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Triterpenoids from Gentianae Scabrae Radix and Gentianae Radix

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For new triterpenoids, uvaol 3-*O*-linoleate (**1**), uvaol 3-*O*-stearate (**2**), erythrodiol 3-*O*-linoleate (**3**) and erythrodiol 3-*O*-stearate (**4**), were isolated from Gentianae Scabrae Radix. Compounds **1** and **2**, and an inseparable mixture of the new triterpenoids, α-amyrin 3-*O*-coriolate (**5**) and α-amyrin 3-*O*-dimorphecolate (**6**), were obtained from Gentianae Radix. The structures of the new compounds were elucidated on the basis of spectral data.

Key words Gentianae Scabrae Radix; Gentianae Radix; Gentianaceae; triterpenoid

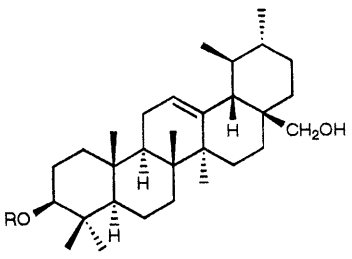
Gentianae Scabrae Radix and Gentianae Radix (Gentianaceae) are used as a stomachic or stimulant of appetite in Chinese medicine.[1,2] In previous papers, we reported the isolation and structural elucidation of secoiridoid glycosides, triterpenoids, sterols and long chain aldehydes from Gentianae Scabrae Radix[3-5] and Gentianae Radix.[6-8] We describe here the isolation and structural elucidation of six new triterpenoids, uvaol 3-*O*-linoleate (**1**), uvaol 3-*O*-stearate (**2**), erythrodiol 3-*O*-linoleate (**3**), erythrodiol 3-*O*-stearate (**4**), α-amyrin 3-*O*-coriolate (**5**) and α-amyrin 3-*O*-dimorphecolate (**6**) from Gentianae Scabrae Radix (compounds **1**－**4**) and Gentianae Radix (compounds **1**, **2**, **5** and **6**). Extraction and isolation were carried out as described in the Experimental section.

Compound **1** was isolated as an amorphous powder. The IR spectrum suggested the presence of a hydroxyl group (3512 cm^{-1}) and an ester group (1719 cm^{-1}). The molecular formula was determined to be $C_{48}H_{80}O_3$ by high-resolution (HR)-EI-MS. The ^1H- and ^{13}C-NMR spectra of **1** closely resembled those of uvaol 3-*O*-palmitate (**7**)[6] except for the presence of linoleoyl group[9] instead of palmitoyl group in **7** (*vide* Experimental). The linoleoyl group was deduced from the EI-MS (*m/z* 425 $[M-C_{18}H_{31}O_2]^+$), ^1H- and ^{13}C-NMR data.[10] Thus, the structure of **1** was determined to be uvaol 3-*O*-linoleate.

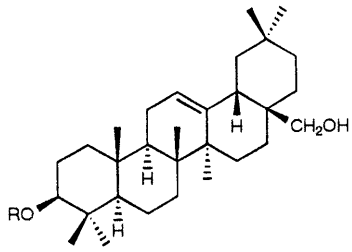
The molecular formula of **2** was determined to be $C_{48}H_{84}O_3$ by HR-EI-MS, which differs from that of **1** by 4 mass units. The ^1H-NMR spectra of **1** and **2** were very similar, but the signals of four olefinic protons of **1** disappeared in the case of **2**. The alkaline hydrolysis of **2** in methanolic KOH yielded methyl stearate. Therefore, the structure of **2** was determined to be uvaol 3-*O*-stearate.

The molecular formulae of **3** and **4** were determined to be $C_{48}H_{80}O_3$ and $C_{48}H_{84}O_3$ by HR-EI-MS, respectively. The ^1H-NMR spectra of **3** and **4** closely resembled those of **1** and **2**, respectively, except for the appearance of two tertiary methyl groups instead of two secondary methyl groups in **1** and **2**. The linoleoyl group of **3** was deduced from the EI-MS (*m/z* 425 $[M-C_{18}H_{31}O_2]^+$), ^1H- and ^{13}C-NMR data.[9,10] The alkaline hydrolysis of **4** in methanolic KOH yielded methyl stearate. Thus, the structures of **3** and **4** were determined to be erythrodiol 3-*O*-linoleate and erythrodiol 3-*O*-stearate, respectively.

