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A PEUCEDANOL GLUCOSIDE FROM *Phlojodicarpus turczaninovii*

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The new coumarin peucedanol 3'-β-D-glucopyranoside (I), $C_{20}H_{26}O_{10}\cdot C_2H_5OH$, mp 160-162°C, has been isolated from an ethanolic extract of the epigeal part of *Phlojodicarpus turczanovii* growing in the Mongolian People's Republic (Gobi-Altai). The acid hydrolysis of (I) formed D-glucose and peucedanol (II), and also decursinol and marmesin. The results of IR, UV, PMR, and ^{13}C NMR spectroscopy are given.

The courmarins [1] peucenidin, libanorin, and buchtarmin have been isolated from *Phlojodicarpus turczaninovii* Sipl. growing in the south of Chitinskaya Province. The same plant collected in the mountains of the Gobi-Altai (Mongolian People's Republic) and erroneously identified previously as *Ph. sibiricus* [2] contains, instead of the coumarins mentioned, the epoxide derivatives phlojodicarpin and isophlojodicarpin.

We now report that in addition to the latter two compounds the Mongolian plant contains a polar coumarin which has been isolated by chromatography on silica gel of the butanol-soluble fraction of the ethanolic extract of the epigeal part of the plant followed by crystallization from ethanol. This compound has been assigned the structure of 3'-O-(β-D-glucopyranosyl)peucedanol (I) on the basis of the following facts.

The hydrolysis of (I) with dilute hydrochloric acid led to glucose and a mixture of three aglycones. Among them a substance with spectral and other characteristics identical with that of peucedanol (II) [3] predominated. It was shown by thin-layer chromatography on Silufol in the presence of markers (in the solvent system chloroform–methanol (10:1)) that minor components of the hydrolysate were decursinol (III) and marmesin (IV). We assume that they were artefacts formed during hydrolysis by the cyclization of (II). The phenolic hydroxyl in (I) is not glycosylated. This follows from the bathochromic shift of the long-wave absorption band in the UV region from 333 to 377 nm on the addition of sodium methanolate.

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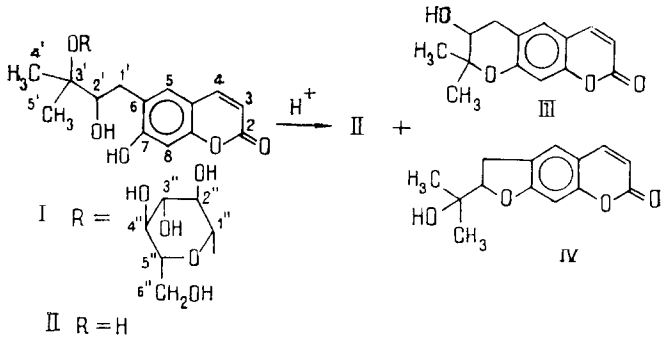
TABLE 1. Chemical Shifts of the Nuclei in the ^{13}C Spectra of (I) and (II)*

No. of the atom	δ, ppm		No. of the atom	δ, ppm		No. of the atom	δ, ppm	
	I	II		I	II		I	II
2	164,2	164,3	8	103,4	103,5	1″	98,5	
3	112,5	112,5	8a	156,0	156,1	2″	75,7	
4	146,5	146,5	1′	33,5	33,7	3″	77,9	
4a	113,3	113,3	2′	78,5†	79,6	4″	71,9	
5	132,0	131,9	3′	81,6	74,1	5″	78,1†	
6	126,7	126,9	4′	23,1	25,5	6″	62,3	
7	161,5	161,7	5′	23,2	25,9			

*The signals at 18.7 and 58.6 ppm in the spectrum belong to ethanol of crystallization.
†Assignment ambiguous.



Quantitative hydrolysis showed that the molecule of (I) contained one glucosyl residue. This sugar is present in the β-pyranose form, as follows from the values of the chemical shift (δ 4.47 ppm) and the spin-spin coupling constant (J = 6.3 Hz) of the anomeric proton [4]. The choice between positions 2 and 3 was made on the basis of the results of a study of the ^{13}C NMR spectra. The assignment of the signals of the carbon atoms in (I) and (II) is given in Table 1. It was made by calculation, confirmed by the INEPT technique, and by comparison with literature information. It can be seen from the table that after the splitting out of glucose the greatest upfield shift (Δδ 7.5 ppm) was observed for the C-3 atom. The signals of the neighboring C-atoms underwent slight downfield shifts. These facts are in harmony with the position of the glycosyl residue at the third carbon atom of the side chain of peucedanol.

EXPERIMENTAL

Melting points were determined on a Kofler block and are not corrected. Mass spectra were taken on a MAT-212 chromato-mass spectrometer, and ^{1}H and ^{13}C NMR spectra on BS-487B and Jeol FX-90Q (89.55 MHz) instruments in deuteromethanol. The results of UV and IR spectroscopy are given for solutions in methanol and in KBr tablets, respectively.

