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# TRITERPENE GLYCOSIDES AND THEIR GENINS FROM *Thalictrum foetidum*.

## IV. STRUCTURE OF CYCLOFOETIGENIN B

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A glycoside isolated from the epigeal part of *Thalictrum foetidum* (Ranunculaceae) has yielded a new genin — cyclofoetigenin B — the structure of which has been established on the basis of chemical transformations and spectral characteristics as 24S-cycloartane-3β,16β,24,25,30-pentaol.

We are continuing the study of the triterpenoids of the plant *Thalictrum foetidum*, L. (Ranunculaceae) [1-3]. The present paper is devoted to a proof of the structure of the genin of glycoside B [1] which we have called cyclofoetigenin B (VI, scheme 1).

The acid hydrolysis of glycoside B (I) gave product (IV) with the composition $C_{30}H_{52}O_5$. The PMR spectrum of this compound showed the signals of seven methyl groups in the strong field and the signal of one olefinic proton at 5.14 ppm (Table 1). It follows from these facts that product (IV) consisted of a tetracyclic triterpenoid including one trisubstituted double bond. The presence of the latter was also shown by an absorption band in the UV spectrum of substance (IV) at 204 nm and by the signals of the corresponding carbon atoms in the $^{13}C$ NMR spectrum at 149.0 and 115.2 ppm (Table 2).

In the PMR spectrum of glycoside B (I) one-proton doublets interacting with one another in the manner of an AB system are observed in the strong field at 0.24 and 0.46 ppm, showing the presence of a cyclopropane ring, and there are the signals of six methyl groups, while there is no signal of an olefinic proton. It can therefore be assumed that product (IV) is not the native genin but an artifact — a derivative of the lanostane series formed in the acid isomerization of the corresponding cycloartane triterpenoids.

The acetylation of the triterpenoid (IV) with acetic anhydride in pyridine gave the tetraacetate (XI) and the pentaacetate (X). Consequently, all the oxygen atoms are present in hydroxy groups and the side chain of compound (IV) has an acyclic structure.

The mass spectrum of the methyl steroid (IV) has the peak of an ion with m/z 329 ($C_{22}H_{33}O_2$) arising as the result of the splitting out of the side chain and the elimination of one molecule of water (scheme 2). Hence, two hydroxy groups are present in the side chain and the other three in the polycyclic part of the molecule.

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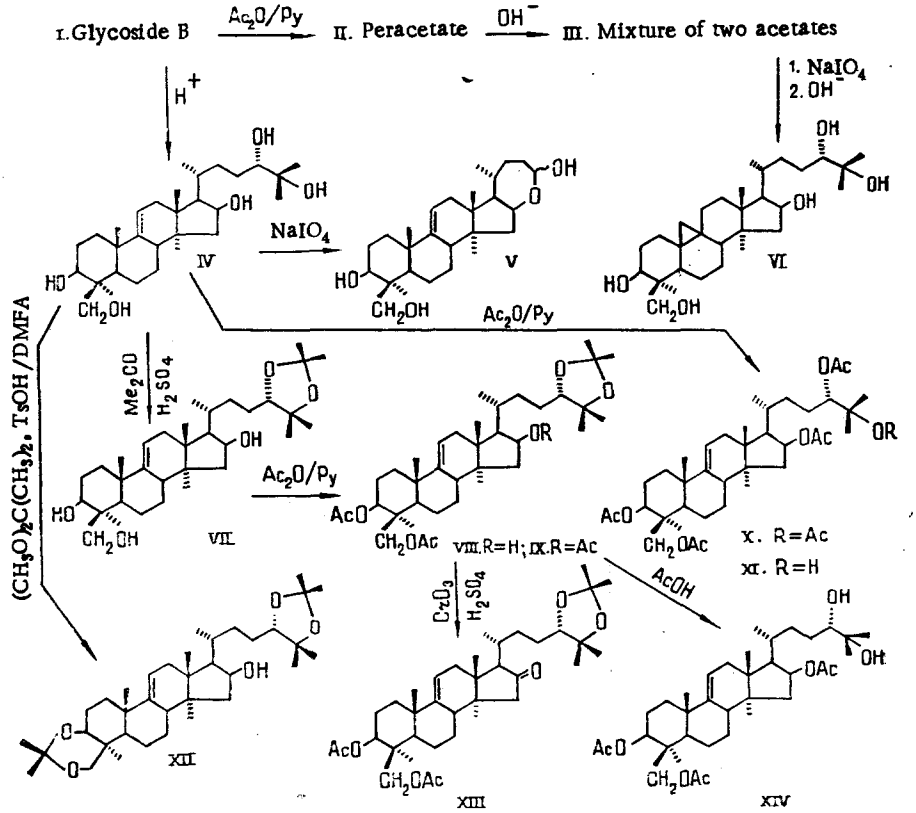



