

the units of the main chain are split once, and that the other half of the units of the main chain, or those at the points of branching, are not split at all.

Experimental

Periodate Oxidation.—Following the method of Hirst, a 400-mg. sample of guaran was dissolved in 100 ml. of potassium chloride solution (5 g. of potassium chloride per 100 ml. of water) in a 500-ml. glass-stoppered bottle. Then 10 ml. of 0.3 *M* sodium periodate solution and 10 ml. of water were added and the mixture shaken at 25° for about one hundred hours. At this point the reaction was complete and ethylene glycol was added to consume the excess periodate. The formic acid present was titrated with 0.01 *N* barium hydroxide solution. One mole of formic acid was produced for 2.7 anhydrohexoside units. Samples of 200 mg. and 100 mg. gave similar values.

The presence of formic acid was confirmed by oxidation with mercuric chloride by the method of Auerbach and Zeglin.⁶ Formic acid (*ca.* 40 mg.) formed from a 400-

mg. sample of guaran was removed from the final reaction mixture by extraction with ether in a liquid-liquid extractor for ten days. A slight excess of sodium hydroxide was added to the ether extract and the mixture concentrated to about 5 ml. to remove ether and then was diluted to 60 ml. with water. After neutralization with 1 *N* hydrochloric acid, 1 ml. excess of acid and 3 g. of sodium acetate were added. The solution was filtered into an Erlenmeyer flask and 20 ml. of 5% mercuric chloride solution was added. The flask was covered with an inverted beaker and the mixture heated on a steam-bath for two hours. Precipitated mercurous chloride was filtered on a medium porosity sintered glass crucible, washed with hot water and ethanol, dried at 100°, and weighed. The weight of the precipitate corresponded to 103% of the formic acid determined by the above method of direct titration.

(6) F. Auerbach and H. Zeglin, *Z. physik. Chem.*, **103**, 161 (1922).

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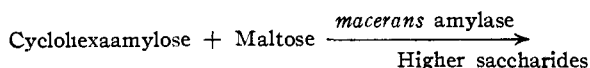
RECEIVED FEBRUARY 28, 1948

COMMUNICATIONS TO THE EDITOR

REVERSIBLE ACTION OF *macerans* AMYLASE¹

Sir:

The action of *Bacillus macerans* amylase² on starch has been interpreted by Cori³ as the exchange of a glycosidic bond in starch for a corresponding bond in a cyclic Schardinger dextrin (cycloamylose) molecule. In view of the small ΔF which would be expected for such an exchange, it might be expected that the reaction should be readily reversible. The reverse type reaction



has been tested with crystalline substrates and verified; *macerans* amylase thus has a synthetic as well as degradative action.

Pure cyclohexaamylose,⁴ 2.0 g., and c. p. maltose, 0.7 g., were dissolved in water, heated to complete mutarotation of the maltose, and treated with four units² of *macerans* amylase. The solution was made up to 100 ml. and the increase in rotation⁵ was followed in the polarimeter: initial rotation, 7.87°; after two hours, 8.10°. At this point the enzyme was inactivated by boiling and the reaction products separated by fractional precipitation. The least soluble fraction, 0.14 g., sirupy, had $[\alpha]_D +163^\circ$; average chain length by

alkaline ferricyanide,⁶ 8.9 glucose units. These values indicate that the sample is probably a mixture of saccharides containing some non-carbohydrate impurities. It gave a slight deepening of the color of I₂-KI solution and no unchanged cyclohexaamylose could be detected by the Tilden micro test.² On treatment with *macerans* amylase the fraction was rapidly reconverted in part into cyclohexaamylose as indicated by the formation of the characteristic I₂-KI complex.

Results indicating a similar synthetic action of *macerans* amylase have been obtained from cyclohexaamylose with glucose, α -methylglucoside, sucrose, cellobiose or maltobionic acid as co-substrates; also from cycloheptaamylose⁴ with maltose or glucose as co-substrates. These studies are being continued and will be reported in full at a later date.

(6) Levine, Foster and Hixon, *ibid.*, **64**, 2331 (1942).

CHEMISTRY SECTION
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RECEIVED AUGUST 10, 1948

FORMATION OF FLUORESCING SUBSTANCES FROM AMINO ACIDS

Sir:

Tauber¹ has reported recently on the formation of a fluorescing compound formed by the reaction of tryptophan with perchloric acid at room tem-

(1) Tauber, *THIS JOURNAL*, **70**, 2615 (1948).

(1) Journal Paper No. J-1581 of the Iowa Agricultural Experiment Station, Ames, Iowa. Project No. 964.

(2) Tilden and Hudson, *J. Bact.*, **43**, 527 (1942).

(3) Cori, *Federation Proc.*, **4**, 226 (1945).

(4) French and Rundle, *THIS JOURNAL*, **64**, 1651 (1942).

(5) McClenahan, Tilden and Hudson, *ibid.*, **64**, 2139 (1942).