tion. It should be further pointed out that Baumgarten[2] suggested that the hydrolysis probably proceeds by way of the dipolar ion.

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EVIDENCE OF NEW LINKAGES IN DEXTRANS

Sir:

We have been able to demonstrate that a significant fraction of the anhydroglucose units in a certain dextran apparently is not attacked by sodium metaperiodate at 25°. Previous investigations[1] of several dextrans showed that substantially all the units were attacked. Methylation studies[2] on dextrans so far investigated indicate that the principal glucosidic linkage is 1,6′, and that, in some cases, 1,4′-linkages are also present. Units at branch points carry linkages on both the 4- and 6-positions. Our results strongly suggest that this dextran contains units linked in the 3-positions, or both the 2- and 4-positions (branch points), or a combination of these possibilities.

This dextran, produced by *Leuconostoc mesenteroides* NRRL B-742, and purified by precipitation between 41 per cent. and 90 per cent. ethyl alcohol, consumed 1.43 moles of periodate and produced 0.64 mole of formic acid per anhydroglucose unit when oxidized at 25°[1] for 250 hours, at which time the consumption of oxidant and production of acid had ceased. Sixty-four per cent. of the glucopyranosyl units are therefore substituted only on the 6-position. Two moles of periodate are consumed by each unit so linked. The percentage of anhydroglucopyranose units consuming only one mole of periodate is then 15% [1.43 − (2 × 0.64)]. These are probably linked on the 4- and 6-positions. According to these calculations, the remaining 21 per cent. of the anhydroglucose units are not oxidized.

To confirm the presence of unoxidized units, a method developed by Smith[3] and his associates at the University of Minnesota has been applied. After removal of salts, the oxidized polymer was catalytically reduced and then hydrolyzed in 2 *N* sulfuric acid on the steam-bath. The only optically active products expected from a polyanhydroglucopyranose treated as above are D-glyceraldehyde, from 2- or 2- and 6-linked units, and D-glucose, from unoxidized units. The optical activity of the hydrolysate, if assumed to be due entirely to glucose, corresponded to 11.7% of unoxidized anhydroglucose units in the original dextran. Catalytic reduction of the neutralized hydrolysate yielded a solution having a small negative optical rotation in good agreement with that expected from the conversion of glucose to sorbitol. Sorbitol was isolated as the pyridine complex[4] and characterized as the hexaacetate, m.p. and mixed m.p., 98–99°; $[\alpha]^{25}D + 10.0°$ (*c*, 3.8; $CHCl_3$). The yield of the hexaacetate corresponded to 5.8% unoxidized anhydroglucopyranose in the original dextran.

The simplest explanation for the lack of oxidation by periodate is the presence of 1,3′-glucosidic linkages. Linkage in the 3-position, regardless of other linkages on the same anhydroglucopyranosyl unit, would prevent oxidation. Oxidation wuld be prevented also by the presence of units at branch points linked in both the 2- and 4-positions. However, the fact that the optical activity of the reduced hydrolysate indicated conversion of D-glucose to sorbitol, rather than of D-glyceraldehyde to glycerol, seems to rule out the presence of 1,2′-glucosidic linkages. Hence, if any 2-linked units are present, they probably occur only at branch points.

Dextran from *L. mesenteroides* NRRL B-742 has been found by Dr. Hellman at this Laboratory to consist of at least two discrete fractions.[5] Periodate analysis of the less soluble fraction, *i.e.*, that portion *precipitated* by 41% ethyl alcohol, does not indicate the presence of unoxidized anhydroglucose units. The fractions have been found by other workers here to differ also in specific rotation, viscosity, and infrared absorption.

Periodate oxidation data on dextrans produced by several other organisms have exhibited similar indications of unoxidized anhydroglucose units. In those cases where calculations indicate the presence of such units, unusual infrared absorption[6] is also found.

Methylation studies are in progress at this Laboratory to establish the positions involved in glycosidic linkage.

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(2) M. Stacey and C. R. Ricketts, *Fortschr. Chem. Org. Naturstoffe*, **8**, 28 (1951).

(3) F. Smith, personal communication.

(4) H. H. Strain, THIS JOURNAL, **56**, 1756 (1934).

(5) N. N. Hellman, in "Report of Working Conference on Dextran," National Research Council, Subcommittee on Shock, and Northern Regional Research Laboratory, Peoria, Illinois, Oct. 29, 1951, p. 36.

(6) S. C. Burket and E. H. Melvin, *Science*, **115**, 516 (1952).

(7) One of the laboratories of the Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture. Article not copyrighted.

STEREOSPECIFIC TOTAL SYNTHESIS OF CORTISONE

Sir:

We should like to report a stereospecific[1] total synthesis of 11-ketoprogesterone, dehydrocorticosterone and cortisone in both the natural and *dl* modifications. *dl*-4b-Methyl-7-ethylenedioxy-1, 2,-3, 4, 4aα, 4b, 5, 6, 7, 8, 10, 10aβ-dodecahydrophenanthrene-4β-ol-1-one[2] (I) with methyl iodide and potassium *t*-butoxide gave the 2-methyl derivative, m.p. 189–192°. *Anal.* Found: C, 70.58; H, 8.42. The latter was alkylated in turn with methallyl iodide to give 2β,4b-dimethyl-2-meth-

(1) "Stereospecific" is taken to mean that in each reaction producing a fixed asymmetric center, the ratio of isomer having the same configuration as the end product to all other isomers is greater than unity. In point of fact, each of such ratios in the present synthesis is 8:1 or greater.

(2) G. I. Poos, G. E. Arth, R. E. Beyler and L. H. Sarett, THIS JOURNAL, in press.