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TRITERPENE SAPONINS FROM *Thalictrum minus*.

V. STRUCTURE OF THALICOSIDE B

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The epigeal part of *Thalictrum minus* L. has yielded a new bidesmoside — thalicoside B — which has the structure of oleanolic acid 28-O- β -D-glucopyranoside 3-O-[O- α -L-rhamnopyranosyl-(1 \rightarrow 2)-O- β -D-glucopyranosyl-(1 \rightarrow 3)- α -L-arabinopyranoside].

We have previously reported the structure of the predominating glycoside of the cycloartane series — thalicoside A — isolated from *Thalictrum minus* [1, 2]. In the present paper we consider the structure of a new triterpenoid glycoside — thalicoside B (I) — isolated from the same plant [1].

The IR spectrum of thalicoside B contains the absorption band of an ester grouping (1740 cm^{-1}). Its PMR spectrum shows the presence in the glycoside of eight methyl groups, one of which is secondary (1.55 ppm, d, $J = 6.1\text{ Hz}$), a proton at double bond (5.33 ppm, m), and four anomeric protons of carbohydrate residues (5.05, d, $J = 6.1\text{ Hz}$, 4.84, m, and 4.65 ppm, 2 H, m).

The acid hydrolysis of thalicoside B led to a genin containing, according to IR spectroscopy and ^1H and ^{13}C NMR spectroscopy, a free carboxy group (1700 cm^{-1} , 180.1 ppm), a trisubstituted double bond (5.42 ppm, m), and seven tertiary methyl groups (0.82, 0.87, 0.93, and 0.94 (2 CH_3) 1.18, and 1.19 ppm). The positions of the ^{13}C NMR signals of the carbon atoms at the double bond (122.5, 144.8 ppm) enabled a choice to be made between the α - and β -amyrin series [3] in favor of the latter. From its physicochemical constants, molecular formula ($\text{C}_{30}\text{H}_{48}\text{O}_3$), and the chemical shifts (CSs) of the carbon atoms in the ^{13}C NMR spectrum [4] (Table 1), the genin was identified as oleanolic acid (II).

Rhamnose, arabinose, and glucose were identified in the hydrophilic fraction of the products of the acid hydrolysis of thalicoside B. The quantitative GLC analysis of the carbohydrates in the form of aldonitrile acetates and alditol acetates showed that the rhamnose, glucose, and arabinose were present in a ratio of 1:2:1. Consequently, in the ^1H NMR spectrum of thalicoside B the doublet at 1.55 ppm belonged to the secondary methyl group of the rhamnose residue.

The alkaline hydrolysis of glycoside (I) led to a progenin with a free carboxy group (1696 cm^{-1}) containing the sugars mentioned in an equimolar ratio (1:1:1). No carbohydrates were detected in the hydrolysate. Thus, one of the two glucose residues is bound to the oleanolic acid through an ester group, and thalicoside B is a bidesmosidic glycoside. The position of attachment of the second carbohydrate chain was obvious and was confirmed by the downfield shift of the C-3 signal in the genin by 11.1 ppm on glycosylation (Table 1).

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TABLE 1. ^{13}C NMR Spectra of the Aglycone Moiety of Thalicoside B (I) and of Oleanolic Acid (II) ($\text{C}_5\text{D}_5\text{N}$, δ , ppm, TMS = 0)

C-atom	I	II	C-atom	I	II
1	59.0	38.9	16	23.8 ^a	23.8
2	26.3	28.1	17	47.1	46.6
3	89.1	78.0	18	41.9	42.0
4	37.6	39.4	19	46.4	46.5
5	56.0	55.8	20	30.7	30.9
6	18.6	18.8	21	34.1	34.2
7	32.6	33.2	22	33.1	33.2
8	40.1	39.7	23	28.3	28.8
9	48.2	48.1	24	16.8	16.5
10	37.1	37.3	25	15.5	15.5
11	23.6 ^a	23.7	26	17.5	17.4
12	122.6	122.5	27	26.1	26.1
13	144.1	144.8	28	176.3	180.1
14	42.3	42.1	29	31.3	33.3
15	28.3	28.3	30	23.8	23.7

a — assignment uncertain within the column.