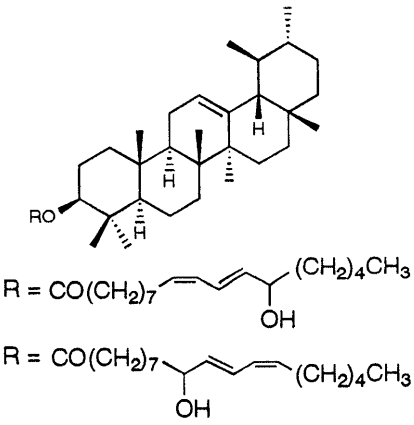
Compounds **5** and **6** were obtained as an inseparable mixture in the approximate ratio of 1 : 1. The HR-EI-MS was consistent with a molecular formula $C_{48}H_{80}O_3$. The ^1H-



1 R = $CO(CH_2)_7$–CH=CH–CH=CH–$(CH_2)_4CH_3$
2 R = $CO(CH_2)_{16}CH_3$
7 R = $CO(CH_2)_{14}CH_3$



3 R = $CO(CH_2)_7$–CH=CH–CH=CH–$(CH_2)_4CH_3$
4 R = $CO(CH_2)_{16}CH_3$



5 R = $CO(CH_2)_7$–CH=CH–CH(OH)–$(CH_2)_4CH_3$
6 R = $CO(CH_2)_7$–CH(OH)–CH=CH–$(CH_2)_4CH_3$

and ^{13}C-NMR spectra indicated the presence of α-amyrin[11] and fatty acid moieties in the form of 3β-*O*-acylated α-amyrin derivatives.[12] The fatty acid ester groups of **5** and **6** were determined to be corioloyl and dimorphecoloyl groups, respectively, by comparison of the UV (λ_{max}: 242 nm), ^{1}H- and ^{13}C-NMR data of methyl coriolate[13,14] and methyl dimorphecolate.[13,15] The EI-MS (*m/z* 409 [M−$C_{18}H_{31}O_3$]$^+$) supported the proposed structures. Thus, **5** and **6** were formulated as α-amyrin 3-*O*-coriolate and α-amyrin 3-*O*-dimorphecolate, respectively. The stereochemistry at C-13' of **5** and C-9' of **6** was not determined.

Experimental

General Optical rotations were determined using a JASCO DIP-360 digital polarimeter. IR spectra were recorded with Perkin-Elmer FT-IR 1725X IR spectrophotometer and UV spectra on a Beckman DU-64 spectrophotometer. ^{1}H- and ^{13}C-NMR spectra were recorded on a JEOL JNM-LA 600 (600 and 150 MHz, respectively) and JNM-LA 400 (400 and 100 MHz, respectivery) spectrometers. Chemical shifts are given on δ (ppm) scale, with tetramethylsilane as an internal standard. EI- and HR-EI-MS were recorded on a JEOL JMS-DX 303 mass spectrometer. Column chromatography was carried out on Silica gel 60 (Merck; 0.040−0.063 mm). Preparative HPLC was carried out on a Tosoh HPLC system (pump, CCPS; detector, RI-8020) using a TSK gel ODS-120T (7.8 mm i.d. ×30 cm) column (Tosoh). HPLC conditions: mobile phase, MeOH; flow rate, 1.0 ml/min; column temperature, 40°C.

Plant Material Gentianae Scabrae Radix (from Jilin, China) and Gentianae Radix (from France) were purchased from Uchida Wakanyaku Co., Ltd., Tokyo, Japan.

Extraction and Isolation Gentianae Scabrae Radix: The powdered Gentianae Scabrae Radix (1.5 kg) was extracted with MeOH at room temperature. The MeOH extract was concentrated under reduced pressure and the residue (160.0 g) was suspended in a small amount of water. This suspension was extracted with $CHCl_3$. The $CHCl_3$-soluble fraction was concentrated under reduced pressure to affored a residue (66.0 g). Part of this residue (29.0 g) was chromatographed on a silica gel column using $CHCl_3$−MeOH−H_2O (30 : 10 : 1), and the eluate was separated into 24 fractions (frs. 1−24). Fraction 3 was purified by preparative HPLC to give **1** (1.5 mg), **2** (0.9 mg), **3** (0.3 mg) and **4** (0.2 mg).

