INVESTIGATION ON PARTHENIOL
A SESQUITERPENE ALCOHOL FROM GUAYULE

Thesis

by

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Table of Contents

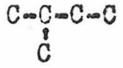
Introduction

Terpenes are the main characteristic constituents of many essential oils, the volatile components of plants. The name "terpen" is commonly considered to have been introduced by Kékulé for hydrocarbons with the empirical formula, $C_{10}H_{16}$. With the abolishing of the use of the broad term camphor to signify crystalline oxygen compounds with empirical formulae, $C_{10}H_{16}O$ and $C_{10}H_{18}O$, the definition of terpene has been extended to cover this group of compounds. The name terpene as it stands today not only implies compounds which are composed of C_5H_8 units and oxygenated derivatives of these compounds, but also cover compounds which contain less hydrogen and those which are more saturated. There are, moreover, exceptions to this classification; for example, santene (C_9H_{14}), is considered a terpene compound because of its resemblance and relation to terpenes.

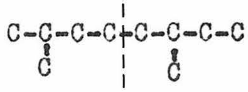
The natural-occurring terpenes are generally complex mixtures of numerous terpenes and their stereoisomers and are usually liquid compounds. For this reason, early investigators found it difficult to identify and classify the various terpenes which were isolated from plants. An outstanding contribution to this field of research was made by Wallach, who, by the preparation of crystalline derivatives, was able to identify several hundred of these compounds. Stimulated by Wallach's work, Semmler and others studied the structure of terpenes and as a result confirmed Berthelot's hypothesis that the hydrocarbons, $C_{10}H_{16}$, $C_{15}H_{24}$, and $C_{20}H_{32}$, are related to isoprene (C_5H_8).

Monoterpenes, which are often referred to as terpenes, in the restricted sense, are composed of two isoprene units and, hence, possesses the empirical formula $C_{10}H_{16}$. Hemiterpenes (C_5H_8) are compounds of single isoprene units and sesquiterpenes ($C_{15}H_{24}$) are composed of three such units. There are also the di-, tri-, tetra-, and polyterpenes, which contain four, six, eight, and numerous isoprene units, respectively. A diagramatic presentation of this classification of terpenes is shown below.

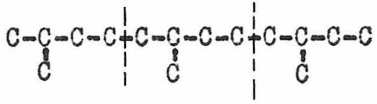
Hemiterpenes (C_5H_8)



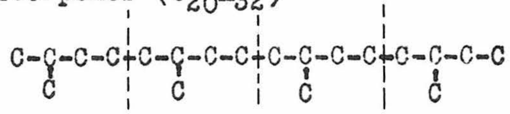
Monoterpenes ($C_{10}H_{16}$)



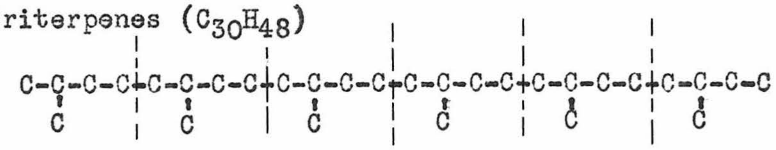
Sesquiterpenes ($C_{15}H_{24}$)



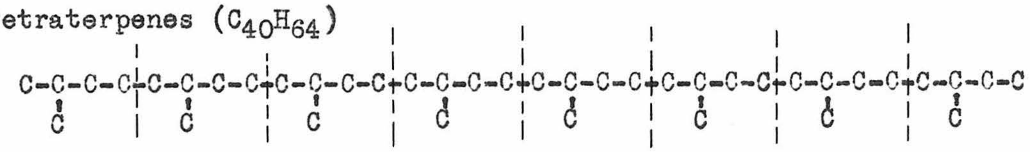
Diterpenes ($C_{20}H_{32}$)



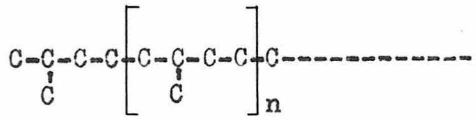
Triterpenes ($C_{30}H_{48}$)



Tetraterpenes ($C_{40}H_{64}$)



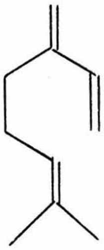
Polyterpenes ($(C_5H_8)_n$)



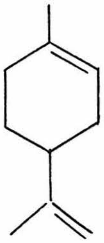
The most common empirical formula for monoterpenes, $C_{10}H_{16}$, shows a lack of six atoms of hydrogen to satisfy the empirical formula for a saturated aliphatic hydrocarbon (C_nH_{2n+2}) with the same number of carbon atoms. This difference in hydrogen content may be accounted for by the presence of double bonds and/or by a cyclic structure. Structures which are in agreement with the empirical formula $C_{10}H_{16}$ are tabulated below.

Structural type	Number of rings	Number of double bonds
acyclic	none	3
monocyclic	1	2
bicyclic	2	1
tricyclic	3	none

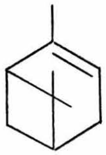
All four of these structures have been found in terpenes; examples for each structural type are cited below.



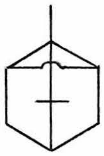
Myrcene
(acyclic)



Limonene
(monocyclic)

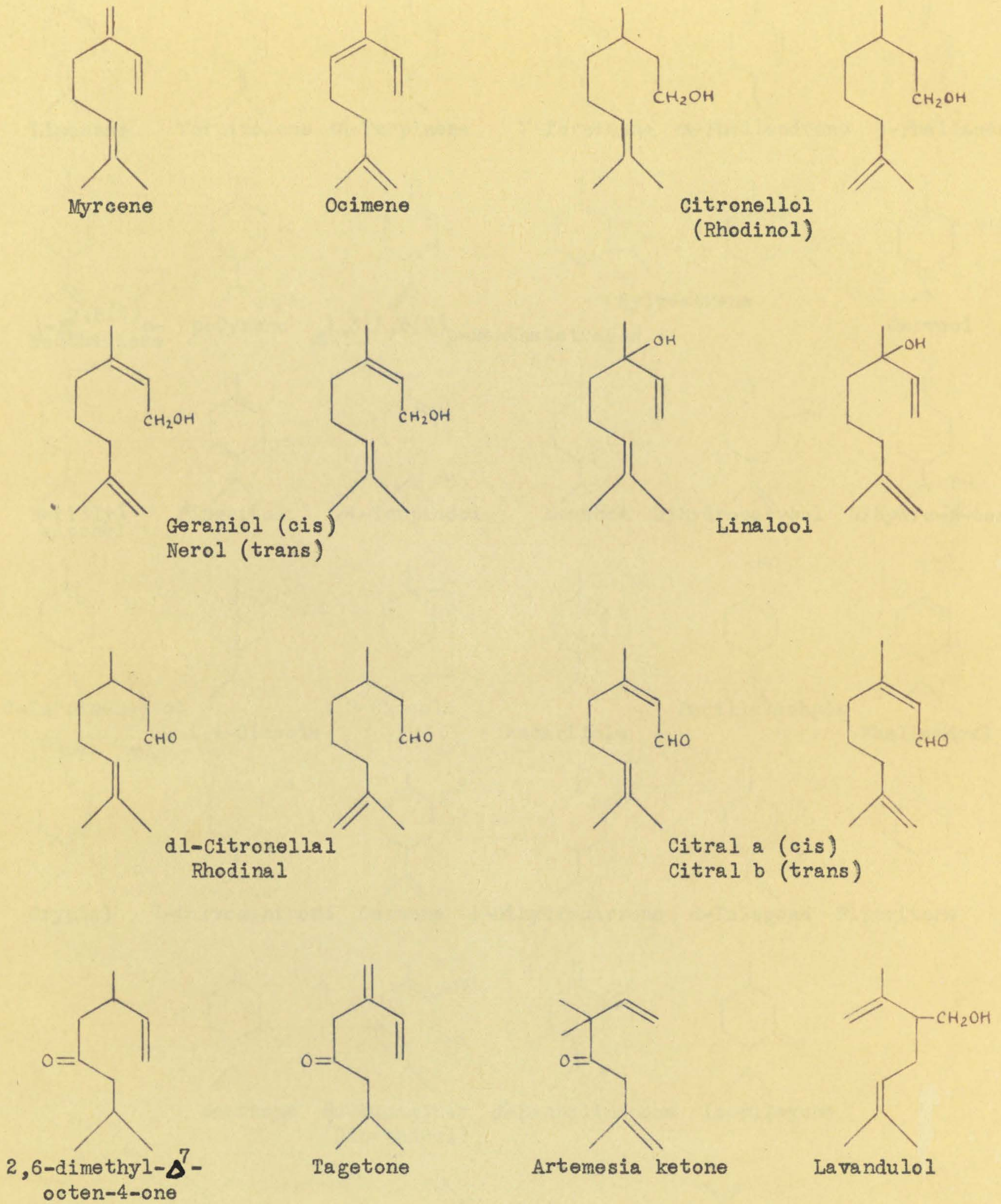


α-Pinene
(bicyclic)



Tricyclene
(tricyclic)

The natural-occurring acyclic, monocyclic, and bicyclic monoterpenes are presented in Figures 1, 2, and 3, respectively.



Myrcene

Ocimene

Citronellol
(Rhodinol)

Geraniol (cis)
Nerol (trans)

Linalool

dl-Citronellal
Rhodinal

Citral a (cis)
Citral b (trans)

2,6-dimethyl-Δ^7-
octen-4-one

Tagetone

Artemesia ketone

Lavandulol

Figure 1. Natural-occurring acyclic monoterpenes

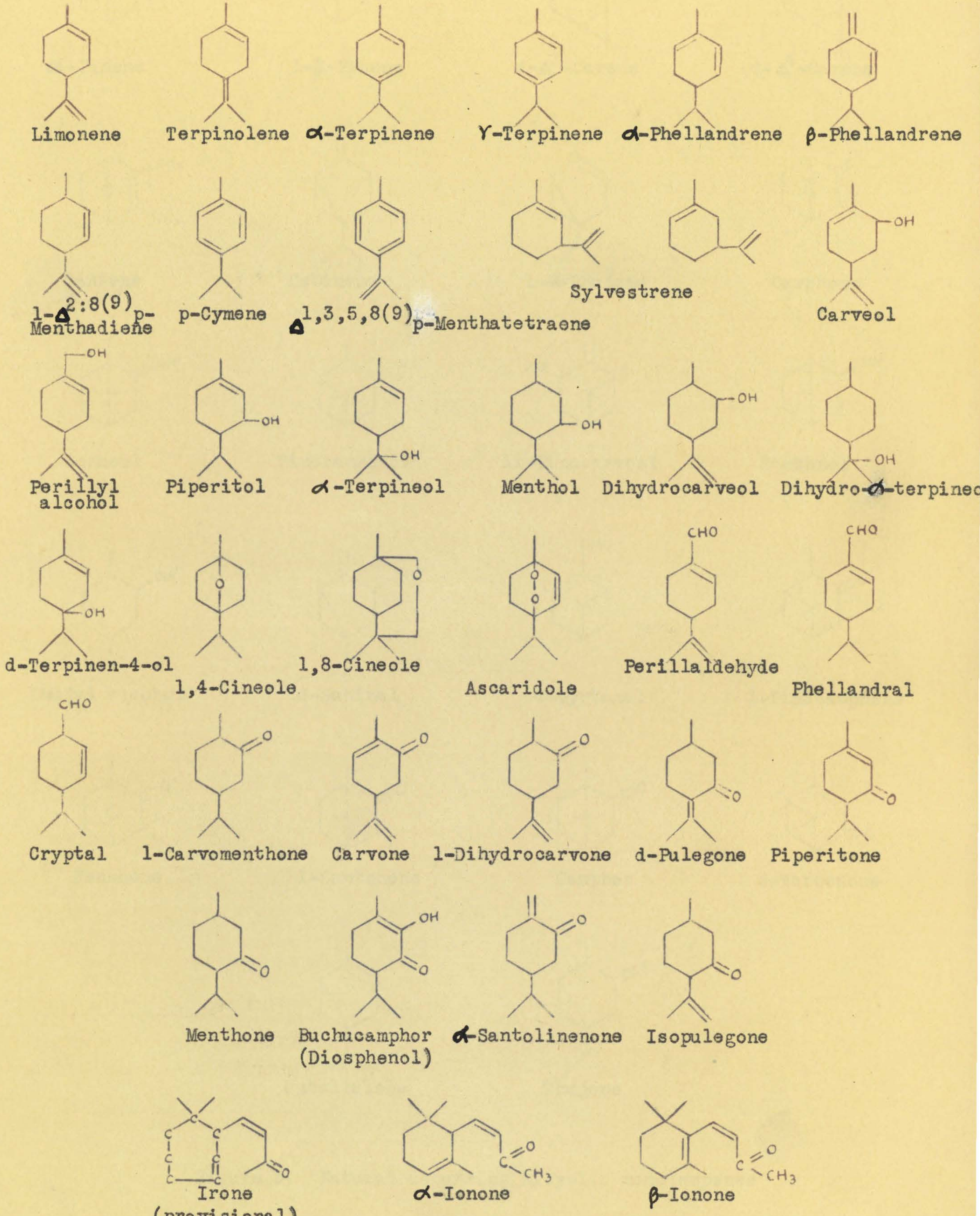
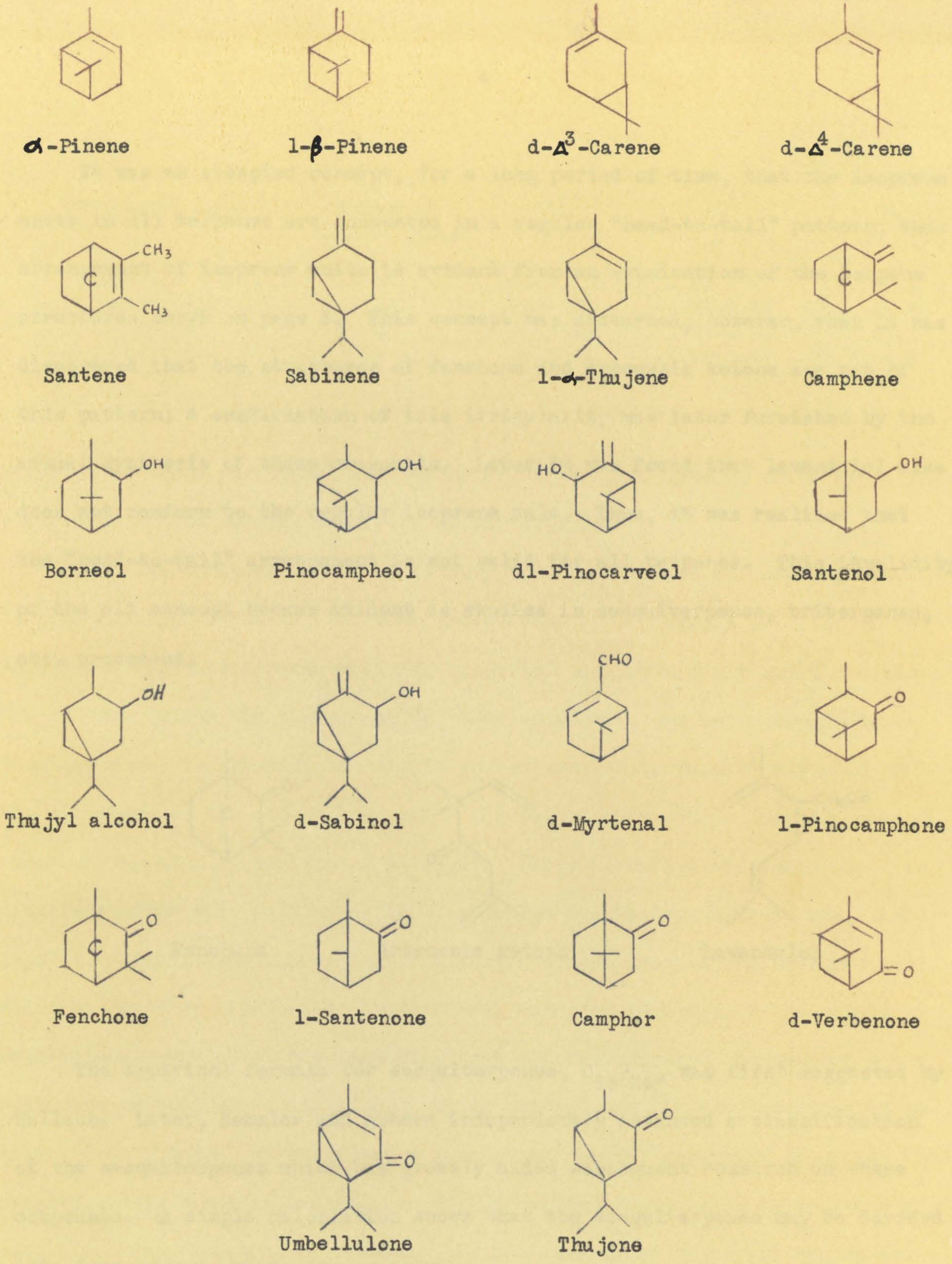


Figure 2. Natural-occurring monocyclic monoterpenes



α-Pinene 1-β-Pinene d-Δ^3-Carene d-Δ^4-Carene

Santene Sabinene 1-α-Thujene Camphene

Borneol Pinocampheol dl-Pinocarveol Santenol

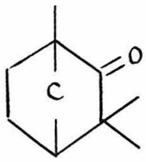
Thujyl alcohol d-Sabinol d-Myrtenal 1-Pinocamphone

Fenchone 1-Santenone Camphor d-Verbenone

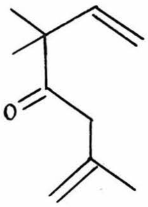
Umbellulone Thujone

Figure 3. Natural-occurring bicyclic monoterpenes

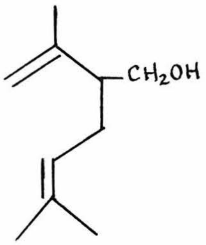
It was an accepted concept, for a long period of time, that the isoprene units in all terpenes are connected in a regular "head-to-tail" pattern; this arrangement of isoprene units is evident from an examination of the terpene structures shown on page 3. This concept was disturbed, however, when it was discovered that the structures of fenchone and artemesia ketone are not of this pattern; a confirmation of this irregularity was later furnished by the actual synthesis of these compounds. Later it was found that lavandulol also does not conform to the regular isoprene rule. Thus, it was realized that the "head-to-tail" arrangement is not valid for all terpenes. This invalidity of the old concept became evident as studies in sesquiterpenes, triterpenes, etc. proceeded.



