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ISOLATION OF 2-(3,7,11-TRIMETHYL-2,6,10-DODECATRIENYL)HYDROQUINONE FROM THE BROWN SEAWEED *DICTYOPTERIS UNDULATA*

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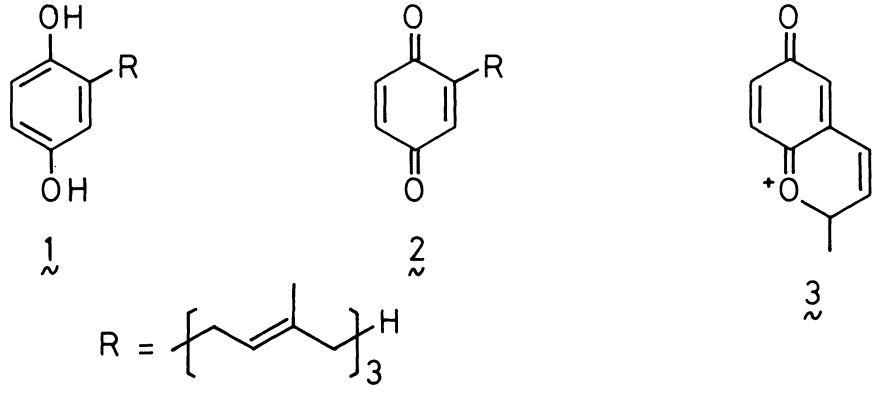
2-(3,7,11-Trimethyl-2,6,10-dodecatrienyl)hydroquinone, a new substance of biogenetic interest, has been isolated from the brown seaweed *D. undulata*. Antimicrobial activity has been tested.

Recent studies on the constituents of the brown seaweed *D. undulata* have resulted in the isolation of several sesquiterpene-substituted phenols.[1] On the other hand, 2-(3,7,11-trimethyl-2,6,10-dodecatrienyl)hydroquinone (1), which is a possible precursor of these phenols, has been the missing member of a series of linear polyprenyl-benzoquinols isolated from the marine organisms.[2] In our continuing search for the antimicrobial components of *D. undulata*, we have isolated this missing one. This compound was found to have a moderate antimicrobial activity against some fungi.[3]

Compound (1) was isolated in 0.015% yield from a methanol extract of the fresh alga by careful silica gel column chromatography as a colorless viscous oil. The structure 1 is assigned for this compound on the basis of the following spectral and chemical evidence.



The molecular formula of (1) ($C_{21}H_{30}O_2$) was established by high resolution mass spectrum (M^+ 314.2232, Calcd 314.2244). The IR spectrum (neat) of (1) shows absorptions at 3320, 1607, 1505, 1195 (Ar-OH), and 1655 (C=C) cm^{-1}. Its ^1H NMR spectrum ($CDCl_3$) exhibits signals due to four vinylic methyl groups at δ 1.61 (6H, s), 1.70 (3H, s), and 1.77 (3H, s), one benzyl methylene group at δ 3.32 (2H, d,

J = 7 Hz), three olefinic protons at δ 5.13 (2H, m) and 5.32 (1H, br t, J = 7 Hz), and three aromatic protons centered at δ 6.61 (3H, m). In the mass spectrum, the fragmentation pattern [ions at m/e 314 (M^+), 245 ($M^+ - C_5H_9$), 191 ($M^+ - C_7H_7O_2$), 177 ($M^+ - C_{10}H_{17}$), 123 ($C_7H_7O_2^+$, dihydroxytropylium ion), and 69 ($C_5H_9^+$, base peak)] points to the presence of a monosubstituted dihydroxybenzene ring and a triprenyl chain.[4] The air-oxidation of (1) yielded a benzoquinone (2) [orange oil, $C_{21}H_{28}O_2$ (M^+ 312), IR (neat) 1655 and 1600 cm^{-1}, UV (EtOH) 248, 310, and 440 nm (ε 16100, 795, and 55), ^1H NMR ($CDCl_3$) δ 6.56 (1H, br s) and 6.75 (2H, br s)] which regenerated (1) by the reduction with $LiAlH_4$. The mass spectrum of (2) displays a prominent peak due to the ion (3) at m/e 161 which reveals the presence of a monosubstituted 1,4-benzoquinone in (2).[4] The chemical shifts of the methyl groups of (1) and (2) [(1): δ 1.61 (x2), 1.70, and 1.77; (2): δ 1.61 (x2), 1.66, and 1.70] indicate that the configuration of the double bonds in the triprenyl chains are trans-trans.[4,5] The ^{13}C NMR data of both compounds are consistent with the assigned structures.[6]

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3) For example, some minimum inhibitory concentrations of (1) determined by dilution method are as follows: *Saccharomyces cerevisiae* (25 μg/ml), *Sclerotinia libertiana* (25 μg/ml), *Aspergillus oryzae* (12.5 μg/ml), and *Aspergillus niger* (12.5 μg/ml).

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6) The ^{13}C NMR data ($CDCl_3$) of (1) and (2) are as follows. (1): δ 149.4 (s), 148.2 (s), 138.7 (s), 135.6 (s), 131.5 (s), 128.5 (s), 124.5 (d), 123.8 (d), 121.4 (d), 116.7 (x2, d), 113.8 (d), 39.8 (x2, t), 29.8 (t), 26.8 (t), 26.5 (t), 25.8 (q), 17.8 (q), 16.4 (q), and 16.2 (q). (2): δ 187.9 (s), 187.6 (s), 148.6 (s), 140.3 (s), 136.8 (d), 136.4 (d), 135.5 (s), 132.4 (d), 131.3 (s), 124.4 (d), 123.8 (d), 117.8 (d), 39.7 (x2, t), 27.5 (t), 26.8 (t), 26.5 (t), 25.8 (q), 17.8 (q), 16.3 (q), and 16.1 (q). The assignments will be discussed in full paper.

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