

PART I

THE SELENIUM DEHYDROGENATION OF FRIEDELINOL

PART II

THE BROMINATION OF FRIEDELIN

BY

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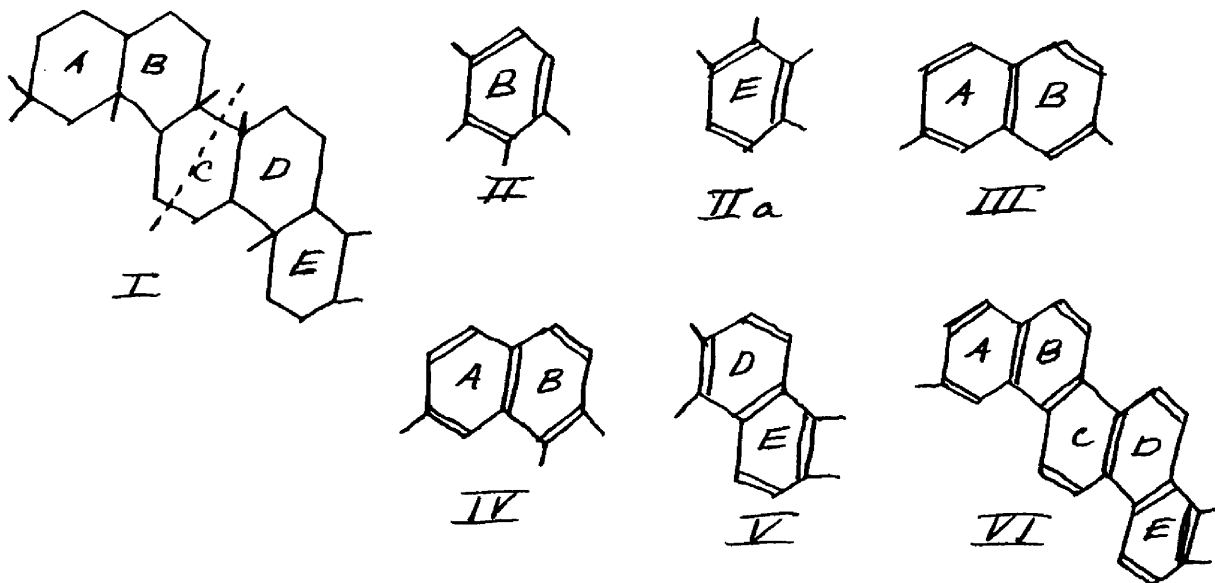
REVIEW OF LITERATURE ON TRITERPENES
FROM 1933 TO DATE*

Ruzicka, previous to 1933, had proposed a structural formula (I) for the carbon skeleton of the triterpenes based on dehydrogenation products. Up to 1933 only comparatively few of the dehydrogenation products had been positively identified and their structures proved correct; namely, 1,2,3,4, tetramethyl benzene, 1,2,7 trimethyl naphthalene (sapotalene) and 2,7 dimethyl naphthalene. Other products had been obtained and tentatively identified but definite proof of their structure was still lacking. The products whose structures were still in doubt were thought to be a tetramethyl naphthalene, an hydroxy trimethyl naphthalene, and a trimethyl picene.

In 1933 Ruzicka¹ attacked the problem of the tetramethyl naphthalene. The relatively high melting point of this compound led him to the conclusion that

* For literature previous to 1933 see H. M. Duvall, Doctor's Thesis, U. of Md., 1936.

the methyl groups were symmetrically arranged in the molecule. It had been previously assumed from the proposed formula (I) that this should be 1,2,5,6 tetramethylnaphthalene (V).



This compound was synthesized and found to be identical to the product obtained by dehydrogenation. Since this compound was the expected one it was concluded that this was good supporting evidence for the hydrogenated picene nucleus of the proposed formula. This picene nucleus was originally assumed on the analogy to the structure of tetracyclosqualene and its behavior toward selenium dehydrogenation, and also that the picene structure was the logical continuation of the phenanthrene ring system in the di-terpenes.

The formula V thus can be a confirmation of the formula VI, if it is true that the formation of IV and V is by the opening of I along the dotted line. (This statement must now be modified as will be shown later.) Ruzicka suggests here that there are many formulae which may be constructed from isoprene units which would also yield these substituted naphthalenes and hence the structure of the trimethyl picene should be determined to establish the ring system.

