Phytochemistry, Vol. 20, No. 8, pp. 2034–2036, 1981.
Printed in Great Britain.

0031-9422/81/082034-03 $02.00/0

A EUDESMANOLIDE AND A GUAIANOLIDE FROM *CYATHOCLINE PURPUREA**

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(*Revised received* 26 *November* 1980)

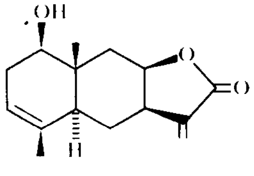
Key Word Index—*Cyathocline purpurea*; Compositae; sesquiterpene lactones; eudesmanolide; guaianolide.

Abstract—Two new sesquiterpene lactones, the eudesmanolide, isoivangustin, and the guaianolide, 6α-hydroxy-4(14),10(15)-guaianadien-8α,12-olide, have been isolated from *Cyathocline purpurea.*

So far one species only of the genus *Cyathocline* (Astereae) has been investigated chemically. However, the volatile compounds only were identified [1]. We have now isolated two new sesquiterpene lactones, the eudesmanolide, isoivangustin (**1**), and a guaianolide, 6α-hydroxy-4(14),10(15)-guaianadien-8α,12-olide (**3**) from *C. purpurea* Kuntze.

The ^{1}H NMR spectral data of **1** (Table 1) and its hydrogenation product clearly showed that we were dealing with a eudesmanolide, as the signals were very close to those of alantolactone [2], ivangustin [3] and a lactone which obviously was epimeric at C-8 only [4]. Furthermore, the ^{1}H NMR spectral data of the hydrogenation product **2** were similar to those of corresponding 1-desoxy compound [5]. The presence of a 1β-hydroxyl group was established by spin decoupling. A critical comparison of the ^{1}H NMR spectral data of **1** with those of ivangustin revealed that **1**, which has an olefinic bond at C-3, differed from the latter in the position of the double bond only and thus was a double bond isomer of ivangustin. The second lactone was isolated from the complex mixture as its acetate (**4**). The ^{1}H NMR spectral data (Table 1) of the latter showed that it was a guaianolide. Careful decoupling allowed the assignment of all signals, which were similar to those of chrysostomalide **5** [6], although some signals were typically different. Especially the coupling $J_{7,8}$ and $J_{8,9}$, as well as the chemical shifts of H-6 and H-9β which suggested the presence of a 8,12-*cis*-lactone ring system. The negative Cotton effect supported this assumption.

The isolation of these sesquiterpene lactones was interesting as, so far, compounds of this type have not been isolated from members of this tribe.



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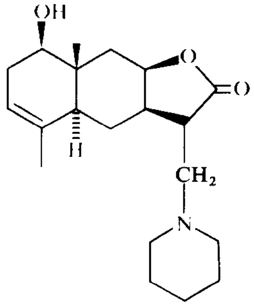

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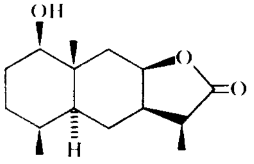

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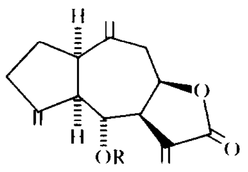

3 R = H
4 R = Ac
5 R = Ac, 8-epi

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*NCL communication No. 2667.

Table 1. ^{1}H NMR spectral data of **1**, **2** and **4** (270 MHz, $CDCl_3$, TMS as internal standard)

	1	**2** (C_6D_6)	Δ*	**4**
1-H	3.51 *dd*	2.91 *dd*	3.91	2.45 *dd* (*br*)
2α-H	1.95 *m*	1.0 *m*		1.70 *dddd*
2β-H	2.30			1.93 *dddd*
3α-H	5.35 *s* (*br*)	1.38 *m*	0.92	2.36 *m*
3β-H				
4-H	—			—
5-H	1.95 *m*			2.36 *m*
6α-H	1.33 *ddd*	0.82 *ddd*	1.01	5.19 *dd*
6β-H	1.95 *m*	1.20 *ddd*	2.74	
7-H	2.99 *ddddd*	1.57 *dddd*	1.15	3.07 *dddd*
8-H	4.59 *ddd*	3.87 *ddd*	1.51	4.48 *ddd*
9α-H	1.45 *dd*	0.92 *dd*	1.38	2.68 *dd* (*br*)
9β-H	2.59 *dd*	2.43 *dd*	3.90	3.23 *d* (*br*)
11-H	—	2.17 *dq*	2.05	—
13-H	6.16 *d*	1.06 *d*	1.39	6.24 *d*
13′-H	5.62 *d*			5.56 *d*
14-H	0.88 *s*	0.97 *s*	2.70	4.98 *s* (*br*)
14′-H				
15-H	1.69 *d*	0.70 *d*	0.79	5.02 *s* (*br*)
15′-H				4.80 *s* (*br*)
OAc	—	—	—	2.13 *s*
OH	1.40 *d*	—	—	—

