Monatshefte für Chemie 130, 887–897 (1999)

Monatshefte für Chemie
Chemical Monthly

Printed in Austria

Synthesis and Haemolytic Activity of Randianin Isomers

Werner Seebacher[1], **Ernst Haslinger**[1,*], **Karin Rauchensteiner**[2], **Johann Jurenitsch**[2], **Armin Presser**[1], and **Robert Weis**[1]

[1] Institute of Pharmaceutical Chemistry, University of Graz, Graz, Austria
[2] Institute of Pharmacognosy, University of Vienna, Vienna, Austria

Summary. Randianin, a haemolytic active saponin from *Randia dumetorum*, and some of its isomers with different carbohydrate side chains have been synthesized from oleanolic acid. The influence of the linkage within the disaccharide residue on the haemolytic activity of these glycosides has been investigated.

Keywords. Glycosidation; Glycosides; Terpenes.

Synthese und hämolytische Aktivität von Isomeren des Randianins

Zusammenfassung. Randianin, ein hämolytisches Saponin aus *Randia dumetorum*, sowie einige dazu isomere Glycoside wurden ausgehend von Oleanolsäure synthetisiert. Der Einfluß der Verknüpfung in der Dissaccharidseitenkette auf die hämolytische Wirkung dieser Glycoside wurde untersucht.

Introduction

Saponins are glycosides of steroids or terpenes, widely distributed in nature and showing important biological and pharmacological activities [1]. The molecular mechanism of most biological activities of these substances is not yet entirely clear. Concerning the haemolytic activity it is accepted that not only their tenside properties are relevant, because no clear correlation between haemolytic power and surface activity has been established. It seems that the first step is an irreversible interaction of the oligosaccharide chain with the membrane of the erythrocytes [2–5]. Therefore, the activity of a saponin strongly depends on its oligosaccharide structure. In the following step enzymatic deglycosidation releases the aglycon, which destroys the membrane locally. For the systematic investigation of structure-activity correlations a synthetic route giving access to several structurally related compounds is desirable. We report the first partial synthesis of randianin (**1**), a glycoside of oleanolic acid, and its isomers **2**, **3**, and **4** (Fig. 1). We have also

* Corresponding author

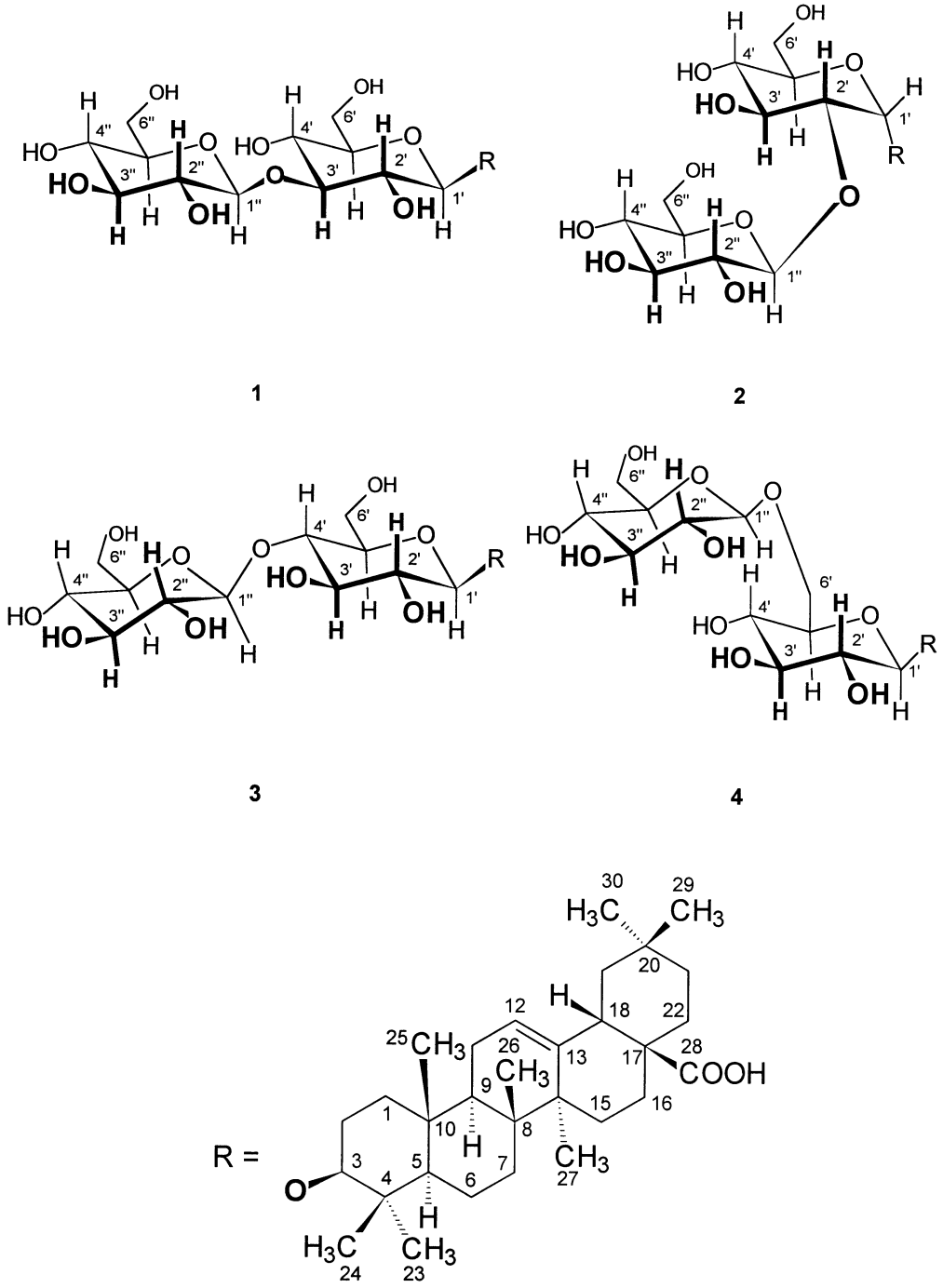


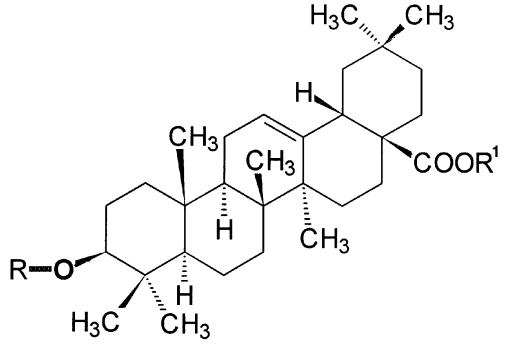
Fig. 1. Structures of glycosides **1**–**4**

determined the haemolytic activity of compounds **1**–**4**. Randianin has been isolated from *Anchusa officinalis* and *Catunaregam nilotica* and described as a haemolytically active [6, 7] and highly molluscidal [8] saponin. **2** is the α-isomer of glycoside E_2 isolated from *Hedera taurica* Carr. [9].

Results and Discussion

Oleanolic acid (**5**)

Oleanolic acid was prepared from cloves according to a procedure given in the literature [10]. The carboxyl group of **5** was protected by esterification with diphenyldiazomethane [11–13], and the diphenylmethyl oleanolate **6** was used as starting material for the glycosidation reactions (Fig. 2).



