

actinomycin D,<sup>26</sup> and oxytocin.<sup>27</sup> Only in the case of *cyclo*-(Pro-Gly)<sub>3</sub> in methylene chloride do these rules fail to agree with previous conclusions, and this failure

(26) D. J. Patel, *et al.*, unpublished results.

(27) A. I. R. Brewster, V. J. Hruby, A. F. Spatola, and F. A. Bovey, *Biochemistry*, **12**, 1643 (1973).

may be due to an unusual dihedral angle  $\psi$ .<sup>24</sup> We believe this application of <sup>13</sup>C nmr spectroscopy will find great importance in future studies of oligo- and polypeptides.

**Registry No.**—*N*-Formylpyrrolidine, 3760-54-1; *N*-acetylpyrrolidine, 4030-18-6.

## Zonarol and Isozonarol, Fungitoxic Hydroquinones from the Brown Seaweed *Dictyopteris zonarioides*<sup>1</sup>

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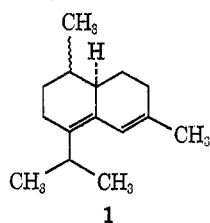
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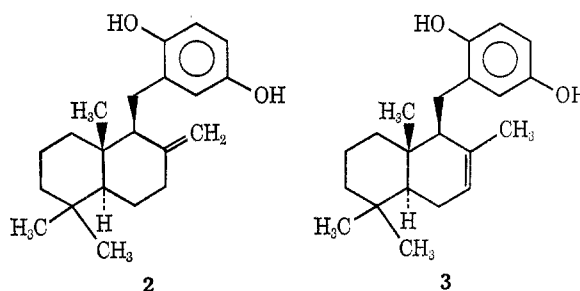
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Zonarol and isozonarol, isomeric C<sub>21</sub> hydroquinones, have been obtained each from separate methanol extracts of *Dictyopteris zonarioides* collected in the Pacific Ocean and in the Gulf of California. The structural assignments were made based upon spectral grounds and by degradation to dihydrotauranic acid and comparison with an authentic sample.

Previous investigations of members of the genus *Dictyopteris* (family Dictyotaceae) have led to the isolation of two new oxygenated sesquiterpenes<sup>3,4</sup> and a novel assortment of nonterpenoid C<sub>11</sub> hydrocarbons and sulfur-containing compounds.<sup>5-8</sup> In an earlier paper<sup>9</sup> we described the structure of zonarene (1),



the major hydrocarbon component of the hexane extract of *D. zonarioides*, an alga indigenous to the Pacific Ocean near southern California and to the Gulf of California. We wish to report here the structures of zonarol (2) and isozonarol (3), hydroquinones obtained from the methanol extract of this alga. Zonarol was the exclusive isomer present in samples collected in the Pacific Ocean, while only isozonarol was obtained from the Gulf of California source. Both methanol extracts also contained 1 and small amounts of the corresponding quinones which are dis-



cussed below. Both 2 and 3 are moderately fungitoxic toward *Phytophthora cinnamomi*, *Rhizoctonia solani*, *Sclerotinia sclerotiorum*, and *Sclerotium rolfsii*.

Column chromatographic separation of the methanol extract of *D. zonarioides*, collected in San Diego, Calif., gave zonarol (2) as a noncrystalline gum. All attempts to crystallize this material failed. The infrared absorptions of this compound clearly showed the presence of hydroxyl (3400 cm<sup>-1</sup>) and an exocyclic double bond (1650 and 908 cm<sup>-1</sup>). While 2 did not give a positive ferric chloride test, it was recognized as a monosubstituted hydroquinone by its eventual oxidation to the corresponding quinone. In addition, its nmr spectrum showed three aromatic protons at  $\delta$  6.55 as a complex band and two hydroxyl protons at solvent-dependent chemical shifts. Two exocyclic methylene protons were recognized by broad bands at  $\delta$  4.64 and 4.75. Multiple bands from  $\delta$  1.0 to 2.8 showed the molecule to contain a variety of saturated methylene hydrogen. Overlapping sharp signals centered at  $\delta$  0.80 indicated three quaternary methyl groups to be present. The mass spectrum of 2 and the integration of the nmr bands described above were consistent ( $P = m/e$  314) in indicating the molecular formula C<sub>21</sub>H<sub>30</sub>O<sub>2</sub>. The uv spectrum<sup>10</sup> also suggested the hydroquinone structure,  $\lambda_{\text{max}}^{\text{MeOH}}$  211 nm ( $\epsilon$  8400) and 295 (3150). Treatment of 2 with Jones reagent<sup>11</sup>

