

SESQUITERPENES FROM LAURENCIA SPP.

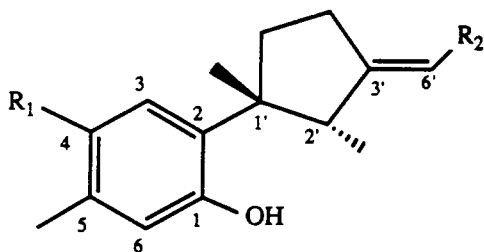
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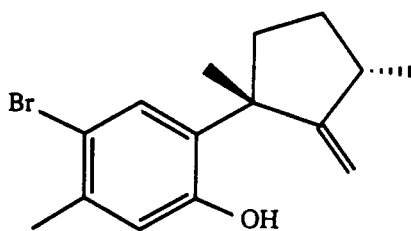
Laurencia (Rhodophyta) is a common genus on southern Australian coasts and includes numerous species which are widespread in this region (1). Most species are clearly defined, but *Laurencia filiformis* (C. Agardh) Montagne includes three main forms, which have been named *filiformis*, *heteroclada*, and *dendritica*, with intergrades between them, and intergrades from it to the related species *Laurencia arbuscula* Sonder and *Laurencia tasmanica* Hooker and Harvey (1). Previous work on two collections of *L. filiformis* f. *heteroclada* has shown that one contained sesquiterpenes based on the laurene skeleton, whereas the other, in addition, contained heterocladol, a halogenated selinane sesquiterpene (2,3). From *L. filiformis* f. *filiformis* we have isolated the snyderanes, aplysiastatin, and 6 β -hydroxyaplysiastatin (4). These results contrast with a report of the occurrence of prepacifenol, a chamigrene ses-

quiterpene, from an unspecified form of *L. filiformis* (5). Because of the ecological importance of this genus, we have examined the constituents of four samples of *L. filiformis* f. *heteroclada* collected at different points along the Western Australian coast. In addition we have identified the major metabolites from *Laurencia majuscula* (Harvey) Lucas occurring in Western Australia. This species is widely distributed in tropical, subtropical, and temperate Pacific and Indian Oceans (1).

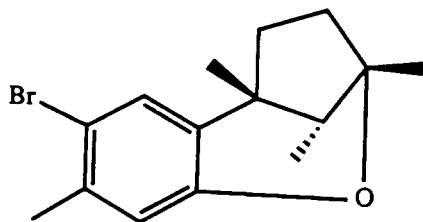
Samples of *L. filiformis* f. *heteroclada* were collected at four sites, Hamelin Bay, Shoalwater Bay (ca. 50 km south of Perth), Cottesloe Beach (Perth), and Lancelin. In each case the alga was found to elaborate laurene sesquiterpenes as the major metabolites. Whereas the sample from Hamelin Bay contained only allolaurinterol [1], those from Lancelin and Cottesloe Beach in addition produc-



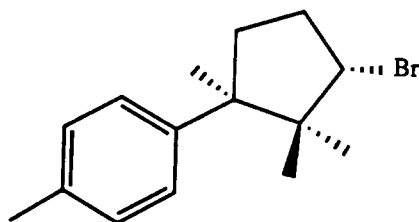
	R ₁	R ₂
1	Br	H
2	H	Br
3	Br	Br



4



5



6

ed laurenisol [2] and bromolaurenisol [3], respectively. In contrast, the Shoalwater Bay sample yielded 2, 3, isolaurinterol [4], filiformin [5], and (-)- α -bromocuparene [6]. Bromolaurenisol [3], which has been described as unstable (6), was transformed to its more stable acetate and characterized (see Experimental). Isolaurinterol [4], which is also unstable unless kept at 0° and free from solvents, was completely characterized for the first time (see Experimental). A minor component 6 isolated from the Shoalwater Bay collection showed spectral characteristics identical with those reported (7) for α -bromocuparene previously isolated from *Laurencia glandulifera*, but differed in the sign for the optical rotation, $[\alpha]_D -23.7^\circ$ (cf. α -bromocuparene, $[\alpha]_D +23^\circ$).

