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THE STRUCTURE OF AKICHENOL AND AKICHENIN

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UDC 547.913.7;547.587.52

Continuing a study of plants of the genus Ferula [1-3], from the roots of Ferula akitschensis B. Fedsch. gathered in July, 1974, in the Susamyr valley, Kirghiz SSR, we have isolated a substance $C_{27}H_{36}O_6$, M^+ 456, mp 162-163°C, $[\alpha]_D^{20} - 8.3°$ (c 0.9; $CHCl_3$). It is readily soluble in ethanol and chloroform, sparingly soluble in petroleum ether, and insoluble in water; its UV spectrum has a maximum at 260 nm (log ε 4.16), which is characteristic for an aromatic nucleus, and its IR spectrum shows absorption bands at 1520, 1590, 1625 cm^{-1} (aromatic nucleus), 1695-1710 cm^{-1} (ester carbonyl), and 3200-3600 cm^{-1} (hydroxy group). The substance is new, and we have called it akichenin (I).

When compound (I) was hydrolyzed by being heated with 5% caustic potash for 2 h, from the acid part of the hydrolyzate we isolated p-hydroxybenzoic acid (II) and by chromatography, and also by NMR spectroscopy, we identified angelic acid (III). From the neutral fraction we obtained a previously unknown triol – akichenol (IV), $C_{15}H_{26}O_3$, M^+ 254, mp 155-156°C, $[\alpha]_D^{20}$ +37.5° (c 1.33; $CHCl_3$), the IR spectrum of which showed absorption bands at 1660 cm^{-1} (double bond) and 3200-3600 cm^{-1} (hydroxy group). On acetylation it formed a diacetate $C_{19}H_{32}O_5$ (V) with mp 105-106°C having in its IR spectrum the absorption band of a hydroxy group, which is tertiary. This is also confirmed by the fact that when the IR spectrum of the deuterated acetate of akichenin (V) was recorded, an absorption band characteristic for the $-O-D$ bond was observed at 2650 cm^{-1} and the intensity of the absorption band at 3590 cm^{-1} had decreased.

The presence, according to the NMR spectrum, of only one double bond in the triol showed its bicyclic structure. When the NMR spectrum of (IV) was compared with that of ferutinol (VI) [4], it was seen that the two compounds are similar. Judging from the nature of the multiplicity and the values of the chemical shifts of the signals of the hemihydroxyl and the olefinic protons and of the C-methyl groups, (IV) differs from (VI) only

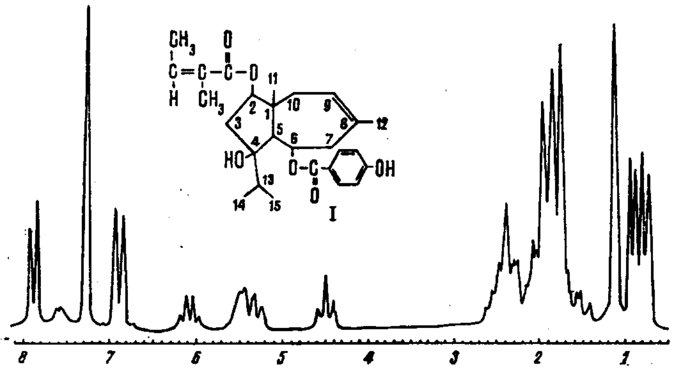

Fig. 1. NMR spectrum of akichenin (in $CDCl_3$).

Institute of the Chemistry of Plant Substances, Academy of Sciences of the Uzbek SSR, Tashkent. Translated from Khimiya Prirodnykh Soedinenii, No. 1, pp. 102-103, January-February, 1976. Original article submitted May 21, 1975.

by one additional secondary hydroxy group. The dehydrogenation of both alcohols (IV) and (VI) gave the one azulene (VII).

The multiplicity of the signal of the secondary hemihydroxyl methine proton in the spectrum of akichenol at 3.3 ppm (q, $J_1 = J_2 = 10$ Hz) shows that it interacts with only two other protons. This pattern can be observed only if this hydroxyl is present at C_2 or C_3. The resistance of akichenol to oxidation with periodic acid excludes the C_3 position.

Thus, it is most likely that akichenol (IV) has the structure of the triol corresponding to (I). When (I) was hydrolyzed with 1% ethanolic caustic potash in the cold for 2 h, we obtained a monoester (VIII) with the composition $C_{20}H_{32}O_4$, M^+ 336, the NMR spectrum of which showed an upfield shift of the sextet at 5.5 ppm (H-6) by 1.6 ppm with a simultaneous disappearance of the signals of the protons of p-hydroxybenzoic acid. It follows from this that the p-hydroxybenzoic residue is present at C_6 and the angelic acid residue at C_2. Consequently, akichenin has the most probable structure (I).

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CATECHIN-7-XYLOSIDE FROM Spirea hypericifolia

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UDC 547.972

As reported previously [1], in an investigation of the stems of S. hypericifolia we found two catechin glycosides. The present paper describes an investigation of a catechin xyloside.

The glycoside extracted from the raw material with methanol was separated from catechins and polyflavones by chromatography on Kapron using methanol–chloroform (9 : 1) as eluent. The separation of the flavan glycosides from one another was achieved by subsequent chromatography on silica gel (with ether and ethyl acetate as eluents).

The glycoside was isolated in the form of colorless needles with the composition $C_{20}H_{22}O_{10}$, mp 165-167°C, $[\alpha]_D^{20}$ −18.0° (c 3.89; acetone). The elementary analyses of the substance itself and of its derivatives corresponded to the calculated figures.

In the products of acid hydrolysis (+)-catechin and xylose were found. Acylation by acetic anhydride in pyridine yielded a heptaacetyl derivative $C_{34}H_{36}O_{17}$ in the form of colorless needles with mp 179-181°C $[\alpha]_D^{20}$ −75.0° (c 0.12; acetone), R_f 0.28 on TLC in benzene–acetone (9 : 1); NMR ($CDCl_3$) δ (ppm): 1.94 (1 alip Ac), 2.02 (3 alip Ac of a sugar), and 2.22 (3 ar Ac). Methylation with diazomethane at room temperature for 120 h gave a trimethyl derivative $C_{23}H_{28}O_{10}$ in the form of plates with mp 172-173°C, $[\alpha]_D^{20}$ −70.0° (c 0.66; methanol); R_f 0.44 in the benzene–acetone (9 : 1) system; NMR ($CDCl_3$), δ (ppm): 3.78 ($1CH_3O$), 3.89 ($2CH_3O$). The acetyl and methyl derivatives were purified on columns of silica gel–Chromaton (5 : 1) using mixtures of benzene and acetone (9 : 1 and 7 : 3) as eluents. A tetraacetyltrimethyl derivative of catechin xyloside was obtained with R_f 0.43 in the benzene–acetone (9 : 1) system; M^+ 632, which corresponds to the calculated molecular weight. The formation of a tri- and not a tetramethyl ether with diazomethane and the presence of the signal of an aliphatic acetyl group at δ 1.94 in the NMR spectrum showed that the sugar is attached to the phenolic hydroxyl.

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