A monoglycoside was extracted from the filtrate with chloroform (4 × 80 ml) and the extract was filtered through a layer of alumina (1 g, activity grade III) and was evaporated. The residue was crystallized from ethanol. The properties of the monoglycoside [mp 221-225°C; $[\alpha]_D^{20}$ − 64.5 ± 3° (s 0.8; MeOH)], corresponded to those of acovenoside A.

The aqueous phase was evaporated to dryness. According to paper chromatography, the residue contained D-glucose. The phenylosazaone of this monosaccharide was obtained, with mp 207-208°C; it was identical with the phenylosazone of D-glucose.

SUMMARY

Six cardenolides have been isolated in the individual state from the leaves of *Acokanthera venenata* G. Don. They include acovenoside A and a new cardiac glycoside which has been named glycoacovenoside B and has been characterized from the results of the investigation as 1β-O-acetyl-3β-(4'-O-β-glucopyranosyl-3'-O-methyl-α-L-talomethylsyloxy)-5β,14β-card-20(22)-enolide.

LITERATURE CITED

1. P. Hauschild-Rogat, E. Weiss, and T. Reichstein, Helv. Chim. Acta, 2, 2612 (1962).
2. T. Reichstein, Helv. Chim. Acta, 8, 2299 (1967).
3. M. B. Fayez and S. A. R. Negm, Chem. Ind. (London), No. 40, 1361 (1968); Ya. V. Rashkes, M. B. Gorovits, G. K. Makarevich, and N. K. Abubakirov, Khim. Prir. Soedin., 747 (1971).
4. K. Tori and K. Avno, Ann. Rept. Shionogi Res. Lab., 15, 130 (1965).
5. N. Sh. Pal'yants and N. K. Abubakirov, Khim. Prir. Soedin., 744 (1981).
6. I. F. Makarevich, Khim. Prir. Soedin., 260 (1969).
7. N. I. Yakubov, Ya. V. Rashkes, and N. Sh. Pal'yants, Khim. Prir. Soedin., 345 (1983).

TRITERPENE GLYCOSIDES OF *Thalictrum squarrosum*

I. STRUCTURE OF SQUARROFURIC ACID

A. S. Gromova, V. I. Lutskii, A. A. Semenov, M. F. Larin, and R. B. Valeev

UDC 547.918:543.422.25

Squarrofuric acid has been isolated from *Thalictrum squarrosum* by the acid hydryolysis of a methanolic extract. It is suggested that is is an artefact formed on hydrolysis and has the structure of 3β,30-dihydroxy-22,25-epoxylanost-9(11)-en-21-oic acid. ^1H and ^{13}C NMR spectra are given for squarrofuric acid and nine of its derivatives. The mass-spectral characteristics and physicochemical constants of the compounds studied are presented.

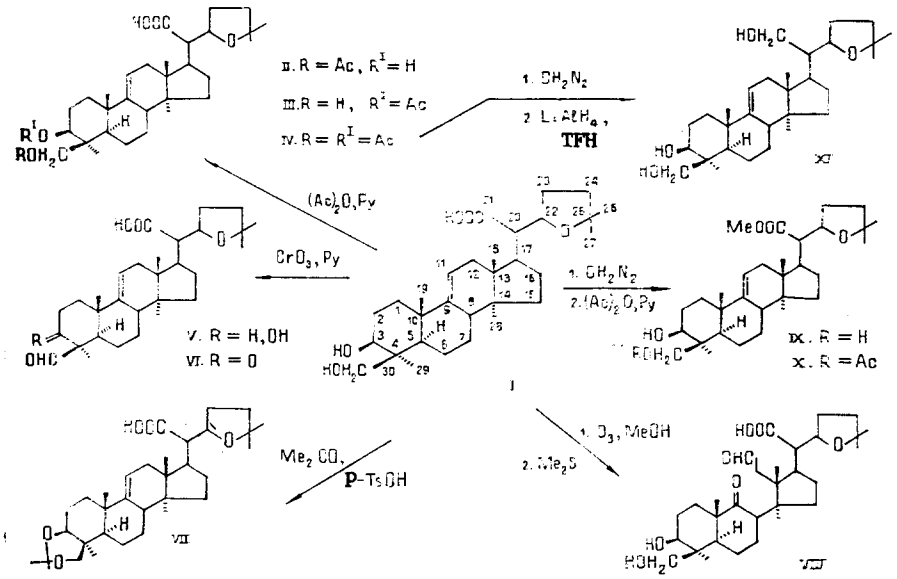
In a study of the saponins of plants of the genus *Thalictrum* [1, 2] we found that *Thalictrum squarrosum* Steph. (nodding meadow rue) contains not less than eight triterpene glycosides (about 1% of the weight of the raw materials). We have called the saponins of this species squarrosides. Some sapogenins of these glycosides belong to the tetracyclic triterpenoids with a cyclopropane ring.