During the next year (1934) Ruzicka continued his work on dehydrogenation of various triterpenoids, describing the dehydrogenation of "Betulin"². This compound was mentioned especially, since along with the usual dehydrogenation products, (I, II, IV, V) was produced an hydrocarbon melting at 324° which analyzed for C₂₅H₂₀ or the same as the so-called trimethyl picene previously obtained which had a melting point of 306°. None of the material melting at 306° was obtained. Ruzicka concluded from this that the new compound was either an isomer or a homologue of the trimethyl picene, and hence that betulin perhaps had a somewhat different carbon skeleton than the other polycyclic terpenes. It may also be noted that no 2,7 dimethyl naphthalene

was isolated from betulin which also points to a somewhat different structure.

Ruzicka reports in this paper² that betulin also gives similar products on dehydrogenation with palladium black as on selenium dehydrogenation. In this case the products were solely 1,2,3,4 tetramethyl benzene, sapotalene, and 1,2,5,6 tetramethyl naphthalene. Palladium dehydrogenation was employed to make a study of the gaseous products. The ratio of hydrogen to methane was found to be 2.5:1 as was the case with the other triterpenes studied.

Hederagenin, oleanolic acid, and sumaresinolic acid were also dehydrogenated³. These produce the usual products already noted together with the $C_{25}H_{20}$ hydrocarbon melting at 306° . Hederagenin also gave a new product $C_{18}H_{18}$, which was shown to be a substituted phenanthrene by the formation of a quinone and a quinoxaline. Oleanolic acid ($C_{30}H_{48}O_3$) also produced a saturated hydrocarbon $C_{29}H_{50}$ (m.p. 175°) formed by the elimination of CO_2 and H_2O .

As a control on the selenium dehydrogenations a series of palladium dehydrogenations were made. This dehydrogenation allows a study of the gas relations involved as previously mentioned. Oleanolic acid gave a

ratio of methane to hydrogen of 4:10, while from the proposed formula (allowing for introduction of one hydroxyl and one carboxyl) a ratio of 4:6 would be expected. The products from palladium and selenium are the same, hence the ratio of methane to hydrogen found can be produced by no other mechanism.

A table of substances dehydrogenated and the products produced follows:

Dehydrogenation Products of Triterpenes

	I	II	III	IV	V	VI	VII	VIII	IX
Betulin + Se	+		+	+	+		VIIa		
Hederagenin + Se	+	+	+	+		+	+		
Hederagenin + Pd	+	+	+	+			+		
Oleanolic acid + Se	+	+	+	+	+		+		
Oleanolic acid + Pd	+	+	+	+			+		
Sumaresinolic acid + Se	+	+	+	+	+		+	+	
Sumaresinolic acid + Pd	+	+	+	+			+		
Siarsesinolic acid + Se	+		+	+	+		+	+	
Gypsogenin + Se		+	+	+			+		+

I - 1,2,3,4 tetramethyl benzene

II - 2,7 dimethylnaphthalene

III - 1,2,7 trimethyl naphthalene (sapotalene)

IV - hydroxy trimethyl naphthalene

V - 1,2,5,6 tetramethylnaphthalene

VI - phenanthrene hydrocarbon C₁₈H₁₈ m.p. 126°

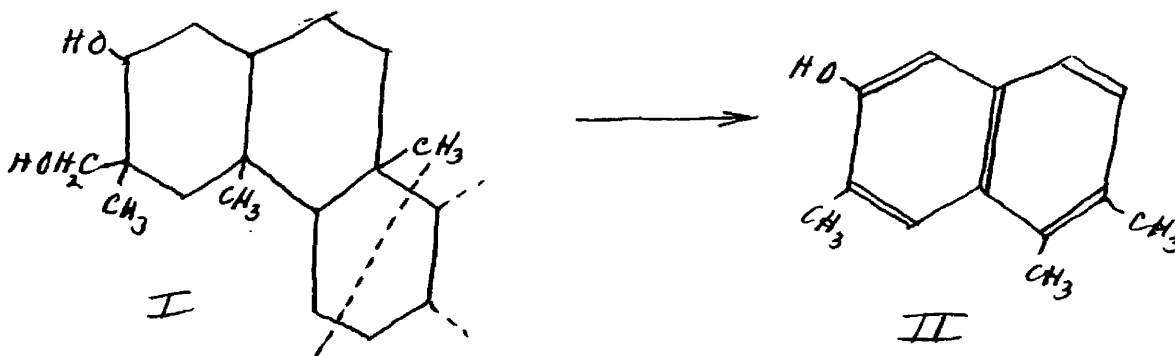
VII - picene hydrocarbon C₂₅H₂₀ m.p. 305°