Fenchone



Artemesia ketone



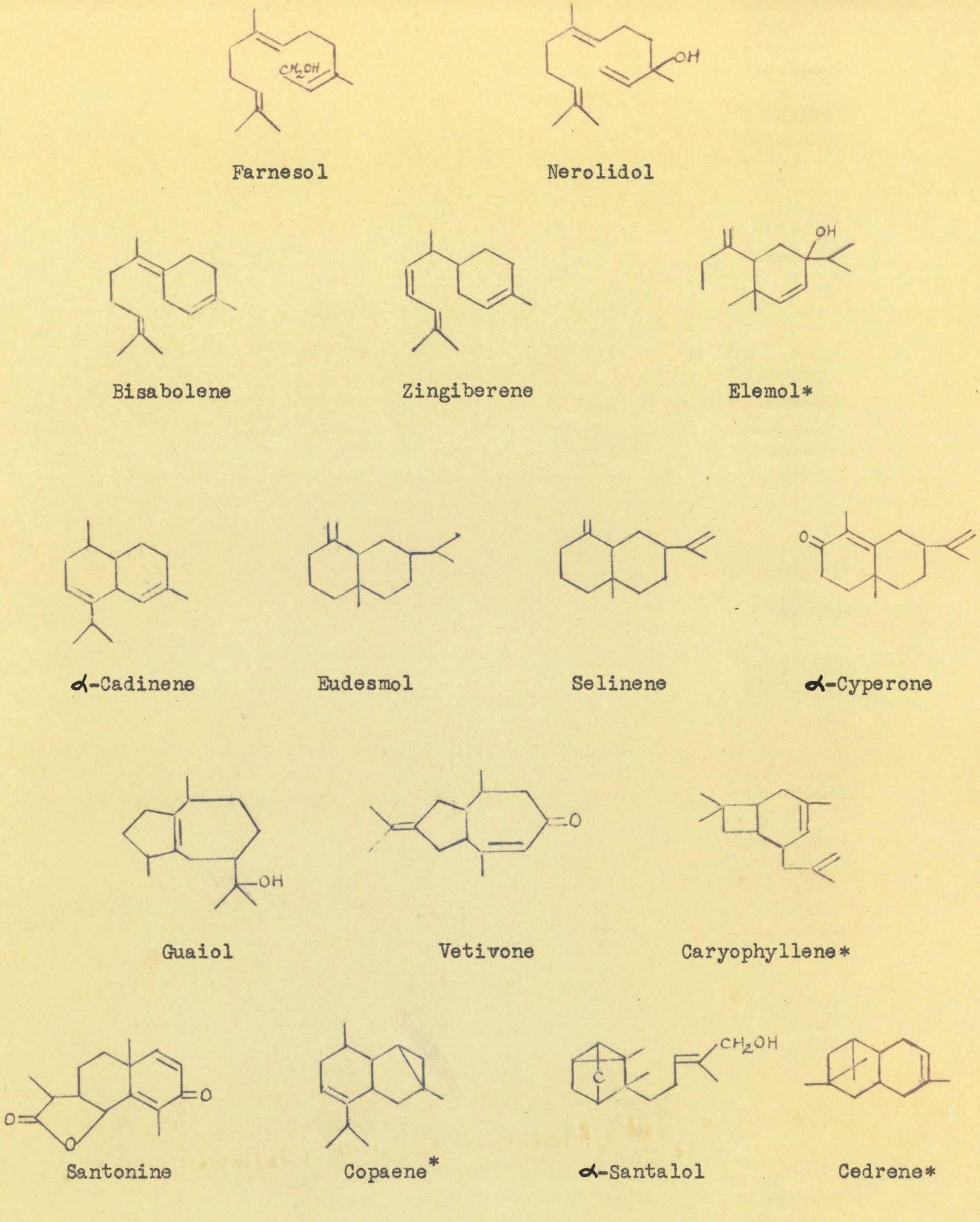
Lavandulol

The empirical formula for sesquiterpenes, $C_{15}H_{24}$, was first suggested by Wallach. Later, Semmler and others independently advanced a classification of the sesquiterpenes which has greatly aided subsequent research on these compounds. A simple calculation shows that the sesquiterpenes may be divided into four groups, which are as shown.

Structural type	Number of double bonds	d^{15°	$n_D^{15^\circ}$	$(M_R)_D$
acyclic	4	0.84	1.53	69.5
monocyclic	3	.89-.87	1.51-1.49	67.8
bicyclic	2	.92-.90	1.51-1.50	66.1
tricyclic	1	.935-.91	1.50-1.49	64.4

Examples of these structural variations are shown in Figure 4, which gives the structures of the natural-occurring sesquiterpenes.

Up to the early part of this century the constitution of only one sesquiterpene alcohol, farnesol, had been determined. The progress of research in this field was slow because ordinary oxidation methods are not usually successful in elucidating the structures of these compounds; the oxidation products obtained were, in general, too simple or too complex to furnish any clue on the structure of the parent compound. A great advancement in sesquiterpene research was made by Ruzicka _et al_ (1,2). These investigators found that, on dehydrogenation with sulfur, cadinene gave the naphthalene hydrocarbon, cadalene (1,6-dimethyl-4-isopropylnaphthalene). By dehydrogenating eudesmol and selinene, another naphthalene hydrocarbon, eudalene (1-methyl-7-isopropylnaphthalene), was obtained. Assuming that all terpenes are composed of whole multiples of isoprene units (C_5H_8), it is evident that in the formation of eudalene from eudesmol or selinene, a loss of one methyl group has occurred. The missing methyl group is probably an angular methyl group which is relatively unstable. The structure of eudalene has been confirmed by actual synthesis.



Farnesol Nerolidol

Bisabolene Zingiberene Elemol*

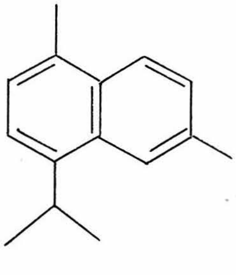
α-Cadinene Eudesmol Selinene α-Cyperone

Guaiol Vetivone Caryophyllene*

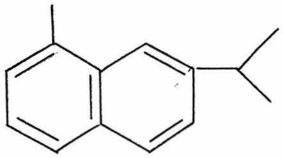
Santonine Copaene* α-Santalol Cedrene*

* These structures have not been definitely established

Figure 4. Natural-occurring sesquiterpenes

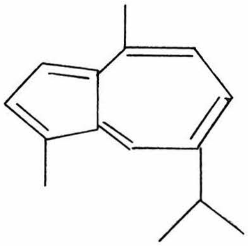


Cadalene



Eudalene

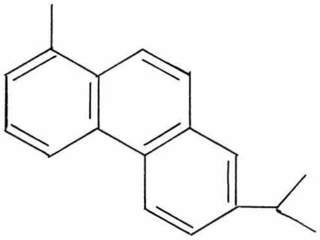
It has been observed that a number of bicyclic sesquiterpenes and their derivatives give rise to azulenes on dehydrogenation. Azulene formation was found possible only in a system which possesses either a cyclopentacycloheptane nucleus or one which could give rise to this bicyclic structure. The formation of S-guaiazulene and vetivazulene from guaiol and vetivone, respectively, shows that azulenes are bicyclic hydrocarbons with probably a cyclopentacycloheptane nucleus containing five conjugated double bonds. This



S-Guaiazulene

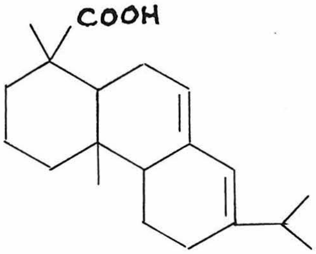
configuration was confirmed by the preparation of characteristic polynitro derivatives of azulenes and by actual syntheses (For a detailed discussion on the chemistry of azulenes see the section on azulenes below). It has been pointed out that the substituted groups in a natural-occurring azulene are so situated in the nucleus that an aliphatic sesquiterpene, as farnesol, could assume the azulene configuration by a rearrangement of its acyclic chain. The investigation of azulenes, along with that of cadalene and eudalene, has been of great value in clarifying the structures of bicyclic sesquiterpenes.

As with the sesquiterpenes, the diterpenes have only recently been investigated and, hence, not much is known. Many of the diterpenes form retene ($C_{18}H_{18}$) on sulfur or selenium dehydrogenation; this characteristic reaction

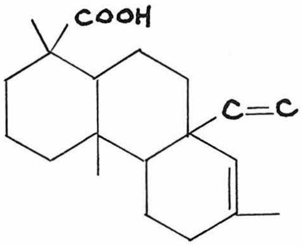


Retene

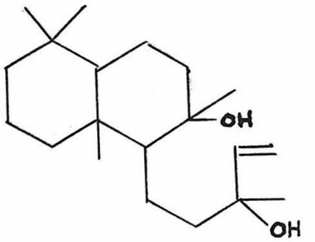
serves as a basis for the structural determination of the diterpenes. The structures of some natural-occurring diterpenes are shown.



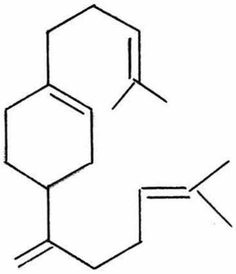
Abietic acid



d-Pimaric acid

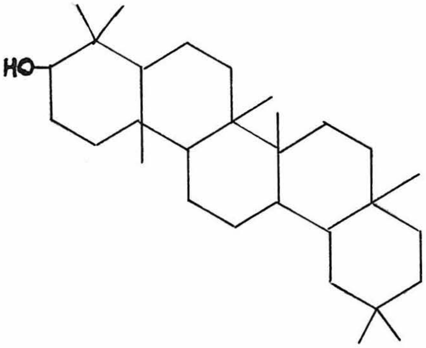


Sclareol

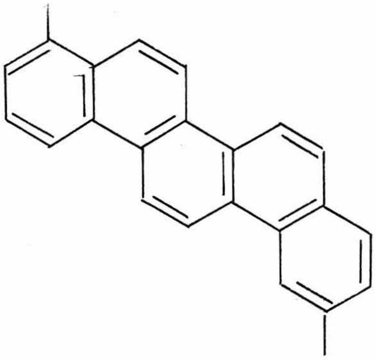


⍺-Camphorene

An acyclic representative of the triterpenes, which are composed of six branched C_5 units, is squalene ($C_{30}H_{50}$), found in shark liver oil and many other oils, as peanut and olive oils. It is interesting to note that squalene may be synthesized from farnesyl bromide. The terpenoid saponins, many with a β-amyrin skeleton, comprise a large portion of the known, natural-occurring triterpenes. A characteristic degradation product from the dehydrogenation of the terpenoid saponins is 1,8-dimethylpicene ($C_{24}H_{18}$).

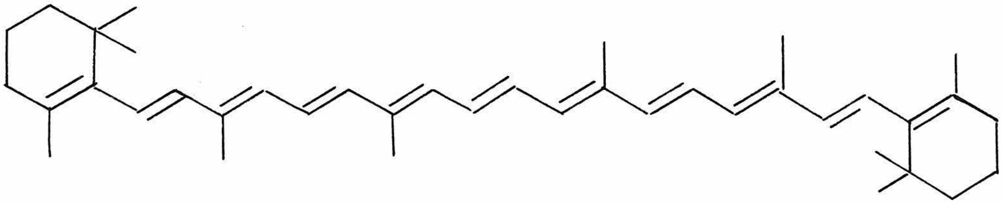


β-Amyrin skeleton



1,8-Dimethylpicene

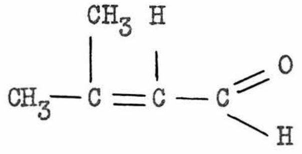
The tetraterpenes, consisting of eight branched C_5 units, are represented by the carotenoids, the plant and animal pigments which are found in various colors, namely, yellow, orange, red, and violet. A well-known example of the carotenoids is β-carotene.



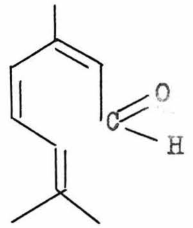
β-Carotene

We have observed that terpenes may be divided into isoprenoid units. Many investigators have speculated that such a unit is the precursor of terpenes in vivo, but there is no definite experimental evidence to support this hypothesis. The first possible precursor proposed for terpenes is isoprene, which is postulated to be formed from the condensation of acetone and acetaldehyde. It was suggested that possibly by the polymerization of these isoprene units terpenes may be formed. In the laboratory dipentene and bisabolene have been obtained from polymerized products of isoprene. Although it is possible to prepare terpenes by the polymerization of isoprene in vitro, there is no direct evidence that isoprene is involved in the formation of terpenes in plants.

The hypothetical precursor, 3-methyl-butenal, has also been postulated for terpenes. From 3-methyl-butenal, Fischer succeeded in synthesizing dehydrocitral with which the synthesis of other terpenes could be easily



3-Methylbutenal



Dehydrocitral

carried out. It has been suggested that 3-methylbutenal is probably formed in nature from the condensation of acetone with pyruvic acid with subsequent decarboxylation. Other precursors which have been considered are isovaleraldehyde, acetoacetic acid-acetone, etc.

The possible precursors of terpenes which have been discussed so far are based on the assumption that the C_5 branched chain is the fundamental building unit of terpenes. It is also hypothetically possible that terpenes may have their origin in larger units. Accordingly, it has been postulated by Emde (3) that terpenes may result from a synthesis from sugars through a coupling of molecules similar to levulinic acid with subsequent decarboxylation and with the addition of smaller products of sugar metabolism. A similar hypothesis was proposed by Hall (4), who suggested that terpenes may be formed from the condensation and degradation of sugar derivatives; "half molecules" which may give the desired structures were postulated.

Undoubtedly enzymes play an important part in the synthesis of terpenes in plants, but the nature of the mechanism involved is obscure.

Previously, it has been shown that most terpenes possess a regular head-to-tail union of isoprenoid units. In later years, an increasing number of terpenes with an irregular union of isoprenoid units have been found. With the desire to add to the limited information on sesquiterpenes the structural investigation of a sesquiterpene alcohol was undertaken. The arrangement of the isoprenoid units in this particular terpene would be of interest.

Experimental Section

Isolation of Partheniol

In extensive studies conducted in our laboratory on the constituents of guayule, a crystalline substance which melts at 125-126° C. was isolated from the entire plant from which the leaves had been removed. Initial isolation of the compound was carried out by exhaustive extraction of the guayule bark with cold alcohol; after the concentration of the extract, the crystalline substance separated out in the cold (0-5° C.).

In later experiments the de-leafed plant was extracted with 86-100° petroleum ether. The concentrated petroleum ether solution was chromatographed on silicic acid columns; development was carried out with petroleum ether. The unknown substance was adsorbed in a band in the lower section of the column. Elution of the compound from the adsorbent was carried out with alcohol. After recrystallization from alcohol the substance gave a melting point of 125-126° C. By qualitative test it was indicated that the crystalline compound was an ester. The test consisted essentially of reacting hydroxylamine with the unknown ester of carboxylic acid to form a hydroxamic acid which gives a colored inner complex iron salt with ferric chloride. The ester, on hydrolysis, yields cinnamic acid and an unknown sesquiterpene alcohol of melting point 127-128° C. Analysis for carbon and hydrogen showed that the empirical formula for the sesquiterpene alcohol is $C_{15}H_{24}O$.

In 1911 Alexander (5) obtained, on prolonged steam distillation of the acetone-soluble portion of guayule, a crystalline product which melted at 127-128° C. Alexander thought that this crystalline solid which liquefied on long standing was a sesquiterpene alcohol. This tendency to liquefy on long standing has also been observed with the unknown sesquiterpene alcohol. It is quite probable that the crystalline alcohol obtained by Alexander is identical with this compound.

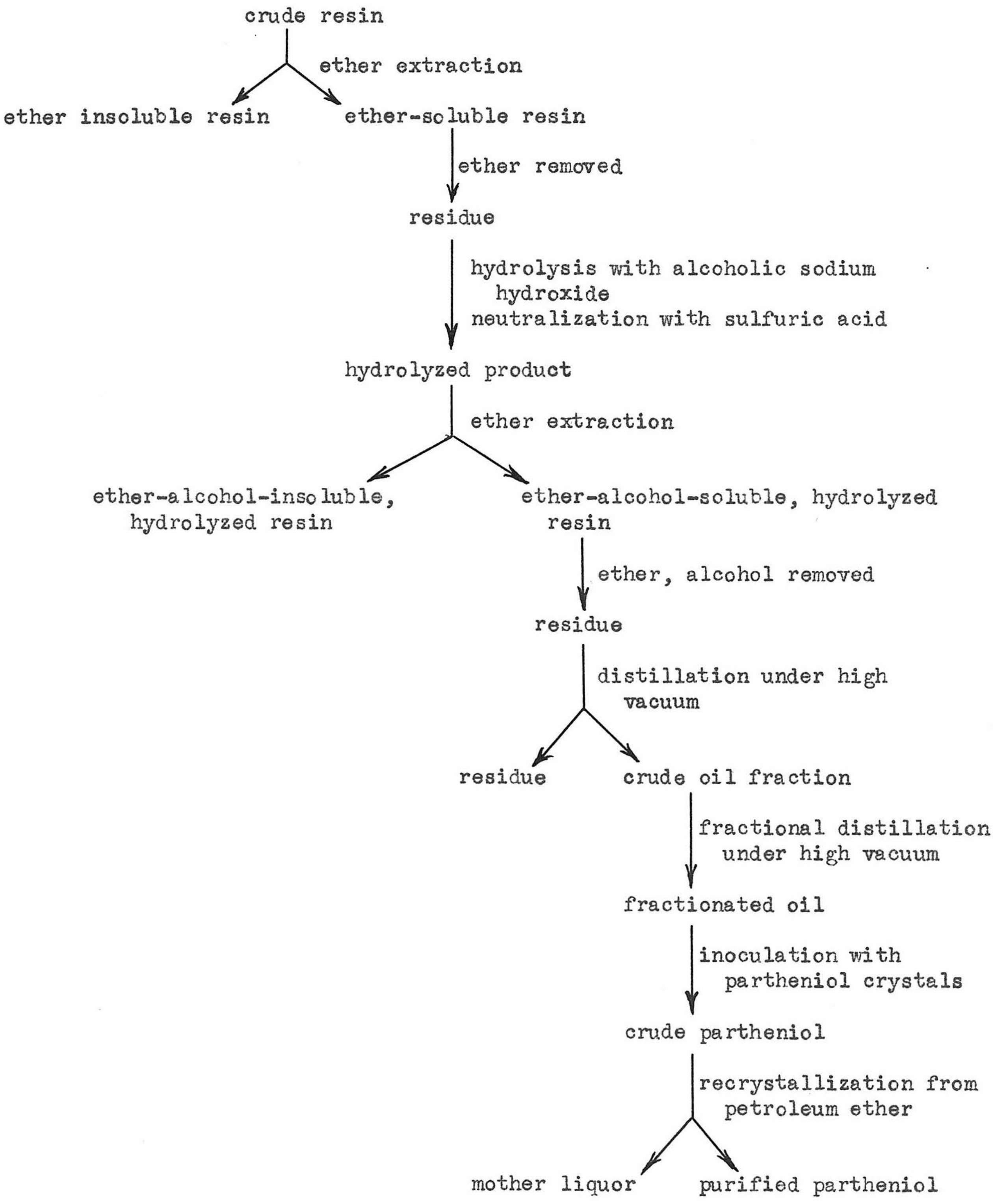
In studies conducted on the isolation and improvement of the quality of rubber Walter (6) isolated an unknown crystalline ester from the sticky exudate of injured roots and bark of the guayule shrub. He also obtained this substance from a concentrated acetone extract of guayule rubber. On recrystallization from acetone the ester gave tetragonal crystals melting at 125-126° C. The substance was soluble in organic solvents and was insoluble in water. Hydrolysis of the ester in an alcoholic alkali solution gave a sesquiterpene alcohol and cinnamic acid. From *Parthenium argentatum, Gray* (guayule) Walter proposed the name partheniol for the sesquiterpene alcohol and parthenyl cinnamate for the ester. Partheniol was obtained in the form of long crystalline needles. The resublimed crystals gave a melting point of 131° C. and were soluble in organic solvents and slightly soluble in hot water. From analysis for carbon and hydrogen Walter proposed $C_{15}H_{26}O$ as the empirical formula for partheniol.