The acid hydrolysis of a metabolic extract of nodding meadow rue gave two predominating sapogenins. In the present communication we consider the structure of the main product of the hydrolysis of the glycosides — genin I, which we have called squarrofuric acid (Scheme on following page).

Squarrofuric acid (I) — $C_{30}H_{48}O_5$, M^+ 488 — is a triterpene acid (IR: 1675 cm^{-1}; ^{13}C NMR: 175.8 ppm) having, according to its PMR spectrum, six methyl groups (0.74, 0.92, 0.97,

Irkutsk Institute of Organic Chemistry, Siberian Branch, Academy of Sciences of the USSR. Irkutsk State University. Translated from Khimiya Prirodnykh Soedinenii, No. 3, pp. 376-384, May-June, 1987. Original article submitted November 25, 1986.

 0009-3130/87/2303-0310$12.50



Scheme of the chemical transformations of squarrofuric acid.

1.15, 1.22, 1.44 ppm), a trisubstituted double bond (5.15 ppm, br.d., ^3J = 6.0 Hz), a primary alcohol group (3.62, 4.46 ppm, d, AB-system, ^2J = 11.0 Hz), and two >CH—O—fragments (3.50 ppm, q, ^3J = 9.0, 4.5 Hz, and 4.28 ppm, q, ^3J = 11.0, 4.5 Hz) (Table 1).

The mass spectra of compound (I) showed, in addition to the molecular ion, the peaks of ions with m/z 330 (M − $C_8H_{14}O_3$, M − the side chain), 299 (330 − CH_2OH + H), and 297 (330 − CH_3 − H_2O). Consequently, genin (I) is a tetracyclic triterpenoid containing two hydroxy groups in the polycyclic fragment. The formation of two monoacetates (II, III) and one diacetate (IV) confirmed this fact.

The Sarett oxidation [3] of genin (I) gave two main products — (V) and (VI). It can be seen from a comparison of the ^{13}C NMR spectra of these compounds that the passage from compound (I) via the aldehyde (V) to the ketoaldehyde (VI) caused a considerable paramagnetic shift of the signal fo the C-4 atom [(I) — 43.6; (V) — 54.0; (VI) — 64.0 ppm]. Consequently, both oxidized groups in compound (VI) were present in the α-position to C-4.

The presence of a 1,3-diol grouping in ring A of squarrofuric acid was also confirmed by the preparations of the 1,3-acetonide (VII) under the action of dry acetone in the presence of p-toluenesulfonic acid on the genin (I) [4].

The β-orientation of the 3-OH group followed from the values of the spin—spin coupling constants (SSCCs) of the H-3 signal (^3J = 9.0 and 4.5 Hz) in the PMR spectrum of compound (I).

Analysis of the ^{13}C NMR spectrum of genin (I) and of literature information for terpenes with 4β- [5, 6] and 4α- [1, 6] -hydroxymethyl groups showed that in squarrofuric acid the hydroxymethyl group at C-4 was present in the axial position and the methyl group in the equatorial position. The values of the chemical shifts (CSs) and the nature of the splitting of the signals of the protons of the 1,3-dioxane ring in the PMR spectrum of the acetonide (VII) confirmed the relative stereochemistry at C-3 and C-4 (Table 1) [4].

The double bond in compound (I) was present in the 9(11) position, as followed from a comparison of the experimental (Table 2) and literature ^{13}C NMR spectra [6, 7].

