The **isopropylamine salt** was obtained by adding at 0° 0.64 ml. of isopropylamine, then 70 ml. of ether to a solution of 4.16 g. of the half-ester in 17 ml. of chloroform. The gummy solid crystallized while standing in the refrigerator; yield 4.47 g. (97%); m.p. 134–137°. Recrystallization from cold ethanol-ether afforded colorless felt-like needles, m.p. 137–139°, $[\alpha]^{20}D$ −91° (*c* 0.61, water), more than 2% soluble in cold water.

Anal. Calcd. for $C_{38}H_{35}NO_{11}\cdot{}^1/_2H_2O$: C, 62.85; H, 5.75; N, 2.22. Found: C, 62.86; H, 5.81; N, 2.16.

Acknowledgment.—The authors wish to thank Mary M. Trail for technical assistance during part of the project and Dr. W. C. Alford and his co-workers for the microanalyses.

BETHESDA 14, MARYLAND

[CONTRIBUTION FROM THE CEREAL CROPS SECTION, NORTHERN UTILIZATION RESEARCH BRANCH[1]]

Interpretation of Periodate Oxidation Data on Degraded Dextran

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RECEIVED JULY 1, 1955

The amount of formic acid produced from reducing end group units of dextrans on oxidation by periodate is different from the amount produced from the other units, and also varies with the position through which the reducing end group is linked to the remainder of the chain. Consideration of this fact, together with the possible structures of dextran and several assumed modes of hydrolytic cleavage, has enabled a more complete interpretation of periodate oxidation analyses of partially degraded dextrans. There appears to be an increase in the proportion of 1,6′-linkages in partially hydrolyzed dextran due to the greater ease of hydrolysis of other linkage types present. Periodate oxidation data on dextran derived from *Leuconostoc mesenteroides* NRRL B-512 are consistent with the simplified modes of degradation depicted while those from the NRRL B-1254 and B-742 dextrans are not.

Measurement of the amount of formic acid produced after oxidation of dextrans with sodium metaperiodate has been used as an index of the proportion of 1,6′-linked anhydroglucose residues.[2,3] In view of current interest in partially acid-hydrolyzed dextran as a blood volume expander[4] the use of periodate oxidation studies for the characterization and/or detection of differences between products will undoubtedly increase. In anticipation of such use the significance of the method, as applied to degraded dextrans, will be discussed in this paper. Emphasis will be placed on the change in periodate oxidation data as a function of the types of linkages broken and the nature of the breakdown (homogeneous *vs.* discard of small fragments resulting from cleavage of a particular type of linkage), on the correction of the periodate oxidation data for the reducing end groups present in the molecule, and on the magnitude of change in periodate oxidation values which may be expected in the degradation of a native dextran to a size suitable for use as a blood-plasma volume expander.

Introduction

Dextran is an anhydroglucose polymer in which most of the glucosidic linkages are α-1,6′. In addition, 1,3′- and 1,4′-linkages are present in at least certain ones of the known dextrans[5] and these apparently are generally but not necessarily at branch points.[6] The various possible types of structures for dextran, involving 1,3′(x)- or 1,4′(x)- and 1,6′-(o)-linkages are shown diagrammatically in Fig. 1. In addition, various combinations of these might be encountered. In the following discussion emphasis generally will be placed on the 1,3′-linkage because it occurs[5e] at the branch point in dextran NRRL B-512 which is of greatest importance at present as a commercial source of blood plasma volume expander.[4]

Structures A, C and D will be recognized as analogous to structures which have been proposed for starch.[7] Thus the "backbone"- or "comb"-type structure (A) was suggested by Staudinger for starch. Structure C is the laminated-type structure used by Haworth. Structure D is the randomly branched or bush-like structure, containing more than one branch on some branches, as proposed by Meyer. For dextran, structure B is a limiting case of the backbone structure A, in which side chains of only one glucose unit are joined to the main chain by 1,3′- or 1,4′-linkages. Similarly, F is a limiting case of structure C.

In these various structures for dextran the main types of chain linkages which would be involved are shown in Fig. 2. In addition, structure B would provide a special type, in which the chain at Y in (b) or (b′) of Fig. 2 is replaced by a hydrogen atom, as shown in (e) and (e′) of Fig. 2.