(1) (a) Marine Natural Products. VII. For Part VI see W. Fenical, J. Sims, and P. Radlick, *Tetrahedron Lett.*, **4**, 313 (1973). (b) Presented in part at the Third International Conference on Food-Drugs from the Sea, Kings-ton, R. I., Aug 1972.

(2) Address correspondence to Institute of Marine Resources, Scripps Institution of Oceanography, La Jolla, Calif. 92037.

(3) T. Irie, K. Yamamoto, and T. Masamune, *Bull. Chem. Soc. Jap.*, **37**, 1053 (1964).

(4) E. Kurosawa, M. Izawa, K. Yamamoto, T. Masamune, and T. Irie, *Bull. Chem. Soc. Jap.*, **39**, 2509 (1966).

(5) R. E. Moore, J. A. Pettus, Jr., and M. S. Doty, *Tetrahedron Lett.*, **46**, 4787 (1968).

(6) J. A. Pettus, Jr., and R. E. Moore, *Chem. Commun.*, 1093 (1970).

(7) J. A. Pettus, Jr., and R. E. Moore, *J. Amer. Chem. Soc.*, **93**, 3087 (1971).

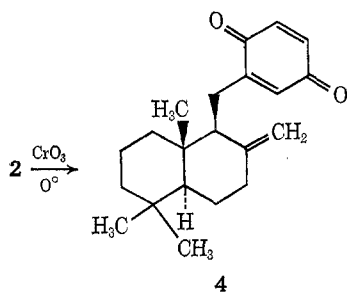
(8) P. Roller, K. Au, and R. E. Moore, *Chem. Commun.*, 503 (1971).

(9) W. Fenical, J. Sims, R. Wing, and P. Radlick, *Phytochemistry*, **11**, 1161 (1972).

(10) A. I. Scott, "Interpretation of the Ultraviolet Spectra of Natural Products," Pergamon Press, Elmsford, N. Y., 1964.

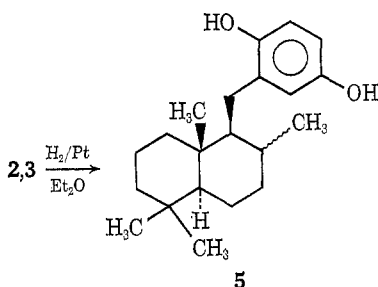
(11) K. Bowden, I. M. Heilbron, E. R. H. Jones, and B. C. L. Weedon, *J. Chem. Soc.*, 39 (1946).

at 0° resulted in quantitative conversion to zonarone (4) which crystallized as long yellow needles from



methanol, mp 125–127°. The uv of this quinone showed  $\lambda_{\text{max}}^{\text{MeOH}}$  248 nm ( $\epsilon$  12,700) and 331 (790), consistent with its structure. The nmr spectrum of 4 exhibited a greater separation of bands and therefore showed more clearly the structural features of this system. Two aromatic protons appeared as a sharp band at  $\delta$  6.65 and the other aromatic as a more broad band at  $\delta$  6.40. The exocyclic olefinic protons appeared as two bands centered at  $\delta$  4.75 and 4.38. Methylene protons spanned between  $\delta$  2.7 and 1.0 and three singlets, sharply resolved at  $\delta$  0.92, 0.87, and 0.80, were assigned to the quaternary methyl groups. The coupling and chemical shifts observed in the nmr of 4 are entirely consonant with those reported for tauranin,<sup>12</sup> a disubstituted quinone with the identical sesquiterpenoid substituent.

