(1H, *br*, 7-H), 3.54 and 3.97 (2H, q_{AB}, J = 12 Hz, $-CH_2OAc$), 5.04 (1H, *br*, 15-H), 5.22 and 5.41 (2H, *br*, $C{=}CH_2$).

Partial synthesis of ent-18-*acetoxykaur*-16-*ene*-3β,7α,15β-*triol* (**2**). (a) Ent-18-*acetoxy*-15β,16β-*epoxykaur*-3β,7α-*diol* (*epoxy-isolinearol*) [4, 5] (**4**). *Ent*-18-acetoxy-3β,7α-dihydrokaur-15-ene (natural isolinearol) (**1**) (150 mg) in Et_2O (100 ml) was treated with *p*-nitroperbenzoic acid (150 mg) at room temp. for 24 hr. After conventional work-up, the epoxy-isolinearol was isolated in good yield; mp 218–220° by comparison with authentic samples, IR superimposable. (b) *Rearrangement of epoxy-isolinearol* (**4**). The epoxide (**4**) (100 mg), dissolved in dry DMSO (20 ml), was treated with freshly distilled BF_3–Et_2O complex (3 drops) and heated at 100° for 20 hr. The soln was then diluted with H_2O (80 ml) and extracted with Et_2O. Evapn of the solvent left a residue (65 mg) which was separated by chromatography on Si gel (cyclohexane–EtOAc, 1:1) giving pure **2** (40 mg) as needles, mp 174–176° (from EtOAc). The IR and ^1H NMR spectra were identical to natural 18-acetoxy-leucanthol isolated from *S. scardica* and then from *S. biflora*.

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STEROLS FROM SOME BASIDIOMYCETES

F. De Simone*, F. Senatore*, D. Sica† and F. Zollo*

* Facoltà di Farmacia, Università di Napoli, 80138 Napoli;
† Istituto di Chimica Organica e Biologica, Università di Napoli, 80134 Napoli, Italy

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Key Word Index—*Armillariella mellea*; *Boletus luridus*; *Pholiota aegerita*; Basidiomycetes; mushroom; sterols; ergosterol; ergost-7-en-3β-ol; ergosta-7,22-dien-3β-ol; ergosta-5,7-dien-3β-ol.

INTRODUCTION

In recent years the sterol mixtures from terrestrial sources have been reinvestigated in detail using modern techniques. Many early studies on sterols from fungal species resulted in the isolation of one or two sterols, but others present in low concentrations were often undetected. Ergosterol is often the major sterol of Basidiomycetes [1–3] which, however, have been examined by modern methods in only a few cases. As a continuation of our studies [4, 5], we have now examined the sterol contents of three species of Basidiomycetes, namely *Armillariella mellea*, *Boletus luridus* and *Pholiota aegerita*.

RESULTS

The unsaponified lipids were obtained by the usual procedure from the Basidiomycetes and the sterol fractions were separated by column chromatography over Si gel. After acetylation, the individual components were separated by column chromatography on Si gel impregnated with $AgNO_3$. The identification of each sterol was based on a comparison of the experimentally derived MS and NMR spectra with those reported in the literature [6, 7] and co-injection with standards. The results are summarized in Table 1. All fungi examined contained ergosterol as the predominant sterol accompanied by the other closely related sterols ergost-7-en-3β-ol, ergosta-7,22-dien-3β-ol and ergosta-5,7-dien-3β-ol. Cholesterol was found only in trace amounts.

Table 1. Sterol composition of Basidiomycetes (%)

Family and species	Sterol present 1	2	3	4
Agaricaceae				
P. aegerita	5.0	4.6	1.3	89.0
Trichelomataceae				
A. mellea	4.4	4.4	11.1	80.0
Polyporaceae				
B. luridus	3.9	9.8	1.2	85.0

1 = Ergost-7-en-3β-ol; **2** = ergosta-7,22-dien-3β-ol; **3** = ergosta-5,7-dien-3β-ol; **4** = ergosterol.

EXPERIMENTAL

The IR spectra were measured in $CHCl_3$. The UV spectra were recorded in EtOH. NMR spectra were recorded in $CDCl_3$ with TMS as internal reference. GLC analyses were on a glass column (2 m × 3 mm) packed with 2.5% OV-1, oven temp. 250°, N_2 50 ml/min; retention times are relative to cholesteryl acetate. The fungi were collected near Naples.

