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A NEW COUMARIN FROM LIBANOTIS SCHRENKIANA

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Libanotis schrenkiana is a perennial herbaceous plant growing in Central Asia. This species has not been subjected to chemical study. From the lactone fraction of an ethanolic extract of L. schrenkiana collected by K. I. Boryaev we have isolated by column chromatography on alumina a substance with the composition $C_{19}H_{20}O_5$, mp 78–79° C (from petroleum ether), $[\alpha]^{16}_D$ +213° (c 1.0; chloroform). The substance has a UV spectrum typical for the coumarins: λ_{max} 250, 261, 237 mμ (log ε 3.65, 3.66, 4.21), and the IR spectrum of the substance (Fig. 1) shows the absence of hydroxyl groups and confirms that it belongs to the coumarin group. Literature data show that the coumarin isolated is a new one; we have proposed for it the name libanorin.

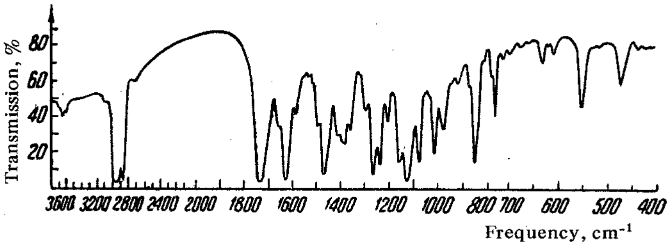


Fig. 1. IR spectrum of libanorin (mull in paraffin oil).

The results of an investigation of the NMR spectrum of libanorin (Fig. 2) enabled the question of its structure to be solved. The presence in the spectrum of the doublets a (δ = 7.62; J = 9.3 Hz) and d (δ = 6.17; J = 9.3 Hz) from H_4 and H_3 and the doublets b (δ = 7.26; J = 8.7 Hz) and c (δ = 6.72; J = 8.7 Hz) from H_5 and H_6, respectively, characterizes libanorin as a 7, 8-disubstituted coumarin [1, 2].

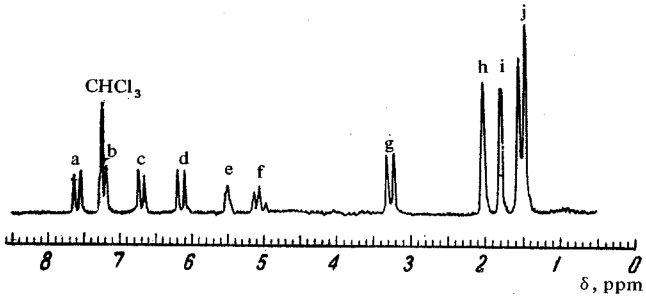
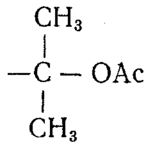
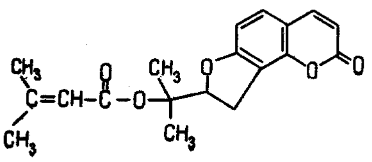


Fig. 2. NMR spectrum of libanorin (solution in $CDCl_3$; O-tetramethylsilane).

The triplet f (δ = 5.13; J = 8.6 Hz) (1 H), the doublet g (δ = 3.32; J = 8.6 Hz) (2 H), and the two peaks j (δ_1 = 1.59; δ_2 = = 1.51) (6 H) belong to the methine, methylene, and methyl protons of a dihydrofuran ring condensed in the 2', 3'-position with a benzene nucleus and containing the grouping  $-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-OAc$ in position 5' [2]. The signals e (δ = 5.55) (1 H), h (δ = 1.08) (3 H), and i (δ = 1.84) (3 H) are due to a residue of β, β-dimethylacrylic (senecioic) acid [3]. Thus, libanorin has the following structure



In full agreement with the proposed structure of libanorin, when it was saponified a substance with the compositon $C_{14}H_{14}O_4$, mp 162–163° C, $[\alpha]^{17}_D$ +193° (c 1; chloroform) identical with zosimol [2, 4], was obtained.