5: R = H, R^1 = H

6: R = H, R^1 = $CH(Ph)_2$

7: R = 3O-β-*D*-(2,3,4,6-Tetraacetyl-*glcp*)-(1→2)-α-*D*-(3,4,6-triacetyl-*glcp*)-(1→, R^1 = $CH(Ph)_2$

8: R = 3O-β-*D*-(2,3,4,6-Tetraacetyl-*glcp*)-(1→3)-β-*D*-(3,4,6-triacetyl-*glcp*)-(1→, R^1 = $CH(Ph)_2$

9: R = 3O-β-*D*-(2,3,4,6-Tetraacetyl-*glcp*)-(1→4)-β-*D*-(3,4,6-triacetyl-*glcp*)-(1→, R^1 = $CH(Ph)_2$

10: R = 3O-β-*D*-(2,3,4,6-Tetraacetyl-*glcp*)-(1→6)-β-*D*-(3,4,6-triacetyl-*glcp*)-(1→, R^1 = $CH(Ph)_2$

Fig. 2. Oleanolic acid and its derivatives

Glycosidation

As glycosyl donors we used the appropriate peracetylglycosyl bromides. For the synthesis of saponin **2**, sophorose obtained from methyl 4,6-O-benzyliden-α-*D*-glucopyranoside and acetobromoglucose was acetylated [13, 14], and the afforded octaacetylsophorose was brominated [15–17] yielding 2,3,4,6-tetraacetyl-β-*D*-glucopyranosyl(1→2)-3,4,6-triacetyl-α-*D*-glucopyranosyl bromide. The latter was used for the glycosidation of **6**. Product **7** was, after removal of the acetyl groups with sodium methanolate, hydrogenated giving saponin **2**. The configuration of the two anomeric carbons was determined by ^{1}H NMR spectroscopy. The resonance of the anomeric proton of the terminal glucose residue exhibited a large vicinal coupling constant ($J = 7.6$ Hz), indicating an axial-axial arrangement of H-1 and

H-2 and, therefore, β-configuration. The second anomeric proton showed a small coupling constant ($J = 3.4$ Hz). From this we conclude α-configuration for this glucose residue.

In a similar procedure, peracetyl laminaribiose obtained from 1,2:5,6-di-O-isopropylidene-α-*D*-glucopyranose and 3,4,6,-Tri-O-acetyl-α-*D*-glucopyranose 1,2-(*tert*-butyl orthoacetate) [18] was converted to α-peracetyl laminaribiose bromide and used for the synthesis of randianin (**1**) *via* **8**. The configuration of the anomeric carbons was determined by NMR spectroscopy as described before. In compounds **8** and **1** the resonances of both anomeric protons exhibited a large axial-axial coupling constant indicating β-configuration.

In an analogous way **3** was obtained from α-acetobromocellobiose *via* **9**. Compound **4** was available from α-acetobromogentiobiose *via* **10**. The configurations of the anomeric carbons of **3**, **4**, **9**, and **10** were investigated by ^{1}H NMR as described above, indicating β-configuration in all cases.

Determination of haemolytic activity

From literature [19–20] it is evident that the haemolytic activity varies considerably with the structure of the glycoside. Monodesmosidic triterpene saponins usually have a high haemolytic activity, whether they are neutral, acidic, or an ester saponin. Polar substitution in ring A and weak polar substitution in rings D and E increases this special effect of lysing the erythrocyte membranes which causes a release of haemoglobin. Bisdesmosidic triterpenes, acylglycosides, and saponins with strong polar substituents in rings D and E exhibit a lower haemolytic activity [21, 22].

Concerning the carbohydrate moiety the situation is less clear. Haemolysis usually decreases with length and increases with branching of the sugar chain; however, diminution due to branching has also been reported [23].

This study deals with the first investigation of the influence of the connectivity within a disaccharide residue on the haemolytic activity. Linkage of the terminal glucose to position 3 of the previous one (saponin **1**) gives the compound with the highest activity. Obviously, the activity decreases if the linkage position is changed to carbon 4 (saponin **3**). Further diminution of the haemolytic activity is observed for linkage to carbon 6 (saponin **4**). Finally, for the saponin **2** only low activity was observed, probably due to the linkage in position 2 and/or to the α-attachment of the first glucose to the aglycone.

The haemolytic indices of compounds **1** to **4** are given in Table 1.

Table 1. Haemolytic activities of compounds **1–4**

Saponin	Sugar combination	*HI*
1	1→3	150000
2	1→2	<10000
3	1→4	80350
4	1→6	37500

Considering the significantly differing haemolytic indices for glycosides **1**–**4**, the investigation of oleanolic acid disaccharide glycosides containing other monosaccharide components seems promising. Furthermore, the influence of the configuration of the anomeric carbon attached to the aglycone should be investigated.

Experimental

General

Melting points; Melting point apparatus Dr. Tottoli, uncorrected; optical rotation: polarimeter 241 MC (Perkin Elmer); MS: Varian MAT 711 spectrometer, 70 eV electron impact and field desorption; IR spectra: infrared spectrometer system 2000 FT (Perkin Elmer); UV/Vis: Lambda 17 UV/Vis spectrometer (Perkin Elmer); NMR spectra: Varian Inova 400, 600 (300 K), 5 mm tubes, solvent resonance as internal standard. ^{1}H and ^{13}C resonances were assigned using ^{1}H, ^{1}H and ^{1}H, ^{13}C correlation spectra and are numbered as given in the formulas. Materials: column chromatography (CC): silica gel 60 (Merck), 70–230 mesh), pore diameter 60 Å; preparative TLC: TLC plates (Merck), silica gel 60 PF_{254}, 1 mm, 200×200 mm; thin layer chromatography (TLC): TLC plates (Merck), silica gel 60 F_{254}, 0.2 mm, 200×200 mm. The substances were detected in UV light at 254 nm and by spraying with methanol/sulfuric acid (9:1) and subsequent heating with a hot gun.

Determination of haemolytic activity

The haemolytic activity (expressed as Haemolytic Index (*HI*)) was evaluated by the method of the *Austrian Pharmacopoeia* (OeAB 1994) using the *Austrian Saponinstandard* ($HI = 30000$) as reference. Due to the low solubility of saponins **2** and **3**, these compounds had first to be dissolved in one droplet of methanol. In these cases, the standard solutions were prepared in the same manner.

Oleanolic acid (**5**)

Acid **5** was obtained as described in Ref. [10]. From 200 g cloves we obtained 1.9 g oleanolic acid.

Diphenylmethyl oleanolate (**6**; $C_{43}H_{58}O_3$)

6 was obtained from **5** and diphenyldiazomethane [11–13].

