TRITERPENE GLYCOSIDES OF ALFALFA.

I. MEDICOSIDE G — A NEW BISDESMOSIDE FROM *Medicago sativa*

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A new triterpene glycoside, medicoside G has been isolated from the roots of the plant *Medicago sativa* L. (family Fabaceae), and its structure has been established as medicagenic acid 3,28-di-O-β-D-glucopyranoside.

Alfalfa or lucerne (*Medicago sativa*, family Fabaceae) is a valuable forage crop. However, on alfalfa pasture ruminants not infrequently suffer from a tumor of the rumen, and alfalfa fodder suppresses the growth of chickens and lowers the egg yield of laying hens. In a field where this crop has previously been sown, the growth of the seeds of other plants is greatly retarded. These long-known properties of alfalfa are ascribed to saponins [1, 2]. At the same time, it has been shown by recent investigations that extracts from alfalfa can be used as effective means for the treatment of hypercholesteremia [3].

The literature on the investigation of the physiological action of the saponins of alfalfa is fairly extensive, but the chemical nature of the triterpene glycosides forming the saponins of the plant has been studied in less detail. The first publications in this direction date to 1954 [4] when an individual sapogenin was first isolated from an extract of the epigeal part of the plant and its physicochemical constants and elementary composition were determined and some derivatives were obtained. Djerassi et al. [5] showed the structure of the sapogenin as 2,3-dihydroxyolean-12-ene-23,28-dicarboxylic acid and called it medicagenic acid. Morric et al. [6], after partial hydrolysis of the saponins from the roots isolated a monoglycoside and determined its structure as medicagenic acid 3-O-β-D-glucopyranoside. Later [7], from alfalfa flowers by the same method a medicagenic acid glycoside with the sugar chain $\beta\text{-Rha}_p\text{-}\beta\text{-GlcUA}_p\text{-}\beta\text{-Glc}_p$ linked to the aglycone in the C-3 position was isolated. Gestetner [8] characterized another triglycoside isolated from alfalfa — medicagenic acid 3-O-β-D-glucopyranosyl-(1 → 6)-β-D-glucopyranosyl-(1 → 3)-β-D-glucopyranoside. There is information on the presence in the plant of glycosides of soyasapogenols A, B, C, D, and E [9], of hederagenin [10], and of oleanolic acid [11].

We are studying the triterpene glycosides of *Medicago sativa* sown in the flood zone of the Central Asian republics as a forage crop. In a methanolic extract of the roots after its purification and fractionation on a column of silica gel, with the aid of thin-layer chromatography (TLC) in various solvent system we have detected the presence of 13 components originally assigned to the pentacyclic triterpenoid series. They have been designated in order of increasing polarity A, B, C, D, E, F, G, H, I, J, K, L, and M. Substances A, D, and G have been isolated in the individual state by column chromatography. In the present paper we consider the determination of the structures of the glycosides A (I) and G (II) (scheme). This is the first time that the latter has been described, and we have called it medicoside G.

It was shown by GLC [12] that glycoside A contains one D-glucose residue and medicoside G two G-glucose residues.

The acid hydrolysis of glycoside A (I) led to the formation of a genin which was identified by its physicochemical constants and IR, mass, and PMR spectra as medicagenic acid (III) [4]. The IR spectrum of compound A (I) lacked the absorption characteristic for an ester grouping. The Hakomori methylation of glycoside A (I) [13] gave the hepta-O-methyl derivative (IV) (M^+ 762). Acid hydrolysis of the ester (IV) yielded the tri-O-methyl derivative

