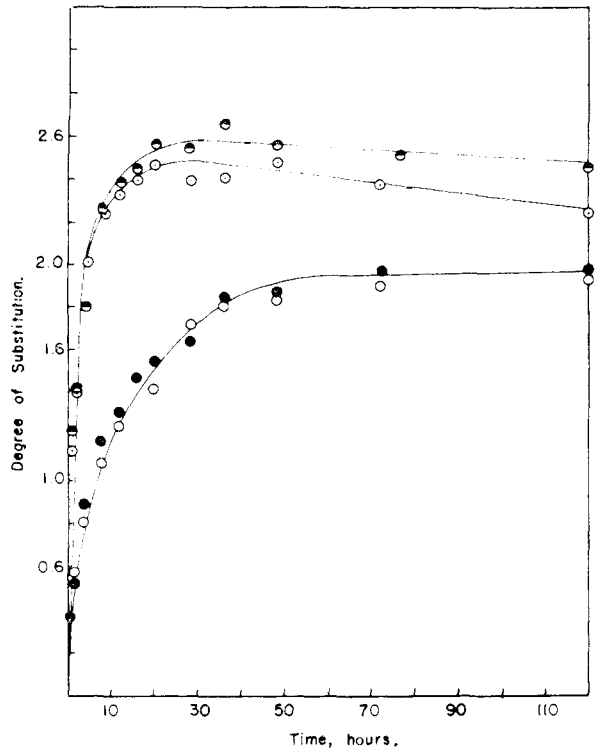


Fig. 2.—Comparative mesylation and tosylation of cellulose, temperature of reaction 28°: mesylation series, ⊖ run 46, ⊙ run 41; tosylation series, ● run 35, O run 41.

agreement regardless of whether the original sample had as little as 0.88 or as much as 2.14 tosyl groups per glucose unit.

Trisubstituted mesylcellulose was prepared in a single step by using a 20:1 molar ratio of mesyl chloride to cellulose; total D.S. values of 2.95, or more, were obtained. When a 10:1 ratio was used, the total D.S. rarely exceeded 2.85. Typical analytical values produced by the 20:1 ratio were 22.9% sulfur and 2.15% chlorine, 22.5% sulfur and 3.18% chlorine. Remesylation of a mesylcellulose having a total D.S. of 2.0 also resulted in the formation of products having a total D.S. of approximately 3.0.

TABLE IV

RE-ESTERIFICATION OF TOSYLCELLULOSE

	Original tosylcellulose	Retosylated tosylcellulose	Mesylated tosylcellulose
	Run A		
Sulfur, %	10.72	14.12	19.00
Chlorine, %	0.28	0.46	1.72
D.S. of tosyl	1.13	2.15	1.13
D.S. of mesyl	..	..	1.65
D.S. of chlorine	0.02	0.06	0.23
Total D.S.	1.15	2.21	3.01
	Run B		
Sulfur, %	9.46	14.06	20.21
Chlorine, %	0.16	0.60	1.62
D.S. of tosyl	0.88	2.18	0.88
D.S. of mesyl	..	..	2.02
D.S. of chlorine	0.08	0.07	0.21
Total D.S.	0.96	2.25	3.11
	Run C		
Sulfur, %	13.93	14.17	16.06
Chlorine, %	0.47	1.50	2.25
D.S. of tosyl	2.14	2.26	2.14
D.S. of mesyl	..	..	0.58
D.S. of chlorine	0.02	0.12	0.34
Total D.S.	2.16	2.38	3.06

The side reaction product, pyridinium methanesulfonate, was ineffectual in causing esterification of the cellulose as was shown by unsuccessful attempts to cause these two materials to react together. The formation of this material simply resulted in a depletion of the active mesylating agent. The active agent was present in the dark brown liquid separated from the solid by-product. Three days after the original mixing of mesyl chloride and pyridine, the liquid portion was still able to introduce about 11% sulfur into a sample of activated cellulose.