VIIa - isomeric C₂₅H₂₀ m.p. 325°

VIII - dinaphthyl hydrocarbon C₂₅H₂₄ m.p. 143°

IX - dinaphthyl ethane (?) hydrocarbon C₂₇H₂₈ m.p. 117°

Ruzicka's next problem was the proof of the structure of the hydroxytrimethyl naphthalene isolated from a number of the triterpene alcohols and hydroxy acids. He had previously assumed this to be a substituted sapotalene with the hydroxyl in the 6 position. This assumption was based on the fact that all the triterpenes that produced this compound exhibit a secondary hydroxyl, and that the hydroxyl of the naphthol represented the secondary alcohol group of the natural substance. From the degradation of hederagenin, one of the alcohols producing hydroxytrimethyl naphthalene, it had been shown that the carbon adjacent to the one carrying the secondary hydroxyl had two methyl groups attached to it, both carbons being part of a ring system. One of these methyl groups also carries a primary hydroxyl group, while in most of the other triterpenes the methyl groups are free of oxygen. Hence the assumption that the cleavage of ring C (I) would produce a 1,2,7 trimethyl 6 hydroxy naphthalene .(II)

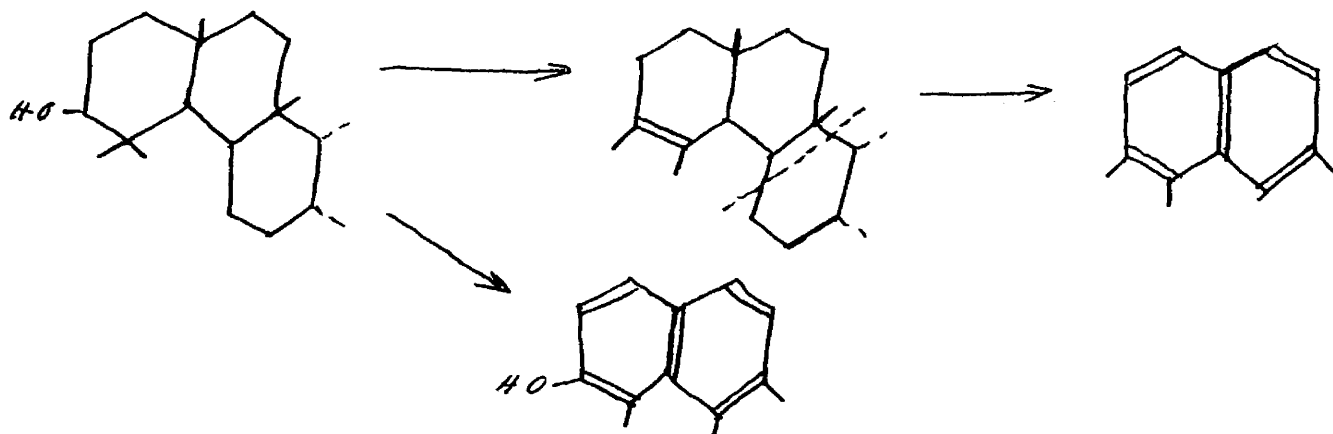


It had also been found that zinc dust distillation of the hydroxy trimethyl naphthalene, or distillation over Ni at 300^o, produced sapotalene. However, when the expected 1,2,7 trimethyl-6-methoxy naphthalene was synthesized it was found to differ from the methoxy derivative of the substance from dehydrogenation. The other four isomeric methoxy sapotalenes were prepared and they too were found not to be the same as the dehydrogenation product. The only conclusion to be drawn is that the substance is not a sapotalene derivative.

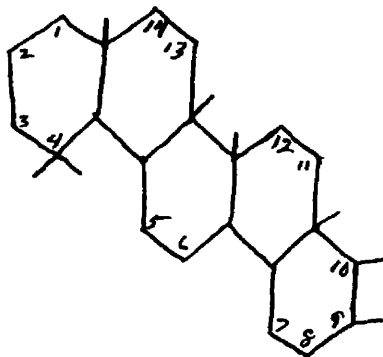
In a later paper⁵ Ruzicka reports the determination of the structure of this hydroxy trimethyl naphthalene. The methoxy derivative of the dehydrogenation product was catalytically hydrogenated by warming slightly with platinum in glacial acetic acid whereby a trimethyl-decahydronaphthalene was produced with the removal of the methoxyl. Since this method is very mild, no rearrangements would be expected. Dehydrogenation of this with palladium black at 300^o gave no sapotalene but 1,2, 8 trimethyl naphthalene. Therefore, the hydroxytrimethyl naphthalene must be 1,2, 8 trimethyl-7-hydroxynaphthalene.

