Chemistry of Natural Compounds and Bioorganic Chemistry

Direct stereospecific synthesis of triterpene and steroid 2-deoxy-α-glycosides

O. B. Flekhter, L. A. Baltina, and G. A. Tolstikov*

Institute of Organic Chemistry, Ufa Scientific Center of the Russian Academy of Sciences, 71 prosp. Oktyabrya, 450054 Ufa, Russian Federation. Fax: 007 (347 2) 35 6066

Stereospecific synthesis of 2-deoxy-α-glycosides of methyl glycyrrhetate, methyl deoxycholate, and cholesterol was performed by glycosylation of the corresponding alcohols with glycal acetates in the presence of a cation-exchange resin (H^+) and LiBr.

Key words: stereo- and regiospecific glycosylation, methyl glycyrrhetate, methyl deoxycholate, cholesterol, glycal acetates, acidic catalysis, 2-deoxyglycosides.

Recently[1–3] we reported the two-step synthesis of 2-deoxyhexopyranosides *via* stereospecific glycosylation of triterpene alcohols with glycal acetates in the presence of iodine-containing activators, such as *N*-iodosuccinimide (NIS) and di(*sym*-collydine)iodonium perchlorate (IDCP). The reaction of glycals with alcohols under the conditions of acidic catalysis,[4] which was used for preparation of 2-deoxyglycosides, allows one to exclude the steps of 2-deoxy-2-iodoglycoside synthesis and deiodination. To synthesize triterpene 2-deoxyglycosides, we used sulfonic acid cationites and LiBr as activators.

Under the conditions mentioned,[5] glycyrrhetinic acid methyl ester (**1a**) was glycosylated with hexa-*O*-acetyllactal (**2**) and hexa-*O*-acetylmaltal (**3**), deoxycholic acid methyl ester (**1b**) was glycosylated with 3,4,6-tri-*O*-acetyl-D-glucal (**4**) and 3,4-di-*O*-acetyl-L-rhamnal (**5**), and cholesterol (**1c**) was glycosylated with 3,4-di-*O*-acetyl-L-rhamnal (**5**).

