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A GERANYLACETONE DERIVATIVE FROM THE BROWN ALGA *CYSTOSEIRA CRINITA*

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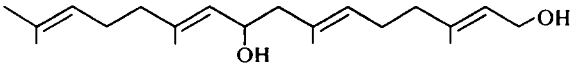
Key Word Index—*Cystoseira crinita*; Cystoseiraceae; terpenoids; 6,10-dimethyl-5,9-undecadien-2,8-dione.

Examination of the lipid components of the marine brown algae of the genus *Cystoseira* has resulted in the isolation of crinitol (**1**) and oxocrinol (**2**) from *C. crinita* [1], and eleganolone (**3**) from *C. elegans* [2]. A re-investigation of the components of *C. crinita* has now resulted in the isolation of the new terpenoid **4**, the structure of which is reported here.

Silica gel chromatography of the chloroform extract of the freeze-dried alga gave, upon elution with increasing concentrations of ether in hexane, fractions which emerged from the column immediately before sterols and contained **4**. Further purification by preparative TLC gave pure **4** (0.0001% dry wt of the alga) as an optically inactive oil, molecular formula $C_{13}H_{20}O_2$ (high resolution MS). The IR spectrum (neat liquid) contained bands at 1715 (ketone), and 1675 and 1615 cm^{-1} (α,β-unsaturated ketone). The UV spectrum showed a strong absorption at 239 nm (EtOH, ε = 10 500, conjugated enone). The ^{13}C NMR ($CDCl_3$, 20.1 MHz) confirmed the presence of 13 carbon atoms with two carbonyl carbons at δ 208.73 (C-2) and 199.38 (C-8), four olefinic carbons at 156.02 (*s*, C-10), 131.29 (*s*, C-6), 127.72 (*d*) and 123.22 (*d*) (C-5 and C-9), three methylene triplets at 55.26 (C-7), 43.48 (C-3), 22.71 (C-4) and four methyl quartets at 29.94 (C-1), 27.69 (C-13), 20.64 (C-11) and 16.64 (C-12). In the mass spectrum, the *m/e* 83 ion ($Me_2C{=}CHCO$) was the base and other intense fragment ions were observed at *m/e* 55 ($Me_2C{=}CH$) and 43 (MeCO). The ^{1}H NMR spectrum ($CDCl_3$, 80 MHz) contained signals at δ 1.62 (3 H, *s*, 3H-12), 1.87 (3 H, *s*, 3H-11), 2.14 (6 H, 3H-1 and 3H-13), 3.02 (2 H, *s*, 2H-7), 5.12 (1 H, *br. t*, *J* = 7 Hz, H-5), 6.08 (1 H, *s*, H-9) and a complex four-proton multiplet at 2.00–2.70. After addition of 0.41 molar equivalent of shift reagent Eu(fod)$_3$, this signal was resolved into a triplet at δ 7.08 (2 H, *t*, *J* = 7 Hz, 2H-3) and a quartet at 6.41 (2 H, *q*, *J* = 7 Hz, 2H-4); the assignments were confirmed by decoupling. The above data led unambiguously to structure **4** for the novel algal metabolite. The stereochemistry of the double bond at C-5 was assumed to be *E* from the chemical shift of the methyl group at C-6 (δ 1.62) [3]. This geranylacetone derivative is presumed to be a truncated diterpene formed from eleganolone (**3**), which co-occurs in the alga by oxidative cleavage of the C-6 double bond.



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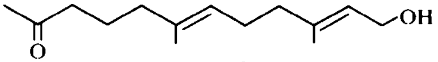

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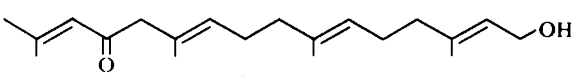

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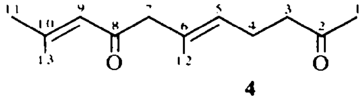

4

During this investigation we observed that eleganolone (**3**) when treated with base suffers a facile retro-aldol reaction with elimination of a six-carbon fragment to give oxocrinol (**2**). Therefore, the high yield of **2**, which now appears to be a minor component of *C. crinita*, from the unsaponifiable lipids of the alga [2] was possibly due to its formation from **3** in alkaline conditions. In every case, considerable quantitative and qualitative variations in the chemical components from the two successive collections of the alga are evident. In particular, the sample examined in the present study is characterized by a much lower concentration of crinitol and a high level of geranylgeraniol, which is, in fact, the main component and was not detected in the collection investigated previously.

