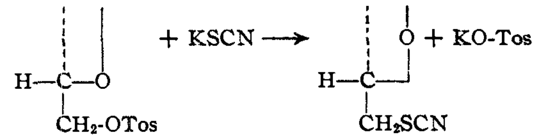
[CONTRIBUTION FROM WESTERN REGIONAL RESEARCH LABORATORY[1]]

The Thiocyanation of Polysaccharide Tosyl Esters

BY J. F. CARSON AND W. DAYTON MACLAY

The replacement of tosyloxy groups in the primary position of carbohydrates by iodine[2] as a method of distinguishing primary from secondary hydroxyl groups has had a wide application. In polysaccharide chemistry, the reaction has been applied quantitatively to cellulose,[3] partially substituted ethyl cellulose[4] and cellulose acetate,[4,5] and to arabogalactan[6] from larch wood. It has now been found that polysaccharide tosyl esters undergo an analogous reaction with alkali thiocyanates to yield thiocyano derivatives. The replacement of tosyloxy in a number of polysaccharide tosyl esters by thiocyanate has been investigated, and the reaction has been found to have approximately the same degree of specificity for primary tosyloxy groups as the familiar iodination reaction.

Müller and Wilhelms[7] found that tetra-acetyl-6-tosyl β-glucose and triacetyl-6-tosyl α-methylglucoside when heated with potassium thiocyanate in acetone at 130° formed the corresponding 6-thiocyanates according to the equation



The 6-thiocyanates were observed to be very stable in contrast to the previously known 1-thiocyanates and showed no tendency to rearrange to the isothiocyanates even at elevated temperatures. A tosyl or mesyl group in the 3 position was found to be unreactive to thiocyanate. The apparent specificity of thiocyanate substitution for primary tosyloxy groups in glucose derivatives cannot be extended to non-carbohydrate materials, since tosyl esters of secondary alcohols have been observed to react with thiocyanates under mild conditions. Cholesterol *p*-toluenesulfonate[8] and ethyl α-tosylpropionate[9] both react with potassium thiocyanate in acetone or alcohol solution to yield the corresponding thiocyano derivatives.

In the present work, potato starch, cellulose, guar mannogalactan, and corn-cob and lima-bean pod hemicelluloses have been tosylated and the esters reacted with sodium thiocyanate in acetonyl acetone at 110–112°. The tosyl esters were also iodinated by heating at 110–112° with sodium iodide in acetonyl acetone, and the primary hydroxyl content as determined by iodine substitution was compared with values obtained by thiocyanation. The results are compiled in Table I.

Discussion of Results

A potato starch tosyl ester, when treated with sodium thiocyanate for varying periods of time, yielded tosyl thiocyano derivatives containing approximately 0.94 equivalent of thiocyanate per anhydroglucose repeating unit. Iodination of the same tosylate likewise yielded iodo compounds containing 0.93 to 0.95 equivalent of iodine per repeating unit.[10]

Thiocyanation and iodination of the cellulose tosyl esters gave more variable results than starch, but approximately one thiocyano group was introduced per anhydroglucose unit. Thiocyanation of a tosyl ester of wood pulp cellulose yielded derivatives containing 0.95 to 1.03 equivalents per repeating unit. Iodination of the same ester for seven hours produced a derivative with 0.98 equivalent of iodine per unit. Thiocyanation of a tosyl ester of regenerated cellulose (Cellophane) yielded derivatives with thiocyanate contents varying from 0.90 to 1.09.

Two different tosyl esters of guar mannogalactan, the water-soluble polysaccharide of guar endosperm (*Cyamopsis tetragonoloba* Taub) when thiocyanated for different periods of time yielded derivatives with thiocyanate contents varying from 0.44 to 0.52 equivalent per anhydrohexose unit. Iodination gave slightly higher replacement values from 0.50 to 0.56 equivalent per anhydrohexose unit. If the two reactions are assumed to be specific for primary hydroxyl in this polysaccharide, approximately half of the primary alcohol groups must be blocked by linkages of the 1,6 type.[11] This observation is at variance with the report of Moe, Miller and Iwen[12] who postulated 1,4 link-

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[1] Bureau of Agricultural and Industrial Chemistry, Agricultural Research Administration, U. S. Department of Agriculture. Article not copyrighted.