To establish the sequence of carbohydrate residues in the glycoside partial hydrolysis with 0.75% sulfuric acid was performed (scheme). Each of the three progenins obtained had a free carboxy group (1700 cm^{-1}).

Progenin III was a monoside containing the residues of an arabinose molecule, of progenin IV, and of a bioside (arabinose and glucose, 1:1), and progenin IV a triside (arabinose, glucose, and rhamnose (1:1:1)). Progenin V was identical with the progenin isolated on alkaline hydrolysis.

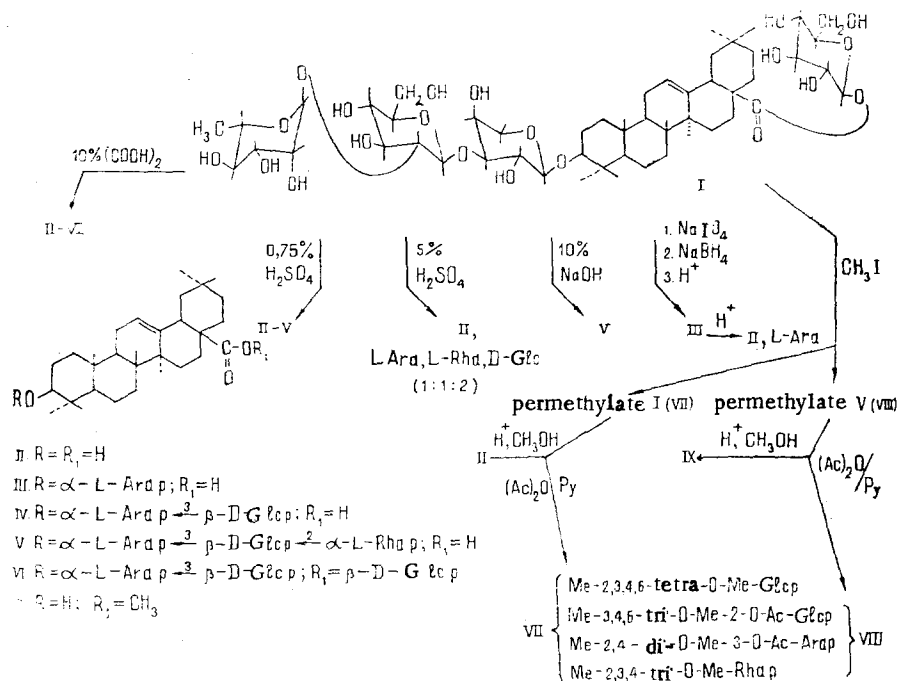
When 10% oxalic acid was used for partial hydrolysis, in addition to the progenins III-V, it was possible to isolate another progenin, VI — also a triside (glucose and arabinose (2:1)) — but with two carbohydrate chains (scheme). Progenin VI had an ester group (1730 cm^{-1}) formed by the attachment of a glucose molecule to the carboxy group. Arabinose and glucose were attached to position 3 of the genin. Consequently, the rhamnose and glucose were the terminal carbohydrate residues in the bisdesmoside.

It must be mentioned that, to determine the composition of each progenin, instead of complete hydrolysis we performed their methanolysis followed by acetylation and the GLC analysis of the methyl acetates obtained. This operation was due to the poor solubility of the progenins under the conditions of acid hydrolysis.

The Hakomori methylation of (I) led to a mixture of two products which, after chromatographic separation, gave compounds (VII) and (VIII) in a ratio of 1:6. Both products proved to be permethylates (IR spectrum). After methanolysis, methyl oleanolate and oleanolic acid, respectively for compounds (VIII) and (VII), were detected in the hydrophobic fractions of the hydrolysate. Consequently, in the methylation of (I) partial alkaline hydrolysis of glycoside B took place with the subsequent methylation of the carboxy group formed. Thus, compound (VII) was a permethylate of thalicoside B and compound (VIII) the permethylate of progenin (V).

