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# NEW GLYCOSIDES FROM PLANTS OF THE GENUS Phlojodicarpus

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From plants of the genus Phlojodicarpus have been isolated the new coumarins umbelliferone β-D-apiosyl(1 → 6)-β-D-glucopyranoside (I) and 8-(2',3'-dihydroxy-3'-methylbutyl)umbelliferone 7-O-β-D-glucopyranoside (II) and also the flavone glycoside diosmetin 7-O-β-D-glucopyranoside (III). The result of IR, UV, PMR, and $^{13}C$ NMR spectroscopy are given.

Investigating the coumarins from plants of the genus Phlojodicarpus, we turned our attention to the fact that the chemical composition of even a single species may undergo considerable changes according to the conditions of growth. Thus, Ph. turczaninovii Sipl. growing in the arid regions of Mongolia contained substances not found in this plant collected on the territory of the USSR [1-3]. In the present paper we describe the isolation and chemical structures of two coumarin glycosides and one flavonoid glycoside from Ph. villosus (Turcz. ex Fischer et Meyer) Ledeb. and Ph. sibiricus (Steph. ex Speng.) K.-Pol.

The first species was collected in the period of flowering in the western part of Mongolia. Decursinol and esters of it have been isolated from it previously [4]. It has now been established that, in addition to these components, the plant contains a polar coumarin with the composition $C_{20}H_{24}O_{12}$. On the basis of the results of IR, UV, PMR, and $^{13}C$ NMR spectroscopy it was assigned the structure of a bioside of umbelliferone (I). The UV spectrum of the compound coincided with the absorption of O-substituted umbelliferone derivatives and no displacement of the absorption bands in the presence of diagnostic additives was observed. The IR spectrum revealed bands typical for the unsaturated lactone ring of a coumarin. In the PMR spectrum, the nature of the spin-spin interactions showed the presence of one substituent in position 7. Hydrolysis with dilute hydrochloric acid formed umbelliferone and two carbohydrates. One of them was identified by paper chromatography as glucose, and the other had the same mobility as rhamnose. However, this should have been a pentose, as follows from the empirical formula of the glycoside and the SSCC of the anomeric proton, 3 Hz. We assumed that the second carbohydrate was apiose which, as is known [5], has the same chromatographic mobility as rhamnose. A study of the $^{13}C$ NMR spectrum confirmed this assumption: the pentose contained two $CH_2O$ groups and one quaternary carbon atom and, consequently, was a branched sugar. The attachment ofthe apiose at position 6 of the glucosyl residue was determined from the chemical shift of the C-6' signal (68.3 ppm). An interpretation of the $^{13}C$ NMR spectrum is given in Table 1.

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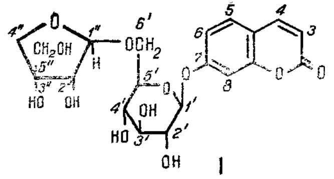
TABLE 1. Chemical Shifts of the Carbon Atoms in the $^{13}C$ NMR Spectra of Compounds (I), (II), (IV), and (V) Taken in DMSO-$d_6$ (ppm relative to TMS)