*After addition of $Eu(fod)_3$.

J (Hz) **1**: 1,2α = 6; 1,2β = 10; 1,OH = 6; 2,2′ = 17; 5,6β = 12; 6α,7 = 6; 6β,7 = 12; 6α,6β = 14; 7,8 = 5; 7,13 = 1.5; 7,13′ = 1; 8,9β = 1.5; 9α,9β = 16; **2**: 1,2α = 5; 1,2β = 10; 4,15 = 7; 5,6α = 5; 5,6β = 12; 6α,6β = 13; 6α,7 = 2; 6β,7 = 12; 7,8 = 5; 7,11 = 7; 8,9α = 4.5; 8,9β = 2; 9α,9β = 15; **4**: 1,2α = 8; 1,2β = 1; 1,5 = 8; 2α,3α = 7; 2α,3β = 10; 2α,2β = 12; 2β,3α = 10; 2β,3β = 7; 5,6 = 10; 6,7 = 10; 7,8 = 9; 7,13 = 3.3; 7,13′ = 3; 8,9α = 4; 8,9β = 11.5; 9,14 = 1.5; 9α,9β = 16.

EXPERIMENTAL

The plant material, collected near Lonavala, Maharashtra, India, during 1978, was shade-dried, powdered and extracted with Me_2CO. 200 g of the Me_2CO extract (300 g) was fractionated over TLC Si gel (grade II activity). By repeated column chromatography two fractions containing sesquiterpene lactones were obtained. The less polar fraction, a complex mixture containing 6α-hydroxy-4(14),10(15)-guaianadien-8α,12-olide (**3**) was acetylated and **4** (1.7 g) isolated by prep. TLC.

6α-*Acetoxy*-4(14),10(15)-*guaianadien*-8α,12-*olide* (**4**). Colourless crystals, mp 128°. IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1770 (γ-lactone), 1740 (OAc); MS *m*/*z* (rel. int.): 288.136 (M^+, 4) 228 (M − HOAc, 100), 213 (228 − Me, 12), 200 (228 − CO, 18); CD (MeCN) $\Delta\varepsilon_{243}$ −0.52;

$$[\alpha]_{24^\circ}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,\text{nm}}{-120.6 \quad -128.0 \quad -145.2 \quad -254.1}$$

($CHCl_3$; $c = 0.17$).

Isoivangustin (**1**). From the more polar fraction a gum containing two sesquiterpene lactones was obtained which, when treated with piperidine and separated by prep. TLC, afforded **1a** as colourless crystals, mp 161–162°. IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3200 (OH), 1750 (lactone); ^{1}H NMR (90 MHz): δ 3.46 (1 H, *dd*, H-1), 1.95 (1 H, *m*, H-2α), 2.30 (H-2β), 5.26 (1 H, *s* (*br*), H-3), 1.95 (1 H, *m*, H-5), 1.21 (1 H, *dd*, H-6α), 1.95 (1 H, *m*, H-6), 2.91 (1 H, *dddd*, H-7), 4.48 (1 H, *ddd*, H-8), 1.45 (1 H, *dd*, H-9α). 2.59 (1 H, *dd*, H-9β), 1.63 (3 H, *s* (*br*), Me-4), 0.82 (3 H, *s*, Me-10), 2.4–2.6 (2 H, *m*, CH_2 of piperidine ring); MS *m*/*z* (rel. int.): 333 (M^+, 100) 248 (M − 85, 48) 230 (248 − H_2O, 12.5) 215 (248 − H_2O − Me, 10).

