Stereoselective synthesis of triterpene and steroid 2-deoxy-α-glycosides using iodonium dicollidine perchlorate

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2-Deoxy-α-glycosides of oleonane type triterpene alcohols and deoxycholic acid were synthesized by glycosylation with glycal acetates in the presence of iodonium dicollidine perchlorate followed by deiodination and deprotection.

Key words: triterpene alcohols, deoxycholic acid, glycal acetates, iodonium dicollidine perchlorate, stereoselective glycosylation, 2-deoxy-α-glycosides.

Earlier we have performed a stereoselective synthesis of 2-deoxy-α-D-*arabino*-hexopyranosides of triterpene alcohols of the oleonane series using D-glycal triacetate as the glycosyl donor and iodine-containing promoters — *N*-iodosuccinimide (NIS)[1] and iodonium dicollidine perchlorate (IDCP).[2] 2,6-Dideoxy-α-L-*arabino*-hexopyranoside of glycyrrhetic acid, which is an analog of natural triterpene glycoside, glycyrrhizic acid, have been synthesized by glycosylation of methyl ester of 18β-glycyrrhetic acid (GLA) (the major biologically active triterpenoid of the extract of licorice roots) with di-*O*-acetyl-L-rhamnal in the presence of NIS and IDCP.[3] The same promoters were successfully used for the synthesis of steroid 2-deoxy-α-glycosides and oligosaccharides.[4,5]

In a continuation of our studies we extended a number of biologically active triterpenes and steroid alcohols used and carried out glycosylation of methyl esters of 18α- (**1a**), 11-deoxo- (**1b**), and 18,19-dehydroglycyrrhetic acids (**1c**) with di-*O*-acetyl-L-rhamnal (**2**) and acetylcholic acid methyl ester (**1d**) with tri-*O*-acetyl-D-glucal (**3**) in the presence of IDCP.

The triterpene 2,6-dideoxy-2-iodoglycosides (**4a—c**) and steroid 2-deoxy-2-iodoglycoside (**4d**), obtained in high yields, underwent deiodination in the presence of 10% Pd/C to give glycosides **5a—d**. Mild deacetylation of glycosides **5a—d** yielded the target triterpene 2,6-dideoxy-α-L-*arabino*-hexopyranosides (**6a—c**) and 2-deoxy-α-D-*arabino*-hexopyranoside of deoxycholic acid (**6d**) (Scheme 1).

The structures of the synthesized compounds were confirmed by elemental analysis and their NMR and UV spectra as well as by comparison of the NMR spectra with those of carbohydrate moieties[3—5] and polycyclic alcohols.[6—9] Thus, the ^{13}C NMR spectra of aglycon parts of glycosides **4a—c** were similar to the spectra of triterpene alcohols **1a—c** [6—8] except for chemical shifts (CS) of the signals of the C(3) carbon, which are shifted downfield. The anomeric C(1′) carbons of glycosides **4a—c** resonate at δ 103.5 as in the spectrum of methyl glycyrrhetate 2,6-dideoxy-2-iodo-α-L-manno-pyranoside.[3] The α-configuration of the *O*-glycosidic bonds and hence the axial orientation of the aglycon in glycosides **4a—c** are confirmed by the coupling constants values $J_{C(1'),H(1')}$ = 169—170 Hz in the ^{13}C NMR spectra measured in the NOE mode.[10] In ^1H NMR spectra of glycosides **4a—c** and **5a—c**, CS values, multiplicity, and coupling constants of the signals of the carbohydrate part are close to those of the corresponding signals in the spectra of methyl glycyrrhetate 2,6-dideoxy-2-iodo-α-L-*manno*-pyranoside and 2,6-dideoxy-α-L-*arabino*-hexapyranoside; characterization of these compounds was reported in detail in Ref. 3.

It should be noted that the ^{13}C NMR spectra of glycosides of stereoisomeric 18α- and 18β-glycyrrhetic acids differ in the CS values of the aglycon carbons (C(11), C(12), C(13), C(18), C(19), C(22), C(28), C(29)); the same fact is also observed for the parent acids themselves.[7] For example, the C(18) signal in glycosides **4a**, **5a**, and **6a** is shifted upfield approximately by 8 ppm as compared to the signal of this carbon in the spectra of glycosides of 18β-GLA.[3]