The carbohydrate fractions of the hydrolysates of (VII) and (VIII) were acetylated and the acetates of partially methylated methyl glucosides so formed were analyzed by GLC-MS. For (VII) the following monosaccharide derivatives were identified (in order of increasing retention time): methyl 2,3,4-tri-O-methylrhamnopyranoside, methyl 2,3,4,6-tetra-O-methyl- α,β -glucopyranoside, methyl 3-O-acetyl-2,4-di-O-methyl- α,β -arabinopyranoside and methyl 2-O-acetyl-3,4,6-tri-O-methyl- α,β -glucopyranoside. Compound (VIII) gave the same set of sugar derivatives as (VII) and, in addition, methyl 2,3,4,6-tetra-O- α,β -glucopyranoside.

As was to be expected, the Smith cleavage of (I) led to the monoside (III), which confirmed the presence of glycosidic bonds in positions 1 and 3 of the arabinose residue.



The glycosylation of the arabinose residue at C-3 was also shown by the displacement of its ^{13}C NMR signal by +4.9 ppm (α -effect) in compounds (I), (IV), and (V) (Table 2) in comparison with methyl arabinoside [5].

The glycosylation of glucose at C-2 causes not only a downfield displacement of this signal by +2.6 ppm (α -effect) but also an upfield shift of the C-1 signal by -1.6 ppm (β -effect) on passing from (IV) to (V) and (I) [5], which is in harmony with information on the existence of a 1 \rightarrow 2 bond between the terminal rhamnose residue and the glucose residue. The chemical shift of the carbon atoms of the terminal carbohydrate residues of thalicoside B correspond to those given in the literature for methyl rhamnoside and glucoside [6], which confirms the presence of glycosidic bonds in these carbohydrate residues only at C-1 position.

The positions of the signals of the anomeric carbon atoms of the arabinose and glucose residues (106.9 and 106.4 ppm) correspond to those of α -L-arabinopyranosides and β -D-glucopyranosides [5]. The anomeric carbon atom of the glucose residue attached in the C-28 position to the genin has a CS of 95.7 ppm, which corresponds to a β -D-glucopyranoside forming an ester bond with the aglycone [6].

In establishing the configuration of the glycosidic bond of the rhamnose residue the characteristic magnitude in the ^{13}C NMR spectrum is the not the CS of the anomeric carbon atom but the CSs of the C-3 and C-5 atoms (α configuration - 72.5 and 69.4; β configuration - 75.4 and 73.5 ppm, respectively [5]). In compounds (I) and (V) the CS of the rhamnose C-3 atom is 72.3 ppm and the CS of the C-5 atom 69.9 ppm and, therefore, the rhamnose residue has the α configuration of the glycosidic center (Table 2).

Calculations of molecular rotation differences according to Klyne for (I-V) correspond to the configurations of the glycosidic centers and the sizes of the oxide rings proposed on the basis of the GLC-MS and ^1H and ^{13}C spectroscopic results.

Thus, thalicoside B has the structure of oleanolic acid 28-O- β -D-glucopyranoside 3-O-[O- α -L-rhamnopyranosyl-(1 \rightarrow 2)-O- β -D-glucopyranosyl-(1 \rightarrow 3)- α -L-arabinopyranoside].

It is interesting to note that the epigeal part of *Thalictrum minus* L. growing in Eastern Siberia contains glycosides the genins of which are both tetracyclic (cycloartanol series) and pentacyclic (β -amyrin series) triterpenoids.

EXPERIMENTAL

General Observations. Melting points were determined on a Boëtius stage and angles of rotation on a Polamat A polarimeter. Mass spectra were recorded on a Varian MAT-212 chromatomass spectrometer, and ^1H and ^{13}C NMR spectra of a Bruker WP-200 instrument in the Fourier

TABLE 2. ^{13}C NMR Spectra of the Carbohydrate Moieties of Compounds (I), (III), (IV) and (V) ($\text{C}_5\text{D}_5\text{H}$, δ , ppm, TMS - 0)

