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FURAN ACIDS IN GORGONARIA CORALS

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Unusual long-chain fatty acids (FA) containing a methyl-substituted furan moiety in the C chain are called furan acids (F-acids) and have been found in marine sponges, algae, invertebrates, lobsters, crabs, and certain fish [1]. It is thought that algae and other plants synthesize the C skeleton of F-acids from linoleic acid (18:2*n*-6) that then elongates to higher homologs. Biosynthesis of F-acids in phototropic bacteria, which are common microflora of many marine animals, has been described [2, 3]. It was proposed that F-acids found in animal tissues migrate there from marine bacteria or algae [2]. A study of the FA composition of marine animals of Viet Nam found F-acids in certain species of soft coral [4]. The presence in coral of long-chain F-acids has not been reported. Our goal was to determine the presence, composition, and structure of F-acids in coral.

Colonies of coral were collected in the coastal zone of Viet Nam (South China Sea). Total lipids were isolated by the method of Bligh and Dyer [5]. Methyl esters of fatty acids (MEFA) were prepared from total lipids by the method of Carreau and Dubacq [6]. The composition of the MEFA was analyzed on a Shimadzu GC-2010 gas chromatograph using a capillary column (30 m × 0.25 mm) with Supelcowax 10, vaporizer and detector (FID) temperature 240°C; column 205°C, He carrier gas. MEFA were identified by GC–MS in a Shimadzu GCMS-QP5050A using a capillary column (30 m × 0.25 mm) with HP-5MS phase, temperature program from 160 to 270°C (2°C/min) then 20 min at 270°C, vaporizer and detector temperature 270°C, He carrier gas, electron-impact ionization (70 eV).

A total of 56 species of soft coral belonging to 24 genera and 13 families were screened for F-acids. We found for the first time in coral 10,13-epoxy-11-methyloctadeca-10,12-dienoic (Me-F18); 12,15-epoxy-13-methyleicosa-12,14-dienoic (Me-F20); 12,15-epoxy-13,14-dimethyleicosa-12,14-dienoic (diMe-F20); 14,17-epoxy-15-methyldocosa-14,16-dienoic (Me-F22); and 14,17-epoxy-15,16-dimethyldocosa-14,16-dienoic (diMe-F22) acids. These characteristically had a furan ring with a fatty acid with 9, 11, and 13 C atoms in one α-position; a pentyl group, in the other. One or two methyls were located in the β-position of the furan ring. Mass spectra of MEFA showed allyl cleavage of an alkylcarboxylic group to give a base peak with *m/z* 179 or 165. Allyl cleavage of the alkyl group gave a characteristic peak for $[M - C_4H_9]^+$ and a peak for the furan-containing fragment with *m/z* 123 or 109 for the di- and monomethyl-substituted acid esters, respectively (Table 1). This fragmentation was characteristic of long-chain F-acids [7]. 12,15-Epoxy-13,14-dimethyloctadeca-12,14-dienoic and 14,17-epoxy-15,16-dimethyleicosa-14,16-dienoic acids were also found in small quantities.

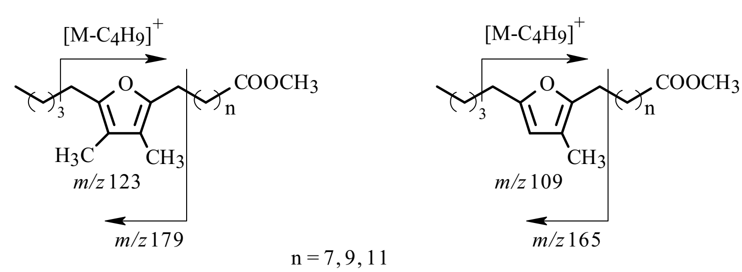

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TABLE 1. Characteristic Ions (m/z, I_{rel}, %) in Mass Spectra of Furan Acid Methyl Esters from Gorgonaria Coral Lipids; n, Number of C Atoms in Alkylester Chain (See Scheme)

	Me-F18	Me-F20	diMe-F20	Me-F22	diMe-F22
n	7	9	9	11	11
M^+	322 (17.7)	350 (18.2)	364 (29.0)	378 (22.9)	392 (35.1)
$[M–MeOH+H]^+$	291 (1.6)	319 (4.1)	333 (4.1)	347 (3.4)	361 (4.8)
$[M–C_4H_9]^+$	265 (4.6)	293 (7.1)	307 (39.4)	321 (6.8)	335 (36.0)
$[M–alkylester]^+$	165 (100)	165 (100)	179 (100)	165 (100)	179 (100)
Furan fragment	109 (17.3)	109 (13.4)	123 (23.5)	109 (14.4)	123 (24.0)

TABLE 2. Total Content and Composition of Principal Furan Acids (% of Total Fatty Acids) of Gorgonaria Corals

Coral species	Total	Me-F18	Me-F20	diMe-F20	Me-F22	diMe-F22
Acabaria erithraea	3.1	2.7	–	–	0.1	0.3
Annella sp.	6.3	0.3	0.7	2.6	0.8	1.6
Bebryce studeri	2.9	0.3	0.8	0.3	0.9	0.6
Chironephthya variabilis	9.7	0.5	0.9	0.8	1.7	5.1
Ellisella plexauroides	8.7	0.5	0.4	0.5	1.6	4.9
Melithaea sp.	3.3	0.4	0.2	0.9	0.6	1.0
Menella praelonga	7.4	0.3	0.5	0.5	2.0	3.7
Paracis sp.	2.8	–	0.5	0.3	0.9	1.1
Siphonogorgia sp.	2.8	0.3	0.5	0.2	0.7	0.9
Viminella sp.	1.3	–	0.2	–	0.8	0.3

F-acids made up from 1.3 to 9.7% of the total FA (Table 2). The concentration of diMe-F22 was greatest in *Chironephthya variabilis* (5.1%). F-acids were found in 10 genera of Gorgonaria corals without zooxanthellae (endosymbiotic microalgae of the genus *Symbiodinium*). F-acids were not found in Gorgonaria with zooxanthellae, alcyonaria and other soft corals. By analogy with other marine animals, a possible source of F-acids in Gorgonaria might have been microalgae occurring in food or bacteria and microalgae associated with the corals. All studied coral specimens had similar food sources. Therefore, the most preferred hypothesis is a temporary nonspecific association of the corals with phototrophic bacteria or microalgae that act as zooxanthellae that are missing in these animals. In this instance, the amount of associated microorganisms could be estimated from the content of F-acid markers.

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