A FLAVONOID AND A PHTHALIDE FROM Helichrysum polyphyllum

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The inflorescences of Helichrysum polyphyllum Lede B. collected in the Khulo region of Upper Adzharia were extracted with methanol. The residue after evaporation was dissolved in water and extracted with petroleum ether and ethyl acetate. After the ethyl acetate had been driven off, the residue was chromatographed on polyamide, whereupon water eluted two substances successively.

Compound (I), composition $C_9H_8O_4$, mp 184.5-185.3°C, UV spectrum: λ_{max} 217, 257, 293, 323 (log ε 4.48, 4.02, 3.56, 2.83). Acetate $C_{11}H_{10}O_5$, mp 140.5-141.5°C, NMR spectrum (100 MHz, TMS, δ scale, solution in $CDCl_3$): singlets at 2.32 ppm (CH_3CO), 3.81 ppm (CH_3O), and 5.10 ppm (CH_2) and two doublets at 6.62 and 6.72 ppm (J = 2 Hz) due to ortho aromatic protons. Thus, compound (I) was identified as 7-hydroxy-5-methoxyphthalide, isolated previously from H. arenarium [1].

Compound (II), composition $C_{21}H_{22}O_{10} \cdot H_2O$, mp 158-161°C, $[\alpha]_D^{20}$ −120° (c 1.27; MeOH), R_f 0.5 (15% AcOH). The maxima in the UV spectra [MeOH, 226 nm (4.47), 284 nm (4.27)] show that substance (II) belongs to the flavonoid group. On the basis of bathochromy, the presence of free hydroxy groups at C-7 and C-4' was established.

The methylation of (II) with dimethyl sulfate gave 6'-hydroxy-2',4,4'-trimethoxychalcone with mp 109°C [1]. The IR spectrum of the chalcone (mull in paraffin oil and solution in CCl_4) had no band of an OH group, but in the NMR spectrum (solution in $CDCl_3$) singlets with δ 3.76, 3.78, and 3.85 ppm correspond in intensity to three CH_3O groups, and the signals of the other protons corresponded to those given in the literature [2].

The acid hydrolysis of (II) gave D-glucose and an aglycone with the composition $C_{15}H_{12}O_5$ (M^+ 272), mp 248-249°C, identical with naringenin (4',5,7-trihydroxyflavanone, III).

In the NMR spectrum of silylated (II), doublets at 7.24 and 6.75 ppm (J = 8.5 Hz) each with an intensity of 2H show the 4'-substitution of the B ring, doublets at 6.05 and 6.03 ppm (J = 2 Hz) the presence of free H-8 and H-6, and a doublet at 4.97 ppm (J = 6 Hz) relates to the anomeric proton of β-glucose, and its other protons give a multiplet with an intensity of 6H at 3.3-3.9 ppm. The nature of the splitting constants of H-2 (quartet at 5.25 ppm) and 2H-3 (quartets, 3_eH at 2.60, 3_ah at 2.88): $J_{2,3e} = 3.5$, $J_{2,3a} = 12$, $J_{3e,3a} = 17$ Hz shows the axial arrangement of the H-3 [3]. The 2,3 coupling constants in the aglycone are unaffected by the presence of the 5-OH group, which, because of a strong hydrogen bond, makes the coplanarity of the carbonyl group with ring A necessary [3].

The facts presented permitted the identification of compound (II) as (−)-naringenin 5-β-D-glucoside, which has been isolated previously from Helichrysum arenarium [4].

LITERATURE CITED

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