spectrum (ppm): 0.78 (s, 3 H); 0.80 (s, 3 H); 0.85 (s, 3 H). ^{13}C spectrum (ppm): 40.8 (C^1), 18.7 (C^2), 42.2 (C^3), 33.5 (C^4), 57.0 (C^5), 18.8 (C^6), 35.7 (C^7), 40.5 (C^8), 51.1 (C^9), 37.6 (C^{10}), 21.4 (C^{11}), 27.8 (C^{12}), 41.6 (C^{13}), 49.0 (C^{14}), 32.1 (C^{15}), 20.9 (C^{16}), 26.7 (C^{17}), 16.2 (C^{18}), 15.6 (C^{19}), 33.5 (C^{28}), 21.6 (C^{29}), 14.8 (C^{30}).

SUMMARY

A partial synthesis of octanor-12β-dammarane — one of the basic compounds for calculating substituent effects in the ^{13}C NMR spectra of tetracyclic triterpenoids of the dammarane series — has been effected from 20(S),24(R)-epoxydammarane-3α,17α,25-triol, isolated from the leaves of *Betula ovalifolia*.

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CATALYTIC REARRANGEMENT OF 1,2-ORTHOACETATES OF α-D-GLUCOSE AND 20(S),24(R)-EPOXYDAMMARANE-3,12β,25-TRIOLS. I.

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UDC 547.455+547.597+547.917+547.918

The catalytic rearrangement of 20(S),24(R)-epoxydammarane-3,12β,25-triol 3-mono and 3,12-di(α-D-glucose 1,2-orthoacetate)s leads to the formation of the corresponding 12-mono- and 12,25-diglucosides. The anomalous regioselectivity of the catalytic rearrangements of orthoesters of 20(S),24(R)-epoxydammarane-3,12β,25-triols is evidently due to the influence of strong intramolecular hydrogen bonds. Details of the IR, PMR, and ^{13}C NMR spectra, and also the physicochemical constants, of the newly obtained compounds are given.

The catalytic isomerization of 1,2-orthoacetates of sugars and of alcohols of noncarbohydrate nature is a well-known method for the "two-stage" 1,2-transglycosylation of lower and some higher monohydric alcohols [1-7]. This rearrangement has not been studied among orthoesters of polyhydric polycyclic alcohols, containing orthoester and free hydroxy groups in the molecule simultaneously. In order to study the isomerization of such orthoesters and also to obtain analogs of ginseng glycosides, we have performed the synthesis of the (α-D-glucose 1,2-orthoacetates) 20(S),24(R)-epoxydammarane-3α-12β,25-triol (I) and of 20(S),24(R)-epoxydammarane-3β,12β,25-triol (II).

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TABLE 1. Conditions of Formation of the Title Orthoesters*

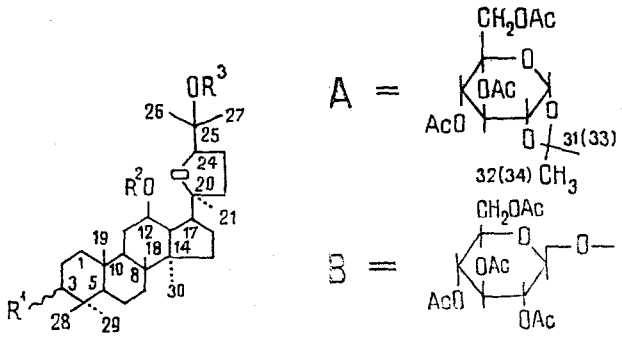
Experiment	Initial alcohol, mmole	α-ABG, mmole	CH_3NO_2, ml	Collidine, ml	Time, h	Reaction product, %
1	(I), 2,0	6,0	10	8	48	(III). 70 (IV). 10
2	(II). 1,0	3.0	10	4	48	(V). 68 (VI). 15

*Experiments 1 and 2 were performed at 25°C.

TABLE 2. Conditions and Results of the Catalytic Rearrangement of the Title Orthoesters in CH_3NO_2*

Experiment	Initial orthoester, mmole	$HgBr_2$, mmole	Time, h	Reaction products, %
3	(IV). 1,0	0,36	1,5	(VIII). 48; (I), 22
4	(VI). 1,0	0,36	1,5	(X). 45; (II), 25
5	(III). 0,42	0,30	1,5	(VII). 42; (VIII). 24
6	(V). 0,60	0,45	1,0	(IX). 32; (X). 34. (XI). 5; (XII). 3

*Experiments 3-6 were performed at 100-105°C.



