XANTHOGALIN — A NEW COUMARIN FROM XANTHOGALUM PURPURASCENS LALLEM.

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In a study of the roots of Xanthogalum purpurascens - a perennial herbaceous plant of the Umbelliferae family - collected in the region of Dombaiskaya Polyana (southern Caucasus), we have isolated 6.6% of lactones of the coumarin group consisting of a mixture of ten substances with R_f values 0.93, 0.83, 0.75, 0.70, 0.57, 0.42, 0.35, 0.25, 0.08, 0.03.

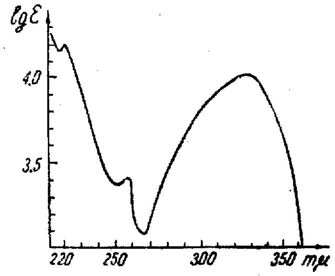


Fig. 1. UV spectrum of xanthogalin

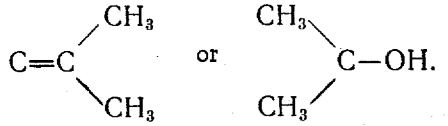
In a chemical study of an alcoholic extract, we isolated a lactone $C_{19}H_{20}O_5$ which was, from its properties and UV spectrum (Fig. 1), a coumarin [1-3]. The lactone contained no mobile hydrogen or methoxy groups, and did not react with carbonyl reagents. The IR spectrum had absorption bands of a lactone carbonyl group (1722 cm^{-1}) and an aromatic nucleus (1610, 1580, 1495 cm^{-1}).

The broad carbonyl band did not exclude the presence of an ester grouping (Fig. 2); judging from its properties, this lactone is a new coumarin which we have called xanthogalin.

The alkaline saponification of xanthogalin gave a lactone $C_{14}H_{14}O_4$, designated xanthogalol, and an unsaturated acid $C_5H_8O_2$ identified by its IR spectrum as trans-1, 2-dimethylacrylic acid. The IR spectrum of xanthogalol (Fig. 2) exhibits bands of a hydroxyl group (3520 cm^{-1}), the presence of which is confirmed by the identification of one atom of labile hydrogen and by the production of a monoacetate, the carbonyl group of a hydroxylactone (1705 cm^{-1}), and an aromatic nucleus (1610, 1582, and 1476 cm^{-1}). The position of the carbonyl band in the IR spectrum of xanthogalol acetate (1747 cm^{-1}) shows the non-phenolic nature of the acetylated hydroxyl group.

In the degradative methylation of xanthogalin with subsequent saponification [2], we obtained o-methoxyxanthogalic acid $C_{16}H_{20}O_5$ with mp 203-204°. Its formation can be explained by the saponification of xanthogalin, the opening of the lactone ring, the methylation of the hydroxyl and carboxyl groups, and the saponification of the methoxycarbonyl group. The production of this acid confirmed that xanthogalin belongs to the coumarin group.

The oxidation of xanthogalin with chromic acid gave acetone identified in the form of dibenzylideneacetone, which showed the presence of the grouping



$$C{=}C(CH_3)_2 \quad \text{or} \quad (CH_3)_2C{-}OH.$$

The investigations carried out show that xanthogalin is an ester of angelic acid and an optically active hydroxylactone containing a hydroxyl group in a side-chain and a $(CH_3)_2C$ —grouping. Of the five oxygen atoms of xanthogalin, two occur in the lactone ring and two have the form of an ester group. Judging from the absence of carbonyl, methoxyl, and hydroxyl groups it may be assumed that the fifth oxygen atom is in a 5- or 6-membered ring or is present in the form of an ether.

Experimental

Paper chromatography. Mobile phase: cyclohexane-benzene-methanol (5:4:1) on paper impregnated with a 10% solution of formamide in methanol; revealing agent - diazotized sulfanilamide [4]. The IR spectra were taken on a UR-10 spectrograph (suspension of the substance in vaseline oil), and the UV spectra on a SF-4 spectrometer.

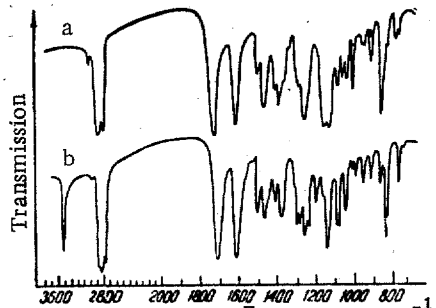


Fig. 2. IR spectra of xanthogalin (a) and xanthogalol (b)

Isolation of xanthogalin. Two kilograms of the dried and comminuted roots were extracted twice with 12-liter and 8-liter portions of alcohol. The extracts were concentrated in vacuum to 500 ml, filtered from the deposit of sugars, diluted with 1 liter of water, and extracted with ether (5 × 250 ml). Distillation of the ethereal extract gave 32.1 g (1.6%) of a yellowish substance which was twice recrystallized from methanol and then from a mixture of ethyl ether and petroleum ether. Coarse colorless cubic crystals with mp 100-125.5°, $[\alpha]_D^{16}$ −41.4° (c 1.6; chloroform), R_f 0.93. The substance is readily soluble in alcohol, chloroform, and ether, and is insoluble in water.