Scheme 1

In dry acetone in the presence of sulfuric acid, the methylsteroid (IV) formed a monoacetonide (VII) which shows the presence of an α-diol grouping. The retention of the ion with m/z 329 in the mass spectrum of the acetonide (VII) indicated that the α-glycol group was located in the side chain. In actual fact, the periodate oxidation of the triterpenoid (IV) formed a product (V) with a molecular weight of 432, which is 60 units less than the molecular weight of the initial compound (IV) ($M^+$ 492). This showed the position of the α-diol group at C-24—C-25. The structure of product (V) will be discussed below.

Acetylation of the acetonide (VII) with acetic anhydride in pyridine gave a diacetate VIII and a triacetate (IX). The Jones oxidation of the diacetate (VIII) [4] led to a monoketone (XIII) ($M^+$ 614). In the IR spectrum of the keto derivative (XIII) the absorption band of the keto function was completely superposed on the absorption band of ester carbonyls at 1740 $cm^{-1}$. This frequency is also characteristic for a five-membered cyclic ketone, which means that the keto function in compound (XIII) and the remaining free hydroxy group in the diacetate (VIII) were present in ring D. A Cotton effect at 302 nm ($\Delta\varepsilon = -5.8$) in the CD spectrum of the substance (XIII) showed the position of the keto function under consideration at C-16 [5]. In the same CD spectrum a Cotton effect due to a 9(11)-double bond was observed at 201 nm ($\Delta\varepsilon = +20.5$) [6, 7].

The increment in the molecular rotations between the acetonide triacetate (IX) and the acetonide diacetate (VIII) {$[M]_{D\text{-}IX} = +658°$, $[M]_{D\text{-}VIII} = 410°$, $\Delta[M]_D = +248°$} shows the β orientation of the hydroxy group at C-16 [8].

Two doublets of an AB system, at 3.54 and 4.40 ppm, in the PMR spectrum of compound (IV), and also a triplet signal at 64.6 ppm, which is characteristic for a primary carbinol carbon in a $^{13}C$ NMR spectrum, indicated the presence of a primary hydroxy group.

The C-30 atoms of cyclofoetigenin A and of thalicogenin resonate in the $^{13}C$ NMR spectra at 14.8 and 11.4 ppm, respectively [2, 9]. In this region of the $^{13}C$ NMR spectrum of compound (IV) there was no signal characteristic of the carbon atom of the 4β-$CH_3$ group. The signals of the quaternary C-4 atom (43.3 ppm) underwent a paramagnetic shift by +2.2 ppm as compared with that in the spectrum of cyclofoetigenin A (41.1 ppm). These facts permitted the assumption that the primary hydroxy group was present at C-30. The chemical shift of the carbon

TABLE 1. Chemical Shifts of the Protons of Cyclofoetigenin B (VI) and Its Derivatives (δ, ppm)

