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## PHENOLIC ACIDS AND FLAVONOIDS OF THE SPORE-BEARING

STEMS OF *Equisetum arvense*

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The spore-bearing stems of *Equisetum arvense* L. (field horsetail) develop earlier than the sterile stems (herbage) and die off after the formation of the spores. Freshly collected spore-bearing stems (Irkutsk region, end of May, moisture content 73-75%) were extracted with methanol, and the extract was treated successively with chloroform, diethyl ether, ethyl acetate, and butanol.

From the ether-soluble fraction by preparative chromatography on polyamide sorbent and elution with water and a mixture of water and ethanol we obtained phenolic acid fractions, and by elution with chloroform and chloroform-methanol (with increasing proportions of methanol from 5 to 30%) fractions enriched with flavonoid compounds.

The phenolic acids and the flavonoids in the form of their TMS ethers were analyzed by GLC on the Tsvet-4 chromatograph with a flame-ionization detector under the conditions described previously [1, 2].

Acids and flavonoids were identified by the method of additives and by comparison of the retention times of the TMS ethers with those of authentic samples. Below we give the relative retention times (RRTs) of the TMS ethers of the phenolic acids.

<u>TMS Derivatives of the Acids</u>	<u>RRT</u>
p-Hydroxybenzoic	0.63
Vanillic*	1.00
Protocatachuic	1.25
p-Coumaric	1.85
Ferulic	3.08
Caffeic	3.78

\*The retention time of the standard was 5 min.

In the flavonoid fraction we identified the following compounds:

<u>TMS Derivatives of the Flavonoids</u>	<u>RRT</u>
Naringenin*	1.03
Dihydrokaempferol	1.24
Dihydroquercetin	1.48
Apigenin	1.95
Luteolin	2.71

\*The retention time of the standard was 7.25 min (column temperature 288°C).

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The relative retention times of the phenolic acids and flavonoids investigated coincided with those of authentic samples. It must be mentioned that, of the phenolic acids, p-hydroxybenzoic, protocatechuic, and p-coumaric predominated quantitatively, while the others were present in only small amounts. Among the flavonoids, the flavones apigenin and luteolin predominated.

In contrast to the herbage of *Equisetum arvense*, no flavonols were detected in the spore-bearing stems.

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#### FLAVONOIDS FROM *Phlomis agraria*

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Continuing a study of the composition of the flavonoids of Siberian species of Jerusalem sage, from the herbage of *Phlomis agraria* Bge. (family Labiatae) we have isolated three flavonoids.

Substance (I): composition  $C_{21}H_{18}O_{12}$ , mp 190-192°C; UV spectrum, nm:  $\lambda_{\max}^{\text{init}}$  350, 276, 255;  $\lambda_{\max}^{+\text{CH}_3\text{COONa}}$  352, 256;  $\lambda_{\max}^{+\text{C}_2\text{H}_5\text{ONa}}$  410, 265 nm;  $\lambda_{\max}^{+\text{AlCl}_3}$  390, 267;  $\lambda_{\max}^{+\text{H}_3\text{BO}_3, +\text{CH}_3\text{COONa}}$  372, 258.

In the products of enzymatic hydrolysis we detected  $\beta$ -glucuronic acid. On the basis of these facts substance (I) was identified as luteolin 7- $\beta$ -glucuronide [1, 3].

Substance (II): had the composition  $C_{21}H_{20}O_{11}$ , mp 255°C. UV spectrum, nm:  $\lambda_{\max}^{\text{init}}$  249, 268, 255;  $\lambda_{\max}^{+\text{CH}_3\text{COONa}}$  352, 268, 257;  $\lambda_{\max}^{+\text{C}_2\text{H}_5\text{ONa}}$  404, 263;  $\lambda_{\max}^{+\text{AlCl}_3}$  416, 278;  $\lambda_{\max}^{+\text{H}_3\text{BO}_3, +\text{CH}_3\text{COONa}}$  374, 259.  $\beta$ -Glucose was detected in the products of enzymatic hydrolysis. These facts permitted substance (II) to be identified as luteolin 7- $\beta$ -glucoside [2, 3].

Substance (III) is also a luteolin O-glycoside, and its study is continuing.

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