Glycals in the Stereoselective Synthesis of Triterpene 2-Deoxy-α-L-Glycosides under Conditions of Acidic Catalysis

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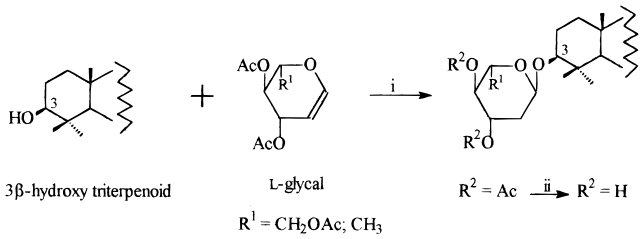
Received June 4, 1999

3β-Hydroxy triterpenes of the oleanane, ursane, and lupane types were successfully glycosylated with acetylated L-glucal and L-rhamnal under conditions of acidic catalysis (anhydrous cation-exchange resin and LiBr). The 2-deoxy- and 2,6-dideoxy-α-L-arabino-hexopyranosides (**1**−**5**) were stereoselectively prepared in 83−90% yields, following deacetylation under mild conditions, which led to the target triterpene 2-deoxy-α-L-glycosides (**6**−**10**).

Naturally occurring saponins isolated from plants of various species and marine invertebrates have many interesting pharmacological and biological activities.[1] Triterpene glycosides of medicinal plants, such as ginseng and licorice, are of particular interest. However, it often happens that synthetic analogues of natural glycosides possess more pronounced effects and a broader spectrum of action.[2−5] In connection with the goals of enantiospecific synthesis of the analogues of natural compounds, the past decade has been marked by an increasing interest in the chemistry of glycals as effective glycosyl donors. Since the discovery of glycal in 1913[6] until the middle of the past decade, these sugars have only a few examples of their potential application in total synthesis.[7] At the present time, the glycal approach is regarded as an extremely useful method to obtain *O*-, *C*-, and *N*-glycosides and, in particular, oligosaccharides. An important contribution to this area was made by new strategies suggested by Danishefsky et al.[8,9] However, there have been relatively few instances of glycosylation of steroid alcohols.[10−12] Earlier, we have used two iodine-containing activators, *N*-iodosuccinimide (NIS) and di(*sym*-collidine)iodonium perchlorate (IDCP), for the synthesis of some 2-deoxy- analogues of glycyrrhizic acid, the major glycoside of the licorice root extract.[13−17] Although the formation of triterpene 2-deoxy-glycosides when NIS and IDCP are used occurs with α-stereospecificity, an additional stage for preparation of 2-deoxy-2-iodo-α-glycosides requires subsidiary reagents, so the yields obtained for the target glycosides are not satisfactory.

An original method of acid catalyzed (sulfonic acid resin and LiBr) preparation of 2-deoxydisaccharides from glycals suggested by Sabesan and Neira[18] was used for the synthesis of triterpene and steroid 2-deoxy-α-D-glycosides.[19,20] In this paper, we demonstrate the remarkable advantages of this method (high stereo- and regioselectivity, good yields, simplicity of experimental conditions) using different natural 3β-hydroxy triterpenes (oleanane, ursane, lupane types) and L-glycals (glucal, rhamnnal)[21] (Scheme 1). The reactions were carried out in a mixture of anhydrous dichloromethane and acetonitrile with an equimolar ratio of each acetylated glycal and triterpene alcohol for 3−4 h with TLC monitoring. Glycosylation resulted in 2-deoxy-**1**, -**2**, -**4**, and 2,6-dideoxy-α-L-glycosides **3**, and **5**, which were isolated as individual products using column chromatography on Si gel with 83−90% yields. Mild

Scheme 1



deacetylation of these products with 5% KOH in methanol afforded the target triterpene α-L-glycosides **6**−**10** (Chart 1) in 87−93% yields. The structures of glycosides were established by NMR spectroscopy.[22] Literature data for triterpene alcohols[23−27] and 2-deoxy-α-glycosides[5,10,15] were used for comparison. TLC and NMR analysis did not show the presence of any β-anomers or rearrangement products. The formation of an α-glycoside bond follows from the magnitudes of the coupling constants $^1J_{C(1'),H(1')} = 168-170$ Hz[16] and the signals of anomeric C-1′ carbon atoms that are observed at δ 99.1−99.8 ppm[15] in the ^{13}C NMR spectra of glycosides **1**−**5**.