| Compound | Positions of the protons | | | | | | |
|---|---|---|---|---|---|---|---|
| | H-3 | H-16 | H-11/2H-19 | H-24 | 2H-30 | $CH_3$ group | OAc |
| IV | [3,39m*] | [4,58m] | [5,14 br.s] | [3,73 q, $^3J$=4 and 9 Hz] | [3,54*; 4,40 d, $^2J$=12,5 Hz] | [0,69; 0,97—1,00 (3×$CH_3$); 1,32; 1,35; 1,40] | — |
| V | [3,66 q, $^3J$=10,9 and 5,1 Hz] | [4,31 q $\Sigma J$=23,1 Hz] | [5,31 br.d, $^3J$=6,0 Hz] | [4,98 q, $^3J$=9,5 and 2,5 Hz.] | [3,72; 4,57 d, $^2J$=11,0 Hz] | [0,78; 0,97 d; 0,93; 1,07; 1,54] | — |
| VI | [3,34 $\Sigma J$=16,2 Hz] | [4,74 sx $\Sigma J$=20,4 Hz] | [0,35; 0,48, $^2J$=4,4 Hz] | [3,95 q, $^3J$=11 and 2,8 Hz.] | [3,83; 4,71 d $^2J$=10,8 Hz] | [0,94; 1,11 d ($^3J$=6,6 Hz); 1,43; 1,47; 1,50; 1,54] | — |
| VII | [3,37 m*] | [4,49 m**] | [5 18 br.s] | [3,71 q, $^3J$=3,8 and 7,5 Hz ] | [3,52*; 4,37**d $^2J$=11,3 Hz ] | [0,70; 0,94 d; 0,99 (2×$CH_3$); 1,06; 1,10; 1,27; 1,35; 1,41] | — |
| VIII | 4,57 q $^3J$=9,2 and 6,4 Hz | 4,47m | 5,27 br.d $^3J$=5,8 Hz | 3,85 q, $^3J$=10,8 and 3,4 Hz | 4,16; 4,42, $^2J$=11,7 Hz | 0,71; 0,84; 0,96 d ($^3J$=6,2 Hz); 1,01; 1,09; 1,12; 1,27; 1,34; 1,42 | 2,04; 2,07 |
| IX | [4,62 m*] | [5,35 m] | [5,07 br.s] | [3,68m] | [4,14; 4,52* d, $^2J$=11,3 Hz] | [0,62; 0,74; 0,87 d; 0,98 (2×$CH_3$); 1,08; 1,18; 1,27; 1,39] | [1,92; 2,00; 2,04] |
| | 4,47 m* | 5,16 m** | 5,13 m** | 3,50 m | 4,04; 4,33* d, $^2J$=12,5 Hz | 0,68; 0,77; 0,90 d; 0,95; 1,02 (2×$CH_3$); 1,16; 1,26; 1,36 | 1,94; 1,98; 1,99 |
| X | 4,53m* | 5,22 br.s** | 5,13m** | 4,99 m** | 4,10; 4,37* d, $^2J$=11,3 Hz | 0,69; 0,77; 0,90 d; 0,96; 1,05; 1,40; 1,44 | 1,91; 1,97; 2,00; 2,02; 2,04 |
| XI | [4,56 m*] | [5,30 m] | [5,03m**] | [5,03m**] | [4,14; 4,51* d, $^2J$=12,5 Hz] | [0,55; 0,70; 0,85 d; 0,97 (2×$CH_3$); 1,30; (2×$CH_3$)] | [1,90; 1,98, (2×$CH_3COO$); 2,01] |
| XII | 3,47 q, $^3J$=10,0 and 3,6 Hz | 4,43m | 5,24 m | 3,83 q, $^3J$=9,0; 4,4 Hz | 3,27; 4,10 d, $^2J$=11,0 Hz | 0,70; 0,82; 0,94 d; 1,10; 1,15; 1,24 (2×$CH_3$); 1,32; 1,37; 1,39; 1,46 | — |
| XIII | 4,58 q, $^3J$=10,6 and 5,2 Hz | — | 5,39 br.d, $^3J$=5,7 Hz | 3,71 q, $^3J$=8,3 and 4,2 Hz | 4,18; 4,40, $^2J$=11,6 Hz | 0,79; 0,93; 0,99 d ($^3J$=6,6 Hz); 1,02; 1,11; 1,12; 1,27; 1,33; 1,42 | 2,05; 2,07 |
| XIV | 4,54 q, $^3J$=10,5 and 5,3 Hz | 5,29 m* | 5,29 m* | 3,29m | 4,14; 4,38 d, $^2J$=11,6 Hz | 0,74; 0,83; 0,93 d ($^3J$=6,5 Hz); 1,01; 1,09; 1,16; 1,20 | 2,02; 2,04; 2,05 |

Note. The spectra were taken in $CDCl_3$ or $C_5D_5N$. The indices given in square brackets were obtained by the use of $C_5D_5N$. The spectra of compounds (V), (VI), (VIII), (XIII), and (XIV) were obtained with TMS as internal standard and the others with HMDS as internal standard. The signals of the horizontal rows marked with asterisks are superposed upon one another. The signals of the methyl groups have a singlet nature with the exception of $CH_3$ at C-20, which has a doublet nature; br.s) broadened singlet; d) doublet; br.d) broadened doublet; t) triplet; q) quartet; sx) sextet; m) multiplet.

