New Glycosphingolipids from the Fungus *Catathelasma ventricosa*

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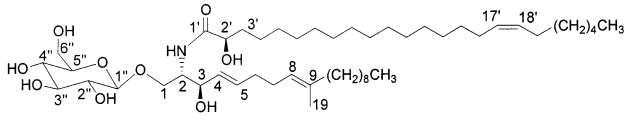
Three new glycosphingolipids with a *cis*-Δ^{17}-fatty acyl moiety, namely, catacerebrosides A−C (**1**−**3**), along with two known glycosphingolipids, cerebrosides B and D, six known ergostane-type sterols, and tyrosamine were isolated from the fungus *Catathelasma ventricosa*. The structures of **1**−**3** were elucidated on the basis of spectroscopic analysis and chemical methods.

Glycosphingolipids and their breakdown products are important components in the cell membranes of animals and plants and are emerging as important second messengers for various cellular processes, such as cell cycle arrest, differentiation, senescence, apoptosis, and others.[1−4] A series of new glycosphingolipids and sphingolipids has been isolated recently from natural sources.[5−8] Glycosphingolipids and sphingolipids possess a variety of biological activities,[1,2] e.g., antihepatotoxic activity,[7] ionophoric activity for Ca^{2+} ions,[9] immunomodulating activity,[10,11] inhibition of the proliferation of lymphocytes stimulated with concanavalin A,[12] and cyclooxygenase-2 inhibition.[13]

The fungus *Catathelasma ventricosa* (PK.) Sing. (Tricholomataceae), mainly distributed in the southwestern region of mainland China, has not been investigated chemically before. In the current study, three new glycosphingolipids with a unique *cis*-Δ^{17}-fatty acyl moiety, namely, catacerebrosides A−C (**1**−**3**), together with cerebroside B, cerebroside D, six sterols, and tyrosamine were isolated from this fungus. The structures of the new glycosphingolipids (**1**−**3**) were elucidated on the basis of spectroscopic analysis and chemical methods.



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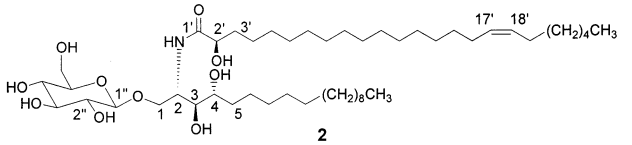

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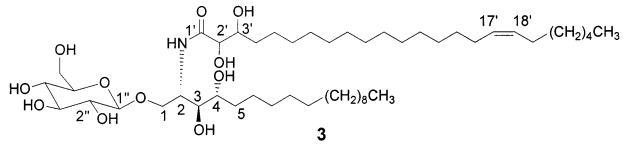

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The ethanolic crude extract of the whole bodies of the fungus was partitioned with ethyl acetate and water to obtain an ethyl acetate-soluble fraction, which was then subjected to extensive column chromatography to afford three new compounds, catacerebrosides A (55 mg), B (41 mg), and C (62 mg), as well as nine known compounds.