$R_f = 0.51$ (benzene: $Et_2O = 1{:}1$); m.p.: 146°C (MeOH/acetone); ^{1}H NMR (400 MHz, δ, $CDCl_3$): 0.27 (s, 3H, 26-H), 0.64–0.69 (m, 1H, 5-H), 0.75 (s, 3H, 24-H), 0.81 (s, 3H, 25-H), 0.88–0.92 (m, 1H, 1-H), 0.90 (s, 3H, 29-H), 0.94 (s, 3H, 30-H), 0.96 (s, 3H, 23-H), 0.98–1.01 (m, 2H, 2-H, 15-H), 1.04–1.06 (m, 1H, 7-H), 1.10 (s, 3H, 27-H), 1.11–1.82 (m, 16H, 1-H, 2-H, 6-H, 7-H, 9-H, 11-H, 15-H, 16-H, 19-H, 21-H, 22-H), 2.00 (ddd, $J = 13.7$, 13.7, 4.1 Hz, 1H, 16-H), 2.96 (dd, $J = 13.8$, 3.9 Hz, 1H, 18-H), 3.18 (dd, $J = 10.4$, 4.3 Hz, 1H, 3-H), 5.26 (t, $J = 3.6$ Hz, 1H, 12-H), 6.83 (s, 1H, Ph_2CH), 7.24–7.37 (m, 10H, aromatic H) ppm; ^{13}C NMR (100 MHz, δ, $CDCl_3$): 15.23 (C-25), 15.55 (C-24), 16.60 (C-26), 18.25 (C-6), 23.17 (C-16), 23.32 (C-11), 23.58 (C-30), 25.78 (C-27), 27.18 (C-2), 27.43 (C-15), 28.07 (C-23), 30.70 (C-20), 32.24 (C-22), 32.66 (C-7), 33.09 (C-29), 33.85 (C-21), 36.93 (C-10), 38.42 (C-1), 38.70 (C-4), 39.16 (C-8), 41.42 (C-18), 41.65 (C-14), 45.94 (C-19), 46.72 (C-17), 47.56 (C-9), 55.16 (C-5), 76.25 (Ph_2CH), 78.98 (C-3), 122.63 (C-12), 127.14, 127.23, 127.56, 127.73, 128.24, 128.40, 140.54 (aromatic C), 143.46 (C-13), 176.28 (C-28) ppm.

Diphenylmethyl 3′,4′,6′,2″,3″,4″,6″-heptaacetyl-β-D-glucopyranosyl-(1→2)-α-D-glucopyranosyl-3-O-oleanolate (**7**, $C_{69}H_{92}O_{20}$)

1 g, (1.6 mmol) **6** was dissolved in $CHCl_3$, and 2.45 g Ag_2O and 4 g drierite were added. This mixture was stirred in the dark in a dry flask for 2.5 h. After addition of 0.2 g I_2, a solution of 0.99 g (1.47 mmol) acetobromosophorose (obtained as described in Ref. [14]) in 10 ml dry $CHCl_3$ was added. This mixture was stirred under Ar for 48 h, filtered, and the $CHCl_3$ was evaporated. From the residue, 0.53 g acetobromosophorose were obtained by recrystallization from $CHCl_3$/petroleum ether. After evaporation of the solvent, 1.5 g solid was obtained. CC over silica gel (150 g) with CH_2Cl_2: EtOAc = 9:1 yielded 0.295 g (16.5%) **7**.

$R_f = 0.16$ (CH_2Cl_2: EtOAc = 9:1); $[\alpha]_D^{20} = +37.6°$, $[\alpha]_{546}^{20} = +45.0°$ ($c = 0.8$, CH_3OH); IR (KBr): $\bar{\nu} = 3436$ (s), 2947 (s), 1750 (s), 1455 (m), 1368 (m), 1232 (s), 1033 (s), 700 (m) cm^{-1}; UV (MeOH); λ (logε) = 215 (4.085), 250 (3.284) nm; ^{1}H NMR (400 MHz, δ, $CDCl_3$): 0.23 (s, 3H, 26-H), 0.63 (d, $J = 10.5$ Hz, 1H, 5-H), 0.78 (s, 3H, 24-H), 0.82 (s, 3H, 25-H), 0.76–0.85 (m, 1H, 1-H), 0.87 (s, 3H, 29-H), 0.91 (s, 3H, 30-H), 0.94 (s, 3H, 23-H), 0.89–0.96 (m, 1H, 15-H), 1.06 (s, 3H, 27-H), 1.09–1.74 (m, 18H, 1-H, 2-H, 6-H, 7-H, 9-H, 11-H, 15-H, 16-H, 19-H, 21-H, 22-H), 1.94–2.00 (m, 1H, 16-H), 1.96 (s, 3H, $COOCH_3$), 1.97 (s, 3H, $COOCH_3$), 1.99 (s, 3H, $COOCH_3$), 2.00 (s, 3H, $COOCH_3$), 2.02 (s, 3H, $COOCH_3$), 2.03 (s, 3H, $COOCH_3$). 2.05 (s, 3H, $COOCH_3$), 2.91–2.96 (m, 1H, 18-H), 3.10 (dd, $J = 11.6$, 4.1 Hz, 1H, 3-H), 3.60–3.65 (m, 1H, 5″-H), 3.71 (dd, $J = 10.0$, 3.7 Hz, 1H, 2′-H), 4.02 (d, $J = 12.0$ Hz, 1H, 6′-H), 4.11–4.23 (m, 4H, 5′-H, 6′-H, 6″-H), 4.58 (d, $J = 7.9$ Hz, 1H, 1″-H), 4.89 (t, $J = 10.0$ Hz, 1H, 2″-H), 4.92 (t, $J = 10.0$ Hz, 1H, 4′-H), 5.00 (d, $J = 3.9$ Hz, 1H, 1′-H), 5.03 (t, $J = 10.5$ Hz, 1H, 4″-H), 5.12 (t, $J = 9.5$ Hz, 1H, 3″-H), 5.24 (s,b, 1H, 12-H), 5.30 (t, $J = 9.7$ Hz, 1H, 3′-H), 6.81 (s, 1H, $CHPh_2$), 7.23–7.33 (m, 10H, aromatic H) ppm; ^{13}C NMR (100 MHz, δ, $CDCl_3$): 15.14 (C-25), 16.62 (C-24, C-26), 18.26 (C-6), 20.27, 20.54, 20.62, 20.70, 20.86, ($COOCH_3$), 22.82 (C-2), 23.13 (C-11), 23.32 (C-16), 23.55 (C-30), 25.74 (C-27), 27.40 (C-15), 28.61 (C-23), 30.68 (C-20), 32.23 (C-22), 32.67 (C-7), 33.06 (C-29), 33.83 (C-21), 36.76 (C-10), 38.25 (C-1), 38.50 (C-4), 39.18 (C-8), 41.41 (C-18), 41.59 (C-14), 45.88 (C-19), 46.69 (C-17), 47.54 (C-9), 55.57 (C-5), 61.72 (C-6″), 62.15 (C-6′), 67.56 (C-5′), 68.31 (C-4″), 68.72 (C-4′), 70.92 (C-2″), 71.89 (C-5″), 72.13 (C-3′), 72.65 (C-3″), 76.22 ($CHPh_2$), 76.38 (C-2′), 87.63 (C-3), 96.70 (C-1′), 100.99 (C-1″), 122.72 (C-12), 127.15, 127.20, 127.57, 127.70, 128.22, 128.38, 140.48, 140.62 (aromatic C), 143.33 (C-13), 168.98, 169.34, 169.66, 169.89, 170.23, 170.42, 170.58 ($COOCH_3$), 176.25 (C-28) ppm; MS (neg. LSIMS, 5 kV): *m/z* (%) = 987 (0.4), 954 (0.6), 821 (0.9), 779 (1.1), 735 (0.5), 643 (0.5), 617 (0.6), 551 (1.2), 481 (1.4), 459 (1.5), 379 (1.3), 367 (3.2), 347 (1.4), 275 (12.0), 239 (2.3), 183 (100.0), 151 (3.8), 91 (51.7), 59 (6.1).

