ISOFLAVONES OF THE OILCAKE OF THE SEEDS OF Glycyne hispida

A. L. Kazakov, E. A. Kechatov, and V. M. Chemerko

UDC 547.972

Isoflavones possess a normalizing activity in experimental atherosclerosis [1, 2] and in view of this may find use in medical practice as a drug. Consequently, the search for sources containing isoflavones is a matter of interest.

It is known that the seeds of Glycyne hispida Max. (cultivated soybean), family Fabaceae, have been found to contain isoflavones [3]. We have investigated oilcake (extracted meal) of soybeans – a production waste of the food industry.

By two-dimensional chromatography on paper of an ethanolic extract from the oilcake in the BAW (4:1:5) and 15% CH_3COOH systems using qualitative reactions we detected two substances of isoflavone nature. The comminuted oilcake after defatting with petroleum ether was extracted with 96% ethanol; the extract was concentrated, and substances (I) and (II) were isolated by fractional crystallization and by preparative chromatography on paper.

Substance (I), $C_{21}H_{20}O_{10}$, formed colorless crystals soluble in methanol and ethanol and insoluble in chloroform with mp 255-256°C, $[\alpha]_D^{20}$ −22.3° (c 0.285; pyridine). The UV spectrum of this substance had one strong and characteristic absorption maximum at 263 nm. By means of ionizing and complex-forming additives the presence of free hydroxy groups in positions 4' and 5 was established.

The appearance of bathochromy as a result of the influence of CH_3COONa on the aglycone after the acid hydrolysis of substance (I) showed the presence of the sugar component (D-glucose) in the C_7 position. The aglycone, with the composition $C_{15}H_{10}O_5$, mp 290-291°C, was identified on the basis of UV spectroscopy and the melting points of the acetyl derivative (197-199°C) and the dimethyl ether (137-138°C) as genistein.

Bands were observed in the IR region characteristic for the β configuration of the glycosidic bond and the pyranose form of the D-glucose. These facts were confirmed by the results of optical rotation, $[M]_D^{20}$ and enzymatic hydrolysis.

In this way, we identified substance (I) as 4',5,7-trihydroxyisoflavone 7-O-β-D-glucopyranoside (genistin).

Substance (II), $C_{21}H_{20}O_9$, formed colorless crystals, soluble in methanol and ethanol and insoluble in chloroform, with mp 235-236°C, $[\alpha]_D^{20}$ −35.6° (c 0.175; 0.02 N KOH). The UV spectra of substance (II) $\lambda_{max}^{C_2H_5OH}$ 258 nm) with ionizing and complex-forming additives showed the presence of a free hydroxy group in position C_4'. Acid hydrolysis gave an aglycone with mp 318-319°C (60.5%) which was identified on the basis of UV spectroscopy and the melting point of the dimethyl ether (157-158°C) as daidzein, the structure of which was confirmed by independent synthesis. D-Glucose was found in the hydrolyzate. On the basis of bathochromy in the UV spectra of the aglycone, it was established that the glucose was present in the C_7 position. From the results of enzymatic hydrolysis (β-hydrolase), molecular optical activity ($[M]_D^{20} \cdot K_P$ = −90.33°) and differential IR spectroscopy, the glucose was found to be present in the pyranose form and to have the β configuration of the glycosidic bond. On the basis of what has been said, we characterized substance (II) as 4',7-dihydroxyisoflavone 7-O-β-D-glucopyranoside (daidzin). The isoflavone content was determined spectrophotometrically [4] in an ethanolic extract from the oilcake. The yield amounted to 1.34% of genistin and 0.81% of daidzin on the weight of the air-dry raw material.

Pyatigorsk Pharmaceutical Institute. Translated from Khimiya Prirodnykh Soedinenii, No. 2, pp. 256-257, March-April, 1975. Original article submitted April 30, 1974.

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