5. T. Norin and Z. Westfelt, Acta Chem. Scand., 17, 1829 (1963).
6. R. Polyudek-Fabina and T. Beirikh, Organic Analysis [in Russian], Nauka, Leningrad (1981), p. 15.
7. W. Herz and S. V. Govindan, J. Org. Chem., 44, 2999 (1979).

GLYCOSYLATION OF TRITERPENE ALCOHOLS OF THE LUPANE SERIES

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The glycosylation of lupeol, allobetulin, 3β-28-dihydroxy-18-lupene, 3β-28-dihydroxy-18β,19β-epoxylupane and of betulin monoacetates in acetonitrile with mercury cyanide has been studied. The 3- and 28-mono- and the 3,28-di-O-β-D-glucopyranosides of 3β-28-dihydroxy-18-lupene and of 3β-28-dihydroxy-18β,19β-epoxylupane have been synthesized for the first time. Preparative methods for the synthesis of glucosides of lupeol, of allobetulin, and of betulin 3- and 28-monoacetates are proposed.

Continuing a study of the glycosylation reaction of triterpenoids of the lupane series [1], we have performed the condensation of lupeol (I), allobetulin (XIII), betulin 28-monoacetate (IV), betulin 3-monoacetate (VI), 3β-28-dihydroxy-18-lupene (Xa), and 3β-28-dihydroxy-18β,19β-epoxylupane (XIV) with α-acetobromoglucose in acetonitrile in the presence of mercury cyanide [2] and also in toluene in the presence of cadmium carbonate for the alcohols (I), (VIII), (IV) and (VI). The results of the experiments are given in Table 1.

The use of mercury cyanide as catalyst led to high yield of glycosylation products and to low recoveries of the initial alcohols (Table 1, experiments 1-6).

On the basis of the results of the investigations by ^1H and ^{13}C NMR, the products obtained were assigned the structures of, respectively, lupeol 3-O-(2',3',4',6'-tetra-O-acetyl-β-D-glucopyranoside) (III), alliobetulin 3-O-(2'3',4',6'-tetra-O-acetyl-β-D-glucopyranoside) (IX), 28-O-acetylbetulin 3-O-(2',3',4',6'-tetra-O-acetyl-β-D-glucopyranoside) (V), 28-O-acetylbetulin 3-O-(2',3',4',6'-tetra-O-acetyl-β-D-glucopyranoside) (Va), 3-O-8-dihydroxy-acetylbetulin 28-O-(2',3',4',6'-tetra-O-acetyl-β-D-glucopyranoside) (VII), 3β-28-dihydroxy-18-lupene 3-O-(2',3',4',6'-tetra-O-acetyl-β-D-glucopyranoside) (XI), 3β-28-dihydroxy-18-lupene 28-O-(2',3',4',6'-tetra-O-acetyl-β-D-glucopyranoside) (XII), 3β-28-dihydroxy-18-lupene 3,28-di-O-(2',3',4',6'-tetra-O-acetyl-β-D-glucopyranoside) (XIIa), 3β-28-dihydroxy-18β,19β-epoxylupane 3-O-(2',3',4',6'-tetra-O-acetyl-β-D-glucopyranoside) (XV), 3β-28-dihydroxy-18β,19β-epoxylupane 28-O-(2',3',4',6'-tetra-O-acetyl-β-D-glucopyranoside) (XVI), and 3β-28-dihydroxy-18β,19β-epoxylupane 3,28-di-O-(2',3',4',6'-tetra-O-acetyl-β-D-glucopyranoside) (XVII).

The β-glucoside acetates (IX), (V), (Va) and (VII) were identified by comparison with authentic samples [1].

In the ^1H spectra of the 3-monoglucosides (III), (XI), (XV) and the diglucosides (XIIa) and (XVII) the doublet signal of the anomeric proton of the sugar component appeared at 4.50-4.53 ppm ($J_{1',2'}$ = 7.8-8.0 Hz), and in the ^1H spectra of the 28-monoglucosides (XII) and (XVI) and of the diglucosides (XIIa) and (XVII) at 4.45-4.48 ppm ($J_{1',2'}$ = 8.0 Hz). For the monoglucosides, the presence of an acetylated sugar component was confirmed by the appearance in the ^1H spectra of these compounds of the signals of the protons of four acetate groups in the 2.00-2.09 ppm region and the signal of six protons in the 3.39-5.33 ppm region, and, for the diglucosides, of the signals of the protons of eight acetate groups (2.00-2.09 ppm) and of 12 protons (3.39-5.34 ppm).

