

228. *Studies in the Sterol Group. Part XIII.*
Hydrocarbons of the Ergosterol Series.

By ISIDOR MORRIS HEILBRON, FRANK STUART SPRING, and ERIC
TAYLOR WEBSTER.

THE only hydrocarbons of the ergosterol series so far described are *allo- α -ergostane*, m. p. 84—85° (Reindel and Walter, *Annalen*, 1928, 460, 212; compare also Reindel and Detzel, *ibid.*, 1929, 475, 78), for which we suggest the simple name ergostane, and two isomeric ergotetraenes (Rygh, *Z. physiol. Chem.*, 1929, 185, 99; Stoll, *ibid.*, 1931, 202, 232).

In continuation of our work on the structure of ergosterol, hydrocarbons corresponding to dihydro- and tetrahydro-ergosterol have now been prepared.

α -Ergostadiene, m. p. 124—125°, is readily obtained either from *ergostadienyl chloride*, m. p. 137°, on treatment with sodium and amyl alcohol or by the reduction of *α -ergostadienone* by Clemmensen's method. It seems probable that it was an impure specimen of this hydrocarbon which Reindel and Walter (*loc. cit.*) isolated from their supposed *α -ergostanol*. Treatment of *α -ergostadiene* with hydrogen chloride yields *β -ergostadiene*, m. p. 66—67°, while hydrogenation in presence of a palladium catalyst gives *α -ergostene*, m. p. 77—78°. The latter hydrocarbon has also been prepared both from *α -ergostenyl chloride* and from *α -ergostenone* by methods similar to those employed for the production of *α -ergostadiene*. *α -Ergostene* gives no coloration either with antimony chloride or with the Rosenheim reagent but responds to the Tortelli-Jaffe reaction (Heilbron and Spring, *Biochem. J.*, 1930, 24, 133).

When *α -ergostadiene* is treated with mercuric acetate in alcoholic acetic acid, it is smoothly dehydrogenated to *ergostatriene-D*, m. p. 134—135°, which hydrocarbon we have also prepared by the Clemmensen reduction of *ergostatrienone-D*. The latter ketone was first described by Windaus and Auhagen (*Annalen*, 1929, 472, 185), who

obtained it by the action of finely divided nickel on dehydroergosterol. We have now prepared it in good yield by treating α -ergostadienone with mercuric acetate. Ergostatriene-D exhibits selective absorption in the ultra-violet region of the spectrum and is characterised by well-defined absorption bands at 235 $m\mu$, 243 $m\mu$, and 252 $m\mu$ identical with those exhibited by ergostatrienone-D and ergosterol-D (Heilbron, Johnstone, and Spring, J., 1929, 2248).

EXPERIMENTAL.

α -Ergostadienyl Chloride.—Dry α -dihydroergosterol (6.5 g.) was triturated with phosphoryl chloride (6.5 g.), added in small quantities during 15 minutes, and the resultant, dark green, pasty mass, after being heated with water, was extracted with ether. The residual material from the dried extract was repeatedly crystallised from benzene-alcohol, *α -ergostadienyl chloride* being obtained in long needles, m. p. 137°, $[\alpha]_D^{25}$ -7° ($c = 4$ in chloroform) (Found : C, 80.6; H, 10.8. $C_{27}H_{43}Cl$ requires C, 80.5; H, 10.7%).

α -Ergostadiene.—A solution of α -ergostadienyl chloride (1 g.) in hot amyl alcohol (40 c.c.) was treated with sodium (3 g.), added in small portions during 1 hour. The whole was then boiled for a further hour; the cold solution was shaken with water, the lower caustic soda layer separated, and the amyl alcohol removed in steam. The residue was extracted with ether and, after drying, the solution was concentrated to 4 c.c. and mixed with alcohol (4 c.c.). The product was recrystallised from alcohol, from which *α -ergostadiene* separated in flat needles, m. p. 124–125°, $[\alpha]_D^{25}$ -10° ($c = 1.8$ in chloroform).

α -Ergostadiene can also be prepared in good yield by boiling α -ergostadienone (1 g.) in xylene (4 c.c.) with amalgamated zinc (50 g.) and concentrated hydrochloric acid (100 c.c.) for 70 hours, removing the xylene in steam, and extracting the residual solid with ether; crystallisation from alcohol-benzene gives the hydrocarbon as described above.

α -Ergostadiene exhibits only general absorption and gives no colour with antimony trichloride, but with the Tortelli-Jaffe reagent an immediate green ring is produced (Found : C, 87.7, 87.8; H, 12.2, 12.2. $C_{27}H_{44}$ requires C, 88.0; H, 12.0%).

β -Ergostadiene.—A solution of α -ergostadiene in chloroform was subjected to a stream of dry hydrogen chloride for 1½ hours. The chloroform was removed under reduced pressure, and the residual oil dissolved in a small volume of alcohol. After standing at 0°, the separated solid was repeatedly crystallised from alcohol, from which *β -ergostadiene* separated in colourless crystals, m. p. 66–67°, $[\alpha]_D^{25}$ -33° . The hydrocarbon can also be prepared by treatment

of β -dihydroergosterol, m. p. 123—124° (Heilbron, Johnstone, and Spring, *loc. cit.*), with phosphoryl chloride and treatment of the oily β -ergostadienyl chloride with sodium and amyl alcohol (Found: C, 87.9, 88.0; H, 11.9, 12.0. $C_{27}H_{44}$ requires C, 88.0; H, 12.0%).

α -Ergostenyl chloride, obtained in an analogous manner to that employed in the preparation of α -ergostadienyl chloride, crystallised from benzene-alcohol in flat needles, m. p. 109—110° (Found: C, 80.2; H, 10.9. $C_{27}H_{45}Cl$ requires C, 80.1; H, 11.1%).

α -Ergostene was prepared from α -ergostenyl chloride in the usual manner, but was more readily obtained directly from α -ergostenone by the Clemmensen method. The residual oil obtained after the reduction product had been worked up solidified rapidly and on recrystallisation from ether-methyl alcohol was obtained as fine needles, m. p. 70—72°. By three further crystallisations from the same mixture or from chloroform-methyl alcohol the melting point gradually rose to a constant value of 77—78°; $[\alpha]_D^{25} + 11^\circ$ ($c = 1$ in chloroform) (Found: C, 87.2, 87.3; H, 12.4, 12.8. $C_{27}H_{46}$ requires C, 87.6; H, 12.4%).

Ergostatrienone-D.—A solution of α -ergostadienone (10 g.) in alcohol (700 c.c.) was refluxed for 2 hours together with mercuric acetate (20 g.) and glacial acetic acid (40 c.c.), the precipitated mercurous acetate separated, and the excess of mercury removed as sulphide. The filtered solution was concentrated and kept in the ice-chest; the crude ketone gradually separated. After repeated crystallisation from alcohol-benzene, ergostatrienone-D was obtained in needles, m. p. 204—205°, $[\alpha]_D + 45^\circ$ ($c = 2$ in chloroform), showing well-defined absorption bands at 235 $m\mu$, 243 $m\mu$, and 252 $m\mu$.

Ergostatriene-D.—Reduction of ergostatrienone-D with amalgamated zinc and concentrated hydrochloric acid in the usual manner gave the *hydrocarbon*, which crystallised from alcohol in needles, m. p. 134—135°, $[\alpha]_D^{25} + 42.7^\circ$ ($c = 1.78$ in chloroform); it gave with antimony chloride a yellow colour, changing fairly rapidly to orange and after some time to red (Found: C, 88.5; H, 11.6. $C_{27}H_{42}$ requires C, 88.5; H, 11.5%).

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