## XANTHONE GLYCOSIDES OF Hedysarum flavescens

V. I. Glyzin, A. I. Ban'kovskii, M. G. Pimenov, and K. I. Boryaev UDC 547.972:547.918

We have previously reported the isolation of xanthone glycosides - mangiferin and isomangiferin - from some species of the genus Hedysarum [1].

I.R=-C- $\beta$ -D-glucobiose , R'=H. III.R=-C- $\beta$ -D-glucose , R'=H II. R'=-C- $\beta$ -D-glucose , R = H. IV. R'=-C- $\beta$ -D-glucose , R = H

The present paper gives the results of the isolation from the epigeal part of <u>H. flavescens</u> of two new xanthone glycosides, which we have called glucomangiferin (I) and glucoisomangiferin (II).

The epigeal part of the plant (50 kg) was extracted with methanol ( $4 \times 200$  liters) with boiling for 4 h. The evaporated extract was treated with hot water, and chromatography was performed on polyamide sorbent (elution with water and 10% ethanol). The fractions containing a mixture of glucoisomangiferin and glucomangiferin were repurified on a column of polyamide sorbent and were separated preparatively on 50 sheets of Fn-18 paper using as the mobile phase a 5% solution of acetic acid. The zones of glucomangiferin with R<sub>f</sub> 0.72 and of glucoisomangiferin (R<sub>f</sub> 0.60) were cut out, and the substances were eluted with methanol and were purified once more on a column of polyamide.

This gave 0.2 g of glucomangiferin and 0.13 g of glucoisomangiferin.

Glucomangiferin (I),  $C_{25}H_{28}O_{16}$ , mp 198-202°C from methanol,  $\lambda_{max}^{CH_3OH}$  242, 257, 317, 360 nm.

NMR spectrum in dimethyl sulfoxide (DMSO, ppm): singlet, 7.73 (1H)(H-8); singlet, 7.23 (1H) (H-5); singlet, 6.78 (1H) (H-4); signals at 4.84 and 5.11 (1H) (protons of the anomeric centers of carbohydrate components).

The hydrolysis of (I) with 2% sulfuric acid gave mangiferin (III),  $C_{19}H_{18}O_{11}$  with mp  $258-260^{\circ}C$ , identified by comparing its IR and NMR spectra with those of a known sample. Glucose was found in the neutralized mother liquor.

Glucomangiferin has free OH groups in positions 1, 3, 6, and 7. In its NMR spectrum, a singlet at 13.61 ppm (1H) is due to the presence of an OH group in position 1.

An ortho-dihydroxy grouping in the 6,7 position was shown by a bathochromic displacement of the maximum of the long-wave band by 57 nm in the presence of boric acid and sodium acetate, and a free hydroxy group in position 3 by a bathochromic shift of the maximum of the long-wave band by 16 nm in the presence of sodium acetate. The results of UV spectroscopy are in harmony with those of the NMR spectroscopy of the acetate of (I). The NMR spectrum of the acetate of (I) has the signals of four acetyl groups in an aromatic ring (2.3-2.4 ppm) and of seven acetyl groups in the carbohydrate moiety (2.0-2.1 ppm).

Thus, the carbohydrate moiety of glucomangiferin is a biose in position 2, and it has the structure of 1,3,6,7-tetrahydroxyxanthone 2-C- $\beta$ -D-glucobioside.

Glucoisomangiferin (II),  $C_{25}H_{28}O_{16}$ , mp 218-221°C from methanol,  $\lambda_{max}^{CH_3OH}$  242, 257, 317, 360 nm.

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NMR spectrum in DMSO (ppm): s 7.57 (1H) (H-8); s 7.17 (1H) (H-5); s 6.53 (1H) (H-2); 4.99 and 5.13 (1H each) (protons of anomeric centers of glucose); s 13.13 (1H) (OH in position 1). The hydrolysis of (II) led to the formation of isomangiferin,  $C_{19}H_{18}O_{11}$ , with mp 249-251°C, and glucose.

Compound (II) differs from (I) by the position of the glucobiose and has the structure of 1,3,6,7-tetra-hydroxyxanthone 4-C- $\beta$ -D-glucobioside.

## LITERATURE CITED

1. V. B. Kuvaev, V. I. Glyzin, G. S. Glyzina, and A. I. Ban'kovskii, Rast. Res., 8, No. 3, 367 (1972).