CCCCXXI.—*The Unsaponifiable Matter from the Oils of Elasmobranch Fish. Part III. Tetracyclosqualene and the Production of a New Naphthalene Hydrocarbon.*

By JOHN HARVEY, ISIDOR MORRIS HEILBRON, and EDWARD DAVID KAMM.

IT was shown by Heilbron, Kamm, and Owens (this vol., p. 1630) that the pyrogenic decomposition of squalene led to the formation, among other terpenes, of a complex sesquiterpene fraction from which, on dehydrogenation with sulphur, a hydrocarbon was isolated which yielded a minute amount of a picrate, possibly cadalene picrate. As all attempts to obtain this compound in larger quantities have proved abortive, we have directed our attention to the tetracyclic isomeride derived from squalene in the hope of obtaining from it, by dehydrogenation, aromatic hydrocarbons in better yield. Whereas squalene itself reacts explosively with sulphur, the reaction with tetra*cyclo*squalene can be controlled and at 200—270° a vigorous evolution of gas occurs. Decomposition took place during the dehydrogenation, and from the mixed products were separated (*a*) a small quantity of a colourless, mobile oil resembling *m*- or *p*-cymene, and (*b*) a colourless oil, b. p. 100—160°/13 mm., which yielded a well-defined, crystalline picrate the analytical values for which agree with the formula $C_{19}H_{17}O_7N_3$. By decomposing this picrate with ammonia, a colourless, solid hydrocarbon (m. p. 33·5°) of formula $C_{13}H_{14}$ was obtained. This substance has a distinct naphthalene-like odour and its identity with a substituted naphthalene compound is suggested both by analogy with the dehydrogenation derivatives of typical sesquiterpenes (compare Ruzicka, *Helv. Chim. Acta*, 1922, **5**, 345) and by the abnormally high value of its molecular refractivity ($\Sigma[R_L]_D = 2{\cdot}75$), which is typical of all such hydrocarbons.

Of the numerous possible hydrocarbons of this formula, α- and β-propyl-, β-*iso*propyl-, and two trimethyl-naphthalenes have been described, but these differ from the compound under discussion.

As the yield of the hydrocarbon was extremely small, and as its formation appeared to be due to the preliminary decomposition of tetra*cyclo*squalene into less complex molecules, the destructive distillation of this compound was studied by the method already described for squalene itself. The complex mixture produced, which was in every way comparable with that obtained from squalene, was fractionated as previously described and a monoterpene fraction was obtained from which a portion closely resembling pinene in odour was isolated. This is being fully investigated.

The whole of the sesquiterpene fraction was treated with sulphur at 200—270° and thereafter the same hydrocarbon of m. p. 33·5° was isolated in 4% yield. Sufficient of this substance has not yet been obtained for the determination of its structure, but larger quantities are being collected for this purpose.

The diterpene fraction also was treated with sulphur, but the dehydrogenated products failed to give crystalline addition compounds with picric acid. This proves definitely that the picrate-forming aromatic hydrocarbon ($C_{13}H_{14}$) is produced from the sesquiterpene portions and hence almost confirms its naphthalene structure.

During the preparation of the comparatively large quantity of tetra*cyclo*squalene required in these experiments, squalene was upon one occasion treated with formic acid which had already been used once for the same purpose. The hydrocarbon produced, even after prolonged boiling with the reagent, differed in physical properties from normal tetra*cyclo*squalene, although it was undoubtedly also a tetracyclic substance. It showed the same exaltation of molecular refractivity and on treatment with sulphur yielded the same $C_{13}H_{14}$ hydrocarbon. It can only be assumed, therefore, that cyclisation in this case must have taken place in a different way, without, however, altering the carbon skeleton of the molecule or the positions of the two remaining ethenoid linkings to which the abnormal molecular refractivity has been ascribed.

EXPERIMENTAL.

*Dehydrogenation of Tetra*cyclo*squalene.* — Tetra*cyclo*squalene (200 g.) and finely-powdered sulphur (100 g.) were heated at 200—270° until, after 14 hours, evolution of hydrogen sulphide and mercaptan had ceased. The viscous, almost black product was separated by distillation into a deep red liquid (58 g.) and an unworkable resinous residue. The distillate was repeatedly distilled over bright metallic sodium until it was colourless and was then fractionated under reduced pressure, whereby the following fractions were obtained.

i. B. p. 70—75°/14 mm. (5 g.). A colourless oil with an odour indistinguishable from that of cymene. B. p. 170—180°/760 mm., $n_D^{20°}$ 1·5080, $d_{20°}^{20°}$ 0·8941. It still contained a trace of sulphur, probably in the combined state. The quantity at our disposal was insufficient for complete purification or further examination.

ii. B. p. 100—160°/13 mm. (25 g.). This portion consisted of a colourless oil giving no definite fractions on distillation. The whole was treated with a hot saturated alcoholic solution of picric acid, whereby gradual precipitation of an orange solid occurred; by treating the mother-liquor with more picric acid, further crops were obtained (total yield of crude substance, 4·3 g.). The picrate crystallised from absolute alcohol, in which it was only moderately easily soluble, in long, orange-red needles, m. p. 139—140° (Found: C, 56·8, 57·0; H, 4·3, 4·3; N, 10·7, 10·6. $C_{19}H_{17}O_7N_3$ requires C, 57·1; H, 4·3; N, 10·5%).

