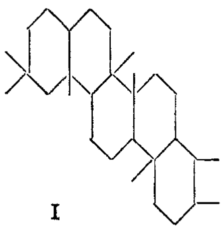
[CONTRIBUTION FROM THE LABORATORY FOR ORGANIC CHEMISTRY OF THE TECHNISCHE HOCHSCHULE, ZÜRICH]

Saponins and Sapogenins. II. The Products of the Selenium Dehydrogenation of Echinocystic Acid

BY C. R. NOLLER[1]

The most fruitful method for gaining an insight into the structure of the polyterpenoids has been the investigation of the products of their dehydrogenation with selenium. Such work has led Ruzicka and his co-workers[2] to postulate the carbon skeleton, I, as characteristic of the triterpenoids. On dehydrogenation this is considered as giving rise to 1,2,3,4-tetramethylbenzene, 2,7-dimethylnaphthalene, 1,2,7-trimethylnaphthalene, 1,2,5,6-tetramethylnaphthalene, a pentamethyldinaphthyl, $C_{25}H_{24}$, and a picene homolog, $C_{25}H_{20}$. In addition most triterpenoids yield the same 1,2,7-trimethylnaphthol. Of the various triterpenoids that have been investigated, only sumaresinolic acid appears to give all of these products.



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Echinocystic acid, $C_{27}H_{42}(CHOH)(CH_2OH)$-$COOH$,[3] on selenium dehydrogenation resembles sumaresinolic acid in that it gives rise to all of these products with the exception of the dinaphthyl homolog of melting point 141.5°. In place of it, however, a new hydrocarbon of melting point 166–167° and of undetermined structure has been isolated in small amount. Analyses of the hydrocarbon and its dipicrate indicate a formula of $C_{26}H_{28}$ or $C_{28}H_{30}$.

Selenium Dehydrogenation.—Two lots of 50 g. each of echinocystic acid, m. p. 305–308°, were heated under an air condenser with 65 g. of selenium at 310–320° for twenty-four hours and at 335–345° for forty-eight hours. The residues were extracted with ether until they could be pulverized readily and the pulverized material again extracted with ether. The ether was removed from the combined extracts by distillation. The ether-insoluble residues were placed in an extraction thimble and continuously extracted with dioxane until the extract was no longer colored. The extract was filtered and the dioxane distilled.

The ether extract was placed in a Claisen flask with a fractionating side arm and distilled at 12 mm., when the following fractions were obtained: (1) 100–130°, 1.0 g.; (2) 130–160°, 7.6 g.; (3) 160–180°, 7.2 g.; (4) 180–210°, 2.5 g. The residue was next distilled at 0.1 mm. to give fractions (5) 150–210°, 0.9 g.; (6) 210–260°, 4.1 g.; and (7) 260–360°, 6.1 g. The first three fractions boiling up to 180° at 12 mm. were refractionated at 0.3 mm. to give fractions (9) below 70°, 1.0 g.; (10) 70–85°, 2.1 g.; (11) 85–95°, 3.9 g.; (12) 95–105°, 2.8 g.; (13) 105–115°, 2.1 g.; (14) 115–120°, 1.0 g.

1,2,3,4-Tetramethylbenzene.—Fraction 9 was redistilled at 12 mm. giving 0.3 g. of liquid boiling at 80–100°. This was treated with a few drops of liquid bromine and the solid product crystallized from alcohol containing a few drops of acetone. After five more crystallizations from alcohol it melted at 209–211° with a preliminary softening at 200°. Because the melting point was somewhat higher than previously reported for 5,6-dibromo-1,2,3,4-tetramethylbenzene, an analysis for bromine content was made.

Anal.[4] Calcd. for $C_{10}H_{12}Br_2$: Br, 54.75. Found: Br, 54.86.

2,7-Dimethylnaphthalene.—Fraction 10 partially solidified. The crystals, twice recrystallized from methyl alcohol, melted at 96.5–97.5°. The picrate melted at 135.5–136.5° and the styphnate at 159–160°.[5]

1,2,7-Trimethylnaphthalene (Sapotalin).—The oil from Fraction 10, together with Fractions 11 and 12, distilled at 12 mm. gave about 4 g. boiling at 140–145°. The purified picrate melted at 128–129°. The hydrocarbon regenerated from the picrate was converted to the styphnate, m. p. 156.5–157.5.

1,2,7-Trimethylnaphthol.—The crystals from fraction 4 were washed with pentane and crystallized five times from hexane. The melting point of 154–155° remained unchanged during the last three crystallizations. The methyl ether, after three crystallizations from methyl alcohol, melted at 89–90°. The addition compound with trinitrobenzene melted at 145–146° after two crystallizations from methyl alcohol.

1,2,5,6-Tetramethylnaphthalene.—Fractions 13 and 14 were crystallized three times from methyl alcohol, when they melted at 116–117°. The picrate, after three crystallizations from methyl alcohol containing a small amount of picric acid, melted at 155–156°. The styphnate melted at 164–165°.