Hence in the dehydrogenation of triterpenes of this

type a pinacolone rearrangement must occur



This lead Ruzicka to propose a new structure for ring A for triterpenes of this type



The structure of the $C_{25}H_{20}$ m.p. 306 hydrocarbon is still unknown, although it is well established that it is a picene homologue. Ruzicka has shown that its ultra-violet absorption spectra is very similar to that of coal tar picene³. He has synthesized two methylated picenes, namely, 3,8 dimethyl, and 3,9,10 trimethyl (see numbering system above), neither of which are identical to the

dehydrogenation product but whose absorption spectra (especially the latter) are very closely related to that of the dehydrogenation product.⁶

INTRODUCTION

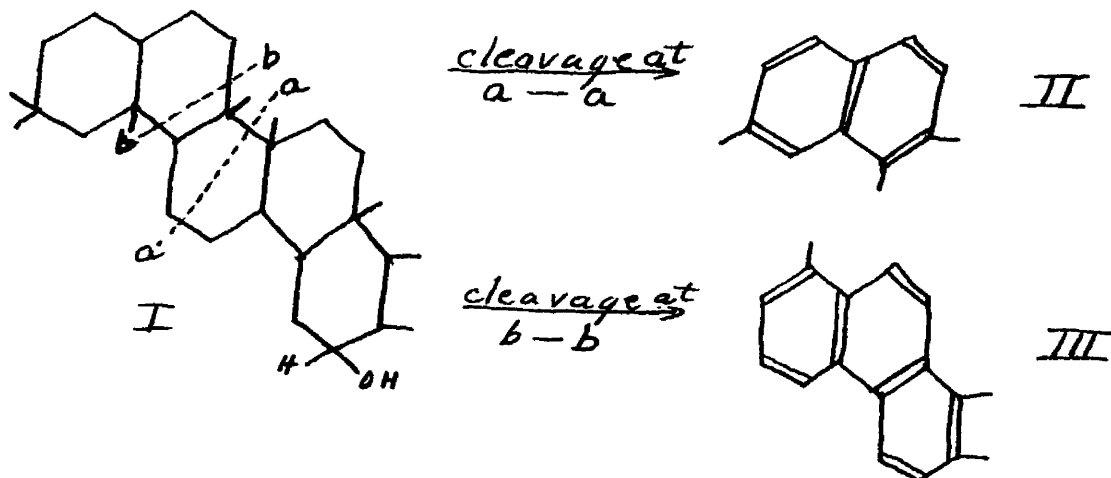
Selenium dehydrogenation has become an important method for the investigation of the nuclear structure of polycyclic hydroaromatic ring systems. Friedelin is such a compound, hence in continuation of the structural investigation of this substance instigated by Drake and Jacobsen⁷, and Drake and Shrader⁸, an attempt has been made to characterize the nuclear structure by this method.

Friedelinol was chosen as the material to be dehydrogenated rather than friedelin itself since ketones do not in general give satisfactory results upon dehydrogenation, especially where the ketone group is part of a ring system. This is due to the ease of attack of the ring itself through the ketone group and the formation of dehydrogenation products too far removed from the original nuclear structure.

The dehydrogenation products obtained from friedelinol are 1,2,7 trimethylnaphthalene (sapotalene), 1,2,8 trimethylphenanthrene, an hydrocarbon $C_{25}H_{20}$ which appears to be identical to the so-called trimethyl picene isolated by Ruzicka and co-workers from a number of

triterpenes,² and an hydrocarbon $C_{11}H_{20}$ which has the properties of an alkyl substituted cyclohexene.

A proposed formula explaining the formation of these products follows:*



Cleavage of the molecule at a - a would produce sapotalene (II) and similarly at b - b, 1,2,8 trimethylphenanthrene. The cleavage at a - a should produce at the same time 1,2,5,6 tetramethylnaphthalene as found by Ruzicka from a number of triterpenes,^{10,5} however this compound was not isolated. This may have been due to the relatively small amounts of friedelinol dehydrogenated, or it may not have been present, since Ruzicka does not

* The location of the hydroxyl is tentative. See Drake and Campbell⁴ on oxidation studies.

report the isolation of the trimethyl phenanthrene from triterpenes which produce the tetramethylnaphthalene. Schulze reports¹¹ 1,2,8 trimethyl phenanthrene as a dehydrogenation product of the triterpene lanosterol, but isolated no tetramethylnaphthalene. It appears, therefore, that there may be more than one basic structure for the triterpenes, one of which produces the tetramethylnaphthalene, and another which produces the trimethyl phenanthrene.

