

a trace of anhydrous copper sulfate and a drop of benzyl cyanide at 150° for six hours. After cooling, dry acetone (100 cc.) was added and the mixture filtered. Removal of the acetone followed by vacuum distillation gave 41.5 g. of benzyl cyanide, b. p. 119–122° (26 mm.).

No appreciable reaction was observed between benzyl chloride and cuprous cyanide at 100° after five hours.

The Action of Cuprous Cyanide on *p*-Methoxybenzyl Chloride.—The addition of *p*-methoxybenzyl chloride (44 g.) to cuprous cyanide (26 g.) at room temperature gave an instantaneous reaction accompanied by heat and gas evolution and the production of a tar. Carrying out the reaction in dry pyridine at –5° and then allowing the mixture to come to room temperature, likewise gave a tar. Treating *p*-methoxybenzyl chloride (26 g.) in acetone (30 cc.) with dry cuprous cyanide (15 g.) at –70° gave no reaction. When the mixture was allowed to reach room temperature, it reacted with an evolution of gas and the formation of a tar.

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The Solubility, Absorption Spectrum and Ionization Constant for Aloe-Emodin

BY K. G. STONE AND N. HOWELL FURMAN

In connection with some other work, it was necessary to know the apparent ionization constant of aloe-emodin. As part of the determination, the solubility and spectrum were required. The results of these measurements are reported here.

Experimental

The aloe-emodin used was prepared by the ferric chloride oxidation of Merck U. S. P. Aloin as described by Cahn and Simonsen.¹ The product after recrystallization from toluene melted at 218° (uncor.). The 0.1 *M* borax-sodium carbonate buffers described by Kolthoff and Vleschouwer² were prepared from c.p. materials which were analyzed where necessary.

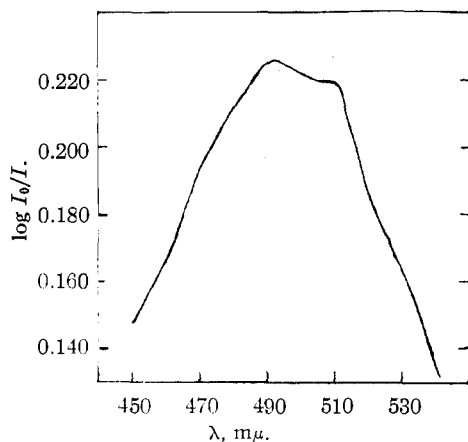


Fig. 1.—Aloe-emodin in pH 11 buffer; concentration, 0.20 mg. per ml.

Optical measurements were made with a Cenco-Sheard Spectrophotometer with an effective slit width of ten millimicrons and 1.0-cm. Corex cells. In all cases solutions containing all reagents except the aloe-emodin were used

(1) R. S. Cahn and J. L. Simonsen, *J. Chem. Soc.*, 2573 (1932).

(2) E. M. Kolthoff and J. J. Vleschouwer, *Biochem. Z.*, **189**, 191 (1927).

as blanks. All volumetric glassware was discarded if it did not meet the customary tolerances.

Saturated solutions of aloe-emodin in the buffer solutions were prepared by intermittent shaking of the buffer with solid aloe-emodin in a glass-stoppered flask in a water-bath at 25.0 ± 0.1°. Standard solutions for colorimetric calibration were prepared by dissolving weighed quantities of aloe-emodin in known volumes of buffer solutions.

Results

The spectrum of aloe-emodin in 0.1 *M* borax-sodium carbonate buffer of pH 11 is given in Fig. 1. The spectra in the buffers of other pH values were almost identical with the spectrum given. Beer's law was followed in all cases in the region from 480 to 510 millimicrons with concentrations up to 0.04 mg. per ml. where the measurements become uncertain.

The solubility measurements given in Table I were obtained by colorimetric analysis of the saturated solutions after dilution with pure buffer if necessary.

TABLE I

SOLUBILITY OF ALOE-EMODIN IN 0.1 *M* BORAX-SODIUM CARBONATE BUFFERS

pH	Moles/liter × 10 ⁵
9.8	7.60
10.0	9.63
10.4	14.8
10.8	28.7
11.0	43.3

The apparent ionization constant of aloe-emodin may be calculated graphically using the method of Davidson.³ By this method it was found that the intrinsic solubility of aloe-emodin is 5.5 × 10⁻⁵ mole per liter and that the apparent *K*_A is 6.8 × 10⁻¹¹.

(3) D. Davidson, *J. Chem. Ed.*, **19**, 221 (1942).

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The Acetylation of *o*-, *m*- and *p*-Nitroacetophenones by the Boron Trifluoride Method¹

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Burgess² reported that the acylation of acetone with ethyl *p*-nitrobenzoate using sodium amide produced only a poor yield of the corresponding β-diketone. The acetylation of *m*-nitroacetophenone with ethyl acetate by this basic reagent method has also been unsatisfactory.³ On the other hand it seemed probable that the acetylation of nitroacetophenones with acetic anhydride by the boron trifluoride method⁴ would be satis-

(1) Paper XXXV on "Condensations"; paper XXXIV, THIS JOURNAL, **68**, 760 (1946).

(2) Burgess, *J. Chem. Soc.*, 2017 (1927).

(3) Mr. D. F. Thompson of this Laboratory obtained apparently none of the β-diketone using sodium amide.

(4) (a) Meerwein and Vossen, *J. prakt. Chem.*, **141**, 157 (1934); (b) Hauser and Adams, THIS JOURNAL, **66**, 345 (1944).