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PISCICIDAL STEROL ACYLGLUCOSIDES FROM *EDGEWORTHIA CHRYSANTHA*

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Key Word Index—*Edgeworthia chrysantha*; Thymelaeaceae; flower; sitosterol-3-*O*-6-linoleoyl- and sitosterol-3-*O*-6-linolenoyl-β-D-glucopyranosides; grasshopper ketone; daphnoretin; piscicidal activity; synthesis of chrysanthoside.

Abstract—New potent piscicidal sterol acylglucosides named chrysanthosides have been obtained from the flower of *Edgeworthia chrysantha*, together with the previously known bis-coumarin and grasshopper ketone and their structures characterized to be sitosterol-3-*O*-6-linoleoyl- and sitosterol-3-*O*-6-linolenoyl-β-D-glucopyranosides by spectral data and synthesis. The natural and synthetic chrysanthosides possess potent piscicidal activity against killie-fish which was killed within 3 hr at a concentration of 0.1 ppm.

INTRODUCTION

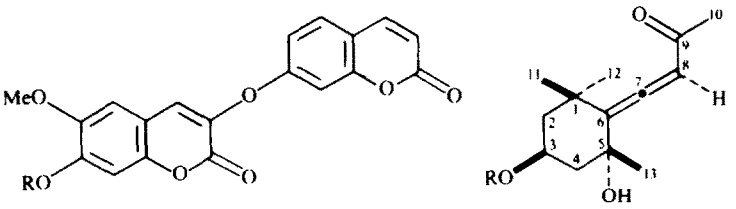
Edgeworthia chrysantha (= *E. papyrifera*) has been used for manufacturing good quality paper, although it produces daphnane-type diterpenoids possessing strong tumour promoting activity [1]. The flowers of this plant also contain odouriferant substances such as benzyl alcohol and nonanal [2]. In the course of our investigation of haemolytic substances of plants [3, 4], we found that the methanolic extract of the flowers of *E. chrysantha* showed an intense piscicidal activity. We report the isolation and characterization of piscicidal sterol acylglucoside from *E. chrysantha* and its synthesis.

RESULTS AND DISCUSSION

The methanol extract was suspended in water and extracted with ethyl acetate and *n*-butanol, successively. The ethyl acetate extract killed killie-fish (= *Oryzia latipes*) within 110 min at a concentration of 100 ppm and 28 hr at 10 ppm. The *n*-butanol extract was inactive against the same fish at a concentration of 100 ppm. The ethyl acetate extract was chromatographed on silica gel using methylene chloride–ethyl acetate gradient to give new piscicidal sterol acylglucosides chrysanthosides (mixture of **3a** and **b**), together with the previously known bis-coumarin, daphnoretin (**1**) [5, 6] and grasshopper ketone (**2**) [7].

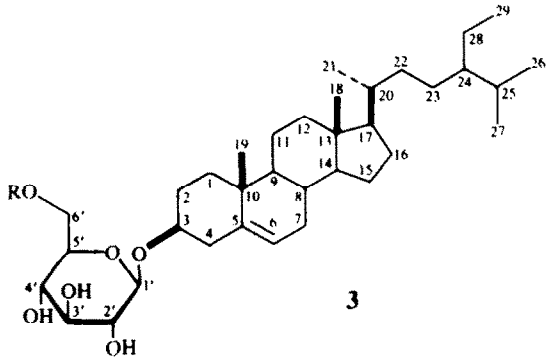
Compound **3** (**3a** and **b**) contained a hydroxyl (3400 cm^{-1}) and an ester group (1725 cm^{-1}). The ^1H NMR spectrum (see Experimental) showed the presence of two tertiary methyls, three secondary methyls and one primary methyl, a methine bearing a hydroxyl group and an olefinic proton, and a glucose moiety which was confirmed by the ^1H–^1H 2D COSY NMR experiment. The ^1H NMR spectrum also contained the signals characteristic of a unsaturated long chain fatty acid (δ_H 0.98, 3H, *t*, $J = 7.6$ Hz; 2.80, *m*; 5.38, *m*). The above spectral data suggested that **3** might be a sterol acylglucoside. In fact, the ^1H NMR spectral data of **3** were quite similar to those of antiulcerogenic sitosterol-3-*O*-6-palmitoyl- and sitosterol-3-*O*-6-oleoyl-β-D-glucopyranosides from *Musa paradisica* [8] and sitosterol-3-*O*-6-stearoyl-β-D-glucopyranoside from *Alisma plantago-aquatica* [9]. Compound **3** was reduced with lithium aluminium hydride, followed by acetylation with acetic anhydride in pyridine to give octadeca-9,12,15-trien-1-yl acetate (**7**) ($[M]^+$ *m/z* 306), octadeca-9,12-dien-1-yl acetate (**8**) ($[M]^+$ *m/z* 308) and sitosterol 2′,3′,4′,6′-tetraacetyl-β-D-glucopyranoside (**6**). The ratio (1.8:1) of **7** and **8** was estimated by GC analysis. The structures (**7** and **8**) were confirmed by the identity of the spectral data with those of authentic samples. The structure (**6**) was also established by its synthesis (see later). The position of the acyl group was established to be at C-6 of glucose, as the methylene protons appeared at lower field than H-2, H-3 and H-4 in the ^1H NMR spectrum of **3** [10]. On the basis of the above chemical and spectral data, compound **3** is a mixture of sitosterol-3-*O*-6-linolenoyl- and sitosterol-3-*O*-6-linoleoyl-β-D-glucopyranosides (**3a** and **b**).