The trimethyl picene would be formed from the dehydrogenation of the molecule leaving the ring structure intact. According to the formula as written the expected trimethyl picene would be substituted in the 3,9,10 positions (VI pg.2). However, this compound has been synthesized by Ruzicka⁶ and found not to be identical with the product isolated from the dehydrogenation of triterpenes.

It is interesting to note that the residue left from the cleavage at b - b (I) would be $C_{11}H_{20}$ which corresponds to the empirical formula found for the alkylcyclohexene isolated.

In any dehydrogenation three factors enter which cause difficulty in determining the original structure

from the compounds produced, namely; (1) alkyl wandering, (2) pinacolone rearrangement, (3) formation of new rings not originally present. Of these three, only the first must be considered in this dehydrogenation. Pinacolone rearrangement is possible only when a secondary hydroxyl group is attached to a carbon adjacent to a carbon holding two alkyl groups, where both carbons are part of a ring system. Campbell⁹ has shown definitely that this structure is not present in friedelinol. Formation of new rings by rupture of rings already present does not occur at temperatures below 350° during selenium dehydrogenation. This dehydrogenation was carried out at 315 - 325°, therefore precluding this factor. However, the first factor, alkyl wandering, cannot be eliminated and hence the proposed formula may be in error as regards the positions of the methyl groups. It is possible to construct a large number of formulae from six isoprene units having the hydrogenated picene nucleus. Of this number, the proposed formula is the most plausible, excluding the possibility of alkyl wandering.

EXPERIMENTAL

Preparation of Materials: - Friedelin

The friedelin was obtained by extracting ground cork with ethyl acetate according to the method described by Drake and Jacobsen⁷. The crude extract which contains both cerin and friedelin was put into solution in boiling chloroform and cooled. The greater part of the cerin was crystallized out by this procedure. The filtrate was evaporated slightly and again cooled to remove the rest of the cerin. The filtrate was then evaporated to a small volume, or until solid started to separate, and an equal volume of acetone added. After cooling and filtering the precipitate was washed with several portions of acetone. This material was designated as "friedelin rich" extract. If the original crude material was light colored this extract was usually pure white and nicely crystalline indicating nearly pure friedelin by its high melting point.

Friedelinol

Friedelinol was prepared from the "friedelin rich" extract by the method described by Campbell.⁹ Ten grams of friedelin rich extract were dissolved in 750 ml. of boiling n-amyl alcohol in a 2 liter flask provided with a reflux condenser. Twenty grams of sodium were added in as large pieces as would conveniently pass through the condenser. The solution was maintained in vigorous ebullition during the reaction period. After the sodium had completely reacted the contents of the flask were steam distilled until the n-amyl alcohol was removed. During the latter part of the distillation the friedelinol separated as a fine white precipitate. The friedelinol was filtered and washed with water until free from alkali; then recrystallized from n-amyl alcohol. Usually one recrystallization was all that was required to obtain a product of sufficient purity for dehydrogenation. In many cases, where the original extract was of good quality, the second crops from the evaporation of the n-amyl alcohol were also of sufficient purity to be used. This method gives an overall yield of 50-60% based on the friedelin rich extract.

Apparatus

The dehydrogenations were carried out in a 200 ml. pyrex flask sealed to a broad U tube 20 mm. in diameter with one arm one meter in length to serve as a reflux condenser. This long arm was provided with a side inlet tube near its upper end to allow the introduction of the charge and the selenium. The shorter arm, about 30 cm. in length, was sealed to a 200 ml. flask to serve as a trap for any volatile products. A side inlet was provided for this flask which led successively to a bubble counter and a calcium chloride tube filled with bleaching powder to decompose the hydrogen selenide.

The reaction flask was placed in a Wood's metal bath heated by a Fisher burner and jacketed with asbestos. The temperature was determined by a thermocouple in the bath.

Dehydrogenation

Two dehydrogenations were carried out. The first consisted of a charge of 40 g. of friedelinol well mixed with 80 g. of powdered selenium. The temperature was maintained between 315-325° and 10 g. portions of selenium

added at twenty-four hour intervals until 40 g. had been added. The reaction was allowed to proceed until evolution of hydrogen selenide ceased. This required a total of two hundred and forty hours.

