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TRITERPENE GLYCOSIDES OF *Astragalus* AND THEIR GENINS
XLV. THE CHEMICAL TRANSFORMATION OF CYCLOARTANES
1. SYNTHESIS OF 25-NORGLYCOSIDES

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Literature information is given on the current state of the study of the chemical transformation of cycloartane triterpenoids. A method has been developed for the transformation of the genin part of glycosides of 20,24-epoxycycloartan-25-ols with retention of the carbohydrate constituents. Three 25-norglycosides have been synthesized from natural cyclosieversigenin glycosides, namely 16β-acetoxy-3β,6α-dihydroxy-20R,25-norcycloartan-20,24-olide 3-O-[O-α-L-arabinopyranosyl-(1→2)-β-D-xylopyranoside] 6-O-β-D-xylopyranoside (VIII), sodium 3β,6α,16β,20-tetrahydroxy-20R,25-norcycloartan-24-oate 6-O-β-D-glucopyranoside 3-O-β-D-xylopyranoside (XII), and 20R,25-norcycloartane-3β,6α,16β,20,24-pentaol 6-O-β-D-glucopyranoside 3-O-β-D-xylopyranoside (XIII).

The 9,19-cyclopropane ring is an attribute of the structure of the carbon skeleton of cycloartane triterpenoids. The chemical transformation of methylsteroids of this series that has been described in the literature is connected in some degree or other with the three-membered ring and is based mainly on the chemical properties of cyclopropane and on those properties of the molecule that are due to the presence of the three-membered ring. Under the conditions of acid catalysis, each of the three carbon–carbon bonds constituting the cyclopropane ring is capable of being cleaved, the cleavage of the 9-19 and 10-19 bonds having been achieved exclusively with the use of Brønsted acids, and that of the 9-10 bond with both Brønsted and Lewis acids. Cleavage of the 9-19 bond leads to lanostene derivatives (I) and cleavage of the ring at the 1-19 bond to compounds of the cucurbitane [19(10→9)-*abeo*-lanostane] series (II) [2-4], while cleavage at the 9-10 bond leads to B-homotriterpenoids (II, IV) [5, 6]. (See scheme at the top of the next page.)

Appearance of olefins as a consequence of opening of the cyclopropane ring by electrophilic attack is practically the only reaction of the three-membered ring of cycloartanes. It is posible that this is a consequence of the extreme difficulty for a nucleophilic attack to compete with the generation of carbocation arising by the cleavage of C–C bond of a protonated cyclopropane. This difficulty is obviously explained by regio- and stereochemical nature of cyclopropane ring in cycloartanes, since a cyclopropane group located in side chain of steroids does undergo nucleophilic attack under analogous conditions [7, 8].

It is true that a product of the nucleophilic attack of cycloart-1-en-3-one — 19-hydroxy-19(10→9)-*abeo*-lanost-1(10)-en-3-one — has been described [4], but this compound may be regarded as the product of the stabilization of the carbocation arising on the cleavage of the cyclopropane ring contrary to the Markovnikov rule.

In their nature, the carbon–carbon bonds of a cyclopropane ring are intermediate between σ- and π-bonds. Consequently, to some degree, cyclopropane behaves similarly to olefins. In view of this the introduction of a keto function into the α-position relative to a cyclopropane ring must be considered as allyl oxidation. Of the two possible α-positions in relation to the cyclopropane ring, the keto function predominantly enters position 11 [9-11]. We may consider the factor that determines the direction of the reaction is that the conjugation of the keto function at C-11 with the cyclopropane ring is more effective because of the suitability of the conformation of ring *C* in this respect.

It is also necessary to introduce a keto function at C-7 [5, 6, 12]. This is probably a result of the fact that the acquisition by the C-7 atom of a state of sp^3 hybridization through the introduction of the keto function decreases the strain of ring *B* caused by the three-membered ring.

