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THE COMPLEXING OF CALCIUM
AND MAGNESIUM BY ORGANIC
PLANT CONSTITUENTS

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ABSTRACT

The definition, occurrence and aetiology of hypomagnesaemic tetany is discussed as an introduction to the practical implications of the present investigation. The current hypotheses, involving an unfavourable pasture chemical composition, accounting for the binding of Ca^{++} and Mg^{++} in the intestinal tract of ruminants are reviewed. The role of undigested or partly-digested plant cell wall materials is advanced as another such hypothesis, and the present investigation of the cell wall polymers of a typical pasture grass is outlined.

The comprehensive analysis of the grass Yorkshire fog (Holcus lanatus) involves, initially, the extraction and purification of pectic substances, lignin, hemicelluloses and cellulose. The non-volatile organic acid content of the grass is also determined.

Analytical methods are developed and evaluated in order to assess the homogeneity of these isolated cell wall fractions, and their chemical constitution investigated to aid in determining any possible relationship between cation complexing and polymer (or monomer) structure.

The pectic fraction isolated from Yorkshire fog is approximately 90% polygalacturonic acid while the hemicelluloses are basically arabinoxylans with varying hexose and uronic acid content. Attempts to fractionate the predominant hemicellulose, hemicellulose B, into homogenous arabinoxylans gives inconclusive results. Most of the chemical evidence, however, indicates the presence of three discreet polysaccharides in this fraction - a simple arabinoxylan, an acidic galactoarabinoxylan and a neutral glucan.

Infrared and ultraviolet spectroscopy is utilised to

determine the purity of the isolated lignin as well as the presence of typical lignin functional groups. Yorkshire fog lignin has a moderate phenolic hydroxyl and -OMe content and, like most other monocotyledonous lignins, gives yields of syringaldehyde, vanillin and p-hydroxybenzaldehyde on alkaline nitrobenzene oxidation. The outstanding feature of the lignin is its appreciable content of etherified hydroxyl groups in the 4-position of the aromatic ring and the low yield of syringaldehyde.

The water-soluble, non-volatile organic acids are quantitatively determined by anion-exchange resin chromatography and their identity confirmed by paper chromatography. The major acid is the tricarboxylic acid, trans-aconitic acid, which is determined spectrophotometrically. The normal plant acids, citric and malic, are present in moderate quantities while the alicyclic acids, quinic and shikimic, are only present in minor amounts.

A limited amount of data on the seasonal fluctuation of these organic fractions in Yorkshire fog is presented.

Electrolytes and the concept of ionic activity are discussed in the introduction to the study of the ability of these plant fractions to bind Ca^{++} and Mg^{++} in an aqueous salt solution of cationic composition similar to that of the intestine of a ruminant. A cation exchange method is developed whereby changes in the activity of Ca^{++} or Mg^{++} on the introduction of a plant fraction into the salt solution are reflected in the cationic composition of the equilibrium resin. An investigation is undertaken of a large number of calibration solutions varying in $[\text{Ca}^{++}]$ and $[\text{Mg}^{++}]$, but constant in $[\text{Na}^+]$, $[\text{K}^+]$ and $[\text{NH}_4^+]$, the latter cations being present in excess as 'swamping' cations.

Regression expressions relating solution cation concentration to the equilibrium resin cation concentrations are derived and used as calibration equations to determine the amounts of bound and ionic Ca^{++} and Mg^{++} in solutions in equilibrium with the plant fractions.

The pectic substances, lignin and the organic acids are effective in complexing a large proportion of the solution Ca in a non-ionic form but only lignin and the organic acids display a significant complexing of solution Mg^{++} . Except for hemicellulose B (branched) at a slightly alkaline pH, the hemicelluloses and cellulose have little ability to complex either Ca^{++} or Mg^{++} .

The complexing results are discussed in terms of the relationship of polymer structure to observed cation affinity. Factors involved in cation binding are:

- the charge and degree of hydration of the cation itself;
- distribution and degree of esterification of carboxyl groups in the polymer;
- monomer conformation;
- type of glycosidic linkage in the polymer;
- the possibility of hydrogen-bonding and non-bonded interactions between substituents on the polymers;
- solution pH.

The in vivo implications of the results are finally discussed in the context of general ruminant nutrition and alkaline-earth metal absorption discussed in the introduction.

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