(I) $R^1 = \alpha$-OH, $R^2 = R^3 = H$
(II) $R^1 = \beta$-OH, $R^2 = R^3 = H$
(III) $R^1 = \alpha$-OA, $R^2 = A$, $R^3 = H$
(IV) $R^1 = \alpha$-OA, $R^2 = R^3 = H$
(V) $R^1 = \beta$-OA, $R^2 = A$, $R^3 = H$
(VI) $R^1 = \beta$-OA, $R^2 = R^3 = H$
(VII) $R^1 = \alpha$-OH, $R^2 = R^3 = B$
(VIII) $R^1 = \alpha$-OH, $R^2 = B$, $R^3 = H$
(IX) $R^1 = \beta$-OH, $R^2 = R^3 = B$
(X) $R^1 = \beta$-OH, $R^2 = B$, $R^3 = H$
(XI) $R^1 = \beta$-OB, $R^2 = B$, $R^3 = H$
(XII) $R^1 = \beta$-OB, $R^2 = R^3 = B$
(XIII) $R^1 = \alpha$-OAc, $R^2 = R^3 = B$
(XIV) $R^1 = \alpha$-OAc, $R^2 = B$, $R^2 = H$
(XV) $R^1 = \beta$-OAc, $R^2 = R^3 = B$
(XVI) $R^1 = \beta$-OA, $R^2 = B$, $R^2 = H$

The reaction of α-acetobromoglucose (α-ABG) with the title alcohols under conditions described previously [8] gave the following 1,2-orthoacetates (Table 1): 20(S),24(R)-epoxydammarane-3α,12β,25-triol 3,12-di(3',4',6'-tri-O-acetyl-α-D-glucopyranose 1,2-orthoacetate) (III), 20(S),24(R)-epoxydammarane-3α,12β,25-triol 3-(3,4,6-tri-O-acetyl-α-D-glucopyranose 1,2-orthoacetate) (IV), 20(S),24(R)-epoxydammarane-3β,12β,25-triol 3,12-di (3,4,6-tri-O-acetyl-α-D-glucopyranose 1,2-orthoacetate) (V), and 20(S),24(R)-epoxydammarane-3-β,12β,25-triol 3-(3,4,6-tri-O-acetyl-α-D-glucopyranose 1,2-orthoacetate) (VI).

The structures of the orthoesters (III)-(VI) were confirmed by the ease of their acid hydrolysis, the results of investigations by ^1H and ^{13}C NMR, and by elementary analysis. The positions of attachment of the orthoester (OE) groups in (III)-(VI) were established by comparing the ^{13}C spectra of the triols (I) and (II) and of the orthoesters (III)-(VI) (Table 3).

The orthoesters (III)-(VI) were subjected to catalytic isomerization under conditions described previously [6] (Table 2). On the basis of the results of investigations by the

TABLE 3. ^{13}C Chemical Shifts of Compounds (I)-(XVI) (ppm relative to TMS)

