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BRYOPHYTA

HEPATICAE

SESQUITERPENES AND OTHER COMPONENTS OF *MYLIA TAYLORII**

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In a systematic study of the components of liverworts, we have isolated during the past few years the following substances from various species: pinguisone,[1] 7-(3-methyl-2-butenyl)indole and 6-(3-methyl-2-butenyl)indole,[2] friedelin and lignoceric acid,[3] saponarin and saponaretin,[4] pellepiphyllin[5] and myliol.[6] The last has been isolated from the liverwort *Mylia taylorii* (Hook) Gray, the other components of which are described in this communication.

RESULTS

Chemical analysis of the components was carried out with the *n*-pentane extract obtained from a collection of this plant from one locality (Adršpach).† The concentrated extract (33 g), from the dry, ground plant (1440 g) was chromatographed on silica gel[7] deactivated with 10% water, affording 5 fractions (*a–e*) which were worked up separately.

* Part VIII in the series "Components of Liverworts". For Part VII see V. BENEŠOVÁ, M. STREIBL, H. M. CHÂU, I. BENEŠ and K. KONEČNÝ, *Coll. Czech. Chem. Commun.* in press.

† *n*-Pentane extracts of two samples of this liverwort, coming from different localities, were investigated. The first was collected in the marshland near the source of the river Úpa in the Giant Mountains (1400 m above sea level), while the second originated from a locality in the Adršpach area (500 m above sea level). Comparison of the two by silica gel TLC showed that ratios of components and groups of substances in the extracts from both samples were practically identical.

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Fraction a. This was a mixture of hydrocarbons (2·5 g) and was separated on a column of silica gel impregnated with silver nitrate[8] to give a saturated (0·2 g) and an olefinic (1·8 g) fraction. The paraffins were analysed by GLC.[9] A branched C_{15} hydrocarbon accounted for 70% of the mixture, while the rest was a homologous series of odd and even paraffins C_{16}–C_{35}. The mixture of the olefinic hydrocarbons was freed from coloured components by distillation, and by analytical GLC.[10] Twenty-one components were detected. On the basis of their boiling points and retention ratios they were classified predominantly as sesquiterpene hydrocarbons. The mixture was separated by preparative GLC[11] into seven fractions (I–VII). A control chromatogram (TLC on silver nitrate impregnated silica gel) indicated that only fractions II, IV and VI were single compounds. The hydrocarbons in fractions IV and VI, however, were very labile and were lost during attempted isolation. Fraction II gave a pure sesquiterpene hydrocarbon (0·13 g), $C_{15}H_{24}$ (M^+ 204). IR: 1363, 1376 cm^{-1} $(CH_3)_2CH$– or CH_3CR; 1614, 1642, 3600 cm^{-1} (C=C); NMR ($CDCl_3$): 0·8–1·05 mt, 2H; 1·08 s, 1·62 mt, 3H, CH_3=C=C–; 5·30 mt, 1H, –CH=C–; 5·40, $J = 3$ Hz, 1H, –CH=C–.[12] The presence of two double bonds, evident from the NMR spectrum, was corroborated by catalytic hydrogenation which gave tetrahydro derivative $C_{15}H_{28}$ (M^+ 208). Work on the determination of the structure of this bicyclic sesquiterpenic hydrocarbon is in progress.

Fraction b. The crystalline fraction (0·1 g), m.p. 70°, having an IR (6% CCl_4) spectrum typical of ester carbonyl (1737, 1176 cm^{-1}) was analysed by GLC.[9] It was shown to contain a homologous series of cerides, from C_{38} to C_{52}, the major component being the C_{42} component.

Fraction c. A pure liquid component was isolated in a very low yield (0·02 g) which gave an IR spectrum (5% CCl_4) having typical absorptions corresponding to an aldehydic (1718, 2730 cm^{-1}) and a hydroxyl group (3530, 3620 cm^{-1}).

Fraction d. The fractions eluted with benzene gave, after concentration, a pure crystalline compound (3·9 g), $C_{15}H_{22}O$ (M^+ 218), which after crystallisation from *n*-pentane had m.p. 110–111° and was shown to be myliol.[6] Myliol is very instable in air at elevated temperatures, and changes rapidly to a liquid, viscous, orange product, soluble only in polar solvents.

Fraction e. This fraction gave a crystalline substance (0·20 g), m.p. 134°, undepressed on admixture of an authentic sample of sitosterol.

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[10] Analytical gas chromatography was carried out on a Perkin–Elmer model F 11 chromatograph with FID and a capillary column of stainless steel, 0·25 mm i.d., length 50 m. The inner walls of the column were coated with Carbowax 20 M. Temperature of the column was 125°, carrier gas nitrogen.

[11] Preparative gas chromatography was carried out on a Fractovap P Carlo Erba, Milano, with FID. Column length 6m, 10 mm i.d., filled with 'Porovina' of 0·2–0·3 mm, impregnated with 4% of Carbowax 20 M. Basic temperature 160° was increased to 180° in the course of the procedure, at a 1·5°/min rate. Carrier gas nitrogen, rate of flow 666 ml/min.

[12] IR spectra were measured on a Zeiss UR 10 spectrophotometer; MS were measured on a MS 902 mass spectrometer; NMR spectra were recorded with a Varian HA-100 spectrometer.