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Chemical Synthesis of a Stereoregular Linear Polysaccharide

Sir:

We wish to report the chemical synthesis of poly-α-(1→6)-anhydro-D-glucopyranose by an essentially stereospecific method. Highly purified 1,6-anhydro-2,3,4-tri-*O*-benzyl-β-D-glucopyranose[1] was dissolved in methylene chloride and treated at −78° with phosphorus pentafluoride freshly generated from an aryldiazonium hexafluorophosphate. All final purifications, transfers, degassings, and the polymerization itself were carried out on the rack using standard high-vacuum techniques. Ranges of 10–20 mole % catalyst to monomer and 20–30% concentrations of monomer resulted in the formation of polymer of number-average molecular weights from 42,000 to 76,600, with molecular rotations from +472 to +489° and intrinsic viscosities from 0.25 to 0.38. Polymerizations of related derivatives were shown to produce broad and variable molecular weight distributions, and apparently the same result was obtained with the tribenzyl derivative, for the intrinsic viscosities of a few reaction products were not directly related to their respective number-average molecular weights.

Debenzylation was accomplished by the slow addition of polymer in pure dimethoxyethane to a solution of a sevenfold excess of sodium in liquid ammonia. After 1 hr of stirring, an equimolar amount of ammonium chloride was added and solvents were removed under a stream of nitrogen. The solids were slurried with methylene chloride, separated, dissolved in water, dialyzed against distilled water, concentrated, clarified by centrifugation, and freeze dried. This debenzylation and work-up gave 80–85% conversion to a water-soluble ash-free dextran-like polymer, which showed no benzylic absorption at 250–270 mμ. Polymers dried *in vacuo* at room temperature retained tenaciously one molecule of water/two glucose units (*Anal.* Calcd for $(C_6H_{10}O_5)_2H_2O$: C, 42.10; H, 6.48. Found: C, 41.92; H, 6.49) and even at 100° failed to lose additional weight.

These polysaccharides, like the natural dextrans,[2] dissolved best in cold water, ∼5°, to form slightly opalescent solutions, but during preparation of solutions at room temperature a small portion crystallized sufficiently to remain insoluble in water. Their intrinsic viscosity in water at 30° ranged from 0.180 to 0.191. From the viscosity–molecular weight relationship determined for natural dextrans which are believed to have only a few short branches[3] and a relatively narrow molecular weight distribution ($\bar{M}_w/\bar{M}_n = 1.58$)[4] this would correspond to $\bar{M}_v$ from 32,400 to 36,500 or $\overline{DP}_v = 200$ to 225.

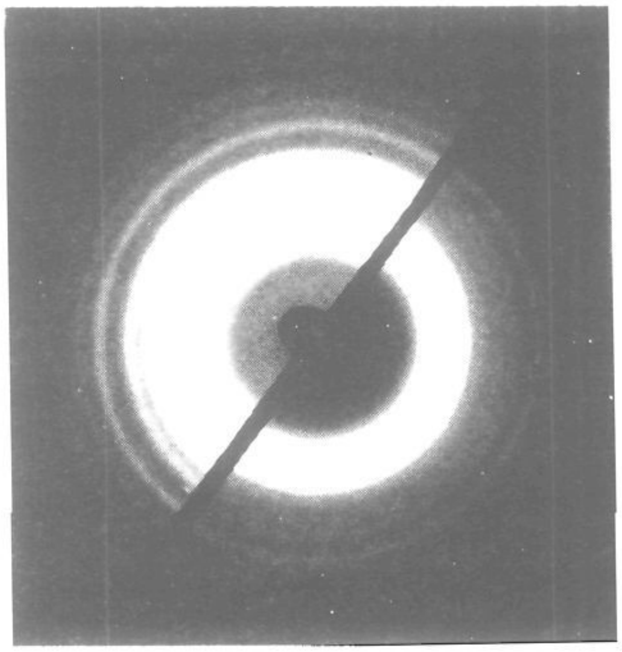

Figure 1. X-Ray powder diagram of synthetic and natural polysaccharides. Upper left, synthetic linear dextran hemihydrate; lower right, natural slightly branched dextran.

The X-ray diagram of films of the synthetic polymer differed from that of a slightly branched natural dextran (Pharmacia Dextran 20 Lot No. To 536) of similar molecular weight, the pattern of the synthetic polymer showing higher crystallinity and different ring spacings (Figure 1).[5] The infrared spectrum resembled that of glucose closely except that the C-1 axial hydrogen deformation band at 891 ± 7 cm^{-1} characteristic of the β linkage[6] appeared to be absent. By solvent precipitation with ethanol, a lower molecular weight fraction (∼10%) was eliminated and the optical rotation of the product was raised from $[\alpha]^{25}$D +196 to +200° (water) (corrected for water content of the polymer). The rotation of both Pharmacia and Northern Regional Research Laboratory B-512 natural dextrans is $[\alpha]^{25}$D +199 (water).[2] It is surprising that the correspondence of the rotational values for the synthetic and natural polymers is so good since the small fraction of α-(1→3) linkages in the natural polymer are more dextrorotatory than the α-(1→6) (see ref 7).[2]

The expanded nmr spectrum of the synthetic deuterated dextran in D_2O contained an intense C-1 equatorial hydrogen resonance at δ 5.05[8] and there was no C-1 axial proton resonance at δ 4.5–4.6,[9,10] although it would have been observed if 1 or 2% of the linkages were of the β configuration. Integration of the spectrum gave the expected proton ratio of six for ring and primary equatorial anomeric hydrogens.

