(IV) were detected residues of 3,4,6-tri-O-methyl-D-glucopyranose (T_{rel} = 2.04; 1.92); 2,3,4, 6-tetra-O-methyl-D-glucopyranose (T_{rel} = 1.26; 1.00); 3,4-di-O-methyl-L-arabinopyranose (T_{rel} = 0.96; 0.86); and 2,3,4-tri-O-methyl-L-arabinopyranose (T_{rel} = 0.58).

SUMMARY

The roots of Medicago sativa L. (family Fabaceae) have yielded a new triterpeneglycoside – medicoside I, for which the structure of hederagenin 3-O-[O-α-L-arabinopyranosyl)-(1 → 2)-O-β-D-glucopyranosyl-(1 → 2)-α-L-arabinopyranoside] 28-O-β-D-glucopyranoside has been established.

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TRITERPENE GLYCOSIDES OF ALFALFA.

IV. MEDICOSIDE J.

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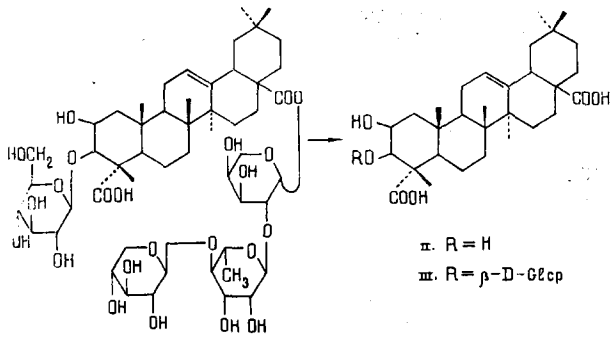
A new triterpene glycoside has been isolated from the roots of Medicago sativa L. (family Fabaceae) – medicoside J, and its structure has been established as a medicagenic acid 3-O-β-D-glucopyranoside 28-O-[O-β-D-xylopyranosyl-(1 → 4)-O-α-L-rhamnopyranosyl-(1 → 2)-β-L-arabinopyranoside].

Continuing a study of the triperpene glycosides of Medicago sativa L (family Fabacaeae) [1-3], we have established the structure of medicoside J (I) isolated previously [3] – one of the main components of the saponin fraction of alfalfa roots.

The acid hydrolysis of glycoside (I) led to medicagenic acid (II). It was established with the aid of GLC that compound (I) contained D-glucose, D-xylose, L-arabinose, and L-rhamnose residues in a ratio of 1:1:1:1.



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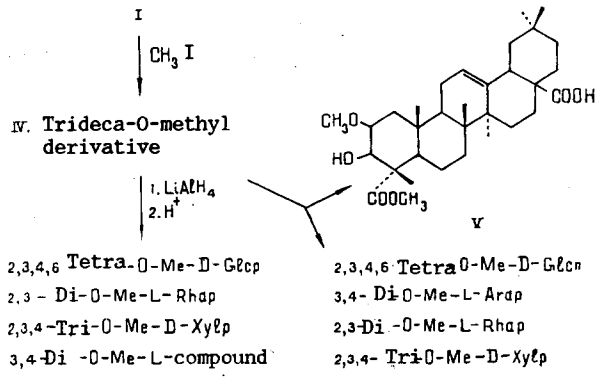

The IR spectrum of medicoside J contained absorption bands of an ester group, which showed the presence of an acyloside sugar chain in the molecule. The alkaline hydrolysis of glycoside (I) gave compound (III), which was identified from its physicochemical constants, spectral characteristics, and R_f value in TLC as medicagenic acid 3-O-β-D-glucopyranoside, isolated previously [1]. Consequently, the acyloside moiety of glycoside (I) was represented by D-xylose, L-arabinose, and L-rhamnose residues.

The periodate oxidation of medicoside J led to the breakdown of all the monosaccharide residues. This fact shows the absence of 1-3 bonds between the monosaccharide units of the acyloside chain and also of branching in it.

