THE STRUCTURE OF PILOPLEURIN – A NEW CHROMONE FROM *Pilopleura kozo-poljanskii*

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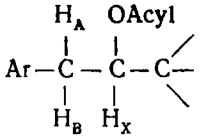
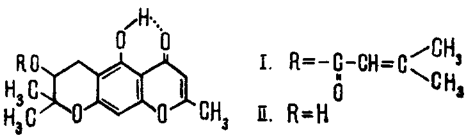
From the roots of Pilopleura kozo-poljanskii Schischk., the only representative of a monotypical genus of the family Umbelliferae which has not previously been studied chemically, we have isolated a new crystalline substance with the composition $C_{20}H_{22}O_6$, mp 130-131°C, $[\alpha]_D^{20}$ −24.8° (c 0.97; ethanol), which we have called pilopleurin (I).

The IR spectrum of the substance [λ_{max} 212, 222 (inflection), 251, 258, 296 nm (log ε 4.48, 4.43, 4.28, 4.27, 3.87)] shows that the substance is a chromone. The presence in the IR spectrum of pilopleurin (Fig. 1) of bands at 1653, 1631, and 1580 cm^{-1} (absorption of γ-pyrone and benzene rings) confirms this conclusion, and a band at 1721 cm^{-1} shows the presence of an ester grouping in the molecule. The fact that pilopleurin is an acylated chromone is also shown by a decrease in the R_f value of the product of the alkaline hydrolysis of (I).

The hydrolysis of (I) gave a chromone $C_{15}H_{16}O_5$ with mp 200-201°C. In its IR spectrum, the absorption band of the ester group had disappeared and the absorption band of a hydroxyl (3523 cm^{-1}) had appeared. The results of a comparison of this substance with hamaudol (II) [1, 2] showed that they were identical. Consequently, pilopleurin is an ester of (II) and an acid C_4H_7COOH. A positive reaction with ferric chloride showed the presence of a free phenolic hydroxyl in the molecule of (I); thus, the hydroxy group in position 3' of the dihydropyran nucleus must be esterified.

The NMR spectrum of pilopleurin (Fig. 2) enables the structure of this compound to be determined unambiguously. A singlet at 2.25 ppm (3H) is caused by a methyl group at C_2 of the chromone nucleus, a signal at 5.81 ppm (1H, s) by a methine proton at C_3, and a singlet at 6.10 ppm (1H) by a proton in position 8; a signal at 12.84 ppm (s, 1H) shows that the molecule contains a phenolic hydroxyl. The structural elements of the dihydropyran ring of hamaudol are responsible for the appearance of the following signals in the NMR spectrum: those of a gem-dimethyl grouping (1.26 and 1.28 ppm, s, 6H); those of a  $Ar-\underset{H_B}{\overset{H_A}{C}}-\underset{H_X}{\overset{OAcyl}{C}}-C\lessgtr$ grouping (d, $\delta_A = 2.89$, $\delta_B = 2.63$, $\delta_X = 5.00$; $J_{AB} = 17.5$ Hz, $J_{AX} = 5.2$ Hz, $J_{BX} = 5.7$ Hz). The remaining signals in the NMR spectrum of pilopleurin (1.82 and 2.09 ppm, doublets, J ≃ 1 Hz, 6H; 5.55 ppm, broadened singlet, 1H) are characteristic for senecioic acid [3].

Consequently, pilopleurin has the structure of 5-hydroxy-2,2',2'-trimethyl-3'-senecioyloxy-3',4'-dihydropyrano-5',6' : 6,7-chromone (I).



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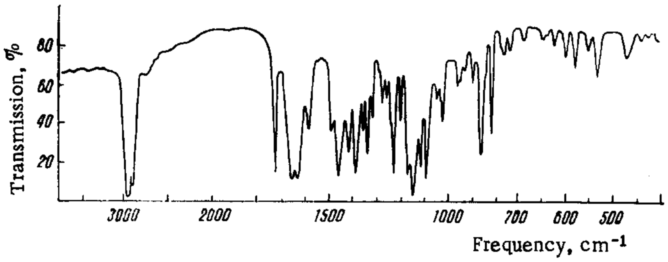

Fig. 1. IR spectrum of pilopleurin (mull in paraffin oil).

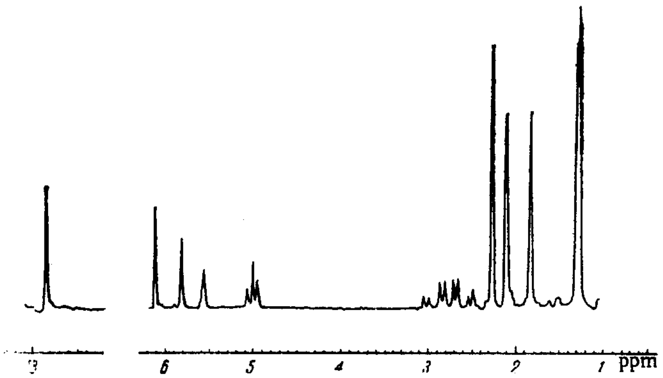

Fig. 2. NMR spectrum of pilopleurin.

EXPERIMENTAL

The UV spectrum of an ethanolic solution of pilopleurin was taken on a Hitachi EPS-3T spectrophotometer, the IR spectrum in paraffin oil on a UR-10 instrument, and the NMR spectrum on a Varian HA-100D instrument (CCl_4, 0 — HMDS). The melting points were determined by Kofler's method. The analyses of all the compounds corresponded to the calculated figures.

Isolation of Pilopleurin. The dried and comminuted roots of Pilopleura kozo-poljanskii (1 kg), collected in August, 1970, in the upper reaches of the river Talas (Kirghizia), were extracted with methanol in 6-, 4-, and 4-liter portions. The resulting extract was evaporated in vacuum and the colorless crystals that deposited were separated off. Yield 32.45 g (3.2%), mp 161-163°C, after recrystallization from ethanol, mp 165-166°C. The substance was identified as mannitol (IR spectrum).

After the separation of the mannitol, the weight of the residue was 208 g. Of this residue, 108 g was treated with water (250 ml), the aqueous layer was decanted off, and the oily residue was heated with petroleum ether (3× 100 ml). When the solution was concentrated, colorless crystals separated out with the composition $C_{20}H_{22}O_6$ (1.95 g, 0.4%), mp 130-131°C (from petroleum ether), R_f 0.60 [Silufol, petroleum ether—ethyl acetate (1 : 1)].

Hydrolysis of Pilopleurin. A solution of 0.50 g of pilopleurin in 2 ml of 5% caustic potash in methanol was boiled for 2 h, cooled, neutralized with 10% sulfuric acid, and diluted with 50 ml of water. Crystals of hamaudol, $C_{15}H_{16}O_5$, deposited. Yield 0.32 g, mp 200-201°C (from methanol).

SUMMARY

From the roots of Pilopleura kozo-poljanskii Schischk. a new chromone has been isolated which has been called pilopleurin. On the basis of the results of hydrolysis and UV, IR, and NMR spectroscopy, it has been established that pilopleurin has the structure 5-hydroxy-2,2',2'-trimethyl-3'-senecioyloxy-3',4'-dihydropyrano-5',6' : 6,7-chromone.

LITERATURE CITED

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