8. R. G. S. Ritchie, N. Cyr, B. Korsch, H. J. Koch, and A. S. Perlin, Can. J. Chem., 53, 1424 (1975).

TRITERPENE GLYCOSIDES OF Thalictrum squarrosum.

IV. STRUCTURES OF SQUARROSIDES A1, A2, B1, AND B2

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Four new cycloartane glycosides have been isolated from a methanolic extract of Thalictrum squarrosum Stephan ex Willd.: squarroside A1 (I) – (21R, 22S, 23R)-3β-(β-D-glucopyranosyloxy)-21α-methoxy-21,23-epoxycycloart-24-ene-22β,30-diol, $C_{30}H_{60}O_{10}$; squarroside A2 (II) – the (21S)-epimer of compound (I); squarroside B1 (III) (21R, 22S, 23R)-3β-[O-α-L-rhamnopyranosyl-(1 → 6)-β-D-glucopyranosyloxy]-21α-methoxy-21,23-epoxycycloart-24-ene-22β,30-diol, $C_{43}H_{70}O_{14}$; and squarroside B2 (IV) – the (21S)-epimer of compound (III). The proposed structures were determined on the basis of ^1H and ^{13}C NMR spectroscopy, FAB mass spectrometry, and chemical transformations.

In the present paper we consider the determination of the structures of four new triterpene glycosides from Thalictrum squarrosum Stephan ex Willd. which have been called squarrosides A1 (I), A2 (II), B1 (III), and B2 (IV).

The separation of the squarrosides that we had isolated into groups A and B was based on their belonging to monoside (group A) or bioside (group B) series. The compounds within each group are stereoisomers, and this has been responsible for the complexity and specificity of their individualization. After a number of attempts to separate the isomeric pairs, and the unfruitfulness of these attempts had become obvious only after the recording of NMR spectra, we came to the conclusion of the possibility of estimating the structures of the compounds without the separation of the isomeric pairs (of decisive importance in this question was an analysis of the NMR spectra obtained). It must be mentioned that chromatography was quite incapable of serving as an indicator in answering the question of the individuality of a particular compound, since the squarrosides of group A have close Rf values and the squarrosides of group B identical ones in, of course, the systems of solvents that we used (see Experimental part).

The proof of the structures of the triterpene glycosides of group A given below was carried out on fractions enriched to different degrees (about 90% of squarroside A1, and, correspondingly, 10% of squarroside A2, and also conversely) and with the use of derivatives. In a number of cases it was possible to obtain the latter in the individual state.

The monosidic nature of at least one of the squarrosides of group A was indicated by the presence, in the FAB mass spectra of enriched fractions, of a signal with m/z 687, corresponding to the cationized molecular ion $[M + Na]^+$ and of a peak of $[M + Na - 162]^+$ with m/z 525 showing that the carbohydrate moiety was a hexose.

The products of the enzymatic hydrolysis of squarrosides 1 and 2 were squarrogenins 1 and 2 (V and VI) – stereoisomers at C-21 [1]. The similarity of the ^{13}C NMR spectra of glycosides (I) and (II) (Table 1) showed the isomeric nature of this pair of compounds.

It can be seen that the spectra of glycosides A1 and A2 differ only by the values of the chemical shifts (CSs) of the signals of the carbon atoms sensitive to epimerization at C-21 (I: C-21, 104.8; C-20, 52.3; C-17, 43.3 ppm); (II: C-21, 108.5; C-20, 55.5; C-17,

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TABLE 1. Chemical Shifts in the ^{13}C NMR Spectra of Compounds (I-XI) (δ, ppm, C_5D_5N)

