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NEW GLYCOSIDIC AND OTHER CONSTITUENTS FROM HULLS OF *Oryza sativa*

I. M. Chung, H. Y. Park, S. C. Chun, J. J. Kim, and A. Ahmad*

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*Three new compounds, 4-hydroxymethylene-7-(9,9,13-trimethylcyclohexyl)-heptanyl-3′,7′,7′-trimethylcyclohexa-2′,4′-dien-1′-oate (**1**), 1-(*n*-hexadec-7-enoxy)-6-(*n*-octadecanoxy)-β-D-glucopyranoside (**2**), and (Z)-12-hydroxy-9-octadecenoic acid-12-β-D-glucopyranoside (**3**), along with the known compound hexacosanoic acid (**4**), were isolated and identified from the rice hulls of* Oryza sativa. *Their structures were elucidated by 1D and 2D NMR spectroscopic techniques (^{1}H-^{1}H COSY, ^{1}H-^{13}C HETCOR, DEPT) aided by EIMS, FABMS, HRFABMS, and IR spectra.*

Key words: *Oryza sativa* L., rice hull composition, 4-hydroxymethylene-7-(9,9,13-trimethylcyclohexyl)-heptanyl-3′,7′,7′-trimethylcyclohexa-2′,4′-dien-1′-oate; 1-(*n*-hexadec-7-enoxy)-6-(*n*-octadecanoxy)-*β*-D-glucopyranoside; (*Z*)-12-hydroxy-9-octadecenoic acid-12-*β*-D-glucopyranoside.

In continuation of our study on rice hulls of *Oryza sativa* constituents, we reported new and known compounds with inhibitory and cytotoxic activities [1–4]. This paper deals with the isolation and characterization of three additional new compounds (**1–3**) of glycosidic and other nature using spectral data analysis and spectral methods, viz., ^{1}H NMR, ^{13}C NMR, COSY, and HETCOR aided by EIMS, FABMS, HRFABMS, and IR and chemical reactions. Compound **3** is a ricinoleic acid glucoside and was reported for the first time as a natural product from rice hulls, while ricinoleic acid is a known compound.

The methanol extract of the *O. sativa* hulls was suspended in water and extracted with ethyl acetate and then *n*-butanol. The ethyl acetate and butanol extract were separated by a combination of column chromatography over silica gel and Lichroprep RP-18 (ODS Si gel) to yield three new compounds and one known compound. For all the molecules studied, relative configurations were suggested on the basis of biogenetic speculations.

The IR spectrum of **1** showed characteristic absorption bands for the ester group at 1730 cm^{-1}, the hydroxyl group at 3448 cm^{-1}, and unsaturation at 1650 cm^{-1}. Its electron impact mass spectrum displayed a molecular ion peak at *m/z* 418 corresponding to a monocyclic homosesquiterpene diol esterified with a cyclohexenoid monoterpenic acid, $C_{27}H_{46}O_3$. It indicated five double bond equivalents; two of them were adjusted in two cyclohexane rings, two in the vinylic linkages, and one in the ester group. The base peak at *m/z* 149 was generated due to cleavage of the ester functional group. The prominent ion peaks at *m/z* 207 $[C_3\text{-}C_4$ fission$]^+$, 167 $[C_4\text{-}C_5$ fission$]^+$, and 293 $[C_7\text{-}C_8$ fission$]^+$ suggested the location of the hydroxylmethylene functional at C-4 and the trimethyl substituted cyclohexane ring at C-7. The mass fragmentation pattern is shown in Fig. 1.

The ^{1}H NMR spectrum of **1** exhibited a one-proton doublet at δ 7.71 (J = 3.5 Hz) and a one-proton doublet of doublets at δ 7.52 (J = 4.5, 3.5 and 4.0 Hz), assigned to vinylic H-4′ and H-5′, respectively. Four one-proton doublets at δ 4.32 (J = 7.0 Hz), 4.30 (J = 7.0 Hz) for H-1_a, H-1_b and δ 4.28 (J = 6.5 Hz), 4.26 (J = 6.5 Hz) for H-14_a, H-14_b were ascribed to oxygenated methylene protons, respectively. Two one-proton doublets at δ 1.73 (J = 4.5 Hz) and 1.69 (J = 4.0 Hz) for H-6′$_a$, H-6′$_b$, respectively, were attributed to methylene protons adjacent to the vinylic carbon. The three-proton broad signal at δ 1.56 was due to C-8′ methyl protons attached to the C-3′ olefinic carbon. A three-proton doublet at δ 0.87 (J = 6.5 Hz) was assigned to the C-17 secondary methyl protons.

