Identification and Total Synthesis of Novel Fatty Acids from the Caribbean Sponge *Calyx podatypa*

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Received April 10, 1998

The phospholipid fatty acid composition of the Caribbean sponge *Calyx podatypa* was studied, and 85 different fatty acids were identified, in particular the 11-methylpentadecanoic acid and 10-tricosenoic acid, which have no literature precedence. Structural characterization was accomplished by means of gas chromatography−mass spectrometry on their corresponding methyl esters and dimethyl disulfide derivatives. The structure of 11-methylpentadecanoic acid was further confirmed by total synthesis (17% overall yield) starting from commercially available 10-hydroxydecanoic acid.

Calyx podatypa Van Soest (Phloeodictyidae) is a common Caribbean sponge rich in cyanobacteria.[1] Several unusual metabolites have been isolated from *C. podatypa*, including proline-derived diketopiperazines,[1] 1,3-diphenylbutanoid compounds,[2] and antimicrobial *N*-methylpyridinium salts related to the xestamines.[3] Just recently, some unusual 2,2,4,6,6-pentasubstituted piperidine alkaloids were also reported from *C. podatypa*.[4] Despite all of these studies, there is only one report on the lipid composition of *C. podatypa*, namely, the isolation and identification of novel sterols with cyclopropene-containing side chains, a probable common feature among *Calyx* species.[5] Motivated by this interesting finding, and under the possibility that unusual sterols might interact with unusual fatty acids in sponge membranes, we studied the complete phospholipid fatty acid composition of *C. podatypa* and found two new fatty acids: 11-methylpentadecanoic acid and 10-tricosenoic acid. Short-chain fatty acids such as 11-methylpentadecanoic acid are of interest because other methyl-branched hexadecanoic acids, such as 13-methylpentadecanoic acid, display antimicrobial activity (MIC = 1.56 μg/mL) against the cariogenic bacterium *Streptococcus mutans*.[6]

C. podatypa presented a typical sponge phospholipid profile. By means of careful ^{31}P NMR on the phospholipid fraction from *C. podatypa*, we identified phosphatidylethanolamine (−1.32 ppm) and phosphatidylserine (−2.05 ppm) as the two most abundant phospholipids. Acid methanolysis of the phospholipids yielded around 85 identifiable fatty acids, which are shown in Table 1. Fatty acid chain lengths ranged between C_{12} and C_{26}, and a wide variety of structural types was identified. In particular, methyl-branched fatty acids were particularly abundant in this sponge, inasmuch as they made up 50% of the total fatty acid composition. For example, a diversified methyl-branched hexadecanoic acid family was identified in *C. podatypa* and included the 3-, 9-, 10-, 11-, and 14-methylpentadecanoic acids. All of these acids were characterized as methyl esters by GC−MS. Moreover, the 11-methylpentadecanoic acid has no literature precedence. Initial characterization of this acid was accomplished through HRMS of its methyl ester **1**. Upon HREIMS the title compound displayed a molecular ion peak at *m*/*z* 270.2554, corresponding to a molecular formula of $C_{17}H_{34}O_2$. In addition, **1** presented an equivalent chain-length (ECL) value of 15.54 in nonpolar capillary GC, indicating unusual methyl branching. A careful inspection of the MS of **1** revealed higher than normal fragmentation peaks at *m*/*z* 185.1542 $[C_{11}H_{21}O_2]^+$ and at *m*/*z* 213.1844 $[C_{13}H_{25}O_2]^+$, as well as a diminished peak at *m*/*z* 199, indicating methyl branching at C-11. Methyl 11-methylpentadecanoate is, therefore, the most probable structure for **1**.

