CHAPTER III : DEXTRINIZATION WITHOUT CATALYST
Roasting of starches in the dry state without any added catalyst results in the formation of British gums or pyrodextrins. Changes in the heat treatment of starch sometimes results in profound changes in the physicochemical properties of the end products. Although several groups of workers have studied the pyrodextrinization of starch in the absence of added catalyst, the results of their work are not strictly comparable inasmuch as some have recorded the temperature of material, while others that of the heating bath. Thus, there is the possibility of a difference of approximately 20° between the reaction temperature employed by different workers. Another factor which introduces variability in reaction conditions is the moisture content of starch.

In the present study, starch, gum guar and their mixtures, in various proportions (9:1, 8:2, 6:4), have been dextrinized at a bath temperature of 213 ± 3°C (temperature material) for 8 hours. The dextrin samples, withdrawn at intervals of one hour, have been evaluated in terms of their solubility in water, reducing power, intrinsic viscosity and 2-amylolysis. In the case of gum guar where considerable decomposition of the gum was observed during dextrinization, heating was restricted to only 2.5 hours.

RESULTS

Solubility

Solubility may be defined as the capacity of two or more substances to form spontaneously a homogeneous, molecular or colloidal dispersion
The solubility behaviour of polymeric substances is much more complex than that of low molecular weight materials. This is due to the size and shape of polymer molecules, the viscosity of their solutions, and the presence of amorphous and crystalline regions. When placed in solution the polymers swell continuously with respect to crystallinity until a homogeneous solution is formed. Thus starch swells and forms a homogeneous dispersion in hot water. Sometimes, partial swelling takes place because of the presence of cross-links, which form a three dimensional network through primary valence bonds.

In homologous series, solubility decreases with increase in molecular weight. Thus, glucose, maltose and glucooligosaccharides show progressive decrease in solubility in water. Apart from molecular size, the nature of the polymer is also important in determining its solubility. Thus, a highly branched molecule will be more soluble than the linear one (e.g. the linear component of starch i.e. amylose is insoluble in water while the branched component, amylopectin, is water soluble.

Solubility Characteristics of Various Dextrins

Fig. 7 shows the changes in solubility that take place during pyrodextrinization of starch, gum guar and starch-guar mixtures in proportions of 9:1, 8:2 and 6:4. It is seen that with progressive heating of starch and starch-guar gum mixtures there is an increase in the solubility. While starch dextrins of high solubility are obtained
Fig. 7

Solubility (%) vs. Heating time in hours

- O Starch
- ● Guar
- ○ Starch:Guar (9:1)
- ● Starch:Guar (8:2)
- ○ Starch:Guar (6:4)
within 3 hours of heating, starch-guar mixtures give dextrins of maximum solubility after about 4 hours of heating. Furthermore, as the proportion of guar gum in the starch-guar gum mixture increases, the extent of loss in solubility after the maximum value is reached decreases. It is also to be noted that with increasing amount of guar gum in the mixture the maximum solubility value and rate of solubilization both decrease. The shape of the solubility curves of starch-guar dextrins is the same as that of starch alone, but all curves lie under it. In all cases once maximum solubility is reached, further roasting results in less soluble products. Another distinctive feature of starch-guar curves is that within first hour the solubility drops but picks up as the dextrinization progresses.

The solubility curve of guar dextrins is markedly different from that of starch dextrins. Instead of increasing, the solubility of guar gum decreases with progressive dextrinization. Thus, guar gum, which had an initial solubility of 63.5%, gave a dextrin after 3 hours whose solubility was only 15%.

Reducing Value

Reducing carbohydrates are polyhydroxy compounds having a potential aldehydic or ketonic function. When a hydroxyl function combines with an aldehydic function within a molecule, a cyclic hemiacetal of pyranose or furanose is formed. In sugars, the hemiacetal function at C₁ is most reactive. It can react with a hydroxyl group of another sugar unit to form a disaccharide. The disaccharide can further react with its terminal functional group to another sugar
residue to form trisaccharide and so on. Thus, on progressive polycondensation, the reducing value (R.V.) of the condensed product diminishes. This is shown in the table, where G represents a glucose unit.