In order to obtain further evidence for the structure of **3**, we carried out the synthesis of **3a** by the glucosylation methods reported by Schmidt *et al.* [11] and Rathore *et al.* [12]. 2,3,4,6-Tetra-*O*-benzyl-D-glucose (**10**) was treated with trichloroacetonitrile in the presence of sodium hydride to give 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl-1-*O*-trichloroacetaimidate (**11**) [11, 12]. Sitosterol (**9**) was glycosylated with **11** in the presence of boron trifluoride etherate to give β-D-glucoside (**12**) and α-D-glucoside (**13**) in the ratio of 3.3:1, the structures of which were established by the differences of the coupling constants ($J = 8.8$ Hz in **12** and 3.4 Hz in **13**) of H-1′ in the ^1H NMR spectra and the difference of the chemical shifts (δ_C 102.2 in **12** and 94.5 in **13**) and coupling constants ($J = 158.1$ in **12** and 169.7 in **13**) of C-1′ in the ^{13}C NMR spectra [13]. Birch reduction [14] of **12** gave sitosterol-3-*O*-β-glucopyranoside (**14**) [15], followed by acetylation to afford the tetraacetate of **14** whose spectral data were identical to those of **6** derived from the natural product **3**. Treatment of **14** with linolenoyl chloride in pyridine gave