Final structural confirmation for **1** was achieved through total synthesis (Scheme 1). Commercially available 10-hydroxydecanoic acid (Aldrich) was converted to methyl 10-hydroxydecanoate in a 99% yield through acid-catalyzed methanolysis.[7] Reaction of the methyl ester with phosphorus tribromide resulted in a 96% yield of methyl 10-bromodecanoate, which was subsequently reacted with triphenylphosphine in benzene, affording the phosphonium salt methyl (9-methoxycarbonylnonyl)triphenyl phosphonium bromide as previously reported (Scheme 1).[7] Subsequent Wittig coupling with 2-hexanone, using potassium *t*-butoxide as base and THF as solvent, afforded a 2:1 cis-trans mixture of methyl 11-methyl-10-pentadecenoate in a low 19% yield. The product ratio was determined by GC, because, in our nonpolar capillary column, fatty acid methyl esters with the trans stereochemistry elute after their cis counterparts, as we previously demonstrated for methyl 7-methyl-6-octadecenoate.[8] Final hydrogenation over PtO_2 resulted in the desired methyl 11-methylpentadecanoate (**1**) in an overall 17% yield, which coeluted on capillary GC with the natural methyl ester from *C. podatypa*. This reaction sequence represents the first synthesis of **1**.

Monounsaturated fatty acids also predominated, up to as much as 11% of the total, in the phospholipid fatty acid mixture from *C. podatypa* (Table 1). One particular monounsaturated fatty acid, 10-tricosenoic acid, became of interest because it has no precedent in the literature. Methyl 10-tricosenoate presented a molecular ion peak

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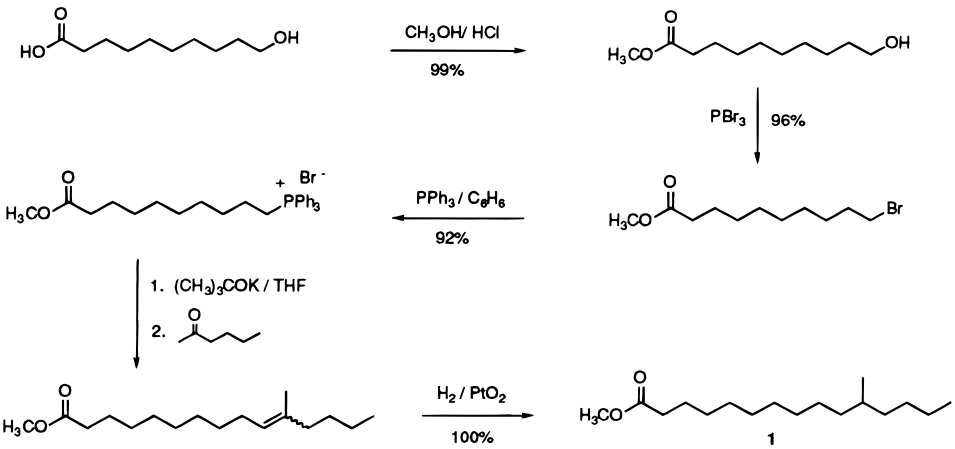
S0163-3864(98)00141-4 CCC: $15.00
Published on Web 07/18/1998

Table 1. Identified Phospholipid Fatty Acids from *C. podatypa*[a]

