4. 24ξ,25-Dimethyl-5α-cholestane-2β,3α,6α-triol-2β,3α,6α-tri(sodium sulfate) (I). Yield 3.5 mg (0.5%), R_f 0.27. ^{1}H NMR spectrum (CD_3OD, δ): 0.49 (CH_3-18, s, 3H); 1.13 (CH_3-19, s, 3H); 0.93 (CH_3-21, d, J = 6.8 Hz, 3H); 0.85 (CH_3-28, d, J = 6.8 Hz, 3H); 0.87 (CH_3-26, -27, -29; s, 9H); 4.78 (C-6, td, 1H); 5.64 (C-2, m, 1H); 5.89 (C-3, m, 1H).

SUMMARY

The inhibiting and membranolytic properties of polysulfated steroids from sponges and of derivatives obtained from them have been studied. It has been shown that in this series of compounds physiological acivity depends on biphilicity.

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GLYCOSYLATION OF TRITERPENOIDS OF THE DAMMARANE SERIES. V. β-D-GLUCOPYRANOSIDES OF 12β-ACETOXY-20(S),24(R)-EPOXYDAMMARANE-3α,25-DIOL AND OF 3-EPIOCOTILLOL

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The synthesis of glucosides from the 12-O-acetyl derivatives of betulafolienetriol oxide and of 3-epiocotillol has been carried out under the conditions of the Koenigs-Knorr reaction and of Helferich's modification. It has been established that glycosylation in the presence of silver zeolite and mercury cyanide takes place nonregioselectively and gives a mixture of the corresponding 3-O- and 25-O-mono- and 3,25-di-O-β-D-glucopyranosides. The structures of all the newly obtained glucosides have been established on the basis of IR and ^{13}C NMR spectroscopy.

The main component of the unsaponifiable fraction of extracts of the leaves of Betula nana L. and B. exilis Sukacz [1] and 3-epiocotillol [20(S),24(R)-epoxydammarane-3α,25-diol (1)], which, as compared with betulafolienetriol oxide (2), lacks a hydroxy group at C^{12}. As reported previously, a decisive influence on the regiochemistry of the glycosylation of the triol (2) and its 3-epimer is exerted by a strong intramolecular hydrogen bond (intraHB) between the proton of the 12β-OH group and the oxygen atom of the tetrahydrofuran ring [2]. A study of the glycosylation of the diol (1) is therefore of interest not only because it is the main component of extracts of these birches but also because it is a compound in which there is no strong intraHB and, consequently, no factor which could appreciably raise the nucleophilicity of the oxygen atom of one of the hydroxy groups.

In the same connection we have studied the glycosylation of the 12-O-acetyl derivative of betulafolienetriol (3), one of the components of extracts of the leaves of B. platyphilla

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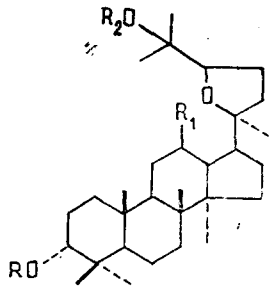
TABLE 1. Conditions and Results of the Condensation of Compounds (1) and (3) with ABG Under Various Conditions

Expt. No.	Initial substances			Reaction conditions*		Reaction products, % †				Recovery† of init., %
	alcohol, mmole	ABG, mmole × n (times)	HBR acceptor, g × n (times)	solvent, ml	time	monoglucosides 3-O-	monoglucosides 25-O-	diglucosides	total yield	
1	(1),1	6×1	Ag zeolite 6	CH_2Cl_2. 15	3 days	11,7 (4)	10,4 (5)	2,5 (6)	24,6	39,0
2	(1),1	1×8	Ag zeolite 2×8	CH_2Cl_2—CH_3NO_2, 20 (1:1)	4 days	20.2 (4)	15,0 (5)	29,6 (6)	64,8	—
3	(1),1	2×4	Ag zeolite 4×4	$(CH_2)_2Cl_2$—CH_3NO_2 17,5 (2,5:1)	8 h	11,3 (4)	14,5 (5)	40,1 (6)	65,9	—
4	(3),1	6×1	Ag zeolite 6	CH_2Cl_2. 15	3 days	10,3 (7)	27,0 (8)	4,0 (9)	41,3	—
5	(3),1	1×8	Ag zeolite 2×8	CH_2Cl_2—CH_3NO_2, 20 (1:1)	2 days	16,5 (7)	22,4 (8)	40,1 (9)	79,0	7,7
6	(1),1	2+2+1	$Hg(CN)_2$, 0,5×2+0,25	$(CH_2)_2Cl_2$—CH_3NO_2, 20 (1:1)	2 days	8,4 (4)	13,6 (5)	6,6 (6)	28,6	26,1
7	(3),1	2+2+1	$Hg(CN)_2$, 0,5×2+0,25	$(CH_2)_2Cl_2$—CH_3NO_2 20 (1:1)	2 days	12,3 (7)	16,5 (8)	11,6 (9)	40,4	20,6
8	(3),1	1	$Hg(CN)_2$, 0,25	CH_3NO_2, 10	1 h	9,6 (7)	30,4 (8)	3,4 (9)	43,4	44,0

