VOLATILES FROM LEPTOLEJEUNEA ELLIPTICA

MITSURU NAKAYAMA*, AKIHIKO MATSUO*, TAKAYASU KAMI† and SHÛICHI HAYASHI*

*Department of Chemistry, Faculty of Science, Hiroshima University, Hiroshima 730, Japan; †Faculty of Fisheries and Animal Husbandry, Hiroshima University, Fukuyama, Hiroshima 720, Japan

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Leptolejeunea elliptica Schiffn. has a characteristic aroma emanating from its surface. In the course of our studies of terpenoids from liverworts [1], a volatile fraction of head space vapours of this liverwort was investigated.

The head space vapours exhibited four peaks on GLC using a PEG 20M-packed column and p-ethylanisole was determined as a major component together with three monoterpenoids, which were identified as α -pinene, camphene and β -pinene. Identification was by GC-MS comparison with authentic samples and with literature data [2, 3]. The relative contents were: p-ethylanisole 81.4%, α -pinene 13.4%, β -pinene 0.3% and camphene 4.9%.

Aromatic esters have previously been noted in liverworts, in *Isotachis japonica* [4], but this is the first report in these plants of an aromatic ether.

EXPERIMENTAL

Material. Fresh liverwort, Leptolejeunea elliptica, was collected at the Valley of Okutani in Iwakuni city, Yamaguchi prefecture,

and put as soon as possible in the round flask with a stopper. The head space vapour in the flask was examined by GLC and GC-MS using PEG 20M-packed column. The GC-MS analyses were performed with a single focus MS under the following conditions: PEG 20M (3%) on Chromosorb AW (60-80 mesh) (3 mm \times 2 m); column temp. 60° (10 min hold) and then programming at 5°/min from 60° to 230°; 1.2 kg/cm² pressure of He carrier; ionizing voltage 70 eV; ion accelerating voltage 1800 eV and ion source temp. 220°.

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(—)-CADALA-1,4,9-TRIENE, A NEW SESQUITERPENIC HYDROCARBON FROM *ACORUS CALAMUS*

MARTIN ROHR and PETER NAEGELI

Givaudan Research Company Ltd., Üeberlandstr. 138, 8600 Düebendorf, Switzerland

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The sesquiterpenic hydrocarbon fraction of sweet flag oil (Acorus calamus) has been investigated extensively in the past, particularly by Sorm and co-workers [1, 2]. These authors reported the isolation and identification of a number of hydrocarbons from a Dutch sample of the essential oil. Our own recent efforts in this field revealed a new major sesquiterpenic hydrocarbon of the cadalane type, which to our knowledge has not as yet been described in the literature.

(-)-Cadala-1,4,9-triene (1)* was isolated as a highly unstable liquid from sweet flag oil of Eastern European

* IUPAC-nomenclature: 1,6-dimethyl-4-(1-methylethyl)-3.4.4*a*,7-tetrahydronaphthalene.

origin, which contained 4.1% of 1 as determined by GLC. Combination of MS and NMR spectroscopy established its molecular formula as $C_{15}H_{22}$. ^{13}C NMR revealed three quaternary (δ 136.9, 132.0, 131.3 ppm) and three tertiary olefinic carbons (124.9, 120.4, 116.9 ppm). The PMR spectrum included the signals of three olefinic protons (δ 5.62 ppm, m), two olefinic (1.82, 1.74 ppm) and two secondary methyl groups (0.93, 0.85 ppm, J=7 Hz each), the latter being attached to the same carbon as demonstrated by double resonance experiments (100 MHz). The skeletal structure of 1 was determined by its total dehydrogenation to 4 using Pd/C 10% in toluene. The spectral properties of 4 were identical in all respects to those of an authentic sample of cadalene and this compound was identified