Defensive Secretion of the Millipede Floridobolus penneri

Athula B. Attygalle, Shang-Cheng Xu, Jerrold Meinwald, and Thomas Eisner

J. Nat. Prod., **1993**, 56 (10), 1700-1706• DOI:
10.1021/np50100a007 • Publication Date (Web): 01 July 2004

Journal of Natural Products
Vol. 56, No. 10, pp. 1700-1706, October 1993

DEFENSIVE SECRETION OF THE MILLIPEDE *FLORIDOBOLUS PENNERI*[1]

ATHULA B. ATTYGALLE,* SHANG-CHENG XU,[2] JERROLD MEINWALD,

Baker Laboratory, Department of Chemistry, Cornell University, Ithaca, New York 14853

and THOMAS EISNER

Section of Neurobiology and Behavior, Cornell University, Ithaca, New York 14853

ABSTRACT.—Six quinones were identified from the defensive secretion of the millipede *Floridobolus penneri*. The two major components, 2-methyl-1,4-benzoquinone [**1**] and 2-methoxy-3-methyl-1,4-benzoquinone [**3**], previously characterized, comprise 95% of the secretion. One of the minor compounds, 2,5-dimethyl-3-methoxy-1,4-benzoquinone [**4**], is a new natural product. Another, 2-hydroxy-3-methyl-1,4-benzoquinone [**2**], had been tentatively characterized from a microbial source. The other two components are 2,3-dimethoxy-1,4-benzoquinone [**5**] and 2,3-dimethoxy-5-methyl-1,4-benzoquinone [**6**]. No sex difference in the composition of the secretion was noted.

Floridobolus penneri (Causey) (Diplopoda, Spirobolida) is an unusual millipede. It is restricted in range to the southern Lake Wales Ridge area of central Florida, a region of interesting faunal composition known as the Florida "scrub," that is rapidly being lost to human encroachment. Taxonomically *F. penneri* is anomalous enough to merit inclusion in a separate family, the Floridobolidae, of which it is the sole member.

Like many millipedes, *F. penneri* produces a defensive secretion from paired segmental glands opening along the sides of the body (1,2). In members of the Spirobolida, the order to which *F. penneri* belongs, this secretion contains 1,4-benzoquinones. Indeed, *F. penneri* itself had previously been shown to secrete 2-methyl-1,4-benzoquinone and 2-methoxy-3-methyl-1,4-benzoquinone (3). Pursuant to the discovery that certain flies that parasitize *F. penneri* appear to be attracted to the quinonoid secretion of their host, we have re-examined the chemistry of this secretion and found it to contain four additional quinones, of which one is a new natural product. We here report these chemical findings.

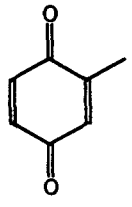
RESULTS

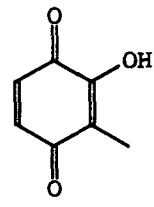
Gc examination of the extracts obtained from the defensive secretions revealed the presence of six well-resolved, volatile components. The relative amounts of these components in secretion samples from three females and one male, along with ms and ir data pertinent to the components, are presented in Table 1. It was evident from ir spectra, which showed strong absorption bands in the 1669–1677 cm^{-1} region, that all six compounds were benzoquinones (4).

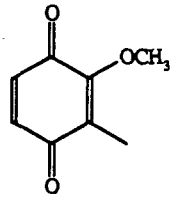
The two major constituents of the secretion, comprising 95% of the total volatiles, were identified as the previously characterized 2-methyl-1,4-benzoquinone [**1**] and 2-methoxy-3-methyl-1,4-benzoquinone [**3**] by their mass spectra, which are very similar to those given in the literature and identical to those obtained from authentic samples (3,5). The gas-phase Ft-ir spectrum of component **3** was identical to that obtained from an authentic sample of 2-methoxy-3-methyl-1,4-benzoquinone. To exclude the possi-

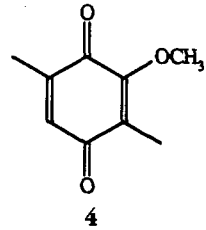
[1]Paper no. 113 of the series Defense Mechanisms of Arthropods. For no. 112 see Lokensgard *et al.*, *Experientia*, **49**, 175 (1993).

