

New aromatic esters of the liverwort, *Trichocolea tomentella*

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Summary. 4 new aromatic esters containing isoprene units have been isolated from the liverwort, *Trichocolea tomentella*, and their structures have been established to be **1**, **2**, **3** and **4**.

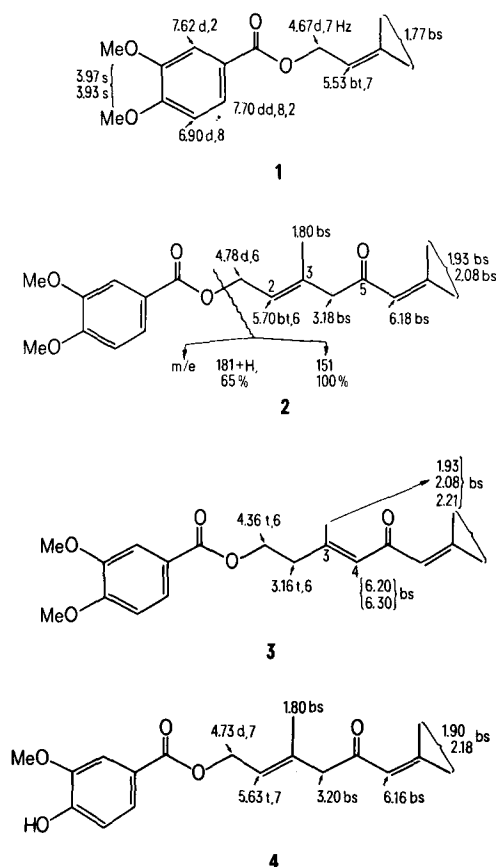
Liverworts often show interesting biological activities, like allergenic contact dermatitis² and cytotoxicity³. We have recently isolated unique sesqui- and diterpene aldehyde responsible for the intense pungency and plant growth inhibitory activity⁴ of *Porella vernicosa* and its species complex, and *Trichocoleopsis sacculata*. Their structures have been elucidated⁵.

Trichocolea tomentella (Trichocoleaceae) contains no pungent substance, but only various aromatic esters. We now wish to describe the isolation and the structures of 4 new aromatic esters, named trichocolein (**1**), tomentellin (**2**), isotomentellin (**3**) and demethoxytomentellin (**4**). *T. tomentella*, growing on the rock, was collected in February 1977. Column and preparative TLC on silica gel of the ether extracts of the air-dried and ground material (72 g) resulted in the isolation of the aromatic esters, **1** (12.2% total weight of the extract), **2** (5.3%), **3** (9.6%) and **4** (5.3%), respectively.

Trichocolein (**1**). $C_{14}H_{18}O_4$ [M^+ 250, m/e 182 (base $C_9H_{10}O_4$)]. The IR- and UV-spectra showed the presence of a benzene ring (1600, 1513, 765 cm^{-1} ; λ_{max} 217 and 259 nm) and an aromatic ester (1715, 1275 cm^{-1} ; λ_{max} 290 nm). The NMR-spectrum (figure) included the signals attributable to a dimethylallyl group, 2 methoxy groups and 3 protons on the benzene ring. Hydrogenation

of **1** in the presence of Pd-C in methanol gave methyl 4-hydroxy-3-methoxy benzoate (65%) and the dihydroderivative of **1** (35%) [δ 1.00 (d, $J = 7$, 6H), 1.25 (m, 1H), 1.82 (m, 2H), 4.15 ppm (t, $J = 6$, 2H); 1715, 1275 cm^{-1}], indicating **1** to be an allyl ester. The dihydroderivative, when hydrolyzed by 5% KOH-MeOH, afforded 3,4-dimethoxy benzoic acid and isoamyl alcohol. On the basis of the above spectral and chemical evidence, the structure of trichocolein was established to be **1**.

Tomentellin (**2**). Careful chromatography of the ester fractions afforded tomentellin as a yellow oil, $C_{19}H_{24}O_5$ (M^+ 332). The IR- (1690 cm^{-1}) and UV- spectra (257 nm, ϵ , 4419) and the formation of a 2,4-dinitrophenylhydrazone (m.p. 119–121°C; λ_{max} 365 nm, ϵ , 7168) suggested the presence of an α,β -unsaturated carbonyl group. The IR-spectrum also showed the presence of an aromatic ester (1712, 1275 cm^{-1}), a trisubstituted double bond (1620, 830 cm^{-1}) and a benzene ring (1600, 1512, 768 cm^{-1}). The NMR- and NMRD-spectra contained the signals for 3 vinyl methyls, 2 olefinic methines, one of which was linked to the carbonyl group, an allylic methylene bearing an ester oxygen, a methylene located between a carbonyl group and a double bond, 2 methoxy groups and 3 protons on a benzene ring. The NMR-signal pattern between 3.99 and 7.85 ppm, except the presence of one olefinic proton (6.18 ppm), was identical to that of **1**, suggesting **2** to be an allyl ester of 3,4-dimethoxy benzoic acid. This is proved by hydrogenolysis of **2** by prerduced PtO_2 to afford methyl 4-hydroxy-3-methoxy benzoate and tetrahydrotomentellin [1710, 1272 cm^{-1} ; 0.90 (d, $J = 8$, 6H), 0.95 (d, $J = 8$, 3H), 0.95–1.25 (m, overlapped, 2H), 1.83 (m, 2H), 2.30 (bd, $J = 8$, 4H), 4.10 (t, $J = 7$, 2H)]. The above spectral evidence coupled with the chemical reaction showed that the compound **2** possessed a further isoprene unit having an enone system linked to one of the vinyl methyl groups of **1**. The location of the carbonyl group at C-5 was confirmed by the bathochromic shift (36 nm, the formation of enolate anion) of the UV-absorption band at 257 nm after addition of 0.1 N NaOH⁶. In the IR-spectrum, the absorption of the double bond (1620 cm^{-1}) was more intense than that of carbonyl group,



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showing **2** to be present in s-cis form (C-5/C-6)⁷. All these data, together with biogenetic considerations, show that tomentellin is most favorably represented by the formula **2**.

