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Polyunsaturated Fatty Acid Methyl Esters from a Soft Coral, *Xenia* sp.

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Abstract

Six polyunsaturated fatty acid methyl esters have been isolated from methanol extract of a soft coral, *Xenia* sp.

Key words: Soft coral, *Xenia* sp., polyunsaturated fatty acid methyl esters

Introduction

Soft corals belonging to the genus *Xenia* have proved to be a rich source of diterpenoids with 9-membered rings named xenia diterpenoids [1]. We have isolated many new xenia diterpenoids from several *Xenia* sp., collected around the Kagoshima area [2]. In the course of our investigation of biologically active compounds from *Xenia* sp., a series of polyunsaturated fatty acid methyl esters have been isolated. In this report, we describe the isolation and structural elucidation of the methyl esters based on spectroscopic methods.

Results and Discussion

Six polyunsaturated methyl esters (1)~(6) have been isolated as oils from the hexane soluble portion of the methanol extract of fresh *Xenia* sp. by use of silica gel and reversed phase HPLC. The molecular formulas in each compounds 1~6 were determined by ^1H , ^{13}C NMR, and mass spectroscopy. The presence of double bonds and a methyl ester in each of these compounds was established by the UV [λ_{max} 206~209 nm (ϵ , 6600~12300)], IR [ν_{max} 1750~1745 cm^{-1}], ^1H NMR [δ ca 3.7 (3H, s)], and ^{13}C NMR [δ 51.5 or 51.9 (COOCH₃), and ca 174 (COOCH₃)] spectra. The stereochemistry of all the double bonds was confirmed as *Z* from the fact that the signal width of the signals (W1/2h: ca 12.5 Hz) in the ^1H NMR spectra were narrow and bands typical of *trans* double bonds were not found in the IR spectrum.

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The ^1H NMR spectrum of **1**, $\text{C}_{21}\text{H}_{34}\text{O}_2$ (M^+ m/z 318) showed signals typical of doubly allylic methylene protons at δ 2.81-2.85 (6H, *m*) and olefinic protons at δ 5.31-5.43 (8H, *m*). A triplet at δ 2.32 (2H, *t*, $J=7.5$ Hz) due to methylene protons adjacent to a carbomethoxyl group was coupled to methylene protons at δ 1.72 (2H, *quint*, $J=7.3$ Hz), which was further coupled to allylic methylene protons at δ 2.11 (2H, *q*, $J=7.0$ Hz). The signals for another allylic methylene groups were observed at δ 2.06 (2H, *q*, $J=7.0$ Hz), which were coupled to methylene protons at δ 1.36 (2H, *quint*, $J=7.7$ Hz). Methyl protons appeared as a triplet at δ 0.89 (3H, $J=6.8$ Hz). The latter two signals were also coupled to two-methylene proton signals at δ 1.30 (2H \times 2, *m*). The above results showed that **1** is methyl 5*Z*, 8*Z*, 11*Z*, 14*Z*-eicosatetraenoate.

The ^1H NMR spectrum of **2**, $\text{C}_{21}\text{H}_{32}\text{O}_2$ was similar to that of **1**, except for two additional doubly allylic protons at δ 2.81-2.86 (2H, *m*) and two olefinic protons at δ 5.28-5.43 (2H, *m*). The methyl resonance at δ 0.98 (3H, *t*, $J=7.5$ Hz) was coupled to an allylic methylene signal at δ 2.07 (2H, *quint*, $J=7.5$ Hz). Thus the structure of **2** was assigned as methyl 5*Z*, 8*Z*, 11*Z*, 14*Z*, 17*Z*-eicosapentaenoate.

Compound **3**, $\text{C}_{19}\text{H}_{32}\text{O}_2$ (M^+ m/z 292) showed the presence of two doubly allylic methylene groups at δ 2.81 (4H, *t*, $J=5.7$ Hz) and three olefinic bonds at δ 5.30-5.43 (6H, *m*) in the ^1H NMR spectrum. Signals due to methylene protons adjacent to a carbomethoxyl group appeared at δ 2.32 (2H, *t*, $J=7.5$ Hz), which was coupled to methylene group resonating at δ 1.65 (2H, *quint*, $J=7.7$ Hz). The latter protons were also coupled to methylene protons resonating at δ 1.40 (2H, *quint*, $J=7.7$ Hz), which were in turn coupled to allylic methylene signal at δ 2.09 (2H, *q*-like, $J=6.2$ Hz). Thus the structure of **3** was determined as methyl 6*Z*, 9*Z*, 12*Z*-octadecatrienoate (methyl γ -linolate).