APPLETON, WISCONSIN

[CONTRIBUTION FROM THE NORTHERN UTILIZATION RESEARCH BRANCH[1]]

Characterization of Dextrans by the Optical Rotation of their Cuprammonium Complexes

BY T. A. SCOTT, N. N. HELLMAN AND F. R. SENTI

RECEIVED OCTOBER 1, 1956

Optical rotations at 4358 Å. in water and cuprammonium solutions have been measured for several dextrans differing widely in their content of 1,6-, 1,4- and 1,3-like linked anhydroglucopyranoside units as determined by periodate oxidation analyses. Based on previous results for the optical rotational shifts of simple glucopyranosides, it is shown how the optical rotational shift data for dextrans can be used to resolve the percentage of 1,4-like linked units derived from periodate oxidation analyses into the proportions of 1,4- and 1,2-linked units. By this method a large proportion of the 1,4-like linked units in NRRL B-1299 and NRRL B-1399 dextrans were found to be linked through position 2. These are the first dextrans to be reported to contain the 1 → 2-linkage. Optical rotation shift data also indicate that NRRL B-1149 and NRRL B-1355 fraction S dextrans have non-1,6-linked units which occur in linear portions of the polysaccharide chain rather than as branch points in the molecule.

Periodate oxidation reaction analyses of a large number of dextrans have shown that the majority of the anhydroglucose units in these polysaccharides are joined through 1→6-glucosidic linkages,

(1) One of the Branches of the Agricultural Research Service, U. S. Department of Agriculture. Article not copyrighted.

the percentage varying from 50 to 97 according to the biological source of the dextran.[2] Differentiation cannot be made by periodate oxidation analyses between 1,2- and 1,4-linked units or between 1,3- and other units having a single free hydroxyl on carbons 2, 3 or 4, and for this reason the content of such units has been reported[2,3] as 1,4-like and 1,3-like, respectively. This ambiguity in structural interpretation can be resolved by methylation analysis, but the procedure is time consuming. It is the purpose of this communication to point out that the optical rotational shift accompanying cuprammonium complex formation of a dextran is an easily measured property which, with certain assumptions, enables the percentage of 1,4-like linked units derived from periodate oxidation analysis to be resolved into the proportions of 1,4- and 1,2-linked units. In some cases further structural information is given by the rotational shift data; in certain dextrans, for example, evidence is provided that part of the non-1→6 linkages are not at branch points. Instead they link units in linear portions of the dextran chain.

Reeves[4] has shown that cuprammonium complex formation at the 2,3-hydroxyl position of glucopyranosides causes a large decrease in optical rotation at 4358 Å., but complex formation at the 3,4-hydroxyl positions produces a large increase in optical rotation. A group attached to the glucopyranoside through the 2-hydroxyl position, for example, caused complete 3,4-complexing and resulted in a molecular rotational shift[5] of +210,000°, whereas a group attached through the 4-hydroxyl position permitted complete 2,3-complexing and gave a molecular rotational shift of −200,000°. When the 3-hydroxyl position was blocked, complex formation was prevented and the specific rotation of a cuprammonium solution of the 3-substituted glucopyranoside was not significantly different from the specific rotation of the aqueous solution. With the 2,3- and 4-hydroxyls all unsubstituted—whether or not the 6-hydroxyl was substituted—a relatively small molecular rotational shift of +25,000° was observed. Presumably this shift is small because both 2,3- and 3,4-complexes were formed so that their opposite optical effects nearly canceled one another. If these results obtained by Reeves on simple glucopyranosides are valid for dextrans, it is apparent that the optical rotational shift should provide a fairly sensitive method of obtaining evidence on the position of linkage of non-1→6-linkages in a dextran. In the present investigation optical rotational shifts have been measured for several dextrans which differ widely in their content of 1,6-, 1,4- and 1,3-like units as determined by periodate analysis.

(2) Allene Jeanes, W. C. Haynes, C. A. Wilham, J. C. Rankin, E. H. Melvin, Marjorie J. Austin, J. E. Cluskey, B. E. Fisher, H. M. Tsuchiya and C. E. Rist, THIS JOURNAL, **76**, 5041 (1954).

(3) J. C. Rankin and Allene Jeanes, *ibid.*, **76**, 4435 (1954).

(4) R. E. Reeves, "Advances in Carbohydrate Chemistry," Academic Press, Inc., New York, N. Y., Vol. 6, 1951, p. 107.

(5) The molecular rotational shift is the product of the molecular weight of the glucopyranoside and the difference in specific rotation at 4358 Å. between cuprammonium and aqueous solutions of the glucopyranoside.