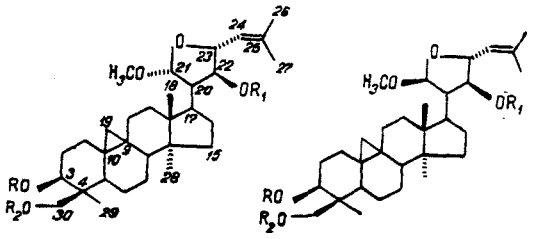
C atom	I, II	I* T=90°	III, IV T=90°	V	VI	VII	VIII, IX	X	XI
1	32,0	32,4	33,2	32,4	32,4	32,0	31,8	32,2	32,3
2a	30,5	31,8	31,1	31,7	31,7	30,1	30,0	31,2	31,4
3	89,1	89,9	90,9	80,1	80,2	89,3	89,3	87,2	87,2
4	44,9	45,8	46,1	43,8	43,8	43,8	43 8	44,8	44,7
5b	48,5	48,7	49,9	48,6	48,7	48,6	48,7	48,7	48,6
6	21,9	22,2	22,6	21,8	21,9	22,7	22,8	22,4	22,5
7c	26,6	27,4	27,9	27,0	26,9	27,0	27,1	27,1	26,7
			27,3						
8b	47,7	48,3	49,1	47,7	47,8	47,8	47,9	47,9	47,9
9	21,2	21,8	22,2	21,7	21,8	21,0	21,1	21,2	21,1
10	25,7	26,0	26,9	26,0	26,0	25,8	25,9	26,0	25,9
11c	25,9	27,0	28,8	26,7	26,5	26,7	25,9	26,7	26,4
			27,9						
12	35,9	36,4	37,2	36,1	35,9	36,1	37,1	36,1	35,9
			37,1				35,4		
13	45,3	45,4	46,7	45,3	45,6	45,3	45,7	45,3	45,4
	45,2		46,6				45,3		
14	48,5	49,1	49,9	48,4	48,5	48,6	48,7	48,7	48,6
15a	29,9	30,2	31,1	30,6	30,5	29,5	30,7	30,2	30,6
16a	29,9	30,2	31,1	30,0	27,8	27,0	29,5	30,0	30,6
	27,6								
17	44,3	41,1	45,8	40,7	44,8	40,8	44,6	40,8	44,7
	40,6		41,9				40,8		
18d	25,7	26,1	27,3	26,3	26,4	26,0	26,1	26,0	25,9
19a	29,9	30,5	32,6	31,3	30,7	31,3	31,2	30,3	30,6
			32,0						
20	55,5	52,9	55,5	52,5	55,6	52,5	55,6	52,5	55,5
	52,3		53,6				52,4		
21	108,5	105,3	109,6	104,9	108,7	104,9	108,2	105,0	108,6
	104,8		106,1				104,9		
22	76,5	75,9	76,4	75,0	76,7	75,0	77,3	75,5	76,5
	74,8		76,1				75,0		
23	80,6	81,1	81,9	80,7	79,0	80,7	80,7	80,7	78,9
	78,8		79,9				78,5		
24**	—	—	—	—	—	—	—	—	—
25**	—	—	—	—	—	—	—	—	—
26d	21,2	21,4	20,9	21,3	21,3	20,5	21,0	21,1	19,7
27d	19,7	20,0	19,7	19,8	19,8	19,8	19,2	19,9	19,5
28d	18,6	19,9	19,5	19,8	18,9	19,8	19,2	19,9	18,8
29d	18,4	18,6	19,5	18,4	18,6	18,5	18,7	18,4	18,6
30e	63,2	63,7	64,6	64,5	64,6	64,7	64,7	63,3	63,2
OCH_3	54,7	54,6	55,9	54,5	54,8	54,5	54,5	54,6	54,7
	54,5		56,4				53,1		
$\underline{COCH_3}$						170,8	170,8		
						170,5	170,4		
						170,4	170,1		
						170,4	169,7		
						169 8			
						169,7			

TABLE 1 (continued)

C atom	I, II	I* T=90°	III, IV T=90°	V	VI	VII	VIII, IX	X	XI
$COCH_3$						20,7	20,7		
1′	106,0	106,4	106,9			103,1	102,7		
2′	75,4	75,3	75,0			72,1	71,3		
3′	78,5	79,0	79,5			73,6	73,6		
4′	71,6	72,5	70,4			69,3	69,9		
5′	78,2	78,3	77,8			72,4	73,6		
6′[e]	62,7	63,5	68,7			62,6	67,7		
1″			103,1				98,7		
2″[f]			72,9				70,1		
3″[f]			73,1				70 1		
4″[f]			73,7				72,5		
5″			69,2				67,2		
CH_3			19,5				17,8		
Split-out carbohydrates									
CHOH								105,5	105,2
								79,1	78,2
CH_2OH								66,7	66,6
								64,5	64,2
								63,9	63,7
								66,7	66,6
								63,1	62,9
CH_3								17,4	17,5

a-f Alternative assignments within a column.
*Progenin of compound (III).
**Signals masked by the solvent.