Extraction and separation. In a typical experiment, the fruit bodies of *A. mellea* (500 g, fr. wt) were cut into small pieces and extracted with Me_2CO (3 × 0.9 l.) at room temp. The combined solns were concd leaving an aq. suspension which was extracted with Et_2O. The extract (3.2 g) was saponified at reflux under N_2 for 2 hr with 10% KOH in 80% EtOH. The unsaponifiable material (1.8 g) was applied to a Sil gel column which was eluted with CH_2Cl_2. The sterol fraction (0.6 g) was acetylated (Ac_2O–C_5H_5N, 12 hr at room temp.) and purified on a Si gel column eluted with petrol (40–70°) C_6H_6 (7:3). The steryl acetates (0.5 g) were fractionated on an $AgNO_3$-Si gel (1:4) column (60 g) and eluted with petrol–C_6H_6 (90:10, 0.6 l.), petrol–C_6H_6 (85:15, 1 l.), petrol–C_6H_6 (80:20, 2 l.), petrol–C_6H_6 (70:30, 0.6 l.), petrol–C_6H_6 (60:40, 0.4 l.), petrol–C_6H_6 (50:50, 0.4 l.) and petrol–C_6H_6 (40:60, 1.5 l.). The fractions (0.1 l.) were monitored by GLC and combined accordingly.

Fractions 19–21 contained ergost-7-en-3β-yl acetate (18 mg); RR_t 1.43; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1730; MS *m/e*: 442 (M^+, base peak), 427, 382, 367, 315, 288, 255, 229, 213; ^1H NMR: δ 0.54 (*s*, C-18), 0.78 (*d*, J = 6.6 Hz, C-28), 0.79 (*d*, J = 6.6 Hz, C-27 or C-26), 0.82 (*s*, C-19), 0.87 (*d*, J = 6.6 Hz, C-26 or C-27), 0.93 (*d*, J = 6.6 Hz, C-21), 2.03 (*s*, $MeCO_2$—), 4.73 (*m*, C-3), 5.18 (*m*, C-7). Fraction 22 (6 mg) contained ergost-7-en-3β-yl acetate (2 mg) and ergosta-7,22-dien-3β-yl acetate (4 mg). Fractions 23–24 contained ergosta-7,22-dien-3β-yl acetate (16 mg); RR_t 1.24; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1730, 972 (Δ^{22} *trans*); MS *m/e*: 440 (M^+, base peak), 425, 397, 380, 365, 342, 315, 313, 288, 255, 253, 229, 213; ^1H NMR: δ 0.54 (*s*, C-18), 0.81 (*s*, C-19), 0.82 (*d*, J = 6.6 Hz, C-27 or C-26), 0.83 (*d*, J = 6.6 Hz, C-26 or C-27), 0.91 (*d*, J = 6.6 Hz, C-28), 1.01 (*d*, J = 6.6 Hz, C-21), 2.03 (*s*, $MeCO_2$—), 4.68 (*m*, C-3), 5.16 (*m*, C-7), 5.21 (*m*, C-22 and C-23). Fractions 35–37 contained ergosta-5,7-dien-3β-yl acetate (36 mg); RR_t 1.43; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1730; UV λ_{max}^{EtOH} nm: 273, 283, 294; MS *m/e*: 440 (M^+), 425, 380 (M^+ − HOAc, base peak), 365, 313, 253, 211, 158, 143; ^1H NMR: δ 0.62 (*s*, C-18), 0.78 (*d*, J = 6.6 Hz, C-28), 0.79 (*d*, J = 6.6 Hz, C-27 or C-26), 0.86 (*d*, J = 6.6 Hz, C-26 or C-27), 0.95 (*d*, J = 6.6 Hz, C-21), 0.96 (*s*, C-19), 2.04 (*s*, $MeCO_2$—), 4.72 (*m*, C-3), 5.39 (*m*, C-7), 5.57 (*m*, C-6). Fractions 38–39 (115 mg) contained ergosta-5,7-dien-3β-yl acetate (15 mg) and ergosteryl acetate (100 mg). Fractions 40–50 contained ergosteryl acetate (266 mg); RR_t 1.22; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1730, 972 (Δ^{22} *trans*); UV λ_{max}^{EtOH} nm: 273, 283, 294; MS *m/e*: 438 (M^+), 423, 378 (M^+ − HOAc, base peak), 363, 335, 313, 253, 251, 211, 158, 143; ^1H NMR: δ 0.63 (*s*, C-18), 0.83 (*d*, J = 6.6 Hz, C-27 or C-26), 0.84 (*d*, J = 6.6 Hz, C-26 or C-27), 0.92 (*d*, J = 6.6 Hz, C-28), 0.96 (*s*, C-19), 1.04 (*d*, J = 6.6 Hz, C-21), 2.04 (*s*, $MeCO_2$—), 4.71 (*m*, C-3), 5.21 (*m*, C-22 and C-23), 5.39 (*m*, C-7) and 5.57 (*m*, C-6).

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