CXV.—*The Unsaponifiable Matter from the Oils of Elasmobranch Fish. Part VI. The Constitution of Squalene as deduced from a Study of the Decahydrosqualenes.*

By Isidor Morris Heilbron and Albert Thompson.

Although the structure of squalene has been largely elucidated as a result of the work described in former communications (especially Part V, preceding paper), additional evidence would nevertheless be welcome, the more so since the larger terpene disintegration products such as bisabolene (Part I) and dihydro-ψ-ionone (preceding paper) were only isolated in very small amount, and consequently their formation is open to possible criticism. It has become abundantly clear that, if further insight is to be gained into the structure of the hydrocarbon, it is necessary in the first instance to render the molecule less liable to complete disruption under the action of oxidising agents. In order to accomplish this, we have now hydrogenated squalene to a point where five of the six ethenoid linkages would theoretically be saturated and then treated the product with ozone. After decomposition with water and removal of peroxides (see experimental), the oxidation products were separated into acid and neutral components. The examination of these has confirmed the work described in Part II of this series (Heilbron, Hilditch, and Kamm, J., 1926, 3131) and proves beyond doubt that the hydrogenation process is not only largely selective but leads to the formation of isomeric decahydrosqualenes. Dodecahydrosqualene (squalane) is also present to the extent of approximately 25%, from which it follows that products hydrogenated to a lesser degree than the decahydrosqualene must also have been formed.

Neutral Products.—(a) *Steam-volatile.* When the whole of the neutral oil was subjected to a short steam distillation, a readily volatile, pleasant-smelling liquid passed over. This was extracted with ether and on fractionation gave as principal fraction a colourless liquid, b. p. 164—166°/765 mm., which we have characterised as methyl *iso*hexyl ketone, $CHMe_2{\cdot}CH_2{\cdot}CH_2{\cdot}CH_2{\cdot}COMe$.

(b) *Non-steam-volatile.* The residue from the steam distillation was collected and separated by distillation under reduced pressure into large primary fractions. Each of these was refractionated and, after suitable distillates had been united, a further fractionation gave the following: (A) b. p. 125—145°/12 mm., (B) 155—175°/3 mm., (C) 200—210°/2 mm.

Fraction A. Further distillation of the fraction yielded a pale yellow liquid, b. p. 119—121°/11 mm. (semicarbazone, m. p. 97—98°), which has been definitely identified as hexahydro-ψ-ionone, $CHMe_2{\cdot}[CH_2]_3{\cdot}CHMe{\cdot}[CH_2]_3{\cdot}COMe$.

Fraction B. After repeated distillation, a definite ketone fraction was obtained, b. p. 136—139°/1·5 mm., $n_D^{20^\circ}$ 1·4461. In view of the isolation of methyl *iso*hexyl ketone and hexahydro-ψ-ionone, it was thought that the product would most likely be the next isoprene homologue, 2 : 6 : 10-trimethyl-14-pentadecanone,

$$CHMe_2{\cdot}[CH_2]_3{\cdot}[CHMe(CH_2)_3]_2{\cdot}COMe.$$

This ketone was accordingly synthesised from farnesol and isolated as a colourless liquid, b. p. 143°/3 mm., $n_D^{20^\circ}$ 1·4435.* The semicarbazones of both ketones were prepared: that from the squalene product melted at 71·5—73·5°; the synthetic semicarbazone melted definitely lower (70—70·5°), but showed no depression when mixed with the former. Despite this fact, results based upon repeated ultimate analyses of the two semicarbazones prove conclusively that they are not identical and that the squalene ketone has the higher molecular formula $C_{19}H_{38}O$.

Fraction C. Analysis of this fraction indicated that it consisted of a mixture of squalane and some oxygen-containing substance, the character of which was shown by its removal by means of sodium bisulphite solution. The regenerated ketone, after distillation in a vacuum, gave analytical results agreeing with the formula $C_{23}H_{46}O$ or $C_{24}H_{48}O$.

Intermediate fractions. The various fractions with boiling points intermediate between those already recorded were each treated with semicarbazide acetate, and the solids formed submitted to very careful fractional crystallisation, without, however, revealing the presence of any semicarbazone other than those already described.