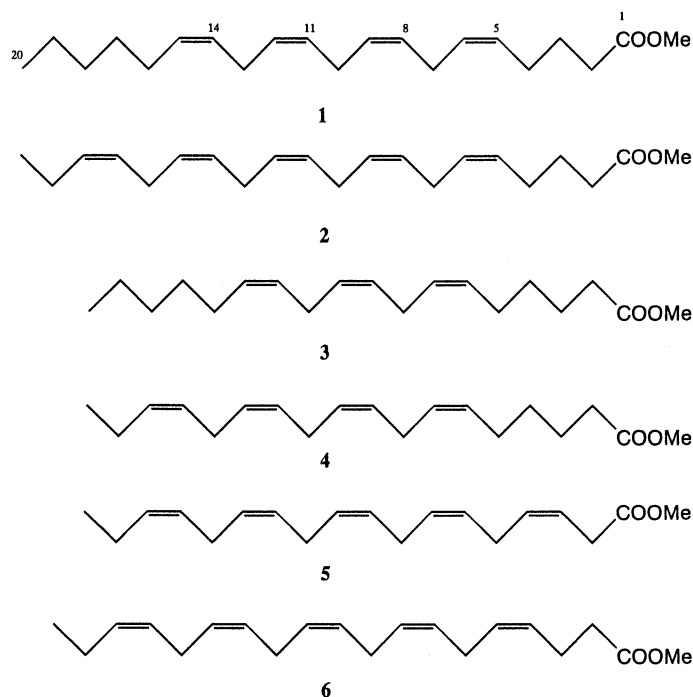
The molecular formula of **4**, $\text{C}_{19}\text{H}_{30}\text{O}_2$ (M^+ m/z 290) has two less hydrogens than that of **3**. In the ^1H NMR spectrum of **4**, signals due to a $-\text{HC}=\text{CH}(\text{CH}_2)_4\text{COOMe}$ moiety were observed [δ 1.40 (2H, *quint*, $J=7.5$ Hz, H-4), 1.65 (2H, *quint*, $J=7.7$ Hz, H-3), 2.09 (2H, *q*, $J=7.3$ Hz, H-5), and 2.32 (2H, *t*, $J=7.5$ Hz, H-2)] as well observed in the case of **3**. Signals due to a $\text{CH}_3\text{CH}_2\text{CH}=\text{CH}$ - moiety at δ 0.98 (3H, *t*, $J=7.7$ Hz, H-18) and 2.07 (2H, *quint*, H-17) were also observed and the remaining nonconjugated *cis* double bonds can only be accommodated by structure **4**, methyl 6*Z*, 9*Z*, 12*Z*, 15*Z*-octadecapentaenoate.

Compound **5**, $\text{C}_{19}\text{H}_{28}\text{O}_2$ (M^+ m/z 288) possessed five double bonds. The ^1H NMR spectrum of **5** exhibited close similarities to those of **4**, except for resonances due to two additional doubly allylic methylene protons at δ 2.80-2.86 (2H, *m*) and two olefinic protons at δ 5.28-5.41 (2H, *m*). Another major difference was that the $-\text{HC}=\text{CH}(\text{CH}_2)_4\text{COOMe}$ moiety in **4** was replaced by a $-\text{HC}=\text{CHCH}_2\text{COOMe}$ moiety, which was confirmed by signals at δ 3.13 (2H, *d*, $J=5.5$ Hz, H-2) in the ^1H NMR spectrum of **5**. Therefore compound **5** is the 3, 4-dehydro derivative of **4**, or methyl 3*Z*, 6*Z*, 9*Z*, 12*Z*, 15*Z*-octadecapentenoate.

The ^1H NMR spectrum of **6** $\text{C}_{20}\text{H}_{30}\text{O}_2$ (M^+ m/z 302) showed the presence of four doubly allylic methylene groups at δ 2.80-2.86 (8H, *m*) and five double bonds at δ 5.28 (10H, *m*). Signals at δ 0.98 (3H, *t*, $J=7.5$ Hz) and 2.08 (2H, *quint*, $J=7.3$ Hz) were assigned to a $\text{CH}_3\text{CH}_2\text{CH}=\text{CH}$ - moiety as observed in the compounds **2**, **4** and **5**. Two groups of methylene

protons in a =CHCH₂CH₂COOMe moiety displayed characteristic resonances at δ 2.35-2.43 (4H), and the structure is proposed to be methyl 4*Z*, 7*Z*, 10*Z*, 13*Z*, 16*Z*-nonadecapentenoate.

Compounds 1~6 may be artifacts of the isolation procedure, and may be formed by methanolysis of biological esters, since they could not be prepared from their acids in the presence of MeOH and silica gel. Compound 5 may be, however, a new one, because we could not find it in the Chemical Abstracts.



