FLAVONOIDS OF Artemisia annua

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We have studied the epigeal part of Artemisia annua (sweet wormwood) of the family Asteraceae collected at the end of fruit-bearing in November, 1984, in the village of Vanovskii, Ashkhabad province.

The air-dry comminuted material was extracted successively with boiling petroleum ether and boiling ethanol. The ethanolic extract was evaporated in vacuum and the residue was chromatographed on silica gel with elution by chloroform and chloroform–ethanol. The chloroform fractions, on recrystallization from ethanol, yielded three methylated flavonoids.

Substance I – $C_{20}H_{20}O_8$, mp 160°C, M^+ 388, R_f 0.85 (Silufol, chloroform–methanol (6:1)), λ_{max} (MeOH: nm); 256, 272 infl., 348.

According to the results of UV spectroscopy with diagnostic reagents, qualitative reactions, a mixed melting point, IR and mass spectra, and R_f values in various systems with an authentic sample, compound (I) was identified as artemetin (5-hydroxy-3,3',4',6,7-pentamethoxyflavone) [1].

Substance II – $C_{19}H_{18}O_8$, mp 186-187°C, R_f 0.74. UV spectrum: λ_{max} (MeOH; nm): 258, 272 infl., 349; NaOMe: 274, 384; NaOAc: 258, 272, 350; $AlCl_3$ and $AlCl_3$ + HCl: 252, 280 infl., 370.

Mass spectrum (m/z, ion, intensity, %): 374 (M^+; 21), 373 (M – 1; 100), 359 (M – 15; 50), 355 (M – 19; 24), 331 (M – 43; 22), 197 (A + 1; 6), 181 (A – 15; 14), 153 (A – 43; 12), 151 (B_1; 9).

Substance (III) – $C_{19}H_{18}O_8$, mp 183-184°C, R_f 0.7. UV spectrum, λ_{max} (MeOH; nm); 257, 272 infl., 349; NaOMe: 273, 400; NaOAc: 257, 272, 350; $AlCl_3$ and $AlCl_3$ + HCl: 260, 368.

Mass spectrum (m/z, ion, intensity, %): 374 (M^+, 100), 373 (M – 1; 40), 359 (M – 15; 60), 355 (M – 19; 15), 331 (M – 43, 22), 197 (A + 1; 5), 181 (A – 15; 8), 153 (A – 43; 8), 151 (B_1; 10).

The molecular weight of 374 permitted substances (II) and (III) to be assigned to the dihydroxytetramethoxyflavones. The fact that on methylation with diazomethane the two substances gave the same product (I) permitted the conclusion that (II) and (III) had identical natures of the substitution of the flavone skeleton and contained, in addition to a 5-OH group, another hydroxyl. Its position was determined by a comparison of UV and mass spectra. The fragmentation of (II) and (III) indicated that substitution in ring A was identical with that of compound (I) and that there were hydroxy and methoxy groups in ring B (the B_1 ion with m/z 151) [2].

The UV spectra confirmed the presence of a 7-OCH_3 group in each of the three substances (test with NaOAc) [1] and also of 5-OH and 6-OCH_3 groups (insignificant bathochromic shift of the long-wave band in the test with $AlCl_3$ + HCl) [3]. Only the nature of the curves and the values of the bathochromic shifts on the addition of sodium methanolate showed a difference between compounds (II) and (III), due to the presence of a hydroxy group at C-4' in (III) and, consequently, at C-3' in (II) [1].

Thus, on the basis of the facts given and a comparison with literature information, substance (II) was identified as casticin (3',5-dihydroxy-3,4',6,7-tetramethoxyflavone [4], and substance (III) as chrysosplenetin (4',5-dihydroxy-3,3',6,7-tetramethoxyflavone) [5].

Artemetin, casticin, and chrysosplenetin have been found previously in other wormwood species [5-8].

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ANTHRAQUINONES OF Gallium articulatum

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We have investigated the roots and rhizomes of the Gallium articulatum L., family Rubiacea, for the presence of anthraquinones. The raw material for the investigation was collected close to Kislovodsk in the environs of the village of Podkumok.

In an ethanolic extract no less than seven substances of anthraquinone nature were detected by paper chromatography in the ethyl acetate–formic acid–water (10:2:3) system. The air-dry raw material was extracted with 96% ethanol by the fractional maceration method. The extract was evaporated in vacuum and was treated successively with water and chloroform. The aqueous fraction, by chromatography on a column of polyamide with elution first with water and then with water–acetone (1:9, 3:7, and 1:1) yielded substance (I) – $C_{25}H_{26}O_{13}$, yellow crystals with mp 256-257°C (from water), R_f 0.39 in the above-mentioned system.

Six anthraquinones were detected in the chloroform fraction. By chromatography on a column of hydrated silicic acid it was possible to isolate only substances (II)-(V). Substance (II) – $C_{14}H_8O_4$, orange-red crystals with mp 289-290°C (from benzene), R_f 0.98; (III) – $C_{14}H_8O_5$, dark red crystals with mp 259-261°C (from ethanol), R_f 0.51; (IV) – $C_{15}H_{10}O_4$, yellow crystals with mp 299-301°C (from chloroform), R_f 0.59; (V) – $C_{15}H_8O_7$, dark red crystals with mp 223-224°C (from chloroform), R_f 0.68.

On the basis of their physical and chemical properties, the results of UV and IR spectroscopy, and hydrolysis products, and a comparison with authentic samples, these substances were identified as ruberitrinic acid (I), alizirin (II), purpurin (III), rubiadin (IV), and pseudopurpurin (V).

The study of the other components isolated from this raw material is continuing.

The results of a quantitative determination of the anthraquinones in various vegetation phases of the plant using a photoelectrocolorimetric method [1] showed that the largest amount of the substances studied in the epigeal part of this bedstraw was present at the period of incipient vegetation (May) – 5.0-5.4%; and during flowering (July) and fruit-bearing (September) – 3.5-3.9 and 2.3-2.7%, respectively.

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