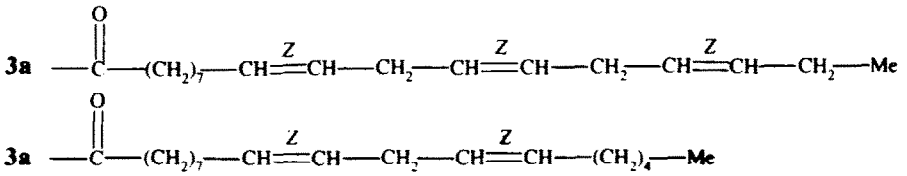


1 R=H
4 R=Ac

2 R=H
5 R=Ac

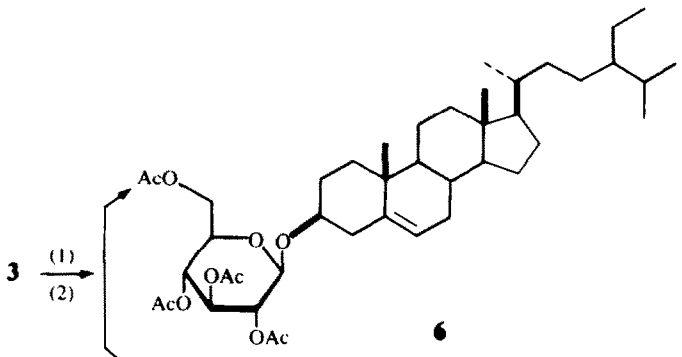


3

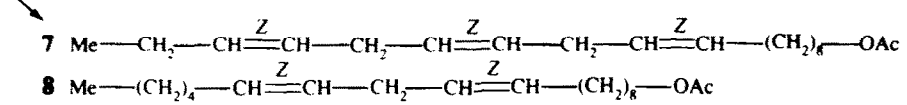


3a

3a



6



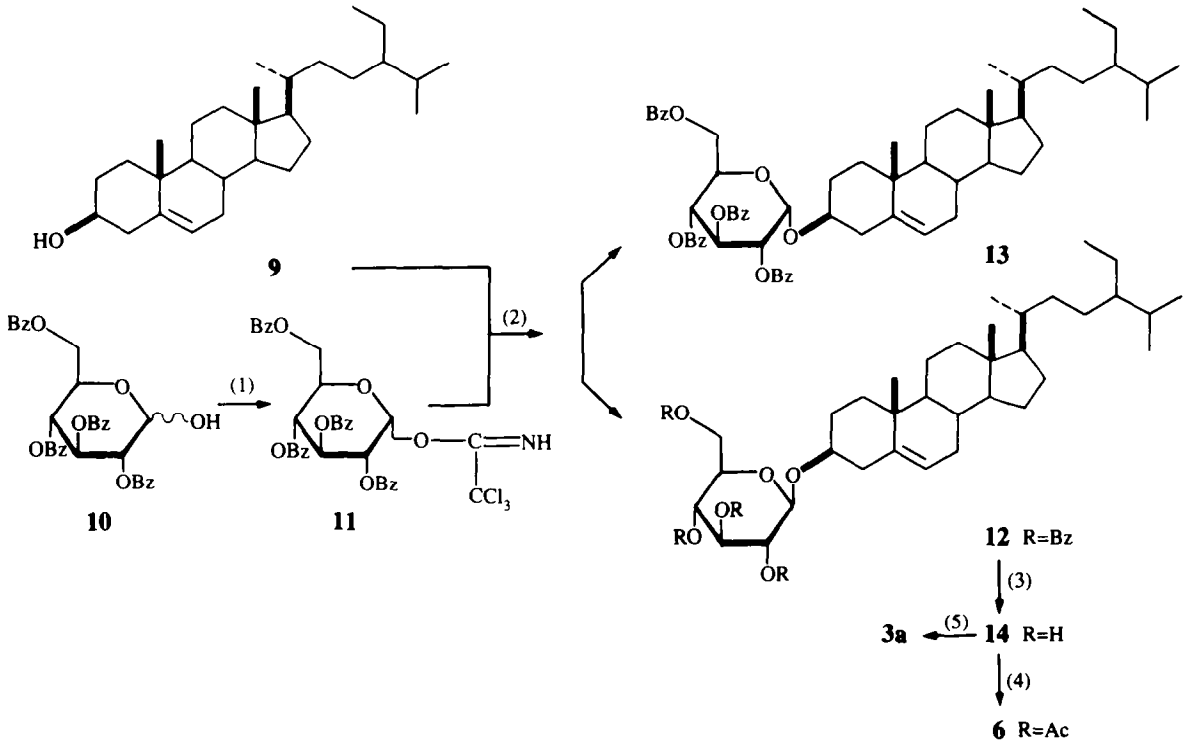
7

8

(1) $LiAlH_4$ (2) Ac_2O/pyridine

sitosterol-3-*O*-6-linolenoyl-β-D-glucopyranoside (**3a**) whose specific optical rotation and spectral data were almost identical to those of compound **3**.

The piscicidal activity of compounds (**1**–**3**, **3a** and **14**) against killie-fish is shown in Table 1. Bis-coumarin (**1**), grasshopper ketone (**2**) and synthetic glucoside (**14**) were inactive at a concentration of 100 ppm. The natural (**3**) and synthetic glucosides (**3a**) showed an intense piscicidal activity and all fish were killed within 3 hr at a concentration of 0.1 ppm. Daphnoretin (**1**) and its acetate (**4**) have been isolated from *E. gardneri* [5, 6]. Grasshopper ketone (**2**), which was initially isolated from the large flightless grasshopper, *Romalea microptera* as a chemical repellent [7], has been isolated from the flower of the present species and from the leaf of *Cissus pheifolia* (Vitaceae) [16].



(1) CCl_3CN/NaH (2) BF_3Et_2O (3) Li/liq.NH_3 (4) Ac_2O pyridine

(5) Me—CH_2—CH=(Z)CH—CH_2—CH=(Z)CH—CH_2—CH=(Z)CH—$(CH_2)_7$—COCl/pyridine

Table 1. Piscicidal activity of the crude extracts and compounds **1**, **2** and **3** from *E. chrysantha* and synthetic **3a** and **14** against killic-fish

Extract and compound	ppm/min*
EtOAc extract	100/110
	10/1680
n-BuOH	100/(−)†
1	100/(−)
	10/(−)
2	100/(−)
	10/(−)
3 and **3a**	5/40
	2.5/50
	1/80
	0.1/180
14	100/(−)

*Concentration at which all fish were killed.