Column chromatographic separation of the methanol extract of *D. zonarioides*, collected in the Gulf of California near Puerto Peñasco, Mexico, gave only the isomeric hydroquinone isozonarol (3).<sup>13</sup> Isozonarol was also obtained as a noncrystalline gum. Spectral information showed 3 to be isomeric with 2, with the obvious difference being the loss of the exocyclic double bond features in both the infrared and nmr spectra. Hydrogenation of 2 and 3 served to confirm the double bond isomer relationship of these two hydroquinones. Each absorbed 1 mol of hydrogen to give a saturated hydroquinone epimeric mixture (5),  $m/e$  316,  $\text{C}_{21}\text{H}_{32}\text{O}_2$ ,

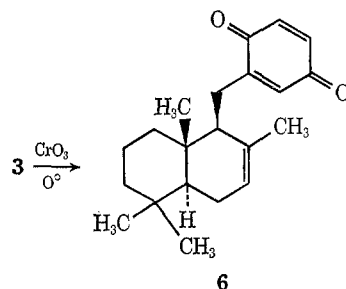


which were identical in all respects. Oxidation of 3 in an analogous fashion as with 2 gave isozonarone (6) as bright yellow plates from methanol, mp 111–112°. The spectral data for this isomer (Experimental Section) exhibited elements in confirmation of its structure.

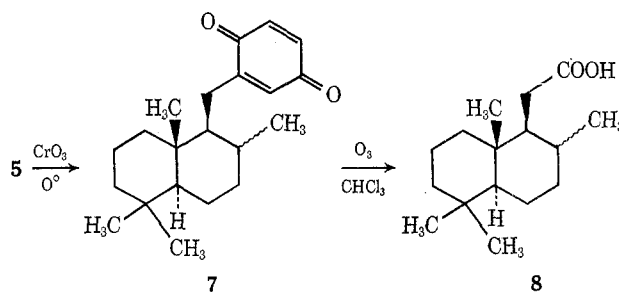
The structural information gained from the spectral features of 2–6 clearly showed the molecules in question to be monosubstituted hydroquinones and quinones. The substituent in each case was a  $\text{C}_{15}\text{H}_{25}$  fragment which contained two rings and a single double bond,

(12) K. Kawashima, K. Nakanishi, and H. Hishikawa, *Chem. Pharm. Bull.*, **12** (7), 796 (1964).

(13) The possibility that 3 is formed from 2 during work-up procedures is discounted since all samples were treated in an identical fashion.



exocyclic in one series and endocyclic in the other. Using a method analogous to that employed by Nakanishi in his structure proof of tauranin,<sup>12</sup> the hydroquinone moiety in zonarol was cleaved *via* an oxidative degradation. To accomplish this, zonarol was first hydrogenated to the saturated epimeric mixture 5. This mixture was then oxidized with Jones reagent to yield the saturated quinone mixture 7. Ozonation of 7 followed by oxidative work-up gave a carboxylic acid mixture 8 which crystallized from acetonitrile, mp



104–105°. This acid gave identical spectra with those reported<sup>12</sup> for the eutectic mixture of dihydrotauranic acids derived from tauranin and from the degradation of ambrein,<sup>14</sup> sclareol,<sup>14</sup> and manöol.<sup>15</sup> A sample of authentic<sup>16</sup> dihydrotauranic acid and the eutectic mixture obtained above were converted to their methyl esters and compared by gas chromatography. Each sample was composed of a 60:40 mixture of epimeric esters whose behaviors were identical including retention times on mixed injection.

