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STRUCTURES OF NEW PLASTOQUINONES FROM THE BROWN ALGA SARGASSUM SERRATIFOLIUM

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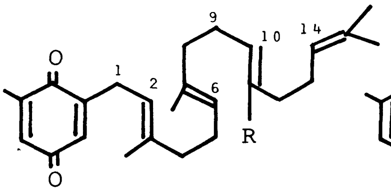
The structures of sargaquinoic acid and sargaquinal, new plastoquinones isolated from the brown alga Sargassum serratifolium, were elucidated as 1a and 2.

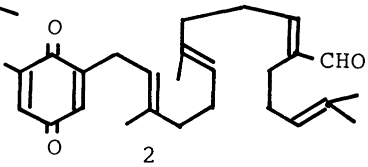
In the course of our investigations on the constituents of algae, we found that methanolic extraction of the fresh brown alga Sargassum serratifolium, followed by chromatographic separation of the extract afforded three new compounds, sargaquinoic acid (1a), sargaquinal (2), and sargachromenol (4).

Sargaquinoic acid (1), oil, $C_{27}H_{36}O_4$, shows the following spectral properties: λ_{max}^{EtOH} 251 nm (ε 14500); NMR($CDCl_3$,δ): 6.56 (1H,dq,J=2 and 0.5 Hz), 6.46 (1H,dt,J=2 and 0.5 Hz), 6.02 (1H,t,J=6 Hz,10-H), 5.16 (3H,m,2-,6-,14-H's), 3.14 (2H,br.d,J=7 Hz, 1-H), 2.62 (2H,q,J=7 Hz,9-H), 2.04 (3H,br.s,quinone Me),1.68(3H,br.s,3-Me), 1.63, 1.61, 1.59 (each 3H,br.s,7-,15-,15-Me's); IR($CHCl_3$): 3400-2500, 1680, 1650, 1610 cm^{-1}. The ^{13}C-NMR ($CDCl_3$) data of sargaquinoic acid showed the presence of five methyls (δ 15.9, 16.0, 16.1, 17.7, 25.7), seven methylenes (26.4, 27.6, 27.9, 28.2, 34.6, 39.1, 39.6) and six trisubstituted olefines (singlets at 130.7, 132.2, 134.6, 139.8, 145.9, 148.5 and doublets at 118.1, 123.5, 124.6, 132.3, 133.2, 145.6), together with benzoquinone carbonyls (188.0) and a carboxyl carbon (173.5). The coupling constant (2 Hz) of the two quinone protons in ^1H-NMR suggested the meta orientation of the methyl group and the C_{20}-side chain. The E-configurations of of the double bonds at C_2-C_3, C_6-C_7, and C_{14}-C_{15} were determined by the chemical shifts of the four vinyl methyls,[1)] and that at C_{10}-C_{11} by comparison of the chemical shifts of the olefinic proton at C_{10} and C_9-methylene protons with those reported[2)] for E- and Z-2-methyl-2-pentenoic acids. The mass spectrum of 1 showed the base peak at m/e 175 due to the fragment (A), typical of such compounds as plastoquinones and ubiquinones.[3a)] The fragments (B) and (C) settled the position of the carboxyl group at C-11.

Sargaquinal (2), oil, $C_{27}H_{36}O_3$, λ_{max}^{EtOH} 250 nm(ε 15000),IR($CHCl_3$):1675,1650 cm^{-1} exhibited similar NMR spectrum to that of 1a. From the molecular formula and a sharp singlet at δ 9.36 in the NMR spectrum, sargaquinal was considered to have an aldehyde function instead of the carboxyl group of 1a. Hence, conversion of 1a into sargaquinal was attempted. Treatment of 1a with zinc-acetic anhydride yielded



1a; R=CO_2H, 1b; R=CH_2OH, 1c; R=CHO



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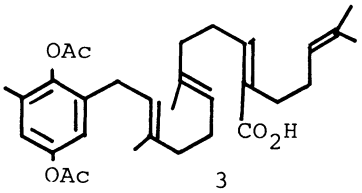

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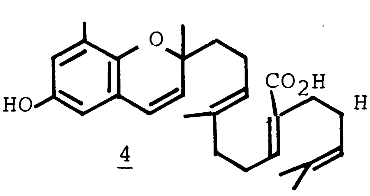

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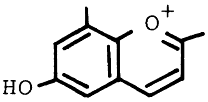
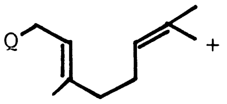
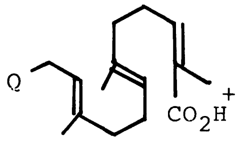


[A] m/e 175.076



[B] m/e 257.154



[C] m/e 355.186

Q = 2-methyl-2,5-cyclohexadiene-1,4-dion-6-yl

diacetate (3), which was reduced with excess lithium aluminum hydride. The resulting hydroquinone was smoothly oxidized by air on standing to afford 1b, primary hydroxyl group of which was oxidized with chromium oxide-pyridine hydrochloride complex. The mass spectrum of the derived aldehyde (1c) was identical with that of sargaquinal (2), but the IR and NMR spectra were different from those of 2; in the NMR spectrum of 1c, the aldehyde and C-9 methylene protons appeared at δ 10.06 and 2.65, respectively, while the corresponding aldehyde and methylene protons of sargaquinal (2) were observed at δ 9.36 and 2.45. These facts indicated that the configurations of the double bonds at C-10 of 1c and 2 are Z and E, respectively.$^{2)}$

Sargachromenol (4), oil, $C_{27}H_{36}O_4$, gives the following data: λ_{max}^{MeOH} 263 (ε4900) and 332 nm (ε 2770); IR($CHCl_3$): 3600, 3500-2500, 1680, 1590 cm^{-1}; NMR(C_6D_6,δ): 6.35 (1H,d,J=2 Hz), 6.25 (1H,d, J=2 Hz), 6.11 (1H,d,J=10 Hz), 5.90 (1H,t,J=7 Hz), 5.31 (1H,d,J=10 Hz), 5.20 (2H,br.t,J=6 Hz), 2.68 (2H,q,J=7 Hz), 2.15 (3H,s), 1.68 (3H,s), 1.56 (6H,s), 1.30 (3H,s). Although sargachromenol (4) has an asymmetric center, it shows no optical activity. When a dilute alcoholic solution of sargaquinoic acid (1a) was allowed to stand at room temperature for one week, 1a was quantitatively converted into sargachromenol. Sargachromenol (4) must therefore be an artifact which was formed during the extraction process with methanol.$^{3b)}$

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