

Polysaccharides of Sugar Beet Pulp, A Review of Their Chemistry

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Dried beet pulp is a stable material of relatively low cost (less than 2 cents per pound) and is available at most American beet sugar factories where manufacturing facilities are usually idle more than half the year. Use of part of their facilities off season to manufacture pulp for some purpose other than feed would be desirable. It seemed worthwhile to review the carbohydrates that make the major proportion of this potential industrial material.

The approximate composition of beet pulp is shown in Table 1. These are average values of samples from beets grown in the United States.

Except for the polysaccharides and acetyl content the analysis of pulp solids is similar to that of other water-leached plant residues. The acetyl content of dried pulp was 4% (19)² essentially the same as in beet pectin.

In spite of the vast quantities of beet pulp available and the high polysaccharide content, these materials have received scant attention since the work of Hirst and Jones more than 20 years ago (22). The early researches of Ehrlich (14, 15, 16) showed araban, galactan, and pectic substances (including galacturonic acid) were closely associated in beet pectin and appeared to be inseparable into pure components unless hydrolyzing conditions were employed.

Table 1.—Approximate composition of beet pulp, dry basis.

Constituent	Percent
Pectin (anhydrouronic acid)	25
Araban	20
Galactan	6
Acetyl	4
Ash	4
Protein (N X 6.25)	10
Crude fiber	25
Other	6

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² Numbers in parentheses refer to literature cited.

Structure of Polysaccharides

Galactan—Plant physiologists were quick to note the similarity in the configuration of galactose, galacturonic acid, and arabinose (Figure 1), and to propose that the three polysac-

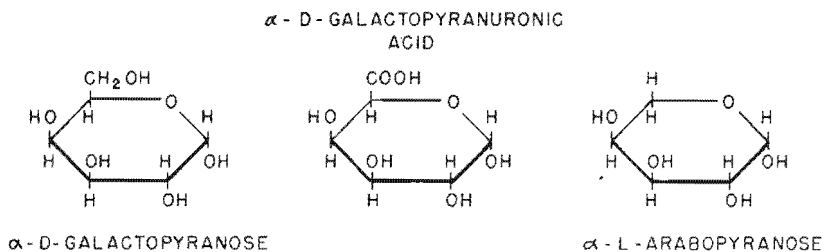


Figure 1.—Space formulas for some monomers as possible constituents of the pectic triad.

charides which make up the pectic triad might be mutually interconvertible in higher plant tissues. Hirst and his co-workers (23, 24) examined the structure of the pectic triad to see if such interconversions were plausible. They chose crude pectic substances particularly rich in one or the other non-uronic moiety, separated it, and then determined its structure by chemical means. Hirst *et al.* (24) studied the galactan of lupine seeds. They first extracted the protein with salt solution. Galactan, pectic substances, and araban were extracted together with dilute sodium hydroxide. The pectic substances were removed by precipitation as insoluble calcium salts. They did not isolate the galactan in pure form at this point but methylated directly. The methylated polysaccharides had different properties which permitted their separation by solvent fractionation and subsequent isolation of 0-methyl galactan. The hydrolysis products were mainly 2,3,6-tri-0-methyl D-galactopyranose and a small amount of 2,3,4,6-tetra-0-methyl D-galactopyranose. From these results and the low negative rotation they concluded that the galactan is a β -linked, unbranched polymer of chain length about 120 units. Figure 2 shows the structure and configuration of lupine galactan. No definite structure determinations of sugar beet galactan have been reported, but the structure of lupine galactan and sugar beet galactan may be similar.

