4. A. Rustaiyan, E. Simozar, A. Ahmadi, M. Grenz, and F. Bohlmann, Phytochemistry, 20, 2772 (1981).
5. W. Vichnewski, R. Murari, and W. Herz, Phytochemistry, 18, No. 1, 129 (1979).
6. H. Wagner, R. Seitz, and H. Lotter, J. Org. Chem., 43, No. 17, 3339 (1978).
7. V. A. Mnatsakanyan, and G. B. Oganesyan, Khim. Prir. Soedin., 727 (1978).

GLYCOSYLATION OF TRITERPENOIDS OF THE DAMMARANE SERIES.

IV. β-D-GLUCOPYRANOSIDES OF BETULAFOLIENETRIOL AND ITS DERIVATIVES

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The glycosylation of betulafolienetriol (dammar-24-ene-3α,12β,20(S)-triol) under the conditions of the Koenigs–Knorr, the Helferich, and the orthoester methods has been studied. It has been shown that the condensation of β-folienetriol and its 3-epimer with α-acetobromoglucose in the presence of silver oxide leads to a mixture of the corresponding 3-, 12-, and 20-mono- and 3,12- and 3,20-di-O-β-pD-glucopyranosides. It has been established that the glycosylation of dammar-24-ene-3α,12β,20(S)-triol under Helferich's conditions and those of the orthoester method is accompanied by a side reaction of dehydration in the side chain and leads to 20-dehydroxy derivatives. The structures of all the newly obtained compounds have been established on the basis of the results of IR and of ^{1}H and ^{13}C NMR spectroscopy.

Pharmacological and biochemical investigations performed in recent years have shown that the stimulating and adaptogenic action of extracts of the roots of *Panax ginseng* is due to the saponins present in it [1-3].

The bulk of the saponins from the roots of *Panax ginseng* is divided into two groups: the ginsenosides R_d, R_c, R_{b_1} and R_{b_2}, the aglycon of which is 20(S)-protopanaxidiol [dammar-24-ene-3α,12β,20(S)-triol] (I) and the ginsenosides R_{g_1}, R_{g_2}, R_e, and R_f, the aglycon of which is 20(S)-protopanaxatriol [dammar-24-ene-3α,6α,12β,20(S)-tetraol] [4, 5]. As a rule, the carbohydrate chains are located at the third, sixth, or twelfth hydroxyls.

A triterpene of the dammarane series, betulafolienetriol (II), which was first isolated by Fischer and Seiler [6] from the European white birch *Betula alba* and was later found in the leaves of Far Eastern species of the genus *Betula* [7], differs from the native genin of the ginsenosides R_{b_1}, R_{b_2}, R_c, and R_d only by the configurationof the hydroxy group at C-3. The unique physiological action of ginseng and its poor distribution in nature makes it desirable to find possible methods of synthesizing glycosides close in structure to the ginsenosides from the comparatively readily available betulafolienetriol (II) and from its 3-epimer (I), which can easily be obtained from (II) by oxidation to the 3-keto derivative (III) followed by reduction.

The extremely limited information available in the literature [8] on the production of glycosides from the triterpenoids isolated from the birch contains no details of the methods of glycosylation used or proofs of the structure and individuality of specific glycosides.

Continuing a study of the glycosylation of dammarane triterpenoids, we have performed the condensation of triols (I) and (II) and their 3-O-acetates (IV) and (V) with α-acetobromoglucose under the conditions of the Koenigs–Knorr reaction. The results of the experiments are given in Table 1.

The glycosylation of the triols (I) and (II) with α-acetobromoglucose in methylene chloride in the presence of silver oxide at room temperature (Table 1, expts. 1 and 2) led to mul-

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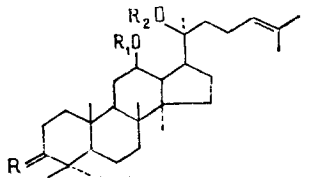
ticomponent mixtures of mono- and diglucosides which were distinguished by instability on prolonged chromatography in a silica gel column.



I. R =  $R_1 = R_2 = H$

II. R = $R_1 = R_2 = H$

III. R = O $R_1 = R_2 = H$

IV. R = $R_1 = R_2 = H$

V. R =  $R_1 = R_2 = H$

VI. R = $R_1 = OAc, R_2 = H$

VII. R =  $R_1 = OAc, R_2 = H$

VIII. R =  $R_1 = R_2 = H$

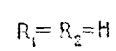
IX. R =  $R_1 = R_2 = H$

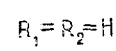
X. R =  $R_1 = Glc(Ac)_4, R_2 = H$

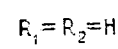
XI. R =  $R_1 = Glc(Ac)_4, R_2 = H$

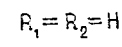
XII. R = $R_1 = H, R_2 = Glc(Ac)_4$

XIII. R =  $R_1 = H, R_2 = Glc(Ac)_4$

XIV. R =  $R_1 = Glc(Ac)_4, R_2 = H$

XV. R =  $R_1 = Glc(Ac)_4, R_2 = H$

XVI. R =  $R_1 = H, R_2 = Glc(Ac)_4$

XVII. R =  $R_1 = H, R_2 = Glc(Ac)_4$

XVIII. R =  $R_1 = OAc, R_2 = Glc(Ac)_4$

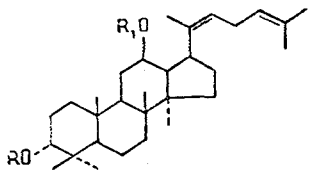
XIX. R =  $R_1 = Glc(Ac)_4, R_2 = H$

XX. R =  $R_1 = Glc(Ac)_4, R_2 = H$

XXI. R =  $R_1 = H, R_2 = Glc(Ac)_4$

XXII. R =  $R_1 = H, R_2 = Glc(Ac)_4$

XXIII. R =  $R_1 = OAc, R_2 = Glc(Ac)_4$



XXIII. R = Ac, $R_1 = Glc(Ac)_4$

XXIV. R = H, $R_1 = Glc(Ac)_4$

XXV. $R = R_1 = Glc(Ac)_4$

XXVI. $R = R_1 = H$

On the basis of the results of an investigation of ^1H and ^{13}C by NMR and elementary analysis, the products obtained were ascribed the respective structures of dammar-24-ene-3α,12β, 20(S)-triol 3-O-(2',3',4',6'-tetra-O-acetyl-β-D-glucopyranoside)(VIII), dammar-24-ene-3α,12β, 20(S)-triol 12-O-(2',3',4',6'-tetra-O-acetyl-β-D-glucopyranoside) (X), dammar-24-ene-3α,12β, 20(S)-triol 20-O-(2',3',4',6'-tetra-O-acetyl-β-D-glucopyranoside) (XII), dammar-24-ene-3α,12β, 20(S)-triol 3,12-di-O-(2',3',4',6'-tetra-O-acetyl-β-D-glucopyranoside) (XIV), dammar-24-ene-3α,12β,20(S)-triol 3,20-di-O-(2',3',4',6'-tetra-O-acetyl-β-D-glucopyranoside) (XVI), dammar-24-ene-3β,12β,20(S)-triol 3-O-(2',3',4',6'-tetra-O-acetyl-β-D-glucopyranoside) (IX), dammar-24-ene-3β,12β,20(S)-triol 12-O-(2',3,'4,'6,'-tetra-O-acetyl-β-D-glucopyranoside) (XI), dammar-24-ene-3β,12β,20(S)-triol 20-O-(2',3',4',6'-tetra-O-acetyl-β-D-glucopyranoside) (XIII), dammar-24-ene-3β,12β,20(S)-triol 3,12-di-O-(2',3',4',6'-tetra-O-acetyl-β-D-glucopyranoside) (XV), and dammar-24-ene-3β,12β,20(S)-triol 3,20-di-O-(2',3',4',6'-tetra-O-acetyl-β-D-glucopyranoside) (XVII).