Experimental

Extraction and isolation. *Xenia* sp. (5.7 Kg) was collected at Bonotsu, Kagoshima prefecture and identified by Dr. Y. Imahara. The animal was extracted three times with MeOH. The combine MeOH solns were concd to afford a brown residue. The residue was diluted with H₂O and extracted with hexane. A portion (4.6 g) of the hexane extract (8.3 g) was absorbed on silica gel and subjected to CC of silica gel packed in hexane, fractions (100 ml) being collected as follows: 1-2 (CH₂Cl₂-hexane, 1:1), 3-4 (CH₂Cl₂), 5-6 (MeOH-CH₂Cl₂, 1:49), 7-8 (MeOH-CH₂Cl₂, 1:19), 9-10 (MeOH-CH₂Cl₂, 1:9), 11-12 (MeOH-CH₂Cl₂, 1:1), and 13-14 (MeOH). Fractions 1-2 (1.15 g) was again chromatographed on silica gel using by EtOAc-hexane (3:97) and then HPLC on ODS with MeOH-H₂O (19:1 to 9:1) to give 1 (47.8 mg), 3 (22.1 mg), 4 (21.1 mg), 2 (17.3 mg), 6 (5.7 mg), and 5 (3.1 mg) in order of polarity.

Compound 1. Oil, UV $\lambda_{\max}^{\text{MeOH}}$ nm (ϵ): 209 (9200); IR ν_{\max}^{film} cm⁻¹: 1750, 1660; ¹H NMR: δ 0.89 (3H, *t*, *J*=6.8 Hz, H-20), 1.3 (4H, *m*, H-18 and 19), 1.36 (2H, *quint*, *J*=7.7 Hz, H-17), 1.72 (2H,

quint, $J=7.3$ Hz, H-3), 2.06 (2H, *q*, $J=7.0$ Hz, H-16), 2.11 (2H, *q*, $J=7.0$ Hz, H-4), 2.32 (2H, *t*, $J=7.5$ Hz, H-2), 2.81-2.85 (6H, *m*, H-7, 10, and 13), 3.66 (3H, *s*, COOMe), 5.31-5.43 (8H, *m*, H-5, 6, 8, 9, 11, 12, 14, and 15); ^{13}C NMR: δ 14.1 (CH_3), 22.6, 24.8, 25.6, 25.7 \times 3, 26.6, 27.2, 29.4, 31.5, and 33.5 (CH_2), 51.5 (COOCH_3), 127.6, 127.9, 128.2, 128.2, 128.6, 128.9, 128.9, and 130.5 ($\text{CH}=\text{CH}$), 174.0 (COOCH_3); EIMS m/z 318 $[\text{M}]^+$.

Compound 2. Oil, UV $\lambda_{\text{max}}^{\text{MeOH}}$ nm (ϵ): 209 (15800), IR $\nu_{\text{max}}^{\text{film}}$ cm^{-1} : 1745, 1650; ^1H NMR: δ 0.98 (3H, *t*, $J=7.5$ Hz, H-20), 1.71 (2H, *quint*, $J=7.5$ Hz, H-3), 2.07 (2H, *quint*, $J=7.5$ Hz, H-19), 2.11 (2H, *q*, $J=7.5$ Hz, H-4), 2.32 (2H, *t*, $J=7.5$ Hz, H-2), 2.81-2.86 (8H, *m*, H-7, 10, 13, and 16), 3.67 (3H, *s*, COOMe), 5.31-5.43 (10H, *m*, H-5, 6, 8, 9, 11, 12, 14, 15, 17, and 18); ^{13}C NMR: δ 14.3 (CH_3), 20.6, 24.8, 25.6, 25.6 \times 3, 26.6, and 33.5 (CH_2), 51.5 (COOCH_3), 127.0, 127.9, 128.1, 128.1, 128.2, 128.3, 128.6, 128.9, 129.0, and 132.1 ($\text{CH}=\text{CH}$), 174.1 (COOCH_3); EIMS m/z 316 $[\text{M}]^+$, 287 $[\text{M-Et}]^+$.