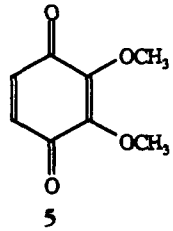
[2]Permanent address: Jiangsu Pesticide Research Institute, Nanjing 210036, People's Republic of China.

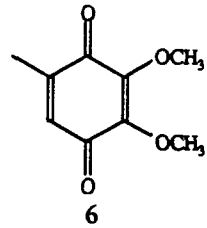

1


2


3


4


5


6

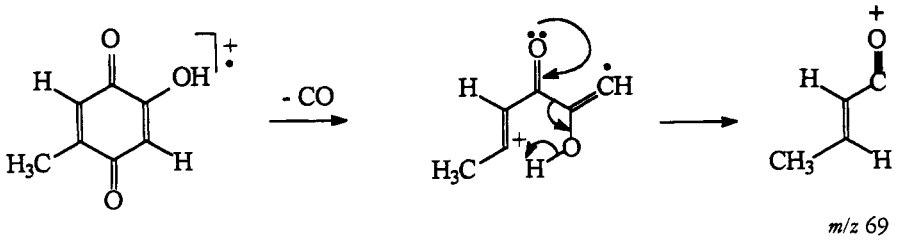
bility that isomeric quinones might possess indistinguishable spectra, the mass and ir spectra of the other two possible methoxymethylbenzoquinones, 2-methoxy-5-methyl-1,4-benzoquinone and 2-methoxy-6-methyl-1,4-benzoquinone, were recorded under similar analytical conditions and compared to those of the natural compound. These new spectra were significantly different from those of 2-methoxy-3-methyl-1,4-benzoquinone. This comparison particularly showed that the ir spectrum of each quinone isomer has a unique absorption profile especially in the region below 1600 cm^{-1}. Finally, 2-methoxy-3-methyl-1,4-benzoquinone was well separated from its positional isomers under the gc conditions used in this study (Kovats indices at 100° on DB-5 for 2,3-, 2,5-, and 2,6-isomers are 1181, 1337, and 1340, respectively).

The ir spectrum corresponding to peak **2** was significantly different from those of the other five components by having an absorption at 3456 cm^{-1} which indicated the presence of an intramolecularly H-bonded hydroxyl group in component **2**. The carbonyl absorption at 1669 cm^{-1}, however, is within the region assigned for benzoquinones without intramolecular H-bonding. This is not surprising, since such a shift was not observed in the spectrum of 2,5-dihydroxy-1,4-benzoquinone (4). The ir information and the ms ($[M]^+$ 138, $C_7H_6O_3$) observed for peak **2** suggested that the compound was a hydroxy methylbenzoquinone. The reported mass spectrum for 2-hydroxy-5-methyl-1,4-benzoquinone, clearly different from that of component **2** (5–7), has a prominent peak at *m/z* 69 (47%), attributed to the rearrangement and fragmentation shown in Scheme 1 (6,8,9).

By analogy, a significant isomeric fragment ion at *m/z* 69 should also be expected for the 2,6-isomer. Interestingly, the spectrum of component **2** (Table 1) had no significant

TABLE 1. The Relative Amounts and Spectrometric Data of Quinones Present in *Floridobolus penneri* Defensive Secretion.

