gradually dissolved. After about two-thirds of the solvent had been removed by distillation, 500 ml. of water was added to the hot solution. After cooling and filtering, the solid was dissolved in ether, and shaken with 10% sodium hydroxide. Sodium salts precipitated in the aqueous layer and were rendered compact at the ether–water interface by the use of a centrifuge. The ether solution was separated and the mixture extracted with a fresh portion of ether. From the combined ether extracts was obtained 0.8 g. of friedelin and 0.2 g. of a resinous material.

The aqueous layer was made acid to Congo red paper, warmed to coagulate the acids and filtered. By recrystallization from aqueous alcohol and finally from 95% alcohol 1.3 g. of a product, which crystallized in narrow laths and melted 206–207°, was obtained.

Anal. Calcd. for $C_{30}H_{50}O_3$: C, 78.54; H, 11.00. Found: C, 78.83, 78.75; H, 10.91, 11.02. *Neutral Equiv.* Calcd. for $C_{28}H_{49}(CO)(COOH)$: 458. Found: 463, 461.

Methyl Friedonate.—This ester was prepared from the crude acid fraction obtained by oxidation of friedelin as above. Esterification was accomplished by heating the sodium salt in absolute ethanol with excess methyl iodide. Methyl friedonate crystallizes from methyl alcohol in narrow laths which melt at 249–251°.

Anal. Calcd. for $C_{31}H_{52}O_3$: C, 78.75; H, 11.09. Found: C, 78.60, 78.85; H, 11.21, 11.42. *Sapon. Equiv.* Calcd. for $C_{29}H_{49}(CO)(COOCH_3)$: 472. Found: 473, 471.

Friedolo Lactone and Norfriedolo Lactone.—Two and four-tenths grams of the lower melting crude acid fraction obtained from the oxidation of friedelin was dissolved in 140 ml. of *n*-propyl alcohol. This solution was heated under reflux and 6 g. of sodium cut in small pieces was added. When all the sodium had dissolved, the solution was diluted with 500 ml. of water, cooled and filtered. The resulting solid was crystallized from ethyl alcohol (160 ml.) and then several times from ethyl acetate. Friedolo lactone crystallizes from ethyl acetate in rods, which melt 309–312°.

Anal. Calcd. for $C_{30}H_{50}O_2$: C, 81.37; H, 11.39. Found: C, 81.24, 81.12; H, 11.26, 11.25.

The alcoholic filtrate from the first crystallization mentioned above was evaporated to half its volume, cooled and filtered. The crystals which separated were purified by further recrystallization from ethyl acetate. The compound norfriedolo lactone crystallizes from ethyl acetate in long needle-like laths, and melts 289–291°. This melting point is considerably depressed by admixture of friedolo lactone.

Anal. Calcd. for $C_{29}H_{48}O_2$: C, 81.24; H, 11.30; sapon. equiv., 428. Found: C, 81.09, 81.29; H, 11.29, 11.34; sapon. equiv., 431, 429.

We should like to acknowledge our indebtedness to R. P. Jacobsen for his analyses of friedelinyl iodide, and to J. R. Spies for analyses of friedelinol and friedelinyl methyl ether.

Summary

1. The oxidation of friedelin and friedelene by chromic anhydride in glacial acetic acid has been studied, and from evidence so obtained the structure $CHCOCH_2$- in the friedelin molecule is deduced.

2. The preparation of friedelinol and of several of its derivatives is described.

3. Several acidic and neutral degradation products of friedelene and friedelin have been prepared.

COLLEGE PARK, MD. RECEIVED JUNE 25, 1936

[CONTRIBUTION FROM THE UNIVERSITY OF MARYLAND]

Cerin and Friedelin. IV. The Dehydrogenation of Friedelinol[1]

BY NATHAN L. DRAKE AND WILLARD T. HASKINS

In continuation of our studies on the structure of cerin and friedelin, we have subjected friedelinol to dehydrogenation by selenium in order to determine the type of aromatic nucleus to which friedelin is related. Friedelinol rather than friedelin was chosen for study because previous investigation had shown that friedelin, like most ketones whose carbonyl forms a part of a ring system, yielded products too complex and too far removed from the original nuclear structure to be a satisfactory substance for dehydrogenation studies.

