This gave three individual compounds, one of which had mp 220-221°C, R_f 0.56 (15% AcOH); $\lambda_{max}^{C_2H_5OH}$ 265, 355 nm. Qualitative reactions and UV spectroscopy showed the presence of free hydroxy groups in positions 3, 4', and 5, and also of a substituent in position 7. On the basis of its physicochemical properties and transformations, the substance was identified as 3,4',5-trihydroxy-7-methoxyflavone, or rhamnocitrin, and the other two compounds also proved to be aglycones and were characterized as quercetin and kaempferol [6, 7].

LITERATURE CITED

1. A. A. Grossgeim, The Flora of the Caucasus [in Russian], Moscow, Vol. VI (1962), p. 126.
2. V. A. Stikhin and A. I. Ban'kovskii, in: The Search for and Chemical Study of Biologically Active Substances. A Collection of Scientific Papers (VILR [All-Union Institute of Medicinal Plants]) [in Russian], Moscow, No. 6 (1973), p. 124.
3. A. V. Gotsiridze and E. P. Kemertelidze, Khim. Prir. Soedin., 114 (1971).
4. A. F. Kovalev, Med. Promst. SSSR, No. 7, 22 (1964).
5. A. F. Kovalev, Farm. Zh., No. 1, 25 (1964).
6. L. K. Klyshev, V. A. Bandyukova, and L. S. Alyukina, Plant Flavonoids [in Russian], Alma-Ata (1978).
7. T. S. Zurabishvili and I. I. Moniava, Khim. Prir. Soedin., 254 (1974).

PHENOLIC COMPOUNDS, STEROLS, AND IRIDOIDS OF VALERIAN. VII. COMPOSITION OF THE PHENOLIC COMPOUNDS, β-SITOSTEROL, AND VALEPOTRIATES OF *Valeriana rossica*

N. S. Fursa

UDC 547.972

In an ethanolic extract of the epigeal part of *Valeriana rossica* P. Smirn (Russian valerian) [1], collected in the Streletskii steppe, Kursk province, there were, according to two-dimensional PC [2], not less than 25 phenolic compounds consisting of flavonoids and hydroxycinnamic acids. Column chromatography on Kapron [polycaprolactam] led to the isolation in the individual state of a number of substances, individual ones of which were identified on the basis of physicochemical investigations as caffeic and chlorogenic acids, apigenin, luteolin, diosmetin, quercetin, and the 7-mono-β-D-glucosides and rutinosides of the first three aglycones. Comparative PC analysis showed that the flavonoid glycosides of the vegetative organs consisted predominantly of derivatives of quercetin, diosmetin, and luteolin. The leaves were also found to contain protocatechuic and p-hydroxybenzoic acids and derivatives of apigenin, of acacetin, and of kaempferol. In the inflorescences the predominating components were biosides of apigenin, of luteolin, and of diosgenin.

When the leaves were extracted with chloroform in a Soxhlet apparatus, a white substance was obtained. After purification on a column of alumina, it consisted of white acicular crystals with the composition $C_{29}H_{50}O$, mp 138-139°C (acetone), giving an acetate melting at 124-125°C. The IR spectra of the substance isolated and of β-sitosterol were identical. In a direct comparison by TLC on silica gel they had the same R_f values.

In a methylene chloride extract of the epigeal organs, by chromatography on Silufol plates [3], we detected a different set of weakly polar substances of the essential oils and no less than eight valepotriates, among which the dominating components were valtrate and the anevaltrate and dihydrovaltrate accompanying it.

According to the results of PC, an ethanolic extract of the hypogeal organs contained considerable amounts of caffeic and chlorogenic acids. Consequently, the qualitative composition of the phenolic compounds an valepotriates of *Valeriana rossica* is close to the composition of other dry-valley valerians from the cycle of common valerian — for example,

Zaporozh'e Medical Institute.

Translated from Khimiya Prirodnykh Soedinenii, No. 4, pp. 525-526, August-September, 1984. Original article submitted January 26, 1984.