Experimental Section

General Experimental Procedures. Chemicals were obtained from Reactive Company, Ufa, Russia, and were used without further purification, unless otherwise noted. Dichloromethane and acetonitrile were double distilled over P_2O_5. KU-2-8 (H^+-form) sulfonic acid cation-exchange resin (Reachim, Moscow, Russia) was dried as described.[18] Molecular sieves (4 Å) were activated at 160−180 °C and 1−5 Torr for 2 h. Melting points were determined on a Boetius heating plate. UV spectra were recorded on a Specord UV M400 spectrophotometer in ethanol. ^1H and ^{13}C NMR spectra were recorded on a Bruker AM-300 spectrometer (300 and 75.5 MHz, respectively) in $CDCl_3$ (Reachim) using TMS as the internal standard. TLC was carried out on Silufol plates (Chemapol, Prague, Czech Republic) using CH_2Cl_2-MeOH, 15:1. The spots were visualized by spraying the plates with a 20% ethanol solution of phosphotungstic acid followed by heating at 100−120 °C for 2−3 min. Preparative column chromatography was carried out on Si gel (40/100 mm) (Chemapol). 3,4,6-Tri-*O*-acetyl-L-glucal and 3,4-di-*O*-acetyl-L-rhamnal were prepared by a procedure similar to that described previously.[28]

Starting Chemicals. Methyl 18β-glycyrrhetinate was obtained by acid hydrolysis of 18β-glycyrrhizic acid in methanol,[29] and its 11-deoxo analogue was synthesized by reduction with Zn/HCl in dioxane.[30] Ursolic acid was extracted from cranberry

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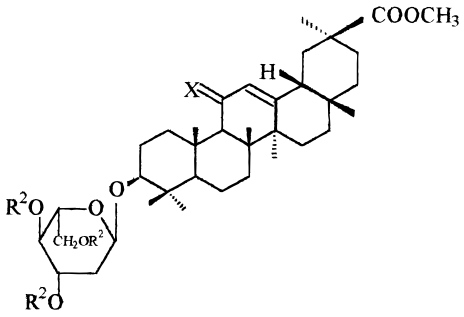
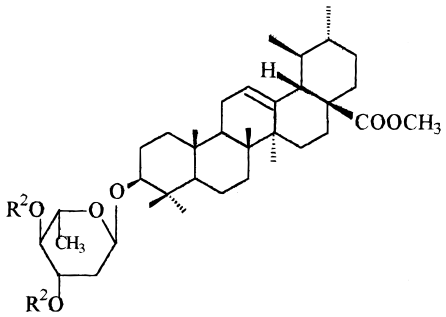
10.1021/np990273b CCC: $19.00
Published on Web 06/23/2000

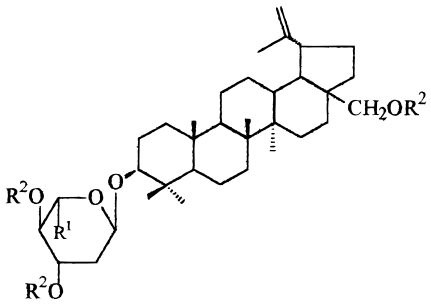
Chart 1



1: R^2 = Ac, X = O
2: R^2 = Ac, X = H_2
6: R^2 = H, X = O
7: R^2 = H, X = H_2



3: R^2 = Ac
8: R^2 = H



4: R^1 = CH_2OAc, R^2 = Ac
5: R^1 = CH_3, R^2 = Ac
9: R^1 = CH_2OH, R^2 = H
10: R^1 = CH_3, R^2 = H

peel (*Oxycoccus quadripetalus* Gilib) with 2-propanol[31] and methylated by CH_2N_2. 28-*O*-Acetylbetulin was synthesized from betulin extracted from birch bark (*Betula pendula* Roth.) with benzene by heating in HOAc.[32]