When glycoside (I) was methylated by Hakomori's method [4], the trideca-O-methyl derivative (IV) (M^+ 1256) was formed. The permethylate (IV) was hydrolyzed with a 4% solution of sulfuric acid. This gave the 2,23-di-O-methyl derivative of medicagenic acid (V) and a mixture of methylated sugars which were identified by GLC and also by TLC with the use of the Bonner reagent [5]. The mixture of methylated sugars included 2,3,4,6-tetra-O-methyl-D-glucopyranose, 3,4-di-O-methyl-L-arabinopyranose, 2,3-di-O-methyl-rhamnopyranose, and 2,3,4-tri-O-methyl-D-xylopyranose. The detection of completely methylated xylose showed that this sugar was terminal in the acyloside sugar chain.

The derivative (IV) was subjected to reductive cleavage and the reaction products were found to contain 2,3,4,6-tetra-O-methyl-D-glucopyranose, 2,3-di-O-methyl-L-rhamnopyranose, and 2,3,4-tri-O-methyl-D-xylopyranose, and also a substance appearing as a single peak on a chromatogram with T_{rel} = 2.68, which was assigned to 3,4-di-O-methylarabitol. Consequently, the L-arabinose residue was attached directly to the carboxy group.

The PMR spectrum (C_5D_5N) of the permethylate (IV) contained doublets of four anomeric protons at (ppm) 4.38 (^3J = 7 Hz), 4.84 (^3J = 6 Hz), 5.46 (^3J = 2 Hz) and 6.19 (^3J = 3 Hz). The first signal related to the D-glucopyranose residue [1]. The value of the chemical shift and the spin-spin coupling constant (SSCC) of the signal at 5.46 ppm (^3J = 2 Hz) showed that it belonged to the L-rhamnopyranose residue. The weakest-field signal at 6.19 ppm related to the monosaccharide attached directly to the carboxy group — L-arabinose. The signal at 4.84 ppm was assigned to the D-xylose residue. The SSCCs of the signals of the anomeric protons showed the β-configurations of the D-xylopyranose and L-arabinopyranose residues and the α-configuration if the L-rhamnopyranose residue [6].

Thus, medicoside J has the structure of medicagenic acid 3-O-β-D-glucopyranoside 28-O-[O-β-D-xylopyranosyl-(1 → 4)-O-α-L-rhamnopyranosyl-(1 → 2)-β-L-arabinopyranoside].

EXPERIMENTAL

For general remarks, see [3]. The following solvent systems were used: 1) chloroform—methanol [a (20:1); b (10:1)]; and 2) benzene—acetone [a (5:1); b) (20:1)].

Medicoside J (substance J, (I)). $C_{52}H_{82}O_{23}$, mp 234-236°C (from methanol, $[\alpha]_D^{27}$ −0 ± 3° (c 0.41; methanol); ν_{max}^{KBr} (cm^{-1}): 3530-3260, 1760-1700, 1265. PMR (C_5D_5N, δ, ppm): 0.78, 0.86, 0.96, 1.11, 1.38, 1.80 (3 H each, s, 6 × CH_3); 1.60 (3 H, d, ^3J = 4 Hz, CH_3 of a L-rhamnopyranose residue); 4.93 (2 H, d, ^3J = 6 Hz, anomeric protons of D-glucopyranose

and D-xylopyranose residues); 5.31 (1 H, broadened s, H-13); 5.55 (1 H, s, anomeric proton of a L-rhamnopyranose residue); 5.32 (1 H, d, ^3J = 2 Hz; anomeric proton of a L-arabinopyranose residue). The GLC analysis of the monosaccharides, performed similarly to that described in [3] showed the glycoside (I) contained D-glucose, D-xylose, L-rhamnose, and L-arabinose residues in a ratio of 1.00:0.87:1.20:1.28.

Medicagenic Acid (II) from (I). A solution of 100 mg of medicoside J (I) in 50 ml of 4% methanolic sulfuric acid was boiled for 3 h. Then the solution was diluted with 50 ml of water and the methanol was evaporated off. The precipitate that deposited was chromatographed on a column with elution by system 1a. This gave 21 mg of medicagenic acid (II), $C_{30}H_{46}O_6$, mp 352-354°C (from chloroform–methanol (20:1)), $[\alpha]_D^{20}$ +111.0 ± 2° (c 0.10); ethanol).