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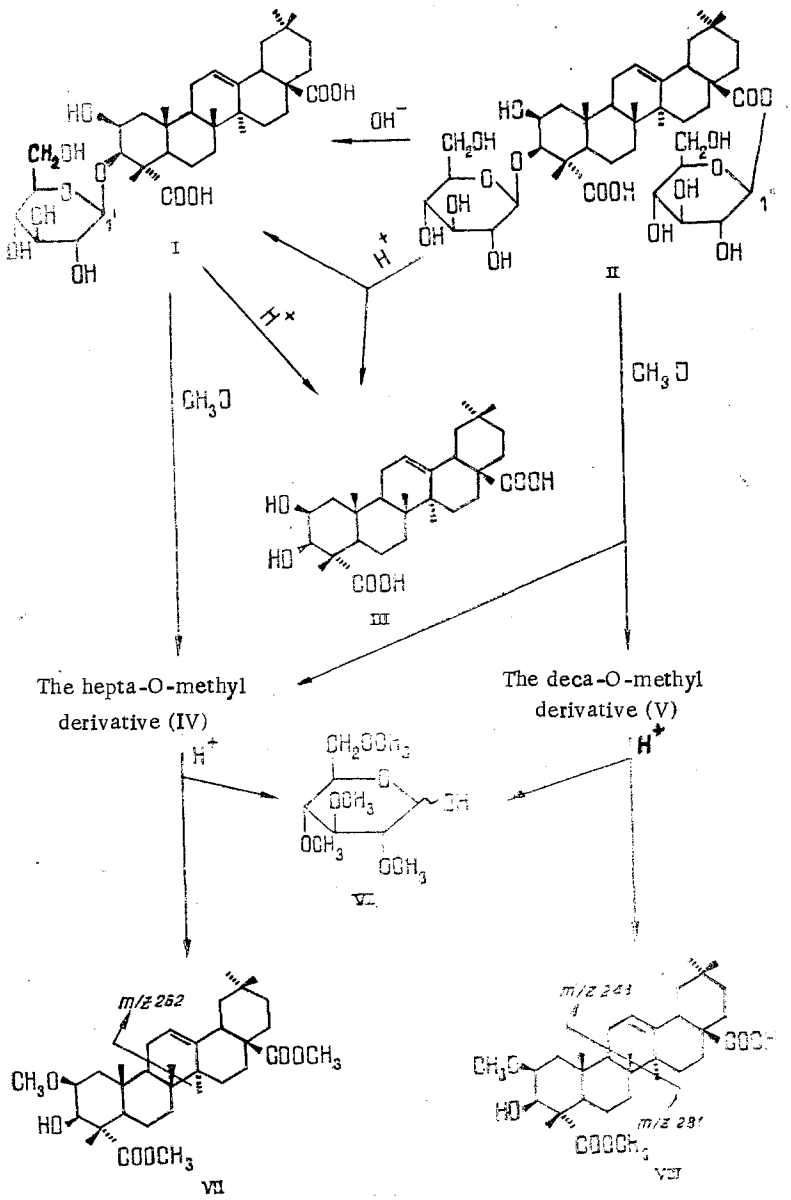
TABLE 1. Chemical Shifts of the Protons of Medicoside G (II) and Its Derivatives (δ, ppm; 0 — HMDS)

Compound	Positions of the protons					
	H-2	H-3	H-12	H-1′	H-1″	CH_3 and OCH_3 groups
I	4,64 m*	4,58 d *	5,31 m $W_{1/2}$ = 10,0 Hz	4,94 d ^3J = 7,5 Hz	—	0,82; 0,87; 0,91; 1,13; 1,47; 1,87
II	4,64 m*	4,54 d *	5,25 m $W_{1/2}$ = 10,0 Hz	4,91 d ^3J = 7,5 Hz	6,10 d ^3J=7,5 Hz	0,87×2; 1,03; 1,12; 1,44; 1,86
III	4,41 m	4,57 d	5,32 m $W_{1/2}$ = 9,0 Hz	—	—	0,80; 0,85; 0,93; 1,14; 1,48; 1,86
IV	[3,82 m]*	[3,92 d]*	[5,17 m $W_{1/2}$ = 9,0 Hz]	[4,09 d ^3J = 7,5 Hz	—	[0,65; 0,88; 0,90; 1,03; 1,15; 1,33—CH_3; 3,24; 3,27; 3,40; 3,43; 3,50; 3,54; 3,61—OCH_3]
V	3,99 m	4,13 d	5,26 m $W_{1/2}$ = 7,5 Hz	4,34 d ^3J = 7,0 Hz	5,65 d ^3J=7,0 Hz	0,75×2; 0,87; 1,12; 1,22; 1,61—CH_3; 3,12; 3,22; 3,29; 3,37×2; 3,44, 3,47; 3,52; 3,55; 3,67—OCH_3
	[3,83 m*]	[3,94 d]*	[5,21 m]*	[4,09 ^3J = 7,5Hz]	[5,29 d]*	[0,71; 0,86×2; 1,05; 1,15; 1,35—CH_3 3,25; 3,28×2; 3,39; 3,43; 3,44×2; 3,52; 3,54; 3,62—OCH_3].
VII	3,66 m *	4,32 d ^3J=4,0 Hz	5,32 m $W_{1/2}$ = 8,0 Hz	—	—	0,74; 0,76; 0,80; 1,07; 1,19; 1,62—CH_3. 3,14; 3,54; 3,56*—OCH_3.
VIII	3,64 m*	4,32 d ^3J=4,0 Hz	5,40 m $W_{1/2}$ = 9,0 Hz.	—	—	0,80; 0,88; 0,92; 1,14×2; 1,61—CH_3. 3,14; 3,54*—OCH_3.

