solvent. The reaction mixture was left at room temperature for 2 days. Then 200 ml of water was added, the methanol was distilled off, and the reaction products were extracted with n-butanol. After the butanolic extract had been washed with water and evaporated to dryness, 20 mg of the glycoside (III) was obtained, with mp 248-249°C (from methanol), $[\alpha]_D^{20}$ + 34.0 ± 2° (c 0.60; methanol), identical with an authentic sample of cyclosiversioside F [3].

Alkaline Hydrolysis of Cyclosiversioside B (II). A solution of 80 mg of cyclosiversioside B in 80 ml of methanol was treated with 80 ml of a 0.5% solution of KOH in the same solvent. The reaction mixture was left at room temperature for 2 days. After a working up procedure similar to that described in the preceding experiment, 37 mg of glycoside (III) was obtained with mp 248-249°C (from methanol), $[\alpha]_D^{22}$ +34.3 ± 2° (c 0.64; methanol), identical with an authentic sample of cyclosiversioside F [3].

SUMMARY

The compositions of the cycloartane glycosides of the plants *Astragalus sieversianus* and *A. basineri* are identical in the qualitative respect. Two new glycosides have been isolated from the roots of *A. basineri* — cyclosiversiosides B and D. It has been shown that cyclosiversioside B is cyclosiversigenin 3-O-(2',3'-di-O-acetyl-β-D-xylopyranoside) 6-O-β-D-glucopyranoside and cyclosiversioside D is cyclosiversigenin 3-O-(2'-O-acetyl-β-D-xylopyranoside) 6-O-β-D-glucopyranoside.

LITERATURE CITED

1. A. N. Svechnikova, R. U. Umarov, N. D. Abdullaev, M. B. Gorovin, T. T. Gorovin, and N. K. Abubakirov, Khim. Prir. Soedin., 460 (1983).
2. A. N. Svechnikova, R. U. Umarov, M. B. Gorovits, and N. K. Abubakirov, Khim. Prir. Soedin., 204 (1982).
3. A. N. Svechnikova, R. U. Umarov, M. B. Gorovits, N. D. Abdullaev, and N. K. Abubakirov, Khim. Prir. Soedin., 208 (1982).
4. A. N. Svechnikova, R. U. Umarov, N. D. Abdulaeev, M. B. Gorovits, and N. K. Abubakirov, Khim. Prir. Soedin., 629 (1982).
5. A. N. Svechnikova, R. U. Umarov, M. B. Gorovits, N. D. Abdullaev, and N. K. Abubakirov, Khim. Prir. Soedin., 312 (1983).
6. A. N. Svechnikova, R. U. Umarov, M. B. Gorovits, K. A. Seitanidi, Ya. V. Rashkes, M. R. Yagudaev, and N. K. Abubakirov, Khim. Prir. Soedin., 67 (1981).

CATALYTIC REARRANGEMENT OF α-D-GLUCOSE 1,2-ORTHOACETATE DERIVATIVES OF PREGNENOLONE AND 16-DEHYDROPREGNENOLONE

N. F. Samoshina, V. A. Denisenko, V. L. Novikov, and N. I. Uvarova

UDC 547.455+547.918:547.922

The rearrangement of pregnenolone and 16-dehydropregnenolone α-D-glucose orthoacetates in the presence of mercuric bromide is, because of the high specific selectivity and satisfactory yields of the desired β-D-glucosides, the most effective method of glycosylating the steroids mentioned.

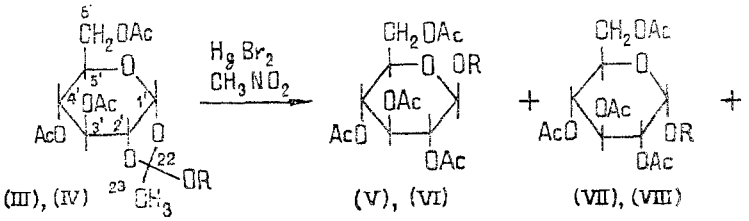
The glycosylation of steroid alcohols is opening up possibilities both for the creation of convenient water-soluble forms of hormone preparations and for the modification of their biological activities. The known methods of glycosylating the alcohols of the title have, however, a number of deficiencies. Thus the glycosylation of (I) by the Koenigs-Knorre method [1, 2] was accompanied by the formation of a mixture of acetylated α- and β-glucosides, and the trans-glycosylation of (II) by the direct orthoester method [3] was accompanied by considerable amounts of 16-dehydropregnenolone acetate with a low yield of the desired