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* After this synthesis was completed, an account of this ketone was published by F. G. Fischer (*Annalen*, 1928, **464**, 69). This author gives the melting point of the semicarbazone as 66—67°. The higher melting point recorded by us was only reached by working with comparatively large quantities and after numerous crystallisations.

Acid Products.—The acid products were converted into their methyl esters and roughly separated by fractional distillation into three distinct fractions and a very high-boiling residue which has not been examined in detail. The lowest-boiling fraction upon redistillation yielded mainly a colourless liquid, b. p. 139—141°/750 mm. The regenerated acid, which gave a solid anilide, m. p. 111—112°, was identified as γ-methyl-*n*-valeric acid.

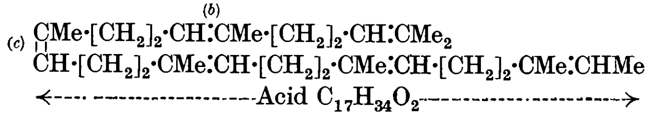
The second main distillate, after further fractionation, was obtained as a colourless liquid, b. p. 105—107°/13 mm., which yielded an amide, m. p. 80—81°. Analytical values for both the ester and the amide pointed to their being derived from an acid $C_{11}H_{22}O_2$. In view of the isolation of γ-methyl-*n*-valeric acid it seemed highly probable that this acid would be 4 : 8-*dimethylnonoic acid*, and this surmise was confirmed by the synthesis of the acid from hexahydro-ψ-ionone by oxidation with chromic acid.

The final definite ester fraction consisted of a pale yellow liquid, b. p. 145—148°/5 mm. As attempts to prepare solid derivatives of the corresponding acid failed, this was carefully fractionated from a Willstätter bulb. The most abundant fraction boiled at 187—192°/2 mm. and gave analytical values in excellent agreement with the formula $C_{17}H_{34}O_2$.

Discussion of Results.

It was pointed out in Part V that all the reactions of squalene could be adequately explained on the assumption that the hydrocarbon exists in the two isomeric forms (I) and (II).

(I.)



$$\begin{array}{l}{}^{(c)}\,\mathrm{CMe{\cdot}[CH_2]_2{\cdot}CH\overset{(b)}{:}CMe{\cdot}[CH_2]_2{\cdot}CH{:}CMe_2}\\ \quad\ \mathrm{CH{\cdot}[CH_2]_2{\cdot}CMe{:}CH{\cdot}[CH_2]_2{\cdot}CMe{:}CH{\cdot}[CH_2]_2{\cdot}CMe{:}CHMe}\\ \quad\ \longleftarrow\text{------------Acid } C_{17}H_{34}O_2\text{------------}\longrightarrow\end{array}$$

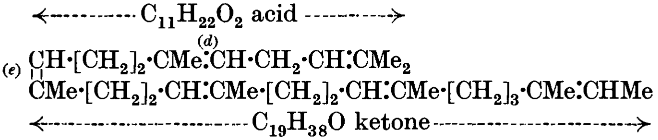
(II.) $\mathrm{CMe_2{:}CH{\cdot}CH_2{\cdot}[CH_2{\cdot}C({:}CH_2){\cdot}CH_2{\cdot}CH_2]_4{\cdot}CH_2{\cdot}CMe{:}CHMe}$

The results now obtained afford striking evidence of the correctness of formula (I). For instance, the isolation in good yield of methyl *iso*hexyl ketone and hexahydro-ψ-ionone conclusively establishes the presence of the ethenoid linkages (*b*) and (*c*). As regards the remaining portion of the molecule, it necessarily follows from the isolation of the latter ketone that an acid constituent having the molecular formula $C_{17}H_{34}O_2$ should also be present. The fact that such an acid has actually been obtained coincides too well with the theoretical requirements to be merely fortuitous, and there can be little doubt that, despite the lack of definite constitutional proof, this acid is 3 : 7 : 11-*trimethyltetradecoic acid.*

