A NEW MONOCYCLIC DITERPENE FROM THE LIVERWORT *JUNGERMANNIA INFUSCA* (MITT.) STEPH.

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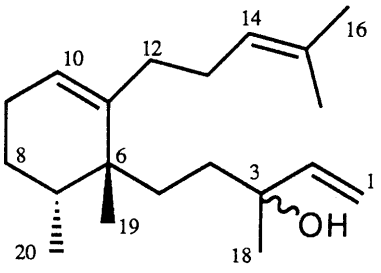
A new monocyclic diterpene, infuscatrienol (**1**), has been isolated from the liverwort *Jungermannia infusca* and its structure determined by extensive spectroscopic analysis.

KEY WORDS *Jungermannia infusca*; liverwort; infuscatrienol; monocyclic diterpene

The liverwort *Jungermannia* species are rich sources of diterpenoids belonging to the pimarane, clerodane and kaurane classes.[1,2] Recently, we reported the isolation of *ent*-kaurane-, labdane- and clerodane-type diterpenoids from *J. infusca* (Mitt.) Steph.[3-6] *J. infusca* has chemically been classified into three chemotypes, one of which mainly produces intensely bitter *ent*-kaurane glucosides.[6] The second type contains *ent*-kaurane- and labdane-type diterpene aglycones as the main components and third one contains clerodane-type diterpene aglycones as the predominant components.[3-5] As part of our search for biologically active substances and the study of the chemical constituents of *Jungermannia* species, we have reinvestigated Japanese *J. infusca* and isolated a new biogenetically interesting monocyclic diterpene **1** along with the known compounds, (-)-kolavelool [7] (**2**) and perrottetin E [8] (**3**), and their structures were established on the basis of spectral evidence.

The ether extract (8.3 g) of *J. infusca* was chromatographed on silica gel, Sephadex LH-20 and preparative HPLC to yield a new monocyclic diterpene, named infuscatrienol (**1**, 59 mg), together with the known compounds, (-)-kolavelool[7] (**2**, 226 mg) and perrottetin E [8] (**3**, 2 g).



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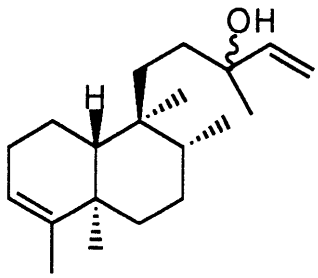

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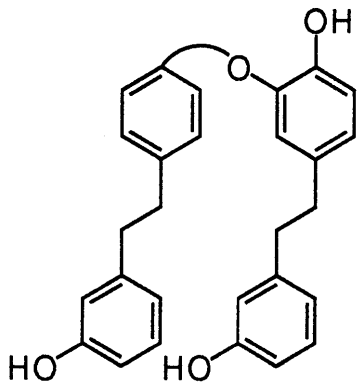

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Compound **1** [9] has the molecular formula $C_{20}H_{34}O$ (*m/z* 290.2610) by high-resolution mass spectrum (HRMS), indicating four degrees of unsaturation. The ^{13}C NMR and IR spectra showed the presence of a tertiary hydroxyl group

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(3450 cm^{-1}, δ_C 73.3 *s*). The ^1H and ^{13}C NMR (C_6D_6) spectra contained the signals of a secondary methyl, two tertiary methyls, two olefinic methyls, two trisubstituted double bonds (δ_H 5.30 *t like* δ_C 125.9 *d*, 131.4 *s* ; δ_H 5.54 *br s* δ_C 122.6 *d*, 143.6 *s*) and a vinyl group (δ 4.95 *dd*, 5.18 *dd* δ_C 111.8 *t*, 146.2 *d*). Analysis of the distortionless enhancement by polarization transfer (DEPT) spectrum also showed the presence of six methylenes, a methine and a quaternary carbon, respectively. The above IR, HRMS and DEPT spectra suggested that **1** is a monocyclic diterpene with a tertiary hydroxyl group. Analysis of ^1H-^1H correlation spectroscopy (COSY), totally correlated spectroscopy (TOSCY) and ^{13}C-^1H COSY spectra indicated the presence of four partial structures, (A) ■-C=CH_2, (B) ■-CH_2-CH_2-■, (C) $(CH_3)_2$C=CH-CH_2-CH_2-■ and (D) ■-(CH_3)CH-CH_2-CH_2-CH=C-■. The connectivity of each partial structure was confirmed by the heteronuclear multiple bond connectivity (HMBC) spectrum as shown in Fig. 1. As the nuclear Overhauser effect spectroscopy (NOESY) of **1** showed NOEs between H-20 and H-5, H-20 and H-8, and H-12 and H-5, the stereochemistry of H-19 and 20 was supported as shown in **1**. Thus, the structure of infuscatrienol was established to be monocyclic diterpene alcohol. However, the stereochemistry of the tertiary alcohol and the absolute configuration of **1** remain to be clarified. Similar monocyclic diterpenoids, generally rare in nature, have been found in the Umbelliferae.[10-12] This is the first report of the isolation of a six-membered ring monocyclic diterpene from bryophytes.[1,2] The present *J. infusca* which contained a bis(bibenzyl), perrottetin E [8] (**3**), as the main component is classified into a new chemotype (fourth chemotype of *J. infusca*).