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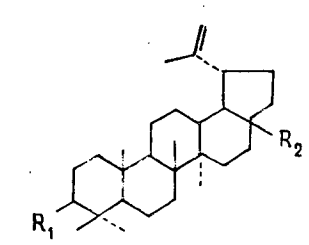
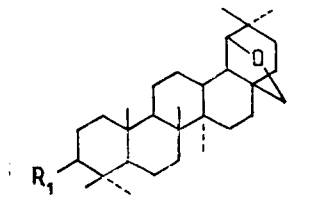
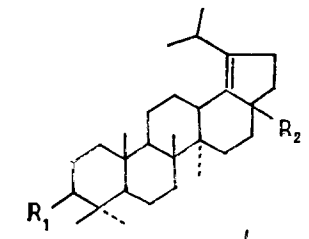


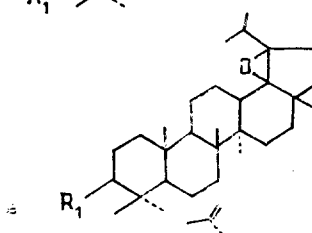
I. R_1 = OH, R_2 = CH_3;
II. R_1 = OAc, R_2 = CH_3;
III. R_1 = OGlc(Ac)$_4$; R_2 = CH_3;
IV. R_1 = OH, R_2 = CH_2OAc;
IVa R_1 = OAc, R_2 = CH_2OAc;
V. R_1 = β-OGlc(Ac)$_4$, R_2 = CH_2OAc;
Va R_1 = α-OGlc(Ac)$_4$, R_2 = CH_2OAc;
VI. R_1 = OAc, R_2 = CH_2OH;
VII R_1 = OAc, R_2 = β-CH_2OGlc(Ac)$_4$;



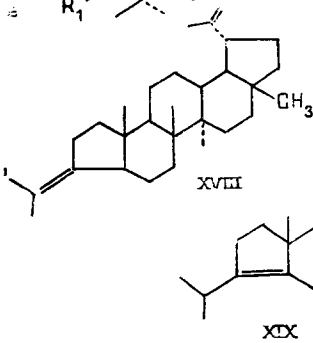
VIII R_1 = OH; VIII a R_1 = OAc;
IX. R_1 = OGlc(Ac)$_4$;



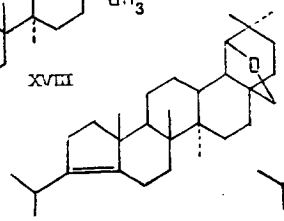
X. R_1 = OAc, R_2 = CH_2OAc;
Xa R_1 = OH, R_2 = CH_2OH;
XI. R_1 = OGlc(Ac)$_4$, R_2 = CH_2OH;
XII R_1 = OH, R_2 = CH_2OGlc(Ac)$_4$;
XIIa R_1 = OGlc(Ac)$_4$, R_2 = CH_2OGlc(Ac)$_4$;



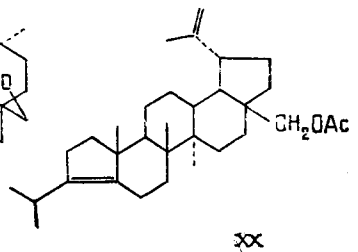
XIII. R_1 = OAc, R_2 = CH_2OAc;
XIV. R_1 = OH, R_2 = CH_2OH;
XV. R_1 = OGlc(Ac)$_4$, R_2 = CH_2OH;
XVI. R_1 = OH, R_2 = CH_2OGlc(Ac)$_4$;
XVII. R_1 = OGlc(Ac)$_4$, R_2 = CH_2OGlc(Ac)$_4$;



XVIII



XIX



XX

A comparison of these ^{13}C spectra of the initial alcohols (I), (Xa), and (XIV), their acetates (II), (X) and (XIII), and the glucosides obtained (III), (XI), (XII), (XIIa), (XV), (XVI) and (XVII) showed a good agreement of almost all the signals of the carbon atoms, with a few exceptions (C-2, C-3, C-4, C-28,...) (Table 2) and enabled the positions of glycosylation to be established.