Inspection shows that hydrolytic cleavage of the linkage between the two units will give from (a) of Fig. 2 a 6-linked reducing end group plus a non-reducing terminal group, (b) and (b′) a 6-linked reducing end group plus a 1,6-linked unit of a chain, (c) a 6-linked reducing end group plus a 1,3-unit of a chain, (c′) a 6-linked reducing end group plus a 1,4-unit of a chain, (d) and (d′) same as (a), and (e) and (e′) D-glucose and a non-reducing end group. The same products as from (e) or (e′) also will be obtained by cleavage of the non-reducing end group if linked 1,6′. Periodate oxidation of the molecular fragments resulting from one of these

(1) One of the Branches of the Agricultural Research Service, U. S. Department of Agriculture.

(2) A. Jeanes and C. A. Wilham, THIS JOURNAL, **72**, 2655 (1950).

(3) P. W. Kent, *Science*, **110**, 689 (1949).

(4) G. H. Bixler, G. E. Hines, R. M. McGhee and R. A. Shurter, *Ind. Eng. Chem.*, **45**, 692 (1953); *cf.* also ref. 15.

(5) (a) I. Levi, W. L. Hawkins and H. Hibbert, THIS JOURNAL, **64**, 1959 (1942); (b) R. Lohmar, *ibid.*, **74**, 4974 (1952); (c) M. Abdel-Akher, J. K. Hamilton, R. Montgomery and F. Smith, *ibid.*, **74**, 4970 (1952); (d) S. A. Barker, E. J. Bourne, G. T. Bruce and M. Stacey, *Chemistry & Industry*, 1156 (1952); (e) J. W. Van Cleve, W. C. Schaefer and C. E. Rist, *Abst. Meetings, Am. Chem. Soc.*, **125**, 8D (1954).

(6) See also R. W. Jones, R. J. Dimler, A. Jeanes, C. A. Wilham and C. E. Rist, *ibid.*, **126**, 13D (1954).

(7) K. Myrbäck, *Wallerstein Lab. Commun.*, **11**, 209 (1948).

bond cleavages will give a higher yield of formic acid per anhydroglucose unit than was obtained from the unhydrolyzed dextran. This increase in formic acid is not necessarily a result of an increase in the ratio of 1,6′- to non-1,6′-linkages as it might be interpreted in the case of high molecular weight native dextrans. At least part of the increase results in all cases from newly formed reducing end groups (or glucose, itself) regardless of whether the cleavage involves disproportionate amounts of the various linkages.

The effect on periodate oxidation data of various assumed modes of degradation of different molecular types of dextran by acid hydrolysis and the types of information which can be obtained from such data are summarized in the following sections.

Theoretical Treatment

The type of mixture obtained by acid hydrolysis of dextran will depend on both the structure of the dextran and the linkages attacked (*i.e.*, 1,3′-, 1,4′- or 1,6′-linkages). Thus, in structures A and B of Fig. 1, hydrolysis of branching or non-1,6′-linkages (x) exclusively would yield a heterogeneous mixture containing the small fragments from side chains (external branches) and the large residual portion of the molecule. In the early stages of breakdown of structures C, D, E and F of Fig. 1, cleavage of the non-1,6′-linkages (x) would give a more nearly homogeneous mixture of partial breakdown products. In the following consideration of particular examples, several simplified and limiting cases are chosen, *e.g.*, exclusive cleavage of 1,3′- or 1,6′-linkages, cleavage at average positions rather than completely at random (always at central linkages rather than occasionally terminal ones), and the presence of only one of the molecular types (Fig. 1) in the dextran.

Homogeneous Cleavage.—In this category will be considered the hydrolysis of structure C, D and E of Fig. 1 by cleavage (a) of 1,3′-linkages only and (b) of 1,6′-linkages only, in both cases yielding large fragments all of which are retained in the recovered product. The presence of only these two linkage types is assumed. Identical results are obtained if 1,4′- instead of 1,3′-linkages are involved.