It must be mentioned that a mixture of the 12-O- and 20-O-monoglucosides (XI) and (XIII) could be separated only after additional acetylation in the form of the acetate derivatives (XVIII) and (XX).

TABLE 1. Conditions and Results of the Condensation of the Triterpenes (I), (II), (IV), and (V) with α-Acetobromoglucoses in the Presence of Silver Oxide

Experiment No.	Initial substances, alcohol	α-acetobromoglucose	Ag_2O	Reaction products, %* monoglucosides	diglucosides	Recovery of the starting material, %
1	(I), 5	15	15	48, (IX) : (XI) : (XIII) 4,5:2,5:1	35 (XV) : (XVII) 1:1	
2	(II), 5	15	15	50, (VIII) : (X) : (XII) 1:4:2	34,5, (XIV) : (XVI) 1:1	
3	(IV), 2	3	3	32,6 (XIX), 24,4 (XXI)	—	20,9
4	(V), 1	1,5	1,5	27,3 (XX), 26,3 (XXII)	—	31,0

*The yields of mixtures of chromatographically homogeneous substances are given. The ratio of the glucosides was determined after additional chromatography.

TABLE 2. ^{13}C Chemical Shifts of the Triol (II) and Its Glucosides (VIII), (X), (XII), (XIV), and (XVI), (δ, ppm relative to TMS)

C atom	Compound II	VIII	X	XII	XIV	XVI
1	33,8	33,8	33,8	33,6	34,1	33,7
2	25,3	20,9	25,4	25,5	21,1	21,0
3	76,0	82,0	75,6	76,3	82,1	82,4
4	37,6	37,1	37,6	37,6	37,2	37,0
5	49,5	49,9	49,4	49,6	50,1	49,9
6	18,3	18,0	18,1	18,3	18,0	18,0
7	34,8	34,5	34,5	34,7	34,7	34,6
8	39,9	40,1	39,9	40,1	40,1	40,1
9	50,0	49,9	49,7	49,6	50,0	49,6
10	37,2	37,0	37,3	37,3	37,3	37,1
11	31,3	31,0	27,1	29,9	27,4	29,9
12	70,8	71,0	78,2	70,2	78,4	70,3
13	47,5	48,0	45,9	48,6	46,2	48,6
14	51,7	51,8	52,2	51,4	52,5	51,4
15	31,0	31,0	31,0	30,3	31,3	30,3
16	26,5	26,5	26,8	26,5	27,0	26,5
17	53,6	53,4	53,2	52,5	53,3	52,7
18	16,0	16,2	16,1	15,8	16,3	16,0
19	15,7	15,7	15,8	15,8	15,9	15,8
20	73,8	74,8	72,7	85,2	72,9	85,2
21	26,7	27,3	26,3	22,2	26,5	22,1
22	34,8	34,5	35,9	35,3	36,3	35,4
23	22,4	22,4	22,4	22,8	22,5	22,9
24	125,3	124,9	125,9	124,7	126,1	124,6
25	131,2	131,9	130,4	131,6	130,6	131,6
26	25,8	27,8	25,8	25,7	25,7	25,7
27	17,7	17,8	17,7	17,7	17,7	17,7
28	28,4	28,6	28,4	28,4	28,6	28,6
29	22,2	22,1	22,1	22,2	22,1	22,3
30	17,0	16,9	17,5	17,1	17,5	17,0

In its physicochemical constants and spectral characteristics, the 20-O-β-D-glucopyranoside hexaacetate (XVIII) was identical with the acetate of the corresponding derivative of 20(S)-protopanaxadiol 20-β-D-glucoside obtained by Japanese workers in the enzymatic hydrolysis of ginsenosides R_{b_1}, R_{b_2}, and R_C [9], while the diglycoside (XVII) is the octaacetate of ginsenoside F_2, which has been isolated from the leaves of *Panax ginseng* [10].

In the ^1H spectrum of each of the monoglucosides (VIII) and (IX) and of the diglucosides (XIV)-(XVII) the doublet signal of the anomeric proton of the sugar component at C^3 appears at 4.50-4.53 ppm ($J_{1',2'}$ = 7.8-8.0 Hz), that of the sugar component at C^{12} in the ^1H spectra of the monoglucosides (X) and (XI) and of the diglucosides (XIV) and (XV), at 4.71-4.73 ppm ($J_{1',2'}$ = 8.0 Hz), and, finally, that at C^{20} in the ^1H spectra of the monoglucosides (XII) and (XIII) and the diglucosides (XVI) and (XVII) at 4.85 ppm ($J_{1',2'}$ = 8.0 Hz). The vlaues of $J_{1',2'}$ show the trans configuration of the glycosidic bonds both in the monoglucosides and in the diglucosides. The positions of attachment of the carbohydrate components were estab-

TABLE 3. ^{13}C Chemical Shifts of the Triol (I) and Its Glucosides (IX), (XI), (XIII), (XV), and (XVII) (δ, ppm relative to TMS)

C Atom	Compound					
	I	IX	XI	XIII	XV	XVII
1	39,1	39,2	39,0	39,1	39,3	39,1
2	27,5	26,2	27,4	27,5	26,1	25,9
3	79,0	90,6	78,8	79,0	90,2	90,8
4	39,1	39,2	39,0	39,1	39,3	38,9
5	56,0	56,5	56,0	56,0	56,5	56,3
6	18,4	18,4	18,3	18,4	18,3	18,3
7	34,8	35,0	34,6	34,7	34,9	34,8
8	39,9	40,0	39,8	39,8	40,0	39,9
9	50,2	50,4	50,0	49,8	50,2	49,8
10	37,2	37,0	37,3	37,3	37,2	36,9
11	31,4	31,2	27,4	31,1	27,6	29,7
12	70,9	70,9	78,4	70,1	78,2	70,1
13	47,8	47,9	46,0	48,7	46,2	48,7
14	51,7	51,7	52,2	51,7	52,3	51,3
15	31,1	31,7	31,1	31,1	31,2	30,3
16	26,9	26,7	26,9	26,9	27,0	26,4
17	53,6	53,9	53,3	53,3	53,6	52,7
18	16,3	16,2	15,9	15,9	16,3	15,5
19	15,8	15,9	15,4	15,4	16,0	15,4
20	74,2	74,1	72,8	85,1	73,0	85,1
21	26,6	26,9	26,4	22,4	26,4	22,3
22	34,8	35,0	36,0	35,3	36,1	35,3
23	22,5	22,5	22,4	22,9	22,5	22,9
24	125,2	125,3	125,9	124,6	126,1	124,6
25	131,6	131,3	130,5	131,6	130,5	131,6
26	25,9	25,9	25,8	25,8	25,9	25,6
27	17,9	17,8	17,7	17,7	17,7	17,7
28	28,2	27,8	28,1	28,1	27,8	27,7
29	15,5	16,2	15,0	15,0	16,3	16,2
30	17,0	17,0	17,4	17,0	17,5	17,0