Turning now to the question of the mode of formation of γ-methyl-

n-valeric acid and 4 : 8-dimethylnonoic acid, it is obvious that these could not possibly be formed directly through fission at the double bond of any of the mono-olefins derived from (I). It is also certain that they have not originated through further oxidation of any of the ketones primarily produced, as the conditions employed in the decomposition of the ozonides wholly preclude this possibility, *i.e.*, 4 : 8-dimethylnonoic acid could not have arisen from secondary oxidation of hexahydro-ψ-ionone but must have resulted from cleavage of the molecule at an ethenoid linkage *already present* in the hydrocarbon. As regards formula (II), it is practically certain, as pointed out in Part II, that the $CH_2\colon C<$ groups would be the primary points for hydrogen addition, in which case ozonisation of the resultant decahydrosqualene could only give rise to an acid of very high molecular weight ($C_{27}H_{54}O_2$). We are thus forced to conclude that squalene exists in still another stable form, the structure of which must correspond to formula (III).

(III.)



$$\begin{array}{l} \xleftarrow{\qquad\qquad} C_{11}H_{22}O_2 \text{ acid} \xrightarrow{\qquad\qquad} \\ {}^{(e)}\ CH\cdot[CH_2]_2\cdot CMe\overset{(d)}{\colon} CH\cdot CH_2\cdot CH\colon CMe_2 \\ \quad\ \ \| \\ \quad\ CMe\cdot[CH_2]_2\cdot CH\colon CMe\cdot[CH_2]_2\cdot CH\colon CMe\cdot[CH_2]_3\cdot CMe\colon CHMe \\ \xleftarrow{\qquad\qquad\qquad\qquad} C_{19}H_{38}O \text{ ketone} \xrightarrow{\qquad\qquad\qquad\qquad} \end{array}$$

Additional evidence of the existence of this isomeride is supplied through the isolation of the $C_{19}H_{38}O$ ketone which, like the above-mentioned acids, cannot be accommodated by formula (I) or (II). Although its structure has not been directly elucidated, its striking similarity to 2 : 6 : 10-trimethyl-14-pentadecanone suggests a closely analogous structure. This fact, taken in conjunction with the formation of 4 : 8-dimethylnonoic acid, leads to the conclusion that the ketone is 3 : 7 : 11-*trimethyl*-15-*hexadecanone* and that it has originated through scission of a decahydrosqualene at the ethenoid linkage (*e*) (formula III). The production of γ-methyl-*n*-valeric acid similarly demands the presence of 3 : 7 : 11 : 15-*tetramethyl*-19-*eicosanone* (scission at *d*), and there is no reason to doubt that the high-boiling ketone separated from dodecahydrosqualene is actually this substance.

Finally, a review of the ketones and acids produced leads to the conclusion that the addition of hydrogen proceeds from that part of the molecule already containing the two hydrogen atoms additional to the simple triterpene formula, *i.e.*, from the terminal group $CMe\colon CHMe$ common to all three isomeric forms. This assumption is necessary in order to explain the absence of any ketone (*i.e.*, 2 : 6 : 10-trimethyl-14-pentadecanone) of higher molecular weight than hexahydro-ψ-ionone from the hydrogenated products from (I) or of fatty acid more complex than 4 : 8-dimethylnonoic acid from (III).

EXPERIMENTAL.

Preparation of the Ozonide.—Squalene obtained by the distillation method from the liver oil of *Centrophorus granulosus* (Heilbron, Kamm, and Owens, J., 1926, 1638) was treated with hydrogen in the presence of nickel catalyst until an absorption of 5 mols. of hydrogen had occurred (compare Heilbron, Hilditch, and Kamm, *loc. cit.*). The crude product was twice distilled, the final distillate boiling at 227—230°/3 mm. (Found : iodine value, 61. Calc. for $C_{30}H_{50}|_{1}^{=}$: iodine value, 62). This was then treated in chloroform solution (150 g. of hydrocarbon in 450 g. of solvent) at 0° with oxygen containing 5% of ozone, the gas being passed in at the rate of 10 litres per hour until a sample no longer absorbed bromine (30 hours). The chloroform was removed under reduced pressure first at the ordinary temperature and then at 100° for 30 minutes. The ozonide formed a clear, colourless, oily liquid lighter than water and possessing a pungent, clinging odour.