The Hydrocarbon $C_{13}H_{14}$.—The picrate was dissolved in ether and decomposed by warming under reflux with dilute aqueous ammonia. The ethereal solution was separated, washed with water, and dried. The colourless oil obtained from it was distilled at 15 mm., almost the whole coming over at 145° and solidifying on cooling. After crystallisation from hot 95% alcohol, it was obtained in centimetrelong, colourless, silky needles, m. p. 33·5°. It is volatile in steam, only slightly soluble in cold methyl or ethyl alcohol, and readily soluble in ether and benzene : $d^{20°}_{20°}$ 1·0103, $n^{20°}_{D}$ 1·6110, $[R_L]_D$ 58·5 (calc. for $C_{13}H_{14}|^{=}_{5}$, 55·7) (Found : C, 91·6; H, 8·3. $C_{13}H_{14}$ requires C, 91·8; H, 8·2%).

*The Destructive Distillation of Tetra*cyclo*squalene*.—Tetra*cyclo*squalene (150 g.) was distilled under the conditions previously given for squalene itself (Heilbron, Kamm, and Owens, *loc. cit.*). The following groups of products were obtained.

	B. p.	Description.	Weight.
1	—	Combustible gas.	(1200 c.c./758 mm.)
2	28— 44°/758 mm.	Mobile, almost colourless oil.	2·5 g.
3	55—100°/20 mm.	Mobile, yellow oil.	44·0 ,,
4	110—180°/20 mm.	,, ,,	42·0 ,,
5	180—210°/20 mm.	Viscous ,,	11·5 ,,
6	210—280°/20 mm.	,, deep yellow oil.	10·0 ,,
7	—	Resinous residue.	25·0 ,,

Of these, groups 1, 2, 6, and 7 have not yet been examined; the liquid comprising group 2 has an odour identical with that of the amylene derived from squalene.

Group 3 was carefully refractionated from a Willstätter flask in a stream of nitrogen and again subdivided. By this means there was obtained a fraction (7·0 g.), b. p. 49—54°/15 mm. Refractionation of this at atmospheric pressure gave, as main portion, a liquid, b. p. 154—158°/758 mm., $d^{20°}_{20°}$ 0·8279, and $n^{20°}_{D}$ 1·4663. The odour closely resembled that of pinene.

Group 4 on refractionation was resolved into two main fractions : (*a*) b. p. 119—125°/14 mm., $d^{18°}_{18°}$ 0·8886, $n^{18°}_{D}$ 1·4940, $[R_L]_D$ 66·83; weight, 7·5 g.; (*b*) b. p. 138—158°/14 mm., $d^{18°}_{18°}$ 0·9111, $n^{18°}_{D}$ 1·5028, $[R_L]_D$ 66·16; weight, 15·0 g. ($[R_L]_D$ calc. for $C_{15}H_{24}|^{=}_{2}$, 66·1).

Each of these fractions was treated with sulphur as previously described, and the purified dehydrogenated product with alcoholic picric acid. From each the picrate, m. p. 139—140°, was isolated. The total yield of the hydrocarbon $C_{13}H_{14}$ given by this method is no better than that obtained from tetra*cyclo*squalene itself, the only advantage of the method being that the monoterpene and diterpene fractions are preserved.

Group 5, which was obviously composed of diterpenes, was treated as a whole with sulphur, but failed to yield a dehydrogenation product that would form a solid picrate.

*Preparation of an Isomeric Tetra*cyclo*squalene*.—On one occasion, for reasons of economy, squalene was caused to cyclise by the use of formic acid which had previously been employed for the same purpose. A comparatively mobile liquid was obtained which could not be further changed by treatment with fresh formic acid : b. p.

228—230°/3 mm., $d_{20^\circ}^{20^\circ}$ 0·9237, $n_D^{20^\circ}$ 1·5098, $[R_L]_D$ 132·7, iodine value 111·3 (calc. for $C_{30}H_{50}|_{2}^{=}$, 124).

On treatment of this new compound (245 g.) with sulphur (140 g.) at 200—280° as described above, 56 g. of volatile products were obtained. These were fractionated into (1) b. p. 70—120°/15 mm., (2) b. p. 120—165°/15 mm., and (3) b. p. 165—185°/15 mm. On treatment of these fractions with alcoholic picric acid, No. 2 readily yielded 4 g. of a picrate, m. p. 139—140°, identical with that already obtained from the compound $C_{13}H_{14}$.

In conclusion, we desire to record our thanks to the Department of Scientific and Industrial Research for grants which enabled this work to be carried out.

THE UNIVERSITY, LIVERPOOL. [*Received, November 2nd*, 1926.]