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# New Plastoquinones from the Brown Alga Sargassum sagamianum var. yezoense

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The structures of sargahydroquinoic acid and yezoquinolide, new plastoquinones isolated from the brown alga Sargassum sagamianum var. yezoense, were elucidated by chemical and spectral methods.

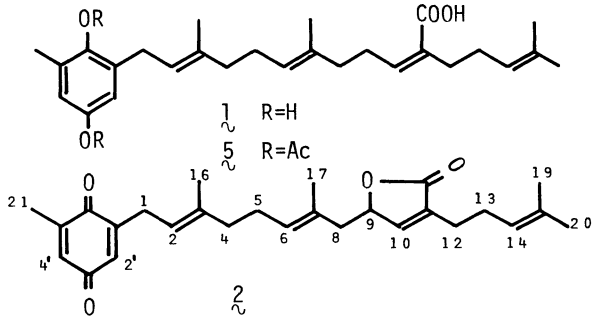
Brown algae of the family Sargassaceae are known to contain unique plastoquinones,[1] chromenols,[2] and bioactive metabolites.[3] We focused our attention on the title alga which is indigenous to Hokkaido.

Two new plastoquinones, designated as sargahydroquinoic acid (1) (0.6% of the ether extracts) and as yezoquinolide (2) (0.5%), were isolated along with two known metabolites, sargaquinoic acid (3)[1] (86%) and sargaquinal (4)[1] (3.9%), from the ethanol extracts of the fresh alga collected in July 1984, at Oshoro Bay.

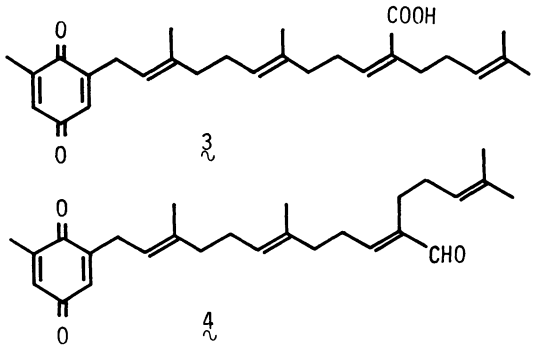
Sargahydroquinoic acid (1), colorless oil, which was smoothly oxidized to 3 by air on standing, showed the following spectral data; IR(film) 3400-2500, 1685, 1630, and 1610 $cm^{-1}$: $^1H$ NMR ($\delta$, $CDCl_3$) 6.46 (2H, br s), 5.98 (1H, t, J=7 Hz), 5.26 (1H, t, J=7 Hz), 5.09 (2H, m), 3.27 (2H, d, J=7 Hz), 2.58 (2H, q, J=7 Hz), 2.17 (3H, br s), 2.3-1.9 (12H, m), 1.74 and 1.66 (each 3H, br s), and 1.58 (6H, br s). Comparison of the spectra of 1 with those of 3 seemed to indicate 1 to be hydroquinone derivative of 3. The structure of 1 was confirmed by direct comparison of its acetate 5[4] with the product of reductive acetylation of 3.

Yezoquinolide (2), pale yellow oil, $[\alpha]_D^{24}$ -23.5° (c 0.52, $CHCl_3$), Found: m/z 422.2455, Calcd for $C_{27}H_{34}O_4$: M, 422.2458, UV $\lambda_{max}$(EtOH) 252 nm ($\varepsilon$ 17000), showed the presence of an $\alpha,\beta$-unsaturated $\gamma$-lactone moiety in its IR spectrum [1760 $cm^{-1}$], and the presence of five methyl groups in its $^1H$ NMR spectrum [1.69 (6H, br s, Me-17 and 20), 1.63 (3H, br s, Me-16), 1.60 (3H, br s, Me-19), and 2.06 (3H, d, J=1.5 Hz, quinone Me)], six methylene groups [2.09 (2H, t, J=6 Hz, H-4), 2.16 (2H, q, J=6 Hz, H-5), 2.23 (2H, q, J=6 Hz, H-13), 2.30 (1H, dd, J=14 and 7 Hz, H-8), 2.31 (2H, tt, J=6 and 1.5 Hz, H-12), 2.37 (1H, dd, J=14 and 7 Hz, H-8), and 3.13 (2H, dd, J=6 and 2 Hz, H-1)], three olefinic protons [5.08 (1H, t sept, J=6 and 1 Hz, H-14), 5.16 (1H, tq, J=6 and 1 Hz, H-2), and 5.23 (1H, tq, J=6 and 1 Hz, H-6)], two quinone protons [6.45 (1H, dt, J=3 and 2 Hz, H-2') and 6.54 (1H, dq, J=3 and 1.5 Hz, H-4')], an olefinic $\beta$ proton of lactone [6.99 (1H, q, J=1.5 Hz, H-10)], and a $\gamma$ proton of lactone [4.97 (1H, tq, J=1.5 Hz, H-9)]. J value of the two quinone protons suggested the meta orientation of the methyl group to the $C_{20}$-side chain. The 2D NMR COSY spectrum and the $^1H$ spin decoupling experiments revealed

the presence of three partial structures, methylquinone-C(3)-C(16), C(4)-C(7)-C(17), and C(8)-C(20). The long range couplings of those two pairs of protons, (H-4, Me-16) and (H-8, Me-17), were observed respectively by the $^1$H spin decoupling experiments, though J values were too small to measure. Both two bonds at C(3)-C(4) and at C(7)-C(8) were supported by the NOEs observed between two pairs of protons, (H-5, Me-16) and (H-9, Me-17). The NOEs observed with respect to those two pairs of protons, (H-1, Me-16) and (H-5, Me-17), revealed that both two double bonds at C(2)-C(3) and at C(6)-C(7) were E-configurations. Therefore, the structure of yezoquinolide is represented by formula 2. Yezoquinolide is the first isolated plastoquinone with butenolide moiety. Biological activity of those metabolites is now under investigation.




2

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4) For 5: colorless oil, Found: m/z 510.2986, Calcd for $C_{31}H_{42}O_6$: M, 510.2983, UV: end absorption, IR(film) 3400-2500, 1765, 1685, 1630, and 1210 cm$^{-1}$, $^1$H NMR (δ, $CDCl_3$) 6.78 (2H, br s), 5.95 (1H, t, J=7 Hz), 5.2-4.9 (3H, m), 3.18 (2H, d, J=7 Hz), 2.56 (2H, q, J=7 Hz), 2.30 and 2.25 (each 3H, s), 2.06 (3H, br s), 2.3-1.9 (10H, m), 1.66 and 1.58 (each 6H, br s).

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