In a study of the glycosylation reaction in toluene in the presence of cadmium carbonate, conditions were developed for the preparative syntheses of the glucosides of lupeol and of allobetulin and of betulin 3- and 28-glucosides. A change in the conditions of glycosylation [1] and of the order of adding the components to the reaction mixture permitted a substantial increase in the yields of the acetylated glucosides and a simplification of the procedure for their isolation. Glucosides (III), (V), (VII) and (IX) were obtained by direct crystallization from the reaction mixture.

The glycosylation of (I) (Table 1, expt. 7) led to the formation of the β-glucoside (III) (70%) and of a weakly polar compound (XVIII), which was assigned the structure of A-nor-$\Delta^{3,4}$-lupeol, known previously under the name of "lipadiene" [3].

A comparison of the ^{13}C NMR spectra of compounds (I) and (XVIII) showed good agreement of the signals of the atoms of rings C and E and of the C-7 signal of ring B. Consequently (I) and (XVIII) differed only by the structure of ring A (Table 3).

TABLE 1. Conditions and Results of the Glycosylation of Compounds (I), (IV), (VI), (VIII), (Xa), (XIV)

Experiment No.	Initial substances mmole			Time, h	Yield*, %		
	alcohol	acetobromoglucose	acceptor		acylglycosides	recovery of starting material	by-products
1	I, (2)	(2)	$Hg(CN)_2$ (2)	1,0	III (88)	—	—
2	VIII, (2)	(2)	$Hg(CN)_2$ (2)	1,5	IX (80)	10	—
3	IV, (1)	(1)	$Hg(CN)_2$ (1)	1,5	V (68), Va (5)	8	—
4	VI, (1)	(1)	$Hg(CN)_2$ (1)	1,5	VII (60)	11	—
5	Xa, (1)	(2)	$Hg(CN)_2$ (2)	2	XI (46), XII (21), XIIa (10)	6	—
6	XIV, (1)	(2)	$Hg(CN)_2$ (2)	1,5	XV (30), XVI (28), XVII (12)	12	—
7	I, (1)	(2)	$CdCO_3$ (2)	2,0	III (70,45**)	—	XVIII (6)
8	VIII, (1)	(2)	$CdCO_3$ (2)	2,0	IX (62,40**)	—	XX (12)
9	IV, (1)	(2)	$CdCO_3$ (2)	2,5	V (72,50**) Va (2,5)	—	IVa (10), XX (8)
10	VI, (1)	(2)	$CdCO_3$ (2)	2,5	VII (60,42**)	—	IVa (8), VIIIa (10), XIX (6)

*The yields are on the chromatographically homogeneous substances.

**Yield of recrystallized product.

TABLE 2. ^{13}C NMR Chemical Shifts of Compounds (I), (Xa), and (XIV), of their Acetates (II), (X), and (XIII), and of their Glucosides (III), (XI), (XII), (XIIa), (XV), (XVI) and (XVII) (δ, ppm relative to TMS)

Compound	C atom								
	1	2	3	4	18	19	20	28	29
I	38,9	27,2	79,0	38,9	48,0	47,9	150,7	18,0	109,9
Xa	39,2	27,2	78,8	39,0	134,5	144,2	26,8	65,6	21,9
XIV	38,8	26,4	78,4	38,9	78,1*	77,1*	28,7	64,4	19,6
II	38,7	23,9	81,2	38,0	48,2	47,9	151,0	18,0	109,5
X	38,7	23,7	81,0	37,8	134,1	143,6	26,6	67,0	21,6
XIII	38,2	23,7	80,8	37,8	77,7*	75,6*	28,6	66,7	16,5
III	38,7	25,9	90,7	39,0	48,2	47,8	150,9	18,0	109,3
XI	38,9	26 0	90,6	39,0	134,1	143,6	26,8	65,6	21,9
XII	39,2	27 2	78,8	39,0	134,6	143,9	26,5	74,6	21,5
XIIa	38,9	26,2	90,7	39,0	134,7	143,6	26,5	74,8	21,6
XV	38,8	26,0	90,7	39,0	78,5*	77,8	28,6	64,5	19,4
XVI	38,8	26,4	78 4	38,9	78,2	77,6	28,9	72,0	19,8
XVII	38,9	26,3	90,6	39,1	78,2	77,7	28,7	72,4	19,3

*Assignment of the signals ambiguous.

