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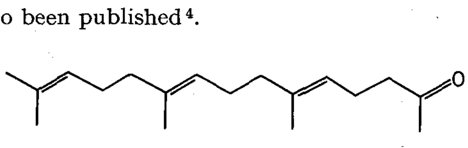
Summary. Farnesylacetone epoxide(**3**) and the isomeric diketone (**4**) have been isolated from the brown alga *Cystophora moniliformis*.

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 extract[3]. The isolation of **2** from marine sediments has also been published[4].



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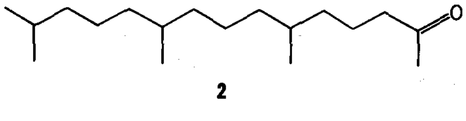

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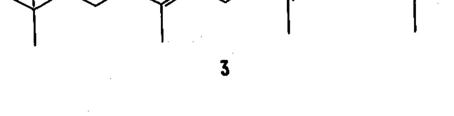

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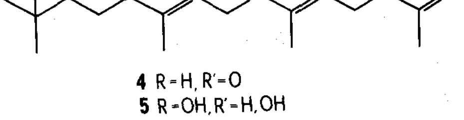

4 R=H, R'=O
5 R=OH, R'=H, OH

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 $C_{18}H_{30}O_2$ of **3**, isolated as an oil $[\alpha]_D$ −3.2°C (c = 1%, $CHCl_3$), was obtained by high resolution MS. The presence of a methyl ketone was established by IR (ν_{max} 1710 cm^{-1}), ^1H-NMR[5] (δ 2.00, 3H, s) and ^{13}C-NMR[5] (δ 208.0, s) and a trisubstituted epoxide grouping was inferred from the ^{13}C-NMR spectrum (δ 63.9, d; 58.0, s)[6]. The remainder of the ^1H-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 ^1H-NMR spectrum of **5**

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

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showed the secondary $\rangle CH$-OH proton at δ 3.30 (J = 12, 4Hz) and 2 sharp methyl singlets at δ 1.16 and 1.19. The absolute configuration of **5** was established by the method of Nakanishi[7]. The CD maxima after addition of Eu(Fod)3 were not well defined at room temperature. However there was a large increase in intensity upon cooling. The longest wavelength maximum at 313.8 nm was strongly negative, $\Delta\varepsilon$ –60.5 (0.74 g/l, –90°C) which established the configuration of **5** at C13 as R. The side chain of 24(R), 25-dihydroxycholesterol, an analogous situation, showed $\Delta\varepsilon$ –11 at 308 nm[8]. Thus the absolute configuration of **3** was R.

A racemic synthetic sample of **3** had slight JH activity[3]. A minor constituent, 6, 10, 14-trimethylpentadeca-5, 9-diene-2, 13-dione (**4**), was isolated as a chromatographically homogenous oil and the formula $C_{18}H_{30}O_2$ established by high resolution MS with major fragment ions at m/e 260 ($M^+ - H_2O$), 192, 125, 97, 71 ($(CH_3)_2$–CH–C≡O$^+$, and 43 (CH_3–C≡O$^+$, base peak). The presence of 2 ketone groups and 2 double bonds was established by ^{13}C-NMR which showed low field resonances at δ 214.3 (s), 208.6 (s), 136.1 (s), 133.8 (s), 124.5 (d) and 122.7 (d). The ^{1}H-NMR showed the presence of a methyl ketone (δ 2.08) and an isopropyl ketone [δ 1.02 (6H, d, J = 7Hz), 2.44 (1H, heptet, J = 7Hz] together with other resonances at δ 5.02 (2H, m), 2.5–1.9 (12H, m) and 1.56 (6H, bs) which was entirely consistent with the proposed structure **4**. When **3** was treated in benzene with strong mineral acids or boron triflouride etherate a complex mixture of cyclic alcohols was formed but no **4** could be detected in this mixture by TLC. It is therefore unlikely that **4** is an artefact by acid catalysed rearrangement of **3**.

The presence of such biologically active compounds in the brown alga *Cystophora moniliformis* is perhaps a chemical defence against predation and is probably analogous to the occurrence of many insect JH and moulting hormone active compounds in vascular plants.

Constituents of propolis

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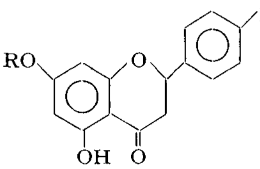
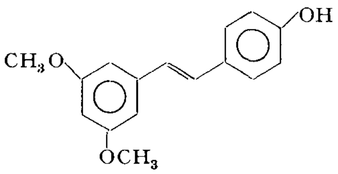
Summary. The major constituents of propolis collected in Western Australia have been isolated and identified as pterostilbene (**5**), xanthorrhoeol (**6**), sakuranetin (**2**) and pinostrobin (**1**).

In recent years there has been renewed interest in the composition of propolis, the resinous substance collected by bees from various plant sources. Bees use propolis for coating hive parts and the cell interiors of the honeycomb and also to seal cracks and crevices in the hive. Propolis has been used for a long time in folk medicine particularly for the cure of respiratory disorders[2], treatment of dermatoses and burns[3] and as a local anaesthetic[4]. Despite numerous reports[5] of the apparent pharmacological activity of extracts of propolis, a limited amount of work has been done on the isolation of the constituents. From samples of European propolis a number of simple aromatic compounds, flavones, flavonols and flavanones have been isolated[6–8]. We have investigated the chemical constituents of Western Australian propolis and the isolation and identification of the major components is the subject of this report.

Propolis[9] (300 g) was extracted with 70% aqueous ethanol and the fraction obtained was dissolved in ether and partitioned into 5% HCl, saturated $NaHCO_3$, 10% Na_2CO_3 and 5% NaOH solutions. The major part (90%) of the material extracted (40 g) was in the NaOH fraction and the remainder was divided almost equally between the other 4 fractions. Apart from the neutral fraction, which appeared to contain mostly fats and sterols, and the $NaHCO_3$ fraction, mostly flavones, all the other fractions were examined in detail. For the isolation and purification of the constituents of each fraction column, analytical and



	R	R¹
1	CH_3	H
2	CH_3	OH
3	H	OCH_3
4	CH_3	OCH_3



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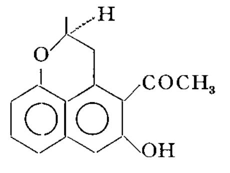

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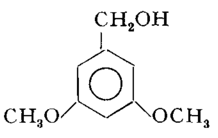

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[1] Acknowledgments. We gratefully acknowledge Dr H. Duewell of the University of Newcastle, New South Wales, for an authentic sample of xanthorrhoeol.

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