LACTONES OF ZOSIMIA ABSINTHIFOLIA (VENT) LINK

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The roots and fruit of Zosimia absinthifolia, a perennial herbaceous plant of the family Umbelliferae, collected on the southern slopes of Mount Mashuk (Northern Caucasus), contain lactones of the coumarin group: 1. 5% in the fruit and 3. 2% in the roots. According to the results of paper chromatography these lactones consist of a mixture of nine substances with R*f* 0. 98, 0. 95; 0. 86; 0. 80; 0. 61; 0. 25; 0. 16; 0. 10, and 0. 0. In attempts to purify the lactones by Späth's method [1], they underwent irreversible changes which could be explained by the presence in them of ester groupings. Two isomeric lactones of composition $C_{19}H_{20}O_5$ were isolated by chromatography.

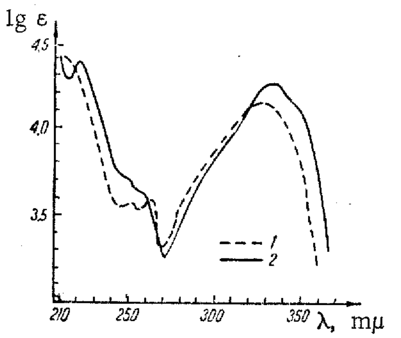

Fig. 1. UV spectra of zosimin (1) and deltoin (2).

Judging from their chemical properties and the UV spectra (Fig. 1), both lactones belonged to the coumarin group. They contained no methoxy groups and did not react with carbonyl reagents.

The IR spectrum of lactone A (Fig. 2) showed the absorption band of the carbonyl group of an unsaturated δ-lactone at 1728 cm^{-1}, a conjugated C=C bond at 1626, an aromatic nucleus at 1587, a $(CH_3)_2C$ group at 1393 and 1374, and an aromatic C—O bond at 1625 cm^{-1}. From the width of the carbonyl band, it could be assumed that the lactone A was an ester. When it was saponified with caustic alkali, a hydroxylactone $C_{14}H_{14}O_4$ was obtained the IR spectrum of which (see Fig. 2) showed adsorption bands for a hydroxyl group at 3408 cm^{-1}, a lactone carbonyl group at 1716, and an aromatic nucleus at 1619 and 1582 cm^{-1}.

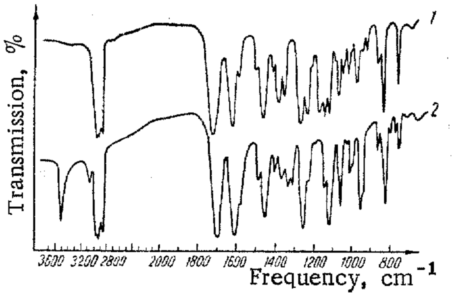

Fig. 2. IR spectra of zosimin (1) and zosimol (2). Mulls in paraffin oil.

Oxidation of the hydroxylactone with chromic acid gave acetone, identified in the form of the dibenzylidene derivative, which showed the presence of a $(CH_3)_2C{=}C$ or a $(CH_3)_2C{-}OH$ grouping. In addition to the hydroxylactone, saponification gave an unsaturated acid $C_5H_8O_2$, identified from its IR spectrum as cis-1, 2-dimethylacrylic acid.

From its composition and the products of its saponification, lactone A corresponded to the dihydrofurocoumarin columbianadin, which has been found in the roots of Lomatium columbianum [2]. However, the optical activity of the substance diverged considerably from that of columbianadin: $[\alpha]_D^{27}$ + + 26. 5°. These facts indicated that the lactone A was, rather, an unknown coumarin; we have called it zosimin, and the corresponding hydroxylactone zosimol [3]. The investigations carried out [4] showed that this lactone is an ester of 2'-t-hydroxyisopropyl-2', 3'-dihydrofuro-4', 5': 8, 7-coumarin and cis-1, 2-dimethylacrylic acid and is therefore an isomer of columbianadin.

Lactone B was identified as deltoin, which we isolated for the first time from deltoid hogfennel.

Thus, the two lactones isolated from zosimin are in fact dihydrofurocoumarin derivatives, and differ from one another by the position of condensation of the dihydrofuran ring with the aromatic nucleus of coumarin and the isomerism of the acids forming the ester groupings.

