FLAVONOIDS AND XANTHONES OF Hedysarum connatum AND H. alpinum

A. N. Komissarenko, T. P. Nadezbina, and N. F. Komissarenko

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The flavonoid and xanthone compositions of the epigeal parts of *Hedysarum connatum* Fedsch. and *H. alpinum* L. (fam. Fabaceae) gathered in Mongolia in 1972 have been studied.

Paper chromatography in the solvent systems butan-1-ol-acetic acid—water (4:1:2), 2% and 15% acetic acid, and benzene—ethyl acetate—acetic acid (74:24:2) formamide revealed the presence in these plants of not less than eight substances of flavonoid nature and two xanthones. In their qualitative compositions the flavonoids and xanthones of these species were very close. The substances that had been detected were isolated by methods described previously [1-3] on neutral, acid, and alkaline Kapron [polycaproamide] powder [4]. As a result, five flavonoids and two xanthones were obtained, and these were designated provisionally as compounds (1-7).

Substance (1), $C_{15}H_{10}O_7$, mp 307-313°C was identified as quercetin from its physicochemical properties, R_f values in various solvent systems, and UV spectra with complex-forming and ionizing reagents [1].

On being subjected to acid hydrolysis with 2% H_2SO_4 , substances (2), $C_{20}H_{18}O_{11}$, mp 254-258°C, $[\alpha]_D$ -38.0°C (methanol); (3), $C_{20}H_{18}O_{11}$, mp 209-212°C, $[\alpha]_D$ -160.0°C (methanol); (4), $C_{21}H_{20}O_{12}$, mp 236-239°C, $[\alpha]_D$ -44.0°C (methanol); and (5), $C_{21}H_{20}O_{11}$, mp 174-177°C, $[\alpha]_D$ -180.0° (methanol) were split into the aglycon quercetin (1) and the sugar components L-arabinose (glycosides (2) and (3)), D-galactose (4), and L-rhamnose (5).

The positions of attachment of the carbohydrate components to quercetin were determined by complex-forming reactions with zirconium nitrate and citric acid [5] and by UV spectroscopy with ionizing and complex-forming reagents [6]. The results obtained showed that in all the glycosides investigated the sugar residue was attached to the OH group at C-3 of quercetin. Substances (2) and (3) had the same aglycon, the same sugar component (L-arabinose) and the same position of its attachment to the aglycon. Nevertheless their physicochemical properties and R_f values in a series of solvent systems differed substantially.

On the basis of exhaustive methylation, NMR and IR spectroscopies, and physicochemical properties, these glycosides were identified as polystachoside (2, quercetin 3-O- β -D-arabinopyranoside) and avicularin (3, quercetin 3-O- β -D-arabinofuranoside), which have been isolated previously from Pontic azalea [7]. Using analogous methods, substances (4) and (5) were identified as hyperoside (quercetin 3-O- β -D-galactopyranoside) [7] and quercitrin (quercetin 3-O- α -L-rhamnopyranoside) [7].

Substance (6), $C_{19}H_{18}O_{11}$, mp 257-262°C, $[\alpha]_D$ +38.5 (pyridine); λ_{max} (ethanol): 365, 315, 258, 241 nm. Substance (7), $C_{19}H_{18}O_{11}$, mp 249-251°, $[\alpha]_D$ +9° (pyridine); λ_{max} (ethanol): 265, 317, 257, 241 nm.

Both substances (6 and 7) were resistant to acid hydrolysis and, from the nature of their UV spectra, were assigned to the xanthones [8]. On being boiled in 5% HCl, substance (6) isomerized into (7), and conversely, which is characteristic for the recyclization isomerism of C-glycosides. The results of the study enabled (6) and (7) to be identified as mangiferin (2-C- β -D-glucopyranosyl-1,3,6,7-tetrahydroxyxanthone, 6) and isomangiferin (4-C- β -D-glucopyranosyl-1,3,6,7-tetrahydroxyxanthone, 7), which have been isolated previously from H. alpinum [3, 9], although the flavonoids of this plant have not ben studied hitherto. This is the first time that the flavonoid and xanthone compositions of the epigeal part of H. connatum have been studied.

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REFERENCES

- 1. N. F. Komissarenko, V. N. Chernobai, and D. G. Kolesnikov, Med. Prom-st SSSR, No. 1, 25 (1965).
- 2. G. S. Glyzina, and N. F. Komissarenko, Khim. Prir. Soedin., 138 (1967).
- 3. N. F. Komissarenko, S. I. Sal'nikova, A. N. Komissarenko, and S. M. Drogovoz, Rast. Res., 29, No., 3, 1 (1993).
- 4. V. N. Spiridonov, Khim.-farm. Zh., No. 5, 43 (1968).
- 5. L. Hörhammer, A. Gehrmann, and I. A. Endres, Arch. Pharm., 292, 113 (1959).
- 6. A. Geissman, The Chemistry of Flavonoid Compounds, Pergamon Press, New York, (1962), p. 108.
- 7. N. F. Komissarenko and I. G. Levashova, Rast. Rest., 16, No. 3, 406 (1980).
- 8. V. I. Glyzin, G. G. Nikolaeva, and T. D. Dargaeva, Natural Xanthones, Novosibirsk (1986).
- 9. V. B. Kuvaev, V. I. Glyzin, G. S. Glyzina, and A. I. Ban'kovskii, Rast. Res., 8, No. 3, 367 (1972).