Experimental

Dextrans.—Except dextran B-523E, which was prepared by the culture-filtrate method,[6] all dextrans were prepared by whole-culture fermentation. Dextrans from strain numbers carrying the superscript *a* in Table I were from preparations described by Jeanes, *et al.*[2] Dextrans from strain B-512F,[7] B-1254 and B-742 were pilot plant preparations. Dextrans were purified as described in reference 2 and were comparable in purity to the dextrans listed there. Samples of the B-512F and B-1254 dextrans were acid hydrolyzed and fractions separated by alcohol precipitation. B-742 dextran was heterogeneous and was separated into two components, S and L, on the basis of their solubility in 41% alcohol.

Optical Rotation of Aqueous and Cuprammonium Solution.—Except samples of B-512 and B-1254 dextrans that had been acid hydrolyzed, the dextrans formed solutions which were too turbid for polarimetric measurements. To reduce their turbidity, these dextrans were sonically degraded to a number-average molecular weight of 50,000 to 150,000. Sonic degradation was effected by subjecting 50 ml. of approximately 2% solution to the action of a 10-kc. Raytheon oscillator[8] for a period of 3 or 4 hours. The solutions were then lyophilized to obtain solid dextran in a readily soluble form. One to 5% aqueous solutions were prepared and their optical rotations were measured in 1- or 2-decimeter tubes. The concentration and tube length depended on the turbidity of the solution. Most of the optical rotations were measured visually on a Bellingham–Stanley polarimeter; the smallest half-shadow angle was used which permitted sufficient light to pass through the solution for matching the field. Two centimeters of cuprammonium solution, the "cupra B" prepared according to Reeves,[4] was used as a light filter for measuring rotations of the aqueous solutions. The cuprammonium–dextran solutions, which were prepared with the same "cupra B," acted as their own filters. Some of the later measurements were made with a photoelectric polarimeter; a Beckman DU spectrophotometer was used to isolate the 4358 Å. line from an H-3 mercury lamp.

After the optical rotations were measured, the dextran concentrations of the solutions were determined by the anthrone method.[9] The cuprammonium solutions were first neutralized with 1 *N* sulfuric acid. Determinations on dextran solutions of known concentration in cuprammonium showed that the copper sulfate present after neutralization did not interfere with the analysis.

Results and Discussion

Rotational shifts for several dextrans on cuprammonium complex formation are given in column 5 of Table I. Periodate oxidation data are listed in columns 6–8; values given for sonically degraded samples are those obtained on the original dextran, but the acid-hydrolyzed samples were analyzed after degradation. The rotation data for samples 2, 3 and 4 of NRRL B-512F dextran permit a comparison of dextran degraded by sonic vibration and acid hydrolysis. Rotational shifts for the 3 samples are identical within experimental error, indicating no detectible difference occurs in the mode of degradation by the two methods. This gives support for our assumption that the periodate oxidation results were unchanged by the sonic degradation since previous work[10,11] has shown that

(6) H. J. Koepsell and H. M. Tsuchiya, *J. Bacteriol.*, **63**, 293 (1952).

(7) In 1950, the B-512F substrain supplanted B-512 for all work at the Northern Utilization Research Branch. Since that time, the dextran from this substrain has been designated inexactly as B-512 in numerous publications. The dextrans from B-512 and B-512F appear to be identical.

(8) 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.

(9) T. A. Scott, Jr., and E. H. Melvin, *Anal. Chem.*, **25**, 1656 (1953).

(10) F. R. Senti, N. N. Hellman, N. H. Ludwig, G. E. Babcock, R. Tobin, C. A. Glass and B. L. Lamberts, *J. Polymer Sci.*, **17**, 527 (1955).

(11) R. J. Dimler, I. A. Wolff, J. W. Sloan and C. E. Rist, THIS JOURNAL, **77**, 6568 (1955).