C-atom	III	IV	V	I
Arabinose				
C-1	107.1	106.9	106.8	106.5
C-2	72.9	74.3	74.5	74.4 ^a
C-3	74.5	79.2	78.8	78.8 ^b
C-4	69.3	71.7	71.8	71.9
C-5	66.4	65.7	65.0	64.7
Glucose				
C-1		106.5	104.8	104.4
C-2		75.7	78.5 ^a	78.7 ^b
C-3		78.5	78.3	78.7
C-4		73.5	72.8	72.8
C-5		78.4	78.1 ^a	78.4
C-6		62.9	62.7	62.8
Rhamnose				
C-1			101.8	101.7
C-2			72.0	72.0
C-3			72.3	72.3
C-4			73.6	73.4
C-5			69.9	69.9
CH ₃			18.5	18.4
Glucose (at C-28)				
C-1				95.7
C-2				74.1 ^a
C-3				77.8
C-4				71.5
C-5				77.8
C-6				62.7

a, b - assignment uncertain within a column.

regime at room temperature. The solvents used were $\text{C}_5\text{D}_5\text{N}$ and CDCl_3 , with TMS as internal standard. IR spectra were recorded on a UR-20 spectrophotometer. The elementary analyses of the compounds corresponded to the calculated figures.

The GLC analysis of the carbohydrates was performed on a Chrom-4 chromatograph with a I-O₂ digital integrator. The detector was of the flame-ionization type and the carrier gas was argon. The rate of flow of hydrogen was 25 ml/min, that of air 500 ml/min, and that of argon 30 ml/min. The temperature of the evaporator was 250°C.

The analysis of the carbohydrates in the form of the corresponding polyol acetates [7] was performed in a glass column (250 × 0.3 cm) with 3% of QF-1 deposited on Chromosorb W (60-80 mesh) as the stationary phase. The column temperature was programmed from 200 to 230°C at the rate of 2°C/min.

Analysis of carbohydrates in the form of the corresponding aldonitrile acetates [8] was performed on a stainless-steel column (250 × 0.3 cm) filled with 5% of XE-60 on Chezasorb AW HMDS (0.25-0.36 mm). The temperature of the thermostat was raised from 180 to 240°C at the rate of 1°C/min.

Analysis of the acetates of the methyl glucosides was performed on the column used for the analysis of the polyol acetates. The temperature was programmed from 170 to 250°C at the rate of 5°C/min.

Chromato-mass-spectrometric analysis was performed on a LKB-900S instrument with a 300 × 0.3 cm column containing 1.5% of QF-1 on Chromaton N-AW-HMDS with helium as the carrier gas (30 ml/min). Conditions of analysis: temperature of the evaporator 275°C; column temperature programmed from 140 to 250°C at the rate of 5°C/min; temperature of the molecular separator 265°C and of the ion source 255°C; ionizing energy 70 eV.

For chromatography we used silica gels L 40/100 (column chromatography) and L 5/40 (TLC), neutral alumina (Brockman activity grade II-IV), and FN-16 chromatographic paper. The paper for PC and the silica gel for TLC analysis of the carbohydrates were impregnated with a 0.3 N solution Na_2HPO_4 . The following solvent systems were used (ratios by volume):

1) ethyl acetate-methanol-water (10:3:2); 2) ethyl acetate-hexane-methanol (6:40:5); 3) benzene-chloroform-methanol (3:2:1); 4) benzene-acetone (5:1); 5) benzene-butan-1-ol-pyridine-water (10:50:30:3); and 6) butanol-ethanol-water (5:3:2).

Thalicoside B (I). Compound (I) was isolated by the procedure described previously [1]. Vitreous powder with mp 213-216°C; $[\alpha]_{578}^{20} +10.49^\circ$ (c 3.58; pyridine); $[\text{M}] +105.8^\circ$. IR spectrum ($\nu_{\text{max}}^{\text{KBr}}$, cm^{-1}): 1740 (ester C=O), 3400-3500 (OH). PMR spectrum (δ , ppm): 0.75 (3 H, s, CH_3); 0.8 (3 H, s, CH_3); 0.83 (3 H, s, CH_3); 0.84 (3 H, s, CH_3); 0.99 (3 H, s, CH_3); 1.12 (3 H, s, CH_3); 1.15 (3 H, s, CH_3); 1.55 (3 H, d, $J = 6.1$ Hz, CH_3); 4.65 (2 H, m, anomeric H's); 4.84 (1 H, m, anomeric H); 5.05 (1 H, d, $J = 6.1$ Hz, anomeric H); 5.33 (1 H, m, $\text{CH}=\text{C}$).

