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CHEMISTRY OF SPONGES, XII. ¹A NEW DIHYDRIC PHENOL FROM THE SPONGE *FASCIOSPONGIA* SP.

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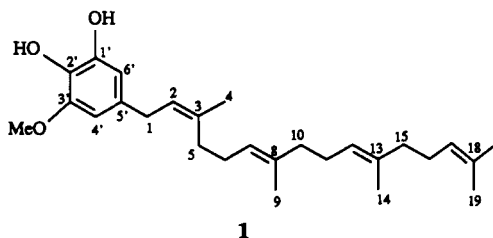
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ABSTRACT.—The new 3-methoxydihydric phenol **1** was isolated from the marine sponge *Fasciospongia* sp.

In a continuation of our investigation of sponges of the order Dictyoceratida we have investigated the metabolites of *Fasciospongia* sp., collected from New Caledonia. Chromatography of the CH₂Cl₂ extract of the freeze-dried sponge afforded the dihydric phenol **1**. Compound **1** was assigned a molecular

dihydric phenol bearing a hydrocarbon chain at C-5. This was indicated by the signals at δ 6.30 and 6.21, which are mutually coupled ($J = 2.7$ Hz), and by correlations observed in the COSY spectrum. The signal at δ 6.30 exhibited long range coupling to the signal due to the methoxyl group [δ 3.83 (s, 3H)]. The



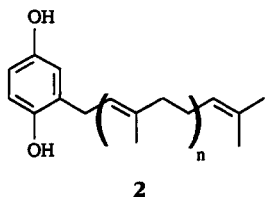
formula C₂₇H₄₀O₃ from its hrms, which showed a molecular ion at m/z 412.3011. The ¹H- and ¹³C-nmr spectra indicated the presence of a 1,2-dihydric phenol as well as a methoxyl group, four trisubstituted double bonds, and five vinyl methyl groups. The ir absorptions at 3400, 1660, and 1605 cm⁻¹ were consistent with the presence of a catechol group and of isolated double bonds. A two-dimensional ¹³C-, ¹H-nmr chemical shift correlation experiment (1) and a ¹H-¹H-COSY spectrum enabled the assignment of most of the protonated carbons. The ¹H-nmr spectrum and COSY correlations suggested a 3-methoxy-1,2-

signals at δ 6.21 and 6.30, which appeared as broad doublets, each had long range coupling to a signal due to a benzylic methylene [δ 3.30 (d, $J = 7$ Hz)] that was, in turn, coupled to signals due to an olefinic proton [δ 5.28 (br t, $J = 7$ Hz, 1H)] and a vinyl methyl group [δ 1.68 (br s, 3H)]. The remainder of the ¹H- and ¹³C-nmr spectra of **1** suggested a linear diterpene chain terminating in an isopropylidene group which required the structure shown. The configuration of the double bonds in **1** was established on the basis of the chemical shifts of the vinyl methyl groups in the ¹³C-nmr spectrum: δ 25.7 (C-4), 23.4 (C-20), 17.7 (C-19), 16.1 (C-9 or C-14), 16.0 (C-14 or C-9). Thus, the configuration of the C-2 double bond was assigned as *Z* from the relatively low field signal for C-4 (2-4), which corresponded well with

*For Part XI, see M. Kernan, R. C. Cambie, and P. R. Bergquist, *J. Nat. Prod.*, **54**, 265 (1991).

those recorded for *cis*-methyl groups in related compounds (5–7). The upfield shifts of the remaining two vinyl methyl groups, other than those of the isopropylidene group, allow assignment of an *E* configuration to the double bonds at C-7 and C-12 (8).

Polyprenylquinols of the general formula **2** have been reported from two species of the sponge genus *Ircinia* (Order Dictyoceratida, Family Spongiidae) (9, 10). Although **2** ($n = 1$) has not been isolated from sponges, some linear diprenylquinones have been reported from a tunicate of the genus *Apolidium* (7). The hydroquinone **1** had a weak antimicrobial activity and inhibited the growth of *Staphylococcus aureus* and *Bacillus subtilis* at 100 $\mu\text{g}/\text{ml}$. A diterpene containing a β -substituted furan group was also isolated from the sponge *Fasciospongia* sp., but the compound decomposed before it could be identified.



EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—Experimental procedures were as described in Part IX (11).

SPONGE.—The genus *Fasciospongia*, which is diagnosed within the Thorectidae by having a fasciculate skeleton and lacking collagenous matrix filaments as in the allied genera *Ircinia* and *Sarcotragus* (12), is predominantly temperate Australian in distribution. Multiple tubular, globular, and fan-shaped or massive growth forms are found among the Australian species. The present species is by far the largest known, growing to a meter high and 14 cm in diameter in the form of a thick-walled tube traversed by a long vestibule. This growth form is unique within *Fasciospongia*, and this report extends the range of the genus to New Caledonia for the first time. The sponge was collected from New Caledonia in 1989, and a voucher specimen (AUZ-NC-15) has been deposited

in the reference collection, Zoology Department, University of Auckland.

ISOLATION OF NATURAL PRODUCTS.—Freeze-dried *Fasciospongia* sp. (27.2 g dry wt) was extracted with CH_2Cl_2 . The crude CH_2Cl_2 extract was purified by cc on Si gel (0–100% EtOAc/hexane) to give the hydroquinone **1** (230 mg, 0.85%) and an unidentified diterpene (123 mg).

HYDROQUINONE [1].—The compound was obtained as an oil: found $[\text{M}]^+$ 412.3011, $\text{C}_{27}\text{H}_{40}\text{O}_3$ requires $[\text{M}]^+$ 412.2977; ir ν max (film) 3400 (br, OH), 1660 (C=C), 1605 cm^{-1} (C=C); ^1H nmr (CDCl_3) δ 6.30 (br d, $J = 2.7$ Hz, H-6'), 6.21 (br d, $J = 2.7$ Hz, H-4'), 5.28 (br t, $J = 7$ Hz, H-2), 5.28 (s, OH), 5.11 (m, H-7, -12, -17), 4.71 (s, OH), 3.83 (s, 3'-OMe), 3.30 (d, $J = 7$ Hz, H-1), 2.10 (q, $J = 6$ Hz, H-5), 2.05 (m, 6H), 1.98 (m, 4H), 1.69 (br s, 3H), 1.68 (br s, Me-4), 1.58 (br s, 9H); ^{13}C nmr (CDCl_3) δ 148.5 (s, C-1', C-2'), 146.7 (s, C-3'), 137.1 (s), 136.6 (s), 135.0 (s), 131.3 (s), 127.7 (s, C-5'), 124.4 (d), 124.1 (d, 2C), 121.7 (d, C-2), 107.4 (d, C-4'), 97.2 (d, C-6'), 56.0 (q, OMe), 39.7 (t, C-6, C-11, C-16), 27.8 (t, C-1), 26.7 (t, C-10, 15), 26.6 (t, C-5), 25.7 (q, C-4), 23.4 (q, C-20), 17.7 (q, C-19), 16.1 (q, C-9 or C-14), 16.0 (q, C-17 or C-9); ms m/z 412 (20% base peak), 191 (15), 153 (30), 69 (100), 41 (80).

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