Catacerebroside A (**1**), a white amorphous solid, showed a protonated molecular ion at *m/z* 838.6887 $[M + H]^+$ (calcd for $C_{49}H_{92}NO_9$, 838.6772) in the positive HRESIMS, corresponding to the molecular formula $C_{49}H_{91}NO_9$. An IR absorption band at 3394 cm^{-1} indicated the existence of hydroxyl and amide groups. The typical IR absorptions at 1647 and 1539 cm^{-1} suggested compound **1** was a secondary amide derivative, which was supported by the presence of a nitrogen-attached carbon signal at δ 55.1 and a carbonyl signal at δ 177.7 in the ^{13}C NMR spectrum (Table 1). In the ^1H NMR spectrum (Table 1), one olefinic proton signal at δ 5.33 (1H, m, H-8), assignable to a trisubstituted double bond, and four olefinic proton signals at δ 5.68 (1H, dd, J = 15.3, 7.4 Hz, H-4), 5.93 (1H, dt, J = 15.3, 5.8 Hz, H-5), and 5.53 (2H, m, H-17′ and H-18′), attributable to the presence of two disubstituted double bonds, were evident. The ^1H NMR spectrum also showed the presence of three methyl groups at δ 1.79 (3H, s, H-19) and 1.07 (6H, t, J = 7.2 Hz, H-18 and H-24′). Comparison of the ^1H and ^{13}C NMR data of **1** with those of cerebrosides A−D[14] indicated that compound **1** is most likely a glycosphingolipid analogue. The amino alcohol moiety could be identified as a sphingosine unit by the characteristic signals that appeared in the ^1H NMR and ^{13}C NMR spectra, especially due to the presence of typical Δ^4 and Δ^8 double bonds and a Me-19 group. A glucopyranosyl moiety could be distinguished in the structure of **1** on the basis of ^1H and ^{13}C NMR spectra. Methanolysis of compound **1** afforded 2-hydroxytetracos-17-enoic acid methyl ester, which was identified by EIMS and ozonolysis. The double bond was located between C-17′ and C-18′ by ozonolysis of 2-hydroxytetracos-17-enoic acid methyl ester to produce heptaldehyde, $C_7H_{14}O$, which was identified by GC-EIMS and co-injection with an authentic sample.

The linkages of the three parts of the molecule of **1** were resolved from the HMBC spectrum. The carbon signal at δ 177.7 (C-1′) correlated with the proton signals at δ 4.19 (H-2) and 4.18 (H-2′). The proton signal at δ 4.19 (H-2) gave cross-peaks with carbon signals at δ 73.4 (C-3) and 70.3 (C-1), and the latter also correlated with the proton signal at δ 4.46 (H-1″). The carbon signal at δ 73.4 (C-3) showed cross-peaks with the proton signals at δ 5.68 (H-4) and 5.93 (H-5). In turn, the proton signal at δ 5.93 (H-5) showed correlations with two methylene carbons at δ 34.9 (C-6) and 29.2 (C-7), while the proton signal at δ 5.33 (H-8) correlated with the carbon signals at δ 137.3 (C-9), 41.3 (C-10), 34.9 (C-6), 29.2 (C-7), and 16.7 (C-19). The planar structure of **1** was thus formulated. The assignments (Table

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Table 1. ^{1}H and ^{13}C NMR Data of Compound **1**[a]

position	δ_H	δ_C	position	δ_H	δ_C
1	4.30 (1H, dd, 10.5, 3.5) 3.90 (1H, dd, 10.5, 7.0)	70.3	3′	1.70, 1.80 (each 1H, m)	36.4
2	4.19 (1H, m)	55.1	4′	1.52 (2H, m)	26.7
3	4.31(1H, t, 6.9)	73.4	5′−15′	1.40−1.50	30.8−31.4
4	5.68 (1H, dd, 15.3, 7.4)	131.6	16′	2.24 (2H, m)	28.5
5	5.93 (1H, dt, 15.3, 5.8)	135.1	17′, 18′	5.53 (2H, m)	131.4
6	2.25 (2H, m)	34.9	19′	2.24 (2H, m)	28.5
7	2.23 (2H, m)	29.2	20′−21′	1.40−1.50	30.8−31.4
8	5.33 (1H, m)	125.3	22′	1.40−1.50	33.6
9		137.3	23′	1.40−1.50	24.2
10	2.17 (2H, t, 7.6)	41.3	24′	1.07 (3H, t, 7.2)	15.0
11	1.48 (2H, m)	29.5	1″	4.46 (1H, d, 8.0)	105.2
12−15	1.40−1.55	30.8−31.4	2″	3.38 (1H, t, 7.8)	75.5
16	1.40−1.55	33.6	3″	3.49 (1H,m)	78.5
17	1.40−1.55	24.2	4″	3.50 (1H, m)	72.0
18	1.07 (3H, t, 7.2)	15.0	5″	3.51 (1H, m)	78.5
19	1.79 (3H, s)	16.7	6″	4.06 (1H, d, 11.7) 3.86 (1H, dd, 11.7, 5.2)	63.2
1′		177.7			
2′	4.18 (1H, m)	73.6			

[a] Spectra were measured in CD_3OD; *J* values are in Hz.

