(100 g.) was added during the reaction to replace that removed by distillation.

The reaction mixture was allowed to cool while it was being neutralized by carbon dioxide (vented into the air stream from 50–100 g. of Dry Ice maintained in a filter flask) diluted with air. The neutralization was completed within one hour as indicated by a neutral reaction to moist Alkacid test paper. Insoluble impurities were removed by centrifugation and soluble colored impurities were removed from the centrifugate by adsorption on a four-inch column of activated alumina previously moistened with benzene. Volatile solvents were removed at room temperature under reduced pressure. The yields, based on tetraethylene glycol, were 75–80% of nearly colorless TEGMA, $n^{20}{}_D$ 1.4631, $d^{20}{}_{20}$ 1.087.

Anal. Calcd. for $C_{16}H_{26}O_7$: C, 58.2; H, 7.9; sapon. equiv., 165; M_D 83.4. Found: C, 57.8; H, 8.2; sapon. equiv., 166, 169; M_D 83.4.

Conductivity measurements (1.14×10^{-8} mho-cm. at 1 Kc.) indicated that ions from the basic catalyst had been largely removed by the purification procedure.

Acid-catalyzed Transesterification Using Picric Acid as Inhibitor.—The same apparatus was used as in the base-catalyzed reaction. The charge consisted of methyl methacrylate (100 g., 1.0 mole, coml.), benzene (75 g., C.P.) and concd. sulfuric acid (10.0 g., 0.098 mole) and picric acid (0.10 g.). The mixture was distilled under hydrogen until no more water was evolved. Tetraethylene glycol (59.5 g., 0.30 mole, redistilled) was added and the reaction was carried out as above for 3.5 hours using hydrogen as an inert atmosphere. At the end of this period nearly the theoretical amount of methanol had been collected. An additional quantity of benzene (50 g.) was added during the reaction.

The reaction mixture was allowed to cool and sodium carbonate (24 g., 0.20 mole) and water (10 g.) were added with vigorous stirring. After 15 minutes there was a sudden color change to the bright yellow color of the picrate ion which indicated complete neutralization. The mixture was diluted with cyclohexane (150 ml.) and all of the insoluble impurities coagulated into a sticky mass leaving a clear supernatant liquid layer which was removed by decantation. Remaining colored impurities were removed from the solution by adsorption on a 4-inch column of activated alumina. Removal of volatile materials under reduced pressure gave a 65–70% yield of TEGMA, $n^{20}{}_D$ 1.4620, sapon. equiv., 164–165.

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Octane-1,1,1,8,8,8-d_6

BY ANDREW STREITWIESER, JR.

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An attractive approach to the assignment of the vibrations of normal aliphatic hydrocarbons into methyl and methylene motions is through the use of a hydrocarbon in which the terminal methyl groups have been replaced by methyl-d_3 groups. Octane-1,1,1,8,8,8-d_6 was thought to be a suitable choice for such a compound because of the length of its methylene chain and of its convenient physical properties.

Dimethyl suberate was reduced with lithium aluminum deuteride to 1,8-octanediol-1,1,8,8-d_4. The glycol was converted to the di-*p*-toluenesulfonate which was further reduced with lithium aluminum deuteride in boiling ether. This final reduction was, however, very sluggish and gave poor yields. More vigorous conditions were considered to be unsatisfactory because of the possible occurrence of undesirable side reactions.[1] The deuterogenolysis of the dihalide may well be a better route at this point.

The density of the product, $d^{25}{}_4$ 0.7354, is close to that calculated for octane-d_6 assuming constancy of molecular volume, $d^{25}{}_4$ 0.7351. Mass spectrographic analysis indicated 90.9% octane-d_6, 7.7% -d_5, 0.6% -d_4 and 0.47% -d_7.[2] The infrared spectrum and its detailed interpretation will be presented elsewhere.[3]

Experimental[4]

1,8-Octanediol-1,1,8,8-d_4.—To 2.0 g. of lithium aluminum deuteride[5] in dry ether was added with vigorous stirring 10.1 g. of dimethyl suberate[6] dissolved in dry ether. Dilute hydrochloric acid was added until the solid inorganic salts separated leaving a clear ether layer which was decanted. The salts were washed with ether and the combined ether layers were evaporated leaving 7.8 g. of crude glycol. Continuous ether extraction of a dilute acid solution of the inorganic salts gave a further 0.3 g. The combined crops were recrystallized from benzene–hexane giving 5.9 g. (79%) of small white crystals, m.p. 56.0–58.0°. A further recrystallization from benzene–hexane raised the m.p. to 58.0–58.5°.

