to 25 cc. gave $\alpha_{5893}^{20}$ +0.95° in a 2-dc. tube; $[\alpha]_{5893}^{20}$ +288°. The rearrangement of the incompletely resolved *l*-amide, $[\alpha]_{5893}^{20}$ −13.8°, was also studied. The corresponding crystalline amine so produced melted at 201–206°; 0.0870 g. dissolved in ethyl alcohol (95%) and made up to a total volume of 25 cc. gave $\alpha_{5893}^{20}$ −0.61° in a 2-dc. tube; $[\alpha]_{5893}^{20}$ −87.7°.

*Anal.* Calcd.: N, 13.6. Found: N, 13.8.

## Conclusions

The Hofmann rearrangement of the amide of an optically active 2,2′-disubstituted 6-carboxydiphenyl has been studied. The corresponding amine so produced was found to be optically active, and to have the same sign for the rotatory power as the amide from which it was prepared. It was also found that the rearrangement took place in such a manner as to produce no appreciable racemization.

These results preclude the possibility of migration of the optically active group in any free form, either as a positive, negative or neutral free radical.

Princeton, New Jersey

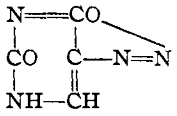
Received January 17, 1933
Published June 6, 1933

# Notes

## A New Color Reaction with Sucrose

By Harry W. Raybin

In studying the chemical properties of diazo-uracil[1] it was observed that in alkaline sucrose solution it produced a blue-green color. Raffinose was the only other sugar found to give a similar but weaker color.



Fructose, glucose, maltose, lactose did not give this test. Preliminary experiments were also negative (mostly yellow to brown-reds) with inulin, melezitose, turanose, as well as for starch, glycogen, pneumococcus polysaccharide Type I, cellobiose, galactose, mannose, arabinose, lyxose, xylose, rhamnose, *l*-fucose, *d*-mannoheptose, mannoketoheptose, *d*-α-glucoheptose, *d*-α-glucoheptulose, lactulose, erythritol, adonitol, dulcitol, *d*-arabitol, perseitol, mannitol, glycerin, formaldehyde, acetone, pyruvic acid, acetoacetic ester, acetone-dicarboxylic acid.

**Experimental Procedure.**—Forty to 50 mg. of sucrose in 5 cc. of *N*/20 sodium hydroxide (10°) is shaken in a corked test-tube with 7 to 10 mg. of diazouracil until the latter dissolves. The blue-green color develops within a few minutes, the solution being kept cold. The addition of magnesium ion gives a stable blue precipitate.

An interesting reaction product with indicator properties has been isolated by salting out from neutral solution.

(1) See *Proc. Nat. Acad. Sci.*, **18**, No. 3, p. 220; This Journal, **55**, 1667 (1933).

Work is being continued on the reaction of diazo oxides with carbohydrates. The author would be glad to hear of the results of others, especially with the uncommon and not readily available sugars.[2]

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(2) The writer is greatly indebted for a number of samples to: Professor C. S. Hudson of the U. S. Public Health Service; Mr. F. Bates of the U. S. Bureau of Standards; Professor W. C. Austin of Loyola Medical School; Professors H. T. Clarke and M. Heidelberger of College of Physicians and Surgeons, Columbia University.

CONTRIBUTION OF THE
NEW YORK CITY DEPARTMENT OF HEALTH
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NEW YORK CITY

RECEIVED FEBRUARY 1, 1933
PUBLISHED JUNE 6, 1933

## The Preparation of Racemic Tartaric Acid

BY ALAN NEWTON CAMPBELL, LOUIS SLOTIN AND STEWART A. JOHNSTON

In preparations of racemic acid by the standard method,[1] we have found that calcium sulfate is an inevitable impurity, despite frequent recrystallizations. This situation is due to the well-known tendency of calcium sulfate to form supersaturated solutions. In previous work[2] it was found that the racemization of active tartrate could be brought about by much lower concentrations of alkali than are used in the standard preparation. A method designed to yield a product free from calcium sulfate was worked out on this basis as follows: 360 g. of *d*-tartaric acid is dissolved in two liters of 4 *N* sodium hydroxide. This solution is gently boiled in a copper flask under reflux for a week. The solution is made distinctly acid with strong hydrochloric acid, and evaporated to a bulk of 500 cc. It is then filtered hot from precipitated sodium chloride and 200 cc. of concentrated hydrochloric acid added to the filtrate. More sodium chloride separates which is again filtered. A liter of 95% alcohol is then added and the precipitated sodium chloride removed. The alcohol is removed by distillation from the steam-bath and the residue allowed to evaporate in an open dish on the steam-bath until the liquid portion has fallen to 150 cc. The thin sirupy liquid obtained is inoculated with a few crystals of racemic acid and allowed to stand overnight. This treatment causes the liquid to set solid. It is macerated with 100 cc. of cold water and filtered. The crude racemic acid thus obtained is dissolved in hot water, boiled with animal charcoal, filtered and allowed to crystallize. The crystals are dried in an oven at 80° to get rid of traces of hydrogen chloride. Further recrystallization from water is necessary to obtain a perfectly pure product. The final product has a melting point, when dehydrated, of 203–204°, is quite inactive and free from chloride. The yield is 150 g. of crystallized product.

