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CEREAL COMPONENTS

A Review of Carbohydrates of Wheat and Other Cereal Grains

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Water-insoluble, pentosanlike material containing uronic acid, arabinose, and xylose residues is present in the outer portion (bran) of the wheat grain. A similar material is present in corn hulls and oat hulls. Within the wheat kernel are found glucose, fructose, maltose, fructosyl-raffinose, a number of glucofructosans (levosine) found also in barley, at least two pentosans (hemicelluloses) composed of arabinose and xylose, and starch, which is the major carbohydrate component of all cereal grains. Wheat germ contains sucrose, raffinose, and traces of glucose and fructose; exposure of wheat kernels to moisture results in a decrease of the concentration of these sugars. Barley and oat grains contain a polyglucosan in which the glucose units are joined by 1,3- and 1,4- linkages.

CEREAL GRAINS form a large and important source of food for both man and animals. It is important, therefore, that the components of the grains, which form the "reactants" of the food technologist, be separated and sub-

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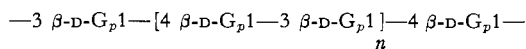
jected to careful study, for only in this way are sustained and far-reaching advances likely to be made.

The physical and chemical behavior of wheat flour, for example, has often been related to either the starch or the protein fractions, which together constitute the major portion of the material. However, it has long been realized that

a number of carbohydrates other than starch are present and may play important roles in the physicochemical properties of the flours. It is principally to these relatively minor carbohydrate components in wheat and other grains that attention has been directed in recent years.

Cereal grains, indeed all plant seeds,

of linkage are present in equal amounts, then one mole of periodate will be consumed by one out of every two glucose residues. The 1,4- and 1,3-linkages in the polyglucosan appear to alternate as



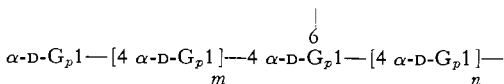
III

in Formula III, since the polyaldehyde, produced by periodate oxidation, gives rise to glucose phenylosazone when treated with phenylhydrazine (24). The presence of glucose residues joined by consecutive 1,3-glycosidic bonds would be revealed by the formation of osazones of one or more glucose oligosaccharides and not simply the osazone of the monosaccharide, glucose.

In the case of a similar glucosan isolated from oats, called oat lichenin (47), periodate oxidation studies have indicated the proportion of 1,4- to 1,3-linkages to be about 3 to 1 (2); a similar polyglucosan with a still higher proportion of 1,4-linkages has been found in Iceland moss (14, 36).

Some support for the presence of 1,3-linked polysaccharides in other cereal grains, if only in small amount, is forthcoming from the observation that an enzyme is present in wheat and many other seeds which is capable of hydrolyzing lichenin and the 1,3- β -linked polysaccharide, laminarin (19, 29, 33, 48). The gradual accumulation of such evidence as this lends some indirect support to the view (7), based on periodate oxidation studies, that a few 1,3-linkages may be present in starch.

Accompanying the poly- β -glucosan in barley gum is an α -glucosan which has been shown by methylation studies to be similar to the amylopectin fraction of starch (25). It differs only in the degree of branching, barley α -glucosan being much more highly branched, with each repeating unit containing on the average eight glucopyranose units (see Formula IV) as compared with an average repeat-



IV

ing unit of about 20 glucopyranose residues found in amylopectin. This has been deduced from the fact that hydrolysis of the methylated polysaccharide yields 2,3,4,6-tetra-*O*-, 2,3,6-tri-*O*-, and 2,3-di-*O*-methyl-*D*-glucose.

The same types of hexosans as the α - and β -glucosans of barley may well be present in all cereal grains.

The outer coating or pericarp of cereal grains contains a high proportion of pentosan material which appears to be more complex than those found in the endosperm. In the case of wheat bran the pentosan is composed of L-arabinose,

D-xylose, *D*-glucuronic acid, and 4-*O*-methyl-*D*-glucuronic acid. Structural studies by the classical methylation technique showed that the methylated pentosan gave rise upon hydrolysis to eight neutral methylated sugars (see Table III) (3).

