Table 1. ^{1}H NMR shifts (δ) of **2**, **3** and **4** in pyridine-d_5

	Me-1	H-2	H-3	H-4	H-5	H-6	H-7α	H-7β	H-8	H-12	Me-12
Aduncin (2)	1.40 *s*	4.93 *d* $J = 3.5$	5.15 *d of d* $J_1 = 0.8$ $J_2 = 3.5$		2.89 *d of d* $J_1 = 0.8$ $J_2 = 5.6$	2.05–2.64	2.19 *d of d* $J_1 = 7.0$ $J_2 = 15$	2.50 *d of d* $J_1 = 3.2$ $J_2 = 15$	4.20 *d* $J = 3.2$	1.50–1.95	1.15 *d* $J = 6$ 1.21 *d* $J = 6$
α-dihydro-picrotoxinin (3)	1.53 *s*	4.88 *d* $J = 3.3$	5.10 *d of d* $J_1 = 3.3$ $J_2 = 5.0$	1.85–2.55	2.97 *d* $J = 4.5$		2.25 *d* $J = 15$	3.15 *d of d* $J_1 = 3.5$ $J_2 = 15$	4.06 *d* $J = 3.5$	1.85–2.55	0.99 *d* $J = 6$ 1.14 *d* $J = 6$
β-dihydro-picrotoxinin (4)	1.53 *s*	4.81 *d* $J = 3.6$	5.13 *d* $J = 3.6$	2.31 *d* $J = 8$	2.92 *s*		2.37 *d* $J = 15$	3.08 *d of d* $J_1 = 3.5$ $J_2 = 15$	4.09 *d* $J = 3.5$	1.45–1.90	0.90 *d* $J = 6$ 0.93 *d* $J = 6$

91(26), 81(10), 79(23), 77(21), 71(36), 69(13), 67(15), 65(17), 55(33), 53(15), 51(10), 44(61), 43(100). (Found: C 61.4; H 6.13; O 32.5. $C_{15}H_{18}O_6$ requires: C 61.2; H 6.16; O 32.6).

α-Dihydropicrotoxinin (**3**). Picrotoxinin was hydrogenated as described by Mercer and Robertson [8] giving **3**, mp 253–254°; $[\alpha]_{578}^{23}$ − 5° (*c* 0.5, Me_2CO). CD, nm ($\Delta\epsilon$): $\lambda_{extrema}$ (methanol) 228 (−3.7). IR: ν_{max} (KBr) 3540(*m*), 3470(*m*), 3050(*w*), 1797(*s*), 1775(*s*) cm^{-1}.

β-Dihydropicrotoxinin (**4**). Picrotoxinin was hydrogenated and the product isolated as described by O'Donnell *et al.* [9] giving **4**, mp 255–257°C; $[\alpha]_D^{23}$ − 24° (*c* 1.0, Me_2CO).

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3β-BROMO-8-EPICAPARRAPI OXIDE, THE MAJOR METABOLITE OF *LAURENCIA OBTUSA*

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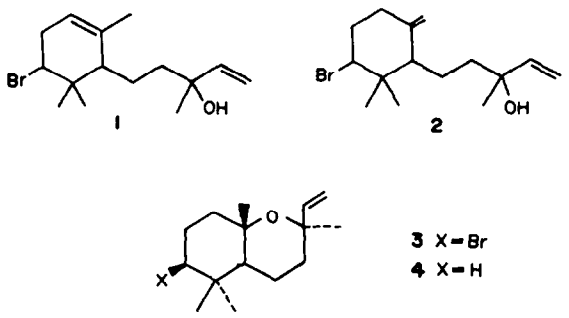
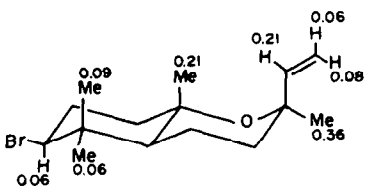
Key Word Index—*Laurencia obtusa*; Rhodomelaceae; brominated sesquiterpene; 3β-bromo-8-epicaparrapi oxide.

Investigations of marine red algae of the genus *Laurencia* (Rhodomelaceae, Rhodophyceae) have resulted in the structural elucidation of many interesting halogenated metabolites [1]. Some recent studies on *Laurencia* metabolites have focused on the possible biosynthetic relationship between the more common halogenated chamigrene derivatives and brominated monocyclofarnesol derivatives [2, 3]. Howard and Fenical [2] have described the structural elucidations of α-snyderol (**1**) and β-snyderol (**2**). α-Snyderol (**1**) was obtained from a sample of *L. obtusa* which was collected in Tossa de Mar, Spain. I wish to report the isolation and identification of 3β-bromo-8-epicaparrapi oxide (**3**), which was the major lipid-soluble metabolite of *L. obtusa* (Huds.) Lamouroux collected from the English Channel.

* The major portion of this research was performed at the University Chemical Laboratory, Cambridge University, Lensfield Road, Cambridge.



