

## Lactitol Dihydrate

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Senderens,<sup>2</sup> who was the first to crystallize lactitol, reported it as a monohydrate of m.p. 78° and  $[\alpha]_D +12.2^\circ$  (water). In our experiences with lactitol a monohydrate has not been detected but instead an anhydrous form and a dihydrate have crystallized.

Lactitol was obtained crystalline<sup>3</sup> from dilute alcohol in the laboratories of The Ohio State University as an anhydrous form; m.p. 146°,  $[\alpha]^{23}_D +14^\circ$  (c 4, water). This form is now found to be metastable and in current preparations in both the Columbus and Bethesda laboratories a hydrated form is obtained; m.p. 72.5–74°,  $[\alpha]^{20}_D +11.5^\circ$  (c 4.5, water). This substance is a dihydrate.

*Anal.* Calcd. for  $C_{12}H_{24}O_{11} \cdot 2H_2O$ : C, 37.87; H, 7.42. Found: C, 37.87; H, 7.60.

Xylitol was first crystallized in the Columbus laboratory<sup>4</sup> as a hygroscopic, metastable form of m.p. 61°. Later preparations in that laboratory and in others now yield the stable dimorph of m.p. 93–94.5°.<sup>5</sup>

(1) Deceased, April 30, 1949.

(2) J. B. Senderens, *Compt. rend.*, **170**, 47 (1920).

(3) M. L. Wolfrom, W. J. Burke, K. R. Brown and R. S. Rose, Jr., *THIS JOURNAL*, **60**, 571 (1938); therein designated "lactositol."

(4) M. L. Wolfrom and E. J. Kohn, *ibid.*, **64**, 1739 (1942).

(5) J. F. Carson, S. W. Waisbrot and F. T. Jones, *ibid.*, **65**, 1777 (1943).

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## 2-Hydroxymethyl-5-hydroxy-6-benzoyl-4-pyrone<sup>1</sup>

By L. L. Woods

A theoretical consideration of the structure of 4-pyrones and an extension of the observations of Wheland<sup>2</sup> indicates that in the presence of acidic reagents polarization of the ring would activate positions 3 and 6. Since the separation of the formal charge between 1 and 3 is great, position 6 should be considerably more active than position 3. If such considerations are valid then acylation in position 6 should be easily effected and demonstrable.

However, the demonstration of the validity of this theory has not been easy due to the fact that kojic acid reacts with benzoyl chloride in the presence of fuming stannic chloride to form chiefly O-benzoylkojic acid.

Experiments have demonstrated that the benzoyl derivative of kojic acid formed by the influence of stannic chloride was not a C-benzoyl compound since it failed to give a chloro derivative with thionyl chloride, failed to participate in a Clemmensen reduction, and failed to be reduced by aluminum isopropoxide.

(1) The author is indebted to the Corn Products Company for the kojic acid used in these experiments and to the Research Corporation for a grant-in-aid on this project.

(2) G. W. Wheland, "The Theory of Resonance," John Wiley and Sons, Inc., New York, N. Y., p. 135.

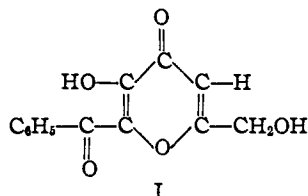
The reaction of kojic acid with benzoyl chloride in the presence of aluminum chloride gave the desired C-acylation. The probable structure 2-hydroxymethyl-5-hydroxy-6-benzoyl-4-pyrone (I) has been assigned to the product.

### Experimental<sup>3</sup>

**O-Benzoylkojic Acid.**—A mixture consisting of 5 g. of kojic acid, 25 ml. of benzoyl chloride and 5 g. of fuming stannic chloride was heated in a Fisher Hi-Temp oil-bath for 4 hours at 74°.

The mixture was then treated with 50 ml. of water and shaken thoroughly; the excess benzoyl chloride was destroyed with about 150 ml. of cold 10% sodium hydroxide. The insoluble material was filtered off, washed repeatedly and air-dried. The crude yield was 12 g. A portion of the crude solid was recrystallized twice from absolute ethanol and analyzed. *Anal.* C, 65.66; H, 4.01. This composition does not conform to any of the calculated derivatives of benzoyl chloride with kojic acid.

Ten grams of the crude solid was placed in a mixture of 75 ml. of ethanol, 40 ml. of water and 5 ml. of concentrated hydrochloric acid, and heated at gentle reflux for 17 hours. The hot solution was decolorized with Norite, filtered and



chilled in the refrigerator overnight; yield 6 g., yellow rosettes. The analytical sample was recrystallized from ethanol, m.p. 128–130°.

*Anal.* Calcd. for  $C_{13}H_{10}O_5$ : C, 63.41; H, 4.06. Found: C, 63.70; H, 3.94.

The compound in an alcohol-water mixture developed a red color with ferric chloride.

**2-Hydroxymethyl-5-hydroxy-6-benzoyl-4-pyrone (6-Benzoylkojic Acid).**—To 200 ml. of carbon disulfide was added 14.2 g. of kojic acid and 40 g. of anhydrous aluminum chloride. The mixture was thoroughly agitated while 15 g. of benzoyl chloride was added from a separatory funnel. The stirring was discontinued in about 20 minutes and, after fully protecting the contents of the flask from atmospheric moisture, the reaction was allowed to proceed at room temperature for 24 hours.

At the end of the reaction period the carbon disulfide was decanted and the residual solid treated with a mixture of 100 ml. of concentrated hydrochloric acid and 100 g. of shaved ice. The solid particles were filtered off and dried. The yield was 9.8 g. after recrystallizing twice from absolute ethanol; m.p. 188°. The compound gave a red coloration with ferric chloride.

*Anal.* Calcd. for  $C_{13}H_{10}O_5$ : C, 63.41; H, 4.05. Found: C, 63.12; H, 4.30.

**Clemmensen Reduction.**—6-Benzoylkojic acid was subjected to Clemmensen reduction by allowing 4 g. of the ketone to react with amalgamated zinc and hydrochloric acid in a solvent mixture of 20 ml. of ethanol and 30 ml. of water.

The reflux time was 7 hours. The mixture was filtered into a crystallizing dish and allowed to stand several days. A rather large amount of soft yellow needles separated; after recrystallization from benzene, in which the (2-hydroxymethyl-5-hydroxy-4-pyrone-6)-phenylmethane was quite soluble, a yield of 1.4 g. was obtained; m.p. 78–80°.

*Anal.* Calcd. for  $C_{13}H_{12}O_4$ : C, 67.24; H, 5.17. Found: C, 67.02; H, 5.31.

**Reaction with Thionyl Chloride.**—A small amount of the compound was allowed to react with a large excess of thionyl chloride in hexane. The hexane and excess thionyl chloride were decanted, and the residual chloro derivative was washed once with hexane. The compound, 2-chloromethyl-5-hydroxy-6-benzoyl-4-pyrone, was recrystallized from ethanol to produce golden yellow crystals; m.p. 185–187°.

(3) All analyses are by Dr. Carl Tiedcke. All melting points were made on a Fisher-Johns melting point assembly.