Araban—As early as 1873, Scheibler (39) isolated a gum from sugar beets that could easily be hydrolyzed to arabinose. Araban from beets was prepared subsequently by others (18, 20, 25, 40, 47). Araban is difficult to separate from galactan

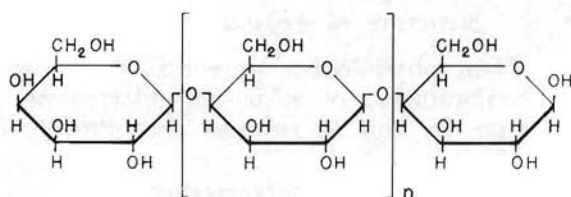
 β -1-4-GALACTAN

Figure 2.—Galactan.

and pectic substances but is slightly soluble in hot 70% ethanol, where the accompanying polysaccharides are not.

In 1948, Hirst and Jones maintained their attack on the pectic polysaccharides and isolated araban in low yields from the pectic substances of sugar beets (23). Again, by procedures of methylation, hydrolysis, and identification of the products, equal amounts of 2,3,5-tri-*O*-methyl, 2,3-di-*O*-methyl, and 2-mono-*O*-methyl L-arabofuranose were isolated. The ease of acidic hydrolysis and the direction of the change of rotation during hydrolysis indicated araban had the structure shown in Figure 3.

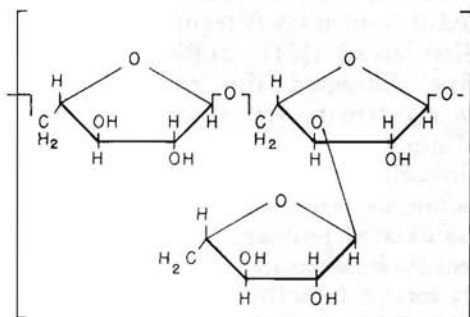
 α -1-5-ARABAN WITH
 α -1-3 BRANCHES

Figure 3.—Araban.

Little was added to the knowledge of sugar beet araban until recent years. Andrews *et al.* (1) confirmed the presence of the 1-3 and 1-5 glycosidic linkages in beet araban from its hydrolysis products separated on charcoal columns. Finan and O'Colla (17) showed by means of periodate oxidation the presence of furanose forms and indicated that beet araban must possess a ramified structure like that shown in Figure 3. Re-

cently, Andrews *et al.* (2) isolated alkali-stable polysaccharides from sugar beet slices. The chief polysaccharide material—molecular weight 12,500—appeared to consist of arabinose, galactose, and rhamnose in a molar ratio of 21:3:1. They were unsuccessful in their attempts to fractionate it and finally suggested that this "araban" exists in a combination with a variety of monosaccharide units.

Goodban and Owens in 1956 published an improved procedure of isolating araban from sugar beet pulp relatively free from pectic substances and contaminated only with traces of galactan (20). They acetylated the crude araban and fractionated the acetate on a charcoal column by elution with acetone and chloroform solution (21). By this means, they developed an elution diagram in which several fractions showed maximum negative rotations, and analysis after deacetylation indicated 95% araban or better. They concluded that this beet araban acetate fractionated according to molecular weight. These conclusions were based upon their specific viscosity measurements, the molecular weight of araban of 10,000 as reported by Ingelman (25), and the statement by Claesson that 10,000 appeared to be the molecular weight of maximum absorption of polymers on charcoal columns (11).

Tomimatsu *et al.* did not agree. In 1958 they measured some of the physical properties of Owens' and Goodban's araban fractions and found araban to be an unusual polysaccharide (43). Although it dissolves easily in water, it rapidly retrogrades and forms macroaggregates. Molecular weight measurements by light-scattering required addition of sodium chloride, alkali, or other hydrogen bond-breaking agents; otherwise molecular weights were anomalous. The weight average molecular weights of charcoal-fractionated araban acetate after deacetylation varied from 18,400 to 37,000. No simple relation existed between the fraction number and the molecular weight, and most of the fractions were heterogeneous in molecular weight.

Pectic Substances

History—The pectic substances offer attractive possibilities for utilization and have been studied widely. As stated by Whistler and Smart (44), the pectic group constitutes a triad of polysaccharide types that occur, are extracted and isolated together. The dominant member of this triad in terms of quantity is galacturonan.

