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MONOTERPENE HYDROCARBONS FROM *JUNGERMANIA CORDIFOLIA* AND *J. OBOVATA**

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Key Word Index—*Jungermania*; Jungermaneceae; liverworts; monoterpenes; α-pinene; camphene; myrcene; α-terpinene; limonene; γ-terpinene; terpinolene; *p*-cymene.

The isolation of longifolene and isolongifolene from the essential oils of some liverworts including *Jungermania cordifolia* was reported.[1] Sesquiterpene hydrocarbons from natural sources generally occur as complex mixtures, difficult to separate even with the most advanced GLC techniques[2–4] and therefore it has not yet been possible to identify the further ten or so sesquiterpenes found in those liverworts investigated.

So far, however, no report has been published concerning the composition of monoterpene fractions from liverworts. I now report the composition of the monoterpene hydrocarbons from the essential oils of *J. cordifolia* and *J. obovata*.

TABLE 1. GLC RETENTION VALUES AND METHOD OF IDENTIFICATION FOR MONOTERPENE HYDROCARBONS OF *Jungermania cordifolia* AND *J. obovata*

Compound	Relative retention time (R_L)*†			Method of identification§	
	A	B	C	*J. cordifolia*	*J. obovata*
Unknown ($C_{10}H_{16}$)	0·37	0·68	0·39	—‡	
α-Pinene	0·38	0·72	0·45		GC, MS
Camphene	0·57	0·77	0·50	GC, MS	
Myrcene	0·75	0·33	0·82		GC, MS
α-Terpinene	0·89	0·86	0·94	GC‖	GC‖,¶
Limonene	1·00	1·00	1·00	GC, MS	GC, MS
γ-Terpinene	1·27	1·08	1·32	GC, MS	GC, NS
Terpinolene	1·57	1·20	1·50	GC, MS	GC, MS
p-Cymene	1·57	0·96	1·41	GC, MS	GC, MS

* Relative retention times to limonene: $R_L = (T_X - T_a)/(T_L - T_a)$, where T_X, T_L and T_a are retention times of hydrocarbon, limonene and air, respectively. T_L = 10·9 min (A), 14·9 min (B) and 3·4 min (C).

† A, B, C are the different columns used (Table 2).

‡ Parent peak *m/e* 136, major peaks at *m/e* 93, 121, 92 and 79. (Probably tricyklene.)

§ All MS were compared with those of authentic samples run under the same conditions.

‖ MS could not be obtained because of the low capacity of the GC–MS apparatus.

¶ Only trace amounts.

RESULTS AND DISCUSSION

Camphene dominates in *J. cordifolia*, while terpinolene and limonene are the main components in *J. obovata* (Table 1). Myrcene and α-pinene are present only in *J. obovata* and

* Part XVII in the series "Chemical Studies on Bryophytes". For Part XVI see *Chem. Scripta* in press.

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[3] TERANISHI, R., FLATH, R. A. and MON, T. R. (1966) *J. Gas Chromatog.* **4**, 77.

[4] WENNINGER, J. A., YATES, R. L. and DOLINSKY, M. (1967) *JAOAC* **50**, 1304.

α-terpinene is a minor component in the same liverwort. In contrast to *J. cordifolia*, *J. obovata* has a very characteristic carrot aroma. Of the 30 terpene hydrocarbons found in *Daucus carota*,[5–7] only sabinene (4% of the whole oil) and myrcene (0·8%) had a carrot root-like odour, the principal monoterpene hydrocarbon being terpinolene (38% of the whole oil). The fact that myrcene is absent from *J. cordifolia* which has no carrot odour, suggests that this compound is at least partly responsible for the carrot-like aroma of *J. obovata*. However, none of the monoterpenes isolated from *J. obovata* has any outstanding carrot odour when examined separately. It is reported that even a concentrated solution of sabinene does not exhibit this special odour.[8] A small peak between α-pinene and myrcene had a retention time which corresponded to that reported for sabinene,[5,6] but it has not been possible to verify this. The small amount found, in relation to the aroma of the hexane extract, might be due to rearrangement of sabinene. No such rearrangement has been reported on alumina but Buttery *et al.*[9] found that sabinene was almost completely rearranged on silica gel to give α- and γ-terpinene.

TABLE 2. GAS CHROMATOGRAPHIC OPERATING CONDITIONS

Parameters	Column A	Column B	Column C§
Dimensions	6 m × 0·8 mm i.d.	6 m × 0·8 mm i.d.	15 m × 0·5 mm i.d.
Support	Chromosorb W-AW-DMCS* 80–100 mesh	Diatom W-AW-DMCS* 80–100 mesh	"SCOT-column"†
Stationary phase	Reoplex 400, 10%	SE 30, 10%	Carbowax 20 TPA
Flow rate, ml/min	N_2: 23 (at 25°)	N_2: 24 (at 25°)	N_2: 1·4 (at 100°)
Temp.	100	Programmed 100–230 at 3°/min	100°

* Acid-washed, silanized.
† Support coated open tubular column.
‡ Carbowax 20 M modified with terephthalic acid.
§ Column C was used together with a capillary injector. Split ratio 1:15.

