

ISOVALONEAIC ACID — A NEW ACID FROM THE TANNING SUBSTANCES

OF *Epilobium hirsutum*

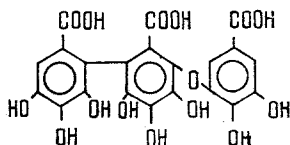
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Continuing a study of the polyphenols of *Epilobium hirsutum* (hairy willow weed), family Onagraceae [1], by acid hydrolysis from the total ellagotannins (5% HCl, 100°C), followed by extraction with ether and ethyl acetate repeated chromatography of the ethyl acetate extract on columns of Sephadex LN-20 with water and aqueous acetone, we have obtained a new phenolic carboxylic acid with the composition $C_{21}H_{14}O_{15}$, decomp. p. 235-237°C, R_f 0.61 in BAW (40:12.5:29) and 0.32 in 15% acetic acid (Filtrak No. 7 paper, ascending chromatography). It formed a deep blue coloration with a 1% solution of ferric ammonium alum (FAA) and gave a positive reaction for bound ellagic acid [2]. Hydrolysis with dilute mineral acid led to the formation of ellagic and gallic acids.

UV spectrum: $\lambda_{\text{max}}^{\text{CH}_3\text{OH}}$ 250, 350 nm. The PMR spectrum (XL-100, DMSO- d_6 , TMS - 0) contains the signals of three aromatic protons in the form of singlets at 7.21, 7.27, and 7.62 ppm. Repeated methylation with an ethereal solution of diazomethane gave the trimethyl ester of the octamethyl derivative of the substance under investigation, with mp 228-230°C, R_f , TLC 0.88 (benzene-acetone (1:4), Silufol). M^+ 661. The PMR spectrum (XL-100, CDCl_3 , TMS-0) of the methyl derivative contained, in addition to the signals of three aromatic protons at (ppm) 6.88 (s), 6.94 (s), and 7.42 (s), the signals of the protons of 11 methoxy groups in the 3.6-4.3-ppm region. The mass spectrum showed intense peaks with m/e 450, 211, 195, 461, 239, and 225.

The nature of the mass-spectrometric fragmentation of the substance [3, 4] shows that it differs from the valoneaic acid isolated by Schmidt et al. [5] by the position of the ether bridge. The acid is a new one not previously described in the literature, and we have called it isovaloneaic acid. It has the following structure:



The NMR and mass spectra were recorded in the V. I. Lenin Tashkent State University.

LITERATURE CITED

1. S. B. Rakhmadieva, M. M. Mukhamed'yarova, and T. K. Chumbalov, in: Chemistry and Chemical Technology [in Russian], No. 22 (1977), p. 99.
2. L. Reichel and A. Schwab, Ann. Chem., 550, 152 (1942).
3. C. Wünsche, A. Sachs, A. Einwiller, and W. Mayer, Tetrahedron, 24, 3407 (1968).
4. C. Wünsche, A. Sachs, and W. Mayer, Tetrahedron, 25, 73 (1969).
5. O. T. Schmidt, Ann. Chem., 591, 156 (1955).

S. M. Kirov Kazakh State University, Alma-Ata. Translated from Khimiya Prirodnykh Soedinenii, No. 5, p. 731, September-October, 1979. Original article submitted April 11, 1979.