C atom	Compound															
	(I)	(II)	(III)	(IV)	(V)	(VI)	(VII)	(VIII)	(IX)	(X)	(XI)	(XII)	(XIII)	(XIV)	(XV)	(XVI)
1	33,7	39,1	34,0	34,0	39,1	39,1	33,8	33,9	39,0	39,0	39,1	39,1	34,5	34,6	38,8	38,8
2	25,5	27,6	23,7	23,7	25,5	25,5	25,5	25,5	27,4	27,5	25,8	26,0	23,0	23,0	23,7	23,7
3	75,9	78,5	78,1	78,2	81,0	81,0	75,8	75,8	78,6	78,6	90,1	90,1	78,1	78,1	80,7	80,6
4	37,5	38,9	38,1	38,0	38,7	38,7	37,6	37,6	39,1	39,0	39,2	39,1	36,9	36,9	37,9	37,9
5	49,5	56,1	50,2	50,2	56,7	56,6	49,5	49,5	56,1	56,0	56,3	56,3	50,8	50,9	56,1	56,1
6	18,3	18,3	18,1	18,1	18,5	18,6	18,2	18,3	18,3	18,3	18,2	18,3	18,1	18,0	18,2	18,2
7	34,8	34,9	34,6	34,6	34,8	34,9	34,6	34,7	34,8	34,7	34,7	34,8	34,5	34,6	34,6	34,6
8	40,0	39,8	39,9	39,9	39,7	39,8	39,8	39,9	39,7	39,6	39,7	39,7	39,8	40,0	39,7	39,7
9	50,3	50,6	50,9	50,2	51,3	50,6	50,3	49,9	50,4	50,0	50,0	50,5	50,4	50,0	49,8	50,0
10	37,3	37,2	37,1	37,2	36,9	37,0	37,4	37,4	37,3	37,2	37,0	37,0	37,3	37,4	37,2	37,2
11	31,2	31,2	33,0	31,3	33,0	31,3	28,3	27,4	27,4	27,5	27,6	27,7	27,6	27,6	27,4	27,6
12	71,0	71,0	75,0	71,1	75,0	71,0	77,1	77,6	77,1	77,5	77,4	77,0	77,1	77,7	77,1	77,5
13	47,9	48,0	48,0	48,0	48,0	48,0	47,7	47,8	47,8	47,8	47,8	47,8	47,6	47,8	47,7	47,8
14	52,2	52,0	52,7	52,2	52,6	52,1	52,2	52,2	52,1	52,1	52,1	52,0	52,1	52,3	52,0	52,1
15	31,2	31,4	31,1	31,3	31,2	31,3	31,5	31,7	31,5	31,7	31,6	31,6	31,5	31,8	31,5	31,7
16	28,6	28,6	28,5	28,6	28,5	28,3	27,2	27,0	28,1	26,9	26,9	26,5	27,3	26,9	28,3	26,9
17	49,3	49,4	47,9	49,4	47,8	49,4	49,7	49,9	50,0	50,0	50,0	50,0	49,7	50,0	50,4	50,0
18	16,2	16,3	16,4	16,4	16,5	16,4	16,1	16,1	16,2	16,2	16,1	16,1	15,9	16,0	16,2	16,3
19	15,4	15,4	15,5	15,5	15,5	15,4	15,7	15,6	15,7	15,5	15,6	15,7	15,7	15,7	15,7	15,6
20	86,5	86,4	85,7	86,5	85,7	86,5	86,5	86,7	86,6	86,6	86,6	86,5	86,5	86,7	86,5	86,6
21	26,1	26,1	27,4	26,2	27,5	26,1	22,0	22,2	22,0	22,2	22,2	22,0	22,0	22,2	22,1	22,2
22	32,6	32,6	33,8	32,6	33,9	32,6	38,7	39,0	39,1	39,0	39,1	38,8	38,8	39,0	38,8	39,0
23	25,0	25,0	26,5	25,1	26,5	25,0	26,3	26,2	26,3	26,2	26,2	26,2	26,3	26,2	26,3	26,2
24	85,4	85,4	84,1	85,5	84,1	85,5	83,3	83,5	82,5	83,5	83,5	82,5	82,5	83,6	82,4	83,5
25	70,1	70,1	70,2	70,1	70,5	70,1	79,7	71,3	79,7	71,2	71,2	79,6	79,6	71,4	79,8	71,3
26	27,8	27,8	28,1	27,9	28,1	27,9	23,8	27,4	23,8	27,5	27,6	23,7	23,9	27,6	23,8	27,6
27	27,6	27,5	24,8	27,7	24,8	27,6	22,8	24,2	23,1	24,2	24,2	23,1	23,1	24,4	22,8	24,2
28	28,4	28,1	28,5	28,6	28,3	27,2	28,3	28,5	28,1	28,1	27,6	28,2	27,9	27,9	28,0	28,0
29	22,0	15,4	22,2	22,3	16,1	16,2	22,0	22,1	15,4	15,4	16,1	16,1	21,7	21,8	16,5	16,5
30	18,3	18,1	19,6	18,5	19,4	18,2	17,8	17,9	17,7	17,4	17,7	17,7	117,8	18,0	17,7	17,8
31	—	—	122,0	122,0	122,0	122,0	—	—	—	—	—	—	70,3	170,3	170,4	170,4
32	—	—	22,2	22,5	22,1	22,4	—	—	—	—	—	—	21,3	21,3	21,3	21,3
33	—	—	121,5	—	121,5	—	—	—	—	—	—	—	—	—	—	—
34	—	—	22,8	—	22,5	—	—	—	—	—	—	—	—	—	—	—

^1H and ^{13}C NMR methods and elementary analysis the products obtained were assigned the following respective structures: 20(S),24(R)-epoxydammarane-3α,12β,25-triol 12,25-di-O-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranoside) (VII), 20(S),24(R)-epoxydammarane-3α-12β,25-triol 12-O-(2,3,4,6-tetra-O-acetyl-α-D-glucopyranoside) (VIII), 20(S),24(R)-epoxydammarane-3β,12β,25-triol 12,25-di-O-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranoside) (IX), and 20(S),24(R), epoxydammarane-3β,12β,25-triol 12-O-(2,3,4,6-tetra-O-acetyl-β-D-glucopyranoside) (X).

A doublet signal of the anomeric proton of the sugar component at C^{12} in the ^1H spectra of (VII)-(X) appears at 4.60-4.63 ppm ($J_{1',2'} \simeq 7.3$ Hz), and the anomeric proton of the sugar component at C^{25} gives a signal at ∿5.0 ppm ($J_{1',2'} \simeq 8.0$ Hz) [9]. The value of $J_{1',2'}$ shows the trans configuration of the glucosidic bonds both in the monoglucosides (VIII) and (X) and in the diglucosides (VII) and (IX). The positions of attachment of the carbohydrate components in (VII)-(X) were established by comparing the ^{13}C spectra of the triols (I) and (II) and of the glucosides (VII)-(X) (Table 3), and also by acetylating (VII)-(X) under mild conditions, which led to the corresponding 3-monoacetates (XIII)-(XVI).

