Chemistry of Natural Compounds and Bioorganic Chemistry

Stereoselective synthesis of triterpene 2-deoxy-α-D-*lyxo*-hexopyranosides

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2-Deoxy-α-D-*lyxo*-hexopyranosides of 18β-glycyrrhetic acid, its 11-deoxo derivative and allobetulin were synthesized by glycosylation of oleonane-type triterpene alcohols with D-galactal acetate in the presence of *N*-iodosuccinimide followed by deiodination and deprotection.

Key words: glycyrrhetic acid, allobetulin, D-galactal acetates, *N*-iodosuccinimide, 2-deoxy-2-iodo-α-D-talopyranosides, 2-deoxy-α-D-*lyxo*-hexopyranosides.

The iodine-containing activators *N*-iodosuccinimide (NIS) and iodonium dicollidine perchlorate (IDCP) were successfully used for the synthesis of oligosaccharides and steroid glycosides.[1,2] We have used these activators for the stereoselective synthesis of triterpene 2-deoxy-α-D-*arabino*- and 2,6-dideoxy-α-L-*arabino*-hexopyranosides.[3—5]

Here we report a stereoselective synthesis of 2-deoxy-α-D-*lyxo*-hexopyranosides by glycosylation of biologically active triterpene alcohols of the oleanane series **1a—c** with D-galactal acetate **2** in the presence of NIS.

Reaction of tri-*O*-acetyl-D-galactal **2** with triterpene alcohols, 18β-glycyrrhetic and 11-deoxo-18β-glycyrrhetic acid methyl esters (**1a,b**), and allobetulin (**1c**), under the conditions reported earlier[4,5] afforded 2-deoxy-2-iodoglycosides **3a—c** in 52—54% yields (Scheme 1).

Deiodination of glycosides **3a—c** by hydrogenolysis in the presence of 10% Pd/C and triethylamine in ethanol or in ethyl acetate led to acetylated 2-deoxy-α-D-*lyxo*-hexopyranosides (**4a—c**) in yields of 90—93%.

Hydrolysis of glycosides **4a,b** with 5% KOH in aqueous ethanol gave 2-deoxy-α-D-*lyxo*-hexopyranosides of 18β-glycyrrhetic acid (**5d**) and its 11-deoxo derivative (**5e**), which are analogs of the natural glycoside from the licorice root extract, glycyrrhizinic acid.

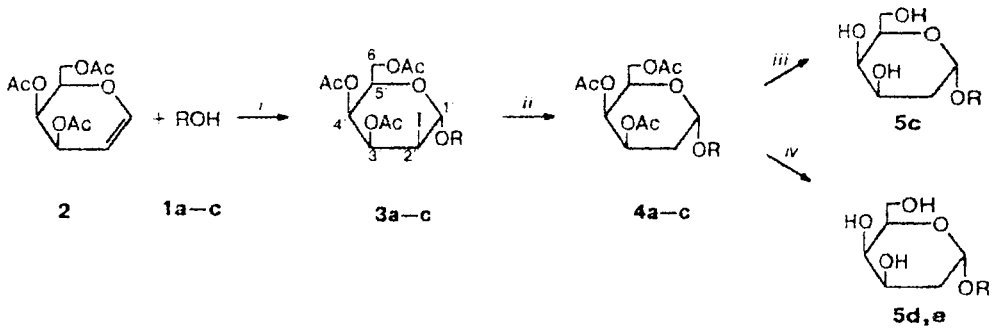
Mild deacetylation of glycoside **4c** with 5% methanolic KOH led to 2-deoxy-α-D-lyxo-hexopyranoside of allobetuline (**5c**).