Decomposition of the Ozonide Mixture.—The ozonide was decomposed by boiling with water (300 c.c.) for 2 hours under reflux in an atmosphere of nitrogen, the gases evolved being passed successively through water and baryta solution; during the decomposition, a small amount of barium carbonate was deposited in the latter. The reaction mixture was acid to litmus, reduced Fehling's solution, and readily liberated iodine from potassium iodide solution, thus showing the presence of organic peroxides. These were decomposed by boiling the mixture with potassium hydroxide solution (75 c.c. of 50%) for 15 minutes, a treatment which simultaneously destroyed the aldehydes. Both the decomposition of the ozonide and the subsequent destruction of the peroxides proceeded smoothly. The reaction mixture was diluted with water and repeatedly extracted with ether. The alkaline portion was acidified with dilute sulphuric acid and the acids were removed by ether extraction and worked up as subsequently described. After removal of solvent from the neutral ethereal solution, the residue was subjected to distillation in steam, 2000 c.c. of distillate being collected. Both the distillate and the residue were saturated with sodium chloride and extracted with ether, and the ethereal solutions dried over anhydrous sodium sulphate. Under these conditions, 450 g. of hydrogenated squalene gave 502 g. of ozonide, from which 16 g. of steam-volatile ketone, 287 g. of neutral, non-steam-volatile matter, including about 35% of squalene, and 178 g. of mixed acids were obtained. The weight of barium carbonate collected amounted to 3·1 g. The aqueous solution through which the gases and low-boiling volatile material had passed was examined for the presence of acetone and formaldehyde, but no trace of either could be detected.

Steam-volatile fraction. The bulk of this distilled at 164—166°/765 mm., forming a colourless, mobile liquid possessing a strong, carraway-like odour (Found : C, 74·7, 74·6; H, 12·7, 12·7. Calc. for $C_8H_{16}O$: C, 75·0; H, 12·5%). It failed to reduce Fehling's solution but readily gave a crystalline addition compound with sodium bisulphite solution. The *semicarbazone*, which was prepared in the usual manner, formed almost immediately and, after three crystallisations from acetone, gave colourless, glistening plates, m. p. 149—150° (Found : C, 58·4, 58·3; H, 10·2, 10·4; N, 22·6. $C_9H_{19}ON_3$ requires C, 58·4; H, 10·3; N, 22·7%). These data agree well with the values for methyl *iso*hexyl ketone, which was synthesised by condensing *iso*amyl iodide with ethyl acetoacetate and hydrolysing the *iso*amylacetoacetic ester produced (compare Clarke, *J. Amer. Chem. Soc.*, 1909, **31**, 3). The ketone gave a semicarbazone, m. p. 152—153°, which showed no depression in melting point in admixture with the semicarbazone described above.

Non-volatile neutral portion. This was first roughly separated into the following fractions, leaving a residue of 18·4 g.

Fract.	Press. (mm.).	Temp.	Wt. (g.).	Fract.	Press. (mm.).	Temp.	Wt. (g.).
1	12·5	80—100°	9·8	4	3·0	170—200°	28·6
2	,,	100—150	17·9	5	,,	200—225	178·5
3	,,	150—200	17·6	6	2·0	225—245	11·3

Redistillation of fraction 1 yielded a further small quantity of methyl *iso*hexyl ketone and a higher-boiling fraction, which was combined with 2. Fraction 3 was similarly divided into a low- and a high-boiling portion, and the former also added to 2. Redistillation of these combined fractions provided a main distillate, b. p. 125—145°/12 mm. (14·5 g.).

Hexahydro-ψ-ionone.—On refractionation of the above, a main portion (5 g.) was collected as a slightly yellow liquid, b. p. 119—121°/11 mm., possessing a faint, clinging odour (Found : C, 78·2, 78·3; H, 13·2, 13·2. Calc. for $C_{12}H_{24}O$: C, 78·3; H, 13·0%. Calc. for $C_{13}H_{26}O$: C, 78·8; H, 13·1%). The ketone, which yielded a crystalline bisulphite addition product, was converted into its semicarbazone, which separated from methyl alcohol in colourless, glistening plates, m. p. 97—98° (Found : C, 65·7; H, 11·6; N, 16·5. Calc. for $C_{13}H_{27}ON_3$: C, 64·7; H, 11·2; N, 17·6%. Calc. for $C_{14}H_{29}ON_3$: C, 65·9; H, 11·4; N, 16·5%). The ketone was regenerated by refluxing the semicarbazone with oxalic acid in aqueous-alcoholic solution and, after distillation, gave the following analytical values: C, 78·6, 78·5; H, 13·3, 13·3%, in excellent agreement with those required for $C_{13}H_{26}O$. Hexahydro-ψ-ionone was synthesised according to Ishizaka's method (*Ber.*, 1914, **47**, 2453), the only modification being that the hydrogenation of the geraniol was carried out at 130° under pressure, a nickel catalyst supported on charcoal being used in place of platinum-black. The semicarbazone obtained from the synthetic ketone melted at 97—98°, alone or mixed with the semicarbazone described above.