Compound	Relative Amount				Ms data *m/z* (%)	Ir data (cm^{-1})
	Specimen 1 (female)	Specimen 2 (female)	Specimen 3 (male)	Specimen 4 (female)		
1	56.0	46.0	57.0	61.0	123 (6), $[M]^+$ 122 (77), 95 (6), 94 (87), 83 (3), 82 (68), 68 (46), 67 (12), 66 (75), 65 (23), 55 (9), 54 (100), 53 (29), 51 (7), 50 (9)	2937 (w), 1673 (s), 1603 (w), 1338 (w), 1284 (m), 1085 (w), 904 (m)
2	0.2	0.1	0.1	0.2	139 (7), $[M]^+$ 138 (100), 110 (9), 109 (6), 83 (14), 82 (40), 81 (15), 56 (14), 55 (33), 54 (28), 53 (17), 43 (9), 39 (15)	3456 (m), 2940 (w), 1669 (s), 1400 (m-s), 1346 (m-s), 1196 (m), 1081 (m), 840 (m)
3	38.0	46.6	39.7	37.3	153 (9), $[M]^+$ 152 (100), 151 (17), 137 (8), 124 (9), 123 (8), 122 (45), 109 (36), 94 (11), 83 (41), 82 (38), 81 $[M-71]^+$ (33), 67 (27), 66 (69), 65 (17), 55 (36), 54 (61), $[M-99]^+$ 53 (89)	2951 (w), 2860 (w), 1671 (s), 1597 (m), 1453 (w), 1382 (w), 1310 (s), 1206 (m), 1069 (w), 1022 (w), 841 (m)
4	0.2	0.5	0.2	trace	167 (10), $[M]^+$ 166 (100), 151 (11), 138 (22), 136 (25), 123 (40), 108 (10), $[M-71]^+$ 95 (34), 83 (43), 80 (29), 79 (31), 77 (14), 69 (11), 68 (21), $[M-99]^+$ 67 (60), 66 (27), 55 (34), 54 (23), 53 (22), 51 (11), 44 (22), 43 (7), 41 (17)	2945 (w), 2859 (w), 1677 (s), 1611 (m), 1451 (w), 1382 (w), 1283 (m), 1199 (m), 1136 (m), 924 (w)
5	5.0	5.3	2.5	1.3	169 (6), $[M]^+$ 168 (59), 153 (32), 125 (19), 124 (8), 123 (100), 122 (11), $[M-71]^+$ 97 (13), 95 (18), 94 (11), 82 (42), $[M-99]^+$ 69 (80), 68 (9), 54 (56), 53 (22), 43 (16)	2954 (w), 2853 (w), 1677 (s), 1590 (m), 1455 (w), 1304 (s), 1207 (m), 1071 (m-s), 841 (w)
6	0.6	1.5	0.5	0.2	183 (9), $[M]^+$ 182 (83), 167 (33), 155 (12), 153 (20), 152 (10), 151 (13), 139 (30), 138 (13), 137 (100), 136 (19), 125 (7), 123 (12), 121 (12), $[M-71]^+$ 111 (29), 109 (12), 96 (19), $[M-99]^+$ 83 (88), 81 (13), 69 (44), 68 (48), 55 (13), 53 (23), 52 (14), 44 (13), 43 (16)	2951 (w), 2850 (w), 1674 (s), 1603 (s) 1455 (w), 1279 (m-s), 1204 (m), 1146 (m), 1088 (w), 988 (w), 922 (w)



SCHEME 1

ion at *m/z* 69; instead a signal at *m/z* 55 (corresponding to the *m/z* 69 fragment minus the methyl substituent) was prominent (Table 1). On this basis, we assigned the structure 2-hydroxy-3-methyl-1,4-benzoquinone to component **2**. This identification was confirmed by synthesizing an authentic sample of this quinone from 2-methylresorcinol (10,11) and comparing the spectral and chromatographic data of the synthetic material with those of the natural compound.

The ms of component **4**, which showed a molecular ion at *m/z* 166 [$C_9H_{10}O_3$], was not congruent with any of the published mass spectra (5). Mass spectra of methoxybenzoquinones characteristically show a pronounced peak at $[M-71]^+$ due to a formal loss of two CO units and a methyl group (6,9). The $[M-71]^+$ species then loses another CO to give a peak at $[M-99]^+$. For example, the spectrum of 2-methoxy-3-methyl-1,4-benzoquinone shows peaks at *m/z* 81 (33%) and 53 (89%), corresponding to $[M-71]^+$ and $[M-99]^+$, respectively (Table 1). It appeared that compound **4** was a methoxyquinone since its spectrum showed $[M-71]^+$ and $[M-99]^+$ peaks (Table 1), and we tentatively identified it as 2,5-dimethyl-3-methoxy-1,4-benzoquinone. Both 2,5-dimethyl-3-methoxy- and 3,5-dimethyl-2-methoxy-1,4-benzoquinone were synthesized for comparison. The ms of both compounds were very similar; however, the ir spectrum of the former was indistinguishable from that of the natural product, while that of the latter differed significantly in the fingerprint region. Although a sample of 2,3-dimethyl-5-methoxy-1,4-benzoquinone was not available for comparison, the ir data alone allows the identification of component **4** as 2,5-dimethyl-3-methoxy-1,4-benzoquinone.