*Experiments 1-7 were performed at room temperature (20-22°C) with vigorous stirring, and experiment 8 at 90°C.

†The yields are given on the chromatographically homogeneous substances.



(1) R=R₁=R₂=H
(2) R=H, R₁=OH, R₂=H
(3) R=R₂=H, R₁=OAc
(4) R=Glc(Ac)₄, R₁=R₂=H
(5) R=R₁=H, R₂=Glc(Ac)₄
(6) R=R₂=Glc(Ac)₄, R₁=H
(7) R=Glc(Ac)₄, R₁=OAc, R₂=H
(8) R=H, R₁=OAc, R₂=Glc(Ac)₄
(9) R=R₂=Glc(Ac)₄, R₁=OAc
(10) R=Glc, R₁=R₂=H
(11) R=R₁=H, R₂=Glc
(12) R=R₂=Glc, R₁=H
(13) R=Glc, R₁=OH, R₂=H
(14) R=H, R₁=OH, R₂=Glc
(15) R=R₂=Glc, R₁=OH

[3] and B. nana [1] in which the intraHB between the proton of the 25-OH group and the oxygen atom of the 12β-OAc group is considerably weaker than the intraHB in the triol (2). The glycosylation of compounds (1) and (3) was performed with α-acetobromoglucose (ABG) in the presence of silver zeolite [4] and of mercury cyanide [5]. The results are presented in Table 1. In all cases, condensation led to mixtures of mono- and diglucosides, to which, on the basis of the results of IR, and of ^1H and ^{13}C spectroscopy and elementary analyses the following respective structures were assigned: 3α-(2',3',4',6'-tetra-O-acetyl-β-D-glucopyranosyloxy)-20(S),24(R)-epoxydammaran-25-ol (4), 25-(2',3',4',6'-tetra-O-acetyl-β-D-glucopyranosyloxy)-20(S),24(R)-epoxydammaran-3α-ol (5), 3β,25-di(2',3',4',6'-tetra-O-acetyl-β-D-glucosopyranosyloxy)-20(S),24(R)-epoxydammarane (6); 12β-acetoxy-3α-(2',3',4',6'-tetra-O-acetyl-β-D-glucopyranosyloxy)-20(S),24(R)-epoxydammaran-25-ol (7), 12β-acetoxy-25-(2',3',4',6'-tetra-O-acetyl-β-D-glucopyranosyloxy)-20(S),24(R)-epoxydammaran-3α-ol (8), and 12β-acetoxy-3α,25-di(2',3',4',6'-tetra-O-acetyl-β-D-glucopyranosyloxy)-20(S),24(R)-epoxydammarane (9). The trans configuration of the glycosidic bond in each case was determined on the basis of the values of the chemical shifts and spin–spin coupling constants of the anomeric protons of the sugar components. A doublet signal of the anomeric proton of the glucose residue at C^3 in the ^1H spectra of the monoglucosides (4) and (7) and of the diglucosides (6) and (19) appeared at 4.49-4.51 ppm ($J_{1',2'}$ = 8.0 Hz) and of that at C^{25} at 4.91 ppm ($J_{1',2'}$ = 8.0 Hz) in the monoglucosides (5) and (8) and the diglucosides (6) and (9). The positions of attachment of the glucose residues were confirmed by comparing the ^{13}C spectra of the initial alcohols (1) and (3) with those of the glucosides obtained (4)-(9) (Table 2).