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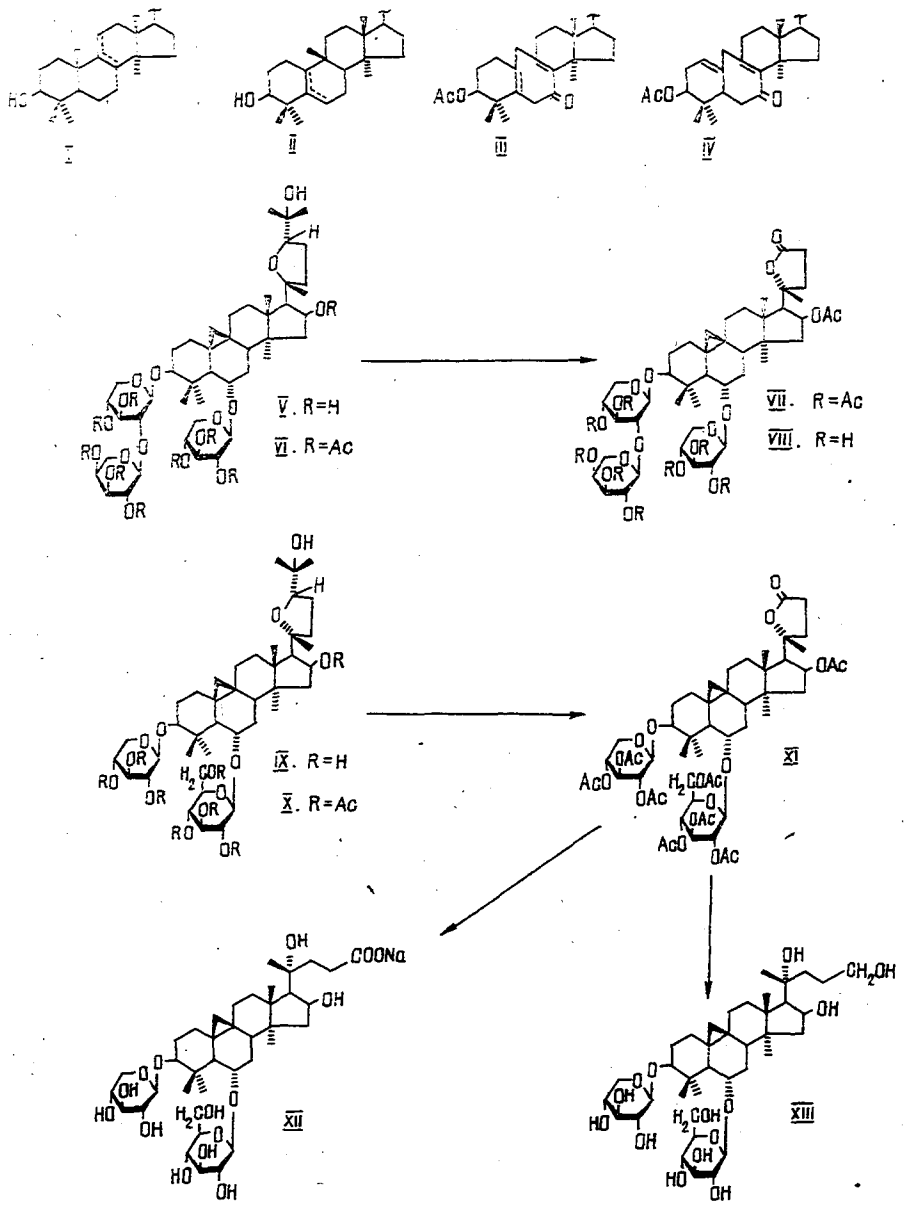

An effective method has been developed for the functionalization of the 4α-methyl group with high regioselectivity which also enables demethylation products to be obtained [13]. In addition, the microbiological transformation of cycloartenol and 24-methylenecycloartenol into androsta-4,18-diene-3,17-dione with the aid of a culture of *Mycobacterium sp.* has been performed. Cycloartenol β-D-glucopyranoside has been synthesized [15].

As a rule, the chemical transformations considered were conducted with monohydric alcohols and their derivatives. The transformation of polyhydroxy compounds and glycosides has not been achieved. Lanostene derivatives of polyhydroxy compounds were formed, to a large degree, as artefacts in the production of genins from glycosides during the proving of their structures [16-19]. The preparation of nor- compounds likewise pursued the aim of structural investigations. Nevertheless, the structure–activity relationship is an important concept of bioorganic chemistry. In view of this, the existence of a large arsenal of cycloartane glycosides suggested the necessity of transforming these compounds in order to follow the changes in their biological activity. This is all the more the case since cardiotonic activity has been detected in cyclosieversioside F (astragaloside IV) [25]. This fact served as the precondition for transformation and search for new cardiotonic drugs among cyclisieversigenin glycosides.