College of Life and Environmental Sciences, Konkuk University, Seoul 143-701, South Korea, fax +82 2 446 7856, e-mail: aahmadc@yahoo.com. Published in Khimiya Prirodnykh Soedinenii, No. 4, pp. 344-347, July-August, 2007. Original article submitted April 20, 2006.

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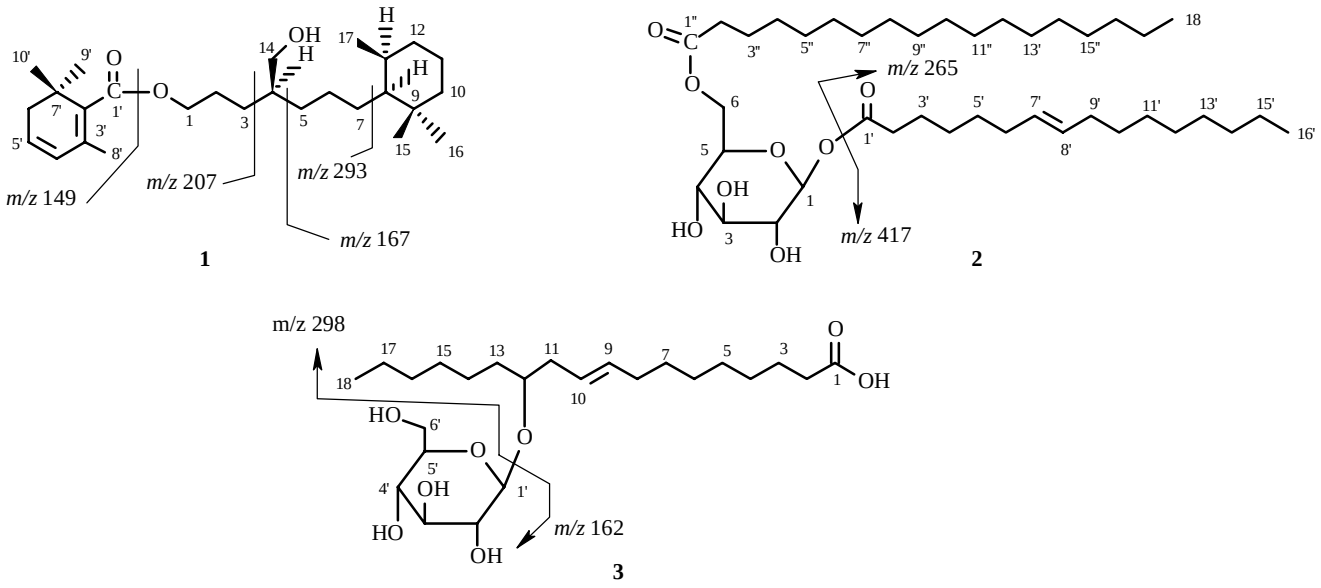

Fig. 1. Mass fragmentation of **1** - **3**.

Four three-protons broad signals at δ 1.25, 0.88, 0.85, and 0.83 were associated correspondingly to tertiary C-9′, C-10′, C-15, and C-16 methyl protons. The remaining methylene and methine protons resonated between δ 1.40–1.12. The ^{13}C NMR spectrum of **1** displayed signals for vinylic carbons at δ 132.55 (C-2′), 129.06 (C-3′), and 131.13 (C-4, C-5′), oxygenated methylene carbons at δ 66.43 (C-1) and 66.12 (C-14), ester carbon at δ 167.94 (C-1′), and methyl carbons at δ 19.39 (C-15), 11.60 (C-16), 10.90 (C-17), 14.34 (C-8′), 26.07 (C-9′), and 19.77 (C-10′). The DEPT spectrum of **1** showed the existence of six methyl, eleven methylene, five methine, and five quaternary carbons. The ^{1}H-^{1}H COSY spectrum showed correlation of H-4′ with H-5′ and H-6′, H-14 with H-4, and H-1 with H-2. The ^{1}H-^{13}C HETCOR spectrum of **1** exhibited correlation of C-1′ with H-1, C-14 with H-4, H-3, and H-5, C-9′ with H-6′, and C-10′ with H-6′.