Complete Acid Hydrolysis of Thalicoside B. The hydrolysis of 4 mg of (I) was performed in 2 ml of 5% sulfuric acid in a sealed tube. The precipitate formed was separated off and was identified by TLC in system 2 as an oleanolic acid. The mother liquor was neutralized with AV-17 anion-exchange resin, and arabinose, rhamnose, and glucose were detected by PC and TLC in systems 5 and 6, respectively. It was established that the GLC of the corresponding aldonitrile and polyol acetates that the arabinose, rhamnose and glucose were present in (I) in a ratio of 1:1:2.

Partial Hydrolysis of Thalicoside B. 1. Hydrolysis with Oxalic Acid. A solution of 1.0 g of (I) in 100 ml of 10% oxalic acid solution was heated at 80°C for 3 h. The hydrolysate was extracted with tert-amyl alcohol and the extracts were washed with water and evaporated. The residue (700 mg) was chromatographed on silica gel in system 1. Rechromatography of the intermediate fractions in the same system yielded the genin (II) (110 mg), progenin III (21 mg), progenin IV (120 mg), progenin V (160 mg), progenin VI (25 mg), and the initial glycoside (I) (60 mg).

Oleanolic Acid (III). $\text{C}_{30}\text{H}_{48}\text{O}_3$, mp 308-309°C (ethanol); $[\alpha]_{578}^{20} +79.53^\circ$ (c 1.92; pyridine). IR spectrum ($\nu_{\text{max}}^{\text{KBr}}$, cm^{-1}): 1690 (acid C=O), 3440 (OH). PMR (δ , ppm): 0.82 (3H, c, CH_3); 0.87 (3H, c, CH_3); 0.93 (3H, c, CH_3); 0.94 (6H, c, 2CH_3); 1.18 (3H, c, CH_3); 1.19 (3H, c, CH_3); 5.42 (1H, m, $\text{CH}=\text{C}$).

Oleanolic Acid 3-O- α -L-Arabinopyranoside (III) from (I). mp 243-246°C (chloroform); $[\alpha]_{578}^{20} +40.0^\circ$ (c 0.40; pyridine); $[\text{M}] +235.2^\circ$. IR spectrum ($\nu_{\text{max}}^{\text{KBr}}$, cm^{-1}): 1690 (acid C=O), 3330-3500 (OH).

According to GLC, (III) contained one arabinose residue.

Oleanolic Acid 3-O-[O- β -D-Glucopyranosyl-(1 \rightarrow 3)- α -L-arabinopyranoside] (IV) from (I). mp 262-264°C (ethyl acetate-methanol), $[\alpha]_{578}^{20} +58.15^\circ$ (c 1.46; pyridine); $[\text{M}] +380.2^\circ$. IR spectrum ($\nu_{\text{max}}^{\text{KBr}}$, cm^{-1}): 1695 (acid C=O), 3340-3500 (OH).

According to GLC, (IV) contained arabinose and glucose residues in a ratio of 1:1.

Oleanolic Acid 3-O-[O- α -L-Rhamnopyranosyl-(1 \rightarrow 2)-O- β -D-glucopyranosyl-(1 \rightarrow 3)- α -L-arabinopyranoside] (V) from (I). mp 249-252°C (methanol), $[\alpha]_{578}^{20} +14.03^\circ$ (c 1.28; pyridine). $[\text{M}] +125.4^\circ$. IR spectrum ($\nu_{\text{max}}^{\text{KBr}}$, cm^{-1}): 1696 (acid C=O), 3340-3450 (OH).

According to GLC, (V) contained arabinose, glucose, and rhamnose residues in a ratio of 1:1:1.

Oleanolic Acid 28-O- β -D-Glucopyranoside 3-O-[O- β -D-Glucopyranosyl-(1 \rightarrow 3)- α -L-arabinopyranoside] (VI) from (I). mp 219-222°C (ethyl acetate-methanol-water); $[\alpha]_{578}^{20} +35.3^\circ$ (c 0.7; pyridine), $[\text{M}] +324.4^\circ$. IR spectrum ($\nu_{\text{max}}^{\text{KBr}}$, cm^{-1}): 1730 (ester C=O), 3450-3500 (OH).