β-D-Glucopyranosyl-(1→2)α-D-glucopyranosyl-3O-oleanolic acid (**2**; $C_{42}H_{68}O_{13}$)

255 mg (0.21 mmol) **7** were dissolved in dry $CHCl_3$, cooled to −20°C, and a solution of 0.26 g Na in 5 ml MeOH cooled to −20° was added. After 1.5 h the mixture was poured into ice water and neutralized with 2 *N* HCl. The organic layer was separated and the mixture extracted three times with $CHCl_3$. The combined organic layers were dried over Na_2SO_4, and the solvent was evaporated. 145 mg of a white residue was obtained; this was dissolved in 10 ml dry MeOH, and 150 mg Pd/C (10%) were added. The mixture was hydrogenated for 12 h at room temperature and 50 psi. After filtration and evaporation 100 mg of a white residue were obtained. Purification by preparative TLC (CH_2Cl_2:MeOH = 8:2) yielded 38 mg (33%) **2**.

M.p.: 244°C (decomp.); $R_f = 0.15$ (CH_2Cl_2:MeOH = 8:2); $[\alpha]_D^{20} = +40.7°$, $[\alpha]_{546}^{20} = -10.8°$ ($c = 0.19$, CH_3OH); IR (KBr): $\bar{\nu} = 3432$ (s), 2929 (m), 1637 (m), 1136 (s), 621 (m) cm^{-1}; ^{1}H NMR (400 MHz, δ, CD_3OD): 0.82 (d, $J = 11.2$ Hz, 1H, 5-H), 0.86 (s, 3H, 24-H), 0.88 (s, 3H, 26-H), 0.93 (s, 3H, 29-H), 0.94–0.97 (m, 1H, 1-H), 0.98, 0.99 (2s, 6H, 25-H, 30-H), 1.07 (s, 3H, 23-H), 1.08–1.10 (m, 1H, 15-H), 1.11–1.15 (m, 1H, 19-H), 1.19 (s, 3H, 27-H), 1.20–1.23 (m, 1H, 21-H), 1.32–2.40 (m, 17H, 1-H, 2-H, 6-H, 7-H, 9-H, 11-H, 15-H, 16-H, 19-H, 21-H, 22-H), 2.91 (dd,

$J = 13.5$, 3.8 Hz, 1H, 18-H), 3.24–3.35 (m, 4H, 3-H, 2″-H, 4″-H, 5″-H), 3.41 (t, $J = 9.1$ Hz, 1H, 3″-H), 3.44 (t, $J = 10.1$ Hz, 1H, 4′-H), 3.49 (dd, $J = 9.7$, 3.2 Hz, 1H, 2′-H), 3.66 (dd, $J = 11.3$, 6.6 Hz, 1H, 6″-H), 3.72–3.81 (m, 3H, 5′-H, 6′-H), 3.87 (t, $J = 9.7$, 1H, 3′-H), 3.93 (d, $J = 11.3$ Hz, 1H, 6″-H), 4.50 (d, $J = 7.6$ Hz, 1H, 1″-H), 5.25 (d, $J = 3.4$ Hz, 1H, 1′-H) ppm; ^{13}C NMR (100 MHz, δ, CD_3OD): 16.24 (C-25), 17.62 (C-24), 18.25 (C-26), 19.81 (C-6), 23.99 (C-2), 24.42 (C-30), 24.56 (C-16), 24.87 (C-11), 26.74 (C-27), 29.30 (C-15), 29.79 (C-23), 31.98 (C-20), 34.02 (C-29), 34.36 (C-7), 34.42 (C-22), 35.44 (C-21), 38.39 (C-10), 39.81 (C-1), 39.92 (C-4), 40.89 (C-8), 43.25 (C-14), 43.33 (C-18), 47.90 (C-19), 48.40 (C-17), 49.30 (C-9), 57.38 (C-5), 62.75 (C-6′), 63.43 (C-6″), 71.72 (C-4′), 72.25 (C-4″), 73.95 (C-3′), 74.01 (C-5′) 75.87 (C-2″), 78.21 (C-3″), 78.37 (C-5″), 82.89 (C-2′), 87.10 (C-3), 98.49 (C-1′), 106.16 (C-1″), 123.47 (C-12), 146.10 (C-13), 183.82 (C-28) ppm; MS (neg. LSIMS, 5 kV): *m/z* (%) = 779 [M-H$^+$] (100.0), 763 (10.6), 687 (5.3), 645 (6.8), 617 (45.3), 599 (9.8), 583 (4.5), 509 (6.0), 483 (10.6), 455 (26.4), 437 (13.6), 423 (6.8), 355 (6.8), 293 (6.0), 265 (13.2), 247 (10.9), 183 (28.3), 101 (19.2), 91 (35.8), 59 (23.8), 45 (6.4).

Diphenylmethyl 2′,4′,6′, 2″,3″,4″,6″-heptaacetyl-β-D-glucopyranosyl-(1→3)-β-D-glucopyranosyl-3O-oleanolate (**8**; $C_{69}H_{92}O_{20}$)

480 mg (0.77 mmol) **6** were dissolved in 5 ml dry $CHCl_3$, and 1 g Ag_2O and 2 g drierite were added. This mixture was stirred in the dark. After addition of 100 mg I_2, a solution of 430 mg (0.61 mmol) acetobromolaminaribiose in 5 ml dry $CHCl_3$ was added. (Acetobromolaminaribiose was obtained by bromination [15] of peracetyllaminaribiose which was prepared from diacetone glucose as described [17, 18]). This mixture was stirred under Ar for 48 h, filtered, and $CHCl_3$ was evaporated. 600 mg of a residue were obtained and purified by CC (CH_2Cl_2) yielding 230 mg (31%) **8** as a yellowish resin.