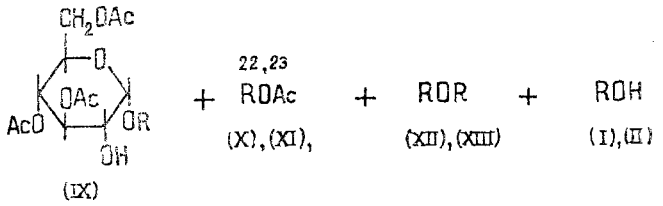
Pacific Ocean Institute of Bioorganic Chemistry, Far Eastern Scientific Center, Academy of Sciences of the USSR, Vladivostok.

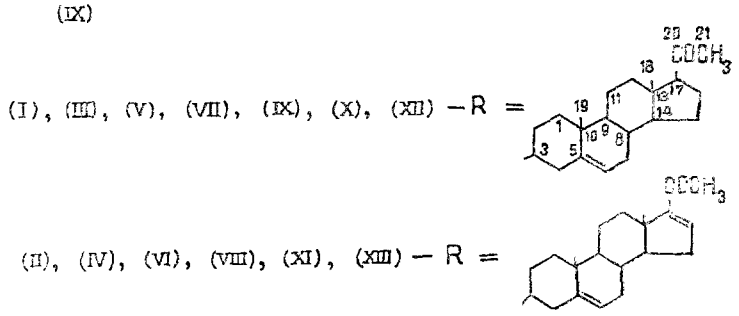
Translated from Khimiya Prirodnykh Soedinenii, No. 2, pp. 191-196, March-April, 1984. Original article submitted February 21, 1983.

0009-3130/84/2002-0177$08.50

β-glucoside. In order to eliminate these deficiencies, we have investigated the two-stage glycosylation of steroid alcohols by the synthesis of α-D-glucose 1,2-orthoacetate derivatives of (I) and (II) and their catalytic rearrangement into the corresponding glycosides.







3',4',6'-Tri-O-acetyl-1',2',O-(pregnenolone-3-yloxyethylidene)-α-D-glucopyranose (III) and 3',4',6'-tri-O-acetyl-1',2'-O-(16-dehydropregnenolone-3-yloxyethylidene)-α-D-glucopyranose (IV) were obtained with yields of 76% and 71%, respectively, by analogy with the procedure of Mazurek and Perlin [4] (experiments 1 and 2). The structures of the orthoesters (III) and (IV) were confirmed by the ease of their acid hydrolysis, by the results of an investigation by ^1H and ^{13}C NMR methods (Table 2), and by elementary analysis. The orthoesters (III) and (IV) were subjected to catalytic rearrangement under the conditions given previously [5].

We have shown previously that the result of the catalytic rearrangement of sterol and triterpene derivatives of α-D-glucose orthoacetates depend on the amount of $HgBr_2$ used as catalyst [5]. The maximum yields of the corresponding β-glycosides were observed with the use of 0.36 mmole of $HgBr_2$ per 1 mmole of orthoester, and a further increase in the amount of $HgBr_2$ led to a decrease in the yield of glucoside. The rearrangement of (III) and (IV) under the optimum conditions (experiments 3 and 4) took place stereoselectively with the formation of the corresponding 1,2-transglucoside tetraacetates (V and VI), but their yields differed substantially (see Table 1). One of the reasons for this could be partial complex-formation between $HgBr_2$ and the polarized enone grouping of the 16-dehydropregnenolone orthoacetate derivative (IV). A doubling of the amount of $HgBr_2$ (experiment 5) in the rearrangement of (IV), however, gave only a slight increase in the yield of (VI) (see Table 1). Together with the 1,2-trans-glycosides (V) and (VI), in the rearrangement of (III) and (IV) the formation of a small amount (~4%) of the 1,2-cis-glycoside tetraacetates (VII and VIII), and, in the case of (III), also of the 1,2-cis-glucoside partially deacetylated at C-2' (IX) (~3%) was observed.