Component **5** was recognized as a dimethoxybenzoquinone by its ms, $[M]^+$ 168. Since this spectrum was different from that of the 2,5-dimethoxy-isomer (6), 2,3-dimethoxy- and 2,6-dimethoxy-1,4-benzoquinone were synthesized for direct comparison. The ir spectrum of the 2,3-isomer was indistinguishable from that of the natural compound, while that of the 2,6-isomer was clearly different particularly in the fingerprint region.

Component **6** was readily identified as 2,3-dimethoxy-5-methyl-1,4-benzoquinone (ubiquinone), previously found in another millipede (12). Direct comparison with an authentic sample confirmed the identification.

The relative amounts of these benzoquinones in the secretions of four specimens, one male and three females, were quantified by integrating gc peak areas. No dramatic qualitative or quantitative differences were observed.

DISCUSSION

A wide variety of benzoquinones have been characterized from plant and microbial sources, as well as from marine animals such as sea urchins, soft corals, and sponges (13). The natural function of these compounds is often obscure, although in some cases they doubtless fulfill antimicrobial and/or antifeedant roles. Among terrestrial animals, 1,4-benzoquinones are widely produced by arthropods including, besides millipedes, a wide

variety of insects and arachnids (1,2). There seems little doubt that in these animals the quinones serve to repel predators (1,2).

The two principal quinones **1** and **3** in the secretion of *F. penneri* are also major components of the secretion of other millipedes known to produce benzoquinones (species of the orders Spirobolida, Spirostreptida, Julida). The four minor components here reported, **2**, **4–6**, may also occur in other millipedes but may have been missed in earlier studies because of lesser sensitivity of instruments then available. Indeed, two of these minor components, **5** and **6**, were previously characterized from an African spiroboloid millipede, *Epibolus pulchripes* (=*Metiche tanganyicense*) (12). Of the two other minor components, 2,5-dimethyl-3-methoxy-1,4-benzoquinone [**4**] is a new natural product; the other, 2-hydroxy-3-methyl-1,4-benzoquinone [**2**], had been tentatively identified on the basis of its uv spectrum as a trace metabolite from the mold *Aspergillus terreus* (14).

The quinonoid defensive fluid of *F. penneri*, like that of millipedes generally, is seemingly devoid of hydrocarbons or other additives that could serve as solvents of the crystalline quinones. The secretion is nonetheless a liquid, a state achieved through mixed melting point depression. In fact, a synthetic mixture made by mixing individual crystalline quinones, in approximately the ratio found in the natural mixture, immediately became a liquid. An optimization principle may be at play in the formulation of quinonoid millipede secretions: the particular isomers of the quinones present in the fluids may be those of lowest melting point. Thus, for instance, compound **3**, a 2,3-methoxy-methyl derivative, has a melting point considerably lower (20–21°) than those of its 2,5 and 2,6 isomers (respectively, 174–176° and 149–150°) (15). Similarly, compound **5**, a 2,3 dimethoxy derivative, melts at 66–67°, while its 2,5 and 2,6 isomers have melting points of 250° and 254–255°, respectively (15). A similar argument may hold for the dimethyl-1,4-benzoquinone in defensive secretions of other arthropods.

EXPERIMENTAL

SAMPLE PREPARATION.—The millipedes were collected at night, on sandy terrain, near Lake Placid, Highlands County, Florida (voucher specimens have been deposited in the Cornell arthropod collection, under lot no. 1212). They were "milked" of secretion by tapping their bodies with a metal rod and collecting the fluid that oozed from their glands with small pieces of filter paper. CH_2Cl_2 extracts of the papers were examined by gc. Secretions were obtained from one male and three females.

CHEMICALS.—2-Methyl-1,4-benzoquinone [**1**], 2-methoxy-5-methyl-1,4-benzoquinone, and 2-methoxy-6-methyl-1,4-benzoquinone were available in our laboratory collection of chemicals. 2,5-Dimethyl-1,4-benzoquinone and 2,3-dimethoxy-5-methyl-1,4-benzoquinone [**6**] were purchased from American Tokyo Kasei Inc. (Portland, OR) and Aldrich Co. (Milwaukee, WI), respectively. The other benzoquinones were synthesized as described below. Melting points are uncorrected. Unless otherwise noted, ^1H- and ^{13}C-nmr spectra were obtained in $CDCl_3$ on Varian X-200 and X-400 instruments, respectively.