TABLE 2. Chemical Shifts of the Carbon Atoms of Cyclofoetigenin B (VI) and Its Derivative (IV) (δ, ppm, O is TMS; $C_5D_5N$)

| C-Atom, multiplicity | Compound IV | Compound VI | C-Atom, multiplicity | Compound IV | Compound VI |
|---|---|---|---|---|---|
| 1t | 36,5 | 32,4 | 16d | 71,8 | 72,1 |
| 2t | 23,7 | 30,7[a] | 17d | 56,0 | 57,5 |
| 3d | 80,2 | 80,3 | 18q | 15,7 | 18,2 |
| 4s | 43,3 | 43,9 | 19t (q) | 23,6 | 31,7[a] |
| 5d | 53,6 | 48,0 | 20d | 28,7 | 28,8 |
| 6t | 21,9 | 21,9 | 21q | 19,4 | 19,5 |
| 7t | 27,9[a] | 26,5[b] | 22t | 33,0 | 33,1 |
| 8d | 42,0 | 48,5 | 23t | 28,9[a] | 28,1 |
| 9s | 149,0 | 21,3 | 24d | 77,2 | 77,3 |
| 10s | 39,5 | 26,4 | 25s | 72,5 | 72,6 |
| 11t (d) | 115,2 | 26,9[b] | 26q | 26,4 | 26,5 |
| 12t | 37,4 | 33,4 | 27q | 25,7 | 25,6 |
| 13s | 44,6 | 45,8 | 28q | 18,4 | 20,4 |
| 14s | 45,1 | 47,1 | 29q | 28,7 | 21,7 |
| 15t | 47,0 | 48,8 | 30t | 64,6 | 64,6 |

Note. The assignment of the signals marked with similar letters within a column is ambiguous. The change in the multiplicity of the signals on passing from (IV) to (VI) is shown in parentheses.

atom of the hydroxymethyl group (64.6 ppm) likewise showed its axial orientation. In the case of the equatorial orientation of the hydroxymethyl group at C-4, the carbon atom of the primary carbinol resonates in a weaker field at 68-72 ppm [9, 10].

The signal of the proton geminal to the remaining unidentified secondary hydroxy function of the polycyclic moiety of the molecule is observed in the PMR spectra of compound (IV) at 3.39 ppm in the form of a multiplet partially superposed on the signal of one of the H-30 atoms. This assignment is based on the fact that the signal of the proton under consideration undergoes a paramagnetic shift in the spectra of the acetonide diacetate (VIII) and of its 16-keto derivative (XIII) and appears at 4.57 ppm ($^3J_1$ = 9.2; $^3J_2$ = 6.4 Hz) and 4.58 ppm ($^3J_1$ = 10.6; $^3J_2$ = 5.2 Hz), respectively in the form of a quartet. The parameters given agree well with those of 3α-H-4α-methyl-4β-hydroxymethyl triterpenoids [11]. Consequently, the hydroxy function located at C-3 has the β orientation.

On reaction with 2,2-dimethoxypropane, the pentaol (IV) gave the diacetonide (XII). The PMR spectral characteristics of the diacetonide (XI) (Table 1) confirmed the conclusion of the location and configuration of the hydroxy and hydroxymethyl groups located in ring A [12].

