

with ether and the oil left after removing the ether was distilled under reduced pressure. There was obtained a 45.7% yield (based on the diazonium fluorosulfonate) of nearly colorless oil, distilling at 135–137° (5 mm.);  $d_{25}^{25}$  1.2905;  $n_D^{25}$  1.5508. When cooled to  $-78^\circ$  the oil crystallized, m. p. 33–34.5° (uncor.). The compound had a slightly aromatic odor and was soluble in acetone, methanol, chloroform, benzene and hexane; it was insoluble in

water and ethylene glycol.

*Anal.* Calcd. for  $C_{12}H_9SO_3F$ : F, 7.53; hydrolysis value, 7.59 ml. of 0.5221 *N* NaOH. Found: F, 7.40; hydrolysis value, 7.27 ml. of 0.5221 *N* NaOH.<sup>3</sup>

CENTRAL RESEARCH DEPARTMENT  
MONSANTO CHEMICAL COMPANY  
DAYTON, OHIO

MARY W. RENOLL

RECEIVED MARCH 2, 1942

## COMMUNICATIONS TO THE EDITOR

### THE SYNTHESSES OF LACTOSE AND ITS EPIMER

*Sir:*

Referring to our articles which describe the syntheses of epi-cellobiose and cellobiose [THIS JOURNAL, **63**, 1724 (1941); **64**, 1289 (1942)], we now report that the combination of acetone-D-mannosan with acetobromo-D-galactose has been accomplished, and that by reactions which are entirely like those used in the indicated syntheses, we have produced, first, the epimer of lactose and, second, lactose itself. The yield of synthetic crystalline  $\alpha$ -epi-lactose octaacetate by the indicated combination was 30% and the deacetylation of the octaacetate generated synthetic epi-lactose which is identical with that produced from lactose. Synthetic epi-lactose octaacetate was converted to acetobromo-epi-lactose, which was in turn reduced to the known lactal hexaacetate, from which  $\beta$ -lactose octaacetate was obtained in good yield by oxidation with perbenzoic acid, followed by acetylation. Deacetylation of this octaacetate generated lactose. Publication of the full details will follow. The syntheses of epi-lactose and lactose were announced at the Memphis meeting of the Society in the Division of Organic Chemistry, April 21, 1942.

DIVISION OF CHEMISTRY  
NATIONAL INSTITUTE OF HEALTH  
BETHESDA, MARYLAND

W. T. HASKINS  
RAYMOND M. HANN  
C. S. HUDSON

RECEIVED MAY 14, 1942

### POLAROGRAPHIC DETERMINATION OF CITRININ<sup>1</sup>

*Sir:*

In view of the growing interest in anti-bacterial substances obtained from molds,<sup>2</sup> it seems desir-

(1) Taken from the thesis of H. W. Hirschy, submitted in partial fulfillment for a Master's Degree in Chemistry, June, 1941.

(2) (a) Abraham, Baker, Chain, Florey, Holiday and Robinsou. *Nature*, **149**, 356 (1942); (b) Dawson, Hobby, Meyer and Chaffee. *Jour. Clin. Invest.*, **20**, 433 (1941); (c) Oxford, Raistrick and Smith. *Chem. and Ind.*, **61**, 22 (1942); (d) Raistrick and Smith, *ibid.*, **60**, 828 (1941); (e) Waksman. *Bact. Rev.*, **5**, 253 (1941); (f) Wiesner. *Nature*, **149**, 356 (1942)

able to publish at this time the results of some preliminary physico-chemical studies on the metabolic product of *Penicillium citrinum*: namely, citrinin, which recently has been shown to inhibit the growth of *Staphylococcus aureus*.<sup>2d</sup>

Citrinin,  $C_{13}H_{14}O_5$ , a yellow crystalline solid, m. p. 170–171° (with decomposition), was isolated and purified by the method of Hethering and Raistrick.<sup>3</sup> It was obtained from the culture, *P. citrinum* #136–5730.6.<sup>4</sup> The characteristic properties of our product were in good agreement with those reported previously.<sup>3</sup>

We have found that citrinin in concentrations of 0.001–0.003 *M* gives well-defined current-voltage curves at the dropping mercury cathode in acid, 75% ethanol solutions, buffered and unbuffered. The limiting current was found to be proportional to the concentration of citrinin. The half-wave potential in the buffered alcoholic solution (*pH* 2.05) is in the range of  $-0.80$  to  $-0.82$  volt applied *versus* the saturated calomel reference electrode. Citrinin is also reduced in 0.1 *N* KCl–75% ethanol solution. It is not reduced in acetate alcoholic buffer (*pH* 6.0) nor in phosphate alcoholic buffer (*pH* 7.4). The manual apparatus used in these studies was similar to that described previously.<sup>5</sup> Attempts to use standard potentiometric procedures with  $TiCl_3$ <sup>6</sup> as a reducing agent proved unsuccessful since stable potentials were never reached within a reasonable and workable length of time.

(3) Hethering and Raistrick, *Roy. Soc. Phil. Trans.*, **B220**, 269 (1931).

(4) Furnished through the courtesy of Dr. K. B. Raper, U. S. Department of Agriculture. The A. T. C. collection #6202 failed to give little more than traces of citrinin.