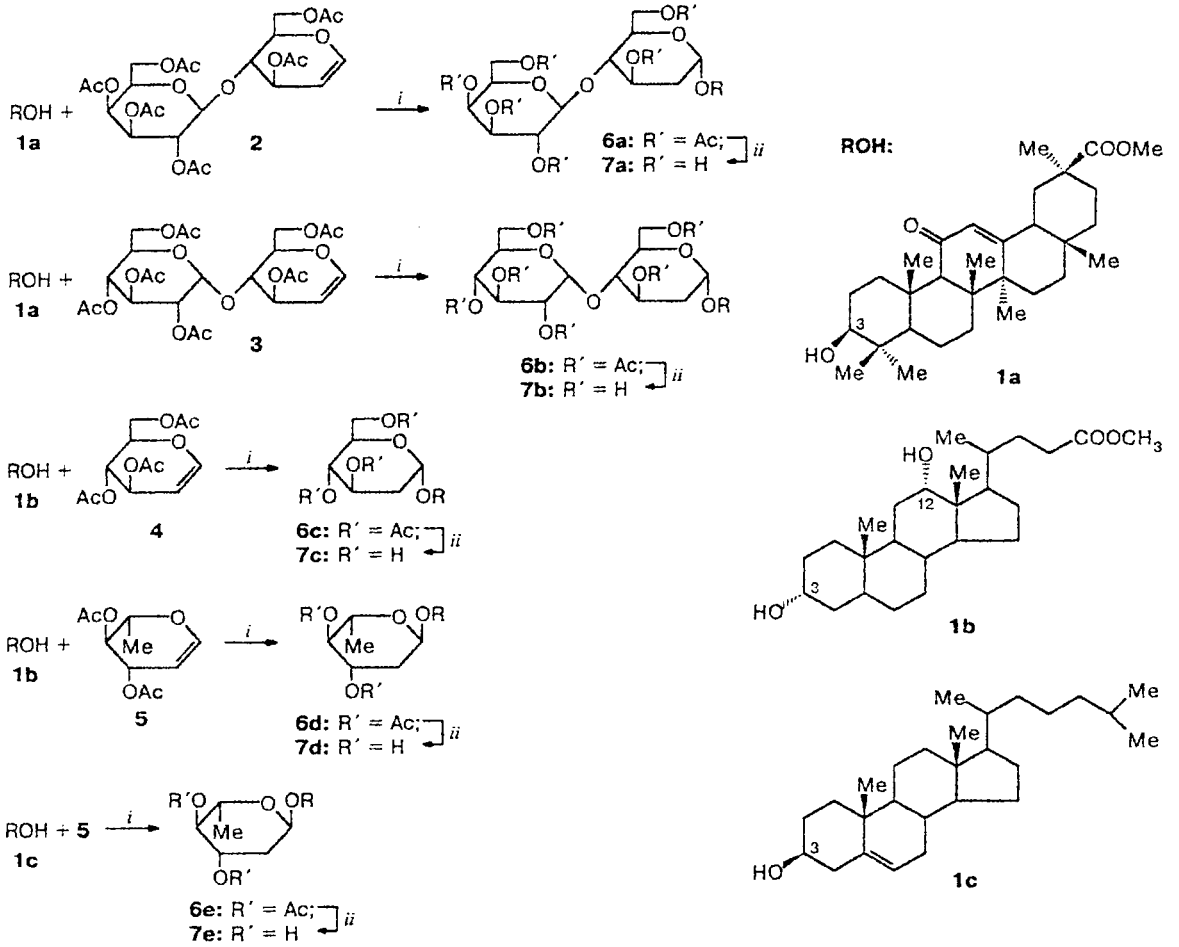
Glycosylation resulted in 2-deoxy-α-glycosides of triterpene (**6a,b**) (54 and 58% yields) and steroid (**6c,d,e**) (~80% yield) alcohols. β-Anomers were not detected by TLC or NMR. Deacetylation of the compounds obtained with KOH in MeOH gave target 4-*O*-(β-D-galactopyranosyl)- and 4-*O*-(α-D-glucopyranosyl)-2-deoxy-α-D-*arabino*-hexopyranosides of 18β-glyccyrrhetinic acid methyl ester (**7a,b**), 2-deoxy-α-D-*arabino*-hexopyranoside of deoxycholic acid methyl ester (**7c**), and 2,6-dideoxy-α-L-*arabino*-hexopyranosides of deoxycholic acid (**7d**) and cholesterol (**7e**) (76—90% yield) (Scheme 1). Compounds **7a,b** are 2-deoxy disaccharide analogs of glyccyrrhizic acid, a natural glycoside from licorice (*Glycyrrhiza*) root extract.

The structure of compounds **6** and **7** was established by NMR spectroscopy and also by comparison of the retention factors and physicochemical characteristics of the compounds obtained with those of glycosides synthesized earlier using IDCP and NIS methods. The signals in the NMR spectra were assigned on the basis of literature data for aglycones[6–9] and carbohydrate moieties.[9–11] The ^{13}C NMR spectra of the aglycone moieties of the glycosides synthesized were the same as

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 7, pp. 1390—1393, July, 1997.

1066-5285/97/4607-1335 $18.00

Scheme 1



Reagents: *i*. KU-2-8 (H^+), LiBr; *ii*. 5% KOH/MeOH

for the starting alcohols **1a—c** except the chemical shifts of C(3) atoms, which were characterized by a down-field shift. The signals of the anomeric C(1′) atoms of glycosides **6a,b** and **7a,b** are present at δ 93.3—93.6 ppm (*cf.* Refs. 5, 12). The signals of CH_3COO groups at δ ~170 ppm are absent in the spectra of compounds **7a—e,** but the signals of the MeOOC group of the aglycone are retained in the spectra of glycosides **7a—d**. The complete assignment of the proton signals in the ^1H NMR spectra of compounds **6a,b** appeared to be hindered by overlap of a number of signals. The signals of the H(1′) protons are doublets with $J_{1',2'}$ = 1.1—1.4 Hz (α-glycosidic bond)[12] in the low-field region (δ 5.10 and 5.15 ppm).