If all bond breakages occur at 3-linked branch points or 1,3′-linkages in a chain (Figs. 2b and 2d, respectively), four additional moles of formic acid will be produced on periodate oxidation as a result of each break. Let D = initial DP[8] of the dextran, d = the final DP, A_D = moles formic acid per anhydroglucose unit (AGU) for the original dextran and A_d = moles formic acid per AGU for the entire degraded dextran. Then D/d = the average number (+1) of bonds broken[9] and the number of molecules formed per molecule of original dextran; A_DD = total formic acid per mole for the original dextran; $A_DD + 4D/d$ = total formic acid of the degraded dextran from a mole of original dextran, which also may be expressed as

$$A_DD + \frac{4D}{d} = A_dD$$

Solving for d

$$d = \frac{4}{A_d - A_D} \qquad (1)$$

Since the apparent ratio of 1,6′- to 1,3′-linkages may be expressed as $R_d = A_d/(1 - A_d)$, equation 1 may also be written in the form

$$R_d = \frac{4 + dA_D}{d(1 - A_D) - 4} \qquad (2)$$

As four additional moles of formic acid per bond broken is the most that can be produced by the cleavage of linkages, Fig. 2a, 2b, 2c and 2d, it follows that equation 1 is an expression for giving the maximum possible degree of polymerization of the hydrolyzed fraction. The only structure which would result in a larger increase of formic acid production would be that of Fig. 2e in which the nonreducing terminal group is linked 1,3′, as in the case of the single-unit external branch which apparently occurs commonly in the dextrans.[6] In this case the 4 would be replaced by 5 in equation 1. Cleavage of

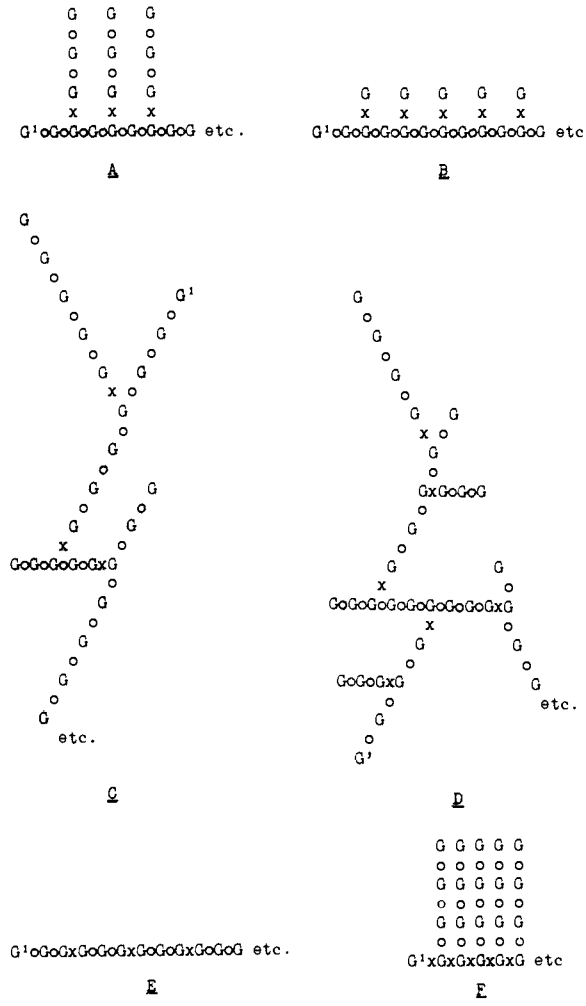

Fig. 1.—Various type structures of dextran in which the anhydroglucose units (G) are linked by α-1,6′-linkages (O) and α-1,3′- or α-1,4′-linkages (X); G′ = reducing end group.

(8) DP is used to designate the number average degree of polymerization.

(9) Since the number of bonds broken will be large in the studies to which the present considerations would be applied, the fact that D/d is numerically one larger than the number of bonds broken has no significance.

