(*s*), 112.3 (*t*), 115.0 (*d*), 119.8 (*d*), 127.7 (*s*), 144.9 (*s*), 147.6 (*s*), 149.6 (*s*).

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HALOGENATED PHLOROGLUCINOLS FROM *RHABDONIA VERTICILLATA*

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Key Word Index—*Rhabdonia verticillata*; Rhabdoniaceae; halogenated phenols; bromo- and chlorophloroglucinols.

Abstract—Six bromo- and/or chloro- derivatives of phloroglucinol have been obtained from the red alga *Rhabdonia verticillata*.

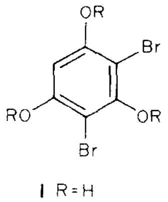
INTRODUCTION

A variety of bromophenols have been isolated from marine organisms, particularly Rhodophyta (red seaweeds) [1, 2]. These compounds have been found to occur primarily in the Rhodomelaceae (Ceramiales). We now report, for the first time, the presence of previously unknown halophenols in a member of the Rhabdoniaceae (Gigartinales).

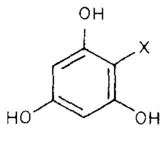
RESULTS AND DISCUSSION

The major compound (0.2%, dry wt) obtained from *Rhabdonia verticillata* was 2,4-dibromo-1,3,5-trihydroxybenzene (dibromophloroglucinol), **1**. Its identity was established by spectroscopic analysis and conversion into 1,3,5-trimethoxybenzene, **3**, via **2** and confirmed by comparison of **1**, **2** and **3** with synthetic materials. Dibromophloroglucinol has not been previously isolated as such from natural sources although the corresponding trimethyl ether, **2**, has been obtained after treatment of the ethanolic extract of *Rytiphlea tinctoria* (Rhodomelaceae) with diazomethane [3].

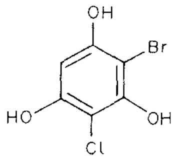
Since *Rhabdonia verticillata* contained smaller amounts of other halogenated phenols which could not be separated from **1** by Si gel chromatography, the crude extract was subjected to GC/MS after forming trimethylsilyl and trimethoxy derivatives. The following halogenated phloroglucinols, in order



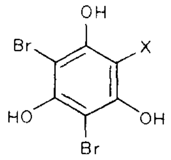
1 R=H
2 R=Me



4 X=Cl
5 X=Br



6



7 X Cl
8 X=Br

of increasing retention time, were found (yields, based on dry wt, are given in parentheses after each compound): 2 - chloro - 1,3,5 - trihydroxybenzene, **4**, (trace); 2 - bromo - 1,3,5 - trihydroxybenzene, **5**, (0.012%); 2 - bromo - 4 - chloro - 1,3,5 - trihydroxybenzene, **6**, (0.005%); 2,4 - dibromo - 1,3,5 - trihydroxybenzene, **1**, (0.214%); 2,4 - dibromo - 6 - chloro - 1,3,5 - trihydroxybenzene, **7**, (trace) and 2,4,6 - tribromo - 1,3,5 - trihydroxybenzene, **8**, (0.004%). The mass spectra of these compounds were identical except for differences due to halogenation. That they were all phloroglucinol derivatives follows from the identification of the major compound and from the absent of any $[M-88]^+$ fragmentation in the mass spectra of the TMSi derivatives which is characteristic of vicinal dihydroxybenzenes[4].

Some algal bromophenols are known to be artifacts resulting from hydrolysis of sulphate esters during the isolation procedure[5]. Application of the method designed to allow isolation of these sulphate esters[5] to *Rhabdonia verticillata* failed to reveal their presence.

The halophenols found in *Rhabdonia verticillata* are probably derived biosynthetically from shikimic acid[1]. This is in contrast to *Plocamium* species (Plocamiaceae), also belonging to the Gigartinales, which are known to elaborate halogenated terpenes[1].

EXPERIMENTAL

Air-dried and powdered *Rhabdonia verticillata* Harvey (4.5 kg), voucher specimen Tasmanian Herbarium No. HO 45370, collected near Smooth Island, Dunalley, Tasmania, was percolated with MeOH. This extract was concd *in vacuo* at 30° to 500 ml and then portioned between petrol–MeOH–H_2O (6:3:1). Extraction of the MeOH phase with Et_2O gave a quantitative separation of crude phenolic material (18.2 g) which was subjected to dry Si gel CC. Elution with petrol–EtOAc of gradually increasing polarity gave **1** (7.3 g), colourless crystals, mp 140–142° (toluene)[6]. (M^+ found 281.8522; $C_6H_4Br_2O_3$ requires 281.8528.) IR $\nu_{\max}^{\mathrm{KBr}}$ cm^{-1}: 3460, 1600, 1490, 1450. ^{1}H NMR (100 MHz, Me_2CO-d_6) $\delta \sim 9$ (3H, *br s*, exch. ArOH), 6.45 (1H, *s*, ArH). EIMS (probe) 70 eV, *m/z* (rel. int.) 282 M^+ (100), 264 (6), 253 (2), 174 (8).

Trimethyl ether. On treatment with CH_2N_2, **1** gave 2,4-dibromo-1,3,5 - trimethoxybenzene, **2**, mp 132°[7]. M^+ at *m/z* 324. This structure was confirmed by spectral and chromatographic comparison with synthetic material.

Debromination. Reaction of **2** with $LiAlH_4$ gave 1,3,5 - trimethoxybenzene mp 48°[8], which was identical with synthetic material.

GC/MS analysis. Powdered, air-dried plant material was extracted with 80% MeOH for 4 hr under reflux. After extraction with EtOAc, TMSi derivatives were prepared[9] and analysed by GC/MS using a 2 m, 4 mm i.d., silanized glass column packed with 3% S.E. – 30 on Chromosorb *Q*. The carrier gas was He at a flow rate of 25 ml/min. Injector and detector temps. were maintained at 250° and 175° respectively. Temp. program 120° to 250° at 6°/min. GC/MS, 70 eV. R_t, *m/z* (rel. int.): 2 - chloro - 1,3,5 - trimethylsiloxybenzene, 10.2 min, 376 (100), 361 (217), 341 (5); 2 - bromo - 1,3,5 - trimethylsiloxybenzene, 11.1 min, 420 (100), 405 (48), 340 (8); 2 - bromo - 4 - chloro - 1,3,5 - trimethylsiloxybenzene, 13.5 min, 454 (100), 439 (37), 419 (8), 375 (6); 2,4 - dibromo - 1,3,5 - trimethylsiloxybenzene, 14.7 min, 498 (100), 483 (50), 404 (32); 2,4 - dibromo - 6 - chloro - 1,3,5 - trimethylsiloxybenzene, 15.4 min, 532 (100), 517 (37); 2,4,6 - tribromo - 1,3,5 - trimethylsiloxybenzene, 16.1 min, 576 (100), 561 (41), 497 (2).

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