TABLE I

FRACTION OF BOND TYPES IN DEXTRANS FROM OPTICAL ROTATIONAL AND PERIODATE OXIDATION DATA

Sample	From strain NRRL B-	Fraction	Spec. rot. $[\alpha]_{4358\text{ Å.}}^{25}$	Rot. shift in cupra. $M\Delta 4358$ n	Fraction of bond types by periodate analysis 1 → 6-like	1 → 4-like	1 → 3-like	Fraction of bond types from rotational data 1 → 4	1 → 2
1[b]	1146[a]		395°	−92,500	0.97	0.03	0.00		
2[b]	512F		395	−90,500	.95	.05	.00		
3[c]	512F		392	−90,400	.95	.05	.00		
4[c]	512F			−90,700	.95	.05	.00		
5[c]	1254		392	−87,000	.93	.07	.00		
6[c]	1254		387	−84,800	.92	.04	.04		
7[b]	523-E		408	−81,800	.85	.11	.04	0.10	0.01
8[b]	523[a]			−27,900	.66	.10	.24	.06	.04
9[b]	742		413	−56,700	.66	.25	.09	.21	.04
10[b]	742	S[d]	431	−40,500	.57	.24	.19	.21	.03
11[b]	742	L[d]	396	−72,000	.80	.20	.00	.14	.06
12[b]	1149[a]			−45,400	.52	.08	.40		− .09
13[b]	1355[a]	S[e]	441	−39,000	.57	.08	.35		− .05
14[b]	1299[a]	L[e]	412	+56,700	.58	.36	.06	.02	.34
15[b]	1299[a]	S[e]		+65,400	.50	.50	.00	.12	.38
16[b]	1399[a]		411	+23,200	.65	.35	.00	.06	.29

[a] Samples described by Jeanes, *et al.*[1] [b] Dextran degraded by sonic treatment. [c] Fractions of acid-hydrolyzed dextran. [d] The letters L and S indicate the dextran was fractioned by solubility in alcohol, L designating the insoluble fraction, and S the soluble fraction at 41% (v./v.) alcohol concentration. [e] Details on the production and characterization of these fractions have been reported by Wilham, Alexander and Jeanes.[12]

degradation to a comparable extent by acid hydrolysis caused no change.

The samples listed in Table I have been selected to provide examples of dextrans representative of the range of structural variation observed in a survey of dextrans from 96 bacterial strains.[2] Structural differences between fractions of a given dextran and between different dextrans, as indicated by the periodate oxidation data, are generally also indicated by the rotational shift data. Samples 5 and 6, for example, are two fractions of acid-hydrolyzed B-1254 dextran which differed in molecular weight. Structural differences between these two fractions are indicated by both the difference in specific rotation and by rotational shift of the two fractions, while the difference in periodate oxidation data borders on significance. The fractions probably reflect some of the structural heterogeneity previously reported[12] for B-1254 dextran.

Analysis of Rotational Shift Data.—The observed rotational shift for a dextran can be taken as the sum of the contributions of each of its constituent anhydroglucopyranoside units, the contributions of each depending on the availability of the hydroxyl groups on carbon atoms 2, 3 and 4 for copper complex formation. An anhydroglucose unit linked through position 3 should be unable to form a copper complex; accordingly, it should make no contribution to the rotational shift. Units linked through positions 2 or 4 should afford maximum opportunity for 3,4- and 2,3-complex formation, respectively, and we have assigned values of +200,000° and −200,000° for the corresponding rotational shifts. These assignments are based on the data for methyl glucosides cited above. Androglucose units linked in a dextran chain through positions 1 and 6 do not afford equal opportunity for complexing at 2,3 and 3,4 and do not produce a resultant null contribution to the rotational shift in cuprammonium solution. This is evident from the observed rotational shift of −92,500 for B-1146 dextran having 97% apparent 1,6-linked units, which shows that the rotational shift for these units must be approximately −90,000°. Scott and Senti[13] observed this negative rotational shift earlier and prepared the methyl glycosides of a series of homologous α-1→6-linked gluco-oligosaccharides in order to determine the rotational shift of a 1,6-linked unit. They found a value of −99,000° which is adopted in the present work.

Preferential complex formation must occur at the 2,3-position to account for the rotational shift of −99,000° for 1,6-linked units on the interior of the dextran chain. This raises the question of the contribution of non-reducing end groups in a dextran, which are linked only through the 1-position and which, therefore, will be subjected to steric influences different from those in 1,6-linked units. Results for the methyl isomaltoside homologous series[13] referred to above showed that either one or both end units must have a rotational shift different from that of the interior units of the 1→6-linked chain. Since the methyl glycoside end unit carries substituents at both positions 1 and 6 whereas the other end unit has a free hydroxyl at position 6, the latter end unit might be expected to differ from interior units in copper complex formation. This is borne out by the rotational shifts observed for some of the dextrans, *e.g.*, B-523, B-1299 fraction L, B-1299 fraction S and B-1399, which require that the contribution of 1-linked units be a less negative value than that found for the 1,6-linked units in the methyl isomaltoside series. The data for these dextrans do not permit the computation of a unique value, however, because such computation would require information, not given by periodate oxidation, on the proportions of 1,2- and 1,4-linked units as well as the extent of branching. For the

(12) C. A. Wilham, B. H. Alexander and Allene Jeanes, *Arch. Biochem. and Biophys.*, **59**, 61 (1955).