<table>
<thead>
<tr>
<th>D.F.</th>
<th>G1, G2, G3, G4, G5, G6, G7, G8, G9, G10</th>
</tr>
</thead>
<tbody>
<tr>
<td>R.V.</td>
<td>305, 243, 176, 147, 123, 105, 87, 75, 63, 66</td>
</tr>
</tbody>
</table>

Several workers have estimated the molecular weight of the polysaccharides by determining the number of reducing end group for a given weight of the sample. However, these methods have been found to be erroneous, when the molecular weight exceeds the value of 15,000.

Ferricyanide method for determining the reducing power is one of the preferred methods in starch chemistry, because it is least influenced by such variables as sample size, time of digestion and weight of oxidant. According to Greenwood, this method is more reliable than those based on copper reagent of Somogyi type.

**Results**

Ferricyanide curves of dextrins prepared from starch, guar and starch-gum guar mixtures are shown in Fig. 8. In all cases, pyrodextrinization results in increase of reducing value. The value increases with time of roasting. It may be noted that the dextrins obtained from mixtures of starch and guar give higher reducing values as compared to starch dextrins, while guar dextrins have higher reducing power as compared to starch and starch-guar dextrins.
Fig. 5: Schematic Presentation of Dextrinization
CHAPTER II: MATERIALS AND METHODS
Ferricyanide number
-oStarch - o ~ Starch: Guar (9:1)
-•-Guar - « & - Siarch'.Guar (8:2)
Fl6c. 8  - o - Search'.Guar (6:4)
Since early work of Staudinger, viscometric data are of interest to organic chemists, because it is possible to relate viscosity to the constitution and geometry of the molecules. Solution viscosity is basically a measure of the size of extension in space of the polymer molecules. Though empirically related to molecular weight only for linear polymers, on account of simplicity and usefulness, viscosity-molecular weight relationships are widely employed for the molecular characterization of polymers. Viscosity data as a function of concentration are extrapolated to infinite dilution by means of Huggins's equation:

\[ \eta \frac{Sp}{C} = \left[ \eta \right] _{sp} K' \left[ \eta \right] C \]

where \( K' \) is a constant for a series of homologous polymers of different molecular weight in a given solvent.

Staudinger had suggested that reduced viscosity, \( \left[ \eta \right]_{sp}/C \), should be proportional to its molecular weight. This concept has undergone some change; reduced viscosity has been substituted by intrinsic viscosity. The reaction is expressed as,

\[ \left[ \eta \right] = K M^\alpha \]

where \( K \) and \( \alpha \) are constants, determined from double logarithmic plot of \( \left[ \eta \right] \) and molecular weight (M) determined by an independent method such as osmometry. The exponent \( \alpha \) varies between 0.5 to 1.0 for coiled polymers depending upon the nature of solvent. Several theories (125-127) of frictional properties of polymer molecules in
solution have come to unanimous conclusion that intrinsic viscosity is proportional to effective hydrodynamic volume of the molecule in solution divided by its molecular weight.

The relation between molecular size and intrinsic viscosity depends upon many factors. The main factors are (1) molecular weight (2) configuration of the chain (3) the unperturbed dimension and (4) the gross chain structure in which degree of branching is the most important variable. Short branches have little effect on molecular size. By controlling some of the variable factors, as mentioned above, degree of branching can be calculated from viscosity measurements. In the case of Huggin's constant $K'$ (equation 1) the effect of chain branching is observed by plotting $\sqrt{\gamma}$ against $S^2$, where $S$ is the slope of the line relating $\gamma$ versus $C$. Harris has observed an increase in value of $K'$ from initial value of 0.58 to 1.02, with increase in molecular weight probably due to the change in the degree of branching.