The UV spectra of glycosides **4a**, **5a**, and **6a** are characterized by a small shift of the absorption maximum (λ_{max} = 245—246.2 nm) as compared to the spectra of glycosides of 18β-GLA (λ_{max} = 246.8—247 nm). We also observed similar changes for other derivatives of 18α- and 18β-glycyrrhetic acids.[11] In the UV spectra of the methyl ester of 18,19-dehydro-GLA glycosides **4c**, **5c**, and **6c**, the absorption maximum is observed at 277.8 — 278.8 nm and its value is close to that of absorption maximum of 18,19-dehydro-GLA acetate (λ_{max} = 282 nm).[12]

In the ^{13}C NMR spectrum of glycoside **4d**, the signal of the C(3) atom is shifted downfield by 7.2 ppm because of the α-effect of glycosylation. The chemical shift of C(12) remains unchanged (δ 73.1); this fact

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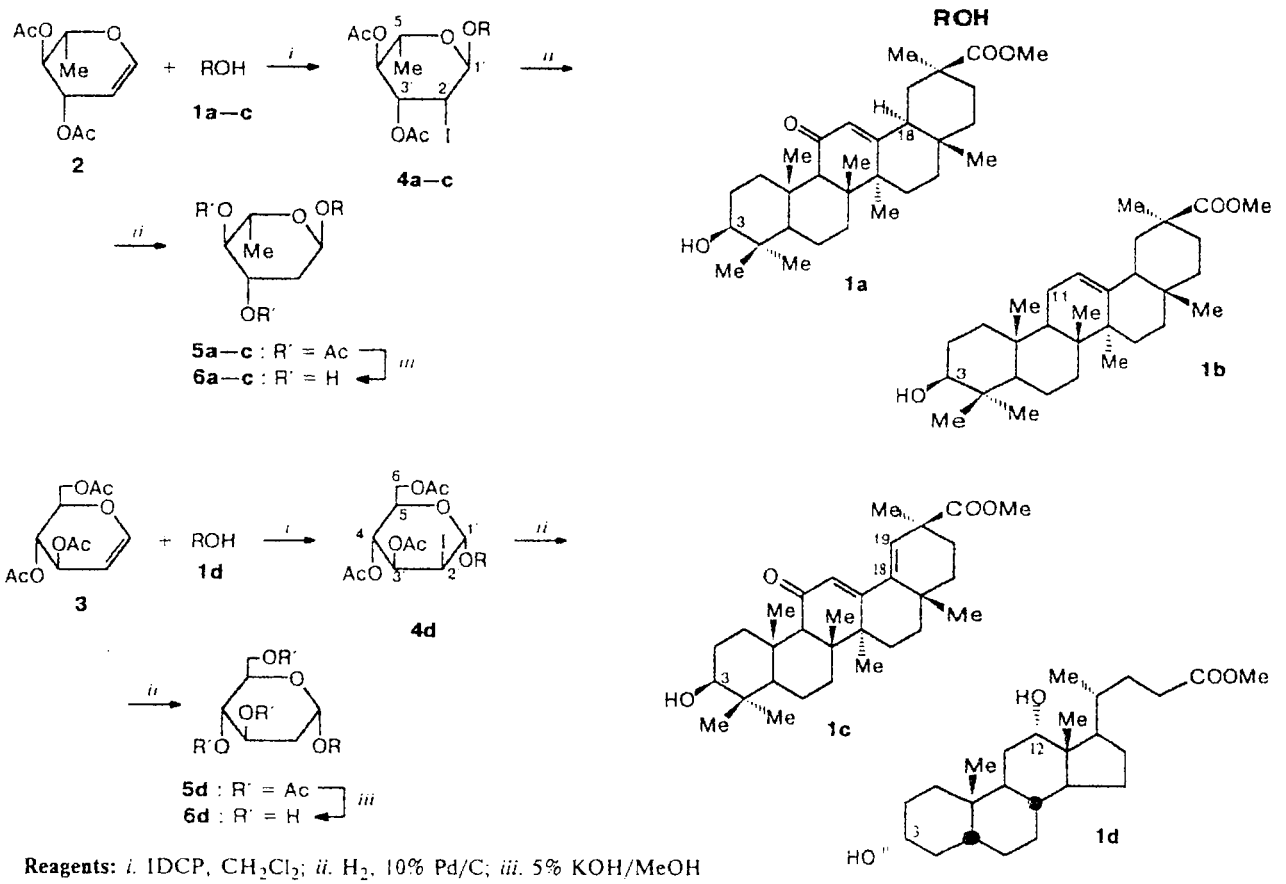
Scheme 1



Reagents: *i.* IDCP, CH_2Cl_2; *ii.* H_2, 10% Pd/C; *iii.* 5% KOH/MeOH

suggests regioselectivity of the glycosylation at C(3), which is apparently due to the steric hindrances of the hydroxy group at C(12). The coupling constant value $J_{C(1'),H(1')}$ = 168 Hz in the ^{13}C NMR spectrum of glycoside **4d** (recorded in the NOE mode) confirms the α-stereoselectivity of the glycosylation[10] and hence the axial positions of the aglycon and the iodine. *Manno-* and *arabino-* configurations of the carbohydrate rings in these compounds are confirmed by the values of the coupling constants of H(2')—H(5') protons in glycoside **4d** and H(3')—H(5') protons in glycoside **5d**, measured from their ^1H NMR spectra.