1) of the ^{1}H NMR and ^{13}C NMR data of **1** were achieved unambiguously from the ^{1}H−^{1}H COSY, HMQC, and HMBC spectra.

The large vicinal coupling constants of H-4 and H-5 (J = 15.3 Hz) clearly indicated an *E*-geometry of the Δ^4 double bond in **1**.[14] The Δ^8 double bond was also assigned as *E* on the basis of the upfield shifted carbon signal of Me-19.[15] The *cis*-configuration of the $\Delta^{17'}$ double bond was evident from the significantly upfield shifted carbon signals of C-16′ (28.5) and C-19′ (28.5)[13,15] and the relatively small coupling constants of H-17′ and H-18′ ($W/2 \approx 3.7$ Hz). The carbon signals of the sugar moiety in the ^{13}C NMR spectrum suggested a β-configuration, which was confirmed by the large coupling constant of H-1″ at δ 4.46 (1H, d, J = 8.0 Hz) and H-2″ at δ 3.38 (1H, t, J = 7.8 Hz). On the basis of biogenetic reasoning, and the co-isolation from *C. ventricosa* of cerebrosides B and D, which have the same sugar with a D-configuration, the sugar moiety of **1** was assigned as β-D-glucopyranosyl. By considering biogenetic[2] and steric factors, the chemical shift of H-2 and the chemical shifts of the carbon signals of C-1 to C-3, C-1′, and C-2′ of glucosphingolipids and sphingolipids may be utilized to determine their absolute stereochemistry.[8,17,18] The proton signal at δ 4.19 (H-2) and the carbon signals at δ 70.3 (C-1), 55.1 (C-2), 73.6 (C-3), 177.7 (C-1′), and 73.4 (C-2′) of **1** were in good agreement with those reported for glycosphingonines (as model structures) with a 2*S*,3*R*,2′*R* configuration.[7,14,16] The structure of **1** was assigned therefore as 1-*O*-β-D-glucopyranosyl-(2*S*,3*R*,4*E*,8*E*)-2-[(2′*R*,17′*Z*)-2′-hydroxy-17′-tetracosenoylamino]-9-methyl-4, 8-octadecadiene-1,3-diol.

Catacerebroside B(**2**) showed the molecular formula $C_{48}H_{93}NO_{10}$, as deduced from the positive HRESIMS at *m*/*z* 844.6862 $[M + H]^+$ (calcd for $C_{48}H_{94}NO_{10}$, 844.6878). The IR absorption band at 3405 cm^{-1} indicated the presence of hydroxyl and amide groups. The typical IR absorptions at 1643 and 1535 cm^{-1} suggested compound **2** was also a secondary amide, as supported by the presence of a nitrogen-attached carbon signal at δ 51.9 and a carbonyl signal at δ 175.8 in the ^{13}C NMR spectrum. The presence of a β-glucopyranosyl moiety and a double bond was evident from the ^{1}H and ^{13}C NMR spectra (Experimental Section). The ^{1}H NMR data showed the presence of two olefinic proton signals at δ 5.50 (2H, m), multiple proton signals between δ 1.26−1.38, and a triplet proton signal at δ 0.93 (6H, t, J = 7.6 Hz), suggesting the presence of two long-chain aliphatic chains, one of which possesses a double bond. Except for the oxygenated carbon signals of the sugar moiety, there were three other oxygenated methine carbon signals (at δ 76.0, 72.7, 72.5) and one secondary carbon signal (δ 70.6) attached to oxygen appearing in the ^{13}C NMR spectrum. Accordingly, compound **2** was seen to be also a glycosphingolipid analogue. Methanolysis of **2** generated 2-hydroxytetracos-17-enoic acid methyl ester, which was identical with the methanolysis product found in compound **1**. Apart from this fatty acid moiety and the sugar unit, the remaining part of the molecule **2** was a moiety of 1,3,4-trihydroxy-2-aminooctadecane. The connectivity of the three moieties was determined from the HMBC spectrum, in which the carbonyl signal at δ 175.8 correlated with proton signals at δ 8.55 (NH), 5.26 (H-2), and 4.60 (H-2′), and the H-1″ proton signal correlated with C-1 at δ 70.6. Both the H-1a and H-1b signals at δ 4.50 and 4.75, respectively, showed cross-peaks with C-1″ at δ 105.7. The full assignments (Experimental Section) of the ^{1}H NMR and ^{13}C NMR data of **2** were determined from the ^{1}H−^{1}H COSY, HMQC, and HMBC spectra.