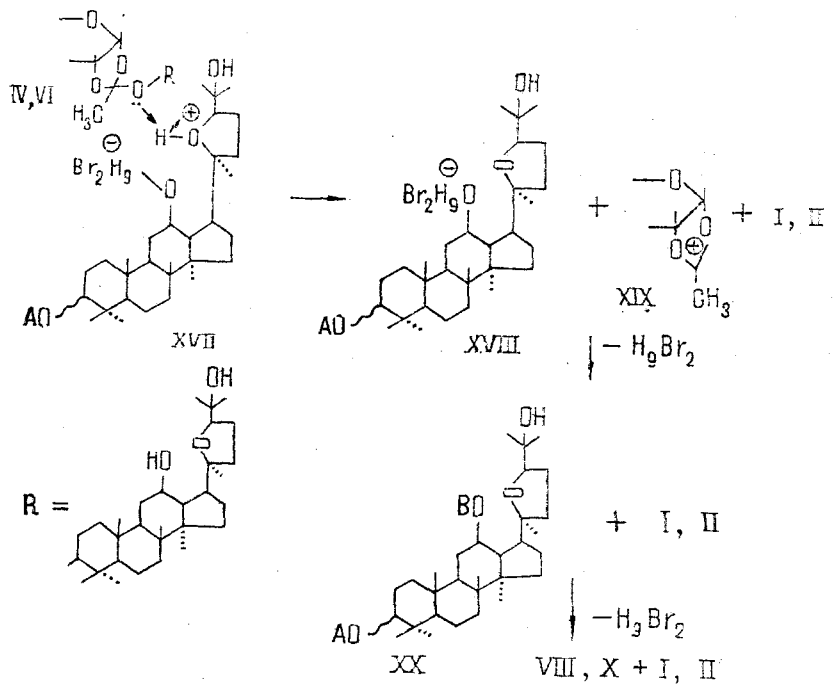
In the absence of $HgBr_2$, no formation of the glucosides (XII)-(X) was observed, and boiling the orthoesters (III)-(VI) in CH_3NO_2 for 1.5 h did not lead to appreciable changes in them, which shows the absence of a possible transesterification of (III)-(VI) at the free hydroxy groups with the subsequent isomerization of the new orthoesters into the corresponding glucosides (VII)-(X).

If we start from the general scheme of the isomerization of orthoesters by $HgBr_2$ in CH_3NO_2 [10], the rearrangement of the 3-mono-orthoesters (IV) and (VI) should lead to the formation of 3-monoglucosides and that of the 3,12-di-orthoesters (III) and (V) to the corresponding 3,12-diglucosides. The absence of these glucosides from the products of the rearrangements of the orthoesters (III)-(VI), with the exception of a small amount (∿5%) of the 3,12-diglucoside (XI) in the case of the orthoester (V), permits the assumption that the anomalous regioselectivity of these rearrangements is connected with a mechanism different from that suggested by Bochkov et al. [10]. In the case of the rearrangements of the mono-orthoesters (IV) and (VI), the first act is apparently the interaction of Lewis acid with the O atom of the hydroxy group at C^{12}, leading in the final account to the formation of an ion pair of type (XVII) (scheme 1). This interaction must be due to the high nucleophilicity of the O^{12} atom, as compared with all the other O atoms on the molecules of (IV) and (VI), which is due to the existence of a strong intermolecular hydrogen bond (intra-HB) between the proton of the 12β-OH group and the O atom of the tetrahydrofuran ring [11]. In actual fact, in the IR spectra of (IV) and (VI) in $CHCl_3$ solution (c, 35.0 and 37.0 mg/ml, respectively) strong broad bands of hydroxyl absorption are observed at 3405 and 3398 cm^{-1}, respectively, not changing their position and intensity with a 23-fold dilution of the solutions. In the ^1H NMR spectra ($CDCl_3$) of (IV) and (VI) broad signals of unit intensity sensitive to the temperature conditions of recording the spectra and disappearing at deutero-exchange are observed.

