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

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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.

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"lower" flavan unit has been established for flavan (I) on the basis of chemical transformations and spectral characteristics.

Several dimeric flavans with two interflavan bonds of this type have been described in the literature — dimers A_1, A_2, and A_3 based on (−)-epicatechin and (+)-catechin [4, 5], dimers based on afzelechin [6], and a biflavonoid based on flavan-3-ol and flavon-3-ol [7].

The dimer that we isolated from *E. lomatolepis*, like the dimer A_2 from the seed husks of the horse chestnut [4], contained (−)-epicatechin in the "lower" half of the molecule. But differences were observed between them in the specific rotations and the PMR spectra of the peracetate, which may be the result both of a different conformation and configuration of the "upper" flavan units of the dimers and also of a different order of the interflavan bond (C_4—C_6 or C_4—C_8).

The investigation of the proanthocyanidins of this ephedra is continuing.

LITERATURE CITED

1. B. M. Zakirova, V. B. Omurkamzinova, and M. S. Erzhanova, Khim. Prir. Soedin., 782 (1982).
2. K. Weinges, W. Bähr, K. Goritz, and H.-D. Marx, Fortschr. Chem. Org. Naturstoffe, 27, 158 (1969).
3. E. Haslam, in: The Flavonoids (ed. B. J. Harborne), Chapman and Hall, London (1975), p. 506.
4. K. Weinges, K. Kaltenhauser, H.-D. Marx, E. Nader, F. Nader, D. Seiler, and J. Perner, Ann. Chem., 711, 184 (1968).
5. D. Jacques and E. Haslam, J. Chem. Soc., Perkin Trans., 2663 (1974).
6. H. Hikimo, N. Shimoyama, G. Kasahara, M. Takanashi, and S. Konno, Heterocycles, 19, No. 8, 1381 (1982).
7. H. Hikino, M. Takanashi, and S. Konno, Tetrahedron Lett., 23, No. 6, 673 (1982).

PHENOLCARBOXYLIC ACIDS OF *Astragalus floccosifolius*

R. K. Yasinov, N. V. Syrovezhko, and G. P. Yakovlev

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From chloroform and aqueous extracts of the epigeal part of *Astragalus floccosifolius* Sumn. collected in the Tadzhik SSR in the flowering phase, by column chromatography and paper chromatography, we have isolated seven phenolcarboxylic acids. All the substances isolated gave positive reactions with a number of reagents for phenolcarboxylic acids [1, 2].

Substance 1 — $C_7H_6O_3$, mp 210-212°C, R_f 0.11 (butan-1-ol—acetic acid—water (4:1:4) — system 1), 0.56 (2% CH_3COOH — system 2), 0.58 (0.1 N hydrochloric acid — system 3). It was identified by comparison with an authentic sample as p-hydroxybenzoic acid.

Substance 2 — $C_9H_8O_3$, mp 207-209°C, R_f 0.88 (system 1), 0.41 (system 2), 0.35 (system 3). Alkaline degradation led to the formation of p-hydroxybenzoic acid. It was identified by comparison with an authentic sample as p-coumaric acid.

Substance 3 — $C_9H_8O_4$, mp 192-194°C, R_f 0.81 (system 1), 0.21 (system 2), 0.20 (system 3). On alkaline degradation with KOH, protocatechuic acid was formed [3]. A mixture with an authentic sample of caffeic acid gave no depression of the melting point.

Substance 4 — $C_{10}H_{10}O_4$, mp 234-236°C, R_f 0.87 (system 1), 0.21 (system 2), 0.38 (system 3). On fusion with KOH, vanillic acid was formed. It was identified by comparison with an authentic sample as isoferulic acid.

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