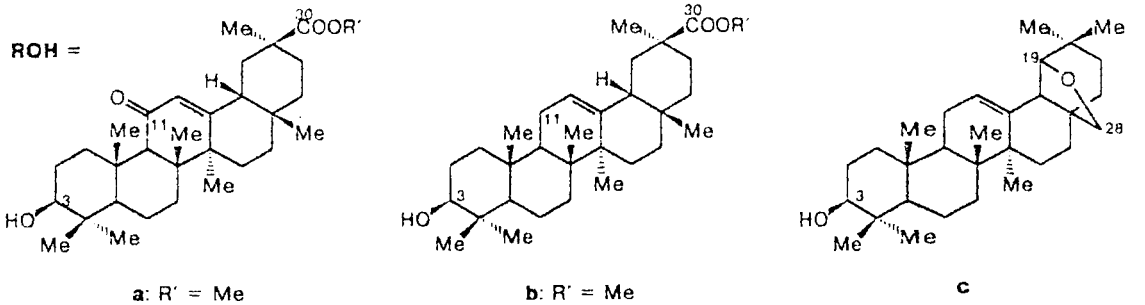
The structures of the synthesized compounds were established using NMR spectroscopy (Table 1). The assignment of signals in the spectra of glycosides **3—5** was based on a comparison with the published data for the aglycons,[6—8] the carbohydrate moieties,[1,2,9] and the spectra of the starting triterpenes **1a—c**. The ^{13}C NMR spectra of aglycon parts of the synthesized glycosides are similar to those of triterpene alcohols, except for the signals of C(3), which are shifted downfield by 5.5—6.3 ppm, and the signals of C(2), which are shifted upfield by 3.8—5.0 ppm. The anomeric C(1′) atoms in the spectra of glycosides **3a—c** resonate at δ 99.8; the signals of H(1′) protons appear in the low field region (δ

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 3, pp. 596—600, March, 1997.

1066-5285/97/4603-0577 $18.00

Scheme 1





a: R' = Me
d: R' = H

b: R' = Me
e: R' = H

c

Reagents: *i.* NIS, CH_2Cl_2—CH_3CN; *ii.* 10% Pd/C; *iii.* 5% KOH/MeOH; *iv.* 5% KOH/EtOH—H_2O (1 : 1)

5.40—5.48) in the form of broadened singlets. The values of coupling constants in the ^{13}C NMR (NOE mode), ($J_{C(1'),H(1')}$ = 167—170 Hz) unambiguously indicate the formation of the α-glycosidic bond and the axial position of the aglycon in glycosides **3 a—c**.[10]

The assignment of the signals of the carbon and hydrogen atoms in the ^{13}C NMR spectra of glycoside **3b** was based on the data of the homonuclear and heteronuclear two-dimensional spectra (Figs. 1 and 2). For example, in the two-dimensional ^1H—^1H

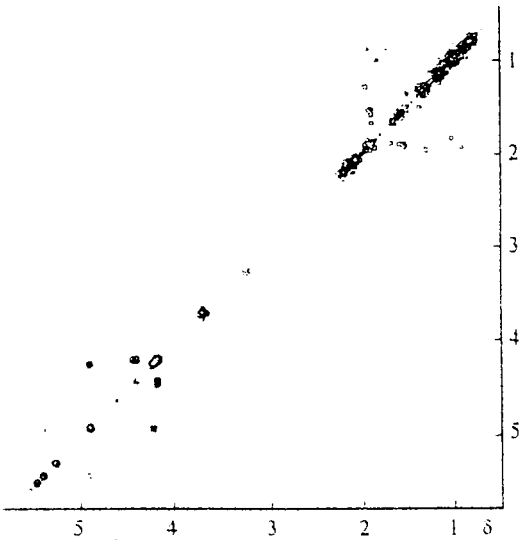


Fig. 1. Two-dimensional ^1H—^1H COSY NMR spectrum of glycoside **3b**

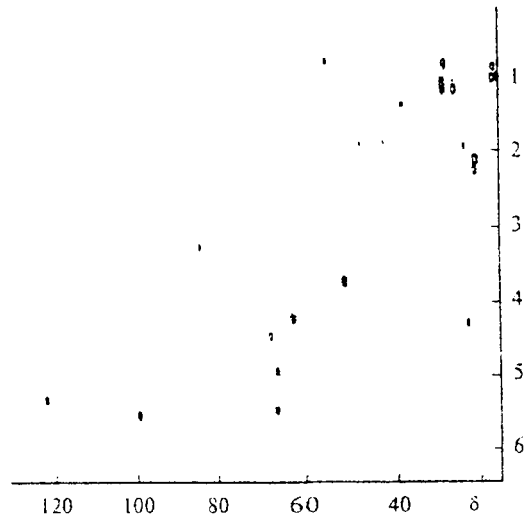


Fig. 2. Two-dimensional ^{13}C—^1H COSY NMR spectrum of glycoside **3b**

Table 1. ^{13}C NMR chemical shifts of glycosides **3**—**5** ($CDCl_3$, δ, 25 °C)

