POLYPHENOL COMPOSITION OF THE EPIGEAL PART OF Potentilla erecta

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From the epigeal part of tormentilla cinquefoil Potentilla erecta (L.) (family Rosaceae) we have previously isolated coumarins (coumarin, scopoletin, umbelliferone [1]) and flavonoids (narcissin, isorhamnetin 3-glucoside 7-rhamnoside, quercetin 3-glucoside 7-rhamnoside [2]). Continuing a study of the chemical composition of the epigeal part of cinquefoil we have investigated the phenolcarboxylic and hydroxycinnamic acids and the catechins. These compounds large determine the effect of the biologically active complex of the plant [3, 4].

Isolation was carried out by the following scheme: 2 kg of air-dry raw material collected in the flowering phase in the environs of Kursk was extracted with 80% ethanol, and then the extract was evaporated to an aqueous residue which was freed from the lipophilic substances that had deposited and was then treated successively with chloroform (800 ml), ethyl acetate (1.3 liters), and butanol (1.6 liters). Coumarins had previously been isolated from the chloroform fraction, and flavonoids from the butanol fraction [2].

We have now investigated the ethyl acetate fraction, the evaporation of which to small volume (120 ml) led to the deposition of a crystalline precipitate of ellagic acid (0.3 g) – $C_{14}H_6O_5$, mp 360°C (decomp.) [5]. After the separation of the ellagic acid, the filtrate was evaporated to a dry residue (26 g).

To isolate the hydroxycinnamic acids, 10 g of the total material obtained from the ethyl acetate fraction was deposited on a column of polyamide sorbent (4.5 × 60 cm) which was washed first with water and then with mixtures of water and ethanol with increasing concentrations of the latter up to 7%.

The process was monitored by paper chromatography in the 5% acetic acid system. Similar fractions were combined, evaporated, and crystallized. As a result the following substances were obtained and identified: p-coumaric acid – $C_9H_6O_3 \cdot H_2O$, mp 212-214°C; 3,4-dihydroxycinnamic (caffeic) acid – $C_9H_8O_4$, mp 195-196°C; 3-hydroxy-4-methoxycinnamic (ferulic) acid – $C_{10}H_{10}O_4$, mp 168-170°C; and 5-O-caffeyl-D-quinic (chlorogenic) acid – $C_{16}H_{18}O_9$, mp 202-204°C, $[\alpha]_D^{20}$ −32° (methanol). Two benzoic acid derivatives were obtained which we characterized as methyl gallate ($C_8H_8O_5$, mp 156-157°C [5]) and gallic acid ($C_7H_6O_5$, mp 253°C [5]).

To isolate catechins, 12 g of the total residual material from the ethyl acetate fraction was deposited on a column of cellulose (4 × 45 cm) which was then washed with 5% acetic acid solution, the fractions so obtained being investigated in the 2% acetic acid and butan-1-ol–acetic acid–water (4:1:2) systems. The elutes obtained were evaporated and the residues were crystallized. Five compounds of flavan nature were obtained which were identified as (+)-catechin – $C_{15}H_{14}O_6$, mp 174-175°C, $[\alpha]_D^{20}$ +18.7° (acetone); (∓)-catechin – $C_{15}H_{14}O_6$, mp 212-214°C; (+)-gallocatechin – $C_{15}H_{14}O_7$ $[\alpha]_D^{20}$ +14° [acetone–water (1:1)]; (−)-epigallocatechin – $C_{15}H_{14}O_7$, mp 218°C, $[\alpha]_D^{20}$ −59° (ethanol); and (−)-epigallocatechin gallate – $C_{22}H_{18}O_{11}$, mp 213°C, $[\alpha]_D^{20}$ −185° (water).

The substances were identified from their physicochemical properties, mixed melting points with authentic samples, R_f values in various solvent systems, the products of alkaline cleavage, and the UV, IR, and PMR spectra of the substances isolated and of their transformation products.

No catechin derivatives have previously been found in the epigeal part of tormentilla cinquefoil.

