AN ION PAIRING H.P.L.C. INVESTIGATION OF THE ACIDITY PRODUCED IN THERMALLY DEGRADED DEXTROSE SOLUTION

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The literature contains conflicting evidence for the source and nature of the acidic product(s) responsible for the pH decrease generally observed during the heating of dextrose solutions. It is widely believed that the acid is formed by subsequent degradation of 5-hydroxymethylfurfuraldehyde (5HMF) (Tahir and Cates 1974; Sturgeon et al 1980). It has also been suggested that the acidity is produced by a second reaction product unrelated to 5HMF (Taylor and Sood 1978). Dextrose solutions (10% $^{w}/_{v}$) were heated at 120°C in sealed ampoules for times up to 6 hours. At intervals, ampoules were removed, cooled and the contents subjected to reverse phase chromatography. A capped ODS stationary phase ODS Hypersil was used with water as solvent and detection was at 254 nm. On the basis of the time dependence of peak heights produced, two major intermediates (I_1, I_2) and two acidic products (A_1, A_2) were detected in addition to the main 5HMF product. A_1 and A_2 were designated acidic products due to their elution at or before the solvent front coupled with the observed increase in their retention times when various quaternary ammonium pairing ions were added to the chromatographic solvent. The addition of pairing ion at different concentrations to the chromatographic solvent markedly improved the retention and separation of A_1 and A_2. The behaviour of A_1 and A_2 followed that shown to be general for carboxylic acids in presence of pairing ion (Hung and Taylor 1980). The use of different pairing ions also allowed a more rigorous comparison of the behaviour of A_1 and A_2 with that of previously suggested acid species namely acetylacrylic, levulinic and formic acids. The observed behaviour did not correspond with any of these. No standard metasaccharinic acid was available but A_1 and A_2 both showed appreciable maximal absorption at 250 nm which was taken to be indicative of a ketocarboxylic acid.

Chromatographic behaviour of A_1 and A_2 without pairing ion but in the presence of solvents of different pH values showed much greater retention at low pH than any of the suggested species and indicated a pKa value for both A_1 and A_2 of approximately 3.0. Isolation of peaks I_1 and I_2 followed by heating in solution and subsequent chromatography with an ion pairing solvent produced peaks corresponding to A_1, A_2 and 5HMF, confirming the intermediate nature of I_1 and I_2. Heating aqueous solutions of 5HMF (0.027% $^{w}/_{v}$) for 8 hours at 120°C in sealed ampoules with subsequent chromatography in ion pairing solvents showed no decomposition of that product, no evidence of A_1 or A_2, nor did the pH of the solution change. The pH decrease generally observed in dextrose was observed to be kinetically consistent with the rise in concentration of the acid products A_1 and A_2. These observations appear to support the contention that the acidity in heated Dextrose solutions is due to acid products formed directly from the intermediates. It has recently been observed, however, following prolonged storage of degraded Dextrose solutions in presence of air at room temperature, that 5HMF originally present appears to be converted to acidic compounds. The complexity of the reaction is further demonstrated by the observation that on heating the isolated intermediates I_1 and I_2, the solution assumes a brown colouration which supports the suggestion (Fleming et al 1969) that an α-diketohexose intermediate itself polymerises and explains the observation that autoclaved dextrose solutions may exhibit brown colouration while containing very small concentrations of 5HMF.

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