Different PMR spectroscopy showed that the olefinic proton (5.15 ppm, br.d, ^3C = 6.0 Hz) in genin I interacted with the two protons at C-12 (1.9 ppm, br.d, ^2J = 18.0, H_a-12; 1.61 ppm, q, ^2J = 18.0 Hz, ^3J = 6.0 Hz, H_e-12). Because the H(11)—C(11)—C(12)—H_a(12) dihedral angle has a value of about 80°, the SSCC of the olefinic proton was close to zero and caused only a broadening of the H-11 signal. Spin—spin coupling with H_e-12 led to the splitting of the H-11 signal with the constant ^3J = 6 Hz).

In the product of the oxonization of squarrofuric acid (VIII), the keto group was located in a six-membered ring (ν = 1720 cm^{-1}). In the α-position to the aldehyde group (10.38 ppm, ^3J = 3.5 Hz) there are two ethylene protons (3.12 ppm ^2J = 18 Hz, ^3J = 3.5 Hz; 2.79 ppm, br.d, ^2J = 18 Hz).

TABLE 1. Chemical Shifts and Spin–Spin Coupling Constants in the ^1H NMR Spectra of Compounds (I-VI) (δ, ppm, C_5D_5N)*

Compound	H-3	H-11	H-22	2H-30	H-20	CHO CH_3OH	CH_3O CH_3COO	CH_3
I	3,50, q, ^3J=4,5; 9,0	5,15, d, ^3J=6,0	4,28, q, ^3J=6,0; 12,0	3,62; 4,46, d, ^2J=11,5	2,65, m	—	—	0,74; 0,92; 0,97; 1,15; 1,22; 1,44
II	4,73, q, ^3J=4,5; 11,5	5,12, d, ^3J=5,0	4,28, q, ^3J=6,0; 13,0	3,95; 4,08, d, ^2J=11,5	2,65, m	—	1,96	0,76; 0,91; 1,08; 1,16 (2 CH_3); 1,23
III	3,42, d, ^3J=6,5; 10,0	5,15, d, ^3J=5,0	4,28, q, ^3J=6,0; 13,0	4,5; 4,7, d, ^2J=11,5	2,65, m	—	2,02	0,76; 0,92; 1,03; 1,16; 1,23; 1,31
IV	4,63, m	5,08, d, ^3J=5,0	4,28, q, ^3J=6,0; 13,0	4,19; 4,55, d, ^2J=11,5	2,65, m	—	1,96; 2,04	0,74; 0,88; 0,94; 0,99; 1,16; 1,23
V	3,53, q, ^3J=4,5; 12,0	5,21, d, ^3J=5,0	4,28, q, ^2J=6,0; 13,0	—	2,65, m	10, 43, s	—	0,73; 0,89; 0,90; 1,15; 1,23; 1,38
VI	—	5,14, d, ^3J=5,2	4,29, q, ^3J=6,5; 13,0	—	2,65, m	9,83, s	—	0,72; 0,90; 1,03; 1,17; 1,24 (2 CH_3)
VII** ($CDCl_3$)	3,43, m	5,21, m	4,03, m	3,21; 4,07, d, ^2J=12,0	2,43, m.	—	—	0,71 (2 CH_3); 1,07; 1,21 (2CH_3); 1,28; 1,33; 1,42
VIII	3,44, m	—	4,27, q, ^3J=6,5; 13,0	3,76; 4,42, d, ^2J=11,0	2,68, m	10,37; d ^3J=3,0	—	0,99; 1,13; 1,16; 1,20; 1,24; 1,39
IX	3,54, q, ^3J=9,0; 15,0	5,18, d, ^3J=6,3	4,11, q, ^3J=6,0; 14,0	3,63; 4,45, d., ^2J=11,0	2,52 M	—	3,66	0,69; 0,74; 0,98; 1,13; 1,16; 1,44
X ($CDCl_3$)	3,26, q, ^3J=5,5; 11,0	5,22, d, ^3J=5,5	4,04, q, ^3J=6,0; 13,0	4,18; 4,32, d, ^2J=11,0	2,42 m	—	3,67; 2,06	0,64; 0,73; 0,99; 1,11; 1,17 (2 CH_3)
XI	3,55, m	5,22, d, ^3J=5,0	4,21, br.t ^3J=7,5	3,63; 4,48, d, ^2J=11,0	***	3,89, q, ^2J=11,0; ^3J=3,0; 4,06, d, ^2J=11,0	—	0,71; 0,73; 1,00; 1,13; 1,18; 1,46