fatty acids	abundance (wt %)	fatty acids	abundance (wt %)
dodecanoic (12:0)	0.1	16-methyloctadecanoic (*ai*-19:0)	1.1
tridecanoic (13:0)	0.1	11-nonadecenoic (19:1)	0.6
12-methyltridecanoic (*i*-14:0)	0.1	nonadecanoic (19:0)	0.2
7-tetradecenoic (14:1)	0.1	5,8,11,14-eicosatetraenoic (20:4 *n*-6)	1.0
tetradecanoic (14:0)	2.4	5,8,11,14,17-eicosapentaenoic (20:5 *n*-3)	2.0
3-methyltetradecanoic (15:0)	0.2	18-methylnonadecanoic (*i*-20:0)	0.7
9-methyltetradecanoic (15:0)	0.3	17-methylnonadecanoic (*ai*-20:0)	0.4
4,8,12-trimethyltridecanoic acid (16:0)	1.9	eicosanoic (20:0)	0.6
13-methyltetradecanoic (*i*-15:0)	6.0	methyleicosanoic (21:0)	0.4
12-methyltetradecanoic (a*i*-15:0)	2.4	19-methyleicosanoic (*i*-21:0)	1.6
pentadecanoic (15:0)	2.3	18-methyleicosanoic (*ai*-21:0)	2.2
3-methylpentadecanoic (16:0)	0.3	heneicosanoic (21:0)	0.2
9-methylpentadecanoic (16:0)	1.3	5,9-docosadienoic (22:2)	0.2
10-methylpentadecanoic (16:0)	1.1	methylheneicosanoic (22:0)	0.2
11-methylpentadecanoic (16:0)[b]	0.2	20-methylheneicosanoic (*i*-22:0)	0.6
5,9-hexadecadienoic (16:2)	1.3	11-docosenoic (22:1)	0.4
14-methylpentadecanoic (*i*-16:0)	1.9	19-methylheneicosanoic (*ai*-22:0)	0.3
9-hexadecenoic (16:1)	0.5	13-docosenoic (22:1)	0.2
11-hexadecenoic (16:1)	1.8	docosanoic (22:0)	3.2
hexadecanoic (16:0)	4.5	methyldocosanoic (br-23:0)	1.9
dimethylpentadecanoic acid (17:0)[c]	0.5	21-methyldocosanoic (*i*-23:0)	2.3
15-methyl-5,9-hexadecadienoic (*i*-17:2)	2.0	20-methyldocosanoic (*ai*-23:0)	1.2
15-methyl-9-hexadecenoic (*i*-17:1)	3.0	10-tricosenoic (23:1)[b]	0.2
10-methylhexadecanoic (17:0)	4.5	15-tricosenoic (23:1)	0.5
15-methylhexadecanoic (*i*-17:0)	2.8	tricosanoic (23:0)	1.3
7-methyl-6-hexadecenoic (17:1)	0.2	22-methyltricosanoic (*i*-24:0)	0.4
14-methylhexadecanoic (*ai*-17:0)	1.3	5,9-tetracosadienoic (24:2)	2.1
3-methylhexadecanoic (17:0)	0.2	21-methyltricosanoic (*ai*-24:0)	0.8
9-heptadecenoic acid (17:1)	0.5	9-tetracosenoic (24:1)	1.1
heptadecanoic (17:0)	0.5	15-tetracosenoic (24:1)	0.7
16-methylheptadecanoic (*i*-18:0)	0.3	17-tetracosenoic (24:1)	0.7
5,9-octadecadienoic (18:2)	0.3	tetracosanoic (24:0)	4.3
6,9,12,15-octadecatetraenoic (18:4 *n*-3)	0.8	23-methyltetracosanoic (*i*-25:0)	1.8
15-methylheptadecanoic (*ai*-18:0)	0.4	5,9-pentacosadienoic (25:2)	1.6
9,12-octadecadienoic (18:2)	0.3	22-methyltetracosanoic (*ai*-25:0)	0.3
9-octadecenoic (18:1)	1.0	pentacosenoic (25:1)	0.8
11-octadecenoic (18:1)	0.9	pentacosanoic (25:0)	0.4
13-octadecenoic (18:1)	0.1	24-methyl-5,9-pentacosadienoic (*i*-26:2)	0.3
octadecanoic (18:0)	1.5	5,9-hexacosadienoic (26:2)	3.9
17-methyl-11-octadecenoic (19:1)	0.5	17-hexacosenoic (26:1)	0.4
10-methyloctadecanoic (19:0)	2.0	19-hexacosenoic (26:1)	0.2
17-methyloctadecanoic (*i*-19:0)	1.5	hexacosanoic (26:0)	0.3

[a] Some minor dimethylated fatty acids were not identified. [b] Unprecedented in nature. [c] Probably 9,14-dimethylpentadecanoic acid.

Scheme 1



at *m*/*z* 368, indicating a monounsaturated methyl tricosenoate. The double bond position was determined by dimethyl disulfide derivatization followed by mass spectrometry.[9] Methyl 10,11-bis(methylthio)tricosanoate presented a molecular ion peak at *m*/*z* 460 and key fragmentations at *m*/*z* 229 $[C_{14}H_{29}S]^+$ and at *m*/*z* 231 $[C_{12}H_{23}SO_2]^+$, together with a peak at *m*/*z* 199 $[C_{11}H_{19}SO]^+$, resulting from the loss of MeOH from the *m*/*z* 231 fragment. This dimethyl disulfide derivative confirmed monounsaturation at C-10 in methyl 10-tricosenoate. Catalytic hydrogenation (PtO_2) of the original methyl ester resulted in methyl tricosanoate, thus excluding the possibility of any methyl branching. All of the above data confirm 10-tricosenoic acid as the most probable structure, which, to the best of our knowledge, also has no literature precedence.