GAS CHROMATOGRAPHY.—Gc was carried out on a Hewlett-Packard (HP) 5890 instrument equipped with a flame ionization detector, and an HP 3396A integrator. Analyses were performed on a 12 m×0.22 mm fused-Si capillary column coated with DB-1 (J&W Scientific).

GC-FT-IR.—Ir spectra were obtained on a HP gas chromatograph linked to an HP 5965A IR detector. Analyses were performed using a 25 m×0.32 mm fused-Si column coated with DB-5.

GC-MS.—Mass spectra were obtained on an HP 5890 gas chromatograph linked to an HP 5970 mass selective detector (MSD). Analyses were performed using a 25 m×0.22 mm fused-Si column coated with DB-5 (J&W Scientific).

SYNTHESIS OF 2-HYDROXY-3-METHYL-1,4-BENZOQUINONE [**2**].—2-Methylresorcinol (1.2 g, Aldrich) was dissolved in HOAc (10 ml) containing about 1% H_2SO_4, and H_2O_2 (30%, 3.5 ml) was added dropwise at 15–20° (10,11). The reaction mixture was stirred at room temperature; after the exothermic reaction, H_2O (25 ml) was added and the mixture was extracted with CH_2Cl_2 (3×) to obtain a crude product (0.94

g) which was sublimed at 90–100° (1 mm) to give yellow needles: mp 129–131° (dec) [lit. (11) 134–135°]; ms *m/z* (%) $[M]^+$ 138 (100), 110 (13), 109 (3), 83 (17), 82 (52), 81 (21), 56 (18), 55 (46), 54 (43), 53 (30); ir (gas phase, cm^{-1}) 3455 (m), 1668 (s), 1400 (m), 1345 (m); ^1H nmr (200 MHz) δ 6.82 (1H, s, removed by D_2O), 6.72 (2H, s), 1.95 (3H, s, -Me); ^{13}C nmr (100.6 MHz) δ 187.73 (C=O), 182.80 (C=O), 151.21, 138.91, 131.72, 117.85, 7.96 (-Me).

SYNTHESIS OF 2-METHOXY-3-METHYL-1,4-BENZOQUINONE [**3**].—H_2O_2 (30%, 3 ml) was added to a solution of 2,6-dimethoxytoluene (1.5 g, Aldrich) and potassium ferricyanide (1.1 g) in HAOc (10 ml) (17). The mixture was stirred overnight, diluted with CH_2Cl_2, and washed with H_2O, $NaHCO_3$ solution, and brine. The usual workup gave a residue which was recrystallized (hexane) to give 2-methoxy-3-methyl-1,4-benzoquinone [**3**]: 740 mg; yellow crystals; mp 19–20° [lit. (15) 20–21°]; ms *m/z* (%) $[M]^+$ 152 (100); ir (gas phase, cm^{-1}), 2950 (w), 1671 (s), 1597 (m), 1310 (s); ^1H nmr (200 MHz) δ 6.69 (1H, d, J=9 Hz), 6.59 (1H, d, J=9 Hz), 4.02 (3H, s, -OMe), 1.95 (3H, s, -Me); ^{13}C nmr (100.6 MHz) δ 188.28 (C=O), 183.23 (C=O), 155.64, 136.30, 134.66, 129.02, 60.83 (-OMe), 8.66 (-Me).

SYNTHESIS OF 2,5-DIMETHYL-3-METHOXY-1,4-BENZOQUINONE [**4**].—Small samples of this compound were prepared by two methods. In the first procedure 2,5-dimethylresorcinol was methylated (16), and the product was oxidized (17).

Procedure I.—2,5-Dimethylresorcinol (420 mg, Aldrich) and MeI (1.7 g) were added to a DMSO (6 ml) solution of KOH (1.4 g) (16). The mixture was stirred for 30 min, poured into H_2O (60 ml), and extracted with CH_2Cl_2. The crude product (500 mg) obtained by evaporating the solvent was purified by cc on Si gel [hexane-CH_2Cl_2 (1:1)]. 1,3-Dimethoxy-2,5-dimethylbenzene: 380 mg; ms *m/z* (%) $[M]^+$ 166 (100), 151 (36), 137 (15), 135 (35), 121 (24), 105 (21), 91(38), 79 (21), 77 (28), 65 (15); ir (gas phase, cm^{-1}) 2943 (m), 1588 (m), 1141 (s).

