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THE *exo*-ANOMERIC EFFECT IN RELATION TO POLYSACCHARIDE CONFORMATION IN SOLUTION

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It has long been recognised that the iodine-binding capacity of glycogen and fractions of starch in aqueous solution is strongly influenced by inorganic co-solutes. For example, potassium iodide diminishes the proportion of iodine that is firmly bound by amylose (Bates *et al.*, 1943) while ammonium sulphate (Sumner & Somers, 1944; Schlamowitz, 1951) and calcium chloride (Deatherage *et al.*, 1955) greatly enhance the iodine-binding capacities of glycogen and branched fractions of starch. Recent studies with many other inorganic salts and mineral acids have confirmed the general nature of the phenomenon (Painter, 1976).

In an early attempt to explain the effect of potassium iodide, it was suggested that it replaced molecular iodine (I_2) by the longer tri-iodide ion (I_3^-) inside the single helix (Baldwin *et al.*, 1944). Later, however, measurements of the formation constants of the respective complexes with the Schardinger α-dextrin (Dube, 1947) and direct analysis of the complex with amylose (Gilbert & Marriott, 1948) made it clear that, under the conditions of the earlier experiments (Baldwin *et al.*, 1944) essentially all of the iodine would have been bound as I_3^-, even at the lowest concentration of potassium iodide that was used.

The phenomenon is therefore still unexplained. It is not a primary salt effect in the ordinary sense, because the salts change the stoichiometry of the reaction and must therefore change the number of binding sites per molecule. Formally, the phenomenon may be brought within the scope of the conventional theory of primary salt effects (Long & McDevit, 1952) by recognising the presence of different binding sites whose sensitivities to salt (analogous to salting-out parameters for small molecules) are different. Consideration of salting-out parameters for small molecules (Long & McDevit, 1952) suggests that differences in *polarity* between different binding sites account best for the observed effects of salts upon starch–iodine complexes (Painter, 1976).

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In the binding of the iodine, the helical conformation of V-amylose (Rundle & French, 1943; Rundle & Edwards, 1943) the glycosidic linkage angles (Rao *et al.*, 1967; Rao *et al.*, 1969; French & Murphy, 1973, 1977*a*, 1977*b*) are close to a position of minimum polarity, as judged from considerations (Painter, 1976) of the *exo*-anomeric effect (Lemieux & Koto, 1974) alone. A more refined, quantum-mechanical analysis may make this approximation better or worse, but there is strong evidence that the *exo*-anomeric effect is the dominant electronic effect in determining linkage conformations (Lemieux & Koto, 1974). We therefore set out to determine whether inorganic ions influence the magnitude of the *exo*-anomeric effect in aqueous solution in a way that would explain the observed effects of salts upon starch–iodine complexes.

The magnitude of the *exo*-anomeric effect is affected by changes in the solvation of the basic, ring- and glycosidic-oxygen atoms, O1 and O5 (Lemieux *et al.*, 1969). Measurements of the effect of salts upon the temperature at which methyl cellulose precipitates from solution (the 'cloud point') gave results closely parallel with the effects of salts upon the starch–iodine reaction, suggesting that there was the common feature of oxygen atoms acting as proton-acceptors in hydrogen bonding (Painter, 1973*a*).

In the case of mineral acids, strong evidence was provided by the finding that the relative rate of hydrolysis (K_β/K_α) of methyl β- and α-D-glucopyranoside was dependent upon both the concentration and the identity of the mineral acid used (Painter, 1973*b*). This quantity, K_β/K_α, is expected to be a unique measure of the magnitude of the anomeric effect, because medium effects on all other parts of the molecule should cancel (Painter, 1973*b*). Similar results were obtained with cellobiose and maltose (Painter, 1973*a*). At 40°C and, by inference, also at lower temperatures, K_β/K_α increased in sulphuric acid and decreased in hydrobromic acid with increasing acid concentration (Painter, 1973*a*), as also did the iodine-binding capacity of starch in the same acids at 20°C (Painter, 1976).

Further evidence on the action of neutral salts was provided by the discovery that they promote a $^4C_1$ to $^1C_4$ conformational transition in the α-L-gulopyranuronate residues of alginate after partial oxidation with periodate (Painter, 1979). Studies of the effects of low pH and esterification upon this transition strongly indicated that it was brought about by changes in the magnitude of the anomeric effect (Painter, 1979).

In conclusion, changes in the magnitude of the *exo*-anomeric effect are probably the main driving force leading to changes in the number of sites in starch and glycogen molecules that can bind iodine strongly. The more polar binding sites that are added or subtracted in the presence of different acids or salts probably occur near branching points or the ends of chains, where their assumption of the less-polar, V-conformation is opposed by steric interactions or the crowding of chain-ends at the periphery of branched molecules. Consistent with this, the salt effects appear to be smaller on fractions rich in amylose, though more experimentation is needed to conform this unequivocally.

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