$R_f = 0.14$ (CH_2Cl_2); $[\alpha]_D^{20} = +3.0°$, $[\alpha]_{546}^{20} = +4.8°$ ($c = 0.3$, CH_3OH); IR (KBr): $\bar{\nu} = 2950$ (m), 1757 (s), 1454 (m), 1436 (m), 1372 (s), 1206 (s), 1160 (s), 1122 (s), 1029 (s), 982 (m), 905 (w), 745 (w), 700 (s), 600 (m) cm^{-1}; UV (MeOH): λ (logε) = 216 (3.562), 259 (3.034) nm; ^{1}H NMR (400 MHz, δ, $CDCl_3$): 0.24 (s, 3H, 26-H), 0.64 (d, $J = 11.4$ Hz, 1H, 5-H), 0.70 (s, 3H, 24-H), 0.79 (s, 3H, 25-H), 0.81–0.82 (m, 1H, 1-H), 0.87 (s, 3H, 23-H), 0.90 (s, 3H, 29-H), 0.94 (s, 3H, 30-H), 0.97–0.99 (m, 1H, 15-H), 1.08 (s, 3H, 27-H), 1.09–1.79 (m, 18H, 1-H, 2-H, 6-H, 7-H, 9-H, 11-H, 15-H, 16-H, 19-H, 21-H, 22-H), 1.94–2.02 (m, 1H, 16-H), 1.98 (s, 3H, $COOCH_3$), 2.01 (s, 6H, 2 $COOCH_3$), 2.02 (s, 3H, $COOCH_3$), 2.06 (s, 3H, $COOCH_3$), 2.07 (s, 3H, $COOCH_3$), 2.12 (s, 3H, $COOCH_3$), 2.94–3.00 (m, 1H, 18-H), 3.01 (dd, $J = 11.8$, 5.1 Hz, 1H, 3-H), 3.64–3.70 (m, 2H, 5′-H, 5″-H), 3.87 (t, $J = 9.3$ Hz, 1H, 3′-H), 4.04 (d, $J = 12.4$ Hz, 1H, 6″-H), 4.11–4.22 (m, 2H, 6′-H), 4.36 (dd, $J = 12.4$, 4.4 Hz, 1H, 6″-H), 4.38 (d, $J = 7.8$ Hz, 1H, 1′-H), 4.60 (d, $J = 8.0$ Hz, 1H, 1″-H), 4.80–4.91 (m, 2H, 2″-H, 4′-H), 5.02 (t, $J = 8.8$ Hz, 1H, 2′-H), 5.08 (t, $J = 9.6$ Hz, 1H, 4″-H), 5.10 (t, $J = 9.3$ Hz, 1H, 3″-H), 5.25 (s, 1H, 12-H), 6.83 (s, 1H, $CHPh_2$), 7.25–7.35 (m, 10H, aromatic H) ppm; ^{13}C NMR (100 MHz, δ, $CDCl_3$): 15.14 (C-25), 16.25 (C-24), 16.56 (C-26), 18.14 (C-6), 20.29, 20.51, 20.54, 20.57, 20.65, 20.78, 21.06 ($COOCH_3$), 23.14 (C-11*), 23.32 (C-16*), 23.58 (C-30), 25.76 (C-2, C-27), 27.41 (C-15), 27.76 (C-23), 30.71 (C-20), 32.24 (C-22), 32.67 (C-7), 33.10 (C-29), 33.84 (C-21), 36.62 (C-10), 38.40 (C-1), 38.83 (C-4), 39.18 (C-8), 41.43 (C-18), 41.62 (C-14), 45.97 (C-19), 46.71 (C-17), 47.58 (C-9), 55.51 (C-5), 61.74 (C-6″), 62.43 (C-6′), 68.09 (C-4″), 68.71 (C-4′), 70.97 (C-2″), 71.38 (C-5′*), 71.66 (C-5″*), 72.95 (C-3″), 73.24 (C-2′), 76.25 ($CHPh_2$), 78.91 (C-3′), 90.52 (C-3), 100.95 (C-1″), 103.05 (C-1′), 122.63 (C-12), 127.21, 127.61, 127.73, 128.25, 128.41, 140.48, 140.62 (aromatic C), 143.43 (C-13), 168.75, 169.22, 169.26, 169.37, 170.40, 170.51, 170.73 ($COOCH_3$), 176.25 (C-28) ppm; MS (neg. LSIMS, 5 kV): *m/z* (%) = 1192 (1.8), 1071 (5.3), 1042 (10.5), 1028 (100.0), 985 (21.1), 882 (3.5), 850 (1.8), 785 (3.5), 769 (4.4), 726 (16.7), 698 (12.3), 619 (14.0), 577 (1.8), 453 (1.8), 437 (26.6), 289 (11.4), 248 (17.5), 203 (42.1), 167 (96.5), 165 (57.9), 127 (15.8), 109 (73.7), 81 (19.3), 43 (100.0), 32 (10.5).

β-D-Glucopyranosyl-(1→3)-β-D-glucopyranosyl-3O-oleanolic acid (**1**, *randianin*: $C_{42}H_{68}O_{13}$)

The same procedure as described for **2** was used. 230 mg (0.19 mmol) **8** dissolved in 6 ml dry $CHCl_3$ yielded after hydrogenation and preparative TLC (CH_2Cl_2:MeOH = 8:2) 32 mg (22%) **1**.

M.p.: 220°C, (decomp.); $R_f = 0.34$ (CH_2Cl_2:MeOH = 8:2); $[\alpha]_D^{20} = +13.2°$, $[\alpha]_{546}^{20} = +17.6°$ ($c = 0.34$, CH_3OH); IR (KBr): $\bar{\nu} = 3375$ (s), 2928 (s), 1577 (s), 1459 (m), 1389 (m), 1077 (s), 890 (w), 827 (w), 789 (w), 649 (w), 621 (w), 472 (w) cm^{-1}; ^1H NMR (400 MHz, δ, CD_3OD): 0.80–0.84 (m, 1H, 5-H), 0.89 (s, 3H, 24-H), 0.90 (s, 3H, 26-H), 0.93 (s, 3H, 29-H), 1.00 (s, 6H, 25-H, 30-H), 1.02–1.08 (m, 2H, 1-H, 15-H), 1.10 (s, 3H, 23-H), 1.19 (s, 3H, 27-H), 1.33–2.10 (m, 19H, 1-H, 2-H, 6-H, 7-H, 9-H, 11-H, 15-H, 16-H, 19-H, 21-H, 22-H), 2.93 (dd, $J = 13.0$, 3.0 Hz, 1H, 18-H), 3.23 (dd, $J = 11.7$, 4.2 Hz, 1H, 3-H), 3.32–3.36 (m, 1H, 5′-H), 3.33 (t, $J = 9.9$ Hz, 2H, 2″-H, 4″-H), 3.36–3.40 (m, 1H, 5″-H), 3.41 (t, $J = 9.9$ Hz, 1H, 2′-H), 3.44 (t, $J = 9.2$ Hz, 1H, 3″-H), 3.45 (t, $J = 8.9$ Hz, 1H, 4′-H), 5.58 (t, $J = 8.9$ Hz, 1H, 3′-H), 3.69 (dd, $J = 11.8$, 5.8 Hz, 1H, 6″-H), 3.74 (dd, $J = 12.0$, 4.6 Hz, 1H, 6′-H), 3.89 (dd, $J = 12.0$, 2.1 Hz, 1H, 6′-H), 3.93 (dd, $J = 11.8$, 2.1 Hz, 1H, 6″-H), 4.42 (d, $J = 7.9$ Hz, 1H, 1′-H), 4.62 (d, $J = 7.5$ Hz, 1H, 1″-H), 5.26 (s, 1H, 12-H) ppm; ^{13}C NMR (100 MHz, δ, CD_3OD): 16.26 (C-25), 17.33 (C-24), 18.36 (C-26), 19.67 (C-6), 24.52 (C-30), 24.69 (C-16), 24.86 (C-11), 26.78 (C-27), 27.27 (C-2), 28.84 (C-23), 29.40 (C-15), 32.03 (C-20), 34.12 (C-29), 34.41 (C-7), 34.52 (C-22), 35.61 (C-21), 38.22 (C-10), 40.09 (C-1), 40.45 (C-4), 40.85 (C-8), 43.26 (C-18), 43.51 (C-14), 48.14 (C-19), 49.45 (C-9), 57.38 (C-5), 62.79 (C-6″), 62.98 (C-6′), 70.37 (C-4′), 71.79 (C-4″), 75.36 (C-2′), 75.75 (C-2″), 77.55 (C-5′), 78.01 (C-3″), 78.42 (C-5″), 88.27 (C-3′), 91.19 (C-3), 105.52 (C-1″), 106.56 (C-1′), 123.14 (C-12), 146.47 (C-13), 184.95 (C-28) ppm; MS (neg. LSIMS, 5 kV): *m/z* (%) = 779 [M^+-H] (22.6), 763 (1.0), 659 (0.5), 645 (0.8), 617 (3.3), 551 (1.0), 483 (1.8), 455 (2.5), 437 (1.8), 367 (4.5), 275 (17.4), 276 (2.3), 205 (1.9), 183 (100.0), 119 (2.3), 91 (80.0), 71 (8.7), 45 (1.5).