The spectra were recorded in C_5D_5N or in $CDCl_3$ (these indices are given in square brackets). The signals denoted by asterisks in the horizontal rows are superposed upon one another. The signals of the methyl groups have a singlet nature; d — doublet; m — multiplet.



of medicagenic acid (VII) (M^+ 544) and a methylated D-glucose. The latter was identified by GLC [14] and TLC in the presence of an authentic sample as 2,3,4,6-tetra-O-methyl-D-glycopyranose (VI).

Analysis of the PMR spectrum (Table 1) of the tri-O-methyl derivative (VII) showed that on methylation the H-2 signal underwent a diamagnetic shift by 0.75 ppm (4.41-3.66) in comparison with the analogous signal of medicagenic acid (III). At the same time, the change in the chemical shift of the H-3 atom was insignificant (4.57 and 4.32 ppm). These results permitted the assumption that in compound (VII) the hydroxy group at C-3 was free. According to this, the product (VII) was the 2,23,28-tri-O-methyl derivative of medicagenic acid. Consequently, in the initial glycoside (I) the D-glucose residue was attached to the genin (III) through the hydroxyl at C-3.

The doublet signals of the anomeric protons (H-1'), with a spin–spin coupling constant (SSCC) of 7.5 Hz, observed in the PMR spectra of glycoside (I) and of the hepta-O-methyl derivative (IV) at 4.94 and 4.09 ppm, respectively, showed the C1 conformation of the D-glucopyranose center.

Thus, glycoside A (I) has the structure of medicagenic acid 3-O-β-D-glucopyranoside. It was stated above that a compound of similar structure has been described in the literature [6]. The discrepancy in the physicochemical constants is apparently due to different degrees of purity of the substances being compared.

As stated above, medicoside G (II) contains two D-glucose residues. The acid hydrolysis of this compound led to medicagenic acid (III) and glycoside (I), identified by its physicochemical constants and a comparison of IR and PMR spectra. When medicoside G (II) was treated with sodium hydroxide, it was likewise converted into glycoside (I). From this followed the conclusion that medicoside G contained an acyloside moiety and was a bisdesmosidic glycoside. Since medicagenic acid (III) has two carbon groups, to determine the position of the acyloside sugar residue glycoside (II) was methylated by Hakomori's method [13]. From the methylation products we isolated a hepta-O-methyl derivative (IV) (M^+ 762) and a deca-O-methyl derivative (V) (M^+ 966).

In the carbohydrate moiety of the products of the acid hydrolysis of the derivative (V), 2,3,4,6-tetra-O-methyl-D-glucopyranose (VI) was detected by GLC [14] and TLC. As was to be expected, from the genin fraction of the hydrolysate we isolated the di-O-methyl derivative of medicagenic acid (VIII) (M^+ 530). The mass spectrum of compound (VIII) showed the presence of ions with m/z 281 and 248 arising as a consequence of a retrodiene decomposition. The formation of the ion with m/z 248 (as in the spectrum of medicagenic acid, this peak was the maximum one) showed that the C-28 carboxy group was not esterified (see scheme) and compound (VIII) had the structure of the 2-O-methyl ether of 23-methyl medicagenate.