Hydrocarbon, M. P. 166–167°.—The fraction from which the hydrocarbon $C_{25}H_{24}$ has previously been isolated[2] boils at 200–220° at 0.2 mm. Echinocystic acid yields very little material boiling in this range so that a cut over a longer range was taken. Fraction 6 was a viscous resin which was dissolved in hot benzene. On dissolving picric acid in the hot solution and cooling, the

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[1] Fellow of the John Simon Guggenheim Memorial Foundation, 1933.

[2] Ruzicka and co-workers, *Helv. Chim. Acta*, **15**, 431, 1496 (1932); **17**, 442 (1934).

[3] Bergsteinsson and Noller, THIS JOURNAL, **56**, 1403 (1934).

[4] Microanalyses by Dr. M. Furter.

[5] In all cases the identity of the hydrocarbons was verified by mixed melting points with authentic specimens of the hydrocarbon and its derivatives.

picrate separated. This was crystallized once from benzene, giving 0.7 g. melting at 202–204°. The hydrocarbon was regenerated from the picrate by means of ammonia, giving approximately 0.2 g. This was recrystallized three times from acetone, once from acetone and a small amount of decolorizing carbon and finally from acetone alone, when it melted at 166–167°.

Anal. Calcd. for $C_{26}H_{28}$: C, 91.71; H, 8.29. For $C_{28}H_{30}$: C, 91.75; H, 8.25. Found: C, 91.67, 91.66; H, 7.85, 8.13.

A portion of the hydrocarbon was converted into the picrate which after one recrystallization from benzene melted at 209–210° with decomposition.

Anal. Calcd. for $C_{38}H_{34}O_{14}N_6$: C, 57.13; H, 4.29. For $C_{40}H_{36}O_{14}N_6$: C, 58.23; H, 4.40. Found: C, 56.84; H, 4.06.

The trinitrobenzenate melted at 219–220° but was insufficient for analysis.

Hydrocarbon, $C_{25}H_{20}$.—The residue from the dioxane extraction was heated very gradually in a flask with a wide low side arm and slowly distilled at 0.1 to 0.3 mm. With the bath at 300° a red liquid distilled which crystallized to a yellow solid in the cooler portion of the side arm. After washing with a little hot pyridine and crystallizing three times from a mixture of pyridine and methyl alcohol and three times from pyridine, a white product melting at 292–293° was obtained. Although not quite pure, it showed no depression in melting point when mixed with a specimen of the $C_{25}H_{20}$ hydrocarbon obtained from sumaresinolic acid, m. p. 296–297°.

Anal. Calcd. for $C_{25}H_{20}$: C, 93.69; H, 6.31. Found: C, 93.42; H, 5.95.

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Summary

Echinocystic acid on dehydrogenation with selenium yields the 1,2,3,4-tetramethylbenzene, 2,7-dimethylnaphthalene, 1,2,7-trimethylnaphthalene, 1,2,7-trimethylnaphthol, 1,2,5,6-tetramethylnaphthalene and the hydrocarbon, $C_{25}H_{20}$, which have previously been obtained by the dehydrogenation of other triterpenoids. The hydrocarbon, $C_{25}H_{24}$, m. p. 141.5°, could not be detected but instead a new hydrocarbon, m. p. 166–167°, has been isolated.

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Rearrangement of Alkyl Phenyl Ethers on Heating at Moderate Temperatures. Synthesis of Tertiary Amyl, Tertiary Butyl and Diisobutyl Phenols

BY SAMUEL NATELSON

Although the author and subsequently others[1] have shown that saturated alkyl phenyl ethers will rearrange in the presence of catalysts, the rearrangement of these compounds in the absence of these catalysts had not been clearly demonstrated.

It was observed that the boiling range and refractive index of *s*-amyl phenyl and cresyl ethers increased with each distillation at atmospheric pressure. In the case of the tertiary octyl phenyl ether (diisobutyl phenyl ether) rearrangement is so rapid that one distillation at atmospheric pressure is capable of bringing about a high conversion to the substituted phenol.[1a]

The substituted phenols are becoming of increasing value and importance as antiseptics and for the preparation of oil soluble resins. Since these alkyl phenyl ethers can be prepared readily by heating alkali with molten phenols and then adding the alkyl halide, this procedure is inexpensive in operation, considering the availability of chlorinated hydrocarbons. If the substituted phenol is desired, the ether need not be isolated but heating may be continued at elevated temperatures until conversion to the substituted phenol has taken place.

Diisobutyl, tertiary amyl and tertiary butyl phenols were therefore prepared by condensing the corresponding alkyl halide with potassium phenolate, adjusting the time of heating and the temperature so as to isolate the substituted phenols. The *t*-amylphenol obtained was identical with *p*-amylphenol, para rearrangement predominating in this case.

The method of preparing ethers by condensing unsaturated hydrocarbons with phenols with the aid of sulfuric acid could also be used to prepare substituted phenols by varying conditions. The poor yield of ethers previously obtained[2] was due

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[1] (a) Samuel Natelson, Ph.D. Thesis, New York University, 1931; (b) Niederl and Natelson, THIS JOURNAL, **53**, 272, 1932 (1931); **54** 1063 (1932); (c) Sowa, Hinton and Nieuwland, *ibid.*, **55**, 3406 (1933); (d) Smith, *ibid.*, **55**, 3720 (1933).

[2] Niederl and Natelson, *ibid.*, **53**, 272 (1931).