The products obtained from friedelinol by dehydrogenation are 1,2,7-trimethylnaphthalene (sapotalene), 1,2,8-trimethylphenanthrene, a hydrocarbon $C_{25}H_{20}$, apparently identical with a polymethyl picene isolated by Ruzicka and coworkers from the dehydrogenation products of a number of triterpenes,[2] and a liquid hydrocarbon, $C_{11}H_{20}$, which has the properties of an alkyl substituted cyclohexene.

The evidence advanced by Ruzicka[3] in support of a picene nucleus in the hydrocarbon $C_{25}H_{20}$ is quite conclusive; consequently there must be in cerin and friedelin a pentacyclic nucleus of the

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[1] From the Ph.D. dissertation of W. T. Haskins.

[2] Ruzicka, Frame, Leicester, Liguori and Brüngger, *Helv. Chim. Acta*, **17**, 426 (1934).

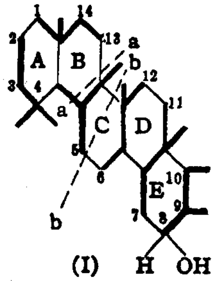
[3] Ruzicka, Hösli and Ehmann, *ibid.*, **17**, 445 (1934).

hydrogenated picene type. The formation of new rings during dehydrogenation is a reaction known to occur, but at the temperatures of our dehydrogenations such ring formation is highly unlikely. Extra cycle formation is most probable at temperatures above 350°,[4] and our dehydrogenations were carried out at temperatures from 315 to 325° (bath temp.).

It seems unlikely that alkyl group rearrangement occasioned by the dehydration of friedelinol occurred prior to the actual dehydrogenation, for both friedelin and friedelene gave the same product, norfriedonic acid[5] on oxidation, and friedelene was prepared at temperatures approximating those employed during the dehydrogenations. It seems logical to conclude, therefore, that the locations of the alkyl groups in the polymethylpicene actually represent the original structure. There is considerable doubt as to the exact number of these methyl groups. Ruzicka has synthesized 3,9,10-trimethylpicene and 3,8-dimethylpicene, neither of which[6] is identical with the product obtained by dehydrogenation, although the absorption bands of the trimethylpicene in the ultraviolet were very much like those of the unknown. All of our analyses on the hydrocarbon obtained from friedelinol and the same substance obtained from ursolic acid are better in accord with $C_{24}H_{18}$ than $C_{25}H_{20}$. Furthermore, our determinations of molecular weight on different specimens of the hydrocarbon from the sources mentioned above are considerably too low for the $C_{25}H_{20}$ formula and check the $C_{24}H_{18}$ formula almost exactly. The concordance of these two sets of determinations carried out by different operators on material from different sources might possibly be fortuitous, but we believe that our findings emphasize the necessity of considering the dimethylpicenes in any attempt to identify the unknown polymethylpicene.

Ruzicka has concluded as a result of certain degradation reactions of hederagenin[7] that the hydroxyl group of the triterpenes must be considered to be adjacent to a carbon atom holding two methyl groups. It is apparent from the behavior of friedelin on oxidation that this structure does not exist in friedelinol.[5]

We suggest as a tentative formula for friedelinol the following (I)



(I)

in which the heavy lines represent isoprene nuclei. This structure corresponds closely to one suggested by Ruzicka for certain triterpenoids,[7b] (p. 391) but differs in the location of the hydroxyl group, and in the absence of the Δ^8 unsaturation. It is entirely possible that the hydroxyl group of cerin corresponds in location to the hydroxyl of those triterpenoids which Ruzicka has studied and should be placed at 3 in Ring A.