The results of mass spectral analysis of the quinones 4 and 6 are worthy of discussion. Under our conditions neither 4 nor 6 gave a clean parent ion. Instead, each quinone gives very large  $\text{P} + 2$  and  $\text{P} + 4$  peaks. For zonarone  $\text{P} + 2$  was 40% parent and for isozonarone  $\text{P} + 2$  was 128% parent intensity. This phenomenon has already been observed<sup>17</sup> with other quinones and is due to the formation of the corresponding hydroquinones *via* reduction upon electron impact. In order to probe the redox nature of these compounds, a cyclic voltametry study of 4 and 6 was initiated. The cyclic voltammogram shows two quasi-reversible electrochemical couples identical for each quinone. One couple has an  $E_{\text{pc}}$  of  $-0.525$  V and an  $E_{\text{pa}}$  of  $-0.45$  V while the other shows an  $E_{\text{pc}}$  of  $-1.35$  V and an  $E_{\text{pa}}$  of  $-1.275$  V. An  $E_{\text{pc}}$  defines the reduction potential for the reaction  $\text{ox.} + ne^- \rightleftharpoons \text{red.}$ , and the

(14) C. C. Asselineau, E. Lederer, D. Mercier, and J. Polonsky, *Bull. Soc. Chim. Fr.*, 720 (1950).

(15) L. Ruzicka, O. Durst, O. Durst, and O. Jeger, *Helv. Chim. Acta*, **30**, 353 (1947).

(16) The authentic sample used was obtained from the degradation of tauranin.<sup>12</sup> We are grateful to Professor K. Nakanishi, Columbia University, for providing us with a sample of the dihydrotauranic acid epimeric mix.

(17) R. T. Alpin and W. T. Pike, *Chem. Ind. (London)*, 2009 (1966).

$E_{pa}$  the oxidation potential of the reverse reaction. These results indicate two one-electron reductions from quinone to semiquinone and from semiquinone to hydroquinone. The low reduction potentials noted above and the reversible nature of the reduction are in complete accord with the ease of reduction under mass spectral conditions.

### Experimental Section

**General Methods.**—All melting points are uncorrected. Infrared spectra were obtained using a Perkin-Elmer Infracord instrument either as thin films or in solvent-cancelling solution as noted. Ultraviolet absorptions were obtained in methanol solution using a Perkin-Elmer Model 202 spectrophotometer. ORD-CD spectra were obtained using a JASCO Model ORD-CD-UV-5 spectrometer. Nmr spectra were recorded in solutions at 60 MHz using a Varian Associates T-60 spectrometer. Mass spectral analyses were all obtained with a Finnigan 1015 SL mass spectrometer. All solvents used were Mallinckrodt AR grade and were used as received with the exception of hexanes, which required distillation. Gas chromatographic analyses were completed with an Aerograph Model A-90-P with the columns and conditions noted.

**Methanol Extraction of *Dictyopteris zonarioides* (Pacific Ocean Source).**—Air-dried *Dictyopteris zonarioides* (127 g) collected intertidally in San Diego, Calif., on September 30, 1970, was ground in a Wiley mill to 1 mm. Extraction was initiated with methanol in a Soxhlet extractor and allowed to continue for 48 hr. The methanol was then removed *in vacuo* and the resulting tar was taken up in an excess of diethyl ether. The ether was dried and concentrated to give 3.2 g of dark tar. The tar was taken up in petroleum ether (bp 30–60°) and chromatographed on a column (250 g) of Davison grade 62 silica gel eluting with petroleum ether, benzene, and varying amounts of diethyl ether in benzene; 3% diethyl ether in benzene eluted zonarol as a noncrystalline gum, 0.450 g. Thin layer chromatography on silica H with 5:1 benzene-ether showed one spot at  $R_f$  0.80. Zonarol was then dissolved in benzene and precipitated by adding petroleum ether, resulting in solids but still noncrystalline. Zonarol had the following spectra, features:  $\nu_{\max}^{\text{CHCl}_3}$  3550, 3400, 2960, 1650, 1490, 1440, 1170 and 910  $\text{cm}^{-1}$ ;  $\nu_{\max}^{\text{MeOH}}$  211 nm ( $\epsilon$  8400), 295 (3150); nmr  $\delta$  3.3 (m, 3 H), 4.7 (s, 2 H), 4.75 (s, 1 H), 4.64 (s, 1 H), 2.60 (m, 2 H), 2.4–1.0 (m, 12 H), 0.85 (m, 9 H); mass spectrum  $m/e$  (rel intensity) 41 (25), 43 (11), 55 (27), 57 (8), 67 (18), 69 (32), 77 (12), 79 (14), 81 (28), 83 (10), 91 (15), 93 (15), 95 (49), 97 (11), 105 (12), 107 (24), 109 (43), 119 (12), 121 (29), 122 (10), 123 (90), 124 (20), 135 (21), 136 (16), 137 (24), 147 (8), 149 (14), 161 (29), 162 (8), 163 (18), 175 (18), 176 (10), 177 (16), 178 (21), 189 (14), 190 (16), 191 (100), 192 (18), 299 (6), 314 (52), 315 (10), 316 (2). In some earlier chromatography fractions very small amounts ( $\sim$ 10 mg) of zonarone were found.