The $\Delta^{17'}$ double bond of **2** was determined to be *Z* by the upfield shifted carbon chemical shifts of C-16′ (27.7) and C-19′ (27.7)[13,15] and the relatively small coupling constant of H-17′ and H-18′ ($W/2 \approx 5.3$ Hz). The proton signal at δ 5.26 (H-2) and the carbon signals at δ 70.6 (C-1), 51.9 (C-2), 76.0 (C-3), 72.5 (C-4), 175.8 (C-1′), and 72.7 (C-2′) of **2** were very close to those of model glycosphingolipids, such as aralia cerebroside[8] and pokeweed cerebrosides[13] with 2*S*,3*S*,4*R*-stereochemistry. The structure of **2** was thus determined as 1-*O*-β-D-glucopyranosyl-(2*S*,3*S*,4*R*)-2-[(2′*R*,-17′*Z*)-2′-hydroxy-17-tetracosenoylamino]octadecane-1,3,4-triol.

Catacerebroside C (**3**) was obtained as a white amorphous powder. The positive HRESIMS revealed a protonated molecular formula of $C_{48}H_{94}NO_{11}$ $[M + H]^+$ (*m*/*z* 860.6841, calcd 860.6827). The IR and ^{1}H and ^{13}C NMR spectra (Experimental Section) of compound **3** were very similar to those of **2** except for the presence of one more hydroxyl group, and suggested compound **3** was an analogue of **2**. Methanolysis of compound **3** afforded 2,3-dihydroxytetracos-17-enoic acid methyl ester, which was identified by EIMS (*m*/*z* 412) and ^{1}H NMR and by analysis of its ozonolysis products on GC-EIMS. A 1,3,4-trihydroxy-2-aminooctadecane moiety was identified by spectral analysis in a manner analogous to that for compound **2**. The

HMBC spectrum showed cross-peaks for the carbonyl signal at δ 174.3 with the proton signals at δ 8.66 (NH), 5.28 (H-2), 4.70 (H-2′), and 4.51 (H-3′). In turn, the H-2 signal at δ 5.28 (H-2) correlated with the carbon signals at δ 70.3 (C-1), 75.8 (C-3), and 174.3 (C-1′), and the H-1″ proton signal at δ 4.97 correlated with C-1 at δ 70.3.

The $\Delta^{17'}$ double bond in the fatty acid moiety was determined to be *Z*, and the stereochemistry of phytosphingosine unit in **3** was assigned as 2*S*,3*S*,4*R* for the same reasons as in **2**. One more hydroxyl was present in the fatty acid moiety of compound **3**, and by comparison with the fatty acid moiety of compound **2**, the chemical shifts of C-1′ and C-2′ were affected. Because there are no suitable models of glycosphingolipids or sphingolipids with a 2′,3′-dihydroxy fatty acyl moiety, the absolute configurations of C-2′ and C-3′ could not readily be established from the available data. The structure of compound **3** was thus assigned as 1-*O*-β-D-glucopyranosyl-(2*S*,3*S*,4*R*)-2-[(17′*Z*),2′,3′-dihydroxy-17-tetracosenoylamino]octadecane-1,3,4-triol. This is the first report of a glycosphingolipid with a 2,3-dihydroxyl fatty acyl moiety.

Cerebrosides B and D were identified on the basis of ^{1}H and ^{13}C NMR spectra and ESIMS.[14] Tyrosamine,[19] 22*E*,-24*R*-ergosta-7,22-diene-3β,5α,6β,9α-tetraol, 22*E*,24*R*-ergosta-7,22-diene-3β,5α,6β,-triol, ergosterol peroxide,[20] 22*E*,24*R*-ergosta-7,22-dien-3β-ol, 22*E*,24*R*-ergosta-7,22-dien-3-*O*-β-D-glucopyranoside,[21] and ergosta-4,6,8(14),22-tetraen-3-one[22,23] were identified on the basis of ^{1}H NMR spectral data and comparison with authentic samples (co-TLC).