*Symbols: s — singlet; d — doublet; br.t — broadened triplet; q — quartet; m — multiplet. The signals of the protons of the CH_3, CH_3O and CH_3COO groups appear as signlets.
†Spectrum taken on a FX-90 Q instrument (JEOL).
†Signal shifted into the region of the methylene hump.

TABLE 2. Chemical Shifts in the ^{13}C NMR Spectra of Compounds (I-VI and IX-XI) [δ, ppm, solvent $CDCl_3$ for (IV, IX, and X); C_5D_5N, for the others]

Proton	I	II	III	IV	V	VI	IX	X	XI
1	36,8	36,6	36,9	35,3	36,1	37,2	35,8	36,2	36,7
2	29,2	24,7	28,7	24,3	28,6	39,2	28,1	27,9	29,1
3	80,4	80,1	78,2	80,0	76,2	208,8	80,6	79,2	80,3
4	43,6	43,3	43,0	41,4	54,0	64,0	42,8	42,6	43,5
5	54,0	54,1	53,8	51,9	54,5	55,8	53,1	53,8	53,8
6	22,2	23,0	22,8	22,3	22,4	23,0	21,3	22,4	22,1
7	27,2	27,3	27,3	27,0	27,2	27,2	26,5	26,6	27,4
8	42,6	42,6	42,7	42,0	42,2	42,2	41,8	42,1	42,4
9	148,6	147,6	147,6	147,4	145,7	145,7	147,8	147,8	147,6
10	39,8	39,6	39,8	39,2	39,6	39,6	39,0	39,2	39,6
11	115,8	115,9	116,0	116,0	116,7	118,1	115,3	115,7	115,7
12*	39,3	39,2	39,2	38,2	39,2	39,2	38,4	38,6	38,9
13*	46,7	46,7	46,8	46,8	46,7	46,6	46,0	46,2	47,2
14*	45,2	45,2	45,1	44,0	45,2	45,4	44,4	44,6	44,9
15	34,2	34,2	34,2	33,3	34,2	34,2	33,8	33,4	34,3
16	29,2	30,0	29,2	28,6	29,2	28,6	28,3	28,6	30,7
17	45,3	45,2	45,1	45,0	45,2	45,0	44,4	44,6	46,8
18	15,1	14,9	15,0	13,7	14,9	14,9	14,5	14,7	14,9
19*	23,5	23,2	23,5	22,6	23,5	21,4	22,4	22,4	23,6
20	54,6	54,6	54,5	53,4	54,7	54,4	53,6	53,5	43,7
21	175,9	175,8	175,7	174,3	176,4	175,8	173,8	173,8	61,4
22	80,4	80,3	80,1	80,0	80,4	80,3	79,3	79,4	81,4
23	32,0	31,9	31,9	30,1	32,0	31,9	31,5	31,6	30,0
24	35,8	35,7	35,8	34,0	35,8	35,8	34,8	35,0	37,0
25	80,2	80,1	80,2	82,4	80,1	80,1	80,0	80,0	80,3
26*	28,5	28,4	28,3	27,7	28,4	28,3	27,9	28,1	27,7
27*	29,3	29,2	29,2	28,6	29,2	29,2	28,6	28,9	29,1
28	19,2	19,1	19,1	18,7	19,1	18,9	18,6	18,8	19,1
29*	23,8	23,0	23,0	22,6	21,7	17,8	23,1	22,9	23,7
30	64,8	63,3	66,2	65,0	207,4	202,5	64,4	65,4	64,7
CH_3COO		21,1; 170,4	21,1; 171,0	21,2 21,1; 170,5; 170,9				21,2 170,4; 51,0	
CH_3O							50,8		

*The assignments of signals 12 and 24, 13 and 14, 19 and 29, and 26 and 27 are alternative.