The two novel acids reported in this work also present two important biological considerations. The 11-methylpentadecanoic acid is of interest because other methyl-branched hexadecanoic acids, in particular the 13-methylpentadecanoic acid, display antimicrobial activity against the cariogenic *Streptococcus mutans*.[6] Moreover, it is also known that 3-methylpentadecanoic acid, which was also identified in *C. podatypa*, has larvicidal activity against the mosquito larvae of *Culex pipiens quinquefasciatus*.[10] In addition, 10-methylpentadecanoic acid, also identified in this *C. podatypa*, has been identified in the phospholipids of the sulfate-reducing bacterium *Desulfobacter*.[11] Despite all of these findings, 11-methylpentadecanoic acid remained elusive until this report. It is very likely that it has a bacterial origin and displays some biological activity, but this will be the subject of future work.

The long-chain fatty acid 10-tricosenoic acid seems to be the result of a previously unrecognized fatty acid biosynthetic sequence in sponges. The 6-nonadecenoic acid was previously reported by us from the Caribbean sponge *Geodia gibberosa*[12] and fits 10-tricosenoic acid (four-carbon extension) in a common biosynthetic sequence belonging to a rare *n*-13 fatty acid family. Work is in progress elucidating the origin of unusual fatty acids in marine sponges.

Experimental Section

General Experimental Procedures. IR spectra were recorded on a Nicolet 600 FT-IR spectrophotometer. ^{1}H NMR, ^{13}C NMR, and ^{31}P NMR spectra were recorded on a General Electric QE−300 or Bruker DPX-300 spectrometers. ^{1}H NMR chemical shifts were recorded with respect to internal $(CH_3)_4Si$, ^{13}C NMR chemical shifts are reported in parts per million relative to $CDCl_3$ (77.0 ppm), and ^{31}P NMR chemical shifts are reported also in parts per million relative to triphenylphosphine (−5.29 ppm) in $CDCl_3$−MeOH (2:1) as solvent. Fatty acid methyl esters were analyzed by GC−MS at 70 eV using a Hewlett-Packard 5972A MS ChemStation equipped with a 30 m × 0.25 mm special performance capillary column (HP-5MS) of polymethyl siloxane cross-linked with 5% phenyl methylpolysiloxane.

Sponge Collection. *Calyx podatypa* Van Soest (class Demospongiae, order Haplosclerida, family Phloeodictyidae) was collected near Mona Island, Puerto Rico, in 1992, at 20 m depth by scuba. A voucher specimen (no. MI-030) is stored at the Chemistry Department of the University of Puerto Rico, Río Piedras campus.

Extraction and Isolation of Phospholipids. The sponge (160.9 g) was carefully cleaned and cut into small pieces. Extraction with 2 × 250 mL of $CHCl_3$−MeOH (1:1) yielded the total lipids (20.5 g). The neutral lipids (4.0 g), glycolipids (1.3 g), and phospholipids (4.2 g) were separated by column chromatography on Si gel (60−200 mesh) using the procedure of Privett et al.[13]

Preparation and Isolation of Fatty Acid Derivatives. The fatty acyl components of the phospholipids were obtained as their methyl esters (0.088 g) by reaction of the phospholipids (0.95 g) with methanolic HCl followed by column chromatography.[12] The double-bond positions in the polyunsaturated fatty acids were determined by preparing the corresponding dimethyl disulfide derivatives.[9] Hydrogenations were carried out in 10 mL of MeOH and catalytic amounts of PtO_2.

Methyl 10-Hydroxydecanoate. 10-Hydroxydecanoic acid (3.77 g, 20.0 mmol) and catalytic amounts of HCl were stirred in refluxing MeOH (25 mL) for 24 h. After this time the solvent was removed in vacuo, affording 3.75 g (99.3%) of the methyl ester, which was used in the next step without further purification.[7]

Methyl 10-Bromodecanoate. Phosphorus tribromide (0.35 mL, 3.7 mmol) was added dropwise to methyl 10-hydroxydecanoate (1.92 g, 9.5 mmol) at 0 °C. After the addition, the reaction mixture was warmed to room temperature and left to stand overnight. Unreacted PBr_3 was then quenched with ice and extracted with ether. The organic layer was washed with brine, dried over Na_2SO_4, and concentrated in vacuo to afford 2.40 g (96% yield) of the bromoester whose spectral data was identical to that previously reported.[7]