Synthesis of Glycosides 1−5. A solution of each 3*β*-hydroxy triterpenoid (1 mmol), acetylated L-glycal (1 mmol) in 30 mL of a CH_2Cl_2−CH_3CN mixture (1:1, v:v) containing activated molecular sieves 4 Å (0.3 g), anhydrous LiBr (0.7 g), and 0.9 g of dried KU-2-8 (H^+-form) resin was stirred for 3−4 h (TLC monitoring), filtered, and quenched with Et_3N. The solvents were removed in vacuo. The residue was dissolved in CH_2Cl_2 (20 mL), washed with cold 1 M HCl and saturated $NaHCO_3$, and dried over Na_2SO_4. The solvent was removed, and the residue was chromatographed using pentane−EtOAc gradient mixtures, 5:1 → 2:1. Compounds **1**−**5** were isolated as homogeneous products with 83−90% yields.

Deacetylation of Glycosides 1−5. Methanolic KOH (5%, 5 mL) was added to a solution of glycosides **1**−**5** (0.5 g) in methanol (30 mL), and the mixture was stirred for 3−4 h (monitoring by TLC). The mixture was treated with a KU-2-8 (H^+-form) resin (until pH 7), the resin was filtered off, the filtrate was diluted with cold water (10 mL), and the product was extracted with $CHCl_3$ (2 × 15 mL). The combined extracts were dried with Na_2SO_4 and concentrated to dryness in vacuo to afford glycosides **6**−**10** in 87−93% yields.

Methyl 3*β*-*O*-(3,4,6-tri-*O*-acetyl-2-deoxy-α-L-arabino-hexopyranosyl)-18*β*-glycyrrhetinate (1): R_f 0.72; mp 188−190 °C; UV λ_{max} (log ϵ) 247 (3.98) nm; ^{1}H NMR δ 0.80, 0.82, 1.12, 1.14, 1.36 (21H, all s, 7 × CH_3), 1.35−2.05 (21H, m, CH_2, CH), 2.08, 2.11, 2.13 (9H, 3s, 3 × OAc), 2.32 (1H, s, H-9), 2.78 (1H, d, J = 13.7 Hz, H-18), 3.16 (1H, dd, J = 4.7, 11.0 Hz, H-3), 3.69 (3H, s, OCH_3), 4.02 (1H, dd, J = 2, 11.8 Hz, H-6′$_a$), 4.10 (1H, ddd, J = 2, 6.3, 9.7 Hz, H-5′), 4.22 (1H, dd, J = 6.3, 11.8 Hz, H-6′$_b$), 4.90 (1H, t, J = 9.7 Hz, H-4′), 5.08 (1H, d, J = 2.5 Hz, H-1′), 5.28 (1H, ddd, J = 5.6, 9.7, 12 Hz, H-3′), 5.66 (1H, s, H-12); ^{13}C NMR δ 21.3 (C-2), 89.5 (C-3), 61.7 (C-9), 200.2 (C-11), 128.5 (C-12), 169.5 (C-13), 48.4 (C-18), 176.9 (C-30), 51.6 (C-31), 99.7 (C-1′), 35.6 (C-2′), 69.2 (C-3′), 67.9 (C-4′), 69.8 (C-5′), 62.6 (C-6′), 170.0, 170.3, 170.7 (O*C*OCH$_3$), 20.5, 20.7, 20.9 (OCO*C*H$_3$); *anal.* C 68.03%, H 8.67%, calcd for $C_{43}H_{64}O_{11}$, C 68.22%, H 8.52%.