In the present study, equation 1 has been employed for intrinsic viscosity determination. Viscosity determinations were carried out in water at 71°C, a temperature at which starch has good dispersibility and practically no retrogradation.

Results

Viscosity changes that take place when starch, gum guar and mixtures of starch-guar are roasted at 213°C are shown in Fig. 9.

In all cases, the same type of viscosity changes take place. Thus, initially within first 1-2 hours of heating there is a steep fall in intrinsic viscosity, after which the values gradually level off. It is
Fig. 9

Heating time in hours

- Starch
- Starch:Guar (9:1)
- Starch:Guar (8:2)
- Guar
- Starch:Guar (6:4)
observed that, in general, starch dextrins show higher viscosity than the corresponding starch-guar dextrins. In the case of 6:4 mixture of starch and guar, viscosity could not be determined after 2 hours since the products did not give homogeneous pastes.

$\beta$-Amylolysis

One of the important properties of starch dextrins is their increased resistance to attack by starch digesting enzymes. Among them, $\beta$-amylase is specific in its action as it attacks starch from the non-reducing ends of its component molecules by endwise action. It successively splits off two glucose units at a time in the form of maltose. (see Fig.10,11). Although the linear polymer (amylose) and the linear portions of branched polymer (amylopectin) undergoing enzymic attack are composed of glucose units joined through $\alpha\ 1 \rightarrow 4$ linkages, the maltose produced is in $\beta$-form due to optical inversion at the point of hydrolysis; hence the enzymic attack is termed "$\beta$-amylolysis". As mentioned earlier, the action of $\beta$-amylase is related to linear portions of starch molecules. Consequently, the action of the enzyme is halted when it encounters a branch point. The resistant core of starch left after the action of $\beta$-amylase is called the "$\beta$-amylase limit dextrin".

Crystalline $\beta$-amylase, obtained from potato, has a molecular weight of 1,52,000, as large as that of amylose fraction. It has been calculated that one molecule of crystalline $\beta$-amylase from malt, can hydrolyse 2,50,000 glucosidic linkages per minute. (132,133)

The enzyme action on $\alpha\ 1 \rightarrow 4$ linkage is attributed to contact
Fig. 10: Action Pattern of Beta-amylase on the Linear Fraction. Asterisk indicates aldehydic End of Chain.

Fig. 11: Action Pattern of Beta-amylase on the Branched Fraction. Asterisk indicates Aldehydic End of Chain.
catalysis, the bond being split by enzyme when it comes in proper juxtaposition with the substrate. The reaction of enzyme with substrate depends upon the specific interaction between them. The "polyaffinity" theory explains to a certain extent the stereochemical specificity of many enzymes.

According to "single chain action" theory, \( \beta \)-amylase attaches itself to single molecules of substrate and degrades it completely. With minimum amount of enzyme, the shorter molecules are attacked first. \( \beta \)-Amylase attacks only monodispersed single molecular chains of starch. Small impurities of retrograded starch impede glycoside bond fission.

The factors which affect the attack of enzyme on granular starch are:
1. the macromolecular structure of enzyme which cannot penetrate into unswollen starch granule cavity and
2. starch granules are highly associated (spherocrystals) in which vulnerable portions are blocked by hydrogen bonding.

Results

The results of \( \beta \)-amylolysis on various dextrins, obtained by dextrinization of starch and starch-guar mixtures, are shown in Fig. 12. It is observed from the figure that when starch is heated at 215°C there is a sharp decrease in the \( \beta \)-amylolysis value. The initial value of 70% after eight hours of roasting falls to 1%. Upto 4 hours the \( \beta \)-amylolysis value of starch dextrin is higher than the corresponding starch-guar dextrins. But after 6 hours of heating the trend changes and starch-guar dextrins show higher value than the corresponding starch dextrins.
Fig. 12
DISCUSSION

It is obvious that, because of the nature of dextrinization process, and the molecular complexity of starch, almost unlimited number of dextrin structures are possible. However, there are two striking structural changes that take place during dextrinization. One is the change in the molecular size of the resulting dextrin and the other is the change in the degree of linearity. The variation in the molecular size or molecular weight influences the viscosity of the dextrin while the change in linearity greatly influences the solubility characteristic of the dextrin.