The reaction flask was cut off the reflux column and broken open to recover the charge. The charge was ground fine in a mortar and exhaustively extracted with ether in a Soxhlet extractor. The reflux tube and trap were rinsed with ether which was then added to the ether extract. The ether was replaced with benzene and the extraction continued until the residue was free of all soluble material.

The ether extract upon evaporation of the solvent yielded 11.1 g. of a dark red oil. The oil was distilled under a pressure of 2 mm., the receivers being changed whenever a considerable temperature rise occurred in the vapor with a corresponding decrease in the rate of distillation.

Fractionation of Ether Extract

Frac- tion	B.P. (vapor temp.)	Amount (gms.)	n_D^{25}	D_{20}^{20}	Phys. Appearance
1	70°	2.0	1.4585	0.8232	Sl. yellow liq.
2	70-125	1.2	1.5686	0.9650	yellow liq.
3	125-170	0.5	1.6067	-	red-yellow liq.
4	170-200	0.8	-	-	yellow semi-solid
5	200-250	1.0	-	-	yellowish solid
Resi- due	250	5.6	-	-	dark resinous solid

The still residue was combined with the benzene extract, and after removal of the benzene, was submitted to low pressure sublimation.

The various fractions from the distillation were converted to the picrates for purification. The details of this purification will be discussed later.

The second dehydrogenation consisted of a charge of 50 g. of friedelinol, well mixed with 15 g. of powdered selenium. The temperature was maintained at 315-325°. Selenium was added in 5 g. portions at intervals of one hour during the day until 150 g. had been added. This dehydrogenation ceased evolving gas at the end of

seventy-five hours.

The treatment of the charge from this point on was exactly as in the previous dehydrogenation. The ether extract weighed 19.2 g. However, 10 g. of this consisted of material whose boiling point at 2 mm. was greater than 250°. It was found impossible to distill at temperatures greater than this due to the bad foaming and bumping of the still contents. The fractions obtained from this distillation corresponded to those obtained from the first dehydrogenation. The still residue and benzene extract were combined and sublimed in vacuo.

The addition of the selenium in small amounts at shorter time intervals appeared to speed up the rate of dehydrogenation considerably, but had little effect on the type and amounts of products, except in the case of the first fraction which was present in less than one third the quantity obtained from the previous dehydrogenation.

Isolation and Characterization of Products

The Alkylcyclohexene

The liquid hydrocarbon boiling at 70° under 2 mm. pressure was redistilled at atmospheric pressure.

Approximately eighty percent distilled between 180-185°.

This fraction was found to have the following properties:

$n_D^{25} = 1.4535$; $D_{20}^{20} = 0.8232$; forms no picrate or styphnate; forms no solid bromide in cold carbon tetrachloride; analysis calculated for $C_{11}H_{20}$

C = 86.74, H ;3.26

found: C = 86.60, 86.32; H = 13.62, 13.61

molecular weight (freezing point of benzene)

calculated for $C_{11}H_{20} = 152$

found 149,152

These properties correspond to reported values for alkyl-substituted cyclohexenes containing eleven carbon atoms, but cannot be used to differentiate between the various isomers, since all are very similar.

The liquid was distilled over platinized asbestos, first at 300° and later at 420°, without being further dehydrogenated. Zelinsky¹⁵ has found that hydro-aromatic six-membered rings containing a quaternary carbon were not aromatized with platinum at temperatures up to 300°. Hence this may be taken as evidence that this alkylcyclohexene contains a quaternary carbon atom. As previously mentioned, the residue from the cleavage at b - b in Figure I would be $C_{11}H_{20}$ and would contain a

quaternary carbon if no dehydrogenation took place before or after the cleavage. It is entirely possible that dehydrogenation might not proceed on this compound since it has a relatively low boiling point. It could easily be held up in the reflux condenser by the higher boiling constituents. Furthermore, its behavior with platinum black shows that it is a difficult compound to dehydrogenate.

The remainder of the material (circa 0.3g) was sealed in a pyrex tube with 1.0 g. of selenium and heated for twenty-four hours at 320° . This accomplished further dehydrogenation as evidenced by the evolution of hydrogen selenide when the tube was opened. The contents were extracted with ether. Upon evaporation of the solvent a yellowish oil remained. $n_D^{25^{\circ}} = 1.4553$, b.p. 187° - 192° . This liquid was cooled to 0° and a small amount of aluminum chloride and a few drops of bromine added. Hydrogen bromide was evolved and the mass partially solidified. It was washed with sodium bisulfite solution, filtered and recrystallized from ethyl alcohol. m.p. 169 - 175° . This melting point does not correspond to any of the brom derivatives of the expected dimethyl ethyl benzene isomers recorded in the literature.