TABLE 3. ^{13}C Chemical Shifts of Compounds (I) [1], (XVIII), and (XIX) (ppm relative to TMS)

Compound	C atom								
	1	2	3	4	5	6	20	28	29
I	38 9	27,2	79,0	38,9	55,6	18,2	150,7	18,0	109,9
XVIII	42,2	27,0	136.6	139,8	56,0	19,0	150,2	62,9	109,8
XIX	42,0	27,4	136.2	26.3	140.0	19,8	36.3	71,3	24,6

In the ^1H NMR spectrum of (XVIII) two additional signals of the protons of methyl groups present on a double bond appear at 1.50 and 1.65 ppm. In the ^{13}C spectrum of (XVIII) the signals of carbon atoms are observed at 136.6 and 139.8 ppm, indicating the presence of a second double bond in the molecule. Thus, compound (XVIII) has the structure of A-nor-$\Delta^{3,4}$-lupeol.

The glycosylation of (VIII) (Table 1, expt. 8) led to the formation of the β-glucoside (IX) (62%) and of a weakly polar product (XIX).

The condensation of betulin 3- and 28-monoacetates with α-acetobromoglucose under these conditions (Table 1, expts. 9 and 10) led to the acetylated glycosides (V), (Va), and (VII) respectively. Compounds (IV), (XIX) and (XX) were isolated as by-products in these syntheses.

The structures of the compounds obtained in experiments 8, 9, and 10 were confirmed by comparison with authentic samples [1].

EXPERIMENTAL

^1H and ^{13}C NMR spectra were measured on a Bruker WM-250 Fourier spectrometer with a working frequency of 250 MHz for ^1H and 62.9 MHz for ^{13}C at 30°C in $CDCl_3$. Chemical shifts are expressed in the δ scale relative to TMS. The accuracy of the measurements was ±1.5 Hz for ^{13}C and ±0.15 Hz for ^1H. Optical rotations were determined on a Perkin-Elmer 141 instrument in a cell 10 cm long at 20°C, and melting points on a Boetius stage.

Column chromatography was carried out on silica gel 100/160 (Chemapol, Czechoslovakia) in hexane–acetone systems, and TLC in a fixed layer of silica gel in the hexane–acetone (2:1) and benzene–chloroform–methanol (3:2:1) systems. The TLC plates were visualized with 10% H_2SO_4 in methanol at 120-150°C.

Acetonitrile was used in the absolute form, and toluene was dried over calcined 4 Å molecular sieves in a Soxhlet apparatus. Acetates (II) and (IV) were obtained by the procedure of [4] and allobetulin by that of [5].

Lupeol (I) was isolated from a chloroform extract of the bark of Betula pubescens followed by chromatography on silica gel and crystallization from ethanol, mp 210-212°C according to the literature [6]: mp 212-213°C.

3β-28-Diacetoxy-18-lupene (X) was obtained by the isomerization of betulin diacetate (IVa) with a solution of HBr in a mixture of acetic acid, acetic anhydride and benzene [7]; mp 210°C. According to the literature [7]: mp 215°C. ^1H spectrum (δ, ppm): 0.835 (s, 3H), 0.845 (s, 3H), 0.890 (s, 6H), 0.904 (d, 3H, J = 6.6 Hz, H-29), 0.994 (d, 3H, J = 6.6 Hz, H-30), 1.059 (s, 3H), 2.045 (s, 3H), 2.052 (s, 3H), 3.136 (m, 1H), 4.0 (q, 2H, J = 11.0 Hz, H-28), 4.484 (m, 1H, H-3), 1.1-2.3 (other H atoms).

3β-28-Dihydroxy-18-lupene (Xa) was obtained by the saponification of (X) with a solution of caustic potash in ethanol; mp 220°C (ethanol). According to the literature [8]: mp 219-220°C (ethanol). ^1H spectrum (δ, ppm); 0.763 (s, 3H), 0.894 (s, 3H), 0.930 (s, 3H), 0.933 (d, 3H, J = 7.0 Hz), 0.964 (s, 3H), 1.009 (d, 3H, J = 7.0 Hz), 1.082 (s, 3H), 3.13-3.25 (m, 2H, H-3 + 1H), 3.416 (d, 1H, J = 11.0 Hz, H-28), 3.526 (d, 1H, J = 11.0 Hz, H-28), 1.1-2.4 (other H atoms).

3β-28-Diacetoxy-18β,19β-epoxylupane (XIII) was obtained by the epoxidation of (X) with a mixture of formic acid and 33% hydrogen peroxide in methylene chloride–ethyl acetate solution [9] with a yield of 62% after purification and crystallization; mp 214-215°C.