3 : 7 : 11-*Trimethyl*-15-*hexadecanone*.—Fraction 4 was combined with the residue of fraction 3 and distilled, giving as main fraction a portion (18 g.), b. p. 155—175°/3 mm. On further fractionation the ketone was obtained as a pale yellow, odourless, oily liquid (7·5 g.), b. p. 136—139°/1·5 mm. (Found: C, 80·3; H, 13·6. Calc. for $C_{18}H_{36}O$: C, 80·6; H, 13·5. Calc. for $C_{19}H_{38}O$: C, 80·9; H, 13·5%). The *semicarbazone* was prepared in the usual manner in methyl-alcoholic solution, a large volume of solvent being necessary in order to maintain the ketone in solution. After 7 days, the reaction mixture was poured into water, and the sticky solid collected and pressed on a porous tile. The semicarbazone was purified with difficulty by repeated crystallisation, first by slow evaporation of a methyl-alcoholic solution, and finally from ice-cold methyl alcohol (ice-jacketed filter). It formed colourless plates, m. p. 71·5—73·5° [Found: (micro), C, 71·2; H, 12·3; N, 12·3, 12·5. $C_{19}H_{39}ON_3$ requires C, 70·2; H, 12·0; N, 12·9%. $C_{20}H_{41}ON_3$ requires C, 70·8; H, 12·1; N, 12·4%].

3 : 7 : 11 : 15-*Tetramethyl*-19-*eicosanone* (?).—This ketone was contained in the high-boiling neutral fraction (146 g.), b. p. 200—210°/2 mm., obtained by refractionation of fraction 5. Analysis of this showed that it consisted of a mixture of squalane and some oxygen-containing substance (Found: C, 84·5; H, 14·6. Calc. for $C_{30}H_{62}$: C, 85·3; H, 14·7%). The oil was diluted with ether and shaken for 30 days with saturated sodium bisulphite solution, and the deposited solid separated by filtration and thoroughly washed with ether. The bisulphite product was decomposed with sodium carbonate solution, and the ketone, isolated by means of ether, was distilled, the main fraction being collected at 195—205°/3 mm. (Found: C, 81·5, 81·7; H, 13·5, 13·7. Calc. for $C_{23}H_{46}O$: C, 81·7; H, 13·6%. Calc. for $C_{24}H_{48}O$: C, 81·8; H, 13·6%).

Hexahydrofarnesol.—Farnesol (50 g.) was hydrogenated at 100° by means of nickel supported on charcoal (5 g. of catalyst containing 15% of nickel). After 2 hours, the absorption of the hydrogen had practically ceased and the mixture was accordingly cooled, filtered, and treated with fresh catalyst (5 g.). When the temperature was now raised to 130°, the theoretical amount of hydrogen was absorbed in 30 minutes. The cooled filtered liquid was fractionated, practically the whole distilling at 125—128°/3 mm. It had $n_D^{18^\circ}$ 1·4469, $d_{4^\circ}^{18^\circ}$ 0·8361, whence $[R_L]_D = 72{\cdot}9$ (Found : C, 78·6, 78·8 ; H, 14·2, 14·2. Calc. for $C_{15}H_{32}O$: C, 79·0 ; H, 14·0% ; $[R_L]_D$, 72·7).