**Oxidation of Zonarol (2).**—2 (0.200 g) was dissolved in 20 ml of cold (0°) acetone and titrated to an oxidation end point with Jones reagent.<sup>11</sup> When the reaction was complete, the solution was poured onto ice and extracted with three 100-ml portions of diethyl ether.

The combined ether extracts were washed with water and dried with anhydrous magnesium sulfate, and the solvent was removed *in vacuo* to leave zonarone (4), 0.190 g, as bright yellow crystals. Crystallization from methanol gave 4 as long yellow needles, mp 126–127°.

*Anal.* Calcd for  $\text{C}_{21}\text{H}_{28}\text{O}_2$ : C, 80.73; H, 9.03. Found: C, 80.98; H, 9.02.

Zonarone had the following spectral features: ORD-CD (MeOH)  $[\alpha]_{425}^{30} -178^\circ$ ,  $[\alpha]_{498}^{30} +279^\circ$ ,  $[\alpha]_{500}^{30} +88.7^\circ$ ;  $\nu_{\max}^{\text{CCl}_4}$  2940, 1660, 1600, 1455, 1430, 1375, 1300, 1210, 1180, 1115, 1075, 1050, 911 and 898  $\text{cm}^{-1}$ ;  $\nu_{\max}^{\text{MeOH}}$  331 nm ( $\epsilon$  790), 248 (12, 700); nmr ( $\text{CCl}_4$ )  $\delta$  6.70 (s, 2 H), 6.45 (s, 1 H), 4.80 (s, 1 H), 4.40 (s, 1 H), 2.60 (m, 2 H), 2.50–1.00 (m, 12 H), 0.90 (s, 3 H), 0.84 (s, 3 H), 0.79 (s, 1 H); mass spectrum  $m/e$  (rel intensity) 27 (15), 28 (26), 29 (22), 32 (10), 36 (10), 39 (24), 41 (100), 42 (8), 43 (30), 51 (9), 53 (30), 54 (14), 55 (80), 56 (8), 57 (16), 65 (12), 66 (8), 67 (41), 68 (8), 69 (79), 77 (36), 78 (14), 79 (36), 81 (63), 82 (14), 83 (12), 91 (54), 92 (10), 93 (34), 94 (12), 95 (63), 97 (10), 103 (10), 105 (31), 107 (36), 108 (10), 109 (31), 115 (16),

117 (13), 119 (27), 120 (10), 121 (26), 122 (11), 123 (75), 124 (19), 128 (10), 129 (10), 131 (15), 133 (24), 134 (22), 135 (19), 136 (12), 137 (64), 138 (8), 145 (10), 147 (16), 149 (22), 157 (8), 159 (8), 160 (8), 161 (36), 162 (10), 163 (12), 173 (12), 174 (22), 175 (21), 176 (14), 188 (7), 189 (67), 190 (16), 191 (12), 201 (10), 227 (8), 312 (19), 313 (7), 314 (7).