The presence of the signals of the MeOOC group carbons in the ^{13}C NMR spectra of glycosides **6a—d**, which are similar to the corresponding signals in the spectra of the alcohols **1a—d**, confirms that the ester group in the aglycon is preserved under the deacetylation conditions used.

Experimental

The UV spectra were obtained in methanol on a Specord UV M400 spectrophotometer. The ^{13}C and ^1H NMR spectra were recorded on a Bruker AM-300 (75.5 and 300 MHz, respectively) in $CDCl_3$. Me_4Si was used as the internal standard.

TLC was carried out on Silufol plates (Czech Republic) using the following eluant systems: CH_2Cl_2—MeOH, 10 : 1 (*A*), AcOEt—petroleum ether, 1 : 1 (*B*), C_6H_6—MeOH, 7 : 3 (*C*). 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. Column chromatography was carried out on Silica gel L (40/100 μm) (Czech Republic).

Melting points were determined on a Boetius heating plate, and specific rotations were measured using a Perkin-Elmer 241 MC polarimeter. Dichloromethane was refluxed over P_2O_5 for 2 h and distilled. Four Å molecular sieves were activated by heating at 160—180 °C and 5 Torr for 2 h.

Di-*O*-acetyl-L-rhamnal (**2**) and tri-*O*-acetyl-D-glucal (**3**) were synthesized from L-rhamnose and D-glucose by the known procedures.[13,14] The 18α-GLA (**1a**) and 11-deoxo-GLA methyl esters (**1b**) were obtained using the published procedures.[15,16] A sample of 18,19-dehydro-GLA was provided to the authors.* Deoxycholic acid (Czech Republic) was methylated with diazomethane. Iodonium dicollidine perchlorate was obtained using the earlier reported procedure;[17] the content of iodine was 25.5—27.0% (94—99% of the theoretical percentage value).

Methyl 3-*O*-(3,4-di-*O*-acetyl-2,6-dideoxy-2-iodo-α-L-mannopyranosyl)-18-α-glycyrrhetate (4a). Activated 4 Å mo-

* The authors thank M. F. Irismetov for providing a sample of 18,19-dehydro-GLA.

lecular sieves (0.43 g) were added to a solution of di-*O*-acetyl-L-rhamnal (**2**) (0.97 g, 2 mmol) and alcohol **1a** (0.97 g, 2 mmol) in CH_2Cl_2 (50 mL), the mixture was stirred for 30 min, and IDCP (1 g, 2.13 mmol) was then added. The resulting mixture was stirred for 4 h (TLC monitoring, system *A*) and filtered. The filtrate was washed with 10% $Na_2S_2O_3$ (20 mL × 2), dried over $MgSO_4$, and evaporated. The residue was chromatographed using a pentane—ethyl acetate gradient (7 : 1, 5 : 1, 3 : 1, 2 : 1, 1 : 1, v/v) as the eluant. Glycoside **4a** (homogeneous according to TLC) was eluted with the 3 : 1 → 2 : 1 gradient mixture. After precipitation with pentane from a solution in CH_2Cl_2, pure compound **4a** was obtained as a white powder; yield 1.40 g, (85.%); R_f 0.70 (*A*), 0.76 (*B*), and 0.69 (*C*); dec.p. 260—262 °C; $[\alpha]_D^{20}$ +73° (*c* 0.07, $CHCl_3$). Found (%): C, 60.1; H, 7.1; I, 15.0. $C_{41}H_{61}IO_9$. Calculated (%): C, 59.7; H, 7.5; I, 15.4. UV, (λ_{max}/nm): 246.2 (lg ε 4.28). ^{1}H NMR, δ (*J*/Hz): 0.67, 0.84, 0.94, 1.11, 1.19, 1.20, 1.21 (all s, 7 CH_3), 1.32 (d, 3 H, H(6′), $J_{6',5'}$ = 6.3), 1.30—2.00 (m, CH_2, CH), 2.06, 2.07 (both s, 6 H, 2 Ac), 2.22 (s, 1 H, H(9)), 2.66 (d, 1 H, H(18), *J* = 13.6), 3.10 (dd, 1 H, H(3), $J_{3,2e}$ = 4.5, $J_{3,2a}$ = 11.0), 3.67 (s, 3 H, OCH_3), 4.07 (dq, 1 H, H(5′), $J_{4',5'}$ = 9.0, $J_{5',6'}$ = 6.3), 4.54—4.60 (m, 2 H, H(2′), H(3′)), 5.13 (t, 1 H, H(4′), $J_{3',4'}$ = $J_{4',5'}$ = 9.0), 5.15 (br.s, 1 H, H(1′)), 5.58 (br.s, 1 H, H(12)). ^{13}C NMR, δ: 22.6 (C-2), 89.8 (C-3), 60.6 (C-9), 199.8 (C-11), 124.2 (C-12), 165.8 (C-13), 40.4 (C-18), 178.8 (C-30), 52.0 (C-31), 103.5 (C-1′), 31.3 (C-2′), 69.4 (C-3′), 72.8 (C-4′), 67.2 (C-5′), 17.3 (C-6′), 169.9, 170.1 ($CH_3\underline{C}O$), 20.9, 21.1 ($\underline{C}H_3CO$).