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STEROID HEXAOL FROM Crossaster papposus

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From an ethanolic extract of the starfish Crossaster papposus by chromatography on Polikhrom-1, silica gel, and Florisil we have isolated a steroid polyol (I). On the basis of spectral characteristics, the structure of 5α-cholestane-3β,6β,8,15α,16β,26-hexaol has been established for (I).

Substance (I), $C_{27}H_{48}O_6$, mp 253-255°C (from chloroform–ethanol), $[\alpha]_{Hg}^{20}$ +40° (C 0.3; methanol) was obtained with a yield of 0.001% on the weight of a lyophilizate of an ethanolic extract of the raw material. The animals were collected in August, 1983, in the Sea of Okhotsk in the littoral of the island of Onekotan (Kurile Islands) from a depth of 100 m. Mass spectrum (m/z, %): 468 (4; M^+); 450 (100); 432 (60); 414 (43); 399 (16); 396 (19); 331 (11); 321 (51); 303 (51); 285 (38); 225 (95); 107 (41). PMR spectrum (C_5D_5N, 250 MHz, δ, TMS, ppm): 1.09 (d, J = 6.7 Hz, CH_3-27); 1.15 (d, J = 7.0 Hz, CH_3-21); 1.45 (dt, J_1 = 2.0 Hz, J_2 = 2.0 Hz, J_3 = 12.0 Hz, H-5); 1.57 (d, J = 10.5 Hz, H-14); 1.60 (s, CH_3-19), 1.60 (dd, J_1 = 7.2 Hz, J_2 = 10.5 Hz, H-17); 1.77 (s, CH_3-18); 2.00 (dm, H-4e); 2.10 (dd, J_1 = 2.5 Hz, J_2 = 14.5 Hz, H-7a); 2.45 (q, J = 11.5 Hz, H-4a); 3.28 (dd, J_1 = 3.0 Hz, J_2 = 14.5 Hz, H-7e); 3.64 (Add, J_1 = 6.2 Hz, J_2 = 10.2 Hz, H-26); 3.77 (Bdd, J_1 = 5.5 Hz, J_2 = 10.2 Hz, H-26'); 4.02 (m, H-3); 4.24 (q, J = 2.2 Hz, H-6); 4.76 (dd, J_1 = 2.0 Hz, J_2 = 7.2 Hz, H-16); 5.06 (dd, J_1 = 2.0 Hz, J_2 = 10.5 Hz, H-15).

^{13}C NMR spectrum (C_5D_5N, 62.9 MHz, δ, TMS, ppm): 40.9 (C-1); 32.1 (C-2); 71.2 (C-3); 37.0 (C-4); 48.6 (C-5); 73.2 (C-6); 45.5 (C-7); 76.1 (C-8); 56.6 (C-9); 36.2 (C-10); 19.3 (C-11); 42.7 (C-12); 44.8 (C-13); 63.9 (C-14); 80.5 (C-15); 82.4 (C-16); 60.3 (C-17); 17.0 (C-18); 15.9 (C-19); 30.0 (C-20); 18.4 (C-21); 36.7 (C-22); 24.4 (C-23); 34.5 (C-24); 36.7 (C-25); 67.5 (C-26); 17.4 (C-27).

The assignment of the signals in the PMR and ^{13}C NMR spectra of (I) was made on the basis of a comparison with the corresponding spectra of 5α-cholestane-3β,6α,8,15α,16β,26-hexaol (II) and asterosaponin P_1 (III) which we had isolated previously from the starfish Patiria pectinfera [1, 2]. The sequence of protons H-4–H-7 was established on the basis of the nature of the H-3 multiplet (4.02 ppm) by spin-decoupling experiments, and the sequence of proteins H-14, H-16, H-17 on the basis of the H-15 signal (5.06 ppm).

The configurations of the hydroxy groups were determined from the SSCCs of the protons. In the PMR spectrum of (I), the H-6 signal was present in the form of a narrow quartet, in contrast to the broad triplet of doublets for H-6 in the analogous spectrum of the steroid (II) [1]. The H-4a signal (2.45 ppm) was shifted downfield, and the H-4e signal (2.00 ppm) upfield, in comparison with the corresponding signals (1.86 and 3.15 ppm), respectively for compound (III) [2]. These facts indicated the β-configuration of the OH group at C-6.

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