

8. V. Srinivasan and E. W. Warnhoff, *Can. J. Chem.*, 54, 1372 (1976).
9. US Patent No. 4,229,599 (1980).
10. V. A. Khan, Yu. V. Gatilov, Zh. V. Dubovenko, and V. A. Pentegova, *Khim. Prir. Soedin.*, 652 (1979).
11. T. Yoshida, J. Nobuhara, M. Uchida, and J. Okuda, *Chem. Pharm. Bull.*, 26, 2535 (1978).
12. Yu. V. Gatilov and Zh. V. Dubovenko, *Zh. Strukt. Khim.*, 20, 320 (1979); L. I. Kurvyakov, Yu. V. Gatilov, V. A. Khan, Zh. V. Dubovenko, and V. A. Pentegova, *Khim. Prir. Soedin.*, 164 (1979).
13. H. Shirahama, A. Osawa, B. R. Chhabra, T. Shimokawa, T. Yokono, T. Kanaiwa, T. Amiya, and T. Matsumoto, *Tetrahedron Lett.*, 22, 1527 (1981).
14. Yu. V. Zefirov and P. M. Zorkii, *Zh. Strukt. Khim.*, 17, 994 (1976).

TRITERPENE SAPONINS FROM *Thalictrum minus*.

II. STRUCTURE OF AN ARTEFACT

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The acid hydrolysis of the predominating saponins isolated from *Thalictrum minus* L. has led to the formation of a triterpenoid (I), which is an artefact of the native genin. The structure of (I) has been established as 22,25-epoxylanost-9(11)-ene-3 $\beta$ ,16 $\beta$ ,29-triol.

The genus *Thalictrum* (family Ranunculaceae) is represented by 85 species, but only two are used in medicinal practice: *Thalictrum minus* L. and *T. foetidum* L. [1].

We have previously reported the isolation from low meadowrue (*T. minus*) of two saponins, A and B, the acid hydrolysis of which led to a triterpenoid (I) and oleanolic acid, respectively [2, 3].

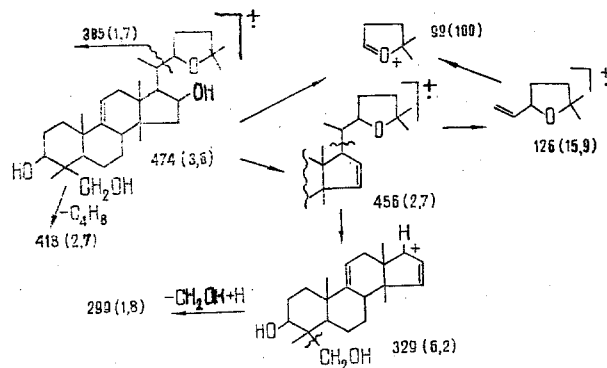
In the present paper we consider the establishment of the structure of the triterpenoid (I), which, as has been found, is an artefact of the native genin of saponin A. This follows from a comparison of the signals in the strong-field region of the PMR spectra of triterpenoid (I) and saponin A.

The PMR spectrum of (I) contains the signals of seven methyl groups one of which ( $\delta = 0.83$  ppm) is split into a doublet ( $J = 8$  Hz). These facts, in combination with the molecular formula  $C_{30}H_{50}O_4$  (elementary analysis and mass spectrometry), and also with the presence in the mass spectrum of strong ions with  $m/z$  126 ( $C_8H_{14}O$ ) and 99 ( $126 - C_2H_3$ ) permitted the compound under investigation to be assigned to the tetracyclic triterpenoids with a tetrahydrofuran ring in the side chain [4].

The results of spectroscopy in the IR (812, 837  $cm^{-1}$ ) and the UV ( $\lambda_{max}$  204 nm) and of PMR spectroscopy (one-proton doublet at  $\delta = 5.15$  ppm,  $J = 4.5$  Hz) indicate the presence in compound of (I) of an isolated trisubstituted double bond. The mass-spectral fragmentation shows that this bond is present in the cyclic system and not in the side chain (scheme).

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The triterpenoid (I) was not oxidized by periodic acid and, consequently, does not contain an  $\alpha$ -glycol grouping.

The structure and stereochemistry of (I) as 22,25-epoxylanost-9(11)-ene-3 $\beta$ ,16 $\beta$ ,29-triol was definitely established by x-ray structural analysis (Figs. 1 and Tables 1 and 2).