Cleavage of the molecule at (a)------(a) would result in the formation of 1,2,8-trimethylphenanthrene and another substance containing eleven carbon atoms, corresponding to the compound $C_{11}H_{20}$, which apparently is a polyalkylcyclohexene. This substance was obtained in small quantity, but possessed properties which were in accord with the suggested structure. It had a refractive index like other known polyalkylcyclohexenes containing eleven carbons, absorbed bromine in cold carbon tetrachloride but yielded no solid bromide, and had a molecular weight and percentage composition which were excellently in accord with the formula $C_{11}H_{20}$. It was distilled several times over platinized asbestos at 300° and later at 420° without being further dehydrogenated. It was possible, however, by heating the substance in a sealed tube with selenium for twenty-four hours at 320° to accomplish further dehydrogenation as evidenced by the escape of hydrogen selenide when the tube was opened. The resulting substance possessed a considerably higher refractive index than the original material and was converted at 0° by the action of bromine in the presence of a bit of aluminum chloride into a solid bromide. The melting point of the bromide did not, however, correspond to that of any of the known derivatives of polyalkylbenzenes. The difficulty of dehydrogenating this material by platinum black is in accord with the findings of Zelinsky,[8] who has examined the

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[4] *Cf.* Diels, *Ann.*, **459**, 1 (1927); *Ber.*, **66**, 487, 1122 (1933); Ruzicka, Thomann, Brandenberger, Furter and Goldberg, *Helv. Chim. Acta*, **17**, 200 (1934).

[5] *Cf.* paper III, THIS JOURNAL, **58**, 1681 (1936).

[6] Ruzicka and Mörgeli, *Helv. Chim. Acta*, **19**, 377 (1936).

[7] (a) Ruzicka and Hofmann, *ibid.*, **19**, 121, 122 (1936); (b) Ruzicka, Hofmann and Frei, *ibid.*, **19**, 387 (1936).

[8] Zelinsky, *Ber.*, **44**, 3121 (1911); **45**, 3678 (1912); **56**, 1716 (1923).

behavior of a number of hydroaromatic rings when subjected to the dehydrogenating influence of platinum at elevated temperatures. Only those rings containing no quaternary carbon atom were aromaticized at temperatures up to 300°.

Cleavage of (I) at (b)----(b) and migration of a methyl group from 4 to 3 would result in the formation of sapotalene. The migration of the alkyl group is certainly within the bounds of reason, for Mayer and Schiffner have shown[9] that α-methylnaphthalenes have a pronounced tendency to rearrange to β-derivatives when distilled over silica gel at temperatures above 400°, and α-phenylnaphthalene rearranges at about 350°.

The location of the hydroxyl group at the 8-position in (I) is based on results obtained in oxidation studies.[5] It is apparent from this work that the secondary hydroxyl of friedelinol must be present in a cycle which contains the unit of structure $CHCHOHCH_2$-; furthermore, we have isolated a lower oxidation product of friedonic acid which apparently is a keto acid containing twenty-seven carbon atoms.[10]

Experimental

Apparatus.—The dehydrogenations were carried out in a 200-ml. Pyrex flask to which was sealed a broad U-tube of 20 mm. tubing. One arm of the U, about a meter long, served as a reflux condenser, the other arm, which was somewhat shorter, was sealed to a small Pyrex flask with a side outlet. This flask served as an auxiliary condenser, and from its side-arm the gaseous products of the reaction were conducted through a small bubble counter to a tube containing moist calcium hypochlorite. The reaction flask was heated by a bath of Wood's metal whose temperature was determined by means of a thermocouple. Selenium was introduced through a short side-arm near the top of the reflux condenser.

Method.—Forty grams of friedelinol,[5] well mixed with 80 g. of powdered selenium, was heated in the reaction flask (metal bath temp. 315–325°), and 10-g. portions of selenium added every twenty-four hours until 40 g. had been added. The heating was continued until hydrogen selenide was no longer evolved (two hundred and forty hours). The reaction flask was then cut from the condenser and broken to recover the charge. The reaction products were finely ground in a mortar and exhaustively extracted with ether in a Soxhlet extractor. The reflux condenser and trap were rinsed with ether and the rinsings added to the ether extract. After extraction by ether was practically complete, the ether was replaced by benzene, and extraction continued until the residue was free from soluble material.