Since parthenyl cinnamate melted at the same temperature as the crystalline ester which we have obtained, it is apparent that the two compounds are identical. Further evidence to support this was the isolation of cinnamic acid from the hydrolyzed ester. Walter has proposed $C_{15}H_{26}O$ for the empirical formula of partheniol, as compared to our formula, $C_{15}H_{24}O$, and has reported a melting point of 131° C. The melting point of partheniol has been found to be 127-128° C. in this laboratory; no change in the melting point was observed after repeated recrystallization of the compound from petroleum ether, benzene, and acetone. Melting points of 129.5-130.5° C. and 132-132.5° C. have been obtained from partheniol which had been recovered from a test for a conjugated double bond; it is probable that molecular rearrangement had occurred during the reaction.

In the early period of the study, partheniol was obtained from the hydrolysis of parthenyl cinnamate isolated from the guayule plant. The maximum yield of parthenyl cinnamate which was obtained from fresh ground plant was approximately 0.05 percent, or about 0.03 percent of partheniol. Upon investigation it was found that a 0.2-0.3 percent yield of partheniol may be obtained from guayule resin which is a concentrated extract of crude guayule rubber. This resin is a by-product in the manufacture of guayule rubber.

The method used for the isolation of partheniol from guayule resin is as follows. About 25 gallons of crude resin was extracted three times with five-gallon portions of ether and twice with a mixture of five gallons of ether and two gallons of methanol. Methanol was used in the last two extractions in order to decrease the solubility of rubber and its oxidized products. After the removal of the solvents from the extract, the ether-soluble portion of the guayule resin was saponified with 0.5-1.0 N alcoholic solution of sodium hydroxide for approximately three hours at a bath temperature of about 90° C. The alkaline alcoholic solution was then neutralized with dilute sulfuric acid. Extraction of the hydrolyzed product was carried out with several two-gallon portions of ether; the solvent was removed at the reduced pressure of an aspirator. The residue (about five gallons) was distilled under high vacuum. In a preliminary distillation, the fraction which distilled up to 150° C. at 1-10 μ pressure was collected; this fraction was approximately two liters. Further fractionation was carried out at 1-10 μ pressure with a short helix-packed column and a variable take-off still head. The fraction which was collected at 100-125° C. was approximately 1.2 liters of viscous oil. By diluting the oil slightly with petroleum ether and inoculating with a few crystals of partheniol a solid mass of partheniol was obtained, after allowing to stand in the cold room for several days. The crystalline partheniol was filtered on a Buchner funnel and the mother liquor was again placed in the cold room in order that further crops of crystals may be obtained. After recrystallizing twice from 60-70° petroleum ether the partheniol was washed with three one-liter portions of hot 30-60° petroleum ether. The washings were carried out by placing the partheniol in the petroleum ether and allowing the solvent to boil vigorously. Subsequently, the mixture was cooled to room temperature and the crystals were filtered on a Buchner funnel. The purified crystalline partheniol was free of oily odor and possessed only a very delicate odor. A total of about 150 g. of purified partheniol, m.p. 127-128° C., was obtained.

The scheme used in the isolation of partheniol from crude guayule resin is summarized in the following diagram.


crude resin
ether extraction
ether insoluble resin
ether-soluble resin
ether removed
residue
hydrolysis with alcoholic sodium hydroxide
neutralization with sulfuric acid
hydrolyzed product
ether extraction
ether-alcohol-insoluble, hydrolyzed resin
ether-alcohol-soluble, hydrolyzed resin
ether, alcohol removed
residue
distillation under high vacuum
residue
crude oil fraction
fractional distillation under high vacuum
fractionated oil
inoculation with partheniol crystals
crude partheniol
recrystallization from petroleum ether
mother liquor
purified partheniol

Quantitative and Qualitative Analyses of Parthenio1*

I. Analysis for carbon and hydrogen

Calculated for $C_{15}H_{24}O$: C, 81.76%; H, 10.98%
Found: (a) C, 81.77%; H, 10.92%
(b) C, 81.73%; H, 10.98%

(a) 2.280 mg. substance gave 6.832 mg. carbon dioxide and 2.226 mg. water

(b) 2.164 mg. substance gave 6.481 mg. carbon dioxide and 2.124 mg. water

II. Determination of molecular weight (Rast)

Calculated for $C_{15}H_{24}O$: M.W., 220.34
Found: M.W., 215.2

0.412 mg. substance in 3.420 mg. camphor gave a depression of 21.5° C.

III. Determination of optical rotations

$$[\alpha]_D^{26^\circ} = 83.6^\circ \text{ (conc. = 1.47\% in absolute alcohol)}$$

$$[\alpha]_D^{25.5^\circ} = 116.5^\circ \text{ (conc. = 1.29\% in chloroform)}$$

IV. Tests for primary and secondary alcohol groups in partheniol

A mixture of 7.8 g. of partheniol and 5.3 g. of phthalic anhydride was heated for 6 1/2 hours at a bath temperature of 130° C. under an atmosphere of nitrogen. No ester of phthalic acid was formed; hence, the alcoholic group was tertiary.

A qualitative test with carbon disufide and sodium hydroxide reagents

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* Micro-analyses were done by G. Oppenheimer, G. Swinehart and B. Dandliker

failed to give a xanthogenate. The failure of the alcohol to react with these reagents again indicates that it is tertiary.

V. Determination of unsaturation of partheniol by hydrogenation

A. 9.404 mg. of partheniol in glacial acetic acid with 3.240 mg. of platinium dioxide took up 1.9 ml. of hydrogen at STP.

Calculated for $C_{15}H_{24}O$: 1.9 ml. hydrogen at STP for 2 double bonds
Found: 1.9 ml. hydrogen at STP; 2 double bonds

B. 13.360 mg. of partheniol in glacial acetic acid with 6.248 mg. of platinium dioxide took up 2.66 ml. of hydrogen at STP.

Calculated for $C_{15}H_{24}O$: 2.72 ml. hydrogen at STP for 2 double bonds
Found: 2.66 ml. hydrogen at STP; 2 double bonds

VI. Tests for conjugated double bonds

A. Reduction with sodium and alcohol

Two grams of partheniol in 10 ml. of amyl alcohol was heated in a 40-ml. flask at a bath temperature of 135° C. for 6 1/4 hours. Sodium (4.5 g.) in small pieces was subsequently added; at periodic intervals more amyl alcohol was introduced until all the sodium had reacted. After allowing to cool, water was slowly added to the reaction mixture; at this point a substance precipitated out. The alcohol phase was separated and combined with an ether solution of the precipitated material. After washing with water till neutral and drying over anhydrous sodium sulfate, the alcohol-ether solution was filtered and the solvent was removed at a reduced pressure. The crystalline residue was recrystallized twice from low boiling petroleum ether; the substance melted at 132-132.5° C. A mixture of the compound and partheniol gave a melting point of 130-130.5° C.

Analysis of recovered product for carbon and hydrogen:

Calculated for $C_{15}H_{24}O$: C, 81.76%; H, 10.98%
$C_{15}H_{26}O$: C, 81.02%; H, 11.79%
Found: C, 81.85%; H, 11.06%; therefore compound is $C_{15}H_{24}O$

It has been shown from the analysis that no reduction of partheniol had occurred; the double bonds in partheniol were, therefore, not conjugated, but isolated. The slightly higher melting point of the recovered partheniol is probably due to molecular rearrangement which may have occurred in the course of the reaction.

B. Reaction with maleic anhydride (Diels-Alder reaction)

A mixture of 600 mg. of partheniol, 300 mg. of maleic anhydride, and 3 ml. of anhydrous benzene in a 10-ml. flask was refluxed at a bath temperature of 100° C. for 10 1/2 hours. After cooling, the precipitated substance was filtered and the benzene filtrate was evaporated at reduced pressure. The remaining oil from the benzene solution was allowed to stand in the refrigerator for several days; no crystals were formed. The solid which had been recovered from the original reaction mixture was washed with two portions of benzene and was subsequently centrifuged; the substance melted at 134-136° C. and decomposed above 136° C. It was shown from the melting point, the decomposition temperature and solubility in water and alcohol that the compound was maleic acid. Hence, it may be concluded that no adduct was formed in the Diels-Alder reaction. A similar experiment, in which 20 mg. of partheniol and an equal amount of ethyl maleate in 0.75 ml. of anhydrous benzene were used, also showed no adduct formation. The recovered partheniol, after recrystallization from cyclohexane gave a melting point of 129.5-130.5° C.

Analysis of recovered product for carbon and hydrogen:

Calculated for $C_{23}H_{36}O$ (conjugated product): C, 70.37%; H, 9.25%
$C_{15}H_{24}O$: C, 81.76%; H, 10.98%
Found: C, 81.96%; H, 10.05%

2.287 mg. substance gave 6.869 mg. carbon dioxide and 2.055 mg. water

VII. Test for homogeneity of partheniol

In the isolation of partheniol from guayule concentrate, repeated recrystallization of the compound from petroleum ether gave a constant melting point of 127-128° C. The constancy of the melting point after further recrystallization from benzene and acetone was determined to check the purity of the compound. In order to further establish the purity of the isolated partheniol and to investigate whether the substance is possibly a mixture of isomers, a chromatographic study of its derivative, parthenyl-p-phenylazobenzoate, was undertaken. The red-orange parthenyl-p-phenylazobenzoate was chromatographed instead of partheniol because its color serves as a convenient index of adsorption.

A. Constancy of melting point of partheniol

About one gram of partheniol (m.p. 127-128° C.) which had been purified by repeated recrystallization from petroleum ether was recrystallized twice from benzene and once from acetone. The melting point of partheniol was 127-128° C. after the first recrystallization from benzene, 128-128.2° C. after the second recrystallization, and 126.5-128° C. after the final recrystallization from acetone. From the constancy of its melting point partheniol appears to be a pure substance.

B. Chromatographic studies

1. Preparation of parthenyl-p-phenylazobenzoate

To 2 g. of partheniol in 15 ml. of pyridine in a 40-ml. flask, 2.4 g. of p-phenylazobenzoyl chloride in 20 ml. of anhydrous benzene was added. The reaction mixture was heated at a bath temperature of 90° C. for 1/2 hour. After allowing to cool the mixture was diluted with alcohol-free ether and washed with four 10-ml. portions of 3 N hydrochloric acid, followed by three 10-ml. portions of 1 N potassium hydroxide. The solution was then thoroughly washed with water and dried over anhydrous sodium sulfate. The residue which remained after the evaporation of the solvent mixture was recrystallized, first, from a mixture of benzene and petroleum ether, then, from acetone. After drying in a vacuum desiccator the parthenyl-p-phenylazobenzoate was used for chromatographic studies.

2. Chromatography of parthenyl-p-phenylazobenzoate

Approximately 1 g. of parthenyl-p-phenylazobenzoate dissolved in a mixture of 10 ml. of benzene and 50 ml. of petroleum ether (85-100° C.) was chromatographed on a silicic acid-Celite column (2:1) which had been initially washed with 250 ml. of petroleum ether. The column was developed with 400 ml. of petroleum ether (85-100° C.) and post-washed with 50 ml. of 30-60° petroleum ether. Two very faint narrow zones which were situated at the top of the column and about 7 cm. from the top, respectively were observed. A main band of parthenyl-p-phenylazobenzoate which was about 5 cm. wide was situated approximately 10 cm. from the top of the column. After extruding the column this zone was cut out and the benzoate was eluted from the adsorbent with ether; the ether solution was dried over anhydrous sodium sulfate, filtered, and the benzoate recovered. The compound was recrystallized three times from acetone; the melting point of the pure parthenyl-p-phenylazobenzoate is 162.5-164° C.

Analysis of recovered parthenyl-p-phenylazobenzoate:

Calculated for $C_{28}H_{32}O_2N_2$: C, 78.47%; H, 7.53%; N, 6.54%
Found: C, 78.48%; H, 7.53%; N, 6.66%

2.675 mg. substance gave 7.693 mg. carbon dioxide and 1.800 mg. water
4.893 mg. substance gave 0.297 ml. nitrogen at 24° C. and 743 mm. Hg

The two very faint bands were probably impurities which were present in either the reagents used in the preparation of the benzoate or in partheniol itself. In any case, the total quantity of these impurities is insignificantly small as compared to the amount of benzoate chromatographically separated. From the above chromatographic study, partheniol appears to be a homogeneous substance.

Absorption Spectrum of Partheniol

The absorption spectrum was determined with the Beckman photoelectric spectrophotometer. A solution of a concentration of 1.76 mg. of partheniol in 100 ml. of absolute alcohol was used. The spectrum, as given in Figure 5, did not show any characteristic maxima or minima within the range of the Beckman photoelectric spectrophotometer.

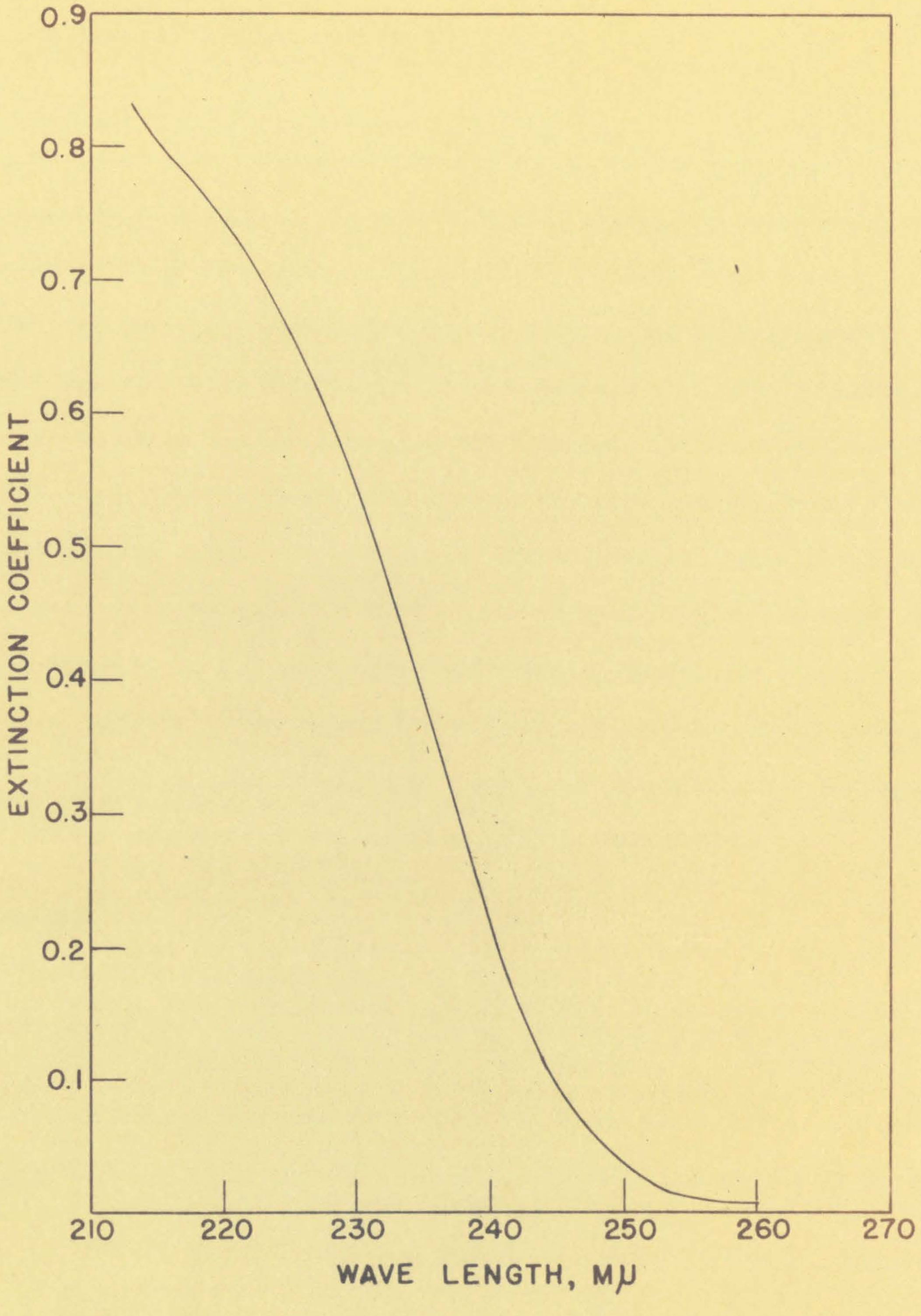


Figure 5. Absorption spectrum of partheniol in absolute ethanol

Preparation of Parthenyl-3,5-dinitrobenzoate

A solution of approximately 150 mg. of partheniol and an equal amount of 3,5-dinitrobenzoyl chloride in a mixture of 2 ml. of dry benzene and 5 ml. of anhydrous pyridine was gently refluxed for 3/4 hour. After cooling, the solution was diluted with alcohol-free ether, then washed with several portions of dilute hydrochloric acid, followed by washing with dilute sodium hydroxide. The ether solution was thoroughly washed with water till neutral and dried over anhydrous sodium sulfate; the solvent was then removed under reduced pressure leaving behind a viscous oil. The oil was diluted with alcohol, then water was added till the solution was turbid. The turbid solution was allowed to stand in the refrigerator for several days. The crystals formed were recrystallized from acetone three times and were then washed with alcohol. After drying under vacuum over phosphorus pentoxide in a drying pistol at 56° C. the substance gave a melting point of 143-144° C.

Analysis:

Calculated for $C_{22}H_{26}N_2O_6$: C, 63.75%; H, 6.31%; N, 6.76%
Found: (a) C, 63.88%; H, 6.61%; N, 6.67%
(b) C, 63.97%; H, 6.51%; N, 6.90%

(a) 3.040 mg. substance gave 7.116 mg. carbon dioxide and 1.795 mg. water
5.635 mg. substance gave 0.341 ml. nitrogen at 22° C. and 742 mm. Hg

(b) 2.806 mg. substance gave 6.577 mg. carbon dioxide and 1.633 mg. water
2.842 mg. substance gave 0.180 ml. nitrogen at 25° C. and 742 mm. Hg

Preparation of Parthenene

A mixture of 5 g. of partheniol and 3.5 g. of fused potassium acid sulfate was heated in a 50-ml. flask fitted with a reflux condenser at a bath temperature of 180-190° C. for 1/2 hour. The oil was extracted with ether and the ether extract was washed with water, then dried over anhydrous sodium sulfate. The ether was removed under reduced pressure and the residual oil was distilled twice over potassium. In the second distillation at 60-65° C. and 100 μ, 1.1 g. of parthenene was obtained.

I. Analysis for carbon and hydrogen

Calculated for $C_{15}H_{22}$: C, 89.04%; H, 10.96%
Found: C, 88.90%; H, 11.15%

2.062 mg. substance gave 6.717 mg. carbon dioxide and 2.054 mg. water

II. Physical constants

$$n_D^{26°} = 1.5120$$

$$d_{4°}^{23.6°} = 0.9194$$

M_R, calculated: 65.67 for 3 double bonds
Found: 66.04
Exaltation: 0.37

III. Absorption spectrum

A solution of 6.0 mg. of parthenene in 100 ml. of absolute ethanol was examined with the Beckman photoelectric spectrophotometer. At 212-330 mμ, the extinction coefficient decreased with the increase of the wave length; no maximum nor minimum was detected.

