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

rotation about the glycosidic linkages (Rees & Skerrett, 1968; Rao, Yathindra & Sundararajan, 1969; Whittington, 1971). If it is assumed that such energies are not appreciably altered by the presence of the more distant neighbours, then from the energy contour map it is possible to calculate the radius of gyration and characteristic ratio of the polysaccharide in solution. In addition, interaction-energy calculations provide information that, when combined with X-ray results, can enable the configuration of the polymer in the fibre to be deduced.

To perform such energy calculations for the galacturonic acid dimer, it is necessary first to decide on the monomer conformation. From evidence provided by the chemical shift of the *O*-acetate methyl signals in the acetyl derivative of polygalacturonic acid and the *O*-methyl signal in the fully methylated derivative, Hirano, Manabe, Miyazaki & Onodera (1968) have suggested that the uronic acid unit is in the 1C conformation. However, it has been reported that it is not possible to fit the X-ray fibre results obtained with pectic acid, whose major constituent is polygalacturonic acid, by a model consisting of a chain of 1C monomers without strong steric interference (Rees, 1969).

By employing the iterative procedure used by Rao, Sundararajan, Ramakrishnan & Ramachandran (1967) to fix the positions of the rotating groups off the sugar ring, the relative energies of the various possible galacturonic acid monomer conformations have been calculated. In addition to the use of a Kitaydorodski function to obtain an estimate of the energy between non-bonded atoms, various hydrogen-bond functions have also been included. The effects of acetylation and methylation on the energies of the monomer conformations are briefly considered.

The energy contour map for the dimer is calculated by employing the appropriate monomer form. A coulombic term is included in the energy function to take into account the interaction between charged groups. The relevance of these results to the solution properties of the polysaccharide and its configuration in fibres is discussed.

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The Conformation of Gramicidin S: Computed Circular-Dichroism Properties

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Several structures have been proposed for the conformation of the cyclic decapeptide antibiotic gramicidin S on the basis of X-ray analysis, spectroscopic measurements and conformational-energy calculations. The structure involving intramolecular hydrogen-bonding (Hodgkin & Oughton, 1957; Schwyzer, 1958) between antiparallel parts of the molecule has received support from n.m.r. (Schwyzer & Ludescher, 1968; Stern, Gibbons & Craig, 1968) and ^3H - ^1H exchange (Laiken, Printz & Craig, 1969a). Initial results of conformational-energy calculations produced three additional possible structures (Liquori, DeSantis, Kovacs & Mazzarella, 1966; Vanderkooi, Leach, Nemethy, Scott & Scheraga, 1966; Scott, Vanderkooi, Tuttle, Shames & Scheraga, 1967). Progressive refinements of the energy calculations (Momany, Vanderkooi, Tuttle & Scheraga, 1969; DeSantis & Liquori, 1971) now favour the Schwyzer (1958) structure as being of lowest energy. The optical-rotatory-dispersion and circular-dichroism findings (Ruttenberg, King & Craig, 1965; Balasubramanian, 1967; Quadrifoglio & Urry, 1967; Laiken, Printz & Craig, 1969b) are consistent with this structure, although they are unusually intense, but the alternative α/β structure proposed by Hodgkin & Oughton (1957) cannot be ruled out. The strong negative rotational strength of the $n-\pi^*$ system indicates a high degree of ordered structure; this is relatively insensitive to organic solvents and to elevated temperatures.

Optical properties have now been computed for various proposed structures. Cyclization of the structures was checked and improved where necessary, preserving twofold symmetry where present. Circular-dichroism properties have been computed by extension of the methods previously described for dipeptides (Bayley, Nielsen & Schellman, 1969). The secular matrix method is expanded to treat the interactions between ten peptide chromophores, with each chromophore containing two transitions ($n-\pi^*$ and $\pi-\pi^*$). Diagonalization of the resultant 20×20 matrix yields eigenvalues and eigenvectors from which the properties of the assembly may be assessed.

Three general results are obtained. (1) The rotational strength of the $n-\pi^*$ system, $R_{n-\pi^*}$, is notably sensitive to molecular conformation,