Medicagenic Acid 3-O-β-D-Glucopyranoside (III) from (I). A solution of 700 mg of medicoside J (I) in 50 ml of 3% aqueous KOH was left at room temperature for two days and was then neutralized with KU-2 cation-exchange resin. The resin was filtered off and was washed with ethanol, and the filtrate was evaporated. The dry residue (700 mg) was chromatographed on a column with elution by system 1b. This gave 96 mg of compound (III), $C_{36}H_{56}O_{11}$, mp 289-292°C (from methanol), $[\alpha]_D^{23}$ + 63.1 ± 2° (c 0.50; ethanol). Glycoside (III) was also identified as medicagenic acid 3-O-β-D-glucopyranoside [1] through its PMR and IR spectra.

The Trideca-O-methyl Derivative (IV) from (I). The Hakomori methylation [4] of 500 mg of glycoside (I) gave 130 mg of the amorphous trideca-O-methyl derivative (IV), $C_{65}H_{108}O_{23}$. $[\alpha]_D^{21}$ +13.1 ± 2° (c 1.45; methanol). In the IR spectrum there was no absorption in the region of hydroxy groups. M^+ 1256. PMR (C_5D_5N, δ, ppm): 0.78, 0.82, 0.94, 1.14, 1.23, 1.63 (3 H each, s, 6 × CH_3); 1.52 (3 H, d, ^3J = 5 Hz, CH_3 of a L-rhamnopyranose resdue); 3.23-3.70 (13 × OCH_3); 4.38 (1 H, d, ^3J = 7 Hz, anomeric proton of a D-glucopyranose residue); 4.84 (1 H, d, ^3J = 6 Hz), anomeric proton of a D-xylopyranose residue); 5.36 (1 H, broadened s, H-12); 5.46 (1 H, d, ^3J = 2 Hz, anomeric proton of a L-rhamnopyranose residue); 6.19 (1 H, d, ^3J = 3 Hz, anomeric proton of a L-arabinopyranose residue). PMR ($CDCl_3$, δ, ppm): 0.69, 0.84, 0.86, 1.06, 1.12, 1.35 (3 H each, s, 6 × CH_3); 1.51 (3 H, d, ^3J = 8 Hz, CH_3 of a L-rhamnopyranose residue); 3.26-3.65 (13 × OCH_3); 4.12 (1 H, d, ^3J = 7 Hz, anomeric proton of a D-glucopyranose residue); 4.52 (1 H, d, ^3J = 7 Hz, anomeric proton of a D-xylopyranose residue); 4.95 (1 H, d, ^3J = 1 Hz, anomeric proton of a L-rhamnopyranose residue). 5.26 (1 H, broadened s, H-12); 5.76 (1 H, d, ^3J = 2 Hz, anomeric proton of L-arabinopyranose).

GLC Analysis of the Methylated Monosaccharides Obtained from the Trideca-O-methyl Derivative (IV). The analysis was performed similarly to that described in [3]. In compound (IV) were found residues of 2,3,4,6-tetra-O-methyl-D-glucopyranose (T_{rel} = 1.24; 1.00); 3,4-di-O-methyl-L-arabinopyranose (T_{rel} = 0.95; 0.85); 2,3-di-O-methyl-L-rhamnopyranose (T_{rel} = 0.95); and 2,3,4-tri-O-methyl-D-xylopyranose (R_{rel} = 0.48; 0.40).

The 2,23-Di-O-methyl Derivative of Medicagenic Acid (V) from (IV). A solution of 50 mg of compound (IV) in 10 ml of a 4% solution of sulfuric acid in methanol was boiled for 5 h, and then 10 ml of water was added to the solution and the methanol was distilled off. The precipitate that deposited (15 mg) was separated off and was chromatographed on a column in system 2b. This gave 120 mg of the 2,23-di-O-methyl derivative of medicagenic acid (V), $C_{32}H_{50}O_6$ $[\alpha]_D^{21}$ + 98.5 ± 2° (c 0.51; chloroform). Compound (V) was also identified on TLC with an authentic sample in system 2a.

