"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

- B. M. Zakirova, V. B. Omurkamzinova, and M. S. Erzhanova, Khim. Prir. Soedin., 782 (1982).
- K. Weinges, W. Bähr, K. Goritz, and H.-D. Marx, Fortschr. Chem. Org. Naturstoffe, <u>27</u>, 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, <u>19</u>, No. 8, 1381 (1982).
- 7. H. Hikino, M. Takanashi, and S. Konno, Tetrahedron Lett., 23, No. 6, 673 (1982).

PHENOLCARBOXYLIC ACIDS OF Astragalus floccosifolius

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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].

<u>Substance 1</u> -  $C_7H_6O_3$ , mp 210-212°C, Rf 0.11 (butan-1-ol-acetic acid-water (4:1:4) - system 1), 0.56 (2% CH<sub>3</sub>COOH - system 2), 0.58 (0.1 N hydrochloric acid - system 3). It was identified by comparison with an authentic sample as p-hydroxybenzoic acid.

<u>Substance 2</u> - C<sub>9</sub>H<sub>8</sub>O<sub>3</sub>, mp 207-209°C, R<sub>f</sub> 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, protocatechnic acid was formed [3]. A mixture with an authentic sample of caffeic acid gave no depression of the melting point.

<u>Substance 4</u> -  $C_{10}H_{10}O_4$ , 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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501

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Substance  $5 - C_{10}H_{10}O_4$ , mp 167-169°C,  $R_f$  0.83 (system 1), 0.32 (system 2), 0.32 (system 3). A mixture of substance 5 with an authentic sample of ferulic acid gave no depression of the melting point.

Substance  $6 - C_{16}H_{18}O_9$ , mp 202-204°C,  $R_f 0.73$  (system 1), 0.56 (system 2), 0.52 (system 3). On fusion with KOH protocatechuic acid was formed. The products of alkaline hydrolysis were investigated by paper chromatography with markers, which revealed the presence of caffeic and D-quinic acid [4]. A mixture with an authentic sample of chlorogenic acid gave no depression of the melting point.

<u>Substance 7</u> -  $C_{16}H_{18}O_9$  - could not be obtained in the crystalline state and was investigated in solution.  $R_f$  0.67 (system 1), 0.63 (system 2), 0.62 (system 3). On alkaline degradation and alkaline hydrolysis, substance 7 also gave protocatechuic, caffeic, and D-quinic acids. The closeness of substance 7 to substance 6 indicated that they were isomers.

This is the first time that any of these phenolcarboxylic acids have been detected in the epigeal part of Astragalus floccosifolius.

## LITERATURE CITED

1. V. A. Bandyukova, Khim. Prir. Soedin., 263 (1983).

- N. V. Sergeeva, G. N. Zemtsova, V. A. Bandyukova, and A. L. Shinkarenko, Izv. Sev.-Kavk. Nauchn. Tsentra Vyssh. Shk., Ser. Estestv. Nauk, No. 3, 72 (1973).
- 3. A. V. Simonyan, V. I. Litvinenko, and A. L. Shinkarenko, Khim. Prir. Soedin., 383 (1972).
- M. J. Michaud, "Révélation différentielle des acids-alcools des depsides hydroxycinnamiques sur les chromatogrammes d'extracts végétaux," Bull. Soc. Pharm., Bordeaux, <u>104</u>, 233 (1961).

THE NATURE OF CHRYSANTHEMYL ACETATE

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An essential oil has been obtained by steam distillation from fresh whole flowering plants of the Arctic pansy *Tanacetum boreale* Fisch. growing in the eastern part of the Kungei-Alatau range (village of Ak-Tyuz). From fractions of this oil obtained by fractional distillation two substances have been isolated by preparative GLC the properties and spectral characteristics of which differ from those given in the literature. One substance, present in the essential oil in a concentration of 10.5%, was an ester (bands at 1741 and 1245 cm<sup>-1</sup> in the IR spectrum) boiling at 81.5-82°C/5 mm and with  $n_D^{2^\circ}$  1.457;  $d_{2^\circ}^{2^\circ}$  0.9208;  $[\alpha]_D^{2^\circ}$  +19.3°, M<sup>+</sup> 196.

Its PMR spectrum (Fig. 1a) showed in the 4.74 ppm region a doublet with J  $\sim$  7.5 Hz) belonging to an olefinic proton and indicating the presence in the molecule of a >CH--CH= C(CH<sub>3</sub>)<sub>2</sub> group the methyl protons of which resonated at 1.59 ppm. The signal of the methine proton of this group consisted of a doublet (J  $\sim$  6 Hz) of doublets (J  $\sim$  7.5 Hz) with its center at 1.05 ppm. It was partially overlapped by the signals of the protons of quaternary groups at 1.05 and 0.96 ppm. The protons of a -CH<sub>2</sub>O group resonated in the 3.50-4.25 ppm region and, being chemically nonequivalent, gave two doublets with centers at 4.11 and 3.77 ppm. These protons interact with one another with J  $\sim$  12 Hz and each, separately, interacts with a third proton with J  $\sim$  7 Hz and J  $\sim$  8 Hz. The signal of the latter was located in a very strong field and formed a doublet of quartets with its center at 0.72 ppm. Such a position of the signal of a methine proton can be explained by the assumption that it was located in a three-membered ring and interreacted not only with the nonequivalent protons of the -CH<sub>2</sub>O group but also with another proton with J  $\sim$  6 Hz. In view of the close-

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502