The interatomic distances of the molecules agree with the lengths of the corresponding bonds in related compounds [5-7]. The C(sp<sup>3</sup>)-C(sp<sup>3</sup>) bonds assume values in the range of 1.488-1.582 Å. In comparison with cyclohexane, some lengthening of the C(5)-C(10) and C(13)-C(14) bonds, by which the linkage of rings A-B and C-D is effected, is observed. The C(4)-C(5) bond in ring A also proves to be lengthened (1.569 Å). The C(16)-C(17) distance is appreciably increased as compared with the bond lengths in cyclopentane (1.546 Å [8]), being 1.582 Å in this structure. The presence of the C(9)-C(11) double bond (1.337 Å) causes some shortening of the C-C distances in rings B and C. This effect appears more strongly in the C(8)-C(9) and C(11)-C(12) bonds conjugated with it than in others. However, the shortest C(sp<sup>3</sup>)-C(sp<sup>3</sup>) bonds are observed in the five-membered heterocycle (1.488 Å) and between C(25) and the methyl carbon atoms (1.480 and 1.499 Å). The extra- and intracyclic interatomic C-O distances practically coincide with one another (1.427, 1.455 Å) and correspond to the standard length of an ordinary bond.

The conformation of the molecule is shown in Fig. 2. Rings A and B have the chair form and are cis-linked, and ring C, in virtue of the double bond between the C(9) and C(11) atoms, has the half-chair conformation. The C(8), C(9), C(11), and C(12) atoms are

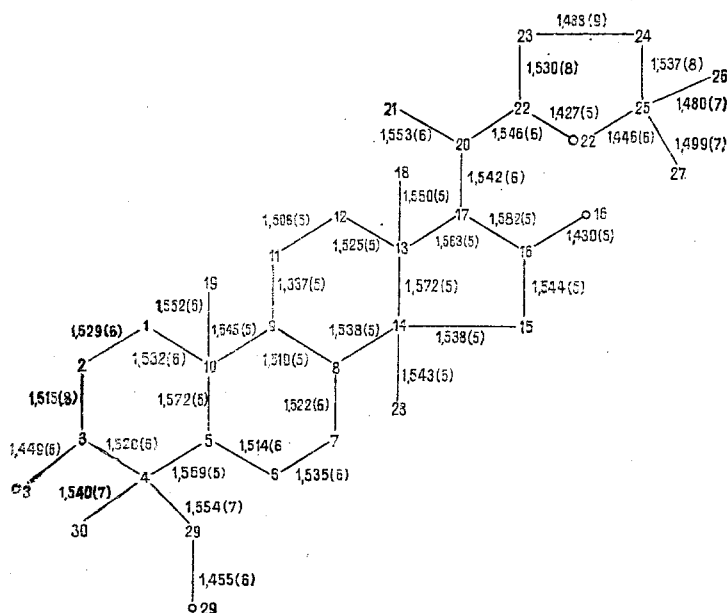


Fig. 1. Interatomic distances, Å.