[2] Oldham and Rutherford, THIS JOURNAL, **54**, 366 (1932).

[3] Honeyman, *J. Chem. Soc.*, 168 (1947).

[4] Cramer and Purves, THIS JOURNAL, **61**, 3458 (1939); Mahoney and Purves, *ibid.*, **64**, 9, 15, 1539 (1942).

[5] Malm, Tanghe and Laird (abstract of paper delivered at Division of Cellulose Chemistry, American Chemical Society, New York, Sept., 1947).

[6] Low and White, THIS JOURNAL, **65**, 2430 (1943).

[7] Müller and Wilhelms, *Ber.*, **74B**, 698 (1941).

[8] Müller and Batyka, *ibid.*, **74B**, 705 (1941).

[9] Gerrard, Kenyon and Phillips, *J. Chem. Soc.*, 153 (1937).

[10] The theoretical thiocyanate or iodine content should be slightly less than unity because of the presence of a small number of 1,6 linkages in the amylopectin component of potato starch.

[11] Swanson (abstract of paper delivered at Division of Sugar Chemistry, American Chemical Society, New York, Sept., 1947) has obtained by hydrolysis of methylated guar polysaccharide 2,3,4,6-tetramethylgalactose and unidentified trimethyl and dimethyl sugars. From the quantities isolated, the author suggests that the polysaccharide consists of a main chain of anhydromannose units with a side unit of galactose attached to every other mannose unit.

[12] Moe, Miller and Iwen, THIS JOURNAL, **69**, 2621 (1947).

TABLE I

THIOCYANATION OF POLYSACCHARIDE TOSYL ESTERS

Tosyl ester			Thiocyanation					Iodination				
Polysaccharide	% S^a	Number of tosyl groups per repeating unit	Reaction time, hr.	% N^b	Equivalents of SCN per repeating unit^c	% S Found^a	% S Calcd.	Time, hr.	% I^d	Equivalents of I per repeating unit^e	% S Found^a	% S Calcd.
White potato starch	13.19	1.82	3	3.72	0.91	16.89	17.2	3.5	30.0	0.95		
			4	3.76	.91	16.98	17.2	7	29.2	.93	6.97	7.16
			6	3.91	.94	17.11	17.4	9	29.7	.94		
			9	3.89	.94	17.09	17.3					
			12	3.96	.95	17.03	17.4					
Cellulose (wood pulp)	13.05	1.77	7	4.06	0.95	16.80	17.3	3.5	29.6	0.92		
			9	4.41	1.01			5	30.2	.94	6.3	6.79
			11	4.52	1.03	17.4	17.8	7	31.6	.98	6.3	6.51
Cellulose (cellophane)	13.38	1.90	7	3.55	0.90	16.9	17.2					
			8	4.23	1.02	17.6	18.0					
			9	4.61	1.09	18.2	18.4					
Guar (mannogalactan)	13.50	1.95	4	1.56	0.46	14.95	15.2	6	15.6	0.54	10.04	10.3
			8	1.72	0.50	15.20	15.4	8	16.1	.56	9.90	10.2
	13.78	2.07	6	1.44	.44	15.15	15.4	3	13.8	0.50		
			9	1.61	.49	15.20	15.5	6	13.7	0.50		
			10	1.73	.52	15.41	15.7	9	15.2	0.55		
			12	1.49	.46	14.83	15.4	12	14.8	0.53		
Lima bean pod hemicellulose	7.67	0.534	6	1.05	.15	8.19	8.32	6	8.58	0.15	5.42	5.73
			7.5	1.01	.15	8.17	8.29					
			9.5	1.06	.16	8.20	8.32					
			12	0.86	.13	8.12	8.20					
	13.03	1.53	5	.81	.20	13.83	13.9	4	10.0	0.29	11.1	11.06
			7	.84	.21	13.89	13.9	6	11.5	.33	10.7	10.73
			8	.82	.21	14.03	13.9					
			9	.98	.24	14.02	14.1					
			11	.92	.23	14.14	14.0					
Corn-cob xylan	13.96	1.81	7	.62	.18			5	5.65	0.18	12.3	12.8
			8.5	.78	.22	14.71	14.8					
			9	.74	.21							
			10	.75	.21	14.80	14.8					