Experimental

The chromatography was carried out on paper impregnated with a 10% solution of formamide in methanol. The mobile phase was cyclohexane-benzene-methanol (5: 4: 1), and the spots were shown up with diazotized sulfanilamide [5]. The IR spectra were recorded on a UR-10 spectrograph (mull of the substance in paraffin oil), and the UV spectra on an SF-4 spectrometer (solution in alcohol). The total amount of lactones in the plant was determined by a recognized method [6].

Isolation of zosimin. Two kilograms of the roots were treated twice with 12-liter portions of 95% alcohol. The extract was concentrated in vacuum to a volume of 0. 5 liter and 1 liter of water was added. The liquid was treated 3 times with 0. 5-liter portions of ether, and the ethereal extracts were evaporated to dryness. The residue (85 g) was mixed with an equal amount of alumina and transferred to a column of the same adsorbent (diameter 8 cm, height 70 cm). The column was first eluted with 6 liters of petroleum ether and then with 2 liters of benzene. Concentration of the benzene eluate gave 5.01 g (0.25%) of colorless needle-shaped crystals with mp 119-120° (from methanol), soluble in petroleum ether and alcohol, and insoluble in water, $[\alpha]_D^{16}$ + 272° (c 1.03; chloroform), R_f 0.98 (orange coloration). UV spectrum, λ_{max}: < 210, 252, 268, 327 mμ (log ε > 4.35, 3.60, 3.61, 4.27).

Found: C 69.90, 70.00; H 6.15, 6.43%; molecular weight (Rast) 295, 315, 330 g-equiv. Calculated for $C_{19}H_{20}O_5$: C 69.51; H 6.14%.

Preparation of zosimol. A mixture of 0.977 g of zosimin and 30 ml of 10% methanolic caustic potash was heated in a water bath for 2 hr, and then the alcohol was distilled off, and the residue was dissolved in water and acidified with 20% sulfuric acid. The precipitate which deposited was crystallized from methanol. This yielded needle-shaped crystals with mp 156-158°, R_f 0.15, $[\alpha]_D^{16}$ + 209.4° (c 0.74; chloroform). Yield 0.60 g. UV spectrum, λ_{max}: 220, 253, 262, 327 mμ (log ε 4.11, 3.25, 3.56, 4.17).

Found: C 66.64, 66.68; H 5.76, 5.88%. Calculated for 1/2 CH_3OH: C 66.40; H 6.14%.

Oxidation of zosimol. 3 ml of an aqueous solution containing 0.5 g of chromic anhydride was added to 0.3160 g of zosimol in 10 ml of acetic acid and the mixture was left for 3 days. The liquid was neutralized and 10 ml was distilled off. The distillate was treated with 5 ml of freshly distilled benzaldehyde in 5 ml of methanol and 5 drops of caustic soda solution. During a day, crystals of dibenzylideneacetone with mp 110° formed.

Preparation of cis-1, 2-dimethylacrylic acid. As described above, 2.14 g of zosimin was saponified with methanolic alkali. The filtrate after the separation of the zosimol was distilled to half its volume, and the distillate was saturated with sodium chloride and extracted with ether. After the solvent had been distilled off, colorless crystals with mp 61° were obtained. IR spectrum: 3520, 2940, 2870, 1697, 1490, 1385, 1345, 1320 cm^{-1}.

Found: C 60.07, 60.19; H 8.01, 8.09%. Calculated for $C_5H_8O_2$: C 59.99; H 8.05%.

Isolation of deltoin. After the elution of the zosimin, the chromatographic column was washed with 7 liters of a 19:1 mixture of benzene and methanol. Concentration of the eluate gave a mixture of crystalline substances with R_f 0.98 and 0.95, which was treated with petroleum ether. The residue was recrystallized from aqueous methanol. This gave 7.55 g (0.37%) of large cubic crystals with mp 104-106°, $[\alpha]_D^{16}$ – 55° (c 1.00; chloroform); R_f 0.95 (purple coloration).

Found: C 69.83, 69.91; H 6.36; 6.25%; molecular weight (Rast) 304, 328 g-equiv. Calculated for $C_{19}H_{20}O_5$: C 69.51; H 6.14%; molecular weight 328.

The spectra were taken by M. E. Perel'son, and the microanalyses were carried out by E. A. Nikonova.

Summary

Two isomeric dihydrofurocoumarins – zosimin and deltoin – have been isolated from the roots of Zosimia absinthifolia, which contain 3.2% of lactones.

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