40.6 ppm). The CSs of the carbon atoms indifferent to C-21 isomerization were identical for the two glycosides (see Table 1).



I. R = β-D-Glucopyranosyl
$R_1 = R_2 = H$

II. R = β-D-Glucopyranosyl
$R_1 = R_2 = H$

III. R = O-α-L-Rhamnopyranosyl-(1→6)-β-D-glucopyranosyl
$R_1 = R_2 = H$

IV. R = O-α-L-Rhamnopyranosyl-(1→6)-β-D-glucopyranosyl
$R_1 = R_2 = H$

V. $R = R_1 = R_2 = H$

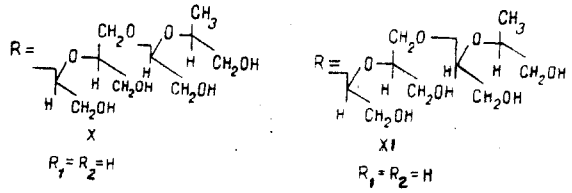
VI. $R = R_1 = R_2 = H$

VII. R = 2,3,4,6-Tetra-O-acetyl-β-D-glucopyranosyl
$R_1 = R_2 = CH_3CO$

VIII. R = O-2,3,4-Tri-O-acetyl-α-L-rhamnopyranosyl-(1→6)-2,3,4-tri-O-acetyl-β-D-glucopyranosyl
$R_1 = R_2 = CH_3CO$

IX. R = O-2,3,4-Tri-O-acetyl-α-L-rhamnopyranosyl-(1→6)-2,3,4,-tri-O-acetyl-β-D-glucopyranosyl
$R_1 = R_2 = CH_3CO$

Thus, the genin of squarroside A1 is squarrogenin 1 – (21R, 22S, 23R)-21α-methoxy-21,23-epoxycycloart-24-ene-3β,22β,30-triol. Squarroside A2 is based on squarrogenin 2 – the (21S)-epimer of compound (V).



X $R_1 = R_2 = H$

XI $R_1 = R_2 = H$

A comparison of the ^{13}C NMR spectra of glycosides (I) and (II) shows the identity of the carbohydrate moieties, and the CS values of these signals coincided with those for methyl β-D-glucopyranoside [2]. The signals of the C-3 atom in squarrosides A1 and A2 were shifted downfield by 9.2 ppm relative to those of the genins. This fact may be the result of the glycosylation of the carbon atom under consideration.

In the ^{13}C NMR spectrum of the peracetate of squarroside A1 (VII) the signals of the C-atoms of the carbohydrate moiety had undergone an upfield shift as a consequence of acetylation, which corresponds to literature information for the 2,3,4,6-tetraacetate of a β-D-glucopyranoside [2]. In this spectrum, the signal of the C-3 atom of the genin was observed at the same CS value as in squarroside A1 (see Table 1). This confirmed the correctness of our conclusion concerning glycosylation at the C-3 atom of the genin.

On the basis of the facts given above, squarroside A1 has the structure of (21R, 22S, 23R)-3β-(β-D-glucopyranosyloxy)-21α-methoxy-21,23-epoxycycloart-24-ene-22β,30-diol, while squarroside A2 is its (21S)-epimer.

As already mentioned, squarrosides B1 and B2 had identical Rf values. From the mass of the quasi-molecular ion 833 $[M + Na]^+$ in the combined FAB mass spectrum of compounds (III) and (IV), they were assigned to the diglycosides. The breakdown of the molecule leading to the fragment with m/z 507 indicated the presence of a hexose and deoxyhexose block [3] splitting out simultaneously with a molecule of water.

Glucose and rhamnose were identified by the TLC method in the products of the acid hydrolysis of the peracetates of compounds of (III) and (IV) (VIII and IX).