In the initial stage of dextrinization moisture is removed from starch, and as the dextrinization progresses the native, water insoluble starch becomes soluble within 2 hours of heating at 215°C. This may be attributed to thermal, random depolymerization of starch component molecules as well as to structural changes that take place in the linear starch component. During dextrinization the linear molecules become branched and the branched molecules become further branched.

The increase in solubility with progressive dextrinization of starch may be, in part, due to rupture of hydrogen bonds. In the starch granule, the crystalline network of hydrogen bonds which prevents the access of water in the cold, decreases with dextrinization. Hence, there is reduced resistance by hydrogen bonds and easier penetration by water in highly amorphous dextrins resulting in high solubility.

The insolubilization of dextrins prepared at high temperatures is
perhaps due to the formation of degraded products and polymers thereof. Some higher D.P. carbohydrate polymers, insoluble in water, are perhaps formed during dextrinization. It is also conceivable that in the dextrinized products there are polymers in which glucose units are joined with furfural derivatives.

The solubility characteristics of products produced on dextrinization of starch and gum guar are very different. Thus, while progressive roasting of starch results in products of greater solubility, guar dextrins are less soluble than the starting material. Similar behaviour has been shown on dextrinization of gum exudates such as gum karaya\(^{136}\) and gum ghatti\(^{136}\), and seed gums such as locust bean gum\(^{137}\), and tamarind kernel polysaccharide.\(^{136}\)

The insolubilization of gum guar upon dextrinization may be due to the following: (1) The guar gum molecule which is composed of a backbone of \(\beta 1 \rightarrow 4\) mannose units, with branches of galactose residues linked to the alternate mannose residues by \(\alpha 1 \rightarrow 6\) linkage, undergoes debranching by cleavage of some of the galactose units. The resultant molecule has a more linear character and therefore there are greater possibilities of molecular association via hydrogen bonds. (2) Gum guar has a fair amount of protein impurity. During roasting the gum may combine with protein component to give insoluble products. Apriori, insolubilization due to debranching appears to be a more plausible explanation.

The increase in reducing power of the dextrins prepared either from starch or gum guar alone or from their mixtures is principally due to cleavage of glycosidic bonds. This is supported by sharp fall in the viscosity. The dark brown colour of the dextrins is indicative of break
down of the polymers beyond the hexose stage. In case of guar dextrins, the dark brown colour may also be due to reaction between sugars and amino acids (Maillard reaction).

If dextrinization were through initial hydrolysis and recombination thereafter, the reducing value at some stage of the reaction should have gone down. This is not observed during dextrinization at 215°C. Thus, at higher temperatures hydrolytic reaction during pyrodextrinization continues throughout, accompanied by some recombination and much transglycosidation. The branched chain nature of dextrins is indicated by their increased resistance towards β-amylase as compared to starch.

As regards mechanism of dextrinization, the data show that continuous hydrolytic degradation (increase in ferricyanide number) is a feature of the reaction although it should be borne in mind that increase in reducing power could also be due to such degradation products as 2-furaldehyde, acetaldehyde etc. Concurrent with the cleavage of glycosidic bonds is the formation of new ones, most probably through the intermediacy of 1,6-anhydro-D-glucopyranose. The formation of the latter derivative requires conformational change of the sugar ring from C1 to C10. Such a change requires input of energy which is readily available under the conditions of dextrinization. The mechanism of dextrinization as proposed by Gardiner is illustrated in Fig.

Some indication of hydrolysis-recombination mechanism is evident from a slight increase in intrinsic viscosity values of starch dextrins at 6 hrs. reaction time as compared to that of the product obtained after 5 hrs.