1,8-Octanediol-1,1,8,8-d_4 Di-*p*-toluenesulfonate.—A solution of 9.73 g. of 1,8-octanediol-1,1,8,8-d_4 in 100 cc. of pyridine was cooled to −10° and 27.7 g. of *p*-toluenesulfonyl chloride was added. After standing in an ice–salt-bath for an hour with frequent swirling, 100 cc. of water was added in portions such that the temperature was kept below 10°. The white granular precipitate was filtered and washed with water. The filtrate contained 4 g. of the monotosylate as a heavy oil which, on further treatment with 5.5 g. of *p*-toluenesulfonyl chloride in the same way, gave an additional quantity of product. After drying, the combined yield of product, m.p. 68.0–70.8°, was 24.9 g. (84%).

Undeuterated material was prepared in the same way from diol prepared by the reduction of dimethyl suberate with lithium aluminum hydride. After one crystallization from benzene the m.p. was 72.8–73.3°.

Anal. Calcd. for $C_{22}H_{30}O_6S_2$: C, 58.1; H, 6.7; S, 14.1. Found: C, 57.9; H, 6.7; S, 14.0.

Octane-1,1,1,8,8,8-d_6.—The ditosylate (20.7 g.) was extracted in a Soxhlet apparatus by a dry ether solution of 1.0 g. of lithium aluminum deuteride. After two days of refluxing the deuteride apparently had reacted completely. Dilute hydrochloric acid was added and the ether layer was separated. Filtration of the aqueous phase gave 3.4 g. of unreacted ditosylate. The ether solution was washed with water and dried with potassium carbonate. The residue after distillation of the ether was mixed with 100 cc. of pure pentane. Filtration of this mixture gave an additional 2.7 g. of unreacted ditosylate. After removal of pentane from the filtrate the residue was distilled from a small flask yielding 0.6 cc. of a crude octane fraction, b.p. 115–124°. The considerable residue from this distillation was undoubtedly the unreacted *p*-toluenesulfonate of 1-octanol-1,1,8,8,8-d_5.

The octane fractions of several runs were combined and redistilled. The distillate was shaken with cold concentrated sulfuric acid,[7] then washed and dried. Distillation gave 1.1

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[1] D. S. Noyce, private communication.

[2] We are indebted to Dr. J. C. Guffy and his associates at the California Research Corp., Richmond, Calif., for the mass spectrum and its analysis.

[3] G. C. Pimentel and W. A. Klemperer, *J. Chem. Phys.*, in press.

[4] Melting points were taken in a Hershberg apparatus and are corrected. Analysis by the Microanalytical Laboratory of the University of California.

[5] Obtained from Metal Hydrides, Inc., Beverly, Mass., on allocation by the United States Atomic Energy Commission.

[6] A. I. Vogel, *J. Chem. Soc.*, 333 (1934).

[7] This treatment is not expected to cause exchange or isomerization of the octane; *cf.*, D. P. Stevenson, *et al.*, THIS JOURNAL, **74**, 3269 (1952).

cc. of octane-1,1,1,8,8,8-d_6, b.p. 121°, $n^{25}D$ 1.3945, d^{25}_4 0.7354.

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Depolymerization of a Dextran with Sonic Vibrations or Ultraviolet Light[1]

BY P. R. WATSON AND I. A. WOLFF

RECEIVED AUGUST 11, 1954

In addition to studies on acid hydrolysis[2] and thermal[3] 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] Stacey[5] and Pautard[6] 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. Pautard[6] suggested that ultrasonic degradation may be analogous to a thermal process. The periodate oxidation data[7] presented here (Table I) are in accord with Pautard's postulation since the sonically degraded samples, like thermally degraded NRRL B-512 dextran[3] 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]	Properties of products: 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).

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. Pautard[9] 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]	Properties of Products: 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 Raytheon[10] (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.

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(1) Article not copyrighted.

(2) I. A. Wolff, C. L. Mehltretter, 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.

(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.

NORTHERN UTILIZATION RESEARCH BRANCH
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Hydroxylation of Δ^{17}-20-Cyanopregnenes by Potassium Permanganate

BY ROGER TULL, R. E. JONES, S. A. ROBINSON AND MAX TISHLER

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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-17α,21-diol-3,11,20-trione 21-acetate (III) an intermediate in Sarett's partial synthesis of cor-