The enzymatic hydrolysis of squarrosides B1 and B2 together gave two genins and a progenin with a Rf value corresponding to squarroside A1. The identity of the genins with squarrogenins 1 and 2 was shown by a comparison of melting points and mass-spectrometric results [1].

According to FAB mass spectroscopy and ^{13}C NMR spectrometry the progenin was identified as squarroside A1 (I). It must be mentioned that for enzymatic hydrolysis we selected experimentally an enzyme (the gastric juice of Helix pomatia) exhibiting rhamnosidase and glucosidase activities in equal measure, so that the predominating reaction products were the genins. The progenin fraction was obtained in considerably smaller amounts. We succeeded in isolating only the progenin of squarroside B1 from it, but we were unable to conclude that this mixture of progenins contained squarroside B2.

As it is not difficult to observe, all the results obtained can be explained in two ways: either we were dealing with a single glycoside and the isolation of two squarrogenins can be ascribed to their interconversion (such a possibility has been shown in [1]) or with two glycosides, isomers, giving two genins in the process of enzymatic hydrolysis.

A definitive and, in our view, convincing choice of the second alternative was based on a comparative analysis of the NMR spectra of squarrosides B1 and B2 and squarrogenins 1 and 2 and also of squarrosides A1 and A2. It follows from this comparison that the ^{13}C NMR spectrum of squarrosides B1 and B2 contained the signals of two compounds, while the genin part of the spectrum coincided with the spectra of squarrosides A1 and A2 and the carbohydrate part contained additional signals which we assigned to a deoxyhexose. From its CS values, this hydrocarbon was identified as rhamnose [2]. To determine the position of attachment of the rhamnose residue, glycosides (III) and (IV) were subjected to Smith oxidation. This gave products (X) and (XI), each containing six CH_2OH groups. The formation of compounds with this number of primary hydroxy groups and having a mass of 707 for the $[M + Na]^+$ ion (FAB mass spectrum) presupposes the attachment of the rhamnose to one of the CH_2OH groups (C-30 of the genin or C-6 of glucose). The signal of one of them underwent a paramagnetic shift by ∿5 ppm (see Table 1).

To choose one of the alternative variants we obtained the peracetates of squarrosides

B1 and B2 (compounds (VIII) and (IX), respectively). In the ^{13}C NMR spectrum of the acetates (VIII) and (IX) the CS of the C-5 glucose atom was 73.6 ppm, while in the peracetate of methyl β-D-glucopyranoside this signal was observed at 71.8 ppm [2]. Such a difference in the CS values is, in our view, the result of attachment of the rhamnose residue to the C-6 glucose atom.

The monodesmosidic nature of glycosides B1 and B2 were shown by their FAB mass spectrometric fragmentation, giving a fragmentary ion with m/z 687 $[M + Na - dHex]^+$ and no peak that could have been ascribed to the analogous fragment from a (nondeoxy-) hexose $[M + Na - Hex]^+$.

Thus, for squarroside B1 we propose the structure of (21R, 22S, 23R)-3β-[O-α-L-rhamnopyranosyl-(1 → 6)-β-D-glucopyranosyloxy]-21α-methoxy-21,23-epoxycycloart-24-ene-22β,30-diol; squarroside B2 is its (21S)-epimer.

EXPERIMENTAL

For general observations see [1].

We used Florisil magnesium silicate, 60-100 mesh, polyamide, and type L40/100 silica gel for column chromatography, and L5/40 and Silufol plates for TLC. The following solvent systems were employed: 1) chloroform–methanol (with an increase in the proportion of ethanol from 0 to 10%); 2) benzene–methanol (with an increase in the proportion of methanol from 0 to 8%); 3) hexane–acetone (with an increase in the proportion of acetone from 0 to 20%); 4) chloroform–methanol–water (70:12:1); 5) chloroform–methanol–water (70:23:4); and 6) hexane–chloroform–methanol (5:10:1).

Isolation of Squarrosides A1 and A2, and B1 and B2. A methanolic extract of Thalictrum squarrosum was chromatographed on a column of silica gel in system 1. Elution of the column with a system containing 5% of methanol gave a fraction of squarrosides A1 and A2, and when the proportion of methanol was increased to 10% a mixture of squarrosides B1 and B2 was isolated.