Experimental Section

General Experimental Procedures. Optical rotations were determined on a Perkin-Elmer 341 polarimeter at room temperature. UV spectra were measured on a Shimadzu UV-210A spectrometer. IR spectra were recorded on a Perkin-Elmer 577 spectrometer using KBr disks. NMR spectra were measured on a Bruker AM-400 spectrometer with TMS as internal standard. EIMS (70 eV) was carried out on a Finnigan-MAT 95 mass spectrometer, and ESIMS was recorded on a Finnigan LCQ^{DECA} mass spectrometer. HRESIMS were measured on a Thermo Electron Corporation FT-mass spectrometer. All solvents used were of analytical grade (Shanghai Chemical Plant, Shanghai, People's Republic of China). Silica gel (200−300 mesh) was used for column chromatography, and precoated silica gel GF254 plates (Qingdao Marine Chemical Plant, Qingdao, People's Republic of China) were used for TLC. C_{18} reversed-phased silica gel (150−200 mesh, Merck) and MCI gel (CHP20P, 75−150 μm, Mitsubishi Chemical Industries Ltd.) were also used for column chromatography.

Fungal Material. *Catathelasma ventricosa* was collected from the Kunming area of Yunnan Province, the People's Republic of China, in late July of 1996, and authenticated by Professor Mu Zang of Kunming Institute of Botany, where a voucher specimen (HKAS30227) was deposited.

Extraction and Isolation. A 7.5 kg quantity of the minced fresh mushroom bodies was extracted with 95% ethanol extensively at room temperature to give a dark crude extract (304 g), which was dissolved in water (3 L) to form a suspension and then partitioned with ethyl acetate to afford an ethyl acetate-soluble fraction E (58 g). This fraction was subjected to column chromatography eluted with petroleum ether containing increasing amounts of acetone to afford fractions 1−6. Fraction 2 (25.2 g) was recrystallized from $CHCl_3$ to yield 22*E*,24*R*-ergosta-7,22-dien-3β-ol (20.5 g). Fraction 3 (6.1 g) was applied to a silica gel column eluted with petroleum ether−ethyl acetate (8:1) to give ergosterol peroxide (125 mg) and ergosta-4,6,8(14),22-tetraen-3-one (78 mg). Fraction 4 (5.5 g) was separated on a silica gel column eluted with $CHCl_3$−MeOH (15:1) to yield 22*E*,24*R*-ergosta-7,22-diene-3β,5α,6β,9α-tetraol (32 mg) and 22*E*,24*R*-ergosta-7,22-diene-3β,5α,6β-triol (190 mg). Fraction 5 (2.5 g) was purified on a silica gel column eluted with $CHCl_3$−MeOH−HCOOH (10:1:0.1) to afford 22*E*,24*R*-ergosta-7,22-dien-3-*O*-β-D-glucopyranoside (21 mg) and tyrosamine (11 mg). Fraction 6 (2.1 g) was subjected to a column containing MCI gel CHP 20P eluted with 90% methanol in water to afford **1** (55 mg), **2** (41 mg), **3** (62 mg), and a mixture of cerebrosides B and D (110 mg), which was further applied to a reversed-phase C_{18} silica gel column, eluted with 90% MeOH in water, to yield cerebroside B (41 mg) and cerebroside D (32 mg).

Catacerebroside A (1): white amorphous powder; $[\alpha]^{20}_D$ −5.0° (*c* 1.1, MeOH); IR (KBr) ν_{max} 3394 (OH), 2922, 1647, 1539 (amide), 1467, 1082 (C−O) cm^{-1}; ^{1}H and ^{13}C NMR (see Table 1); positive ESIMS *m*/*z* 860 $[M + Na]^+$; positive HRESIMS *m*/*z* 838.6887 $[M + H]^+$ (calcd for $C_{49}H_{92}NO_9$, 838.6772).