Partial Hydrogenation of Partheniol with Raney Nickel

A 5.04-g. sample of partheniol dissolved in 50 ml. of absolute ethanol was hydrogenated with approximately 2 g. of Raney nickel as catalyst at room temperature and at a pressure slightly above atmospheric. The rate at which the hydrogenation proceeded was about 30 ml. of hydrogen per hour for the first 15 hours and decreased thereafter; at the end of 27 hours the rate was 5 ml. of hydrogen per hour. The hydrogenation was stopped shortly after the required amount of hydrogen was taken up. For the 5.04-g. sample, 514 ml. of hydrogen is required at STP; in the hydrogenation 582 ml. of hydrogen was taken up at STP, giving 1.1 double bonds. After the removal of the Raney nickel and the ethanol, the remaining oil was distilled at 92-102° C. at 100 μ; a total of 3.5 g. of dihydropartheniol was obtained.

I. Analysis for carbon and hydrogen

Calculated for $C_{15}H_{26}O$: C, 81.02%; H, 11.79%
Found: C, 81.05%; H, 11.96%

2.036 mg. substance gave 6.047 mg. carbon dioxide and 2.177 mg. water

II. Hydrogenation

12.955 mg. substance and 5.947 mg. platinium dioxide in cyclohexane gave no uptake of hydrogen

10.259 mg. substance and 5.063 mg. platinium dioxide in methylcyclohexane-glacial acetic acid (1:1) took up 1.84 ml. hydrogen at STP

Calculated for $C_{15}H_{26}O$: 1.04 ml. hydrogen at STP for 1 double bond;
2.08 ml. hydrogen at STP for 2 double bonds
Found: 1.84 ml. hydrogen at STP; 2 double bonds (probably reduction of the hydroxyl group)

III. Physical constants

$n_D^{26^\circ} = 1.5035$

$d_{4^\circ}^{23.6^\circ} = 0.9614$

M_R, calculated: 68.13 ($C_{15}H_{26}O$), for 1 hydroxyl group
Found: 68.50

IV. Preparation of dihydroparthenyl-p-phenylazobenzoate

Approximately 1 g. of dihydropartheniol in 15 ml. of dry pyridine was added to 1.3 g. of p-phenylazobenzoyl chloride in benzene-pyridine. The reaction mixture was heated at a bath temperature of 100° C. for 1/4 hour and was then diluted with alcohol-free ether. The pyridine was removed with 3 N hydrochloric acid; the p-phenylazobenzoic acid with 1 N potassium hydroxide. The ether-benzene solution was washed with water, dried over anhydrous sodium sulfate, and the solvents were removed under reduced pressure. In order to separate the substance from its impurities, the dihydroparthenyl-p-phenylazobenzoate was dissolved in 30 ml. of 85-100° petroleum ether and chromatographed on a column of silicic acid-Celite (2:1), 4.5 cm. x 20 cm., which had been pre-washed with about 250 ml. of 85-100° petrol ether. The chromatogram was developed with 150 ml. of 1:1 85-100° petroleum ether-100-130° petroleum ether. The main zone of the azobenzoate was about 15 cm. from the top of the column; three small zones all of which were more strongly adsorbed than and well separated from the benzoate were observed. The main zone was cut out and the substance was eluted from the adsorbent with ether. The ether solution was dried over anhydrous sodium sulfate and the ether was removed. The recovered dihydroparthenyl-p-phenylazobenzoate gave a m.p. of 121.5-122.5° C., after three recrystallizations from acetone.

Analysis for carbon and hydrogen:

Calculated for $C_{28}H_{34}O_2N_2$: C, 78.20%; H, 7.96%; N, 6.51%
Found: C, 78.40%; H, 8.20%; N, 6.58%

2.708 mg. substance gave 7.781 mg. carbon dioxide and 1.984 mg. water
4.884 mg. substance gave 0.293 ml. nitrogen at 24° C. and 743 mm. Hg

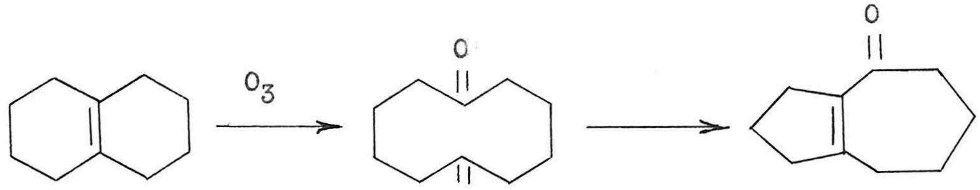
V. Conclusion

It has been shown that one of the double bonds in partheniol is easily hydrogenated.

Preparation of Azulenes from Partheniol

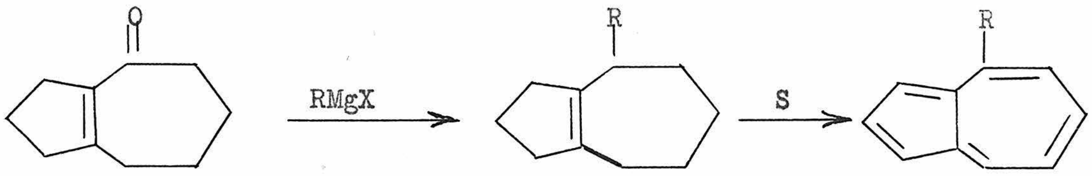
There are found in literature many references to blue colored fractions in essential oils. In 1894 Piese gave the name *Azulene* to the blue substance obtained from wormwood oil. The general trend of thought at that time was that the blue oil was an oxygenated compound of alcoholic nature. From the properties of azulene its nucleus was considered to be related to the sesquiterpene skeleton. Later, it was found that azulenes were bicyclic hydrocarbons. Since the only simple colored hydrocarbons known at that time were fulvene and its derivatives, the benzofulvene structure was proposed for azulenes. Many of the reactions of azulenes were explained on the basis of a benzofulvene structure. With the actual synthesis of azulenes, however, this concept of a benzofulvene structure was discarded in favor of a conjugated cyclopentacycloheptene nucleus.

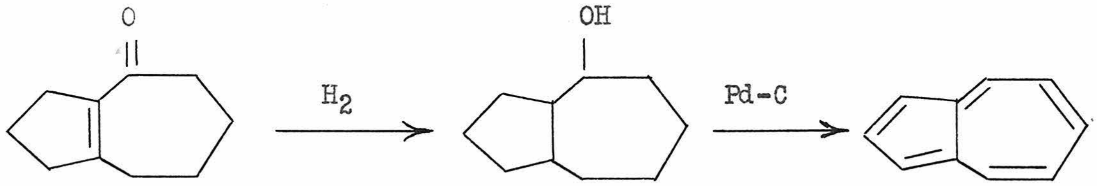
Hückel *et al* (7,8) were the first to synthesize cyclopentenocycloheptanone by ozonizing octalin to form a diketone which was subsequently treated with aqueous sodium carbonate or dilute sodium hydroxide. The reactions are as presented below.



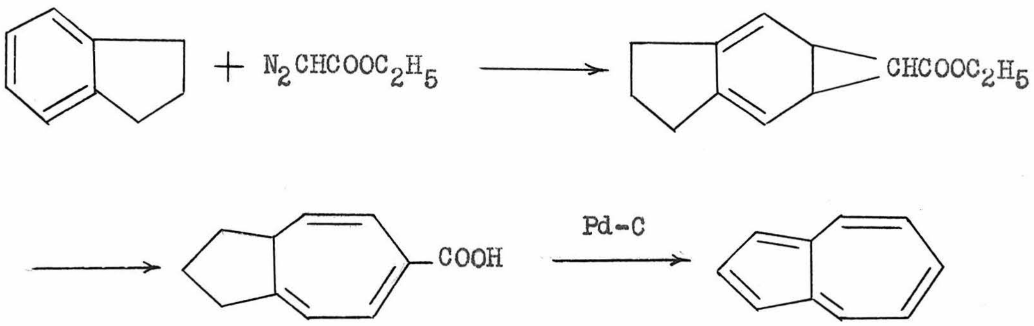
$\Delta^{9,10}$octalin

Pfau and Plattner (9) condensed cyclopentenocycloheptanone with various Grignard reagents and dehydrogenated the products with nickel or sulfur to form various azulenes with different substituted groups. These investigators (10) also prepared the parent azulene by reducing the cyclopentenocycloheptanone, first, to the dihydro compound, then, to the carbinol which was subsequently dehydrogenated with palladium-charcoal. The reactions involved are given below.

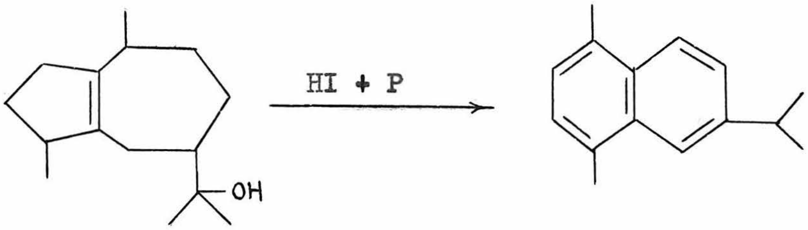




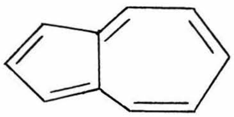
A recent method for the synthesis of azulene is to treat the desired substituted indane with diazo-acetic ester, followed by hydrolysis of the ester. The bicyclic acid is then decarboxylated and dehydrogenated with palladium-charcoal or sulfur to form the desired azulene. The reactions are as follows.

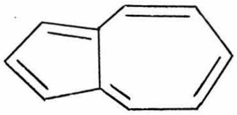


From bond energy considerations* it may be shown that the azulene nucleus is less stable than that of the naphthalene nucleus. Hence, it is not surprising that an azulene may be readily transformed into a naphthalene derivative by treatment with hydroiodic acid and red phosphorus, as given below.



Two stable valence bond structures may be formulated for the parent azulene; these are as given.





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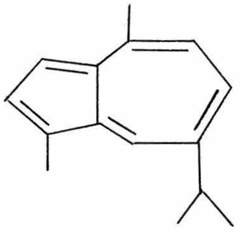
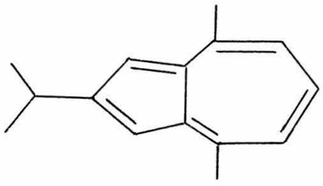
* Heats of combustion of 1,4-dimethyl-7-isopropylazulene and 3,8-dimethyl-5-isopropylnaphthalene are 2022.9 and 1993.4 Cals., respectively (Perrottet, Traub, and Briner, Helv. Chim. Acta 23, 1260-8, 1940).

Generally azulenes may be formed from essential oils by dehydrogenation with sulfur, selenium, palladium-charcoal or nickel. There may be found reported in literature a number of azulenes each of which was named after the natural oil from which it is derived. Among these supposedly different azulenes are possibly identical compounds, since the chemical nature of most of these azulenes apparently has not been investigated. In an investigation on a number of azulenes Ruzicka and Haagen-Smit (11) suggested that kessazulene is identical to S-guaiazulene. The number of actually different azulenes which may be derived from natural sources is probably limited; a few which have been reported are briefly discussed below.

S-Guaiazulene (m.p. 30° C.) which is obtained by the S-dehydrogenation of guaiol is a blue compound. It may be derived also from <u>Eucalyptus globulus</u> and other essential oils. Camazulene (m.p. 132° C.), the structure of which has not been entirely elucidated, has been obtained from camomile oil. Vetivazulene (m.p. 32° C.), a violet compound, is derived from sulfur dehydrogenation of vetivone or vetiver oil. The structural formulae of S-guaiazulene and vetivazulene are presented in I and II, respectively.



I



II

In studies on azulenes, the phosphoric acid method of isolating the azulene has been extensively used. Azulenes are usually characterized by such addition products as the picrates and the styphnates. More stable crystalline addition products with trinitrobenzene and trinitrotoluene also may be prepared. The purification of an azulene is afforded by the easily decomposable polynitro addition products; the separation of the regenerated azulene from the polynitro reagent is accomplished by chromatographic adsorption on activated alumina.

In the investigation of the structure of partheniol, the selenium dehydrogenation of a small sample of the sesquiterpene alcohol was carried out; a blue violet azulene was obtained. The induction of an azulene from partheniol suggests that the sesquiterpene alcohol possesses a cyclopentacycloheptane nucleus. In a more extensive study of the preparation of azulenes from partheniol, it has been found that dehydrogenation with sulfur and with selenium yield azulenes which are not identical. Previous studies by Ruzicka and Haagen-Smit on guaiol (11) have shown that dehydrogenation of guaiol with sulfur and selenium also yielded different azulenes. With sulfur, the blue S-guaiazulene was formed; with selenium, a violet azulene, or probably a mixture of azulenes was obtained.

The preparation of and the studies made on the azulenes from partheniol are presented in this section.

I. Dehydration of partheniol

Twenty grams of partheniol and 12.5 g. of fused potassium acid sulfate were placed in a 200-ml. flask and heated at a bath temperature of 165-170° C. for an hour. The reaction mixture was transferred into a distilling flask and the reaction flask was rinsed with ether; the ether washings were combined with the main fraction in the distilling flask. After the removal of the solvent by distillation, the remaining oil was fractionally distilled under high vacuum. The crude parthenene which distilled at 78-100° C. and 0.15 mm. Hg was collected and dehydrogenated as described below.

In a separate experiment, 24.6 g. of crude parthenene was prepared from 30 g. of partheniol according to the procedure described above.

II. Dehydrogenation of parthenene with sulfur (9,12)

Fifteen grams of crude parthenene was heated with 4.7 g. of sulfur under a reduced pressure of 30-50 mm. Hg at a bath temperature of 180-185° C. for 3 hours. The blue azulene which was formed was distilled directly from the reaction flask. The fraction obtained at 70-100° C. and 10-15 mm. Hg was 7.0 g.

A. Purification of S-azulene by the phosphoric acid method

The crude blue azulene was dissolved in five times its volume of purified petrol ether and the solution was cooled to below 0° C. in an ice-salt bath. Approximately 0.3-ml. portions of 85% phosphoric acid were added with thorough agitation of the mixture after each addition. The addition of the phosphoric acid reagent was continued until the petrol ether solution was practically discolored; a total of 2.5-3.0 ml. of the reagent was used. The petrol ether solution was then drawn off and the phosphoric acid addition product which was formed was washed with four 15-ml. portions of petrol ether.

To decompose the addition product finely crushed ice was added. The liberated azulene was taken up in about 25 ml. of peroxide-free ether. The ether solution was washed, first, with several 5-ml. portions of 1 N sodium hydroxide, then, with water until a neutral reaction with litmus was obtained.

The ether was evaporated and the azulene was steam distilled. The steam distillate containing the azulene was extracted with peroxide-free ether, the ether solution was dried over anhydrous sodium sulfate, filtered and the ether removed. The azulene was transferred into a micro-claisen flask and distilled over sodium; the fraction which distilled at 140-150° C. (bath temperature) and 50 μ pressure was approximately 250 mg. The percentage yield based on crude parthenene is about 1.7 percent.

B. Purification of azulene by means of the 1,3,5-trinitrobenzene addition product

Approximately 250 mg. of the blue azulene obtained from S-dehydrogenation, 300 mg. of 1,3,5-trinitrobenzene and 1.5 ml. of absolute alcohol were placed in a small test tube and heated to boiling. The stoppered test tube and its contents were allowed to cool in the refrigerator. After approximately an hour the crystalline trinitrobenzene addition product which had formed was filtered, washed with several small portions of absolute alcohol and the excess alcohol was removed by suction. The thoroughly dried addition product was placed on a chromatographic column 2 cm. in diameter and packed with activated alumina 14 cm. high. On the addition of purified petrol ether to the column the trinitrobenzene addition product of azulene immediately decomposed into the original azulene and trinitrobenzene. The trinitrobenzene, being strongly adsorbed on alumina, formed a zone at the top of the column. The azulene was adsorbed a short distance below the trinitrobenzene zone. By continued addition of petrol ether to the column the azulene zone was washed free of weakly adsorbed contaminating substances; a total of 75 ml. of petrol ether was used. To elute the azulene from the adsorbent about 60 ml. of a mixture of 1:1 benzene-petrol ether was passed through the column. The filtrate containing the azulene was collected and the solvent was distilled off. A trinitrobenzene addition product of the recovered azulene was again prepared and the cycle of the decomposition and the regeneration of the azulene was repeated.

The final product of azulene was distilled under reduced pressure. Approximately 125 mg. of the purified blue azulene was obtained.

Analysis of purified azulene:

Calculated for $C_{15}H_{18}$: C, 90.85%; H, 9.15%
Found: C, 90.93%; H, 9.24%

1.934 mg. substance gave 6.444 mg. carbon dioxide and 1.596 mg. water

C. Absorption spectrum of azulene obtained from sulfur dehydrogenation of parthenene

A solution of 3.62 mg. of S-azulene in purified hexane was made up to a total volume of 10 ml. The absorption spectrum of the azulene in hexane was determined with a Beckman photoelectric spectrophotometer using a slit width of 0.02 to 0.30 mm. The spectrum was characterized by three maxima at 603, 656, and 728 mμ and undulations at 557, 582, 630, and 698 mμ, as shown in Figure 6.

The absorption spectrum of S-guaiazulene, as reported by Plattner, is characterized by three maxima at 603, 661, and 732 mμ and undulations at 556, 577, 631, and 699 mμ (13).