Gentianae Radix: The powdered Gentianae Radix (1.5 kg) was extracted with MeOH at room temperature. The MeOH extract was concentrated under reduced pressure and the residue (160.0 g) was suspended in a small amount of water. This suspension was extracted with $CHCl_3$. The $CHCl_3$-soluble fraction was concentrated under reduced

pressure to afforded a residue (67.0 g). Part of this residue (44.0 g) was chromatographed on a silica gel column using $CHCl_3$—MeOH—H_2O (30 : 10 : 1), and the eluate was separated into 35 fractions (frs. 1—35). Fraction 3 was purified by preparative HPLC to give **1** (0.6 mg), **2** (0.5 mg) and the mixture of **5** and **6** (1.3 mg).

Uvaol 3-*O*-linoleate (1): Amorphous powder. $[\alpha]_D^{25}$ +30.3° (*c* = 0.15, $CHCl_3$). IR ν_{max} ($CHCl_3$) cm^{-1}: 3512, 1719. EI-MS *m/z*: 704 ($[M]^+$), 425 ($[M-C_{18}H_{31}O_2]^+$), 234, 203. HR-EI-MS *m/z*: 704.6089 ($[M]^+$, calcd for $C_{48}H_{80}O_3$; 704.6107). ^{1}H-NMR (600 MHz, $CDCl_3$) δ: 0.81 (3H, d, *J* = 5.9 Hz, H_3-29), 0.868 (3H, s, H_3-23), 0.870 (3H, s, H_3-24), 0.89 (3H, t, *J* = 7.0 Hz, H_3-18'), 0.94 (3H, d, *J* = 6.2 Hz, H_3-30), 0.98 (3H, s, H_3-25), 0.99 (3H, s, H_3-26), 1.10 (3H, s, H_3-27), 1.25 (16H, br. s, H_2-3'—H_2-7', H_2-15'—H_2-17'), 2.04 (2H, br. t, *J* = 7.0 Hz, H_2-14'), 2.05 (2H, br. t, *J* = 7.0 Hz, H_2-8'), 2.29 (2H, t, *J* = 7.0 Hz, H_2-2'), 2.77 (2H, t, *J* = 7.0 Hz, H_2-11'), 3.20 (1H, d, *J* = 11.0 Hz, H-28a), 3.53 (1H, d, *J* = 11.0 Hz, H-28b), 4.50 (1H, dd, *J* = 10.6, 5.5 Hz, H-3), 5.14 (1H, br. t, *J* = 3.7 Hz, H-12), 5.34 (4H, m, H-9', H-10', H-12', H-13'). ^{13}C-NMR (150 MHz, $CDCl_3$) δ: 14.1 (C-18'), 15.8 (C-25), 16.8 (C-24, C-29), 17.4 (C-26), 18.2 (C-6), 21.3 (C-30), 22.6 (C-16, C-17'), 23.3, 23.4 (C-11, C-27), 23.6 (C-2), 25.0 (C-3'), 25.7 (C-11'), 27.2 (C-8', C-14'), 28.1 (C-23), 29.1—29.6 (C-4'—C-7'), 29.2 (C-15), 29.4 (C-15'), 30.6 (C-21, C-22), 31.6 (C-16'), 32.8 (C-7), 34.1 (C-2'), 36.8 (C-17), 37.8 (C-10), 38.0 (C-1), 38.5 (C-4), 39.4 (C-19, C-20), 40.0 (C-8), 42.1 (C-14), 47.6 (C-9), 54.0 (C-18), 55.3 (C-5), 70.0 (C-28), 80.6 (C-3), 125.0 (C-12), 127.9 (C-12'), 128.1 (C-10'), 130.1 (C-9'), 130.2 (C-13'), 138.8 (C-13), 174.3 (C-1').

Uvaol 3-*O*-stearate (2): Amorphous powder. EI-MS *m/z*: 708 ($[M]^+$), 424 ($[M-C_{18}H_{36}O_2]^+$), 234, 203. HR-EI-MS *m/z*: 708.6448 ($[M]^+$, calcd for $C_{48}H_{84}O_3$; 708.6420). ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 0.81 (3H, d, *J* = 5.9 Hz, H_3-29), 0.87 (6H, s, H_3-23, H_3-24), 0.88 (3H, t, *J* = 6.6 Hz, H_3-18'), 0.95 (3H, d, *J* = 5.4 Hz, H_3-30), 0.98 (3H, s, H_3-25), 0.99 (3H, s, H_3-26), 1.10 (3H, s, H_3-27), 1.25 (30H, br. s, H_2-3'—H_2-17'), 2.29 (2H, t, *J* = 7.6 Hz, H_2-2'), 3.20 (1H, dd, *J* = 11.0, 4.6 Hz, H-28a), 3.54 (1H, dd, *J* = 11.0, 3.7 Hz, H-28b), 4.50 (1H, dd, *J* = 10.7, 5.6 Hz, H-3), 5.14 (1H, br. t, *J* = 3.9 Hz, H-12).