TABLE 4. ^{13}C Chemical Shifts of Compounds (IV), (V), and (VII) and of Their Glucosides (XVIII)-(XXII) (δ, ppm, relative to TMS)

C atom	Compound							
	IV	V	VII	XVIII	XIX	XX	XXI	XXII
1	34,0	38,7	38,6	38,6	34,7	39,0	34,2	38,7
2	23,0	23,7	23,6	23,7	23,0	23,7	22,9	23,8
3	78,3	80,8	80,5	80,8	78,2	80,8	78,4	80,9
4	36,8	37,8	38,0	38,0	37,0	38,0	36,8	37,9
5	50,8	56,0	56,0	56,0	51,1	56,1	49,6	56,0
6	18,2	18,2	18,2	18,2	18,2	18,2	18,2	18,2
7	34,9	34,8	34,6	34,6	34,7	34,9	34,6	34,7
8	40,0	39,8	39,8	39,7	40,1	40,0	40,0	39,9
9	50,0	50,0	50,0	50,1	50,0	50,6	50,8	49,7
10	37,2	37,0	37,2	37,1	37,5	37,3	37,2	37,1
11	31,0	31,0	28,3	29,2	27,5	27,8	29,9	30,0
12	70,8	70,6	76,5	75,3	78,4	77,9	70,1	70,1
13	47,6	47,6	45,0	45,7	46,2	46,0	48,6	48,7
14	51,7	51,5	52,8	53,2	52,5	52,3	51,4	51,2
15	31,1	31,3	31,5	31,8	31,3	31,2	30,3	30,3
16	26,5	26,4	27,2	26,5	27,0	27,0	26,5	26,5
17	53,7	53,7	53,0	47,9	53,4	53,4	52,7	52,6
18	16,0	16,5	16,6	16,[illegible]	16,0	16,0	15,8	16,5
19	15,8	15,2	16,3	16,2	15,9	15,9	15,8	16,1
20	73,8	73,7	73,7	83,4	72,9	72,8	85,2	85,2
21	26,7	26,6	26,3	22,0	26,6	26,5	22,3	22,2
22	34,3	34,8	36,2	39,1	36,3	36,2	35,3	35,3
23	22,4	22,4	22,4	22,9	22,5	22,5	23,0	22,8
24	125,4	125,2	125,3	124,7	126,1	126,1	124,6	124,6
25	131,1	131,1	131,1	131,6	130,7	130,6	131,6	131,6
26	25,8	25,7	25,8	25,7	25,8	25,8	25,7	25,7
27	17,8	17,7	17,6	17,7	17,7	17,7	17,7	17,7
28	28,0	28,0	28,0	28,0	27,9	27,9	27,9	28,0
29	15,7	15,7	15,7	15,5	21,8	16,3	21,8	15,8
30	17,3	16,8	17,3	18,1	17,7	17,5	17,2	17,1

TABLE 5. ^{13}C Chemical Shifts of Compound (XXVI) and Its Glucosides (XXIII)-(XXV) (δ, ppm, relative to TMS)

C atom	Compound				C atom	Compound			
	XXIII	XXIV	XXV	XXVI		XXIII	XXIV	XXV	XXVI
1	34,2	33,9	34,1	33,7	16	27,4	27,1	27,1	27,0
2	22,9	25,3	21,1	25,5	17	50,2	50,2	50,2	50,1
3	77,9	76,0	82,1	76,0	18	16,1	16,1	16,1	16,1
4	36,8	37,6	37,2	37,6	19	15,7	15,7	15,7	15,7
5	49,3	49,5	50,1	49,5	20	137,4	137,6	137,6	140,2
6	18,1	18,2	18,0	18,2	21	12,7	12,7	12,7	12,5
7	34,8	34,8	34,7	34,9	22	122,9	122,9	122,9	122,2
8	40,2	40,2	40,1	40,3	23	27,6	27,6	27,6	27,4
9	50,0	49,5	50,0	50,1	24	124,0	124,0	124,0	124,6
10	37,4	37,4	37,3	37,4	25	130,4	130,4	130,4	131,7
11	28,5	27,9	27,4	30,3	26	25,7	25,7	25,7	25,7
12	78,1	77,7	78,4	73,4	27	17,7	17,7	17,7	17,7
13	47,6	47,4	47,6	50,1	28	27,9	28,4	28,6	28,4
14	50,9	51,1	51,1	50,6	29	21,8	22,2	22,1	22,2
15	32,4	32,2	32,2	32,4	30	17,1	16,9	17,0	16,9

TABLE 6. ^{13}C Chemical Shifts of the Sugar Components of the Glucosides (VIII)-(XXV), (δ, ppm, relative to TMS)

Compound	C atom					
	1′	2′	3′	4′	5′	6′
VIII	98,0	71,6	73,1	69,1	71,6	62,2
IX	103,0	71,8	73,1	69,0	71,7	62,3
X	96,9	71,9	73,1	69,1	72,4	62,2
XI	96,6	71,6	72,8	68,8	72,1	62,0
XII	94,8	72,0	73,2	68,8	72,3	62,5
XIII	94,8	72,1	72,8	68,8	72,1	62,5
	98,1	71,8	73,2	69,3	72,1	62,4
XIV	97,0	71,9	73,0	69,0	72,4	62,1
	103,0	71,8	73,1	69,0	71,7	62,4
XV	97,0	71,9	73,1	69,0	72,1	62,1
XVI	98,2	71,6	73,2	69,2	71,6	62,3
	94,8	72,2	73,2	68,8	72,1	62,5
XVII	103,0	71,8	73,1	69,0	71,7	62,4
	94,8	72,3	73,05	68,8	72,1	62,4
XVIII	94,9	71,7	73,5	69,1	72,1	62,8
XIX	96,9	71,8	73,1	69,1	72,3	62,2
XX	97,9	71,8	73,2	69,0	72,5	62,3
XXI	94,8	72,2	73,1	68,8	72,0	62,5
XXII	94,8	72,0	73,2	68,8	72,3	62,5
XXIII	96,9	71,8	73,1	69,6	72,3	62,2
XXIV	96,9	71,9	73,2	69,0	72,3	62,2
	98,1	71,8	73,1	69,3	72,1	62,4
XXV	96,9	71,8	73,1	66,0	72,4	62,2

lished by comparing the ^{13}C spectra of the initial triols (I) and (II) and of the glucosides (VIII)-(XVII) obtained (Tables 2 and 3).

The absence of regioselectivity on glycosylation under the Koenigs—Knorr conditions complicated the isolation of individual glucosides but, on the other hand, it permitted a set of almost all possible structures to be obtained.

The condensation of the 3-O-acetyl derivatives (IV) and (V) with α-acetobromoglucose under the same conditions (experiments 3 and 4) gave mixtures of the corresponding 12-O- and 20-O-β-D-glucopyranosides (XIX)-(XXII).

An attempt to perform the glycosylation of the diacetates (VI) and (VII) under the same conditions led to the quantitative recovery of the initial alcohols.

The glycosylation of the triol (II) with α-acetobromoglucose in the presence of mercury cyanide in nitromethane [11] was complicated by a side reaction and gave the 20-dehydroxy glucosides (XXIII)-(XXV).