We have developed methods of transforming the most readily available cyclosieversigenin glycosides in two directions: 1) transformation of the genin moiety with retention of the carbohydrate chains; and 2) growth of the monosaccharide residues — selective glycosylation. In the present paper we consider syntheses by the first direction.

TABLE 1. Chemical Shifts of the Carbon Atoms of Glycosides (V, VIII, IX, XII, XIII) (δ, ppm; C_5H_5N; 0 — TMS)*

C atom	Compound				
	V	VIII	IX	XII	XIII
1	31.84	31.82	32.12	32.30	32.25
2	27.98	29.05	28.95	29.16	28.96
3	87.69	87.54	88.48	89.89	88.59
4	42.72	42.62	42.58	41.68	42.64
5	51.94	51.78	52.46	51.69	52.57
6	77.59	77.46	79.21	80.92	79.24
7	32.94	32.99	34.55	34.20	34.42
8	43.08	43.05	45.02[a]	45.98	45.29
9	21.37	20.99	21.07	20.74	21.18
10	30.10	29.95	30.12	29.49	29.97
11	26.56	26.12	26.14	25.59	26.37
12	33.58	33.19	33.36	32.51	33.35
13	45.29	46.27	45.02[a]	46.10	46.87
14	45.64	46.57	45.65	46.43	47.25
15	46.20	43.88	46.17	46.97	48.35
16	73.49	75.24	73.37	73.87	74.01
17	58.08	56.41	58.17	54.59	55.77
18	20.13	20.90*	19.80	19.43	20.04[a]
19	25.36	25.89	28.52	31.57	30.16
20	87.39	89.04	87.20	78.12	76.72
21	28.23	14.93*	28.10	27.48	28.84
22	34.95	27.67	34.86	37.14	38.88
23	26.34	32.83	26.40	28.93	28.59[b]
24	81.68	176.39	81.64	183.53	63.19[c]
25	71.33	—	71.16	—	—
26	27.18*	—	27.02*	—	—
27	27.57*	—	28.52*	—	—
28	19.58	19.18	21.07	19.78	20.04[a]
29	28.69	28.14	28.81	27.19	28.59[b]
30	16.40	16.38	16.50	15.76	16.62
	3-O-β-D-Xylp				
1	105.38	105.27	107.51	105.61	107.62
2	83.73	83.54	75.48[b]	74.50	75.63
3	77.21	77.05	78.37	76.86	78.49
4	71.04	70.97	71.24	69.56	71.26
5	66.67	66.55	66.92	65.14	67.03
	α-L-Arap		β-D-Glcp		
1	106.64	106.67	105.12	103.03	105.23
2	73.77	73.61	75.48[b]	73.89	75.57
3	74.35	74.25	79.04	76.09	79.18
4	69.21	69.10	71.79	69.84	71.93
5	66.97	66.82	77.98	75.87	78.11
6			63.02	61.16	63.19[c]

*The spectrum of compound (XII) was obtained in heavy water. Signals marked with the same letter were superposed on one another, and those marked with asterisks have been assigned uncertainly.

The absence of a clear idea on the fine mechanism of the action of cyclosieversioside F permitted us to assume that the creation of a γ-lactone ring in the side chain of cyclosieversigenin glycosides will possibly lead to an enhancement of cardiotonic action in view of the fact that a butenolide side chain is a necessary structural element of the cardenolides.

In order to create a γ-lactone ring, we used the possibility of splitting out a hydroxyisopropyl fragment of a side chain with a 20,24-epoxy-25-ol structure on oxidation with chromium trioxide. For this purpose we selected the optimum conditions of oxidation by the Jones reagent [26].