These results taken together with those reported previously (2-4) suggest that the forma *heteroclada*, in terms of the laurene sesquiterpene metabolites it produces, is clearly distinct from the forma *filiformis*. It seems likely that the third forma of the *L. filiformis* complex, f. *dendritica*, is also distinct, and it is this forma which produces prepacifenol, a chamigrene sesquiterpene (5). In this context it is interesting to note that *L. tasmanica*, which can be regarded as an extreme form of the *L. filiformis* complex bordering f. *dendritica*, has been shown to produce pacifenol (5). It seems probable that the *L. filiformis* samples reported to contain laurenisol [2] and (-)- α -bromocuparene [6] by Erickson (8, p. 160 and p. 155, respectively) belong to f. *heteroclada*.

In contrast to the *L. filiformis* "complex," *L. majuscula* is a distinctive species widely distributed along the southern Australian coast including Tasmania (1). *L. majuscula*, collected from Woodmans Point (ca. 320 km south of Perth), was found to elaborate the known chamigrene sesquiterpenes obtusane, obtusol, elatol, and isoobtusol (8). Although these compounds have been isolated from various *Laurencia*

species, they have not been reported before from *L. majuscula* and differ from the chamigrenes present in the Mediterranean (9) and Japanese varieties (10,11).

EXPERIMENTAL

General experimental procedures have been described previously (12).

COLLECTION, EXTRACTION, AND ISOLATION.—Samples of *L. filiformis* f. *heteroclada* were collected at Hamelin Bay, Shoalwater Bay (ca. 50 km south of Perth), Cottesloe Beach (Perth), and Lancelin. Voucher specimens have been deposited with the Botany Department, The University of Western Australia. Samples of the alga were extracted with CH_2Cl_2 -MeOH (1:1). The CH_2Cl_2 -soluble extract was adsorbed on a column of silicic acid and eluted with a petroleum ether/ CH_2Cl_2 gradient. The compounds isolated (yields as % of dry wt) from samples of *L. filiformis* f. *heteroclada* include laurenisol [2] (0.3%) and allolaurinterol [1] (0.4%) (Lancelin); 1 (1.1%) and bromolaurenisol [3] (0.01%) (Cottesloe); 1 (0.9%) (Hamelin Bay); and isolaurinterol [4] (0.6%), filiformin [5] (0.01%), 3 (0.01%), 2 (0.01%), and (-)- α -bromocuparene [6] (0.02%) (Shoalwater Bay).

The sample of *L. majuscula* was collected at a depth of 0.5-1.0 m off the rocks at Woodman's Point (30 km south of Perth). A voucher specimen has been deposited (No. A52710) with the Department of Botany, Adelaide University. A sample of *L. majuscula* was extracted, and the CH_2Cl_2 solubles (13.6 g from 109 g dry wt, 12.5%) adsorbed on a column of alumina (activity III, neutral). Elution with petroleum ether afforded obtusane (26 mg, 0.02%). Preparative hplc [μ -porasil, hexane- CH_2Cl_2 (1:1)] of the fraction eluted with petroleum ether- CH_2Cl_2 (1:1) yielded obtusol (1.3 g, 1.2%), elatol (0.77 g, 0.7%), and isoobtusol (5 mg, 0.05%).

IDENTIFICATION OF THE METABOLITES.—*Laurenisol* [2].—Characterized as its acetate, mp 102-103°, $[\alpha]_D +85^\circ$ ($c=0.1$, CHCl_3) [lit. (13) mp 102.5-103°, $[\alpha]_D +85^\circ$], with $^1\text{H-nmr}$ characteristics as reported (13).

Allolaurinterol [1].—A clear oil with $^1\text{H-nmr}$ and ms characteristics as reported (2). Characterized as its acetate which recrystallized from MeOH as needles, mp 82-84.5°, $[\alpha]_D +46^\circ$ ($c=0.4$, CHCl_3) [lit. (2) mp 86.6-89.1°, $[\alpha]_D +48.2^\circ$]. Found C 60.71, H 6.72, $\text{C}_{17}\text{H}_{21}\text{O}_2\text{Br}$ requires C 60.54, H 6.28; $^1\text{H-nmr}$ and ms characteristics as reported (2).