| C atom | Compound |  |  |  | C atom | Compound |  |  |  |
|---|---|---|---|---|---|---|---|---|---|
|  | I | II | IV | V |  | I | II | IV | V |
| 2 | 160,9 | 161,0 | 164,9 | 163,4 | 3′ | 76,8* | 72,7 | 147,7 | 146,8 |
| 3 | 114,0* | 112,2 | 104,6 | 103,6 | 4′ | 70,7 | 26,0* | 152.2 | 151,2 |
| 4 | 144,8 | 145,2 | 182,6 | 181,7 | 5′ | 77,2* | 26,5* | 113,1 | 112,2 |
| 4a | 114,1* | 117,9 | 106.2 | 103,7 | 6′ | 68.3 |  | 119,7 | 123.8 |
| 5 | 130.2 | 127,6 | 161,9 | 157.3 | 1″ | 110,1 | 102,4 | 100,9* |  |
| 6 | 114,2* | 113,7 | 100,4* | 98,9 | 2″ | 76,4* | 74,4 | 73,9 |  |
| 7 | 160,9 | 159,8 | 163,9 | 164,2 | 3″ | 79.4 | 77,7* | 77,2* |  |
| 8 | 104,2 | 114,4 | 95,7 | 93,9 | 4″ | 74,2 | 70,6 | 70,5 |  |
| 8a | 155,7 | 157,0 | 157,8 | 161,4 | 5″ | 64.3 | 78,1* | 78,0* |  |
| 1′ | 101,0 | 25.5 | 123,7 | 118 7 | 6″ |  | 61.6″ | 61,5 |  |
| 2′ | 73,9 | 77,1 | 114,0 | 113,0 | $OCH_3$ |  |  | 56,6 | 58,3 |

*Assignment ambiguous within a column.

Thus, the bioside from Ph. villosus has the structure of umbelliferone β-D-apiosyl-(1 → 6)-β-D-glucopyranoside. We found the same bioside in considerably larger amount in Ph. sibiricus growing in the environs of Ulan-Bator and in Yakutia. Several other phenolic compounds glycosylated by apiosylglucose are known; see, for example, [6, 7]. Some results from these papers were used in the assignment of the signals in the $^{13}C$ NMR spectrum of compound (I).

A prenylated coumarin glycoside for which the chemical structure (II) has been proposed has been isolated from this same species of Phlojodicarpus, Ph. sibiricus var. eudahuricus (M. Popov) Serg., but collected in the south of Chita province. Its glycosidic nature followed from the empirical formula $C_{20}H_{26}O_{10}$ and the PMR spectrum in DMSO-$d_6$, in which there were the signals of six hydroxy groups and an anomeric proton. The type of substitution in the coumarin nucleus followed from an analysis of the spin-spin couplings in the PMR spectrum. The hydrolysis of (II) with dilute hydrochloric acid gave glucose and two aglycones: lomatin, and 8-(2',3'-dihydroxy-3'-methylbutyl)-7-hydroxycoumarin (III), previously isolated from Seseli tortuosum. The structure of the side chain and the site of attachment of the substituents to the benzene ring followed from the formation on hydrolysis of the artifact lomatin, in addition to (III), and from the $^{13}C$ spectrum (see Table 1).



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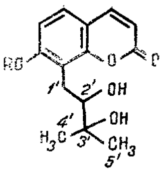
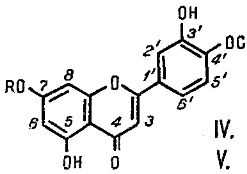


II. R=β-D-Glc
III. R=H



IV. R=β-D-Glc
V. R=H

The flavone glycoside (IV) was also isolated from Ph. sibiricus growing in the environs of Ulan-Bator. On acid hydrolysis it decomposed into glucose and an aglycone with the composition $C_{16}H_{12}O_6$ which, on the basis of UV and PMR spectroscopy, was identified as diosmetin (V) [9, 10]. One of the hydroxyls of (IV) gave a signal at δ 12.93 ppm in the PMR spectrum taken in DMSO-$d_6$ solution, which showed the presence of an unsubstituted OH group at C-5.

The absence of a bathochromic shift in the electronic spectrum on the addition of sodium acetate indicated the attachment of the glucosyl residue to the C-7 atom. The configuration and size of the sugar ring were determined on the basis of the positions of the signals of the anomeric center in the PMR and $^{13}C$ NMR spectra of (IV): 5.08 (J = 7.5 Hz) and 100.9 ppm, respectively. The other spectral characteristics also agreed with the structure of diosgenin 7-O-β-D-glucopyranoside for (V). This is the first time that this compound has been found in plants of the genus Phlojodicarpus. The isolation of the 7-O-α-D-glucofuranoside of (V) from Ferula samarkandica has been reported previously [11].