As was described previously,[13] diol **1b** is glycosylated regiospecifically at O(3) to yield glycosides **6c,d**. This is confirmed by the fact that the C(3) signals in the ^{13}C NMR spectra shifted down-field after glycosylation, while the position of the C(12) signals remained unchanged. The yields of glycosides **6c** and **6e** are higher than those of **6c,e** obtained *via* 2-deoxy-2-iodo derivatives.[9, 13]

The signal of the anomeric C(1′) atom in the spectrum of glycoside **6c** is located at δ 95.2 ppm as in the spectra of this compound obtained by the IDCP procedure.[13] The signals of the C(1′) atoms in the ^{13}C NMR spectra of glycosides **6d** and **6e** are present at δ 98.2 and 99.2 ppm. This was previously observed in the spectrum of triterpene 2,6-deoxy-α-L-*arabino*-hexopyranoside.[3] The ^1H NMR spectra of glycosides **6c** and **6e** agreed with those obtained for these compounds synthesized by IDCP[13] and NIS[9] methods. The signal of the H(1′) proton at the anomeric center in the ^1H NMR spectrum of glycoside **6d** is present in the low-field region at δ 4.90 ppm as a doublet with $J_{1',2'}$ = 1.8 Hz. This suggests its equatorial position and α-glycosidic linkage.

Experimental

IR spectra were recorded on a Specord M80 spectrophotometer in Nujol. UV spectra were recorded on a Specord UV M400 spectrophotometer in methanol. ^{13}C and ^1H NMR spectra were registered on a Bruker AM-300 instrument (75.5

and 300 MHz, respectively) in $CDCl_3$ with tetramethylsilane as the internal standard.

TLC was performed on Silufol (Czech Republic) plates using CH_2Cl_2—MeOH (10 : 1) (A) and AcOEt—pentane (1 : 1) (B) as developing systems. The compounds were visualized by treating the plates with 20% phosphotungstic acid in ethanol and subsequent heating at 100—120 °C for 2—3 min. Column chromatography was performed on Silica gel L 40/100 mm (Czech Republic).

Melting points were determined on a Boetius instrument. Specific optical rotations were taken on a Perkin-Elmer 241 MC polarimeter.

Solvents (CH_2Cl_2 and MeCN) were refluxed over P_2O_5 for 2 h and then distilled. Molecular sieves 4 Å were activated at 160—180 °C and 1—5 Torr for 3 h. Cation-exchange resin KU-2-8 (H^+) was dried as described in Ref. 4. 18β-Glycyrrhetinic acid methyl ester **1a** was obtained by the method[14] from β-glycyrrhizic acid. Glycals **2**—**5** were prepared by the procedure similar to that described previously.[15]

Synthesis of glycosides 6a—e. Anhydrous LiBr (0.7 g), alcohol **1a—c**, activated molecular sieves 4 Å, and 0.9 g of dried cation-exchange resin were added to a solution of glycal **2**—**5** in 30 mL of a CH_2Cl_2—CH_3CN mixture (1 : 1 vol.). The reaction mixture was stirred for 3 h (monitoring by TLC, A), filtered, and quenched with Et_3N. The solvents were removed *in vacuo*. A residue was dissolved in CH_2Cl_2 (20 mL), washed with cold 1 *M* HCl solution and saturated $NaHCO_3$, and dried over Na_2SO_4. The solvent was removed, and the residue was chromatographed in pentane—AcOEt. A resulting product was reprecipitated with ether or hexane from $CHCl_3$ or CH_2Cl_2.

