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VOLATILES FROM *LEPTOLEJEUNEA ELLIPTICA*

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Key Word Index—*Leptolejeunea elliptica*; Lejeuneaceae; Hepaticae; volatiles; *p*-ethylanisole; monoterpenoids.

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 × 2 m); column temp. 60° (10 min hold) and then programming at 5°/min from 60° to 230°; 1.2 kg/cm^2 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*

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Key Word Index—*Acorus calamus*; Araceae; sweet flag oil; new cadalane type sesquiterpene; cadala-1,4,9-triene.

The sesquiterpenic hydrocarbon fraction of sweet flag oil (*Acorus calamus*) has been investigated extensively in the past, particularly by Šorm 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 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 (δ5.62 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

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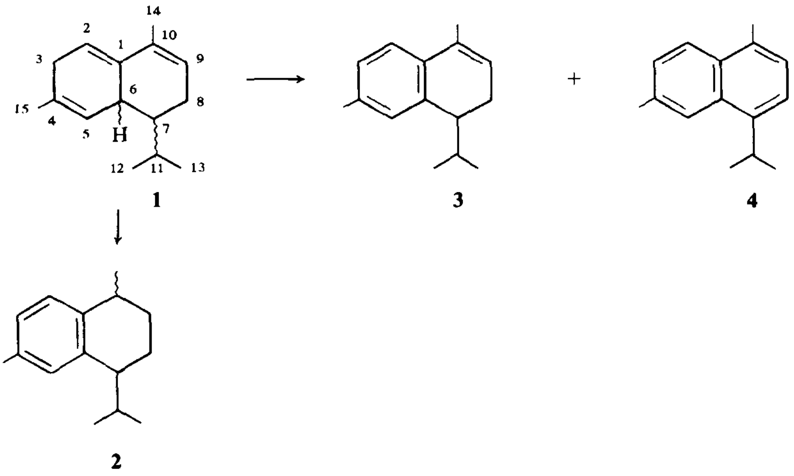
* IUPAC-nomenclature: 1,6-dimethyl-4-(1-methylethyl)-3,4,4*a*,7-tetrahydronaphthalene.



as a minor constituent of sweet flag oil. The UV spectrum of **1** showed a maximum at 242 nm clearly indicating the presence of a heteroannular diene system (λ_{max} calc. 239–244 nm). Since **1** possesses a cadalane skeleton, its three double bonds consequently must be placed at the (1,2)- (4,5)- and (9,10)-positions. Additional evidence supporting structure **1** for the new hydrocarbon was obtained by its partial dehydrogenation under mild conditions to afford besides cadalene (**4**) and starting **1** α-calacorene (**3**) [2]. The identity of **3** was established by GC–MS and GLC coinjection with authentic material. Furthermore **1** readily underwent isomerization upon treatment with catalytic amounts of *p*-toluenesulfonic acid in benzene to furnish a mixture of *cis*- and *trans*-calamenenes (**2**) [3] in a ratio near 3:2 [4]. However, no configurational assignments for **1** could be made on the basis of the spectroscopical evidence available. Inspection of molecular models indicated a remarkable conformational flexibility for both stereoisomers possible. Therefore any statement about the steric relationship between C-6 and C-7 protons based on PMR experiments would be of highly speculative character.

EXPERIMENTAL

Preparative GLC: 5% Carbowax 20M on Chromosorb G, 3.8 × 16 mm glass column; temp. 200°; N_2 at 260 ml/min. Analytical GLC: Carbowax 20M ($BaCO_3$-layer) 29 m × 0.27 mm WCOT glass column; temp. 150°; He at 2–3 ml/min. PMR and ^{13}C NMR were recorded at 100 MHz and 25 MHz, respectively, and spectra are for $CDCl_3$ with TMS set at δ = 0.00 ppm. Merck Si gel 60 (70–230 mesh) was used for CC.

Isolation of (−)-*cadala*-1,4,9-*triene* (**1**). A wide distillation cut (129–138°/0.03 mm; 350 g) of sweet flag oil of Eastern European origin was chromatographed on Si gel (6 kg) using hexane as eluant. Head fractions containing mainly (**1**) and α-calacorene (**3**) [2] were separated by preparative GLC to afford **1** as an air-sensitive, colourless oil, bp 80°/0.01 mm. $[\alpha]_D^{22}$ − 156.4° ($CHCl_3$, *c* 1.07); UV λ_{max}^{EtOH} nm (log ε): 242 (3.985); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 2980, 1460, 1435, 1380, 1360, 940, 820; PMR: δ 5.62 (3H, *m*), 2.68 (3H, *m*, C-3, C-6), 2.20 (1H, *m*), 1.98 (2H, *m*), 1.82 (3H, *bs*), 1.74 (3H, *bs*), 1.54 (1H, *m*, C-11), 0.93 (3H, *d*, *J* = 7 Hz), 0.85 (3H, *d*, *J* = 7 Hz); ^{13}C NMR: δ 136.859*s*, 131.998*s*, 131.307*s*, 124.859*d*, 120.424*d*, 116.860*d*, 44.892*d*, 37.997*d*, 31.796*t*, 26.413*d*, 25.248*t*, 23.413*q*, 21.036*q*, 19.445*q*, 14.782*q*; MS *m/e* (rel. int.): 202 [M^+] (30), 187(2), 159(100), 145(17), 131(40), 119(7), 117(9), 115(9), 105(15), 91(10), 77(5), 67(4), 55(2), 41(7).

Dehydrogenation of **1**. (a) To Pd/C 10% (20 mg) in toluene (2 ml) was added **1** (13 mg) and the mixture heated to reflux for 3 hr. Filtration, evapn and separation by PLC (hexane) afforded **4** (6 mg) as a colourless oil, bp 70°/0.01 mm, identical in all respects (IR, PMR, MS, GLC) to an authentic sample of cadalene.

(b) To Pd/C 10% (10 mg) in toluene (2 ml) was added **1** (15 mg) and the mixture kept at 90° for 3 hr. GC–MS of the recovered product revealed a mixture of starting **1**, α-calacorene (**3**) and cadalene (**4**) in a ratio of 2:1:0.5. The identity of the components was confirmed by GLC coinjection with authentic materials.

Isomerization of **1**. A soln of **1** (10 mg) and *p*-toluenesulfonic acid (2 mg) in C_6H_6 (1 ml) was heated to reflux for 10 min. Recovery of the product by washing with aq. $NaHCO_3$, evapn and purification by PLC (hexane) gave calamenene (**2**) (8 mg), bp 60°/0.01 mm. $[\alpha]_D^{22}$ − 10° ($CHCl_3$, *c* 0.22), identical by IR, MS and GLC with an authentic sample of *trans*-calamenene. PMR revealed a mixture of *cis*- and *trans*-stereoisomers in a ratio of *ca* 3:2 (see ref. [4]).

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