THE STRUCTURE OF CHUIN, A NEW COUMARIN FROM THE ROOTS OF Seseli tschuense

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We have previously reported the isolation from the roots of Seseli tschuense E. Nik, sp. novo, of the new coumarin chuin [1]. The present paper gives the results of a chemical study of this component and of the determination of its structure. Chuin (I), $C_{22}H_{18}O_7$, with mp 212-213.5°C, $[\alpha]_D^{26}-225°$ (c 0.2; ethanol), as was shown previously, is an acylated furocoumarin. The IR spectrum of (I) has absorption bands at (cm^{-1}) 3320-3400 (hydroxy group), 1720 (C =O of an α-pyrone and an ester), 1690 (carbonyl of an Ar−CO−R ketone), and 1636, 1620, and 1580 cm^{-1} (C =C bond of an aromatic system).

The presence in the NMR spectrum of (I) (Figure 1) of doublets at 6.13 and 7.80 ppm (J = 9.5 Hz) and of singlets at 7.32 and 6.72 ppm (the latter superposed on one of the components of a doublet at 6.52 ppm) shows that the substance is a 6,7-substituted coumarin. A singlet at 1.54 ppm (6 H), a two-proton doublet with its center at 3.10 ppm (J = 8 Hz), and a one-proton triplet at 5.05 ppm are due to gem-dimethyl, methylene, and methine protons of a dihydrofuran ring. Thus, (I) is a linear dihydrofurocoumarin acylated with an aromatic acid.

Doublets at 6.52 and 7.04 ppm (J = 8.5 Hz) each with an intensity of two proton units are due to two pairs of ortho-interacting protons in an aromatic nucleus. The paramagnetic shift of the signal at 7.04 ppm relative to the chemical shift of the protons of an unsubstituted benzene ring is caused by the carbonyl group of an ester, and the diamagnetic shift of the signal of the protons at 6.52 ppm is due to the donor influence of a hydroxy group. This shows that the hydroxy group in the acid residue is present in the para position. The presence of a phenolic hydroxyl in (I) is confirmed by the formation on its treatment with diazomethane of a methyl ester $C_{23}H_{20}O_7$, with mp 69-71°C, and a bathochromic shift by 33 nm of the long-wave maximum in the UV spectrum recorded in the presence of alkali, and also by an absorption band at 3320-3400 cm^{-1} in the IR spectrum. Chuin reacts with 2,4-dinitrophenylhydrazine to form the corresponding hydrazone with mp 216-218°C (from ethanol). This shows that its molecule contains an oxo group.

The mass spectrum of (I) shows the peaks of the molecular ion M^+ with m/e 394 and of fragments corresponding to a hydroxycoumarin with m/e 246 and to an oxo acid with m/e 149.

By the alkaline methanolysis of (I) we obtained a hydroxylactone with the composition $C_{14}H_{14}O_4$, mp 186-188°C (ethanol), and an oxo acid with mp 176-177°C, $[\alpha]_D^{22}-26°$ (chloroform), R_f 0.74.

The lactone was identified as nodakenetin from its IR and mass spectra and also by a mixed melting point.

The acid was identified as p-hydroxyphenylglyoxylic acid from its composition, melting point, the methyl ether (mp 85-86°C) obtained by the hydrolysis of O-methylchuin, the methyl ether of its methyl ester, and its mass spectrum [2]. When the acid was heated in vacuum, it split out CO and was converted to p-hydroxybenzoic acid with mp 210-212°C.

Thus, substance (I) is an ester of nodakenetin and p-hydroxyphenylglyoxylic acid and has the structure shown in Fig. 1.

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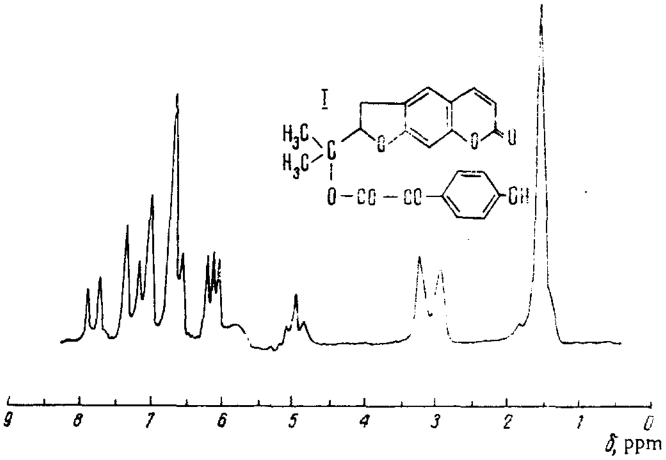

Fig. 1. NMR spectrum of chuin.

