COUMARINS AND FLAVONOIDS OF THE FLOWERS OF Helichrysum italicum

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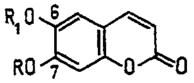
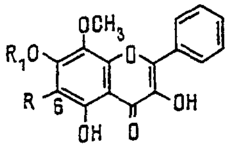
A number of flavonoid glycosides and acylglycosides and hydroxycinnamic and caffeoylquinic acids, and also a series of other compounds, have previously been isolated from the flowers of <u>Helichrysum italicum</u> grown in the Crimea [1, 2]. In a further investigation of the weakly polar compounds of a chloroform extract of <u>Helichrysum italicum</u> flowers using chromatography on silica gel (mixtures of chlf and methanol and of chlf and petroleum ether) we have isolated coumarins (I-III) and flavonoids (IV-VI).



I. R = R_1=H

II. R_1= CH_3; R=H

III. R_1= H; R=CH_3



V. R = R_1=H

VI. R = OCH_3; R_1=CH_3

<u>Compound (I)</u>, light yellow crystals from chlf—methanol (98:2), mp 248-249°c, $C_9H_6O_4$, (M^+ 178); λ_{max}^{MeOH} 229, 257, 299, 349 nm, ν_{CO} 1712 cm^{-1}. ^{1}H NMR spectrum in acetone-d_6 (100 MHz), δ: 7.76 (d, 10.Hz, H-4), 7.00 (s, H-5), 6.76 (s, H-8), 6.32 (d, 10 Hz, H-3), 3.4 (br. s., 2OH).

In UV light (366 nm), compound (I) exhibited a bright blue fluorescence, and on comparison with an authentic sample it was identified as 6,7-dihydroxycoumarin (esculetin).

<u>Compound (II)</u>, colorless needles from water or chloroform, mp 205-207°C, $C_{10}H_8O_4$, (M^+ 192), CNC-5, rp. λ_{max}^{EtOH} 229, 260, 298, 346 mn, ν_{CO} 1700 cm^{-1}. This compound also exhibited a bright blue fluorescence, while its NMR spectrum, as compared with that of compound (I), contained an additional singlet of a methoxy group (δ 3.86 ppm), and its properties were identical with those of an authentic sample of 7-hydroxy-6-methoxycoumarin (scopoletin).

<u>Compound (III)</u>, light yellow acicular crystals with a greenish tinge from chloroform, mp 185-187°C, $C_{10}H_8O_4$, (M^+ 192), λ_{max}^{EtOH} 274, 360 nm. ^{1}H NMR spectrum in $CDCl_3$ (100 Mhz), δ: 7.76 and 6.27 (doublets, 9.6 Hz, H-4 and H-3) singlets at 6.92 S(H-5), 6.85 (H-8), 3.96 (CH_3O), and 6.16 (OH). The compound exhibited a bright green fluorescence. On acetylation it formed a monoacetate, $C_{12}H_{10}O_5$ (M^+ 234), the NMR spectrum of which included the signals of an aromatic acetoxy group (δ 2.35).

Compounds (II) and (III) had practically identical NMR and mass spectra but differed considerably in their fluorescence and their UV spectra (λ_{max} 360 and 346 nm, respectively). These differences corresponded to the UV spectra given in the literature for 6-hydroxcoumarin (344 nm) and 7-hydroxycoumarin (319 nm).

Thus, compound (III) was an isomer of compound (II) and was in fact 6-hydroxy-7-methoxycoumarin (isoscopoletin) [4].

<u>Compound (IV)</u>, light yellow crystals with mp 285-287°C, $C_{15}H_{10}O_6$ (M^+ 286), was identified from its UV, NMR, and mass spectra as kaempferol (3,4',5,7-tetrahydroxyflavone).

<u>Compound (V)</u>, yellow crystals with mp 227-229°C (from alcohol), $C_{16}H_{12}O_6$ (M^+ 300), λ_{max}^{EtOH} 274, 309 sh, 372 nm. ^{1}H NMR spectrum in $CDCl_3$ (200 MHz) δ: 11.5 (s, 5-OH), 8.23 (dd,

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2 and 8 Hz, H-2',6'), 7.54 (m, 3H, H-3',4',5'), 6.71 (s, OH), 6.45 (s, H-6), 6.37 (s, OH), 4.05 (s, CH_3O).

Triacetate of (V), $C_{22}H_{18}O_9$ (M^+ 426), mp 155-157°C (from alcohol).

Compound (VI), yellow crystals with the composition $C_{18}H_{16}O_7$ (M^+ 344), mp 151-152°C (from alcohol), λ_{max}^{EtOH} 278, 327, 377 nm. ^1H NMR spectrum in $CDCl_3$ (200 MHz) δ: 11.5 (s, 5-OH), 8.25 (dd, 2 and 8 Hz, H-2',6'), 7.54 (m, 3H, H-3',4'5'), 6.74 (s, 3-OH), 4.14 (s, CH_3O), 3.98 (s, CH_3O), 3.95 (s, CH_3O).

Diacetate of (VI), $C_{22}H_{20}O_9$ (M^+ 426), mp 168-170°C.

The mass spectra of compounds (V) and (VI) contained the intense peaks of the (M − 15) ions that are characteristic for 6- and 8-methoxylated flavenoids [5]. In the NMR spectra of the two compounds there were te same signals of an unsubstituted B ring of a flavonoid and of a 5-OH group. In addition, in the NMR spectrum of compound (V) singlets were observed from H-6 and one CH_3O group, and in that of compound (VI) singlets from three CH_3O groups.

A comparison of the results obtained with information in the literature permitted compound (V) to be identified as 3,5,7-trihydroxy-8-methoxyflavone, which has been described only for Adenostoma sparsifolium [6].

Compound (VI) was identified as 3,5-dihydroxy-6,7,8-trimethoxyflavone, which has been isolated previously from other Helichrysum species [7-9], although its structure has twice been reconsidered because of the unusual features of its spectral and chemical properties [7, 10]. Thus, flavonol (VI) does not react with Mg + HCl, which earlier led to an erroneous conclusion concerning its structure [10]. Flavonoid (V) behaved similarly under the conditions of this reaction. Furthermore, we have observed an anomolous behavior of substances (V) and (VI) on Silufol plates in UV light at 366 nm: the dark spots did not acquire the yellow-green fluorescence in the presence of $AlCl_3$ that is characteristic for flavonols, although their UV spectra and the zirconyl test [5] characterized substances (V) and (VI) as flavonols with free 3-OH groups.

In our view, the peculiarities found deserve attention since they do not fall within classical ideas on the properties of flavonoids.

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