TABLE 1. Values of the Valence Angles on the Molecule

Angle	Value, degrees	Angle	Value, degrees
C ( 1) — C ( 2) — C ( 3)	109.7 (4)	C ( 8) — C ( 9) — C (11)	121.1 (3)
C ( 2) — C ( 3) — C ( 4)	114.1 (4)	C ( 8) — C (14) — C (28)	109.9 (3)
C ( 2) — C ( 3) — O ( 3)	107.1 (4)	C (14) — C ( 8) — C ( 7)	113.2 (3)
O ( 3) — C ( 3) — C ( 4)	112.0 (4)	C (12) — C (13) — C (18)	109.0 (3)
C ( 3) — C ( 4) — C ( 5)	107.9 (3)	C (18) — C (13) — C (17)	109.1 (3)
C ( 3) — C ( 4) — C (30)	111.2 (4)	C (13) — C (14) — C (15)	102.5 (3)
C (30) — C ( 4) — C (29)	107.2 (3)	C (14) — C (15) — C (16)	106.4 (3)
C ( 4) — C (29) — O (29)	111.9 (4)	C (15) — C (16) — C (17)	105.9 (3)
C (29) — C ( 4) — C ( 5)	106.4 (3)	C (16) — C (17) — C (13)	103.7 (3)
C ( 4) — C ( 5) — C (10)	116.6 (3)	C (13) — C (17) — C (20)	118.0 (3)
C ( 5) — C (10) — C ( 1)	109.0 (3)	C (20) — C (17) — C (16)	114.9 (3)
C (10) — C ( 1) — C ( 2)	113.4 (4)	C (17) — C (16) — O (16)	113.5 (3)
C ( 4) — C ( 5) — C ( 6)	114.2 (3)	O (16) — C (16) — C (15)	106.9 (3)
C ( 5) — C ( 6) — C ( 7)	110.1 (3)	C (15) — C (14) — C (28)	108.4 (3)
C ( 6) — C ( 7) — C ( 8)	113.1 (4)	C ( 7) — C ( 8) — C (14)	1 3.2 (3)
C ( 7) — C ( 8) — C ( 9)	114.2 (3)	C (17) — C (20) — C (21)	111.0 (3)
C ( 8) — C ( 9) — C (10)	116.6 (3)	C (21) — C (20) — C (22)	106.9 (3)
C ( 9) — C (10) — C ( 5)	108.5 (3)	C (17) — C (20) — C (22)	115.3 (3)
C (10) — C ( 5) — C ( 6)	111.2 (3)	C (20) — C (22) — C (23)	117.5 (4)
C ( 1) — C (10) — C (19)	108.3 (4)	C (20) — C (22) — O (22)	111.1 (3)
C (19) — C (10) — C ( 9)	105.5 (3)	O (22) — C (22) — C (23)	105.7 (4)
C (10) — C ( 9) — C (11)	121.9 (3)	C (22) — C (23) — C (24)	105.0 (4)
C ( 9) — C (11) — C (12)	125.9 (4)	C (23) — C (24) — C (25)	105.8 (5)
C (11) — C (12) — C (13)	110.6 (3)	C (24) — C (25) — O (22)	101.3 (4)
C (12) — C (13) — C (14)	106.9 (3)	C (25) — O (22) — C (22)	109.1 (3)
C (13) — C (14) — C ( 8)	111.8 (3)	O (22) — C (25) — C (27)	106.0 (4)
C (14) — C ( 8) — C ( 9)	111.2 (3)	C (27) — C (25) — C (26)	111.4 (4)
		C (24) — C (25) — C (26)	114.2 (5)

TABLE 2. Torsion Angles in the Rings,  $\tau$ , deg

Ring	Angle	Ring	Angle		
A	C (1) — C ( 2) — C ( 3) — C (4)	60.4	D	C (17) — C (13) — C (14) — C (15)	44.8
	C (2) — C ( 3) — C ( 4) — C (5)	-54.5		C (13) — C (14) — C (15) — C (16)	-33.7
	C (3) — C ( 4) — C ( 5) — C (10)	49.0		C (14) — C (15) — C (16) — C (17)	9.5
	C (4) — C ( 5) — C (10) — C (1)	-48.1		C (15) — C (16) — C (17) — C (13)	18.6
	C (5) — C (10) — C ( 1) — C (2)	51.5		C (16) — C (17) — C (13) — C (14)	-38.7
	C (10) — C (1) — C (2) — C (3)	-58.2			
B	C (9) — C (10) — C (5) — C (6)	56.7	E	C (23) — C (22) — O (22) — C (25)	27.7
	C (10) — C (5) — C (6) — C (7)	-61.5		C (22) — O (22) — C (25) — C (24)	-36.8
	C (5) — C (6) — C (7) — C (8)	55.0		O (22) — C (25) — C (24) — C (23)	31.6
	C (6) — C (7) — C (8) — C (9)	-45.4		C (25) — C (24) — C (23) — C (22)	-15.8
	C (7) — C (8) — C (9) — C (10)	43.2		C (24) — C (23) — C (22) — O (22)	-6.1
	C (8) — C (9) — C (10) — C (5)	-47.6			
C	C (12) — C (11) — C (9) — C (8)	-2.9			
	C (11) — C (9) — C (8) — C (14)	-14.8			
	C (9) — C (8) — C (14) — C (13)	49.6			
	C (8) — C (14) — C (13) — C (12)	-68.1			
	C (14) — C (13) — C (12) — C (11)	49.1			
	C (13) — C (12) — C (11) — C (9)	-15.9			

approximately in one plane. The C(8)–C(9)–C(11)–C(12) torsion angle is 2.9°. The C(13) and C(14) atoms are displaced on different sides of this plane by 0.44 and 0.41 Å. The two five-membered rings have intermediate conformations between the envelope and twist forms [9].

Two intramolecular hydrogen bonds are observed in the structure. One of them is formed between the O(16) and O(22) atoms, with a O...O distance of 2.698 Å. The other connects the O(3) and O(29) atoms, the distance between which is 2.609 Å (Fig. 3).