[a] Sulfur was determined gravimetrically by the Parr bomb method. [b] Nitrogen was determined by the Kjeldahl method. [c] The number of equivalents of thiocyanate (m) per repeating unit was calculated from nitrogen analyses by the formula

$$m = \frac{u + 154.18n}{113.11 + (1401/N)}$$

where n = number of tosyl groups per repeating unit in original ester; N = % nitrogen; and u = average repeating unit, *i. e.*, 162.1 for a hexosan. For the corncob and lima bean pod hemicelluloses, the calculated values of u were, respectively, 137 and 141, on the assumption that the material unaccounted for as xylan, uronic anhydride, and methoxyl is hexosan. The theoretical percentage of sulfur was calculated by the formula:

$$\% \text{ S} = \frac{3206n}{u + 154.18n - 113.11n}$$

Calculation of thiocyanate content from sulfur analyses would have yielded slightly lower values in each case. [d] Iodine was estimated by the method of Clark, "Semimicro Quantitative Analysis," Academic Press, New York, N. Y., 1943, p. 62. [e] The number of equivalents of iodine per repeating unit was calculated from iodine analyses assuming no loss of tosyl ester except by replacement.

ages from the observation that guar mannogalactan consumes one mole of periodate.[13]

Thiocyanation and iodination of a corn-cob hemicellulose tosylate gave unexpectedly high values for thiocyanate and iodine substitution. Analysis of the hemicellulose indicated that approximately 96% could be determined as xylan[14] and methoxy uronide. Lignin content was not greater than 1%. Since the anhydroxylose units

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(13) Investigations in this Laboratory of the periodate oxidation of mannogalactan are also in disagreement with the report of Moe, *et al.*[11] It has been observed that in the oxidation of guar polysaccharide, formic acid is always produced (0.3 to 0.4 mole per equivalent of polysaccharide) and that consumption of paraperiodic acid (buffered at *p*H 5) or of sodium metaperiodate at temperatures from 5° to 25° was greater than one mole, the rate curve having such a shape that it was difficult to determine the exact consumption of oxidant.

(14) Bennett (*J. Agr. Res.*, **76**, [1] 43 (1947)), in investigations of an unfractionated sample of corn cob hemicellulose, reported the presence of a trace of L-arabinose in the acid hydrolysate. Our hemicellulose fraction was found to be free of arabinose to the extent that no test could be obtained with diphenylhydrazine or benzylphenylhydrazine.

of the xylans are considered to be in the pyranose form,[15] the actual replacement by iodine or thiocyanate should not be greater than 0.04 equivalent per average repeating unit. A tosyl ester containing 1.81 tosyl groups per average repeating unit yielded thiocyanates containing 0.18 to 0.22 equivalent of thiocyanate per repeating unit and iodination gave a replacement of 0.18 equivalent.