According to GLC, (VI) contained arabinose and glucose residues in a ratio of 1:2.

2. Hydrolysis with Sulfuric Acid. A solution of 1.5 g of (I) in 70 ml of 0.75% sulfuric acid was heated at 90°C for 3 h. Then the mixture was cooled, and the precipitate that deposited was separated off and washed with water. The mother liquor was extracted with butanol. The extracts were washed with water, the butanol was evaporated off, and the residue was

combined with the previous precipitate. The hydrolysis product (950 mg) was chromatographed on silica gel in system 1. This led to the isolation of oleanolic acid (II) (190 mg), progenin III (15 mg), progenin IV (48 mg), progenin V, (30 mg), and the initial glycoside (I) (160 mg).

The physicochemical constants of the progenins obtained on the hydrolysis of (I) with sulfuric acid agreed with those for the corresponding progenins III-V isolated when (I) was hydrolyzed with oxalic acid.

Alkaline Hydrolysis. A solution of 200 mg of (I) in 10 ml of a 10% solution of KOH in 70% ethanol was heated at 90°C for 3 h. Then it was neutralized with KU-1 cation-exchange resin, evaporated until the ethanol had been eliminated completely, diluted with water, and extracted with butanol. The butanolic extracts were evaporated and the residue was chromatographed on silica gel in system 1. This led to the isolation of 110 mg of a progenin which, according to IR and TLC and the absence of a depression of the melting point with an authentic sample was shown to be identical with progenin V. The aqueous part of the hydrolysate was evaporated, the residue was dissolved in 5 ml of 5% sulfuric acid, and the solution was heated at 90°C for 4 h. The hydrolysate was neutralized with AV-17 anion-exchange resin and was analyzed by PC and TLC in systems 5 and 6, respectively. No carbohydrates were detected.

Methanolysis of Compounds (III) and (IV). The methanolysis of 3-4 mg of each of these substances was performed in absolute methanol saturated with 10% HCl. The reaction was performed in sealed tubes at 68°C for 4 h. Then the hydrolysate was evaporated and to each flask was added 1 ml of pyridine and 0.5 ml of acetic anhydride and the mixture was left for 12 h. After the usual working up, the methyl glycoside acetates were analyzed by GLC.

Hakomori Methylation. With constant stirring, 1 g of sodium hydride was added in small portions to 1.2 g of (I) in 30 ml of dimethyl sulfoxide. After 40 min, 15 ml of methyl iodide was added dropwise to the reaction mixture and it was stirred at room temperature for 3 h. Then the reaction mixture was poured into 0.5 liter of a 2% solution of sodium thiosulfate and was exhaustively extracted with chloroform. The extracts were washed with water and evaporated. The reaction product (1.57 g) was chromatographed on alumina in system 4. This gave 96 mg of the permethylate of (V), (VIII), and 629 mg of the permethylate of (I), (VII). The IR spectra of (VII) and (VIII) showed no absorption due to hydroxy groups.

Compounds (VII) (629 mg) and (VIII) (96 mg) were dissolved in 7% HClO₄ in methanol and the solutions were heated at 90°C for 8 h. The precipitates were filtered off and washed with water. For the permethylate (VII), 170 mg of (II) was obtained, and for the permethylate (VIII), 29 mg of (IX). Compound (II) was identified by TLC in system 2 as oleanolic acid. Compound (IX) was purified on a silica gel column in system 3, which yielded 19 mg of methyl oleanolate (IX).

Methyl Oleanolate (IX). C₃₁H₅₀O₃, mp 198-200°C (ethanol); mass spectrum (m/z, %): M⁺ 470 (79.7), 452 (6.5), 262 (100), 203 (70.3), 190 (21.6). IR spectrum ($\nu_{\text{max}}^{\text{KBr}}$, cm⁻¹): 1738 (C=O), 3330 (OH). The mother liquors after the separation of (II) and (IX) were neutralized with AV-17 anion-exchange resin, evaporated, and poured into a mixture of 1 ml each of pyridine and acetic anhydride. The reaction mixtures were heated at 60°C for 3 h. After the usual working up, GLC, and GLC-MS showed the presence in the reaction products from (VIII) of methyl 2,3,4-tri-O-methylrhamnoside, methyl 3-O-acetyl-2,4-di-O-methyl- α,β -arabinosides, and methyl 2-O-acetyl-3,4,6-tri-O-methyl- α,β -glucopyranoside, and for (VII), in addition to the derivatives mentioned above, methyl 2,3,4,6-tetra-O-methyl- α,β -glucopyranosides.

