STUDY OF SOLVATO COMPLEXES OF POLYPHENOLS BY UV SPECTROSCOPY

E. N. Gritsenko

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Electron spectroscopy is widely used in the study of intermolecular interaction. Investigating the interaction of certain polyphenols with low-molecular-mass and polymeric compounds by UV spectroscopy, we have studied their specific interaction with solvents, to which the position of the electronic spectra is extremely sensitive [1, 2]. We have used chromatographically pure samples of flavonoids and phenolcarboxylic acids. The medium for the interaction was water which adequately reflects the real conditions of the interaction of natural compounds in biological materials. However, many polyphenols are practically insoluble in water. In these cases, the aqueous solutions were prepared by the successive dilution with water of solutions of the initial substance in ethanol (pharmacopeal quality containing 95-95% of ethanol), and also by boiling the substance with water for 10-15 min and cooling to the temperature of the experiment (20±2°C). The electronic spectra were recorded on a Specord M-40 UV-VIS spectrophotometer in cells with a layer thickness of 10 mm 1.5-3 h after the preparation of the solutions. For the alcoholic solutions the comparison solution was ethanol, and for the aqueous solutions it was water.

The results of the investigations showed that the addition of water to alcoholic solutions and the method of preparing aqueous solutions exerted different effects on the positions of the maxima in the UV spectrum of individual polyphenols. The UV spectrum of quercetin ($\lambda_{max}^{ethanol}$: 256, 374 nm) varied little with a decrease in the concentration of ethanol in the range of 90-20%, although a fall in the intensity of absorption was in fact observed. For solutions containing less than 10% of ethanol (λ_{max}: 254, 366 nm) a hypsochromic shift of band I by an average of 8 nm with only a slight change in the position of band II was observed.

Previously, a shift of the maxima into the shorter-wave region with a decrease in the intensity of absorption after the addition of water to alcoholic solutions has been described for systems in which complex-forming reactions of the flavonoids with $AlCl_3$ took place, and the phenomenon observed was explained by the hydrolytic decomposition of the weak complexes [3]. As far as concerns the flavonoid–solvent systems, for them only a scatter of values was shown (for example, quercetin λ_{max} 370±3 and 255±2 nm) and a fall in the specific absorption as a function of the solvent [4].

In our experiments, the scatter of the results likewise amounted to ±2 nm, but it was referred to the reduced mean values of λ_{max}. The UV spectrum of an aqueous solution of quercetin obtained by boiling differed sharply from those given above by hypsochromic shifts of both bands: λ_{max} 251, 290 nm. Such shifts could be connected either with the formation of an aqua complex or with the decomposition of the substance on heating. However, boiling the initial alcoholic solution with subsequent dilution by water did not lead to such changes in the spectrum, and the chromatographic behaviours on paper of quercetin deposited in the form of alcoholic and aqueous (boiling) solutions in the BAW (4:1:2), 95% ethanol, and 15% acetic acid systems were identical. Consequently, quercetin forms solvato complexes with different properties.

The UV spectra of solutions of kaempferol in ethanol, water (dilution) and water (boiling) were, respectively, λ_{max}: 267, 367, sh.; 243, 263, 355; and 243, 292 nm; and for isorhamnetin they were: 254, 372; 254, 363; and 250, 290 nm. That is, the solvatochromism of flavonols is shown mainly in a displacement of band I, particularly after boiling with water.

The UV spectra of the corresponding solutions of luteolin, λ_{max}, nm, were: 255, 266 sh.,

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352; 255 sh., 265, 349; and 255 sh., 266, 349, solvatochromism being shown in a change in the form of band II and slight hypsochromism of (I). For wogonin – λ_{max}, nm: 276; 275; and 275 – no influence of the solvent and boiling on the position of the spectra was shown. For rutin – 258, 361; 256, 353; and 263, 353 nm – the formation of an aqua complex was reflected in the position of band I, while on boiling band II reacted, which is obviously connected with the substitution of the OH group in position 3 of quercetin. Biorobin – 267, 351; 265, 346; and 265, 346 nm. Cynaroside – 256, 266 sh., 352; 266, 351; and 265, 346 nm. Baicalin – 278, 315; 275, 315; and 276, 315 nm. Consequently, flavonoid glycosides change their spectral characteristics little under the influence of water, and their solvatocomplexes are stable on boiling.

Solvatochromism is also pronounced for phenolcarboxylic acids. For example, the UV spectra of caffeic acid in the corresponding solvents had λ_{max}, nm: 234, 299 sh., 326; 286, 311; and 286, 310.

Thus, the intermolecular interaction of polyphenols with a solvent is expressed in their electronic absorption spectra. The clearest change in the energetic state of the compounds is shown in the UV spectra of the aqua complexes of flavonols and caffeic acid.

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PHENOLIC COMPOUNDS OF Helichrysum italicum

G. G. Zapesochnaya, T. V. Dzyadevich, and B. S. Karasartov

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Continuing a chemical study of Italian everlasting Helichrysum italicum G. Don., family Asteraceae, introduced into the Crimean Zonal Experimental Station of the All-Union Institute of Medicinal Plants [1, 2, 4], from the flowers of the plant we have isolated an additional six substances of phenolic nature: hydroxycinnamic acids (I)-(III), a caffeoylquinic acid (IV), a phthalide (V), and a coumaran (VI).

To identify the substances isolated we used UV, IR, PMR, and mass spectroscopy and also direct comparison with authentic samples of (I)-(V).

p-Coumaric acid (I) – colorless crystals with the composition $C_9H_8O_3$ (M^+ 164), mp 207-209°C (from water), λ_{max} 312 nm.

Caffeic acid (II) – light yellow crystals with the composition $C_9H_8O_4$ (M^+ 180), mp 194-198°C (decomp), λ_{max} 325 nm.

Ferulic acid (III) – colorless crystals with the composition $C_{10}H_{10}O_4$ (M^+ 194), mp 168-171°C, λ_{max} 323 nm.

Chlorogenic (5-O-caffeoylquinic) acid (IV) – colorless crystals with the composition $C_{16}H_{18}O_9$, mp 205-207°C (from water), λ_{max} 329 nm, ν_{CO} 1720, 1710, 1690 cm^{-1}. According to PMR results, the full acetate of compound (IV) contained two aromatic and three aliphatic acetoxy groups. The attachment of the caffeic acid residue to the 5-hydroxyl of quinic acid

All-Union Scientific-Research Institute of Medicinal Plants Scientific Industrial Association, Moscow.

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