†Concentration at which all fish were not killed after 24 hr.

EXPERIMENTAL

Mps: uncorr. The solvents used for spectral measurements were TMS–$CDCl_3$ [^{1}H (400 MHz); ^{13}C NMR (100 MHz)]; $CHCl_3$ ($[\alpha]_D$ and EtOH (CD and UV), unless otherwise stated. IR spectra were measured as KBr tablets unless otherwise stated. EIMS were carried out at 70 eV (ionizing potential) and 5 kV (accelerating voltage).

Bioassay. Piscicidal activity was tested using a modified method of ref. [17] in which Me_2CO was used as the solvent in place of MeOH.

Plant material. Edgeworthia chrysantha Lindl. (= *E. papyrifera* Sieb. et Zucc.) was collected in Ichiu-son, Tokushima, in April 1985. The voucher specimen is deposited at the Institute of Pharmacognosy, Tokushima Bunri University.

Extraction and isolation. Edgeworthia chrysantha was extracted with MeOH for 1 month. The crude extract, after removal of the solvent, was suspended in H_2O and extracted with EtOAc and *n*-BuOH, successively. Evaporation of the solvents gave EtOAc extract (47.79 g) and *n*-BuOH extract (36.20 g). The former extract was chromatographed on silica gel using a CH_2Cl_2–EtOAc gradient. From the 40% EtOAc–CH_2Cl_2 fr., daphnoretin (**1**) (501 mg) was obtained as pale yellow needles, mp 244–246° (lit. [5] 244–245°); HRMS: found: 352.0580; $C_{19}H_{12}O_7$ requires 352.0583; (found: C, 64.98; H, 3.41, $C_{19}H_{12}O_7$ requires: C, 64.77; H, 3.43). 7-*O*-acetyldaphnoretin (**4**): needles, mp 230–232.5° (lit. [6] 230–232°); HRMS: found: 394.0670; $C_{21}H_{14}O_8$ requires 394.0689. The spectral data of **1** and **4** were identical to those of reported data [5, 6]. From the 60% EtOAc–CH_2Cl_2 fr., the mixtures of sterol acylglucoside (**3**) (319 mg) was obtained as a viscous oil. Grasshopper ketone (**2**) was isolated from the 80% EtOAc–CH_2Cl_2 fr. as crystals, mp 128–129.5° (lit. [7] 128–128.5); $[\alpha]_D$ −41° (c 0.72); IR ν_{max} cm^{-1}: 3350, 1940 (C=C=C), 1680, 1455, 1360, 1230, 1160, 1035; UV λ_{max} nm (log ε): 206 (4.05), 233 (4.16); CD: $\Delta\varepsilon_{258\,nm}$ −5.10,