Atom	Glycoside								
	3a	**3b**	**3c**	**4a**	**4b**	**4c**	**5c**	**5d**	**5e**
C(2)	22.3	22.3	22.5	21.8	21.8	22.2	21.7	21.3	21.4
C(3)	84.4	84.6	84.5	82.6	82.9	83.5	81.7	81.2	81.3
C(9)	61.9	48.3	51.2	61.9	48.2	51.2	51.1	61.6	48.2
C(10)	37.1	36.9	37.2	37.0	36.9	37.4	37.2	36.7	36.9
C(11)	200.1	36.3	21.1	200.3	23.5	21.2	21.0	200.1	23.5
C(12)	128.6	122.6	26.3	128.5	122.5	26.4	26.3	127.7	122.6
C(13)	169.3	144.5	36.8	169.4	144.4	36.9	36.8	170.9	144.5
C(18)	48.5	47.8	46.9	48.5	47.7	47.0	46.8	48.2	47.6
C(19)	41.2	43.0	88.0	41.2	42.8	88.1	88.0	40.9	42.8
C(20)	44.1	44.4	36.3	44.0	44.3	36.3	36.2	43.4	43.3
C(28)	28.6	28.3	71.3	28.5	28.6	71.4	71.3	28.4	28.7
C(30)	177.0	176.8	28.9	177.0	177.7	28.9	28.8	181.5	181.8
C(31)	51.8	51.6		51.8	51.6				
C(1′)	99.8	99.8	99.8	93.6	93.2	93.4	93.4	93.2	93.3
C(2′)	22.8	22.9	22.9	30.7	30.8	30.9	34.9	33.4	33.5
C(3′)	65.5	65.5	65.5	66.5	66.5	66.6	68.4	65.8	65.8
C(4′)	65.5	65.6	65.6	66.8	66.9	66.8	65.2	69.4	69.6
C(5′)	67.2	67.2	67.1	67.0	67.1	67.2	70.3	70.2	70.1
C(6′)	62.2	62.3	62.2	62.6	62.5	62.6	64.2	61.8	61.7
$OC\underline{O}CH_3$	170.2	169.6	170.2	169.8	169.6				
	170.4	170.2	170.5	170.2	170.1				
	170.6	170.5	170.6	170.8	170.6				
$OCO\underline{C}H_3$	20.8	20.8	20.8	20.8	20.8				
	20.9	21.0	20.9	21.0	20.9				
	21.1	21.1	21.0	21.1	21.0				

COSY NMR spectrum (Fig. 1), no cross peak between H(1′) and H(2′) (δ 5.48 and 4.22) is observed due to the low coupling constant value (H(1′) and H(2′) protons are equatorial). The H(3′) proton (δ 4.89, triplet) exhibits pronounced cross-peaks with H(2′) and H(4′) protons (δ 5.40), while the value of the coupling constant (J = 4.7 Hz) confirms the axial position of H(3′) proton between equatorial H(2′) and H(4′) protons. The olefinic H(12) proton of the aglycon at δ 5.27, which appears as a broadened singlet, has a cross-peak with H(11) protons, resonating in the high field at δ 1.9. As can be seen in Fig. 2, which presents the two-dimensional ^{13}C—^1H COSY NMR spectrum of glycoside **3b**, the signal of H(1′) proton correlates directly with the C(1′) signal at δ 99.8, and the C(2′) atom (δ 22.9) has a cross-peak with the H(2′) proton at δ 4.22. On the basis of the positions of the cross-peaks in the ^{13}C—^1H COSY NMR spectrum and the exact determination of the chemical shifts of the proton signals in the ^1H NMR spectrum, the signals of the other carbons of the carbohydrate ring were assigned unequivocally. Thus, compounds **3a**—**c** are 2-deoxy-2-iodo-α-D-*talo*-hexopyranosides.

