

DITERPENOIDS FROM LIVERWORTS*

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Dedicated to Professor F. Šantavý on the occasion of his 60th birthday.

Six diterpenoids were isolated from the light petroleum extracts of three liverworts, *Jungermannia sphaerocarpa* HOOK. [syn. *Solenostoma* s. (HOOK.) STEPH.], *Pellia endiviifolia* (DICKS.) DUM., and *Mylia anomala* (HOOK.) S. GRAY.

In the course of a systematic investigation of liverworts we mainly concentrated on their sesquiterpenic components¹⁻⁵. However, during these studies we did not neglect other substances either, which were the major components⁶⁻⁸ of these as yet little studied plants. In this paper we describe substances of diterpenoid character which are — as is evident from our extensive study — represented in this group of plants in smaller quantities than sesquiterpenes. A similar line of research was also followed by other authors studying diterpenoids which were isolated from the liverworts of *Jungermanniaceae*^{9,10}, or *Antheliaceae*¹¹ and *Marchantiaceae*¹² families.

EXPERIMENTAL AND RESULTS

The melting points were determined on a Kofler block and they are not corrected. The IR spectra were measured in chloroform by means of a Zeiss UR 10 spectrophotometer (Jena), the UV spectra on a CF 4 apparatus (Optica Milano), and the mass spectra on an AEI MS 902 spectrometer. The PMR spectra in deuteriochloroform were recorded with a Varian HA-100 apparatus using tetramethylsilane as internal standard. Silica gel for column chromatography was prepared according to Pitra and Štěrba¹³ and was deactivated with 10% of water. The neutral alumina used (Laborchemie Apolda) had activity grade V according to Brockmann¹⁴.

Jungermannia sphaerocarpa HOOK. [syn. *Solenostoma* s. (HOOK.) STEPH.].
(*Jungermanniaceae*)

Origin. Valley of Černá Nisa near Rudolfovo (Liberec), Czechoslovakia. The liverwort (3600 g) was dried at room temperature, ground, and extracted with light petroleum (b.p. 40–60°C);

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from the concentrated extract a residue (16 g) was obtained, which was chromatographed on silica gel¹³ using a mixture of benzene and diethyl ether (5–10%) for elution. A mixture of crystalline compounds was eluted, which was separated by chromatography on alumina (act. V., neutral). Elution with light petroleum gave component *A* (356 mg), m.p. 110–111°C (benzene), R_F 0.63 (benzene–diethyl ether 7 : 3 on silica gel G). IR (6% in chloroform): 897, 928, 976, 989, 1018, 1044, 1052, 1092, 1115, 1132, 1195, 1229 (ester), 1270, 1290, 1372, 1412, 1443, 1462, 1656 (C=C), 1746 (ester), 2845, 2865, 2910, 2930, 3580 (OH) cm^{-1} ; MS: M^+ 346, $\text{C}_{22}\text{H}_{34}\text{O}_3$; PMR (CDCl_3): 0.80 s, 0.86 s, 0.91 s, $3 \times 3 \text{ H}$, $3 \times \text{CH}_3\text{—C—}$; 2.19 s, 3 H, $\text{CH}_3\text{—C=O}$; 2.5–2.7 mt, 2 H; 3.81 mt, W = 24, 1 H, >CH—O— ; 4.94 mt, 5.14 mt, $2 \times 1 \text{ H}$, >C=CH_2 , $J_{\text{gem}} = 0$; 5.30 t, 1 H, CHOCOCH_3 , shifts in δ -scale.

Elution with light petroleum containing 5% of benzene has given substance *B* (42 mg), m.p. 131–132°C (benzene), R_F 0.40 (light petroleum–acetone 8 : 2; alumina Woelm neutral for TLC), or R_F 0.59 (benzene–diethyl ether 7 : 3; silica gel G). IR (6% in chloroform); 795, 940, 977, 1029, 1052, 1060, 1114, 1180, 1186, 1235, 1260, 1342, 1370, 1390, 1450, 1460, 1645 (C=C), 1722 (C=O), 2780, 2935, 3000, 3080, 3480 (OH), 3595 (OH), 3660 cm^{-1} ; UV (ethanol): 238 nm ($\log \epsilon$ 3.81); MS: M^+ 302, $\text{C}_{20}\text{H}_{30}\text{O}_2$; PMR (CDCl_3): 0.82 s, 0.90 s, 1.02 s, $3 \times 3 \text{ H}$, $3 \times \text{CH}_3\text{—C—}$; 2.40 d, $J = 12.3$, 1 H; 3.04 mt, 1 H, allylic H; 4.05 d, $J = 5$, 1 H, >CH—O— ; 5.25 mt, 5.86 mt, $2 \times 1 \text{ H}$, >C=CH_2 , $J_{\text{gem}} = 1.0$, shifts in δ -scale.

Elution with light petroleum containing 30% of benzene gave substance *C* (295 mg), m.p. 192–194°C (benzene), R_F 0.43 (benzene–diethyl ether 7 : 3; silica gel G). IR (6% in chloroform): 831, 850, 866, 894, 923, 948, 963, 992, 1014, 1028, 1040, 1056, 1068, 1077, 1091, 1111, 1133, 1193, 1239, 1242, 1275, 1371, 1390, 1442, 1462, 1580, 1658 (C=C), 2674, 2845, 2870, 2930, 2955, 3070 (C=C), 3430 (OH), 3590 (OH) cm^{-1} ; MS: M^+ 304, $\text{C}_{20}\text{H}_{32}\text{O}_2$; PMR (CDCl_3): 0.82 s, 0.88 s, 0.95 s, $3 \times 3 \text{ H}$, $3 \times \text{CH}_3\text{—C—}$; 2.62 mt, 1 H, allylic proton; 3.58 mt, W = 8, 1 H, >CH—O— ; 4.01 d, $J = 5$, 1 H, >CH—O— ; 5.02 bs + 5.12 bs, >C=CH_2 , shifts in δ -scale.

