evapd to dryness. The residue was then chromatographed on Si gel in Et_2O to give the hexa-acetate (**3**) of **2** (37 mg) as an amorphous powder, $[\alpha]_D^{25}$ −103° (MeOH; *c* 0.4). (Found: C, 52.63; H, 5.83. $C_{27}H_{36}O_{16}$ requires: C, 52.59; H, 5.88%.) ^1H NMR ($CDCl_3$): δ 6.20 (1 H, *dd*, $J_{3,4}$ = 6.3, $J_{3,5}$ = 2 Hz, H-3), 5.50 (1 H, *d*, $J_{1,9}$ = 2.5 Hz, H-1), 5.3–4.8 (H-6), 4.95 (1 H, *dd*, $J_{3,4}$ = 6.3 Hz, H-4), 4.20 (2 H, *br s*, 2 H-10), 2.80 (2 H, *br s*, H-5 and H-9), 2.2–1.9 (2 H-7 and AcO signals).

Hepta-acetate (**4**) *of* (**2**). Compound **2** (120 mg) was treated with dry pyridine (0.5 ml) and Ac_2O (1 ml) for 3 days at room temp. The usual work-up gave a residue which when chromatographed on Si gel in Et_2O–C_6H_6 (7:3) gave the hepta-acetate (**4**) of **2** (70 mg) as an amorphous powder, $[\alpha]_D^{25}$ −116° (MeOH; *c* 0.4). (Found: C, 52.77; H, 5.71. $C_{29}H_{38}O_{17}$ requires: C, 52.88; H, 5.82%.) ^1H NMR ($CDCl_3$): δ 6.20 (1 H, *dd*, $J_{3,4}$ = 6, $J_{3,5}$ = 2 Hz, H-3), 5.90 (1 H, *br s*, H-1), 5.3–4.5 (H-6), 5.0–4.6 (H-4), 4.5–4.0 (2 H-10), 3.05 (1 H, *br d*, H-9), 2.80 (1 H, *br d*, $J_{5,9}$ = 8.3 Hz, H-5), 2.4–2.1 (2 H-7), 2.1–1.9 (AcO signals).

Reduction of catalpol-hexa-acetate (**9**) *with* $LiAlH_4$. **9** (100 mg) was dissolved in dry THF (7 ml) and then treated with $LiAlH_4$ (20 mg) at 70° with stirring for 5 hr. After cooling in an ice-bath, MeOH was added (3 ml) and the soln neutralized with 6 M HCl. After addition of H_2O (8 ml) the soln was evapd to an aq. suspension, which was treated with charcoal and stratified on a Gooch funnel. After removal of salts with H_2O, elution with MeOH gave a residue (70 mg) which was chromatographed on Si gel in $CHCl_3$–MeOH (7:3) to give small amounts (8 mg) of catalpol and the reduction product (45 mg) whose physical data (^1H and ^{13}C NMR) were identical to those of **2**.

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NOTE ADDED IN PROOF

The unexpected coincidence observed for C-4 C.S. values in **2** and **6** (in epimers at C-6 this value differs by *ca* 3 ppm) prompted us to check the correct stereochemistry of ajugol. The succesful transformation of ajugol penta-acetate to give linaride (10-deoxyaucubin) penta-acetate unequivocally proves that the configuration at C-6 of ajugol must be reversed (data of next publication).

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(+)-*ENT*-EPICUBENOL FROM THE LIVERWORT *SCAPANIA UNDULATA*

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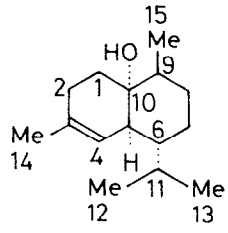
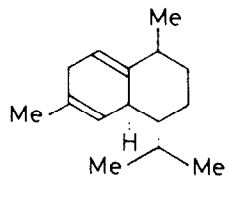
Key Word Index—*Scapania undulata*; Hepaticae; liverwort; sesquiterpene alcohol; (+)-*ent*-epicubenol.