In the PMR spectra (Table 1) of medicoside G (II) and of the deca-O-methyl derivative (V) at 6.10 ppm (^3J = 7.5 Hz) and 5.65 ppm (^3J = 7.0 Hz), respectively, doublets of anomeric protons were observed, including the anomeric proton of D-glucopyranose residue bound by an acyloside bond. Consequently, this D-glucose residue also had the C-1 conformation and the β configuration.

The calculation of molecular rotation increments according to Klyne [15] confirmed the conclusion concerning the β configuration of the glycosidic bonds.

Medicoside G (II) has the structure of medicagenic acid 3,28-di-O-β-D-glucopyranoside.

EXPERIMENTAL

General Remarks. For thin-layer chromatography (TLC) we used type KSK silica gel (<63 mμ) containing 13% of gypsum and Silufol plates, and for column chromatography silica gels of types KSK and L (63-100 mμ). The triterpenoids were detected on the plates by spraying them with a 25% methanolic solution of molybdophosphoric acid followed by heating for 5-10 min at 100°C. The following solvent systems were used: 1) chloroform–methanol–water (65:35:8) (a) and (65:23:4) (b); 2) chloroform–methanol (20:1) (a) and (10:1) (b); 3) chloroform; 4) benzene–acetone (20:1) (a) and (10:1) (b).

Mass spectra were taken on a MKh-1310 instrument at an ionizing voltage of 50 V and a temperature of 130-170°C; IR spectra on a UR-20 spectrometer in KBr; and PMR spectra on JNM-4H-100/100 MHz and Varian XL-100-15 instruments with HMDS as internal standard, δ scale. GLC was performed on a Chrom-5 chromatograph. Sugars were chromatographed in the form of methyl glycoside trimethylsilyl ethers [12] on a column (3.2 m × 3 mm) with Interton AW-DMCS, impregnated with 5% of the silicone phase SE-30. The temperature of the thermostat was 175°C, and the carrier gas was helium at the rate of 60 ml/min. The methyl derivatives of the sugars were identified in the form of their methyl glycosides [14]. They were chromatographed on a column (12. m × 3 mm) containing Chromaton N-AW with 10% of 5F-4E poly(phenyl ether) at a thermostat temperature of 198°C with helium as carrier gas at a rate of 50 ml/min.

Isolation of the Glycosides. Alfalfa roots collected in May, 1981, were dried in the dark and comminuted in the form of shavings. The raw material prepared in this way (10 g) was treated three times with chloroform at room temperature and was then exhaustively extracted with hot methanol. The methanolic extract was evaporated to dryness. The dry residue was dissolved in 2 liters of water and the solution was repeatedly extracted with butanol. The butanolic extracts were combined and washed with water. The butanolic solution, after the distillation of the solvent, yielded 150 g of combined extractive substances (1.5%; here and below the yields have been calculated on the air-dry raw material), which included 13 components (TLC on Silufol plates, system 1b) denoted in order of increasing polarity as A, B, C, D, E, F, G, H, I, J, K, L, and M.

Part of the combined material obtained (50 g) was chromatographed on a column of KSK-silica gel using system 1a. The mixture was separated into four fractions. Then the frac-

tion containing substances A, D, and G was rechromatographed on a column of silica gel L using system 1b. The following substances were isolated: A — 0.29 g (0.0087%); d — 0.02 g (0.0006%); and G — 0.92 g (0.0276%).

Medicagenic Acid 3-O-β-D-Glucopyranoside (Substance A, I). $C_{36}H_{56}O_{11}$, mp 289-292°C (methanol), $[\alpha]_D^{24}$ +64.0 ± 2° (c 0.50; ethanol). ν_{max}^{KBr} (cm^{-1}: 3340-3495 (OH), 1710 (C=O of carboxy groups); soluble in methanol and ethanol, sparingly soluble in acetone, chloroform, and water. According to the literature [6]: mp 255 ± 1° (from aqueous ethanol), $[\alpha]_D^{26}$ +70° (absolute ethanol).