## EXPERIMENTAL

For general observations, see [1, 2]. The following solvent systems were used for chromatography: 1) chloroform—methanol (10:1); 2) chloroform—methanol (4:1); and 3) butanol—pyridine—water (6:3:1).

Isolation of (I). The air-dry epigeal part of Ph. villosus (2.5 kg) was extracted three times with 96% ethanol. The extract was evaporated to a volume of about 1 liter, diluted with water, and extracted successively with petroleum ether and diethyl ether. The aqueous phase was evaporated to dryness and the residue (75 g) was chromatographed on 1 kg of silica gel L 100/160. Elution was performed with chloroform and with mixtures of chloroform and methanol with increasing proportions of the latter. Compound (I) was eluted at the (9:1) composition of the mixture. After two recrystallizations from methanol, 2.3 g of umbelliferone 7-O-[O-β-D-apiofuranosyl-(1 → 6)-β-D-glucopyranoside] (I), $C_{20}H_{24}O_{12}$, was obtained with mp 204-205°C, $[\alpha]_D^{22}$ +169° [c 0.59; $CH_3OH:H_2O$ (1:1)]. UV spectrum ($CH_3OH$), $\lambda_{max}$: 248, 292, 318 nm. IR spectrum: $\nu_{max}^{KBr}$ 3360 (OH), 1718 (CO), 1620 (C = C). PMR spectrum, δ (DMSO-$d_6$): 7.99 (d, J = 10 Hz), $H_4$; 7.65 (d, J = 9 Hz), H-5; 7.04, m, H-6 and H-8; 6.32, d, J = 10 Hz, H-3; 5.02 (d, J = 7 Hz), H-1'; 4.80 (d, J= 3 Hz); 3.88-3.15, m, OH and CH of a disaccharide.

Hydrolysis of (I). A mixture of 0.02 g of the bioside (I) and 4 ml of 3% HCl was heated in the boiling water bath for 2 h. The completeness of hydrolysis was checked by TLC on Silufol plates in system 1. The aglycone that deposited on cooling was filtered off and crystallized from chloroform. This gave a substance with mp 224-226°C, $M^+$ 164, identical with umbelliferone. The aqueous filtrate was neutralized with AV-17 ion-exchange resin and was extracted with ethyl acetate. Carbohydrates were identified in the aqueous layer by PC in system 3.

Isolation of (II). The extract obtained by the treatment of 2.6 kg of the epigeal part of Ph. sibiricus collected in Chita province with 96% ethanol was evaporated to a volume of about 1 liter. The crystalline precipitate that deposited when this concentrate was allowed to stand in the cold was filtered off. The concentrated mother liquor was diluted with water and was washed free from nonpolar substances with petroleum ether and diethyl ether. The aqueous phase was evaporated to dryness and the residue was chromatographed on 1.2 kg of silica gel L 100/160. A mixture of chloroform and methanol (9:1) eluted 8-(2',3'-dihydroxy-3'-methylbutyl)-7-β-D-glucopyranosyloxycoumarin (II), $C_{20}H_{26}O_{10}$, mp 224-226°C (from methanol). UV spectrum $\lambda_{max}^{CH_3OH}$ 314 nm.

PMR spectrum, δ (DMSO-$d_6$): 7.98 (d, J = 10 Hz), H-4; 7.53 (d, J = 8.5 Hz), H-5; 7.15 (d, J = 8.5 Hz), H-6; 6.30 (d, J = 10 Hz), H-3; 4.87 (d, J = 7.5 Hz), H-1"; 5.30 d, 5.08 m, 4.64 m, 4.43 d, 4.28 s, OH and CH of a glucose residue; 3.44 m and 2.85 m, CH and $CH_2$ of the side chain; 1.17 s, 2 × $CH_3$.