Hexahydrofarnesyl Bromide (12-bromo-2:6:10-trimethyldodecane).—This was prepared substantially as described by Fischer (*loc. cit.*). It formed a colourless, mobile liquid with a faint odour, b. p. 122°/4 mm., $n_D^{18^\circ}$ 1·4605, $d_{4^\circ}^{18^\circ}$ 1·001 (Found : Br, 27·4, 27·5. Calc. for $C_{15}H_{31}Br$: Br, 27·5%).

Hexahydrofarnesylacetoacetic ester formed a colourless liquid, b. p. 175—178°/3 mm., $n_D^{18^\circ}$ 1·4484, $d_{4^\circ}^{18^\circ}$ 0·9014 (Found : C, 74·3, 74·1 ; H, 12·0, 12·1. Calc. for $C_{21}H_{40}O_3$: C, 74·1 ; H, 11·4%).

2 : 6 : 10-*Trimethyl*-14-*pentadecanone*.—The preceding ester was decomposed by alcoholic potassium hydroxide solution at room temperature substantially as recorded by Fischer (*loc. cit.*). The ketone (10·5 g.) formed a colourless, odourless liquid, b. p. 142—143°/3 mm., $n_D^{19^\circ}$ 1·4435, $d_{4^\circ}^{19^\circ}$ 0·8403, whence $[R_L]_D = 84{\cdot}6$ (Found : C, 80·6, 80·5 ; H, 13·3, 13·4. Calc. for $C_{18}H_{36}O$: C, 80·6 ; H, 13·5% ; $[R_L]_D$, 85·1). The semicarbazone was obtained after many crystallisations from ice-cold methyl alcohol in colourless, glistening plates, m. p. 70—70·5° (Found : C, 70·3 ; H, 12·2 ; N, 12·9. Calc. for $C_{19}H_{39}ON_3$: C, 70·2 ; H, 12·0 ; N, 12·9%).

Acid Products.—The crude acid mixture was esterified by means of methyl alcohol and sulphuric acid, giving a brownish-yellow liquid (170 g.) with an odour reminiscent of *iso*butyric acid. The esters were separated by distillation at 15 mm. into the following fractions : (1) up to 110° (31 g.), (2) 110—150° (32 g.), (3) 150—200° (39 g.), (4) 200—245° (53 g.), residue (13 g.). Each was again distilled and, after suitable fractions had been united, a further series of distillations resulted in the formation of the following three portions : (a) 155—165°/756 mm. (5 g.), (b) 100—110°/13 mm. (17 g.), (c) 140—150°/5 mm. (17 g.).

γ-Methyl-n-*valeric Acid*.—Fraction (a) consisted of a colourless liquid which upon fractionation distilled almost wholly at 139—141°/750 mm. (3·9 g.) (Found : C, 64·4 ; H, 11·0 ; sap. equiv., 136. Calc. for $C_7H_{14}O_2$: C, 64·7 ; H, 10·8% ; sap. equiv., 130). The ester was hydrolysed, and the acid converted into the anilide by refluxing with twice its weight of distilled aniline for 24 hours. The crude product was crystallised from aqueous alcohol in presence of animal charcoal, separating in long, colourless needles, m. p. 110—112° (Found : C, 75·3, 75·5 ; H, 9·1, 9·1 ; N, 7·6. Calc. for

$C_{12}H_{17}ON$: C, 75·4; H, 8·9; N, 7·3%). These data are in good agreement with those recorded for γ-methyl-*n*-valeric acid, which was synthesised from malonic ester and *iso*butyl iodide (compare Bentley and Perkin, J., 1898, **73**, 48) and converted into its anilide, m. p. 111—112°. A mixed m. p. determination of the two anilides showed no depression.