(9-Methoxycarbonylnonyl)triphenylphosphonium Bromide. To a stirred solution of triphenylphosphine (1.07 g, 4.1 mmol) in benzene was slowly added methyl 10-bromodecanoate (1.09 g, 4.1 mmol). The mixture was refluxed under nitrogen for 5 h. After cooling, the C_6H_6 was removed in vacuo. The crude product was dissolved in CH_2Cl_2 (20 mL) and precipitated by slow dilution with ether (100 mL) to give the salt (1.9 g, 92% yield) as a clear syrup.[7] ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.83−7.69 (15H, m, $-C_6H_5$), 3.62 (3H, s, $-OCH_3$), 2.28 (2H, m, H-2), 1.58 (6H, m, H-3, H-9, H-10), 1.20 (10H, m, H-4, H-5, H-6, H-7, H-8); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 174.3 (s, C-1), 135.1 (s), 133.7 (d), 133.5 (d), 130.4 (d), 51.34 (q, $-OCH_3$), 34.29 (t), 33.99 (t), 30.42 (t), 30.21 (t), 29.00 (t), 28.91 (t), 28.37 (t), 24.79 (t), 24.71 (t).

Methyl 11-Methyl-10-pentadecenoate. To a stirred solution of (9-methoxycarbonylnonyl) triphenylphosphonium bromide (1.05 g, 2.0 mmol) in THF (20 mL) at 0 °C, and under a nitrogen atmosphere, was added potassium *t*-butoxide (1.80 g, 2.0 mmol). The solution was stirred for 10 min, and then a solution of 2-hexanone (0.21 g, 2.1 mmol) in THF (10 mL) was added. The reaction mixture was allowed to stand overnight, and then it was quenched with a saturated ammonium chloride solution (25 mL), extracted with ether (2 × 50 mL), and dried over Na_2SO_4. After evaporation of the solvent in vacuo, the crude product was chromatographed on Si gel, eluting with hexane−ether (8:2, v/v) and afforded the desired product [0.1 g, 18.6% yield of a mixture of 2:1 (*Z*/*E*) isomers]: IR (neat) υ_{max} 3018 (=CH, olefinic), 2965, 2954, 2942, 2926, 2856, 1745 (C=O), 1652, 1605, 1512, 1460, 1388, 1295, 1243 cm^{-1}; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 5.10 [1H, br t, J_{9-10} = 6.6 Hz, H-10, (*E*) and (*Z*)], 3.66 [3H, s, $-OCH_3$, (*E*) and (*Z*)], 2.30 [2H, t, J = 7.5 Hz, H-2, (*E*) and (*Z*)], 2.02−1.97 [4H, m, H-9, H-12, (*E*) and (*Z*)], 1.67 [3H, br s, Me-16, (*Z*)], 1.58 [2H, m, H-3, (*E*) and (*Z*)], 1.44 [3H, br s, Me-16, (*E*)], 1.28 [14H, m, (*E*) and (*Z*)], 0.80 [3H, br t, J = 7.0 Hz, Me-15, (*E*) and (*Z*)]; ^{13}C NMR ($CDCl_3$, 75 MHz) δ 174.3 [s, C-1, (*E*) and (*Z*)], 135.4 [s, C-11, (*Z*)], 135.1 [s, C-11, (*E*)], 125.2 [d, C-10, (*Z*)], 124.5 [d, C-10, (*E*)], 51.4 [q, $-OCH_3$, (*E*) and (*Z*)], 39.4 [t, (*E*) and (*Z*)], 34.1 [t, (*E*) and (*Z*)], 30.3 [t, (*E*) and (*Z*)], 30.2 [t, (*E*) and (*Z*)], 30.1 [t, (*E*) and (*Z*)], 29.9 [t, (*E*) and (*Z*)], 29.4 [t, C-5,

(*Z*)], 29.3 [t, C-5, (*E*)], 29.2 [t, C-4, (*Z*)], 29.1 [t, C-4, (*E*)], 27.9 [t, C-9, (*E*)], 27.7 [t, C-9, (*Z*)], 24.9 [t, (*E*) and (*Z*)], 23.8 [q, C-16, (*Z*)], 22.7 [t, C-14, (*Z*)], 22.3 [t, C-14, (*E*)], 16.3 [q, C-16, (*E*)], 14.1 [q, C-15, (*Z*)], 14.0 [q, C-15, (*E*)].