Methyl 3*β*-*O*-(3,4,6-tri-*O*-acetyl-2-deoxy-α-L-arabino-hexopyranosyl)-11-deoxo-18*β*-glycyrrhetinate (2): R_f 0.68; mp 224−226 °C; ^{1}H NMR δ 0.79, 0.82, 0.91, 0.95, 1.12 (21H, all s, 7 × CH_3), 1.15−1.95 (25H, m, CH_2, CH), 2.02, 2.06, 2.08 (9H, 3s, 3 × OAc), 3.10 (1H, dd, J = 4.4, 10.5 Hz, H-3), 3.68 (3H, s, OCH_3), 4.06 (1H, dd, J = 2, 12 Hz, H-6′$_a$), 4.15 (1H, ddd, J = 2, 6.4, 9.8 Hz, H-5′), 4.38 (1H, dd, J = 6.4, 12 Hz, H-6′$_b$), 4.97 (1H, t, J = 9.8 Hz, H-4′), 5.02 (1H, d, J = 2.7 Hz, H-1′), 5.27 (1H, br s, H-12), 5.33 (1H, ddd, J = 9.8, 11.7, 5.4 Hz, H-3′); ^{13}C NMR δ 21.4 (C-2), 89.6 (C-3), 48.2 (C-9), 23.5 (C-11), 122.6 (C-12), 144.5 (C-13), 47.7 (C-18), 176.8 (C-30), 51.7 (C-31), 99.8 (C-1′), 35.7 (C-2′), 69.3 (C-3′), 67.9 (C-4′), 69.9 (C-5′), 62.7 (C-6′), 170.1, 170.4, 170.9 (O*C*OCH$_3$), 20.9, 21.0, 21.2 (OCO*C*H$_3$); *anal.* C 69.28%, H 9.12%, calcd for $C_{43}H_{66}O_{10}$, C 69.51%, H 8.95%.

Methyl 3*β*-*O*-(3,4-di-*O*-acetyl-2,6-dideoxy-α-L-arabino-hexopyranosyl)-ursolate (3): R_f 0.69; mp 148−150 °C; ^{1}H NMR δ 0.68, 0.85, 0.88, 0.90, 1.01 (15H, 5s, 5 × CH_3), 0.75 (3H, d, J = 5.5 Hz, H-29), 0.80 (3H, d, J = 6.2 Hz, H-30), 1.05−1.95 (18H, m, CH_2, CH), 1.35 (3H, d, J = 6.0 Hz, H-6′), 1.95, 1.99 (6H, 2s, 2 × OAc), 2.18 (1H, d, J = 11.6 Hz, H-18), 3.00 (1H, dq, J = 6.0, 9.8 Hz, H-5′), 4.67 (1H, t, J = 9.8 Hz, H-4′), 4.86 (1H, d, J = 2.9 Hz, H-1′), 5.17−5.26 (2H, m, H-3′, H-12); ^{13}C NMR δ 23.0 (C-2), 88.8 (C-3), 47.9 (C-9), 16.9 (C-11), 125.3 (C-12), 137.9 (C-13), 52.7 (C-18), 39.2 (C-19), 38.7 (C-20), 177.6 (C-28), 20.5 (C-30), 51.1 (C-31), 99.2 (C-1′), 35.6 (C-2′), 69.0 (C-3′), 74.9 (C-4′), 65.4 (C-5′), 17.1 (C-6′), 169.3, 169.9 (O*C*OCH$_3$), 20.7, 20.9 (OCO*C*H$_3$); *anal.* C 72.11%, H 9.73%, calcd for $C_{41}H_{64}O_8$, C 71.89%, H 9.42%.