D. Preparation of polynitro derivatives of the sulfur azulene from partheniol

1. Trinitrobenzene addition product of S-azulene from partheniol

A mixture of approximately 42 mg. of purified S-azulene, an equal amount

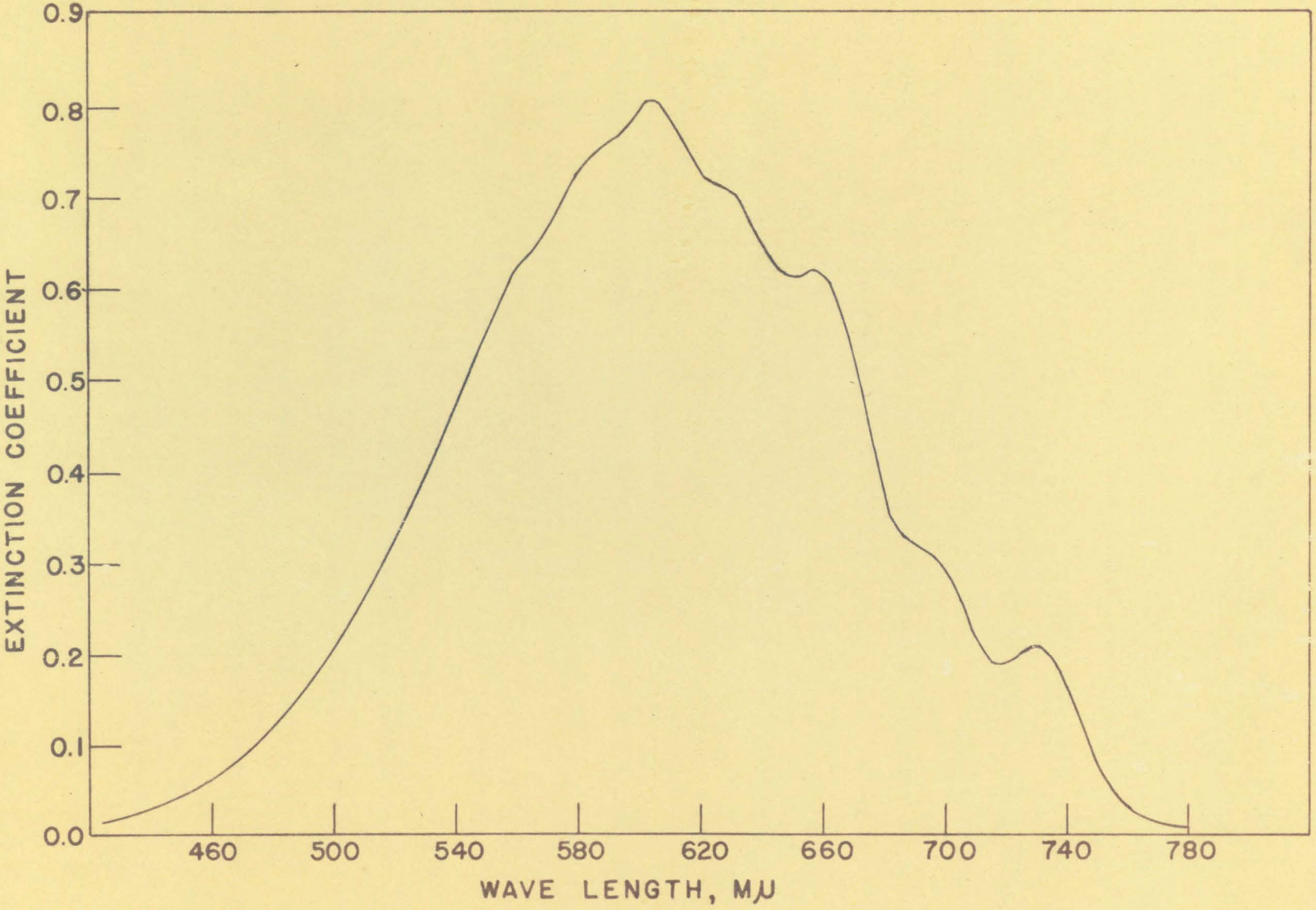


Figure 6. Absorption spectrum of S-guaiazulene prepared from S-dehydrogenation of parthenene (hexane solution).

of trinitrobenzene, and 0.75 ml. of absolute ethyl alcohol was heated to boiling. The trinitrobenzene addition product which was formed was allowed to crystallize at a temperature of -10° C. The crystals were filtered, washed with absolute alcohol and dried. Recrystallization of the trinitrobenzene addition product was carried out three times from absolute ethyl alcohol and once from absolute methyl alcohol. The crystals were dried over phosphoric pentoxide for several days. The purified 1,3,5-trinitrobenzene addition product of the sulfur azulene melted at 150-151° C. The melting point of the corresponding addition product of S-guaiazulene, as reported in literature, is 151-151.5° C. (9)

Analysis of the trinitrobenzene addition product:

Calculated for $C_{21}H_{21}N_3O_6$: C, 61.34%; H, 5.14%; N, 10.21%
Found: C, 61.61%; H, 4.99%; N, 10.12%

2.993 mg. substance gave 6.757 mg. carbon dioxide and 1.333 mg. water
2.760 mg. substance gave 0.254 ml. nitrogen at 23° C. and 742 mm. Hg

2. Picrate of S-azulene from partheniol

Approximately 26 mg. of the purified S-azulene, 26 mg. of picric acid, and 0.3 ml. of absolute ethanol were placed in a test tube and heated to boiling. The stoppered tube with its contents was allowed to cool in the cold room. The picrate of the azulene which precipitated from the reaction mixture was filtered, washed with absolute ethanol and recrystallized from the same solvent. The melting point of the picrate was 120.5-121° C.; that of the picrate of S-guaiazulene, as reported in literature, is 122.5-123° C. (9).

Analysis of picrate of S-azulene:

Calculated for $C_{21}H_{21}N_3O_7$: C, 59.01%; H, 4.95%; N, 9.83%
Found: C, 58.79%; H, 4.88%; N, 10.09%

2.947 mg. substance gave 6.349 mg. carbon dioxide and 1.286 mg. water
2.810 mg. substance gave 0.258 ml. nitrogen at 24° C. and 744 mm. Hg

3. Trinitrotoluene addition product of S-azulene from partheniol

A mixture of 30 mg. of the purified azulene, 30 mg. of trinitrotoluene, and 0.3 ml. of absolute ethanol was heated to boiling and the trinitrotoluene addition product which was formed was allowed to crystallize in the cold room at 0° C. The crystals were filtered, washed with absolute ethanol, and dried. The melting point of the trinitrotoluene addition product after recrystallization from absolute ethanol was 88-89° C.; that of the corresponding addition product of S-guaiazulene was reported in literature to be 89° C. (9)

Analysis of trinitrotoluene addition product of S-azulene from partheniol:

Calculated for $C_{22}H_{23}N_3O_6$: C, 62.11%; H, 5.45%; N, 9.88%
Found: C, 62.30%; H, 5.74%; N, 10.06%

2.786 mg. substance gave 6.360 mg. carbon dioxide and 1.430 mg. water
2.922 mg. substance gave 0.267 ml. nitrogen at 24° C. and 745 mm. Hg

E. Conclusion

The azulene obtained from the sulfur dehydrogenation of parthenene has been characterized by various polynitro derivatives which agree with those reported for S-guaiazulene. The absorption spectrum is also identical with that of S-guaiazulene. It is concluded that the sulfur azulene from partheniol is S-guaiazulene, and hence, partheniol possesses a 1,4-dimethyl,7-isopropylcyclopentacycloheptane configuration as in guaiol.

III. Selenium dehydrogenation of parthenene

A mixture of 24.6 g. of crude parthenene which was prepared from 30 g. of partheniol and 19 g. of selenium was heated in a 100-ml. flask in a metal bath at a bath temperature of 285-295° C. for 7 hours. The reaction product was transferred to a claisen flask, rinsing the flask with a small amount of ether. The ether was evaporated and the azulene was distilled under reduced pressure. A total of 14.5 g. of crude purple azulene which distilled at 90-100° C. and 1 mm. Hg was obtained. A preliminary purification of the crude azulene was carried out by means of the phosphoric acid method which was used for the purification of the sulfur azulene (Section II-A). Distillation of the azulene over metallic sodium gave further purification. At this stage 0.5 g. of azulene was obtained. Still further purification of the azulene was made by means of the trinitrobenzene addition product decomposition method as described in Section II-B in connection with the work on the S-azulene from partheniol. This process of purification was repeated; the final yield of pure Se-azulene was 350 mg., which is 1.4 percent of the crude parthenene originally used.

Analysis of purified Se-azulene:

Calculated for $C_{15}H_{18}$: C, 90.85%; H, 9.15%
Found: C, 90.93%; H, 9.34%

1.925 mg. substance gave 6.414 mg. carbon dioxide and 1.606 mg. water

A. Absorption spectrum of Se-azulene

A solution of 1.75 mg. of purified azulene in hexane was made up to a total volume of 5 ml. The absorption spectrum of Se-azulene in hexane, as determined by means of a Beckman photoelectric spectrophotometer, is characterized by three maxima at 553, 567, and 578 mμ and undulations at 490, 500, 533, 603, 616, 627, and 664 mμ, as shown in Figure 7.

B. Preparation of polynitro addition products of Se-azulene from partheniol

1. Preparation of the trinitrobenzene addition product

The 1,3,5-trinitrobenzene addition product of the Se-azulene from partheniol was prepared from 78 mg. of the azulene according to the procedure used for the preparation of the corresponding addition product of S-azulene and is as described in Section II-D. The melting point of the crystalline addition product was 103-104° C.

Analysis of trinitrobenzene addition product of Se-azulene from partheniol:

Calculated for $C_{21}H_{21}N_3O_6$: C, 61.34%; H, 5.14%; N, 10.21%
Found: C, 61.10%; H, 5.07%; N, 10.18%

2.884 mg. substance gave 6.457 mg. carbon dioxide and 1.306 mg. water
3.535 mg. substance gave 0.329 ml. nitrogen at 24° C. and 742 mm. Hg

2. Preparation of the picrate of Se-azulene from partheniol

A mixture of 60 mg. of azulene and 50 mg. of picrate was used in the preparation of the picrate of Se-azulene according to the procedure given in Section II-D. Recrystallization from absolute ethanol gave a product with a melting point of 105.5-107.5° C.

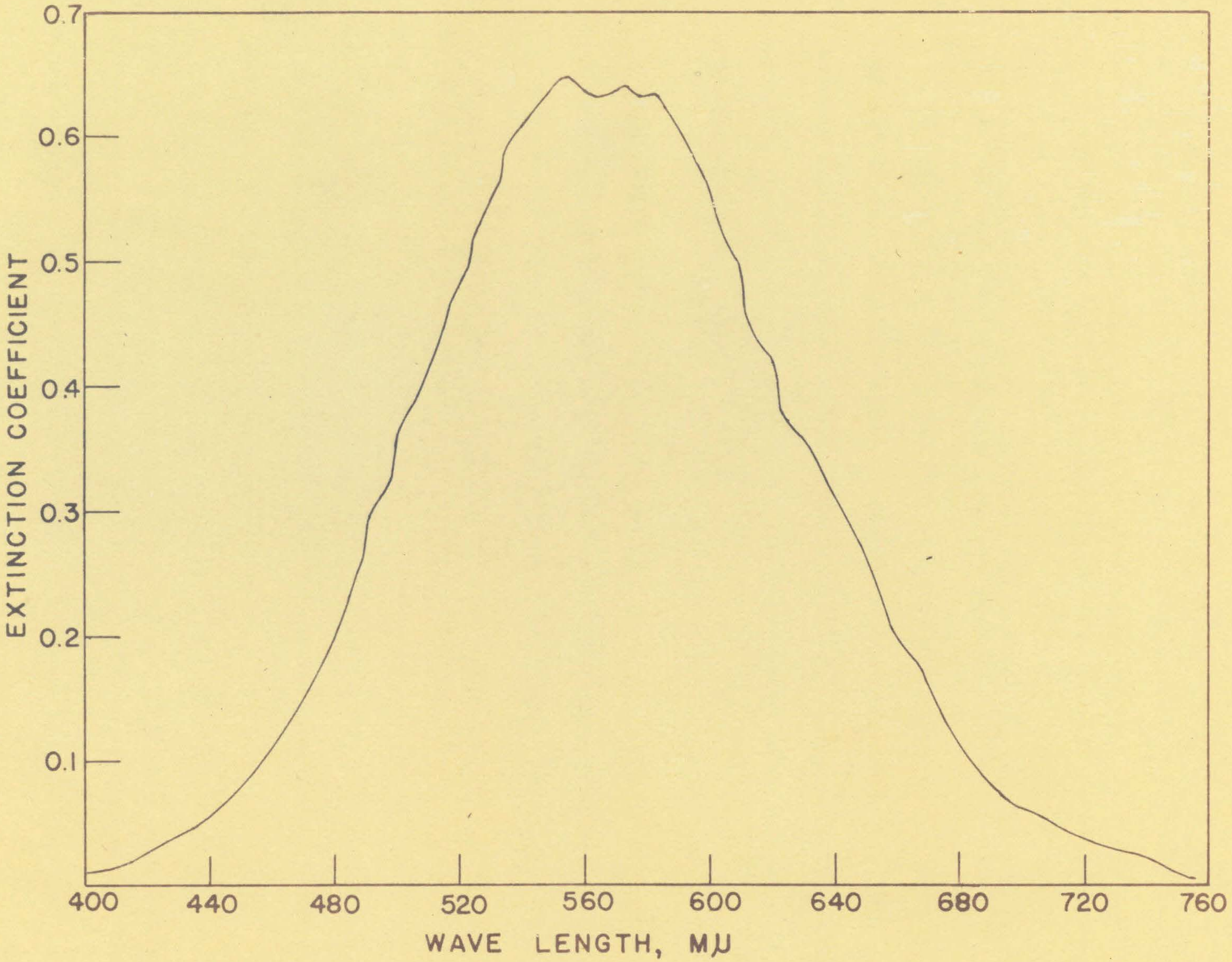


Figure 7. Absorption spectrum of azulene prepared from Se-dehydrogenation of parthenene (hexane solution).

Analysis of picrate of Se-azulene from partheniol:

Calculated for $C_{21}H_{21}N_3O_7$: C, 59.01%; H, 4.95%; N, 9.83%
Found: C, 58.68%; H, 4.75%; N, 9.87%

2.978 mg. substance gave 6.404 mg. carbon dioxide and 1.264 mg. water
2.840 mg. substance gave 0.254 ml. nitrogen at 23° C. and 745 mm Hg

3. Preparation of the styphnate (2,4,6-trinitroresorcinol addition product) of Se-azulene from partheniol

The styphnate of Se-azulene was prepared according to the general procedure used for the preparation of polynitro addition products. The melting point of the compound was found to be 110-111° C. Because the quantity of the styphnate obtained was small, it was not possible to carry out an analysis of the substance.

C. Conclusion

The azulene obtained from the selenium dehydrogenation of parthenene has not been identified; it is probably admixed with other azulenes.

Preliminary Qualitative Ozonization of Partheniol and Tetrahydroparthenene

I. Ozonization of partheniol

Five grams of partheniol was ozonized in glacial acetic acid. The ozonide was decomposed by hydrogenation in 1:1 acetic acid-ether with a platinium catalyst (Adams) at below 0° C. Because the decomposition of an ozonide with catalytic hydrogen is exothermic, the reaction mixture was cooled in an ice-salt bath during the first phase of the hydrogenation in order that a secondary reaction of "acid rearrangement" of the ozonide would not occur to any appreciable extent. The hydrogenation was later allowed to proceed at room temperature till the required amount of hydrogen was taken up. A test for formaldehyde in the gas wash bottle with dimedon reagent was positive, while a test for acetone with p-nitrophenylhydrazine was negative. It was thus shown that probably a methylene group was present in partheniol and, hence, one of the two double bonds in the compound is possibly exocyclic.

From the ozonized product was separated a neutral fraction by making the solution alkaline and extracting with ether. An acid fraction was obtained by acidifying the alkaline solution and extracting with ether. A qualitative test for methyl ketone in the neutral fraction was positive; a qualitative test for aldehyde with Schiff's reagent was also positive.

By distilling at 0.6 mm. Hg and 98-100° C., 0.5 g. of the neutral fraction was collected. A greater portion of the neutral fraction was not distillable. The amount of acid fraction was negligible.

A. Analysis of neutral fraction

1. Analysis for carbon and hydrogen

Calculated for $C_{15}H_{24}O_4$: C, 67.13%; H, 9.01%
$C_{14}H_{22}O_4$: C, 66.11%; H, 8.72%
Found: C, 66.74%; H, 8.69%

2.117 mg. substance gave 5.177 mg. carbon dioxide and 1.644 mg. water

2. Determination of active hydrogen and carbonyl group (Zerewitinoff)

25.166 mg. substance gave 1.90 ml. methane at STP; 4.05 ml. methane missing (STP)

Calculated for $C_{14}H_{22}O_4$ (254.3): 2.21 ml. methane at STP for 1 hydroxyl group; 4.46 ml. methane missing (STP) for 2 carbonyl groups

3. Determination of methyl ketone group

7.4 mg. substance used up 42.14 mg. iodine, equivalent to 1.90 or 2 CH_3CO- groups for $C_{14}H_{22}O_4$ (MW = 254.3)

4. Physical constants

$$n_D^{24^\circ} = 1.4762$$

$$d_{4^\circ}^{24^\circ} = 1.062$$

M_R, calculated for $C_{14}H_{22}O_4$: 66.20, for 1 hydroxyl group and 3 carbonyl groups
Found: 67.5

II. Ozonization of tetrahydroparthenene

Approximately 0.4 g. of tetrahydroparthenene was ozonized in carbon tetrachloride; the ozonide was decomposed by adding a small amount of water and heating to a boil in a water bath. A test for formaldehyde in the wash bottle with dimedon reagent was positive; a test for acetone with p-nitrophenylhydrazine was negative. It is thus indicated that a methylene group was probably present in tetrahydroparthenene. Hence, it is possible that in partheniol a tertiary alcohol group and a methyl group are attached to the same carbon atom.

Quantitative Determination of Methylene Group in Partheniol and in Tetrahydroparthenene by Ozonization

In preliminary qualitative ozonization experiments which were described in the previous section, it was indicated that one of the double bonds in partheniol is possibly exocyclic. It was also shown that probably the tertiary hydroxyl group and a methyl group are attached to the same carbon atom. In order to determine whether these preliminary observations are justified quantitative oxonization experiments were carried out; these experiments are described below.

I. Ozonization of partheniol

A 1.5-g. sample of partheniol was ozonized in 25 ml. of glacial acetic acid at 17° C. for 40 minutes (O_3 conc., 1.24 g./hr.). The formaldehyde was collected in a wash bottle containing water and the carbon dioxide liberated was absorbed in two ascarite tubes. At the completion of the ozonization, 50 ml. of water was introduced into the reaction flask without disconnecting the system. Decomposition of the ozonide was carried out by heating this aqueous solution at a bath temperature of 100° C. for 2 3/4 hours. A suspension of mercuric oxide in water was then added from a separatory funnel and the reaction mixture was heated in a boiling water bath for an additional hour.

When the reaction was complete, an excess of buffered dimedon reagent was added to the water in the wash bottle and the mixture was allowed to stand overnight. The amount of formaldehyde dimedon which precipitated out on standing was negligible. The quantity of carbon dioxide which was absorbed in the ascarite tubes was determined gravimetrically and was found to be 121 mg., expressed as formaldehyde. Theoretically, from 1.5 g. of partheniol, which is assumed to possess one exocyclic double bond, 205 mg. of formaldehyde should be formed. Experimentally, only 121 mg. of formaldehyde was obtained, thus accounting for 60 percent of an exocyclic double bond.

II. Ozonization of tetrahydroparthenene

A 0.85-g. sample of tetrahydroparthenene was ozonized in 25 ml. of glacial acetic acid for 14 minutes (O_3 conc., 1.24 g./hr.). The formaldehyde and carbon dioxide which were formed were determined gravimetrically. The amount of formaldehyde which was precipitated with dimedon was negligible; the quantity of carbon dioxide expressed as formaldehyde was 80 mg. Assuming the compound contains one exocyclic double bond, the theoretical amount of formaldehyde formed is 124 mg. Hence, 64 percent of the exocyclic double bond in tetrahydroparthenene was accounted for.

III. Conclusion

It was again indicated by quantitative ozonization that one of the double bonds in partheniol is probably exocyclic and thus gives rise to a methylene group. It is not known at this stage whether the methylene group is attached to the nucleus of the molecule as a separate unit, or is part of an isopropylene side chain.

As shown in the quantitative as well as the qualitative experiments, the tertiary hydroxyl group in partheniol is probably attached to the same carbon atom as a methyl group, thus accounting for the methylene group in tetrahydroparthenene.

Determination of the Position of the Hydroxyl Group in Partheniol

A scheme of reactions which was used for the determination of the position of the hydroxyl group in partheniol is essentially as follows. Partheniol is first saturated with hydrogen to form tetrahydropartheniol which is subsequently dehydrated into tetrahydroparthenene. As the hydroxyl group is probably on the same carbon atom as a methyl group (work described in previous section) there are three possible positions at which the double bond may be formed in the tetrahydro compound. It was thought that the double bond may be predominantly in a given position; in this case, by cleavage of the molecule at the double bond by means of ozonization, the major products of the cleavage may be obtained for study. By characterizing these products, it is possible to locate the hydroxyl group in partheniol.

In another series of experiments designed to determine the position of the hydroxyl group in partheniol, a chromic acid oxidation procedure was used. As in the ozonization experiments, characterization of the products of oxidation was desired in order to place the hydroxyl group.

I. Preparation of tetrahydropartheniol

In a typical experiment 32.8 g. of partheniol was hydrogenated in approximately 200 ml. of glacial acetic acid with 0.4 g. of platinium dioxide as catalyst. The reaction was carried out at room temperature and at a pressure slightly above atmospheric. When no further uptake of hydrogen was observed, the reaction was assumed complete. After the removal of the catalyst by filtration, the glacial acetic acid solution was concentrated under vacuum.

