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

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UDC 615.322:582.998:547.9

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

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Translated from Khimiya Prirodnykh Soedinenii, No. 3, pp. 409-410, May-June, 1990. Original article submitted June 26, 1989.

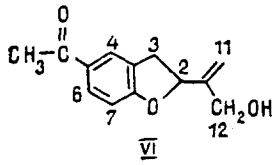
0009-3130/90/2603-0342$12.50

was determined from characteristic signals in the PMR spectrum of the initial substance (IV) [3].

7-Hydroxy-5-methoxyphthalide (V) – colorless crystals with the composition $C_9H_8O_4$ (M^+ 180), mp 184-185°C (from chloroform), λ_{max} 293 nm.

Bitalin A (IV) – light yellow oil, λ_{max} 281 nm. PMR spectrum ($CDCl_3$): δ 7.78 (dd and 2 Hz, H-6), 7.74 (d, 2 Hz, H-4), 6.82 (d, 9 Hz, H-7), 5.42 (t, 9 Hz, H-2), 5.28 (br, s, 2H-11), 4.24 (br.s, 2H-12), 3.44 (dd, 16 and 9 Hz, H-3), 3.14 (dd 16 and 9 Hz, H-3'), 2.53 (s, CH_3CO). Mass spectrum, m/z (int. %): M^+ 218(100) ($C_{13}H_{14}O_3$), M – Me 203(51), M – CH_2OH 187(40), 187 – CH_2CO 145(99).

The structure of bitalin A, a new tremetone derivative followed from the spectral characteristics given. The PMR spectrum of (VI) indicated the presence of a trisubstituted aromatic ring and an acetyl group that was very close to the spectrum of tremetone [5], except that the signal of the olefinic methyl was replaced by the signal (δ 4.24) of a methylene group linked with a hydroxyl. The signals of the protons at C-2, C-3, C-11, and C-12 correspond t the analogous signals of related coumaran derivatives [5-7]. The mass spectrum confirmed the proposed structure of 12-hydroxy tremetone for compound (VI).



VI

This is the first time that any of these substances, with the exception of the phthalide (V), has been isolated from the given plant. In the course of investigations of the flowers of Italian everlasting we also isolated a mixture of dicaffeoylquinic acids the structures of which are now being studied.

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