was heated to reflux for 96 h. The solvent was evaporated under reduced pressure and the residue was chromatographed on a silica gel column, eluted with chloroform-ethyl acetate (3:1). Yield: 25 mg (77 %). MS: $M^+ = 203$; NMR (dimethyl sulfoxide-d_6): broad NH at 13.07 (1H), aldehyde singlet at 9.42 (1H), aromatic singlet at 8.36 (1H, H-3), doublet ($J = 7$ Hz) at 8.19 (1H, H-6), triplet ($J = 7$ Hz) at 7.75 (1H, H-7), doublet ($J = 7$ Hz) at 7.40 (1H, H-8), and singlet at 2.35 (3H, CH_3) ppm.

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Methylation Studies on Levans

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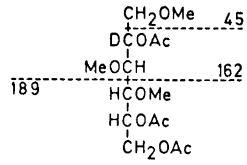
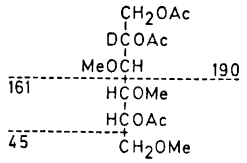
Levan, which is an essentially (2→6)-linked β-fructan, is antigenic in man and is precipitated by some myeloma proteins.[1] Different preparations show variations in their immunochemical behaviour[1,2] which must be due to structural differences. We now report methylation studies on some levan preparations of different origins.

Qualitative and quantitative analysis of the methylated sugars obtained on hydrolysis of a methylated polysaccharide is preferably performed by GLC-MS of the derived alditol acetates.[3,4] Some difficulties might be expected in working with ketoses since reduction of each partially methylated ketose should give rise to two alditol derivatives. None of the pairs of D-glucitol and D-mannitol derivatives obtained from 1,3,4,6-tetra-*O*-methyl-, 1,3,4-tri-*O*-methyl-, or 3,4-di-*O*-methyl-D-fructose separated, however, on the chromatographic columns used. Another possible source of difficulty is that the alditols derived from the 1,3,4- and 3,4,6-isomers of tri-*O*-methyl-D-fructose might not be distinguishable. When the conversion to





alditols is carried out with sodium borodeuteride, however, these substances give different mass spectra. The origin of some pertinent primary fragments is indicated above for the D-glucitol derivatives. When this method is used, a small proportion of 3,4,6-tri-*O*-methyl-D-fructose in the 1,3,4-tri-*O*-methyl-D-fructose might be overlooked. Therefore GLC was used to compare the acetates of the free sugars obtained on hydrolysis of methylated inulin with those obtained from the methylated levans B512 PP2, "Coryne", "Hestrin", and "Rye grass". The 1,3,4- and 3,4,6-tri-*O*-methyl-D-fructose acetates gave only one peak each on GLC and these were well separated (retention times relative to 1,5-di-*O*-acetyl-2,3,4,6-tetra-

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Table 1. Methylation analysis of levans.

Polysaccharide	Methylated sugar, % 1,3,4,6-Fru[a] $T^b=0.82$	2,3,4,6-Glu $T=1.00$	1,3,4-Fru $T=1.82$	3,4,6-Fru $T=1.82$	3,4-Fru $T=4.31$
Inulin	4	3	–	92	1
P6	4	1	85	–	10
B512 E	10	–	68	–	22
B512 PP2	11	–	68	–	21
Coryne	3	–	91	–	6
Hestrin	16	–	66	–	18
Rye grass	7	–	87	–	6

[a] 1,3,4,6-Fru= 1,3,4,6-tetra-*O*-methyl-D-fructose, *etc.*
[b] Retention times of the corresponding alditol acetates relative to 1,5-di-*O*-acetyl-2,3,4,6-tetra-*O*-methyl-D-glucitol on an OV-225 column.

O-methyl-D-glucitol 1.07 and 1.16, respectively). Only the 1,3,4-derivative was obtained from the levans investigated. The results of the methylation analyses of inulin and the different levans are summarized in Table 1.

According to previous results the levans are essentially (2→6)-linked, with some branches in the 1-position,[5] in contradistinction to inulin which is essentially (2→1)-linked. The mode of biosynthesis of these polysaccharides indicates that each molecule should contain a sucrose residue with D-glucose as the non-reducing end-group.

The results in the table show that all the levans have the expected structure (although the non-reducing D-glucose end-group is found only in the analysis of levan P6), a chain of (2→6)-linked D-fructose residues with some branching in the 1-positions. Since all the polysaccharides have strong negative rotations, the linkages must have the β-configuration. The degree of branching is proportional to the percentage of 3,4-di-*O*-methyl-D-fructose. For polysaccharides of high molecular weight the percentage of branch points should be equal to that of fructose non-reducing end-groups. The agreement between these figures is good for inulin and the rye grass levan, but not for the five bacterial levans. Losses of volatile 1,3,4,6-tetra-*O*-methyl-D-fructose and derivatives may partially explain this discrepancy which is, however, larger than expected. Therefore it is possible that these levans contain some minor structural feature which has been overlooked in these studies. Phosphate groups are excluded as levans B512 PP2, B512E, P6, „Hestrin", and "Rye grass" contained no phosphate.