H_2O_2 (30%, 1 ml) was added to a solution of 1,3-dimethoxy-2,5-dimethylbenzene (380 mg) and potassium ferricyanide (300 mg) in HOAc (4 ml) (17). The reaction mixture was stirred for 10 h and diluted with CH_2Cl_2. After the usual workup, the residue was purified by cc on Si gel [hexane-CH_2Cl_2 (1:1)] followed by recrystallization (hexane). 2,5-Dimethyl-3-methoxy-1,4-benzoquinone [**4**]: 90 mg; yellow needles; mp 61–62°; ms *m/z* (%), $[M]^+$ 166 (100), 138 (9), 136 (18), 123 (40), 95 (26), 83 (38), 80 (29), 79 (28), 69 (11), 68 (25), 67 (67); ir (gas phase, cm^{-1}) 2944 (w), 1667 (s), 1611 (m), 1283 (m), 1135 (m); ^1H nmr δ 6.52 (1H, s), 3.98 (3H, s, -OMe), 2.03 (3H, s, -Me), 1.93 (3H, s, -Me); ^{13}C nmr δ 188.34 (C=O), 183.69 (C=O), 155.91, 143.69, 133.07, 129.02, 60.79 (-OMe), 15.39 (-Me), 8.58 (-Me).

Procedure II.—Direct methoxylation gave a mixture of compounds (18). BF_3/MeOH complex (10 μl) was added to a solution of 2,5-dimethyl-1,4-benzoquinone (1 mg) in dry MeOH (100 μl) and heated in a closed container for 1 h. After 3 h at room temperature, H_2O was added and products were extracted into CH_2Cl_2. Gc-ms examination of the extract showed that the conversion of the starting material was poor. Nevertheless the desired compound **4** was present as a minor peak (ms and ir data similar to those given above for **4**). The major product was 2,5-dimethyl-4-methoxyphenol: ms *m/z* (%) $[M]^+$ 152 (64); 137 (100), 121 (4), 109 (12), 91 (11), 81 (21), 79 (15), 69 (10); ir (gas phase, cm^{-1}) 3653 (m), 2939 (m), 1676 (w), 1510 (s), 1409 (m), 1195 (s), 1019 (m); ^1H nmr δ 6.59 (2H, s), 4.36 (1H, br, -OH), 3.76 (3H, s, -OMe), 2.21 (3H, s, -Me), 2.14 (3H, s, -Me).

SYNTHESIS OF 3,5-DIMETHYL-2-METHOXY-1,4-BENZOQUINONE.—A small sample of this compound was obtained as a mixture by the methoxylation procedure described above (18). 2,6-Dimethyl-1,4-benzoquinone (Aldrich) was used as the starting material, and the gas chromatogram obtained from the product showed two peaks in 2:8 ratio. The minor peak represented the desired 3,5-dimethyl-2-methoxy-1,4-benzoquinone: ms *m/z* (%) $[M]^+$ 166 (10), 151 (10), 136 (24), 123 (40), 95 (23), 83 (50), 80 (41), 79 (42); ir (gas phase, cm^{-1}) 2953 (w), 1668 (s), 1611 (m), 1318 (m), 1207 (M), 1152 (m). The major product was 2,6-dimethyl-4-methoxyphenol (19): ms *m/z* (%) $[M]^+$ 152 (79), 137 (100), 109 (17), 91 (17), 81 (30), 79 (18), 77 (16); ir (gas phase, cm^{-1}) 3655 (m), 2939 (m), 1607 (w), 1488 (s), 1324 (m), 1191 (s); ^1H nmr (DMSO) δ 7.66 (1H, br, -OH), 6.47 (2H, s), 3.61 (3H, s, -OMe), 2.11 (6H, s, -Me×2).

