FLAVONOIDS OF HYPERICUM MACULATUM AND H. INODORUM

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We have carried out a comparative chemical study of two species of St. Johnswort, Hypericum maculatum Crantz [H. quadrangulum L.], collected in 1962 in Moscow Oblast, and Hypericum inodorum Willd, collected in 1961 in Transcaucasia.

The results of paper chromatography [1] have shown that H. maculatum contains chlorogenic and caffeic acids, hyperoside, quercitrin, and quercetin, and also substances of the dianthrone type [2].

Hypericum maculatum. 0.27 kg of the dry flowering herb was exhaustively extracted with hot methanol. The extract was evaporated in vacuum, the residue was diluted with water to 200 ml, separated from resin, and transferred to a column of polyamide $(5 \times 40 \text{ cm})$. The column was washed with water and then with aqueous ethanol of increasing ethanol concentration. The eluates were analyzed by means of color reactions [3] and paper [4-7] and thin-layer chromatography [6].

The systems of solvents for paper chromatography were: 1) 1-butanol-acetic acid-water (4: 1: 5), and 2) ethyl acetate-formic acid-water (10: 2: 3); and for thin-layer chromatography: 3) methanol, and 4) methanol-water (6: 4).

After being treated with 1% AlCl₃ solution or ZrOCl₂, the dried chromatograms were observed in UV light. The fractions were concentrated in vacuum. The flavonoids isolated and the products of their acid hydrolysis [4, 5] were identified with authentic samples.

The 15% ethanol fraction yielded 0.35 g (0.13%) of quercitrin and the 30% ethanol eluted 1.92 g (0.71%) of hyperoside. The 75% ethanol fraction contained 0.24 g (0.09%) of quercetin. An additional 0.57 g (0.21%) of quercetin was isolated from the resin that separated from the aqueous solution by the method described previously [8].

The 80-95% ethanolic eluate gave 0.30 g (0.11%) of a mixture of hypericin and pseudohypericin, which was identified by its charactistic crimson fluorescence in UV light, its reaction with alkalies (brown coloration), and by a comparison with reference materials [2].

The intermediate fractions contained very small amounts of flavonoids, which we did not identify. The total yield of flavonoids isolated was 3.08 g (1.14%).

Hypericum inodorum. 0.2 kg of the dry flowers was extracted with 70% ethanol. After the alcohol had been eliminated in vacuum, the aqueous solution was filtered and transferred to a column of polyamide (8 \times 40 cm), which was washed with water and then with aqueous ethanol. 20% ethanol eluted 0.24 g (0.12%) of isoquercitrin. The 30% ethanolic eluate gave 0.48 g (0.24%) of hyperoside.

The ethanolic fraction yielded 0.21 g (0.1%) of quercetin, and the resin from the initial aqueous solution gave, by a published method [4], with supplementary chromatography on polyamide, 0.54 g (0.27%) of the same substance. The total yield of flavonoids was 1.47 g (0.73%).

Thus, H. maculatum contains quercitrin, hyperoside, quercetin, and a mixture of hypericin and pseudohypericin, and H. inodorum contains isoquercitrin, hyperoside, and quercetin.

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