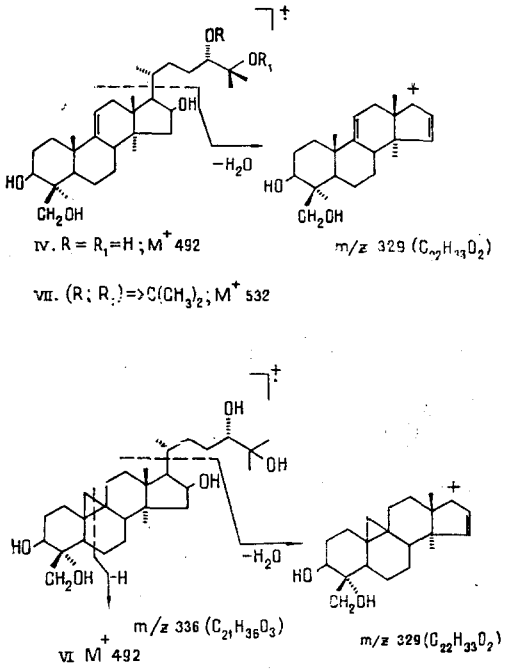
The configuration of the C-24 asymmetric center was established by a modification of Nakanishi's method [13]. For this purpose, the triacetate of the acetonide (IX) was treated with 50% acetic acid, and the 24,25-diol (XIV) was obtained. The CD spectrum of compound (XIV) taken with the addition of $Eu(fod)_3$ showed a positive Cotton effect at 325 nm ($\Delta\varepsilon$ = +1.97). Consequently, the chiral C-24 atom has the S configuration [14]. This conclusion was also confirmed by the practical identity of the C-24 chemical shifts in the $^{13}C$ NMR spectra of compound (IV) (77.2 ppm) and of cyclofoetigenin A (77.2 ppm) [2].

Thus, compound (IV) is 24S-lanost-9(11)-ene-3β,16β,24,25,30-pentaol.

According to its IR and PMR spectra, compound (V) was a 24,16-semiacetal. We have obtained a similar product previously from cyclofoetigenin A [2]. Consequently, compound (V) has the structure of 16β,24ξ-epoxy-25-norlanost-9(11)-ene-3β,24,30-triol.

As mentioned above, the triterpenoid (IV) was an artifact. To obtain the native genin, glycoside B (I) was converted into the peracetate (II). Treatment of the latter with an ethanolic solution of potassium hydroxide led to a mixture of two acetyl derivatives of glycoside (I), each obviously containing an acetyl group at C-25. The periodate oxidation of the mixture of acetates (III) followed by alkaline hydrolysis led to cyclofoetigenin B (VI).

Cyclofoetigenin B (VI) has the same elementary composition, $C_{30}H_{52}O_5$, and molecular weight ($M^+$ 492) as compound (IV). An analysis of the $^1H$ and $^{13}C$ NMR spectra of these compounds showed that the molecule of cyclofoetigenin B (VI) retained a 9,19 three-membered ring and, in agreement with this, there was no double bond and, as was to be expected, there were six methyl




Scheme 2

groups (Tables 1 and 2). The other structural elements of cyclofoetigenin B (VI) and the artifact (IV) obtained from it were identical.

The mass-spectrometric fragmentation of cyclofoetigenin B (scheme 2) agreed with the suggested structure.

Thus, cyclofoetigenin B has the structure of 24S-cycloartane-3β,16β,24,25,30-pentaol.

## EXPERIMENTAL

For general observations, see [1]. The following solvent systems were used: 1) chloroform–methanol (20:1); 2) chloroform–ethyl acetate (1:3); 3) benzene–chloroform–ethyl acetate (10:1:1); 4) benzene–chloroform–ethylacetate (5:1:1); 5) benzene–ethyl acetate (3:1); 6) benzene–ethyl acetate (2:1); and 7) hexane–acetone (2:1).

$^1H$ and $^{13}C$ NMR spectra were obtained on XL-200 (Varian), JNM-4H-100/100 MHz, and FX 90Q (Jeol), Bruker WP-200, and CFT-20 (Varian) instruments in deuterochloroform or in deuteropyridine (δ, ppm, 0 — HMDS or TMS).

CD spectra were taken on a Jasco J-20 spectropolarimeter.

For the isolation of the triterpene glycosides of *Thalictrum foetidum* L., see [1].

24S-Lanost-9(11)-ene-3β,16β,24,25,30-pentaol (IV) from (I). Glycoside B (2 g) was hydrolyzed in 100 ml of a 0.5% methanolic solution of sulfuric acid at the boiling point of the reaction mixture for 9.5 h. Then the solution was diluted with two volumes of water and the methanol was evaporated off. The precipitate that had deposited was filtered off and was chromatographed on a column with elution in system 1. This gave 400 mg of substance (IV), $C_{30}H_{52}O_5$, mp 243-245°C (from methanol), $[\alpha]_D^{30}$ +52 ± 2° (c 1.65; methanol). $\nu_{max}^{KBr}$, $cm^{-1}$: 3510-3320; (OH); 3050 (=C–), $\lambda_{max}^{C_2H_5OH}$, : 204 nm (ε 4920). Mass spectrum, m/z (%): $M^+$ 492 (10.9), 474 (34.8), 459 (54.3), 456 (43.5), 441 (100), 423 (47.8), 415 (19.6), 405 (19.6), 397 (26.1), 379 (15.2), 329 (91.3), 311 (39.1).