On the basis of these, the structure of **1** has been formulated as 4-hydroxymethylene-7-(9,9,13-trimethyl-cyclohexyl)-heptanyl-3′,7′,7′-trimethylcyclohexa-2′,4′-dien-1′-oate.

Compound **2** was obtained as a yellow semi-solid mass from ethyl acetate–methanol (9:1) eluants. Its IR spectrum showed characteristic absorption bands for the hydroxyl group at 3450 and 3375 cm^{-1}, the ester group at 1730 cm^{-1}, and unsaturation at 1640 cm^{-1}. Its molecular formula ($C_{40}H_{74}O_8$) was established by positive ion HRFABMS. Its FAB-MS showed a molecular ion peak at *m/z* 683 $[M+H]^+$ corresponding to the molecular formula $C_{40}H_{74}O_8$. The prominent ion peaks at *m/z* 265 $[CO(CH_2)_5CH{=}CH(CH_2)_7CH_3]^+$ and *m/z* 417 $[M-265]^+$ in EIMS indicated that one of the fatty acids attached to the glucose moiety was palmitoleic acid. The mass fragmentation pattern is shown in Fig. 1.

The ^{1}H NMR spectrum of **2** showed a one-proton broad signal at δ 5.31 assigned to anomeric H-1 proton. Two one-proton multiplets at δ 5.34 and 5.31 were ascribed to vinylic protons H-7′ and H-8′, respectively. Two one-proton doublets at δ 4.25 (J = 7.2 Hz) and 4.23 (J = 7.2 Hz) were attributed to oxygenated methylene protons H-6$_a$ and H-6$_b$, respectively, and deshielding effects of the methylene protons suggested the attachment of the other fatty acid molecule at the hydroxyl group of the C-6 methylene group. A one-proton doublet at δ 4.09 (J = 7.7 Hz) was associated with the glucose methine H-2. The other protons of the glucose moiety appeared as multiplets at δ 3.99, 3.67, and 3.51, all integrated for one proton. Four one-proton doublets at δ 2.31 (J = 7.2 Hz) and 2.29 (J = 7.2 Hz) for H-2′$_a$ and H-2′$_b$ and at δ 2.01 (J = 7.8 Hz) and 1.99 (J = 7.8 Hz) for H-2″$_a$ and H-2″$_b$, respectively, were ascribed to methylene protons attached to ester groups. Two three-proton triplets at δ 0.85 (J = 6.78 Hz) and 0.81 (J = 6.1 Hz) were attributed to the primary methyl protons Me-16′ and Me-18″, respectively. The remaining methylene protons resonated at δ 1.57 (2H), 1.37 (2H), 1.28 (2H), and 1.23 (46H).

The ^{13}C NMR spectrum of **2** exhibited two deshielded carbon signals at δ 176.39 and 174.98 assigned to ester carbonyl carbon C-1′ and C-1″, respectively. The carbon signals for the sugar moiety appeared between δ 103.65–70.55. The deshielding of the carbon signal of the oxygenated methylene group from δ 62.0 to 70.55 supported the presence of one of the fatty acid moiety at this group. The deshielded carbon signals at δ 130.68 and 129.94 were associated with the vinylic carbons of the

palmitoleic acid moiety. The terminal primary methyl carbons of the fatty acid moieties appeared at δ 14.41 and 12.32. The remaining methylene carbon signals resonated between δ 39.89–20.15. The multiplicity of the methylene carbons was determined with the DEPT experiments. The ^{1}H-^{1}H COSY spectrum showed the correlation of H-7′ and H-8′ with the adjacent methylene protons, anomeric H-1 with H-2′, H-6 with H-2″, H-2 with H-1, H-3, H-4, and H-5, and H-16′ and H-18″ with the adjacent methylene carbons. In the HMBC spectrum the correlation of the ester carbon with deshielded methylene carbons and anomeric C-1 carbon with hydroxymethine carbons of the sugar and methylene carbons of the fatty acid was noted. In the ^{1}H-^{13}C HETCOR spectrum there were interactions of the vinyl carbons with H-7′ and H-8′, C-1 with H-1, sugar carbons with sugar carbons, and methyl carbons with methyl protons.

On the basis of the spectral data analysis, the structure of **2** has been formulated as 1-(*n*-hexadec-7-enoxy)-6-(*n*-octadecanoxy)-*β*-D-glucopyranoside.