Abstract—(+)-*Ent*-epicubenol has been isolated from the liverwort *Scapania undulata*.

The liverwort *Scapania undulata* (L.) Dum. (Family: Scapaniaceae) has been analysed several times and the following sesquiterpenes have been found: (−)-longifolene [1–4], (−)-longiborneol [1–3], (−)-α-longipinene [2–4], (+)−α−himachalene [2–4], γ-himachalene, (−)-α-ylangene, β-farnesene, (−)-longicyclene, sativene, sibirene, (−)-β-longipinene, (−)-α-caryophyllene, (−)-α-helmiscapene, β-helmiscapene, α_1-bisabolene, α_2-bisabolene, aequilobene, scapanene, β-gymnomitrene, (+)-α-chamigrene, β-chamigrene, γ-cadinene, asperene, undulatene and (−)-longipinanol [3]. During the course of a chemotaxonomic study of European *S. undulata* (Huneck, S., Jänicke, S. and Meinunger, L., unpublished work), we found a chemical race containing a further sesquiterpene alcohol which could be isolated from the essential oil by column chromatography. This alcohol was shown to be the hitherto unknown (+)-*ent*-epicubenol (**1**) by comparison of the spectroscopic data with the data of (−)-epicubenol which was isolated from the oil of *Piper cubeba* L. several years ago [5]. The identity with epicubenol was confirmed by conversion of **1** into (+)-cubenene (**2**). The isolation of **1**



1



2

from *S. undulata* is a further example of the occurrence in liverworts of sesquiterpenoids enantiomeric to the corresponding compounds from higher plants.

EXPERIMENTAL

Isolation of (+)-ent-*epicubenol* (**1**). The essential oil (3 g) from *S. undulata* (leg. et det. S.H., GDR, Thuringian Forest, Kerngrund near Oberhof, 23.7.1980; this chemical race occurs widely in Scotland (Rycroft, D. S., unpublished work), prepared by steam distillation, was chromatographed on Si gel (80 g, with 5% H_2O). Elution with *n*-hexane (1.5 l.) and *n*-hexane–Et_2O (19:1) (500 ml) yielded an oily mixture. Subsequent elution with *n*-hexane–Et_2O (9:1) (500 ml) gave (+)-*ent*-epicubenol (**1**) as an oil with $[\alpha]_D^{24}$ +111.6° ($CHCl_3$; *c* 4.705), n_D^{24} 1.5027 and R_f 0.64 [Si gel PF, *n*-hexane–Et_2O–HCO_2H (30:25:6), AcOH + SO_3HCl, 150°, violet spot]. $C_{15}H_{26}O$ (222). MS *m/z* (rel. int.): 222 $[M]^+$ (48), 207 $[M - Me]^+$ (40), 205 (70), 204.1877 ($[M - H_2O]^+$, calc. 204.1877) (92), 189 $[M - Me - H_2O]^+$ (44), 179 $[M - Me{-}CH{-}Me]^+$ (86), 162 (76), 161 $[M - H_2O - Me\ CH{-}Me]^+$, 153 (35), 147 (46), 137 (58), 135 (56), 133 (52), 123 (76), 122 (75), 121 (75), 120 (82), 119 (100), 111 (74), 110 (74), 109 (79), 107 (77), 105 (95), 95 (88), 93 (90); IR ν_{max}^{film} cm^{-1}: 840, 854, 896, 924, 950, 968, 990, 1024, 1074, 1130, 1144, 1186, 1208, 1226, 1260, 1280, 1310, 1372, 1450, 2990, 3600; ^1H NMR (60 MHz, $CDCl_3$): δ 0.75, 0.85, 0.95 (3 × *sec* Me), 1.67 (3H, *s*, vinyl Me), 5.37 (1H, *d* (*br*), H-4); ^{13}C NMR ($CDCl_3$): δ 15.2 (*q*), 15.2 (*q*), 21.7 (*q*), 22.1 (*t*), 23.5 (*q*), 24.1 (*t*), 26.8 (*t*), 27.0 (*d*), 31.2 (*t*), 42.0 (*d*), 48.2 (*d*), 49.3 (*d*), 72.7 (*s*), 122.2 (*d*), 133.9 (*s*).