$\Delta\varepsilon_{231\,nm}$ +5.88, $\Delta\varepsilon_{208\,nm}$ −6.51; ^{1}H NMR: δ 1.16 (3H, s, Me-1), 1.39 (3H, s, Me-1), 1.44 (3H, s, Me-5), 2.19 (3H, s, Me-9), 4.35 (1H, tt, J = 11.5, 4.2 Hz, H-3), 5.86 (1H, s, H-8); ^{13}C NMR: δ 26.4 (q, C-10), 29.1, 31.0 (each q, C-11 or C-12), 31.7 (q, C-13), 36.2 (s, C-1), 48.4 (d, C-2 or C-4), 49.1 (d, C-2 or C-4), 63.6 (d, C-3), 72.4 (s, C-5), 100.9 (d, C-8), 118.4 (s, C-6), 198.2 (s, C-9), 209.6 (s, C-7); EIMS: m/z (rel. int.): 224 $[M]^+$ (1), 209 (34), 163 (41), 152 (14), 151 (18), 149 (34), 125 (31), 123 (54), 121 (21), 109 (43), 107 (23), 95 (35), 43 (100); HRMS: found: 224.1408; $C_{13}H_{20}O_3$ requires 224.1448. 3-Acetyl grass hopper ketone (**5**): mp 76.0–78.5; $[\alpha]_D$ −36° (*c* 0.6); IR ν_{max} cm^{-1}: 3450, 2950, 1940, 1730, 1670, 1355, 1235, 1175, 1155, 1065, 1020; UV λ_{max} nm (log ε): 206 (3.96), 233 (4.11); CD: $\Delta\varepsilon_{253\,nm}$ −7.50, $\Delta\varepsilon_{228\,nm}$ +9.39, $\Delta\varepsilon_{208\,nm}$ −5.70; ^{1}H NMR: 1.16 (3H, s, Me-1), 1.43 (3H, s, Me-1 or Me-5), 1.44 (3H, s, Me-1 or Me-5), 2.05 (3H, s, OAc-3), 2.19 (3H, s, Me-9), 5.38 (1H, tt, J = 11.5, 4.2, H-3), 5.87 (1H, s, H-8); ^{13}C NMR: δ 21.3 (q, OAc), 26.3 (q, C-10), 28.8, 30.7 (each q, C-11 or C-12), 31.6 (q, C-13), 36.0 (s, C-1), 44.9 (d, C-2 or C-4), 45.0 (d, C-2 or C-4), 67.5 (d, C-3), 71.8 (s, C-5), 100.8 (d, C-8), 118.3 (s, C-6), 170.4 (s, OAc), 198.2 (s, C-9), 209.6 (s, C-7); EIMS: (rel. int.): 266 $[M]^+$ (1), 207 (17), 191 (39), 164 (24), 163 (40), 149 (15), 145 (12), 131 (20), 123 (86), 122 (19), 121 (18), 107 (13), 85 (13), 43 (100); HRMS: found: 266.1524; $C_{15}H_{22}O_4$ requires 266.1518. Compound **3** (the mixtures of **3a** and **3b**): $[\alpha]_D$ −42.5° (*c* 1.2); IR ν_{max}^{neat} cm^{-1}: 3400, 2925, 1725, 1620, 1455, 1430, 1370, 1230, 1155, 1050; ^{1}H NMR: δ 0.68 (3H, s, Me-18), 0.81 (3H, d, J = 6.8, Me-26 or Me-27), 0.83 (3H, d, J = 6.8 Hz, Me-26 or Me-27), 0.86 (3H, t, J = 6.8 Hz, Me-29), 0.92 (3H, d, J = 6.6 Hz, Me-21), 0.98 (3H, t, J = 7.6 Hz, Me-$(CH_2)_n$–), 1.01 (3H, s, Me-19), 1.31 (m, –$(CH_2)_n$–), 2.36 (m, –CH_2–CO_2–), 2.80 (m, –CH=CH–CH_2–), 3.35 (1H, dd, J = 9.0, 7.6 Hz, H-2'), 3.39 (1H, dd, J = 9.0, 9.0 Hz, H-4'), 3.44 (1H, m, H-3), 3.57 (1H, dd, J = 9.0, 9.0 Hz, H-3'), 3.60 (1H, m, H-5'), 4.25 (1H, dd, J = 12.0, 2.0 Hz, H-6'), 4.38 (1H, d, J = 7.6 Hz, H-1'), 4.50 (1H, dd, J = 12.0, 4.0 Hz, H-6'), 5.36 (1H, br t, J = 1.9 Hz, H-6), 5.38 (m, –CH=CH–).

Reduction of compound **3** *and acetylation of reduced product.* To a suspension of $LiAlH_4$ (50 mg) in Et_2O (10 ml) was added **3** (110 mg) dropwise for 10 min with stirring. To the resultant solution was added EtOAc (5 ml) and then 1 M HCl (20 ml) at 0–5°, followed by filtration through Celite and the filtrate partitioned between EtOAc and H_2O. The EtOAc layer, after being dried over $MgSO_4$ and concd, was acetylated with Ac_2O–pyridine (each 3 ml) to give the crude acetate (121 mg) which was purified by prep. TLC (C_6H_6–EtOAc, 4:1) to afford sterol-3-*O*-β-D-glucopyranoside (**6**) (35 mg) [14], and the monoacetate mixtures (**7** and **8**, the ratio 1.8:1 in GC) (31 mg) the structures of which were confirmed by identity of R_f of GC and mass spectra (GC-MS) with those of authentic samples.