From the characteristics of the above substances it follows that they are of diterpenic character. In the case of substance *A* it is a hydroxy acetate, substance *B* is a hydroxy ketone, and substance *C* is a diol.*

Pellia endiviifolia (DICKS.) DUM. (*Pelliaceae*)

Origin. Srbsko (Karlštejn), Czechoslovakia. The liverwort (1300 g) was dried at room temperature, then ground and extracted with light petroleum (b.p. 40–60°C); the concentrate (5 g) was chromatographed on silica gel² deactivated with 15% of water, using a 1 : 1 mixture of light petroleum and benzene for elution. A substance (20 mg) was obtained, m.p. 120°C (light petroleum), R_F 0.35 (benzene–diethyl ether 95 : 5; silica gel G). IR (5% in tetrachloromethane): 865,

* From the liverwort *Solenostoma triste* (NEES) K. MÜLL. (= *Jungermannia atrovirens* DUM.) Connolly and Thornton isolated recently four diterpenoids and assigned then the structures derived from 11 β -hydroxylated ent-kaurene¹⁵.

924, 955, 980, 1070, 1109, 1130, 1174, 1192, 1208, 1255, 1300, 1344, 1365, 1386, 1422, 1466, 1636 (C=C), 1689 (C=C-C=O), 1714 (-CHO), 2730 cm^{-1} ; MS: M^+ 302, $\text{C}_{20}\text{H}_{30}\text{O}_2$; PMR (CDCl_3): 0.95 s, 0.97 s, $2 \times 3 \text{ H}$, $2 \times \text{CH}_3-\text{C}-$; 1.58 bs, 1.67 bs, $2 \times 3 \text{ H}$, $2 \times \text{CH}_3-\text{C}=\text{C}$; 2.46 mt, 2 H, 2.85 mt, 1 H, 5.06 mt, 1 H, $-\text{CH}=\text{C}-$; 7.12 mt, 1 H, $-\text{CH}=\text{C}-$; 9.47 s, 1 H, $-\text{CH}-\text{C}-$; 9.47 s, 1 H, $-\text{C}-\text{CH}=\text{O}$; 9.51 d, $J = 4.0$, 1 H, $-\text{CH}-\text{CH}=\text{O}$, shifts in δ -scale.

From the characteristic data of the above diterpenoid it follows that it is a dialdehyde.

Mylia anomala (HOOK.) s. GRAY (*Jungermanniaceae*)

Origin: Mount Sv. Sebastian (Chomutov), Czechoslovakia. The liverwort (130 g) was dried at room temperature, then ground and extracted with light petroleum (b.p. 40–60°C); from the concentrate of the light petroleum extract a crystalline mixture separated which, after filtration of the mother liquors was separated chromatographically on silica gel² deactivated by 10% of water. Elution with benzene gave substance *A* (100 mg), m.p. 153°C (benzene-diethyl ether), R_f 0.46 (benzene; silica gel G). IR (6% in chloroform): 858, 941, 970, 1015, 1035, 1075, 1100, 1122, 1162, 1306, 1321, 1365, 1386, 1455, 1464, 3 060 (cyclopropane ring), 3 620 (OH) cm^{-1} ; MS: M^+ 306, $\text{C}_{20}\text{H}_{34}\text{O}_2$; PMR (CDCl_3): 0.18 t, $J_{\text{gem}} = 4.5$, 1 H, 0.43 dd, $J_{\text{gem}} = 4.5$, $J_{\text{vic}} = 8.5$, 1 H, two geminal cyclopropane protons; 0.76 s, 1.03 s, 1.19 s, $3 \times 3 \text{ H}$, $3 \times \text{CH}_3-\text{C}-$; 0.86 d, $J = 6.7$, 0.91 d, $J = 6.7$, $2 \times 3 \text{ H}$, $2 \times \text{CH}_3-\text{CH}-$; 3.65 mt, 2 H, $2 \times >\text{CH}-\text{O}-\text{H}$, shifts in δ -scale.

Elution with benzene containing 20% of diethyl ether gave substance *B* (10 mg), m.p. 157°C (benzene), R_f 0.18 (benzene; silica gel G). IR (6% in chloroform): 857, 904, 915, 950, 975, 990, 1035, 1070, 1092, 1118, 1168, 1305, 1333, 1385, 1412, 1462, 1636 (C=C), 3090 (C=C), 3620 (OH) cm^{-1} ; MS: M^+ 322, $\text{C}_{20}\text{H}_{34}\text{O}_3$; PMR (CDCl_3): 0.91 s, 0.95 s, 1.25 s, 1.30 s, $4 \times 3 \text{ H}$, $4 \times \text{CH}_3-\text{C}-$; 3.74 mt, 1 H, 3.89 mt, 1 H, $2 \times >\text{CH}-\text{O}-$; 4.82 dd, $J_{\text{cis}} = 11$, $J_{\text{gem}} = 1.5$, 1 H, 4.88 dd, $J_{\text{trans}} = 17$, $J_{\text{gem}} = 1.5$, 1 H, 5.76 dd, $J_{\text{trans}} = 17$, $J_{\text{cis}} = 11$, 1 H, $\text{CH}_2=\text{CH}-\text{C}-$.

From the data for the mentioned diterpenoids from *M. anomala* it follows that substance *A* is a diol, while substance *B* is a triol.

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