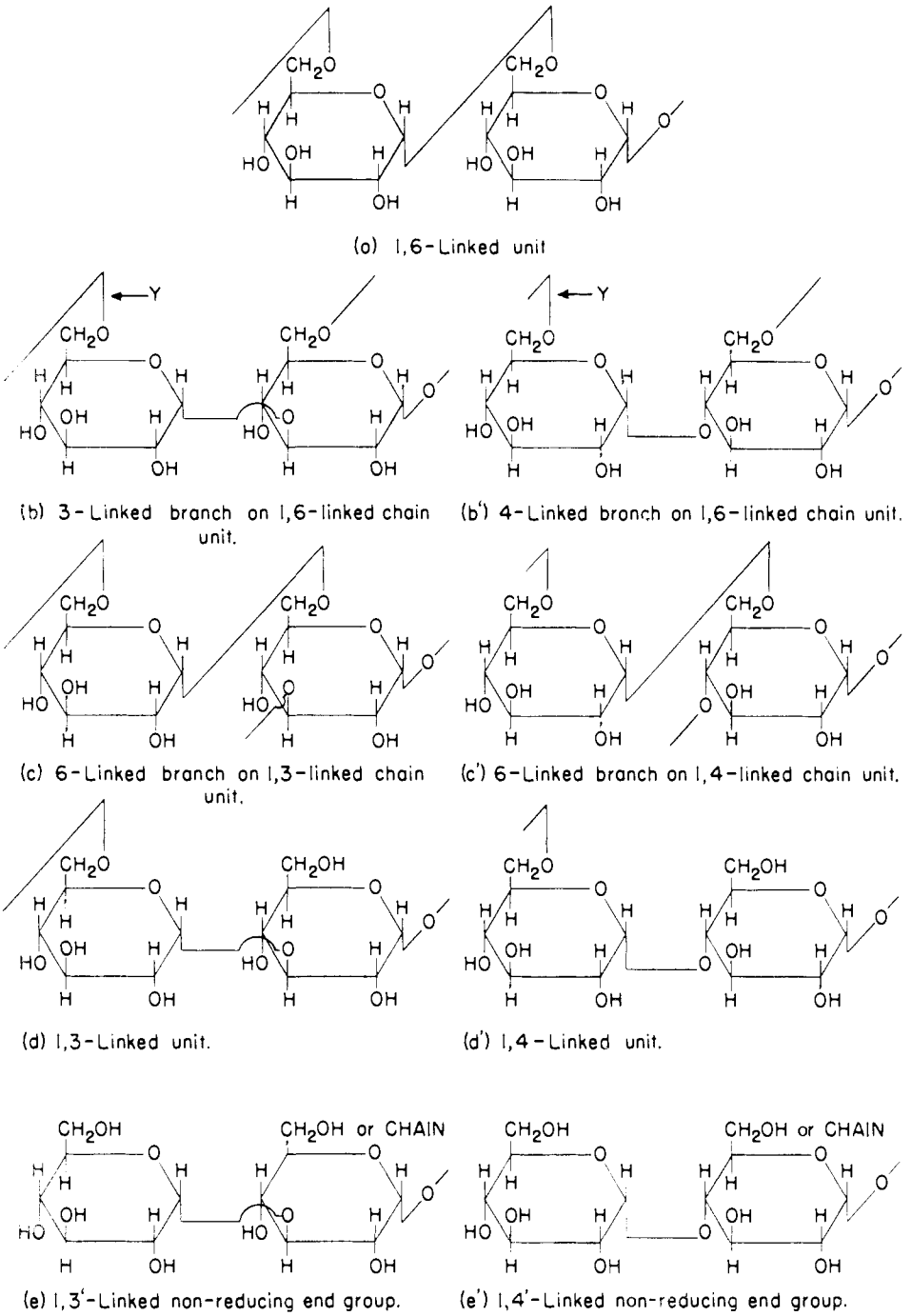

Fig. 2.—Main types of unit linkage for different dextran structures.

a non-reducing terminal 1,6′-linked unit, however, would produce only four additional moles of formic acid, corresponding to equation 1.