Isotomentellin (**3**). M.p. 79–80°C (fine needles). The UV- and IR-spectra are quite similar to those of tomentellin **2**. The NMR- and NMDR-spectra showed the presence of a 3,4-dimethoxy benzoate group, 2 methylenes located between ester oxygen and double bond, 2 olefinic methines bearing a carbonyl group and 3 vinyl methyls. Treatment of **3** with prereduced PtO_2 afforded only a tetrahydroderivative, whose spectral data were completely identical to those of tetrahydrotomentellin. The above spectral and chemical data indicated that **3** was the C-3/C-4 double bond isomer of **2**. The correctness of this conclusion was also confirmed by the absence of bathochromic shift of the absorption band (262 nm) in the UV-spectrum corresponding to the conjugated carbonyl group after addition of 0.1 N NaOH. Thus, the structure of iso-tomentellin was determined to be **3**.

Demethoxytomentellin (**4**). The spectral data (UV, IR and NMR) of the most polar aromatic ester were quite similar to those of tomentellin (**2**), except for the presence

of a hydroxyl group (3550 cm^{-1}) and the absence of one methoxy group. The NMR-signal pattern in the aromatic region was identical to that of the 4-hydroxy-3-methoxy benzoate system, indicating **4** to be the demethoxy compound of **2**. Alkaline hydrolysis of **4** gave white crystal, whose m.p. and the spectral data were completely identical to vanillic acid. Methylation of **4** with diazomethane afforded tomentellin. Thus, demethoxytomentellin was established to have structure **4**.

In recent 10 years, various mono-, sesqui- and diterpenes have been isolated from many liverworts; on the other hand, occurrence of the aromatic esters is rare and one example only has been known in *Isotachis japonica*⁸. As far as we are aware, the present results are the first reports of aromatic esters containing isoprene units in Bryophytes.

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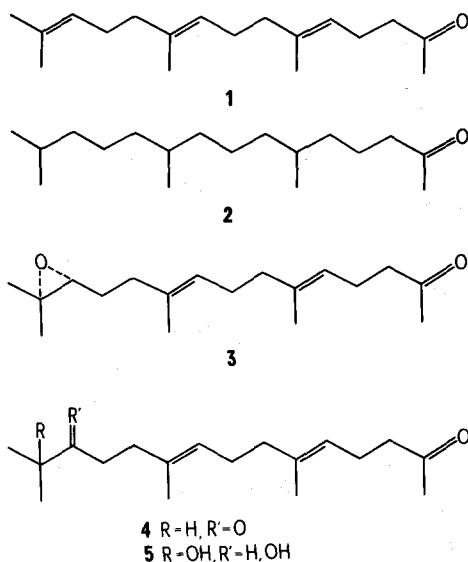
Two derivatives of farnesylacetone from the brown alga *Cystophora moniliformis*

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Summary. Farnesylacetone epoxide(**3**) and the isomeric diketone (**4**) have been isolated from the brown alga *Cystophora moniliformis*.

A recent report has described the isolation of farnesylacetone (**1**) and the hexahydro-derivative (**2**) from the androgenic glands of male specimens of the crab, *Carcinus maenas*². **1** and **2** showed 2 of the 3 previously documented biological activities shown by the crude gland extract. Significant juvenile hormone activity was also shown by **1** and **2** in the *Galleria* wax test but neither compound showed as high an activity as that demonstrated by the crude extract³. The isolation of **2** from marine sediments has also been published⁴.



We now report the isolation of the farnesylacetone epoxide (**3**) and the related dione (**4**) from the brown alga *Cystophora moniliformis* in significant yield. Extraction of the freeze dried alga with dichloromethane yielded a 1% extract from which **3** and **4** were isolated in 60% and 5% yield respectively by chromatography on silica gel.

The formula $\text{C}_{18}\text{H}_{30}\text{O}_2$ of **3**, isolated as an oil $[\alpha]_D -3.2^\circ\text{C}$ ($c = 1\%$, CHCl_3), was obtained by high resolution MS. The presence of a methyl ketone was established by IR ($\nu_{\text{max}} 1710\text{ cm}^{-1}$), $^1\text{H-NMR}^5$ (δ 2.00, 3H, s) and $^{13}\text{C-NMR}^6$ (δ 208.0, s) and a trisubstituted epoxide grouping was inferred from the $^{13}\text{C-NMR}$ spectrum (δ 63.9, d; 58.0, s)⁶. The remainder of the $^1\text{H-NMR}$ spectrum of **3** consisted of 2 methyl singlets (δ 1.18 and 1.21), a 6 proton singlet (δ 1.58) and vinyl protons centred at δ 4.96 and 5.04 (each 1H, bt) with other signals at 2.48 (1H, dd, J 5.5, 5.5 Hz), 2.4–1.9 (10H, m) and 1.50 (2H, m). These data were fully consistent with structure **3**. Further confirmation came from the hydrolysis of **3** to the diol **5** with aqueous HClO_4 in glyme. The $^1\text{H-NMR}$ spectrum of **5**

- 1 Acknowledgment. We thank Dr K. Noack for CD measurements and interpretations and Mr K. Harada for algal identification.
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