The doublet signals of the anomeric protons of the sugar components on the PMR spectra of (V) and (VI) appeared at 4.59 ppm ($J_{1',2'}$ = 7.4 and 7.7 Hz, respectively). The $J_{1',2'}$ values showed the trans configuration of the glycosidic bonds in (V) and (VI). The PMR spectra of (VII) and (VIII) showed a marked downfield shift of the signal of the anomeric proton of the sugar component (5.23 ppm) as compared with its position in the spectra of (V) and (VI). The chemical shifts (CSs) of this signal and the values of $J_{1',2'}$ (3.5 and 3.8 Hz, respectively) showed the cis configuration of the glycosidic bond in (VII) and (VIII). A similar conclusion follows from an analysis of the PMR spectrum of the glycoside (IX), the doublet signal of the anomeric proton in which appears at 5.05 ppm ($J_{1',2'}$ = 4.1 Hz).

The cis configuration of the glycosidic bonds in (VII) and (VIII) was also confirmed by an analysis of the ^{13}C CSs of the sugar components (Table 3). An upfield shift of the C-1'

TABLE 1. Conditions and Results of the Catalytic Rearrangement of the Orthoesters of the Title*

Experiment No.	Initial orthoester, mmole	$HgBr_2$, mmole	Time, min	Reaction product, %			
				acylated glycosides	ROAc	ROR	ROH
3	III, 1	0,36	60	(V), 56.5 (VII), 4 (IX), 3	(X), 5	(XII), 9	(I), 2
4	IV, 1	0,36	60	(VI), 36.3 (VIII), 4	(XI), 8	(XIII), 14	(II), 2
5	IV, 1	0,72	20	(VI), 41.9	(XI), 6	(XIII), 11	—

*Experiments 3-5 were performed in CH_3NO_2 at 90°C.

signal by 5.2 ppm (94.4 ppm) in comparison with its position in the spectrum of (V) (99.6 ppm) is connected with the disappearance of the $\gamma_{H,H}$ interaction between H-1' and H-3 in the glucoside with the α-configuration of the glycosidic bond.

As in the glycosylation of (II) by the direct orthoester method [3], in the case of the rearrangement of the orthoesters (III and IV), the formation of appreciable amounts (see Table 1) of by-products of nonglycosidic nature was observed: the free alcohols (I and II) the orthoesters of which were subject to rearrangement, and also their acetates (X and XI) and ethers (XII and XIII). The yields of the by-products in the rearrangement of the 16-dehydropregnenolone orthoester derivative (IV) were higher than for the pregnenolone orthoester derivatives (III). A doubling of the amount of Lewis acid in the rearrangement (IV) (experiment 5) led not only to an increase in the yield of glucoside (IV) but also to an appreciable fall in the yield of the by-products of nonglycosidic nature. The structures of compounds (X-XIII) were established by an analysis of their IR spectra and a comparison of their ^1H and ^{13}C NMR spectra (see Table 2) with those of (I) and (II).

Thus, because of its high stereoselectivity, the catalytic rearrangement of orthoester derivatives of 16-dehydropregnenolone and of pregnenolone possesses an undoubted advantage over the glycosylation of steroid alcohols by the Koenigs-Knorre method. It also has an advantage over the direct orthoester method of glycosylation since the yield of the desired 16-dehydropregnenolone β-glucoside (VI) is considerably higher (41.9%) and the amount of by-products of nonglycosidic nature is considerably lower (6% of (XI) and 11% of (XIII)) than in the direct glycosylation of (II) with tert-butyl α-D-glucose orthoacetate (27.4% of VI) and 33.7% of (XI) [3].