Methanolysis of Catacerebroside A (1). An aliquot (10.3 mg) of **1** was dissolved in 5 mL of methanol containing 5% HCl and refluxed for 18 h. The reaction mixture was neutralized with $NaHCO_3$ and diluted with 10 mL of water. The aqueous solution was extracted with *n*-hexane three times, and the organic phase was dried with anhydrous Na_2SO_4. After removal of solvent, 3.8 mg of 2-hydroxytetracos-17-enoic acid methyl ester was afforded: EIMS *m*/*z* 396 $[M]^+$ (48), 365 (31), 337 $[M - COOCH_3]^+$ (55), 111 (52), 97 (88), 83 (95), 69 (92), 55 (100).

Ozonolysis of 2-Hydroxytetracos-17-enoic Acid Methyl Ester. Ozone was passed into a stirred solution of 2-hydroxytetracos-17-enoic acid methyl ester (3 mg) in 5 mL of anhydrous MeOH−CH_2Cl_2 (1:1) at −78 °C, and the ozonolysis was contained until the solution became blue. The solution was purged with nitrogen and allowed to come to room temperature. Heptaldehyde, $C_7H_{14}O$, produced by ozonolysis was identified by GC−MS at *m*/*z* 114 ($C_7H_{14}O$, t_R 6.23 min) and by co-injection with an authentic sample.

Catacerebroside B (2): white amorphous powder; $[\alpha]^{20}_D$ +5.0° (*c* 3.0, C_5H_5N); IR (KBr) ν_{max} 3405 (OH), 2922, 1643, 1535 (amide), 1467, 1080 (C−O) cm^{-1}; ^{1}H NMR (C_5D_5N, 400 MHz) δ 8.55 (1H, d, *J* = 9.1 Hz, NH), 5.50 (each 1H, m, H-17′, H-18′), 5.26 (1H, m, H-2), 4.94 (1H, d, *J* = 7.7 Hz, H-1″), 4.75 (1H, dd, *J* = 10.7, 6.6 Hz, H-1a), 4.60 (1H, m, H-2′), 4.52 (1H, d, *J* = 11.6 Hz, H-6a″), 4.50 (1H, dd, *J* = 10.7, 4.5 Hz, H-1b), 4.34 (1H, m, H-3), 4.32 (1H, dd, *J* = 11.6, 5.5 Hz, H-6b″), 4.22 (1H, m, H-4), 4.20 (1H, m, H-4″), 4.19 (1H, m, H-3″), 4.01 (1H, t, *J* = 8.0 Hz, H-2″), 3.87 (1H, m, H-5″), 2.11 (1H, m, H-5a), 2.10 (1H, m, H-3a′), 2.07 (each 2H, m, H-16′, H-19′), 2.00 (1H, m, H-3b′), 1.97 (1H, m, H-5b), 1.85 (2H, m, H-4′), 1.80 (2H, m, H-6), 1.26−1.38 (52H, m, H-7−H-17, H-5′−H-15′, H-20′−H-23′), 0.93 (each 3H, t, *J* = 7.6 Hz, H-18, H-24′); ^{13}C NMR (C_5D_5N, 100 MHz) δ 175.8 (C-1′), 130.4 (C-17′, C-18′), 105.7 (C-1″), 78.6 (C-3″, C-5″), 76.0 (C-3), 75.3 (C-2″), 72.7 (C-2′), 72.5 (C-4), 71.6 (C-4″), 70.6 (C-1), 62.8 (C-6″), 51.9 (C-2), 35.7 (C-3′), 34.1 (C-5), 32.2 (C-16, C-22′), 29.5−30.5 (C-7−C-15, C-5′−C-15′, C-20′−C-21′), 27.7 (C-16′, C-19′), 26.7 (C-4′), 26.5 (C-6), 23.1 (C-17, C-23′), 14.5 (C-18, C-24′); negative ESIMS *m*/*z* 842 $[M - H]^-$; positive HRESIMS *m*/*z* 844.6862 $[M + H]^+$ (calcd for $C_{48}H_{94}NO_{10}$, 844.6878).

