Sesquiterpene Hydrocarbons of the Liverwort, *Dumortiera hirsuta*

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Liverwort (Hepaticae), Sesquiterpene Hydrocarbons, Mass Spectra

Sesquiterpene hydrocarbons of the hexane extract from *Dumortiera hirsuta* were analyzed by a combining method of gas chromatography and mass spectrometry, and ten sesquiterpene hydrocarbons, δ-elemene, α-copaene, β-bourbonene, β-elemene, γ-elemene, β-pompene, γ-muurolene, α-muurolene, bazzanene and cuparene, were identified.

The liverworts *(Hepaticae)* are classfied as a unique division in the plant kingdom. The usual plant bodies of these plants are haploidal (gamethophyte) growing from the spores and contain characteristic oil bodies in each cell. Accordingly, the occurrence of novel compounds is expecting in these plants. The investigation on the chemical constituents of the plants, however, has hardly carried out for the reason that the collection of a sufficient amount of the plants to examine their constituents are very difficult. In connection with our previous papers [1], the investigation on the constituents of a hexane extract from a thallus liverwort, *Dumortiera hirsuta* (Swartz) R.B.N. (Japanes name Kezeni-goke), belonging to the marchantiaceae was undertaken. The present paper deals with the analytical result of the hydrocarbon fraction.

The hexane extract was chromatographed over a silica gel column with hexane to separate a hydrocarbon fraction which showed one spot (R_F 0.80) in TLC using a silica gel plate and a mixed solvent of hexane and ethyl acetate (4 : 1) and exhibited several absorption bands attributable to only C – H bonding in the infrared spectrum. The hydrocarbon fraction, however, was very small in the amount and exhibited 11 peaks in gas chromatography using a PEG 20M-packed column as shown in Fig. 1. For that reason, the analysis of the fraction was performed by a combining instrument of a gas chromatograph and mass spectrometer (GC-MS). Thus, ten sesquiterpene hydrocarbons of δ-elemene [2, 3], α-copaene [3], β-bourbonene [5], β-elemene [2, 3], γ-elemene [2], β-pompene (= gymnomitrene) [6, 7], γ-muurolene [4], α-muurolene [2, 4], bazzanene [5] and cuparene [5] were identified based on agreement of the mass spectra (*cf* Table) with the authentic ones.

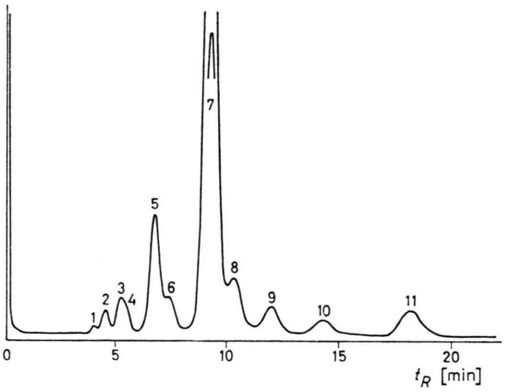

Fig. 1. Gas chromatogram of the sesquiterpene hydrocarbons from *Dumortiera hirsuta.* 1. δ-elemene; 2. α-copaene; 3. β-bourbonene; 4. $C_{15}H_{24}$; 5. β-elemene; 6. γ-elemene; 7. β-pompene; 8. γ-muurolene; 9. α-muurolene; 10. bazzanene; 11. cuparene.

Amoung them β-bourbonene, β-pompene, bazzanene and cuparene had already been detected in another liverworts. This liverwort, however, is the first instance, in which such many kinds of sesquiterpene hydrocarbons have been detected in the same liverwort.

Table. Abundant ions in mass spectra of identified sesquiterpene hydrocarbons [a].

Compound	M [%]	H_1	H_2 [%]	H_3 [%]
δ-elemene	204 (28)	121	93 (79)	136 (76)
α-copaene	204 (35)	105	41 (92)	119 (89)
β-bourbonene	204 (10)	81	82 (75)	123 (62)
β-elemene	204 (23)	93	41 (95)	81 (86)
γ-elemene	204 (28)	121	41 (86)	93 (83)
β-pompene	204 (12)	96	108 (95)	93 (83)
γ-muurolene	204 (24)	161	93 (94)	105 (81)
α-muurolene	204 (45)	105	161 (62)	41 (54)
bazzanene	204 (6)	109	108 (55)	67 (43)
cuparene	202 (13)	132	131 (44)	145 (32)

[a] Percentages in parentheses represent the relative abundance.

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Experimental

Separation of a sesquiterpene hydrocarbon fraction

The liverwort collected at the suburbs of Hiroshima City was dried in the shade for several days. The dried plant (510 g) was digested with hexane (5 l) to obtain a brown viscous substance (2.4 g) in a 0.47% yield, which was chromatographed through a silica gel column (1.5 × 35 cm) with hexane, and a hydrocarbon fraction (0.27 g) eluted quickly was collected.

Gas chromatography

The gas chromatograms were determined on a apparatus equipped with a flame-ionization detector in connection with a separation column packed with PEG 20M (3%) on Chromosorb AW (60 – 80 mesh); the column temperature was regulated at 140 °C and the pressure of nitrogen gas at 1.0 kg/cm^2.

The analysis by a combining instrument of a gas chromatograph and mass spectrometer

The hydrocarbon fraction was analyzed with a combining instrument of a gas chromatograph and mass spectrometer, Hitachi RMU-6E, using a separation column packed with PEG 20M (4 mm × 2 m). The column temperature was programmed at a rate of 3 °C/min from 120 to 220 °C and a helium carrier was used. The column effluent was admitted to an ion source *via* a heated line and Watson-Biemann type helium separator. The mass spectrometer was operated at 70 eV ionization voltage, 80 μA total emission, 1800 eV ion accelerating voltage and 220 °C ion source temperature.

Identification of the constituents

From each of the mass spectra thus determined, the mass units and intensity of four abundant ions, molecular (M), base (H_1), second-highest (H_2) and third-highest (H_3) ions, were read as shown in Table. Based on agreement of these spectral patterns with the authentic ones the identification was carried out.

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