Medicagenic Acid (III) from (I). A solution of 100 mg of glycoside (I) in 20 ml of methanol was treated with 7 ml of a 20% solution of sulfuric acid, and the reaction mixture was heated at 100°C for 15 h. Then 20 ml of water was added and the methanol was evaporated off. The resulting precipitate was filtered off, washed with water to neutrality, and chromatographed on a column with elution by system 2a. This yielded 40 mg of medicagenic acid (III), $C_{30}H_{46}O_6$, mp 352-354°C (from chloroform–methanol (20:1); $[\alpha]_D^{24}$ +12 ± 2° (c 0.10; ethanol). ν_{max}^{KBr} (cm^{-1}); 3340-3510 (OH); 1700 (C=O of carboxy groups). Mass spectrum, m/z (%): 502 (M^+, 10), 456 (4), 253 (7), 249 (27), 248 (100), 286 (5), 235 (7), 233 (10), 219 (6), 205 (5), 204 (19), 203 (75), 202 (8), 189 (14), 187 (7), 173 (8). According to the literature [14]: mp 349-350°C; $[\alpha]_D^{26}$ +111° (c 0.192; ethanol).

The Hepta-O-methyl Derivative (IV) from (I). With stirring, 0.12 g of sodium hydride was added to a solution of 120 mg of the glycoside (I) in 12 ml of dimethyl sulfoxide. After 2 h, 1.5 ml of methyl iodide was added dropwise and the reaction mixture was stirred for another 4 h. Then it was poured into 50 ml of 2% sodium hyposulfite and the reaction products were extracted with chloroform. The residue obtained after the evaporation of the combined and water-washed chloroform extracts was chromatographed on a column with elution by system 4a. This yielded 83 mg of the amorphous hepta-O-methyl derivative (IV), $C_{43}H_{70}O_{11}$, $[\alpha]_D^{24}$ +40.1 ± 2° (c 0.60; chloroform). There was no absorption in the hydroxy group region of the IR spectrum. Mass spectrum, m/z (%): 762 (M^+; 0.9), 760 (3), 703 (1), 599 (4), 587 (3), 561 (3), 542 (4), 529 (9), 528 (37), 527 (93), 511 (3), 496 (11), 495 (30), 468 (12), 467 (30), 463 (4), 451 (3), 436 (3), 435 (8), 369 (11), 281 (16), 280 (4), 265 (6), 264 (5), 263 (22), 262 (81), 249 (15), 248 (5), 247 (12), 234 (4), 233 (10), 232 (4), 219 (15), 215 (4), 201 (6), 202 (19), 203 (100), 204 (22), 190 (4), 189 (15), 188 (10), 187 (81).

The 3,23,28-Tri-O-methyl Derivative of Medicagenic Acid (VII) from (IV). A solution of 53 mg of the hepta-O-methyl derivative (IV) in 10 ml of methanol was treated with 3 ml of a 20% methanolic solution of sulfuric acid, and the reaction mixture was heated at 100°C for 7 h. Then 10 ml of water was added to the solution and the methanol was distilled off. The precipitate that deposited (47 mg) was chromatographed on a column with elution by system 3. This yielded 16 mg of the amorphous 2,23-28-tri-O-methyl derivative of medicagenic acid (VII), $C_{33}H_{52}O_6$, $[\alpha]_D^{24}$ +63.3 ± 2° (c 0.24; chloroform). ν_{max}^{KBr} (cm^{-1}): 3490-3560 (OH), 1725, 1260 (ester group). Mass spectrum, m/z (%): 544 (M^+, 2), 512 (1), 484 (24), 453 (13), 282 (2), 281 (10), 262 (63), 261 (18), 249 (10), 203 (100), 189 (19), 187 (8), 178 (8).

The aqueous solution was heated at 100°C for 2 h and was neutralized with barium carbonate, after which the precipitate was eliminated and the filtrate was evaporated. 2,3,4,6-Tetra-O-methyl-D-glucose was detected in the residue with the aid of TLC in system 4b in the presence of an authentic sample, and also by GLC [14].