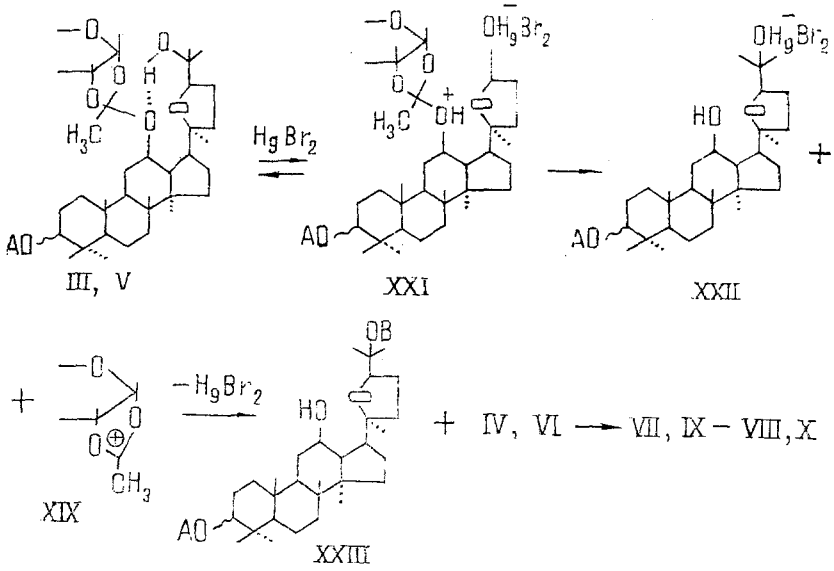
The intermolecular attack of the electron pair of the alkoxy carbon atom of the orthoester grouping of (IV) or (VI) on the oxonium proton of the zwitter ion (XVII) probably leads to the formation of the anion (XVIII), the acyloxonium ion (XIX;, and the free triols (I) and (II) (scheme 1). The acyloxonium ion (XIX) then disappears, apparently either as the result of an attack of the anion (XVIII) on its glycosidic center, which leads to the intermediate (XX), or as the result of the ejection of a proton and the formation of ketene acetal. The subsequent reaction of (I) or (II) with $HgBr_2$ must again lead to bipolar ions of type (XVII), the reaction of which with (XX) will, according to scheme 1, give the monoglucosides (VIII) and (X). Under the conditions of equiprobability of the two pathways for the destruction of the acyloxonium ion (XIX), the ratio of (XX) and (I) or (II) in the intermediate stage of the reaction will be close to 1:2, which, in the final account, determines the observed ratio of the end-products of the rearrangement of (IV) and (VI). The formation of ketene acetals has been assumed previously for acyloxonium ions of both carbohydrate [12, 13] and noncarbohydrate [14] nature.

Thus, in the case of rearrangement of the mono-orthoesters (IV) and (VI) under the action of $HgBr_2$, latent proton catalysis obviously takes place and the role of the $HgBr_2$ reduces to generating a mobile oxonium proton through interaction with the nucleophilic O^{12} atom of the initial orthoester.

This applies in equal measure to the rearrangement of the 3,12-di-orthoesters (III) and (V), although in this case intramolecular protonic catalysis of the rearrangement of one of



Scheme 1



Scheme 2

the orthoester groups may take place as the result of the existence of a strong intra-HB between the proton of the hydroxy group at C^{25} and the alkoxy oxygen atom of the orthoester grouping at C^{12} (scheme 2). In the IR spectrum of (III) there is a strong broad band at 3410 cm^{-1} independent of the concentration of the solution in $CHCl_3$, and in the ^1H spectrum there is a broad signal of unit intensity at 3.65 ppm which appears on deuterium exchange.

The attack of the Lewis acid on the O^{25} atom, the nucleophility of which is raised through an intra-HB, must lead in the final account to the bipolar ion (XXI) (scheme 2). By analogy with the rearrangement of (IV) and (VI) (scheme 1), the interaction of the anion (XXII) with the acyloxonium ion (XIX) will probably lead to the intermediate (XXIII) and the mono-orthoester (IV) or (VI). The further interaction of two molecules of (XXIII), or of a molecule of (XXIII) with a molecule of (IV) or (VI), will apparently lead, by analogy with scheme 1, to the 12,25-diglucosides (VII) and (IX). Similarly, the interaction of two molecules of (IV) or (VI) can give the 12-monoglucosides (VIII) and (X).

In principle, other combinations of the interactions of the intermediates under consideration with one another are possible, leading to the formation of the final rearrangement

TABLE 4. ^{13}C Chemical Shifts of the Sugar Components of the Orthoesters (III)-(VI) and of the Glucosides (VII)-(XVI) (ppm relative to TMS*

C atom	Compound															
	(III)		(IV)	(V)		(VI)	(VII)		(VIII)	(IX)		(X)				
1	96.6	96.7	96.9	97.0	96.7	97.0	93.8	96.0	97.2	96.9	69.1	97.2				
2	68.3	68.6	68.3	68.2	68.5	68.2	71.3	71.7	71.3	71.3	71.7	71.3				
3	70.5	70.2	70.3	70.5	70.2	70.5	73.0	73.4	73.1	73.0	73.5	73.1				
4	73.8	72.8	73.5	73.6	72.7	73.5	68.6	68.4	69.6	68.8	69.0	68.6				
5	67.4	66.8	67.2	67.5	66.8	67.4	71.7	71.7	71.7	71.7	71.7	71.7				
6	63.0	63.0	63.2	63.1	63.1	63.1	63.0	61.6	61.9	61.7	62.1	61.9				

*The signals of the ^{13}C nuclei of the acetate groups of the sugar components of compounds (III)-(XVI) appear in the 170.0-170.6 and 20.8-21.6 ppm regions.

products of the 3,12-di-orthoesters (III) and (V). Thus, the formation of (VIII) and (IX) can probably take place by analogy with scheme 1 but even by intermediates of type (XX), since the IR spectra of (VIII) and (X) likewise show intra-HB between the protons of the hydroxy group at C^{25} and alkoxy O atom of the glycosidic grouping at C^{12} (bands at 3548 and 3543 cm^{-1}, respectively, not depending on the concentration of the solution in $CHCl_3$). Although these intra-HBs are weaker than in (III), (IV), (V), and (VI) (the peaks and integral intensities of these bands are considerably smaller than those of the corresponding bands in the IR spectra of the mono- and di-orthoesters), they may nevertheless promote the glycosylation at C^{25} of intermediates of type (XX).

