

diphenyl-bromobismuthine, suggesting that organic radicals are readily liberated from their compounds with bismuth.

Exchange of metal atoms will probably occur with many typical organo-metallic compounds, where the link between carbon and metal is weaker than that between carbon and a non-metal of the same group of the Periodic Table; also, the strength of binding decreases with increasing atomic weight of the central atom.

1 Station Hill,
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¹ NATURE, 135, 828, May 18, 1935.

² Ber., 46, 1685; 1913.

³ J. Chem. Soc., 105, 2210; 1914.

Synthesis of Dehydroandrosterone by the Decomposition of γ -Sitosterol from Soya Beans

Two substances have been isolated from the urine of men which resemble the male hormone in their ability to stimulate the growth of the capon's comb¹. One of these, androsterone, described in detail by Butenandt and Tscherning², has been produced artificially by Ruzicka and his collaborators³ by means of the oxidative decomposition of epi-dihydrocholesterol acetate, and has thereby been recognised as 3-epi-oxy- Δ^5 -cholestanone-(17). A second oxyketone containing two hydrogen atoms less has been obtained by Butenandt and Dannenbaum⁴ from an unsaturated chloroketone, $C_{27}H_{45}OCl$, occurring in extracts of urine, by replacement of the chlorine atom by a hydroxyl group. On carrying out the analogous replacement reaction using the saturated chloroketone, androsterone was obtained. These reactions leave the question unanswered as to the position of the double bond and the steric position of the hydroxyl group.

I have elucidated this by carrying out the synthesis of the hormone by means of the decomposition of one of the known sterols. Acetylated sitosterol obtained from soya beans was chlorinated in the 5,6-position in order to protect the double bond, and the side chain was afterwards removed by vigorous oxidation with chromic acid, more or less according to the classical method of Ruzicka by which the identity of the ring system of sitosterol and cholesterol has been determined⁵. From the dechlorinated and saponified reaction mixture, a sparingly soluble semicarbazone was obtained; this, after hydrolysis, gave beautiful crystals of an oxyketone which proved to be chemically and physiologically identical with dehydroandrosterone obtained from urine in this laboratory. This oxyketone has a melting point at 147°–148° C. (corr.), the mixed melting point with dehydroandrosterone showing no depression; oxime, leaflets or needles, melting point and mixed m.p. 190° C. (corr.); benzoate, melting point 252°–253° C. (corr.); specific rotation, $+13.5^\circ$ in absolute alcohol. The capon unit is about 210 γ , which is the same as the dose required of natural dehydroandrosterone (androsterone = 70 γ). Dehydroandrosterone is therefore 3-oxy- Δ^5 -6- Δ^5 -cholestanone-(17).

This configuration of the ring system is similar to that of sitosterol and cholesterol, which is interesting in as much as it has been found possible, by a modification of the existing process (K. David⁶) to

prepare, in this laboratory, dehydroandrosterone from urine in almost the same quantity as androsterone.

The details of this work will be published elsewhere.
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¹ J. Pharm., 40, 27; 1930.
² Z. physiol. Chem., 229, 167; 1934.
³ Helv. Chim. Acta, 17, 1389; 1934.
⁴ Z. physiol. Chem., 229, 192; 1934.
⁵ Helv. Chim. Acta, 18, 430; 1935.
⁶ Acta. brev. Neerl., 5, 1–2, 31; 1935.

Selective Accumulation of Lipochrome

It is well known that different animals deal with carotenoids derived from vegetable sources in various ways. The adipose tissue of the horse and the cow contain considerable amounts of polyene-hydrocarbons (carotenes), but it does not accumulate polyene-alcohols (xanthophylls). A precisely opposite selection would appear to take place in the fat of the hen.

We tried to locate the organ in which this selection takes place and chose the horse for the following experiment. The blood serum of the horse is free from xanthophyll, and therefore the elimination of this carotenoid takes place before it enters the general circulation. So the question arises, whether the polyene-alcohols are not absorbed at all by the gut, or whether they reach the liver and are transformed or eliminated there. To choose between these alternatives, we took blood samples, therefore, while absorption of large amounts of green food was going on, from the portal vein of a narcotised horse. No xanthophyll was found in the serum, the lipochrome of which was identical with that taken from the jugular vein; but the carotene content was found to be increased.

This observation makes it quite probable that xanthophylls do not cross the wall of the gut and that selection already takes place in the digestive organs of the horse.

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Keratin Digestion in the Larvæ of the Clothes Moth

THE digestion of keratin in the larvæ of the ordinary clothes moth, *Tineola biselliella*, was investigated by means of the micro-methods developed by Linderstrøm-Lang and Holter. In the secretion of the middle intestine a powerful proteinase was found having a pH optimum about 9.3 (40°, splitting up casein) and, contrary to animal trypsin-kinase, being but little sensitive to addition of thiol compounds (sodium sulphide, sodium thioglycolate). The pH of the secretion of animals fed with wool was about 10 (measured with the glass electrode in a carbon dioxide free chamber) and gave a strong nitroprusside reaction which was most clearly visible in the half-digested hairs present as contamination in the secretion. The reaction disappeared soon after the secretion had been exposed to the air; only a very small further visible change of the hairs was