

A DITERPENE FROM *LAURENCIA OBTUSA*

M. D. HIGGS and D. JOHN FAULKNER

Scripps Institution of Oceanography, La Jolla, CA 92093, U.S.A.

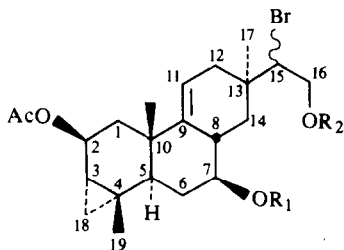
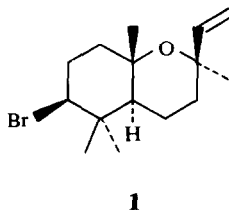
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Key Word Index—*Laurencia obtusa*; Rhodomelaceae; brominated diterpene; 15-Bromo-2,16-diacetoxy-7-hydroxy-9(11)-paraguarene.

Abstract—*Laurencia obtusa* collected at Kimmeridge Bay, Dorset contained 15-bromo-2,16-diacetoxy-7-hydroxy-9(11)-paraguarene as a major metabolite. Closely related compounds have recently been isolated from the sea hare *Aplysia dactylomela* collected at La Parguera, Puerto Rico.

INTRODUCTION

We have previously reported that 3 β -bromo-8-epicaparrapi oxide (1) was the major metabolite of *Laurencia obtusa* collected at Kimmeridge Bay, Dorset [1]. From the remaining metabolites, we isolated a diterpene diacetate to which we tentatively assigned the structure 2. Our interest in this compound was rekindled when Schmitz *et al.* [2] described a related diterpene monoacetate 3 from *Aplysia dactylomela* collected at La Parguera, Puerto Rico. We have subsequently confirmed the relationship between the two compounds by comparison of spectral data for samples of the triacetate 4.



2 $R_1 = H$ $R_2 = Ac$

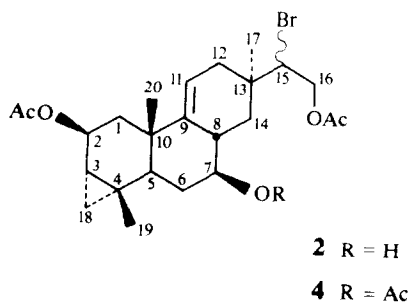
3 $R_1 = H$ $R_2 = H$

4 $R_1 = Ac$ $R_2 = Ac$

RESULTS AND DISCUSSION

The diacetate **2** had the molecular formula $C_{24}H_{35}BrO_5$. The IR spectrum contained bands at 3360 (hydroxyl) and 1725 cm^{-1} (acetate). The ^{13}C NMR spectrum contained two acetate carbonyl signals at δ 170.4 and 169.7 and two olefinic carbon signals at 144.1 (*s*) and 117.1 (*d*). The diacetate **2** was therefore tetracyclic. The signals at δ 17.2 (*s*), 21.8 (*t*) and 24.1 (*d*) indicated that one of the rings was a 1,1,2-trisubstituted cyclopropane. The 1H NMR spectrum (Table 1) contained signals at δ 0.03 and 0.67 (C-18) coupled to a signal at 0.80 (C-3) that was in turn coupled to an α -acetoxy proton signal at 5.31 (C-2). Since there were only three methyl signals at δ 1.05, 1.08 and 1.14, it seemed reasonable to propose that the cyclopropyl group had resulted from cyclization of a methyl group to a ring carbon in one of the more common tricyclic diterpene ring systems. The 1H NMR spectrum contained an isolated ABX system at δ 4.29 (*m*, 2H) and 4.58 (*m*, 1H). These signals could be assigned to either a 1-bromo-2-acetoxyethyl or 1-acetoxy-2-bromoethyl side chain attached at a fully substituted carbon atom. The ^{13}C NMR signals at δ 66.2 (*t*) and 60.3 (*d*) clearly required a primary acetate and secondary bromide; calculated values were $R-CHBr-CH_2OAc$, δ 67.7 (*t*), 59.1 (*d*); $R-CHOAc-CH_2Br$, 84.1 (*d*), 31.7 (*t*). The presence of the two carbon side-chain indicated that the carbon skeleton of the diterpene diacetate was probably based on either the pimarane or rosane skeletons. Cyclopropane formation between C-3 and C-18 of pimarane gave an appropriate skeleton for a complete and unambiguous assignment of the 1H NMR spectrum (see Table 1). The ^{13}C NMR spectrum was consistent with the structure proposed.

