Met-Asp-Phe, Trp-Met-Asp-Phe and β -Ala-Trp-Met-Asp-Phe. These peptides seem to exist in a relatively narrow range of conformational populations centred around $\phi = 95^\circ$, and the population distribution is described quite well by the potential-energy map given by Scott & Scheraga (1966). This series of peptides will also be used to show how n.m.r. can give precise information on the populations of the different rotamers about the side-chain α -CH- β -CH₂ bond, and finally a possible method by which n.m.r. may be able to give information about the other backbone dihedral angle, ψ , will be discussed.

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Conformations of Crystalline Alginic Acids and their Salts

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The physical properties of alginates, e.g. viscosity, gel formation, ion-selectivity etc., are known to be dependent on the proportions of mannuronic acid and guluronic acid in a given sample (Smidsrød & Haug, 1968), but the relationships between these properties and the molecular structures of alginates are poorly understood.

In the partially crystalline fibrous form, poly- β -D-mannuronic acid and poly- α -L-guluronic acid are stereochemically very different (Atkins, Mackie, Parker & Smolko, 1971). Polymannuronic acid is a flat ribbon-like chain whose molecular repeat of 10.3 Å contains two diequatorially (1eq,4eq)-linked β -D-mannuronic acid units in the C1 chair form. In contrast, polyguluronic acid has a repeat of 8.7 Å also containing two α -L-guluronic acid units, but in the 1C chair form. Thus the sugar units are diaxially (1ax,4ax)-linked and the chain has a rod-like conformation.

The study of oriented specimens of salts of these substances by X-ray diffraction has revealed some other interesting differences. In the polymannuronates (lithium, sodium, potassium and calcium salts) the fibre repeating value is about 15 Å. The chain is now a helix, though still close to maximum extension, in which one turn contains three monosaccharide units in the C1 chair. These structures are reminiscent of β -(1 $\rightarrow$ 4)-linked xylan, which also has three D-xylose units in a repeat of 14.8 Å

(Marchessault & Sarko, 1967). In contrast, the X-ray-diffraction photographs of ammonium polyguluronate and potassium polyguluronate clearly show that the twofold repeat of 8.7 Å (and therefore the 1C chair) is maintained in these structures. The X-ray-diffraction photographs of other salts (including the calcium salt) are poorly resolved at present, but these show the same general features of the ammonium and potassium salts. It is therefore to be expected that they too have the sugar units in the 1C chair form and similar overall chain conformations. The results also provide evidence that polymannuronate may be a more flexible structure than polyguluronate, in the sense that rotations can occur about the glycosidic bonds in the former, whereas the units are more rigidly held in potassium polyguluronate chains. [The related substance polygalacturonate is similar to polyguluronate in having (1ax,4ax)-linked units, but is also like polymannuronate in having three sugar units in a molecular repeat of 13 Å.]

Alginates may serve as ion-exchangers and structural materials in the natural state, and it is thought that they are largely co-polymers made up of blocks of the type $(-M-)_n$, $(-G-)_n$ and $(-M-G-)_n$ (where M is mannuronic acid and G is guluronic acid) (Haug, Larsen & Smidsrød, 1966) whose proportions may vary according to the physical requirements of particular tissues in particular environments. In a qualitative sense it is noteworthy that alginates enriched in $(-M-)_n$ appear to be characteristic of more flexible tissues, whereas those enriched in $(-G-)_n$ are found in tissues (such as cell walls) that require more rigidity (Frei & Preston, 1962).

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The Conformation of Polygalacturonic Acid Subunits

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Several workers have employed computational methods to obtain an estimate of the energy of a disaccharide as a function of the two angles of