These studies give information on the degree of branching of the different samples but not on the lengths of the side chains which, from the immunochemical point of view, may be of equal or greater importance.

Experimental. General methods. Concentrations were carried out under diminished pressure at bath temperatures which did not exceed 40°. For gas chromatography a Perkin-Elmer 990 instrument fitted with a flame-ionization detector was used. Separations were carried out on glass-columns 180 × 0.15 cm containing (a) 3 % OV-225 on Gas Chrom Q (100/120 mesh) at 170° (partially methylated alditol acetates) or (b) 3 % ECNSS-M on Gas Chrom Q (100/120 mesh) at 160° (partially methylated monosaccharide acetates). For mass spectrometry a Perkin-Elmer 270 GLC-MS instrument fitted with an OV-225 S.C.O.T. column (15 m × 0.5 mm) used at 190° was employed. Mass spectra were recorded at an ionization potential of 70 eV, an ionization current of 80 μA and an ion source temperature of 80°.

Materials. Five of the levans investigated were the same as preparations used by Allen and Kabat.[1] P6 is produced by an unidentified microorganism, B512 PP2 and B512 E by strains of *Leuconostoc mesenteroides*, and "Hestrin" by *Aerobacter levanicum*. "Rye grass" is a perennial rye grass levan. "Coryne" is produced by a *Corynebacterium* species.[6] The inulin investigated was a commercial sample.

Methylation analyses. The polysaccharide (2 mg) was methylated by Hakomori's method[3,7] and recovered by dialysis against running tap-water and concentration to dryness. The product was then treated on the steam-bath with 90 % formic acid (1 ml) for 30 min, diluted with 10 volumes of water, and returned to the steam-bath for 3,5 h. The solution was then concentrated to a small volume and the remaining formic acid was removed by co-distillation with additional water (3 × 5 ml). Finally the product was either reduced with sodium borodeuteride and acetylated or part of it was treated in this way, and the remainder was acetylated without reduction as described below. For acetylation pyridine (1 ml) and acetic anhydride (1 ml) were added to the dry product and after 10 min at room temperature the flask was moved to the steam-bath for 20 min. The acetylating agents were then removed by co-distillation with toluene (3 × 5 ml) and the product was examined by GLC.

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The Molecular Structure of Trichlorotrimethylamine-aluminium, $Cl_3AlN(CH_3)_3$ by Gas Phase Electron Diffraction

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Recently we have determined the molecular structures of the complexes Me_3AlNMe_3[1] (Me = CH_3) and H_3AlNMe_3[2] by means of gas phase electron diffraction. We now report the results of a similar study of Cl_3AlNMe_3. This complex has previously been studied by X-ray crystallography,[3] but we hoped to improve on the accuracy.

The electron scattering pattern from gaseous Cl_3AlNMe_3 was recorded on the Oslo electron diffraction unit [4] with a nozzle temperature of about 330°C. Exposures were made with a nozzle-to-photographic-plate distance of about 48 cm. The intensity data thus obtained extended from $s = 1.50$ Å^{-1} to $s = 18.00$ Å^{-1}. A radial distribution (RD) curve obtained by Fourier inversion of the modified molecular intensity curve [5] is shown in Fig. 1. A.

The molecular structure was refined under the assumption that the molecular symmetry is C_{3v} with the Cl atoms of the acceptor and the Me groups of the donor staggered with respect to rotation about the Al – N bond (as they are in the crystal). The Me groups were assumed to have C_{3v} symmetry and to be oriented in such a way that the C – H bonds are staggered with respect to the bonds radiating from the N atom. The molecular structure is then determined by seven independent parameters, *e.g.* the Al – Cl, Al – N, N – C, and C – H bond distances and the ∠N – Al – Cl, ∠Al – N – C, and ∠N – C – H valance angles. The latter was fixed at 109.8°, the angle found in free NMe_3.[6] Since it was anticipated that large amplitude libration about the Al – N bond might lead to an average value of the Cl···C(*trans*) distance that was significantly smaller than that calculated for the equilibrium geometry, the shrinkage of this distance was included in the refinement as an additional independent parameter. The vibrational amplitude of the Al – N bond distance was fixed at the value found