It was obtained as a yellow semisolid mass from ethyl acetate–methanol (9:1) eluants. It yielded effervescences with sodium bicarbonate solution and decolorized bromine water. Its IR spectrum showed characteristic absorption bands of the carboxylic group at 3380 and 1695 cm^{-1}, hydroxyl group at 3435 cm^{-1}, and unsaturation at 1640 cm^{-1}. The FAB mass spectrum showed a molecular ion peak at *m/z* 460 corresponding to a C_{18}-fatty acid glycoside, $C_{24}H_{44}O_8$. The mass fragmentation pattern is shown in Fig. 1.

The ^{1}H NMR spectrum of **3** displayed two one-proton multiplets at δ 6.82 and 6.76 assigned to vinylic H-10 and H-9, respectively. A one-proton doublet at δ 5.38 (J = 2.8 Hz) was ascribed to the carbinol proton signals, and values between δ 3.95–3.30 were attributed to the glucose protons. Two one-proton doublets at δ 2.32 (J = 7.2 Hz) and 2.30 (J = 7.2 Hz) for H-2_a, H-2_b, respectively, accounted for the methylene protons adjacent to the carboxylic group. Two one-proton double doublets at δ 2.15 (J = 7.2, 7.2 Hz), and 2.12 (J = 7.2, 7.8 Hz) for H-11_a H-11_b, respectively, were assigned to methylene protons. Two one-proton broad signals at δ 2.05 and 2.02 were assigned to methylene H-8 adjacent to the vinylic carbons. A one-proton multiplet at δ 3.85 was ascribed to oxygenated methine H-12 proton. A three- proton triplet at δ 0.89 accounted for the primary C-18 methyl protons. The remaining methylene proton signals resonated at δ 1.52 (6H), 1.32 (6H), and 1.28 (8H).

The ^{13}C NMR spectrum of **3** displayed important carbon signals for the carboxylic group at 180.72 (C-1), vinylic carbons at δ 116.77 (C-9) and 115.98 (C-10), carbinol carbons at δ 75.16 (C-12), anomeric carbons at δ 99.01 (C-1′), sugar carbons between δ 81.35–64.38, and the remaining methyl and methylene carbons in the range δ 38.65–24.28. The multiplicity of each carbon was determined by DEPT experiments. The ^{1}H-^{1}H COSY spectrum of **3** displayed the correlation of H-12 with H-11, H-10, H-9, and H-13; H-9 with H-10, H-11, and H-8; H-18 with H-17, H-16, and H-15; and H-1′ with H-2′, H-3′, H-5′, and H-12. The ^{1}H-^{13}C HETCOR spectrum showed correlation of C-1 with H-2 and H-3, and Me-18 with H-17, H-16, and H-15. The HSQC spectrum of **3** showed long-range coupling of C-1′ with H-2. Hydrolysis of **3** with dilute HCl yielded *β*-D-glucose and ricinoleic acid (TLC comparable).

On the basis of spectral data analysis and chemical reactions, the structure of **3** has been established as (*Z*)-12-hydroxy-9-octadecenoic acid-12-*β*-D-glucopyranoside.

EXPERIMENTAL

Melting points were determined on an Electrochemical Engineering melting point apparatus (Electrochemical Engineering Ltd., model No. IA9100 Electrothermal, Seoul, South Korea). Optical rotation was measured on an AA-10 model polarimeter (Instruments Ltd., Seoul, South Korea). Both ^{1}H and ^{13}C NMR spectra were obtained with a Bruker Avance model DRX-500 spectrometer operating at 500 and 125 MHz, respectively. This NMR machine available at Seoul National University, Seoul, South Korea and all NMR spectra was done at SNU. NMR spectra were obtained in deuterated chloroform, pyridine, and methanol using tetramethylsilane (TMS) as internal standard, with chemical shifts expressed in ppm (δ) and coupling constants (J) in Hz. EI/MS were recorded on a JEOL JMS-SX 102 A spectrometer, and FAB/MS on a JEOL JMS-AX 505 WA. This mass machine available at Seoul National University, Seoul, South Korea, and all mass spectra were done in SNU. IR spectra were recorded on a Thermo Mattson, Infinity Gold FT-IR (German) model 60-AR spectrophotometer. This IR machine is available at Korea Institute of Science and Technology (KIST) Seoul, South Korea.