Methyl 3-*O*-(3,4-di-*O*-acetyl-2,6-dideoxy-2-iodo-α-L-mannopyranosyl)-11-deoxo-18-β-glycyrrhetate (4b). Glycoside **4b** (1.35 g, 83.7%) was obtained similarly as a white powder from **2** (0.43 g) and alcohol **1b** (0.97 g). R_f 0.75 (*A*), 0.74 (*B*); m.p. 222—224 °C (dioxane); $[\alpha]_D^{20}$ +104° (*c* 0.08, $CHCl_3$). Found (%): C, 60.4; H, 8.0; I, 15.1. $C_{41}H_{63}IO_8$. Calculated (%): C, 60.7; H, 7.8; I, 15.6. ^{1}H NMR, δ (*J*/Hz): 0.77, 0.83, 0.95, 1.11, 1.12, 1.18, 1.20 (all s, 7 CH_3), 1.31 (d, 3 H, H(6′), $J_{6',5'}$ = 6.3), 1.20—2.05 (m, CH_2, CH), 2.05, 2.07 (both s, 6 H, 2 Ac), 3.13 (dd, 1 H, H(3), $J_{3,2e}$ = 4.2, $J_{3,2a}$ = 11.3), 3.68 (s, 3 H, OCH_3), 4.07 (dq, 1 H, H(5′), $J_{4',5'}$ = 9.1, $J_{5',6'}$ = 6.3), 4.53—4.62 (m, 2 H, H(2′), H(3′)), 5.13 (t, 1 H, H(4′), $J_{3',4'}$ = $J_{4',5'}$ = 9.1), 5.17 (br.s, 1 H, H(1′)), 5.28 (br.s., 1 H, H(12)). ^{13}C NMR, δ: 22.6 (C-2), 90.0 (C-3), 48.3 (C-9), 23.6 (C-11), 122.6 (C-12), 144.5 (C-13), 47.7 (C-18), 177.7 (C-30), 51.6 (C-31), 103.5 (C-1′), 31.2 (C-2′), 69.4 (C-3′), 72.9 (C-4′), 67.2 (C-5′), 17.5 (C-6′), 169.8, 170.0 ($CH_3\underline{C}O$), 20.8, 21.0 ($\underline{C}H_3CO$).

