Short Communications

A Steroidal Glycol, 22-Hydroxycholesterol from *Narthecium ossifragum* Huds.

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In the course of an investigation of the pigments of the flowering parts of *Narthecium ossifragum*, — a tiny lily supposed to be the cause of a sheep disease of photodynamic nature, — there was, during the chromatographic separation of the crude hypophasic carotenoids also isolated a colourless compound (I), which, from the following summary of its reactions, will be seen to be one of the two stereomeric forms of the hitherto unknown 22-hydroxy-cholesterols, m.p. 186° (corr.), [α]_D^20 = 39, CHCl_3 (Anal. Calc. for C_{37}H_{46}O_4: C 80.5; H 11.52. Found: C 80.0; H 11.83). The glycolic nature is demonstrated by the formation of a diacetate, m.p. 101°, [α]_D^20 = 33 (Anal. Calc. for C_{42}H_{44}O_4: C 76.5; H 10.35. Found: C 76.5; H 10.50), and a dibenzoate, m.p. 256°, [α]_D^20 = 9 (Anal. Calc. for C_{48}H_{48}O_4: C 80.6; H 8.91. Found: C 80.6; H 8.83). Catalytic hydrogenation furnished a dihydroglycol (II), m.p. 176.5°, [α]_D^20 = 18; diacetate, m.p. 76°, [α]_D^20 = 14; dibenzoate, m.p. 215—17°, [α]_D^20 = 16.

Careful oxidation of (I) with chromium trioxide gave a compound (III) of m.p. 142.5°—43.5°, [α]_D^20 = 58. The I.R. spectrum of this oxidation product indicated an unsaturated hydroxy-ketone. The found data were close to those given by Cole and Julian 1 for 22-keto-cholesterol, (m.p. 142°—43°, [α]_D^20 = 55). Dr. Cole had the kindness to furnish a sample of this substance with m.p. 142—43°, [α]_D^20 = 60, and supposed by Dr. Cole to be a purer one. Mixed m.p. confirmed the identity of the two substances. Mixed m.p. of the acetate of (III) with the acetate of 22-keto-cholesterol, also kindly provided by Dr. Cole, furnished additional evidence for the identity.

The dihydroglycol (II) was oxidised with chromium trioxide to a diketone, m.p. 148°, [α]_D^20 = 16, which must be the previously unknown cholestan-3,22-dione. Reduction by the Clemmensen method afforded cholestan, m.p. 80°, undepressed on admixture with cholestan prepared from cholesterol.

The saponins of *Narthecium ossifragum* are presently being investigated. They seem to contain no 22-hydroxy-cholesterol. Their sapogenins have an ordinary number of oxygen atoms.

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