16β,24ξ-Epoxy-25-norlanost-9(11)-ene-3β,24,30-triol (V) from (IV). To 34 mg of substance (IV) in 3 ml of methanol was added 100 mg of sodium periodate in 0.5 ml of water. The reaction mixture was stirred for 5 h. Then it was diluted with water containing a few drops of ethylene glycol and was extracted with chloroform. The chloroform extract was washed with water and evaporated. The residue was chromatographed on a column with elution in system 1. This gave 20 mg of the nor product (V), $C_{27}H_{44}O_4$, mp 138-140°C (from methanol), $[\alpha]_D^{30}$ +22 ± 2° (c 0.72; chloroform–methanol (1:1)). $\nu_{max}^{KBr}$, $cm^{-1}$: 3520-3300 (OH); 3055 (=CH–). Mass spectrum, m/z (%):

$M^+$ 432 (18.4), 417 (15.8), 414 (23.6), 399 (42.0), 383 (31.6), 381 (36.8), 365 (23.6), 321 (23.6), 284 (21.0), 279 (18.4), 260 (97.3), 223 (42.0), 213 (68.4), 199 (57.8), 185 (100).

24S-Lanost-9(11)-ene-3β,16β,24,25,30-pentaol 24,25-Acetonide (VII) from (IV). To 150 mg of substance (IV) was added 5 ml of acetone containing 0.2% of sulfuric acid, and the mixture was stirred at room temperature for 2 h. Then it was poured into water and extracted with ethyl acetate. The residue after evaporation of the solvent was chromatographed on a column with elution by system 2. This gave 172 mg of the acetonide (VII), $C_{33}H_{56}O_5$, mp 229-231°C (from ethyl acetate–methanol (1:1)), $[\alpha]_D^{16}$ +77.7 ± 2° (c 0.9; methanol), $\nu_{max}^{KBr}$, $cm^{-1}$ 3500-3400 (OH); 3050 (=C–). Mass spectrum, m/z (%): $M^+$ 532 (10.6), 517 (69.7), 474 (30.3), 456 (93.9), 441 (100), 423 (36.4), 401 (22.7), 329 (78.8), 311 (42.4).

24S-Lanost-9(11)-ene-3β,16β,24,25,30-pentaol 3,16,30-Triacetate 24,25-Acetonide (IX) from (VII). The acetonide (VII) (60 mg) was acetylated with 1 ml of acetic anhydride in 2 ml of pyridine at room temperature for 48 h. After evaporation of the solvents, the residue was chromatographed on a column with elution by system 3. This gave 63 mg of the acetonide triacetate (IX), $C_{39}H_{62}O_8$, mp 122-125°C (from methanol), $[\alpha]_D^{23}$ +100 ± 2° (c 0.7; methanol). $\nu_{max}^{KBr}$, $cm^{-1}$; 3050 (=C–); 1740, 1250 (ester group). Mass spectrum, m/z (%): $M^+$ 658 (0.94), 643 (60.9), 583 (4.3), 539 (43.4), 525 (36.9), 467 (14.2), 465 (6.1), 421 (10.4), 413 (100), 405 (21.7), 399 (4.7), 353 (7.1), 311 (5.2), 293 (18.9).

24S-Lanost-9(11)-ene-3β,16β,24,25,30-pentaol 3,30-Diacetate 24,25-Acetonide (VIII) from (VII). The acetonide (VII) (27 mg) was acetylated with 0.25 ml of acetic anhydride in 0.5 ml of pyridine at room temperature for 1.5 h. After evaporation of the solvents, the residue was chromatographed on a column with elution by system 4. This gave 13.5 mg of the acetonide diacetate (VIII), $C_{37}H_{60}O_7$, mp 185-187°C (from chloroform–methanol (1:1)), $[\alpha]_D^{24}$ +66.6 ± 2° (c 0.94; methanol), $\nu_{max}^{KBr}$, $cm^{-1}$: 3540 (OH); 3050 (=CH–); 1740, 1255, 1230 (ester group). Mass spectrum, m/z (%): $M^+$ 616 (1.1), 601 (39.5), 558 (10.5), 540 (55.3), 525 (100), 485 (10.5), 433 (15.8), 413 (73.7), 293 (28.9).