The above-mentioned multiplicity of the H-12 signals in genin (I) and in the aldehyde (VIII) showed the quaternary nature of the C-13 atom. On the other hand, it was possible to show by the procedure of selective double ^{13}C-{^1H} resonance that in (I) there was a proton (2.35 ppm) and not a methyl group at the C-8 carbon atom (42.6 ppm). Consequently, of the seven possible types of structures of tetracyclic triterpenes [8], the dammarane, fusicane and meliacin series can be excluded for squarrofuric acid.

It followed from the indications hydrogen unsaturation (five rings, one double bound), the ^{13}C NMR spectra (80.4; 80.2 ppm, s, CH–O–C group) and mass-spectral fragmentation (m/z 99, 100%, $C_6H_{11}O$) [9] that genin (I) contained a tetrahydrofuran ring with geminal methyl groups at C-25.

The signals of a proton at 4.28 ppm (q, ^3J = 12.0; ^3J = 6.0 Hz) and of a carbon atom at 80.4 ppm in the ^1H and ^{13}C NMR spectra of genin (I) were assigned to H-22 and C-22, respectively, of the tetrahydrofuran ring, since the passage from compound (I) to its acetate (II-V) did not lead to changes in the CSs of the CH-22 group (see Tables 1 and 2).

It was shown by the methods of double resonance (PMR) and selective ^{13}C-{^1H} double resonance that the H-22 proton exhibited spin–spin coupling (^3J = 12.0 Hz) with a proton at C-20 (2.65 ppm, m). The strong descreening of the H-20 proton indicated that it was adjacent to a carboxy group. In actual fact, the reduction of the acid (I) to the alcohol (XI) caused a diamagnetic shift of the H-22 signal in the PMR spectrum of (XI). In the ^{13}C NMR spectrum, passage from the acid (I) to the alcohol (XI) led to an upfield shift of the C-20 signal by 10.9 ppm (see Table 2). Consequently, the carboxy group was present at C-21.

In order to assign the signals of the methyl groups in the PMR spectra of genin (I) we studied the spectra of its derivative (X) having a complex-forming center at C-3, with the

TABLE 3. Chemical Shifts of the Protons Induced on the Addition of $Eu(dpm)_3$ in the ^1H NMR Spectrum of Compound (X) ($CDCl_3$, δ, ppm)

Mk/Ms*	CH_3-19	CH_3-29	CH_3-18**	CH_3-28**	CH_3-26	CH_3-27	H-3	2H-30
0	0,99	1,11	0,64	0,73	1,17	1,17	3,26	4,32; 4,18
0,024	1,0	1,13	0,65	0,74	1,17	1,17	3,6	4,33; 4,20
0,064	1,03	1,21	0,65	0,74	1,17	1,17	3,6	4,44; 4,28
0,106	1,09	1,36	0,67	0,76	1,17	1,17	3,6	4,69; 4,42
Δ	0,1	0,25	0,03	0,03	0	0	0,34	0,37; 0,24
Δ Hz.	20	50	6	6	0	0	68	74; 48

*Mk/Ms — $Eu(dpm)_3$/substrate molecular ratio.
**Assignment alternative.

addition of the shift reagent $Eu(dpm)_3$. As can be seen from Table 3, the greatest paramagnetic shift was experienced by the protons of the CH_3-19 and CH_3-29 methyl groups. The methyl groups at C-13 and C-14 are more remote from the center of complex-formation and the addition of the $Eu(dpm)_3$ caused a considerably smaller downfield shift of their protons (6 Hz). The signals of the geminal methyl groups in the tetrahydrofuran ring did not change their positions at all because of their great distance from the $Eu(dpm)_3$.

It is impossible on the basis of the available information to determine the configurations of the substituents at C-13, C-14, C-17, and C-20 and, consequently, to make a choice between lanostane, euphane, and tirucillane structures. However, in view of the nature of the genins of other *Thalictrum* species studied previously [1, 5, 10], the most probable structure for squarrofuric acid is that of 3β,30-dihydroxy-22,25-epoxylanost-9(11)-3n-21-oic acid (I). On the basis of analogies [1, 5], it must be assumed that triterpenoid (I) is an artefact formed during hydrolysis under the action of the mineral acid on a genin of the cycloartane series.