0009-3130/84/2004-0499$08.50

V. stolonifera Czern. and *V. dubia* Bge. The differences, particularly in the accumulation of the minor components are probably due to the conditions of growth [4].

LITERATURE CITED

1. V. N. Voroshilov, Common Valerian [in Russian], Moscow (1959).
2. M. S. Fursa and L. Yu. Belyaeva, Ukr. Bot. Zh., 11, No. 4, 36 (1983).
3. S. D. Trzhetsins'kii, M. S. Fursa, T. M. Vishnevs'ka, and V. V. Petrenko, Farm. Zh., No. 5, 67 (1983).
4. N. S. Fursa, Rast. Resur., 19, No. 2, 216 (1983).

PROANTHOCYANIDINS OF *Ephedra lomatolepis*

V. B. Omurkamzinova, L. T. Pashinina, and M. S. Erzhanova

UDC 547.972+978

Continuing a study of the chemical composition of herb *Ephedra lomatolepis* Schrenk. [1] from a methanolic extract by adsorption chromatography on polyamide with elution by chloroform–methanol we have isolated two flavans in addition to flavonol glycosides.

The substances gave positive proanthocyanidin reaction and underwent acid cleavage with the formation of (–)-epicatechin, phloroglucinol, and the pigment cyanidin (λ_{max} 535 nm), which enabled us to assign it to the dimeric proanthocyanidins [2]. The formation of phloroglucinol on hydrolysis and also the resistance of the flavans to the action of thioglycolic acid suggested that the flavans belonged to the dimers of group A [3].

Since the substances isolated were labile, their separation was performed through the peracetates (acetic anhydride in absolute pyridine) by chromatography on the adsorbent Chromaton–silicic acid (1:5) with elution by benzene–acetone (1:1 and 1:2).

We give the results of a study of flavan (I). The peracetate of flavan (I) was an amorphous white powder with mp 156-157°C (from ethanol) $[\alpha]_D^{22}$ –32.04° (c 0.79; methanol). The heptamethyl diacetate of flavan (I) was an amorphous cream-colored powder with M^+ 758.

In the PMR spectrum of the peracetate ($CDCl_3$, δ, ppm) in the strong-field region the signals of the protons of seven aromatic acetyl groups (2.3 — 18 H; 1.5 — 3 H) and two aliphatic acetyl groups (1.94 — 3 H; 1.78 — 3 H) were observed. Thus, of the ten hydroxy groups of the two catechin molecules, nine were acylated. In the strong-field region, the signals of two protons of ring A of the "upper" half of the molecule of the dimer were observed in the form of one-proton doublets at 6.75 and 6.4, J = 2 Hz, which is characteristic for meta interaction. The presence of an unsplit signal of a proton of ring A of the "lower" half (6.48, s) indicated that a second carbon atom of this ring (C_6 or C_8) participated in the formation of the interflavan bond.

All six protons of rings B of the dimer resonated in the 7.4-7.55 ppm region. Of the eight protons of the heterorings of the dimer the signals of six were detected in the spectrum. The C-2 proton of the "lower" half resonated in the form of a singlet at 5.22 ppm, which corresponds to its cis arrangement relative to the C-3 proton (5.02 ppm). This was confirmed by the formation of (–)-epicatechin on the acid cleavage of the dimer. The C-3 proton of the "upper" half resonated in the form of a doublet at 5.45 ppm with J = 5 Hz.

Of the four protons of the methylene groups of the heterorings three were recorded in the spectrum: at 4.75 ppm (1 h, J = 5 Hz) and at 2.85 ppm (2 H, d, J = 2 Hz). The absence of the fourth proton of the methylene groups indicated the participation of C-4 in the formation of the interflavan bond.

The structure of a dimer of a 3,3',4',5,7-pentahydroxyflavan with a C_4–C_8 (or C_6) and C_2–O–C_7 interflavan bonds and the 2R,3R configuration of the asymmetric centers of the

S. M. Kirov Kazakh State University, Alma-Ata.

Translated from Khimiya Prirodnykh Soedinenii, No. 4, pp. 526-527, August-September, 1984. Original article submitted January 27, 1984.

0009-3130/84/2004-0500$08.50