3β,24,25,30-Trihydroxy-24S-lanost-9(11)-en-16-one 3,30-Diacetate 24,25-Acetonide (XIII) from (VIII). Compound (VIII) (10 mg) in 3 ml of acetone was oxidized with 3 drops of the Jones reagent [4] at –5°C for 10 min. The excess of oxidant was decomposed with 1 ml of methanol. The reaction mixture was diluted with water and extracted with water. The chloroform extract was washed with water and evaporated. After recrystallization from methanol, 7 mg of substance (XIII) was obtained: $C_{37}H_{58}O_7$, mp 155-157°C, $[\alpha]_D^{30}$ –33 ± 2° (c 0.42; methanol). $\nu_{max}^{KBr}$, $cm^{-1}$: 3055 (=CH–); 1740 (C=O at C-16); 1740, 1255 (ester group). CD (c 0.1; methanol), $\Delta\varepsilon$ = –5.8 (302 nm); $\Delta\varepsilon$ = +20.5 (201 nm). Mass spectrum, m/z (%): $M^+$ 614 (0.1), 599 (14.8), 556 (9.1), 541 (31.8), 539 (29.5), 485 (46.6), 457 (5.7), 415 (10.2), 373 (10.2), 363 (8.0), 313 (4.5), 253 (27.2), 149 (100).

24S-Lanost-9(11)-ene-3β,16β,24,25,30-pentaol 3,16,24,25,30-Pentacetate (X) and 24S-Lanost-9(11)-ene-3β,16β,24,25,30-pentaol 3,16,24,30-Tetraacetate (XI) from (IV). Substance (IV) (58 mg) was acetylated with 1 ml of acetic anhydride in 2 ml of pyridine at room temperature for two days. The residue after the solvents had been distilled off was chromatographed on a column with elution by system 5. This gave 6 mg of the pentaacetate (X), $C_{40}H_{62}O_{10}$, mp 99-100°C (from methanol), $[\alpha]_D^{26}$ +107 ± 2° (c 1.2; methanol). $\nu_{max}^{KBr}$, $cm^{-1}$: 3040 (=CH–); 1740, 1250 (ester group). Mass spectrum, m/z (%): $M^+$ 702 (0.3), 642 (41.6), 627 (10.4), 582 (11.7), 567 (24.7), 540 (9.1), 523 (27.3), 499 (5.2), 471 (16.9), 413 (100), 353 (19.5), 293 (50.6), 279 (14.3), 253 (26.0), 149 (86.4).

Continuing the elution of the column with the same system, we obtained 65 mg of the tetraacetate (XI), $C_{38}H_{60}O_9$, mp 121-123°C (from methanol), $[\alpha]_D^{30}$ +89.7 ± 2° (c 1.16; methanol). $\nu_{max}^{KBr}$, $cm^{-1}$: 3510-3420 (OH); 3060 (=CH–); 1730, 1250 (ester group). Mass spectrum, m/z (%): $M^+$ 660 (1.7), 642 (15.8), 600 (78.6), 585 (53.6), 582 (6.7), 567 (14.2), 540 (60.7), 525 (96.4), 507 (17.5), 465 (38.3), 439 (14.2), 414 (92.9), 413 (92.9), 405 (57.1), 399 (35.7), 353 (42.8), 293 (100).

24S-Lanost-9(11)-ene-3β,16β,24,25,30-pentaol 3,16,30-Triacetate (XIV) from (IX). The acetonide triacetate (IX) (23 mg) in 5 ml of 50% acetic acid was heated in the water bath for 5 h. Then the reaction mixture was diluted with water and the reaction products were extracted with chloroform. The chloroform extract was washed with water and evaporated. The residue was chromatographed on a column with elution by system 6. This gave 16 mg of the triacetate (XIV), $C_{36}H_{58}O_8$, mp 92°C (from methanol), $[\alpha]_D^{30}$ +69 ± 2° (c 0.88; methanol). $\nu_{max}^{KBr}$, $cm^{-1}$: 3570-3310 (OH); 3050 (=CH–); 1735, 1260-1240 (ester group). Mass spectrum, m/z (%): $M^+$ 618 (2.5), 600

(1.9), 558 (54.5), 543 (50.0), 540 (31.8), 525 (27.3), 500 (40.9), 483 (38.6), 414 (95.5), 413 (95.5), 405 (68.2), 399 (18.2), 379 (36.4), 353 (38.6), 311 (31.8), 293 (100).

