may be confirmatory evidence of the biogenetic disassociation of borneol and cineole. The derivatives of glycol VI have been found most abundantly in plant structures of leaf or fruit type, and are frequently accompanied widely by derivatives of glycol III.

The occurrence of α-pinene and limonene in both these apparently important series must have a great deal to do with the wide occurrence of these compounds.

The possible derivation of the olefinic terpenes, myrcene and ocimene, from glycerol B is given in figure 11. Clearly, myrcene can be derived from either the 1,3,4- or the 1,3,8-glycerol, although ocimene can be derived only from the latter. Also, both geraniol and linaloöl can be derived from glycerols A and B, but only geraniol from C and D.

CONCLUSIONS

The predominant family of terpenes and near relatives in the plant world is the pinene group.

Family I: α-Pinene
β-Pinene
Limonene
Dipentene
$\left\{\begin{array}{l}\text{Carenes}\\ \text{Terpinolene}\\ \text{Crithmene}\end{array}\right\}$ (not specific)
1,8-Cineole
α-Terpineol
Borneol (camphor)
Dihydrocarveol

According to association and derivation from glycols III and VI, which are the only glycols with hydroxyl on carbon atom 8, this family should be subdivided as follows:

Subfamily IA: α-Pinene
β-Pinene
Limonene
Dipentene
$\left\{\begin{array}{l}\text{Carenes}\\ \text{Terpinolene}\\ \text{Crithmene}\end{array}\right\}$
1,8-Cineole
α-Terpineol

Subfamily IB: α-Pinene
Limonene
Dipentene
$\left\{\begin{array}{l}\text{Carenes}\\ \text{Terpinolene}\end{array}\right\}$
α-Terpineol
Borneol (camphor)
Dihydrocarveol

Second in importance as to occurrence is the phellandrene group, derivable from glycol I.

Family II: α-Phellandrene
β-Phellandrene
$\left\{\begin{array}{l}\text{Carenes}\\ \text{Terpinenes}\end{array}\right\}$
Piperitol (piperitone)

Family II is more often associated with subfamily IA than with any other group.

Less prevalent than the others, but associated mostly with family I, is family III.

Family III:	Terpinenes	1,4-Cineole
	Sabinene	Terpinenol-4
	Thujene	Thujyl alcohol (thujone)[2]
	Terpinolene	
	Crithmene	

According to association and derivation from glycols II and IV, which are marked by possessing hydroxyl on carbon atom 4, this family should be subdivided as follows:

Subfamily IIIA:	Terpinenes	1,4-Cineole
	Sabinene	Terpinenol-4
	Thujene	
	Terpinolene	
	Crithmene	
Subfamily IIIB:	Terpinenes	Terpinenol-4
	Thujene	Thujyl alcohol (thujone)

If the biogenesis of these substances occurs along the lines indicated, which hypothesis is supported by the evidence accumulated, it is clear that small changes in intercellular mechanism may shift the composition of the resultant oil considerably, but the classification of the oil according to the above scheme should remain the same. This classification should be of some value in working out differences in closely related species.

The mechanism of the formation of the hypothetical glycerols can not yet be logically explained on the basis of our present knowledge. Further research on the water-soluble components of plants yielding volatile oils may yield substantiating evidence for the above hypothesis. For the present, the classification given has only the support of the evidence of biological association submitted. This, however, has the definite merit of following actual occurrence rather than an artificial structural classification, and should prove to be of value in isolation studies as well as furnish a unified basis for the study of terpene chemistry.

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[2] Structure and occurrence do not conform.

Perhaps future work will isolate certain of the compounds now indicated as undiscovered, as well as others whose formulas have been omitted. Should they be associated as indicated here, considerably more weight will be added to this classification.

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