METHOXYFLAVONES OF SOME SPECIES OF Centaurea

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We have studied the flavonoids of the epigeal part of three species of Centaurea collected in the flowering stage in Armenia. The substances were isolated by extracting the plants with hot water followed by chromatography of chloroform extracts on silica gel in the chloroform–methanol (95:5) system. From Centaurea pseudomaculosa Dobrocz. we isolated a compound (I), from C. aggregata Fisch. et Mey compounds (I) and (II) (minor component), and from C. salicifolia Bieb. compound (III).

Compound (I), $C_{19}H_{18}O_7$, mp 189-190°C, ν_{CO} 1660 cm^{-1}, λ_{max}^{MeOH}, nm; 241, 254 (shoulder), 277, 341; in the presence of $AlCl_3$/HCl: 262, 290, 368. In the mass spectrum, the strongest peaks were those of ions with m/e 358 (M^+) and 343 $(M - CH_3)^+$. PMR spectrum in $CDCl_3$: singlets of four CH_3O groups (3.92 ppm, 9 H and 3.87 ppm, 3H), a 5-OH group (12.77 ppm, 1 H), and the signals of five aromatic protons, three of which show the 3',4'-substitution of the B ring in the structure of (I) with the flavone skeleton, and two singlets at 6.46 and 6.42 ppm which are characteristic for a flavonoid with a trisubstituted ring A. A positive Gibbs test (with 2,6-dibromobenzoquinone chloroimide) showed the presence of a free position 8 in (I). The acetylation of (I) gave a monoacetate, $C_{21}H_{20}O_8$, M^+ 400, mp 182-185°C; ν_{CO} 1630, 1764 cm^{-1}. PMR spectrum in $CDCl_3$: signals of 5-OAc at 2.49 ppm, H-3 at 6.49 ppm, and H-8 at 6.88 ppm.

Thus, compound (I) has the structure of 5-hydroxy-3',4',6,7-tetramethoxyflavone which has been described as a semisynthetic product [1]; we have isolated it from natural sources for the first time.

Compound (II), $C_{18}H_{16}O_7$, M^+ 344, mp 190-193°C; gives a blue coloration with the Gibbs reagent. The PMR spectrum of (II) in $CDCl_3$ differed from the spectrum of (I) only by the form of the signals of the CH_3O groups (9H). According to the shifts of the signals in the PMR spectrum (II) in C_6D_6, the methoxy groups were assigned in the following way: 3.87 ppm (6-OMe), 3.31 ppm (4'-OMe), and 3.16 ppm (7-OMe). These facts, and also the maxima of the UV spectra, coincide with those given in the literature for eupatorin (3',5-dihydroxy-4',6,7-trimethoxyflavone [6]. This is the first time that eupatorin has been isolated from plants of the genus Centaurea.

Compound (III), $C_{18}H_{16}O_8$, M^+ 360, mp 167-168°C, λ_{max}^{MeOH} 257, 272, 354 nm. PMR spectrum of the TMS ether of (III) in CCl_4: the singlets of three methoxy groups (3.86, 3.84, 3.82 ppm), signals of aromatic protons of a 3',4'-substituted ring B (flavone skeleton), and a singlet at 6.32 ppm which can be assigned to H-3 or one of the protons of the trisubstituted ring A.

The acetylation of compound (III) gave a triacetate, $C_{24}H_{22}O_{11}$, M^+ 486, mp 163-165°C. PMR spectrum in $CDCl_3$: signals of three acetoxy groups (2.31, 2.34, 2.49 ppm), of three methoxy groups (3.77, 3.84, 3.87 ppm), and of four aromatic protons, the one-proton singlet being displaced to 7.18 ppm.

The presence of a 3-OCH_3 group was shown by the formation of flavones when compound (III) was demethylated with pyridine hydrochloride [3]. The product obtained was identified as quercetin (3,3',4',5,6,7-hexahydroxyflavone): $C_{15}H_{10}O_8$, M^+ 318, mp 306-308°C, λ_{max}^{MeOH} 259, 276, 366 nm; a negative gossypetone reaction and a positive Gibbs test confirmed that position 8 in the compound is free.