The selective acetylation of askenoside D (V) [27] with acetic anhydride in pyridine enabled us to obtain the nonaacetate (VI). The IR spectrum of (VI) included the absorption band of a hydroxy group Its PMR spectrum contained the signals of nine acetyl groups. Obviously, the tertiary hydroxy group (at C-25) had remained free. In actual fact the mass spectrum of the acetate (VI) showed the peak of an ion with m/z 143, corresponding to the unacetylated side chain.

The nonaacetate (VI) was oxidized by the Jones reagent [26] to give product (VII). In the IR spectrum of the oxidation product (VII), the absorption band of the γ-lactone ring was masked by a broad band of ester groups. As was to be expected, in the high-field region of the PMR spectrum of compound (VII), together with the resonance lines of the protons of the cyclopropane methylene, the signals of only five methyls remained. These facts showed that compound (VII) was the nonaacetateof3β,6α,16β-trihydroxy-20R,25-norcycloartan-20,24-olide3-O-[O-α-arabinopyranosyl-(1→2)-β-D-xylopyranoside) 6-O-β-D-xylopyranoside].

Saponification of the lactone nonaacetate (VII) with 0.1% methanolic sodium hydroxide at room temperature for 15 min gave the lactone (VIII in a yield, calculated to the initial askenoside D (V) of 47.4%. The IR spectrum of (VIII) showed absorption bands characteristic for a γ-lactone and an ester group. The ^{1}H and ^{13}C NMR spectra of compound (VIII) (Table 1), which contained a three-proton singlet at 2.05 ppm and the signals of carbon atoms at 19.97 and 169.50 ppm showed that the derivative under consideration was a monoacetate. The proton geminal to the acetoxy group resonated at 5.65 ppm in the form of a quartet with an intensity ratio of 1:3:3:1 and with $^{3}J_1 = {}^{3}J_2 = {}^{3}J_3 = 7.5$ Hz. These parameters are characteristic for H-16 [27], which means that the acetyl group was located at C-16. In actual fact, the C-16 atom experienced the α-effect of acetylation, and the C-15 and C-17 atoms the β-effect. Because of this, the signal of the C-16 atom in the ^{13}C NMR spectrum was shifted downfield and the signals of C-15 and C-17 upfield and were observed at 75.24, 43.88, and 56.41 ppm, respectively. Resonance lines at 89.04 and 176.39 ppm related to the C-20 and C-24 atoms of the γ-lactone ring.

Thus, we are justified in assuming that the compound (VIII) that we had obtained had the structure of 16β-acetoxy-3β,6α-dihydroxy-20R,25-norcycloartan-20,24-olide 3-O-[O-α-L-arabinopyranosyl-(1→2)-β-D-xylopyranoside] 6-O-β-D-xylopyranoside.

Glycosides (XII) and (XIII) were synthesized with the aim of improving the solubility of cyclosieversigenin glycosides in water.

Acetylation of cyclosieversioside F (IX) with acetic anhydride in pyridine gave the acetate (X). The IR spectrum of the latter had the absorption band of a hydroxy group. Its PMR spectrum clearly showed the signals of eight acetoxy groups, seven methyl groups, and two anomeric protons. Consequently, compound (X) was the octaacetate of cyclosieversioside F. It is obvious that in the molecule of octaacetate (X) the tertiary hydroxy group at C-25 had remained free. In actual fact, the oxidation of the octacetate (X) with the Jones reagent [26] at room temperature gave the nor- compound (XI). The PMR spectrum of the nor- compound showed the signals of five methyl groups, eight acetyl groups, and two anomeric protons. The IR spectrum of substance (XI) lacked the absorption band of a hydroxy group, and the absorption band of the γ-lactone ring was superposed on the broad band of ester groups. The facts mentioned determine substance (XI) as the octaacetate of the lactone from cyclosieversioside F. On the deacetylation of the octaacetate (XI) with a 1% methanolic solution of sodium hydroxide at room temperature for more than a day, the sodium salt (XII) crystallized out from the reaction mixture. The yield of the salt (XII) was 50%, calculated on the initial octaacetate (X).

