

in 5 minutes, about 2 times as the native, and then gradually decreased. After 3 hours, the height became lower than that of the control. In 60°C water-bath this alkaline effect was so rapid that the height in 10 minutes corresponded to that in 24 hrs. Besides the temperature, the slope of this denaturation-time curve was found to be influenced regularly by KOH concentration; the higher the concentration, the steeper the slope.

The quantity of serum protein acted merely as a deciding factor of magnitude of this curve; but a protein-corrected test on a case of hypoproteinemia showed lower wave height. Therefore, Brdicka reaction is considered to be that of qualitative change after all. Furthermore, we found some interesting facts that the curve flattened and the peak (maximum activation) lagged in the pathologic serum such as cancer or portal cirrhosis. From the above results, it may be said that the denaturation, especially alkaline one, might be a combination of two phases, i. e. phase of activation and that of inactivation, which will be characterized by temperature, agent and the nature of serum itself.

References:

- 1) Brdicka, R.; Klin. Wochenschr, 18, 305 (1939).
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70. Studies on the Mechanism of the Formation of Polysaccharides. (XIII)

On the Carbohydrate Activator of Starch Formation by Potato Phosphorylase. (1).

*Yoshiyuki Inouye, Konoshin Onodera, Hiromu Kisaki
and Keizo Hayashiya.*

It has been recently reported (Cori and Cori, J. Biol. Chem., 137, 773 (1940); Hanes, Proc. Roy. Soc., B, 119, 174 (1940); Green and Stumpf, J. Biol. Chem., 142, 335 (1942); Hidy and Day, J. Biol. Chem., 160, 273 (1945); Swanson and Cori, J. Biol. Chem., 172, 815 (1948)) that potato phosphorylase needs some amount of polysaccharide as an activator in the process of starch formation and that the activity of the activator depends on the chain length of the polysaccharide. No detailed description is, however, found about the methods of preparing the activator and the determination of the chain length.

The experiments reported in this paper are concerned with the ability, as activator, of polysaccharides prepared from potato starch which had been hydrolyzed under mild condition, and fractionated successively with ethanol of different

concentration.

Potato phosphorylase was prepared from 3 l. potato juice by repeated fractional precipitation with ammonium sulfate. The final fraction was 1.105—1.125 in specific gravity. The phosphorylase obtained proved to have almost no ability of starch formation when no activator was added.

20 g. of potato starch was boiled in 100 cc. of 1% H₂SO₄ for 20 minutes; then H₂SO₄ was removed with BaCO₃. The filtered solution was concentrated to a thick syrup under reduced pressure and dried in a vacuum desiccator. 10 g. of the product (polysaccharide mixture) was extracted with each 100 cc. of 90, 80, 60, 40 and 20% ethanol successively and finally with water under reflux condenser. The chain length of the polysaccharides thus prepared were 1.5, 2.9, 5.0, 8.0, 10.8 and 42.2 glucose units respectively (as calculated on the determination of reducing power).

It is concluded that, among these polysaccharides, the fraction of 5.0 glucose units shows the highest activating ability while the natural starch, such as sweet potato, rice and glutinous rice, and synthetic starch prepared in our laboratory (Inouye, Onodera and Kisaki, Rep. Inst. Chem. Res. Kyoto Univ., 18, 39 (1949)) show lower activating ability than their hydrolyzed products.

71. Studies on the α , β -Transformation of Glycosides. (II)

The Transformation of β -ethylglucoside.

Yoshiyuki Inouye, Konoshin Onodera and Ikuo Karasawa.

In the previous paper (Rep. Inst. Chem. Res. Kyoto Univ., 18, 37 (1949)) it was reported that β -methylglucoside is transformed to α -methyl-glucoside by means of SbCl₅ which is found to be more convenient than SnCl₄ (E. Pacsu, Ber., 61, 137 (1928)) or TiCl₄ (Ber., 61, 1508 (1928); J. Am. Chem. Soc., 52, 2563 (1930)). Recently B. Lindberg (C. A., 43, 3785 (1949)) reported on the transformation of β -glucosides to α -form by means of BF₃. The present paper is a report on the transformation of β -ethylglucoside to α -form catalyzed by SbCl₅.

Tetraacetyl- β -ethylglucoside (m. p. 106—107°, $[\alpha]_D^{20}$ -22.7° (CHCl₃); E. Fischer, Ber., 49, 584 (1916)) was dissolved in purified chloroform (alcohol-free), and SbCl₅ dissolved in chloroform was added. After a definite time, the chloroform layer was shaken with distilled water, treated with a small amount of BaCO₃ and filtered. The filtrate was dried, filtered, and then concentrated to a thick syrup under a reduced pressure, a small amount of abs. ethanol was added and cooled with ice for several hours. The β -form which was not transformed was crystallized out and filtered off. After addition of a small amount of dist.