SYNTHESIS OF 2,3-DIMETHOXY-1,4-BENZOQUINONE [**5**] AND 2,6-DIMETHOXY-1,4-BENZOQUINONE.—These were obtained by hexacyanoferrate-catalyzed oxidation of 1,2,3-trimethoxybenzene (1.7 g, Aldrich) with 30% H_2O_2 (17). The two products were isolated by the procedure of Matsumoto and Kobayashi (17). 2,3-Dimethoxy-1,4-benzoquinone [**5**] (160 mg): red needles; mp 66° [lit. (17) 66–67°], ms *m/z* (%) $[M]^+$ 168 (58), 153 (32), 123 (100), 97 (15), 95 (22), 82 (45), 69 (84), 54 (60); ir (gas phase, cm^{-1}) 2954 (w), 1677 (s), 1590 (m), 1304 (s), 1207 (m); ^1H nmr δ 6.60 (2H, s), 4.02 (6H, s, -OMe×2); ^{13}C nmr δ 184.01 (C=O), 145.01, 134.58, 61.24 (OMe). 2,6-Dimethoxy-1,4-benzoquinone (320 mg): yellow needles; mp 248° [lit. (17) 240–242°]; ms *m/z* (%) $[M]^+$ 168 (29), 140 (9), 138 (10), 125 (12), 97 (11), 80 (24), 69 (100); ir (gas phase, cm^{-1}) 2940 (w), 1709 (m), 1656 (s), 1598 (s), 1212 (s), 1107 (s); ^1H nmr δ 5.85 (2H, s), 3.81 (6H, s, -OMe×2); ^{13}C nmr δ 186.81 (C=O), 176.05 (C=O), 157.25, 107.39, 56.48 (-OMe).

ACKNOWLEDGMENTS

We thank K.D. McCormick for his help with nmr spectra and staff of the Archbold Biological Station, Lake Placid, Florida, for numerous kindnesses. Support of this research by NIH grants AI 12020 and AI 02908 is acknowledged with pleasure.

LITERATURE CITED

1. T. Eisner, D. Alsop, K. Hicks, and J. Meinwald, in: "Arthropod Venoms." Ed. by S. Bettini, Springer Verlag, Berlin, 1978.
2. M.S. Blum, "Chemical Defenses of Arthropods," Academic Press, New York, 1981.
3. A. Monro, M. Chadha, J. Meinwald, and T. Eisner, *Ann. Entomol. Soc. Am.*, **55**, 261 (1962).
4. R.A. Nyquist, "The List of Vapor Phase Infrared Spectra," Sadtler Research Laboratories, Philadelphia, 1984, p. 311.
5. F.W. McLafferty and D.B. Stauffer, "The Wiley/NBS Registry of Mass Spectral Data," John Wiley, New York, 1989.
6. J.H. Bowie, D.W. Cameron, R.G.F. Giles, and D.H. Williams, *J. Chem. Soc. B*, 335 (1966).
7. T.G. Olagbemiro, L. Lajide, K.M. Sani, and B.W. Staddon, *Experientia*, **44**, 1022 (1988).
8. H. Budzikiewicz, C. Djerassi, and D.H. Williams, "Mass Spectrometry of Organic Compounds," Holden-Day, San Francisco, 1967.
9. H. Dieks and K. Beyer, *J. Labelled Compd. Radiopharm.*, **9**, 1093 (1990).
10. D. Bryce-Smith and A. Gilbert, *J. Chem. Soc.*, 873 (1964).
11. A. Rashid and G. Read, *J. Chem. Soc. C*, 1323 (1967).
12. W.F. Wood, J. Shepherd, B. Chong, and J. Meinwald, *Nature*, **253**, 625 (1975).
13. R.H. Thomson, "Naturally Occuring Quinones III," Chapman and Hall, New York, 1987.
14. T. Subramanian, K. Namasivayam, K. Mohan, and E.R.B. Shanmugasundaram, *Proc. Indian Acad. Sci., Sect. B*, **87**, 177 (1978).
15. "Dictionary of Organic Compounds," Chapman and Hall, London, 1982.
16. R.A.W. Johnstone and M.E. Rose, *Tetrahedron*, **35**, 2169 (1979).
17. M. Matsumoto and H. Kobayashi, *J. Org. Chem.*, **50**, 1766 (1985).
18. J. Kopecky, D. Saman, and L. Novotny, *Collect. Czech. Chem. Commun.*, **52**, 223 (1987).
19. M. Fujio, M. Mishima, Y. Tsuno, Y. Yukawa, and Y. Takai, *Bull. Chem. Soc. Jpn.*, **48**, 2127 (1975).

Received 19 January 1993