Qualitative tests indicated that esterification of partheniol had occurred during the hydrogenation. To hydrolyze the parthenyl acetate, approximately 100 ml. of a 0.5 N alcoholic solution of potassium hydroxide was added; the reaction mixture was heated for two hours in a water bath. After neutralization of the base, the alcohol was evaporated under vacuum. The crude tetrahydropartheniol was extracted with ether and the ether solution was dried over anhydrous sodium sulfate. The ether having been removed, the hydrogenated product was distilled under high vacuum; the main fraction of tetrahydropartheniol, 28.1 g., was distilled at 70-85° C. and 0.01 mm. Hg.

A. Analysis of tetrahydropartheniol

1. Analysis for carbon and hydrogen

Calculated for $C_{15}H_{28}O$: C, 80.29%; H, 12.58%
Found: C, 80.16%; H, 12.72%

2.424 mg. substance gave 7.209 mg. carbon dioxide and 2.707 mg. water

2. Physical constants

$n_D^{25.5^\circ} = 1.4820$

$d_{4^\circ}^{25.4^\circ} = 0.9342$

M_R, calculated = 68.60, for 1 hydroxyl group
Found = 68.47

II. Preparation of tetrahydroparthenene

A mixture of approximately 38.5 g. of tetrahydropartheniol and 24 g. of fused powdered potassium bisulfate was heated for 45 minutes at a bath temperature of about 160° C. After allowing the reaction mixture to cool, the crude dehydrated product was extracted with ether. The ether solution was washed, first, with a very dilute solution of sodium hydroxide, then, with water till the solution was free from alkali. After drying over sodium sulfate, the ether solution was filtered and the ether removed. Distillation of the crude hydrocarbon was carried out under high vacuum. The hydrocarbon was distilled three times, twice over potassium. The main fraction which was obtained from a final distillation over potassium was distilled at 59-64° C. and a pressure of 0.02 mm. Hg; a yield of 23 g. was obtained.

A. Analysis of tetrahydroparthenene

1. Analysis for carbon and hydrogen

Calculated for $C_{15}H_{26}$: C, 87.30%; H, 12.70%
Found: C, 87.31%; H, 12.83%

2.303 mg. substance gave 7.368 mg. carbon dioxide and 2.640 mg. water

2. Physical constants

$n_D^{25^\circ} = 1.4880$

$d_{4^\circ}^{25^\circ} = 0.9025$

M_R, calculated = 66.6, for one double bond
Found = 65.9

3. Hydrogenation

25.504 mg. substance and 6.799 mg. platinium dioxide in glacial acetic acid took up 2.77 ml. hydrogen at STP

Calculated for $C_{15}H_{26}O$: 2.77 ml. hydrogen at STP for 1 double bond
Found: 2.77 ml. hydrogen at STP; 1 double bond

III. Ozonization of tetrahydroparthenene (14)

A. An 18.2-g. sample of tetrahydroparthenene in approximately 40 ml. of glacial acetic acid was ozonized at about 15° C. for 3 hours. To decompose the ozonide, 18 g. of zinc dust suspended in a small amount of water was slowly added; the reaction temperature was kept at 50-70° C. for approximately 1/2 to 1 hour. A test for peroxides was made with titanic sulfate and dilute sulfuric acid; no peroxides were found. The excess zinc and zinc salts were removed by filtration on a sintered glass funnel. The acetic acid solution was neutralized with a slight excess of dilute potassium hydroxide and the neutral solution was extracted with several portions of ether. An acid fraction was obtained by acidifying the aqueous phase remaining from the ether extraction with dilute sulfuric acid and extracting with several portions of ether. The neutral and acid ether fractions were both thoroughly washed and dried over anhydrous sodium sulfate. After filtering and removing the ether, the neutral fraction was distilled at 0.125-0.150 mm. Hg; the fractions collected were redistilled at 5-50 μ.

1. First fractionation of neutral fraction at 0.125-0.150 mm. Hg

A	68-78° C.	6.4 g.
B	78-93° C.	1.4 g.
C	93-108° C.	2.4 g.
D	108-120° C.	2.8 g.

(a) Analysis of neutral fraction A for carbon and hydrogen

Calculated for $C_{14}H_{24}O$: C, 80.71%; H, 11.61%
Found: C, 83.83%; H, 12.51%

1.724 mg. substance gave 5.296 mg. carbon dioxide and 1.927 mg. water

(b) Analysis of neutral fraction B for carbon and hydrogen

Calculated for $C_{14}H_{24}O$: C, 80.71%; H, 11.61%
$C_{15}H_{26}O_2$: C, 75.58%; H, 11.00%
Found: C, 77.56%; H, 11.36%

3.098 mg. substance gave 8.805 mg. carbon dioxide and 3.145 mg. water

(c) Analysis of neutral fraction C for carbon and hydrogen

Calculated for $C_{15}H_{26}O_2$: C, 75.58%; H, 11.00%
Found: C, 75.17%; H, 11.37%

2.345 mg. substance gave 6.459 mg. carbon dioxide and 2.383 mg. water

2. Second fractionation of neutral fractions at 5-50 μ

1.	51-61° C.	2.1 g.
2.	61-76° C.	0.8 g.
3.	76-96° C.	1.3 g.
4.	96-135° C.	1.8 g.
5.	135-140° C.	3.0 g.
6.	residue	0.7 g.

(a) Analysis of neutral fraction 1

(i) Analysis for carbon and hydrogen

Calculated for $C_{14}H_{24}O$: C, 80.71%; H, 11.61%
$C_{15}H_{26}O_2$: C, 75.58%; H, 11.00%
Found: C, 83.48%; H, 12.99%

2.177 mg. substance gave 6.660 mg. carbon dioxide and 2.528 mg. water

(ii) Active hydrogen and carbonyl group determination (Zerewitinoff)

22.766 mg. substance gave 0.40 ml. methane at STP; 0.77 ml. methane missing (STP)

Calculated for $C_{14}H_{24}O$ (208.3): 2.45 ml. methane missing (STP) for 1 carbonyl group
$C_{15}H_{26}O_2$ (238.4): 4.28 ml. methane missing (STP) for 2 carbonyl groups

(iii) Methyl ketone group determination

21.7 mg. substance used up 20.96 mg. iodine; equivalent to 0.3 CH_3CO- group for $C_{15}H_{26}O_2$ (MW = 238) and 0.27 CH_3CO- group for $C_{14}H_{24}O$ (MW = 208)

(b) Analysis of neutral fraction 2

(i) Analysis for carbon and hydrogen

Calculated for $C_{14}H_{24}O$: C, 80.71%; H, 11.61%
$C_{15}H_{26}O_2$: C, 75.58%; H, 11.00%
Found: C, 81.59%; H, 12.92%

1.947 mg. substance gave 5.821 mg. carbon dioxide and 2.247 mg. water

(ii) Active hydrogen and carbonyl group determination (Zerewitinoff)

19.535 mg. substance gave 0.52 ml. methane at STP; 0.60 ml. methane missing (STP)

Calculated for $C_{14}H_{24}O$ (208.3): 2.10 ml. methane missing (STP) for 1 carbonyl group
$C_{15}H_{26}O_2$ (238.4): 3.67 ml. methane missing (STP) for 2 carbonyl groups

(iii) Methyl ketone group determination

14.0 mg. substance used up 7.74 mg. iodine; equivalent to 0.1 CH_3CO- group for $C_{15}H_{26}O_2$ (MW = 238) and 0.15 CH_3CO- group for $C_{14}H_{24}O$ (MW = 208.3)

(c) Analysis of neutral fraction 3

(i) Analysis for carbon and hydrogen

Calculated for $C_{14}H_{24}O$: C, 80.71%; H, 11.61%
$C_{15}H_{26}O_2$: C, 75.58%; H, 11.00%
Found: C, 77.47%; H, 11.99%

2.098 mg. substance gave 5.956 mg. carbon dioxide and 2.248 mg. water

(ii) Active hydrogen and carbonyl group determination (Zerewitinoff)

19.794 mg. substance gave 1.25 ml. methane at STP; 1.88 ml. methane missing (STP)

Calculated for $C_{14}H_{24}O$ (208.3): 2.13 ml. methane missing (STP) for 1 carbonyl group
$C_{15}H_{26}O_2$ (238.4): 1.87 ml. methane missing (STP) for 1 carbonyl group; 3.74 ml. methane missing (STP) for 2 carbonyl groups

(iii) Methyl ketone group determination

9.5 mg. substance used up 12.11 mg. iodine; equivalent to 0.4 CH_3CO- group for $C_{15}H_{26}O_2$ (MW = 238)

B. In another experiment, 23 g. of tetrahydroparthenene was ozonized in 60 ml. of glacial acetic acid. The solution was tested for unsaturation with a 5-percent solution of bromine in carbon tetrachloride; the test was negative indicating that the reaction was complete. For the reductive decomposition of the ozonide, the zinc-acetic acid method was used. The ozone reaction products were separated into a neutral and an acid fraction. From the distillation of the acid fraction at 145-165° C. and 75 μ pressure a 2.3-g. fraction was obtained.

Fractions from distillation of neutral fraction at 10-20 μ:

1.	60-80° C.	6.0 g.
2.	80-105° C.	3.5 g.
3.	105-120° C.	2.0 g.
4.	residue	2.6 g.

Both neutral and acid fractions showed a strong positive qualitative test for the aceto or methyl ketone group.

Investigation of the contents of the water wash bottle showed that only formaldehyde was present. The formaldehyde was identified by means of its dimedon derivative and its 2,4-dinitrophenylhydrazone derivative.

1. Carbonyl derivatives of the neutral fractions

Attempts to prepare a semicarbazone from the neutral fractions by means of an alcoholic acid-buffered solution of semicarbazide have been unsuccessful thus far. The preparation of a 2,4-dinitrophenylhydrazone also proved unsuccessful.

2. Absorption spectra of neutral ozone fractions

The spectra of the three neutral ozone fractions in ethanolic solutions were determined with the Beckman photoelectric spectrophotometer. All three samples showed maxima in the region 230-236 mμ, as shown below.

Neutral fractions	Position of maxima wave length, mμ
1. 60-80° C.	236.5
2. 80-105° C.	235
3. 105-120° C.	230

3. Hydrogenation of the carbonyl compound (neutral fraction)

Neutral fractions 2 and 3 were combined with a neutral ozone fraction from a previous ozonization. This combined fraction (10.3 g.) was hydrogenated in 100 ml. of absolute alcohol at room temperature under a pressure of 2.7 atmospheres. When no further drop in pressure was observed, the reaction was stopped. The catalyst was filtered out and the alcohol removed under reduced pressure. The remaining residue was then distilled under high vacuum; the three fractions collected are listed below.

Distillation at 50 μ:

1.	88-95° C.	0.6 g.
2.	95-115° C.	2.0 g.
3.	115-135° C.	4.6 g.

Fractions 2 and 3 were combined and taken as the principal alcohol fraction; this combined fraction was dehydrated to form a hydrocarbon which was subsequently dehydrogenated with sulfur. The procedures for these reactions are given in the following sections.

(a) Dehydration of the alcohol

A mixture of 6.5 g. of the alcohol (fractions 2 and 3 combined) and 4 g. of fused potassium acid sulfate was heated at a bath temperature of 200° C. for 1/2 hour. The reaction mixture was extracted with ether and the ether solution was dried over anhydrous sodium sulfate. The oil remaining after the removal of the solvent was fractionally distilled; the fractions collected are given below.

Distillation at 75 μ:

1.	90-115° C.	2.4 g.
2.	115-140° C.	0.9 g.

Analysis of fraction 2:

(1) Analysis for carbon and hydrogen

Calculated for $C_{15}H_{30}O_2$: C, 74.32%; H, 12.48%
Found: C, 73.99%; H, 12.44%

2.677 mg. substance gave 7.258 mg. carbon dioxide and 2.977 mg. water

(2) Active hydrogen and carbonyl group determination

19.712 mg. substance gave 2.36 ml. methane at STP; 0.95 ml. methane missing (STP)

Calculated for $C_{15}H_{30}O_2$ (242.4): 3.64 ml. methane missing (STP) for 2 carbonyl groups; 1.82 ml. methane missing (STP) for 1 carbonyl group

(b) Dehydrogenation with sulfur

A mixture of 2.4 g. of fraction 1 and 1.5 g. of sulfur was heated for 5 hours at a bath temperature of 230° C. The crude product was transferred into a micro claisen flask and distilled under vacuum. The distilled product was dissolved in petroleum ether and chromatographed on an activated alumina column. No trace of azulene was detected on the column.

4. Acid ozone fraction

Distillation of the acid ozone fraction was carried out at 75 μ and 145-165° C.; 2.3 g. was obtained. The acid fraction gave a positive qualitative test for methyl ketone, thus indicating that it is probably a keto acid. This fraction was combined with an acid fraction from a previous ozonization giving a total of 3.2 g.

(a) Degradation of the keto acid with potassium hypobromite (Haloform reaction)

A reagent solution containing 29 g. of potassium hydroxide, 6.8 ml. of bromine, and 170 ml. of water was prepared at 0° C. The keto acid (3.2 g.) was added to the potassium hypobromite reagent and the mixture was allowed to come to room temperature. The reaction mixture was agitated for two hours on a shaking machine after which the excess potassium hypobromite was decomposed with sodium bisulfite; the bromoform was removed by extraction with ether. The aqueous solution was then made acid and extracted with ether. The ether solution was thoroughly washed with water, dried over anhydrous sodium sulfate, and the solvent was distilled. The residue was combined with a crude acid fraction (less than 2 g.) which was obtained from a haloform reaction on a mixture of 6 g. of a neutral ozone fraction and 2.6 g. of a similar neutral fraction from a chromic-acid oxidation; qualitative tests showed that each of the latter fractions contained methyl ketone and aldehyde. Distillation of the combined acid fraction was carried out as shown below.

Distillation at 50 μ:

1.	100-140° C.	0.9 g.
2.	140-155° C.	0.3 g.
3.	155-170° C.	2.2 g.

(i) Analysis of fraction 1

Calculated for $C_{14}H_{24}O_3$: C, 69.96%; H, 10.07%
Found: C, 67.66%; H, 9.94%; Br, 6.13%; equivalent weight, 228

2.401 mg. substance gave 5.953 mg. carbon dioxide and 2.132 mg. water
6.379 mg. substance gave 0.919 mg. silver bromide
10.275 mg. substance required 4.49 ml. 0.01 N sodium hydroxide

(ii) Analysis of fraction 3

Calculated for $C_{14}H_{23}O_4Br$: C, 50.16%; H, 6.92%; Br, 23.84%
Found: C, 49.59%; H, 7.47%; Br, 29.53%; equivalent weight, 192; saponification equivalent, 129

2.565 mg. substance gave 4.661 mg. carbon dioxide and 1.712 mg. water
6.945 mg. substance gave 4.819 mg. silver bromide
12.569 mg. substance required 6.54 ml. 0.01 N sodium hydroxide
84.1 mg. substance saponified 35 minutes at 125° C. with potassium hydroxide in diethylene glycol required 6.50 ml. 0.1 N hydrochloric acid

(b) Reaction of dicarboxylic acid (acid fraction 3) with acetic anhydride (Blanc's reaction (15))

The bromodicarboxylic acid (acid fraction 3), about 400 mg., was debrominated with 18 ml. of a 1 N alcoholic solution of potassium hydroxide. The alkali was neutralized with dilute sulfuric acid and the alcohol was removed under reduced pressure. After acidifying with dilute sulfuric acid the residue was extracted with ether; the ether extract was washed with three small portions of water, dried over anhydrous sodium sulfate and the ether was removed under reduced pressure. An attempt to hydrogenate the residual liquid in glacial acetic acid with platinium dioxide as catalyst resulted in the uptake of only 2 ml. of hydrogen. The dicarboxylic acid was recovered by filtering out the catalyst and removing the glacial acetic acid under vacuum. About 1 ml. of acetic anhydride was then added to the recovered acid and the mixture was refluxed for an hour. The mixture was transferred to a micro claisen flask and the acetic acid and acetic anhydride were removed under the reduced pressure of an aspirator. One milliliter of absolute ether was used to wash out the acetic anhydride in the side arm of the micro claisen flask; the ether was subsequently removed under vacuum. The remaining oil was distilled at a bath temperature of 240° C. and a pressure of 0.5 mm. Hg. A drop of oil was obtained and was analyzed.

Analysis:

Calculated for $C_{13}H_{20}O$ (cyclic ketone): C, 81.20%; H, 10.48%
Found: C, 54.18%; H, 8.03%

2.847 mg. substance gave 5.653 mg. carbon dioxide and 2.044 mg. water

C. Since the results obtained from the Blanc reaction described above were not conclusive the experiment was repeated. A 10.5-g. sample of tetrahydroparthenene was ozonized in 20 ml. of glacial acetic acid for 1 1/2 hour (1.45 g. O_3/ hr.). Since the acid fraction was desired the ozonide was decomposed with a 7-percent solution of hydrogen peroxide by heating in a water bath for an hour. Decomposition of the excess hydrogen peroxide was carried out by heating for an additional 1/2 hour in the presence of traces of platinium black. The mixture was concentrated in order to remove the excess acid. A neutral and an acid fraction were obtained by making the concentrate basic and acid respectively and extracting with ether. On testing the neutral fraction with Schiff's reagent for aldehyde a positive reaction was obtained; the oxidation was apparently incomplete. The neutral fraction was thus further reacted with a 5-percent solution of hydrogen peroxide in glacial acetic acid for an hour in a hot water bath with vigorous stirring. The excess peroxide was again decomposed with traces of platinium black and the mixture was concentrated and separated into a neutral and an acid fraction. The total acid fraction obtained was 2.5 g.; the neutral fraction, 4.5 g. Distillation of the acid fraction was carried out as shown below.

Distillation at 75 μ:

A.	176-190° C.	0.65 g.
B.	190-210° C.	0.5 g.

Analyses for carbon and hydrogen:

Fraction A:

Calculated for $C_{15}H_{26}O_3$: C, 70.82%; H, 10.30%
$C_{14}H_{24}O_4$: C, 65.60%; H, 9.44%
Found: C, 68.36%; H, 9.95%

2.098 mg. substance gave 5.256 mg. carbon dioxide and 1.866 mg. water

Fraction B:

Calculated for $C_{14}H_{24}O_4$: C, 65.60%; H, 9.44%
Found: C, 66.51%; H, 9.70%

2.074 mg. substance gave 5.055 mg. carbon dioxide and 1.798 mg. water

1. Reaction with sodium hypobromite (Haloform reaction)

Fractions A and B were reacted separately with sodium hypobromite (1.7 g. NaOH, 2 g. Br_2, and 23 ml. water) for 2 hours. The excess sodium hypobromite was decomposed with a small amount of sodium bisulfite. After removing the neutral fraction containing bromoform the alkaline solution was acidified with sulfuric acid and an acid fraction was extracted with ether.

The acid fractions obtained from original fractions A and B were distilled separately. Distillation of fraction A at 10 μ and a bath temperature of 190-200° C. gave 0.3 g. of oil; the distillation of fraction B at the same pressure and at a bath temperature of 200-230° C. gave 0.15 g. of oil.