Methyl 11-Methyl-10(*Z*)-pentadecenoate: t_R = 12.13 min, GC−MS (70 eV) *m*/*z* 268 [M^+] (4), 237 (2), 211 (1), 194 (3), 179 (4), 171 (6), 161 (2), 152 (2), 139 (8), 125 (2), 121 (2), 115 (2), 111 (7), 109 (5), 98 (25), 95 (14), 83 (18), 81 (15), 74 (20), 69 (74), 67 (21), 56 (44), 55 (100).

Methyl 11-Methyl-10(*E*)-pentadecenoate: t_R = 12.27 min, GC−MS (70 eV) *m*/*z* 268 [M^+] (4), 237 (3), 211 (2), 194 (3), 179 (3), 171 (6), 161 (2), 152 (2), 139 (8), 125 (2), 121 (2), 115 (2), 111 (6), 109 (6), 98 (24), 95 (14), 83 (17), 81 (14), 74 (15), 69 (72), 67 (22), 56 (42), 55 (100).

Methyl 11-Methylpentadecanoate (1): distilled MeOH (10 mL) and catalytic amounts of PtO_2 were added to 0.003 g (0.01 mmol) of methyl 11-methyl-10-pentadecenoate. The reaction mixture was allowed to react for 24 h under a hydrogen-filled balloon. Then, it was filtered, washed with ether, and the solvent evaporated in vacuo affording the saturated ester in a quantitative yield: (0.003 g, 100% yield): IR (neat) υ_{max} 2937, 2862, 1508, 1736, 1460, 1446, 1363 cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 3.66 (3H, s, $-OCH_3$), 2.29 (2H, t, J = 7.5 Hz, H-2), 1.33−1.23 (23H, br s, CH_2, H-11), 0.94−0.82 (6H, m, Me-15, Me-16); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 174.3 (s, C-1), 51.4 (q, $-OCH_3$), 37.1 (t, C-10), 36.8 (t, C-12), 34.1 (t, C-2), 32.7 (d, C-11), 31.9 (t, C-9), 31.6 (t, C-8), 29.9 (t), 29.7 (t), 29.4 (t, C-5), 29.3 (t), 29.2 (t), 24.9 (t), 22.7 (t, C-14), 19.7 (q, C-16), 14.1 (q, C-15); GC−MS (70 eV) *m*/*z* 270 [M^+] (20), 239 (5), 227 (10), 213 (7), 199 (1), 186 (3), 185 (5), 171 (1), 163 (6), 157 (2), 143 (19), 129 (7), 111 (6), 109 (6), 97 (17), 87 (73), 85 (19), 83 (23), 81 (10), 75 (19), 74 (100), 69 (34), 59 (6), 57 (84), 55 (51); HREIMS *m*/*z* 270.2554 (calcd for $C_{17}H_{34}O_2$, 270.2559).

Methyl 10-Tricosenoate (2): GC−MS (70 eV) *m*/*z* 368 [M^+] (1), 334 (1), 267 (1), 250 (10), 227 (8), 208 (3), 195 (3), 177 (4), 166 (4), 154 (7), 143 (8), 139 (9), 125 (7), 111 (16), 98 (20), 97 (33), 87 (32), 83 (42), 74 (58), 69 (66), 57 (46), 55 (100).

Methyl 10,11-Bis(methylthio)tricosanoate: GC−MS (70 eV) *m*/*z* 460 [M^+] (2), 398 (3), 369 (4), 327 (2), 281 (6), 253 (5), 231 (16), 229 (9), 208 (12), 199 (9), 163 (6), 149 (9), 111 (16), 97 (36), 87 (93), 85 (41), 74 (100), 69 (55), 57 (94), 55 (79).

Acknowledgment. This work was supported by the National Institutes of Health (NIH) under grant no. 5SO6GM08102. HREIMS spectral determinations were performed at the Nebraska Center for Mass Spectrometry at the University of Nebraska. We thank Dr. Vance Vicente for the taxonomic classification.

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NP9801413