It is apparent from these results and relative hydrolysis rates of the arabinose residues that some of these are part of the central portion of the hemicellulose molecule. The isolation of 2,3,5-tri-*O*-methyl-L-arabinose and 2,3,4-tri-*O*-methyl-*D*-xylose shows that the end groups in the polysaccharide are composed of both L-arabofuranose and *D*-xylopyranose units. Both of these structural features are in contrast to those of the wheat endosperm hemicellulose, which contains L-arabofuranose only as terminal units. A further difference between the two hemicelluloses is the pres-

Table III. Neutral Cleavage Fragments of Methylated Wheat Bran Hemicellulose (3)

Component	Proportions
L-Arabinose	
2,3,5-Tri- <i>O</i> -methyl-	6
2,5-Di- <i>O</i> -methyl-	7
3- <i>O</i> -Methyl-	(?) 3
5- <i>O</i> -Methyl-	3
<i>D</i> -Xylose	
2,3,4-Tri- <i>O</i> -methyl-	5
2,3-Di- <i>O</i> -methyl-	4
2- <i>O</i> -Methyl-	4

Table IV. Carbohydrate Components of Wheat

Glucose	Glucofructosans
Fructose	Araboxylans
Sucrose	Amylopectin
Maltose	Amylose
Raffinose	Other glucosans
Fructosyl-raffinose	

ence of acidic groups in that from the bran. By partial acid hydrolysis of the bran hemicellulose the acidic components have been isolated as aldobiouronic acids, in which the acidic moiety has been shown to be linked through its reducing group to a *D*-xylose unit at position 2 (4). It is probable that these

acidic residues also form end groups in the hemicellulose, and as they are probably present as salts, the explanation for the higher ash content of the bran as compared to the endosperm becomes apparent. A similar hemicellulose, $[\alpha]_D^{25} - 96^\circ$ (1*N* sodium hydroxide), may be extracted from oat hulls with dilute alkali (58).

A similar hemicellulose extracted from the pericarp of corn with dilute alkali is composed of arabinose, xylose, galactose, and glucuronic acid (40, 63). This polysaccharide forms gummy solutions in water, which, though lower in viscosity than those of similar concentration

made from gum Karaya and tragacanth, are considerably higher than those of gum arabic (63). Like wheat bran hemicellulose, the corn hull polysaccharide has been shown by methylation studies (40) to have end groups of arabinose, xylose, and glucuronic acid. The L-arabinose and *D*-xylose have been obtained as the 2,3,5-tri- and the 2,3,4-tri-*O*-methyl derivatives, respectively. The nonreducing end groups of *D*-glucuronic acid were obtained as a partially methylated aldobiouronic acid from the methylated polysaccharide and characterized, after reduction, with lithium aluminum hydride as crystalline 2-*O*-(2,3,4-tri-*O*-methyl-*D*-glucopyranosyl)-3-*O*-methyl-*D*-xylose. The characterization of the latter also proved that the terminal units of *D*-glucuronic acid were joined directly to the main structural xylan framework of the polysaccharide. This corn hull hemicellulose differs from wheat bran hemicellulose in also having the galactose residues as nonreducing end groups. The framework of corn pericarp hemicellulose, like that from wheat bran, is composed principally of *D*-xylopyranose residues linked through positions 1 and 4 and from which are subtended multiunit side chains containing arabinose residues. This follows from the characterization of 2,3-di and 2-*O*-methyl-*D*-xylose among the cleavage products of the methylated polysaccharide. Similar results have been obtained by other investigators, who have carried out methylation (10) and degradation (59) studies on a corn "fiber" hemicellulose which is very similar if not identical with the substance referred to above as corn hull hemicellulose.

Conclusion

In order to illustrate the diversity of the carbohydrate components in cereal grains, those found thus far in wheat are listed in Table IV. There are the simple sugars and oligosaccharides, including the recently identified fructosyl-raffinose (67); the glucofructosans, which may be considered as a spectrum of oligosaccharides with sucrose as the simplest member; the highly branched araboxylans, which represent what might be termed the cellular cement of most plants; the branched and linear components of wheat starch, which, together, represent by far the principal carbohydrates in wheat; and, finally, the other glucosans about which little is known as yet. No mention is made here of the glycoproteins, which undoubtedly play a major role in cereals and other plant products.

It is the authors' belief, however, that the full chemical and food technological utilization of the vast store of carbohydrates, proteins, lipides, and their complexes present in wheat and other cereal grains, which in contrast to other natural

sources of organic chemicals like oil is reproducible annually, will not be realized until the fundamental approaches to the separation, identification, and structure determination of their components have been fully exploited.

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MILK ANALYSIS

Direct Microdetermination of Calcium in Milk

A RAPID MICROMETHOD for the determination of calcium was required for studies on ionic equilibria in milk. The method had to be suitable for the analysis of small aliquots of synthetic mixtures resembling milk serum but con-

taining as little as 10 γ of calcium per ml. Gravimetric, colorimetric, and titrimetric methods (7) were unsatisfactory because they were time-consuming or lacked sensitivity with the limited aliquots of test solution available.

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The method of Saifer and Clark (2), which estimates from 40 to 280 γ of calcium in water, was studied in detail with the aim of adapting it to milk and milk serum. A successful modified method, with increased sensitivity, measures from