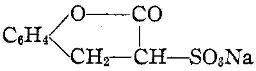
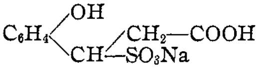
Some Derivatives of Coumarin. II.—The reaction of coumarin with acid sulfite solutions was found by the writer[1] to result in the formation of sulfonic derivatives of hydrocoumarin, the sodium salt, for example, having the composition $NaSO_3C_9H_7O_2 \cdot H_2O$, and probably the structure



More recently, Dey and Row[2], by treating coumarin with sodium sulfite and subsequent acidification, obtained a salt $NaSO_3C_9H_9O_3 \cdot H_2O$, to which they assigned the structure



Inasmuch as the writer had not previously observed the occurrence of an acid salt of this type, and Dey and Row make no reference to the lactone salt already described, it seemed desirable to repeat some of this work in order to characterize more exactly the salt or salts in question. The result of the examination has confirmed the previous work of the writer, and also, to a certain extent, that of Dey and Row.

The lactone salt is obtained by treating coumarin with a solution of sodium acid sulfite. It crystallizes in flat prisms with rectangular ends, under the microscope apparently orthorhombic. The crystals effloresce at the ordinary temperature, and are soluble in about five parts of water at 20°. The fresh solution is neutral to litmus and gives no color with ferric chloride. Addition of salt to the solution precipitates the lactone salt almost completely.

The acid salt is readily prepared as follows: coumarin (20 g.) is dissolved, by moderate heating, in about 100 g. of sodium sulfite solution (25% $Na_2SO_3 \cdot 7H_2O$). If the solution becomes alkaline to phenolphthalein, it may be neutralized with acid sulfite. When all the coumarin is dissolved, the solution is filtered, diluted to about 160 g., 35 cc. of about 4 *N* hydrochloric acid added and the mixture allowed to crystallize in the cold, or, if large crystals are desired, by slow evaporation at the ordinary temperature.

The acid salt is deposited in large transparent prisms with pyramidal terminations, or, more rarely, in rhombic prisms with basal planes. Sections perpendicular to the prism faces show in convergent polarized light the characteristic interference figure of orthorhombic crystals. The crystals contain $3H_2O$, do not effloresce and are soluble in about three parts of water at 20°. The solution is strongly acid and is not precipitated by the addition of salt.

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[1] Dodge, THIS JOURNAL, **38**, 446 (1916).

[2] Dey and Row, *J. Chem. Soc.*, **125**, 554 (1924).

Anal. 2.00 g. at 105–110° lost 16.63%, 2.001 g. lost 16.55% of water. Calcd. for $3H_2O$: 16.77%. *Titration.* Subs., 1.998, 1.667, 1.4365: 12.4, 10.8, 9.0 cc. of 0.5 *N* KOH. Calcd. acid value: 170.8. Found: 173, 181, 175. Subs., 1.998: Na_2SO_4, 21.4%. Calcd.: 22%.

The slightly high acid values are probably due to the phenolic hydroxyl, as similar high values are obtained in titrating coumaric acid.

The writer was unable to obtain the monohydrated salt described by Dey and Row. In several batches, however, the large prisms were accompanied by groups of silky needles, which could not be readily purified; these also often appear in recrystallizing the pure trihydrate.

With ferric chloride solution the acid salt gives a very characteristic bright blue coloration. A *fresh* solution of the lactone salt shows, as already stated, no color with this reagent. If, however, the solution is allowed to stand, after a few hours a greenish-blue color is obtained, and after twenty-four hours, a bright blue, indistinguishable from that of the acid salt. This indicates that the lactone salt, in solution, is gradually hydrolyzed to the acid salt, which is exactly what would be expected. For the hydrocoumarin ring, being a saturated δ-lactone, has no longer the characteristic stability of the coumarin ring, but in solution tends to an equilibrium between lactone and acid.

Excess of mineral acid throws the equilibrium point toward the lactone stage, which explains the fact that from the mother liquor of the trihydrate acid salt, some lactone salt can be obtained by salting out.

Very strong acid causes a partial hydrolysis to coumarin. For example, 10 g. of concentrated hydrochloric acid was added to a solution of 6 g. of acid salt in 10 g. of warm water and the mixture evaporated to dryness. On dissolving the residue in 30 cc. of water, 0.8 g. of coumarin remained; the filtrate on addition of salt gave an abundant precipitate of lactone salt.

On heating above 120°, the acid salt, like the lactone salt, yields coumarin.

Summary.—From coumarin, by addition of sodium bisulfite, two distinct salts are obtained: one, a lactone corresponding to hydrocoumarin, the other an acid salt corresponding to hydrocoumaric acid.

CONTRIBUTION FROM THE
LABORATORY OF THE
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RECEIVED DECEMBER 3, 1929
PUBLISHED APRIL 7, 1930