Some Recent Trends in the Chemistry of the Carbohydrates

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It has been calculated by the National Farm Chemurgic Council that something over 84,000,000 tons of by-products of agriculture are being wasted annually. This list includes wheat straw, corn stover, cotton stems and pods, oat hulls, and corn cobs. "Research is plugging away," according to Gustavus J. Esselen, "at this problem, patiently, persistently. . . . Hulls and pods and straw and stems—who knows what the magic of chemistry may eventually work with these waste products?"

The magic of chemistry has already been at work in this field. From burrs, cobs, hulls, stalks, and straw, a vast array of products have already been produced and some of these have found their way into commercial production. Substitute woods, "which range from those as hard as stone to others as soft as cork bark, some denser than the heaviest teak wood and others lighter and stronger than balsa wood," have been fabricated from waste agricultural products.

Wood has been subjected to hydrogenolysis to give water-white liquids which can be fractionated without decomposition to yield important raw materials for further synthesis. This may be one of the answers to the replacement of our petroleum supply, which, according to the organic theory, came originally from carbohydrate material. The other alternative is to apply adequate heat and pressure to carbohydrate material to convert it into petroleum-like products. An energetic worker in the carbohydrate field recently wrote: "It is very interesting that plants and animals are able to make almost anything from the sugars. . . . It is about time for us to be able to do more of these things in the laboratory." The chemist out-did nature in the synthesis of indigo, yet there are innumerable analogous opportunities in the field of carbohydrate chemistry.

The production of lumber utilizes only about 20% of the forests whereas the new technic for the disintegration of wood to fibers and the subsequent recombination of these under heat and pressure to give pressed board, makes use of about 93% of the forest crop. This represents a saving of 73% and tremendously simplifies the important problem of reforestration.

Etholcel, which is probably obtained by treatment of sodium cellulose with ethyl chloride, was developed in 1936 and is now being marketed by the Dow Chemical Company as a competitive material for cellulose acetate, cellulose nitrate, and similar products.

Director Stine, of du Pont, is responsible for the statement that "there are ten thousand different products of cellulose being produced and the industry is still in its infancy".

Starch acetates are now available on pilot plant scale in three types: (1) those soluble in water, (2) those soluble in both water and organic solvents, and (3) those that are soluble only in certain organic solvents.

These appear to be of interest as chemicals for sizing, for flotation, for films, and allied uses. The lower starch ethers have been prepared in the laboratory, but enough is not known at this time of their properties to predict their use if any in our industrial program.

Among the newer food products are Dri-Dex, Fro-Dex, Liquid Sugar, Malto-Dextrine, and Sweetose. The Dri-Dex, Fro-Dex, and Malto-Dextrine are all produced by the vacuum pan drying of appropriate corn syrups. Liquid sugar is produced by an acid hydrolysis of starch in the presence of molybdenum salts, whereas Sweetose is produced by a combined enzymeacid hydrolysis of starch.

Levulinic or 4-ketopentanoic acid is obtained from waste sugars and starch by a special type of reductive hydrolysis.

Starch is being depolymerized by either (a) the wet process or (b) the dry process. In the wet process the nature of the end product is determined by the type of starch, the hydrogen ion concentration, and the time of heating, whereas in the dry process there are two additional variables: the moisture content of the starch and the temperature of the reaction. By proper control of all of these variables, it appears possible to produce a starch product for a large variety of needs.

Among the newer uses for starch should be mentioned that of torrefying the starch in situ in the fabrication of corrugated cardboard. In 1939, according to Dr. G. E. Hilbert, this accounted for the consumption of 80,000,000 pounds of starch. Another rapidly expanding outlet for starch is the sizing of painted walls, which may be washed in turn and resized as needed by the use of a dilute starch solution. It is reputedly reported, furthermore, that definite progress has been made in the design and construction of an engine which operates on pulverized starch.

The discovery, by Denny and co-workers at the Boyce Thompson Institute, of a rather large number of chemicals that will stimulate budding and root growth has received a large amount of publicity, but it is not generally known that these workers have been able to show that when ethylene chlorohydrin is used as such a stimulate it is detoxicated by the plant by glycoside formation. In the study of potato tubers and gladiolus corms it was observed that gentiobiose, not normally present or at most in a minimum concentration, is produced to detoxicate the ethylene chlorohydrin by the formation of the corresponding gentiobioside. These workers have, moreover, found that it is possible to dormatize tubers by treatment with either a dilute solution of potassium naphthaleneacetate or the vapors of methyl naphthaleneacetate. These dormatized tubers may be dedormitized at will by treatment with ethylene chlorhydrin or other stimulating chemicals. This work is of paramount importance, if it can be adequately controlled, in that it will enable storage without danger of germination.

Three new approaches are now available for continued study of the size and structure of the starch molecule. By the preparation of the thioacetal, which takes place only at the free aldehyde group, it is possible to estimate by mercury or sulfur determination, the terminal aldehyde groups at any given time in the hydrolysis. Similiar measurements seem possible by use of the dropping mercury cathode and by the

use of complete alkylation, followed by high vacuum fractionation of the alkylated residues. As a result of these studies it appears that some of the starch molecules may be very highly branched.

The various sugars can now be separated analytically by complete methylation of the mixture, followed by fractional distillation and identification of the various fractions. The technic has been extended to the analysis of the ingredients of dextrins and corn syrups.

A synthesis of some interest to the vitamin chemists is that of ascorbic acid or vitamin C from D⁻-threose and ethyl bioxylate in the presence of mild alkali as a condensing agent. The first step in the reaction appears to be addition, which is followed by the loss of water and ethyl alcohol.

The hydrogenolysis of D+-glucose is being thoroughly investigated in the quest of a new source for the polyalcohols and other synthetic intermediates.

The technic for the production of lactic acid, from either milk or starch, has been improved and a high grade is now available for either the food or the synthetic-products industries. The various esters of lactic acid as well as their derivaties, the acrylic esters, are being used in increasing amounts in the lacquer and allied trades.

The condensation of the simple sugars with phenolic compounds to give complex cyclic structures, by Niederl and collaborators, may suggest how nature synthesizes some of its complex colored substances.

Aside from the items indicated here, mention should be made of the twenty-seven pages devoted to the Chemistry of the Carbohydrates and Glycosides in the Annual Review of Biochemistry, Vol. IX, 1940.

The magic of chemistry is at work and the diligence of the research worker in the field of carbohydrate chemistry is being awarded by these mile posts of progress.