Deiodination and deprotection result in upfield shifts of the signals of the anomeric C(1′) atoms and the aglycon C(3) carbons (by 6.4—6.6 and 2.8—3.4 ppm, respectively) in the ^{13}C NMR spectra of 2-deoxy-α-D-*lyxo*-hexopyranosides **4a**—**c**, **5c**—**e**; while the signals of C(2′) carbons of pyranose rings undergo downfield shifts by 10.6—12 ppm. Catalytic hydrogenolysis does not lead to changes in the aglycon part of glycosides **4a**,**b** (C=O and C=C). This fact is confirmed by retaining the low field signals of C(11)—C(13) atoms in the ^{13}C NMR spectrum of glycoside **4a** and C(12), C(13) atoms in the spectrum of glycoside **4b**. In the ^1H NMR spectra of compounds **4a** and **4b**, the low field signals of H(12), which are typical of triterpenes of the olean-12-enone type, also were retained.[8]

Alkaline hydrolysis of the ester groups in glycosides **4a**,**b** gives glycosides of triterpene acids **5d** and **5e**, in ^{13}C NMR spectra of which the C(30) signal is in a lower field (δ 181.5—181.8) than that in the spectra of the methyl esters **4a**,**b**. A similar C(30) signal of the carboxyl group is observed in the spectrum of glycyrrhizinic acid.[11] Configuration of the proton at C(18) carbon of the aglycon in glycosides **5d** and **5e** remained unchanged during alkaline hydrolysis, as was demonstrated earlier.[12]

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. IR spectra were recorded on a Specord M80 for Nujol mulls. The elemental analysis data were consistent with the calculated values.

TLC was carried out on Silufol plates (Czech Republic) using the following solvent 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 in ethanol followed by heating at 100—120 °C for 2—3 min. Preparative 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 and acetonitrile were refluxed over P_2O_5 for 2 h and distilled. Molecular sieves 4 Å were activated at 160—180 °C and 5 Torr for 2 h.

N-Iodosuccinimide was obtained using the earlier reported procedure,[13] with an iodine content of 55.8—51.6% (98—99% of the theoretical value).

Methyl esters of 18β- and 11-deoxo-18β-glycyrrhetic acids **1a** and **1b** were obtained using the previously published procedures.[14,15] Allobetulin was synthesized according to the previously published procedure[16] from the extract of birch bark (*Betula pendula*). Tri-*O*-acetyl-D-galactal (**2**) was synthesized according to the previously published procedure.[17]

Synthesis of glycosides 3 and 4 (general procedure). *A.* Activated molecular sieves 4 Å (0.55 g) were added to a solution of tri-*O*-acetyl-D-galactal (**2**) (0.55 g, 2 mmol) and an equimolar amount of triterpene alcohol **1a—c** in a mixture of CH_2Cl_2 and CH_3CN (1 : 1, v/v) (50 mL). The resulting mixture was cooled to 0 °C and *N*-iodosuccinimide (0.52 g, 2.3 mmol) was added with stirring in the dark. The temperature was allowed to attain *ca.* 20 °C and the mixture was stirred for 70 h (TLC monitoring, system A). The sieves were filtered off and the solvent was distilled off *in vacuo*, and the residue was dissolved CH_2Cl_2 (50 mL). The resulting solution was washed with 10% $Na_2S_2O_3$ (20 mL × 2), dried over $MgSO_4$, and evaporated to dryness. The residue was chromatographed on a column to give analytically pure samples of the corresponding glycosides **3a—c**.

B. Several drops of triethylamine were added to a solution of acetate **3a—c** (0.5—1.00 g, 0.6—1.1 mmol) in methanol, ethanol, or ethyl acetate (20—35 mL). The reaction mixture was hydrogenated for 6—8 days (p = 1 atm) in the presence of 10% Pd/C (the catalyst quantity was equal to the mass of the glycoside used). The catalyst was filtered off, the solvent was distilled off *in vacuo*, and the residue was precipitated or recrystallized to yield analytically pure samples of glycosides **4a—c**.

