

663. *The Scope and Mechanism of Carbohydrate Osotriazole Formation. Part VIII.*¹ *Azo-dyes from Aminophenylosotriazoles.*

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Aminophenylosotriazoles, obtained by nitration and reduction of monosaccharide phenylosotriazoles, have been converted into azo-dyes that react with cellulose treated with cyanuric chloride.

It was expected^{1,2} that aminophenylosotriazoles, when converted into dyes, would acquire affinity towards cellulose owing to their sugar residues. We have now prepared some azo-dyes from aminophenylosotriazoles and as expected they possessed considerably more affinity towards cellulose than the corresponding aniline dyes. More important is that they react with cellulose fibres treated with cyanuric chloride. The chloride reacts with the hydroxyl groups of both the cellulose and the sugar osotriazole dye, and leads to quite fast colours. It is thus possible to confer the stability on reactive dyes while avoiding their delicate isolation.

The aminophenylosotriazoles needed were prepared by reducing the nitro-derivatives,

¹ Part VII, *J.*, 1962, 3154.

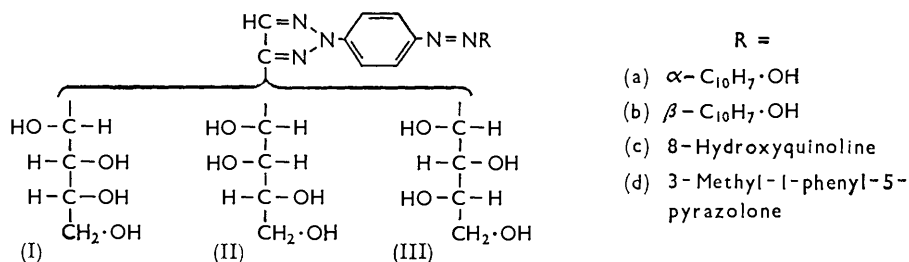
² El Khadem and Meshreki, *Nature*, 1962, **194**, 373.

which were obtained by nitrating phenylosotriazole acetates. As with the glucose derivatives previously investigated,¹ nitration took place in the 4-position when this was free; otherwise, the nitro-group entered the 3-position. For example, glucose *m*-fluorophenylosotriazole tetra-acetate, on nitration and hydrolysis, yielded the 3-fluoro-4-nitrophenylosotriazole, and the *p*-fluoro-derivative yielded the 4-fluoro-3-nitrophenylosotriazole. D-Galactose, L-sorbose, D-xylose, L-arabinose, and L-rhamnose phenylosotriazole acetates yielded the *p*-nitrophenylosotriazoles. The position of the nitro-group was determined by oxidation with periodic acid to 4-formyl-*p*-nitrophenyl-1,2,3-triazole³ or with potassium permanganate to 2-*p*-nitrophenyl-1,2,3-triazole-4-carboxylic acid.^{1,3} Maltose phenylosotriazole hepta-acetate, on nitration and hydrolysis, lost water and afforded an anhydromaltose nitrophenylosotriazole (at present under study).

Reduction was carried out catalytically on the nitrophenylosotriazole acetates. D-Galactose and L-sorbose *p*-nitrophenylosotriazole tetra-acetates yielded the corresponding *p*-aminophenylosotriazole tetra-acetates. The L-arabinose and L-rhamnose derivatives could not be obtained crystalline, but the latter was converted into its *N*-acetyl derivative.

Azo-dyes were prepared from the *p*-aminophenylosotriazoles and their acetates. In the latter case, care was taken to remove the dye immediately after coupling, to avoid hydrolysis. Thus, azo-dye (Ia) and its acetate were prepared by diazotising D-glucose *p*-aminophenylosotriazole and its tetra-acetate and coupling it with α -naphthol. Seven other dyes, shown in Table 4, were similarly prepared.

The spectra of the dyes in the visible and the ultraviolet region are shifted towards higher wavelength with rise of pH.



EXPERIMENTAL

Absorption spectra were determined for ethanolic solutions with a Unicam S.P. 500 spectrophotometer.