This appears to be the first reported stereospecific chemical synthesis of a linear polysaccharide. The high stereospecificity of the process is understandable

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from both mechanistic and thermodynamic considerations.[11,12]

Enzymic degradation of the polymer is being investigated by Dr. Elwyn T. Reese at the U. S. Army Natick Laboratories.

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The Circular Dichroism of the $[PtCl_4]^{2-}$ Ion

Sir:

The weak-to-moderate intensity d $\rightarrow$ d transitions of dissymmetric metal complexes show strong circular dichroism when the transition is magnetic dipole allowed in the donor group microsymmetry of the complex.[1] This selection rule has been employed[2] in the assignment and the interpretation of these spectra, but, except for one reported example,[3] the use of this criterion has been restricted to complexes which are dissymmetric. We wish here to draw attention to the possibility of extending this method to complexes which are formally optically inactive and, in the present example, to determining the polarization direction of the transition.

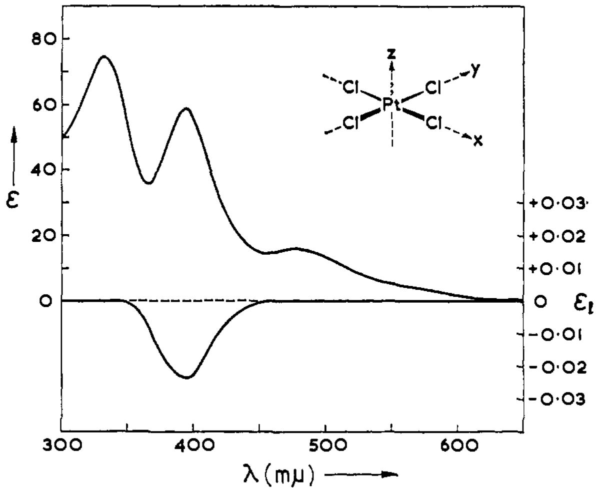

Figure 1. The visible absorption spectrum and circular dichroism of the $[PtCl_4]^{2-}$ ion in D(−)-2,3-butanediol. Shown in the inset is the coordinate frame of the ion referred to in the text.

When the complex $Na_2[PtCl_4]$ is dissolved in D(−)-2,3-butanediol, the unpolarized electronic absorption spectrum of a fresh solution of the ion is hardly altered in position and intensity from that found in the solid and in aqueous solution, but circular dichroism is observed at one of the d $\rightarrow$ d transitions (Figure 1).

The square-planar d^8 diamagnetic ion $[PtCl_4]^{2-}$ has three spin-allowed d $\rightarrow$ d transitions, $^1A_{1g} \rightarrow {}^1B_{1g}$, $^1A_{2g}$, ^1E_g, which have been assigned with some certainty.[4,5] The $^1A_{1g} \rightarrow {}^1A_{2g}$ transition has been shown[4] by a vibronic analysis of the polarized crystal spectrum to occur at about 390 mμ, and from the magnetic circular dichroism of the ion the $^1A_{1g} \rightarrow {}^1E_g$ transition has been shown[5] to occur at about 335 mμ (Figure 1). It can be shown that the $^1A_{1g} \rightarrow {}^1A_{2g}$ transition is magnetic dipole allowed in z-axis polarization while the $^1A_{1g} \rightarrow {}^1E_g$ transition should be allowed in the x,y plane of the axis system shown in Figure 1. The $^1A_{1g} \rightarrow {}^1B_{1g}$ transition (at 480 mμ) is forbidden in magnetic dipole radiation fields, and we would expect that if this band shows any circular dichroism it should be very much weaker than that exhibited by the other two.

Experiment shows that only the $^1A_{1g} \rightarrow {}^1A_{2g}$ (z-polarized) band has any detectable circular dichroism, suggesting that the dissymmetric influences of the solvent are concentrated and directed at the tetragonal ($+z$ and $-z$) positions of the ion. Although this may indicate weak coordination of the solvent in these positions, the extent of covalent participation must be extremely small since the spectrum of the ion is not appreciably altered by this effect. Alternatively, it seems unlikely that the appearance of circular dichroism is due to dissymmetric distortion of the molecular framework of the ion by the solvent, because under these circumstances we would expect to see the appearance of circular dichroism in both the z- and x,y-polarized transitions and not only in the unique polarization which is observed.

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A New Reaction of Diborane with Carbon Monoxide Catalyzed by Sodium Borohydride. A Convenient Synthesis of Trimethylboroxine

Sir:

In 1937 it was reported by Schlesinger and Burg that diborane reacts with carbon monoxide at 100° in a sealed tube under 20 atm pressure to form a simple addition compound, borane carbonyl.[1] The product is a gas, stable at low temperatures, but largely dissociated into its components at ordinary temperatures and pressures (eq 1). This reaction and its product

$$B_2H_6 + 2CO \rightleftharpoons 2H_3B{:}CO \tag{1}$$

have since been the subject of numerous investigations.[2]

We have examined the reaction of carbon monoxide with diborane in tetrahydrofuran solution, following the rate of absorption by adapting the automatic hydrogenator previously described.[3] In the absence of sodium borohydride only a small quantity of carbon monoxide

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