(13) T. A. Scott and F. R. Senti, THIS JOURNAL, **77**, 3816 (1955).

purposes of this paper, the contribution of a non-reducing end group in dextran was assumed to be that found for methyl glucoside, *i.e.*, +25,000°, since in both cases the anhydroglucose unit is linked through the 1-position and steric influences on copper complex formation should be similar.

An equation for the rotational shift in terms of the contributions of the variously linked anhydroglucose units may be written as

$$M\Delta\alpha/n = -99{,}000^\circ F_{1,6} + 25{,}000^\circ F_1 + 200{,}000^\circ F_{1,2} - 200{,}000^\circ F_{1,4} + 0 \cdot F_{1,3} \quad (1)$$

where M is the molecular weight of the dextran, n is the degree of polymerization, $\Delta\alpha$ the shift in specific rotation in cuprammonium solution, $F_{1,6}$ the fraction of anhydroglucose units linked only through carbon atoms 1 and 6, F_1 the fraction of non-reducing end units, $F_{1,2}$ the fraction of units linked through positions 1 and 2 or 1, 2 and 6, $F_{1,4}$ the fraction of units linked through positions 1 and 4 or 1, 4 and 6, and $F_{1,3}$ the fraction of units bonded through 1→3-like linkages.

To adapt equation 1 for convenient application to the results of periodate oxidation analysis as commonly reported, we let $F'_{1,6}$ represent the fraction of 1,6-like units, *i.e.*, $F'_{1,6} = F_{1,6} + F_1$, and we assume that all anhydroglucose units involved in linkages other than 1→6 linkages are branched units. If only singly branched units are assumed to be present at branch-points, there is a non-reducing end for each branch-point unit and F_1 may be replaced by $1 - F'_{1,6}$ and equation 1 becomes

$$M\Delta\alpha/n = -99{,}000^\circ (2F'_{1,6} - 1) + 25{,}000^\circ (1 - F'_{1,6}) + 200{,}000^\circ (F_{1,2} - F_{1,4}) \quad (2)$$

Using the additional condition that $F_{1,2} + F_{1,4}$ is the fraction of 1,4- like units determined in periodate oxidation analysis, we can solve equation 2 for $F_{1,2}$ and $F_{1,4}$. Results for the dextrans studied in the present work are given in the last two columns of Table I. No resolution of 1,4-like units has been made for the first six samples because the uncertainty in the content of 1,4-like units, as determined by periodate analysis, may be as great as the value reported.[3]

Results for dextrans B-1299 fraction L, B-1299 fraction S and B-1399 definitely indicate the presence of anhydroglucose units linked through position 2. In fact, in these dextrans it appears that 1,2-linkages comprise the greater proportion of the 1,4-like linkages as determined by periodate oxidation analysis. In view of the assumptions made, the interpretation is less certain for the samples 7–11 from B-523 and B-742 dextrans, but the results suggest that some 1,2-linked units occur in these dextrans. Alternatively, the apparent 1,2-linked units could be accounted for by a larger fraction of 1,3-linked units than indicated by the periodate data for these dextrans.

For two dextrans, B-1149 and B-1355 fraction S, equation 2 proved to be inconsistent with the experimental data, requiring negative fractions of 1,2-linked units for its solution. In effect, this means that the sum of the first two terms on the right-hand side of equation 2 should be a larger negative number to account for the observed rotational shift. Rather than assume new values for rotational shifts characteristic of various units in these dextrans, an alternative interpretation that seems more likely is that not all non-1→6-linkages comprise branch points in the dextran chain. If we accept this interpretation, then about 70% of the 1,3-like or 1,4-like linked units in B-1149 dextran must be bonded only to two other units and do not represent branching units in the structure. Similarly, about 50% of the non-1→6-linkages in B-1355 fraction S dextran are not involved in branching but join units in linear portions of the dextran chain. Jones, *et al*,[14] also concluded from the yields of mono-, di-, tri- and tetrasaccharides from B-1355 dextran on limited acid hydrolysis that the majority of the non-1→6-linkages did not comprise branch points. Preliminary methylation structure studies[15] on this dextran confirm these conclusions.