**Methanol Extraction of *Dictyopteris zonarioides* (Gulf of California Source).**—Air-dried *Dictyopteris zonarioides* (3100 g) collected intertidally near Puerto Peñasco, Mexico, on March 27, 1971 was ground to 1 mm with a Wiley mill. The powdered plant was extracted for 48 hr with methanol in a Soxhlet extractor and the methanol was then removed. The resulting dark tar was taken up in diethyl ether, the solution was dried with anhydrous magnesium sulfate, and the ether was removed to yield 67 g of dark solids. This tar (25 g) was taken up in petroleum ether and chromatographed on 480 g of Davison grade 62 silica gel. Varying solvents from petroleum ether to ether in benzene gave a clean separation of isozonarol (3), 3.1 g, as a noncrystalline gum. In a prior fraction (benzene) 25 mg of isozonarone was obtained. Isozonarol showed the following spectral characteristics:  $\nu_{\max}^{\text{CHCl}_3}$  3570, 3340, 2920, 1605, 1500, 1450, 1377, 1290, 1170, 1095, 955, and 872  $\text{cm}^{-1}$ ;  $\nu_{\max}^{\text{MeOH}}$  209 nm ( $\epsilon$  8210), 296 (2700); nmr ( $\text{CDCl}_3$ )  $\delta$  6.80 (s, 1 H), 6.60 (s, 2 H), 5.45 (m, 1 H), 4.90 (m, 2 H), 2.60 (m, 2 H), 1.0–2.5 (m, 12 H), 0.90 (m, 9 H); mass spectrum  $m/e$  (rel intensity) 39 (17), 41 (76), 42 (7), 43 (39), 53 (15), 55 (55), 57 (13), 65 (11), 67 (41), 69 (43), 77 (22), 79 (23), 81 (23), 83 (10), 91 (29), 93 (21), 95 (57), 97 (11), 105 (19), 107 (29), 109 (72), 119 (15), 121 (32), 123 (74), 124 (13), 135 (29), 147 (9), 149 (10), (161) (24), 163 (11), 173 (11), 175 (32), 190 (13), 191 (100), 192 (13), 314 (17), 315 (5), 316 (1).

**Oxidation of Isozonarol (3).**—Isozonarol (1.0 g) was oxidized with Jones reagent in a fashion identical with that given above for zonarol. The yield of isozonarone (6) was essentially quantitative. Recrystallization from methanol gave 6 as bright yellow plates, mp 111–112°.

*Anal.* Calcd for  $\text{C}_{21}\text{H}_{28}\text{O}_2$ : C, 80.73; H, 9.03. Found: C, 80.74; H, 9.15.

Isozonarone showed the following spectral characteristics: ORD-CD (MeOH)  $[\alpha]_{424}^{30} -261^\circ$ ,  $[\alpha]_{498}^{30} +341^\circ$ ,  $[\alpha]_{500}^{30} +95.2^\circ$ ;  $\nu_{\max}^{\text{CHCl}_3}$  2940, 1660, 1595, 1445, 1375, 1300, 1075, and 910  $\text{cm}^{-1}$ ;  $\nu_{\max}^{\text{MeOH}}$  248 nm ( $\epsilon$  21,500), 330 (1430); nmr ( $\text{CDCl}_3$ )  $\delta$  6.75 (m, 3 H), 5.47 (m, 1 H), 2.49 (m, 2 H), 1.0–2.3 (m, 13 H), 0.90 (m, 9 H); mass spectrum  $m/e$  (rel intensity) 39 (14), 41 (61), 43 (18), 53 (12), 55 (50), 65 (11), 67 (18), 69 (21), 77 (15), 79 (17), 81 (17), 83 (10), 91 (26), 93 (13), 95 (17), 105 (20), 107 (15), 109 (38), 119 (100), 120 (20), 121 (13), 124 (25), 125 (39), 133 (20), 147 (10), 161 (9), 173 (9), 189 (37), 190 (8), 312 (<1), 313 (<1), 314 (<1), 315 (<1).