Plant Material. *Oryza sativa* cultivar "Ilpumbyeo" was grown at Konkuk University experimental field in South Korea and harvested in October, 2002. A voucher specimen of hulls (reference code KKU 121, Ilpumbyeo) has been deposited in the herbarium of the Department of Applied Life Science, Konkuk University, Seoul, South Korea. The hulls from the harvested

plants were separated on a milling machine and dried at room temperature (25°C) for 7 days. Dried rice hulls were ground or powdered with a Wiley mill through a 40-mesh screen.

Extraction of Rice Hulls. The powdered hulls of *O. sativa* (10 kg) were immersed in methanol (60 L) for 1 week at room temperature and then concentrated *in vacuo* to yield 150 g of extract. This material was suspended in water and extracted with ethyl acetate and *n*-butanol successively to produce 35 g of ethyl acetate and 19 g of butanol extract.

Isolation of Compounds from Ethyl Acetate Extract. The entire ethyl acetate extract was subjected to normal phase CC over silica gel (800 g) to yield 40 fractions (each of 500 mL) with the following eluants: fraction 1 with *n*-hexane, fractions 2–5 with *n*-hexane–ethyl acetate (9:1), fractions 6–11 with *n*-hexane–ethyl acetate (8:2), fractions 12–15 with *n*-hexane–ethyl acetate (7:3), fractions 16–20 with *n*-hexane–ethyl acetate (1:1), fractions 21–22 with ethyl acetate, fractions 23–28 with ethyl acetate–methanol (9.5:0.5), fractions 29–30 with ethyl acetate–methanol (9:1), fractions 31–36 with ethyl acetate–methanol (7:3), and fractions 37–40 with methanol. All fractions were examined by TLC. Fraction 1 was subjected to CC over silica gel (50 g; each fraction 100 mL) and TLC, then eluted with *n*-hexane–ethyl acetate to yield pure hentriacontane (50 mg). Fractions 2–5 were bulked (1.2 g) and subjected to CC over silica gel (100 g; each fraction 200 mL) and TLC, then eluted with dichloromethane and dichloromethane–methanol mixtures (99.8:0.2, 99.6:0.4, 99.4:0.6, 99.2:0.8 and 99:1) to yield six fractions; 1-tetratriacontanol (50 mg) was obtained from the initial fraction. Fraction 6 (2.8 g) was crystallized and, after purification by CC, yielded β-sitosterol (200 mg), the identity of which was confirmed through comparison with an authentic sample by co-chromatography (TLC) and spectroscopic data. Fraction 11 (2.1 g) was further purified by CC over silica gel (100 g; each fraction 200 mL) and eluted with dichloromethane and dichloromethane–methanol mixtures (99.8:0.2, 99.6:0.4, 99.4:0.6, 99.2:0.8 and 99:1) to afford two pure compounds, momilactone A (80 mg) and momilactone B (70 mg), and a new compound **1** (13 mg). Fraction 12 (3.4 g) was subjected to CC over silica gel (80 g; each fraction 150 mL) using dichloromethane and methanol as eluants to yield three compounds identified as tricin (10 mg), β-sitosterol-3-*O*-β-glucuronoside (50 mg), and 3,7-dimethyl-*n*-octan-1-yl benzoate (15 mg). Fraction 23 (1.2 g), after CC over silica gel (100 g; each fraction 100 mL) and elution with chloroform and methanol, yielded pure β-sitosterol-3-*O*-β-D-glucoside (50 mg). Fractions 29–30 of the 1st column from ethyl acetate extract was re-chromatographed over Lichroprep RP18 (ODS silica gel; 50 g; each fraction 100 mL) eluted sequentially with methanol containing 80, 60, 40 20, 10, and 0% water to yield two novel compounds in small quantities, namely, **2** (16 mg), **3** (18 mg), and the known hexacosanoic acid **4** (25 mg).

Acid Hydrolysis of 3. Compound **3** (6 mg) was refluxed with 2 mL of 1 M hydrochloric acid–dioxane (1:1, v/v) in a water bath for 4 h. The reaction mixture was evaporated to dryness and partitioned between chloroform and water four times. The chloroform extract was concentrated and contained the aglycone portion while the water extract contained D-glucose (co-chromatographed on TLC with authentic sample).