The IR spectrum of compound (XII) included absorption bands at 1610-1530 and 1415-1385 cm^{-1} that are characterisic of a carboxylic acid salt [28]. In the PMR spectrum, taken in heavy water, the signals of two protons of a cyclopropane ring and of five methyls and two anomeric protons were clearly traced. The ^{13}C NMR spectrum contained a signal at 183.53 ppm belonging to the carbon atom of a carboxylate anion. On the basis of these facts, we were justified in concluding that compound (XII)wassodium3β,6α,16β,20-tetrahydroxy-20R,25-norcycloartan-24-oate6-O-β-D-glucopyranoside3-O-β-D-xylopyranoside.

The reductive opening of the lactone ring in compound (XI) was carried out with lithium tetrahydroaluminate. The yield of the reduced glycoside (XIII) was 10%, calculated on the initial lactone (XI).

As was to be expected, the IR spectrum of glycoside (XIII) lacked the absorption band of a γ-lactone ring. The PMR spectrum of the norglycoside (XIII) retained the signals of two cyclopropane protons, five methyls, and two anomeric protons.

The ^{13}C NMR spectrum of this glycoside contained the signals of tertiary and primary carbinol carbon atoms at 76.72 and 63.19 ppm, assigned to the C-20 and C-24 atoms, respectively. The spectral characteristics given unambiguously determined glycoside (XIII) as 20R,25-norcycloartane-3β,6α,16β,20,24-pentaol 6-O-β-D-glucopyranoside 3-O-β-D-xylopyranoside

EXPERIMENTAL

For general observations, see [29]. The following solvent systems were used: 1) chloroform–methanol (100:1); 2) chloroform–methanol–water (70:12:1); and 3) chloroform–methanol–water (70:23:4).

The PMR spectra of compounds (VI), (VII), (X), and (XI) were obtained on a Tesla BS-567 A instrument, and the ^1H and ^{13}C NMR spectra of the other substances on a Bruker AM-400. The ^{13}C NMR spectra were taken with complete decoupling of C–H interactions and also under J-modulation conditions. To interpret the spectra, in individual cases we also used the 2D NMR spectra with correlation of the $^1H-^1H$ and $^1H-^{13}C$ chemical shifts (δ, ppm).

The Nonaacetate of Askenoside D (VI) from (V). Askenoside D (V, 2.5 g) was acetylated with 12 ml of acetic anhydride and 12 ml of absolute pyridine at room temperature for 10 days. The reaction mixture was poured into ice water, and the resulting precipitate was filtered off, washed with water, and dried. The reaction products were chromatographed on a column of silica gel with elution by system 1. This gave 3.4 g of the nonaacetate (VI), $C_{63}H_{92}O_{26}$, mp, 152-153°C (from methanol)), $[\alpha]_D^{20}$ + 10.4 ± 2° (c 0.77; methanol). ν_{max}^{KBr}, cm^{-1}: 3610-3370 (OH), 3050 (CH_2 of cyclopropane ring), 1760, 1260-1220 (ester groups). PMR spectrum (C_5D_5N, 0 — HMDS): 0.08 and 0.42 (2H-19, d, ^2J = 4 Hz), 0.84; 1.12; 1.22; 1.26; 1.26; 1.33 (7 × CH_3, s), 1.81; 1.86; 1.86; 1.86; 1.94; 1.97; 2.02; 2.18; 2.28 (9 × CH_3COO, s), 4.68; 4.83; 4.89 (3 anomeric protons, d, ^3J = 6 Hz).

3β,6α,16β-Trihydroxy-20R,25-norcycloartan-20,24-olide 3-O-[O-α-L-arabinopyranoside-(1→2)-β-D-xylopyranoside) 6-O-β-D-Xylopyranoside Nonaacetate (VII) from (VI). At room temperature, 105 mg of the nonaacetate was oxidized with 0.1 ml of the Jones reagent [26] for 15 min. The excess of oxidant was decomposed by the addition of 1 ml of methanol, and, after the usual working up the reaction product was subjected to column chromatography with elution by system 1, which gave 85 mg of the lactone (VII). $C_{60}H_{84}O_{26}$, mp 168-171°C (from methanol), $[\alpha]_D^{24}$ — 23.8 2° (c 0.67; methanol). ν_{max}^{KBr} cm^{-1}: 1770-1740; 1260-1230 (γ-lactone and ester groups)> PMR sprectrum (C_5D_5N, 0 — HMDS): 0.11 and 0.43 (2H-19, d, ^2J = 4 Hz), 0.84; 1.13; 1.13; 1.34; 1.34 (5 × CH_3, s), 1.82; 1.86; 1.86; 1.88; 1.92; 1.98; 2.04; 2.19; 2.29 (9 × CH_3COO, s), 4.68 (1 anomeric proton, d, ^3J = 6 Hz), 4.86 (2 anomeric proton, m).