The condensation of (II) with D-glucose (tert-butyl orthoacetate) with azeotropic distillation in chlorobenzene in the presence of 2,4,6-collidinium perchlorate [12] led to the same glucosides. The absence from the glycosylation products of the 12-O-mono-, 12,20-di-, and 3, 12,20-triglucosides, the formation of which might have been expected, is connected with the competing process of dehydration through the splitting out of a molecule of water in the side

chain of the initial triterpenoids by the action of such dehydrating agents as $HgBr_2$ under Helferich's conditions and azeotropic distillation under the conditions of the orthoester method.

In a control experiment in which the initial triol (II) was boiled with a catalytic amount of 2,4,6-collidinium perchlorate under the conditions of the orthoester method for 15 min, a mixture of weakly polar substances was formed with a predominance of the dehydration product dammar-20(22),24-diene-3α,12β-diol (XXVI) (58.3%). Under Helferich's conditions, mercury cyanide caused no change in the initial triterpene (II), but under the action of $HgBr_2$, which is formed as the result of the interaction of the acetobromoglucose and the mercury cyanide, the aglycon was likewise converted into a mixture of weakly polar substances.

EXPERIMENTAL

IR spectra were recorded on a Specord 75 IR spectrophotometer in $CHCl_3$ solution, and ^1H and ^{13}C NMR spectra were measured on a Bruker WM-250 Fourier spectrometer with working frequencies of 250 MHz for ^1H and 62.9 MHz for ^{13}C at 30°C in $CDCl_3$. The chemical shifts are expressed in the δ scale relative to TMS. The accuracy of measurement was ±1.5Hz for ^{13}C and ±0.15 Hz for ^1H. The assignment of the signals in the ^{13}C spectra was made by the method of off-resonance spin decoupling and on the basis of literature analogies [5]. Optical rotations were determined in a Perkin-Elmer 141 instrument in a cell 10 cm long at 20°C, and the melting points of the substances on a Boëtius stage.

Column chromatography was performed on KSK silica gel (120-150 mesh) in the hexane—acetone, (15:1) → (5:1), and the benzene—methanol, (250:1) → (80:1), systems.

The individuality of the substances was checked with the aid of TLC in a fixed layer of silica gel in the benzene—chloroform—methanol (6:4:1), benzene—ethanol (10:1), and hexane—acetone (2:1) and (3:2) systems. The substances were revealed with 10% H_2SO_4 in ethanol followed by heating at 100-200°C.

The results of elementary analysis for all the compounds obtained for the first time agreed with the calculated figures. The deacetylation of (VIII)-(XVII) with a 0.1 N solution of sodium methanolate in methanol led to the corresponding free glucosides (yields 90-95%).

Betulafolienetriol [dammar-24-ene-3α,12β,20(S)-triol] (II) was isolated from an ethereal extract of the leaves of *Betula platyphylla* followed by chromatography on silica gel and crystallization from acetone; mp 195-196°C. According to the literature [6]: mp 197-198°C.

12β,20(S)-Dihydroxydammar-24-en-3-one (III) was obtained by the oxidation of (II) with chromium trioxide in pyridine; mp 196-198°C (acetone), according to the literature [6]: mp 202-203°C (methanol); [13]: mp 196-199°C (acetone).

Dammar-24-ene-3β,12β,20(S)-triol (I) was obtained by the reduction of (III) with sodium tetrahydroborate in isopropanol; mp 197-198°C (acetone); $[\alpha]_D^{20}$ +26.7° (c 1.0; chloroform). According to the literature [14]: mp 197-200°C (benzene).

Dammar-24-ene-3α,12β,20(S)-triol 3,12-di-O-acetate (VI) was obtained by the acetylation of (II) with acetic anhydride in pyridine at room temperature for a day; amorphous, $[\alpha]_D^{20}$ −15.1° (c 1.0; chloroform). IR spectrum (ν, cm^{-1}): 1598, 1720, 3535. ^1H spectrum (δ, ppm): 0.84 (s, 3 H), 0.88 (s, 3 H), 0.89 (s, 3 H), 0.99 (s, 3 H), 1.02 (s, 3 H), 1.14 (s, 3 H), 1.64 (s, 3 H), 1.72 (s, 3 H), 2.06 (s, 3 H, OAc), 2.10 (s, 3 H, OAc), 3.11 (s, 1 H, OH), 4.63 (t, 1 H, J = 1.8 Hz, H_e^3); 4.74 (t-d, 1 H, H_a^{12}), 5.16 (t, 1 H, H^{24}).

Dammar-24-ene-3α,12β,20(S)-triol 3-O-acetate (IV) was obtained by the partial deacetylation of (VI) with a 0.1 N solution of sodium methanolate in methanol at room temperature for 4-5 h (TLC monitoring) mp 216-218°C (acetone), $[\alpha]_D^{20}$ −6.9° (c 1.0; chloroform). IR spectrum (ν, cm^{-1}): 1599, 1717, 3373, 3611. ^1H spectrum, (δ, ppm): 0.84 (s, 3 H), 0.89 (s, 3 H), 0.90 (s, 3 H), 0.93 (s, 3 H), 1.00 (s, 3 H), 1.20 (s, 3 H), 1.63 (s, 3 H), 1.70 (s, 3 H), 2.06 (s, 3 H, OAc), 3.61 (t-d, 1 H, H_a^{12}), 4.63 (t, J = 1.8 Hz, 1 H, H_e^3), 5.17 (t, 1 H, H^{24}). According to the literature [15]: mp 216-218°C (acetone).

Dammar-24-ene-3β,12β,20(S)-triol 3,12-di-O-acetate (VII) was obtained by the acetylation of (I) with acetic anhydride in pyridine at room temperature for a day mp 172-173°C (acetone), $[\alpha]_D^{20}$ +9.8° (c 1.0; chloroform). IR spectrum (ν, cm^{-1}): 1598, 1720, 3535, ^1H spectrum (δ, ppm): 0.85 (s, 6 H), 0.88 (s, 3 H), 0.95 (s, 3 H), 1.01 (s, 3 H), 1.13 (s, 3 H), 1.64 (s, 3 H), 1.71 (s, 3 H), 2.04 (s, 3 H, OAc), 2.05 (s, 3 H,OAc), 3.04 (s, 1 H, OH), 4.48 (m, 1 H, H_a^3), 4.73 (t-d, 1 H, H_a^{12}), 5.16 (t, 1 H, H^{24}).

Dammar-24-ene-3β,12β,20(S)-triol 3-O-acetate (V) was obtained by the partial deacetylation of (VII) with a 0.1 N solution of sodium methanolate in methanol at room temperature for 4-5 h; mp 175-177°C (acetone), $[\alpha]_D^{20}$ +33.5° (c 1.0; chloroform). IR spectrum (ν, cm^{-1}) 1600, 1718, 3372, 3600. ^1H spectrum (δ, ppm): 0.86 (s, 6 H), 0.89 (s, 3 H), 0.91 (s, 3 H), 0.99 (s, 3 H), 1.20 (s, 3 H), 1.64 (s, 3 H), 1.70 (s, 3 H), 2.07 (s, 3 H, OAc), 3.60 (t-d, 1 H, H_a^{12}), 4.48 (m, 1 H, H_a^3), 5.17 (t, 1 H, H^{24}).