EXPERIMENTAL

^1H and ^{13}C NMR spectra were recorded on a Bruker HX-90E spectrometer in the Fourier regime at 30°C using 8% solutions of the substances in $CDCl_3$ at a working frequency of 90.0 MHz for ^1H and 22.63 MHz for ^{13}C. TMS was used as internal standard. The accuracy of the measurements was ±0.15 Hz for ^1H and ±1.5 Hz for ^{13}C. The assignment of the signals in the ^{13}C spectra was carried out by the method of off-resonance spin decoupling and on the basis of literature analogies [6, 7]. The melting points of the substances were determined on a Boëtius stage. Nitromethane was prepared as in [8]. $HgBr_2$ was purified by sublimation. The hydrolytic test for sugar orthoesters was carried out under the conditions of [8].

Column chromatography was performed on KSK SiO_2, 65-100 mesh, that had been treated in accordance with [9] in the petroleum ether—acetone (45:1)—(10:1) system, and TLC in a fixed layer of SiO_2 in the petroleum ether—acetone (3:1) system. The TLC plates were stained with a mixture of concentrated H_2SO_4 and MeOH (1:10) at 100-200°C.

Experiment 1. A mixture of 1.26 g (4 mmole) of (I), 2.4 g (6 mmole) of α-acetobromoglucose, 6 ml of collidine, and 10 ml of CH_3NO_2 was stirred at room temperature for 3 days. The precipitate was separated off and washed with benzene, and the combined filtrate was evaporated to dryness. The residue was dissolved in $CHCl_3$, the solution was washed with water and dried over Na_2SO_4, and the solvent was driven off. The new residue was chromatographed on a column of SiO_2 and was crystallized from methanol. This gave 1.98 g of (III) (76%). mp 151-153°C, $C_{35}H_{50}O_{11}$. ^1H spectrum (δ, ppm): 0.63 (s, 3 H, C^{13}—CH_3); 0.98 (s, 3 H, C^{10}—CH_3); 1.73 (s, 3 H, C^{22}—CH_3); 2.10 (s, 6 H, 2 × OAc); 2.12 (s, 6 H, OAc and $COCH_3$); 3.42 (m, 1 H, $\Sigma J \simeq 32$ Hz, H_a^3); 3.97 (q, 1 H, J = 9.6 and 4.0 Hz, H^5); 4.20 (d, 2 H, J = 4.0 Hz,

TABLE 2. ^{13}C Chemical Shifts of Compounds (I-VII) and (X-XIII) (ppm relative to TMS)

C atom	Compound										
	I	II	III	IV	V	VI	VII	X	XI	XII	XIII
1	37,2	37,1	37,4	37,2	37,2	37,0	37,1	37,0	36,9	37,4	37,2
2	31,6	31,6	29,8	29,8	29,4	29,4	29,8	27,7	27,7	29,4	29,3
3	71,6	71,6	73,6	73,6	79,8	80,0	78,8	73,8	73,8	76,2	76,3
4	42,2	42,2	40,4	40,4	38,8	39,0	40,0	38,1	38,1	40,0	40,1
5	140,8	141,4	140,5	141,2	140,2	140,9	140,4	139,6	140,2	141,3	141,8
6	121,3	120,9	121,7	121,4	121,8	121,5	121,9	122,2	121,9	121,0	120,7
7	31,8	31,6	31,8	31,6	31,8	31,6	31,9	31,8	31,5	31,8	31,6
8	31,8	30,2	31,8	30,2	31,8	30,2	31,9	31,8	30,1	31,8	30,2
9	50,0	50,5	50,1	50,6	50,0	50,6	50,1	50,0	50,4	50,1	50,6
10	36,5	36,7	36,6	36,7	36,7	36,9	36,8	36,6	36,9	36,8	37,0
11	21,1	20,7	21,1	20,8	21,1	20,7	21,1	21,1	20,7	21,1	20,7
12	38,9	34,6	38,9	34,7	38,8	34,6	38,9	38,8	34,6	38,9	34,6
13	44,0	46,1	43,9	46,1	43,9	46,1	44,1	43,9	46,1	43,9	46,1
14	56,9	56,4	56,9	56,5	56,9	56,4	57,0	56,8	56,3	56,9	56,5
15	24,5	32,2	24,5	32,3	24,4	32,2	24,6	24,4	32,2	24,5	32,2
16	31,6	144,4	31,5	144,3	31,4	144,2	31,5	31,4	144,3	31,5	144,3
17	63,7	155,3	63,7	155,4	63,6	155,4	63,8	63,6	155,3	63,7	155,4
18	13,2	15,7	13,3	15,7	13,2	15,7	13,3	13,2	15,7	13,2	15,7
19	19,4	19,3	19,3	19,2	19,3	19,2	19,4	19,2	19,2	19,4	19,3
20	209,5	196,8	209,0	196,7	209,0	196,6	209,3	209,1	196,6	209,3	196,7
21	22,8	27,1	22,9	27,2	22,8	27,1	22,9	22,8	27,1	22,8	27,1
22	—	—	121,4	121,4	—	—	—	170,3	170,3		—
23	—	—	21,7	21,7	—	—	—	21,3	21,4	—	—

