

## BRIEF COMMUNICATIONS

### PHENOLCARBOXYLIC ACIDS OF THE GENUS *Thymus*

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A preliminary chromatographic analysis of aqueous extracts of some plants of the genus *Thymus* L. (thyme) growing in the Caucasus has shown that they contain phenolcarboxylic acids, as well as flavone glycosides [1]. By hot-water extraction we have isolated four compounds from plants of each of the species *Th. dimorphus* Klok., *Th. nummularius* Bieb., *Th. transcaucasicus* Ronn. and *Th. kotschyanus* Boiss. et Hohen.

The aqueous extract after concentration was acidified with hydrochloric acid to pH 3.0. The precipitate that deposited was separated off, washed with water, and transferred to a column of polyamide sorbent. The compounds were eluted with aqueous ethanol having increasing concentrations of ethanol. The fractions were monitored by paper chromatography in the 0.1 N HCl and 2% CH<sub>3</sub>COOH systems.

Substance I consists of light yellow crystals soluble in alcohols and insoluble in water with the composition C<sub>9</sub>H<sub>8</sub>O<sub>4</sub>, mp 195–196°C (ethanol–water). The alkaline degradation of (I) formed protocatechuic acid. The acetyl derivative of the substance has mp 197–198°C. A mixture of it with caffeic acid gave no depression of the melting point.

Substance (II), with the composition C<sub>15</sub>H<sub>18</sub>O<sub>8</sub>, forms yellow crystals soluble in alcohols and insoluble in water, mp 96–98°C,  $[\alpha]_D^{20}$  –47° (c 0.1; ethanol). A mixture of (II) with 1-caffeoylglucose gave no depression of the melting point.

Substance (III), with the composition C<sub>15</sub>H<sub>18</sub>O<sub>8</sub>, forms a light yellow amorphous powder. By its physicochemical properties it was characterized as 6-caffeoylglucose.

Substance (IV), with the composition C<sub>24</sub>H<sub>24</sub>O<sub>12</sub>, mp 127–129°C, forms light yellow crystals readily soluble in alcohols and pyridine and sparingly soluble in water. The acid and alkaline hydrolysis of (IV) gave caffeic acid (60%) and D-glucose,  $[\alpha]_D^{20}$  –81° (c 0.1; ethanol). IR spectrum,  $\lambda_{\max}$ , cm<sup>–1</sup>: 3400 (–OH); 2970–2900 (=CH– and =CH<sub>2</sub> of the aliphatic part of the molecule); 1720, 1690 (ester groupings); 1640 (–CH=CH–); 1090, 1070, 1040 (pyranose form of the sugar residue), 887 ( $\beta$  configuration of the glycosidic linkage); and 860–815 cm<sup>–1</sup> (1,2,4-substitution in an aromatic ring).

On mild alkaline hydrolysis 1-caffeoylglucose was obtained, and on stepwise hydrolysis 6-caffeoylglucose. Substance (IV) was therefore identified as harashengin [2].

As a result of a comparative chromatographic analysis of aqueous extracts from *Th. pseudonum-mularius* Klok. et Shost., *Th. caucasicus* Willd., *Th. tiflisiensis* Klok. et Shost., *Th. elisabethae* Klok. et Shost., *Th. karamarianicus* Klok. et Shost., *Th. pastoralis* Hjin., *Th. marschallianus* Willd., *Th. migricus* Klok. et Shost., *Th. collinus* Bieb., *Th. rariflorus* C. Koch., *Th. ziaratinus* Klok. et Shost., *Th. ararati-minoris* Klok. et Shost., *Th. fominii* Klok. et Shost., *Th. trautvetteri* Klok. et Shost., *Th. desyatoviae* Ronn., *Th. dagestanicus* Klok., et Shost., and *Th. sosnowskyi* Grossh. with samples of the phenolcarboxylic acids obtained, in all the species studied caffeic acid and also, probably, 1-caffeoylglucose, 6-caffeoylglucose, and harashengin were found. In addition to this, according to chromatographic analysis, all the species of the genus contain a caffeic acid derivative – rosmarinic acid – isolated by Herrmann from thyme [3].

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The presence in representatives of this genus of derivatives of caffeic and quinic acids, in addition to caffeic and rosmarinic acids, has been reported. However, on investigating the species of thyme mentioned we found only derivatives of caffeic acid with glucose. This is the first time that all the compounds described have been isolated from these plants, and it is the first description of compounds (II-IV) from the genus Thymus.

#### LITERATURE CITED

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