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(1) Cohen, "Practical Organic Chemistry," 1928 ed., p. 145; Holleman, *Rec. trav. chim.*, **17**, 66 (1898).

(2) Campbell and Campbell, THIS JOURNAL, **54**, 3834 (1932).

The method is in constant use in this Laboratory. Although the procedure is long, it is actually less cumbersome to manipulate than the standard method and much more certain in its results.

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RECEIVED FEBRUARY 3, 1933
PUBLISHED JUNE 6, 1933

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## Note on the Esterase Character of Pectase (Pectin-demethoxylase)

BY Z. I. KERTESZ

Von Euler[1] proposed the name pecto-lipase for the enzyme pectase, which splits off methoxy groups from pectin and forms a gel from it under suitable conditions. Though this name indicates the esterase character of pectase, it does not specify its action. Other compounds (acetic acid) might also be attached to the molecule by ester linkages, but it is likely that the splitting off of these groups is indifferent from the standpoint of gel formation.

It was of considerable interest to see whether other ester-splitting enzymes are able to produce gels from pectin solutions, a fact of importance in the classification of enzymes. In the course of some work started at this Station several years ago enzymes of different origin and type were tested for their action on pectin. Gels of stiff consistency were obtained by the use of some typical esterases. A preparation from castor beans was used in the first case. The beans were crushed, extracted with ether and dried. This crude preparation forms a gel from apple or lemon pectin in the presence of calcium ion at *P*H 5 and 8, but not at *P*H 3. A commercial lipase preparation (Difco, from pancrease) was also applied, with the same results.

The fact that from pectin gel could be formed by the use of typical ester-hydrolyzing enzymes verifies the earlier assumption about the esterase character of pectase. The more specific name pectin-demethoxylase is proposed for this enzyme.

(1) Von Euler, *Chemie der Enzyme*, Teil 2, Absch. 1, 457 (1928).

GENEVA, NEW YORK

RECEIVED FEBRUARY 16, 1933
PUBLISHED JUNE 6, 1933

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## Note on the Preparation of Dibenzoyl-*d*-tartaric Acid

BY C. L. BUTLER AND LEONARD H. CRETCHER

Considerable quantities of dibenzoyl-*d*-tartaric acid were needed for use in research on the cinchona alkaloids which is in progress in this Laboratory. The only detailed directions for the preparation of this substance which could be found in the literature were in a paper by Zetzsche and Hubacher.[1]

(1) Zetzsche and Hubacher, *Helv. Chim. Acta*, **9**, 291 (1926).

These authors heated one molecular proportion of tartaric acid with two and seven-tenths moles of benzoyl chloride in order to obtain the desired product. No statement of yield is to be found in any of the papers on the subject. When the directions of Zetzsche and Hubacher[1] were followed exactly, yields of 30 to 37% were obtained.

Since the reaction product of benzoyl chloride and tartaric acid under these conditions is a benzoylated anhydride and not a free acid, it is clear that a dehydration accompanies the benzoylation. It seemed reasonable therefore to suspect that at least three moles of benzoyl chloride (two for benzoylation and one for dehydration) should be used. With this thought in mind, the experiment was repeated according to the following modified directions and a yield close to quantitative was obtained.

One hundred fifty grams of tartaric acid (1 mole) and 450 g. of benzoyl chloride (3.2 moles) were heated in an Erlenmeyer flask slowly up to 150°. Reaction took place mainly between 135 and 140°. The total time of heating was three hours. The contents of the flask were removed and ground in a mortar. Benzoic acid and the excess of benzoyl chloride were removed by extracting with benzene in the following manner. Three hundred cc. of solvent was added, the mixture was warmed, with agitation, just short of the boiling point and then cooled to room temperature. The product was filtered and the extraction was repeated. The material was then washed with several portions of cold benzene. The yield of crude dibenzoyl-*d*-tartaric anhydride, dried at 100°, was 348 g., melting point 155 to 160°. A strictly pure product melting at 173° may be obtained by crystallizing from xylene.

The crude benzene extracted product was placed in a flask with 1500 cc. of water and the mixture was gently boiled for one-half hour, during which time dibenzoyl-*d*-tartaric acid monohydrate collected on the bottom of the flask as a heavy oil. When allowed to stand overnight, the oily product solidified in a crystalline cake. However, if a few crystals of acid from a previous run were added to the aqueous mixture and the mixture was shaken vigorously for a few minutes, the product solidified in small lumps. It was filtered, air-dried and ground. The yield was 359 g., or 93% of the theoretical amount. The substance melted at 84 to 85°, and was sufficiently pure for our purposes. A purer product, melting at 88 to 89°, $[\alpha]_D$ −116.0°, may be obtained if desired by crystallizing from benzene, or more conveniently by washing with a little cold benzene.

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Received February 20, 1933
Published June 6, 1933