Cleavage of the 1,6′-linkage in Fig. 2a and c produces three additional moles of formic acid per bond broken. By a similar derivation to the above, the minimum possible degree of polymerization of a hydrolyzed dextran fraction would be

$$d_{\text{min.}} = \frac{3}{A_d - A_D} \qquad (3)^{10}$$

(10) Equations 1 through 4 are not valid when the number of bonds broken approaches one, or for small values of d.

and as before

$$R_d = \frac{3 + d\,A_D}{d\,(1 - A_D) - 3} \qquad (4)$$

As a result of equations 1 and 3 it is possible from periodate oxidation data alone to ascertain, within the restrictions imposed by the assumptions made above, the limits within which the average molecular size of a degraded dextran lies. Alternatively (equations 2 and 4) the apparent ratio of 1,6′- to 1,3′-linkages of degraded dextrans which one might expect to derive from periodate oxidation

data can be calculated from the formic acid value of the original undegraded dextran and the number average molecular size (obtained by an independent method) of the degraded dextran. The results of typical calculations for two different dextrans from equation 2 showing how the apparent linkage ratio varies with molecular size are shown in Fig. 3. The hyperbolic curves[11] demonstrate that the apparent ratio of 1,6′- to 1,3′-linkages changes little with DP (or extent of hydrolysis) until rather extensive hydrolytic degradation has occurred, even though only 1,3′-linkages are assumed to be hydrolyzed. After passing through a range in which the ratio changes sensitively with DP, the ratio rises so rapidly with decrease in DP as to be of no value in terms of types of linkage since the increased formic acid produced at reducing end groups becomes the predominant factor. The range in which the ratio is responsive to changes in DP shifts toward higher molecular weights as the 1,6′- to 1,3′-linkage ratio in the original dextran increases.

Non-homogeneous Cleavage and Fractionation of Products.—In actual practice the hydrolysis of dextrans will depart from both of the ideals stipulated for the above discussion. Thus the attack on linkages will be more or less at random, both in terms of their position in the molecule and in the kind of linkage. While there will be differences in the hydrolysis rate constants for 1,6′- and non-1,6′-linkages and differences in the numbers of each type hydrolyzed (because of both the difference in rate constants and the difference in their "concentration" or departure of their ratio from unity), there always will be hydrolysis of all the types of linkage present, rather than of one type to the exclusion of the others. In addition, distribution of molecular sizes resulting from the non-homogeneous cleavage of bonds makes fractionation a necessary step in the isolation of the degraded dextran. The fraction isolated need not be representative of the bulk of the hydrolysis mixture.

The effect of the occurrence of single-unit external branches[6] is of particular interest, since evidence for this type of structure has been found for several dextrans.[12] Cleavage of the non-1,6′-linkage in such a structure, exemplified by Fig. 1-B, would liberate a molecule of D-glucose. Periodate oxidation then would give a larger amount of formic acid than otherwise predicted, as pointed out above in connection with equations 1 and 2 for homogeneous cleavage.

Correction of Periodate Data for Reducing End Groups.—A more valid indication of the ratio of 1,6′- to non-1,6′-linkages in degraded dextran fractions would be obtained by correcting for the "extra" formic acid arising from oxidation of the reducing end group, probably linked through position 6. Since this anhydroglucose unit yields four moles of formic acid instead of the usual one mole, the observed formic acid production, A_F, per AGU will be high by the amount $3/F$, where F is the degree of polymerization of the dextran fraction. The

(11) J. W. Mellor, "Higher Mathematics for Students of Chemistry and Physics," Longmans, Green and Co., London, 1931, pp. 120–121.

(12) R. J. Dimler and R. W. Jones, unpublished data obtained by use of methods reported in ref. 6.

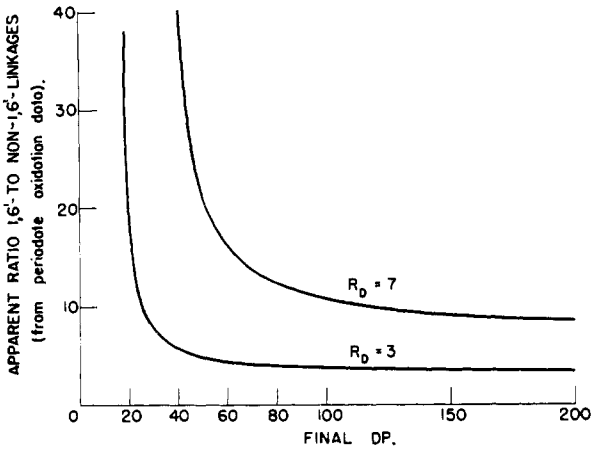

Fig. 3.—Variation of apparent proportion of 1,6′-linkages with molecular size.