3*β*-*O*-(3,4,6-Tri-*O*-acetyl-2-deoxy-α-L-arabino-hexopyranosyl)-28-acetyl-20(29)-lupene (4): R_f 0.78; mp 105−107 °C; ^{1}H NMR δ 0.73, 0.77, 0.81, 0.90, 0.96 (15H, 5s, 5 × CH_3), 1.00−1.90 (26H, m, CH_2, CH), 1.63 (3H, s, CH_3), 1.90, 1.96, 1.99 (12H, 3s, 4 × OAc), 2.38 (1H, ddd, J = 5.5, 11.7, 11.7 Hz, H-19), 2.98 (1H, dd, J = 5.9, 10.6 Hz, H-3), 3.78 (1H, d, J = 11 Hz, H-28), 3.97 (1H, dd, J = 2, 12 Hz, H-6′$_a$), 4.06 (1H, ddd, J = 9.8, 2, 6.2 Hz, H-5′), 4.19 (1H, dd, J = 6.2, 12 Hz, H-6′$_b$), 4.21

(1H, d, J = 11 Hz, H-28), 4.51 and 4.63 (2H, each d, J = 2 Hz, H-29), 4.88 (1H, t, J = 9.8 Hz, H-4′), 4.9.3 (1H, d, J = 2.8 Hz, H-1′), 5.25 (1H, ddd, J = 5.3, 11.8, 9.8 Hz, H-3′); ^{13}C NMR δ 25.2 (C-2), 89.3 (C-3), 20.5 (C-11), 149.8 (C-20), 62.4 (C-28), 109.8 (C-29), 18.9 (C-30), 99.5 (C-1′), 35.4 (C-2′), 69.0 (C-3′), 67.7 (C-4′), 70.8 (C-5′), 62.5 (C-6′), 169.7, 169.9, 170.1, 171.2 ($OCOCH_3$), 20.6, 20.7, 20.8, 20.9 ($OCOCH_3$); *anal*. C 70.05%, H 8.89%, calcd for $C_{44}H_{68}O_{10,}$ C 69.81%, H 9.05%.

3*β*-*O*-(3,4-Di-*O*-acetyl-2,6-dideoxy-α-L-arabino-hexopyranosyl)-28-acetyl-20(29)-lupene (5): R_f 0.77; mp 98−100 °C; ^{1}H NMR δ 0.75, 0.82, 0.88, 0.97, 1.05 (5C, 15H, 5 × CH_3), 1.00−2.15 (26H, m, CH_2, CH), 1.29 (3H, d, J = 6.3 Hz, H-6′), 1.60 (3H, s, CH_3), 1.95, 1.96, 1.98 (9H, 3s, 3 × OAc), 2.32−2.40 (1H, m, H-19), 2.93 (1H, dd, J = 6, 10.1 Hz, H-3), 3.77 (1H, d, J = 11 Hz, H-28), 3.96 (1H, dq, J = 9.7, 6.3 Hz, H-5′), 4.16 (1H, d, J = 11 Hz, H-28), 4.48−4.53 and 4.58−4.62 (2H, each br s, H-29), 4.64 (1H, t, J = 9.7 Hz, H-4′), 4.82 (1H, d, J = 2.1 Hz, H-1′), 5.20 (1H, ddd, J = 5.5, 11.7, 9.7 Hz, H-3′); ^{13}C NMR δ 24.2 (C-2), 88.7 (C-3), 20.4 (C-11), 149.6 (C-20), 62.3 (C-28), 109.6 (C-29), 18.8 (C-30), 99.1 (C-1′), 35.6 (C-2′), 68.9 (C-3′), 74.8 (C-4′), 65.3 (C-5′), 17.6 (C-6′), 169.8, 170.4, 171.0 ($OCOCH_3$), 20.5, 20.6, 20.9 ($OCOCH_3$); *anal*. C 71.95%, H 9.33%, calcd for $C_{42}H_{66}O_8$, C 72.17%, H 9.52%.

