FLAVONOIDS OF THE FLOWERS OF *Cyclachaena xanthifolia*

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We have previously isolated sesquiterpene lactones from *Cyclachaena xanthifolia* (Nutt.) Fresen., family Asteraceae [1]. We have now studied the flavonoids of the flowers of this plant gathered in the environs of Kuibyshev in August, 1981. The flowers were extracted with 70% ethanol and the vacuum-evaporated extract was chromatographed twice on polyamide using mixtures of water and ethanol and of chloroform and methanol.

The final purification of substance (I) obtained was carried out by recrystallization from aqueous ethanol, and that of the minor substance (II-IV) by additional chromatography on silica gel.

Compound (I) (yield 0.1%, mp 175-177°C, $[\alpha]_D^{20}$ −32.9°, c 0.3; methanol) was identified from its UV spectra, the results of acid and enzymatic hydrolysis, and comparison with an authentic sample as astragalin (kaempferol 3-O-glucoside).

Kaempferol [compound (II), mp 275-278°C, M^+ 286] was obtained by the hydrolysis of (I) and was also isolated from the plant in the free form (yield 0.01%).

Compound (III), mp 274-277°C, mass spectrum (m/z, intensity, %): M^+ 330 (79), $(M-15)^+$ 315 (100), $(M-43)^+$ 287 (21), 197 (23), 169 (26), 121 (15), 118 (9). Maxima in the UV spectra, nm: MeOH 256 sh, 281, 335; + NaOMe, 283, 334, 400; + NaOAc, 285, 316 sh, 339 sh, 392; + NaOAc + H_3BO_4, 284, 319 sh., 340 sh; + $AlCl_3$, 265 sh, 289 sh, 311, 360; + $AlCl_3$ + HCl, 265 sh, 290 sh, 311, 355. PMR spectrum in deuteroacetone (ppm): 13.0 (s, 5-OH); 7.95 (d, J = 9 Hz, H-2',6'); 7.02 (d, J = 9 Hz, H-3',5'), 6.62 (s, H-3); 3.94 and 3.83 (singlets, 2 OCH_3).

Compound (IV), mp 264-268°C, mass spectrum (m/z, intensity, %): M^+ 346 (80%), $(M-15)^+$ 331 (100), $(M-43)^+$ 303 (20), 197 (24), 169 (28), 137 (7), 134 (10). Maxima in the UV spectra, nm: MeOH, 259 sh, 279, 350; + NaOMe, 280, 339 sh, 414, + NaOAc, 283, 400; + NaOAc + H_3BO_3, 267, 278 sh, 380; + $AlCl_3$, 283, 310 sh, 431; + $AlCl_3$ + HCl, 263 sh, 290, 302, 370.

The spectral characteristics showed that compounds (III) and (IV) differed only in the structure of ring B: In (III) there was a 4'-OH group (λ_{max} with MeONa 400 nm; m/z 121, 118; two-proton doublets with J = 9 Hz), and in (IV) a 3',4'-dihydroxy group. The singlet signal in the PMR spectrum at 6.62 ppm may belong with equal probability to a proton at C-8 or at C-3. However, the negative Gibbs reaction [2] indicated that position 8 in compound (III) was occupied. Compound (IV) reacted with the Gibbs reagent through the hydrogen at C-6', which was activated by the 3'-hydroxy group, in the para position.

There were no signals of aromatic protons of rings A in the PMR spectra, and therefore compounds (III) and (IV) belong to the flavones with completely substituted A rings. Judging from the PMR and mass spectra, the substances each contained two methoxy groups, which were assigned to positions 6 and 8 on the basis of the following facts. A small bathochromic shift of the long-wave band of the UV spectrum with $AlCl_3$ (HCl) [$\Delta\lambda$ = 20 nm] that is characteristic for 5-hydroxy-6-methoxyflavones [6]. The negative gossypetone test with p-benzoquinone for (III) and (IV) characterized them as 8-methoxy derivatives. A free 7-OH group was also confirmed by the bathochromic shift in the UV spectrum with NaOAc ($\Delta\lambda$ = 4 nm).

Thus, the compounds under consideration have the structures (III) and (IV):

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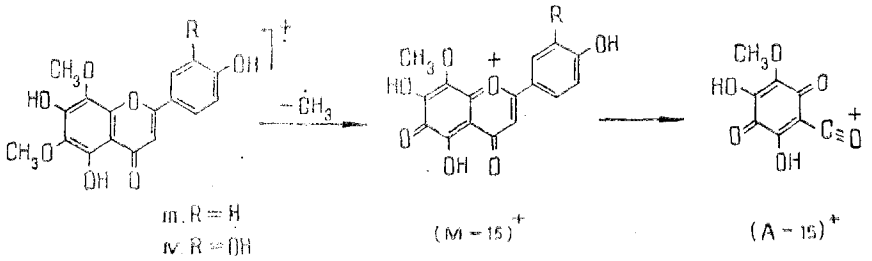

III. R = H
IV. R = OH

A mass-spectrometric study of compounds (III) and (IV) confirmed their structures. The main process of fragmentation of flavones with 6- or 8-OR groups (R = CH_3) was a pathway leading to the loss of the radical and the formation of the ion (M − R), which is not infrequently the main peak of the spectrum. The subsequent loss of CO from this ion produced the fragment (M − R − CO). This process was completed by the quinoid ions (A − R) and (A − R − CO) [4] formed from peak A in the decomposition of the ion (M − R).

It is just these ions that were present in the mass spectra of (III) and (IV), the ions (A − 15) with m/z 197 and (A − 43) with m/z 169 having identical masses in each case, since this part of the spectrum is common to the two compounds.

It must be mentioned that flavonoids with completely substituted rings A are comparatively rare in nature. Thus, 3',4',5,7-tetrahydroxy-6,8-dimethoxyflavone (IV) has previously been isolated only from the gardenia (family Rubiaceae) [5], and 4',5,7-trihydroxy-6,8-dimethoxyflavone (III) from only three plants [6].

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FLAVONOIDS OF THE RHIZOMES OF *Rhodiola rosea*. III.

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Derivatives of tricin and herbacetin have been isolated previously from the rhizomes of *Rhodiola rosea* L. (roseroot stonecrop), family Crassulaceae [1, 2]. Continuing an investigation of the rhizomes of this plant, we have isolated another four flavonoid compounds (I-IV) and a gallic acid derivative (V).

Compound (I) forms yellow crystals from aqueous acetone with the composition $C_{16}H_{12}O_7$, M^+ 316, mp 262-264°C (decomp.). The PMR spectrum of this compound (in deuteroacetone) contained the signals of the protons of a herbacetin skeleton [two doublets J = 9 Hz at 8.23 ppm (H-2',6') and 7.06 ppm (H-3',5'), and a singlet of H-6 at 6.34 ppm] and the singlet signal of one methoxy group at 3.99 ppm.

The mass-spectrometric fragmentation of (I) with the formation of the ions $(M - 15)^+$, 301 (100%), A − 15, with m/z 167, and A − 43 with m/z 139, indicated the presence of a methoxy group in ring A [3]. The small bathochromic shifts ($\Delta\lambda$ = 9 mm) of the short-wave maximum in the UV spectrum in the presence of sodium acetate indicated the presence of free 7-OH group. The long-wave maximum in the UV spectrum in MeOH at 374 nm permitted this com-

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