When (1) was condensed with acetobromoglucose in the presence of silver zeolite (Table 1, experiments 1-3), the amount of acylhalogenose added, the order of its addition, and the system of solvent used were varied. The addition of the acylhalogenose to the reaction mixture in portions and also the use of a mixture of solvents (Table 1, experiments 2 and 3) increased the conversion of the initial alcohol, while the replacement of methylene chloride by dichloroethane (Table 1, experiment 3) led to an appreciable rise in the yield of the diglucoside (6). In all the experiments, the ratio of the monoglucosides (4) and (5) was approximately the same.

When compound (3) was glycosylated under the same conditions (Table 1, experiments 4 and 5), the same laws were observed: The yield of the diglucoside (9) and the degree of conversion of the initial alcohol rose with an increase in its solubility through the use of a mixture of solvents, and also when the α-acetobromoglucose was added to the reaction mixture in several portions. In both cases, the yield of the 25-O-glucoside (8) was greater than that of the 3-O-glucoside (7), which can apparently be explained by the increased nucleophilicity of the oxygen atom of the 25-OH group through the existence of a weak intraHB between the proton of the 25-OH group and the oxygen atom of the 12β-OAc group. The IR spectrum of the initial alcohol (3) showed a band of hydroxyl absorption at 3567 cm^{-1} which did not disappear and did not change its position or intensity when the solution was diluted ten times. To confirm this hypothesis we performed the glycosylation of (3) by analogy with the regioselective glycosylation of (2) [6] under the conditions of the previous formation of an ion pair with mercury cyanide and subsequent treatment with α-acetobromoglucose (Table 1, experiment 8). In this case the predominant formation of the 25-O-glucoside (8) was observed, its yield being more than three times as great as that of the 3-O-glucoside (7).

EXPERIMENTAL

IR spectra were recorded on a Specord 75 IR spectrophotometer in chloroform solution, and ^1H and ^{13}C NMR spectra were measured on a Bruker WM-250 spectrometer with a working

TABLE 2. ^{13}C Chemical Shifts of the Initial Alcohols (1) and (3) and their Glucosides (4)-(9) (δ, ppm relative to TMS)

C Atom	Compound							
	(1)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
1	33,7	33,5	33,9	33,9	34,0	33.7	33.6	33,7
2	25.4	25,4	21,0	25,5	20,7	20,9	25.5	21,6
3	76,1	76,0	81,9	76,6	82.4	81,8	76,1	81,9
4	37,6	37,6	37.2	37.8	37,1	37,1	37.4	36.9
5	49,5	49.4	49,9	49,8	50.0	49,7	49,7	49.7
6	18,2	18,2	17,9	18,3	18.1	17.9	18,3	18,0
7	34,5	34,5	35,2	35,6	35,3	34.6	34.7	34.6
8	40.6	39,8	40.7	40,8	40.9	39,9	40,0	40,0
9	50.6	50,5	50.9	50,4	50,0	50,4	49,7	51,1
10	37.3	37.3	37,0	37,5	37,1	36,9	37,7	37,1
11	21,4	28.3	21,5	21.5	23.1	28,3	28,3	28,1
12	27.4	75,6	27,5	27,3	27.5	75,6	76,0	75.7
13	42,9	46.3	43,0	43,1	43.1	46.4	46,3	46,3
14	50,2	52.3	50,2	50,0	51,0	52,4	52,4	52.3
15	31,5	31,2	31,5	31,5	31,6	31.3	31.0	31,1
16	25,7	26,8	25,8	25,5	25,8	26.8	26,0	28,1
17	49.5	49.7	49,6	50,8	50.0	49,7	51,4	49,7
18	16,1	15,9	16.4	16,1	16.4	16,2	16,0	16 2
19	15,5	15,6	15,5	15,7	15.7	15.6	15.7	15,7
20	86 4	85,8	86,5	86,6	86,7	85,8	86 2	85,8
21	23 6	22,3	23,9	23,1	23.1	22,3	22,2	22,0
22	35,7	38,9	35,6	36,0	35,8	38,9	39,1	39,1
23	26,2	26,1	26.2	27,5	27,5	26,1	28.3	26.0
24	83,3	83,4	83,4	82,4	82,4	83.4	82,7	82,3
25	71,4	71,0	71.5	80.2	80,3	71,0	80,0	79.8
26	27,4	27 5	27,5	23,1	23,1	27.5	23,2	23,0
27	24,3	24,2	24,4	22,8	23 1	24.2	23,2	23,0
28	28.4	28,3	28,6	28,5	28,7	28,5	28,5	28,6
29	22,1	21.1	22,2	22,3	22,2	21,8	21.9	21.8
30	16.6	17,7	16,6	16,6	16.4	17,7	17,5	17.4