2 × $H^{6'}$); 4.36 (q, 1 H, J = 5.0 and 3.0 Hz, $H^{2'}$); 4.90 (q, 1 H, J = 9.6 and 3.0 Hz, $H^{4'}$); 5.18 (t, 1 H, J = 3.0 Hz, $H^{3'}$); 5.37 (d, 1 H, J = 4.4 Hz, H^{6}); 5.69 (d, 1 H, J = 5.0 Hz, $H^{1'}$).

Experiment 2. Under conditions similar to those described in Experiment 1, 1.26 g of (II) yielded 1.84 g of (IV) (71%). mp 106-107°C (MeOH). Lit [10]: mp 104-106°C. ^1H spectrum (δ, ppm): 0.91 (s, 3 H, C^{13}—CH_3); 1.02 (s, 3 H, C^{10}—CH_3); 1.73 (s, 3 H C^{22}—CH_3); 2.10 (s, 6 H, 2 × OAc); 2.11 (s, 3 H, OAc); 2.26 (s, 3 H, $COCH_3$); 3.43 (m, 1 H, ΣJ ≃ 32 Hz, H_a^3); 3.95 (q, 1 H, J = 9.5 and 4.0 Hz, $H^{5'}$); 4.19 (d, 2 H, J = 4.0 Hz, 2 × $H^{6'}$); 4.35 (q, 1 H, J = 5.0 and 3.0 Hz, $H^{2'}$); 4.91 (q, 1 H, J = 9.5 and 3.0 Hz, $H^{4'}$); 5.19 (t, 1 H, J = 3.0 Hz, $H^{3'}$); 5.37 (d, 1 H, J = 4.2 Hz, H^{6}); 5.69 (d, 1 H, J = 5.0 Hz, H^{1}); 6.71 (dd, 1 H, J = 2.4 and 3.4 Hz, H^{16}).

Experiment 3. From a solution of 646 mg (1 mmole) of (III) in 10 ml of CH_3NO_2 was distilled off 5 ml of CH_3NO_2, and then a solution of 130 mg (0.36 mmole) of $HgBr_2$ in 5 ml of CH_3NO_2 was added. The reaction mixture was heated at 90°C for 1 h. After the addition of a few drops of C_5H_5N, the solvent was driven off complete, the residue was washed four times with hot water and dried, and it was chromatographed on a column of SiO_2. This led to the isolation of:

The β-D-glucoside tetraacetate (V), 365 mg (56.5%), mp 216-218°C (C_2H_5OH), lit [2]: mp 190-192°C, $C_{35}H_{50}O_{11}$. ^1H spectrum (δ, ppm): 0.63 (s, 3 H, C^{13}—CH_3); 0.99 (s, 3 H, C^{10}—CH_3); 2.01 (s, 3 H, OAc); 2.02 (s, 3 H, OAc); 2.05 (s, 3 H, OAc); 2.08 (s, 3 H, OAc); 2.12 (s, 3 H, $COCH_3$); 3.40 (m, 1H, ΣJ ≃ 32 Hz, H_a^3); 3.64 (m, 1 H, $H^{5'}$); 4.19 (m, 2 H, 2 × $H^{6'}$); 4.59 (d, 1 H, J = 7.4 Hz, $H_i^{1'}$); 4.80-5.32 (m, 3 H, $H^{2'}$, $H^{3'}$, $H^{4'}$); 5.36 (d, 1 H, J = 4.2 Hz, H^{6}).