EXPERIMENTAL

IR spectra were recorded on an IR-75 spectrophotometer in $CHCl_3$ solution, and ^1H and ^{13}C NMR spectra on a Bruker HX-90E spectrometer in the Fourier regime at 30°C for 8% solutions of the substances in $CDCl_3$ at a working frequency of 90.0 MHz for ^1H and 22.63 MHz for ^{13}C. The accuracy of the measurements was ±0.15 Hz for ^1H and ±1.5 Hz for ^{13}C. The assignment of the signals in the ^{13}C spectra was performed by the method of off-resonance spin decoupling and on the basis of literature analogies [15-19]. Optical rotations were determined on a Perkin-Elmer instrument in a cell 10 cm long. The melting points of the substances were determined on a Boëtius stage. Solvents were prepared as described in the literature [20]. Column chromatography was performed on KSK SiO_2, 100-115 mesh, treated as described by Wulf and Schmidt [4], in petroleum ether–acetone (40:1) → (5:1) systems, and TLC in a fixed layer of SiO_2 in the petroleum ether–acetone (3:1) and (2:1) systems. The TLC plates were treated for visualization with a mixture of concentrated H_2SO_4 and MeOH (1:10) at 100-200°C. The hydrolytic test for orthoesters was performed under the conditions given by Kochetkov et al. [20]. The results of the elementary analyses of the compounds obtained for the first time corresponded to the calculated figures.

The triterpene (I) was isolated from the leaves of the Far-Eastern species *Betula platyphylla*, mp 235-237°C (acetone). According to the literature [21]: mp 237-240°C. The triterpene (II) was obtained from (I) as described previously [22], mp 218-220°C (acetone). According to the literature [23]: mp 225-226°C (aqueous MeOH). The acetates (XIII)-(XVI) were obtained by treating the corresponding alcohols with $(CH_3CO)_2O$ in C_5H_5N at 25°C for a day.

The 3,12-Di-orthoester (III). Amorphous substance, $C_{58}H_{88}O_{22}$, $[\alpha]_D^{20}$ +15.8° (c 1.0; C_5H_5N). ^1H spectrum (δ, ppm): 0.84 (s, 6H), 0.95 (s, 6H), 1.07 (s, 3H), 1.19 (s, 3H), 1.26 (s, 3H), 1.28 (s, 3H), 1.74 (s, 3H, C^{31}–CH_3), 1.77 (s, 3H, C^{31}–CH_3), 2.08 (s, 6H, 2 × OAc), 2.10 (s, 6H, 2 × OAc), 2.11 (s, 6H, 2 × OAc), 3.37 (t, 1H, J = 2.0 Hz, H_e^3), 3.65 (br. singlet, 1H, OH), 3.68 (t, 1H, J = 6.8 Hz, H^{24}), 3.93 (sextet, 1H, $J_{a,a} = J_{a,a} = 9.0$, $J_{a,e} = 4.0$ Hz, H_a^{12}), 3.95 (m, 2H, J = 9.7 and 4.0 Hz, 2 × H_2'), 4.19 (d, 4H, J = 4.0 Hz, 4 × H_6', 4.44 m, 2H, J = 2.7, 2.9, 5.0 and 4.7 Hz, 2 × H_2'), 4.89 (q, 2H, J = 2.5 and 9.7 Hz, 2 × H_4'), 5.12 (t, 1H, J = 2.7 Hz, H_3') 5.22 (t, 1H, J = 2.9 Hz, H_3'), 5.68 (d, 1H, J = 4.7 Hz, H_1') 5.73 (d, 1H, J = 5.0 Hz, H_1').

The 3-Mono-orthoester (IV). Amorphous substance, $C_{44}H_{70}O_{13}$, $[\alpha]_D^{20}$ +19.7° (c, 1.0; C_5H_5N). ^1H spectrum (δ, ppm): 0.85 (s, 9H), 0.93 (s, 3H), 0.97 (s, 3H), 1.09 (s, 3H), 1.27 (s, 6H), 1.74 (s, 3H, C^{31}–CH_3), 2.09 (s, 6H, 2 × OAc), 2.13 (s, 3H, OAc), 3.33 (t, 1H, J = 2.3 Hz, H_e^3), 3.51 (sextet, 1H, $J_{a,a} = J_{a,a} = 10.0$, $J_{a,e} = 5.0$ Hz, H_a^{12}), 3.71 (br. singlet, 1H, OH),

3.96 (q, 1H, J = 4.0 and 9.2 Hz, H_5'), 4.19 (d, 2H, J = 4.0 Hz, 2 × H_6'), 4.33 (q, 1H, J = 3.0 and 5.0 Hz, H_2'), 4.88 (q, 1H, J = 2.6 and 9.2 Hz, H_4'), 5.18 (t, 1H, J = 3.0 Hz, H_3'), 5.42 (br. singlet, 1H, OH), 5.68 (d, 1H, J = 5.0 Hz, H_1').