To measure the CD curve, aliquot volumes of 0.0002 M solutions of $Eu(fod)_3$ and of substances (XIV) in absolute carbon tetrachloride were taken [13, 14]; $\Delta\varepsilon$ = +1.97 (325 nm).

24S-Lanost-9(11)-ene-3β,16β,24,25,30-pentaol 3,30:24,25-Diacetonide (XII) from (IV). To 20 mg of substance (IV) were added 2 ml of 2,2-dimethoxypropane and 2 ml of dimethylformamide, and then 5 mg of p-toluenesulfonic acid, and the mixture was heated at 80°C for 3 h. After the solvents had been distilled off, the reaction mixture was extracted with chloroform. The chloroform extract was washed with water and evaporated to give 22 mg of the diacetonide (XII), $C_{36}H_{60}O_5$, mp 234-236°C (from ethanol). Mass spectrum, m/z (%): $M^+$ 572 (3.4), 557 (100), 539 (3.6), 514 (4.5), 499 (18.0), 481 (23.3), 441 (21.8), 439 (15.0), 423 (30.0), 421 (25.6), 405 (9.8), 369 (9.0), 339 (6.0), 327 (7.5), 311 (27.0).

Cyclofoetigenin B (VI) from (I). Glycoside B (I) (3 g) was acetylated with 30 mg of acetic anhydride in 50 ml of pyridine at a temperature of 38-40°C for 30 days. After the solvents had been distilled off, the residue was chromatographed on a column with elution by system 7. This gave 3.2 g of the amorphous peracetate (II), $C_{71}H_{104}O_{30}$, $[\alpha]_D^{27}$ +1.4 ± 2° (c 1.01; methanol). Its IR spectrum lacked the absorption of hydroxy groups.

The peracetate (II) (3 g) was dissolved in 20 ml of methanol and hydrolyzed with 15 ml of 1% potassium hydroxide in methanol at 10-15°C for 1 h. The reaction mixture was diluted with water, the methanol was evaporated off, and the aqueous residue was extracted with butanol. The residue after the evaporation of the solvents in 50 ml of methanol, which consisted of two components (III, 2g, TLC), was treated with 2 g of sodium periodate in 10 ml of water. The mixture was stirred for 10 h, and then 1 ml of ethylene glycol and 30 ml of water were added. The mixture was extracted with chloroform and the solvent was evaporated to dryness. The residue (1.6 g) was hydrolyzed with 30 ml of a 1% methanolic solution of potassium hydroxide for 7 h. The hydrolysate was diluted with water, the methanol was distilled off, and the reaction product was extracted with chloroform. After the chloroform had been distilled off, the dry residue was chromatographed on a column with elution by system 1. This gave 62 mg of cyclofoetigenin B (VI), $C_{30}H_{52}O_5$, mp 240-242°C (from acetone), $[\alpha]_D^{22}$ +72 ± 2° (c 0.5; methanol). $\nu_{max}^{KBr}$, $cm^{-1}$: 3530-3250 (OH); 3040 ($CH_2$ of a cyclopropane ring). Mass spectrum, m/z (%): $M^+$ 492 (0.8), 474 (55.6), 459 (74.6), 456 (63.5), 441 (49.2), 433 (44.4), 423 (46.0), 415 (31.7), 405 (19.0), 397 (31.7), 379 (19.0), 371 (57.1), 353 (63.5), 329 (30.2), 311 (66.6), 173 (100).

## SUMMARY

The ordinary acid hydrolysis of glycoside B isolated from the epigeal part of *Thalictrum foetidum* L. (Ranunculaceae) leads to a substance having the structure of 24S-lanost-9(11)-ene-3β,16β,24,25,30-pentaol. The native aglycon of this glycoside — cyclofoetigenin B — obtained by a more complex route, is 24S-cycloartane-3β,16β,24,25,30-pentaol.

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