Laurencia obtusa was collected at Kimmeridge, Dorset in July 1975. Florisil chromatography of hexane extracts of the air-dried alga gave 3β-bromo-8-epicaparrapi oxide (**3**) as the major metabolite (0.28% of dry weight). 3β-Bromo-8-epicaparrapi oxide, $[\alpha]_D^{21}$ + 30.4° (c = 1.46), was obtained as an oil, which slowly solidified at −20°. The molecular formula, $C_{15}H_{25}OBr$, was inferred from high resolution mass measurements of the (M^+ − Me) doublet since the molecular ion doublet observed at low resolution was not sufficiently intense to allow accurate mass measurement. The IR spectrum contained bands indicative of olefinic (1640 cm^{-1}) and ether (1100, 1080 cm^{-1}) functionality. The NMR spectrum contained four methyl singlets at δ 0.83, 1.06, 1.12 and 1.24, a double doublet at 3.97 (J = 11,5 Hz) due to an α-bromo proton, and three double doublets at 4.94 (J = 11,2 Hz), 4.98 (J = 18,2 Hz) and 5.99 (J = 11,18 Hz) due to an isolated vinyl group. The chemical shift and coupling constants of the α-bromo proton indicate that the bromine atom is located in a cyclohexane ring adjacent to a fully substituted carbon atom. These data indicated that the unknown molecule, an isomer of the snyderols, was a brominated caparrapi oxide. In order to define the stereochemistry of the molecule and confirm the position of the bromine atom, the Eu(fod)$_3$-induced shifts for eight signals in the proton NMR spectrum were measured. The best fit between observed and calculated [4] europium-induced shifts was obtained for 3β-bromo-8-epicaparrapi oxide (**3**).



Scheme 2. Observed Eu(fod)$_3$-induced shifts for 3β-bromo-8-epicaparrapi oxide (**3**)

Reduction of 3β-bromo-8-epicaparrapi oxide (**3**) with $LiAlH_4$ in refluxing dioxan gave a 90% yield of 8-epicaparrapi oxide (**4**), $[\alpha]_D^{21}$ + 43° (c = 1.08), having spectral data identical to those reported by Cookson and Lombardi [5].

It is interesting that *L. obtusa* from two locations should have closely related but different major metabolites. Since both studies were based on single collections, this difference cannot be rationalised. In addition to 3β-bromo-8-epicaparrapi oxide (**3**), *L. obtusa* also contains diterpene and acetylenic components.

EXPERIMENTAL

Laurencia obtusa was collected from shallow water (0–2 ft) at Kimmeridge Bay, Dorset on 12 July, 1975. Powdered air-dried alga (500 g) was Soxhlet extracted with hexane. The concentrated extract was chromatographed on florisil (300 g). Five fractions eluted with C_6H_6 were combined to give 3β-bromo-8-epicaparrapi oxide (1.4 g, 0.28% of dry material) in >95% purity. The impurities were removed by rechromatography on thick layer Si gel plates.

3β-Bromo-8-epicaparrapi oxide (**3**). This was obtained as an oil which solidified at −20°C; $[\alpha]_D^{21}$ + 30.4 (c = 1.46, EtOH); IR (film) 1640, 1100, 1080 cm^{-1}; PMR (CCl_4) δ 0.83, 1.06, 1.12, 1.24 (*s*, 3, Me each), 3.97 (*dd*, 1, J 11,5 Hz), 4.94 (*dd*, 1, J 11,2 Hz), 4.98 (*dd*, 1, J 18,2 Hz), 5.99 (*dd*, 1, J 11,18 Hz); MS *m/e* 302, 300 (M^+), 287, 285 (M^+ − Me): *m/e* 287.0835 ($C_{14}H_{22}O^{81}Br$ requires 287.0834).

8-Epicaparrapi oxide (**4**). A soln of 3β-bromo-8-epicaparrapi oxide (220 mg, 0.73 mmol) in dry dioxan (5 ml) was added to $LiAlH_4$ (100 mg) in dry dioxan (45 ml). The stirred mixture was heated under reflux for 18 hr. 0.1 N NaOH was added to the cooled soln until evolution of H_2 no longer occurred. Aluminium salts were removed by filtration and solvent evaporated to yield 8-epicaparrapi oxide (**4**) as an oil; $[\alpha]_D^{21}$ + 43.0° (c = 1.08, EtOH); IR (film) 1640, 1105, 1050 cm^{-1}; PMR ($CDCl_3$) δ 0.73, 0.90, 1.15, 1.23 (*s*, 3, Me each), 4.91 (*dd*, 1, J 11,2 Hz), 4.97 (*dd*, 1, J 18,2 Hz), 6.02 (*dd*, 1, J 18,11 Hz); MS *m/e* 222 (M^+), 207 (M^+ − Me); *m/e* 207.1746 ($C_{14}H_{23}O$ requires 207.1748). The IR and PMR spectra were identical to those of (±) 8-epicaparrapi oxide obtained by Lombardi and Cookson [5] and were appreciably different from the other three possible isomers [6].

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