TABLE 3. ^{13}C Chemical Shifts of the Sugar Component of Glucosides (4)-(9)(δ, ppm relative to TMS)

Compound	C atom					
	1′	2′	3′	4′	5′	6′
(4)	97,8	71,7	73 2	69,1	71,7	62,3
(5)	96,2	71,9	73,6	69,2	71,9	62,7
(6)	98,2	71,9	73,4	69.3	71,9	62,5
	96,1	71,7	73,4	69,3	71,9	62,7
(7)	97,8	71,6	73,0	69 1	71,6	62,1
(8)	96,3	71,9	73,6	69,2	71,9	62,7
(9)	98,0	71,6	73,1	69,0	71,6	62,2
	95,9	71,6	73,3	69,1	71,6	62,5

Note. The ^{13}C signals of the acetate groups are found in the 170.1-170.4 and 20.6-20.8 ppm regions.

frequency of 250 MHz for ^{1}H and 62.9 MHz for ^{13}C at 30°C in deuterochloroform with tetramethylsilane as internal standard. 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 [7]. Optical rotations were determined on 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 carried out on KSK silica gel (120-150 mesh) in the hexane–acetone (30:1) → (5:1) system. The individuality of the substances was checked with the aid of TLC in a fixed layer of silica gel in the hexane–acetone (2:1) and (3:1) and benzene–chloroform–methanol (6:4:1) and (3:2:1) systems. The spots were detected with 10% H_2SO_4 in ethanol with heating at 100-200°C.

The results of the elementary analyses of all the newly obtained compounds agreed with the calculated figures. The deacetylation of (4)-(9) with a 0.1 N solution of sodium methanolate in methanol led to the corresponding free glucosides (10)-(15) with yields of 90-95%.

3-Epicotillol (20(S),24(R)-epoxydammarane-3α,25-diol) (1) was isolated from the unsaponifiable part of an ethereal extract of the leaves of B. nana and B. exilis, mp 160-162°C (acetone). According to the literature [8]: mp 167-169°C (acetone).

12β-Acetoxy-20(S),24(R)-epoxydammarane-3α,25-diol (3) was isolated from the unsaponifiable fraction of an extract of the leaves of B. platyphylla and B. nana, mp 139-145°C (hexane).

General Procedure for Performing Condensations in the Presence of Silver Zeolite (Table 1, Experiments 1-5). Silver zeolite and α-acetobromoglucose were added in one or several portions with continuous stirring to 1 mmole of the initial alcohol in a suitable solvent or mixture of solvents. The reaction was carried out at room temperature until one of the initial reactants had disappeared (monitoring by TLC). The reaction mixture was filtered from insoluble silver compounds, the filtrate was evaporated, and the residue was dried. The dry residue was chromatographed on a column of silica gel.

General Procedure for Performing Condensations in the Presence of Mercury Cyanide (Table 1, Experiments 6 and 7). A mixture of 1 mmole of the initial alcohol, 2 mmole of α-acetobromoglucose, and 2 mmole of mercury cyanide in 20 ml of a mixture of dichloroethane and nitromethane (1:1) was stirred at room temperature until the α-acetobromoglucose had disappeared from the reaction mixture (monitoring by TLC). Then another 2 mmole of mercury cyanide and 1 mmole of α-acetobromoglucose were added in two portions. The reaction mixture was diluted with chloroform and was filtered from insoluble mercury compounds. The filtrate was washed several times with water, dried with anhydrous Na_2SO_4, and evaporated. The dry residue was chromatographed on a column of silica gel.