Methyl 3-*O*-(3,4-di-*O*-acetyl-2,6-dideoxy-2-iodo-α-L-mannopyranosyl)-18,19-dehydroglycyrrhetate (4c). Glycoside **4c** (1.25 g, 76.0%) was obtained similarly as a white powder from **2** (0.43 g) and alcohol **1c** (0.97) after precipitation with petroleum ether from a chloroform solution. R_f 0.68 (*A*), 0.75 (*B*), 0.69 (*C*); dec.p. 245—247 °C; $[\alpha]_D^{20}$ +92° (*c* 0.04, $CHCl_3$). Found (%): C, 59.6; H, 6.9; I, 15.2. $C_{41}H_{59}IO_9$. Calculated (%): C, 59.8; H, 7.2; I, 15.4. UV, λ_{max}/nm: 277.8 (lgε 4.19). ^{1}H NMR, δ (*J*/Hz): 0.85, 0.94, 1.16, 1.18, 1.22 (all s, 7 CH_3), 1.32 (d, 3 H, H(6′), $J_{6',5'}$ = 6.2), 1.35—1.90 (m, CH_2, CH), 2.07, 2.08 (both s, 6 H, 2 Ac), 2.24 (s, 1 H, H(9)), 3.11 (dd, 1 H, H(3), $J_{3,2e}$ = 4.0, $J_{3,2a}$ = 10.1), 3.68 (s, 3 H, OCH_3), 4.07 (dq, 1 H, H(5′), $J_{4',5'}$ = 9.1, $J_{5',6'}$ = 6.2), 4.53—4.61 (m, 2 H, H(2′), H(3′)), 5.14 (t, 1 H, H(4′), $J_{3',4'}$ = $J_{4',5'}$ = 9.1), 5.16 (br.s, 1 H, H(1′)), 5.53 (br.s, 1 H, H(12)), 5.79 (s, 1 H, H(19)). ^{13}C NMR, δ: 22.5 (C-2), 89.8 (C-3), 60.9 (C-9), 200.2 (C-11), 129.7 (C-12), 162.9 (C-13), 142.9 (C-18), 124.2 (C-19), 176.8 (C-30), 52.3 (C-31), 103.5 (C-1′), 30.3 (C-2′), 69.8 (C-3′), 72.6 (C-4′), 67.2 (C-5′), 17.6 (C-6′), 170.0, 170.1 ($CH_3\underline{C}O$), 20.9, 21.1 ($\underline{C}H_3CO$).

Methyl 3-*O*-(3,4,6-tri-*O*-acetyl-2-deoxy-2-iodo-α-D-mannopyranosyl)-deoxycholic acid (4d). Glycoside **4d** (0.63 g, 79.0%) was obtained similarly as an amorphous powder from tri-*O*-acetyl-D-glucal (**3**) (0.55 g, 2 mmol) and alcohol **1d** (0.41 g, 1 mmol). R_f 0.66 (*A*). Found (%): C, 55.6; H, 6.9; I, 15.3. $C_{37}H_{57}IO_{11}$. Calculated (%): C, 55.2; H, 7.1; I, 15.8. $[\alpha]_D^{20}$ +48° (*c* 0.08, $CHCl_3$). ^{1}H NMR, δ(*J*/Hz): 0.68 (s, 3 H, H(18)), 0.90 (s, 3 H, H(19)), 0.98 (d, 3 H, H(21), *J* = 5.9), 1.04—2.35 (m, CH_2, CH), 2.07, 2.08, 2.10 (all s, 9 H, 3 Ac), 3.66 (s, 3 H, OCH_3), 3.99 (br.s, 1 H, H(12)), 4.12—4.23 (m, 3 H, H(5′), H_a(6′), H_b(6′)), 4.49 (dd, 1 H, H(2′), $J_{2',1'}$ = 1.3, $J_{2',3'}$ = 4.3), 4.64 (dd, 1 H, H(3′), $J_{2',3'}$ = 4.3, $J_{3',4'}$ = 9.3), 5.30 (d, 1 H, H(1′), $J_{1',2'}$ = 1.3), 5.35 (t, 1 H, H(4′), $J_{3',4'}$ = $J_{4',5'}$ = 9.3). ^{13}C NMR, δ: 27.1 (C-2), 79.2 (C-3), 28.7 (C-11), 73.1 (C-12), 174.8 и 51.6 (COOMe), 100.0 (C-1′), 30.8 (C-2′), 69.2 (C-3′), 68.0 (C-4′), 69.4 (C-5′), 62.5 (C-6′), 170.0, 170.1, 170.4 ($CH_3\underline{C}O$), 20.7, 20.9, 21.0 ($\underline{C}H_3CO$).

