

cc. of octane-1,1,1,8,8,8-*d*₆, b.p. 121°, *n*_D²⁵ 1.3945, *d*₄²⁵ 0.7354.

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Depolymerization of a Dextran with Sonic Vibrations or Ultraviolet Light¹

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In addition to studies on acid hydrolysis² and thermal³ procedures for partial depolymerization of the dextran produced by *Leuconostoc mesenteroides* NRRL B-512, limited attention has been given at this Laboratory to dextran depolymerization with sonic vibrations or with ultraviolet light. This paper records our experiments with these latter procedures.

Lockwood, *et al.*,⁴ Stacey⁵ and Pautard⁶ have investigated the ultrasonic degradation of a highly branched dextran and stated that the degraded dextrans produced in the course of the reaction were less polydisperse than an acid-hydrolyzed dextran. However, no data were presented on the percentage of 1,6'-glucosidic linkages in the resulting products. Pautard⁶ suggested that ultrasonic degradation may be analogous to a thermal process. The periodate oxidation data⁷ presented here (Table I) are in accord with Pautard's postulation since the sonically degraded samples, like thermally degraded NRRL B-512 dextran³ and in contrast with fractions prepared from acid-hydrolyzed material, have a lower percentage of 1,6'-linkages than the parent raw material. It also is seen in Table I that under the conditions of irradiation used, a more extended time of treatment would be required for preparation of a fraction of inherent viscosity near 0.25, of suitable molecular size for injection purposes.⁸

TABLE I
PROPERTIES OF SONICALLY DEPOLYMERIZED NRRL B-512 DEXTRAN

Treatment time, min.	Max. power, %	Properties of products	
		Inherent viscosity ^a	1,6'-like ^b links, %
0	..	1.17	94.6
5	100	0.78	..
10	100	.59	..
15	100	.52	93.8
5	50	.82	92.4
10	50	.67	..
30	50	.45	92.5

^a Measured in water at 25° at a relative viscosity of 1.1-1.2. ^b Those units (linked at position 1 only or at positions 1 and 6) which give formic acid on periodate oxidation (reducing end-groups disregarded).

(1) Article not copyrighted.

(2) I. A. Wolff, C. L. Mehlretter, R. L. Mellies, P. R. Watson, B. T. Hofreiter, P. L. Patrick and C. E. Rist, *Ind. Eng. Chem.*, **46**, 370 (1954).

(3) I. A. Wolff, P. R. Watson, J. W. Sloan and C. E. Rist, *ibid.*, **45**, 755 (1953).

(4) A. R. Lockwood, A. E. Jones and F. G. Pautard, *Research (London)*, **4**, 46 (1951).

(5) M. Stacey, *ibid.*, **4**, 48 (1951).

(6) F. G. Pautard, *Chemistry & Industry*, 1316 (1953).

(7) Allene Jeanes and C. A. Wilham, *This Journal*, **72**, 2655 (1950).

(8) U. S. Government military medical purchase description for dextran injection, stock number 1-161-890, May 24, 1951.

Solid B-512 dextran on irradiation with ultraviolet light was partially depolymerized (Table II). Oxidation probably took place concurrently since the products were slightly acidic and discolored during moisture-determination analysis at 100° *in vacuo*. The apparent percentage of 1,6'-linkages is increased with time of exposure to the light, but the formic acid values from periodate oxidation studies should be accepted with reservation in view of our incomplete knowledge of the structure of the irradiated products. The irradiated samples were water-soluble. Pautard⁹ has reported that irradiation of dextran sensitized with dichromate caused its insolubilization.

TABLE II
PROPERTIES OF NRRL B-512 DEXTRAN IRRADIATED WITH ULTRAVIOLET LIGHT

Treatment time, hr.	Properties of Products	
	Inherent viscosity ^a	1,6'-like ^a links, %
0	1.17	94.6
4	1.07	94.6
8	0.91	95.1 ^b
15	.84	95.9 ^b
24	.90	96.9 ^b

^a Terms have same meaning as in Table I. ^b Corrected for acidity of the original sample.

Experimental

Sonic treatments were carried out in a Raytheon¹⁰ (specification number T-049A, model 10 KC, power output 200 watts) instrument on 2% solutions of native NRRL B-512 dextran, which had been produced in whole culture. Cooling water was used to prevent excessive temperature rise of the solutions being treated. The degraded dextrans were recovered in solid form by alcoholic precipitation.

Ultraviolet light treatment involved exposure of air-equilibrated solid dextran, in the form of a finely divided powder, to radiation from a high-pressure, quartz, mercury arc lamp operated without a filter. The dextran was exposed in thin layers (0.5 g. dextran spread over 33.2 sq. cm.), 20 inches from the light source.

Acknowledgment—The assistance of B. H. Alexander and J. C. Rankin in carrying out the periodate oxidation analyses is gratefully acknowledged.

(9) F. G. Pautard, *Nature*, **171**, 302 (1953).

(10) Mention of firm names or trade products does not imply they are endorsed or recommended by the U. S. Department of Agriculture over other firms or similar products not mentioned.

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Hydroxylation of Δ^{17} -20-Cyanopregnenes by Potassium Permanganate

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A search for hydroxylating agents other than osmium tetroxide for the introduction of a hydroxyl group into position-17 of the pregnane molecule led to a practical method for the utilization of potassium permanganate in the conversion of Δ^{17} -20-cyanopregnene-21-ol-3,11-dione acetate (I) into pregnane-17 α ,21-diol-3,11,20-trione 21-acetate (III) an intermediate in Sarett's partial synthesis of cor-