

PHENOLIC COMPOUNDS OF *Antitoxicum sibiricum*

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In the epigeal part of *Antitoxicum sibiricum* Poled., family Asclepiadaceae, we found six flavonoid compounds and no less than seven phenolic carboxylic acids.

By chromatographic methods we have isolated in the individual state two flavonoids and six hydroxycinnamic acids.

Substance (I) (mp 250-254°C; UV spectrum: $\lambda_{\max}^{\text{ethanol}}$ 255, 352 nm, $\lambda_{\max}^{\text{KOH}}$ 275, 385 nm, $\lambda_{\max}^{\text{CH}_3\text{COONa}}$ 255, 356 nm, $\lambda_{\max}^{\text{CH}_3\text{COONa} + \text{H}_3\text{BO}_3}$ 255, 360 nm; IR spectrum, cm^{-1} : 1662, 1005, 1030, 1095, 1595, 1562, 2855, 3300 $R_f^{15\% \text{ CH}_3\text{COOH}}$ 0.73, gives the characteristic reactions for flavonoid compounds. It was readily hydrolyzed by 1% sulfuric acid with cooling and by 5% acetic acid on heating. The aglycone so obtained (mp 264-267°C; $\lambda_{\max}^{\text{ethanol}}$ 255, 360 nm) was identified as kaempferol. The carbohydrate components were identified as D-glucose, D-xylose, and L-arabinose. Incubation of the substance with the enzyme β -glycosidase (24 h, 37°C, pH 6.0) led to the formation of kaempferol and the sugars mentioned above. On the basis of an analysis of the UV spectra, qualitative reactions, and the rate of hydrolysis, it may be assumed that the sugar components are attached at C₃ of the aglycone. Consequently, substance (I) has the most probable structure of kaempferol 3-O-D-glucosyl-D-xylo-L-arabinoside and is a new kaempferol derivative.

Substance (II) (UV spectrum; $\lambda_{\max}^{\text{ethanol}}$ 258, 360 nm; $\lambda_{\max}^{\text{KOH}}$ 280, 400 nm, $\lambda_{\max}^{\text{CH}_3\text{COONa}}$ 257, 382 nm; $\lambda_{\max}^{\text{CH}_3\text{COONa} + \text{H}_3\text{BO}_3}$ 261, 390 nm; $R_f^{15\% \text{ CH}_3\text{COOH}}$ 0.64) was also readily hydrolyzed under the conditions given for substance (I). The aglycone (mp 310-312°C; UV spectrum: $\lambda_{\max}^{\text{ethanol}}$ 255, 372 nm) was identified as quercetin, and the sugar component as D-glucose. The ratio of $E_{1\text{cm}}^{1\%}$ for the glycoside to $E_{1\text{cm}}^{1\%}$ of the aglycone, equalling 0.40, characterizes the substance as a diglucoside. An analysis of the properties of the flavonoid provides grounds for assuming that the sugar components are located at C₃ and consist of gentiobiose or sophorose.

Substances (III)-(VII) were identified on the basis of an analysis of their physicochemical properties, their chemical reactions, and comparison with authentic samples as the hydroxycinnamic acids: ferulic acid [C₁₀H₁₀O₄, mp 169°C, $\lambda_{\max}^{\text{ethanol}}$ 236, (290) 318 nm]; isoferulic acid [C₁₀H₁₀O₄, mp 234-235°C, λ_{\max} 255, (300), 315 nm]; sinapic acid C₁₁H₁₂O₅ mp 200-202°C, λ_{\max} 235, (300), 320 nm]; 3-feruloylquinic acid ($[\alpha]_D^{25}$ -40°, ethanol; λ_{\max} 260, (298), 325 nm; $\lambda_{\max}^{\text{KOH}}$ 277, 295, 375 nm); and 1-feruloylglucose (λ_{\max} 318 nm; $\lambda_{\max}^{\text{KOH}}$ 250, 355 nm).

Substance (VIII) ($[\alpha]_D^{24}$ -35°, ethanol; λ_{\max} 250, (295), 325 nm; $\lambda_{\max}^{\text{KOH}}$ 255, 295, 375 nm; $R_f^{2\% \text{ CH}_3\text{COOH}}$ 0.49) on alkaline hydrolysis (0.1 N KOH, 100°C, 30 min) formed equimolar ratios of sinapic and quinic acids. The considerable bathochromic shift (50 nm) of the absorption maximum in an alkaline medium shows the presence of an ester bond. The magnitude of the optical rotation permits the compound under investigation to be assigned to quinic acid derivatives substituted in position 3. Thus, the compound studied is 3-O-sinapoyl-D-quinic acid and is a new hydroxycinnamoyl derivative.

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