After being heated for 4 h, the filtrate was neutralized with EDE-10p anion-exchange resin, the solvent was distilled off, and in the dry residue with the aid of TLC in system 1b were identified: 2,3,4,6-tetra-O-methyl-D-glucopyranose (R_f 0.84); 2,3,4-tri-O-methyl-D-xylopyranose (R_f 0.76); 2,4-di-O-methyl-L-rhamnopyranose (R_f 0.47); and 3,4-di-O-methyl-L-arabinopyranose (R_f 0.33). The last spot was revealed with the Bonner reagent [5].

Reductive Cleavage of the Trideca-O-methyl Derivative (IV). A solution of 25 mg of compound (IV) in 5 ml of absolute ether was treated with 40 mg of lithium tetrahydroaluminate, and the mixture was boiled for 8 h. The solid matter was filtered off and the filtrate was evaporated. The methylated monosaccharides in the residue were analyzed by GLC as described in [3]. The following were identified in the product of the reductive cleavage of the derivative (IV): 2,3,4,6-tetra-O-methyl-D-glucopyranose, (T_{rel} = 1.20; 1.00); 3,4-

di-O-methyl-L-rhamnopyranose, (T_{rel} = 0.94); 2,3,4-tri-O-methyl-D-xylopyranose (T_{rel} = 0.46; 0.39); and 3,4-di-O-methyl-L-arabitol (T_{rel} = 2.68).

Periodate Oxidation of Medicoside J (I). A solution of 50 mg of glycoside (I) in 5 ml of 5% $NaIO_4$ was left at roomtemperature for 4 h. Then chloroform was added and the precipitate that deposited was separated off and was analyzed with the aid of GLC as described in [3]. No sugars were detected.

SUMMARY

The roots of Medicago sativa L. (family Fabaceae) have yielded a new triterpene glycoside – medicoside J – for which the structure of medicagenic acid 3-O-β-D-glucopyranoside 28-O-[O-β-D-xylopyranosyl-(1 → 4)-O-α-L-rhamnopyranosyl-(1 → 2)-β-L-arabinopyranoside) has been established.

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TRITERPENE GLYCOSIDES OF Astragalus AND THEIR GENINS.

XXI. CIRCULAR DICHROISM OF CYCLOARTANE KETONES

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The CD spectra of a number of natural and synthetic cycloartane ketones have been studied. The influence of 6α-hydroxy group on the Cotton effect due to a 3-keto function has been found. The Cotton effect has been determined for 6-oxo- and 11-oxocycloartanes.

In the present paper we consider some features of the circular dichroism (CD) spectra of cycloartane ketones.

In the CD spectra of oxocycloartanes a Cotton effect is observed in the 280-320 nm region which is due to the $n \rightarrow \pi^*$ transition in the carbonyl function. It is known that 3-oxocycloartanes unsubstituted in ring B are characterized by a negative Cotton effect. For example, in the case of cycloartenone (cycloart-24-en-3-one) an effect is observed at 315 nm ($\Delta\varepsilon$ = −0.99) [1], and in the case of the 3-oxo derivative (II) one at 296 nm ($\Delta\varepsilon$ = −1.39) (Table 1 and Fig. 1a). At the same time, as follows from the CD spectra of the 6α-hydroxy-3-oxocycloartanes (III-VI and VIII), the effect due to the 3-oxo function acquires a complex form: on the long-wave side (315-322 nm) a negative minimum appears, and in the region of shorter waves (280-290 nm) a positive maximum. This change in the nature of the CD curve is obviously caused by the presence of the 6α-hydroxy group [2]. Actually, one of the factors responsible for the negative sign of the effect for 4,4-dimethyl-3-oxo-5α-steroids is the interaction of the 4α-CH_3 group with the 6α-H atom [3]. There is no doubt that the replacement of the 6α-hydrogen atom by a hydroxy group will lead to a distortion

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