Erythrodiol 3-*O*-linoleate (3): Amorphous powder. $[\alpha]_D^{25}$ +36.9° (*c* = 0.09, $CHCl_3$). IR ν_{max} ($CHCl_3$) cm^{-1}: 3512, 1718. EI-MS *m/z*: 704 ($[M]^+$), 425 ($[M-C_{18}H_{31}O_2]^+$), 234, 203. HR-EI-MS *m/z*: 704.6107 ($[M]^+$, calcd for $C_{48}H_{80}O_3$; 704.6107). ^{1}H-NMR (600 MHz, $CDCl_3$) δ: 0.866 (3H, s, H_3-23), 0.869 (3H, s, H_3-24), 0.875 (3H, s, H_3-30), 0.88 (3H, t, *J* = 7.0 Hz, H_3-18'), 0.89 (3H, s, H_3-29), 0.94 (3H, s, H_3-25), 0.96 (3H, s, H_3-26), 1.17 (3H, s, H_3-27), 1.25 (16H, br. s, H_2-3'—H_2-7', H_2-15'—H_2-17'), 2.04 (2H, br. t, *J* = 7.0 Hz, H_2-14'), 2.05 (2H, br. t, *J* = 7.0 Hz, H_2-8'), 2.29 (2H, t, *J* = 7.0 Hz, H_2-2'), 2.77 (2H, t, *J* = 7.0 Hz, H_2-11'), 3.22 (1H, d, *J* = 11.0 Hz, H-28a), 3.55 (1H, d, *J* = 11.0 Hz, H-28b), 4.50 (1H, dd, *J* = 10.6, 5.5 Hz, H-3), 5.19 (1H, br. t, *J* = 3.7 Hz, H-12), 5.35 (4H, m, H-9', H-10', H-12', H-13'). ^{13}C-NMR (150 MHz, $CDCl_3$) δ: 14.1 (C-18'), 15.6 (C-25), 16.7 (C-24), 16.8 (C-26), 18.2 (C-6), 22.0 (C-16), 22.6 (C-17'), 23.5, 23.6 (C-2, C-11, C-30), 25.2 (C-3'), 25.5 (C-15), 25.6 (C-11'), 25.9 (C-27), 27.2 (C-8', C-14'), 28.1 (C-23), 29.1—29.7 (C-4'—C-7'), 29.4 (C-15'), 31.0 (C-20, C-22), 31.5 (C-16'), 32.5 (C-7), 33.3 (C-29), 34.1 (C-21), 34.9 (C-2'), 36.8 (C-17), 36.9 (C-10), 37.8 (C-1), 38.3 (C-4), 39.8 (C-8), 41.7 (C-14), 42.3 (C-18), 46.4 (C-19), 47.5 (C-9), 55.2 (C-5), 69.7 (C-28), 80.6 (C-3), 122.3 (C-12), 127.9 (C-12'), 128.0 (C-10'), 130.1 (C-9'), 130.2 (C-13'), 144.2 (C-13), 173.7 (C-1').

Erythrodiol 3-*O*-stearate (4): Amorphous powder. EI-MS *m/z*: 708 ($[M]^+$), 424 ($[M-C_{18}H_{36}O_2]^+$), 234, 203. HR-EI-MS *m/z*: 708.6438 ($[M]^+$, calcd for $C_{48}H_{84}O_3$; 708.6420). ^{1}H-NMR (400 MHz, $CDCl_3$) δ: 0.865 (3H, s, H_3-23), 0.869 (3H, s, H_3-24), 0.874 (3H, s, H_3-30), 0.88 (3H, t, *J* = 6.1 Hz, H_3-18'), 0.89 (3H, s, H_3-29), 0.94 (3H, s, H_3-25), 0.96 (3H, s, H_3-26), 1.16 (3H, s, H_3-27), 1.25 (30H, br. s, H_2-3'—H_2-17'), 2.29 (2H, t, *J* = 7.1 Hz, H_2-2'), 3.21 (1H, d, *J* = 10.7 Hz, H-28a), 3.54 (1H, d, *J* = 10.7 Hz, H-28b), 4.49 (1H, dd, *J* = 10.6, 5.5 Hz, H-3), 5.19 (1H, br. t, *J* = 3.4 Hz, H-12).