EXPERIMENTAL

IR spectra were recorded on a Specord UV-VIS instrument in paraffin oil. ^1H NMR spectra were recorded on a Bruker WP-200 spectrometer (200.13 MHz) and ^{13}C NMR spectra on a Jeol FX-90Q spectrometer (22.49 MHz). Temperature 25°C; internal standard — HMDS.

The assignment of the signals of the carbon atoms was made with the use of the INEPT procedure and by selective double resonance [11] according to the characteristic shifts of the signals with a change in the functional groups, and also on the basis of literature analogies [1, 5, 6]. Mass spectra were taken on a Varian MAT-212 instrument (70 eV). Melting points were determined on a Boetius stage. Specific optical rotations were measured in pyridine on a Zeiss polarimeter.

Type L 40/100 μ silica gel was used for column chromatography and L 5/40 μ silica gel for TLS with the following systems: 1) chloroform—methanol (with increasing proportions of methanol from 0 to 25%; 2) chloroform—ethyl acetate—methanol (10:20:1); 3) benzene—chloroform—ethyl acetate (3:2:5); 4) benzene—ethyl acetate (with an increase in the proportion of ethyl acetate from 5 to 20%); and 5) hexane—acetone (with an increase in the proporation of acetone from 0 to 30%).

Isolation of the Squarrogenins. The epigeal part of nodding meadow rue was gathered in the flowering phase in the Transbaikal region of Chita province (village of Khara Nor). The evaporated aqueous methanolic (1:1) extract was hydrolyzed with 15% sulfuric acid on the water, evaporated until the methanol had been completely eliminated, and exhaustively extracted with chloroform. The chloroform extract was washed with water, concentrated, and chromatographed on silica gel column. Elution with system 1 gave a fraction containing genins. Squarrofuric acid (I) was isolated from this fraction by repeated chromatography in systems 1 and 2.

Squarrofuric Acid (I). $C_3OH_{48}O_5$, mp 298-200°C (chloroform—methanol), $[\alpha]_D^{20}$ + 20.1° (s 0.5; pyridine). IR spectrum, ν_{max}, cm^{-1}: 1675 (C=O), 2500-2800 (COOH), 3468, 3580 (OH). Mass spectrum, m/z (%): 488 (3.3), 473 (2.9), 270 (3.1), 455 (1.8), 427 (2.8), 409 (1.5), 330 (2.2), 329 (1.7), 299 (1.1), 99 (100). The ^1H and ^{13}C NMR spectra are given in Tables 1 and 2.

Acetylation of Squarrofuric Acid (I). A solution of 250 mg of genin (I) in 2 ml of pyridine was treated with 1 ml of acetic anhydride. After 2 h, the reaction mixture was poured into ice water and was extracted with chloroform. The chloroform extract was evaporated and chromatographed on a column of silica gel. Elution with system 5 gave 70 mg of 3,30-diacetoxysquarrofuric acid (IV) and 25 mg of 3-acetoxysquarrofuric acid (III).

When elution of the column with system 5 was continued, 50 mg of 30-acetoxysquarrofuric acid (II) and 90 mg of squarrofuric acid were isolated.

30-Acetoxysquarrofuric Acid (II). $C_{32}H_{50}O_6$, mp 235°C (hexane–acetone), $[\alpha]_{589}^{22}$ + 31.8° (s 1.2; pyridine). Mass spectrum, m/z: 530, 515, 497, 484, 464, 455, 437, 414, 373, 99. The ^1H and the ^{13}C NMR spectra are given in Tables 1 and 2.

3-Acetoxysquarrofuric Acid (III). $C_{32}H_{50}O_6$, mp 224°C (hexane–acetone), $[\alpha]_{546}^{22}$ + 19.7° (s 0.95; pyridine). IR spectrum, ν_{max}, cm^{-1}: 1720, 1735 (C=O), 3430 (OH). Mass spectrum, m/z: 530, 151, 484, 468, 437, 414, 373, 99. The ^1H and ^{13}C NMR spectra are given in Tables 1 and 2.