16β-Acetoxy-3β,6α-dihydroxy-20R,25-norcycloartan-20,24-olide 3-O-[O-α-L-arabinopyranosyl-(1→2)-β-D-xylopyranoside] 6-O-β-D-xylopyranoside (VIII) from (VII). The lactone nonaacetate (VII) (502 mg) was saponified with 50 ml of a 0.1% methanolic solution of sodium hydroxide at room temperature for 15 min. The reaction mixture was diluted with water, the methanol was evaporatd off, and the residue was extracted with n-butyl alcohol. The butanol extract was washed with water and evaporated. The residue was subjected to column chromatography with elution by system 2, giving 216 mg of compound (VIII) (the yield calculated on the initial askenoside D was 47.4%). Lactone (VIII), $C_{44}H_{68}O_{18}$, mp 198-200°C (from methanol), $[\alpha]_D^{25}$ + 72 ± 2° (c 0.5; methanol). ν_{max}^{KBr}, cm^{-1}: 3600-3270 (OH), 1770-1740, 1270 (γ-lactone and ester groups). PMR spectrum (C_5D_5N, 0 — TMS): 0.13 and 0.59 (2H-19, d, ^2J = 4 Hz), 1.03; 1.22; 1.34; 1.42; 1.79 (5 × CH_3, s), 2.05 (CH_3COO at C-16, s), 3.38 (H-3, dd, $^3J_1$ = 12 Hz, $^3J_2$ = 4 Hz), 4.78 and 4.82 (anomeric protons od D-glucopyranoses, d, ^3J = 7.4 Hz), 5.16 (anomeric proton of L-aranopyranoses, d, ^3J = 6.6 Hz), 5.65 (H-16, q, $^3J_1$ = $^3J_2$ = $^3J_3$ = 7.5 Hz). For the ^{13}C NMR spectrum, see Table 1.

Cyclosieversioside F Octaacetate (X) from (IX). Cyclosieversioside F (5 g) was acetylated with 25 ml of acetic anhydride in 25 ml of absolute pyridine at room temperature for 12 days. Then the reaction mixture was poured into ice water, and the resulting precipitate was filtered off, washed with water, and dried. The reaction products were chromatographed on a column of silica gel with elution by system 1, and 6.5 g of the octaacetate (X) was isolated. $C_{57}H_{84}O_{22}$ $[\alpha]_D^{27}$ + 14.5 ± 2° (c 1.1; methanol). ν_{max}^{KBr}, cm^{-1}: 3600-3370 (OH), 3045 (CH_2 of cyclopropane ring)., 1770-1730, 1270-1210 (ester groups). PMR spectrum (C_5D_5N, 0 — HMDS): 0.08 and 0.04 (2H-19, d, ^2J = 4 Hz), 0.84; 0.95; 1.16; 1.22; 1.27; 1.27; 1.27 (7 × CH_3, s), 1.83; 1.87; 1.88; 1.89; 2.00; 2.00; 2.04; 2.05 (8 × CH_3COO, s), 4.73 and 4.83 (anomeric protons, d, ^3J = 7.5 Hz).

3β,6α,16β-Trihydroxy-20R,25-norcycloartan-20,24-olide 6-O-β-D-Glucopyranoside 3-O-β-D-Xylopyranoside Octaacetate (XI) from (X). The octaacetate (X) (5 g) in 200 ml of acetone was oxidized with 5 ml of the Jones reagent [26] with constant stirring at room temperature for 20 min. The reaction was stopped by the addition of 5 ml of methanol, the