Methyl 3-*O*-(3,4,6-tri-*O*-acetyl-2-deoxy-2-iodo-α-D-*talo*-pyranosyl)-18β-glycyrrhetate (3a). Crude product (1.57 g) obtained from alcohol **1a** (0.97 g) by the above procedure (*A*) was chromatographed, pentane—ethyl acetate mixtures (7 : 1, 5 : 1, 3 : 1, 2 : 1, 1 : 1 v/v) being used for elution. Glycoside **3a** (homogeneous according to TLC) was eluted with the 3 : 1 → 2 : 1 mixtures and isolated as an amorphous powder. Yield 0.92 g (52%). $C_{43}H_{63}IO_{11}$. R_f 0.67 (A); 0.73 (B); 0.72 (C). $[\alpha]_D^{20}$ +76° (*c* 0.09, $CHCl_3$). UV, λ_{max}/nm: 248.2 (lgε 3.59). ^{1}H NMR, δ: 0.80, 0.82, 1.00, 1.14, 1.35, 1.65 × 2 (all s, 7 CH_3), 1.30—2.00 (m, CH_2, CH), 2.03, 2.06, 2.17 (all s, 3 Ac), 2.31 (s, 1 H, H(9)), 2.85 (d, 1 H, H(18), J = 13.8 Hz), 3.23 (dd, 1 H, H(3), $J_{3,2e}$ = 4.5 Hz, $J_{3,2a}$ = 11.3 Hz), 3.68 (s, 3 H, OCH_3), 4.16 (d, 2 H, H(6′), $J_{6',5'}$ = 6.4 Hz), 4.21 (d, 1 H, H(2′), $J_{2',3'}$ = 4.6 Hz), 4.39 (td, 1 H, H(5′), $J_{5',6'a}$ = $J_{5',6'b}$ = 6.4 Hz, $J_{4',5'}$ = 1.7 Hz), 4.89 (t, 1 H, H(3′), $J_{2',3'}$ = $J_{3',4'}$ = 4.6 Hz), 5.29 (br. s, 1 H, H(4′)), 5.47 (br.s, 1 H, H(1′)), 5.66 (s, 1 H, H(12)).

Methyl 3-*O*-(3,4,6-tri-*O*-acetyl-2-deoxy-2-iodo-α-D-*talo*-pyranosyl)-11-deoxo-18β-glycyrrhetate (3b). Crude product (1.58 g) obtained from alcohol **1b** (0.94 g) using procedure *A* was chromatographed, chloroform and chloroform—methanol mixtures (200 : 1, 150 : 1, 100 : 1, 50 : 1, v/v) being successively used for elution. Glycoside **3b** (homogeneous according to TLC) was eluted with the 150 : 1 → 100 : 1 mixtures and crystallized from dioxane to give **3b** as a white powder (0.9 g, 54%). $C_{43}H_{65}IO_{10}$. R_f 0.69 (A), 0.71 (B); m.p. 206—208 °C; $[\alpha]_D^{20}$ +85° (*c* 0.08, $CHCl_3$). ^{1}H NMR, δ: 0.77, 0.81, 0.95, 0.96, 1.00, 1.12, 1.55 (all s, 7 CH_3), 1.20—2.00 (m, CH_2, CH), 1.99, 2.04, 2.14 (all s, 3 Ac), 3.23 (dd, 1 H, H(3), $J_{3,2e}$ = 4.0 Hz, $J_{3,2a}$ = 11.5 Hz), 3.68 (s, 3 H, OCH_3), 4.17 (d, 2 H, H(6′), $J_{6',5'}$ = 6.4 Hz), 4.22 (d, 1 H, H(2′), $J_{2',3'}$ = 4.7 Hz), 4.41 (td, 1 H, H(5′), $J_{5',6'a}$ = $J_{5',6'b}$ = 6.4 Hz, $J_{4',5'}$ = 1.8 Hz), 4.89 (t, 1 H, H(3′), $J_{2',3'}$ = $J_{3',4'}$ = 4.7 Hz), 5.27 (s, 1 H, H(12)), 5.40 (br.s, 1 H, H(4′)), 5.48 (br.s, 1 H, H(1′)).

