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FLAVONOIDS FROM *Gleditsia triacanthos*

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The genus *Gleditsia* L. (Fabaceae) numbers from 8 to 12 species according to different sources [1]. Young leaves and fruits from *G. triacanthos* are medicinal raw materials. The pharmacological activity of the leaves is due to the alkaloid triacanthin, which exhibits spasmolytic activity, reduces arterial pressure, and expands coronary vessels. The spasmolytic activity is highest for smooth intestinal muscle and bronchi. Anthraglycosides in the plant pericarp have laxative activity [2, 3]. The contents of biologically active compounds in leaves depend on the collection time (from June to September), e.g., flavonoids 2.75–2.23%; hydroxycinnamic acids, 1.80–1.77%; and phenolic compounds, 4.91–3.36%. The quality of the raw material is unaffected by insignificant oscillations of biologically active compounds from June to September and allows leaves to be collected as they are falling [4].

The goal of the present work was to study the flavonoid composition of *G. triacanthos* leaves collected in June in Kharkov Oblast.

Plant leaves (1.5 kg) were exhaustively extracted with EtOH (70%) by combining maceration (24 h) and subsequent thermal extraction at 85–90°C. The aqueous EtOH extracts were combined, evaporated *in vacuo* to a thick residue (~700 mL), and left in a refrigerator at 4–5°C for 1 d. The resinous residue was separated by filtration and rinsed with hot H_2O. The rinsings were combined with the filtrate and evaporated to the initial volume. The purified aqueous solution was worked up sequentially with $CHCl_3$, EtOAc, and *n*-BuOH.

The solvents were distilled to afford $CHCl_3$ (86.0 g), EtOAc (38.1 g), *n*-BuOH (46.4 g), and aqueous (81.2 g) fractions.

Compounds in the EtOAc and *n*-BuOH fractions were separated using absorption chromatography over a polyamide column with elution by H_2O and aqueous EtOH with gradually increasing EtOH concentrations. This isolated flavonoids **1**–**12** from the EtOAc fraction and **13**–**16** from the *n*-BuOH fraction.

Comparisons of the results with the literature and authentic samples identified **1** as quercetin; **2**, isorhamnetin; **3**, myricetin; **6**, rutin; **11**, apigenin; **12**, sapigenin-7-*O*-β-D-glucoside; **13**, luteolin; **14**, vitexin; **15**, saponaretin; **16**, orientin; and **17**, homoorientin [4–8].

Myricetin-3-*O*-β-D-rutinoside (4). $C_{27}H_{30}O_{17}$, mp 190–192°C (70% MeOH). UV (λ_{max}, nm): 256, 308, 363. IR spectrum (KBr, ν_{max}, cm^{-1}): 2960 (OH), 1672 (C=O), 1615, 1570, 1500 (C=C), 1080–1010, 885 (β-glycoside bond). Acid hydrolysis of **4** produced myricetin in addition to D-glucose and L-rhamnose.

Myricetin-3-*O*-β-D-glucoside (5). $C_{21}H_{20}O_{13}$, mp 275–277°C (MeOH). UV (λ_{max}, nm): 256, 304, 360. IR spectrum (KBr, ν_{max}, cm^{-1}): 2940 (OH), 1670 (C=C), 1620, 1560, 1542 (C=C), 1070–1000, 885 (β-glycoside bond). Acid hydrolysis of **5** produced myricetin and D-glucose.

Quercetin-3-*O*-β-D-gentiobioside (7). $C_{27}H_{30}O_{17}$, mp 180–182°C (70% MeOH). UV (λ_{max}, nm): 258, 267, 367. IR spectrum (KBr, ν_{max}, cm^{-1}): 3350 (OH), 1662 (C=O), 1600–1445 (C=C), 1100–1010, 890 (β-glycoside bond). Enzymatic hydrolysis by rhamnodiastase produced quercetin and gentiobiose. Isoquercitrin and D-glucose resulted from stepwise acid hydrolysis by H_2SO_4 (2%).

Isoquercitrin (8). $C_{21}H_{20}O_{12}$, mp 248–250°C. Acid hydrolysis of **8** produced quercetin and D-glucose.

Isorhamnetin-3-*O*-β-D-gentiobioside (9). $C_{28}H_{32}O_{17}$, mp 198–201°C (70% MeOH). UV (λ_{max}, nm): 257, 268, 357. IR spectrum (KBr, ν_{max}, cm^{-1}): 3285 (OH), 1670 (C=O), 1625–1514 (C=C), 2920, 2852 (OCH_3), 1100–1010, 890 (β-glycoside bond). Stepwise acid hydrolysis produced isorhamnetin-3-*O*-glucoside and D-glucose. Enzymatic hydrolysis by rhamnodiastase produced isorhamnetin and gentiobiose.

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Isorhamnetin-3-*O*-β-D-glucoside (10). $C_{22}H_{22}O_{12}$, mp 250–252°C (MeOH). Acid hydrolysis of **10** produced isorhamnetin and D-glucose [4, 5].

Compounds **2–5** and **7–10** were isolated for the first time from *G. triacanthos* leaves. Myricetin and apigenin glycosides prevailed according to quantitative HPLC.

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