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INSTABILITY OF PECTIN IN NEUTRAL SOLUTIONS

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Pectin is usually thought to be stable in acid, whereas its instability in alkali has been known for some time (Kertesz, 1951). It has now been found, however, that pectin solutions are extremely sensitive to elevated temperatures in neutral and weakly acidic solutions. Under such conditions the pectin breaks down to lower molecular weight products. The instability of pectin at natural pH levels suggests that over extended periods of time it may lose part of its ability to strengthen the cell wall.

The present observation is also of practical importance. Stoĭkov (1958), for example, reports that pectin extracted from sunflower heads at a pH of approximately 7 has a lower jellying power than pectins extracted by more acidic solutions. The present investigations show that extraction of pectin under such conditions will result in considerable degradation of the polymer.

The viscosity of pectin solutions at various pH levels was investigated by Myers and Baker in 1927, Malsch in 1941, and many others. These investigations disclosed a slight drop in viscosity as the pH approached neutrality and significant decreases under alkaline conditions. The change in viscosity was attributed to variations in the hydrogen ion concentration. A number of investigators, including Weber (1944), have observed limited degradation of pectin by submitting solutions to elevated temperatures at

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various unbuffered pH levels. Vollmert (1950) and Neukom and Deuel (1958) have demonstrated the extreme lability of pectin, both in the cold and at elevated temperatures, under alkaline conditions.

Experimental

Unless otherwise stated a 2% solution of 70% esterified commercial citrus pectin was used for all determinations. Solution of the pectin was aided by prewetting the powder with a small amount of ethanol. The solution was filtered thru a sintered glass funnel before using. All viscosity measurements were obtained by diluting 10 ml of pectin with an equal volume of buffer. A standard McIlvaine buffer was used for the pH curves of Figure 1. The curves of Figure 2 were obtained by using 0.2 M sodium phosphate buffer at pH 6.8. The solutions were heated by inserting a large test tube containing the 20 ml volume into a water bath of the appropriate temperature. The length of heating was measured from the time of insertion of the test tube in the water bath. The volume of the samples was corrected after heating for loss due to evaporation. The same procedure was followed when testing substances other than citrus pectin.

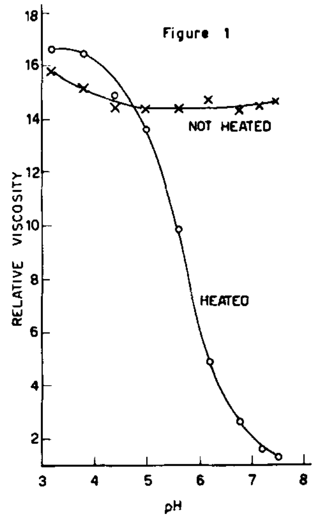
Figure 1

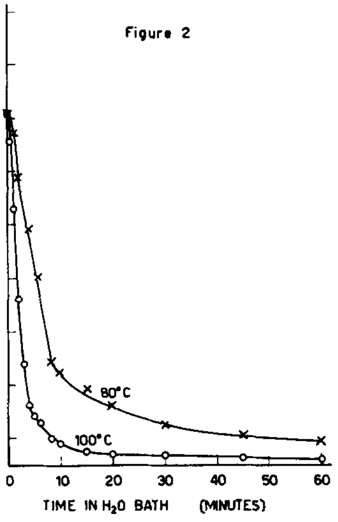
Figure 2

All viscosity measurements were obtained at 20°C by employing a capillary (Ubbelohde type) viscosimeter. Flow time for distilled water in the particular viscosimeter used was 31 seconds.

Results and Discussion

The curves of Figure 1 demonstrate the dependence of degradation of pectin solutions (6 minutes in boiling water bath) on the pH. The viscosity of the solution is only slightly dependent on the buffer before heating, but is reduced to practically that of water following the heat treatment at pH 6.8. The samples heated at pH 7.2 and 7.5 showed the characteristic yellowing of alkaline degradation.

The curves of Figure 2 follow the rapid reduction in viscosity caused by heating of pectin solutions at pH 6.8. Even in an 80°C water bath the viscosity is reduced by half in less than 7 minutes. Such a rapid loss in viscosity can only be due to a breaking of internal linkages. It requires an hour of heating at 80°C before yellowing of the solution is detectable.

Table 1

The effect of ten minutes in a boiling water bath on the viscosity of polyuronides in the presence of various buffers

Solution Tested	Buffer	pH	Relative Viscosity Before Heating	Relative Viscosity After Heating
1% citrus pectin	0.1 M Na Phosphate	6.8	14.3	1.7
1% citrus pectin	0.1 M Na Phosphate	4.5	13.9	13.1
1% citrus pectin	0.1 M Na Acetate	6.8	16.9	2.1
1% citrus pectin	0.1 M Na Citrate	6.8	13.2	1.7
1% apple pectin	0.1 M Na Phosphate	6.8	7.8	1.3
0.5% apple pectic acid (neutralized with NaOH)	0.1 M Na Phosphate	6.8	5.1	5.1
0.5% glycol ester of alginic acid *	0.1 M Na Phosphate	6.8	14.6	2.7

* commercially sold as "manucol"

The data of Table 1 show the effectiveness of several buffers at pH 6.8 on citrus pectin as well as the equal effectiveness of phosphate buffer at pH 6.8 on apple pectin and on the glycol ester of alginic acid. Apple pectic acid is completely unaffected by this treatment. The viscosity of a citrus pectin solution heated at pH 4.5 is only slightly reduced.

It is of interest that this is not the first unexpected reaction involving uronic acids to be observed this year. Fischer and Schmidt (1959) found that uronic acids readily undergo inversion of configuration at carbon 5 when submitted to the same reaction conditions necessary for pectin degradation. A striking difference between these reactions is that polyuronide breakdown seems to require the carboxyl groups to be esterified while epimerization is readily achieved by the free acid.

The mechanism of the degradation of pectin is currently being studied.

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