Diphenylmethyl 2′,3′,6′,2″,3″,4″,6″-heptaacetyl-β-D-glucopyranosyl-(1→4)-β-D-glucopyranosyl-3O-oleanolate (**9**; $C_{69}H_{92}O_{20}$)

1.3 g (2.1 mmol) **6** were dissolved in a mixture of 50 ml dry benzene and 50 ml dry nitromethane. The solution was heated to 50°C, and two thirds of the solvent were evaporated. Thereafter, 1.6 g (6.3 mmol) $Hg(CN)_2$ and 900 mg (1.3 mmol) acetobromocellobiose (obtained from octaacetylcellobioside [15, 17]) dissolved in 20 ml of benzene:CH_3NO_2 = 1:1 were added. The mixture was heated under Ar to 100°C and stirred for 3 h. After cooling to room temperature, $CHCl_3$ was added, and the solution was washed three times with 5% aqueous KJ, twice with 10% $NaHCO_3$, and twice with water. The organic phase was dried over Na_2SO_4 and evaporated. 2 g crude **9** were obtained and purified by CC with CH_2Cl_2: ethyl acetate = 9:1 yielding 550 mg (34%) **9**.

$R_f = 0.15$ (CH_2Cl_2:ethyl acetate = 9:1); $[\alpha]_D^{20} = +7.3°$, $[\alpha]_{546}^{20} = +5.0°$ ($c = 0.2$, CH_3OH); IR (KBr): $\bar{\nu} = 2948$ (m), 1758 (s), 1456 (w), 1367 (m), 1231 (s), 1159 (w), 1122 (w), 1038 (s), 700 (w) cm^{-1}; UV (MeOH); λ (logε) = 214 (4.412), 257 (4.064) nm; ^1H NMR (400 MHz, δ, $CDCl_3$): 0.21 (s, 3H, 26-H), 0.61 (d, $J = 11.2$ Hz, 1H, 5-H), 0.66 (s, 3H, 24-H), 0.75 (s, 3H, 25-H), 0.77–0.80 (m, 1H, 1-H), 0.83 (s, 3H, 23-H), 0.86 (s, 3H, 29-H), 0.89 (s, 3H, 30-H), 0.91–0.95 (m, 1H, 15-H), 1.04 (s, 3H, 27-H), 1.08–1.74 (m, 18H, 1-H, 2-H, 6-H, 7-H, 9-H, 11-H, 15-H, 16-H, 19-H, 21-H, 22-H), 1.93–2.00 (m, 1H, 16-H), 1.94 (s, 3H, $COOCH_3$), 1.96 (s, 3H, $COOCH_3$), 1.92 (s, 6H, 2 $COOCH_3$), 1.99 (s, 3H, $COOCH_3$), 2.04 (s, 3H, $COOCH_3$), 2.05 (s, 3H, $COOCH_3$), 2.91 (dd, $J = 13.6$, 3.3 Hz, 1H, 18-H), 3.00 (dd, $J = 11.3$, 4.5 Hz, 1H, 3-H), 3.50–3.55 (m, 1H, 5′-H), 3.62 (ddd, $J = 9.8$, 4.3, 2.3 Hz, 1H, 5″-H), 3.67 (t, $J = 9.5$ Hz, 1H, 4′-H), 4.00 (d, $J = 12.4$ Hz, 1H, 6″-H), 4.06 (dd, $J = 11.9$, 5.7 Hz, 1H, 6′-H), 4.31 (dd, $J = 12.4$, 4.3 Hz, 1H, 6″-H), 4.42–4.45 (m, 1H, 6′-H), 4.44 (d, $J = 8.3$ Hz, 1H, 1′-H), 4.46 (d, $J = 8.6$ Hz, 1H, 1″-H), 4.88 (t, $J = 8.6$ Hz, 1H, 2″-H), 4.89 (dd, $J = 9.3$, 8.3 Hz, 1H, 2′-H), 5.01 (t, $J = 9.7$ Hz, 1H, 4″-H), 5.10 (t, $J = 9.3$ Hz, 1H, 3″-H), 5.13 (t, $J = 9.3$ Hz, 1H, 3′-H), 6.78 (s, 1H, $CHPh_2$), 7.19–7.30 (m, 10H, aromatic H) ppm; ^{13}C NMR (100 MHz, δ, $CDCl_3$): 15.07 (C-25), 16.24 (C-24), 16.47 (C-26), 18.02 (C-6), 20.44 (3 $COOCH_3$), 20.48, 20.54, 20.62,

20.74 ($COOCH_3$), 23.05 (C-16), 23.23 (C-11), 23.50 (C-30), 25.57 (C-2), 25.66 (C-27), 27.30 (C-15), 27.59 (C-23), 30.61 (C-20), 32.14 (C-22), 32.55 (C-7), 33.00 (C-29), 33.75 (C-21), 36.53 (C-10), 38.28 (C-1), 38.71 (C-4), 39.08 (C-8), 41.33 (C-18), 41.53 (C-14), 45.86 (C-19), 46.61 (C-17), 47.45 (C-9), 55.34 (C-5), 61.49 (C-6″), 61.91 (C-6′), 67.73 (C-4″), 71.54 (C-2″), 71.80 (C-2′), 71.83 (C-5″), 72.33 (C-5′), 72.44 (C-3′), 72.82 (C-3″), 76.16 ($CHPh_2$), 76.73 (C-4′), 90.50 (C-3), 100.64 (C-1″), 100.72 (C-1′), 122.51 (C-12), 127.06, 127.12, 127.50, 127.64, 128.15, 128.31, 140.42, 140.52 (aromatic C), 143.39 (C-13), 168.93, 169.19, 169.30, 169.76, 170.09, 170.16, 170.38 ($COOCH_3$), 176.14 (C-28) ppm; MS (neg. LSIMS, 5 kV): *m/z* (%) = 827 (0.2), 735 (0.5), 653 (0.2), 643 (0.8), 607 (0.3), 551 (1.1), 471 (1.1), 459 (1.7), 423 (0.9), 367 (3.5), 331 (1.3), 275 (12.8), 256 (1.5), 183 (100.0), 151 (3.0), 91 (30.2), 89 (5.7).

β-D-Glucopyranosyl-(1→4)-β-D-glucopyranosyl-3O-oleanolic acid (**3**; $C_{42}H_{68}O_{13}$)

The same procedure as described for **2** was used. 550 mg (0.44 mmol) **9** dissolved in 10 ml dry $CHCl_3$ yielded after hydrogenation and recrystallization from acetone: MeOH = 1:1 90 mg (26%) **3**.

