528. *The Chemistry of Triterpenes and Related Compounds. Part XXXIII.* The Isolation of Ergosta-7 : 22-dien-3-one from* Fomes fomentarius.

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A simple steroid ketone, ergosta-7 : 22-diene-3-one, has been isolated from *Fomes fomentarius*.

In continuation of our investigation of the wood-rotting fungi we have examined *Fomes fomentarius*, a large perennial fungus found in the British Isles only in the north of Scotland. Extraction of the fungus with light petroleum gave about 0·75% of a yellow paste which was separated by chromatography into two main fractions eluted with benzene and ether–methanol. The former yielded a ketone whose analysis indicated that it was either a steroid or triterpene containing 28 or 29 carbon atoms and no oxygen other that in the keto-group. Reduction with sodium borohydride gave two alcohols. Ozonolysis of the lower-melting alcohol gave 2 : 3-dimethylbutyraldehyde; on hydrogenation in acetic acid this alcohol absorbed one mol. of hydrogen but the intensity of the low-wavelength ultraviolet absorption of the product was greater than that of the starting material, indicating that a second double bond was being isomerised. These results suggested that the ketone and alcohols were ergosta-7 : 22-diene derivatives, the 7 : 8-double bond

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isomerising to the 8 : 14-position during hydrogenation.[1] Comparison of the constants of the ketone and the alcohols with those of ergosta-7 : 22-dien-3-one and the derived 3α- and 3β-alcohols (see Table), and direct comparison of the ketone and 3β-alcohol, proved the identity of the ketone.

This is the first time to our knowledge that a simple steroid ketone, as distinct from a triterpene, has been isolated from a natural source. Ergosta-7 : 22-dien-3β-ol has been isolated from Spanish grape-seed oil[3] and occurs as one of the minor sterols of yeast.[2]

	Found		Recorded	
	M. p.	$[\alpha]_D$	M. p.	$[\alpha]_D$
Ergosta-7 : 22-dien-3-one	184—187°	+6	177°,[a] 184·5 [1]	+1·5°,[a] +2° [1]
Ergosta-7 : 22-dien-3β-ol	171—174	−22	176 [1]	−19; −20
acetate	179—181	−15	178—180 [1]	−19
Ergosta-7 : 22-dien-3α-ol	214—215	−9	215—216 [b]	−4·4
acetate	146—148	0	156 [b]	+4

[a] Bladon, Henbest, and Wood, *J.*, 1952, 2737. [b] Windaus, Dithmar, Murke, and Suckfüll, *Annalen*, 1931, **488**, 91.

Experimental

M. p.s were determined of a Kofler block and are corrected. Rotations were determined for $CHCl_3$ solutions at room temperature. The alumina used for chromatography was of activity I—II unless otherwise stated. Light petroleum refers to the fraction with b. p. 60—80°.

Extraction of Fomes fomentarius *with Light Petroleum.*—The fungus (8 kg.) was cut into small pieces and extracted with light petroleum (30 l.) at 20° for three days. The extract was filtered and evaporated under reduced pressure, to give a yellow paste (60 g.). This was chromatographed on alumina (1 kg.), elution with benzene giving a white solid (20 g.) and elution with ether–methanol (9 : 1) a yellow paste (20 g.). By a tedious combination of chromatography and crystallisation from acetone the former solid was divided into fractions: (i) m. p. 100—205° (2·5 g.) and (ii) needles (5·0 g.), m. p. 175—179° (from acetone), raised by further crystallisation to 184—187°, $[\alpha]_D$ +6° (Found: C, 84·75; H, 11·3. Calc. for $C_{28}H_{44}O$: C, 84·8; H, 11·2%), $\nu_{max.}$ 1710 cm.$^{-1}$.

Reduction of the Ketone.—The ketone of m. p. 175—179° (0·512 g.) in dioxan–methanol (2 : 1, 30 ml.) was treated with sodium borohydride (0·3 g.) at 50° for 2 hr. Dilution with water and acidification with dilute sulphuric acid afforded a solid (0·52 g.) which was adsorbed from light petroleum on alumina (activity III; 50 g.). Elution with light petroleum–benzene (1 : 1; 350 c.c.) gave a solid (0·045 g.) which crystallised from acetone as needles, m. p. 201—205°, $[\alpha]_D$ −7°. After further elution with light petroleum–benzene (1 : 1; 150 c.c.) and benzene (300 c.c.), elution with benzene–ether (10 : 1; 200 c.c.; and 4 : 1; 700 c.c.) gave a solid (0·46 g.) which crystallised from acetone as prisms, m. p. 171—174°, $[\alpha]_D$ −22°. The infrared spectra indicated that both were alcohols. The two alcohols were more conveniently obtained directly from the benzene-eluted fraction resulting from chromatography of the light petroleum extract of the fungus. The fraction (1·0 g.) was dissolved in dioxan (20 c.c.) and methanol (10 c.c.). Sodium borohydride (1·0 g.) in dioxan (10 c.c.) and methanol (10 c.c.) was added and the mixture was boiled under reflux for 1 hr., then kept at *ca.* 40° for 3 hr. Most of the solvent was removed under reduced pressure, and water and dilute sulphuric acid were added. The white precipitate was collected, washed, and dried. It was adsorbed from light petroleum–benzene (2 : 1; 150 c.c.) on alumina (65 g.) deactivated with 5% of 10% aqueous acetic acid. Elution with light petroleum–benzene (1 : 1; 300 c.c.) gave only traces of oil and wax. After further elution with benzene (300 c.c.), benzene–ether (99 : 1; 400 c.c.) gave a fraction (0·055 g.) which crystallised from benzene and from acetone as needles, m. p. 214—215°, $[\alpha]_D$ −9° (Found: C, 84·5; H, 11·4. Calc. for $C_{28}H_{46}O$: C, 84·35; H, 11·65%). Acetylation gave the acetate which crystallised from acetone as prisms, m. p. 146—148°, $[\alpha]_D$ ±0° (Found: C, 81·6; H, 11·1. Calc. for $C_{30}H_{48}O_2$: C, 81·75; H, 11·0%). After further elution with benzene–ether (99 : 1; 450 c.c.), benzene–ether (9 : 1; 150 c.c.) gave a fraction (0·314 g.) which crystallised