General Procedure for the Performance of Condensation in the Presence of Silver Oxide. The initial alcohol and 1/3 of the total amount of silver oxide and of α-acetobromoglucose in absolute methylene chloride were stirred at room temperature until the α-acetobromoglucose had disappeared from the reaction mixture (monitoring by TLC), and then the remaining amount of the silver oxide and the α-acetobromoglucose was added in two portions. The reaction was continued until one of the starting materials had disappeared from the reaction mixture, which was then diluted with methyl chloride and was filtered from the silver compounds. The solvent was distilled off and the dry residue was chromatographed on a column of silica gel.

3-Monoglucoside (VIII): mp 214-217°C (ethanol), $[\alpha]_D^{20}$ −21.1° (c 1.0; chloroform). IR spectrum (ν, cm^{-1}): 1594, 1751, 3366, 3594. ^1H spectrum (δ, ppm): 0.83 (s, 3 H), 0.88 (s, 3 H), 0.90 (s, 6 H), 0.97 (s, 3 H), 1.20 (s, 3 H), 1.64 (s, 3 H), 1.70 (s, 3 H), 2.02 (s, 3 H, OAc), 2.04 (s, 6 H, 2 × OAc), 2.10 (s, 3 H, OAc), 3.34 (t, 1 H, 2 × J = 1.8 Hz, H_e^3), 3.55 (t-d, 1 H, H_a^{12}), 3.64 (m, 1 H, $H^{5'}$), 4.14 — 4.24 (m, 2 × H, $2H^{6'}$), 4.50 (d, 1 H, J = 7.8 Hz, $H^{1'}$), 4.91 (s, 1 H, OH), 5.01 (d-d, 1 H, J = 7.5 Hz, J = 9.0 1 Hz, $H^{2'}$), 5.08 (t, 2 × J = 9.5 Hz, $H^{4'}$), 5.17 (t, 1 H, H^{24}), 5.22 (t, J = 9.5 Hz, J = 9.5 Hz, $H^{3'}$).

3-Monoglucoside (IX): mp 212-214°C (ethanol), $[\alpha]_D^{20}$ +12.5° (c 1.0; chloroform). IR spectrum (ν, cm^{-1}): 1595, 1750, 3367, 3595. ^1H spectrum (δ, ppm): 0.74 (s, 3 H), 0.87 (s, 6 H), 0.90 (s, 3 H), 0.98 (s, 3 H), 1.20 (s, 3 H), 1.64 (s, 3 H), 1.70 (s, 3 H), 2.01 (s, 3 H, OAc), 2.03 (s, 3 H, OAc), 2.04 (s, 3 H, OAc), 2.09 (s, 3 H, OAc), 3.08 (d-d, 1 H, J = 4.9 Hz, J = 10.8 Hz, H_a^3), 3.59 (t-d, 1 H, J = 10 Hz, J = 10 Hz, J = 5 Hz, H_a^{12}), 3.68 (m, 1 H, $H^{5'}$), 4.11-4.25 (m, 2H, 2 × $H^{6'}$), 4.53 (d, 1 H, J = 7.9 Hz, $H^{1'}$), 5.04-5.25 (m, $H^{2'}$, $H^{3'}$, $H^{4'}$, H^{24}, OH).

12-Monoglucoside (X): IR spectrum (ν, cm^{-1}): 1599, 1754, 3474, 3634. ^1H spectrum (δ, ppm): 0.85 (s, 3 H), 0.88 (s, 3 H), 0.90 (s, 3 H), 0.95 (s, 3 H), 0.97 (s, 3 H), 1.11 (s 3 H), 1.66 (s, 3 H), 1.72 (s, 3 H), 2.00 (s, 3 H, OAc), 2.02 (s, 3 H, OAc), 2.04 (s, 3 H, OAc), 2.10 (s, 3 H, OAc), 3.43 (s, 1 H, J = 2.8 Hz, H_e^3), 3.66 (m, 1 H, $H^{5'}$), 3.81 (t-d, 1 H, 2 × J = 10.0 Hz, J = 5.0 Hz, H_a^{12}), 4.03 (s, 1 H, OH), 4.21 (d, 2 H, J = 3.8 Hz, 2 × $H^{6'}$), 4.73 (d, 1 H, J = 8.1 Hz, $H^{1'}$), 4.92-5.22 (m, $H^{2'}$, $H^{3'}$, $H^{4'}$, H^{24}).

The acetylation of the monoglucoside (X) with acetic anhydride in pyridine at room temperature for a day led to a compound identical with the glucoside (XIX) from Experiment 3.

20-Monoglucoside (XII): IR spectrum (ν, cm^{-1}): 1599, 1754, 3474, 3634. ^1H spectru (δ, ppm): 0.84 (s, 3 H), 0.88 (s, 6 H), 0.94 (s, 3 H), 0.97 (s, 3 H), 1.18 (s, 3 H), 1.59 (s, 3 H), 1.67 (s, 3 H), 2.00 (s, 3 H, OAc), 2.02 (s, 3 H, OAc), 2.04 (s, 3 H, OAc), 2.05 (s, 3 H, OAc), 3.41 (t, 1 H, H_e^3). 3.52 (t-d, 1 H, H_a^{12}), 3.67 (m, 1 H, $H^{5'}$), 4.12 (d, 2 H, 2 × $H^{6'}$), 4.31 (s, 1 H, OH), 4.85 (d, 1 H, J = 8.0 Hz, $H^{1'}$), 4.95-5.24 (m, $H^{2'}$, $H^{3'}$, $H^{4'}$, H^{24}). The acetylation of (XII) by acetic anhydride in pyridine at 90°C for 7 h led to the 3,12-diacetate (XXVII), with mp 108-110°C (hexane), $[\alpha]_D^{20}$ −22.4° (c 0.8; chloroform). ^1H spectrum (δ, ppm): 0.84 (s, 3 H), 0.87 (s, 3 H), 0.88 (s, 3 H), 0.97 (s, 6 H), 1.18 (s, 3 H), 1.59 (s, 3 H), 1.65 (3, 3 H), 2.00-2.11 (s, 18 H, 6 × OAc), 3.66 (m, 1 H, $H^{5'}$), 4.12 (t, 2 H, 2 × $H^{6'}$), 4.62 (t, 1 H, H_e^3), 4.67 (d, 1 H, J = 8.0 Hz, $H^{1'}$), 4.84 (t-d, 1 H, H_a^{12}), 4.91-5.23 (m, $H^{2'}$, $H^{3'}$, $H^{4'}$, H^{24}).

Acetylation of the Mixture of Monoglucosides (XI) and (XIII). The mixture of monoglucosides (XI) and (XIII) (280 g) was acetylated with acetic anhydride (0.7 ml) in 1.5 ml of pyridine for 3 days at room temperature. After the usual working up, the reaction mixture was chromatographed on a column of silica gel in the hexane—acetone (10:1) system. This yielded 74 mg of (XVIII) and 164 mg of (XX) (30.1 and 69.9%, respectively).

