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BRYOPHYTA

JUNGERMANNINAE

ESSENTIAL OILS FROM SOME LIVERWORTS*

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IN ORDER to study the occurrence of sesquiterpenes in liverworts we have, in collaboration with Dr. Huneck, investigated the volatile extract from *Scapania undulata* from which he has earlier isolated (−)-longifolene and (−)-longiborneol.[1] By capillary GLC and mass spectrometry the extract has been shown to contain not less than seven sesquiterpenes, all of which have the parent peak *m/e* 204. The fragmentation patterns are all characteristic of sesquiterpene hydrocarbons ($C_{15}H_{24}$). Besides longifolene, isolongifolene has also been identified.

Some additional liverworts have also been investigated for their sesquiterpenes. Their GLC chromatograms suggest complex mixtures, mostly consisting of sesquiterpenes. Their isolongifolene and longifolene contents are given in Table 1. The identities of longifolene and isolongifolene were determined by gas co-chromatography with authentic specimens (one chromatographic run for each specimen).

TABLE 1. THE OCCURRENCE OF ISOLONGIFOLENE AND LONGIFOLENE IN SOME LIVERWORTS

Liverwort	Isolongifolene	Longifolene
Jungermania cordifolia	—	Trace
Scapania nemorosa	—	+
*S. subalpina**	Trace	+
S. uliginosa	+	+
*S. undulata**	+	+

* Contains also (−)-longiborneol.

The GLC analysis of *Jungermania cordifolia* indicated the presence of only one main component (MS: *m/e* 204 parent peak and base peak). The fragmentation pattern was characteristic of sesquiterpene hydrocarbons.

EXPERIMENTAL

Plant material. (Origin and collection month): *Jungermania cordifolia*, Kuhevagge, Björkliden, Aug. 1970; *Scapania nemorosa*, Växjö, Oct. 1970; *Scapania subalpina*, Sälen, Aug. 1970; *Scapania uliginosa*, Sälen, Aug. 1970; *Scapania undulata*, Växjö, Oct. 1970.

* Part XIII of the series "Chemical Studies on *Bryophytes*". For Part XII see *Phytochem.* **11**, 1161 (1972).

[1] S. HUNECK and E. KLEIN, *Phytochem.* **6**, 383 (1967).

The reference compounds were obtained as follows: longiborneol, gift from Dr. Huneck; longifolene, from Dr. Huneck and also isolated by preparative GLC from *Scapania undulata*; isolongifolene, prepared from longifolene by acid-catalysed isomerization.[2-3]

Isolation of volatile compounds, general procedure. 20–25 g of liverwort, air dried and ground, was extracted (2 × 24 hr) with hexane (2 × 150 ml) at 22°. The extract was evaporated and the residue chromatographed on 20 g alumina (Akt I, neutral). The results of the chromatographic separations performed on the liverworts listed above are given in Table 2. The sesquiterpene fractions were then analysed by GLC.

TABLE 2. CHROMATOGRAPHY OF HEXANE EXTRACTS FROM LIVERWORTS

Fraction No.	Solvent (ml)	Eluate
1	Hexane (100)	Sesquiterpenes
2	Hexane (100)	Sesquiterpenes (only traces)
3	Benzene (100)	Yellow wax
4	Benzene (100)	Trace of wax
5	Ether (100)	*
6	Ether (100)	*

* Crystals (*Scap. subalpina* and *Scap. undulata*) besides a yellow wax.

From the ether fraction of *Scapania subalpina* (−)-longiborneol was isolated, which after repeated recrystallization from pentane had m.p. 108–109° and $[\alpha]_D^{20}$ −14·5° (c = 2·15, EtOH).[1]

Gas chromatography. Analytical GLC was performed on a Perkin–Elmer model 900 gas chromatograph equipped with two flame ionization detectors. Two stainless steel support coated open tubular columns 50 ft × 0·02 in. were used. 1. *CW 20 M—TPA* (Carbowax modified with terephthalic acid) 2. *OV 1* (Methylsilicone-gum). *Carrier gas.* N_2 in both cases fed at a rate of 2·6 ml/min at 135°. *Column temp.* 135°. *Detector temp.* 250°. *Injection temp.* 210°.

Preparative GLC separations were made on a Perkin–Elmer model F 21 preparative gas chromatograph (flame ionization detector) fitted with stainless steel columns (2·7 m × ⅜ in.) packed with either 20% Carbowax 20 M or 20% Reoplex 400 on Chromosorb A (45–60 mesh). *Carrier gas.* N_2 170 ml/min at 140°. (Reoplex) *Column temp.* 140°. (Reoplex) *Detector temp.* 250°. *Injection temp.* 210°.

Mass spectrometry. The mass spectra were recorded at 70 eV on a Perkin–Elmer model 270 combined GLC–MS apparatus equipped with a 50 ft × 0·02 in. stainless steel SCOT-column coated with CW 20 M. For some mass spectral analyses we also used the LKB 9000 combination instrument.

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[2] U. R. NAYAK and S. DEV, *Tetrahedron* **8**, 42 (1960).
[3] *Chem. Abs.* **71**, 39217 s (1969).

Key Word Index—Scapania; Jungermania; Bryophyta; liverworts; sesquiterpenes; longifolene; isolongifolene.