A CHEMICAL STUDY OF ANGELICA SACHALINENSIS MAXIM.

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We have investigated the roots of Angelica sachalinensis Maxim. (Sakhalinian angelica), a perennial herbaceous plant of the Umbelliferae family growing in Sakhalin. A preliminary evaluation showed that the roots contained about 13.1% of lactones of the coumarin group consisting of a mixture of 11 components with R_f 0.97; 0.85; 0.79; 0.72; 0.62; 0.47; 0.38; 0.24; 0.18; 0.12; 0.0. This mixture, in the form of an amber-colored mass which caked on storage, did not undergo separation on vacuum distillation or on fractional crystallization.

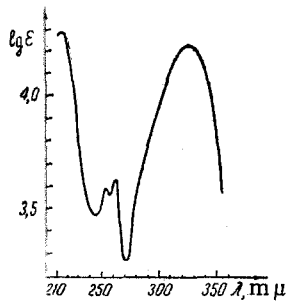

Fig. 1.

We isolated two individual substances by two-fold chromatography; $C_{29}H_{50}O$ (mp 130-132°) and $C_{18}H_{16}O_5$ (mp 132-134°). The third was neutral, gave the Lieberman-Burchardt reaction for steroids, and on drying in vacuum lost its solvent of crystallization with difficulty giving a product with mp 137-139°. The IR spectrum contained absorption bands of a hydroxyl group at 3444 and 3336 cm^{-1}, and this was confirmed by determining the labile hydrogen. From its IR spectrum and a mixed melting point, the substance was identified as β-sitosterol.

From its chemical properties, the second substance was a lactone of the coumarin group and from the UV spectrum (Fig. 1) it had the coumarin skeleton [1, 2]. The IR spectrum exhibited hydroxyl absorption bands, the presence of these being confirmed also by the determination of three atoms of labile hydrogen (Fig. 2). Attempts to methylate these hydroxyl groups with diazomethane and methyl iodide were unsuccessful. Acid hydrolysis with acetic and sulfuric acids gave a substance $C_{13}H_{12}O_4$ containing no hydroxyl groups. The IR spectrum of the product of acid hydrolysis exhibited a band at 1756 cm^{-1} corresponding to the carbonyl group of an ester (acetate) formed as a result of hydrolysis and subsequent acetylation of the hydroxyl group. Judging from the frequency of this band, it may be assumed that the hydroxyl group is not phenolic and is present in a side-chain, and the product formed consists of the acetate of coumarylethanol: $(C_9H_5O_2)$—CH_2CH_2OH. From its properties, the lactone obtained is a new coumarin; we have called it sakhalinin.

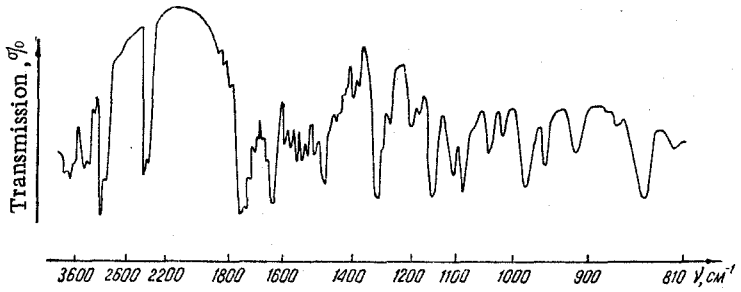

Fig. 2.

EXPERIMENTAL

The content of lactones was determined by a method described previously [3], and the labile hydrogen by the gasometric method [4]. Chromatography was carried out with a mobile phase consisting of cyclohexane-benzene-methanol (5:4:1) on paper impregnated with a 10% solution of formamide in methanol, and the spots were revealed by means of a 10% alcoholic solution of caustic potash and diazotization with a solution of sulfanilamide.

Isolation of β-sitosterol. The extraction of 10.2 kg of roots was carried out twice with 60-liter portions of 95% alcohol, and the extract was concentrated to 4 liters, diluted with 8 liters of water, and repeatedly treated with ether (1-liter portions). The ethereal extracts were evaporated to 1.5 liters, 5 liters of 15% alcoholic caustic potash was added, and the mixture was left for 48 hr. The liquid was diluted with water (1:1), extracted with ether (preextraction), acidified with 20% sulfuric acid, and again treated with ether. The ethereal extracts were washed with 5% sodium carbonate solution and evaporated to dryness. This gave 1 kg of a vitreous mass consisting of lactones.

One hundred grams of the lactones was chromatographed on a column of acidic Al_2O_3 (Brockman activity II) 80 cm high and 5.5 cm in diameter, the column being washed with 12 liters of benzene and 2 liters of methanol. The

methanolic eluate was concentrated and rechromatographed on a fresh portion of adsorbent, the column being washed with methanol containing 5% HCl. The eluate was concentrated and mixed with acetone (1:1). This gave almost 1 g of substance with mp 130-132° (from methanol) or 137-139° (anhydrous).

Found %: C 83.60, 83.10; H 12.32, 12.10; H (labile) 0.67, 0.54; mol. wt. (Rast) 347, 323. $C_{29}H_{50}O \cdot 1/4CH_3OH$. Calculated %: C 83.17; H 12.08.

Isolation of sakhalinin. After the removal of the β-sitosterol, the methanolic-acetonic filtrate was evaporated to dryness in vacuum, and the residue was dissolved in water and extracted with ether. Concentration of the extract gave 2.5 g of a crystalline substance with mp 132-134° (from methanol), R_f = 0.12. The lactone is readily soluble in chloroform, less readily in alcohol, and insoluble in water.

Found %: C69.10, 69.15; H 5.24, 5.19; H (labile) 0.89; 0.86; mol. wt. 257, 292. $C_{18}H_{16}O_5$. Calculated %: 23; C 69.23; H 5.12: 3 H (labile) 0.96; mol. wt 3.12.

UV spectrum: λ_{max} 214; 252; 261; 325 mμ (log ε > 4.29; 3.58; 3.64; 2.22).

IR spectrum: 3384; 3324; 3160 (hydroxyl), 1739 (carbonyl of a lactone); 1626; 1582 (aromatic nucleus); 898; 855; 831 cm^{-1}.

Acid hydrolysis of sakhalinin. Ten drops of conc. H_2SO_4 was added to 0.113 g of substance in 8 ml of acetic acid. The solution was heated in a water bath for 6 hr. The mixture was diluted with water and extracted with ether, and the extract was evaporated to dryness. This gave about 0.05 g of substance with mp 70.5-71° (from aqueous methanol).

Found %: C 67.49; 67.61; H 5.06; 5.39; mol. wt. 222, 248. $C_{13}H_{12}O_4$. Calculated %: C 67.24; H 5.17.

IR spectrum: 1756 (carbonyl of an ester); 1732 (carbonyl of a lactone); 1655; 1624; 905; 841; 828 cm^{-1}.

SUMMARY

The presence of lactones of the coumarin group, consisting of a mixture of 11 components, has been established in the roots of Sakhalinian angelica. From the lactone fraction a new coumarin $C_{18}H_{16}O_5$ has been isolated which has been given the name sakhalinin and is, apparently, an ester of coumarylethanol, together with β-sitosterol.

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