The lima bean pod hemicellulose fraction had analyses indicating that 82% of the polysaccharide could be accounted for as xylan, uronic anhydride and methoxyl. Arabinose could not be detected. On the assumption that the material unaccounted for by these analyses is hexosan, the maximum degree of replacement should be approximately 0.18 equivalent per average repeating unit (weighted average of xylan, methoxy uronide and hexosan). Thiocyanation and iodination of a tosylate with a low ester content (0.53 equivalent of tosyl per unit) seemed to confirm this supposition. Both reactions proceeded to the extent of 0.15 equivalent per unit. However, iodination of a tosyl ester having a higher tosyl content (1.53 equivalents per unit) gave higher values which would indicate a primary hydroxyl content of 0.29 to 0.33. Thiocyanate substitution was also significantly higher than before, 0.20 to 0.24 equivalent per repeating unit.

When these reactions are applied to polysaccharides, two conditions are presupposed: (1) that substantially all of the primary alcohol groups are tosylated and (2) that the replacement occurs only at the primary position. Complete tosylation of the polysaccharide would automatically satisfy the first condition, but this often leads to dark-colored degraded products containing some nitrogen and chlorine. Purves and co-workers[16] have measured the relative rates of tosylation in the unsubstituted positions of cellulose acetate and ethyl cellulose and found them to be in the ratios, respectively, of 2.2:0.11:23 and 2.3:0.07:15 for the 2,3 and 6 hydroxyls. Other polysaccharides may not have such a favorable ratio for attaining complete esterification of the primary alcohol groups. On the other hand, lima bean pod hemicellulose tosylate appeared to undergo iodination and the corncob hemicellulose tosylate apparently underwent both iodination and thiocyanation in secondary positions. Malm, *et al.*,[5] have reported that in the tosylation and subsequent iodination of cellulose acetate or regenerated cellulose, the amount of iodine introduced increased when the time of reaction in either the tosylation or the iodination step was extended. These discrepancies would be particularly significant in assigning structures to polysaccharides with a low primary hydroxyl content and would restrict the utility of the reactions to very crude approximations of primary hydroxyl content.

Acknowledgment.—The authors wish to thank L. M. White and A. Bevenue for the determinations of nitrogen and sulfur.

Experimental

Polysaccharides

Potato Starch.—A commercial sample was used without purification.

Cellulose samples used were Dupont Cellophane and Brown Co. "Solka Floc," a purified wood pulp in a finely divided form. The latter had a xylan content of 2.5%.

Lima Bean Pod Hemicellulose.—The pods from lima beans of normal canning maturity were extracted successively with benzene–ethanol (2:1), boiling water and boiling 0.5% ammonium oxalate. The material was delignified by the sodium chlorite procedure of Wise, *et al.*,[17] and the holocellulose extracted successively with boiling water, 2% sodium carbonate, and 5% potassium hydroxide at room temperature for one hour under nitrogen. The hemicellulose isolated from the potassium hydroxide extraction was re-dissolved in alkali and precipitated with copper sulfate according to the directions of Angell and Norris.[18]

Anal. Uronic anhydride, 9.0%; xylan, 72%; methoxyl, 1.4%; and $[\alpha]^{20}\mathrm{D}$ −45.3 (*c*, 1.28 in 2% potassium hydroxide).[19]

Corn-cob Hemicellulose.—This material was prepared in the same manner as the lima bean pod hemicellulose. *Anal.* Uronic anhydride, 6.2%; xylan, 89.3%; methoxyl, 0.7%; and $[\alpha]^{20}\mathrm{D}$ −98.2 (*c*, 0.917 in 2% potassium hydroxide).[19]

Guar Mannogalactan.—The water-soluble fraction was isolated from guar flour (*Cyamopsis tetragonoloba* Taub) obtained from General Mills, Inc. An aqueous dispersion of the flour was first digested with trypsin to remove proteins, then centrifuged, and the extract was clarified by filtration. The polysaccharide was isolated as a white fibrous precipitate when the filtrate (after concentration *in vacuo* to a 0.4% solution) was poured into two and one-half volumes of ethanol. It was purified by washing with 70% ethanol–1% hydrochloric acid, neutral 70% ethanol, 95% ethanol and acetone. *Anal.* Nitrogen, 0.07%; anhydromannose, 59%[20]; anhydrogalactose, 32%; uronic anhydride, 3.5%; pentosan <1%; and $[\alpha]^{20}\mathrm{D}$ +61° (*c*, 0.57 in water).[19]