The two last-mentioned atoms also participate in the formation of intermolecular hydrogen bonds which link the molecules into infinite chains. Crystallographically, the molecules in these chains are translated into one another by twofold screw axes. The O(3)...O(29') distance is 2.700 Å (Fig. 3).

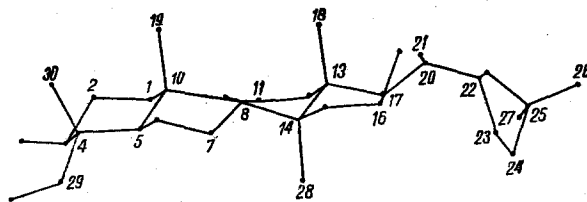


Fig. 2. Conformation of the molecule.

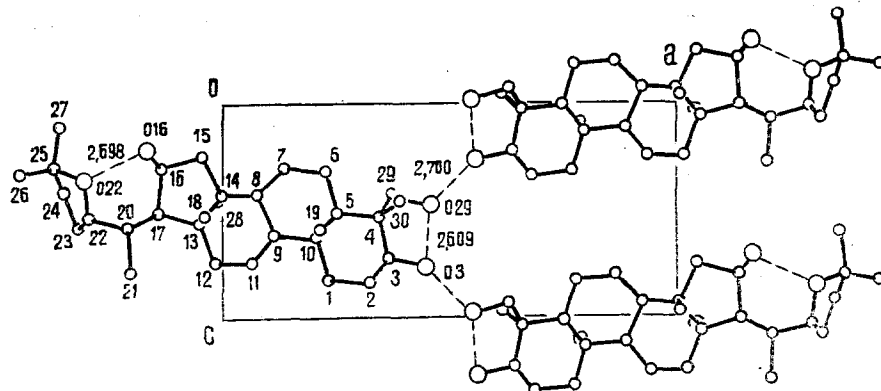


Fig. 3. Projection of the structure of the (010) plane.

#### EXPERIMENTAL

The physicochemical constants were obtained on the instrument and under the conditions described previously [2].

22,25-Epoxy lanost-9(11)-ene-3 $\beta$ ,16 $\beta$ ,29-triol. C<sub>30</sub>H<sub>50</sub>O<sub>4</sub>; M<sup>t</sup> 474; mp 262–263°C (ethanol) [ $\alpha$ ]<sub>D</sub><sup>20</sup> +70.98° (c 2.04; pyridine);  $\lambda$ <sub>max</sub><sup>MeOH</sup> 204 nm ( $\epsilon$  4244); IR (KBr),  $\nu$ : 3040, 837, 812 cm<sup>-1</sup> (CH=C); <sup>1</sup>H NMR,  $\delta$ , ppm (DMS, 0): six tertiary methyl groups at 0.58, 0.67, 0.77, 1.01, 1.15, 1.18; secondary methyl group at 0.83 (d, J = 6 Hz); olefinic proton at 5.15 (d, J = 4.5 Hz). Mass spectrum, m/z: 474 (3.6), 456 (2.7), 418 (2.7), 385 (1.7), 329 (6.2), 312 (0.8), 299 (1.8), 213 (1.9), 126 (15.9), 99 (100), 81 (25.8).

For x-ray structural analysis, crystals were grown from ethyl acetate solution. Crystals of the orthorhombic system,  $a = 33.360(17)$ ,  $b = 10.611(5)$ ,  $c = 7.664(4)$  Å;  $V = 2707(1)$  Å<sup>3</sup>,  $\mu(\text{CuK}\alpha) = 5.1$  cm<sup>-1</sup>,  $\rho_{\text{calc}} = 1.7$  g·cm<sup>-3</sup>; space group P2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>. The cell contains four C<sub>30</sub>H<sub>50</sub>O<sub>4</sub> formula units.

The parameters of the elementary cell and the intensities of 2002 independent reflections with  $I > 2\sigma$  were measured from a sample with prismatic habitus and dimensions of 0.1 × 0.15 × 1.5 mm on a DAR-UMB diffractometer with equal-inclination geometry (CuK $\alpha$  radiation; graphite monochromator). No correction for absorption was introduced.