Dammar-24-ene-3β,12β,20(S)-triol 3,12-di-O-Acetate 20-O-(2',3',4',6'-Tetra-O-acetyl-β-D-glucopyranoside) (XVIII): mp 176-177°C (ethanol), $[\alpha]_D^{20}$ +7.5° (c 0.83; chloroform). IR spectrum (ν, cm^{-1}): 5 1597, 1753 [sic]. ^1H spectrum (δ, ppm): 0.84 (s, 6 H), 0.87 (s, 3 H), 0.92 (s, 3 H), 0.96 (s, 3 H), 1.17 (s, 3 H), 1.59 (s, 3 H), 1.65 (s, 3 H), 1.98 (s, 3 H: OAc), 2.00 (s, 3 H, OAc), 2.03 (s, 3 H, OAc), 2.04 (s, 3 H, OAc), 2.0 (s, 3 H, OAc), 2.06 (s, 3 H, OAc), 3.65 (m, 1 H, $H^{5'}$), 4.11 (t, 2 H, 2 × $H^{6'}$), 4.48 (m, 1 H, H_a^3), 4.66 (d, 1 H, J = 8.2 Hz, $H^{1'}$), 4.83 (t-d, 1 H, H_a^{12}), 4.92-5.19 (m, $H^{2'}$, $H^{3'}$, $H^{4'}$, H^{24}). According to the literature [9]: mp 177-178°C.

Dammar-24-ene-3β,12β,20(S)-triol 3-O-Acetate12-O-(2',3',4',6'-Tetra-O-acetyl-β-D-glucopyranoside) (XX): mp 137-140°C (ethanol), $[\alpha]_D^{20}$ +20.0° (c 0.75; chloroform). IR spectrum (ν, cm^{-1}): 1600, 1718, 1752, 3474. ^1H spectrum (δ, ppm): 0.87 (s, 6 H), 0.88 (s, 3 H), 0.89 (s, 3 H), 0.97 (s, 3 H), 1.11 (s, 3 H), 1.64 (s, 3 H), 1.70 (s, 3 H), 1.98 (s, 3 H, OAc), 2.01 (s, 3 H, OAc), 2.03 (s, 3 H, OAc), 2.06 (s, 3 H, OAc), 2.09 (s, 3 H, OAc), 3.67 (m, 1 H, $H^{5'}$), 3.85 (t-d, 1 H, H_a^{12}), 3.95 (s, 1 H, OH), 4.22 (d, 2 H, J = 3.9 Hz, 2 × $H^{6'}$), 4.48 (m, 1 H, H_a^3), 4.74 (d, 1 H, J = 8.2 Hz, $H^{1'}$), 4.92-5.23 (m, $H^{2'}$, $H^{3'}$, $H^{4'}$, H^{24}).

3,12-Diglucoside (XIV): mp 158-160°C (ethanol), $[\alpha]_D^{20}$ −22.9° (c 0.66; chloroform). IR spectrum (ν, cm^{-1}): 1600, 1752, 3474. ^1H spectrum (δ, ppm): 0.84 (s, 3 H), 0.87 (s, 3 H), 0.90 (s, 3 H), 0.92 (s, 3 H), 0.95 (s, 3 H), 1.11 (s, 3 H), 1.64 (s, 3 H), 1.70 (s, 3 H), 2.00-2.10 (s, 24 H, 8 × OAc), 3.38 (t, 1 H, H_e^3), 3.64 (m, 2 H, 2 × $H^{5'}$), 3.79 (t-d, 1 H, H_a^{12}), 3.99 (s, 1 H, OH), 4.12-4.24 (m, 4 H, 4 × $H^{6'}$), 4.53 (d, 1 H, J = 8.0 Hz, $H^{1'} - C^3$), 4.71 (d, 1 H, J = 8.0 Hz, $H^{1'} - C^{12}$), 4.91-5.23 (m, $2H^{2'}$, $2H^{3'}$, $3H^{4'}$, H^{24}).

3,12-Diglucoside (XV): mp 193-195°C (ethanol), $[\alpha]_D^{20}$ +8.7° (c 1.0; chloroform). IR spectrum (ν, cm^{-1}): 1600, 1752, 3474. ^1H spectrum (δ, ppm): 0.86 (s, 3 H), 0.88 (s, 6 H), 0.91 (s, 3 H), 0.99 (s, 3 H), 1.11 (s, 3 H), 1.64 (s, 3 H), 1.70 (s, 3 H), 2.00 (s, 3 H, OAc), 2.02 (s, 9 H, 3 × OAc), 2.05 (s, 6 H, 2 × OAc), 2.10 (s, 3 H, OAc), 2.12 (s, 3 H, OAc), 3.09 (d-d, 1 H, J = 4.7 Hz, J = 11.0 Hz, H_a^3), 3.64 (m, 2 H, 2 $H^{5'}$), 3.80 (t-d, 1 H, H_a^{12}), 3.98 (s, 1 H, OH), 4.12-4.24 (m, 4 H, 4 × $H^{6'}$), 4.50 (d, 1 H, J = 8.0 Hz, $H^{1'} - C^3$), 4.73 (d, 1 H, J = 8.0 Hz, $H^{1'} - C^{12}$), 4.91-5.23 (m, $2H^{2'}$, $2H^{3'}$, $2H^{4'}$, H^{24}).

3,20-Diglucoside (XVI): mp 169-173°C (hexane), $[\alpha]_D^{20}$ −12.0° (c 1.0; chloroform). IR spectrum (ν, cm^{-1}): 1600, 1755, 3470. ^1H spectrum (δ, ppm): 0.83 (s, 3 H), 0.87 (s 6 H), 0.90 (s, 3 H), 0.95 (s, 3 H), 1.27 (s, 3 H), 1.59 (s, 3 H), 1.67 (s, 3 H), 2.00-2.09 (s, 24 H, 8 × OAc), 3.32 (t, 1 H, 2 × J = 1.8 Hz, H_e^3), 3.50 (t-d, 1 H, H_a^{12}), 3.59-3.62 (m, 2 H, 2 × $H^{5'}$), 4.11 (d, 2 H, J = 4.0 Hz, 2 × $H^{6'}$ at C^{20}), 4.15-4.24 (m, 2 H, 2 × $H^{6'}$ at C^3), 4.49 (d, 1 H, J = 8.0 Hz, $H^{1'}$ at C^3), 4.85 (d, 1 H, J = 8.0 Hz, $H^{1'}$ at C^{20}), 4.90-5.22 (m, 2 × $H^{2'}$, 2 × $H^{3'}$, 2 × $H^{4'}$, H^{24}).

3,20-Diglucoside (XVII): mp 120-125°C (hexane—acetone), $[\alpha]_D^{20}$ +19.8° (c 0.75; chloroform). IR spectrum (ν, cm^{-1}): 1600, 1755, 3470. ^1H spectrum (δ, ppm): 0.74 (s, 3 H), 0.85 (s, 3 H), 0.86 (s, 3 H), 0.90 (s, 3 H), 1.06 (s, 3 H), 1.26 (s, 3 H), 1.59 (s, 3 H), 1.67 (s, 3 H), 2.01-2.09 (s, 24 H, 8 × OAc), 3.07 (d-d, 1 H, H_a^3), 3.50 (t-d, 1 H, H_a^{12}), 3.68 (m, 2 H, 2 × $H^{5'}$), 4.11 (d, 2 H, 2 × $H^{6'}$ at C^{20}), 4.14-4.26 (m, 2 H, 2 × $H^{6'}$ at C^3), 4.33 (s, 1 H, OH), 4.53 (d, 1 H, J = 8.0 Hz, $H^{1'}$ at C^3), 4.85 (d, 1 H, J = 8.0 Hz, $H^{1'}$ at C^{20}), 4.01-5.23 (m, 2 × $H^{2'}$, 2 × $H^{3'}$, 2 × $H^{4'}$, H^{24}).

