Isolation and Biosynthesis of Ergosta-5,7,9(11),22-tetraen-3β-ol from *Mucor rouxii*

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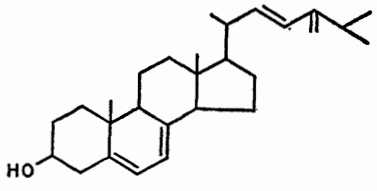
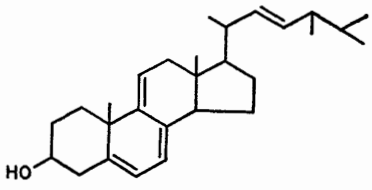
Summary Biosynthetic studies have shown that ergosta-5,7,9(11),22-tetraen-3β-ol, isolated from the fungus *Mucor rouxii*, is derived from ergosterol presumably *via* a biological dehydrogenation (oxidation) reaction.

IN our studies on the growth and composition of fungi[1,2] examination of the sterol content of aerobically grown *M. rouxii* revealed that the major compounds present were ergosterol (96%, M^+ 396) and a dehydroergosterol derivative (4%, M^+ 394). Recently the isolation,[3,4] synthesis,[4,5] and biosynthesis[4] of a dehydroergosterol derivative, ergosta-5,7,22,24(28)-tetraen-3β-ol, (I), have been reported and this sterol was shown to be an intermediate in the biosynthesis of ergosterol in yeast. The physical properties of the sterol from *M. rouxii* and the yeast sterol showed that the former compound contained a conjugated triene system (λ_{max} 325 nm) and three double bonds in the



(I)



(II)

ABCD ring nucleus (*m/e* 394, 251)[6] whereas the yeast sterol exhibited a conjugated diene chromophore (λ_{max} 294 nm) and two double bonds in the ABCD ring system (*m/e* 394, 253). The data suggested that the new fungal sterol was similar to ergosta-5,7,9(11),22-tetraen-3β-ol (II) which is readily prepared by treatment of ergosterol acetate with mercuric acetate[7] followed by hydrolysis. Comparison of the i.r., n.m.r., u.v., and mass spectra of (II) and the fungal sterol confirmed the structure of the natural product as (II).

[4,4-$^3H_2$]Ergosterol (prepared as described)[4a] was fed to aerobically grown *M. rouxii* (30% incorporation into the cells) and the overall incorporation into the tetraene (II) was 0·55%. In another experiment [4,4-$^3H_2$]ergosta-5,7,9(11),-22-tetraen-3β-ol† was readily incorporated into the mycelium (28%) of *M. rouxii*, but after repeated crystallization of the ergosterol fraction only $<$0·001% was found to be incorporated into ergosterol. Thus it seems likely that the tetraene (II) is not an intermediate in the biosynthesis of ergosterol but is formed from ergosterol *via* a biological dehydrogenation (oxidation) reaction.

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† Prepared by treatment of [4,4-$^3H_2$]ergosteryl acetate[7] with no loss in the specific activity of the product.

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