Analysis of distillate from fraction A:

Calculated for $C_{14}H_{24}O_4$: C, 65.60%; H, 9.44%
Found: C, 64.34%; H, 9.52%

2.181 mg. substance gave 5.143 mg. carbon dioxide and 1.855 mg. water

2. Reaction of dicarboxylic acid with acetic anhydride

A mixture of 0.3 g. of dicarboxylic acid from fraction A and 0.5-0.7 ml. of acetic anhydride was heated in a sealed Carius tube for 1/2 hour at 240° C. (bath temperature). The cooled tube was opened and its contents was transferred into a micro-claisen flask with ether. The acetic anhydride was removed and the remaining oil was distilled under high vacuum. A fraction of approximately 50 mg. which distilled at 10 μ pressure and a bath temperature of 200-210° C. was obtained.

Analysis for carbon and hydrogen:

Calculated for $C_{14}H_{24}O_4$ (acid): C, 65.60%; H, 9.44%
$C_{14}H_{22}O_3$ (anhydride): C, 70.55%; H, 9.30%
$C_{13}H_{20}O$ (ketone): C, 81.20%; H, 10.48%
Found: C, 68.17%; H, 9.17%

2.147 mg. substance gave 5.363 mg. carbon dioxide and 1.759 mg. water

3. Conclusion

The analysis of the product obtained from Blanc's reaction on the dicarboxylic acid shows that it is probably a mixture of the original acid and its anhydride. Since a ketone was not formed from the dicarboxylic acid, it is indicated that the hydroxyl group in partheniol is situated in the 5-membered ring.

IV. Oxidation of tetrahydropartheniol with chromic acid (16)

A 22.4-g. sample of tetrahydropartheniol in 112 ml. of glacial acetic acid was treated dropwise with a solution of 19.5 g. of chromic trioxide in a mixture of 112 ml. of water and 240 ml. of glacial acetic acid. The addition of the oxidizing agent was completed in an hour; the oxidation, in three hours. The volatile products were steam distilled; the distillate was extracted with ether and the ether solution was thoroughly shaken with an aqueous solution of sodium carbonate. After this treatment the ether solution was washed with water till neutral, dried over anhydrous sodium sulfate, filtered and the ether was removed. A crude neutral fraction of 14.8 g. was obtained. This fraction was distilled twice; the final distillation at 20 μ (0.02 mm. Hg) gave the following fractions.

Distillation at 20 μ:

1.	57-70° C.	2.6 g.
2.	70-85° C.	3.8 g.
3.	85-95° C.	3.3 g.

Analysis of fraction 2:

Found: C, 82.86%; H, 13.34%

2.001 mg. substance gave 6.080 mg. carbon dioxide and 2.385 mg. water

Qualitative tests for the methyl ketone or aceto- (CH_3CO-) group showed that fraction 1 was strongly positive while fractions 2 and 3 were weakly positive. A qualitative test for the carbonyl group with azobenzenephenylhydrazine sulfonic acid showed fraction 1 to be strongly positive; fractions 2 and 3 were also positive.

A. Absorption spectra of the neutral fractions

The absorption spectra of the neutral fractions were recorded with a Beckman photoelectric spectrophotometer, using absolute alcohol as the solvent. The nature of the absorption spectra of the three neutral fractions are as shown.

Neutral fractions	Position of maxima wave length, mμ
1. 57-70° C.	no maxima
2. 70-85° C.	293
3. 85-95° C.	286

B. Carbonyl derivatives of the neutral fractions

Attempts to prepare a semicarbazone from the neutral fractions by means of an alcoholic, acid-buffered solution of semicarbazide or an alcoholic-pyridine solution of semicarbazide have proved unsuccessful thus far.

The preparation of a 2,4-dinitrophenylhydrazone has likewise proved unsuccessful.

C. Hydrogenation of the neutral fraction

Approximately 6.6 g. of a neutral fraction (ketone fractions 2 and 3 combined) was hydrogenated in 60 ml. of absolute alcohol under 2.4 atmospheres of pressure with 6 g. of Raney nickel as catalyst. A total of 0.15 moles of hydrogen was taken up. The catalyst was filtered out and the filtrate containing the hydrogenated product was concentrated. The alcohol obtained from the hydrogenation was fractionally distilled under high vacuum.

Distillation at 100 μ (0.1 mm. Hg):

1.	63-70° C.	0.9 g.
2.	70-80° C.	3.55 g.

1. Analysis of fraction 2

(a) Analysis for carbon and hydrogen

Calculated for $C_{14}H_{26}O$: C, 79.93%; H, 12.46%
Found: C, 79.89%; H, 12.12%

2.018 mg. substance gave 5.908 mg. carbon dioxide and 2.186 mg. water

(b) Optical rotation

$$[\alpha]_D^{26^\circ} = 15.7^\circ \text{ (Conc. = 1.02\%, in absolute alcohol)}$$

2. Dehydration of the alcohol with potassium acid sulfate

A mixture of 4.3 g. of combined fractions 1 and 2 and 2.9 g. of potassium acid sulfate was heated for 35 minutes at 200-210° C. The hydrocarbon which was formed was directly distilled from the reaction flask at 80-95° C. and a pressure of 0.5 mm. Hg; 3.5 g. of light blue oil was obtained.

3. Dehydrogenation of the hydrocarbon

A mixture of the hydrocarbon (3.5 g.) and 2.4 g. of sulfur was heated for 4 hours at 230° C. After the evolution of hydrogen sulfide had ceased, the reaction product was directly distilled at 90-100° C. and 50 μ (0.05 mm. Hg); a 1.5-g. fraction was collected.

A 1.1-g. sample of this substance was further dehydrogenated by heating with 0.3 g. of selenium at 300° C. for 5 hours. The crude product was transferred into a claisen flask and distilled; 0.6 g. of slightly blue distillate was obtained. No addition product with trinitrobenzene could be prepared from this fraction; the amount of azulene present was evidently not more than a trace. In order to isolate this small quantity of azulene, the entire fraction was dissolved in petrol ether and chromatographed on a column of activated alumina. A diffuse zone of azulene, which was formed on the column was eluted with a petrol ether-benzene mixture. The chromatographic procedure was repeated three times. The solvent mixture was distilled from the final eluate and the azulene recovered was dissolved in purified hexane. The absorption spectrum of the purified azulene in hexane, as recorded with a Beckman photoelectric spectrophotometer, is characterized by a principal maximum at 580 mμ with three other maxima at 540, 635, and 672 mμ, as shown in Figure 8. The azulene has not been identified.

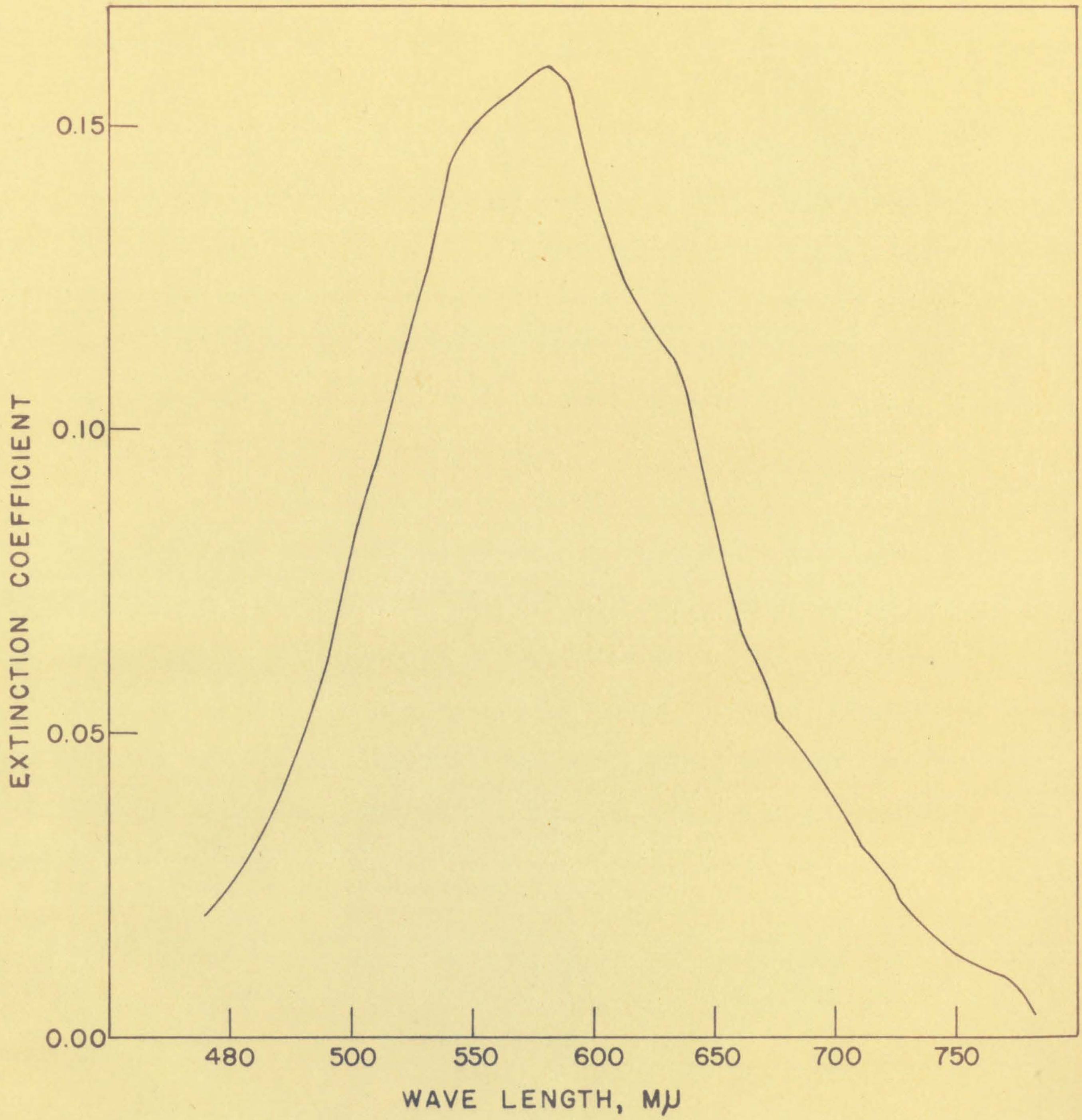


Figure 8. Absorption spectrum of azulene prepared from neutral fraction from chromic acid oxidation of tetrahydropartheniol (hexane solution).

Determination of the Positions of the Double Bonds

I. Partial ozonization of partheniol in petroleum ether

Twenty grams of partheniol was ozonized in 5-g. portions in purified petroleum ether at about 10° C. The ozonization time required for the cleavage of one double bond was determined by calculations. During the ozonization, a portion of the ozonide precipitated out as a gelatinous mass. At the completion of the ozonization, the solvent was recovered and used for the ozonization of the next 5-g. sample.

The ozonide was decomposed immediately after ozonization with water, zinc dust and traces of silver nitrate and hydroquinone. Decomposition at the boiling point of water was carried out for 2.5-3.0 hours; the reaction mixture was allowed to stand overnight at room temperature. The ozone reaction products were separated into a neutral and an acid fraction. By continuous extraction an additional 2 g. of neutral fraction was recovered from the mother liquor. The neutral fractions gave positive methyl ketone and aldehyde tests.

Distillation of neutral fraction at 10 μ:

1.	98-140° C.	4.9 g.
2.	140-160° C.	1.2 g.

Refractionation of neutral fraction 1 at 5 μ:

A.	85-92° C.	0.6 g.
B.	92-110° C.	0.9 g.
C.	110-130° C.	2.75 g.

Distillation of recovered neutral fraction at 40-60 μ:

a.	75-95° C.	1.4 g.
b.	95-120° C.	0.4 g.

A. Analysis of neutral fractions

1. Fraction A

(a) Analysis for carbon and hydrogen

Calculated for $C_{15}H_{24}O_3$: C, 71.39%; H, 9.59%
Found: C, 72.58%; H, 9.30%

1.951 mg. substance gave 5.189 mg. carbon dioxide and 1.622 mg. water

(b) Active hydrogen and carbonyl group determination (Zerewitinoff)

11.047 mg. substance gave 1.18 ml. methane at STP; 1.98 ml. methane missing (STP)

Calculated for $C_{15}H_{24}O_3$ (252.3): 0.98 ml. methane at STP for 1 hydroxyl group; 1.96 ml. methane missing (STP) for 2 carbonyl groups

(c) Methyl ketone group determination

11.1 mg. substance used up 37.82 mg. iodine; equivalent to 1.1 CH_3CO-groups for $C_{15}H_{24}O_3$ (MW = 252)

(d) Physical constants

$$n_D^{25^\circ} = 1.4962$$

$$d_{4^\circ}^{25^\circ} = 1.028$$

M_R, calculated: 70.35 ($C_{15}H_{24}O_3$), for 1 hydroxyl group, 1 double bond, and 2 carbonyl groups
Found: 71.78

2. Fraction B

(a) Analysis for carbon and hydrogen

Calculated for $C_{15}H_{24}O_3$: C, 71.39%; H, 9.59%
$C_{14}H_{22}O_2$: C, 75.63%; H, 9.97%
Found: C, 73.79%; H, 9.70%

2.119 mg. substance gave 5.730 mg. carbon dioxide and 1.836 mg. water

(b) Active hydrogen and carbonyl group determination (Zerewitinoff)

12.440 mg. substance gave 1.27 ml. methane at STP; 2.45 ml. methane missing (STP)

Calculated for $C_{15}H_{24}O_3$ (252.3): 1.1 ml. methane at STP for 1 hydroxyl group; 2.5 ml. methane missing (STP) for 2 carbonyl groups

(c) Methyl ketone group determination

26 mg. substance used up 110.3 mg. iodine; equivalent to 1.4 CH_3CO-groups for $C_{15}H_{24}O_3$ (MW = 252)

12.4 mg. substance used up 50.89 mg. iodine; equivalent to 1.36 CH_3CO-groups for $C_{15}H_{24}O_3$ (MW = 252)

(d) Physical constants

$n_D^{25°} = 1.4992$

$d_{4°}^{24°} = 1.031$

M_R, calculated: 70.35 ($C_{15}H_{24}O_3$), for 1 hydroxyl group, 1 double bond, and 2 carbonyl groups

Found: 71.77

3. Fraction C

(a) Analysis for carbon and hydrogen

Calculated for $C_{15}H_{24}O_3$: C, 71.39%; H, 9.59%

Found: C, 72.23%; H, 9.62%

2.443 mg. substance gave 6.466 mg. carbon dioxide and 2.101 mg. water

(b) Active hydrogen and carbonyl group determination (Zerewitinoff)

10.913 mg. substance gave 1.21 ml. methane at STP; 2.30 ml. methane missing (STP)

Calculated for $C_{15}H_{24}O_3$ (252.3): 0.97 ml. methane at STP for 1 hydroxyl group; 1.94 ml. methane missing (STP) for 2 carbonyl groups

(c) Hydrogenation

23.927 mg. substance took up 7.94 ml. hydrogen at STP

Calculated for $C_{15}H_{24}O_3$ (252): 6.38 ml. hydrogen at STP for 2 carbonyl groups and 1 double bond, 8.50 ml. if tertiary hydroxyl group was reduced

Found: $F_{3.74} = F_4$

(d) Physical constants

$n_D^{25°} = 1.4960$

$d_{4°}^{24°} = 1.033$

M_R, calculated: 70.35 ($C_{15}H_{24}O_3$), for 1 hydroxyl group, 1 double bond, and 2 carbonyl groups

Found: 71.43

4. Fraction a

(a) Analysis for carbon and hydrogen

Calculated for $C_{15}H_{24}O_3$: C, 71.39%; H, 9.59%
Found: C, 71.61%; H, 8.88%

2.053 mg. substance gave 5.387 mg. carbon dioxide and 1.629 mg. water

(b) Methyl ketone determination

14.0 mg. substance used up 66.25 mg. iodine; equivalent to 1.6 CH_3CO-groups for $C_{15}H_{24}O_3$ (MW = 252)

5. Fraction b

Calculated for $C_{15}H_{24}O_3$: C, 71.39%; H, 9.59%
Found: C, 68.50%; H, 9.27%

2.206 mg. substance gave 5.538 mg. carbon dioxide and 1.827 mg. water

B. Degradation of methyl ketone group in fraction C with potassium hypobromite

Fraction C was reacted with a solution of potassium hypobromite in the usual manner. From the reaction 1.3 g. of crude acid was obtained. An attempt to distill the hydroxyl acid under high vacuum was unsuccessful because the compound decomposed during the distillation.

Discussion

Partheniol has been found to possess two double bonds by hydrogenation experiments in glacial acetic acid with platinium dioxide as catalyst. The hydrogenation of dihydropartheniol in methylcyclohexane-acetic acid showed, however, an uptake of two moles of hydrogen. This is probably caused by the reduction of the hydroxyl group. Such a reaction has been reported in experiments on guaiol (17,18); it was found that on hydrogenating guaiol in cyclohexane with platinium dioxide one mole of hydrogen was taken up, while on hydrogenating in glacial acetic acid with platinium black as catalyst two moles of hydrogen was consumed.

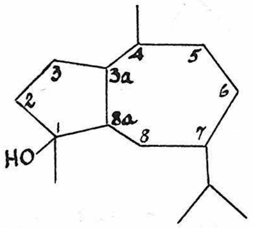
Parthenene which contains three double bonds did not show any maxima or minima in its absorption spectrum, as determined with the Beckman photoelectric spectrophotometer; it is thus indicated that the compound does not possess any conjugated double bond. The determination of molecular refractivity showed, however, an exaltation of 0.37. It is possible that the exaltation is due to a semicyclic double bond; such small exaltations of semicyclic double bonds have been reported for β-pinene and for camphene which give an exaltation of 0.2 and 0.5, respectively.

Azulenes have been formed from parthenene by selenium and sulfur dehydrogenation. By selenium dehydrogenation an unknown violet azulene was obtained. The melting points of the polynitro derivatives of the Se-azulene are as follows: trinitrobenzene addition product, m.p. 103-104° C.; picrate, m.p. 105.5-107.5° C.; styphnate, m.p. 110-111° C. The absorption spectrum of Se-azulene is characterized by three maxima at 553, 567, 578 mμ and undulations at 490, 500, 533, 603, 616, 627, and 664 mμ.

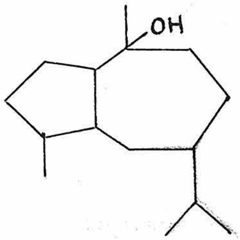
Plattner (13), in a comprehensive study on azulenes, found that the absorption spectrum of an azulene is influenced by the introduction of alkyl substituents. Plattner further states that the position rather than the size of the alkyl substituent is responsible for variations in the absorption of the azulene. By the comparision of the absorption bands of various violet azulenes, Plattner was able to deduce that Se-guaiazulene, a violet azulene, is probably substituted in the 2,4,7-positions. Since the violet azulenes investigated by Plattner have been found to possess a 2-substituent, it may be speculated that , as the Se-azulene from partheniol is violet in color, possibly a shift of the substituent from the 1-position to the 2-position had occurred during the process of dehydrogenation. It is also possible that in the Se-dehydrogenation of partheniol, a mixture of azulenes rather than a single azulene was formed.

The azulene obtained from the sulfur dehydrogenation of parthenene has been characterized by various polynitro derivatives and by its absorption spectrum and has been identified as S-guaiazulene. From this finding the configuration of partheniol has been elucidated as 1,4-dimethyl-7-isopropylcyclopentacycloheptane (I) as in guaiol. With the configuration known the positions of the hydroxyl group and the two double bonds remained to be determined. This problem has been approached by means of ozone and chromic acid oxidation experiments.