M.p.: 250–257°C (decomp.); $R_f = 0.18$ (CH_2Cl_2:MeOH = 8:2); $[\alpha]_D^{20} = 13.9°$, $[\alpha]_{546}^{20} = 10.0°$ ($c = 0.18$, CH_3OH); IR (KBr): $\bar{\nu} = 3423$ (s), 2944 (s), 1697 (m), 1637 (w), 1459 (w), 1387 (w), 1162 (m), 1032 (s), 642 (w) cm^{-1}; ^1H NMR (400 MHz, δ, CD_3OD): 0.81–0.82 (m, 1H, 5-H), 0.85 (s, 3H, 26-H), 0.89 (s, 3H, 24-H), 0.95 (s, 3H, 29-H), 0.98 (s, 3H, 30-H), 0.99 (s, 3H, 25-H), 1.00–1.03 (m, 1H, 1-H), 1.10 (s, 3H, 23-H), 1.12–1.15 (m, 1H, 15-H), 1.20 (s, 3H, 27-H), 1.24–1.26 (m, 1H, 21-H), 1.30–1.80 (m, 17H, 1-H, 2-H, 6-H, 7-H, 9-H, 11-H, 15-H, 16-H, 19-H, 21-H, 22-H), 2.05 (dt, $J = 13.2$, 3.3 Hz, 1H, 16-H), 2.88 (dd, $J = 13.2$, 3.5 Hz, 1H, 18-H), 3.22 (dd, $J = 11.8$, 4.2 Hz, 1H, 3-H), 3.24–3.45 (m, 6H, 2′-H, 2″-H, 3″-H, 4″-H, 5′-H, 5″-H), 3.54 (t, $J = 9.0$ Hz, 1H, 3′-H), 3.14 (t, $J = 9.1$ Hz, 1H, 4′-H), 3.71 (dd, $J = 11.7$, 5.6 Hz, 1H, 6″-H), 3.89–3.95 (m, 3H, 6′-H, 6″-H), 4.40 (d, $J = 7.9$ Hz, 1H, 1′-H), 4.47 (d, $J = 7.9$ Hz, 1H, 1″-H), 5.28 (s, b, 1H, 12-H) ppm; ^{13}C NMR (100 MHz, δ, CD_3OD): 16.23 (C-25), 17.27 (C-24), 18.02 (C-26), 19.61 (C-6), 24.27 (C-30), 24.34 (C-16), 24.83 (C-11), 26.68 (C-27), 27.31 (C-2), 28.80 (C-23), 29.12 (C-15), 31.90 (C-20), 33.86 (C-29), 34.11 (C-22), 34.30 (C-7), 35.19 (C-21), 38.19 (C-10), 40.07 (C-1), 40.44 (C-4), 40.87 (C-8), 43.03 (C-18), 43.18 (C-14), 47.54 (C-19), 47.94 (C-17), 49.30 (C-9), 57.33 (C-5), 62.22 (C-6′), 62.62 (C-6″), 71.65 (C-4″), 75.21 (C-2″), 75.67 (C-2′), 76.51 (C-3″), 76.75 (C-3′), 78.07 (C-5′), 78.38 (C-5″), 80.93 (C-4′), 91.19 (C-3), 104.84 (C-1″), 106.81 (C-1′), 123.92 (C-12), 145.49 (C-13), 182.15 (C-28) ppm; MS (neg. LSIMS, 5 kV): *m/z* (%) = 779 [M-H$^+$] (11.8), 763 (12.5), 689 (1.3), 645 (1.6), 617 (4.5), 551 (1.8), 497 (2.3), 455 (4.0), 389 (2.3), 367 (2.8), 311 (2.5), 275 (11.3), 219 (6.8), 183 (100.0), 151 (6.0), 127 (12.1), 91 (30.9), 59 (9.1), 45 (1.9).

Diphenylmethyl 2′,3′,4′,2″,3″,4″,6″-Heptaacetyl-β-D-glucopyranosyl-(1→6)-β-D-glucopyranosyl-3-O-oleanolate (**10**; $C_{69}H_{92}O_{20}$)

The same procedure as described for **8** was used. From 400 mg (0.64 mmol) **6** and 450 mg (0.64 mmol) acetobromogentiobiose (obtained from 1,2,3,4-tetraacetyl-β-*D*-glucopyranose and acetobromoglucose [15, 17, 24]) we obtained 200 mg (25%) **10** after purification by CC (CH_2Cl_2).

$R_f = 0.2$ (CH_2Cl_2; $[\alpha]_D^{20} = 18.8°$, $[\alpha]_{546}^{20} = 23.8°$ ($c = 0.4$, CH_3OH); IR (KBr): $\bar{\nu} = 3438$ (m), 2949 (m), 2874 (w), 1757 (s), 1456 (w), 1439 (w), 1372 (m), 1222 (s), 1167 (m), 1039 (s), 986 (w), 753 (w), 701 (w) cm^{-1}; UV (MeOH): λ (logε) = 220 (3.462), 260 (3.072) nm; ^1H NMR (400 MHz, δ, $CDCl_3$): 0.23 (s, 3H, 26-H), 0.65 (d, $J = 12.0$ Hz, 1H, 5-H), 0.69 (s, 3H, 24-H), 0.79 (s, 3H, 25-H), 0.87 (s, 6H, 23-H, 29-H), 0.91 (s, 3H, 30-H), 0.93–0.96 (m, 2H, 1-H, 15-H), 1.04 (s, 3H, 27-H), 1.06–1.86 (m, 18H, 1-H, 2-H, 6-H, 7-H, 9-H, 11-H, 15-H, 16-H, 19-H, 21-H, 22-H), 1.98–2.02 (m, 1H, 16-H), 1.98 (s, 3H, $COOCH_3$), 1.99 (s, 3H, $COOCH_3$), 2.02 (s, 6H, 2$COOCH_3$), 2.03 (s, 3H, $COOCH_3$), 2.05 (s, 3H, $COOCH_3$), 2.10 (s, 3H, $COOCH_3$), 2.93 (dd, $J = 13.8$, 3.9 Hz, 1H, 18-H), 3.08 (dd, $J = 10.9$, 5.5 Hz, 1H, 3-H), 3.61–3.71 (m, 3H, 5′-H, 5″-H, 6′-H), 3.73–3.78 (m, 1H, 6′-H),

4.10 (dd, $J = 12.3$, 2.4 Hz, 1H, 6″-H), 4.22 (dd, $J = 12.3$, 4.2 Hz, 1H, 6″-H), 4.50 (d, $J = 8.0$ Hz, 1H, 1′-H), 4.61 (d, $J = 8.0$ Hz, 1H, 1″-H), 4.83 (t, $J = 9.6$ Hz, 1H, 4′-H), 4.94 (t, $J = 8.9$ Hz, 1H, 2″-H), 4.95 (dd, $J = 9.6$, 8.0 Hz, 1H, 2′-H), 5.03 (t, $J = 9.6$ Hz, 1H, 4″-H), 5.12 (t, $J = 9.5$ Hz, 1H, 3″-H), 5.15 (t, $J = 9.6$ Hz, 1H, 3″-H), 5.24 (t, $J = 3.4$ Hz, 1H, 12-H), 6.83 (s, 1H, $CHPh_2$), 7.25–7.34 (m, 10H, aromatic H) ppm; ^{13}C NMR (100 MHz, δ, $CDCl_3$): 15.17 (C-25), 16.34 (C-24), 16.56 (C-26), 18.08 (C-6), 20.51, 20.61, 20.71 ($COOCH_3$), 23.14 (C-11*), 23.25 (C-16*), 23.58 (C-30), 25.64 (C-27), 25.86 (C-2), 27.37 (C-15), 27.75 (C-23), 30.68 (C-20), 32.22 (C-22), 32.64 (C-7), 33.09 (C-29), 33.82 (C-21), 36.62 (C-10), 38.37 (C-1), 38.88 (C-4), 39.16 (C-8), 41.39 (C-18), 41.60 (C-14), 45.99 (C-19), 46.68 (C-17), 47.54 (C-9), 55.40 (C-5), 61.84 (C-6″), 67.80 (C-6′), 68.29 (C-4″), 69.11 (C-4′), 71.09 (C-2′*), 71.68 (C-2″*), 71.94 (C-5″), 72.73 (C-3′*), 72.79 (C-3″*), 73.59 (C-5′), 76.25 ($CHPh_2$), 90.20 (C-3), 100.39 (C-1″), 102.65 (C-1′), 122.76 (C-12), 127.13, 127.21, 127.57, 127.71, 128.23, 128.39, 140.50 (aromatic C), 143.25 (C-13), 169.14, 169.39, 169.56, 170.27, 170.56 ($COOCH_3$), 176.24 (C-28) ppm; MS (70 eV): m/z (%) = 1071 (3.5), 1028 (8.8), 767 (5.3), 725 (7.1), 698 (1.8), 620 (8.8), 619 (100.0), 567 (3.5), 438 (38.1), 437 (98.2), 391 (4.4), 333 (1.8), 330 (70.8), 317 (1.8), 271 (7.1), 247 (7.1), 203 (12.4), 169 (63.7), 167 (100.0), 145 (5.3), 109 (10.6), 81 (5.3), 43 (17.7).