Methyl 3-*O*-(3,4-di-*O*-acetyl-2,6-dideoxy-α-L-*arabino*-hexopyranosyl)-18-α-glycyrrhetate (5a). Several drops of Et_3N and 0.96 g of 10% Pd/C were added to a solution of glycoside **4a** in methanol (35 mL), and the mixture was hydrogenated for 8 days (*p* = 1 bar). The catalyst was filtered off, the solvent was evaporated, the residue was precipitated with hexane from a solution in CH_2Cl_2 to afford glycoside **5a** (0.49 g, 89.6%) as a white powder. R_f 0.62 (*A*); dec.p. 215—217 °C. $[\alpha]_D^{20}$ +89° (*c* 0.06, $CHCl_3$). Found (%): C, 70.1; H, 9.2. $C_{41}H_{62}O_9$. Calculated (%): C, 70.5; H, 8.9. UV, λ_{max}/nm: 246.0 (lg ε 4.27). ^{1}H NMR, δ (*J*/Hz): 0.69, 0.81, 0.89, 1.10, 1.12, 1.18, 1.20 (all s, 7 CH_3), 1.31 (d, 3 H, H(6′), $J_{6',5'}$ = 6.5), 1.40—1.95 (d, CH_2, 9 CH aglycon CH, H(2′)), 1.98, 2.04 (both s, 6 H, 2 Ac), 2.30 (s, 1 H, H(9)), 2.64 (d, 1 H, H(18), *J* = 13.4), 3.03 (dd, 1 H, H(3), $J_{3,2e}$ = 4.9, $J_{3,2a}$ = 11.0), 3.67 (s, 3 H, OCH_3), 3.99 (dq, 1 H, H(5′), $J_{4',5'}$ = 9.6, $J_{5',6'}$ = 6.5), 4.70 (t, 1 H, H(4′), $J_{3',4'}$ = $J_{4',5'}$ = 9.6), 4.89 (d, 1 H, H(1′), $J_{1',2'a}$ = 3.0), 5.26 (ddd, 1 H, H(3′), $J_{2'e,3'}$ = 5.0, $J_{2'a,3'}$ = 11.6, $J_{3',4'}$ = 9.6), 5.54 (br.s, 1 H, H(12)). ^{13}C NMR, δ: 22.4 (C-2), 88.9 (C-3), 60.7 (C-9), 200.2 (C-11), 124.2 (C-12), 165.9 (C-13), 40.4 (C-18), 178.9 (C-30), 52.0 (C-31), 99.5 (C-1′), 35.9 (C-2′), 69.3 (C-3′), 75.1 (C-4′), 65.6 (C-5′), 17.3 (C-6′), 170.2, 170.3 ($CH_3\underline{C}O$), 20.9, 21.1 ($\underline{C}H_3CO$).

Methyl 3-*O*-(3,4-di-*O*-acetyl-2,6-dideoxy-α-L-*arabino*-hexopyranosyl)-11-deoxo-18-β-glycyrrhetate (5b). Several drops of Et_3N and 0.75 g of 10% Pd/C were added to a solution of glycoside **4b** in ethyl acetate (40 mL), and the mixture was hydrogenated for 7 days (*p* = 1 bar). The catalyst was filtered off, the solvent was evaporated, and the residue was recrystallized from dioxane to give glycoside **5b** (0.58 g, 91.8%) as a white powder. R_f 0.70 (*A*); m.p. 218—220 °C. $[\alpha]_D^{20}$ +100° (*c* 0.08, $CHCl_3$). Found (%): C, 71.5; H, 9.2. $C_{41}H_{64}O_9$. Calculated (%): C, 71.9; H, 9.4. ^{1}H NMR, δ (*J*/Hz): 0.78, 0.81, 0.91, 0.98, 1.13, 1.15 (all s, 7 CH_3), 1.33 (d, 3 H, H(6′), $J_{6',5'}$ = 6.2), 1.10—1.95 (m, CH_2, CH aglycon CH, H(2′), 2.02, 2.06 (both s, 6 H, 2 Ac), 3.10 (dd, 1 H, H(3), $J_{3,2e}$ = 4.3, $J_{3,2a}$ = 11.2), 3.68 (s, 3 H, OCH_3), 4.01 (dq, 1 H, H(5′), $J_{4',5'}$ = 9.6, $J_{5',6'}$ = 6.2), 4.73 (t, 1 H, H(4′), $J_{3',4'}$ = $J_{4',5'}$ = 9.6), 4.93 (dd, 1 H, H(1′), $J_{1',2'e}$ = 1.0, $J_{1',2'a}$ = 3.0), 5.25-5.32 (m, 1 H, H(3′)), 5.27 (br.s, 1 H, H(12)). ^{13}C NMR, δ: 23.2 (C-2), 89.2 (C-3), 48.3 (C-9), 23.6 (C-11), 122.7 (C-12), 144.5 (C-13), 47.8 (C-18), 177.7 (C-30), 51.6 (C-31), 99.6 (C-1′), 36.0 (C-2′), 69.4 (C-3′), 75.3 (C-4′), 65.8 (C-5′), 17.5 (C-6′), 170.3, 170.4 ($CH_3\underline{C}O$), 20.9, 21.1 ($\underline{C}H_3CO$).