Isolation of (I). The air-dry epigeal part of *Phlojodicarpus turczaninovii* (Gobi, Altai, Mongolian People's Republic, flowering period) (2.3 kg) was extracted three times with 10-liter portions of ethanol. The extract was filtered, evaporated in vacuum to a volume of ~1 liter, and diluted with water. The precipitate that deposited was separated off, and the solution was extracted with n-butanol. After the solvent had been evaporated off, the resulting residue (11.3 g) was chromatographed on a column containing 450 g of silica gel L 100/160. Elution was carried out with benzene containing increasing amounts of methanol. The glucoside (I) was desorbed by benzene–methanol (9:1). After two crystallizations from ethanol, 0.5 g (0.02%) of colorless crystals was obtained.

3′-O-(β-D-Glucopyranosyl)peucedenol, $C_{20}H_{26}O_{10}\cdot C_2H_5OH$, mp 160-162°C. Found, %: C 55.72; 56.12; H 6.66; 6.67. Calculated, %: C 55.93; H 6.78. UV spectrum, $\lambda_{max}^{CH_3OH}$ (nm): 224, 258, 333 (377) in sodium methanolate solution). IR spectrum, ν_{max}^{KBr}, cm^{-1}: 3350 (OH); 1690 (CO); 1610 (C=C). PMR spectrum, δ, ppm: 7.72, d, H-4, J = 9 Hz; 7.30, s, H-5; 6.63, s, H-8; 6.08, d, H-3, J = 9 Hz; 5.18, s, OH-7; 4.47, d, H-1″, J = 6.3 Hz; 3.40-2.90, m, 2.64, m, 2H-1; 1.30 and 1.26, s, 2 CH_3; 1.11, t, CH_3 (ethanol).

Hydrolysis of (I). A mixture of 0.1 g of the glucoside of 2 ml of 3% HCl was heated in the boiling water bath for 1.5 h. The completeness of hydrolysis was confirmed by thin-layer chromatography on Silufol in the chloroform-methanol (10:1) system. The aglycone that deposited on cooling was filtered off. The filtrate was neutralized with anion-exchange resin, separated from the resin, and extracted with ethyl acetate. An additional amount of aglycone (making a total of 0.06 g) passed into the organic extract. The substance recrystallized from ethyl acetate at mp 184-186°C, M^+ 264. The PMR spectrum, mass-spectrometric fragmentation, and other characteristics coincided with those reported [3] for peucedanol (II).

The mother liquor from the crystallization of (II) contained another two coumarins. In their mobility on Silufol in the solvent system given above they corresponded to authentic samples of (III) and (IV).

SUMMARY

A new coumarin, 3'-β-D-glucopyranoside peucedanol, has been isolated from the epigeal part of *Phlojodicarpus turczaninovii*. Its structure has been established by chemical and spectral methods.

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FLAVONOIDS OF *Haplophyllum perforatum*.

NEW GLYCOSIDES OF LIMOCITRIN

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Two new glycosides of limocitrin have been isolated from the epigeal part of *Haplophyllum perforatum* (M. B.) Kar. et Kir. On the basis of chemical transformations and spectral characteristics the structures of the substances isolated have been established as 7-(6"-acetyl-β-D-glucopyranosyloxy)-3,4',5-trihydroxy-3',8-dimethoxyflavone and 7-[O-α-L-rhamnopyranosyl-(1 → 2)-β-D-glucopyranosyloxy]-3,4',5-trihydroxy-3',8-dimethoxyflavone.

We have previously demonstrated the presence of flavonoids in the plant *Haplophyllum perforatum* (M. B.) Kar. et Kir. [1, 2]. A further study of the components of ethyl acetate and butanol fractions of an ethanolic extract of the epigeal part has led to the isolation of another four new flavonoids. In the present paper we report on the determination of the structures of two of them.

The compounds, with the composition $C_{25}H_{26}O_{14}$ (I) and $C_{29}H_{34}O_{17}$ (II), were assigned on the basis of their UV spectra, qualitative reactions with zirconium oxychloride in citric acid, and their bright yellow fluorescence in UV light to the group of flavonols with free hydroxyls at C-3. According to the results of acid hydrolysis, both substances were glycosides. It was established by TLC and GLC that the carbohydrate moiety of (I) consisted of D-glucose and that of (II) D-glucose and L-rhamnose. The aglycones of the glycosides (I) and (II) proved to be the same compound with the composition $C_{17}H_{14}O_8$, M^+ 346 (III). UV spectra with diagnostic additives showed the presence of free phenolic hydroxy groups in the C-3, C-5, C-7, and C-4' positions of the aglycone [3].

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