FLAVONOIDS OF Stizolophus coronopifolius

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UDC 547.972

Of the two species of Stizolophus growing in the USSR [1], only one – S. balsamita Lam. (A. Takht) – has been studied previously for its flavonoid content (Utkin [2]). In our investigation we have used the leaves of Stizolophus coronopifolius (Lam.), collected in the vegetation phase (May, 1972, Azerbaidzhan SSR).

The air-dry raw material (0.5 kg) was treated with isopropanol with heating. The alcoholic extracts were combined and were concentrated in vacuum, and the residue was treated with a small amount of hot water and then with chloroform. The aqueous solution was concentrated, diluted with ethanol, and left at room temperature for several days. Substance (I), $C_{22}H_{22}O_{12}$, mp 165-166°C (from 70% ethanol), $[\alpha]_D^{22}$ −116.5° (c 0.0973; ethanol) precipitated with a yield of about 0.1%. Two-dimensional chromatography on paper in the 15% CH_3COOH and BAW (4 : 1 : 5) systems showed the presence of a single substance with R_f 0.29 and 0.63, respectively. In UV light, the glycoside had a blue fluorescence which changed to intense bright yellow under the action of NH_3 vapors. The acetyl derivative of the glycoside in pyridine had mp 198-200°C (ethanol). UV spectrum of the glycoside: $\lambda_{max}^{C_2H_5OH}$ 351, 252 nm; λ_{max}^{+AcONa} 365, 267 nm, $\lambda_{max}^{+AlCl_3}$ 352, 252 nm, $\lambda_{max}^{+AlCl_3+HCl}$ 352, 252 nm; $\lambda_{max}^{+AcONa+H_3BO_3}$ 377, 265 nm, $\lambda_{max}^{+C_3H_3ONa}$ 407, 265 nm.

We determined the molecular weight by the UV spectroscopy of the reduction products [3]. The action of a 5% solution of H_2SO_4 in aqueous ethanol led to the formation of the aglycone (II) (identified as quercetin 3-methyl ether) and D-glucose (phenylosazone, mp 204-205°C). In the IR region there were bands characteristic for the β-configuration of the glycosidic bond and for a pyranose ring of the carbohydrate component. These features were confirmed by the results of a determination of the value of $[M]_D^{20}$ and by enzymatic hydrolysis. Analysis of the UV spectra with ionizing and complex-forming additives showed the presence of free hydroxy groups in positions 3' and 4'. The absence of bathochromy under the influence of $AlCl_3$ and $AlCl_3$+HCl shows the presence of substituents in positions 3 and 5.

After acid hydrolysis a free hydroxyl appeared in the molecule of the aglycone [substance (II)] in the C_5 position. Consequently, substance (I) is a glycoside at C_5 of the flavone nucleus.

Substance (II) was obtained from the mother solution by chromatography on a column of polyamide. Yellow needles with mp 258-262°C (90% ethanol) having the composition $C_{16}H_{12}O_7$; acetate with mp 182-183°C (from ethanol). Demethylation with HI+AcO_2O+P (by the Delofe–Herrero method [4]) led to the formation of quercetin.

UV spectrum of the aglycone: $\lambda_{max}^{C_2H_5OH}$ 360, 257 nm, λ_{max}^{+AcONa} 377, 265 nm; $\lambda_{max}^{+AlCl_3}$ 401, 365, 270; $\lambda_{max}^{AlCl_3+HCl}$ 360, 269; $\lambda_{max}^{+AcO\ Na+H_3BO_3}$ 383, 262 nm; $\lambda_{max}^{C_2H\ ONa}$ 410, 271 nm.

The curve of the UV spectral analysis of the products of the cyanidin reaction of the aglycone of the glycoside had a specific shoulder, which shows the presence of a free OH group at C_7 [5]. From the results of quantitative hydrolysis, alkaline degradation, and a mixed melting point with authentic samples (kindly provided by Professor L. M. Utkin), compound (I) was characterized as 3-O-methylquercetin 5-O-β-D-glucopyranoside, or stizoloside, and (II) as 3-O-methylquercetin.

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