According to the literature [9], mp 222-223°C. ^1H spectrum (δ, ppm): 0.85-1.10 (21H, 7 × CH_3), 2.05 (s, 6H, 2 × CH_3), 3.90 (d, J = 10.6 Hz, 1H, H-28), 4.48 (m, 1H, H-3), 4.52 (d, 1H, J = 10.6 Hz, H-28), 1.2-2.4 (other H atoms).

3β-28-Dihydroxy-18β,19β-epoxylupane (XIV) was obtained by the saponification of (XIII) with a methanolic solution of caustic potash at the boil [9]; mp 246°C. According to the literature [9]: mp 245°C (ethanol). ^1H spectrum (δ, ppm): 0.758 (s, 3H), 0.888 (s, 3H), 0.956 (s, 3H), 1.024 (d, 3H, J = 6.7 Hz, H-29), 1.106 (d, 3H, J = 6.7 Hz, H-30), 1.128 (s, 3H), 2.156 (m, 1H), 2.35 (m, 1H), 3.145 (m, 1H), 3.345 (m, 1H, H-3), 3.442 (d, 1H, J = 10.6 Hz, H-28), 3.870 (d, 1H, J = 10.6 Hz, H-28), 1.1-1.9 (other H atoms).

General Procedure for Glycosylation in the Presence of Mercury Cyanide. The initial alcohol and the necessary amounts of α-acetobromoglucose and of mercury cyanide (Table 1, expts. 1-6) in 20 ml of acetonitrile were stirred with a magnetic stirrer at 90°C. The reaction was continued until the initial alcohol had disappeared from the reaction mixture. After the end of the reaction, the solution was diluted with chloroform, washed with water, dried and evaporated. The dry residue was chromatographed on silica gel.

The 3-Monoglucoside (III). mp 132-134°C (ethanol), $[\alpha]_D^{20}$ +38.5° (c 1.0; chloroform). ^1H spectrum (δ, ppm): 0.83 (s, 3H), 0.88 (s, 3H), 0.91 (s, 3H), 0.96 (s, 3H), 1.65 (s, 3H), 2.00 (s, 3H, OAc), 2.02 (s, 3H, OAc), 2.04 (s, 3H, OAc), 2.08 (s, 3H, OAc), 3.06 (t, 1H), 3.7 (m, 1H, H-5'), 4.09-4.3 (m, 2H, H-6'), 4.53 (d, 1H, J = 8.0 Hz, H-1' at C-3).

The 3-Monoglucoside (IX). mp 205-208°C (ethanol), $[\alpha]_D^{20}$ +18.4° (c 1.0; chloroform). ^1H spectrum (δ, ppm): 0.76 (s, 3H), 0.84 (s, 3H), 0.89 (s, 3H), 0.93 (s, 3H), 0.95 (d, 3H,

J = 7.0 Hz), 0.97 (s, 3H), 1.08 (d, 3H, J = 7.0 Hz), 2.00 (s, 3H, OAc), 2.06 (s, 3H, OAc), 2.08 (s, 3H, OAc), 2.09 (s, 3H, OAc), 3.18 (m, 1H, H-3), 3.48 (d, 1H, J = 11.0 Hz, H-28), 3.64 (m, 1H, H-5'), 4.12-4.24 (m, 2H, 2H-6'), 4.50 (d, 1H, J = 7.8 Hz, H-1' at C-3).

The 28-Monoglucoside (XII). mp 214-216°C (ethanol), $[\alpha]_D^{20}$+25.1° (c 1.0; chloroform). ^{1}H spectrum (δ, ppm): 0.740 (s, 3H), 0.840 (s, 3H), 0.882 (s, 3H), 0.958 (d, 3H, J = 7.0 Hz), 0.970 (s, 3H), 1.068 (d, 3H, J = 7.0 Hz), 2.01 (s, 3H, OAc), 2.03 (s, 3H, OAc), 2.04 (s, 3H, OAc), 2.06 (s, 3H, OAc), 3.16 (m, 1H, H-3), 3.49 (d, 1H, J = 11.0 Hz, H-28), 3.59 (m, 1H, H-5'), 4.14-4.29 (m, 2H, 2 × H-6'), 4.48 (d, 1H, J = 8.0 Hz, H-1' at C-28).