We recently learned that Schmitz *et al.* [2] had proposed the same carbon skeleton for a monoacetate **3** isolated from the sea hare *Aplysia dactylomela* collected at La Parguera, Puerto Rico. Comparison of spectral data showed that the triacetate **4** from the

Table 1. ^1H NMR data for diacetate **2** and triacetate **4**

H at C No.	2	Multiplicity	<i>J</i> (Hz)	4
1 α	1.23	<i>dd</i>	15, 5, 5	1.25
1 β	1.90	<i>dd</i>	15, 1	1.90
2	5.31	<i>br d</i>	5.5	5.31
3	0.80	<i>m</i>	10, 4, 1	0.80
5	1.09	<i>dd</i>	13, 4	1.14
6 α	2.14	<i>dt</i>	13, 4.5, 4	2.18
6 β	1.71	<i>dt</i>	13, 13, 11	1.70
7	3.17	<i>td</i>	11, 11, 4.5	4.40
8	2.35	<i>m</i>	11, 10, 6, 4, 2, 2	2.58
11	5.34	<i>dt</i>	4, 2, 2	5.38
12 α	1.81	<i>ddd</i>	15, 4, 2	1.82
12 β	2.44	<i>m</i>	15, 4, 2, 1	2.45
14 α	2.30	<i>dd</i>	13, 6	2.02
14 β	1.38	<i>br dd</i>	13, 10, 1	1.32
15	4.58	<i>m</i>	†	4.52
16	4.29	<i>m</i>	†	4.29
17	1.14*	<i>s</i>		1.15*
18 α	0.03	<i>dd</i>	6, 4	0.03
18 β	0.62	<i>dd</i>	10, 6	0.67
19	1.08*	<i>s</i>		1.05*
20	1.05*	<i>s</i>		1.03*
-OAc	2.08	<i>s</i>		2.07
-OAc	2.12	<i>s</i>		2.09
-OAc	—	<i>s</i>		2.13

*May be interchanged.

†Complex patterns—not first order.

diacetate **2** was identical in all respects with a sample prepared from monoacetate **3**. Schmitz has suggested the name parguerane for the 3,18-cyclopimarane carbon skeleton: the diacetate **2** is therefore 15-bromo-2,16-diacetoxy-7-hydroxy-9(11)-parguerane. Sea hares are known to consume large quantities of red algae [3] suggesting that the parguerols may have originated in a Puerto Rican *Laurencia* species, perhaps *L. obtusa*. Since there have been many previous studies of *L. obtusa* [4], it is surprising that diterpenes of this class have not been described previously.

EXPERIMENTAL

For general procedures, see ref. [5]. Additional NMR spectra were recorded at Shell Research Laboratories on a Bruker 360 MHz spectrometer.

Laurencia obtusa was collected from shallow water at Kimmeridge Bay, Dorset, during July 1975 and Sept. 1980. Both samples contained the same array of major metabolites. The air-dried alga (200 g) was powdered and Soxhlet-extracted with hexane (2 l.), CH_2Cl_2 (2 l.) and MeOH (2 l.). The combined hexane and CH_2Cl_2 solubles (3.11 g) were chromatographed on TLC grade Si gel using solvents of increasing polarity from hexane through Et_2O to EtOAc. The fractions eluted with hexane and 5% Et_2O in hexane contained predominantly 3 β -bromo-8-epicaparrapi oxide [1]. The fraction eluted with Et_2O was rechromatographed on a Lobar (310–325) Si gel column using Et_2O as eluant to obtain the diacetate **2** (165 mg, 0.08% dry wt): oil; $[\alpha]_{\text{D}} -48^\circ$ (MeOH; *c* 0.1); IR (neat) 3360, 1725 cm^{-1} ; ^1H NMR (CDCl_3): see Table 1; ^{13}C NMR (C_6D_6): δ 170.4 (*s*), 169.7 (*s*), 144.1 (*s*), 117.1 (*d*), 76.9 (*d*), 69.1 (*d*), 66.2 (*t*), 60.4 (*d*), 46.7 (*d*), 39.2 (*t*), 38.6 (*d*), 38.54 (*t*), 38.49 (*t*), 37.2 (*s*), 35.6 (*s*), 34.9