Pregnenolone acetate (X), 18 mg (5%), mp 144-146°C (C_2H_5OH), lit [11]: mp 147°C.

Dipregnenolone-yl ether (XII), 28 mg (9%). mp 218-219°C ($CHCl_3$—MeOH). ^1H NMR spectrum (δ, ppm): 0.63 (s, 3 H, C^{13}—CH_3); 1.00 (s, 3 H, C^{10}—CH_3); 2.12 (s, 3 H, $COCH_3$); 3.25 (m, 1 H, ΣJ ≃ 31 Hz, H_a^3); 5.32 (d, 1 H, J = 4.4 Hz, H^{6}).

The α-D-glucoside tetraacetate (VII), 26 mg (4%), mp 108-110°C (C_2H_5OH), lit [2]: mp 94-95°C. ^1H spectrum (δ, ppm): 0.63 (s, 3 H, C^{13}—CH_3); 1.01 (s, 3 H, C^{10}—CH_3); 2.02 (s, 3 H, OAc); 2.04 (s, 3 H, OAc); 2.06 (s, 3 H, OAc); 2.09 (s, 3 H, OAc); 2.12 (s, 3 H, $COCH_3$); 3.38 (m, 1 H, ΣJ ≃ 31 Hz, H_a^3); 4.18 (m, 3 H, $H^{5'}$, 2 × $H^{6'}$); 4.79 (q, 1 H, J = 3.5 and 10.0 Hz, $H^{2'}$); 5.23 (d, 1 H, J = 3.5 Hz, $H^{1'}$); 5.03-5.60 (m, 2 H, $H^{3'}$ and $H^{4'}$); 5.35 (d, 1 H, J = 4.5 Hz, H^{6}).

Pregnenolone (I), 6.5 mg (2%).

3-O-(3',4',6'-Tri-O-acetyl-α-D-glucopyranosyl)pregnenolone (IX), 18 mg (3%). ^1H spectrum (δ, ppm): 0.63 (s, 3 H, C^{13}—CH_3); 1.01 (s, 3 H, C^{10}—CH_3); 2.04 (s, 3 H, OAc); 2.08 (s,

TABLE 3. ^{13}C Chemical Shifts of the Sugar Components of Compounds (III-VII) (ppm relative to TMS)*

C atom	Compound				
	III	IV	V	VI	VII
1′	97,0	96,9	99,6	99,6	94 4
2′	68,3	68,3	71 5	71,6	67,4
3′	70,3	70,3	72,9	72,9	70,3
4′	73,2	73,0	68,6	68,6	68,9
5′	67,1	67,0	71,7	71,8	71 2
6′	63,1	63,1	62,1	62,1	62,2

*The ^{13}C signals of the acetate groups of the sugar components of compounds (III-VII) appeared in the 169.0-170.0 and 20.5-20.8 ppm regions.

6 H, 2 × OAc); 2.13 (s, 3 H, $COCH_3$); 3.53 (m, 1 H, $\Sigma J \simeq 32$ Hz, H_a^3); 5.05 (d, 1 H, J = 4.1 Hz, $H^{1'}$); 3.90-5.25 (m, 6 $H^{2'}$, $H^{3'}$, $H^{4'}$, $H^{5'}$, 2 × $H^{6'}$); 5.35 (d, 1 H, J = 4.2 Hz, H^6).

Experiment 4. The rearrangement of 644 mg (1 mmole) of (IV) under conditions similar to those described in experiment 3 gave:

The β-D-glycoside tetraacetate (VI), 235 mg (36.3%), mp 228-231°C (C_2H_5OH), lit [1]: mp 234-237°C; lit [3]: mp 230-232°C (C_2H_5OH). ^1H spectrum (δ, ppm): 0.92 (s, 3 H, C^{13}—CH_3); 1.03 (s, 3 H, C^{10}—CH_3); 2.01 (s, 3 H, OAc); 2.02 (s, 3 H, OAc); 2.05 (s, 3 H, OAc); 2.07 (s, 3 H, OAc); 2.26 (s, 3 H, $COCH_3$); 3.65 (m, 1 H, $H^{5'}$); 4.18 (m, 2 H, 2 × $H^{6'}$); 4.59 (d, 1 H, J = 7.7 Hz, $H^{1'}$); 4.80-5.32 (m, 3 H, $H^{2'}$, $H^{3'}$, $H^{4'}$); 5.36 (d, 1 H, J = 4.1 Hz, H^6); 6.71 (dd, 1 H, J = 2.5 and 3.4 Hz, H^{16}).

