A PHENOLCARBOXYLIC ACID FROM THE TANNIN SUBSTANCES OF Chamaenerium angustifolium

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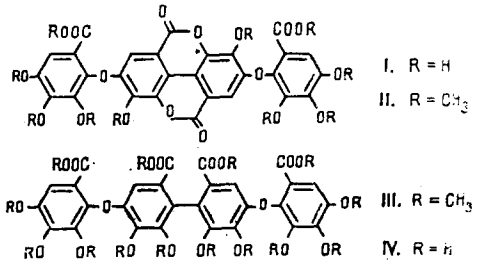
On the hydrolysis with 2 N HCl of the total tannins isolated from the flower heads of Chamaenerium angustifolium (L.) Holub. (fireweed), a mixture of phenolcarboxylic acids was obtained. By chromatography on Sephadex LH-20, a phenolcarboxyic acid (I) was isolated from the mixture with the composition $C_{28}H_{14}O_{18}$, decomp. p. 300°C, Rf 0.65 (BAW, 40:12.5:29), 0.29 (15% acetic acid, FN-16 paper). UV spectrum: $\lambda_{max}^{CH_3OH}$ 216, 258 nm. IR spectrum, cm^{-1}: 3400 (OH), 1710 (COO), 1610 (aromatic ring). PMR spectrum of (I) (here and below 360 MHz, TMS, δ, ppm): aromatic protons, 6.98 (2 H) and 6.99 (2 H), $(CD_3)_2SO$. The alkaline decomposition of (I) [1] led to the formation of gallic and ellagic acids, while partial degradation (2% Na_2CO_3, 100°C, 10 min) formed gallic and ellagic acids and the dilactone of valoneaic acid.

The methylation of (I) (CH_2N_2) followed by chromatography on silica gel [chloroform–hexane (1:1)] yielded a decamethyl derivative $C_{38}H_{34}O_{18}$, mp 213°C, M^+ 778 (II). PMR spectra of (II) ($CDCl_3$), ppm: 7.35 (s, 2 H), 7.20 (s, 2 H) – aromatic protons; 4.31 (s, 6 H), 3.99 (s, 6 H), 3.97 (s, 6 H), 3.79 (s, 6 H), and 3.74 (s, 6 H) – the signals of ten methoxy protons.

A comparison of the mass spectra of (II) and the heptamethyl derivative of the dilactone of valoneaic acid showed the presence of an additional gallic acid residue in (II). The PMR spectrum showed a similarity of (I) to valoneaic acid and differences from sanguisorbic [2] and alnusinic [3] acids.



On the basis of the facts given, we proposed structure (I) for the compound isolated. The numbers of signals of aromatic protons and methoxy groups in the PMR spectra of (I) and (II) may be half the numbers corresponding to the formulas if the signals are superposed in view of the symmetry of the structure of the molecules.

The total tannins were methylated (CH_2N_2) and the products were subjected to methanolysis with sodium methanolate. From the mixture of methyl derivatives of methylated phenolcarboxylic acid the tetramethyl derivative (III) isolated by preparative TLC on silica gel, with $[\alpha]_D^{20}$ +15.6° (c 0.56; chloroform); M^+ 870. PMR spectrum ($CDCl_3$): 7.29 (s, 2 H), 6.91 (s, 2 H) – aromatic protons; 4.07 (6 H), 3.97 (6 H), 3.94 (6 H), 3.77 (12 H), 3.67 (6 H), 3.46 (6 H)– the signals of 14 methoxy groups. The new tetraphenolcarboxylic acid (IV) is a component of the tannin which we have called chamaenerium tannin. Compounds (I-IV) have not been described in the literature previously.

LITERATURE CITED

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