FLAVANS OF Spiraea hypericifolia

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We have investigated S. hypericifolia L. collected in November in the foothills of the Trans-Ili Ala-Tau. By paper chromatography in the solvent systems butan-1-ol–acetic acid–water (40:12.5:29) (1) and 2% acetic acid (2) we found in the stems of this plant a considerable amount of flavonoids and four flavans. The fact that these substances were flavans was shown by the orange red and pink colors which their spots on chromatograms developed with 1% of vanillin in concentrated HCl and with iron ammonium alum, respectively.

The flavans from the stems freed from bark were extracted with methanol after the elimination of resins and waxes by steeping with benzene and with chloroform. The aqueous methanolic extract was concentrated under vacuum at 30-35°C and the flavans present in it were extracted successively with ether and ethyl acetate.

To separate the mixture of substances of the ethereal extract, we used partition chromatography on KSK silica gel previously treated by a method described earlier [1]. As the stationary solvent we used water and as the mobile solvent, ethyl ether. The aglycones of the flavonoids were eluted in the first fractions, and then, successively, flavan 1 and flavan 2. Phloroglucinol and protocatechuic acid were found in the products of alkaline fusion. Flavan 1 has R_f 0.66 (system 1) and 0.34 (system 2) mp 177°C, $[\alpha]_D^{22}+17.0°$ [c 0.3; acetone–water (1:1); flavan 2 has R_f 0.58 (system 1) and 0.30 (system 2), mp 236-237°C, $[\alpha]_D^{22}-62.0$ (c 0.34; acetone–water (1:1)]. The constants obtained correspond to literature information for (+)-catechin and (-)-epicatechin [2].

The substances from the ethyl acetate extract were also separated by partition chromatography on silica gel. After the elimination of the flavonoid aglycones and traces of the catechins by ether, flavans 3 and 4 were eluted successively with ethyl acetate. Complete separation of the substances was achieved by repeated rechromatography of the fractions. Then the flavans were freed from accompanying substances by chromatography on Sephadex LH20 using ethanol as the eluant.

Flavan 3 had R_f 060 (system 1) and 0.63 (system 2); flavan 4 had R_f 0.53 (system 1) and 0.56 (system 2). Flavan 3 ($C_{21}H_{24}O_{10}$) was isolated in the form of a white powder with $[\alpha]_D^{23}-86.2°$ (c 3.48; acetone). (+)-Catechin and rhamnose were found in the products of the mild acid hydrolysis of flavan 3. Consequently, flavan 3 is (+)-catechin rhamnoside, which has not previously been found in plants.

Flavan 4, $C_{20}H_{22}O_{10}$, formed a white powder with $[\alpha]_D^{20}-18.0$ (c 3.89; acetone). (+)-Catechin and arabinose were found in the products of its mild acid hydrolysis. This showed that this substance is (+)-catechin arabinoside. Catechin arabinoside has been obtained previously by synthesis [3], and (+)-catechin 7-arabinoside has been isolated only from Polypodium vulgare [4].

LITERATURE CITED

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