16-Dehydropregnenolone acetate (XI), 28 mg (8%), mp 172-174°C (C_2H_5OH), lit [3]: mp 174-175°C.

Di-16-dehydropregnenolone-2-yl ether (XIII), 40 mg (14%), mp 207-212°C ($CHCl_3$—MeOH), $C_{42}H_{58}O_3 \cdot 1/2CH_3OH$. ^1H spectrum (δ, ppm): 0.92 (s, 3 H, C^{13}—CH_3); 1.04 (s, 3 H, C^{10}—CH_3); 2.26 (s, 3 H, $COCH_3$); 3.24 (m, 1 H, $\Sigma J \simeq 32$ Hz, H_a^3); 5.33 (d, 1 H, J = 4.4 Hz, H^6); 6.71 (dd, 1 H, J = 2.5 and 3.5 Hz, H^{16}).

3-O-(2′,3′,4′,6′-Tetra-O-acetyl-α-D-glucopyranosyl)-16-dehydropregnenolone (VIII), 25 mg (4%). ^1H spectrum (δ, ppm); 0.92 (s, 3 H, C^{13}—CH_3); 1.05 (s, 3 H, C^{10}—CH_3); 2.02 (s, 3 H, OAc); 2.04 (s, 3 H, OAc); 2.07 (s, 3 H, OAc); 2.09 (s, 3 H, OAc); 2.26 (s, 3 H, $COCH_3$); 3.36 (m, 1 H, $\Sigma J \simeq 31$ Hz, H_a^3); 4.17 (m, 3 H, $H^{5'}$, 2 × $H^{6'}$); 4.80 (q, 1 H, 3.8 and 9.6 Hz, $H^{2'}$); 5.05-5.65 (m, 2 H, $H^{3'}$, $H^{4'}$); 5.23 (d, 1 H, J = 3.8 Hz, $H^{1'}$); 5.36 (d, 1 H, J = 4.2 Hz, H^6); 6.71 (dd, 1 H, J = 2.4 and 3.3 Hz, H^6).

16-Dehydropregnenolone (II), 6 mg (25%).

Experiment 5. The rearrangement of 644 mg (1 mmole) of (IV) in the presence of 260 mg (0.72 mmole) of $HgBr_2$ under conditions similar to those described in experiment 3 gave 270 mg (41.9%) of (VI), 20 mg (6%) of (XI), and 30 mg (11%) of (XIII).

SUMMARY

The rearrangement of the α-D-glucose orthoacetate derivatives of pregnenolone and of 16-dehydropregnenolone in the presence of mercuric bromide is, in view of its high stereoselectivity and satisfactory yields of the desired β-D-glucosides, the most effective method of glycosylating the steroids mentioned.

LITERATURE CITED

1. B. Pal and M. Gyorgy, Magy. Kem. Folyoirat, 72, 201 (1966).
2. R. Kocovsky, K. K. Kosoev, and Z. Proshazka, Collect. Czech. Chem. Commun., 38, 3273 (1973).
3. N. I. Uvarova, G. I. Oshitok, and G. B. Elyakov, Carbohydr. Res., 27, 79 (1973).
4. M. Mazurek and A. S. Perlin, Can. J. Chem., 43, 1918 (1965).

5. N. F. Samoshina and N. I. Uvarova, Khim. Prir. Soedin., 334 (1979).
6. H. Eggert, C. L. Van Antwerp, N. S. Bhacca, and C. Djerassi, J. Org. Chem., 41, 71 (1976).
7. J. W. Blunt and J. B. Stothers, Org. Magn. Reson., 9, 439 (1977).
8. N. K. Kochetkov, A. Ya. Khorlin, and A. F. Bochkov, Tetrahedron, 23, 693 (1967).
9. G. Wulf, and W. Schmidt, Carbohydr. Res., 53, 33 (1977).
10. N. I. Uvarova, N. F. Samoshina, G. I. Oshitok, and G. B. Elyakov, Izv. Akad. Nauk SSSR, Ser. Khim., 1907 (1975).
11. L. Fieser and M. Fieser, Steroids, Reinhold, New York (1959).