Dammar-24-ene-3α,12β,20(S)-triol 3-O-Acetate 12-O-(2',3',4',6'-Tetra-O-acetyl-β-D-glucopyranoside) (XIX): mp 188-191°C (ethanol), $[\alpha]_D^{20}$ −18.8° (c 0.9; chloroform). IR spectrum (ν, cm^{-1}): 1597, 1718, 1751, 3469. ^1H spectrum (δ, ppm): 0.86 (s, 3 H), 0.89 (s, 3 H), 0.91 (s, 3 H), 0.94 (s, 3 H), 0.98 (s, 3 H), 1.12 (s, 3 H), 1.64 (s, 3 H), 1.70 (s, 3 H), 2.00 (s, 3 H, OAc), 2.02 (s, 3 H, OAc), 2.04 (s, 3 H, OAc), 2.09 (s, 3 H, OAc), 2.10 (s, 3 H, OAc), 3.67 (m, 1 H, $H^{5'}$), 3.85 (t-d, 1 H, H_a^{12}), 4.01 (s, 1 H, OH), 4.22 (d, 2 H, J = 3.9 Hz, 2 × $H^{6'}$), 4.67 (t, 1 H, J = 3.0 Hz, H_e^3), 4.74 (d, 1 H, J = 8.2 Hz, $H^{1'}$), 4.92-5.23 (m, $H^{2'}$, $H^{3'}$, $H^{4'}$, H^{24}).

Dammar-24-ene-3α,12β,20(S)-triol 3-O-Acetate 20-O-(2',3',4',6'-tetra-O-acetyl-β-D-glucopyranoside) (XXI): mp 168-172°C (ethanol), $[\alpha]_D^{20}$ −19.1° (c 1.0 chloroform). IR spectrum (ν, cm^{-1}): 1597, 1718, 1751, 3469. ^1H spectrum (δ, ppm): 0.84 (s, 3 H), 0.89 (s, 6 H), 0.92, (s, 3 H), 0.98 (s, 3 H), 1.12 (s, 3 H), 1.60 (s, 3 H), 1.67 (s, 3 H), 2.00 (s, 3 H, OAc), 2.02 (s, 3 H, OAc), 2.04 (s, 3 H, OAc), 2.09 (s, 3 H, OAc), 2.10 (s, 3 H, OAc), 3.68 (m, 1 H, $H^{5'}$), 3.58 (t-d, 1 H, H_a^{12}), 4.11 (d, 2 H, J = 4.0 Hz, 2 × $H^{6'}$), 4.31 (s, 1 H, OH), 4.63 (t, 1 H, J = 3.0 Hz, H_e^3), 4.85 (d, 1 H, J = 8.2 Hz, $H^{1'}$), 4.92-5.23 (m, $H^{2'}$, $H^{3'}$, $H^{4'}$, H^{24}).

Dammar-24-ene-3β,12β,20(S)-triol 3-O-Acetate 20-O-(2',3',4',6'-tetra-O-acetyl-β-D-glucopyranoside) (XXII): Amorphous. $[\alpha]_D^{20}$ +21.5° (c 1.0; chloroform). IR spectrum (ν, cm^{-1}): 1597, 1718, 1753, 3472. ^1H spectrum (δ, ppm): 0.85 (s, 6 H), 0.86 (s, 3 H), 0.89 (s, 3 H), 0.97 (s, 3 H), 1.27 (s, 3 H), 1.59 (s, 3 H), 1.67 (s, 3 H), 1.99-2.09 (s, 15 H, 5 × OAc), 3.53 (t-d, 1 H, H_a^{12}), 3.68 (m, 1 H, $H^{5'}$), 4.12 (d, 2 H, J = 4.0 Hz, 2 × $H^{6'}$), 4.31 (s, 1 H, OH), 4.49 (m, 1 H, H_a^3), 4.87 (d, 1 H, J = 8.0 Hz, $H^{1'}$), 4.91-5.22 (m, $H^{2'}$, $H^{3'}$, $H^{4'}$, H^{24}).

Condensation of (II) with D-Glucose (tert-Butyl Orthoacetate) in the Presence of 2,4,6-Collidinium Perchlorate. A mixture of 460 mg of the triol (II) and 10 ml of absolute chlorobenzene was boiled with azeotropic distillation for 10 min, and then, in three portions with

an interval of 20 min, 2,4,6-collidinium perchlorate (4 mg in each portion) and D-glucose tert-butyl orthoacetate (1 mmole in each portion) were added and the reaction mixture was then boiled under the same conditions for another 20 min and was evaporated and the residue was dried. The dry residue was chromatographed with the hexane–acetone (40:1) → (5:1) system. Fractions of chromatographically homogeneous compounds were obtained: 180 mg (22.1%) of (XXIII) and 530 mg (48.1%) of (XXV).

Dammar-20(22),24-diene-3α,12β-diol 3-O-Acetate 12-O-(2',3',4',6'-Tetra-O-acetyl-β-D-glucopyranoside) (XXIII): IR spectrum (ν, cm^{-1}): 1600, 1625, 1725, 1750. ^1H spectrum (δ, ppm): 0.84 (s, 3 H), 0.89 (s, 6 H), 0.92 (s, 3 H), 1.00 (s, 3 H), 1.61 (s, 3 H), 1.66 (s, 3 H), 1.70 (s, 3 H), 2.00-2.09 (s, 15 H, 5 × OAc), 3.65 (m, 1 H, $H^{5'}$), 3.74 (t-d, 1 H, H_a^{12}), 4.22 (m, 2 H, 2 × $H^{6'}$), 4.67 (t, 1 H, H_e^3), 4.42 (d, 1 H, J = 8.0 Hz, $H^{1'}$), 4.96-5.23 (m, $H^{2'}$, $H^{3'}$, $H^{4'}$, H^{22}, H^{24}).

Dammar-20(22),24-diene-3α,12β-diol 3,12-Di-O-(2',3',4',6'-Tetra-O-acetyl-β-D-glucopyranoside) (XXV): IR spectrum (ν, cm^{-1}): 1600, 1625, 1750. ^1H spectrum (δ, ppm): 0.84 (s, 3 H), 0.86 (s, 3 H), 0.87 (s, 3 H), 0.91 (s, 3 H), 0.97 (s, 3 H), 1.50 (s, 3 H), 1.58 (s, 3 H), 1.69 (s, 3 H), 2.00-2.09 (s, 24 H, 8 × OAc), 3.37 (t, 1 H, H_e^3), 3.65 (m, 2 H, 2 × $H^{5'}$), 3.74 (t-d, 1 H, H_a^{12}), 4.11-4.22 (m, 4 H, 2 × 2$H^{6'}$), 4.53 (d, 1 H, J = 8.0 Hz, $H^{1'}$ at C^3), 4.42 (d, 1 H, J = 8.0 Hz, $H^{1'}$ at C^{12}), 4.98-5.23 (m, $H^{2'}$, $H^{3'}$, $H^{4'}$, H^{22}, H^{24}).

Condensation of (II) with α-Acetobromoglucose in the Presence of Mercury Cyanide. A mixture of 460 mg (1 mole) of the triol (II), 820 mg (2 mmole) of α-acetobromoglucose, and 500 mg of mercury cyanide in 10 ml of absolute nitromethane was stirred at room temperature for 4 h and the solution was then diluted with chloroform, washed with water, dried and evaporated. The dry residue was chromatographed in the hexane–acetic acid (40:1) → (5:1) system. Chromatographically homogeneous substances were isolated: 70 mg (8.6%) of (XXIII), 150 mg (19.4%) of (XXIV), and 290 mg (26.3% of (XXV).