Found %: C 69.18, 69.30; H 6.20, 6.12; M 325 (Rast). Calculated % for $C_{19}H_{20}O_5$: C 69.54; H 6.14.

UV spectrum: λ_{max}: 220, 257, 328 mμ (lg ε 4.17; 3.38; 4.01).

Preparation of xanthogalol. One gram of xanthogalin was dissolved in 30 ml of a 1 N solution of caustic potash in methanol. The mixture was heated for 2 hr in a boiling water bath, diluted with water, acidified with 10% sulfuric acid, and extracted with three 25-ml portions of ethyl ether. Distillation of the ethereal extracts gave a crystalline substance with mp 183-185° (from methanol), $[\alpha]_D^{16}$ + 13.7 (c 0.9; chloroform), R_f 0 20.

Found %: C 68.08, 68.45; H 5.91, 5.94; H_{act} 0.60, 0.57; M 261 (Rast). Calculated % for $C_{14}H_{14}O_4$: C 68.29; H 5.58; H_{act} 0.71.

Xanthogalol acetate was obtained by heating the substance with acetic anhydride and fused sodium acetate for 3 hr. Needlelike crystals with mp 138.5-140° deposited.

Found %: C 66.56, 66.99; H 5.76, 5.84. Calculated % for $C_{16}H_{16}O_5$: C 66.66; H 5.55.

IR spectrum: 1747, 1626, 1577 cm^{-1}.

Production of angelic acid. One gram of xanthogalin was saponified with aqueous alkali as described above. The liquid was diluted with twice its volume of water, the alcohol was distilled off, the residual aqueous alkaline solution was acidified, and the xanthogalol which deposited was filtered off. The filtrate was evaporated, and the distillate was saturated with sodium chloride and treated with ether. Concentration of the ethereal extract gave a syrupy crystallizing mass with a characteristic odor, readily solubile in water, alcohol, and ether.

Found %: C 60.02, 60.07; H 7.69, 7.92; H_{act} 0.80, 0.79. Calculated % for $C_5H_8O_2$: C 59.99; H 8.05; H_{act} 1.01.

IR spectrum: 3526:, 1695, 1650, 1465, 1425, 1385, 1355, 1280, 1165, 1090 cm^{-1}.

Production of o-methoxyxanthogalic acid. A mixture of a solution of 0.75 g of xanthogalin in 6.6 ml of 5% sodium methoxide solution and 1.7 ml of a solution of dimethyl sulfate in methanol was shaken until the dimethyl sulfate dissolved, and then more sodium methoxide and dimethyl sulfate were added (15 times). The methanol was distilled off in vacuum, and the residue was dissolved in 50 ml of water and extracted with ether. The alkaline solution was acidified with 20% sulfuric acid and extracted with ether. The residue after the distillation of the ether was dissolved in 30 ml of a 10% solution of caustic potash in methanol, and the mixture was boiled for 2 hr. The methanol was distilled off, the residue was dissolved in water, and the solution was acidified with sulfuric acid and treated with ether. The acid was extracted from the ethereal solution with 5% sodium carbonate solution. The extract was acidified and treated with ether. The elimination of the ether gave a crystalline substance with mp 203-204° (from aqueous methanol), readily soluble in water. Yield 0.2 g.

Found %: C 65.59, 65.77; H 6.77, 6.96; H_{act} 0.14. Calculated % for $C_{16}H_{20}O_5$: C 65.76; H 6.89; H_{act} 0.34.

IR spectrum: 2727, 2630, 1686, 2636, 1582, 1261 cm^{-1}.

Oxidation of xanthogalin with chromic acid. A solution of 0.5 g of chromic anhydride in 5 ml of water was added to 0.5 g of the substance in 20 ml of acetic acid and the mixture was left for 3 days. The liquid was neutralized with 20% alkali and 10 ml was distilled off. To 5 ml of the distillate were added 5 ml of methanol and 4 drops each of freshly-distilled benzaldehyde and 10% caustic soda solution. The precipitate which deposited after a day was filtered off and washed with water. The crystals separated had mp 111-112.5°

Found %: C 86.80; H 6.16. Calculated % for $C_{17}H_{14}O$: C 87.14; H 6.02.

Summary

A new coumarin $C_{19}H_{20}O_5$, designated xanthogalin, has been isolated from the roots of Xanthogalum purpurascens. It is an ester of a new hydroxycoumarin, xanthogalol $C_{14}H_{14}O_4$, and trans-1, 2-dimethylacrylic (angelic) acid.

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