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PHLOMOSIDE D — AN IRIDOID GLYCOSIDE FROM *Phlomis regelii*

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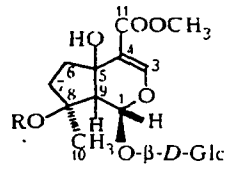
A new iridoid — phlomoside D — has been isolated from the epigeal organs of Phlomis regelii *(M. Pop). Its structure has been established on the basis of chemical transformations and spectral characteristics.*

We have previously [1] reported the presence in the epigeal organs of *Phlomis regelii* M. Pop. (fam. Lamiaceae) of ipolamiidoside (**1**), phlomosides A (**2**) and B (**4**), ipolamiide (**3**) and lamiide (**5**).

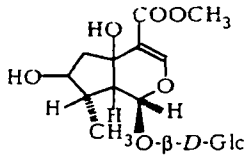
By rechromatography on a column of silica gel of the mother solutions obtained in the isolation of the above substances we have now isolated two new iridoid glycosides — phlomosides C and D. In the present paper we consider the determination of the structure of phlomoside D (**6**).

The IR spectrum of iridoid (**6**) contained a broad absorption band at 3240 cm^{-1} (OH group), a maximum at 1634 cm^{-1} (C=C), and absorption bands at 1706 and 1281 cm^{-1} (ester) and at 1452, 1071, and 714 cm^{-1} (benzene ring), to which the signal of five aromatic protons at 7.54 ppm (3H) and 8.14 ppm (2H) in the PMR spectrum corresponded.

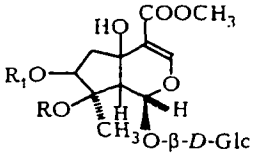
In the neutral fraction of the product of the alkaline saponification of iridoid (**6**) we identified lamiide (**5**) [1, 3], and in the acid part of the hydrolysate we found benzoic acid. The acid hydrolysis of iridoid (**6**) led to *D*-glucose and a black decomposition product of the aglycon moiety of the iridoid.



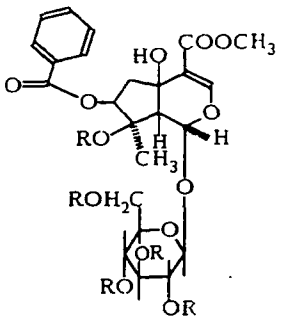
1. R=Ac
3. R=H



2



4. R=R_1=Ac
5. R=R_1=H



6. R=H
7. R=Ac

On comparing the characteristics of the PMR spectra of lamiide (**5**) and iridoid (**6**) it can be seen that the signal of H-7 proton in the spectrum of (**6**) is shifted downfield by 1.5 ppm (Table 1). This fact and also the paramagnetic displacements of the H-9 and CH_3-10 signals show the position of the benzoate group at C-7.

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TABLE 1. Chemical Shifts (ppm) and SSCCs (J, Hz) of the Protons in the PMR Spectrum of Lamiide (**5**) and Phlomoside D (**6**) in CD_3OD and of the Pentaacetyl Derivative (**7**) of the Latter in $CDCl_3$ Relative to TMS

Protons	Compound		
	5	6	7
H-1	5.81, s	5.85, s	5.96, s
H-3	7.42, s	7.46, s	7.38, s
H-6	2.37, d.d J=15.5, 5 Hz	2.49, br.d	2.53, br.d
H-6	2.22, d.d J=15.5, 4.5 Hz	2.49, br.d	2.53, br.d
H-7	3.52, d.d J=5, 3.4 Hz	5.02, t ΣJ=6.5 Hz	5.38, t ΣJ=8.0 Hz
H-9	2.78, br.s	3.01, br.s	3.37, br.s
CH_3-10	1.08, s	1.22, s	1.52, s
$COOCH_3$	3.72, s	3.75, s	3.78, s
H-1′	4.59, d J=7.9 Hz	4.64, d J=7.5 Hz	5.06, d J=8.0 Hz
Ar	–	7.54(3H), 8.14(2H)	7.50(3H), 7.99(2H)
$OCOCH_3$	–	–	1.96(6H), 2.02, 2.05, 2.09

The acetylation of iridoid (**6**) with acetic anhydride in pyridine gave the pentaacetyl derivative (**7**).

In the PMR spectrum of (**7**) we observed an additional paramagnetic displacement of the H-7 and CH_3-10 signals relative to those in (**6**), which was due to the introduction of an acetyl group at C-10. These results also confirmed the conclusion concerning the position of the benzoate group. The anomeric proton, H-1′, of the carbohydrate moiety of the iridoid resonated at 4.65 ppm in the form of a doublet with J = 7.5 Hz (see Table 1), which showed the β-configuration of the glycosidic center.

Thus, phlomoside D (**6**) is 7-O-benzoyllamiide.

EXPERIMENTAL

For **general observations**, see [1, 2]. For column chromatography we used KSK and L 40/100 μm (Czech Republic) silica gels and the solvent systems chloroform–methanol 50:1 (1) and 100:1 (2).

Isolation of the Iridoids. The mother solutions obtained in the isolation of the iridoids described previously from 660 g of *P. regelii* [1] were combined and chromatographed on a column of silica gel. Elution with system 1 yielded 170 mg of a mixture of two iridoids. Rechromatography of this mixture on a column of silica gel with the same solvent system led to the isolation of 65 mg (0.011% on the weight of the air-dry raw material) of phlomoside D (**6**), $C_{24}H_{30}O_{13}$ (amorphous).

Alkaline Hydrolysis of Phlomoside D (6). A solution of 10 mg of iridoid (**6**) in 3 ml of methanol was treated with 25 mg of potassium bicarbonate in 2 ml of water. The reaction mixture was left at room temperature for three days. Then it was diluted with water (15 ml), neutralized, and extracted with ethyl acetate. The solvent was distilled off to dryness, giving 5 mg of a substance which was identified as lamiide [1] by TLC and IR spectroscopy in comparison with an authentic specimen. Benzoic acid with mp 122°C was isolated from the aqueous solution after acidification with dilute (1:1) hydrochloric acid and extraction with ethyl acetate.

Acid Hydrolysis of Phlomoside D (6). A solution of 8 mg of the iridoid glycoside was hydrolyzed in 5 ml of 5% sulfuric acid at 100°C for 3 h. The precipitate that had formed was separated off. In the hydrolysate, after its neutralization with barium carbonate and concentration in vacuum, glucose was detected by paper chromatography in the butanol–pyridine–water (6:4:3) system.

Acetylation of Phlomoside D (6). The acetylation of 20 mg of phlomoside D in 0.8 ml of pyridine with 0.8 ml of acetic anhydride was conducted at room temperature for 48 h. Then the reaction mixture was diluted with water, and the precipitate that deposited (20.7 g) was filtered off on a column of silica gel [sic]. Elution with system 2 yielded 19 mg of phlomoside D pentaacetate, $C_{34}H_{40}O_{18}$, mp 164-166°C (from methanol), $[\alpha]_D^{22}$ 0±2° (*c* 0.56; chloroform).

IR spectrum (KBr, ν, cm^{-1}): 3539 (OH); 1630 (C=C); 1742, 1723, 1272, 1232 (ester); 1603, 1452, 1113, 716 (benzene ring).

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