PHENOLIC COMPOUNDS OF Eleutherococcus senticosus

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An extract of the roots of prickly eleutherococcus Eleutherococcus senticosus (Rupr. et Maxim.) Maxim. (family Araliaceae) is widely used in medical practice [1]. There are reports in the literature on a study of the chemical compositions of the roots [2-4] and of a prepration [5] of prickly eleutherococcus.

We have investigated the composition of an industrial extract and a number of samples of industrial batches of the raw material of prickly eleutherococcus. The extracts were seprated by column chromatography on a succession of sorbents (silica gel L 40/100, Sephadex LH-020, Woelm polyamide) using mixed eluents (chloroform–methanol and water–ethanol in various ratios). This permitted the isolation of 15 compounds (I-XV). For their identification we used their UV, PMR, and mass spectra, and also, in the case of substances (I-X, XII, and XIII), direct comparison with authentic samples.

p-Hydroxybenzoic acid (I) – white crystals with the composition $C_7H_6O_3$ (M^+ 138), mp 213-214°C (aqueous alcohol).

Vanillic acid (II) – colorless crystals with the composition $C_8H_8O_4$ (M^+ 168), mp 210-212°C (aqueous alcohol).

Syringic acid (III) – colorless crystals with the composition $C_9H_{10}O_5$ (M^+ 198), mp 203-205°C (aqueous alcohol).

Vanillin (IV) – white crystals with the composition $C_8H_8O_3$ (M^+ 152), mp 79-81°C (ethanol).

p-Coumaric acid (V) – light yellow crystals with the composition $C_9H_8O_3$ (M^+ 164), mp 207-209°C (chlf–MeOH).

Caffeic acid (VI) – light yellow crystals with the composition $C_9H_8O_4$ (M^+ 180), mp 220-222°C (aqueous alcohol).

Ferulic acid (VII) – colorless crystals with the composition $C_{10}H_{10}O_4$ (M^+ 194), mp 168-170°C (aqueous alcohol).

Chlorogenic acid (VIII) – white crystals with the composition $C_{16}H_{18}O_9$, mp 203-205°C (water), λ_{max}^{EtOH} 243, 300 sh., 330 nm.

Coniferin (IX) – white crystals with the composition $C_{16}H_{22}O_8$, mp 184-185°C (ethanol), λ_{max}^{EtOH} 266 sh, 258 nm. Compound (IX) was hydrolyzed by β-glucosidase with the formation of coniferyl alcohol (M^+ 180) and glucose.

Syringin (eleutheroside B) (X) – white acicular crystals with the composition $C_{17}H_{24}O_9$, mp 192-193°C (water), λ_{max}^{EtOH} 266 nm. Compound (X) was hydrolyzed by β-glucosidase with the formation of sinapyl alcohol (M^+ 210) and glucose.

Coniferyl alcohol (XI) – light yellow syrupy substance with the composition $C_{10}H_{10}O_5$ (M^+ 178).

Isofraxidin (XII) – light yellow crystals with the composition $C_{11}H_{10}O_5$ (M^+ 222), mp 146-149°C (aqueous alcohol).

Isofraxidin Glucoside (eleutheroside B_1) (XIII) – light yellow crystals with the composition $C_{17}H_{20}O_{10}$, mp 211-213°C (aqueous alcohol). Compound (XIII) was hydrolyzed by β-glucosidase with he formation of isofraxidin (XII) and glucose.

Syringaresinol (XIV) – light yellow amorphous substance with the composition $C_{22}H_{26}O_8$ (M^+ 418), λ_{max}^{EtOH} 237, 273 nm.

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Syringaresinol diglucoside (eleutheroside D) (XV) – white acicular crystals with the composition $C_{33}H_{38}O_{13}$, mp 255-257°C (aqueous alcohol), λ_{max}^{EtOH} 234, 271 nm, $[\alpha]_D^{23}$ −6.1° (0.4; 50% ethanol).

Compound (XV) was hydrolyzed by β-glucosidase with the formation of syringaresinol (XIV) and glucose.

The results presented show that we are the first to have isolated compounds (I-IX) from this plant, while we have confirmed the presence of compounds (X-XV) [2, 3, 5]. At the same time, it must be mentioned that we did not detect certain compounds described previously for this plant: the lignan sesamin [4, 5], ethyl caffeate [5], and sinapyl alcohol [5].

The fact deserves attention that the chlorogenic acid (VIII) detected previously by the TLC method [5] and successfully isolated by us is one of the dominating components of the plant and (together with lignans and other phenylpropanoids) affects the nature of the UV absorption curve of an extract of prickly eleutherococcus (λ_{max}^{EtOH} 284 and 330 nm).

The greatest practical interest is presented by syringin (X), giving on Silufol UV 254 plates [chlf–MeOH–H_2O (26:14:3)] a bright blue coloration on treatment with 16% sulfuric acid (110°C). This method (using a standard sample of syringin) may be used for determining the authenticity of the raw material and of eleutherococcus preparations and also of those from other plants containing syringin (lilac, mistletoe).

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PROTOLYTIC PROPERTIES OF THE PHYTOMELANIN PIGMENTS OF Helianthus annuus

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One of the main problems of the chemistry of phytomelanin pigments (PMPs) holding back their use in medicine and the pharmacological, chemical, and food industries is the structural-group differentiation of the protogenic oxygen functional groups, without which the standardization of PMP preparations is impossible. The amounts of these functional groups and the determination of their capacity for ionization have been little studied in practice in view of the difficulties due to the statistical copolymeric structure, the polymolecularity, and the limited solubility of the pigments [1].

As an illustration of these difficulties we may give the molecular absorption spectra of the PMPs, which have unresolved structures in the UV and VIS regions of the spectrum.

Taking as an example a study of the protolytic equilibria of the H, NH_4, and Na forms of the PMPs of the husks of black seeds of Helianthus annuus in dilute (0.005-0.01%) aqueous solutions in the pH range of 3-12, we have shown the possibility of a differentiation of carboxylic and phenolic functional groups with respect to their ionization constants (pK) and their mass fractions (W). To find these parameters we used the methods of direct and

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