EXPERIMENTAL

Plant material. Jungermania cordifolia was collected in Kärkevagge in the Torneträsk area in July 1972 and *J. obovata* was collected in the parish of Sälen (northwestern Dalecarlia) in September 1971. Both liverworts grew in small mountain streams. The liverworts were stored at −20°, if not used in fresh condition. Reference compounds for GLC and MS were obtained from commercial sources.

Extraction and isolation of volatile oils. 250–350 g Liverwort, air dried and ground, was extracted (4 × 24 hr) with redist. hexane (4 × 1 l.) at 22°. A green, viscous extract (2·1–2·4%*) remained after solvent evaporation. The hydrocarbon fraction in hexane was separated from the more polar constituents of the oil by column chromatography on 200–250 g neutral alumina (Merck, Akt. I). The hydrocarbons were eluted from the column with hexane and the eluate was collected in two 500 ml fractions. The hydrocarbons in each fraction were recovered by removal of the hexane at reduced pressure.

Headspace experiment. 80 g Liverwort, air dried and ground, was filled in a glass column (52 × 3 cm). Purified N_2 was blown through the column and the headspace vapours were collected in three glass traps, which were

* Since the solvent was not removed completely to avoid losses of volatile material, the yields (in % of dry wt of the plant material) given for the various fractions are only approximate.

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[6] BUTTERY, R. G., SEIFERT, R. M., GUADAGNI, D. G., BLACK, D. R. and LING, L. C. (1968) *J. Agric. Food Chem.* **16**, 1009.
[7] WILLIAMS, C. A. and HARBORNE, J. B. (1972) *Phytochemistry* **11**, 1981.
[8] WHITTAKER, D. private communication.
[9] Ref. 6, p. 1012.

connected to the outlet of the column and cooled in a mixture of dry ice-acetone. The condensed headspace vapours were then injected into the gas chromatograph.

Gas chromatography. Analytical GLC separations were carried out on a Perkin-Elmer model 900 gas chromatograph equipped with a FID and intermittently also with a capillary injector (Table 2).

MS. The MS were recorded at 70 eV on an LKB 9000 combined GC–MS apparatus equipped with a 3 m × 6 mm (o.d.) glass column filled with 7·5% SE 30 on Chromosorb W-AW-DMCS 80–100 mesh.

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ALKALOIDS OF *LYCOPODIUM THYOIDES* AND *L. CONTIGUUM*

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Plants. Lycopodium thyoides H. B. Willd. and *L. contiguum* Klotzsch. *Source.* Collected near Bogota, Columbia in June 1970 by Dr. J. H. Wilce. Voucher specimens (*L. thyoides*, No. 41359; *L. contiguum*, No. 41358) deposited in the University of Alberta Herbarium.

Present work. Ground, dried, whole plant was extracted (Soxhlet) with MeOH, concentrated, and taken up in 1% aq. HCl. The acidic soln was washed with Et_2O, basified with aq. NH_3, and extracted with $CHCl_3$. In the case of *L. thyoides* TLC (aluminum oxide G, $CHCl_3$–MeOH, 49:1, Dragendorffs reagent) indicated at least five components. These were separated by chromatography over alumina (eluent $CHCl_3$–MeOH, 49:1) and identified, in order of elution, as follows: (a) lycopodine (**1**),[1] identified as the hydrochloride, m.p. > 300°, by comparison (IR) with an authentic sample, and as the free base (IR, MS, TLC identical with an authentic sample); (b) *O*-acetylfawcettiine (**2**),[2] IR identical with that of an authentic specimen, further characterized as the methiodide, m.p. 271–272° (from MeOH), ν_{max} 1738 cm^{-1}; (c) *O*-acetyldihydrolycopodine (**3**),[3] m.p. 94–96° (lit.[4] 95–96°), hydroperchlorate, m.p. 246–247° (lit.[4] 246–247°), identified by comparison (IR, and in the case of the free base, TLC and MS) with authentic samples; (d) fawcettiine (**4**),[5] identified by comparison (IR) of its methiodide, m.p. 293–294° (from CH_2Cl_2–MeOH) (lit.[6] 296–297°) with an authentic sample. The free base was not obtained crystalline, but it showed TLC behavior identical with authentic fawcettiine; (e) the final component eluted formed

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[3] Ref. 1, p. 334.
[4] Ref. 1, p. 311.
[5] ANET, F. A. L. (1960) *Tetrahedron Letters* (20) 13.