The fraction containing squarrosides A1 and A2 was subjected to liquid-liquid separation in a two-phase chloroform–methanol–water (20:10:7.5) system. Separation was carried out in test tubes for 30 min. Six transfers were carried out in the course of the separation. The bottom phase from the first and second transfers was evaporated and the residue was extracted with diethyl ether. The residue after extraction was repeatedly chromatographed on silica gel in systems 1 and 2, followed by filtration of the fraction through Florisil. This gave a fraction of squarrosides A1 and A2 the yield of which amounted to 0.1% on the air-dry plant.

The combined squarrosides B1 and B2 were rechromatographed on polyamide in system 1. The saponins so isolated were subjected to countercurrent separation in the chloroform–methanol–water (5:6:4) system. The separation was carried out as described above. The evaporated bottom phase of the first two transfers was chromatographed successively on silica gel in systems 1, 4, and 5. This gave squarrosides B1 and B2. The yield of squarrosides B1 and B2 was 0.5% on the air-dry raw material.

Squarrosides A1 and A2 (I and (II). $C_{37}H_{60}O_{10}$. IR spectrum ν_{max}^{KBr}, cm^{-1}: 3040 (CH_2 of a cyclopropane ring), 3350-3500 (OH). FAB mass spectrum, m/z: 703 $[M + K]^+$, 687 $[M + Na]^+$, 541 $[M + K - 162]^+$, 525 $[M + Na - 162]^+$. The ^{13}C NMR spectrum is given in Table 1.

Squarrosides B1 and B2 (III and IV). $C_{43}H_{70}O_{14}$, mp 200-202°C (ethanol). IR spectrum, ν_{max}^{KBr}, cm^{-1}: 3040 (CH_2 of a cyclopropane ring); 3440 (OH). FAB mass spectrum, m/z: $[M + Na]^+$, 687 $[M + Na - 146]^+$, 507 $[M + Na - 308 - H_2O]^+$. The ^{13}C NMR spectrum is given in Table 1.

Acetylation of Squarroside A1. A solution in 4 ml of pyridine of 700 mg of the fraction enriched with squarroside A1 was treated with 2 ml of acetic anhydride, and the reaction mixture was kept at room temperature for 24 h. After the usual working up, the acetylation products were chromatographed on a silica gel column in system 3. This gave 400 mg of 22,30-di-O-acetylsquarrogenin 1 2,3,4,6-tetra-O-acetyl-β-D-glucopyranoside (VII), $C_{49}H_{72}O_{16}$, mp 192-194°C (hexane–acetone), $[\alpha]_{546}^{20}$ +52.70° (c 1.2; pyridine). IR spectrum, ν_{max}^{KBr}: 1720-1735 cm^{-1} (C=O). ^1H NMR spectrum (δ, ppm; J, Hz; $CDCl_3$; 0 – TMS): 0.38, 0.51 (d, AB system, ^2J = 4.0 Hz; 2H-19); 0.90, 0.98, 1.21, 1.67, 1.76 (s, CH_3 × 5); 1.96, 1.98, 1.98, 2.00, 2.03, 2.06 (s, $\underline{CH_3}CO$ × 6); 3.28 (s, CH_3O); 4.52 (d, ^3J = 8 Hz, anomeric H of glucose); 4.78 (d, ^3J = 4.0 Hz, H-21); 5.35 (br.d., ^2J = ~8 Hz, H-24). The ^{13}C NMR spectrum is given in Table 1.

Acetylation of Squarrosides B1 and B2 (III and IV). A soution in 4 ml of pyridine of 1100 mg of the mixture of squarrosides B1 and B2 was treated with 2 ml of acetic anhydride, and the reaction mixture was kept at room temperature for 24 h. After the usual working up, the acetylation products were chromatographed on a silica gel column in system 3. This gave 650 mg of the combined O-2,3,4-tri-O-acetyl-α-L-rhamnopyranosyl-(1 → 6)-2,3,4-tri-O-acetyl-β-D-glucopyranosides of 22,23-di-O-acetylsquarrogenins 1 and 2 (VIII and IX, respectively). $C_{59}H_{86}O_{12}$. IR spectrum: ν_{max}^{KBr}, 1725-1740 cm^{-1} (C=O). ^1H NMR spectrum (δ, ppm; J, Hz; $CDCl_3$; 0 – TMS): 0.39, 0.47 (d, AB system, ^2J =4.0 Hz, 2 H-19); 1.19 (d, ^3J = 4 Hz, CH_3 of rhamnose); 1.91, 1.95, 1.99, 2.00, 2.00, 2.03, 2.08, 2.11 (s, CH_3CO × 8); 3.60 (s, CH_3O); 4.50 (d, ^3J = 8 Hz, anomeric H of glucose); 4.77 (d, ^3J = 4 Hz, H-21); 5.34 (br.d., ^3J = ∿8 Hz, H-24). The ^{13}C NMR spectrum is given in Table 1.

