CXL. THE STRUCTURE OF VITAMIN A.

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It has already been shown [Edisbury *et al.*, 1932] that it is possible to obtain by several methods, and especially with acid reagents, a product from vitamin A exhibiting highly characteristic narrow absorption bands. On the basis of the structure (I) suggested by Karrer, Morf and Schöpp [1931] for the vitamin it seemed to us that the new product was probably formed by intramolecular condensation whereby a hydronaphthalene (II) might result.

As is well known, many hydronaphthalene compounds can readily be dehydrogenated by sulphur, or better by the Diels method employing selenium, to yield true aromatic naphthalene hydrocarbons. Thus cadalene (1 : 6-dimethyl-4-*isopropyl*naphthalene) or eudalene (1-methyl-7-*isopropyl*naphthalene) is formed from many bicyclic sesquiterpenes [Ruzicka *et al.*, 1922].

On the other hand, ionene (III) [Ruzicka and Rudolf, 1927] and tetracyclosqualene (IV) [Heilbron and Wilkinson, 1930; Ruzicka *et al.*, 1932], both of which contain *gem*-dimethyl groupings attached to quaternary carbon atoms,

yield on dehydrogenation 1 : 6- and 1 : 2 : 5-trimethylnaphthalene respectively.

On the basis of this, we anticipated that the suggested hydronaphthalene derivative (II) would yield with selenium either one or other of the above methylnaphthalenes. On submitting this idea to experimental test we have found that on treatment of the product obtained from a rich concentrate by the action of alcoholic hydrochloric acid with selenium at 300–330°, a good yield of 1 : 6-dimethylnaphthalene results.

The extraordinary ease with which vitamin A is transformed into a cyclised product prompted us to attempt the dehydrogenation with the vitamin itself, with the result that an equally high yield of 1 : 6-dimethylnaphthalene was obtained. It is thus evident that the intramolecular change is due either to the elevated temperature at which the reaction is carried out [cf. Heilbron *et al.*, 1932] or to the action of hydrogen selenide, the presence of which can be observed even at comparatively low temperatures.

EXPERIMENTAL.

A vitamin A concentrate, $E_{1\text{cm}}^{1\%}$ 617 $m\mu$, 3140, (7.4 g.), mixed with finely powdered selenium (7.4 g.), was heated under a long air condenser at 300–330° for 48 hours. The cooled viscous product was repeatedly extracted with boiling ether, the combined extracts were filtered and the solvent was removed. The residual oil was then distilled over metallic sodium, whereby the following fractions were obtained.

A. B.P. 120–200°/20 mm. (1.6 g.); redistillation of this fraction over sodium yielded a colourless oil, B.P. 70–110°/5 mm. (1.2 g.).

B. A high boiling fraction, B.P. 200–300°/20 mm. This fraction was obtained as a viscous orange oil which rapidly darkened on standing (1 g.).

1 : 6-Dimethylnaphthalene. A warm solution of oil (A) was treated with an alcoholic solution of picric acid (1 g. in 15 cc.), when a slight darkening in colour was immediately observed. On standing the liquid solidified almost completely yielding orange crystals (1 g.) m.p. 100–110°. After recrystallisation from absolute alcohol long orange needles (m.p. 113–114°) were obtained. (Found: C, 56.0; H, 4.2: $C_{18}H_{16}O_7N_3$ requires C, 56.1; H, 3.9 %.) A mixed melting-point with authentic 1 : 6-dimethylnaphthalene picrate (m.p. 112–113°) gave no depression. The hydrocarbon was obtained by shaking an ethereal solution of the picrate with aqueous ammonia. Its absorption spectrum was compared with that of pure 1 : 6-dimethylnaphthalene (Fig. 1) and found to be qualitatively and quantitatively identical.

The *styphnate* was also prepared and forms yellow needles, m.p. 120°. (Found: C, 53.8; H, 3.5. $C_{18}H_{15}O_8N_3$ requires C, 53.9; H, 3.7 %.)

The high boiling fraction (B) failed to give any crystalline derivative with either picric or styphnic acid.

Cyclisation of vitamin A. This was carried out by treating the vitamin A concentrate (11 g.) in alcohol (500 cc.) with concentrated hydrochloric acid (6 cc.). The solution was allowed to stand for 20 minutes at room temperature during which time the pale yellow colour changed to dark brown. Solid sodium carbonate was added until the solution reacted alkaline, when the colour immediately reverted to light yellow. Excess sodium carbonate was filtered off, and the alcohol removed under reduced pressure. The residue was taken up in light petroleum and the petroleum extract repeatedly washed with water. After drying and removal of solvent a light brown viscous oil remained which on spectroscopic examination was found to exhibit well defined absorption bands at 392, 369, 350 and 333 $m\mu$. Treatment of this product with selenium by the method already described above gave 1 : 6-dimethylnaphthalene in a yield of approximately 3.5 %.

The isolation of 1 : 6-dimethylnaphthalene in good yield by the dehydrogenation of vitamin A definitely establishes the terpenoid nature of the vitamin and the presence in the richest concentrates of a material possessing a constitution which, as far as the fourteenth carbon atom, must be identical with the constitution (I) advanced by Karrer, Morf and Schöpp [1931] for vitamin A.

Fig. 1. 1 : 6-Dimethylnaphthalene in hexane.

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