Of the three hydroxy groups in (III), one is located at C-5 (singlet at 12.7 ppm in the PMR spectrum taken in DMSO), the second at C-7 (λ max 274 nm with NaOAc), and the third in ring B (mass spectrum) at C-4' (λ max 414 nm with NaOMe). Consequently, compound (III) has the structure of 4',5,7-trihydroxy-3,3',6-trimethoxyflavone, i.e., jaceidin; however, its mp is given in the literature as 127-133°C [4].

It must be mentioned that C. aggregata and C. Pseudomaculosa which contain compound (I) that is new for the genus Centaurea, belong to the same subgenus, Acrolophus. Centaurea salicifolia contains jaceidin

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(III), which has been isolated previously from C. jacea. Both these species of Centaurea belong to the subgenus Jacea.

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ESTERS OF Ferula ceratophylla

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The isolation of angrendiol from Ferula ceratophylla Regel et Schmalh. has been reported previously [1]. In a methanolic extract of the roots of F. ceratophylla collected in the mountains of Karatau, Kazakh SSR, in the fruit-bearing period, we found no angrendiol but detected two substances with Rf 0.35 and 0.5 giving a crimson coloration when chromatograms were treated with a 1% solution of vanillin in sulfuric acid (Silufol; chloroform system).

By chromatography on type KSK silica gel with elution by hexane–benzene (5 : 1) of a phenolic fraction obtained from a methanolic extract of the roots by a known method [2] we isolated both substances, which proved to be new esters and we have called them ferocin and ferocinin.

Ferocin (I), $C_{22}H_{28}O_3$, mp 127-128°C [hexane–ether (5 : 1)], M^+ 340, $[\alpha]_D^{20}$ −200° (c 1.0; benzene); ferocinin (II) $C_{23}H_{30}O_3$, mp 107-108° M^+ 370, $[\alpha]_D^{20}$ −197° (c 1.0; benzene). Both compounds are readily soluble in benzene and chloroform, moderately soluble in ether and methanol, sparingly soluble in hexane, and insoluble in water.

The UV spectrum of (I) showed a maximum at 253 nm (log ε 4.43) and that of (II) showed maxima at 252 nm (log ε 4.31) and 295 nm (log ε 3.94), which are characteristic for p-hydroxybenzoyl and p-hydroxy-m-methoxybenzoyl chromophores, respectively. In the presence of alkali, the short-wave maxima under went bathochromic shifts by 51 and 64 nm, respectively, which shows that these substances belong to the phenol group. This was confirmed by the fact that (I) and (II) dissolve in alkalis and on acidification separate out in unchanged form, and also by the brown coloration that they give with $FeCl_3$.

The IR spectra of ferocin and ferocinin show the absorption bands of the carbonyl of an ester of an aromatic acid (1680 and 1705 cm^{-1}, respectively), and also those of an aromatic nucleus and of hydroxy groups.

On severe alkaline hydrolysis with a 15% methanolic solution of KOH, both compounds yielded the same terpenoid alcohol with the composition $C_{15}H_{24}O$, mp 82-83°C (hexane), M^+ 220, which we have called fecerol, and ferocin gave p-hydroxybenzoic acid and ferocinin gave vanillic acid.

The NMR spectrum of fecerol showed the signals of the protons of an exomethylene group (quadruplet, 4.75 ppm, $J_1 = 7.5$ Hz, $J_2 = 2.5$ Hz, 2H) an olefinic proton in a $-CH=\overset{|}{C}-$grouping (triplet, 5.17 ppm, J = 6 Hz, 1H), of trans protons in a $-CH=CH-$grouping (doublets at 5.74 and 5.32 ppm, 1H each, J = 15 Hz), and of a hemihydroxylic proton (multiplet, 3.48 ppm, 1H).

On the basis of its composition and NMR spectrum, it may be assumed that fecerol is a secondary alcohol containing three double bonds and having a monocyclic structure.

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