3-*O*-(3,4,6-Tri-*O*-acetyl-2-deoxy-2-iodo-α-D-*talo*-pyranosyl)allobetulin (3c). A crude product (1.55 g) obtained from alcohol **1c** (0.89 g) by procedure *A* was chromatographed under conditions similar to those used for **3b** to give 0.89 g of **3c** (53%). $C_{42}H_{65}IO_9$. R_f 0.70 (A), 0.72 (B); m.p. 232—234 °C; $[\alpha]_D^{20}$ +20° (*c* 0.05, $CHCl_3$). ^{1}H NMR, δ: 0.77, 0,79, 0.84, 0.89, 0.92, 0.97 × 2 (all s, 21 H, 7 CH_3), 1.00—2.05 (m, CH_2, CH), 2.05, 2.06, 2.17 (all s, C, 9 H, 3 Ac), 3.19—3.23 (br.s, 1 H, H(3)), 3.43 (d, 1 H, H(28), ^2J = 7.7 Hz), 3.51 (s, 1 H, H(19)), 3.76 (d, 1 H, H(28), ^2J = 7.7 Hz), 4.16 (d, 2 H, H(6′), $J_{6',5'}$ = 6.5 Hz), 4.21 (d, 1 H, H(2′), $J_{2',3'}$ = 4.4 Hz), 4.40 (td, 1 H, H(5′), $J_{5',6'a}$ = $J_{5',6'b}$ = 6.5 Hz, $J_{4',5'}$ = 1.8 Hz), 4.88 (t, 1 H, H(3′), $J_{2',3'}$ = $J_{3',4'}$ = 4.4 Hz), 5.30 (br.s, 1 H, H(4′)), 5.40 (br.s, 1 H, H(1′)).

Methyl 3-*O*-(3,4,6-tri-*O*-acetyl-2-deoxy-α-D-*lyxo*-hexopyranosyl)-18β-glycyrrhetate (4a). A solution of glycoside **3a** (1.0 g, 1.13 mmol) in 35 mL of methanol was hydrogenated for 8 days according to procedure *B*. After reprecipitation of the residue from a chloroform solution with hexane, glycoside **4a** was obtained (0.76 g, 90%). $C_{43}H_{64}IO_{11}$. R_f 0.67 (A), 0.74 (B); m.p. 240—241 °C; $[\alpha]_D^{20}$ +79° (*c* 0.06, $CHCl_3$). UV, λ_{max}/nm: 248.2 (lgε 3.66). IR, ν/cm^{-1}: 1760—1750 (OAc), 1730—1720 ($COOCH_3$), 1650 (C(11)=O). ^{1}H NMR, δ: 0.80, 0.82, 1.01, 1.13, 1.16 × 2, 1.35 (all s, 7 CH_3), 1.25—2.30 (m, CH_2, CH-aglycon, H(2′)), 1.99, 2.04, 2.14 (all s, 3 Ac), 2.31 (s, 1 H, H(9)), 2.83 (d, 1 H, H(18), J = 13.6 Hz), 3.20 (dd, 1 H, H(3), $J_{3,2e}$ = 4.5 Hz, $J_{3,2a}$ = 11.3 Hz), 3.69 (s, 3 H, OCH_3), 4.07—4.12 (m, 2 H, H(6′)), 4.27 (td, 1 H, H(5′), $J_{5',6'a}$ = $J_{5',6'b}$ = 6.3 Hz, $J_{4',5'}$ = 1.6 Hz), 5.19—5.33 (m, 2 H, H(1′), H(3′)), 5.36 (br.s, 1 H, H(4′)), 5.66 (s, 1 H, H(12)).

Methyl 3-*O*-(3,4,6-tri-*O*-acetyl-2-deoxy-α-D-*lyxo*-hexopyranosyl)-11-deoxo-18β-glycyrrhetate (4b). A solution of glycoside **3b** (0.9 g, 1.03 mmol) in 35 mL of AcOEt was hydrogenated for 10 days according to procedure *B*. After recrystallization from dioxane, glycoside **4b** (0.72 g, 93%) was obtained as a white powder. $C_{43}H_{66}IO_{10}$. R_f 0.67 (A); m.p. 201—203 °C; $[\alpha]_D^{20}$ +77° (*c* 0.04, $CHCl_3$). IR, ν/cm^{-1}: 1760—1750 (OAc), 1730—1720 ($COOCH_3$). ^{1}H NMR, δ: 0.77, 0.81, 0.89, 0.95, 0.96, 1.00, 1.12 (all s, 7-CH_3), 1.15—2.00 (m, CH_2, CH-aglycon, H(2′)), 1.99, 2.05, 2.17 (all s, 3 Ac), 3.20 (dd, 1 H, H(3), $J_{3,2e}$ = 4.0, $J_{3,2a}$ = 11.0), 3.68 (s, 3 H, OCH_3), 4.02—4.15 (m, 2 H, H(6′)), 4.28 (td, 1 H, H(5′), $J_{4',5'}$ = 1.5, $J_{5',6'a}$ = $J_{5',6'b}$ = 6.3), 5.18—5.32 (m, 2 H, H(1′), H(3′)), 5.27 (s, 1 H, H(12)), 5.35 (br.s, 1 H, H(4′)).

