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Sesquiterpene Hydrocarbons of the Liverwort, *Scapania parvitexta*

Akihiko Matsuo, Mitsuru Nakayama, and Shûichi Hayashi
Department of Chemistry, Faculty of Science, Hiroshima University, Higashisenda, Hiroshima 730

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The liverworts (*Hepaticae*), which are phylogenetically placed between the vascular plants and the algae, and which contain several oil bodies in each cell, form a unique division in the plant kingdom. About 8500 species of the plants are distributed throughout the world. The essential oils of liverworts have hardly been investigated at all to date because of the difficulty of collecting a sufficient amount of the plants to examine their constituents. In the course of our studies of the constituents of *Hepaticae*,[1] the present investigation was undertaken on the essential oil of a leafy liverwort, *Scapania parvitexta* Steph. (Japanese name, Koamimehishakugoke), belonging to the *Scapaniaceae* family; we were able to identify nine sesquiterpene hydrocarbons.

The hexane extract of the liverwort was subjected to fractional distillation under reduced pressure, followed by elution chromatography; we thus obtained a hydrocarbon fraction, which showed thirteen peaks in gas chromatography with a Golay column, as is shown in Fig. 1. Since the fraction was very small in amount, its analysis depended upon a method combining a gas chromatograph and a mass spectrometer (GC-MS); by a comparison of the mass spectra thus obtained (*cf.* Table 1) with the previously-reported data, nine sesquiterpene hydrocarbons of β-bourbonene,[2] β-ylan-

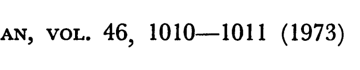

Fig. 1. Gas chromatogram of the sesquiterpene hydrocarbon fraction of *Scapania parvitexta*.
1. β-bourbonene 2. $C_{15}H_{24}$ 3. $C_{15}H_{24}$ 4. β-ylangene 5. β-cubene 6. $C_{15}H_{24}$ 7. $C_{15}H_{24}$ 8. γ-cuprenene 9. calamenene 10. β-chamigrane 11. β-selinene 12. bazzanene 13. cuparene

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[1] Chemical constituents from *Hepaticae*, Part XII: Part XI, A. Matsuo, M. Nakayama, J. Ono, and S. Hayashi, *Z. Naturforsch.*, *B*, **27**, 1437 (1972).

[2] K. Morikawa and Y. Hirose, Abstract of the 14th Symposium on the Chemistry of Terpenes, Essential Oils, and Aromatics, Kitami, p. 27 (1970).

Table 1. Abundant ions in mass spectra of identified sesquiterpene hydrocarbons[a]

Compound	M (%)	H_1	H_2 (%)	H_3 (%)
β-Bourbonene	204(9)	81	80(74)	123(63)
β-Ylangene	204(35)	161	41(82)	204(35)
β-Cubebene	204(45)	161	119(60)	105(55)
γ-Cuprenene	204(25)	119	93(53)	105(40)
Calamenene	202(12)	159	157(35)	142(18)
β-Chamigrene	204(55)	189	41(90)	93(75)
β-Selinene	204(100)	204	41(85)	105(80)
Bazzanene	204(5)	109	108(52)	67(31)
Cuparene	202(15)	132	131(42)	145(30)

a) Percentages in parentheses represent the relative abundance.

gene,[3] β-cubebene,[4] γ-cuprenene,[4] calamenene,[5] β-chamigrene,[6] β-selinene,[7] bazzanene,[8] and cuparene,[9] were identified.

The biogenetic pathways of the hydrocarbons may be shown as in Chart 1: β-chamigrene (VI), γ-cuprenene (VII), bazzanene (VIII), and cuparene (IX) are synthesized from *cis*-farnesol (I) *via* the (III) cation, and β-ylangene (X), β-cubebene (XI), and calamenene (XII), from the same precursor *via* the (IV) cation, whereas the other compounds, β-selinene (XIII) and β-bourbonene (XIV), are synthesized from *trans*-farnesol (II) *via* the (V) cation. Although most of these biogenetic courses have already been known in higher plants,[10,11] it is very interesting that so many kinds of sesquiterpene hydrocarbons were also detected in the liverwort.

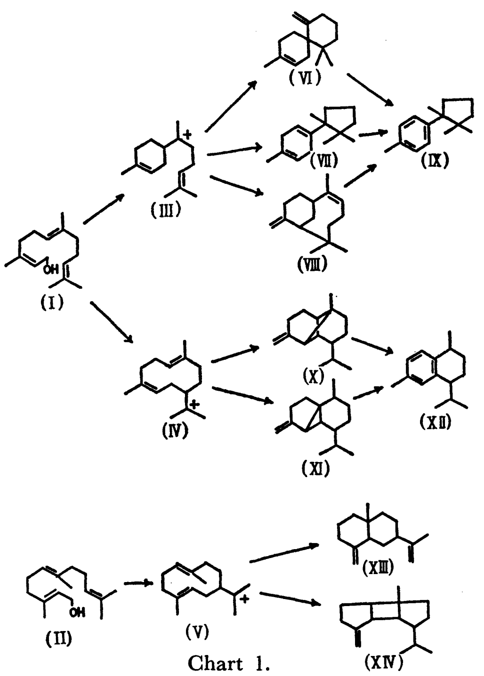

Chart 1.

Experimental

Separation of a Sesquiterpene Hydrocarbon Fraction. Liverwort collected at Yaku Island in Kagoshima Prefecture (October, 1969) was dried in the shade for a week; the plants (3.85 kg) were then digested with hexane (15 l) to obtain a dark brown, viscous matter (5.3 g) in a 0.14% yield. This matter was subjected to distillation under reduced pressure by using a small-type distillation column packed with single-turn spirals of stainless steel. The distillate (bp 70—90°C/2 mm Hg; 0.45 g) thus obtained was then chromatographed over a silica gel column (1.5×25 cm) to collect a hydrocarbon fraction (0.37 g), which was then quickly eluted with hexane.

Gas Chromatography. The gas chromatograms were taken on a Hitachi K–53 gas chromatograph equipped with a flame-ionization detector in connection with a Golay column (coating, PEG–20 M; 0.5 mm×45 m): the column temperature was programmed from 120 to 170°C at a rate of 2°C/min, and the carrier (nitrogen gas) had a pressure of 1.0 kg/cm^2.

An Apparatus Combining a Gas Chromatograph and a Mass Spectrometer. The hydrocarbon fraction described above was analyzed with an instrument combining a gas chromatograph and a mass spectrometer, Hitachi RMU-6E Model, using a Golay column (PEG–20 M, 0.5 mm×45 m); the gas-chromatograph part was operated under the same conditions as above, except that helium was used instead of nitrogen gas as the carrier gas. The column effluent was admitted to an ion source *via* a heated line and a Watson-Biemann-type helium separator. The mass spectrometer part was operated under the following conditions: 70 eV, ionization voltage; 100 μA, total emission; 1800 eV, ion-accelerating voltage, and 220°C, ion source temperature.

Mass Spectrum of Each Constituent. From the mass spectra thus taken, four abundant ions of molecular (M), base (H_1), second-highest (H_2), and third-highest (H_3) ions and their abundance were read, as is shown in Table 1. These spectral patterns were then a compared with the respective reported spectra, and the listed sesquiterpene were identified.

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