3-*O*-[3,6-Di-*O*-acetyl-2-deoxy-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-galactopyranosyl)-α-D-*arabino*-hexopyranosyl]-18β-glycyrrhetinic acid methyl ester (6a). Glycoside **6a** (0.56 g, 54.2 %, cream-colored powder) was obtained from hexa-*O*-acetyllactal **2** (0.56 g, 1 mmol) and alcohol **1a** (0.48 g, 1 mmol). R_f 0.65 (A); 0.59 (B); decomp.p. 232—234 °C; $[\alpha]_D^{20}$ +36° (*c* 0.09, $CHCl_3$). Found (%): C, 60.2; H, 7.7. $C_{55}H_{80}O_{19}$. Calculated (%): C, 63.2; H, 7.7. UV (MeOH), λ_{max}/nm: 248.4 (lgε 3.97). IR, ν/cm^{-1}: 1760—1750 (OAc), 1730—1720 ($COOCH_3$), 1660 (—C(11)=O). ^{1}H NMR (δ, ppm, *J*/Hz): 0.80, 0.92, 1.11, 1.12, 1.15, 1.36 (all s, 21 H, 7 CH_3); 1.20—2.00 (m, CH_2, aglycone CH, H(2′)); 2.03, 2.05, 2.08, 2.10, 2.13 (all s, 18 H, 6 Ac); 2.32 (s, 1 H, H(9)); 2.75 (d, 1 H, H(18), J = 13.5); 3.25 (dd, 1 H, H(3), $J_{3,2e}$ = 4.5, $J_{3,2a}$ = 11.4); 3.69 (s, 3 H, OCH_3); 4.15—4.36 (m, 6 H, H(5′), H(6′a,b), H(5″), H(6″a,b)); 4.41 (t, 1 H, H(4′), $J_{4',3'}$ = $J_{4',5'}$ = 9.9); 4.72 (dd, 1 H, H(3″), $J_{3'',4''}$ = 3.6, $J_{3'',2''}$ = 10.2); 5.15 (d, 1 H, H(1′), $J_{1',2'e}$ = 1.1); 5.22 (dd, 1 H, H(4″), $J_{4'',3''}$ = 3.6, $J_{4'',5''}$ = 1.2); 5.33 (ddd, 1 H, H(3′), $J_{3',4'}$ = 9.9, $J_{3',2'e}$ = 11.5); 5.43 (d, 1 H, H(1″), $J_{1'',2''}$ = 8.1); 5.56—5.61 (m, 2 H, H(2″), H(12)). ^{13}C NMR (δ, ppm): 21.9 (C(2)); 82.7 (C(3)); 200.3 (C(11)); 128.6 (C(12)); 169.7 (C(13)); 177.8 (C(30)); 51.7 (C(31)); 93.4 (C(1′)); 36.9 (C(2′)); 69.9 (C(3′)); 79.1 (C(4′)); 71.7 (C(5′)); 62.8 (C(6′)); 101.6 (C(1″)); 72.8 (C(2″)); 73.5 (C(3″)); 69.8 (C(4″)); 76.6 (C(5″)); 62.8 (C(6″)); 169.9, 170.1, 170.2, 170.6, 170.9 ($OCOCH_3$)); 20.7, 20.8, 20.9, 21.0 ($OCOCH_3$).

3-*O*-[3,6-Di-*O*-acetyl-2-deoxy-4-*O*-(2,3,4,6-tetra-*O*-acetyl-α-D-glucopyranosyl)-α-D-*arabino*-hexopyranosyl]-18β-glycyrrhetinic acid methyl ester (6b). Glycoside **6b** (0.60 g, 58 %, cream-colored powder) was obtained from hexa-*O*-acetylmaltal **3** (0.56 g, 1 mmol) and alcohol **1a** (0.48 g, 1 mmol). R_f 0.64 (A); 0.61 (B); decomp.p. 187—190 °C; $[\alpha]_D^{20}$ +53° (*c* 0.06, $CHCl_3$). Found (%): C, 60.1; H, 7.0. $C_{55}H_{80}O_{19}$. Calculated (%): C, 63.2; H, 7.7. UV (MeOH), λ_{max}/nm: 247.8 (lgε 4.05). IR, ν/cm^{-1}: 1760—1750 (OAc); 1730—1720 ($COOCH_3$); 1660 (—C_{11}=O). ^{1}H NMR (δ, ppm, *J*/Hz): 0.63, 0.74, 0.77, 0.96, 1.06, 1.08, 1.30 (all s, 21 H, 7 CH_3); 1.10—1.90 (m, CH_2, aglycone CH, H(2′)); 1.95, 1.98, 2.03 (all s, 18 H, 6 Ac); 2.27 (s, 1 H, H(9)); 2.75 (d, 1 H, H(18), J = 13.8); 3.26 (dd, 1 H, $J_{3,2e}$ = 4.4, $J_{3,2a}$ = 11.3); 3.63 (s, 3 H, OCH_3); 4.00—4.25 (m, 8 H, H(4′), H(5′), H(6′a,b), H(4″), H(5″), H(6″a,b)); 4.90—5.00 (m, 1 H, H(2″)); 5.10 (d, 1 H, H(1′), $J_{1',2'e}$ = 1.4); 5.20—5.30 (m, 2 H, H(3′), H(3″)); 5.50 (d, 1 H, H(1″), $J_{1'',2''}$ = 4.0); 5.60 (s 1 H, H(12)). ^{13}C NMR (δ, ppm): 21.7 (C(2)); 82.6 (C(3)); 200.0 (C(11)); 128.6 (C(12)); 169.1 (C(13)); 176.8 (C(30)); 51.7 (C(31)); 93.3 (C(1′)); 35.4 (C(2′)); 67.6 (C(3′)); 76.6 (C(4′)); 66.8 (C(5′)); 62.4 (C(6′)); 94.2 (C(1″)); 69.2 (C(2″)); 68.4 (C(3″)); 69.4 (C(4″)); 69.6 (C(5″)); 62.4 (C(6″)); 169.8, 170.1, 170.6, 170.7, 170.8 ($OCOCH_3$)); 20.6, 20.7, 20.8, 20.9 ($OCOCH_3$).