α-Amyrin 3-*O*-coriolate (5) and α-amyrin 3-*O*-dimorphecolate (6): Amorphous powder. $[\alpha]_D^{25}$ +32.8° (*c* = 0.13, $CHCl_3$). UV λ_{max} (MeOH) nm (log ε): 242 (3.4). EI-MS *m/z*: 704 ($[M]^+$), 409 ($[M-C_{18}H_{31}O_3]^+$),

218, 203. HR-EI-MS *m/z*: 704.6091 ($[M]^+$, calcd for $C_{48}H_{80}O_3$; 704.6107). ^{1}H-NMR (600 MHz, $CDCl_3$) α-amyrin moiety δ: 0.80 (3H, d, *J* = 7.0 Hz, H_3-29), 0.80 (3H, s, H_3-28), 0.87 (6H, s, H_3-23, H_3-24), 0.92 (3H, d, *J* = 6.2 Hz, H_3-30), 0.98 (3H, s, H_3-25), 1.01 (3H, s, H_3-26), 1.07 (3H, s, H_3-27), 4.51 (1H, dd, *J* = 7.0, 5.5 Hz, H-3), 5.13 (1H, m, H-12); fatty acid moiety of **5** δ: 0.89 (3H, t, *J* = 7.0 Hz, H_3-18'), 1.25 (16H, br. s, H_2-3'－H_2-7', H_2-15'－H_2-17'), 2.17 (2H, br. q, *J* = 7.7 Hz, H_2-8'), 2.29 (2H, t, *J* = 7.3 Hz, H_2-2'), 4.16 (1H, m, H-13'), 5.44 (1H, dt, *J* = 11.4, 7.3 Hz, H-9'), 5.66 (1H, dd, *J* = 15.0, 6.6 Hz, H-12'), 5.97 (1H, br. t, *J* = 11.4 Hz, H-10'), 6.48 (1H, ddd, *J* = 15.0, 11.0, 0.7 Hz, H-11'); fatty acid moiety of **6** δ: 0.89 (3H, t, *J* = 7.0 Hz, H_3-18'), 1.25 (16H, br. s, H_2-3'－H_2-7', H_2-15'－H_2-17'), 2.17 (2H, br. q, *J* = 7.7 Hz, H_2-14'), 2.29 (2H, t, *J* = 7.3 Hz, H_2-2'), 4.16 (1H, m, H-9'), 5.44 (1H, dt, *J* = 11.4, 7.3 Hz, H-13'), 5.66 (1H, dd, *J* = 15.0, 6.6 Hz, H-10'), 5.97 (1H, br. t, *J* = 11.4 Hz, H-12'), 6.48 (1H, ddd, *J* = 15.0, 11.0, 0.7 Hz, H-11'). ^{13}C-NMR (150 MHz, $CDCl_3$) α-amyrin moiety δ: 15.7 (C-25), 16.8 (C-24), 16.9 (C-26), 17.5 (C-29), 18.2 (C-6), 21.4 (C-30), 23.2 (C-27), 23.4 (C-11), 23.6 (C-2), 26.6 (C-16), 28.1 (C-23, C-28), 31.3 (C-21), 32.9 (C-7), 33.8 (C-17), 36.8 (C-10), 37.8 (C-4), 38.4 (C-1), 39.6, 39.7 (C-19, C-20), 40.0 (C-8), 41.5 (C-22), 42.1 (C-14), 47.6 (C-9), 55.3 (C-5), 59.1 (C-18), 80.6 (C-3), 124.3 (C-12), 139.6 (C-13); fatty acid moiety of **5** δ: 14.1 (C-18'), 22.6 (C-17'), 25.1 (C-3', C-15'), 27.7 (C-8'), 28.9, 29.1 (C-5', C-6'), 29.5 (C-4'), 29.7 (C-7'), 31.8 (C-16'), 34.8 (C-2'), 37.3 (C-14'), 72.9 (C-13'), 125.8 (C-11'), 127.8 (C-10'), 132.8 (C-9'), 135.9 (C-12'), 173.7 (C-1'); fatty acid moiety of **6** δ: 14.1 (C-18'), 22.6 (C-17'), 25.1 (C-3'), 25.4 (C-7'), 27.8 (C-14'), 29.1, 29.2 (C-5', C-6'), 29.3 (C-15'), 29.4 (C-4'), 31.5 (C-16'), 34.8 (C-2'), 37.3 (C-8'), 72.9 (C-9'), 125.9 (C-11'), 127.7 (C-12'), 133.1 (C-13'), 135.7 (C-10'), 173.7 (C-1').