From the detection of a methylene group in the preliminary ozonization of tetrahydroparthenene it was deduced that the hydroxyl group is probably situated on the same carbon atom as a methyl group; in this case, the hydroxyl group is situated either in the 1- or 4-position in the partheniol configuration or in the isopropyl side chain as shown in diagrams III, IV, and V.



III



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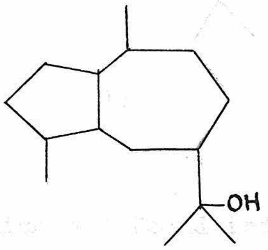
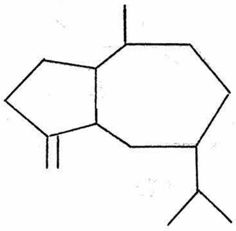


V

Formula V may be eliminated, however, because no acetone was detected. Confirmation of this deduction has been furnished by the subsequent quantitative determination of the methylene group in tetrahydroparthenene by an ozonization procedure in which 64 percent of an exocyclic double bond was accounted for. In the dehydration of tetrahydropartheniol the double bond which is formed could be situated in three possible positions; the three possible structures of tetrahydroparthenene are as presented in diagrams VI, VII, and VIII, if the hydroxyl group is originally in the 1-position and are as given in diagrams IX, X, and XI, if the hydroxyl group is originally in the 4-position. It



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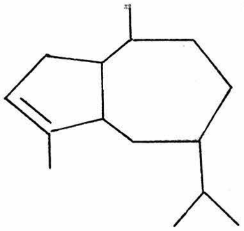

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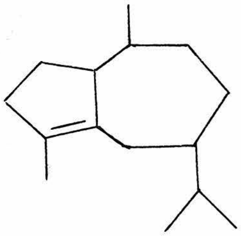

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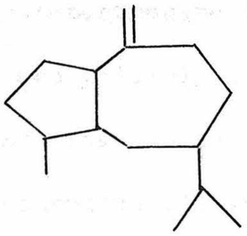

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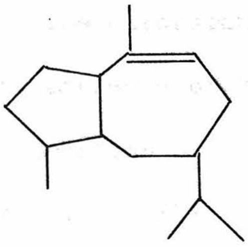

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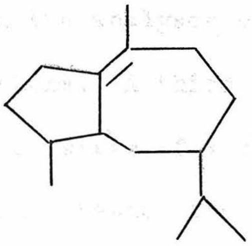
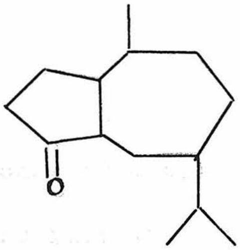


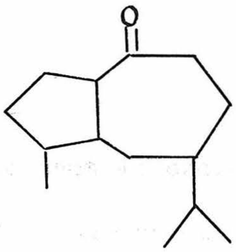
XI

is plausible that 64 percent of a methylene group which was found indicates a predominance of the exocyclic double bond. It is also conceivable that the value 64 percent may be too low; in consideration of the experimental error in general quantitative ozonization procedures this fairly wide discrepancy is acceptable.

In the ozonization experiments on tetrahydroparthenene formaldehyde and methyl ketone have been detected; it is thus substantiated that the hydroxyl group and a methyl group are attached to the same carbon atom. From a study of the analytical data it appears that one or the other of the two cyclic ketones, XII and XIII, depending on the position of the hydroxyl group, probably

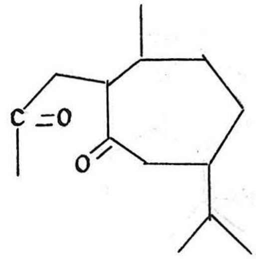


XII

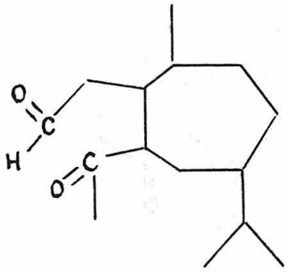


XIII

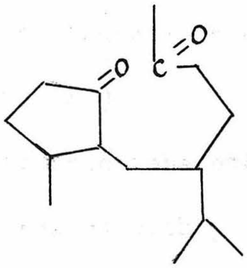
constitutes two fractions, 1 and 2, which were obtained from the ozonization of tetrahydroparthenene (p. 51). The discrepancies in the analyses of these fractions are possibly due to the presence of hydrocarbons. A third fraction from the ozonization experiment (fraction 3) probably consists of a mixture of carbonyl compounds XIV and XV or XVI and XVII, depending whether the hydroxyl group in partheniol is in position 1 or 4.



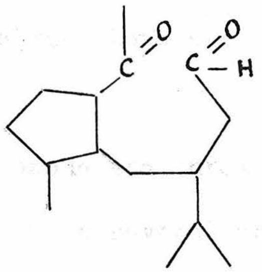
XIV



XV

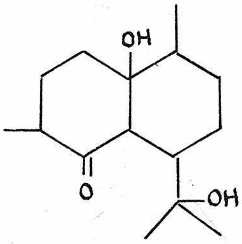


XVI

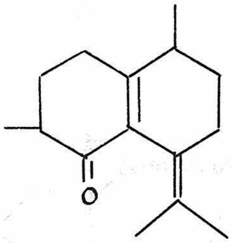


XVII

The presence of active hydrogen in the neutral ozone fractions of tetrahydroparthenene indicates that the aldehyde group probably was partially reduced to an alcohol group during the course of the reduction of the ozonide with zinc and acetic acid. The spectra of the neutral ozone fractions in alcohol showed maxima at 230-236.5 mμ; the position of the maxima is lower than that usually shown by a carbonyl group, which is about 280 mμ. It has been found in ozonization experiments on guaiol (19) that the dihydroxyl ketone, XVIII, showed a maximum at 281.5 mμ in an alcoholic solution, whereas, the corresponding dehydrated compound, XIX, which is an unsaturated ketone, gave a spectrum in alcohol with a maximum at 265 mμ. It is possible that the absorption spectra of the neutral ozone fractions showed maxima at lower wave lengths because of tautomeric equilibrium between keto and enol forms of the carbonyl compound (20).



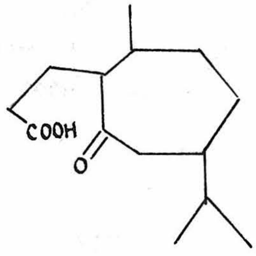
XVIII



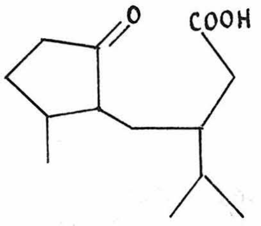
XIX

From neutral fractions which were from ozone and chromic acid oxidations and which were treated with potassium hypobromite several acid fractions showing the presence of bromine were obtained. The analysis of the first fraction gave 67.66 percent carbon, 9.94 percent hydrogen, and 6.13 percent bromine (p. 57); excluding the small amount of bromine, the data agree reasonably well with the empirical formula, $C_{14}H_{24}O_3$ (69.96% C, 10.07% H). Taking into consideration the finding that the tertiary hydroxyl group is probably on the same carbon atom as a methyl group, formulae XX and XXI may be proposed for the

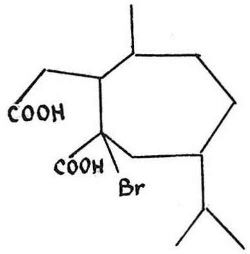
$C_{14}H_{24}O_3$ compound. For the third acid fraction (fraction 3, p. 57) the formula of $C_{14}H_{23}O_4Br$, XXII and XXIII, may be proposed.



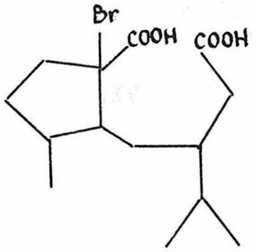
XX



XXI

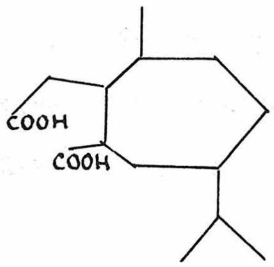


XXII

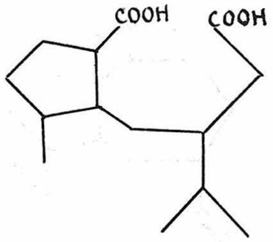


XXIII

Ozonization and oxidation products have not been able to elucidate whether the hydroxyl group in partheniol is in the 1- or 4-position. To determine the exact position of the hydroxyl group Blanc's reaction was carried out on the dicarboxylic acid which was obtained from the oxidation of tetrahydroparthenene; the structure of the acid is either XXIV or XXV, depending on the position of the hydroxyl group. Blanc's rule states that when dicarboxylic acids are heated with acetic anhydride and the resulting product slowly distilled, ketones are obtained from 1,6- or 1,7-dicarboxylic acids



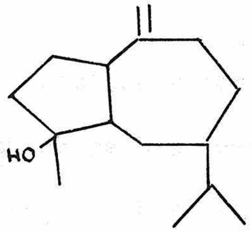
XXIV



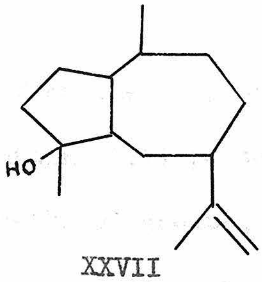
XXV

while anhydrides are formed from 1,4- and 1,5-dicarboxylic acids. Accordingly, if the two carboxylic groups in the dicarboxylic acid from tetrahydroparthenene were situated in the 7-membered ring a ketone would be obtained; if the two carboxylic groups were situated in the 5-membered ring an anhydride would result. Apparently, no ketone was obtained from the reaction of the dicarboxylic acid with acetic anhydride; this indicates that the carboxylic groups in the dicarboxylic acid are not situated in the 7-membered ring but are situated in the 5-membered ring as in structure XXIV. Hence, it probable that the structure of tetrahydroparthenіol is as shown in diagram III, with the hydroxyl group at the 1-position.

The presence of a methylene group has been detected in the ozonization experiments on partheniol, thus indicating that one of the two double bonds is exocyclic. As the hydroxyl group is probably in the 1-position, the position of the exocyclic double bond is restricted to two positions as shown in diagrams XXVI and XXVII.



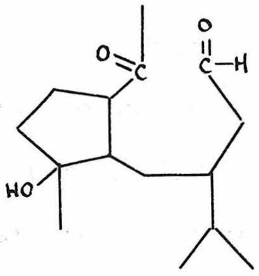
XXVI



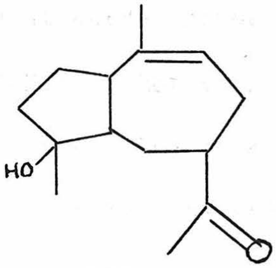
XXVII

Further indication of an exocyclic double bond was shown in the partial hydrogenation of partheniol in alcohol with Raney nickel catalyst. The relative rapid uptake of one mole of hydrogen is indicative of an exocyclic double bond.

In the partial ozonization of partheniol in petroleum ether which was carried out for the purpose of the selective cleavage of the exocyclic double bond, it was found that the neutral fraction is probably a mixture of $C_{15}H_{24}O_3$ and $C_{14}H_{22}O_2$. The structure of $C_{15}H_{24}O_3$ is probably as given in diagram XXVIII; the formula $C_{14}H_{22}O_2$ may be represented by structure XXIX. The formation of a mixture of products, namely, $C_{15}H_{24}O_3$ and $C_{14}H_{22}O_2$, from the partial ozonization experiment in petroleum ether shows that the degradation products resulting from the cleavage of both the exocyclic and cyclic double bonds were obtained.

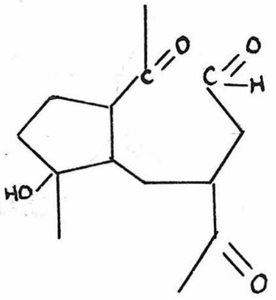


XXVIII

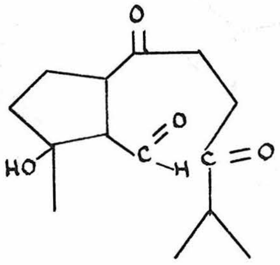


XXIX

A neutral fraction which was obtained from the complete oxidation of partheniol with ozone has been found to contain 66.74 percent carbon, 8.69 percent hydrogen, one hydroxyl group, two carbonyl groups, and two methyl ketone groups. Two empirical formulae, $C_{15}H_{24}O_4$ and $C_{14}H_{22}O_4$, agree reasonably well with the carbon and hydrogen values. The formula, $C_{15}H_{24}O_4$, cannot represent, however, a possible ozonized product of partheniol because for two cyclic double bonds and one hydroxyl group the compound should contain five atoms of oxygen. The formula, $C_{14}H_{22}O_4$, which indicates one exocyclic double bond, is acceptable and is structurally as shown in XXX and XXXI, depending on the position of the exocyclic double bond. These structures are in

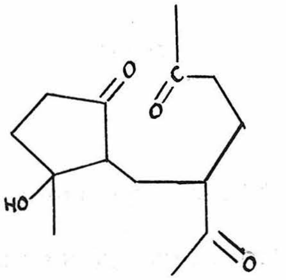


XXX

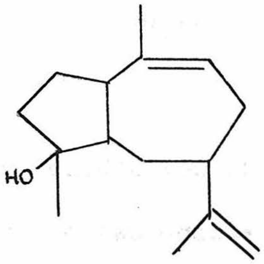


XXXI

accordance with the Zerewitinoff determination which showed the presence of at least two carbonyl groups. Formula XXXI is discarded since it does not contain two methyl ketone groups and formula XXXII is not considered because an aldehyde test with Schiff's reagent was positive. The remaining formula, XXX, indicates that the structure of partheniol is as represented in XXXIII.

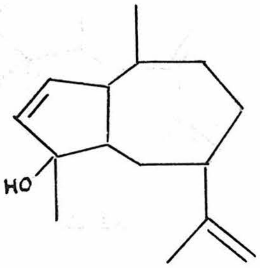


XXXII

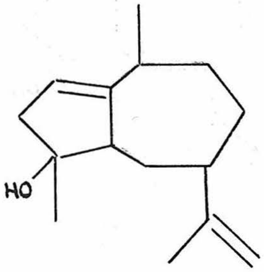


XXXIII

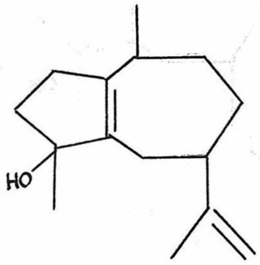
Structures XXXIV, XXXV, XXXVI, XXXVII, and XXXVIII may be eliminated because no conjugated double bond system is present in parthenene. The absence of a conjugated double bond in parthenene has been indicated by spectral studies.



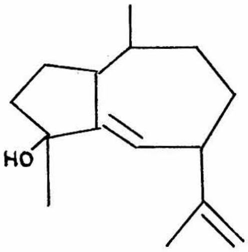
XXXIV



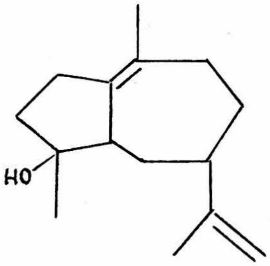
XXXV



XXXVI

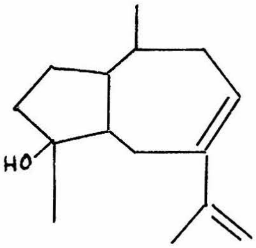


XXXVII

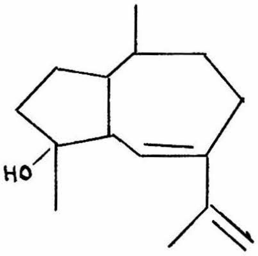


XXXVIII

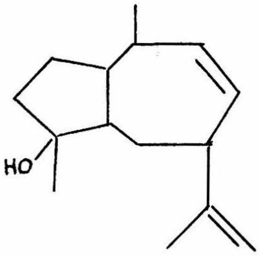
This is also shown by the difficulty in the dehydration of partheniol. Since it has been shown by qualitative tests that the two double bonds in partheniol are not conjugated formulae XXXIX and XL may also be eliminated. Structure XLI is not considered because the oxidized product of such a compound would not give two methyl ketone groups which have been found in the degradation



XXXIX



XL



XLI

products from the ozonization of partheniol. The remaining possible structure, XXXIII, is in agreement with the oxidized product XXX and hence may be proposed as the probable structure for partheniol.

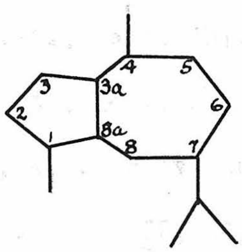
Summary

1. Partheniol, a sesquiterpene alcohol (m.p. 127-128° C.), has been isolated from guayule.

2. Partheniol has been found to possess two double bonds, one of which is exocyclic.

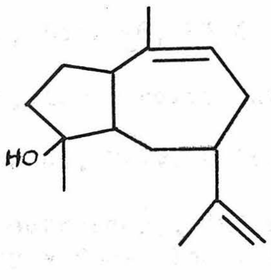
3. An unknown azulene or a mixture of azulenes has been obtained from the selenium dehydrogenation of parthenene.

4. S-guaiazulene has been obtained from the sulfur dehydrogenation of parthenene; hence, the skeletal structure of partheniol is as follows.



5. The hydroxyl group in partheniol has been found to be tertiary and is probably situated at the 1-position.

6. The proposed structure of partheniol is presented below.



Bibliography

(1) Ruzicka, L., Meyer, J., Helv. Chim. Acta 4, 505 (1921)

(2) Ruzicka, L., Meyer, J., Mingazzini, M., Helv. Chim. Acta 5, 345 (1922)

(3) Emde, H., Pharm. Acta Helv. 4, 121-8 (1929)

(4) Hall, J.A., Relationship in Phytochemistry, Chem. Rev. 20, 305 (1937)

(5) Alexander, P., Ber. 44, 2320-28 (1911)

(6) Walter, E.D., J. Am. Chem. Soc. 66, 419-21 (1944)

(7) Hückel, W., Gercke, A., Gross, A., Ber. 66, 563 (1933)

(8) Huckel, W., Schnitzpahn, L., Ann 505, 274 (1933)

(9) Pfau, A.S., Plattner, Pl. A., Helv. Chim. Acta 19, 858 (1936)

(10) Pfau, A.S., Plattner, Pl. A., Helv. Chim. Acta 20, 224 (1937)

(11) Ruzicka, L., Haagen-Smit, A.J., Helv. Chim. Acta 14, 1104 (1931)

(12) Melville, J., J. Am. Chem. Soc., 55, 2462 (1933)

(13) Plattner, Pl. A., Helv. Chim. Acta 24, 283-94E (1941)

(14) Plattner, Pl. A., Lemay, L., Helv. Chim. Acta 23, 897 (1940)

(15) Blanc, H.G., Compt. Rend. 144, 1356 (1907)
Gilman, Org. Chem., 2nd ed., Vol. II, p. 1358
(John Wiley & Sons, Inc., 1944)

(16) Plattner, Pl. A., Magyar, G., Helv. Chim. Acta 25, 581 (1942)

(17) Semmler, F.W., Risse, F., Ber. 46, 2305 (1913)

(18) Ruzicka, L., Haagen-Smit, A.J., Helv. Chim. Acta 14, 1131 (1931)

(19) Plattner, Pl. A., Magyar, G., Helv. Chim. Acta 24, 191 (1941)

(20) Brode, W.R., Chemical Spectroscopy, 2nd ed., p. 221-222
(John Wiley & Sons, Inc., 1943)