Isolation and Properties of Sugar Beet Araban

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For more than 80 years it has been known that sugar beet pulp contains a gum which may be hydrolyzed to give a high proportion of arabinose (1)[2]. Later work has shown that this araban is a relatively low molecular weight polysaccharide, soluble in water. Its importance to the sugar beet industry is twofold; first, it is water soluble and can be extracted during the diffusion process and interferes with purification and crystallization of sucrose; and second, it composes from 15 percent to 20 percent of the marc solids and may be a useful by-product of sucrose production. Beet molasses contains an alcohol-insoluble polysaccharide which has been shown to have a very marked depressant effect on the rate of crystallization of sucrose (2). This material yields, upon hydrolysis, arabinose, galactose, dextrose, and mannose. Ingleman (3) also found that the alcohol insolubles from sugar beet molasses were inhibitors of sucrose crystallization. Since the original discovery of araban in the pulp was made by extracting the beets with lime water, it is apparent that conventional purification methods will not remove araban but allow it to be carried along to the crystallizers.

Extraction

We were interested in the extraction of araban from the standpoint of both the conditions necessary to give a good yield of representative material, and also the conditions which might be encountered in the factory which would allow araban to be extracted into the diffusion juice. The pulp used was a supply of factory cossettes which had been preserved in boiling isopropyl alcohol. The cossettes were ground and extracted with boiling 70 percent alcohol until the extract contained less than 1 percent sucrose. No arabinose was detected by paper chromatography of the hydrolyzed extract.

To determine the total amount of arabinose-containing polysaccharide in the pulp, portions were refluxed with 1N or 3N HCl for periods of 30 minutes to 24 hours. The extracts were analyzed chromatographically and the arabinose estimated by reflectance of the spot after development with aniline trichloracetate (4). The maximum arabinose was about 20 percent, obtained in 1 hour with 3N or 4 hours with 1N acid.

Extraction of the pulp was investigated by heating the pulp with 50 volumes of extractant, neutralizing the filtrate, and concentrating before hydrolysis. Arabinose was determined on the hydrolyzate. Extraction was for 40 or 120 minutes at pH 6, pH 9, or pH 11, and a temperature of 70° or 100° C. High-temperature electrodes were used to measure the pH during extraction, and 1N NaOH was added to maintain the desired pH. At pH 9 or pH 11, the de-esterification and degradation of pectin occur very rapidly and it is necessary to add alkali to neutralize the acid produced. The results of the extractions are shown in Table 1. Extraction at pH 6 is slight in comparison to the higher pH extractions, and 100° is more effective than 70°. Apparently the extraction of araban is correlated with the breakdown of the pectin in the cell wall, since pH 6 extraction also

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[2] Numbers in parentheses refer to literature cited.

Table I.—Extraction of Araban from Sugar Beet Pulp.

pH	Temperature °C	Time Min.	Yield of Arabinose Percent on Pulp
6	70	40	.63
		120	.64
	100	40	1.1
		120	1.9
9	70	40	3.3
		120	4.3
	100	40	10.8
		120	12.0
11	100	40	19.3

fails to remove pectin. It is of interest to note that the pulp becomes slimy and difficult to filter when extracted at pH 9. This might be an explanation for the observed deterioration of pulp at high battery supply water temperatures. The battery supply water is usually alkaline because of condensate return, and this, coupled with the higher temperature, causes the degradation of pectin and the solution of araban. From these results it would seem desirable to control the alkalinity of the battery supply water to improve the pressability of the pulp and to minimize the extraction of araban.

Extractions also have been made with saturated lime water at 100°. The arabinose obtained was 13.5 percent in 40 minutes, and 18.5 percent in two hours. Since this is close to the total arabinose in the pulp, lime water was chosen as the extracting medium because of simplified control of conditions, ease of removal of excess calcium, and because the pectic acids produced form insoluble lime salts.

Purification and Isolation

The preparation of araban was undertaken in order to study the effect of this material on purification and crystallization studies in our processing laboratory. For our purposes it was desirable to obtain pure araban, or the purest arabinose-containing polysaccharide possible, in order to isolate the effects due to araban from those of the other colloidal materials in the beet.