(5) Smith, Kolthoff, Wawzonek and Ruoff, THIS JOURNAL, **63**, 1018 (1941).

(6) (a) Kolthoff and Furman, "Potentiometric Titrations," John Wiley and Sons, Inc., New York, N. Y., 1931, p. 355; (b) Knecht and Hibbert, "Volumetric Analysis," Longmans, Green and Co. London, 1925, p. 53.

In addition, citrinin was found to be a fairly strong acid ( $K_a$   $5.5 \times 10^{-4}$  at  $21^\circ$  in 95% ethanol). Using a Beckman pH meter, Model M, we noted that below a pH of 4.6 the solution of citrinin was colored a characteristic bright lemon-yellow with green fluorescence. At pH 4.6, the color began to fade and at pH 5.6–5.8 it changed sharply to an orange-pink. Above pH 9.9 the color again changed sharply from an orange-pink to a cherry-red.

Investigations on citrinin and on synthetic compounds believed to be related structurally to citrinin are being continued.

We wish to acknowledge our appreciation to Professor C. C. Carpenter, Plant Science Department, Syracuse University, for assistance rendered in the microbiological procedures.

DEPARTMENT OF CHEMISTRY  
SYRACUSE UNIVERSITY  
SYRACUSE, N. Y.

H. W. HIRSCHY  
P. M. RUOFF

RECEIVED MAY 18, 1942

## NEW BOOKS

**The Technology of Natural Resins.** By C. L. MANTELL, Ph.D., Consulting Chemical Engineer, Director, Netherlands Indies Laboratories, and C. W. KOPF, B.Ch.E., J. L. Curtis and E. M. Rogers, B.A., Associates, Netherlands Indies Laboratories, New York. John Wiley and Sons, Inc., 440 Fourth Ave., New York, N. Y., 1942. vii + 506 pp. 81 figs.  $15.5 \times 23.5$  cm. Price, \$7.00.

The title of this volume is a little misleading as two of our most important natural resins, common rosin and shellac, are not included. The authors state: "Although an extensive literature exists on the synthetic resins, a corresponding development of the much older field of the natural materials is lacking. Volumes specifically devoted to shellac and rosin are in existence, but there is a decided gap in our technical literature concerning the important damar, copal, East India, and related resins from the viewpoint of their properties, their applications, industrial uses, development, and technology. This volume is an attempt to fill the gap."

The volume contains much information not published elsewhere or found only in scattered special articles.

One is reminded that the source territory of many of the natural resins discussed by the authors is now held by Japan. Our supply of Manila copal, damar, elemi and the East Indies batu, black and pale, are cut off for the duration. Much of our supply of shellac is similarly cut off.

The authors discuss the value of these natural resins in lacquer formulation and claim that in lacquer and oil varnishes they have not been satisfactorily replaced by synthetic resins. The present war situation of course requires their replacement by synthetic or other materials.

In the discussion of the removal of coloring matter from resins in solution by filtering through fuller's earth, it is implied that the loss by adsorption of resin by the earth precludes the commercial use of such a method. However, rosin in naphtha solution has successfully been decolorized in this way on a large scale for many years.

Technical monographs on special subjects, bringing the subject matter up to date, are always welcome, particularly when well done as in this volume. The authors are naturally interested in promoting the use of the particular

natural resins in which they are commercially interested. The book, however, is not less valuable on that account.

B. T. BROOKS

**Qualitative Analysis.** By H. V. ANDERSON, B.Ch.E., M.S., Professor of Chemistry, and T. H. HAZLEHURST, A.B., Ph.D., Associate Professor of Chemistry, Lehigh University. Third, revised edition. Prentice-Hall, Inc., 70 Fifth Avenue, New York, N. Y., 1941. xi + 266 pp. 14 figs.  $15.5 \times 23.5$  cm. Price, \$3.70.

In revising the second edition of this popular text [reviewed in *THIS JOURNAL*, 60, 2010 (1938)], the authors state that "certain changes in the presentation . . . have seemed advisable: . . . a more thorough treatment of acid-base reactions . . . and also a more detailed discussion of oxidation-reduction reactions and their analogy to acid-base reactions. . . . While endorsing the modern swing to semimicro technique, . . . in making this edition available to schools using semimicro methods, no change in the scheme of analysis has been advanced. . . . Therefore, along with the directions for procedures on the usual scale, there appear . . . quantities and occasionally special notes appropriate to semimicro methods. . . . Ionic equations have been used regularly. . . ." A slight increase in page length has more than taken up the small expansion, to give ten fewer pages.

The subject is presented under the chapter headings: Fundamental Theory, Solutions, Le Chatelier's Principle, Theory of Precipitation—The Solubility Product Principle, The Physical Process of Precipitation, Acids and Bases, Oxidation and Reduction, Cations of Groups I, II, III, IV and V, Reactions of Anions, Analysis of Solutions, Solids and Alloys, Appendix. The text treatment and literary presentation are clear and direct; well-planned format and good typography combine to produce an attractive book, its appearance being marred slightly by use of full capitals for certain terms (AWU, SPC, SOLID, LIQUID, etc.) and the cutting in of ionic charge symbols directly over subscripts instead of following them (which must have caused the typesetters hours of unnecessary labor).

ALLEN D. BLISS