1,2,7 trimethylnaphthalene (Sapotalene)

The liquid fractions boiling from 70-125° and 125-170° were converted to the picrate by adding an equal weight of picric acid and recrystallizing from ethyl alcohol. After eight recrystallizations the orange needles of the picrate reached a constant m.p. of 126-127°.

Analysis calculated for $C_{19}H_{17}N_3O_7$: C = 57.13;
H = 4.29

found: C = 57.27, 56.87; H = 4.04, 4.14

The corresponding fractions from the second dehydrogenation were converted to the styphnate and recrystallized from ethyl alcohol several times. m.p. 153-154°.

Since the density, refractive index and boiling point of the crude fractions from which this material was obtained also are approximately those of sapotalene, it was concluded that the principal constituent of these fractions was 1,2,7 trimethylnaphthalene. (Reported values¹⁰ by Ruzicka $b_{16} = 148^\circ$, $d_4^{15} = 1.008$, $n_D^{15} = 1.6093$, picrate 129°, styphnate 157°.)

1,2,8 trimethylphenanthrene

The fraction boiling from 170-200° at 2 mm. pressure was converted to the picrate, but this picrate was found to decompose spontaneously after several recrystallizations from methyl alcohol. In this way a small amount of a white fluffy hydrocarbon was obtained, m.p. 141-142°. A similar treatment of the corresponding fraction from the second dehydrogenation yielded the same hydrocarbon, m.p. 142-143°. A mixed m.p. of these two showed no depression.

Analysis calculated for C₁₇H₁₆; C = 92.73, H = 7.27

found C = 92.90, 92.45, H = 7.49, 7.23

Molecular weight (Rast's method) Calculated for

C₁₇H₁₆ = 220 found = 204, 202.

It was found that the picrate could be recrystallized from ethyl alcohol saturated with picric acid at 0° without decomposition. The picrate prepared in this manner melted at 162-163°.

The solid fractions distilling at 200-250° at 2 mm. pressure were recrystallized from ethyl alcohol five times. The resulting hydrocarbon was the same as that obtained from the previous fraction. Three hundredths of a gram of this was dissolved in boiling glacial acetic

acid and 0.05 g. of chromic anhydride added in glacial acetic acid solution over a period of ten minutes. The mixture was refluxed for thirty minutes, cooled, and water added. An orange precipitate was filtered off and recrystallized from ethyl alcohol. A small amount of the quinone in the form of orange needles was obtained. m.p. 189-190°.

The quinone was dissolved in ethyl alcohol, an excess of o-phenylenediamine added, and the solution evaporated to dryness. The residue was taken up in ether and extracted with one percent hydrochloric acid to remove the unreacted diamine. After evaporation of the ether the product was recrystallized from ethyl alcohol. The quinoxaline thus obtained appeared as fine, pale yellow crystals. m.p. 129-131°.

Reported melting points of derivatives of 1,2,8 trimethylphenanthrene

	Hydrocarbon	Picrate	Quinone	Quinoxalin
Haworth ¹²	144-145°	163°	196-197°	131-132°
Ruzicka ¹³	142-143°	161-163°	194°	131-132°
Found	142-143°	162-163°	189-190°	129-131°

Trimethylpicene

The combined still residues from the ether

extracts and the benzene extracts were submitted to sublimation at 300° under low pressure. The sublimed material was recrystallized several times from benzene. The crystals separating in the first crystallization were colored red with selenium which was removed in the subsequent recrystallization by decolorizing carbon. The final product was shiny flat platelets with a bluish lustre. m.p. $305-306^{\circ}$.

Analysis calculated for $C_{25}H_{20}$ C = 93.70, H = 6.30

found C = 93.80, 93.97; H = 6.17, 6.11.

Molecular weight (Rast's method) calculated for

$C_{25}H_{20}$ = 320 found 306, 309.

(It was necessary to use 20-30 times as much camphor as sample due to the low solubility of this hydrocarbon.)

A few crystals dissolved in concentrated sulfuric acid produced a deep emerald green. This color is also given by picene¹⁴.

A small amount of the hydrocarbon was oxidized with chromic anhydride in boiling glacial acetic acid and yielded a deep reddish orange quinone, having no melting point. (Picene quinone has no melting point). The quinone was recrystallized from dioxan and the intermediate crop analyzed.