Medicoside G (substance G, II), $C_{42}H_{66}O_{16}$, mp 242-243°C (from methanol), $[\alpha]_D^{24}$ +35.2 ± 2° (c 0.53; 50% aqueous ethanol). ν_{max}^{KBr} (cm^{-1}): 3340-3490 (OH), 1730, 1260 (ester group). Soluble in methanol and ethanol; sparingly soluble in acetone, water, and chloroform.

Medicagenic Acid (III) and Medicagenic Acid 3-O-β-D-Glucopyranoside (I) from (II). A solution of 150 mg of medicoside G (II) in 30 ml of methanol was treated with 10 ml of 20% sulfuric acid and the reaction mixture was heated at 100°C for 5 h. Then 30 ml of water was added and the methanol was evaporated off. The precipitate that deposited (106 mg) was chromatographed on a column with elution by system 2a. This gave 50 mg of medicagenic acid (III) with mp 352-354°C, $[\alpha]_D^{24}$ +112.0 ± 2° (c 0.10, ethanol), identical with an authentic sample obtained by the hydrolysis of glycoside (I), and also identified by its IR spectrum and its R_f value in TLC (system 2b).

On continuing the elution of the column with the same solvent system, 40 mg of glucoside (I) with mp 276-278°C (from methanol) was isolated, and this was shown to be identical with

a sample isolated directly from the plant by means of its IR spectrum and its R_f value on TLC on systems 1b and 2b.

Alkaline Hydrolysis of Medicoside G [(I) from (II)]. A solution of 50 mg of glycoside (II) in 20 ml of 50% ethanol was treated with a solution of 2.75 g of KOH in 5 ml of water. The reaction mixture was left at room temperature for 2 days. Then 100 ml of water was added, the ethanol was distilled off, and the reaction products were extracted with n-butanol. The butanolic extracts were combined, washed with water, and evaporated, and the dry residue was chromatographed on a column using system 2b. In this way, 35 mg of medicagenic acid 3-O-β-D-glucopyranoside (I) with mp 279-281°C was isolated, and it was shown by a mixed melting point and by means of its IR spectrum and R_f values on TLC in systems 1b and 2b to be identical with the analogous compound from the preceding experiment.

The Hepta-O-methyl Derivative (IV) and the Deca-O-methyl Derivative (V) from (II). With stirring, 0.5 g of sodium hydride was added in portions over 15 min to a solution of 0.5 g of medicoside G (II) and 50 ml of dimethyl sulfoxide. After 2 h, 6 ml of methyl iodide was added dropwise and the reaction mixture was stirred for another 4 h. Then it was poured into 200 ml of 2% sodium hyposulfite solution and the reaction products were extracted with chloroform. The residue obtained after the evaporation of the chloroform extract was chromatographed on a column with elution by system 4a. This gave 57 mg of the amorphous hepta-O-methyl derivative (IV), $[\alpha]_D^{24}$ +39.4 ± 2° (c 0.64; chloroform), which was shown with the aid of TLC and also from the results of IR, PMR, and mass spectroscopy to be identical with the sample obtained from glycoside (I).

On continuing the elution of the column with the same system, 119 mg of the deca-O-methyl derivative (V), $C_{52}H_{86}O_{16}$, was isolated with $[\alpha]_D^{24}$ +43.4 ± 2° (c 0.54; chloroform) in the IR spectrum of which there was no absorption in the region of hydroxy groups. Mass spectrum, m/z (%): 966 (M^+, 0.7), 747 (3), 732 (4), 717 (2), 703 (18), 685 (1), 527 (3), 512 (12), 497 (2), 481 (4), 467 (15), 453 (5), 435 (12), 422 (3), 407 (7), 375 (2), 353 (2), 325 (2), 309 (5), 303 (9), 281 (10), 265 (10), 263 (7), 249 (10), 248 (10), 233 (5), 231 (5), 219 (59), 205 (9), 204 (10), 203 (26), 187 (100).