Compound 3. Oil, UV $\lambda_{\text{max}}^{\text{MeOH}}$ nm (ϵ): 209 (6600); IR $\nu_{\text{max}}^{\text{film}}$ cm^{-1} : 1750, 1650; ^1H NMR: δ 0.89 (3H, *t*, $J=6.8$ Hz, H-18), 1.30 (6H, *m*, H-15, 16, and 17), 1.40 (2H, *quint*, $J=7.7$ Hz, H-4), 1.65 (2H, *quint*, $J=7.7$ Hz, H-3), 2.07 (2H, *q*, $J=7.5$ Hz, H-14), 2.09 (2H, *q*, $J=6.2$ Hz, H-5), 2.32 (2H, *t*, $J=7.0$ Hz, H-2), 2.81 (4H, *t*, $J=5.7$ Hz, H-8 and 11), 3.67 (3H, *s*, COOMe), 5.30-5.43 (6H, *m*, H-6, 7, 9, 10, 12, and 13); ^{13}C NMR: δ 14.1 (CH_3), 22.6, 24.6, 25.7 \times 2, 26.9, 27.2, 29.1, 29.4, 31.5, and 34.0 (CH_2), 51.5 (COOCH_3), 127.6, 128.1, 128.3, 128.4, 129.6, and 130.5 ($\text{CH}=\text{CH}$), 174.1 (COOCH_3); EIMS m/z : 292 $[\text{M}]^+$.

Compound 4. Oil, UV $\lambda_{\text{max}}^{\text{MeOH}}$ nm (ϵ): 208 (8800); IR $\nu_{\text{max}}^{\text{film}}$ cm^{-1} : 1745, 1650; ^1H NMR: δ 0.98 (3H, *t*, $J=7.7$ Hz, H-18), 1.40 (2H, *quint*, $J=7.5$ Hz, H-4), 1.65 (2H, *quint*, $J=7.7$ Hz, H-3), 2.07 (2H, *quint*, $J=7.3$ Hz, H-17), 2.09 (2H, *q*, $J=6.6$ Hz, H-5), 2.32 (2H, *t*, $J=7.5$ Hz, H-2), 2.80-2.84 (6H, *m*, H-7, 10, and 14), 3.67 (3H, *s*, COOMe), 5.28-5.43 (8H, *m*, H-6, 7, 9, 10, 12, 13, 15, and 16); ^{13}C NMR: δ 14.3 (CH_3), 20.6, 24.6, 25.6, 25.7, 26.9, 29.1, and 34.0 (CH_2), 51.5 (COOCH_3), 127.1, 127.9, 128.1, 128.2, 128.3, 128.5, 129.7, and 132.0 ($\text{CH}=\text{CH}$), 174.1 (COOCH_3); EIMS m/z : 290 $[\text{M}]^+$, 261 $[\text{M-Et}]^+$.

Compound 5. Oil, UV $\lambda_{\text{max}}^{\text{MeOH}}$ nm (ϵ): 208 (11500), IR $\nu_{\text{max}}^{\text{film}}$ cm^{-1} : 1745, 1650; ^1H NMR: δ 0.98 (3H, *t*, $J=7.5$ Hz, H-18), 2.08 (2H, *quint*, $J=7.3$ Hz, H-17), 2.80-2.86 (8H, *m*, H-5, 8, 11, and 14), 3.69 (3H, *s*, COOMe), 5.28-5.41 (6H, *m*, H-4, 6, 7, 9, 10, 12, 13, and 15), 5.60 (2H, *m*, H-3 and 16); ^{13}C NMR: δ 14.3 (CH_3), 20.6, 25.6, 25.6 \times 2, 25.8, and 32.8 (CH_2); 51.9 (COOCH_3), 121.3, 127.0, 127.4, 127.8, 127.9, 128.4, 128.6, 128.7, 131.4, and 132.1 ($\text{CH}=\text{CH}$), 172.2 (COOCH_3); EIMS m/z : 288 $[\text{M}]^+$, 259 $[\text{M-Et}]^+$.

Compound 6. Oil, UV $\lambda_{\text{max}}^{\text{MeOH}}$ nm (ϵ): 206 (12300), IR $\nu_{\text{max}}^{\text{film}}$ cm^{-1} : 1750, 1650; ^1H NMR: δ 0.98 (3H, *t*, $J=7.5$ Hz, H-19), 2.08 (2H, *quint*, $J=7.3$ Hz, H-18), 2.35-2.43 (4H, *m*, H-2 and 3), 2.80-2.86 (8H, *m*, H-6, 9, 12, and 15), 3.68 (3H, *s*, COOMe), 5.28-5.45 (10H, *m*, H-4, 5, 7, 8, 10, 11, 13, 14, 16, and 17); ^{13}C NMR: δ 14.3 (CH_3), 20.6, 22.8, 25.6 \times 2, 25.7 \times 2 and 34.0 (CH_2), 51.6 (COOCH_3), 127.0, 127.9, 128.1, 128.2, 128.2, 128.3, 128.3, 128.6, 129.3, and 132.1 ($\text{CH}=\text{CH}$), 173.6 (COOCH_3); EIMS m/z : 302 $[\text{M}]^+$, 273 $[\text{M-Et}]^+$.

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