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A PHENOL FROM THE BROWN ALGA *PERITHALIA CAUDATA*

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Key Word Index—*Peritholia caudata*, Phaeophyta, Sporochnaceae, phenol, 2,4-bis(3-methylbut-2-enyl)phenol

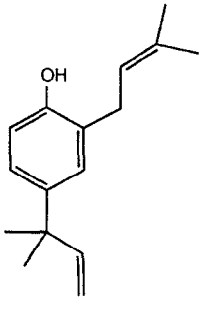
Abstract—The diprenylated phenol 2,4-bis(3-methylbut-2-enyl)phenol as well as the previously described isomeric 4-(1,1-dimethylprop-2-enyl)-2-(3-methylbut-2-enyl)phenol have been isolated from the brown alga *Peritholia caudata*. The relative proportions of these two phenols varies considerably between individual plants.

INTRODUCTION

In an earlier paper we reported that the main secondary metabolite from *Peritholia caudata* (Lab.), a brown seaweed (order Sporochnales) which is common around the coast of southern Australia, was 4-(1,1-dimethylprop-2-enyl)-2-(3-methylbut-2-enyl)phenol (**1**), a diprenylphenol containing a 'reverse' isoprene unit at the 4-position as well as a 'normal' unit at the 2-position [1] The phenol was isolated from a combined collection of the alga A number of plants had been collected, combined and processed to give an oil (1 8% dry weight) consisting of a mixture of **1** (90%) and a second component (9%), which at the time could not be separated This second component has now been obtained pure and identified as 2,4-bis(3-methylbut-2-enyl)phenol (**2**)

RESULTS AND DISCUSSION

Analysis of individual plants, collected at the same location as those in the previous study, has now revealed that there is a considerable variation in the distribution of compounds **1** and **2** in *Peritholia caudata*. Five plants were freeze-dried and powdered Representative samples of each were analysed by GC-MS; relative amounts of **1** and **2**, based on total ion chromatogram measurements, varied from 7.3 . 1 to 0 37 : 1 No other isomeric phenols were detected. The plant extract richest in the second component was subjected to preparative gas chromatography allowing **2** to be obtained in a pure state The molecular formula of **2** was established as $C_{16}H_{22}O$ by high resolution mass spectroscopy, showing that **2** was isomeric with **1**. The low field region of the ^1H NMR spectrum of **2** was quite similar to that of **1**; the three aromatic protons formed an ABX system revealing that **2** was also a 2,4-disubstituted phenol Differences in the rest of the spectrum indicated that the substituents were two nonequivalent 3-methylbut-2-enyl groups, so both of the isoprene units were attached in the normal manner rather than one of them being reversed as in **1** This is the first report of **2** as a natural product although it has previously been synthesized [2, 3]



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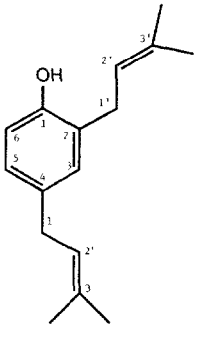

2

The co-occurrence of **1** and **2** is of interest as is the variability of these compounds in individual plants. The plants analysed were collected at the same location and time; they were all of similar appearance and occurred in the same habitat Intraspecific variability of seaweed secondary metabolites has been previously reported but in only a few cases have individual plants been analysed Secondary metabolites are frequently obtained from combined collections of plants and when differences have been found they have usually been from geographically distinct collections Seaweeds of the family Plocamiaceae and from the genus *Laurencia* (both Rhodophyta) have been most extensively investigated and many examples of geographical variation observed [4, 5]. In one of the few cases where individuals have been analysed, *Plocamium cartilagineum* plants from the same location on the USA west coast gave three different chemical patterns [6]. More recently, individual plants of *P. cartilagineum* collected over a 50 mile region of the eastern coast of Australia showed no difference in composition of metabolites although a few samples contained no metabolites [7]. The factors responsible for the variability of phenol composition in *P. caudata* are unknown

EXPERIMENTAL

Peruthalia caudata was collected at Ninepin Point, D'Entrecasteaux Channel, Tasmania (43° 16 7′ S, 147° 10′ E) at a depth of 2 m in Oct 1986 A voucher specimen (HO 100792) has been lodged at the Tasmanian Herbarium, Hobart

Analysis of individual plants Individual plants were collected, freeze-dried, milled and the resulting powder thoroughly mixed. A representative sample (0 5 g) was extracted with CH_2Cl_2 (3 × 1 ml) and the extract analysed by GC-MS on a methylsilicone-fused silica column using methods described in ref [8].

Extraction and isolation. Freeze-dried plant material (100 g) was milled and extracted at room temp with CH_2Cl_2 The extract was concd under red pres and partly purified by silica gel CC using CH_2Cl_2 The fraction containing the phenols was further purified by prep TLC (silica gel using CH_2Cl_2–heptane, 1 · 1) to give a mixture of **1** and **2** as a colourless oil (1 46 g, 45% of **1** and 55% of **2** by GC, this represents 0 66 and 0 80% dry weight of the alga, respectively) A small portion of this oil was purified by prep. GC. A 2 m × 0.25 cm od 3% OV-1 Chromosorb column was used isothermally at 190°. The carrier gas was N_2 at a flow rate of *ca* 30 ml/min. The GC column effluent was split with a ratio of *ca* 50 1 Fractions were collected using a temp gradient fraction collector in thin walled glass capillary tubes.

2,4-Bis(3-methylbut-2-enyl)phenol (**2**). Colourless oil High resolution EIMS found 230 1675, $C_{16}H_{22}O$ requires 230 1670 Low resolution EIMS and IR spectra were in agreement with published data [2, 3]. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.71 (3H, *s*, 3′ or 3″-Me), 1.74 (3H, *d*, J = 1 0 Hz, 3′ or 3″-Me), 1 77 (3H, *d*, J = 1.2 Hz, 3′ or 3″-Me), 1 78 (3H, *s*, 3′ or 3″-Me), 3 24 (2H, *d*, J = 7.6 Hz, H-1′ or H-1″), 3 32 (2H, *d*, J = 7.1 Hz, H-1′ or H-1″), 4.91 (1H, *s*, OH), 5.30 (2H, *m*, H-2′ and H-2″), 6 71 (1H, *d*, J = 8.5 Hz, H-6), 6 89–6 92 (2H, *m*, H-3 and H-5).

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