(*t*), 24.4 (*q*), 24.1 (*d*), 23.3 (*q*), 21.8 (*t*), 21.2 (*q*), 20.5 (*q*), 20.0 (*q*), 17.2 (*s*); mass spectrum m/z 464 ($M - H_2O$), 325, 265, 239; high-resolution mass measurement, observed m/z 464.1563, $C_{24}H_{33}^{79}BrO_4$ requires 464.1562.

Acetylation of diacetate 2. A soln of the diacetate **2** (10 mg, 0.021 mmol) in Ac_2O (0.56 ml) and pyridine (1.0 ml) was allowed to stand at room temp. overnight. The reagents were evapd under high vacuum and the residue dissolved in Et_2O and passed through a short plug of Si gel to obtain the triacetate **4** (11 mg, quantitative), having spectral data, particularly 1H NMR, identical with those of a sample prepared by Schmitz *et al.* [2] from the monoacetate **3**.

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PHLOROGLUCINOL DERIVATIVES FROM *LEUCANTHEMOPSIS PULVERULENTA*

J. DE PASCUAL-T., M. A. MORENO VALLE, M. S. GONZÁLEZ and I. S. BELLIDO

Department of Organic Chemistry, Salamanca University, Spain

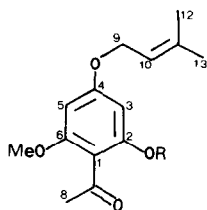
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Key Word Index—*Leucanthemopsis pulverulenta*; Compositae; roots; phloroglucinol derivatives.

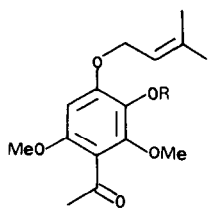
Abstract—From roots of *Leucanthemopsis pulverulenta*, two new phloroglucinol derivatives and (+) sesamin, have been isolated. The new compounds were identified as 1 - acetyl - 4 - isopentenyl - 6 - methylphloroglucinol and 1 - acetyl - 3 - hydroxy - 2,6 - dimethyl - 4 - isopentenylphloroglucinol.

Leucanthemopsis is a small genus, belonging to the Anthemideae tribe (Compositae) with only 6 species, most of them, widely distributed in Spain and Portugal. They have not as yet been examined for chemical constituents and we are now beginning their study with *Leucanthemopsis pulverulenta*, collected at the end of May, near Ledesma (Salamanca, W. Spain).

From the roots of *L. pulverulenta*, we have isolated (+)sesamin [1, 2] and two new phloroglucinol derivatives, **2** and **3**.



2 R=H
2a R=Ac



3 R=H
3a R=Ac

Compound **2**, shows a M^+ in the mass spectrum, at m/z 250, in agreement with the formula $C_{14}H_{18}O_4$. Its UV spectrum is characteristic of a polyhydroxy-acetophenone derivative (see Experimental). Acetylation of **2** yields the monoacetate **2a**. The bathochromic shift (20 nm) induced in the UV of **2**, by addition of $AlCl_3-HCl$ to the ethanolic solution, is indicative of an OH *ortho* to a COMe group [3]. The substituents were identified by 1H NMR, which showed the presence of a 1,2,4,6-tetrasubstituted aromatic ring, with -COMe, -OH, -OMe and *O*-isopentenyl groups as substituents (Table 1). The signal at 3.75 ppm for the -OMe group on C-6, so that the *O*-isopentenyl group must be on C-4 [4, 5].

Compound **3**, had a M^+ at m/z 280, in agreement with the formula $C_{15}H_{20}O_5$. Its UV spectrum was similar to that of **2**, but there was no induced shift on addition of $AlCl_3-HCl$, although the acetylation yields a monoacetate, **3a**. Thus, the free hydroxyl group is not at C-2 or C-6 [3]. The 1H NMR spectrum of **3** confirms the presence of a 1,2,3,4,6-pentasubstituted aromatic ring, with -COMe, -OH, -*O*-isopentenyl