Experiment 8 (Table 1). A mixture of 1 mmole of the initial alcohol (3) and 1 mmole of mercury cyanide in 10 ml of absolute nitromethane was kept at 90°C for one hour. Then a solution of 1 mmole of α-acetobromoglucose in 5 ml of absolute nitromethane was added over 10 min, and the mixture was kept at the same temperature for another 1 h. Then it was worked up as in the preceding experiment.

3-Monoglucoside (4). mp 184-186°C (ethanol), $[\alpha]_D^{20}$ −30.1° (c 0.77; chloroform). IR spectrum (ν, cm^{-1}): 1756. ^1H spectrum (δ, ppm): 0.82 (s, 3H), 0.84 (s, 3H), 0.90 (s, 3H), 0.97 (s, 6H), 1.09 (s, 3H), 1.18 (s, 6H), 2.00 (s, 6H, 2 ×)Ac), 2.02 (s, 3H, OAc), 2.07 (s, 3H, OAc), 3.32 (t, 1H, J = 2.8 Hz, H_e^3), 3.65 (m, 1H, $H^{5'}$), 3.72 (t, 1H, J = 6.8 Hz, H^{24}), 4.12 (d-d, 1H, J = 2.6 Hz, J = −12.0 Hz, $H^{6'}$), 4.22 (d-d, 1H, J = 4.7 Hz, J = −12.0 Hz, $H^{6'}$), 4.49 (d, 1H, J = 7.3 Hz, $H^{1'}$), 5.01 (d-d, 1H, J = 7.5 Hz, J = 9.0 Hz, $H^{2'}$), 5.08 (t, 1H; J = 9.5 Hz, J = 9.5 Hz, $H^{4'}$), 5.22 (t, 1H, J = 9.5 Hz, J = 9.5 Hz, $H^{3'}$).

The 25-Monoglucoside (5). mp 159-162°C (ethanol), $[\alpha]_D^{20}$ +5.71° (c 0.77; chloroform). IR spectrum (ν, cm^{-1}): 1753, 3600. ^1H spectrum (δ, ppm): 0.84 (s, 3H), 0.86 (s, 3H), 0.90 (s, 3H), 0.94 (s, 3H), 0.97 (s, 3H), 1.08 (s, 3H), 1.13 (s, 3H), 1.19 (s, 3H), 2.00-2.06 (s, 12H, 4 × OAc), 3.39 (t, 1H, J = 2.8 Hz, H_e^3), 3.68 (m, 1H, $H^{5'}$), 3.89 (t, 1H, J = 7.0 Hz, H^{24}), 4.12 (d-d, 1H, J = 2.6 Hz, J = −12.0 Hz, $H^{6'}$), 4.22 (d-d, 1H, J = 4.7 Hz, J = −12.0 Hz, $H^{6'}$), 4.92 (d, 1H, J = 8.2 Hz, $H^{1'}$), 4.95-5.16 (m, $H^{2'}$, $H^{3'}$, $H^{4'}$).

The 3,25-Diglucoside (6). mp 206-208°C (ethanol), $[\alpha]_D^{20}$ −15.8° (c 0.77; chloroform). IR spectrum (ν, cm^{-1}): 1755. ^1H spectrum (δ, ppm): 0.83 (s, 3H), 0.85 (s, 3H), 0.89 (s, 6H), 0.95 (s, 3H), 1.08 (s, 3H), 1.11 (s, 3H), 1.19 (s, 3H), 2.01-2.07 (s, 24H, 8 × OAc), 3.34 (t, 1H, J = 2.8 Hz, H_e^3); 3.65 (m, 1H, $H^{5'}$), 3.89 (t, 1H, J = 7.0 Hz, H^{24}), 4.12-4.24 (m, 4H, 4 × $H^{6'}$), 4.51 (d, 1H, J = 7.1 Hz, $H^{1'}$ at C^3), 4.91 (d, 1H, J = 8.2 Hz, $H^{1'}$ at C^{25}), 4.95-5.23 (m, 2 × $H^{2'}$, 2 × $H^{3'}$, 2 × $H^{4'}$).

