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## TRIFOLIN FROM LESPEDEZA TOMENTOSA

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The herb *Lespedeza tomentosa* (Thunb.) Sieb. (woolly *Lespedeza*) collected in 1964 in the Far East (1.4 kg) was comminuted and extracted with methanol, the solvent was distilled off in vacuum, and the residue was dissolved in water and transferred to a column of polyamide. The column was washed with water and then 10% alcohol eluted 4.5 g of a substance with a flavonoid structure, which was rechromatographed on polyamide. Yield 1.8 g (0.13%; from alcohol), mp 241°-242° C, composition  $C_{21}H_{20}O_{11} \cdot 3/2H_2O$ ,  $\lambda_{max}$  268 and 354 m $\mu$ .

The acid hydrolysis of the substance gave galactose, which was identified by paper chromatography [1] and kaempferol with mp 283°-284° C,  $\lambda_{max}$  267, 323, 366 m $\mu$ , tetraacetate with mp 184°-185° C.

The position of the sugar residue in the kaempferol was ascertained by methylation and subsequent splitting off of the sugar [1]. This gave 5, 7, 4'-trimethylkaempferol with mp 146°-147° C, which was confirmed by the zirconium test [2].

Thus, a comparison of the physicochemical constants and the IR and UV spectra with literature data has shown that the substance isolated is kaempferol 3-galactoside (trifolin).

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## STRUCTURE OF THE FLAVONOIDS OF CRATAEGUS CURVISEPALA

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We have previously reported the isolation from the leaves of *Crataegus curvisepala* Lindm. of the total flavonoids [1] and of eight individual flavonoids B, D, E, F, G, I, J, and K [2, 3]. Flavonoids B, D, E, G, and J were isolated from hawthorn for the first time [2]. Flavonoid G, which we have called cratenacin is a new C-glycoside containing an acetyl group [4].

The present paper gives the results of a chemical study of flavonoids F, J, D, B, and E (table).

The aglycone of the flavonoid glycoside F was identified as vitexin. It was established by oxidative degradation with sodium metaperiodate [4] that the sugar component of the glycoside is rhamnose attached to the glucose molecule of vitexin through C<sub>4</sub>. Thus, the results of a chemical and spectroscopic investigation show that the flavonoid that we have isolated is 5, 7, 4'-trihydroxyflavone 8-C- [ $\beta$ -D-glucopyranosyl (1  $\rightarrow$  4)]- $\alpha$ -L-rhamnopyranoside, i. e., deacetyl-

Basic Physicochemical Properties of the Flavonoids of Crataegus curvisepala

Substance	Composition	Mp, ° C	$[\alpha]_D^{20}$ (in alcohol), degrees	$\lambda_{max}$ , m $\mu$
Deacetylcratenacin (F)	C <sub>27</sub> H <sub>30</sub> O <sub>14</sub>	214—215	— 35	{ 334 (log $\epsilon$ 4.15) 270 (log $\epsilon$ 4.17)
Apigenin 7- $\beta$ -D-glucopyranoside (J)	C <sub>21</sub> H <sub>20</sub> O <sub>10</sub>	253—256	—125	{ 337 (log $\epsilon$ 4.30) 268 (log $\epsilon$ 4.26)
Rhamnoepigenin (D)	C <sub>21</sub> H <sub>20</sub> O <sub>9</sub>	284—285	—130	{ 339 (log $\epsilon$ 4.11) 266 (log $\epsilon$ 4.03)
Glucoluteolin (B)	C <sub>21</sub> H <sub>20</sub> O <sub>11</sub>	255—258	— 80	{ 355 (log $\epsilon$ 4.30) 265 (log $\epsilon$ 4.43)
Quercitrin (E)	C <sub>21</sub> H <sub>20</sub> O <sub>11</sub>	187—190	— 20	{ 360 (log $\epsilon$ 3.88) 261 (log $\epsilon$ 3.98)

Apigenin was isolated from the products of the acid hydrolysis of flavonoids J and D. From a chemical and spectroscopic study (with the addition of sodium acetate, sodium ethoxide, and other reagents) it was found that the first of them is 5, 4'-dihydroxyflavone 7- $\beta$ -D-glucopyranoside (apigenin 7- $\beta$ -D-glucopyranoside) and the second is 5, 4'-dihydroxyflavone 7- $\alpha$ -L-rhamnopyranoside (rhamnoapigenin).

Flavonoid B is one of the luteolin flavonoids which is difficult to hydrolyze and was identified as 5, 3', 4'-trihydroxyflavone 7- $\beta$ -D-glucopyranoside (glucoluteolin). The presence of a hydroxy group at C<sub>8</sub> of flavonoid B, a chemical study of which we have reported previously [2], was not confirmed.

The results of a chemical and spectroscopic investigation have shown that flavonoid E is a glycoside of quercetin and is 5, 7, 3', 4'-tetrahydroxyflavone 3- $\alpha$ -L-rhamnopyranoside (quercitrin).

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Khar'kov Chemical and Pharmaceutical  
Scientific Research InstituteINVESTIGATION OF THE TANNING SUBSTANCES OF AGRIMONIA ASIATICA

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Aggrimonia asiatica Juz., family Rosaceae, is used in popular medicine as an astringent in bowel diseases [1]. We have confirmed this feature by showing that agrimony contains tanning substances which accumulate in all phases of the growth of the plant and particularly in the flowering period (table). In order to investigate the substances of the polyphenolic complex of the hypogeeal organs of Asiatic agrimony collected in Western Tien Shan, we studied the precursors of the tanning substances (phenolcarboxylic acids, polyphenols) and particularly the tannides, leucoanthocyanidins, and catechins. Benzoic acid was found among the free acids.

The tannides proper were identified from the products of acid hydrolysis of the extracts, the alkaline hydrolysis of the phlobaphenes, and the pyrolysis of the tanning preparation obtained. Gallic and benzoic acids and catechol were