Synthesis of **12** *and* **13**. To a suspension of NaH (230 mg) and dry CH_2Cl_2 (10 ml) was added 2,3,4,6-tetra-*O*-benzyl-D-glucopyranose (**10**) (2.75 g) in dry CH_2Cl_2 (30 ml) dropwise and stirred for 20 min at room temp. To the reactant mixture was added CCl_3CN (2.3 ml) and stirred for 1 hr, followed by filtration through the mixtures of Celite (5 g) and silica gel (10 g) and the filtrate concd to give 2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl-1-*O*-trichloroacetimidate (**11**) (2.89 g) [11, 12]. To compound (**11**) in CH_2Cl_2 (30 ml) was added sitosterol (**9**) (2.0 g) in CH_2Cl_2 (20 ml) and then $BF_3 \cdot Et_2O$ (0.2 ml) at 0 to −10°. The resulting mixture was stirred for 1 hr and poured into ice H_2O and extracted with CH_2Cl_2. The extract was dried over $MgSO_4$, concd to give the residue (5.35 g) which was chromatographed on silica gel using *n*-hexane–EtOAc gradient to furnish 3-[(2,3,4,6-tetra-*O*-benzyl-β-D-glucopyranosyl)oxy]- (**12**) (1.488 g, 42.9%), 3-[2,3,4,6-tetra-*O*-benzyl-α-D-glucopyranosyl)oxy]-sitosterol (**13**) (454 mg, 13.1%) and sitosterol (**9**) (485 mg, 24.3%) recovered, respectively. Compound **12**: mp 85.5–87.0°; $[\alpha]_D$ −1.3° (*c* 1.17); IR ν_{max} cm^{-1}: 3050, 2950, 1610, 1495, 1450, 1355, 1060, 1020, 725, 690; ^{1}H NMR: δ 0.68 (3H, s, Me-18), 0.81 (3H, d, J = 7.1 Hz, Me-26 or Me-27), 0.83 (3H, d, J = 7.1 Hz, Me-26 or Me-27), 0.85 (3H, t, J = 7.8 Hz, Me-29), 0.93 (3H, d, J = 6.3 Hz, Me-21), 1.03 (3H, s, Me-19), 4.65 (1H, m, H-3), 3.46 (2H, m, H-6'), 4.51 (1H, dd, J = 8.8, 8.8 Hz, H-2'), 4.56 (1H, dd, J = 8.8, 8, 8 Hz, H-4'), 4.85 (1H, dd, J = 8.8, 8.8 Hz, H-3'), 3.73 (1H, m, H-5'), 4.57 (1H, d, J = 8.8 Hz, H-1'), 4.49–4.99 (8H, m, O–CH_2–C_6H_6), 5.34 (1H, m, H-6), 7.16–7.36 (20H, m, aromatic protons); ^{13}C NMR: δ 11.8 (q, C-18), 11.9 (q, C-29), 18.8 (q, C-26 or C-27), 19.0 (q, C-21), 19.4 (q, C-26 or C-27), 19.8 (q, C-19), 21.0 (t, C-11), 23.0 (t, C-28), 24.3 (t, C-15), 26.0 (d, C-23), 28.2 (t, C-12), 29.1 (d, C-25), 29.9 (d, C-2), 31.8 (t, C-7 or C-8), 31.9 (t, C-7 or C-8), 33.9 (t, C-22), 36.1 (d, C-20), 36.7 (s, C-10), 37.3 (t, C-1), 39.1 (t, C-4), 39.7 (t, C-16), 42.3 (s, C-13), 45.7 (d, C-24), 50.1 (d, C-9), 56.0 (d, C-17), 56.7 (d, C-14), 69.0 (t, C-6'), 73.3, 74.7, 74.9 (t, –CH_2–C_6H_5), 75.6 (d, C-4'), 77.9 (d, C-3), 79.6 (d, C-2'), 82.3 (d, C-3') 84.8 (d, C-5'), 102.2 (d, C-1'), 121.9 (d, C-6), 127.5, 127.6, 127.8, 127.9, 128.2, 128.3 (d, aromatic carbons), 138.1, 138.2, 138.5, 138.6 (s, aromatic carbons), 140.5 (s, C-5); $J_{1'-C-H}$ = 158.1 Hz. (Found: C, 81.17; H, 9.02, $C_{63}H_{84}O_6$ requires C, 80.73; H, 9.03). Compound **13**: mp 134.5–136.0°; $[\alpha]_D$ +42° (*c* 1.21); IR ν_{max} cm^{-1}: 3025, 2950, 2850, 1610, 1495, 1450, 1355, 1065, 1030, 745, 725, 690; ^{1}H NMR: δ 0.68 (3H, s, Me-18), 0.81 (3H, d, J = 7.1 Hz, Me-26 or Me-27), 0.83 (3H, d, J = 7.1, Me-26 or Me-27), 0.85 (3H, d, J = 7.8 Hz, Me-29), 0.93 (3H, d, J = 6.3 Hz, Me-21), 1.03 (3H, s, Me-19), 3.47 (1H, m, H-3), 3.55 (1H, dd, J = 9.5, 3.4, H-6'), 3.64 (2H, m, H-2' and H-4'), 3.74 (1H, dd, J = 9.5, 3.2 Hz, H-6'), 4.93 (1H, d, J = 3.4 Hz, H-1'), 4.43–5.02 (8H, m, O–CH_2–C_6H_5), 6.98–7.35 (20H, m, aromatic protons); ^{13}C NMR: 11.8 (q, C-18), 12.0 (q, C-29), 18.8 (q, C-26 or C-27), 19.0 (q, C-21), 19.3 (C-26 or C-27), 19.8 (q, C-19), 21.0 (t, C-11), 23.0 (t, C-28), 24.2 (t, C-15), 26.0 (d, C-23), 28.2 (t, C-12), 29.1 (d, C-25), 30.2 (d, C-2), 31.8 (t, C-7 or C-8), 31.9 (t, C-7 or C-8), 33.9 (t, C-22), 36.1 (d, C-20), 36.7 (s, C-10), 37.0 (t, C-1), 38.7 (t, C-4), 39.7 (t, C-16), 42.2 (s, C-13), 45.7 (d, C-24), 50.0 (d, C-9), 55.9 (d, C-17), 56.7 (d, C-14), 68.5 (t, C-6'), 70.0 (d, C-3), 73.0, 73.3, 75.0, 75.6 (t, O–CH_2–C_6H_5), 76.4 (d, C-4'), 77.8 (d, C-2'), 79.8 (d, C-3'), 82.0 (d, C-5'), 94.5 (d, C-1'), 121.6 (d, C-6), 127.4, 127.6, 127.8, 127.9, 128.2, 128.3 (s, aromatic carbons), 137.9, 138.2, 138.9 (s, aromatic carbons), 140.7 (s, C-5); $J_{1'-C-H}$ = 169.68 Hz. (Found: C, 80.42; H, 8.99, $C_{63}H_{84}O_6$ requires C, 80.73; H, 9.03).