The 3-Monoglucoside (7). mp 229-231°C (ethanol), $[\alpha]_D^{20}$ −16.9° (c 0.77; chloroform). IR spectrum (ν, cm^{-1}): 1753. ^1H spectrum (δ, ppm): 0.83 (s, 6H), 0.88 (s, 6H), 0.93 (s, 3H), 1.12 (s, 6H), 1.20 (s, 3H), 2.00-2.07 (s, 15H, 5 × OAc), 3.34 (t, 1H, J = 2.8 Hz, H_e^3), 3.65 (m, 2H, $H^{5'}$, H^{24}), 4.12 (d-d, 1H, J = 2.6 Hz, J = −12.0 Hz, $H^{6'}$), 4.22 (d-d, 1H, J = 4.7 Hz, J = −12.0 Hz, $H^{6'}$), 4.50 (d, 1H, J = 7.3 Hz, $H^{1'}$), 4.85 (t-d, 1H, J = 10.0 Hz, J = 10.0 Hz, J = 5.0, H_a^{12}), 5.01-5.22 (m, 3H, $H^{2'}$, $H^{3'}$, $H^{4'}$).

The 25-Monoglucoside (8). mp 180-183°C (ethanol), $[\alpha]_D^{20}$ −18.2° (c 0.77; chloroform). IR spectrum (ν, cm^{-1}): 1753. ^1H spectrum (δ, ppm): 0.83 (s, 3H), 0.86 (s, 3H), 0.94 (s, 3H), 0.96 (s, 3H), 1.00 (s, 3H), 1.12 (s, 3H), 1.14 (s, 3H), 1.16 (s, 3H), 2.00-2.06 (s, 15H, 5 × OAc), 3.39 t, 1H, J = 2.8 Hz, H_e^3), 3.66 (m, 1H, $H^{5'}$), 3.90 (t, 1H, H = 6.8 Hz, H^{24}), 4.12 (d-d, 1H, J = 2.6 Hz, J = −12.0 Hz, $H^{6''}$), 4.22 (d-d, 1H, J = 4.7 Hz, J = −12.0 Hz, $H^{6'}$), 4.87 (t-d, 1H, J = 10.0 Hz, J = 10.0 Hz, J = 5.0 Hz, H_a^{12}), 4.91 (d, 1H, J = 8.0 Hz, $H^{1'}$), 4.95-5.17 (m, 3H, $H^{2'}$, $H^{3'}$, $H^{4'}$).

The 3,25-Diglucoside (9). mp 270-271°C (ethanol), $[\alpha]_D^{20}$ −29.8° (c 0.77; chloroform). IR spectrum (ν, cm^{-1}): 1755. ^1H spectrum (δ, ppm): 0.82 (s, 3H), 0.84 (s, 3H), 0.90 (s, 3H), 0.96 (s, 6H), 1.10 (s, 3H), 2.00-2.10 (s, 27H, 9 × OAc), 3.31 (t, 1H, J = 2.8 Hz, H_e^3), 3.67 (m, 2H, 2 × $H^{5''}$), 3.82 (t, 1H, J = 6.8 Hz, H^{24}), 4.12-4.24 (m, 4H, 2 × $H^{6'}$), 4.49 (d, 1H, J = 7.6 Hz, $H^{1'}$ at C^3), 4.86 (t-d, 1H, J = 10.0 Hz, J = 10.0 Hz, J = 5.0 Hz, H^{12}), 4.91 (d, 1H, J = 7.7 Hz, $H^{1'}$ at C^{25}), 4.95-5.22 (m, 6H, 2 × $H^{2'}$, 2 × $H^{3'}$, 2 × $H^{4''}$).

SUMMARY

1. The glycoslylation of 3-epiocotillol and of 12β-acetoxy-20(S),24(R)-epoxydammarane-3α,25-diol with α-acetobromoglucose in the presence of silver zeolite and of mercury cyanide has been studied.

2. It has been shown that the synthesis of glucosides from 3-epiocotillol and 12β-acetoxy-20(S),24(R)-epoxydammarane-3α,25-diol, both under the conditions of the Koenigs-Knorr reaction and under those of Helferich's modification, takes place nonregioselectively and gives mixtures of the corresponding 3-O- and 25-O-mono- and 3,25-di-O-β-D-glucopyranosides.

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