Analysis calculated for $C_{25}H_{18}O_2$ C = 82.70; H = 5.18

Found C = 81.38, H = 4.89

Apparently this sample was contaminated with some compound with a lower carbon content, perhaps formed by the oxidation of one of the methyl groups to a carboxyl. (Picene quinone prepared from coal tar picene is contaminated with a compound containing one more carbon atom in the form of a carboxyl, supposedly due to the oxidation of a methyl picene.)

This hydrocarbon seems to be identical to the "trimethylpicene" isolated by Ruzicka from a number of polyterpenes.^{10,2}

CONCLUSIONS

It may be definitely concluded that 1,2,8 trimethylphenanthrene and 1,2,7 trimethylanthracene are produced by the selenium dehydrogenation of friedelinol. This classifies friedelin as a triterpenoid.^{10,11} Hence it would appear that friedelin contains five six-membered rings and no double bond rather than four rings and one double bond as assumed by Drake and Jacobsen⁷. These five rings are probably present in the form of an hydrogenated picene.

SUMMARY

1. A proposed structural formula for friedelinol has been given.
2. The selenium dehydrogenation of friedelinol has been described.
3. The isolation and characterization of 1,2,7 trimethylnaphthalene and 1,2,8 trimethylphenanthrene has been described.
4. The isolation of two other products, supposed to be an alkylcyclohexene and trimethylpicene, together with all their available characteristics, has been given.
5. The classification of friedelin as a triterpenoid has been established.

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PART II

INTRODUCTION

Friedelin was found to react readily with bromine with the evolution of hydrogen bromide by Jacobsen*. He concluded that several bromo derivatives were formed concurrently since the products were complex mixtures containing varying amounts of bromine depending on the solvent and temperature employed.

This work is a continuation of the investigation of the bromination reaction in an attempt to find the proper conditions for the preparation of a pure mono - or dibromide.

It was assumed that the bromination took place first, by addition to the double bond of the enol form with a subsequent elimination of a molecule of hydrogen bromide. If the reaction ceased at this point a monobromide would result. However, if additional hydrogen atoms are available for enolization, the reaction may

* R. P. Jacobsen - Doctor's Thesis, U. of Md. (1935).

proceed with the formation of a dibromide, or even to a tribromide. Campbell* has shown that the structure $\text{CH} - \text{CO} - \text{CH}_2$ - is present in friedelin, and hence there are available three hydrogens for enolization in this reaction. However, it cannot be definitely concluded that the bromination proceeds in this way due to the diversity of products obtained. In a molecule of this size and complexity it is extremely difficult to predict the ease with which bromine might substitute rather than add even though the addition to the double bond of the enol form might at first seem to be the most logical reaction. Furthermore, the existence of tertiary hydrogens near the positions entered by the bromine may complicate the reaction by the elimination of bromine as hydrogen bromide with the formation of double bonds.

* Campbell, W. P. - Doctor's Thesis, U. of Md. (1936).

EXPERIMENTAL

The following table is a summary of the brominations carried out. These reactions were carried out in a flask painted black on the outside to exclude all light which might act as a substitution catalyst. The reagents were all carefully dried before use. The solvent in each case was glacial acetic acid. This solvent was employed because Jacobsen found that it gave products whose bromine content was nearest that of the monobromide.

Quant. Br ₂	Temp.	Time	M.P. Product	% Br
1 equimol slight excess	45-55°	35 min.	189-190(1st crop) 198-199(last crop)	11.18, 11.24 15.18, 15.32
2 equimol slight excess	45-55°	4 hrs.	223-224(1st crop) 217-218(last crop)	24.82 22.35
3 equimol slight excess	25-30°	68 hrs.	210° - 210.5°	18.15
4 equimol	25-30°	17 hrs.	193-197°	not det.

Calculated for C₃₀H₄₉OBr, Br = 15.81

Calculated for C₃₀H₄₈OBr, Br = 27.34

The bromination products were recrystallized from ethylacetate, and in some cases were fractionally crystallized as noted in the table.

The material melting at 193-197° from the last bromination was treated with potassium hydroxide in boiling n-propyl alcohol in an attempt to prepare the unsaturated ketone. However, after evaporation of the solvent a resinous material remained. By wetting this resin with ether and allowing to evaporate slowly, it was induced to solidify. m.p. 115-142°. This material was insoluble in alkali and gave no Beilstein test for halogen. It was found impossible to further purify this, since in all solvents which it would dissolve it was reprecipitated as a resin.

CONCLUSIONS

It may be concluded that the bromination of friedelin leads to the formation of no pure mono - or dibromide, but rather to mixtures which are impossible to separate by crystallization.