1 was regenerated from its piperidine adduct by the method of Jain *et al.* [7] to yield colourless crystals (0.018 %), mp 141°. IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3620 (OH), 1770 (γ-lactone); MS *m*/*z* (rel. int.): 248.141 (M^+, 68; $C_{15}H_{20}O_3$), 230 (M − H_2O, 21), 206 (M − CO_2, 20), 81 (100);

$$[\alpha]_{24^\circ}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,\text{nm}}{+120.8 \quad +125.4 \quad +143.1 \quad +255.4}$$

($CHCl_3$; $c = 0.26$).

Compound **2**. Isoivangustin (50 mg) was hydrogenated in the presence of PtO_2 (50 mg) and HOAc (30 ml) at room temp./atmosphere to give **2** as colourless crystals, mp 151°. IR $\nu_{max}^{CHCl_3}$cm^{-1}: 3620 (OH), 1775 (γ-lactone); MS *m*/*z* (rel. int.): 252.173 (M^+, 100), 234 (M − H_2O, 10), 219 (234 − Me, 8), 208 (M − CO_2, 18), 193 (208 − Me, 83).

Acknowledgement—We thank the Authorities of the Botanical Survey of India, Pune, for the identification of the plant.

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Phytochemistry, Vol. 20, No. 8, pp. 2036–2037, 1981.
Printed in Great Britain.

0031-9422/81/082036-02 $02.00/0

SEASONAL CHEMICAL EVOLUTION OF THE ALGA *CYSTOSEIRA ELEGANS*

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(*Received* 14 *November* 1980)

Key Word Index—*Cystoseira elegans*; Cystoseiraceae; Phaeophyceae; eleganolone; acyclic diterpenoids.

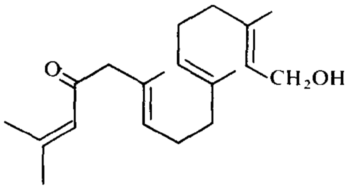
Abstract—Among the Mediterranean algae belonging to the family Cystoseiraceae analysed for diterpenic compounds, only *Cystoseira elegans* contains eleganolone, epoxy-eleganolone and elegandiol, as does the Atlantic alga *Bifurcaria bifurcata.* Surprisingly, for the seasonal *Cystoseira elegans*, these compounds are present only at the beginning of growth of the alga during Spring and they disappear in the Summer yielding important seasonal variation data for diterpenoids, and also for sterols, alginic acid, mannitol and cellulose.

INTRODUCTION

The brown alga *Cystoseira elgans* is a very typical plant of the Catalan Mediterranean coast near Banyuls sur Mer. In Autumn the alga is at rest, branches and leaves appearing at the beginning of Spring and disappearing in August. From April to July, we have observed a seasonal chemical variation of alginic acid, mannitol, cellulose and sterols, these compounds being analysed by previously described methods. The acyclic diterpenoids already identified from *Cystoseira elegans*, and from another Cystoseiraceae *Bifurcaria bifurcata* [1–3], eleganolone (**1**), the related epoxy-eleganolone (**2**) and elegandiol (**3**), are also analysed. An analytical method utilizing IR spectrometry and GLC has been developed for a rapid and easy identification of these compounds in extracts of algae.

RESULTS AND DISCUSSION

Cystoseira elegans is the only Mediterranean *Cystoseira* species analysed which was found to contain the diterpenoid compounds **1**, **2** and **3** (Table 1). These compounds were also present in *Bifurcaria bifurcata. B. bifurcata*, an Atlantic, perennial Cystoseiraceae, showed a seasonal variation of eleganolone (**1**) from January (1.5 % dry wt) to July (3 % dry wt). For *C. elegans*, which is a



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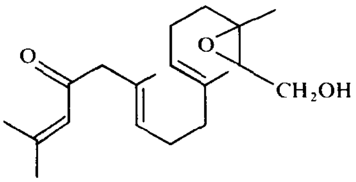

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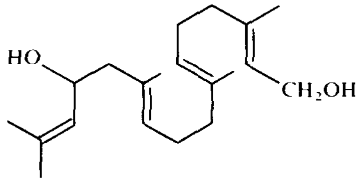

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