corrected ratio, R'_F, of 1,6′- to non-1,6′-linkages will be

$$R'_F = \frac{A_F - (3/F)}{1 - A_F + (3/F)} \qquad (5)$$

In a homogeneous breakdown of dextran, correction of the formic acid values for reducing end groups leads to equations which indicate the maximum increase that can be obtained in the actual ratio of 1,6′- to non-1,6′-linkages. Thus for homogeneous breakdown with cleavage of 1,3′-linkages only, introducing such a correction in equation 2 gives the corrected ratio R'_d

$$R'_d = \frac{1 + d\,A_D}{d\,(1 - A_D) - 1}$$

while with cleavage of 1,6′-linkages, correction of equation 4 would result in

$$R'_d = \frac{A_D}{1 - A_D} = R_D$$

In actual practice, then, an increase in the corrected ratio to a value higher than that calculated above, or by an amount greater than

$$R_D - R'_d = \frac{1}{d\,(1 - A_D)^2 - (1 - A_D)}$$

would indicate departure from the homogeneous-type cleavage. It might also indicate the presence of molecular types other than the linear or the randomly branched types for which homogeneous cleavage would be expected to obtain.

Experimental

Three different types of dextrans were isolated by procedures previously described,[13] and were hydrolyzed in 5% solution at 80° with sulfuric acid at *p*H 1 to predetermined relative viscosities. Further details of the acid hydrolysis of dextran and fractionation of the hydrolyzates to yield clinical-type material[14] are described elsewhere.[15]

Results of the periodate oxidation of several dextrans and degraded dextrans and of determinations of the number average degree of polymerization of these materials by the Somogyi procedure[16] are summarized in Table I. The "total

(13) A. Jeanes, C. A. Wilham and J. C. Miers, *J. Biol. Chem.*, **176**, 603 (1948).

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

(15) (a) 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); (b) I. A. Wolff, *et al.*, *ibid.*, **46**, 2605 (1954).

TABLE I

PERIODATE OXIDATION OF NATIVE AND DEGRADED DEXTRANS

Dextran	DPN	HCOOH formed after 96 hr. oxidation, Moles/anhydroglucose unit	Ratio 1,6′- to non-1,6′-linkages	Ratio 1,6′- to non-1,6′-linkages cor. for reducing end groups (eq. 5)	Calcd. DPN Max. (eq. 1)	Calcd. DPN Min. (eq. 3)
L. mesenteroides, NRRL B-512						
Native	Probably > 10^4	0.949	19	.....	..	..
Total hydrolyzate	54	1.019	..	27 (0.963)[a]	57	43
Clinical-size fraction	238	0.964	27	19 (0.951)	267	200
S. dextranicum, NRRL B-1254						
Native	Probably > 10^4	0.886	7.8	.....	..	..
Clinical-size fraction	258	0.924	1.2	10 (0.912)	105	79
L. mesenteroides, NRRL B-742						
Native	Probably > 10^4	0.689	2.2	.....	..	..
Clinical-size fraction	194	0.738	2.8	2.6 (0.723)	82	61
L. mesenteroides, NRRL B-742 fraction of undegraded dextran pptd. between 41 and 90% ethanol [5b] (B-742-S)						
Native	Probably > 10^4	0.580	1.4	.....	..	..
Total hydrolyzate	20	0.836	5.1	2.2 (0.686)	16	12
Clinical-size fraction	247	0.649	1.8	1.8 (0.637)	58	43

[a] Corrected yield of formic acid.

hydrolyzates'' were deionized by passage through columns of Duolite A-4[16] resin prior to oxidation analysis.

Interpretation of Data

Results of the application of the appropriate equations derived in preceding sections to the periodate oxidation data obtained on the several dextran samples are included in Table I.

Properties of Entire Hydrolyzate.—The total hydrolyzates (B-512 and B-742-S) show an increased ratio of 1,6′- to non-1,6′-linkages, even after correction for the additional contribution of the reducing end groups to formic acid production. The correction leaves the reducing end group equivalent to a 1,6′-linked unit, therefore cleavage of 1,6′-linked units would give no change in the *corrected* ratio (except when D-glucose is the fragment liberated). The observed increase thus shows that non-1,6′-linkages have been hydrolyzed and/or D-glucose molecules formed.