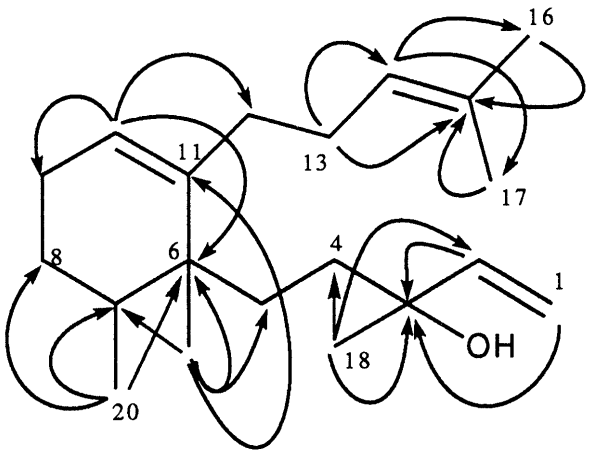

Fig. 1. ^1H-^{13}C Correlations of **1**

The tentative biogenetic pathways for compound **1** is shown in Fig. 2. Compound **1** might be formed from the cyclization of geranylgeranyl pyrophosphate [13] *via* methyl migration and deprotonation (route a) or from a labdane-type intermediate [13] *via* methyl migration, cleavage of a single bond and deprotonation (route b).

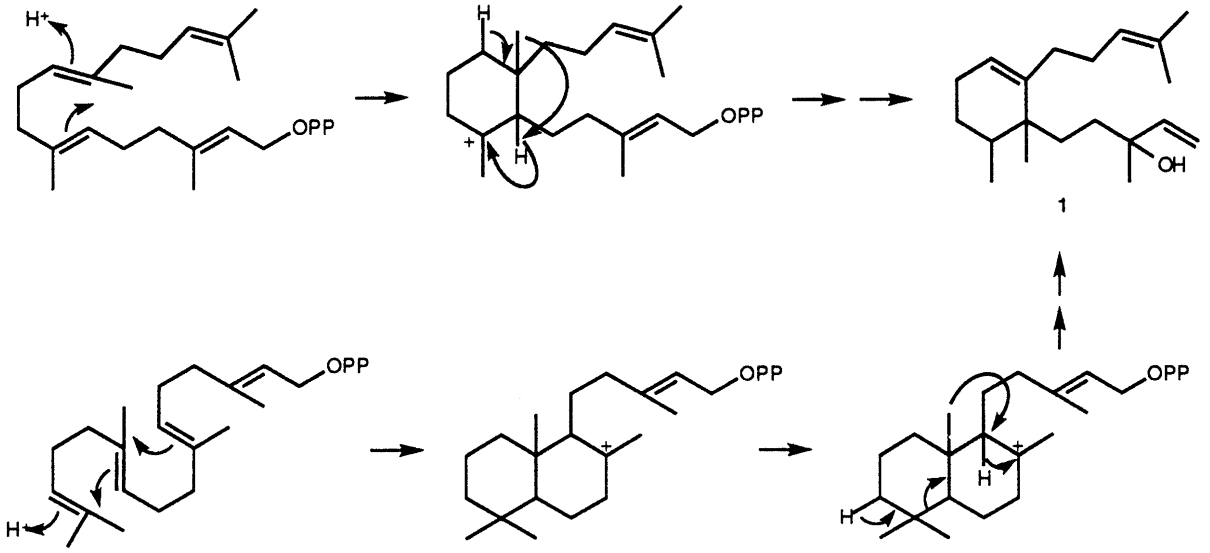

Fig. 2. Tentative Biogenetic Pathway of **1**

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9) $[\alpha]_D^{22}$ +29.2° (c 0.90, $CHCl_3$); HRMS; *m/z* 290.2610 $C_{20}H_{34}O$ requires 290.2609 ; IR: 3450, 1470, 1390 cm^{-1}; δ_H (C_6D_6) 4.95 (1H, *dd*, *J*=10.7, 1.7 Hz, H-1a), 5.18 (1H, *dd*, *J*=17.3, 1.7 Hz, H-1b), 5.79 (1H, *dd*, *J*=17.3, 10.7 Hz, H-2), 1.26 (1H, *ddd*, *J*=12.7, 12.7, 4.2 Hz, H-4), 1.45-1.57 (3H, *m*, H-4 and H-5), 1.70 (1H, *m*, H-7), 1.42 (2H, *m*, H-8), 1.99 (2H, *m*, H-9), 5.54 (1H, *br s*, H-10), 2.05 (2H, *t like*, H-12), 2.24 (2H, *br s like*, H-13), 5.30 (1H, *t like*, H-14), 1.68 (3H, *d*, *J*=1.2 Hz, H-16), 1.59 (3H, *s*, H-17), 1.12 (3H, *s*, H-18), 0.91 (3H, *s*, H-19), 0.87 (3H, *d*, *J*=6.8 Hz, H-20) ; δ_C (C_6D_6) 111.8 (C-1), 146.2 (C-2), 73.3 (C-3), 37.4 (C-4), 31.1 (C-5), 41.1 (C-6), 34.3 (C-7), 27.6 (C-8), 26.2 (C-9), 122.6 (C-10), 143.6 (C-11), 31.2 (C-12), 28.3 (C-13), 125.9 (C-14), 131.4 (C-15), 18.2 (C-16), 26.3 (C-17), 28.5 (C-18), 22.1 (C-19), 16.6 (C-20).

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