[CONTRIBUTION FROM THE DANIEL SIEFF RESEARCH INSTITUTE]

The Strophanthidin Dehydrogenation Product $C_{21}H_{16}$

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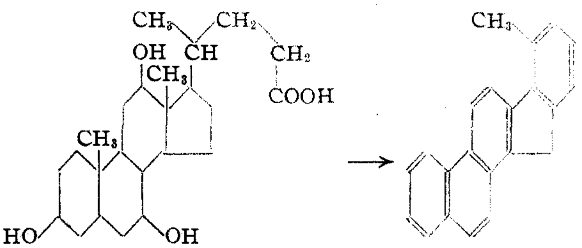
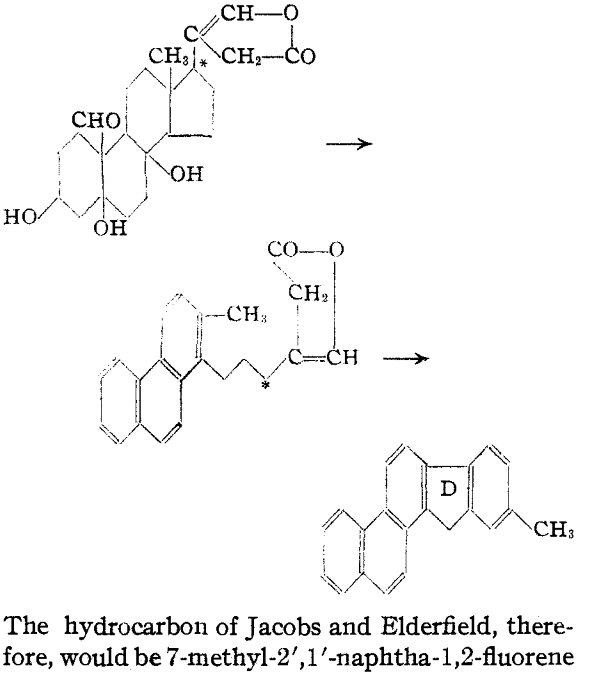
By selenium dehydrogenation of strophanthidin, Jacobs and Elderfield[1] obtained *inter al.* a hydrocarbon, m. p. 296°, to which they ascribed the formula $C_{21}H_{16}$. Their tentative suggestion that it may be 1,2-cyclopentenotriphenylene has been ruled out by synthetic work carried out in this Laboratory.[2] Further work in this direction has led to the assumption that the above hydrocarbon belongs to the 2′,1′-naphtha-1,2-fluorene derivatives, which have been obtained from cholic acid, cholesterol, ergosterol and sitosterol.[3] First of all, the absorption spectrum of the above hydrocarbon, a few milligrams of which we owe to the courtesy of Professor Jacobs, shows a definite resemblance to those of pure naphthafluorene derivatives.[4] Absorption maxima have been observed at λ 2720, 2800, 2980, 3150, and lower ones at 3200, 3400 and 3600.

With regard to the formation of the hydrocarbon from cholic acid, Bachmann, Cook, Hewett and Iball[3] have presented conclusive evidence for the scheme



but they point out that "this identification of Ruzicka's hydrocarbon throws no further light on the structure of the pentacyclic hydrocarbons of analogous structure obtained by dehydrogenation of sterols," as cholesterol does not yield 5-methyl-8-isopropyl-2′,1′-naphtha-1,2-fluorene, to be expected according to the given scheme. We may add that strophanthidin could not give rise to a pentacyclic system at all according to the scheme of the English authors, as only a three-carbon side-chain, containing one methyl group, is available.

The carbon atom lacking for the construction of the pentacyclic system can only be the quaternary methyl group at C_{13} which is used in an analogous way in the synthesis of chrysene from cholic acid[5] or oestrone.[6] There, the cyclopentane system opens and gives a six-membered ring by subsequent recyclization. Here, the new ring (D) formed is again a five-membered one, and the number of the chain atoms is increased by one, so that the possibility is given for additional six-membered ring formation:



The hydrocarbon of Jacobs and Elderfield, therefore, would be 7-methyl-2′,1′-naphtha-1,2-fluorene and have the formula $C_{22}H_{16}$ instead of $C_{21}H_{16}$; combustion analysis would not be able to differentiate between the two formulas. In fact, the hydrocarbon prepared from strophanthidin proved identical with 7-methylnaphthafluorene, prepared according to Cook and co-workers,[3] on the follow-

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[1] Jacobs and Elderfield, *J. Biol. Chem.*, **107**, 143 (1934).

[2] E. Bergmann and O. Blum-Bergmann, THIS JOURNAL, **58**, 1678 (1936); E. Bergmann and F. Bergmann, *ibid.*, **60**, 1805 (1938).