Sugar p-Nitrophenylosotriazoles.—The following experiment is typical. To a stirred, cooled solution of the osotriazole acetate (20 g.) in glacial acetic acid (40 ml.) and sulphuric acid (*d* 1.84) (40 ml.), nitric acid (*d* 1.52) (12 ml.) was added dropwise during 1 hr., the temperature being kept below 20°. After a further hour's stirring, the mixture was poured on ice and extracted with chloroform, and the chloroform layer washed, dried, and evaporated. The D-galactose and L-sorbose *p*-nitrophenylosotriazole tetra-acetate separated at this stage and were crystallised from dilute ethanol. The nitro-acetate was then hydrolysed by boiling 10% alcoholic sodium hydroxide (150 ml.) for 15 min. or by methanolic ammonia (200 ml.) at room temperature for 24 hr. The *nitrophenylosotriazoles* which separated recrystallised from dilute ethanol (see Table 1); they were soluble in boiling ethanol or methanol, and insoluble in ether and water.

Sugar p-Nitrophenylosotriazole Acetates.—A solution of the osotriazole (2 g.) in dry pyridine (30 ml.) was treated with acetic anhydride (30 ml.) and left for 24 hr. at room temperature, then poured on ice and extracted with ether. The ether layer was washed, dried, and evaporated. The *products* (see Table 2) crystallised from dilute ethanol and were soluble in cold ethanol, methanol, and ether, and insoluble in water.

³ Bishop, *Science*, 1953, **117**, 715.

TABLE I.
Sugar *p*-nitrophenylosotriazoles.

Starting phenylosotriazole acetate	Subst. of aryl in product	M. p.	Yield (%)	Found (%)			Formula	Required (%)		
				C	H	N		C	H	N
D-Xylose ⁴	<i>p</i> -NO ₂	166°	45	47.8	4.6	19.8	C ₁₁ H ₁₂ N ₄ O ₅	47.2	4.4	20.0
L-Rhamnose ⁵	<i>p</i> -NO ₂	190	50	49.5	4.7	18.9	C ₁₂ H ₁₄ N ₄ O ₅	49.0	4.8	19.0
D-Glucose <i>m</i> -F ⁶	4-NO ₂ -3-F	222	30	44.2	4.4	—	C ₁₂ H ₁₃ FN ₄ O ₆	43.9	4.0	—
D-Glucose <i>p</i> -F ⁶	3-NO ₂ -4-F	172	36	44.3	4.3	17.1	C ₁₂ H ₁₃ FN ₄ O ₆	43.9	4.0	17.1
D-Galactose ⁴	<i>p</i> -NO ₂	238	56	46.7	4.7	18.1	C ₁₂ H ₁₄ N ₄ O ₆	46.5	4.5	18.1
L-Sorbose ⁴	<i>p</i> -NO ₂	236	42	46.9	4.7	18.2	C ₁₂ H ₁₄ N ₄ O ₆	46.5	4.5	18.1
Maltose ⁷	<i>p</i> -NO ₂	190	20	48.0	5.0	12.7	C ₁₈ H ₂₂ N ₄ O ₁₀	47.6	4.9	12.3

TABLE 2.
Sugar substituted phenylosotriazole acetates.

Sugar	Subst. in Ph	M. p.	Yield (%)	Found (%)			Formula	Required (%)		
				C	H	N		C	H	N
L-Arabinose	<i>p</i> -NO ₂	124°	40	49.9	4.4	14.1	C ₁₇ H ₁₈ N ₄ O ₈	50.2	4.4	13.8
L-Rhamnose	<i>p</i> -NO ₂	174	72	51.2	4.8	13.1	C ₁₈ H ₂₀ N ₄ O ₈	51.4	4.8	13.3
L-Rhamnose	<i>p</i> -NHAc	140	80	55.4	5.6	13.2	C ₂₀ H ₂₄ N ₄ O ₇	55.6	5.6	13.0
D-Galactose	<i>p</i> -NO ₂	168	64	50.1	4.5	11.6	C ₂₀ H ₂₂ N ₄ O ₁₀	50.2	4.6	11.7
D-Galactose	<i>p</i> -NHAc	154	85	54.0	5.6	11.5	C ₂₂ H ₂₆ N ₄ O ₉	53.9	5.3	11.4
L-Sorbose	<i>p</i> -NO ₂	148	68	50.3	4.7	11.7	C ₂₀ H ₂₂ N ₄ O ₁₀	50.2	4.6	11.7
Anhydromaltose	<i>p</i> -NO ₂	165	25	51.2	4.4	8.6	C ₂₈ H ₃₂ N ₄ O ₁₀	50.6	4.8	8.4

Monosaccharide p-Aminophenylosotriazole Tetra-acetates.—The monosaccharide *p*-nitrophenylosotriazole tetra-acetate (5 g.) in ethanol (150 ml.) was hydrogenated⁸ at 1 atm. over palladium-barium sulphate⁹ (2 g.) within 4 hr.; 600 ml. of hydrogen were absorbed. The mixture was filtered and concentrated. The *monosaccharide p-aminophenylosotriazole tetra-acetate* separated (see Table 3) and crystallised from dilute ethanol, the solubility being as for the other acetates.