Hydrolysis of (II). The glucoside (II) (0.02 g) was hydrolyzed by being heated in 3% HCl for 1.5 h. The crystalline precipitate that deposited on cooling was filtered off. Lomatin and compound (III) were isolated from it by preparative thin-layer chromatography; the lomatin was identified by comparison with an authentic sample and the (III) from its mass spectrum: m/z (%): $M^+$ 264 (112), 196 (29), 178 (100), 166 (79).

Isolation of (IV). Glucoside (IV) was isolated in a similar manner to (I) and (II) from the epigeal part of Ph. sibiricus collected in the Ulan-Bator region. It was eluted with chloroform—methanol (19:1). Diosmetin 7-O-β-D-glucopyranoside (IV), $C_{21}H_{22}O_{11}$, mp 265-266°C (from $CH_3OH$). UV spectrum $\lambda_{max}^{CH_3OH}$: 254, 269, 345 nm. IR spectrum, $\nu_{max}^{par.oil}$, $cm^{-1}$: 3420 (OH), 1674 (CO), 1620 (C=C). PMR spectrum, δ (DMSO-$d_6$), ppm: 12.93, s, 5-OH; 9.47, s, 3'-OH; 7.57 (dd, J = 8; 2.5 Hz), H-6'; 7.44 (d, J = 2.5 Hz), H-2'; 7.12 (d, J = 8 Hz, H-5'; 6.83, s, H-3; 6.81 (d, J = 2.5 Hz), H-8; 6.44 (d, J = 2.5 Hz), H-6; 5.08 (d, J = 7.5 Hz), H-1"; 3.87, s, $OCH_3$.

Hydrolysis of (IV). Glucoside (IV) (23 mg) was hydrolyzed by heating with 5 ml of 10% HCl in the water bath for 4 h. The completeness of hydrolysis was checked by the TLC method using Silufol with system 2. The aglycone (V) that deposited upon cooling was filtered off and was identified as diosmetin by its UV and $^1H$ and $^{13}C$ NMR spectra [9, 10]. The filtrate was neutralized, and glucose was identified in it by PC in system 3.

## SUMMARY

1. Umbelliferone 7-O-[O-β-D-apiofuranosyl-(1 → 6)-β-D-glucopyranoside, 8-(2',3'-dihydroxy-3'-methylbutyl)-7-β-D-glucopyranosyloxycoumarin, and diosmetin 7-O-β-D-glucopyranoside have been isolated from the epigeal parts of Phlojodicarpus villosus and Ph. sibiricus.

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# A NEW ISOFLAVONOSTILBENE FROM THE HEARTWOOD OF Maackia amurensis

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A new isoflavonostilbene which has been called maackiasin has been isolated from an ethanolic extract of the heartwood of Maackia amurensis and its structure has been established by spectral methods. The maackiasin molecule is constructed of fragments of the isoflavone retusin and of 3,3',4',5-tetrahydroxystilbene linked by a diether bond. The dioxane grouping connecting the two fragments is constructed from the hydroxyls at C-7 and C-8 of the isoflavone and the vinyl grouping of the stilbene. Maackiasin is the first representative of a new type of natural polyphenols.

We have previously reported the isolation of three isoflavones – formononetin, genistein, and retusin – and two stilbenes – resveratrol and 3,3',4',5-tetrahydroxystilbene – from the ethyl acetate fraction of an ethanolic extract of the wood of maackia (Maackia amurensis Rupr. et Maxim) growing in Maritime Territory [1].

Among the phenolic compounds isolated there was also a substance M-6 corresponding on its elementary composition to the formula $C_{30}H_{22}O_9$ and issuing from a chromatographic column after the substances mentioned above. In the present paper we give the results of the determination of the structure of this compound.

Compound M-6 was optically inactive. No fluorescence was observed under UV, which indicated the absence of a stilbene structure in the molecule of this compound. The $^{13}C$ NMR spectrum (Table 1) contained the signals of 30 carbon atoms, which correspond to the formula

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