3,30-Diacetoxysquarrofuric Acid (IV). $C_{34}H_{52}O_7$, mp 246-247°C (hexane–acetone), $[\alpha]_{589}^{22}$ + 289° (s 0.85; pyridine). IR spectrum, ν_{max}^{KBr}, cm^{-1}: 1705, 1740 (C=O). Mass spectrum m/z: 572, 552, 512, 496, 437, 414, 391, 99. The ^1H and ^{13}C NMR spectra are given in Tables 1 and 2.

Sarett Oxidation [3] of Squarrofuric Acid (I). Over 5 h, Sarett's reagent (3 ml) was added dropwise to a solution of the genin (I) (20 mg) in pyridine (2 ml). The reaction mixture was cooled to +10°C for the first hour and then the reaction was performed at room temperature. The reaction products were extracted with diethyl ether, and, after evaporation, the ethereal extracts were chromatographed repeatedly in system 4. In this way, 23 mg of the ketoaldehyde (VI) and 19 mg of the aldehyde (V) were isolated.

30-Aldosquarrofuric Acid (V). $C_{30}H_{46}O_5$, mp 241-242°C (benzene–acetone), $[\alpha]_{546}^{22}$ + 9.8° (s 1.1; pyridine). IR spectrum, ν_{max}, cm^{-1}: 1738 (C=O), 3340 (OH). Mass spectrum, m/z: 486, 468, 425, 329, 99. The ^1H and ^{13}C NMR spectra are given in Tables 1 and 2.

30-Aldo-3-ketosquarrofuric Acid (VI). $C_{30}H_{44}O_5$, mp 260°C (benzene–ethyl acetate), $[\alpha]_{546}^{22}$ + 2.4° (s 0.95; pyridine). IR spectrum, ν_{max}, cm^{-1}: 1700, 1725, 1738 (C=O), 3340 (OH). The ^1H and ^{13}C NMR spectra are given in Tables 1 and 2.

Squarrofuric Acid 3,30-Acetonide (VII) [4]. A solution of 30 mg of genin (I) in acetone (5 ml) was treated with p-toluenesulfonic acid and the mixture was left for 24 h. The acetone was distilled off and the residue was washed with water and dissolved in chloroform (5 ml), and the solution was washed twice with water. The chloroform was evaporated off and the residue was chromatographed on a silica gel column. Elution with system 5 gave 23 mg of the acetonide (VII), $C_{33}H_{52}O_5$, mp 280-282°C (chloroform).

Mass Spectrum, m/z: 528, 513, 495, 455, 453, 437, 410, 339, 332, 156, 158, 99. The PMR spectrum is given in Table 1.

Ozonization of Squarrofuric Acid (I) [12]. A solution of 250 mg (0.05 mole) of the genin (I) in 90 ml of methanol was cooled to −70°C and, with stirring, ozone was passed through the solution (for 8 min at the rate of 6 mmole/h), which was then flushed with argon and was treated with dimethyl sulfide (2 ml). The temperature of the reaction mixture was brought to that of the room over 2 h and it was then left for 20 h. The methanol was distilled off and the residue was treated three times with ethyl acetate. This gave 45 mg of a white crystalline product (VIII). $C_{30}H_{48}O_7$, mp 232-234°C (methanol). IR spectrum ν_{max}, cm^{-1}: 1694, 1710, 1725 (C=O). 3440, 3470 (OH). Mass spectrum, m/z: 520, 502, 487, 430, 391, 321, 276, 99. The PMR spectrum is given in Table 1.

Methyl Squarrofurate (IX). A solution of 45 mg of genin (I) in 15 ml of diethyl ether saturated with diazomethane was left for 24 h with the periodic (three times) addition of an ethereal solution of diazomethane. After the ether had been driven off, the residue was chromatographed on silica gel. Elution with system 4 gave 50 mg of compounds (IX), $C_{31}H_{50}O_5$, mp 229-230°C (benzene–ethyl acetate), $[\alpha]_{546}^{22}$ + 23.8° (s 2.49; pyridine). IR spectrum, ν_{max}, cm^{-1}; 1705 (C=O), 3250, 3320 (OH). Mass spectrum, m/z: 502, 487, 441, 329, 99. The ^1H and ^{13}C NMR spectra are given in Tables 1 and 2.