reaction mixture was diluted with water and the product was extracted with chloroform. The chloroform extracts were combined, washed with water to neutrality, dried with anhydrous sodium sulfate, and evaporated. The residue was chromatographed on a column of silica gel with elution by system 1. This gave 4.5 g of product (XI), $C_{54}H_{76}O_{22}$, mp 249-251°C (from methanol), $[\alpha]_D^{27}$ + 12.6 ± 2° (c 0.88; methanol). ν_{max}^{KBr}, cm^{-1}; 3065 (CH_2 of a cyclopropane ring), 1780-1720, 1230-1210, (γ-lactone and ester groups). PMR spectrum (C_5D_5N, 0 — HMDS: 0.41 (H-19, d, ^2J = 4 Hz), 0.85; 0.94; 1.16; 1.16; 1.35 (5 × CH_3, s), 1.84-2.05 (8 × CH_3COO), 4.74 and 4.86 (anomeric protons, d, ^3J = 7.5 Hz).

Sodium 3β,6α,16β,20-Tetrahydroxy-20R,25-norcycloartan-24-oate 6-O-β-D-glucopyranoside 3-O-β-D-xylopyranoside (XII) from (XI). A solution of 160 mg of the lactone octaacetate (XI) in 20 ml of 1% methanolic sodium hydroxide was left at room temperature. The product that crystallized out was filtered off and washed with methanol. This gave 80 g of the salt (XII), $C_{38}H_{61}O_{15}$, mp. 261-264°C (from methanol), $[\alpha]_D^{25}$ + 42.0 ± 2° (c 0.7; water). ν_{max}^{KBr}, cm^{-1}: 3530-3200 (OH), 3055 (CH_2 of a cyclopropane ring), 1610-1530, 1415-1385 (carboxylate). PMR spectrum (D_2O): 0.31 and 0.50 (2H-19, d, ^2J = 4 Hz), 0.82; 0.89; 1.15; 1.25; 1.26 (5 × CH_3, s), 4.36 and 4.38 (anomeric protons, d, ^3J = 7.8 and 7.9 Hz respectively). For the ^{13}C NMR spectrum, see Table 1.

20R,25-Norcycloartane-3β,6α,16β,20,24-pentaol 6-O-β-D-Glucopyranoside 3-O-β-D-Xylopyranoside (XIII) from (XI). To 300 mg of compound (XI) in 50 ml of absolute ethyl ether was added 300 mg of lithium tetrahydroaluminate, and the mixture was boiled for 48 h. Then 5 ml of ethyl acetate was added to decompose the excess of reducing agent, and the reaction mixture was poured into water. The products were extracted with n-butyl alcohol, and the extract was evaporated The residue was chromatographed on a column, with elution by system 3. This gave 30 mg of glycoside (XIII), $C_{38}H_{64}O_{14}$, mp, 231-234° (from ethanol), $[\alpha]_D^{26}$ + 0 ± 3° (c 0.5; methanol). ν_{max}^{KBr}, cm^{-1}: 3560-3200 (OH), 3050 (CH_2 of a cyclopropane ring). PMR spectrum (C_5D_5N, 0 — TMS): 0.18 and 0.58 (2H-19, d, ^2J = 4 Hz), 0.96; 1.35; 1.67; 1.79; 2.01 (5 × CH_3, s), 3.52 (H-3, dd, ^3J = 12 Hz, $^3J_2$ = 4 Hz), 3.68 (H-5a of D-xylose, t, ^2J = ^3J = 10 Hz), 3.80 (H-6, td, $^3J_1$ = $^3J_2$ = 8 Hz), $^3J_3$ = 4 Hz), 3.89 (H-5 of D-glucose, m), 3.97-4.20 (H-2, H-3, H-4 of monosaccharides, 2H-24), 4.27 (H-6 of D-glucose, dd, ^2J = 12 Hz, ^3J = 6 Hz), 4.34 (H-5e of D-xyglose, dd, ^2J = 10 Hz, ^3J = 6 Hz), 4.44 (H-6′ of D-glucose, dd, ^2J = 12 Hz, ^3J = 3 Hz), 4.83 (H-1 of D-xyglose, d, ^3J = 8 Hz), 4.90 (H-1 of D-glucose, d, ^3J = 8 Hz), 4.95 (H-16, q, $^3J_1$ = $^3J_2$= $^3J_3$ = 7 Hz). For the ^{13}C NMR spectrum, see Table 1.

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