(+)-ent-*Cubenene* (**2**). To a soln of **1** (0.3 g) in pyridine (5 ml) was added $SOCl_2$ (1.5 ml) at 0°. After 30 min the mixture was poured into ice-cold aq. 10% $NaHCO_3$ and extracted with Et_2O. The ethereal soln was washed with 10% H_2SO_4, H_2O, $NaHCO_3$ soln and H_2O, dried with Na_2SO_4, the Et_2O removed *in vacuo* and the residue chromatographed on Si gel (10 g, with 10% $AgNO_3$). *n*-Hexane (400 ml) and *n*-hexane–Et_2O (46:1) (100 ml) eluted an oily mixture. Further elution with *n*-hexane–Et_2O (46:1) (100 ml) gave (+)-*ent*-cubenene (**2**) as an oil with $[\alpha]_D^{24}$ + 22.3° ($CHCl_3$; *c* 1.50) and R_f 0.60 [$AgNO_3$–Si gel (1:9), *n*-hexane–Et_2O (19:1), AcOH + SO_3HCl, 150°, violet spot]. $C_{15}H_{24}$ (204). MS *m/z* (rel. int.): 204.1880 ($[M]^+$, calc. 204.1878) (72), 189 $[M - Me]^+$ (15), 161 $[M - Me{-}CH{-}Me]^+$ (88), 147 (26), 133 (33), 121 (62), 120 (64), 119 (100), 105 (86), 93 (50), 92 (53), 91 (39); IR ν_{max}^{film} cm^{-1}: 790, 824, 852, 888, 944, 1030, 1112, 1170, 1272, 1364, 1380, 1450, 2900, 2960; ^1H NMR (CCl_4): δ 0.82, 0.87, 0.99 (3 × *sec* Me), 1.65 (3H, *s*, vinyl Me), 5.21 (1H, *m*, H-1), 5.41 (1H, *m*, H-4); ^{13}C NMR (CCl_4): δ 15.1 (*q*), 18.2 (*q*), 21.5 (*q*), 23.4 (*q*), 24.6 (*t*), 26.6 (*d*), 31.5 (*t*), 36.8 (*t*), 37.6 (*d*), 41.9 (*d*), 51.2 (*d*), 112.6 (*d*), 121.2 (*d*), 131.3 (*s*), 143.1 (*s*).

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STEROLS OF *CANDIDA TROPICALIS* GROWN ON *N*-ALKANES

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Key Word Index—*Candida tropicalis*; Ascomycetes; fungi; ergosterol; ergost-7-en-3β-ol; (22*E*)-ergosta-7,22-dien-3β-ol; ergosta-7,24(28)-dien-3β-ol; cholesta-8,24-dien-3β-ol; (22*E*)-ergosta-5,7,9(11),22-tetraen-3β-ol.

Abstract—Six sterols isolated from the yeast *Candida tropicalis* were identified as ergosterol (major component), (22*E*)-ergosta-5,7,9(11),22-tetraen-3β-ol, ergost-7-en-3β-ol, (22*E*)-ergosta-7,22-dien-3β-ol, ergosta-7,24(28)-dien-3β-ol and cholesta-8,24-dien-3β-ol.

In continuation of our work on sterols [1, 2], we have now examined the sterol fraction of *Candida tropicalis*, a yeast that has attracted commercial interest for protein production by micro-organisms [3].

The unsaponifiable fraction of the crude extract of *C. tropicalis* was chromatographed on Si gel and the sterol fraction, after acetylation, was further fractionated on Si gel to give the 4-demethyl sterol fraction. Preliminary capillary GLC analysis on OV-101 of the steryl acetates indicated the presence of six sterols which were identified