**Hydrogenation of Zonarol and Isozonarol (2 and 3).**—The hydrogenations of both 2 and 3 were run in an identical fashion. In each case 0.1–1.0 g of 2 or 3 was dissolved in 50 ml of diethyl ether, 25 mg of platinum oxide was added, and the solution was placed in a 125-ml filter flask. The neck was fitted with a large serum cap and the side arm was fitted with a balloon to act as a hydrogen reservoir. The flask and side arm were filled with hydrogen and stirred for 24 hr. The contents were then filtered and the solvent was removed *in vacuo* to give a saturated hydroquinone mixture. On prolonged sitting very fine needles were observed. Both 2 and 3 gave the identical saturated hydroquinone mixture (5), characterized by the following spectral information: parent  $m/e$  316;  $\nu_{\max}^{\text{CHCl}_3}$  3550, 3350, 2960, 1600, 1490, 1450, 1380, 1300, 1175, 1100, 975, 875, and 840  $\text{cm}^{-1}$ ; nmr ( $\text{CDCl}_3$ )  $\delta$  6.52 (m, 3 H), 2.50 (m, 2 H), 1.0–2.2 (m, 15 H), 0.70–1.00 (m, 12 H).

**Oxidation of the Hydroquinone 5.**—The oxidation of 5 was carried out as described for zonarol. In a typical run 0.500 g of hydroquinone was converted to the quinone mixture in quantitative yield. The crystalline mixture was confirmed as the saturated structure 6 by the following spectral information:  $\nu_{\max}^{\text{CHCl}_3}$  1650, 1590, 1280, 1070, and 909  $\text{cm}^{-1}$ ; nmr  $\delta$  6.60 (m, 3 H), 2.50 (m, 2 H), 1.0–2.0 (m, 13 H), 0.90 (m, 12 H); parent  $m/e$  314.

**Ozonation of Quinone 6. Dihydrotauronic Acid (8)**—The saturated quinone mixture 5 (0.400 g) was dissolved in 50 ml of ethanol-free chloroform. A stream of 1–2% ozone was directed into the flask, which was stirred and cooled to 0°. After 2 hr the solvent was removed at 0° under low pressure and the contents were mixed with 200 ml of 1%  $\text{H}_2\text{O}_2$  and warmed for 1 hr on a

steam bath. Ether extraction gave 0.200 g of a viscous oil which crystallized from acetonitrile. Repeated recrystallization gave colorless needles of dihydrotauranic acid epimeric mixture, mp 104–105° (lit.<sup>12</sup> mp 107°).

The nmr of this product was identical with that reported;<sup>12</sup>  $\delta$  (CDCl<sub>3</sub>) 0.79 (d, 1.5 H), 0.82 (s, 3 H), 0.86 (s, 6 H), 1.02 (s, 1.5 H), 1.0–2.6 (m, 15 H), 9.98 (s, 1 H).

**Gas Chromatography of Methyl Dihydrotauranates.**—The samples of dihydrotauranic acid obtained above, mp 104–105°, and an authentic sample,<sup>13</sup> mp 107°, were converted to their respective methyl esters *via* treatment with thionyl chloride and anhydrous methanol. Analysis of each ester mixture by gas chromatography on a 0.25 in.  $\times$  3 m 10% DC-11 silicon grease on Chromosorb W 60/80 column at 200° showed a 60:40 mixture of two epimeric esters. At this temperature their retention times were 25.7 and 28.6 min. Equal amounts of the esters from each source were combined and injected; identical results were obtained. A comparison was also completed on a 0.25 in.  $\times$  2 m 15% butanediol succinate on Chromosorb P 60/80 column at 215°. The esters had identical retention times of 8.8 and 10.0 min.