3α-*O*-(3,4,6-Tri-*O*-acetyl-2-deoxy-α-D-*arabino*-hexopyranosyl)deoxycholic acid methyl ester (6c). Glycoside **6c** (0.54 g, 79.1 %, powder) was obtained from 3,4,6-tri-*O*-acetyl-D-glucal **4** (0.54 g, 2 mmol) and alcohol **1b** (0.41 g, 1 mmol). R_f 0.62 (A); 0.70 (B); decomp.p. 95—97 °C; $[\alpha]_D^{20}$ +62° (*c* 0.09, $CHCl_3$). Ref.[13]: decomp.p. 93—95 °C; $[\alpha]_D^{20}$ +64° (*c* 0.07, $CHCl_3$).

3α-*O*-(3,4-Di-*O*-acetyl-2,6-dideoxy-α-D-*arabino*-hexopyranosyl)deoxycholic acid methyl ester (6d). Glycoside **6d** (0.5 g, 80.8 %, amorphous powder) was obtained from 3,4-di-*O*-acetyl-L-rhamnal **5** (0.42 g, 2 mmol) and alcohol **1b** (0.41 g, 1 mmol). R_f 0.61 (A); 0.73 (B). Found (%): C, 68.0; H, 8.7. $C_{35}H_{56}O_9$. Calculated (%): C, 67.7; H, 9.1. ^{13}C NMR (δ, ppm): 27.2 (C(2)); 85.5 (C(3)); 28.7 (C(11)); 73.2 (C(12)); 174.4 (C(24)); 51.5 (C(25)); 98.2 (C(1′)); 35.6 (C(2′)); 69.2 (C(3′)); 75.0 (C(4′)); 65.5 (C(5′)); 17.8 (C(6′)); 169.6, 169.7 ($OCOCH_3$)); 20.8, 20.9 ($OCOCH_3$). ^{1}H NMR (δ, ppm, *J*/Hz): 0.64 (s, 3 H, H(18)); 0.88 (s, 3 H, H(19)); 1.13 (d, 3 H, H(21), J = 6.3); 1.21 (d, 3 H, H(6′), J = 6.7); 1.10—2.50 (m, CH_2, CH); 2.09, 2.10 (2 s, 6 H, 2 Ac); 3.63 (s, 3 H, OCH_3); 3.90 (dq, 1 H, H(5′), $J_{5',4'}$ = 9.3, $J_{5',6'}$ = 6.5); 4.75 (t, 1 H, H(4′), $J_{4',3'}$ = $J_{4',5'}$ = 9.3); 4.90 (d, 1 H, H(1′), $J_{1',2'e}$ = 1.8); 5.25—5.30 (m, 1 H, H(3′)).

3-*O*-(3,4-Di-*O*-acetyl-2,6-dideoxy-α-L-*arabino*-hexopyranosyl)cholest-5-en-3β-ol (6e). Glycoside **6e** (0.49 g, 81.1 %, cream-colored powder) was obtained from 3,4-di-*O*-acetyl-L-rhamnal **5** (0.56 g, 1 mmol) and cholesterol **1c** (0.38 g, 1 mmol) after reprecipitation with hexane from $CHCl_3$. R_f 0.66 (A); m.p. 125—127 °C; $[\alpha]_D^{20}$ −96° (*c* 0.08, $CHCl_3$). Found (%): C, 74.2; H, 10.4. $C_{37}H_{60}O_6$. Calculated (%): C, 73.9; H, 10.1. ^{13}C NMR (δ, ppm): 27.6 (C(2)); 76.7 (C(3)); 140.3 (C(5)); 122.1 (C(6)); 99.2 (C(1′)); 34.5 (C(2′)); 69.4 (C(3′)); 74.7 (C(4′)); 65.7 (C(5′)); 17.9 (C(6′)); 170.0, 170.7 ($OCOCH_3$); 20.9, 21.5 ($OCOCH_3$). Ref.[9]: m.p. 123 °C; $[\alpha]_D^{20}$ −103° (*c* 0.335, $CHCl_3$).