Bromolaurenisol [3].—Characterized as its acetate, a clear oil, $[\alpha]_D +43^\circ$ ($c=0.5$, CHCl_3). Found (ms) 413.979, $\text{C}_{17}\text{H}_{20}^{79}\text{Br}_2\text{O}_2$ requires

$[M]^+$ 413.983; 1H nmr ($CDCl_3$, 80 MHz) δ 0.72 (d, $J = 7.0$ Hz, $2'-CH_3$), 1.13 (s, $1'-CH_3$), 2.35, 2.32 (2s, $5-CH_3$ and $OCOCH_3$), 2.88 (q, $J = 7.0$ Hz, $H-2'$), 6.07 (bs, $H-6'$), 6.95 (s, $H-6$), 7.38 (s, $H-3$); ir ν max (CCl_4) 3080, 1770, 1650, 1480, 1455, 1435, and 1370 cm^{-1} ; uv λ max (EtOH) 275 (ϵ 1000), 279 nm (1100); eims m/z (rel. int.) 414, 416, 418 $[M]^+$ (11), 372, 374, 376 (20), 335, 337 (41), 292, 293, 294, 295 (49), 214 (100), 201 (29), 199 (43).

Isolaurinterol [4] (14).—A clear oil, bp 144° (bath)/1.3 mm, $[\alpha]_D -82^\circ$ ($c = 1.5$, $CHCl_3$) Found C 61.31, H 6.51, $C_{15}H_{19}BrO$ requires C 61.03, H 6.49; 1H nmr ($CDCl_3$, 90 MHz) 1.20 (d, $J = 7.0$ Hz, $3'-CH_3$), 1.46 (s, $1'-CH_3$), 2.30 (s, $5-CH_3$), 2.83 (q, $J = 7.0$ Hz, $H-3'$), 4.94, 5.10 (2d, $J = 2.5$ Hz, $2'-CH_2$), 5.57 (s, OH), 6.72 (s, $H-6$), 7.45 (s, $H-3$); ir ν max (film) 3460, 3080, 1648, 1615, 1170, 908, 878 cm^{-1} ; uv λ max (EtOH) 287 nm (ϵ 2300); eims m/z (rel. int.) 294, 296 $[M]^+$ (75), 279, 281 (100), 265, 267 (8), 251, 253 (10), 237, 239 (30), 226, 228 (12), 201 (13), 200 (43), 199 (10), 159 (32), 145 (12).

Filiformin [5].—Recrystallized from hexane as prisms, mp 86–87°, $[\alpha]_D -19.5^\circ$ ($c = 0.6$, $CHCl_3$) [lit. (2) mp 86.4–87.3°, $[\alpha]_D -20^\circ$] with 1H -nmr characteristics as reported (2).

(-)- α -*Bromocuparene* [6].—An oil, $[\alpha]_D -23.7^\circ$ ($c = 0.2$, $CHCl_3$) [lit. (7) $[\alpha]_D +23^\circ$], which appeared homogeneous by glc and had 1H -nmr and ir spectra identical with those of authentic (+)- α -bromocuparene.

Obtusane.—A crystalline solid, mp 163–167°, $[\alpha]_D +27^\circ$ ($c = 0.1$, $CHCl_3$) [lit. (15) mp 174–175°, $[\alpha]_D +38^\circ$] with 1H -nmr, ir, and ms characteristics as reported (15).

Obtusol.—Recrystallized from MeOH/ H_2O as white needles, mp 145–146°, $[\alpha]_D +12^\circ$ ($c = 0.2$, $CHCl_3$) [lit. (16) mp 145–146°, $[\alpha]_D +10^\circ$] with 1H -nmr, ir, and ms characteristics as reported (17).

Elatol.—A clear oil, bp 180° (bath)/0.4 mm, $[\alpha]_D +110^\circ$ ($c = 1.2$, $CHCl_3$) [lit. (18) $[\alpha]_D +83.5^\circ$] with 1H -nmr characteristics as reported (19). Ir ν max (CCl_4) 3590, 3100 cm^{-1} ; eims m/z (rel. int.) 237, 235 $[M - Br - H_2O]^+$ (61), 209, 207 (22), 199 (22), 91 (61), 85 (100). Elatol formed a crystalline acetate, recrystallized from hexane as clear prisms, 155–157° [lit. (19) mp 157–158°].

Isoobtusol.—A semi-crystalline oil with 1H -nmr and ms characteristics as reported (17).

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