EXPERIMENTAL

The UV spectra were taken on a Hitachi spectrometer, the IR spectra on a UR-10 spectrometer (KBr), the mass spectra on an MKh-1303 instrument, and the NMR spectra on a JNM-4H-100/100 MHz instrument in DMSO (region from 5 to 10 ppm) and in pyridine (from 1 to 6 ppm), the chemical shifts being given in the δ scale from the signal of HMDS taken as 0.

The acids were chromatographed in a thin layer of cellulose and on type "C" ["fast"] paper in the ethanol–ammonia–water (95 : 5 : 5) system with Bromphenol Blue as the chromogenic agent. The results of elementary analysis corresponded to the calculated figures.

Isolation of Chuin (I). The comminuted roots of Seseli tschuense (3 kg) were treated with methanol (3 × 10 liters), and the combined extract was concentrated to two liters, diluted with water (1 : 2), and extracted with diethyl ether (5 × 0.5 liter). The ethereal extract was distilled, giving 40 g of a viscous product, which was deposited on a chromatographic column filled with KSK silica gel (h = 40, d = 9 cm), and the column was eluted with a mixture of petroleum ether and ethyl acetate with gradually increasing concentrations of the latter, the volume of each fraction collected being 0.6 liter.

Fractions 21-28 (10% of ethyl acetate in petroleum ether) yielded 0.5 g of a crystalline substance, $C_{22}H_{18}O_7$, with mp 212-213°C (MeOH), $[\alpha]_D^{26} -225°$ (c 0.2; ethanol).

2,4-Dinitrophenylhydrazone of (I). A freshly prepared solution of 2,4-dinitrophenylhydrazine was added to a solution of 0.03 g of the substance in ethanol. After a day, crystals deposited with mp 216-218°C (ethanol).

Methyl Ether of (I). A solution of diazomethane in ether was added to a solution of 0.1 g of the substance in the same solvent. The mixture was left for 12 h, and then the ether was evaporated off and the residue was washed with ether. A substance with mp 69-70°C was obtained.

Nodakenetin. A solution of 0.2 g of chuin in a 5% solution of KOH in methanol was heated on the water bath for 3 h. The liquid was diluted with water, the methanol was distilled off in vacuum, and the solution was acidified with 5% H_2SO_4 and was treated with ether (3 × 50 ml). The ethereal extract was washed with 3% Na_2CO_3 solution, dried, and distilled. This gave a substance with mp 186-188°C (ethanol), $[\alpha]_D^{22} -26°$ (chloroform).

p-Hydroxyphenylglyoxylic Acid. Solution A was acidified and treated with ether (3 × 30 ml), and the solvent was distilled off. Colorless acicular crystals deposited with mp 176-177°C (benzene), R_f 0.74.

p-Methoxyphenylglyoxylic Acid. The methyl ether of chuin (0.5 g) was treated as described above, giving an acid with mp 85-86°C and R_f 0.42.

Methyl p-Methoxyphenylglyoxylate. Methyl p-hydroxyphenylglyoxylate was dissolved in acetone, an excess of diazomethane was added, the mixture was left for 12 h, and the solvent was evaporated. An oily neutral substance with M^+ 194 was obtained.

SUMMARY

The roots of Seseli tschuense E. Nik., sp. novo, have yielded a new coumarin $C_{22}H_{18}O_7$ with mp 212-213.5°C, $[\alpha]_D^{26} -225$ (c 0.2; ethanol), which has been called chuin. On the basis of NMR, mass, IR, and UV spectra and the products of alkaline methanolysis, and derivatives, it has been established that chuin is an ester of p-hydroxyphenylglyoxylic acid and nodakenetin.

This is the first time that p-hydroxyphenylglyoxylic acid has been found in acylated coumarins.

LITERATURE CITED

1. A. M. Aminov and G. K. Nikonov, Khim. Prirodn. Soedin., 799 (1972).
2. J. Heilbron, Dictionary of Organic Compounds, 2nd ed., Eyre and Spottiswoode, London (1943-4).