The 2,23-Di-O-methyl Derivative of Medicagenic Acid (VIII) from (V). A solution of 42 mg of the deca-O-methyl derivative (V) in 10 ml of methanol was treated with 10 ml of 20% methanolic sulfuric acid and the reaction mixture was heated at 100°C for 7 h. Then 20 ml of water was added to the solution, the methanol was distilled off, and the resulting precipitate was separated off and washed with water, after which it was chromatographed on a column with elution by system 4a. This yielded 18 mg of the amorphous 2,23-dimethyl derivative of medicagenic acid (VIII), $C_{32}H_{50}O_6$, $[\alpha]_D^{24}$ +99.6 ± 2° (c 0.50; chloroform). ν_{max}^{KBr} (cm^{-1}): 3400-3580 (OH), 1725, 1250 (ester group). Mass spectrum, m/z (%): 530 (M^+, 1), 484 (30), 281 (13), 249 (20), 248 (100), 233 (15), 203 (84), 189 (16), 187 (20).

The aqueous solution was heated to 100°C for 2 h and was neutralized with barium carbonate, the precipitate was filtered off, and the filtrate was evaporated. In the residue, the presence of 2,3,4,6-tetra-O-methyl-D-glucose (VI) was shown by TLC in system 4b in the presence of an authentic sample, and it was also revealed by the GLC method [14].

SUMMARY

A new triterpene glycoside has been isolated from the roots of *Medicago sativa* — medicoside G — and its structure has been established as medicagenic acid 3,28-di-O-β-D-glucopyranoside.

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TRITERPENE GLYCOSIDES AND THEIR GENINS FROM *Thalictrum foetidum*.

I. THE STRUCTURE OF FOETOSIDE C

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A new glycoside — foetoside C — has been isolated from the epigeal part of *Thalictrum foetidum* L. and, on the basis of chemical transformations and spectral characteristics its structure has been established as oleanolic acid 28-[O-α-D-glycopyranosyl-(1 → 6)-O-β-D-glucopyranoside] 3-O-[O-β-D-xylopyranosyl-(1 → 3)-O-α-L-rhamnopyranosyl-(1 → 2)-α-L-arabinopyranoside].

From the epigeal part of *Thalictrum foetidum* L. (Ranunculaceae) we have isolated triterpene glycosides A, B, and C. In the present paper we consider the structure of the glycoside that we have called foetoside C (I). When glycoside (I) was subjected to acid hydrolysis, oleanolic acid (V) was identified as the aglycone [1]. It was found by GLC [2] that foetoside C contains D-glucose, D-xylose, L-arabinose, and L-rhamnose residues in a ratio of 2:1:1:1.

The alkaline hydrolysis of the pentaoside (I) led to the formation of the progenin (II), the carbohydrate components of which were, according to GLC [2], D-xylose, L-arabinose, and L-rhamnose (1:1:1). Consequently, foetoside C is a bisdesmosidic glycoside the acyloside chain of which includes two D-glucose residues.

The Smith degradation of glycoside (I) [3] led to the formation of oleanolic acid (V), which showed the absence of branching in the sugar chain.

Glycoside (II) was subjected to stepwise hydrolysis. From the hydrolysis products were isolated substance (VI), identified as oleanolic acid 3-O-α-L-arabinopyranoside [4], and a progenin (VII) containing L-arabinose and L-rhamnose residues.

The Hakomori methylation of glycoside (VII) [5] gave the hexa-O-methyl derivative (IX) (M^+ 818). From the products of the methanolysis of the permethylated (IX) was isolated methyl oleanolate (VIII). In a hydrolysate 2,3,4-tri-O-methyl-L-rhamnopyranose and 3,4-dimethyl-L-arabinopyranose were detected by GLC [6]. The presence of the latter compound was confirmed by a positive Bonner reaction [7]. A calculation of molecular rotation differences showed the α configuration of the anomeric carbon atom of the L-rhamnopyranose residue [8].

The facts given determine the glycoside (VII) as oleanolic acid 3-O-[O-α-L-rhamnopyranosyl-(1 → 2)-α-L-arabinopyranoside], which has been described previously [4]. A good

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