EXPERIMENTAL

Isolation of constituents. The freeze-dried and ground alga (600 g) was extracted with $CHCl_3$ at room temp. The extract was concd *in vacuo* and the residue (48 g) chromatographed on a Si gel column (800 g). Elution with increasing concns of Et_2O in hexane yielded, in order, the following compounds: geranylgeraniol acetate, eleganolone acetate, oxocrinol acetate, geranylgeraniol, compound **4**, eleganolone and crinitol. When necessary, the isolated compounds were further purified by CC or TLC.

Geranylgeraniol acetate (550 mg), showed spectral data identical to the literature data [4].

Eleganolone acetate (1.38 g), identical to an authentic sample prepared from eleganolone by the standard procedure: IR $\nu_{max}^{neat\ liq}$ cm^{-1}: 1740, 1690, 1623, 1235; UV λ_{max}^{EtOH} nm: 242 (ε = 11 200). ^{1}H NMR (60 MHz, $CDCl_3$, TMS): δ 1.66 (6 H, *br. s*), 1.76 (3 H, *s*), 1.93 (3 H, *s*), 2.10 (3 H, *s*), 2.13 (3 H, *s*), 2.20 (8 H, *br. s*), 3.10 (2 H, *s*), 4.67 (2 H, *d*), 5.23, 5.34, 5.46 (1 H each, *t*), 6.23 (1 H, *br. s*).

Oxocrinol acetate (48 mg), identical in all respects to an authentic sample.

Geranylgeraniol (3.4 g), spectroscopic data identical to those reported in the literature [4].

6,10-Dimethyl-5,9-undecadien-2,8-dione (**4**) (65 mg), viscous oil, MS (high resolution) found 208.1468, calc. for $C_{13}H_{20}O_2$ 208.1463.

Eleganolone (2.97 g), showed spectral data identical to the literature data [4].

Crinitol (62 mg), was identical to an authentic sample.

Treatment of **3** *with base to produce* **2**. **3** (100 mg) was heated at reflux with 10% KOH (in EtOH H_2O, 4:1; 1 ml) for 1.5 hr. The soln was diluted with H_2O and extracted with Et_2O (3 ×). The extract was washed with H_2O, evapd and purified by TLC (hexane Et_2O, 1:1) to give oxocrinol (41 mg).

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A DITHIENYLACETYLENE FROM *POROPHYLLUM RUDERALE*[*]

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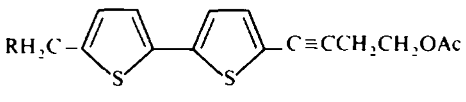
Key Word Index *Porophyllum ruderale*, Compositae; new dithienyl-acetylene diacetate.

In addition to compounds isolated previously [1], the dithienyl derivatives **1** and **2** were isolated from the aerial parts of *Porophyllum ruderale* (Jacq.) Cass. (tribe Tageteae, Compositae). While **1** is present in *Dyssodia setifolia* [2] belonging to the same tribe, **2** has not been described before. The structure is readily deduced from the spectral data. The broad UV maximum at 336 nm is identical with that of **1** and also the ^1H NMR data of **1** and **2** are very similar. In the spectrum of **2**, however, the methyl group in **1** must be replaced by CH_2OAc (5.21 *s(br)*). In the mass spectrum the elimination of AcOH and OAc can be observed. The latter is characteristic for compounds of this type. The isolation of **1** and **2** again supports the close morphological relationship of *Porophyllum* to *Dyssodia* and *Tagetes*.



1 R = H **2** R = OAc

EXPERIMENTAL

The air dried aerial parts (100 g) (collected in north-eastern Brazil, voucher RMK 8010) was extracted with Et_2O petrol. TLC (Et_2O petrol, 1:3) afforded 5 mg terthienyl, 3 mg but-1-en-3-inyldithienyl, 10 mg **1** and 5 mg **2**.

5'-Acetoxymethylen-2-[4-acetoxy-but-3-inyl]-dithiophene (**2**). Yellow gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1750, 1240 (OAc); MS: M^+ *m/e* (rel. int.) 348.049 (15) ($C_{17}H_{16}O_4S_2$); 288 (71) (M − AcOH); 229 (100) (288 − OAc). ^1H NMR ($CDCl_3$, 270 MHz): 7.04 *d* ($J = 3.5$); 7.02 *d* ($J = 3.5$); 6.98 *d* (2H, $J = 3.5$); 5.21 *s(br)* (2H), 4.25 *t* (2H, $J = 7$); 2.79 *t* (2H, $J = 7$); 2.10 *s* (3H); 2.10 *s* (3H).

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[*] Part 258 in the series "Polyacetylene Compounds"; for Part 257 see: Bohlmann, F., Abraham, W.-R., King, R. M. and Robinson, H. (1980) *Phytochemistry* (in press).