The observed DP_N for the total hydrolyzate of dextran B-742-S (Table I) is significantly higher than the predicted maximum DP_N calculated from the periodate data using equation 1. This suggests a marked departure from the pattern of hydrolysis (homogeneous cleavage) on which equations 1 and 3 were based. The observed results are accounted for readily on the basis of the high yields of D-glucose which have been observed in other hydrolysis studies and which have led to the proposal for this and other dextrans of a structure in which the external branches predominantly are only one glucose unit in length,[6,12] analogous to Fig. 1B. Data on the composition of hydrolyzates of dextran B-742-S similar to the one given here showed that about 75% of the bonds cleaved yielded D-glucose and that most of such bonds probably were non-1,6′-linkages.[12] A combination of 75% of such cleavage and 25% of homogeneous cleavage of 1,6′-linkages yielding larger fragments would give a calculated DP_N of 18, which approaches reasonably closely to the observed value of 20.

In contrast, for the hydrolyzate of dextran B-512 the observed DP_N falls between the maximum and minimum calculated from the periodate oxidation data. This can be accounted for on the basis of a much lower extent of formation of D-glucose, together with hydrolysis of 1,6′-linkages as well as non-1,6′-linkages, more or less in proportion to their frequency of occurrence. Quantitative measurements of the amount of D-glucose formed have shown[6] that only about 20% of the bond cleavages give rise to D-glucose in the range of extent of hydrolysis used here. This extent of D-glucose formation apparently is not sufficient to overshadow the hydrolysis of 1,6′-linkages, so that the formic acid production on oxidation is not even as high as would be predicted for homogeneous cleavage of only non-1,6′-linkages.

Properties of Isolated Clinical Fraction.—Comparisons of apparent ratio of 1,6′- to non-1,6′-linkages frequently will be made between the original dextran and isolated degradation fractions, such as a clinical-size fraction. Correction of the periodate oxidation data will involve a change in the observed yield of formic acid dependent on the DP of the fraction. As seen in Table I, this correction amounts to between 0.015 and 0.012 mole of formic acid per anhydroglucose unit in the DP range of 200 to 250. The magnitude of the effect of this correction on the calculated ratio of 1,6′- to non-1,6′-linkages varies with the apparent ratio, being quite large for higher ratios such as for dextran B-512 (see Table I) and becoming less than 0.1 as the ratio approaches 1.0. For the most critical comparison of periodate data on degradation products, however, it is imperative that a correction always be made for the additional formic acid obtained from the reducing end group.

After correction for the reducing end group, the

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

clinical-size fractions still give a higher ratio of 1,6′- to non-1,6′-linkages, with the possible exception of dextran B-512. Several possible explanations could be advanced to account for the usual increase in ratio. For example, molecular heterogeneity may have existed in the original dextran,[15b] the degradation changing the properties sufficiently to permit a fractionation on the basis of structure which was not accomplished before hydrolysis. In the absence of fractionation on a structural basis, hydrolysis of non-1,6′-linkages will in most cases cause an increase in apparent ratio, regardless of whether the hydrolysis rate constant of non-1,6′-linkages or the relative number broken were higher or lower than for 1,6′-linkages. Thus, there is a multiplicity of factors which may influence the apparent ratio for the isolated fraction. The absence of a significant change in the ratio for dextran B-512[15a] undoubtedly reflects the relatively small proportion of non-1,6′-linkages present and the resulting fact that most of the degradation of the polymer would be as a result of hydrolysis of 1,6′-linkages, for which no change in formic acid production would be obtained on the corrected basis.

The calculation of maximum and minimum DP_N from the periodate oxidation data on the original dextran and the isolated fraction, using equations 1 and 3, is of interest as further evidence of whether the fraction is a result of a relatively homogeneous-type cleavage. The clinical-size fraction from dextran B-512 has a DP_N between the calculated extremes and, therefore, could be a product of an essentially homogeneous cleavage. The observed values for the other three products, Table I, are significantly higher than the calculated maximum DP_N. This suggests a departure from homogeneous-type cleavage or a fractionation of the products on the basis of structure. Evidence from other studies[12] indicates that at least one contribution to the results is the fact that apparently removal of external branches by cleavage of non-1,6′-linkages leads to the formation of D-glucose and some oligosaccharides, which then are discarded in the isolation of the clinical-size fraction. While the same process apparently occurs with dextran B-512, it represents a minor part of the total bond cleavage[6] and has little influence on the periodate oxidation properties of the product.