WITHASTEROIDS OF *Physalis*.

IV. 28-HYDROWITHAPHYSANOLIDE. ^{13}C NMR SPECTRUM OF 14-α-HYDROXYWITHASTEROIDS

N. D. Abdullaev, E. A. Maslennikova,
R. N. Tursunova, N. K. Abubakirov,
and M. R. Yagudaev

UDC 547.926+543.422+541.67

A new withasteroid has been isolated from *Physalis viscosa* L. — 28-hydroxywithaphysanolide, with mp 234°C, composition $C_{28}H_{38}O_8$. The ^{13}C NMR spectra of a number of withasteroids have been investigated. For 28-hydroxywithaphysanolide we propose the structure 4β,14α,17β,20R,28-pentahydroxy-1-oxo-22R-witha-2,5,24-trienolide. The corresponding corrections have been made in the structural formulas of withaphysanolide and physalactone.

Structure of 28-Hydroxywithaphysanolide (I)

From an aqueous extract of the epigeal part of *Physalis viscosa* L. [1] we have isolated a new polar withasteroid (I) with the composition $C_{28}H_{38}O_8$ (M^+ 502). A strong maximum in the UV spectrum at 212 nm (log ε 4.10) and the presence in its mass spectrum of ions with m/z 185 and 141 indicate the presence of an additional oxygen function in an unsaturated lactone ring. The peak of the ion with m/z 185 has the maximum intensity, which shows the cleavage of the bond between C-17 and C-20 that is characteristic for withasteroids containing a diol grouping at the position of cleavage [2]. With acetic anhydride, the new withasteroid (I) formed a di-O-acetate (II). When compound (II) was oxidized with the Jones reagent, a lactone (XIII) and 4β-acetoxy-14α-hydroxy-1,17-dioxoandrostane-2,5-diene (XIV) were obtained. Precisely the same derivative of androstane-2,5-diene was obtained previously by the oxidation of withaphysanolide acetate (III), but compound (XIV) was ascribed a somewhat different structure [2]. The ease of degradation of (II) by chromium trioxide is a new confirmation of the presence of a diol grouping at C-17 and C-20.

In the PMR spectrum, the positions of five one-proton signals depended to a considerable degree on the temperature of the solution of the substance which showed that they belonged to five hydroxy groups. Three of them appeared at 30°C in the form of singlets (tertiary OH groups) at 5.16, 6.19, and 6.97 ppm, and the other two were split into a doublet (7.23 ppm, ^3J = 4.4 Hz), and a triplet (7.05 ppm, ^3J = 12.1 Hz). In the spectrum taken at 50°C, the same signals appeared at 4.60, 5.81, 6.84, 6.86, and 6.76 ppm, respectively. The doublet and triplet splitting of the weak-field signals is due to spin–spin coupling between the hydroxylic protons and the methine and methylene protons arranged geminally to them. Consequently, in (I) the two oxygen functions are represented by secondary and primary hydroxy groups. The components of the two doublet signals of the methylene proton of the CH_2OH group were additionally split through coupling with the proton of the hydroxy group (triplet at 7.05 ppm). They appeared in the form of quartets at 4.40 ppm ($^2J_{gem}$ = 14.5 and $^3J_{CHH'-OH}$ = 6.5 Hz) and 4.17 ppm ($^2J_{gem}$ = 14.5 and $^3J_{CHH'-OH}$ = 5.6 Hz). In the spectrum of the acetate (II) the signals were shifted downfield (4.75 and 5.01 ppm) and appeared in the form of two AB doublets with $^2J_{gem}$ = 13.6 Hz.

Institute of the Chemistry of Plant Substances, Academy of Sciences of the Uzbek SSR, Tashkent. Translated from Khimiya Prirodnykh Soedinenii, No. 2, pp. 197-207, March-April, 1984. Original article submitted March 15, 1983.

 0009-3130/84/2002-0182$08.50