Chemical Derivatives of Starch and Their Industrial Use

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The natural starches of maize, wheat, tapioca etc. have been used for many years in a variety of industrial products. They have, however, a number of deficiencies, which limit their use for present-day manufacturing processes.

Modification of the raw starch, by the introduc-

tion of various chemical groups into the molecule, changes the cooked paste characteristics and improves their performance for many applications.

The development of the techniques for cross-linking, ether and ester formation, together with the commercial development of the so-called waxy varieties of maize, sorghum and, more recently, rice, now enable the starch manufacturer to offer a range of products of varied flexibility.

A selection of these chemical derivatives of starch is discussed and their roles in the paper/textile and food/feed fields are commented on.

COMMUNICATIONS

Control by Light of Starch Degradation and Cell-Wall Biosynthesis in *Platymonas tetrahele*

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The planktonic unicellular alga *Platymonas tetrahele* stores starch as grains in the chloroplast and around the pyrenoid. Its cell wall has been shown to be made of pectin-like material, with galactose, galacturonic acid and arabinose as major components. During synchronous culture in a light-dark regime the cells divide and the new cell walls are formed in the light just before the beginning of the dark period. Exogenously supplied D-[U-¹⁴C]-glucose is taken up and incorporated into polysaccharides, but is not used as a respiratory substrate. Short-term electron-microscopic radioautographs show that D-[6-³H]glucose is quickly incorporated into starch and that during cell division radioactivity appears in developing cell-wall components in the Golgi bodies and later in the cell walls themselves. Comparison of the radioautographs with longer-term incorporation studies with D-[U-¹⁴C]glucose indicates that the stored starch is utilized to form the cell-wall polysaccharides. There is no detectable loss of starch after incubation of the algae for long periods in the dark on agar containing 1% glucose.

Control by light of starch breakdown has been reported in a mutant of *Chlamydomonas* (Ohad, Siekevitz & Palade, 1967), in a moss (Hahn & Miller, 1966) and in higher plants (Price, Mitrakos & Klein, 1965), and in the last two cases has been ascribed to a phytochrome system. It is possible that this is a widespread phenomenon that is often masked by other processes, although in the present case it is not clear whether the starch breakdown is directly controlled by light or whether it is a secondary effect of light-mediated biosynthesis of cell-wall polysaccharides.

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The Amino Acid Composition of a Wheat-Based Brewing Syrup

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The amino acid composition of the brewer's wort is important, as it affects the metabolism of the yeast and consequently the character of the beer (Rainbow, 1970). The presence of certain amino acids is particularly important as their keto acids are essential at some stage of the fermentation (Jones & Pierce, 1969). Any brewing adjunct that is to be added to the wort should not significantly alter this composition. A brewing syrup that was prepared from wheat by using commercially available enzymes had an overall composition that was similar to that of a malt wort. In particular, the free amino acid composition of the syrup, calculated as a percentage of the total amino acid content, showed few differences to the malt wort. Serine, threonine, glutamine and asparagine were measured together and were 3% higher in the syrup. Of the remaining amino acids seven differed by more than 1% and only three by more than 2%: proline was 17.7% higher in the malt wort, and both tyrosine (5.1%) and lysine (15.8%) were higher in the syrup. Proline, serine, threonine, glutamine and asparagine are not essential amino acids, as they can be formed throughout the fermentation by the

yeast (Jones, & Pierce, 1964). Tyrosine is absorbed only during the latter stages of fermentation, because of competition for the permease sites in the yeast cell wall (Jones & Pierce, 1964), so the excess present in the syrup should not effect the yeast metabolism. Lysine could block the transport of several amino acids, as it is preferentially absorbed by the yeast permease system (Jones & Pierce, 1964). Consequently the excess of lysine might affect the quality of the beer if a major percentage of the wort was derived from the wheat syrup. However, small-scale brewing trials have shown that the use of a wheat-based syrup to replace 30% of a malt wort produced beers that could not be distinguished organoleptically from the all-malt wort control beers.

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The Reaction of Malonaldehyde with Wheat Flour Proteins

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Recent studies on lipid-protein interaction in dry systems (Roubal & Tappel, 1966; Roubal, 1970) have demonstrated that the free radicals derived from oxidizing lipids are the dominant cause of reactions leading to protein polymerization and amino acid destruction. However, there is some evidence that the difunctional aldehydes malonaldehyde and glutaraldehyde, products of the oxidation of polyunsaturated fatty acids, are able to react with proteins (Menzel, 1967; Ewart, 1968) and amino acids (Buttkus, 1968) directly. This communication confirms previous findings and demonstrates the reaction mechanism of malonaldehyde-protein in wheat flour systems.

Malonaldehyde was prepared from 1,1,3,3-tetraethoxypropane (Kwon & Watts, 1963) and allowed to react with wheat flour gliadin under the conditions described by Ewart (1968) for gliadin-glutaraldehyde reaction. The modified protein was hydrolysed with 6M-hydrochloric acid for 18h at 105°C, and amino acid analyses were carried out as described by Ewart (1967). Results demonstrate that the treatment of gliadin with malonaldehyde results in the destruction of all the detectable tyrosine, in contrast with other workers, who have reported losses of lysine and tyrosine (Ewart, 1968), of cysteine and methionine (Buttkus, 1968) and of methionine (Tannenbaum, Barth & Le Roux, 1969).

Glycerol tri[U-¹⁴C]linolenate was synthesized (Daubert & Baldwin, 1944) via the acyl chloride (Wood, Jackson, Baldwin & Longenecker, 1944) and stored with a mixture of wheat flour proteins for 35 days at 30°C (80% relative humidity). Portions of the mixture were withdrawn at intervals, exhaustively defatted and fractionated by polyacrylamide discontinuous gel electrophoresis. The developed gels were sliced into 1mm sections and the radioactivities counted. During storage significant amounts of radioactivity became associated with the more mobile proteins. After storage the mixture was slurried with water and the more volatile components, containing 70% of the residual radioactivity, were isolated by steam-distillation. All of the radioactivity in this isolate was associated with a compound whose properties were identical with those of malonaldehyde. A sample of [U-¹⁴C]-malonaldehyde was prepared from [U-¹⁴C]linolenic acid and dispersed with unlabelled aldehyde on to a similar protein mixture. Subsequent isolation and counting of radioactivity showed the pattern of radioactivity-protein combination to be identical with that observed in stored glycerol tri-linolenate-protein mixtures.

This evidence supports the view that the aldehydes released from oxidizing lipids combine directly with proteins.

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The Isolation of Plant Root Protoplasts and their Use in the Separation of Subcellular Components

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Power & Cocking (1968) described a method for the isolation of large numbers of protoplasts from fully expanded tobacco leaves. This method has been adapted for use on roots, either for the production of intact protoplasts or for the release of