The nomenclature of the pectic substances was quite confused in the early literature until 1926 when committees of the

American Chemical Society established rules of nomenclature essentially as follows:

"Pectic substances" is a group designation for these complex colloidal carbohydrate derivatives which occur in or are prepared from plants and contain a large proportion of anhydrogalactopyranuronic acid units which are thought to exist in a chainlike combination. The carboxyl groups of the polyuronic acids may be partly esterified by methyl alcohol and partly or completely neutralized by one or more bases.

"Pectinic acid" was the term used for colloidal polygalactopyranuronic acids containing more than a negligible proportion of methyl ester groups. Pectinic acids under suitable conditions can form gels with sugar and acid or, if suitably low in methoxyl, with certain metallic ions. The salts of pectinic acids are either normal or acid pectinates.

"Pectic acids" are completely de-esterified pectic substances and exist either as acids, salts, or a mixture.

"Protopectin" is applied to those water-insoluble pectic substances that occur in plants and that, upon partial hydrolysis, are converted to pectin.

Kertesz summarized researches on the pectic substances up to 1951 (27) and Joslyn reviewed developments up to 1962 (26). Confusion still exists as to the exact constitution of galacturonan as it exists in plants. The difficulty of separation of the accompanying polysaccharides, frequently referred to as ballast, has led most workers to conclude that integral nonuronic sugars are attached to the main galacturonan chain of most pectic substances. Numerous reports have appeared in the literature of neutral sugars including arabinose, galactose, rhamnose, xylose, and others identified chromatographically among the products of hydrolysis of carefully purified pectic substances (1, 3, 4, 7-10, 12, 19, 22, 27, 30-32, 34, 35, 42, 45). Only two reports of the isolation of pure galacturonan have appeared; one from sunflower heads (8) and one from fir bark (7).

Zitko and Bishop fractionated pectins from sugar beet, apple and citrus into acid-soluble and acid-insoluble polysaccharides (46). The acid-soluble polysaccharides were shown by moving-boundary electrophoresis to be complex mixtures of several polysaccharides. Zitko and Bishop fractionated pectic acids by precipitation with sodium acetate and examined them by electrophoresis. Each of the pectic acids showed two acidic components: one a pure galacturonan and the other a galacturonan containing neutral sugars as part of the molecule.

The constitution of citrus and apple pectic substances has been studied extensively and the basic structure of degraded pectic acids established through the work of Beaven and Jones (5, 6), Luckett and Smith (29), Smith (41), and Levene and Kreider (28). The galacturonan consists of α ,1,4-D-galactopyranuronic acid units combined in unbranched chains. Methylation fractionations have not been very satisfactory because the galacturonans are insoluble in the methylation agents and unstable to alkali. Extremely low yields of methylated galacturonan derivatives have so far been obtained (29). Methylated pectic acid yields 2,3-di-O-methyl-, but no 2,3,4-tri-O-methyl D-galactopyranuronic acid upon hydrolysis, so that end group assays of

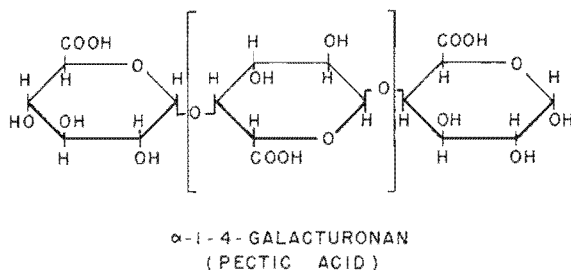


Figure 4.—Galacturonan.

chain length of the material have not been possible. Figure 4 shows the structure of pectic acid. Meyer and Mark (33) and Palmer and Hartzog (36) developed a space configuration in which the pectic acid molecule shows three-fold screw symmetry.