The above examples illustrate the structural information on dextrans that can be gained from cuprammonium rotational shift data in conjunction with periodate oxidation analyses. In the application of equation 2, however, it must be kept in mind that the coefficients of the second and third terms on the right-hand side have not been determined from dextrans of known structure and, accordingly, some reservations must be held with respect to the accuracy of results computed from the equation. Better values for these coefficients must await methylation or other complete structural analysis of several dextrans, preferably each having a large proportion of a single type of non-1,6-linked unit.

Limitations on the accuracy of the periodate oxidation data as pointed out by Rankin and Jeanes[2] also should be recognized. In the case of B-512F dextran, for example, methylation analysis[16] shows that the 5% non-1→6-linkages are 1→3- rather than 1→4-like linkages as given by periodate oxidation analyses.

Allowing an error of +0.05 in the proportion of 1→4-like linkages does not affect the principal findings with respect to structure of the dextrans investigated in the present study. These are that B-1149 and B-1355 fraction S dextrans have non-1,6-linked units in linear portions of the polysaccharide chain, and that a large proportion of the 1,4-like linked units in B-1299 and B-1399 dextrans are actually linked through position 2. The latter dextrans are the first to be reported to contain the 1→2-linkage; non-1→6-linkages found in other dextrans by methylation analysis have been either the 1→4- or 1→3-type. Dextrans containing relatively large proportions of 1→2-linkages as the dominant non-1→6-linkage are easily recognized by their positive rotational shift in cuprammonium as exemplified by B-1299 and B-1399 dextrans.

(14) R. W. Jones, R. J. Dimler, Allene Jeanes, C. A. Wilham and C. E. Rist, Abstracts of Meeting of American Chemical Society, **126**, p. 13D (1954).

(15) R. J. Dimler, R. W. Jones, W. C. Schaefer and J. W. Van Cleve, Abstracts of Meeting American Chemical Society, **129**, p. 2D (1956).

(16) J. W. Van Cleve, W. C. Schaefer and C. E. Rist, Abstracts of 125th Meeting of American Chemical Society, Kansas City, Missouri (1954), p. 8D.

Similarly, one could expect a dextran containing a large proportion of 1→4-linkages as the principal non-1→6-linkage to show a large negative rotational shift as compared to the value −99,000° for a dextran in which only 1,6-linked units are present.

Acknowledgments.—The authors would like to thank Drs. Allene Jeanes and R. L. Lohmar for many of the dextran samples used in this investigation.

PEORIA, ILLINOIS

[CONTRIBUTION FROM THE NATIONAL INSTITUTE OF ARTHRITIS AND METABOLIC DISEASES, NATIONAL INSTITUTES OF HEALTH]

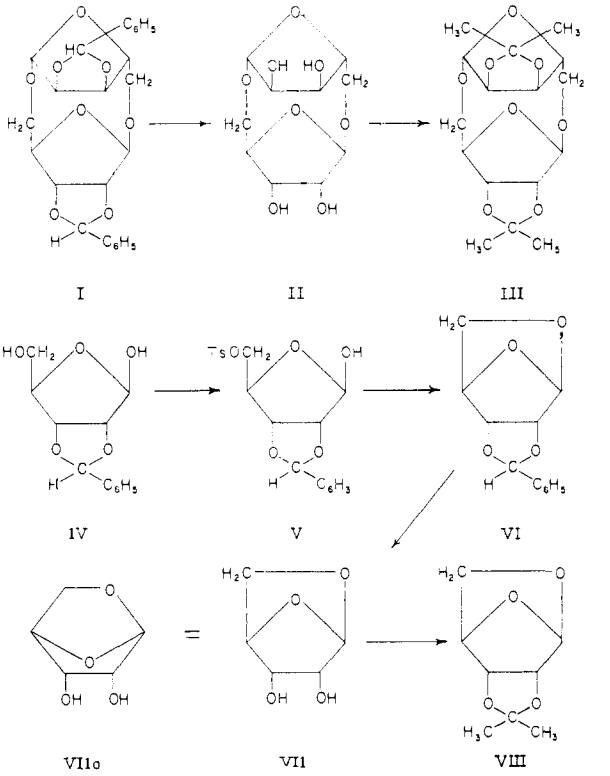
1,5-Anhydro-β-D-ribofuranose and the "Monoacetone Anhydroriboses" of Levene and Stiller

BY ERIK VIS[1] AND HEWITT G. FLETCHER, JR.