[3] Diels, Gaedke and Koerding, *Ann.*, **459**, 1 (1927); Ruzicka and co-workers, *Helv. Chim. Acta*, **16**, 216, 812 (1933); **17**, 200 (1934); Cook and co-workers, *J. Chem. Soc.*, 1727 (1934); 1319 (1935); 54 (1936).

[4] Compare Cook and co-workers;[3] Mayneord and Roe, *Proc. Roy. Soc.* (London), **158A**, 634 (1937). For comparing the spectra, I am very much indebted to Dr. Frieda Goldschmidt of this Institute.

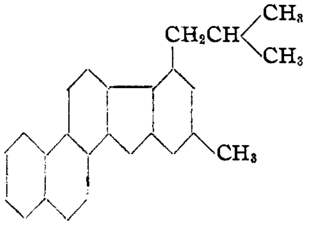
[5] Diels and Karstens, *Ann.*, **478**, 129 (1930); *cf. Ber.*, **66**, 487 (1933); Ruzicka and co-workers, *Helv. Chim. Acta*, **17**, 200 (1934). For cholesterol, see Diels, *et al.*, *Ber.*, **60**, 140 (1927); *Ann.*, **459**, 1 (1927); Raudnitz and co-workers, *Z. physiol. Chem.*, **209**, 103 (1932); *Ber.*, **66**, 879 (1933).

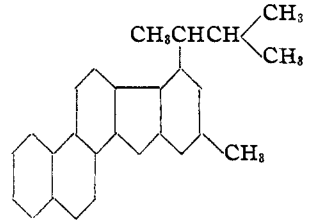
[6] Butenandt and Thompson, *ibid.*, **67**, 140 (1934).

ing evidence. They have the same m. p. 301° (on slow heating);[7] the melting point of their mixture is not depressed; the solubilities in various solvents are identical. Due to the extreme scarcity of material, it was impossible to compare derivatives of the two products; so the evidence presented is somewhat unsatisfactory, were it not for the immanent probability of the above hypothesis.

It is a curious coincidence that the naphthafluorene hydrocarbon derived from cholic acid, too, had been formulated $C_{21}H_{16}$ at first, the correct formula being $C_{22}H_{16}$ according to Cook and co-workers[3] and to Bernal and Crowfoot.[8]

In view of the reported result, the hydrocarbons obtained from cholesterol and ergosterol, respectively, have to be formulated as follows





In accordance with Ruzicka's results,[3] the two sterols would yield different naphthafluorene derivatives, and the contradictory view of Diels and co-workers[9] would be untenable. The possibilities of synthesizing 7-methyl-9-isobutyl- and 7-methyl-9-(α,β-dimethylpropyl)-naphthafluorene are being investigated in this Laboratory.

With the elucidation of the mechanism of naphthafluorene formation from steroids, all the possibilities of their aromatization seem to be clear: the methyl at C_{13} is eliminated in the formation of methylcholanthrene, picene[10] and of 5-methyl-naphthafluorene from cholic acid (see above); it is used for conversion of the cyclopentano ring into a six-membered system in the formation of chrysene[5,6] and for the formation of a new cyclopentano ring in the case of the naphthafluorene derivatives studied above; it migrates in the formation of γ-methyl-1,2-cyclopenteno-phenanthrene from various steroids.[11] The quaternary methyl at C_{10} is generally eliminated in dehydrogenation processes.

Summary

The polycyclic hydrocarbon obtained by dehydrogenation of strophanthidin is 7-methyl-2′,1′-naphtha-1,2-fluorene and has the formula $C_{22}H_{16}$ (not $C_{21}H_{16}$). The mechanism of its formation is discussed and formulas for the analogous derivatives of cholesterol and ergosterol, respectively, are suggested.

The various aromatization mechanisms for steroids are enumerated.

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[7] Cook and co-workers give 334–336° in a bath preheated to 300°.

[8] Bernal and Crowfoot, *J. Chem. Soc.*, 93 (1935).

[9] Diels and co-workers, *Ann.*, **459**, 1 (1927); **478**, 129 (1930); *Ber.*, **66**, 1122 (1933); **67**, 113 (1934); *cf.* Ruzicka, *et al.*, *Helv. Chim. Acta*, **16**, 818 (1933); **17**, 200 (1934); **18**, 434 (1935). Recently, Diels and Stephan [*Ann.*, **527**, 279 (1937)] admit that the dehydrogenation of ergosterol does *not* give at least exclusively the same naphthafluorene derivative as the dehydrogenation of cholesterol.

[10] Compare Fieser, "Natural Products Related to Phenanthrene," Reinhold Publishing Corp., New York, 1936, p. 159.

[11] E. Bergmann and Hillemann, *Ber.*, **66**, 1302 (1933); E. Bergmann, *Chemistry and Industry*, **54**, 175 (1935); Cohen, Cook and Hewett, *J. Chem. Soc.*, 445 (1935); E. Bergmann and F. Bergmann, *Chemistry and Industry*, **55**, 272 (1936), and unpublished results.