Methanolysis of 2. Methanolysis of **2** (5.5 mg) by the procedure described for compound **1** also afforded 2-hydroxytetracos-17-enoic acid methyl ester (1.6 mg).

Catacerebroside C (3): white amorphous powder; $[\alpha]^{20}_D$ +3.0° (*c* 1.0, C_5H_5N); IR (KBr) ν_{max} 3363 (OH), 2920, 1628, 1541 (amide), 1467, 1078 (C−O) cm^{-1}; ^{1}H NMR (C_5D_5N, 400 MHz) δ 8.66 (1H, d, *J* = 9.2 Hz, NH), 5.51 (each 1H, m, H-17′, H-18′), 5.28 (1H, m, H-2), 4.97 (1H, d, *J* = 7.7 Hz, H-1″), 4.70 (1H, dd, *J* = 10.6 Hz, 6.0 Hz, H-1a), 4.70 (1H, m, H-2′), 4.52 (1H, d, *J* = 11.7 Hz, H-6a″), 4.51 (1H, m, H-3′), 4.50 (1H, dd, *J* = 10.6, 4.6 Hz, H-1b), 4.31 (1H, dd, *J* = 11.7, 5.4 Hz, H-6b″), 4.29 (1H, m, H-3), 4.23 (1H, m, H-4), 4.19 (1H, m, H-4″), 4.17 (1H, m, H-3″), 3.98 (1H, m, H-2″), 3.84 (1H, m, H-5″), 2.23 (1H, m, H-5a), 2.13 (each 2H, m, H-4′, H-16′, H-19′), 1.93 (1H, m, H-5b), 1.85 (each 2H, m, H-6, H-5′), 1.25−1.45 (50H, m, H-7−H-17, H-6′−H-15′, H-20′−H-23′), 0.87 (each 3H, t, *J* = 6.8 Hz, H-18, H-24′); ^{13}C NMR (C_5D_5N, 100 MHz) δ 174.3 (C-1′), 130.3 (C-17′, C-18′), 105.5 (C-1″), 78.5 (C-3″), 78.4 (C-5″), 76.2 (C-2′), 75.8 (C-3), 75.1 (C-2″), 73.6 (C-3′), 72.6 (C-4), 71.5 (C-4″), 70.3

(C-1), 62.7 (C-6″), 51.8 (C-2), 34.3 (C-5), 32.7 (C-4′), 32.1 (C-16, C-22′), 29.6−30.5 (C-7−C-15, C-6′−C-15′, C-20′−C-21′), 27.6 (C-16′, C-19′), 26.6 (C-6, C-5′), 23.0 (C-17, C-23′), 14.3 (C-18, C-24′); positive ESIMS *m*/*z* 882 $[M + Na]^+$; positive HRESIMS *m*/*z* 860.6841 $[M + H]^+$ (calcd for $C_{48}H_{94}NO_{11}$, 860.6827).

Methanolysis of 3. Methanolysis of **3** (20.5 mg) by the procedure described for compound **1** afforded 2,3-dihydroxytetracos-17-enoic acid methyl ester (6.6 mg): ^{1}H NMR ($CDCl_3$) δ 5.34 (2H, t-like, J = 4.8 Hz, H-17, H-18), 4.23 (1H, d, J = 3.5 Hz, H-2), 3.81 (1H, m, H-3), 3.79 (3H, s, $-OCH_3$), 2.00 (4H, m, H-16, H-19), 1.25 (long chain), 0.85 (3H, t, J = 7.0, H-24); EIMS *m*/*z* 412 $[M]^+$ (14), 394 $[M - H_2O]^+$ (8), 376 $[M - 2H_2O]^+$ (2), 317 $[M - 2H_2O - COOCH_3]^+$ (13), 111 (10), 97 (17), 90 (100), 83 (20), 69 (24), 55 (25). Ozonolysis of 2,3-dihydroxytetracos-17-enoic acid methyl ester also yielded heptaldehyde, $C_7H_{14}O$, identified by GC−MS at *m*/*z* 114 ($C_7H_{14}O$, t_R 6.23 min) and by co-injection with an authentic sample.

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