

Previously, from the leaves of *Plantago major* var. *asiatica* Linn. (rippleseed plantain, Asian variety) apigenin, luteolin 7-glucoside and luteolin 7-glucuronide have been isolated [1]. Continuing a study of the flavonoid composition of this plant, we have isolated another five substances. Substances (IV) formed lemon-yellow crystals,  $C_{16}H_{12}O_6$ , mp 282-285°C (from methanol), mol. wt. 300,  $R_f$  0.38 [Silufol; system 1: chloroform-methanol (9:1)];  $\lambda_{max}$  274, 336 nm (in methanol).

On the basis of its IR, UV, and NMR spectra, the substance isolated was identified as 4',5,7-trihydroxy-6-methoxyflavone, or hispidulin [2].

Substance (V) formed yellow acicular crystals with the composition  $C_{22}H_{22}O_{11}$ , mp 255-258°C (from methanol),  $[\alpha]_D^{20}$  -43.64° (c 0.55; pyridine);  $R_f$  0.58 [Silufol; system 2: chloroform-methanol (8:2)]  $\lambda_{max}$  276, 333 nm (in methanol). The hydrolysis of substance (V) with 10%  $H_2SO_4$  and with emulsin formed (IV) and D-glucose.

On the basis of the results of IR, UV, and NMR spectroscopy, and also of enzymatic and acid hydrolysis, substance (V) was characterized as 4',5,7-trihydroxy-6-methoxyflavone 7-O- $\beta$ -D-glucopyranoside, or homoplantaginin.

From an ethyl acetate fraction of the ethanol extract by chromatography on polyamide sorbent with elution by chloroform and aqueous methanol we isolated three flavonoid glycosides - (VI), (VII), and (VIII).

Substance (VI) formed yellow crystals,  $C_{22}H_{22}O_{12}$ , mp 229-233°C (from methanol),  $R_f$  0.65 [system 3; ethyl acetate-formic acid-water (10:2:3)];  $\lambda_{max}$  255 sh, 275, 344 nm (in methanol).

On the basis of its IR, UV, and NMR spectra, the substance was characterized as 3',4',5,7-tetrahydroxy-6-methoxyflavone 7-O- $\beta$ -D-glucopyranoside, or nepitrin [1].

Substance (VII) formed yellow crystals with the composition  $C_{21}H_{20}O_{10}$ , mp 233-234°C (from methanol)  $[\alpha]_D^{20}$  22.82°, c 0.80; (pyridine),  $\lambda_{max}$  285, 335 nm (in methanol),  $R_f$  0.53 (system 3). Hydrolysis with 10%  $H_2SO_4$  led to the formation of scutellarein and L-rhamnose.

Substance (VII) was characterized as 4',5,6,7-tetrahydroxy-6-methoxyflavone 7-O- $\alpha$ -L-rhamnopyranoside.

Substance (VIII) formed yellow crystals with the composition  $C_{21}H_{20}O_{12}$ , mp 197-199°C (from methanol). The molecular weight of the aglycone was 302 (mass spectrometry);  $\lambda_{max}$  257 sh, 285, 346 nm (in methanol);  $R_f$  0.27 (system 3).

On the basis of IR, UV, NMR, and mass spectra, substance (VIII) was characterized as 3',4',5,6,7-pentahydroxyflavone 7-O- $\beta$ -D-glucopyranoside.

This is the first time that these substances have been isolated from the Asian variety of rippleseed plantain.

## LITERATURE CITED

1. V. I. Lebedev-Kosov, *Khim. Prirodn. Soedin.*, 812 (1976).
2. J. Mabry, K. R. Markham, and M. B. Thomas, *The Systematic Identification of Flavonoids*, Springer Verlag, New York (1970).

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