The 3,28-Diglucoside (XIIa). mp 218-219°C (ethanol), $[\alpha]_D^{20}$ +14.3° (c 1.0; chloroform). ^{1}H spectrum (δ, ppm): 0.710 (s, 3H), 0.842 (s, 3H), 0.890 (s, 3H), 0.95 (s, 3H), 0.96 (d, 3H, J = 7.0 Hz), 0.98 (s, 3H), 1.09 (d, 3H, J = 7.0 Hz), 2.00-2.09 (s, 24H, 8 × OAc), 3.16 (m, 1H, H-3), 3.48 (d, 1H, J = 11.0 Hz, H-28), 3.61 (m, 2H, 2 × H-5'), 4.10-4.24 (m, 4H, 4 × H-6'), 4.53 (d, 1H, J = 7.8 Hz, H-1' at C-3), 4.48 (d, 1H, J = 8.0 Hz, H-1' at C-28).

The 3-Monoglucoside (XV). mp 198-201°C (ethanol), $[\alpha]_D^{20}$ +139.9° (c 1.0; chloroform). ^{1}H spectrum (δ, ppm): 0.76 (s, 3H), 0.85 (s, 3H), 0.96 (s, 3H), 1.03 (d, 3H, J = 6.7 Hz, 3 × H-3), 1.11 (d, J = 6.7 Hz, 3H-30), 1.12 (s, 3H), 1.13 (s, 3H), 2.00-2.07 (s, 12H, 4 × OAc), 3.34 (m, 1H, H-3), 3.50 (m, 1H, H-5'), 3.53 (d, 1H, J = 10.6 Hz, H-28), 4.10-4.20 (m, 2H, 2 × H-6'), 4.53 (d, 1H, J = 7.8 Hz, H-1' at C-3).

The 28-Monoglucoside (XVI). mp 186-189°C (ethanol), $[\alpha]_D^{20}$ +17.8° (c 1.0; chloroform). ^{1}H spectrum (δ, ppm): 0.73 (s, 3H), 0.84 (s, 3H), 0.96 (s, 3H), 1.03 (d, 3H, J = 6.7 Hz, H-29), 1.08 (d, 3H, J = 6.7 Hz, H-30), 1.10 (s, 3H), 1.13 (s, 3H), 2.02-2.07 (s, 12H, 4 × OAc), 3.32 (m, 1H, H-3), 3.49 (d, 1H, J = 10.6 Hz, H-28), 3.56 (m, 1H, H-5'), 4.10-4.20 (m, 2H), 4.47 (d, 1H, J = 8.0 Hz, H-1' at C-28).

The 3,28-Diglucoside (XVII). mp 220-224°C (ethanol), $[\alpha]_D^{20}$ +19.6° (c 1.0; chloroform). ^{1}H spectrum (δ, ppm): 0.76 (s, 3H), 0.82 (s, 3H), 0.86 (s, 3H), 0.98 (s, 3H), 1.00 (d, 3H, J = 6.7 Hz, H-29), 1.08 (d, 3H, J = 6.7 Hz, H-30), 1.11 (s, 3H), 2.01-2.08 (s, 24H, 8 × OAc), 3.30 (m, 1H, H-3), 3.48 (d, 1H, J = 10.6 Hz, H-28), 3.61 (m, 2H, H-5'), 4.12-4.24 (m, 4H, H-6'), 4.53 (d, 1H, J = 7.8 Hz; H-1' at C-3), 4.47 (d, 1H, J = 8.0 Hz, H-1' at C-28).

A-Nor-$\Delta^{3,4}$-lupeol (XVIII). mp 178-181°C (ethanol). According to the literature [3]: mp 180-181°C. ^{1}H spectrum (δ, ppm): 0.80 (s, 3H), 0.85 (s, 3H), 0.91 (s, 3H), 0.96 (s, 3H), 1.50 (s, 3H), 1.65 (s, 3H), 1.70 (s, 3H).

General Procedure for Performing Condensation in the Presence of Cadmium Carbonate. The reaction was performed in a Soxhlet apparatus over freshly calcined 4 Å molecular sieves. A solution of α-acetobromoglucose (2 mmole) and the initial alcohol (1 mmole) was added dropwise over one hour to a boiling suspension of cadmium carbonate in toluene. After the end of the reaction (monitoring by the TLC method), the mixture was cooled, and the precipitate was separated off and was washed with chloroform. The evaporated dry filtrate was washed several times with hot distilled water, carefully dried, and treated with a small amount of methanol. The precipitate that deposited on cooling was filtered off and was washed successively with cold methanol and hexane and was recrystallized from ethanol. The yields of the glucoside acetates (III), (IX), (V), and (VII) were, respectively, 45, 40, 50, and 42% (Table 1, expts. 7-10).