Methyl 3-*O*-(3,4-di-*O*-acetyl-2,6-dideoxy-α-L-*arabino*-hexopyranosyl)-18,19-dehydroglycyrrhetate (5c). Several drops

of Et_3N and 0.40 g of 10% Pd/C were added to a solution of glycoside **4c** (0.40 g) in ethyl acetate (15 mL) and the mixture was hydrogenated for 6 days. The catalyst was filtered off, the solvent was evaporated, and the residue was precipitated with hexane from a solution in $CHCl_3$ to afford glycoside **5c** (0.30 g, 89.4%) as a cream colored powder. R_f 0.66 (*A*); dec.p. 210—212 °C. $[\alpha]^{20}_D$ +90° (*c* 0.07, $CHCl_3$). Found (%): C, 70.9; H, 8.2. $C_{37}H_{60}O_9$. Calculated (%):C, 70.6; H, 8.7. ^{1}H NMR, δ (*J*/Hz): 0.82, 0.91, 0.94, 1.11, 1.20 (all s, 7 CH_3), 1.30 (d, 3 H, H(6′), $J_{6',5'}$ = 6.2), 1.30—2.00 (m, CH_2, aglycon CH, H(2′), 2.03, 2.05 (both s, 6 H, 2 Ac), 2.24 (s, 1 H, H(9)),3.09 (dd, 1 H, H(3), $J_{3,2e}$ = 4.4, $J_{3,2a}$ = 11.1), 3.68 (s, 3 H, OCH_3), 4.03 (dq, 1 H, H(5′), $J_{4',5'}$ = 9.6, $J_{5',6'}$ = 6.3), 4.72 (t, 1 H, H(4′), $J_{3',4'}$ = $J_{4',5'}$ = 9.6), 4.92 (br.s, C, 1 H, H(1′)), 5.25— 5.31 (m, 1 H, H(3′)), 5.56 (br.s, 1 H, H(12)). ^{13}C NMR, δ: 23.1 (C-2), 88.9 (C-3), 60.9 (C-9), 200.4 (C-11), 129.6 (C-12), 162.8 (C-13), 142.9 (C-18), 124.3 (C-19), 176.9 (C-30), 52.3 (C-31), 99.5 (C-1′), 35.9 (C-2′), 69.3 (C-3′), 75.1 (C-4′), 65.6 (C-5′), 17.6 (C-6′), 170.4, 170.5 ($CH_3\underline{C}O$), 20.9, 21.2 ($\underline{C}H_3CO$).

Methyl 3-*O*-(3,4,6-tri-*O*-acetyl-2-deoxy-α-D-*arabino*-hexopyranosyl)-deoxycholate (5d). Several drops of Et_3N and 0.96 g of 10% Pd/C were added to a solution of glycoside **4d** (0.96 g) in ethanol (25 mL) and the mixture was hydrogenated for 7 days. The catalyst was filtered off, the solvent was evaporated, and the residue was precipitated with hexane from a solution in CH_2Cl_2 to afford glycoside **5d** (0.45 g, 90%) as a cream colored powder. R_f 0.62 (*A*); dec.p. 93—95 °C. $[\alpha]_D^{20}$ +64° (*c* 0.07, $CHCl_3$). Found (%): C, 65.2; H, 9.0. $C_{37}H_{58}O_{11}$. Calculated (%): C, 65.5; H, 8.6. ^{1}H NMR, δ (*J*/Hz): 0.67 (s, 3 H, H(18)), 0.89 (C, 3 H, H(19)), 0.96 (d, 3 H, H(21), *J* = 6.1), 1.00— 2.40 (m, CH_2, aglycon CH, H(2′), 1.99, 2.02, 2.07 (all s, 9 H, 3 Ac), 3.65 (s, 3 H, OCH_3), 3.97 (br.s, C, 1 H, H(12)), 4.00—4.10 (m, 2 H, H(6′)), 4.26 (dt, 1 H, H(5′), $J_{4',5'}$ = 9.8, $J_{5',6'a}$ = $J_{5',6'b}$ = 5.4), 4.96 (t, 1 H, H(4′), $J_{3',4'}$ = $J_{4',5'}$ = 9.8), 5.17 (br.s, 1 H, H(1′)), 5.25—5.38 (m, 1 H, H(3′)). ^{13}C NMR, δ: 27.2 (C-2), 77.5 (C-3), 28.8 (C-11), 73.1 (C-12), 174.8 and 51.5 (COOMe), 95.3 (C-1′), 35.8 (C-2′), 69.3 (C-3′), 68.2 (C-4′), 69.8 (C-5′), 62.7 (C-6′), 170.1, 170.2, 170.3 ($CH_3\underline{C}O$), 20.8, 21.0, 21.1 ($\underline{C}H_3CO$).

