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; 0.03 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.

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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 Hoŏsli, *Helv. Chim. Acta*, **15**, 431 (1932).

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

Experimental

Purification of Ursolic Acid.—Two hundred grams of crude ursolic acid was dissolved in a hot solution of 50 g. of potassium hydroxide in approximately 600 ml. of methanol and 300 ml. of water. A small quantity of insoluble brown material was skimmed off and the solution filtered with suction while hot through a large Büchner funnel. The hot filtered solution was then treated with 40 g. of decolorizing charcoal, filtered, and the charcoal treatment repeated twice. The resulting solution was next heated on the steam-bath to remove some of the methyl alcohol (not enough to cause separation of potassium ursolate); 1500 ml. of hot water was then added and the ursolate salted out by the addition of 50% potassium hydroxide solution (about 50 g. of potassium hydroxide in 50 ml. of water was necessary).

The precipitated potassium ursolate was collected on a large Büchner funnel, sucked dry, and then dissolved in 500–600 ml. of hot methanol. This solution, after filtration while hot, was acidified to Congo red by 6 *N* hydrochloric acid. The resulting precipitate was filtered and washed carefully twice by stirring it in a beaker with about a liter of boiling water acidified with hydrochloric acid. One recrystallization from ethyl alcohol yielded a product which melted 278–280°.[4] Further recrystallization raised the melting point to 283–284°.

Anal. Calcd. for $C_{30}H_{48}O_3$: C, 78.88; H, 10.60. Found: C, 79.05, 78.86; H, 10.69, 10.53.

The Dehydrogenations.—Two 50-g. portions and one 200-g. portion of ursolic acid were dehydrogenated. The apparatus and procedure were essentially as in our earlier work.[5] The products of the second and third dehydrogenations were worked up together; 59.5 g. of ether-soluble products and 13.7 g. of benzene-soluble products were so obtained.

Fractionation of the Ether-Soluble Products.—The ether-soluble material was distilled from a 200-ml. flask with a sausage side-arm. Fractions with the following boiling ranges, weights and physical states, were obtained (l. = liquid; s. = solid): 115–150° at 12 mm., 2.5 g., l.; 150–175° at 11 mm., 3.6 g., l.; 175–200° at 12 mm., 21.1 g., l.; 200–250° at 12 mm., 8.9 g., l.; 265–285° at 6–8 mm., 8.0 g., l. and s.; 285–310° at 2 mm., 7.9 g., s.; 350–365° at 3 mm., 6.1 g., s.

By redistillation at 11–12 mm. in a small Claisen flask, fractions 1, 2, 3 and 4 were separated into a principal fraction boiling from 130–140°, and a number of lower and higher boiling fractions. This principal fraction was then subjected to careful fractionation at 1–2 mm. in a column about 92 cm. in height packed with Wilson rings. After a small fore-run, the bulk of the material had a refractive index of n^{25}_D 1.5997-1.6001. This material was combined with other fractions of nearly the same index and used for preparation of derivatives of sapotalene.

The lower boiling fractions from the second distillation were likewise carefully fractionated in the ring-packed column. From the intermediate fractions of this distillation a solid was obtained, which after further purification proved to be 2,7-dimethylnaphthalene.

2,7-Dimethylnaphthalene.—This substance, isolated as described directly above, had a melting point of 96.5°; its picrate melted at 135–136°, and its styphnate at 159–160°. The corresponding values given in the literature[2] are 97, 136 and 159°, respectively.

Anal. Calcd. for $C_{12}H_{12}$: C, 92.25; H, 7.75. Found: C, 91.93; H, 7.70. Calcd. for $C_{18}H_{15}O_7N_3$: C, 56.09; H, 3.93. Found: C, 56.25; H, 3.95. Calcd. for $C_{18}H_{15}O_8N_3$: C, 53.85; H, 3.77. Found: C, 53.84; H, 3.89.

1,2,7-Trimethylnaphthalene.—It did not prove feasible to purify sapotalene as such, so the substance was converted into picrate and purified by crystallization. The picrate was then decomposed by dilute aqueous ammonia and the styphnate prepared. The picrate melted at 128–129°, the styphnate at 157–157.5°; the melting points of these substances given in the literature[2] are 129 and 157°, respectively.

Anal. Calcd. for $C_{19}H_{17}O_7N_3$: C, 57.13; H, 4.27. Found: C, 57.42, 57.24; H, 4.53, 4.35. Calcd. for $C_{19}H_{17}O_8N_3$: C, 54.92; H, 4.11. Found: C, 55.19, 55.13; H, 4.19, 4.22.

The Polymethylpicene.—The fourth, fifth and sixth fractions from the initial distillation contained solid material. This solid was purified by recrystallization from benzene, and its melting point found to be 304°.

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: C, 94.07, 93.80; H, 5.92, 6.03; mol. wt. (Rast), 300, 296.

This hydrocarbon gave the same characteristic green color when treated with sulfuric acid as does picene,[6] and was oxidized by chromic anhydride in glacial acetic acid to a quinone which reacted with *o*-phenylenediamine to give a quinoxaline. To date we have not been able to obtain either quinone or quinoxaline in a state of analytical purity.

Summary

1, Sapotalene, 2,7-dimethylnaphthalene and a polymethyl picene have been obtained from ursolic acid by selenium dehydrogenation.

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[4] All melting points are corrected.

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

[6] Beilstein, 4th ed., Julius Springer, Berlin, Vol. V, 1918, p. 735.