Methyl 30-O-Acetylsquarrofurate (X). Compound (III) (30 mg) was methylated as described for (IX). The product obtained, (X), was chromatographed in the system 5. This gave 31 mg of triterpenoid (X), $C_{33}H_{52}O_6$, mp 214-216°C (hexane–acetone). IR spectrum, ν_{max}, cm^{-1}: 1690,

1725 (C=O), 3475 (OH). Mass spectrum, m/z 544, 529, 511, 484, 468, 414, 373, 99. The ^{1}H and ^{13}C spectra are given in Tables 1 and 2.

Reduction of Squarrofuric Acid 3,30-Diacetate (IV). The methylation of 50 mg of the diacetate (IV) was carried out as described above. With stirring, a solution of 55 mg of the methyl ester of the diacetate in 20 ml of absolute tetrahydrofuran (THF) was added dropwise to 25 mg of $LiALH_4$ in 10 mol of THF. The reaction was carried out in the boiling solvent for 12 h. The excess of $LiAlH_4$ was decomposed with ice water, and the precipitate of aluminum hydroxide was dissolved in 10% H_2SO_4.

After the elimination of the THF, product (XI) was extracted with diethyl ether and was chromatographed on silica gel in system 4. This gave 10 mg of compound (XI). $C_{30}H_{50}O_4$, M^+ 472, mp 243-246°C (benzene–ethyl acetate), $[\alpha]_{546}^{22}$ + 67.5 (s 0.95; pyridine). Mass spectrum, m/z: 474, 457, 439, 359, 329. 99. The ^{1}H and ^{13}C spectra are given in Tables 1 and 2.

SUMMARY

Squarrofuric acid has been isolated from *Thalictrum squarrosum* by the acid hydrolysis of a methanolic extract. It is suggested that it is an artefact formed in hydrolysis and has the structure of 3β,30-dihydroxy-22,25-epoxylanost-9(11)-en-21-oic acid.

LITERATURE CITED

1. A. S. Gromova, V. I. Lutskii, A. A. Semenov, V. A. Denisenko, and V. Isakov, Khim. Prir. Soedin., 207, 213 (1984).
2. T. V. Ganenko, M. I. Isaev, T. T. Gorovich, A. S. Gromova, V. I. Lutskii, A. A. Semenov, and N. K. Abubakirov, Khim. Prir. Soedin., 458 (1984).
3. G. I. Poos, G. E. Arth, R. E. Beyler and L. H. Sarett, J. Am. Chem. Soc., 75, 422 (1952).
4. Y. Tsuda, T. Sano, K. Isobe, and M. Miyauchi, Chem. Pharm. Bull., 22, 2396 (1974).
5. T. V. Ganenko, M. I. Isaev, A. S. Gromova, V. I. Lutskii, M. F. Larin, N. D. Abdullaev, A. A. Semenov, M. B. Gorovich and N. K. Abubakirov, Khim. Prir. Soedin., 312 (1986).
6. F. W. Wehrli and T. Nishida, Fortschr. Chem. Org., 36, 1-229 (1979).
7. H. Bejerbeck, J. K. Saunders, J. W. AsSimon, Can J. Chem., 55, 2813 (1977).
8. M. S. Das and S. B. Mahato, Phytochemistry, 22, 1071 (1983).
9. C. Singh. J. Singh, and S. Dev, Tetrahedron, 33, 1759 (1977).
10. T. V. Ganenko, M. I. Isaev, V. I. Lutskii, A. A. Semenov, N. D. Abdullaev, M. B. Gorovich, and N. K. Abubakirov, Khim. Prir. Soedin., 66 (1986).
11. G. A. Morris and R. Freeman, J. Am. Chem. Soc., 101, 760 (1979).
12. V. N. Odinokov and G. A. Tolstikov, Usp. Khim., 50, 1207 (1981).