3-*O*-(3,4,6-Tri-*O*-acetyl-2-deoxy-α-D-*lyxo*-hexopyranosyl)allobetulin (4c). A solution of glycoside **3c** (0.45 g, 0.53 mmol) in 20 mL of ethanol was hydrogenated for 9 days according to procedure *B*. After recrystallization from ethanol, glycoside **4c** (0.34 g, 90%) was obtained as a yellow powder. $C_{42}H_{66}IO_9$. R_f 0.69 (A); m.p. 215—217 °C; $[\alpha]_D^{20}$ +13° (*c* 0.08, $CHCl_3$). IR, ν/cm^{-1}: 1760—1750 (OAc). ^{1}H NMR, δ:

0.77, 0.78, 0.86, 0.91, 0.93, 0.97 × 2 (all s, 21 H, 7 CH_3), 1.00—1.90 (m, CH_2, CH aglycon, H(2')), 2.05, 2.06, 2.08 (all s, 9 H, 3 Ac), 3.16—3.22 (br. s, 1 H, H(3)), 3.44 (d, 1 H, H(28), ^2J = 7.8 Hz), 3.52 (C, 1 H, H(19)), 3.78 (d, 1 H, H(28), ^2J = 7.8 Hz), 4.05—4.18 (m, 2 H, H(6')), 4.25 (t d, 1 H, H(5'), $J_{4',5'}$ = 1.6, $J_{5',6'a}$ = $J_{5',6'b}$ = 6.8), 5.20 (br.s, 1 H, H(1')), 5.21—5.30 (m, 1 H, H(3')), 5.36 (br.s, 1 H, H(4')).

3-*O*-(2-Deoxy-α-D-*lyxo*-hexopyranosyl)allobetulin (5c). A solution of glycoside **4c** in methanol (50 mL) was deacylated with 5% methanolic KOH (8 mL) according to the procedure reported in Ref. 4. After recrystallization from ethanol, glycoside **5c** (0.15 g, 85%) was obtained as a cream-colored powder. $C_{36}H_{60}IO_6$. R_f 0.32 (*A*); m.p. 205—207 °C; $[\alpha]_D^{20}$ +14° (*c* 0.03, $CHCl_3$). IR, ν/cm^{-1}: 3600—3200 (OH).

3-*O*-(2-Deoxy-α-D-*lyxo*-hexopyranosyl)-18β-glycyrrhetic acid (5d). A solution of glycoside **4a** (0.38 g, 0.5 mmol) in a 5% KOH solution in an EtOH—H_2O mixture (1 : 1, v/v, 13 mL) was kept at *ca.* 20 °C for 10 h and then boiled for 2 h. The mixture was diluted with water (5 mL), treated with cation exchange resin (H^+-form), and evaporated to dryness. We chromatographed the residue eluting with chloroform—methanol mixtures (200 : 1, 150 : 1, 100 : 1, 50 : 1, 25 : 1, v/v). Glycoside **5d** (homogeneous according to TLC) was eluted with a 50 : 1 → 25 : 1 mixture as a white powder. Yield 0.20 g (67%). $C_{36}H_{56}IO_8$. R_f 0.24 (A), 0.26 (B); m.p. 212—215 °C; $[\alpha]_D^{20}$ +117° (*c* 0.08, $CHCl_3$). UV, λ_{max}/nm: 248.0 (lg ε 3.78). IR, ν/cm^{-1}: 3600—3200 (OH), 1710—1700 (COOH), 1650 (C(11) = O).

3-*O*-(2-Deoxy-α-D-*lyxo*-hexopyranosyl)-18β-glycyrrhetic acid (5e). Glycoside **4b** (0.37 g, 0.5 mmol) was deacylated as reported above. After purification, glycoside **5e** (0.21 g, 68%) was obtained as a white powder. $C_{36}H_{58}IO_7$. R_f 0.25 (A); m.p. 183—185 °C; $[\alpha]_D^{20}$ +110° (*c* 0.06, $CHCl_3$). IR, ν/cm^{-1}: 3600—3200 (OH), 1710—1700 (COOH).

This work was financially supported by the Russian Foundation for Basic Research (Project No. 96-03-33240).

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Received June 8, 1996;
in revised form — January 21, 1997