Smith Cleavage of Thalicoside B. A solution of 60 mg of (I) in 20 ml of water was treated with 200 ml of 0.025 M solution of sodium metaperiodate and the mixture was left at 5°C for 62 h. Then 5 ml of ethylene glycol was added to it, and it was evaporated with chloroform. The chloroform was distilled off, and the residue was heated with 30 ml of 50% ethanol and 20 mg of sodium tetrahydroborate at 80°C for 3 h. The reaction mixture was acidified to pH 4 and the boric acid was eliminated in the form of methyl borates by adding methanol to the residue in portions and then removing the solvent in vacuum. The residue was dissolved in 30 ml of 50% ethanol, and 2 ml of concentrated HCl was added; after 30 min, progenin III was detected in the solution (TLC, system 1). After 2 hours, the reaction mixture was neutralized with AV-17 anion-exchange resin, evaporated until the ethanol had been driven off completely, and extracted with chloroform. In the hydrophobic fraction of the hydrolysate oleanolic acid was identified by TLC in system 2, and in the hydrophilic part of the hydrolysate arabinose was detected by TLC in system 5 and PC in system 6.

SUMMARY

The structure of a new triterpene bisdesmolide isolated from low meadow rue has been established. The bisdesmolide, which has been called thalicoside B, has the structure of oleanolic acid 28-O- β -D-glucopyranoside 3-O-[O- α -L-rhamnopyranosyl-(1 \rightarrow 2)-O- β -D-glucopyranosyl-(1 \rightarrow 3)- α -L-arabinopyranoside].

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CARDENOLIDES OF *Coronilla glauca* AND *C. scorpioides*

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The cardenolide glycosides glucocorotoxigenin, scorpioside, and coronillobioside and a new compound which has been called glucocoroglaucigenin have been isolated from the seeds of *Coronilla glauca* L. for the first time. The new glycoside has the structure of 3 β -(β -D-glucopyranosyloxy)-14,19-dihydroxy-5 α -card-20(22)-enolide. This glycoside has also been isolated from the seeds of *C. scorpioides*.

The present paper gives the results of a study of the cardenolides of the seeds of *Coronilla glauca* L. (honey coronilla) and *Coronilla scorpioides* (L.) Koch. (scorpion coronilla) [1-4]. The glycosides were isolated from the comminuted seeds as described in [5].

From the seeds of honey coronilla we obtained and identified the aglycone corotoxigenin (I), the glycosides glucocorotoxigenin (III), scorpioside (V) and coronillobioside (VI), and a new substance which we have called glucocoroglaucigenin (IV). From scorpion coronilla, in addition to those known previously and mentioned above we have obtained for the first time coroglaucigenin and substance (IV). The UV spectrum of the substance exhibited a single maximum in the 219 nm region ($\log \epsilon$ 4.12), which is characteristic for the butenolide ring of a cardenolide.

Compound (IV) was not reduced by sodium tetrahydroborate, which indicated the absence of carbonyl groups from the molecule. On enzymatic hydrolysis (scheme), the glycoside was cleaved into D-glucose (I) and an aglycone (II) which was identified by its physicochemical properties, color reactions with 84% sulfuric acid, R_f values in various solvent systems, and a mixed melting point as 3 β ,14 β ,19-trihydroxy-5 α -card-20(22)-enolide (coroglaucigenin).

A β -glycosidic bond was found in the glycoside (IV) on the basis of Klyne's rule [4]. Difficulty in acid hydrolysis with 0.05 N sulfuric acid showed the pyranose form of the carbohydrate moiety of the substance being studied.

To confirm the results obtained, glucocorotoxigenin (III) was reduced with sodium tetrahydroborate. The substance obtained proved to be identical with the glucoside isolated.

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