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The Occurrence of Ergosterol in the Lichen *Cornicularia normoerica* (Gunnerus) Lynge

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Dedicated to Professor *Holger Erdtman* on his 60th birthday

A substance has been isolated from *Cornicularia normoerica* which by direct comparison was identified as ergosterol.

In the literature there are several references to the occurrence of ergosterol in lichens: In *Lobaria pulmonaria*,[1] in *Parmelia saxatilis*,[2] in *Peltigera canina* L.[3], in *Cladonia rangiferina* (L) Hoffm.[4], in *Alectoria ochroleuca* Ehrh.[5], in *Parmelia physodes*[6], in *Gyrophora Dillenii* (Tuck.) Müll. Arg. and *Parmelia furfuracea* L.[7], in *Cetraria islandica*[8], and in *Roccella montagnei*[9]. Ref.[4] lists several other lichens in which the presence of ergosterol was indicated by colour reactions. Of the occurrences the ones reported in Ref.[4,7,9] appear to be the best authenticated, but, curiously, none appear to have made a direct comparison with ergosterol.

During an investigation of the lichen *Cornicularia normoerica* (Gunnerus) Lynge one of us isolated mannitol and minute amounts of a substance which gave colour reactions and a UV spectrum similar to those of ergosterol[10]. We now have repeated the work on larger amounts of material.

The lichen has a very low content of matter which can be extracted with ether, 10.3 g from 4.45 kg of lichen, and subsequent extractions with acetone and with methanol gave comparable amounts of extract. The ether extract appeared to be very complex in composition, and the only substance which was obtained in a reasonably pure, crystalline state, was ergosterol, characterised by m.p. and mixed m.p. with authentic material, optical activity, UV and IR spectra, and by preparation of a benzoate, the m.p. and IR spectrum of which were compared with those of authentic ergosteryl benzoate; for details see Experimental.

EXPERIMENTAL

UV spectra were measured on a Perkin-Elmer Model 13 spectrophotometer in ethanol. IR spectra were measured on a Perkin-Elmer Model 21 Spectrophotometer in KBr. Optical activity was measured in chloroform in a 1 dm tube. In mixed m.p. determinations the m.p.'s of the three samples to be compared were measured at the same time.

The lichen material was collected at the mountain Munken on the northern side of the Trondheim Fjord during April-August 1960. The air dry material, 4.45 kg, contained 13—14 % of moisture as determined by drying at 110°, and an ignition residue of 5—6 %. The ignition residue of carefully cleaned lichen was about 1 %.

The material was extracted with ether in a Soxhlet apparatus for 24 h. Removal of the solvent left 10.3 g of extract. Of this material 4.9 g were neutral towards alkali. It was dissolved in a small volume of acetone, and after standing for some days at low temperature large, needle-like crystals had separated. They melted at 146—150° and absorbed in the UV as did ergosterol. Three more crystallisations from acetone afforded 30 mg of white needles which melted at 149—153°. A mixture with ergosterol melted at 147—150°. $[\alpha]_D$ −122°(*c*, 1.70). λ_{max} 2710, 2800 and 2930 Å, ε 10 500, 11 000 and 6500, respectively. Our comparison sample was a commercial ergosterol which had been crystallised once from acetone and then had the following constants: m.p. 147—151°, $[\alpha]_D$ −121°(*c*, 1.72), λ_{max} 2710, 2810 and 2930 Å, ε 12 500, 13 000 and 7500, respectively. "Elsevier" gives [11] m.p. usually in the 162—167° region with the reservation that it varies with the water content and $[\alpha]_D$ −129° for the monohydrate in chloroform. Barton and Cox [12] give λ_{max} 2710, 2820 and 2920 Å, ε 11 900, 12 500 and 5950, respectively, in ethanol. The IR spectra of the two substances were identical.

The benzoate was prepared with benzoyl chloride in pyridine with boiling for 1 h. It was purified by filtration through alumina in benzene and crystallisation from petroleum ether to give 1.1 mg of benzoate melting at 150—153°. A mixture with ergosteryl benzoate (m.p. 155—156°, prepared in the same way from the commercial ergosterol) melted at 150—153°. The IR spectra of the two substances were essentially identical.

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