Tosylation

Potato starch, guar mannogalactan, and the hemicelluloses were pretreated by pasting with boiling water, coagulating with pyridine, and removing the water by washing with pyridine to obtain the polysaccharide in a reactive form. The wood-pulp and the Cellophane were steeped in 25 to 30 parts of 5% sodium hydroxide for one hour at 20°, and were then washed with water until free of alkali and the water was replaced by pyridine.

Esterification was performed in a mixture of pyridine and *p*-toluenesulfonyl chloride, the latter in an excess of four to five times the calculated quantity. Tosylation was allowed to proceed at 20–23° (after initial cooling of the reaction mixture) for periods of time varying from two days to three weeks. The esters were isolated and purified in the usual manner. Under these conditions, starch and guar polysaccharide could be tosylated to a degree of 1.7 to 2.0 tosyl groups per repeating unit in forty-eight

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[15] Hampton, Haworth and Hirst, *J. Chem. Soc.*, 1739 (1929); Haworth and Percival, *ibid.*, 2850 (1931); Haworth, Hirst and Oliver, *ibid.*, 1917 (1934); Bywater, Haworth, Hirst and Peat, *ibid.*, 1983 (1937).

[16] Mahoney and Purves, THIS JOURNAL, **64**, 9 (1942); Gardner and Purves, *ibid.*, **64**, 1539 (1942).

[17] Wise, Murphy and D'Addieco, *Paper Trade Journal*, **122** [2], 35 (1946).

[18] Angell and Norris, *Biochem. J.*, **30**, 2155 (1936).

[19] Specific rotations were determined by measuring the rotations in 2 dm. tubes with the D line of sodium at 20°.

[20] Mannose was estimated by a modification of Bertrand's method, and galactose was estimated by the differential fermentation procedure of Wise and Appling (*Ind. Eng. Chem., Anal. Ed.*, **16**, 28 (1944)).

hours on a shaking machine. Cellulose samples required from four to five days at 20° with shaking for the same degree of esterification; the hemicelluloses reacted very slowly, a high degree of tosylation requiring from two to three weeks. The esters had nitrogen contents of 0.05% or less.

Thiocyanation and Iodination

Replacement of tosyloxy by thiocyanate was effected by heating a mixture of 2 g. of tosyl ester, 200 ml. of freshly distilled acetonyl acetone, and 6 g. of sodium thiocyanate (dried *in vacuo* at 100°) under anhydrous conditions at 110–112° for periods of time as indicated in Table I. Low values for nitrogen were usually obtained unless the reaction mixture was heated for at least five hours.

The starch and mannogalactan tosylates were almost completely soluble in the hot reaction medium, the cellulose tosylates were partly soluble and the hemicellulose esters swelled without appreciable solution. The thiocyanotosylates were recovered in quantitative yields by pouring into four volumes of ice water. The esters were washed repeatedly with distilled water, 95% ethanol, and finally with ether. For analyses, they were dried *in vacuo* at 70° over phosphorus pentoxide. The thiocyano derivatives when dried were powdery materials, white to a light grey in color. Their solubility behavior was very similar to that of the corresponding iodo compounds.

Iodination was performed under conditions comparable to the thiocyanation procedure. Five grams of sodium iodide was used for each gram of tosyl ester and 100 ml. of acetonyl acetone. No apparent difference was noted in iodination at 100 and 110°, although thiocyanation at the lower temperature was, in some cases, slightly slower than at 110°.

Summary

The replacement of tosyloxy in the primary position by thiocyanate has been found to be applicable to several polysaccharide tosyl esters. When applied to potato starch, cellulose, and guar mannogalactan, the reaction had approximately the same degree of specificity for replacement of the tosyloxy group in the primary position as the iodination reaction.