The 3,12-Di-orthoester (V). Amorphous substance, $C_{58}H_{88}O_{22}$, $[\alpha]_D^{20}$ +26.0° (c 1.0, C_5H_5N). ^1H spectrum (δ, ppm): 0.75 (s, 3H), 0.85 (s, 3H), 0.92 (s, 3H), 0.93 (s, 3H), 0.94 (s, 3H), 1.07 (s, 3H), 1.18 (s, 3H), 1.27 (s, 3H), 1.74 (s, 6H, 2 × $C^{31} - CH_3$), 2.09 (s, 12H, 4 × OAc), 2.10 (s, 6H, 2 × OAc), 3.14 (q, 1H, J = 5.2 and 9.4 Hz, H_a^3), 3.59 (br. singlet, 1H, OH), 3.65 (t, 1H, J = 6.3 Hz, H^{24}), 3.89 (m, 3H, H_a^{12}, 2 × H_5'), 4.19 (d, 4H, J = 4.0, 4 × H_6'), 4.34 (q, 1H, J = 3.4 and 5.0 Hz, H_2'), 4.49 (q, 1H, J = 3.2 and 5.2 Hz, H_2'), 4.92 (q, 2H, J = 3.2 and 9.4 Hz, 2 × H_4'), 5.11 (t, 1H, J = 3.0 Hz, H_3'), 5.19 (t, 1H, J = 3.4 Hz, H_3'), 5.69 (d, 1H, J = 5.0 Hz, H_1') 5.73 (d, 1H, J = 4.7 Hz, H_1').

The 3-Mono-orthoester (VI). Amorphous substance, $C_{44}H_{70}O_{13}$, $[\alpha]_D^{20}$ +18.0° (c 1.0; C_5H_5N). ^1H spectrum (δ, ppm): 0.74 (s, 3H), 0.85 (s, 3H), 0.90 (s, 6H), 0.97 (s, 3H), 1.09 (s, 3H), 1.27 (s, 6H), 1.73 (s, 3H, $C^{31} - CH_3$), 2.08 (s, 3H, OAc), 2.09 (s, 3H, OAc), 2.11 (s, 3H, OAc), 3.13 (q, 1H, J = 6.0 and 10.0 Hz, H_a^3), 3.49 (sextet, 1H, $J_{a,a} = J_{a,a} = 10.0$ and $J_{a,e} = 4.5$ Hz, H_a^{12}), 3.85 (br. singlet, 1H, OH), 3.85 (t, 1H, J = 5.0 Hz, H^{24}), 3.97 (q, 1H, J = 4.0 Hz and 9.3 Hz, H_5'), 4.19 (d, 2H, J = 4.0 Hz, 2 × H_6'), 4.34 (q, 1H, J = 3.3 and 5.3 Hz, H_2'), 4.89 (q, 1H, J = 3.3 and 9.3 Hz, H_4'), 5.18 (t, 1H, J = 3.3 Hz, H_3'), 5.60 (br. singlet, 1H, OH), 5.68 (d, 1H, J = 5.3 Hz, H_1').

The 12,25-Diglucoside (VII). mp. 222-224° (MeOH), $[\alpha]_D^{20}$ −15.0° (c 0.78; $CHCl_3$) $C_{58}H_{88}O_{22}$. ^1H spectrum (δ, ppm): 0.86 (s, 3H), 0.88 (s, 3H), 0.91 (s, 3H), 0.96 (s, 6H), 1.04 (s, 3H), 1.14 (s, 6H), 2.00 (s, 3H, OAc), 2.02 (s, 18H, 6 × OAc), 2.07 (s, 3H, OAc), 3.48 (m, 1H, ΣJ = 5.0 Hz, H_e^3), 3.69 (m, 4H, H_a^{12}, H^{24}, 2 × H_5'), 4.18 (m, 4H, 4 × H_6'), 4.61 (d, 1H, J = 7.0 Hz, H_1'), 5.00 (d, 1H, J ≃ 8.0 Hz, H_1'), 4.80-5.32 (m, 6H, 2 × H_2', 2 × H_3', 2 × H_4').

The 12-Monoglucoside (VIII). mp. 190-193° (C_2H_5OH) $[\alpha]_D^{20}$ −12.9° (c 1.0; $CHCl_3$). $C_{44}H_{70}O_{13}$. ^1H spectrum (δ, ppm): 0.88 (s, 9H), 0.95 (s, 6H), 1.09 (s, 6H) 1.18 (s, 3H), 2.03 (s, 9H, 3 × OAc), 2.07 (s, 3H, OAc), 3.42 (t,1H, J = 2.4 Hz, H_e^3) 3.65 (m, 3H, H_a^{12}, H^{24}, H_5'), 4.19 (m, 2H, 2 × H_6'), 4.60 (d, 1H, J = 7.7 Hz, H_1'), 4.82-5.31 (m, 3H, H_2', H_3', H_4').