Glycosides 7a—e were obtained by deacetylation of glycosides **6a—e** with 5% KOH in MeOH according to the procedure reported in Ref. 1. The target compounds were chromatographed (pentane—ethyl acetate) and reprecipitated with pentane or hexane from $CHCl_3$ or CH_2Cl_2.

3-*O*-[2-Deoxy-4-*O*-(β-D-galactopyranosyl)-α-D-*arabino*-hexopyranosyl]-18β-glycyrrhetinic acid methyl ester (7a). Glycoside **7a** (0.31 g, 78.0 %, cream-colored powder) was obtained from glycoside **6a** (0.50 g). R_f 0.22 (A); decomp.p. 221—223 °C; $[\alpha]_D^{20}$ +47° (*c* 0.04, $CHCl_3$). Found (%): C, 64.2; H, 8.9. $C_{43}H_{68}O_{14}$. Calculated (%): C, 63.8; H, 8.5. UV (MeOH), λ_{max}/nm: 247.6 (lgε 4.02). IR, ν/cm^{-1}: 3600—3200 (OH); 1730—1720 ($COOCH_3$); 1660 (—C(11)=O). ^{13}C NMR (δ, ppm): 20.8 (C(2)); 81.7 (C(3)); 200.4 (C(11));

128.6 (C(12)); 169.4 (C(13)); 176.1 (C(30)); 51.9 (C(31)); 93.6 (C(1′)); 38.1 (C(2′)); 69.2 (C(3′)); 78.4 (C(4′)); 71.5 (C(5′)); 62.2 (C(6′)); 100.5 (C(1″)); 71.1 (C(2″)); 72.3 (C(3″)); 69.2 (C(4″)); 75.7 (C(5″)); 62.2 (C(6″)).

3-*O*-[2-Deoxy-4-*O*-(α-D-glucopyranosyl)-α-D-*arabino*-hexopyranosyl]-18β-glycyrrhetinic acid methyl ester (7b). Glycoside **7b** (0.25 g, 66.0 %, cream-colored powder) was obtained from glycoside **6b** (0.50 g). R_f 0.25 (A); decomp.p. 165—167 °C; $[\alpha]_D^{20}$ +58° (*c* 0.06, $CHCl_3$). Found (%): C, 64.4; H, 8.1. $C_{43}H_{68}O_{14}$. Calculated (%): C, 63.8; H, 8.5. UV (MeOH), λ_{max}/nm: 246.8 (lgε 3.92). IR, ν/cm^{-1}: 3600—3200 (OH); 1730—1720 ($COOCH_3$); 1660 (—C(11)=O). ^{13}C NMR (δ, ppm): 20.9 (C(2)); 81.8 (C(3)); 200.4 (C(11)); 128.6 (C(12)); 169.5 (C(13)); 177.1 (C(30)); 51.8 (C(31)); 93.5 (C(1′)); 38.2 (C(2′)); 69.2 (C(3′)); 75.4 (C(4′)); 69.2 (C(5′)); 62.2 (C(6′)); 93.5 (C(1″)); 72.1 (C(2″)); 72.5 (C(3″)); 72.1 (C(4″)); 71.6 (C(5″)); 62.2 (C(6″).

3α-*O*-(2-Deoxy-α-D-*arabino*-hexopyranosyl)deoxycholic acid methyl ester (7c). Glycoside **7c** (0.43 g, 88.9 %, white powder) was obtained from glycoside **6c** (0.6 g). R_f 0.35 (A); decomp.p. 104—105 °C; $[\alpha]_D^{20}$ +85° (*c* 0.07, $CHCl_3$). Ref.[13]: decomp.p. 103—105 °C; $[\alpha]_D^{20}$ +83° (*c* 0.08, $CHCl_3$).

3α-*O*-(2,6-Dideoxy-α-D-*arabino*-hexopyranosyl)deoxycholic acid methyl ester (7d). Glycoside **7d** (0.23 g, 89.9 %, amorphous powder) was obtained from glycoside **6d** (0.30 g). R_f 0.30 (A). Found (%): C, 69.8; H, 10.1. $C_{31}H_{52}O_7$. Calculated (%): C, 69.4; H, 9.8. ^{13}C NMR (δ, ppm): 27.3 (C(2)); 82.3 (C(3)); 28.7 (C(11)); 73.3 (C(12)); 174.6 (C(24)); 51.5 (C(25)); 99.5 (C(1′)); 38.4 (C(2′)); 69.4 (C(3′)); 78.3 (C(4′)); 67.5 (C(5′)); 17.6 (C(6′)).