4-Hydroxymethylene-7-(9,9,13-trimethylcyclohexyl)-heptanyl-3′,7′,7′-trimethylcyclohexa-2′,4′-dien-1′-oate (1). IR spectrum (KBr, ν, cm^{-1}): 3448, 3395, 2959, 2922, 2853, 1730, 1650, 1462, 1345, 1263, 1077, 955, 803 cm^{-1}.

PMR (500 MHz, $CDCl_3$, δ, ppm, J/Hz): 7.71 (1H, d, J = 3.5, H-4′), 7.52 (1H, ddd, J = 4.5, 3.5, 4.0, H-5′), 4.32 (1H, d, J = 7.0, H-1_a), 4.30 (1H, d, J = 7.0, H-1_b), 4.28 (1H, d, J = 6.5, H-14_a), 4.26 (1H, d, J = 6.5, H_2-14_b), 1.73 (1H, d, J = 4.5, H-$6'_a$), 1.69 (1H, d, J = 4.0, H-$6'_b$), 1.56 (3H, br.s, Me-8′), 1.40 (1H, m, H-4), 1.38 (1H, m, H-8a), 1.36 (1H, m, H-13a), 1.33 (2H, m, H-2), 1.32 (2H, m, H-10), 1.29 (2H, m, H-3), 1.28 (2H, m, H-11), 1.26 (2H, m, H-12), 1.25 (3H, br.s, Me-9′), 1.12 (4H, m, H-5, H-6), 0.97 (2H, m, H-7), 0.88 (3H, br.s, Me-10′), 0.87 (3H, d, J = 6.5, Me-17), 0.85 (3H, br.s, Me-15), 0.83 (3H, br.s, Me-16).

^{13}C NMR (125 MHz, $CDCl_3$, δ, ppm): 66.43 (C-1), 33.85 (C-2), 33.32 (C-3), 36.70 (C-4), 29.92 (C-5), 29.48 (C-6), 28.81 (C-7), 32.98 (C-8), 25.70 (C-9), 26.99 (C-10), 29.31 (C-11), 19.39 (C-12), 26.54 (C-13), 66.12 (C-14), 19.39 (C-15), 11.60 (C-16), 10.90 (C-17), 167.94 (C-1′), 132.55 (C-2′), 129.06 (C-3′), 131.13 (C-4′), 131.13 (C-5′), 36.80 (C-6′), 23.21 (C-7′), 14.34 (C-8′), 26.07 (C-9′), 19.77 (C-10′); EIMS *m/z* (rel. int.) 418 $[M]^+$ ($C_{27}H_{46}O_3$) (3.6), 293 (75.2), 275 (5.1), 221 (3.9), 207 (1.3), 167 (28.3), 149 (100), 127 (37.1), 113 (3.8), 97 (11.0), 71 (37.8), 57 (31.1). FAB MS (positive ion mode) *m/z* 419 $[M+H]^+$ ($C_{27}H_{47}O_3$).

1-(*n*-Hexadec-7-enoxy)-6-(*n*-octadecanoxy)-β-D-glucopyranoside (2), IR spectrum (KBr, ν, cm^{-1}): 3450, 3375, 2955, 2845, 1730, 1640, 1414, 1260, 1080 cm^{-1}.

PMR (600 MHz, CD_3OD, δ, ppm, J/Hz): 5.37 (1H, br.s, H-1), 5.34 (1H, m, H-7′), 5.31 (1H, m, H-8′), 4.24 (1H, d, J = 7.2, H-6_a), 4.23 (1H, d, J = 7.2, H-6_b), 4.09 (1H, d, J = 7.7, H-2), 3.99 (1H, m, H-5), 3.67 (1H, m, H-4), 3.51 (1H, m, H-3), 2.31 (1H, d, J = 7.2, H-$2'_a$), 2.29 (1H, d, J = 7.2, H-$2'_b$), 2.01 (1H, d, J = 7.8, H-$2''_a$), 1.99 (1H, d, J = 7.8, H-$2''_b$), 1.66 (2H, m,

H-6′), 1.57 (2H, m, H-9′), 1.37 (2H, m, H-3′), 1.28 (2H, m, H-3″), 1.23 (46 H, br.s, 23 × CH_2), 0.85 (3H, t, J = 6.78, Me-16′), 0.81 (3H, t, J = 6.1, Me-18″).