Although the presence of a high proportion of arabinose in a gum from sugar beet pulp was known as early as 1873 (1), the first report of the isolation of an araban from sugar beets was by Gaponenkov (5) in 1936. This material was obtained by extraction of hydropectin by 70 percent ethanol and yielded 98 percent arabinose on hydrolysis. It is claimed by Schneider and Bock (6) that this extraction procedure, which has been used by other workers, actually extracts only the lower-molecular-weight arabans, and indeed the material isolated by Gaponenkov was fractionated by precipitation with 80 percent, 75 percent, and 70 percent alcohol into fractions with molecular weights of 5,700, 6,600, and 7,700 respectively. In 1945 Ingelman (3) purified an araban from sugar beets by dialysis and electrophoresis and determined the molecular weight to be about 10,000, and the specific rotation to be —129°. Hirst and Jones (7) have reported on the structure of sugar beet araban. It is a highly branched chain of L-arabo-furanoside residues, ⅔ of the units linked through positions 1 and 5, the remainder being terminal groups linked through positions 1 and 3.

We have found that extraction of pulp with lime water and precipitation of araban with alcohol yields an impure araban, as noted by Hirst and Jones. We have resorted to fractionation of the acetylated araban followed by de-acetylation to give a purified araban.

In a typical isolation, 120 grams of sugar-free beet pulp was extracted for two hours at 100° in 1500 ml. of saturated lime water. The extract was treated with CO_2 to pH 8, filtered, and the residual ions removed with ion exchange resins. After concentration to 200 ml., araban was precipitated with 9 volumes of 95 percent EtOH, washed, and dried. Yield was 17.5 grams of araban; 14.9 grams of this crude araban was acetylated by the method of Carson and Maclay (8), using formamide as a dispersing agent. The product was precipitated in ice water, washed, and dried. The yield was 23 grams of almost white material, anhydroarabinose .48 percent, calc. for araban diacetate 60.2 percent.

Crude araban acetate prepared in this manner was fractionated by two methods, column fractionation on charcoal or fractional precipitation from acetone by the addition of petroleum ether. Details of the fractionations are being published elsewhere (9). Columnar fractionation was somewhat superior to the fractional precipitation.

Table 2.—Araban Recovered from Fractions of Acetate on a Charcoal Column.

	Araban Acetate		
Fraction	**(α)D**	**Purity Percent**	**Araban (α)D**
6	—56[1]	68[2]	
11	—116	92	—131[3]
20	—84		—99
Original	—95	80	—113

[1] About 0.5 percent in chloroform.
[2] Calculated from arabinose content by orcinol-ferric chloride determination.
[3] About 0.5 percent in H_2O.

To recover araban from the acetate, samples were treated with 1N KOH for several days at room temperature until solution was complete. KOH was neutralized with excess acetic acid, then 8 volumes of EtOH were added. The precipitated araban was reprecipitated from aqueous solution to remove KOAc and dried. The yield was essentially quantitative. Data on fractions from a charcoal column are given in Table 2. The specific rotation is the best measure of the purity of the fractions. Fractions 6 and 11 were obtained by elution of the column with acetone-chloroform mixtures, fraction 20 by elution of the column with dioxane. The purities reported were calculated from the pentose values by the orcinol-ferric chloride method (10), which has consistently given results about 5 percent to 10 percent higher than paper chromatographic determination. A second fractionation, starting with an 89 percent araban acetate, gave fractions with a maximum purity of 95 percent, and a specific rotation of —122°. This material has not been deacetylated. Although even the best araban from these fractions still shows evidence of the presence of galactose and possibly a trace of rhamnose, it is probably suitable for use in studying the effect of araban on processing characteristics of sugar beet juices.

It is probable that the arabinose in sugar beet pulp is present largely as a true araban, since the yield of araban acetate with a purity of greater

than 90 percent was about 35 grams from 75 grams of starting material. The possibility of the presence of an arabo-galactan is certainly not excluded by these results, however, for none of the preparations were completely free of galactose, which is the principal impurity in the various materials prepared in this study.

Extraction of Commercial Grade Araban

There is another aspect to the araban in sugar beet pulp; namely, its value as a by product. Although araban from sugar beets is low in molecular weight, it may be useful, just as are other plant gums and mucilages, as an adhesive, a dispersing agent for emulsions, as a suspending agent in lotions, creams, etc. The drawback to the use of araban from sugar beet pulp is the expense of the usual alcohol precipitation. If $Ca(OH)_2$ is used as the extracting medium, the pectin is degraded to pectic acids which form insoluble calcium salts and can be separated by filtration. The excess calcium may be removed, along with the proteins, by carbonation in the usual manner. Araban can then be obtained by evaporation of the filtrate. This procedure has been followed in this laboratory to obtain crude araban as a light-brown powder. The use of carbon may be necessary to produce a light-colored product. The cost of this operation would be very low, since existing equipment in the factory could be used for almost the entire process.

Summary

The isolation of araban from sugar beet pulp has been described, and the conditions under which araban is extracted from the pulp have been investigated. The use of araban as a by product of the production of sugar is discussed, and an economical method for its preparation is outlined.

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