After evaporation of the ether from the first extract there remained 11.1 g. of dark red oil. A second dehydrogenation was conducted in the same apparatus using 50 g. of friedelinol mixed with 15 g. of powdered selenium as the initial charge. Selenium was added in 5-g. portions at intervals of an hour during the daytime until 150 g. in all had been added. Evolution of hydrogen selenide ceased at the end of seventy-five hours. The ether extract weighed 19.2 g., but 10 g. consisted of material boiling above 250° under 2 mm. pressure. The addition of selenium in small amounts appeared to speed up the dehydrogenation considerably, but had little effect on the type and amounts of products except that the first fraction described below was less than one-third as large in the second dehydrogenation as in the first.

Fractionation of the Ether Soluble Products.—The ether-soluble products were distilled under a pressure of 2 mm. in a Claisen flask with a short fractionating column. Fractions with the following boiling ranges, weights, $n^{25}D$ and d^{20}_{20} were obtained: up to 70°, 2 g., 1.4585, 0.8232, sl. yellow liq.; 70–125°, 1.2 g., 1.5686, 0.9650, yellow liq.; 125–170°, 0.5 g., 1.6067, red-yellow liq.; 170–200°, 0.8 g., yellowish semi-solid; 200–250°, 1.0 g., yellowish solid; residue, 5.6 g., dark resinous solid.

The still residue was combined with the benzene extract, and the material left after removal of the benzene was sublimed under low pressure.

The Alkylcyclohexene.—The liquid hydrocarbon boiling up to 70° at 2 mm. pressure was redistilled at atmospheric pressure. Approximately 80% of the substance distilled from 180 to 185°. This substance would not form a solid bromide when treated with bromine in cold carbon tetrachloride, nor would it yield a picrate or a styphnate.

Anal. Calcd. for $C_{11}H_{20}$: C, 86.74; H, 13.26; mol. wt., 152. Found: C, 86.60, 86.32; H, 13.62, 13.61; mol. wt. (f. p. of benzene), 149, 152; $n^{25}D$ 1.4535; d^{20}_{20} 0.8232.

The liquid was distilled several times over platinized asbestos at 300 and at 420°, but no dehydrogenation occurred. About 0.3 g. of the liquid was heated to 320° with 1.0 g. of selenium in a small sealed Pyrex tube for twenty-four hours. When the tube was opened hydrogen selenide escaped, proving dehydrogenation. The product was extracted with ether and later distilled; it boiled 187–192°, and had a considerably higher refractive index than before heating ($n^{25}D$ 1.4553). The 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. After removal of excess bromine and recrystallization from alcohol the solid melted 169–175°. The melting point does not correspond to that of any of the recorded bromo derivatives of the polyalkylbenzenes.

1,2,7-Trimethylnaphthalene.—The liquid fractions which boiled from 70–125° and from 125–170° were converted into picrate, and recrystallized from ethyl alcohol. After eight recrystallizations a constant melting point of 125–127° was attained.

Anal. Calcd. 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 into styphnate and the latter

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[9] Mayer and Schiffner, *Ber.*, **67**, 67 (1934).

[10] Unpublished work.

recrystallized from ethyl alcohol to a constant melting point of 153–154°.[11]

1,2,8-Trimethylphenanthrene.—The fraction which boiled 170–200° was converted to picrate, but this derivative dissociated readily after a few recrystallizations from methyl alcohol had removed excess picric acid. The fluffy white hydrocarbon so obtained melted at 141–142°. Similar treatment of the corresponding fraction from the second dehydrogenation yielded more of the same substance.

Anal. Calcd. for $C_{17}H_{16}$: C, 92.73; H, 7.27; mol. wt., 220. Found: C, 92.90, 92.45; H, 7.49, 7.23; mol. wt. (Rast), 204, 202.

The picrate of this hydrocarbon was crystallized from ethyl alcohol saturated at 0° with picric acid. The picrate melted 162–163°.