[1] Barton and Cox, *J.*, 1948, 1354; Fieser and Fieser, " Natural Products Related to Phenanthrene," Reinhold Publ. Corp., New York, 1949, p. 243.

[2] Elsevier's " Encyclopaedia of Organic Chemistry," 1954, Vol. XIV, Suppl., p. 1758 S; Wieland, Rath, and Hesse, *Annalen*, 1941, **548**, 34; Barton and Cox, *J.*, 1948, 1357.

[3] See ref. *a* of Table.

from benzene and from acetone as prisms, m. p. 171—174°, $[\alpha]_D$ −22°. Acetylation gave the acetate, plates (from acetone), m. p. 179—181°, $[\alpha]_D$ −15°.

Ozonolysis of the Alcohol of m. p. 171—174°.—Ozonised oxygen was passed for 30 min. through a solution of the alcohol (500 mg.) in chloroform (50 ml.), and then the mixture was steam-distilled. The distillate was collected in aqueous dimedone solution, and this was then distilled with steam. The distillate was collected in a solution of 2 : 4-dinitrophenylhydrazine (400 mg.) in methanol (40 ml.) and sulphuric acid (0·25 ml.), and the resulting mixture was extracted with chloroform. The residue obtained after distillation of the chloroform was extracted with benzene. Evaporation of the benzene solution yielded an orange solid (65 mg.) which, after chromatography in benzene over alumina and crystallisation from methanol, gave 2 : 3-dimethylbutyraldehyde 2 : 4-dinitrophenylhydrazone as needles, m. p. and mixed m. p. 126—127°.

Hydrogenation of the Acetate of the Alcohol of m. p. 171—174°.—The acetate (0·150 g.; light absorption in *cyclo*hexane: ε_{2130} 3150; ε_{2150} 3000; ε_{2200} 1350; ε_{2230} 710) in chloroform (10 c.c.) and acetic acid (30 c.c.) was added to pre-reduced Adams catalyst (80 mg.) in acetic acid (10 c.c.) and hydrogenated at atmospheric pressure; ~1 mol. of hydrogen was taken up. After removal of catalyst, evaporation under reduced pressure gave a glass which crystallised from acetone as plates, m. p. 105—110°, light absorption in *cyclo*hexane: ε_{2130} 5530; ε_{2150} 5270; ε_{2200} 3850; ε_{2230} 2780.

Ergosta-7 : 22-dien-3β-yl Acetate.—This was prepared by Barton and Cox's method [1] and crystallised from methanol as plates, m. p. 177—179° (undepressed on admixture with the acetate of the alcohol of m. p. 171—174°), $[\alpha]_D$ −22°. The acetate (2·5 g.) was suspended in ether (100 c.c.), lithium aluminium hydride (0·5 g.) added, and the mixture heated under reflux for 2 hr. After addition of methanol and sulphuric acid ether-extraction afforded ergosta-7 : 22-dien-3β-ol, plates (from acetone), m. p. 175·5—176·5°, undepressed on admixture with the alcohol of m. p. 171—174°.

Ergosta-7 : 22-dien-3-one.[1,3]—Ergosta-7 : 22-dien-3β-ol (1·52 g.) in acetone (200 c.c.) was titrated with chromic acid solution as described by Bowers *et al.*[4] The product (1·4 g.), m. p. 165—166°, was adsorbed from light petroleum on alumina (activity I—II) which had been deactivated with 5% of 10% acetic acid. Elution with benzene–light petroleum (1 : 9) gave ergosta-7 : 22-dien-3-one (0·8 g.), needles (from acetone), m. p. 183—185° (undepressed on admixture with the ketone of m. p. 184—187° obtained from *Fomes fomentarius*), $[\alpha]_D$ +1°.

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[4] Bowers, Halsall, Jones, and Lemin, *J.*, 1953, 2555.