**Cyclic Voltammetry of Zonarone (4).**—The cyclic voltammetric measurements were done using a three-electrode system in a degassed electrochemical cell with dimethyl sulfoxide as solvent and tetraethylammonium perchlorate (0.1 *F*) as supported electrolyte. A Beckman platinum-inlay electrode was em-

ployed as the working electrode. An aqueous silver–silver chloride electrode in 0.4 *F* tetramethylammonium chloride was used as a reference with a potential of 0.00 V *vs.* the saturated calomel electrode. Potentials recorded for two-electron reduction of zonarone were:  $E_{pc}$  –0.525 V,  $E_{pa}$  –0.450 V and  $E_{po}$  –1.350 V,  $E_{pa}$  –1.275 V.

**Registry No.**—2, 39707-54-5; 3, 39707-55-6; 4, 39707-56-7; 5 isomer A, 39707-57-8; 5 isomer B, 39707-58-9; 6, 39707-59-0.

**Acknowledgment.**—The authors are indebted to Mr. James Stewart and Dr. Ralph Lewin, Scripps Institution of Oceanography, for aid in collecting and identifying this alga. Thanks are extended to Dr. James Gerber, Department of Chemistry, UCR, for running the cyclic voltammetry experiments. This work is a result of research sponsored by NOAA Office of Sea Grant, Department of Commerce, under Grant USDC 2-35208 with the Institute of Marine Resources. The U. S. Government is authorized to produce and distribute reprints for governmental purposes notwithstanding any copyright notation that may appear within.

## The Pschorr Reaction by Electrochemical Generation of Free Radicals. II. Benzophenone Series. An Alternative Mechanism<sup>1</sup>

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Diazonium salts of 2-amino-*R'*-benzophenone ( $R' = 4\text{-CH}_3, 4\text{-OCH}_3, 3\text{-NO}_2$ ) were decomposed electrolytically, thermally, and by the iodide ion. Protic and aprotic solvents were employed, with a variety of catalysts and over a range of temperatures. Using our results and published data, a general inter- or intramolecular one-electron redox mechanism is proposed. Based on experimental results and theoretical calculations, this proposal alleviates many of the previously encountered difficulties in explaining the behavior of diazonium salts under varied conditions and specifically clarifies the Pschorr cyclization mechanism.

Phenyl radicals produced by the electrochemical reduction of benzenediazonium salts have been used for phenylation of aromatic substrates.<sup>2</sup> This technique was used in a new approach to the Pschorr reaction, in which intramolecular arylation occurred upon reduction of diazonium salts of 2-amino- $\alpha$ -(*R'*)-phenylcinnamic acids giving near quantitative yields of phenanthrene derivatives.<sup>3</sup> However, when this technique was applied to diazonium salts of 2-amino-*R'*-benzophenones to obtain fluorenone derivatives, some surprising results were obtained.

Various literature surveys<sup>4–9</sup> have revealed a long history of mechanistic studies on Pschorr-like systems. All agree that, depending on the reaction conditions, homolytic or heterolytic mechanisms, or a combination of the two, could explain the type and yield of products.

However, aryl diazonium cations have been shown to be strong oxidizing agents,<sup>10</sup> which upon reduction (electrolytically or thermally) release nitrogen and produce aryl radicals. This redox model has been used to explain the salient fact of diazonium salt chemistry.<sup>11</sup>

We now believe there are indeed two mechanisms operating in the Pschorr reaction: one is the conventional homolytic mechanism and the other is a substitute for the classical heterolytic mechanism. Both mechanisms involve a one-electron redox reaction: the homolytic one results from external reduction of the diazonium moiety, while the other invokes an *internal* or intramolecular reduction in which the system goes through an intramolecular charge-transfer or redox state.

### Results

**A. Electrolytic Reductions of Unsubstituted Diazonium Salts (Table I).**—Protic and aprotic media were employed at different potentials. In aprotic media at 0.0 V cyclization was poor, while abstraction and attack on the electrode produced the major products. At higher potential attack on the cathode was reduced,

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