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BINDING OF TOXIC CATIONS TO PECTIN, ITS OLIGOMERIC FRAGMENTS AND PLANT TISSUES

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Pectin, occurring in fruits, vegetables and some important industrial plants, is a component of our daily food. In view of the role of pectin in the physiology of nutrition, pectin is today held to be an essential part of the diet. It favourably influences the cholesterol level in blood and the metabolism of saccharides and also acts as a natural prophylactic substance against poisoning with toxic cations. Pectin has been shown to be effective in removing lead and mercury from the gastrointestinal tract, and respiratory organs. It has been suggested that the binding of lead cations to monomeric galacturonic acid, produced by enzymic degradation of pectin, is important in the urinary excretion of lead.

With regard to all these areas, the binding of toxic cations was investigated not only on macromolecular pectins (Sr^{2+}, Cd^{2+}, Pb^{2+}), but also on well defined oligomeric fragments of pectin (Sr^{2+}, Cd^{2+}, Pb^{2+}, Cu^{2+}) and plant tissues (Pb^{2+}) isolated from some nutritionally important vegetables (carrots, cabbage) and fruits (apples).

The interaction of cations with the carboxyl groups of these substances was evaluated on the basis of counter-ion activity and the results were interpreted by using the multiple equilibria law. The following experimental techniques were used: dialysis, the metal-indicator method (tetramethylmurexide), ion-specific electrodes and polarography. The advantages and disadvantages of each method were discussed.

The stability constant (K) of cadmium pectinates decreased strongly with increasing degree of esterification (E) of pectin, i.e. with decreasing linear charge density (Malovìkovà & Kohn, 1982). The cadmium cations are bound to pectin with a high degree of esterification ($E \sim 85\%$) by pure electrostatic bonds, while in low methoxyl pectins ($E = 0$ and $E = 25\%$) there is an intermolecular chelate bond which results in aggregation.

In contrast, the stability constants for lead pectinates (Malovìkovà & Kohn, 1979) do not change over a degree of esterification from $E = 0$ to $E = 50\%$; the stability

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constants are thus independent of the linear charge density which is not in agreement with classical polyelectrolyte behaviour and is probably due to the formation of an intramolecular chelate bond with lead cations. Results relating to the binding of Sr^{2+} ions on pectin and oligogalacturonates have been discussed earlier (Kohn & Luknár, 1975). The interaction of Cd^{2+} and Pb^{2+} ions with pectin is governed by the multiple equilibria law. Conclusions for the practical application of pectin as a prophylactic agent were discussed.

The binding of Pb^{2+} ions to plant tissues isolated from cabbage, carrots and three varieties of apples has been studied (Kohn *et al.*, 1981). The binding capacity of carrot and cabbage tissue for lead ions is high and several times greater than that of apple tissues. This low binding capacity is due to the very high degree of esterification of apple pectin (85%). The lead cations are strongly preferentially bound to the vegetable tissues even in the presence of a large excess of calcium ions. Both types of vegetable can therefore be used as an active component in a prophylactic diet against poisoning with lead cations. The binding mechanism of lead ions to plant tissues is complicated due to the presence of buffer substances and inhibitors in plant tissues which interfere with the cation binding. Lead ions are bound to plant pectins by a strong chelate bond only at the higher pH values corresponding to the pH of the small intestine, the resorption organ of the human body. At the low pHs found in the stomach the binding of lead cations is relatively small.

The binding of bivalent cations on oligogalacturonic acids (K^+ form) with a degree of polymerisation (n) of 1-9 has been studied (Kohn, 1982; Kohn *et al.*, 1982). These oligomeric fragments of pectin displayed strong selectivity in their cation binding, decreasing in the order: lead > copper > cadmium > calcium, strontium, zinc. No selectivity was observed between calcium, strontium and zinc ions, which are bound to oligomers electrostatically. These cations are bound to the monomeric D-galacturonic acid in very small amounts, close to the limit which can be detected experimentally. The relatively high amounts of lead, copper and cadmium bound to these low molecular fragments of pectin, especially the monomer, dimer and trimer, prove that these substances can really take part in removing toxic cations from the respiratory organs, i.e. outside the gastrointestinal tract. It was confirmed (Kohn *et al.*, 1982) that copper ions are bound on mono- and oligogalacturonates stoichiometrically in accordance with the multiple equilibria law. These results are not in agreement with the suggested formation of a positively charged complex of Cu^{2+} (as well as Pb^{2+} Cd^{2+}) ions with monogalacturonic acid.

In the last part of the lecture some theoretical problems concerning cation binding by polymeric acids in general were elucidated (Kohn & Malovíková, 1981). The interpretation of activity coefficients $\gamma_{Ca^{2+}}$ determined in solutions of calcium oligogalacturonates and oligoguluronates led to the conclusion that the binding of Ca^{2+} to isolated macromolecules of D-galacturonan and L-guluronan is of a purely electrostatic nature, in contrast to the intermolecular chelate binding, which occurs in aggregates of macromolecules containing these uronans.

The linearity of the functions $\gamma_{Ca^{2+}} = f(1/n)$ and $\gamma_{Ca^{2+}} = f((n-2)/n)$ (Freudenberg's equation) proved the validity of the additivity rule in predicting the contribution of $a_{Ca^{2+}}$ corresponding to individual uronic acid units, to the total activity of Ca^{2+} counter-ions in oligo- and polygalacturonates and guluronates. The additivity rule can be applied only to cations bound electrostatically on polyelectrolytes with relatively stiff chains (L-guluronan, D-galacturonan). With polyelectrolytes having a more flexible chain (e.g. D-mannuronan) the additivity rule is not valid.

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