RECEIVED SEPTEMBER 26, 1956

Among the products arising from the condensation of D-ribose with benzaldehyde in the presence of zinc chloride–acetic acid has now been found an anhydrobenzylidenepentose. The same substance has been synthesized through treatment of 2,3-*O*-benzylidene-5-*O*-*p*-tolylsulfonyl-D-ribofuranose with alkali, showing its structure to be 1,5-anhydro-2,3-*O*-benzylidene-β-D-ribofuranose. Hydrogenolysis afforded the parent 1,5-anhydro-β-D-ribofuranose (synonym: 1,4-anhydro-α-D-ribopyranose) in crystalline form. Condensation of this anhydride with acetone under mild conditions has given the 1,5-anhydro-2,3-*O*-isopropylidene-β-D-ribofuranose which Levene and Stiller reported as a by-product in the acetonation of D-ribose. Condensation of the known di-β-D-ribofuranose 1,5′:1′,5-dianhydride with acetone under mild conditions has given di-(2,3-*O*-isopropylidene-β-D-ribofuranose) 1,5′:1′,5-dianhydride which is probably identical with the second "monoacetone anhydroribose" mentioned by Levene and Stiller. Phenyl β-D-ribofuranoside and its tribenzoate are described.

In a recent paper from this Laboratory[2] the benzylidenation of D-ribose in the presence of zinc chloride–acetic acid as catalyst was shown to give rise to 2,3-*O*-benzylidene-β-D-ribofuranose (IV)[3] and di-(2,3-*O*-benzylidene-β-D-ribofuranose) 1,5′:1′,-5-dianhydride (I). Chromatography of this rather complex reaction mixture has now led to the isolation in 7% yield of a second crystalline substance having the composition of an anhydrobenzylidenepentose. Hydrogenolysis afforded the parent anhydride which was further characterized through its dibenzoate. In contrast to the known dimolecular anhydride II obtained through the hydrogenolysis of I, the new substance proved to have the molecular weight of a monomeric anhydride. Like levoglucosan it was stable to Fehling solution but was converted rapidly to a reducing mixture on brief treatment with acid. Preliminary experiments showed that acid hydrolysis gave a sugar which migrated at the same rate as D-ribose on a paper chromatogram. When methylation preceded hydrolysis the product migrated at the same rate as 2,3-di-*O*-methyl-D-ribose. This evidence seemed to indicate that the anhydride might be 1,5-anhydro-β-D-ribofuranose (VII) and so its synthesis from 2,3-*O*-benzylidene-β-D-ribofuranose (IV) was attempted. Tosylation provided the monotosyl ester V[4]; treatment of this ester with sodium isopropoxide afforded 1,5-anhydro-2,3-*O*-benzylidene-β-D-ribofuranose (VI), identical with the product obtained through the benzylidenation of D-ribose. This identity was confirmed through conversion of the product VI thus made to the free anhydride VII and its dibenzoate. These latter two substances were identical with those derived *via* the benzylidenation of D-ribose.



I II III

IV V VI

VIIo = VII VIII

An unsubstituted, monomeric, non-reducing anhydropentose has not to our knowledge been reported before[5] although Micheel and Micheel[6] have described a substance to which they assigned a

(1) Chemical Foundation Fellow, 1956–1957.

(2) H. B. Wood, Jr., H. W. Diehl and H. G. Fletcher, Jr., THIS JOURNAL, **78**, 4715 (1956).

(3) This substance was found independently by G. R. Barker and J. W. Spoors, *J. Chem. Soc.*, 1192 (1956), who employed zinc chloride alone as a catalyst.

(4) In view of the relative reactivities of a primary hydroxyl group in a sugar and the hemiacetal hydroxyl in an aldose it seems reasonable to assume that the tosyl group here is at C_5.

(5) The dimeric anhydride II was originally assumed to be 1,5-anhydro-β-D-ribofuranose by its discoverers [H. Bredereck, M. Köthnig and E. Berger, *Ber.*, **73**, 956 (1940)] but later work showed clearly that the substance contained two D-ribose residues [G. R. Barker and M. V. Lock, *J. Chem. Soc.*, 23 (1950); R. W. Jeanloz, G. R. Barker and M. V. Lock, *Nature*, **167**, 42 (1951)].

(6) F. Micheel and H. Micheel, *Ber.*, **63**, 2861 (1930).