STRUCTURE AND CONFIGURATION OF POLYANTHIN AND POLYANTHININ – NEW COUMARINS FROM THE ROOTS OF Ferula polyantha

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From the roots of Ferula polyantha Eug. Kor., collected at the end of July, 1973, in the Fergana oblast (valley of the River Shakhimardan) we have isolated two new coumarins with the compositions $C_{26}H_{32}O_5$, mp 148-149°C, $[\alpha]_D^{20} -50°$ (c 0.8; chloroform) and $C_{26}H_{32}O_5$ mp 127-129°C. $[\alpha]_D^{20} -32°$ (c 1; ethanol), which we have named polyanthin (I) and polyanthinin (II), respectively. The UV spectra of both substances have maxima at λ_{max} 323, 297, and 250 nm (log ε 4.15, 3.9, 3.29), which show that they are derivatives of 7-hydroxycoumarin.

The IR spectra of (I) and (II) show absorption bands at 1730, 1640, 1615, 1560, 1390, 1370, 1250, 895, and 840 cm^{-1}. The broadened carbonyl adsorption band at 1250 cm^{-1} has permitted their assignment to the acylated coumarins [1, 2]. In fact, when (I) and (II) were treated with a 5% solution of caustic potash, they underwent hydrolysis; from the hydrolyzate of (I) we obtained a hydroxycoumarin $C_{24}H_{30}O_4$ with mp 157-159°C $[\alpha]_D^{20} -56°$ (c 1; ethanol) and from the hydrolyzate of (II) a hydroxycoumarin $C_{24}H_{30}O_4$ with mp 176-177°C $[\alpha]_D^{20} -54°$ (c 1; 0; chloroform). By comparing the physicochemical constants and IR spectra of the hydroxylactones obtained, mogoltadin [3] and gummosin [4, 5] – terpeneoid coumarins of the iresane group – were identified. By TLC, acetic acid was found in the hydrolyzates of both substances. These results permit the conclusion that (I) and (II) are natural acetates of mogoltadin and gummosin.

The proposed structures agree completely with the results of mass and NMR spectroscopy. The mass spectra of (I) and (II) show the peaks of ions with m/e 424 (M^+), 381 $(M-43)^+$, 364 $(M-60)^+$, 221 (M−Ar−O−CH_3CO) and 162 $(ArOH)^+$.

In the NMR spectrum of polyanthin there are signals from tertiary methyl groups at 0.85, 0.9, and 0.98 ppm (s, 3H each), a broadened triplet 4.43 ppm ($W_{1/2}$ = 16 Hz) from a hemiacyl proton in the axial orientation, two quartets with centers at 3.95 and 4.25 ppm from the methylene protons in an $Ar-O-CH_2-$ grouping (J_1 = 10.5 Hz; J_2 = 6 Hz), and broadened singlets at 4.62 and 4.72 ppm from the protons of an exocyclic methylene group. In addition, signals from the five protons of a 7-hydroxy substituted coumarin can be seen in the 6.05-7.45-ppm region.

The NMR spectrum of polyanthinin differs from that of polyanthin by the fact that the hemiacyl proton appears in the form of a broadened singlet at 4.65 ppm, with $W_{1/2}$ = 6 Hz, this being superposed in the signal of a vinyl proton corresponding to its equatorial orientation [3, 4].

Thus, compounds (I) and (II) are stereoisomeric compounds, (I) having the configuration analogous to mogoltadin and (II), to gummosin.

On the basis of what has been said above, we propose the following most probable structures and configurations for polyanthin (I) and polyanthinin (II). (See scheme on following page.)

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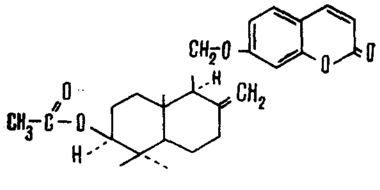

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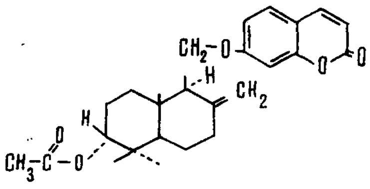

II

We have also isolated polyanthin from the roots of *F. mogoltavica* [3, 4].

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