Both thiocyanation and iodination of the tosylate of the water-soluble polysaccharide of guar indicate that approximately half of the primary hydroxyl groups are involved in linkages.

Thiocyanation and iodination of a corn-cob hemicellulose tosyl ester and iodination of a lima bean pod hemicellulose tosylate yielded substitution to a greater extent than was expected, from the structure of these materials, indicating that possibly some secondary tosyloxy groups were replaced.

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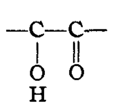
Oxidation Processes. XXI.[1] The Autoxidation of the *p*-Phenylenediamines

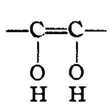
BY JAMES E. LUVALLE, DUDLEY B. GLASS AND ARNOLD WEISSBERGER

Introduction

Previous papers of this series discussed the autoxidation of α-ketols, I,[2] enediols, II,[3] hydroquinones, III,[4] and α-aminoketones, IV.[5] The present paper deals with the autoxidation of *p*-phenylenediamines, VI, and, briefly, of *p*-aminophenols, V.



I



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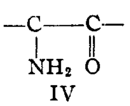
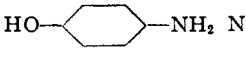


IV



V

VI

Like the dihydroxy compounds, these substances react with molecular oxygen, and the reaction proceeds in two univalent steps.[6] From the results of earlier papers of this series,[3,4,5] the rate of the over-all reactions can be expected to depend upon the rate of formation of the semiquinone, upon its concentration in the various equilibria involved, and upon its reactivity with oxygen.

$$R + O_2 \longrightarrow T + H_2O_2 \qquad (1)$$

The intensely colored intermediate products of *p*-phenylenediamines, *Wurster's salts*, exist as free radicals, semiquinones, in dilute solution,[6] and as dimers or higher polymers in higher concentration.[6c] These semiquinones are much more stable than the corresponding fully oxidized quinonediimines,[6b,7] and quinoneimines[7] which are readily hydrolyzed to the corresponding quinones. Moreover, the higher N-methylated diamines undergo a demethylation reaction when oxidized. Thus, N,N'-tetramethyl-*p*-phenylenediimine loses a methyl group with formation of N,N'-trimethyl-*p*-phenylenediamine and formaldehyde,[6,7] and N,N'-tetramethyl-, N,N'-trimethyl-, and N-dimethyl-*p*-phenylenediamine couple in oxidizing solutions with a *p*-substituted phenol to give an identical indoaniline dye.[8] The latter reaction shows that the trimethyl-*p*-phenylenedi-

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[1] XX. LuValle and Weissberger, THIS JOURNAL, **69**, 1821 (1947).

[2] (a) Weissberger, Mainz and Strasser, *Ber.*, **62**, 1942 (1929); (b) Weissberger and Bach, *J. Chem. Soc.*, 226 (1935).

[3] Weissberger and LuValle, THIS JOURNAL, **66**, 700 (1944).

[4] (a) James and Weissberger, *ibid.*, **60**, 98 (1938); (b) James, Snell and Weissberger, *ibid.*, **60**, 2084 (1938); (c) LuValle and Weissberger, Part XIX, *ibid.*, **69**, 1576 (1947).

[5] James and Weissberger, *ibid.*, **59**, 2040 (1937).

[6] (a) Michaelis and Hill, *ibid.*, **55**, 1487 (1933); (b) Michaelis, Schubert and Granick, *ibid.*, **61**, 1981 (1939); (c) Michaelis and Granick, *ibid.*, **65**, 1747 (1943).

[7] (a) Willstätter and Meyer, *Ber.*, **37**, 1494 (1904); (b) Willstätter and Pfannenstiel, *ibid.*, **37**, 4605 (1904); (c) Willstätter and Kubli, *ibid.*, **42**, 4135 (1909).

[8] W. R. Ruby. of these Laboratories. private communication.