The solid fractions which boiled at 200–250° under 2 mm. pressure were recrystallized from ethyl alcohol five times. The resulting hydrocarbon was the same as the one described directly above; 0.08 g. of this substance was dissolved in boiling glacial acetic acid and 0.05 g. of chromic anhydride was added. The mixture was heated under reflux for thirty minutes, then cooled, and diluted with water. A small amount of an orange colored quinone which melted 189–190° was obtained. This quinone was dissolved in ethyl alcohol, an excess of *o*-phenylenediamine was added, and the solution was evaporated to dryness. The residue was taken up in ether, and extracted with 1% hydrochloric acid to remove unreacted diamine. Evaporation of the ether solution left a pale yellow quinoxaline which melted 129–131°. The melting points of hydrocarbon and the derivatives mentioned above (in the order discussed) are reported by Haworth[12] as 144–145, 163, 196–197, 131–132°, and by Ruzicka[13] as 142–143, 161–163, 194, 131–132°.

The Polymethylpicene.—The combined still residues from the ether extracts and the benzene extracts were sublimed at 300° under low pressure. The sublimed material was crystallized several times from benzene. After treatment with decolorizing carbon and further recrystallization, a product which melted 305–306° and crystallized in shiny flat platelets with a bluish luster was obtained.

Anal. Calcd. for $C_{25}H_{20}$: mol. wt., 320; C, 93.70; H, 6.30; for $C_{24}H_{18}$: mol. wt., 306; C, 94.09; H, 5.91. Found: mol. wt. (Rast), 306, 309; C, 93.80, 93.97; H, 6.17, 6.11.

The hydrocarbon dissolves in concentrated sulfuric acid with the production of a deep emerald green color, a reaction also given by picene,[14] and it is oxidized by chromic anhydride in glacial acetic acid to a reddish orange quinone which possesses no definite melting point (like picene quinone). Analysis of a sample of this quinone which had been recrystallized from dioxane indicated that it contained a considerable quantity of a substance richer in oxygen. Lack of material prevented further purification.

Summary

1. 1,2,7-Trimethylnaphthalene, 1,2,8-trimethylphenanthrene, a polymethylpicene and a polyalkylcyclohexene have been shown to be present among the products formed by dehydrogenating friedelinol by selenium.
2. Cerin and friedelin should be classed with the triterpenoids. They contain a hydrogenated pentacyclic nucleus.
3. A tentative structure has been assigned to friedelinol, the reduction product of the ketone, friedelin.

COLLEGE PARK, MD.

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[11] Ruzicka [*Helv. Chim. Acta*, **15**, 431 (1932)] gives the following melting points: picrate, 129°; styphnate, 157°.

[12] Haworth and Mavin, *J. Chem. Soc.*, **141**, 2720 (1932).

[13] Ruzicka and Hosking, *Helv. Chim. Acta*, **14**, 203 (1931).

[14] Burg, *Ber.*, **13**, 1834 (1880).

[CONTRIBUTION FROM THE UNIVERSITY OF MARYLAND]

The Dehydrogenation of Ursolic Acid by Selenium[1]

BY NATHAN L. DRAKE AND HARRY M. DUVALL

During his study of polyterpenoid substances, Ruzicka dehydrogenated a small quantity (5 g.) of ursolic acid by means of selenium[2] and identified 1,2,7-trimethylnaphthalene (sapotalene) as one of the dehydrogenation products. In connection with certain other work in progress in this Laboratory, it seemed desirable to repeat this work using larger quantities of material, and we were very fortunate in obtaining for this purpose, through the courtesy of Drs. C. E. Sando and K. S. Markley of the U. S. Department of Agriculture, a considerable quantity of crude ursolic acid.

In addition to sapotalene we have obtained two other substances by the action of selenium at 320–340° on ursolic acid, *viz.*, 2,7-dimethylnaphthalene, and a polymethylpicene, apparently identical with a substituted picene obtained by Ruzicka[2] from related triterpenoid substances. This polymethylpicene is identical with the compound obtained by Drake and Haskins by the dehydrogenation of friedelinol.[3]

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[1] From the Ph.D. dissertation of H. M. Duvall.

[2] Ruzicka, Brüngger, Egli, Ehmann, Furter and Hoösli, *Helv. Chim. Acta*, **15**, 431 (1932).

[3] Drake and Haskins, THIS JOURNAL, **58**, 1684 (1936).