Enzymatic Hydrolysis of Squarrosides A1 and A2, and B1 and B2. The enzymatic hydrolysis of squarrosides A1 and A2 was described in [1]. A suspension of 2 g of squarrosides B1 and B2 in 500 ml of water was treated with 200 mg of the unpurified enzyme of Helix pomatia and a few drops of toluene. The reaction mixture was kept in a thermostat at 36°C with constant stirring for 14 days with the periodic addition of more enzyme (50-mg portions). Monitoring was carried out by TLC in system 5. The reaction products were exhaustively extracted with chloroform. The chloroform extracts were washed with water. This gave 590 mg of dry extract. The residue after extraction with chloroform was exhaustively extracted with butanol. The butanolic extract after evaporation of the solvent was subjected to enzymatic hydrolysis under the conditions described above. The weight of the chloroform extracts from the second enzymolysis was 320 mg.

The reaction products were combined and chromatographed on a column of silica gel in system 1. At a 3% concentration of methanol a mixture of genins (V) and (VI) was eluted, and when the concentration of methanol was increased to 5% the progenin of squarroside B1 was obtained – squarrogenin 1 3-O-β-D-glucopyranoside (I). $C_{37}H_{60}O_{10}$, mp 254-256°C (in methanol), $[\alpha]_{546}^{20}$ +25.16° (c 1.5; pyridine). FAB mass spectrum, m/z: 703 $[M + K]^+$, 687 $[M + Na]^+$, 709 $[M + 2Na - H]^+$, 507 $[M + Na - 162 - H_2O]^+$. The ^{13}C NMR spectrum is given in Table 1.

The mixture of genins was rechromatographed in silica gel in system 3. The eluent containing 13% of acetone eluted 50 mg of squarrogenin 1 (V), $C_{31}H_{50}O_5$, mp 169-171°C (hexane–acetone), $[\alpha]_{546}^{20}$ +11.06° (c 4.52; pyridine), FAB mass spectrum, m/z: 525 $[M + Na]^+$, 503 $[M + H]^+$, 485 $[M + H - H_2O]^+$, 471 $[M + H - CH_3OH]^+$, 453 $[M + H - CH_3OH - H_2O]^+$, 435 $[M + H - CH_3OH - 2H_2O]^+$. An increase in the concentration of acetone to 14% gave 46 mg of squarrogenin 2 (VI), $C_{31}H_{50}O_5$, mp 190-193°C (hexane–acetone), $[\alpha]_{546}^{20}$ +106.6 (c 0.3; pyridine). FAB mass spectrum, m/z: 525 $[M + Na]^+$, 503 $[M + H]^+$, 485, 471, 453, 435.

Smith Oxidation [4] of Squarrosides B1 and B2. A solution of 800 mg of squarrosides B1 and B2 in 82 ml of methanol was treated with a solution of 2.7 g of sodium periodate in 15 ml of water, and the mixture was stirred at room temperature for 18 h. After the excess of oxidant had been decomposed with glycerol, the reaction mixture was diluted with water and the methanol was evaporated off. The aqueous residue was extracted with chloroform.

The evaporated chloroform extract was dissolved in 50 ml of methanol, and 2.7 g of sodium tetrahydroborate was added. After 5 h the reaction products were diluted with water (1:1), the methanol was evaporated off, and the aqueous residue was extracted with chloroform. The chloroform extracts were washed with water. This gave 520 mg of reaction products, and they were repeatedly chromatographed on silica gel columns in systems 1 and 6, which led to the isolation of 46 mg of the product of the oxidation of squarroside B1 (XI) and 25 mg of the product of the oxidation of squarroside B2 (X). Their ^{13}C NMR spectra are given in Table 1.