Methyl 3*β*-*O*-(2-deoxy-α-L-arabino-hexopyranosyl)-18*β*-glycyrrhetinate (6): R_f 0.33; mp 152−154 °C; UV λ_{max} (log ϵ) 246 (4.09) nm; ^{13}C NMR δ 20.8 (C-2), 88.8 (C-3), 61.9 (C-9), 200.4 (C-11), 128.6 (C-12), 169.4 (C-13), 48.5 (C-18), 177.0 (C-30), 51.9 (C-31), 100.5 (C-1′), 38.1 (C-2′), 71.4 (C-3′), 67.3 (C-4′), 73.1 (C-5′), 62.4 (C-6′); *anal*. C 70.15%, H 9.42%, calcd for $C_{37}H_{58}O_{8,}$ C 70.44%, H 9.26%.

Methyl 3*β*-*O*-(2-deoxy-α-L-arabino-hexopyranosyl)-11-deoxo-18*β*-glycyrrhetinate (7): R_f 0.28; mp 213-215 °C; ^{13}C NMR δ 20.9 (C-2), 89.0 (C-3), 48.2 (C-9), 23.5 (C-11), 122.6 (C-12), 144.3 (C-13), 47.6 (C-18), 177.8 (C-30), 51.6 (C-31), 100.5 (C-1′), 38.1 (C-2′), 71.0 (C-3′), 69.2 (C-4′), 72.5 (C-5′), 62.4 (C-6′); *anal*. C 71.82%, H 10.07%, calcd for $C_{37}H_{60}O_{7,}$ C 72.04%, H 9.80%.

Methyl 3*β*-*O*-(2,6-dideoxy-α-L-arabino-hexopyranosyl)-ursolate (8): R_f 0.36; mp 136−138 °C; ^{13}C NMR δ 23.6 (C-2), 88.4 (C-3), 47.6 (C-9), 16.9 (C-11), 125.7 (C-12), 138.1 (C-13), 52.9 (C-18), 38.9 (C-19), 38.7 (C-20), 178.2 (C-28), 21.2 (C-30), 51.5 (C-31), 100.2 (C-1′), 38.4 (C-2′), 69.5 (C-3′), 78.4 (C-4′), 67.5 (C-5′), 17.6 (C-6′); *anal*. C 74.22%, H 9.75%, calcd for $C_{37}H_{60}O_{6,}$ C 73.96%, H 10.06%.

3*β*-*O*-(2-Deoxy-α-L-arabino-hexopyranosyl)-28-hydroxy-20(29)-lupene (9): R_f 0.35; mp 184−186 °C; ^{13}C NMR δ 25.1 (C-2), 88.4 (C-3), 20.5 (C-11), 150.1 (C-20), 60.8 (C-28), 109.8 (C-29), 19.0 (C-30), 100.0 (C-1′), 36.4 (C-2′), 69.3 (C-3′), 68.3 (C-4′), 71.6 (C-5′), 61.8 (C-6′); *anal*. C 73.68%, H 9.97%, calcd for $C_{36}H_{60}O_{6,}$ C 73.43%, H 10.27%.

3*β*-*O*-(2,6-Dideoxy-α-L-arabino-hexopyranosyl)-28-hydroxy-20(29)-lupene (10): R_f 0.36; mp 186−188 °C; ^{13}C NMR δ 25.1 (C-2), 88.7 (C-3), 20.8 (C-11), 150.4 (C-20), 60.4 (C-28), 109.6 (C-29), 19.0 (C-30), 100.0 (C-1′), 39.0 (C-2′), 69.2 (C-3′), 78.1 (C-4′), 67.5 (C-5′), 17.5 (C-6′); *anal*. C 75.27%, H 10.83%, calcd for $C_{36}H_{60}O_5$, C 75.48%, H 10.56%.

Acknowledgment. This work was supported by the Russian Foundation for Basic Research (no. 96-03-33240).

References and Notes

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(21) We believe that triterpene glycosides containing L-sugar fragments should have more pronounced activity than their D-analogues. For example, the effects of 18*β*-glycyrrhetic acid 2-deoxy-α-L-arabino-hexopyranoside on the regeneration of skin and the stomach mucous membrane were more pronounced in a comparison with its α-D-analogue and glycyrrhizic acid containing a D-glucuronic acid fragment (unpublished data).
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NP990273B