The 12,25-Diglucoside (IX). mp. 203-205° (C_2H_5OH), $[\alpha]_D^{20}$ −16.0° (c 1.0; $CHCl_3$), $C_{58}H_{88}O_{22}$. ^1H Spectrum (δ, ppm): 0.79 (s, 3H), 0.87 (s, 3H), 0.90 (s, 3H), 0.96 (s, 3H), 0.93 (s, 3H), 1.05 (s, 3H), 1.14 (s, 6H), 2.01 (s, 3H, OAc), 2.03 (s, 15H, 5 × OAc), 2.07 (s, 3H, OAc), 2.08 (s, 3H, OAc), 3.20 (m, 1H, ΣJ ≃15.0 Hz, H_a^3), 3.71 (m, 4H, H_a^{12}, H^{24}, 2 × H_5'), 4.18 (m, 4H, 4 × H_6'), 4.62 (d, 1H, J = 7.2 Hz, H_1'), 5.00 (d, 1H, J ≃8.0 Hz, H_1'), 4.80-5.32 (m, 6H, 2 × H_2', 2 × H_3', 2 × H_4').

The 12-Monoglucoside (X). mp. 197-198° (C_2H_5OH). $[\alpha]_D^{20}$ −12.0° (c 1.0; $CHCl_3$), $C_{44}H_{70}O_{13}$. ^1H spectrum (δ, ppm): 0.78 (s, 3H), 0.86 (s, 6H), 0.95 (s, 3H), 0.98 (s, 3H), 1.09 (s, 6H), 1.19 (s, 3H), 2.00 (s, 3H, OAc), 2.02 (s, 6H, 2 × OAc), 2.07 (s, 3H, OAc), 3.21 (m, 1H, ΣJ ≃ 15.0 Hz, H_a^3), 3.65 (m, 3H, H_a^{12}, H^{24}, H_5'), 4.18 (m, 2H, 2 × H_6'), 4.60 (d, 1H, J = 7.6 Hz, H_1'), 4.81-5.32 (m, 3H, H_2', H_3', H_4').

20(S),24(R)-Epoxydammarane-3β,12β,25-triol 3,12-Di-O-:2,3,4,6-tetra-O-acetyl-β-glucopyranoside) (XI). $[\alpha]_D^{20}$ −3.8° (c, 1.6 $CHCl_3$, $C_{58}H_{88}O_{22}$. ^1H spectrum (δ, ppm): 0.74 (s, 3H), 0.86 (s, 6H), 0.91 (s, 3H), 0.94 (s, 3H), 1.09 (s, 6H), 1.19 (s, 3H), 2.01 (s, 6H, 2 × OAc), 2.03 (s, 12H, 4 × OAc), 2.07 (s, 3H, OAc), 2.11 (s, 3H, OAc), 3.07 (m, 1H, ΣJ ≃15.0 Hz, H_a^3), 3.65 (m, 4H, H_a^{12}, H^{24}, 2 × H_5'), 4.19 (m, 4H, 4 × H_6'), 4.55 (d, 1H, J = 7.2 Hz, H_1'), 4.60 (d, 1H, J = 7.2 Hz, H_1'), 4.80-5.33 (m, 6H, 2 × H_2', 2 × H_3', 2 × H_4').

The 3,12,25-Triglucoside (XII) (lit. [22]). $C_{72}H_{106}O_{31}$, $[\alpha]_D$ −8.3° (c 1.0; $CHCl_3$). ^1H spectrum (δ, ppm): 0.75 (s, 3H), 0.86 (s, 3H), 0.89 (s, 3H), 0.91 (s, 3H), 0.95 (s, 3H), 1.04 (s, 3H), 1.14 (s, 6H), 2.01 (s, 3H, OAc), 2.03 (s, 27H, 9 × OAc), 2.07 (s, 3H, OAc), 2.11 (s, 3H, OAc), 3.02 (m, 1H, ΣJ ≃15.0 Hz, H_a^3), 3.68 (m, 5H, H_a^{12}, H^{24}, 3 × H_5'), 4.18 (m, 6H, 6 × H_6'), 4.54 (d, 1H, J = 7.6 Hz, H_1'), 4.61 (d, 1H, J = 7.7 Hz, H_1'), 5.00 (d, 1H, J ≃8.0 Hz, H_1'), 4.80-5.30 (m, 9H, 3 × H_3', 3 × H_3', 3 × H_4').

SUMMARY

1. The catalytic rearrangement of 20(S),24(R)-epoxydammarane-3,12β,25-triol 3-mono and 3,12-di(glucose orthoester)s leads to the formation of the corresponding 12-mono- and 12,25-diglucosides.

2. The anomalous regioselectivity of the catalytic rearrangements of orthoesters of 20(S),24(R)-epoxydammarane-3,12β,25-triols is evidently due to the influence of strong intramolecular hydrogen bonds.

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