^{13}C NMR (150 MHz, CD_3OD, δ, ppm): 103.65 (C-1), 76.91 (C-2), 74.01 (C-3), 72.46 (C-4), 78.14 (C-5), 70.55 (C-6), 176.39 (C-1′), 39.89 (C-2′), 33.84 (C-3′), 32.43 (C-4′), 30.19 (C-5′), 37.51 (C-6′), 130.68 (C-7′), 129.94 (C-8′), 34.95 (C-9′), 29.86 (C-10′), 29.86 (C-11′), 29.68 (C-12′), 26.56 (C-13′), 20.15 (C-14′), 19.38 (C-15′), 14.41 (C-16′), 174.78 (C-1″), 37.93 (C-2″), 32.70 (C-3″), 32.43 (C-4″), 30.19 (C-5″), 30.19 (C-6″), 30.19 (C-7″), 29.86 (C-8″), 29.86 (C-9″), 29.86 (C-10″), 28.48 (C-11″), 27.75 (C-12″), 25.71 (C-13″), 25.30 (C-14″), 23.46 (C-15″), 23.16 (C-16″), 23.05 (C-17″), 12.32 (C-18″); EI-MS *m/z* (rel.int.): 682 $[M]^+$ ($C_{40}H_{74}O_8$) (not observed); 431 (7.7), 417 $[M–C_{16}H_{29}O]^+$ (100), 389 (13.4), 339 (48.8), 265 (9.1), 179 (6.4), 137 (13.0), 125 (17.5), 97 (30.4), 85 (21.5), 83 (29.2), 57 (41.5), 71 (29.5), 69 (29.0); FAB-MS (positive ion mode): *m/z* 683 $[M+H]^+$; HRFABMS (positive ion mode): *m/z* 683.5418 (calculated for $C_{40}H_{75}O_8$ with – 0.4 ppm error).

(*Z*)-12-Hydroxy-9-octadecenoic Acid-12-*β*-D-glucopyranoside (3). IR spectrum (KBr, ν, cm^{-1}): 3435, 3380, 2960, 2845, 1695, 1640, 1564, 1415, 1360, 1250, 1120, 801.

PMR (600 MHz, CD_3OD, δ, ppm, J/Hz): 6.82 (1H, m, H-10), 6.76 (1H, m, H-9), 5.38 (1H, d, J = 2.8, H-1′), 3.95 (1H, m, H-2′), 3.88 (1H, m, H-5′), 3.85 (1H, m, H-12), 3.65 (1H, m, H-3′), 3.60 (1H, m, H-4′), 3.30 (2H, br.s, H-6′), 2.32 (1H, d, J = 7.2, H-2_a), 2.30 (1H, d, J = 7.2, H-2_b), 2.15 (1H, dd, J =7.2, 7.2, H-11_a), 2.12 (1H, dd, J = 7.2, 7.8, H-11_b), 2.05 (1H, br. s, H-8_a), 2.02 (1H, br.s, H-8_b), 1.52 (6H, br.m, 3 × CH_2), 1.32 (6H, br.s, 3 × CH_2), 1.28 (8H, br. s, 4 × CH_2), 0.89 (3H, t, J = 6.0, Me-18).

^{13}C NMR (150 MHz, CD_3OD, δ, ppm): 180.72 (C-1), 38.65 (C-2), 30.84 (C-3), 30.84 (C-4), 30.84 (C-5), 30.58 (C-6), 30.65 (C-7), 36.21 (C-8), 116.77 (C-9), 115.98 (C-10), 35.23 (C-11), 75.16 (C-12), 30.84 (C-13), 30.58 (C-14), 30.65 (C-15), 27.79 (C-16), 26.11 (C-17), 24.28 (C-18), 99.01 (C-1′), 81.35 (C-2′), 68.19 (C-3′), 67.52 (C-4′), 77.63 (C-5′), 64.38 (C-6′); EI-MS *m/z* (rel. int.): 460 $[M]^+$ ($C_{24}H_{44}O_8$) (not observed); FAB-MS (positive mode) *m/z* 461 $[M]^+$ ($C_{24}H_{45}O_8$).

Hexacosanoic Acid (4). Colorless solid; mp 89–90°C; EIMS *m/z* (rel. int.) 396 $[M]^+$ ($C_{26}H_{52}O_2$); FAB MS (positive ion mode) *m/z* 397 $[M+H]^+$ ($C_{26}H_{53}O_2$).

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