Dammar-20(22),24-diene-3α,12β-diol 12-O-(2',3',4',6'-Tetra-O-acetyl-β-D-glucopyranoside) (XXIV). IR spectrum (ν, cm^{-1}): 1610, 1630, 1750, 3600. ^1H spectrum (δ, ppm): 0.87 (s, 3 H), 0.89 (s, 6 H), 0.96 (s, 3 H), 1.00 (s, 3 H), 1.54 (s, 3 H), 1.62 (s, 3 H), 1.70 (s, 3 H), 1.98-2.10 (s, 12 H, 4 × OAc), 3.38 (t, 1 H, H_e^3), 3.62 (m, 1 H, $H^{5'}$), 3.74 (m, 1 H, H_a^{12}), 4.03 (s, 1 H, OH), 4.21 (m, 2 H, 2 × $H^{6'}$), 4.42 (d, 1 H, J = 8.0 Hz, $H^{1'}$), 4.95-5.23 (m, $H^{2'}$, $H^{3'}$, $H^{4'}$. H^{22}, H^{24}).

Control Experiment. A mixture of 150 mg of (II), 2 mg of 2,4,6-collidinium perchlorate, and 5 ml of absolute chlorobenzene was boiled with azeotropic distillation for 15 min. Then the solution was evaporated. The residue was dried and was chromatographed on a column of silica gel in the hexane–acetone (30:1) system. This gave 84 mg (58.3%) of compound (XXVI). ^1H spectrum (δ, ppm): 0.84 (s, 3 H), 0.89 (s, 6 H), 0.94 (s, 3 H), 1.02 (s, 3 H), 1.61 (s, 3 H), 1.66 (s, 3 H), 1.66 (s, 3 H), 3.39 (t, 1 H, H_e^3), 3.74 (t-d, 1 H, H_a^{12}), 5.06 (t, 1 H, J = 7.2 Hz, H^{24}), 5.39 (t, 1 H, J = 6.8 Hz, H^{22}).

SUMMARY

1. The glycosylation of betulafolienetriol (dammar-24-ene-3α,12β,20(S)-triol) under the conditions of the Koenigs–Knorr, the Helferich, and the orthoester methods has been studied.

2. The 3-, 12-, and 20-mono- and 3,12- and 3,20-di-O-β-D-glucopyranosides of betulafolienetriol and of its 3-epimer have been synthesized for the first time.

3. It has been established that the glycosylation of dammar-24-ene-3α,12β,20(S)-triol under the conditions of the Helferich and the orthoester methods is accompanied by a side reaction of dehydration in the side chain and leads to the corresponding 20-dehydroxy derivatives.

LITERATURE CITED

1. T. Yokozawa, T. Kobayashi, A. Kawai, N. Oura, and Y. Kawashima, Chem. Pharm. Bull., 33, No. 2, 722 (1985).
2. V. K. Singh, C. X. George, N. Singh, S. S. Agarwal, and B. M. Gupta, Planta Medica, 47, 234 (1983).
3. Y. Takemoto, T. Ueyama, H. Saito, S. Horio, S. Sanada, J. Shoji, S. Yahara, O. Tanaka, S. Shibata, Chem. Pharm. Bull., 32, No. 8, 3128 (1984).
4. J. Asakawa, R. Kasai, K. Yamasaki, and O. Tanaka, Tetrahedron, 33, 1935 (1977).

5. N. Nagai, O. Tanaka, and S. Shibata, Tetrahedron, 27, 881 (1971).
6. F. G. Fischer and N. Seiler, Ann. Chem., 626, 185 (1959).
7. N. I. Uvarova, G. V. Malinovskaya, Yu. N. El'kin, V. V. Isakov, A. K. Dzizenko, and G. B. Elyakov, Khim. Prir. Soedin., 757 (1976).
8. M. Salome, W. German Patent No. 2,732,749; Chem. Abstr., 90, No. 26, 210111w (1979).
9. I. Yoshioka, T. Sugawara, K. Imai, and I. Kitagawa, Chem. Pharm. Bull., 20, No. 11, 2418 (1972).
10. S. Yahara, O. Tanaka, and T. Komori, Chem. Pharm. Bull., 24, (9), 2204 (1976).
11. B. Helferich and K. Weis, Chem. Ber., 89, 314 (1956).
12. N. K. Kochetkov, A. F. Bochkov, T. A. Sokolovskaya, and V. I. Snyatkova, Carbohydr. Res., 16, 17 (1971).
13. M. Nagai, N. Tanaka, O. Tanaka, and S. Ishikawa, Chem Pharm. Bull., 9, 2061 (1973).
14. R. Kasai, K. Shinzo, and O. Tanaka, Chem. Pharm. Bull., 24, No. 3, 400 (1976).
15. R. Kasai, K. Shinzo, O. Tanaka, and K. Kakai, Chem. Pharm. Bull., 22, No. 5, 1213 (1974).

TRITERPENE GLYCOSIDES AND THEIR GENINS FROM *Thalictrum foetidum*.

IV. STRUCTURE OF CYCLOFOETIGENIN B

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A glycoside isolated from the epigeal part of *Thalictrum foetidum* (Ranunculaceae) has yielded a new genin — cyclofoetigenin B — the structure of which has been established on the basis of chemical transformations and spectral characteristics as 24S-cycloartane-3β,16β,24,25,30-pentaol.

We are continuing the study of the triterpenoids of the plant *Thalictrum foetidum*, L. (Ranunculaceae) [1-3]. The present paper is devoted to a proof of the structure of the genin of glycoside B [1] which we have called cyclofoetigenin B (VI, scheme 1).

The acid hydrolysis of glycoside B (I) gave product (IV) with the composition $C_{30}H_{52}O_5$. The PMR spectrum of this compound showed the signals of seven methyl groups in the strong field and the signal of one olefinic proton at 5.14 ppm (Table 1). It follows from these facts that product (IV) consisted of a tetracyclic triterpenoid including one trisubstituted double bond. The presence of the latter was also shown by an absorption band in the UV spectrum of substance (IV) at 204 nm and by the signals of the corresponding carbon atoms in the ^{13}C NMR spectrum at 149.0 and 115.2 ppm (Table 2).

In the PMR spectrum of glycoside B (I) one-proton doublets interacting with one another in the manner of an AB system are observed in the strong field at 0.24 and 0.46 ppm, showing the presence of a cyclopropane ring, and there are the signals of six methyl groups, while there is no signal of an olefinic proton. It can therefore be assumed that product (IV) is not the native genin but an artifact — a derivative of the lanostane series formed in the acid isomerization of the corresponding cycloartane triterpenoids.

The acetylation of the triterpenoid (IV) with acetic anhydride in pyridine gave the tetraacetate (XI) and the pentaacetate (X). Consequently, all the oxygen atoms are present in hydroxy groups and the side chain of compound (IV) has an acyclic structure.

The mass spectrum of the methyl steroid (IV) has the peak of an ion with m/z 329 ($C_{22}H_{33}O_2$) arising as the result of the splitting out of the side chain and the elimination of one molecule of water (scheme 2). Hence, two hydroxy groups are present in the side chain and the other three in the polycyclic part of the molecule.

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