Methyl 3-*O*-(2,6-dideoxy-α-L-*arabino*-hexopyranosyl)-18-α-glycyrrhetate (6a). Glycoside **5a** (0.30 g) was deacetylated using the procedure reported in Ref. 1. Glycoside **6a** (0.23 g, 90.5%) was isolated as a white powder after precipitation with hexane from a solution in $CHCl_3$. R_f 0.29 (*A*); dec.p. 183—185 °C; $[\alpha]_D^{20}$ +64° (*c* 0.09, $CHCl_3$). Found (%): C, 71.9; H, 9.1. $C_{37}H_{58}O_7$. Calculated (%): C, 72.3; H, 9.5. UV, λ_{max}/nm: 245.0 (lg ε 4.28). ^{13}C NMR, δ: 22.0 (C-2), 88.5 (C-3), 60.4 (C-9), 199.9 (C-11), 124.2 (C-12), 165.8 (C-13), 40.5 (C-18), 178.8 (C-30), 52.0 (C-31), 100.1 (C-1′), 38.4 (C-2′), 69.2 (C-3′), 78.3 (C-4′), 67.6 (C-5′), 17.5 (C-6′).

Methyl 3-*O*-(2,6-dideoxy-α-L-*arabino*-hexopyranosyl)-18-β-glycyrrhetate (6b). Glycoside **5b** (0.95 g) was deacetylated using the procedure reported in Ref. 1. After crystallization from dioxane glycoside **6b** (0.75 g, 90.3%) was obtained as a white powder. R_f 0.30 (*A*); m.p. 214—216 °C; $[\alpha]_D^{20}$ +93° (*c* 0.05, $CHCl_3$). Found (%): C, 74.3; H, 9.8. $C_{37}H_{60}O_6$. Calculated (%): C, 74.0; H, 10.1. ^{13}C NMR, δ: 22.3 (C-2), 88.6 (C-3), 48.4 (C-9), 23.7 (C-11), 122.6 (C-12), 144.4 (C-13), 47.7 (C-18), 177.9 (C-30), 51.6 (C-31), 100.2 (C-1′), 38.4 (C-2′), 69.5 12 (C-3′), 78.4 (C-4′), 67.5 (C-5′), 17.5 (C-6′).

Methyl 3-*O*-(2,6-dideoxy-α-L-*arabino*-hexopyranosyl)-18,19-dehydroglycyrrhetate (6c). Glycoside **5c** (0.15 g) was deacetylated using the procedure reported in Ref. 1. Glycoside **6c** (0.11 g, 86.5%) was obtained after precipitation from its $CHCl_3$ solution with petroleum ether as a cream colored powder. R_f 0.27 (*A*); dec.p. 180—182 °C; $[\alpha]_D^{20}$ +87° (*c* 0.07, $CHCl_3$). Found (%): C, 72.2; H, 8.9. $C_{37}H_{56}O_7$. Calculated (%): C, 72.5; H, 9.2. UV, λ_{max}/nm: 278.8 (lg ε 4.31). ^{13}C NMR, δ: 20.8 (C-2), 88.4 (C-3), 60.9 (C-9), 200.3 (C-11), 129.6 (C-12), 162.8 (C-13), 142.8 (C-18), 124.2 (C-19), 176.9 (C-30), 52.2 (C-31), 100.1 (C-1′), 38.6 (C-2′), 69.2 (C-3′), 78.2 (C-4′), 67.8 (C-5′), 17.6 (C-6′).

Methyl 3-*O*-(2-deoxy-α-D-*arabino*-hexopyranosyl)-deoxycholate (6d). Glycoside **5d** (0.6 g) was deacetylated using the procedure reported in Ref. 1. Glycoside **6d** (0.43 g, 89%) was obtained as a white powder. R_f 0.35 (*A*); dec.p. 103—105 °C; $[\alpha]_D^{20}$ +83° (*c* 0.08, $CHCl_3$). Found (%):C, 67.8; H, 9.8. $C_{31}H_{52}O_8$. Calculated (%): C, 67.4; H, 9.5. ^{13}C NMR, δ: 27.3 (C-2), 77.4 (C-3), 29.0 (C-11), 73.2 (C-12), 174.9 (C-24), 51.6 (C-25), 96.2 (C-1′), 38.2 (C-2′), 72.0 (C-3′), 68.9 (C-4′), 73.4 (C-5′), 62.0 (C-6′).

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