Acid Hydrolysis of the Peracetates (VIII) and (IX). A solution of 40 mg of the peracetates (VIII) and (IX) in 3 ml of ethanol was treated with 3 ml of 1% sulfuric acid. After 3 h, the concentration of acid in the solution was increased to 20%, and the reaction mixture was heated at 70°C for 2 h. The excess of acid in the solution was neutralized with AV-17 anion-exchange resin.

The reaction products were extracted with chloroform. The residue after extraction was analyzed by TLC for carbohydrates. When the chromatogram was run in system 5 with authentic samples, glucose and rhamnose were identified.

SUMMARY

Four new cycloartane glycosides have been isolated from a methanolic extract of Thalictrum squarrosum Stephan ex. Willd. The following structures have been established for them: squarroside A1 (I) – (21R, 22S, 23R)-3β-(β-D-glucopyranosyloxy)-21α-methoxy-21,23-epoxycycloart-24-ene-22β,30-diol; squarroside A2 (II) is the (21S)-epimer of compound (I); squarroside B1 (III) is (21R, 22S, 23R)-3β-[O-α-L-rhamnopyranosyl-(1→6)-β-D-glucopyranosyloxy]-21α-methoxy-21,23-epoxycycloart-24-ene-22β,30-diol; and squarroside B2 (IV) is the (21S)-epimer of compound (III).

LITERATURE CITED

1. V. I. Lutskii, E. A. Khamidullina, A. S. Gromova, and A. A. Semenov, Khim. Prir. Soedin., 510 (1989) [in this issue].
2. S. Seo, J. Tomita, K. Tori, and Y. Yashimura, J. Am. Chem. Soc., 100, 3331 (1978).
3. M. Adinolfi, J. Mangoni, G. Marino, M. Parrilli, and R. Self, Biomed. Mass Spectrom., 11, 310 (1984).
4. M. Abdel-Akner, J. K. Hamilton, R. Montgomery, and F. Smith, J. Am. Chem. Soc., 74, 4970 (1952).

ANODIC BEHAVIOR OF EPHEDRINE AT SOLID ELECTRODES

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The electrooxidation of the alkaloid ephedrine at solid electrodes in a wide range of concentrations and pH values of solutions has been studied by the methods of potentiodynamic voltammetric curves, preparative electrolysis, and quantum-chemical calculations by the SCF MO LCAO method in the MINDO/3 approximation. A quantitative basis has been given for the sequence of stages in the electrooxidation of ephedrine proposed previously by the authors of one of the cited papers. Good agreement has been established between the values found theoretically and experimentally.

In electrochemical methods of extracting alkaloids from plant raw materials [1, 2] a large role is played by the choice of the material of the electrode and the nature of the medium. Continuing investigations on the electrochemistry of ephedrine [3], we have studied its electrochemical oxidation at platinum, graphite, and vitreous carbon in Britton-Robinson aqueous buffer solutions with various pH values [4].

As the results of the experiments have shown, the voltammetric curves of the oxidation of ephedrine have the form of distinctly expressed current maxima, the greatest value of which is observed in an alkaline medium. The nature of the effective oxidation curve depends on the material of the electrode (Fig. 1). The electrooxidation of ephedrine on platinum takes place with greater difficulty than on graphite and on vitreous carbon electrodes. On the voltammetric curves taken in more concentrated solutions of ephedrine ($C > 2 \cdot 10^{-3}$ M) at a graphite electrode a second electrode wave appears (Fig. 1c). This shows the further electrooxidation of the products of the initial oxidation of ephedrine. The treatment of the curves by Semerano's criterion [5] showed in all the solutions studied a linear relationship between the peak current and the square root of the rate of scanning the potential, which is characteristic for diffusion processes. However, such a relationship may also be observed in a number of other cases; for example, on the slow transfer of charge or on desorption of a primary oxidation product [6]. The values of $(\partial \log i/\partial \log v)_{c,T}$ calculated from these

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