PEORIA, ILLINOIS

[JOINT CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE OHIO STATE UNIVERSITY AND THE BALLISTIC RESEARCH LABORATORIES OF ABERDEEN PROVING GROUND]

The Controlled Thermal Decomposition of Cellulose Nitrate. I[1,2]

BY M. L. WOLFROM, J. H. FRAZER, L. P. KUHN, E. E. DICKEY, S. M. OLIN, D. O. HOFFMAN, R. S. BOWER, A. CHANEY, ELOISE CARPENTER AND P. MCWAIN

RECEIVED JULY 15, 1955

The thermal decomposition of propellant cellulose nitrate (12.6% N), under ignition conditions, has been investigated at 2–3 mm. A solid residue is formed which has been characterized analytically and which on denitration and hydrolysis yielded cellobiose, D-glucose, D-gluconic acid, D-erythrose and glyoxal. These results establish the material as a fragmented type of oxycellulose nitrate of an extremely low degree of polymerization. The results are interpreted on the basis of homolytic bond scission.

Since the initial preparation of cellulose nitrate by Pelouze[3] in 1838 and the recognition of its military importance by Schönbein[4] in the following decade, there has been an increasing amount of research on the decomposition of this substance. The action of chemical agents such as acids, bases and reducing substances has been investigated under a variety of conditions; a number of simple and a few complex reaction products have been identified.[5] A list[6] of the substances produced by the chemical agents follows (to provide comparison with those afforded by thermal decomposition): inorganic nitrites and nitrates; nitrogen[7]; cyanide[8]; oxides of nitrogen (N_2O,[7] NO[7] and NO_2) and carbon (CO[7,8] and CO_2); ammonia[8]; oxalic, malic, formic,[8] glycolic, butyric, malonic, tartaric,[8] trihydroxyglutaric, dihydroxybutyric, hydroxypyruvic,[8] isosaccharinic and tartronic acids; glucose; modified and degraded celluloses[9] and their nitrates.

The thermal decomposition of cellulose nitrate at 108° has been found to produce carbon dioxide and monoxide, nitric and nitrous oxides, methane and nitrogen.[10] Hydrogen cyanide was found by

(1) This work was carried out under contract (OEMsc-1152 with the Office of Emergency Management, Office of Scientific Research and Development; W-33-019-ord-3978 and -6279, and DA-33-019-ord-11, -163, -727 and -1466 with the Ordnance Department, United States Army) by The Ohio State University Research Foundation (Projects 170, 212, 313, 402, 458, 496 and 589). Preliminary investigations were performed by D. O. Hoffman and Prof. R. C. Elderfield in the Department of Chemistry of Columbia University, New York, N. Y.

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(3) T. J. Peiouze, *Compt. rend.*, **7**, 713 (1838).

(4) C. F. Schönbein, *Phil. Mag.*, **31**, 7 (1847).

(5) J. Barsha, in "Cellulose and Cellulose Derivatives," "High Polymers," Vol. V, 2nd edition, E. Ott, H. M. Spurlin and Mildred W. Grafflin, Ed., Interscience Publishers, Inc., New York, N. Y., 1954, p. 751, gives an excellent review on the action of chemical agents on cellulose nitrate and cites many references to the original literature.

(6) References are cited only for the products not noted by Barsha in reference 5.

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(8) E. Knecht and B. R. Bostock, *J. Soc. Chem. Ind.*, **39**, 163T (1920).

(9) B. Rassow and E. Dörr, *J. prakt. Chem.*, **108**, 113 (1924); T. Tomonari, *Z. Elektrochem.*, **40**, 207 (1934); A. Nadai, *Z. physik. Chem.*, **136**, 289 (1928).

(10) R. Vandoni, *Compt. rend.*, **201**, 674 (1935).