3-*O*-(2,6-Dideoxy-α-L-*arabino*-hexopyranosyl)cholest-5-en-3β-ol (7e). Glycoside **7e** (0.30 g, 81.6 %, amorphous powder) was obtained from glycoside **6e** (0.43 g). R_f 0.31 (A); m.p. 128—129 °C; $[\alpha]_D^{20}$ −107° (*c* 0.07, $CHCl_3$). Found (%): C, 76.9; H, 11.4. $C_{33}H_{56}O_4$. Calculated (%): C, 76.7; H, 10.9.^{13}C NMR (δ, ppm): 28.6 (C(2)); 76.3 (C(3)); 140.7 (C(5)); 121.9 (C(6)); 95.3 (C(1′)); 38.7 (C(2′)); 69.3 (C(3′)); 78.2 (C(4′)); 67.7 (C(5′)); 17.8 (C(6′)).

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

References

1. L. A. Baltina, O. B. Flekhter, E. V. Vasiljieva, and G. A. Tolstikov, *Izv. Akad. Nauk, Ser. Khim.*, 1996, 2340 [*Russ. Chem. Bull*, 1996, **45**, 2843 (Engl. Transl.)].
2. O. B. Flekhter, L. A. Baltina, E. V. Vasiljieva, and G. A. Tolstikov, *Izv. Akad. Nauk, Ser. Khim.*, 1996, 2993 [*Russ. Chem. Bull.*, 1996, **45** (Engl. Transl.)].
3. L. A. Baltina, O. B. Flekhter, and E. V. Vasiljieva, *Mendeleev Commun.*, 1996, 63.
4. S. Sabesan and S. Neira, *J. Org. Chem.*, 1991, **56**, 5468.
5. O. B. Flekhter, L. A. Baltina, E. V. Vasiljieva, and G. A. Tolstikov, *Mendeleev Commun.*, 1997, 3.
6. G. A. Tolstikov, L. M. Khalilov, L. A. Baltina, R. M. Kondratenko, A. A. Panasenko, E. V. Vasiljieva, *Khim. Prir. Soed.*, 1985, 645 [*Chem. Nat. Comp.*, 1985 (Engl. Transl.)].
7. J. W. Blunt and J. W. Stothers, *Org. Magn. Res.*, 1977, **8**, 439.
8. J. Goto, K. Suzaki, and T. Nambara, *Chem. Pharm. Bull.*, 1980, **4**, 1258.
9. J. Thiem, S. Kopper, and J. Schwenther, *Liebigs Ann. Chem.*, 1985, 2135.
10. E. Breitmaier, W. Voelter, *^{13}C NMR spectroscopy*, Verlag Chemie, 1974, 303 p.
11. A. K. Dzizenko, V. V. Isakov, N. I. Ouvarova, G. I. Oshitok, and G. B. Elyakov, *Dokl. Akad. Nauk SSSR*, 1972, **207**, 1351 [*Dokl. USSR Chem.*, 1972, **207** (Engl. Transl.)].
12. S. Saito, Sh. Sumita, Y. Kanda, and Y. Sasaki, *Chem. Pharm. Bull.*, 1994, **42**, 1016.
13. L. A. Baltina, O. B. Flekhter, E. V. Vasiljieva, and G. A. Tolstikov, *Izv. Akad. Nauk, Ser. Khim.*, 1997, 601 [*Russ. Chem. Bull.*, 1997, **46**, 582 (Engl. Transl.)].
14. L. A. Baltina, O. B. Flekhter, Zh. M. Putieva, R. M. Kondratenko, L. V. Krasnova, and G. A. Tolstikov,, *Khim.-farm., Zh.*, 1996, **30**, 47.
15. Yu. A. Zhdanov, G. N. Dorofeenko, G. A. Krol'chenko, and G. V. Bogdanova, *Praktikum po khimii uglevodov* [*Laboratory Course on Carbohydrate Chemistry*], Rosvuzisdat, 1963, 199 pp.

Received December 6, 1996;
in revised form March 5, 1997