Hydrolysis of 2 and 4 Compounds **2** and **4** were refluxed with 5% methanolic KOH for 3h. The reaction mixture was extracted with $CHCl_3$, and the $CHCl_3$ layer was concentrated under reduced pressure to yield methyl stearate. This compound was identified by GC comparison with the authentic sample. GC conditions: column, 3% SE-52 on Chromosorb W (AW) (60－80 mesh), 3 mm i.d. ×2 m; carrier gas, N_2; flow rate, 1.0 kg/cm^2; detector, FID; column temperature, 190°C. Methyl stearate, t_R 5.8 min.

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10) Methyl linoleate; ^{13}C-NMR (150 MHz, $CDCl_3$) δ: 14.1 (C-18), 22.6 (C-17), 25.2 (C-3), 25.6 (C-11), 27.2 (C-8, C-14), 29.1 - 29.7 (C-4 - C-7), 29.4 (C-15), 31.5 (C-16), 34.9 (C-2), 51.4 ($COO\underline{C}H_3$), 127.9 (C-12), 128.1 (C-10), 130.1 (C-9), 130.2 (C-13), 173.7 (C-1).
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Masao, Abstracts of papers, the 41st Annual Meeting of Tohoku Branch, the Pharmaceutical Society of Japan, Hirosaki, October 13, 2002, p. 39.

14) Methyl coriolate; ^{1}H-NMR (600 MHz, $CDCl_3$) δ: 0.89 (3H, t, J = 7.0 Hz, H_3-18), 1.25 (16H, br. s, H_2-3－H_2-7, H_2-15－H_2-17), 2.17 (2H, br. q, J = 7.6 Hz, H_2-8), 2.30 (2H, t, J = 7.6 Hz, H_2-2), 3.66 (3H, s, $COOCH_3$), 4.15 (1H, m, H-13), 5.45 (1H, dt, J = 11.0, 7.7 Hz, H-9), 5.66 (1H, dd, J = 15.2, 7.7 Hz, H-12), 5.97 (1H, t, J = 11.0 Hz, H-10), 6.48 (1H, dd, J = 15.2, 11.0 Hz, H-11); ^{13}C-NMR (150 MHz, $CDCl_3$) δ: 14.1 (C-18), 22.6 (C-17), 24.9 (C-3), 25.1 (C-15), 27.7 (C-8), 28.9, 29.1 (C-5, C-6), 29.5 (C-4), 29.7 (C-7), 31.8 (C-16), 34.1 (C-2), 37.3 (C-14), 51.5 ($COO\underline{C}H_3$), 72.9 (C-13), 125.8 (C-11), 127.8 (C-10), 132.8 (C-9), 135.9 (C-12), 174.4 (C-1).

15) Methyl dimorphecolate; ^{1}H-NMR (600 MHz, $CDCl_3$) δ: 0.89 (3H, t, J = 7.0 Hz, H_3-18), 1.25 (16H, br. s, H_2-3－H_2-7, H_2-15－H_2-17), 2.18 (2H, q, J = 7.7 Hz, H_2-14), 2.30 (2H, t, J = 7.7 Hz, H_2-2), 3.67 (3H, s, $COOCH_3$), 4.15 (1H, m, H-9), 5.45 (1H, dt, J = 11.0, 7.7 Hz, H-13), 5.66 (1H, dd, J = 15.0, 7.0 Hz, H-10), 5.97 (1H, t, J = 11.0 Hz, H-12), 6.48 (1H, dd, J = 15.0, 11.0 Hz, H-11); ^{13}C-NMR (150 MHz, $CDCl_3$) δ: 14.1 (C-18), 22.6 (C-17), 24.9 (C-3'), 25.4 (C-7), 27.8 (C-14), 29.1, 29.2 (C-5, C-6), 29.3 (C-4, C-15), 31.5 (C-16), 34.1 (C-2), 37.3 (C-8), 51.5 ($COO\underline{C}H_3$), 72.9 (C-9), 125.9 (C-11), 127.7 (C-12), 133.1 (C-13), 135.7 (C-10), 174.3 (C-1).