Pectic acid is an α -1,4-D-galactopyranuronide, araban is a branched α -1,5-L-arabofuranoside, and galactan is a β -1,4-D-galactopyranoside. Hirst and Jones (22) concluded that no direct interconversions of these three polymers can occur.

Hirst and Jones (22) stated clearly that only highly degraded pectic acids were essentially pure polygalacturonans, and that undegraded pectin may have side chains of nonuronide materials. Their results have often been carelessly interpreted as implying that all nonuronide material may be removed from pectic acid physically.

Sugar Beet Pectin Sugar beet pectin differs from most known fruit and vegetable pectins studied in that it cannot be extracted in high yields under conditions used successfully for citrus and apples. Once extracted and isolated sugar beet pectin does not gel easily. Roboz and Van Hook (38) suggested that the presence of acetyl on a relatively small molecule might prevent

beet pectin from gelling. Phippen *et al.* (37) showed that the introduction of but 2.6% of acetyl—one group per eight uronic acid units—prevented citrus pectin from gelling. Partial acid hydrolysis of the acetyl restored the gelation power to the pectin. Partial acid hydrolysis also changed sugar beet pectin so that it gelled fairly well.

Deuel and co-workers reported that sugar beet sodium pectate, extracted after alkaline treatment of pulp, had a high molecular weight and formed firm gels with calcium ions (13).

Gee *et al.* (19) showed that beet pulp contains about 4% acetyl. If the acetyl of pulp solids is all associated with the secondary hydroxyl groups of pectin, beet pectin *in situ* contains about 16% acetyl. This means that more than half of the secondary hydroxyl groups of beet pectin are acetylated. Its high acetylation partly explains why its solubility and alkali lability differ from those of fruit pectin or of sugar beet pectin partially deacetylated by conventional methods of extraction.

In addition to acetyl ester groups, beet pulp contains 25% pectin whose carboxyl groups are 50% esterified. Both the carbomethoxyl and acetyl groups are important to ammoniation of beet pulp to increase its nitrogen content for feeding sheep and cattle. Assuming that pulp has 4% acetyl and 25% pectin, about 3.5% N might be fixed through reactions of ammonia to form pectinate salts, pectin amides, and acetamide.

Beet Pulp Resources

Some knowledge is available on the chemical structure of the chief polysaccharides of beet pulp, but much less is known about their properties or possible uses. Sustained research is needed on extraction, isolation, and uses of beet pulp polysaccharides. Table 2 shows the calculated amounts of these materials

Table 2.—Potentially available beet polysaccharides in pulp produced in 1963 compared with some imported carbohydrate polymers consumed in the United States.

Beet polysaccharides	Millions of pounds
Pectin	580
Araban	464
Cellulose (crude fiber)	580
Galactan	139
Gums	
Gum tragacanth ¹	1.6
Gum karaya ¹	8
Locust bean ¹	11
Citrus and apple pectin ²	15
Gum arabic ¹	22
Guar gum ¹	26

¹ U. S. Bureau of the Census as reported in Oil Paint and Drug Reporter.

² Estimated from U. S. census (1957).

as compared with some of the foreign and domestic gums and pectic substances presently consumed in the United States.

A potential 139 million pounds of galactan is present in the available sugar beet pulp. Research might demonstrate an economical means of obtaining sugar beet galactan with useful properties.

Araban is an unusual polysaccharide, but no practical commercial uses have developed for it at this writing. Should research demonstrate its usefulness, 464 million pounds of this material exist in beet pulp.

By the same calculation as that used for araban and galactan, 580 million pounds of pectin is present in the sugar beet pulp currently available. This amount exceeds by 40-fold the current production and use of pectin from fruit cannery wastes.

Summary

Four carbohydrate polymers make up 76% of the dry weight of beet pulp in the following proportions: 6% galactan, 20% araban, 25% cellulose, and 25% pectin. The structure and properties of these materials are discussed.

Reference to a company or product name does not imply approval or recommendation of the product by the U. S. Department of Agriculture to the exclusion of others that may be suitable.

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