The total yields of reaction products were determined after column chromatography on silica gel.

SUMMARY

1. The glycosylation of lupeol, allobetulin, 3β,28-dihydroxy-18-lupene, 3β,28-dihydroxy-18β,19β-epoxylupane, and betulin monoacetates with α-acetobromoglucose in acetonitrile in the presence of mercury cyanide has been studied. It has been shown that under these conditions tetraacetates of β-glucosides of the initial alcohols are formed.

2. 3β,28-Dihydroxy-18-lupene and 3β,28-dihydroxy-18β,19β-epoxylupane 3,28-mono- and 3,28-di-O-β-Di-glucopyransides have been synthesized for the first time.

3. Preparative methods for the synthesis of lupeol, allobetulin and betulin 3- and 28-monoacetates have been proposed.

LITERATURE CITED

1. L. É. Odinokova, G. I. Oshitok, V. A. Denisenko, V. F. Anufriev, A. M. Tolkach and N. I. Uvarova, Khim. Prir. Soedin, 182 (1984).
2. A. V. Nikolaev, A. S. Shashkov, B. A. Dmitriev, and N. K. Kochetkov, Bioorg. Khim. 7, No. 6, 914 (1981).
3. J. L. Simonsen and W. C. J. Ross, The Terpenes, Cambridge University Press, Cambridge, Vol. 4 (1957), p. 304.
4. L. Ruzicka, A. H. Lamberton and E. W. Christe, Helv. Chim. Acta, 21, 1706-1717 (1938).
5. A. Vystrcil, E. Stejskolova-Vondraskova and J. Cerny, Collect. Czech. Chem. Commun., 24, No. 10, 3279 (1959).
6. H. W. Kircher, Phytochemistry, 19, No. 12, 2707 (1980).
7. E. Suokas and T. Hase, Acta Chem. Scand., B29, No. 1, 139 (1975).
8. E. Suokas and T. Hase, Acta Chem. Scand., B28, No. 7, 793 (1974).
9. E. Suokas and T. Hase, Acta Chem. Scand., B31, No. 3, 231 (1977).

STEROIDS OF THE SPIROSTAN AND FUROSTAN SERIES FROM PLANTS OF THE GENUS Allium.

XXV. STRUCTURE OF ANZUROGENIN B FROM Allium suvorovii AND Allium Stipitatum

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A new genin of the spirostan series – anzurogenin B having the structure of 2α,5α-epoxy-(25R)-spirostan-3β,6β-diol – has been isolated form the collective fruit of the cocultivated Allium suvorovii Rgl. and Allium stipitatum Rgl. (family Liliaceae).

In a preceding communication [1] we showed that the collective fruit of the cocultivated Allium survorovii Rgl. and Allium stipitatum Rgl. (family Liliaceae) – local name anzur – was the source of five aglycons of the spirostan series. Two of them proved to be new. They were called anzurogenins A [1] and B. The present publication is devoted to a proof of the structure of anzurogenin B (I).

The characteristic color reaction with vanillin–phosphoric acid [2, 3] and a distinctive series of bands in the 800-1000 cm^{-1} region of the IR spectrum [3-5] permitted genin (I) to be assigned to derivatives of the (25R)-spirostan series.

The correctness of this assignment was also shown by the elementary composition of the molecular ion M^+ 446 ($C_{27}H_{42}O_5$), the nature of its mass-spectrometric fragmentation [6], and its ^{13}C and ^1H NMR spectra (Tables 1 and 2, respectively) [3, 7].

In the ^{13}C NMR spectrum of anzurogenin B taken with retention of carbon-proton interaction (GD spectrum), there are six signals in the region of resonance of the carbon atoms linked to one oxygen atom. One of them has triplet splitting and a chemical shift (CS) of 66.96 ppm, which are characteristic for C-26 of genins of the spirostan series. A signal with a CS of 90.42 ppm is a singlet and the other four are doublets. Three signals are worthy of note: the above-mentioned singlet at 90.42 ppm, and two doublets at 81.26 ppm and 80.38 ppm. While one of the doublets is naturally assigned to the C-16 resonance, the CSs of the second doublet and of the singlet must be regarded as unusual for carbon atoms with unsubstituted secondary and tertiary OH groups, respectively.

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