The structure was deciphered by the direct method and was refined by the MLS with an experimental weighting scheme taking into account the anisotropy of the thermal motions of the nonhydrogen atoms by the YANX program (INEOS AN SSR [Institute of Organometallic Compounds of the Academy of Sciences of the USSR]) to  $R = 0.054$ . The positions of the hydrogen atoms in the CH, CH<sub>2</sub>, and CH<sub>3</sub> groups were calculated geometrically. The last two groups were refined as rigid fragments with fixed C–H distances (1.08 Å) and fixed H–C–H angles (109.5°). The hydrogen atoms of the OH groups were localized in an electron-density difference synthesis, and the positional parameters for them were refined. The general isotropic temperature parameters for the hydrogen atoms in the CH<sub>3</sub> groups and for the other H atoms were refined separately. The coordinates of the basis atoms ( $\times 10^4$ ) are given below:

Atom	x	y	z
C (1)	1148 (1)	5953 (6)	8256 (6)
C (2)	1604 (1)	6023 (6)	8463 (6)
C (3)	1801 (1)	5056 (6)	7286 (6)
O (3)	2227 (1)	5089 (5)	7652 (6)
C (4)	1713 (1)	5237 (4)	5352 (5)
C (5)	1246 (1)	5272 (4)	5116 (5)
C (6)	1110 (1)	5430 (5)	3240 (5)
C (7)	665 (1)	5083 (4)	3070 (6)
C (8)	397 (1)	5819 (4)	4316 (5)
C (9)	554 (1)	5897 (3)	6164 (4)
C (10)	1007 (1)	6171 (4)	6375 (5)
C (11)	305 (1)	5877 (4)	7534 (5)
C (12)	-146 (1)	5836 (4)	7446 (5)
C (13)	-292 (1)	6189 (3)	5619 (4)
C (14)	-42 (1)	5377 (3)	4283 (4)
C (15)	-264 (1)	5609 (4)	2555 (5)
C (16)	-712 (1)	5758 (4)	3022 (5)
O (16)	-850 (1)	6875 (3)	2167 (4)
C (17)	-730 (1)	5838 (4)	5086 (5)
C (18)	-226 (1)	7620 (3)	5331 (5)
C (19)	1058 (1)	7590 (4)	5939 (6)
C (20)	-1075 (1)	6653 (4)	5816 (5)
C (21)	-1054 (1)	6729 (5)	7842 (6)
C (22)	-1591 (1)	6198 (4)	5345 (5)
O (22)	-1577 (1)	6335 (3)	3518 (3)
C (23)	-1610 (1)	4834 (6)	5787 (7)
C (24)	-1787 (2)	4314 (6)	4153 (9)
C (25)	-1888 (1)	5461 (5)	3007 (6)
C (26)	-2290 (1)	6003 (8)	3332 (8)
C (27)	-1823 (2)	5206 (6)	1100 (8)
C (28)	-65 (1)	3958 (3)	4717 (5)
C (29)	1864 (1)	4071 (5)	4315 (6)
O (29)	2267 (1)	3704 (5)	4839 (5)
C (30)	1934 (1)	6398 (5)	4621 (6)

#### SUMMARY

The predominating saponin has been isolated from *Thalictrum minus* L., and its acid hydrolysis has led to a triterpenoid (I). The latter has the structure of 22,25-epoxy-lanost-9(11)-ene-3 $\beta$ ,16 $\beta$ ,29-triol, and is an artefact of the native genin.

#### LITERATURE CITED

1. A. F. Gapperman, G. N. Kadaev, M. D. Shupinskaya, and A. A. Yatsenko-Khmelevskii, Medicinal Plants [in Russian], Moscow (1973), p. 173.
2. A. S. Gromova, V. I. Lutskii, E. V. Kostyleva, N. N. Dedkova, and A. A. Semenov, Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim. Nauk, Series No. 4, Issue No. 9, 129 (1981).
3. A. A. Semenov, V. I. Lutskii, A. S. Gromova, E. V. Slavuanov, and V. N. Biyushkin, in: First International Conference on the Chemistry and Biotechnology of Biologically Active Products, Sofia, Vol. 3, Part I (1981), p. 135.
4. C. Singh, J. Singh, and S. Dev, Tetrahedron, 33, 1759 (1977).
5. L. G. Vorontsova, Zh. Strukt. Khim., 20, 882 (1979).
6. D. C. Rohrer, Acta Crystallogr., B36, 1565 (1980).
7. J. E. Berg, B. Karlsson, A.-M. Pilotti, and A.-C. Soderholm, Acta Crystallogr., B33, 2927 (1977).
8. W. J. Adams, H. I. Geise, and L. S. Bartel, J. Am. Chem. Soc., 92, 5013 (1970).
9. K. S. Pitzer and W. E. Donath, J. Am. Chem. Soc., 81, 3213 (1959).