4 : 8-*Dimethylnonoic Acid.*—Further distillation of fraction (b) gave as main fraction a colourless liquid, b. p. 105—108°/3 mm. (7·8 g.), having a more pleasant though fainter odour than the first fraction (Found : C, 71·2; H, 11·8; sap. equiv., 189. Calc. for $C_{11}H_{22}O_2$: C, 71·0; H, 11·8%; sap. equiv., 186. Calc. for $C_{12}H_{24}O_2$: C, 72·0; H, 12·0%; sap. equiv., 200). The ester was hydrolysed, and the acid further purified by conversion into its sparingly soluble calcium salt, whereupon a small quantity of a more soluble salt (probably the salt of a dicarboxylic acid) was removed; but it was not further investigated. The regenerated acid was then distilled and analysed, figures in good agreement with the formula $C_{11}H_{22}O_2$ being obtained (Found : C, 70·6, 70·5; H, 11·9, 11·9%; equivalent, 182). This was confirmed by the preparation of the *amide* through the acid chloride in the following manner. A solution of the acid (2·5 g.) in a mixture of dry benzene (10 c.c.) and light petroleum (25 c.c.) was heated under reflux with thionyl chloride (5 g.) until the action was completed. The crude acid chloride, after removal of solvent and excess of reagent, was mixed with alcoholic ammonia, and the amide, which solidified on standing, was repeatedly crystallised from ether–light petroleum, yielding colourless plates, m. p. 80—81° (Found : C, 71·1, 71·2; H, 12·6, 12·5; N, 7·7. $C_{11}H_{23}ON$ requires C, 71·3; H, 12·4; N, 7·6%).

4 : 8-Dimethylnonoic acid was synthesised by heating a solution of synthetic hexahydro-ψ-ionone (2·5 g.) in glacial acetic acid for 4 hours at 80° with a solution of chromic acid (5 g.) in the same solvent. This treatment yielded 0·8 g. of acid and 1·3 g. of unchanged ketone, which was again treated in the same manner. The acid was converted into its amide, m. p. 77—79° (Found : N, 8·0%), as described above. The compound was identical in all respects with the amide from the natural product and showed no depression of melting point in admixture.

3 : 7 : 11-*Trimethyltetradecoic Acid* (?).—Fraction (c) on redistillation gave mainly a yellowish oil, b. p. 145—148°/5 mm. (15 g.) (Found : C, 74·6; H, 12·6; sap. equiv., 236. Calc. for $C_{15}H_{30}O_2$: C, 74·4; H, 12·4%; sap. equiv., 242. Calc. for $C_{16}H_{32}O_2$: C, 75·0; H, 12·5%; sap. equiv., 256. Calc. for $C_{17}H_{34}O_2$: C, 75·4; H, 12·6%; sap. equiv., 270). The ester was hydrolysed and attempts were made to obtain a solid derivative without success.

As it seemed probable that some dicarboxylic acid might be present, fractional distillation of the acid itself was carried out and fractions were collected for every 5° rise of temperature. This fractionation showed that the acid was indeed a mixture. The two bulkiest fractions, (a) b. p. 182—187°/5 mm. (3·0 g.), and (b) 187—192°/5 mm. (4·5 g.), were analysed [Found: (a) C, 75·1; H, 12·5%; equivalent, 261. (b) C, 75·3; H, 12·8%; equivalent, 264]. These results show that the acid has the formula $C_{17}H_{34}O_2$, and, taken in conjunction with the isolation of hexahydro-ψ-ionone, lead almost inevitably to the conclusion that it is in effect 3 : 7 : 11-*trimethyltetradecoic acid*. The low values for carbon and hydrogen given by the methyl ester are probably due to contamination with small quantities of the ester of a keto- or dicarboxylic acid, either of which would originate through oxidation of some of the lesser hydrogenated squalene products to which attention has already been drawn (p. 883).

4 : 8-*Dimethylnonaldehyde* (?).—In certain experiments the reaction mixture, after the decomposition of the ozonide with water, was worked up without removal of the peroxides. Under these conditions certain fractions of the neutral portion (boiling between methyl *iso*hexyl ketone and hexahydro-ψ-ionone), on being treated with semicarbazide acetate, yielded, in addition to methyl *iso*hexyl ketone semicarbazone, a small quantity of a more soluble *semicarbazone*, which crystallised from acetone in colourless plates, m. p. 115—116° (Found: C, 63·1; H, 11·0; N, 18·8. $C_{12}H_{25}ON_3$ requires C, 63·4; H, 11·0; N, 18·4%). Hydrolysis of the semicarbazone yielded a liquid which readily reduced Fehling's solution. These results lead to the conclusion that the substance is 4 : 8-dimethylnonaldehyde. Unfortunately the quantity of aldehyde regenerated was too small to allow of further work being carried out.

THE UNIVERSITY, LIVERPOOL.

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