Birch reduction [14] of **12**. To liq. NH_3 (*ca* 40 ml) was added Li (2.0 g) and stirred for 30 min. To this solution was added **12** (1.30 g) in dry THF (10 ml) dropwise for 20 min and stirred for 2 hr at −78° and further for 30 min and allowed to stand for 30 min at room temp. and then NH_4Cl (10 g) and H_2O (50 ml) were added to the reaction mixture and extracted with EtOAc, dried over $MgSO_4$, filtered and concd to afford the residue (1.015 g) which was chromatographed on Sephadex LH-20 ($CHCl_3$–MeOH 1:1) to furnish sitosterol-3-*O*-β-D-glucopyranoside (**14**) (781 mg, 97.6%), mp 287–290° (lit. [15] 290–295°).

Acetylation of compound **14**. Compound **14** (30 mg) was acetylated with Ac_2O–pyridine (each 1 ml) to give a tetraacetate (29 mg), mp 166.5–168° (lit. [15] 167–168°); $[\alpha]_D$ −25.4° (*c* 0.71) (lit. [15] −25.1°), whose spectral data were identical to those of the tetraacetate (**6**) derived from the natural product (**3**).

Linolenoylation of compound **14**. Linolenic acid (1 g) was treated with $SOCl_2$ (0.4 ml) in dry C_6H_6 (5 ml) under reflux to give linolenoyl chloride (1.05 g) to which **14** (200 mg) was added and stirred for 2 hr at room temp. Work-up as usual gave the residue (485 mg) which was further purified by a combination of Sephadex LH-20 ($CHCl_3$–MeOH, 1:1) and prep. TLC to furnish sitosterol-3-*O*-6-linolenoyl-β-D-glucopyranoside (**3a**) (32 mg). $[\alpha]_D$ −41° (*c* 0.85), the spectral data of which were almost identical to those of **3**.

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