Recently, a paper [5] has appeared in the literature on the identity of zosimin and columbianadin and the products of their saponification, zosimol and columbianetin. The considerable difference in the specific rotations of the last two substances (+209.4° for zosimol in chloroform and +20.0° for columbianetin in dioxane [6]) the authors explained by the solvent effect. However, our determination has shown that for zosimol $[\alpha]_D^{17}$ +190° (c 1.0; dioxane). Apparently the specific rotation of columbianetin given by Willette and Soine [6] does not correspond with reality.

Experimental

Isolation of libanorin. 2.5 kg of the comminuted roots of L. schrenkiana were exhaustively extracted with methanol. The solvent was distilled off in a vacuum-distillation apparatus. This gave 231 g of a dark resinous residue. To separate the essential and fatty oils, 20 g of this extract was treated with petroleum ether (bp 40–60° C). The residue was dissolved in 250 ml of diethyl ether and the solution was washed with 0.5% caustic potash solution (5 × 50 ml) and with water (2 × 25 ml). The ethereal solution was dried with anhydrous sodium sulfate and the solvent was distilled off. The residue of neutral substances (6.9 g) was chromatographed on a column of alumina (75 × 4 cm, 700 g, activity grade III). The fractions obtained by elution with a mixture of benzene and petroleum ether (2 : 1), after evaporation of the solvent, yielded coarse colorless crystals (3 g) with mp 78–79° C (from petroleum ether), R_f 0.81 (TLC: Al_2O_3, activity grade III, benzene–isobutyl acetate (2 : 1)). The substance is readily soluble in chloroform, acetone, ethyl acetate, ether, alcohols, and ethanolic alkali, $[\alpha]_D^{16}$ +213° (c 1.00; chloroform).

Found, %: C 69.78, 69.68; H 6.14, 6.27; mol. wt. 319 (by spectrophotometry) [7]. Calculated for $C_{19}H_{20}O_5$, %: C 69.28; H 6.14; mol. wt. 328.35.

Alkaline hydrolysis of libanorin. A solution of 0.54 g of the substance in 20 ml of a 1 N solution of caustic potash in ethanol was heated at 70° C in the water bath for 1.5 hr. The solvent was distilled off under reduced pressure and the residue was dissolved in water, and the solution was acidified with 20% sulfuric acid and extracted with chloroform (4 × 20 ml). The chloroform solution was washed several times with 2% sodium bicarbonate solution and with water and was then dried with anhydrous sodium sulfate and distilled. This gave 0.37 g of a crystalline residue which, after recrystallization from methanol and ether, gave colorless needles with mp 162–163° C, $[\alpha]_D^{17}$ +193° (c 1.00; chloroform); +190° (c 1.00; dioxane). For analysis, the substance was dried in vacuum at 82° C for 10 hr.

Found, %: C 68.25, 68.20; H 5.79, 5.83. Calculated for $C_{14}H_{14}O_4$, %: C 68.28; H 5.73.

A mixture of the hydroxylactone obtained and zosimol gave no depression of the melting point and the IR spectra of the two substances were identical.

The sodium carbonate extract of the products of alkaline saponification were acidified with 20% H_2SO_4 and extracted with diethyl ether (4 × 20 ml). The ethereal solution was washed with water (2 × 10 ml), dried with anhydrous sodium sulfate, and distilled. A sirupy liquid residue (0.12 g) with a sharp acidic odor was obtained which, on paper chromatography in the form of the diethylamine salt in the water-saturated butanol system gave a spot with R_f 0.52 corresponding to the position of β, β-dimethylacrylic acid (Leningrad type "M" paper; spot revealed with 0.2% Bromophenol Blue solution).

Conclusions

A new coumarin $C_{19}H_{20}O_5$ with mp 78–79° C, $[\alpha]_D^{16}$ + 213° (c 1.00; chloroform) has been isolated from the roots of Libanotis schrenkiana, and we have called it libanorin. On the basis of chemical and spectral characteristics, the structure of the β, β-dimethylacrylic ester of zosimol (columbianetin) has been proposed for libanorin.

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