β-D-Glucopyranosyl-(1→6)-β-D-glucopyranosyl-3O-oleanolic acid (**4**; $C_{42}H_{68}O_{13}$)

The same procedure as described for **2** was used. 200 mg (0.16 mmol) **10** dissolved in 6 ml dry $CHCl_3$ yielded after hydrogenation and preparative TLC (CH_2Cl_2: MeOH = 8:2) 20 mg (16%) **4**.

M.p.: 220°C (decomp.); $R_f = 0.25$ (CH_2Cl_2:MeOH = 8:2); $[\alpha]_D^{20} = +4.2°$, $[\alpha]_{546}^{20} = +5.0°$ ($c = 0.24$, CH_3OH); IR (KBr): $\bar{\nu} = 3375$ (s), 2943 (s), 1559 (m), 1459 (m), 1385 (s), 1311 (m), 1074 (s), 1032 (s), 913 (w), 630 (w) cm^{-1}; ^{1}H NMR (400 MHz, δ, CD_3OD): 0.79 (d, $J = 10.9$ Hz, 1H, 5-H), 0.85 (s, 3H, 24-H), 0.86 (s, 3H, 26-H), 0.88 (s, 3H, 29-H), 0.95 (s, 6H, 25-H, 30-H), 0.98–1.02 (m, 2H, 1-H, 15-H), 1.06 (s, 3H, 23-H), 1.14 (s, 3H, 27-H), 1.28–1.95 (m, 19H, 1-H, 2-H, 6-H, 7-H, 9-H, 11-H, 15-H, 16-H, 19-H, 21-H, 22-H), 2.90 (dd, $J = 13.1$, 3.2 Hz, 1H, 18-H), 3.16–3.23 (m, 1H, 3-H), 3.24 (t, $J = 7.9$ Hz, 1H, 2′-H), 3.26 (t, $J = 8.5$ Hz, 1H, 2″-H), 3.28–3.31 (m, 1H, 5″-H), 3.32–3.37 (m, 3H, 3′-H, 4′-H, 4″-H), 3.41 (t, $J = 8.6$ Hz, 1H, 3″-H), 3.47–3.50 (m, 1H, 5′-H), 3.68 (dd, $J = 12.0$, 5.5 Hz, 1H, 6″-H), 3.80 (dd, $J = 12.0$, 5.5 Hz, 1H, 6′-H), 3.87 (dd, $J = 12.0$, 2.1 Hz, 1H, 6″-H), 4.10 (dd, $J = 12.0$, 1.7 Hz, 1H, 6′-H), 4.34 (d, $J = 7.9$ Hz, 1H, 1′-H), 4.40 (d, $J = 7.9$ Hz, 1H, 1″-H), 5.22 (t, $J = 3.4$ Hz, 1H, 12-H) ppm; ^{13}C NMR (100 MHz, δ, CD_3OD): 16.28 (C-25), 17.33 (C-24), 18.45 (C-26), 19.70 (C-6), 24.59 (C-30), 24.78 (C-16), 24.87 (C-11), 26.77 (C-27), 27.39 (C-2), 28.85 (C-23), 29.50 (C-15), 32.07 (C-20), 34.19 (C-29), 34.45 (C-7), 34.62 (C-22), 35.71 (C-21), 38.26 (C-10), 40.11 (C-1), 40.47 (C-4), 40.86 (C-8), 43.31 (C-14), 43.65 (C-18), 48.32 (C-19), 49.44 (C-9), 57.37 (C-5), 63.02 (C-6″), 70.13 (C-6′), 71.84, 71.91 (C-4′, C-4″), 75.42 (C-2′*), 75.92 (C-2″*), 77.15 (C-5′), 78.25, 78.38 (C-3′, C-3″, C-5″), 91.23 (C-3), 105.08 (C-1″), 107.03 (C-1′), 123.03 (C-12), 146.65 (C-13), 185.60 (C-28) ppm; MS (neg. LSIMS, 5 kV): m/z (%) = 779 [M^+-H] (18.4), 777 (2.5), 733 (0.5), 645 (0.6), 617 (3.0), 551 (0.8), 497 (0.5), 483 (1.3), 455 (2.8), 437 (1.3), 367 (6.0), 331 (0.8), 275 (24.2), 273 (5.3), 183 (100.0), 151 (6.0), 91 (100.0), 71 (12.1), 45 (1.5).

Acknowledgements

This work was supported by FWF grant Nr. P12540-CHE.

References

[1] Frohne D, Pfänder HJ (1987) In: Giftpflanzen, 3. Auflage. Wissenschaftliche Verlagsgesellschaft, Stuttgart, p 32

[2] Segal R, Milo-Goldzweig I (1975) Biochem Pharmacol **24**: 77

[3] Segal R, Milo-Goldzweig I, Seiffe M (1972) Life Sci **11**: 61
[4] Segal R, Schlösser E (1975) Arch Microbiol **104**: 147
[5] Segal R, Shatovski P, Milo-Goldzweig I (1974) Biochem Pharmacol **23**: 973
[6] Romussi G, Chirallo G, Falcone G, Schneider C (1979) Liebigs Ann Chem **12**: 2028
[7] Sotheeswaran S, Bokel M, Kraus W (1989) Phytochemistry **28**: 1544
[8] Lemmich E, Cornett C, Furu P, Jorstian CL, Knudsen AD, Olsen CE, Salhi A, Thilborg ST (1995) Phytochemistry **39**: 63
[9] Loloiko AA, Grishkovets VI, Shashkov AS, Chirva VY (1988) Chem of Natural Compounds **24**: 614
[10] Stahl E, Schild W (1986) In: Isolierung und Charakterisierung von Naturstoffen. G. Fischer, Stuttgart New York, p 132
[11] Staudinger H, Anthes E, Pfenninger F (1917) Ber Chem **49**: 1928
[12] Coleman GH, Gilman H, Adams CE, Pratt PE (1939) J Org Chem **3**: 99
[13] Hardegger E, EI Heweihi Z, Robinet FG (1948) Helv Chim Acta **31**: 439
[14] Coxon B, Fletcher HG (1961) J Org Chem **26**: 2892
[15] Brauns DH (1927) J Am Chem Soc **49**: 3170
[16] Freudenberg K, Soff K (1936) Ber Chem **69**: 1245
[17] Rychener M, Bigler P, Pfander H (1984) Hely Chim Acta **67**: 378
[18] Kochetkov NK, Bochkov AF, Sokolovska TA, Snyatkova VJ (1971) Carbohydr Res **16**: 17
[19] Hostettmann K, Marston A (1995) Saponins. Cambridge University Press, Cambridge, p 232
[20] Zechmeister L (1973) In: Fortschritte der Chemie organischer Naturstoffe, vol 30. Springer, Wien New York, p 564
[21] Romussi G, Cafaggi S, Bignardi G (1980) Pharmazie **35**: 498
[22] Hase J, Kobashi K, Mitsui K, Namba T, Yoshizaki M, Tomimori T (1981) J Pharmacobio-Dyn **4**: 833
[23] Schloesser E, Wulff G (1969) Z Naturforsch B **24**: 1284
[24] Reynolds DD, Evans WL (1938) J Am Chem Soc **60**: 2559

Received November 23, 1998. Accepted December 7, 1998