TABLE 3.
Monosaccharide *p*-aminophenylosotriazole tetra-acetates.

Monosaccharide	M. p.	Yield (%)	Found (%)			Formula	Required (%)		
			C	H	N		C	H	N
D-Galactose	108°	46	53.6	5.7	12.6	C ₂₀ H ₂₄ N ₄ O ₈	53.6	5.4	12.5
L-Sorbose	125	35	—	—	12.4	C ₂₀ H ₂₄ N ₄ O ₈	—	—	12.5

TABLE 4.
Azo-dyes.

Dye	Sugar in <i>p</i> -amino-phenylosotriazole	Phenol coupled	M. p.	Yield (%)	Found (%)			Formula	Required (%)		
					C	H	N		C	H	N
Ia	D-Glucose	α -Naphthol	253°	50	60.2	5.2	—	C ₂₂ H ₂₁ N ₅ O ₅	60.7	4.8	—
	D-Glucose acetate	α -Naphthol	195	40	59.6	4.6	12.1	C ₃₀ H ₂₉ N ₅ O ₉	59.7	4.8	11.6
Ib	D-Glucose	β -Naphthol	255	70	60.4	5.0	—	C ₂₂ H ₂₁ N ₅ O ₅	60.7	4.8	—
	D-Glucose acetate	β -Naphthol	180	42	59.1	4.9	11.7	C ₃₀ H ₂₉ N ₅ O ₉	59.7	4.8	11.6
IIb	D-Galactose	β -Naphthol	208	65	60.8	5.2	16.0	C ₂₂ H ₂₁ N ₅ O ₅	60.7	4.8	16.1
	D-Galactose acetate	β -Naphthol	170	55	59.4	5.1	12.0	C ₃₀ H ₂₉ N ₅ O ₉	59.7	4.8	11.6
IIIb	L-Sorbose	β -Naphthol	250	75	60.6	5.1	16.0	C ₂₂ H ₂₁ N ₅ O ₅	60.7	4.8	16.1
Ic	D-Glucose	8-Hydroxyquinoline	235	40	57.0	4.7	18.7	C ₂₁ H ₂₀ N ₆ O ₅ · $\frac{1}{2}$ H ₂ O	56.6	4.7	18.9
Id	D-Glucose acetate	3-Methyl-1-phenyl-5-pyrazolone	173	35	56.5	4.9	—	C ₃₀ H ₃₁ N ₇ O ₉	56.9	4.9	—

⁴ Haskins, Hann, and Hudson, *J. Amer. Chem. Soc.*, 1945, **67**, 939.⁵ Hardegger and El Khadem, *Helv. Chim. Acta*, 1947, **30**, 900; Haskins, Hann, and Hudson, *J. Amer. Chem. Soc.*, 1947, **69**, 1461.⁶ El Khadem, Kolkaila, and Meshreki, following paper.⁷ Hudson, *J. Org. Chem.*, 1944, **9**, 474.⁸ Vogel, "A Textbook of Practical Organic Chemistry," Longmans, Green, London, 1959, p. 472.⁹ *Org. Synth.*, Coll. Vol. III, p. 685.

Azo-dyes.—Hexose *p*-aminophenylosotriazoles or their tetra-acetates (0.2 g.) were diazotised at 0° and coupled with the calculated amount of the phenolic compound dissolved in 5% aqueous sodium hydroxide. The sodium salt of the dye was filtered off, washed with distilled water and ethanol, dried, and purified by repeated crystallisation from hot ethanol containing a few drops of glacial acetic acid to liberate the free *azo-dye* (see Table 4). They were all extremely difficultly soluble in water and organic solvents.

Absorption Spectra.—These are recorded in Table 5.

TABLE 5.
Ultraviolet spectra.

Dye	In 0.01N-ethanolic NaOH				In ethanol				In 0.01N-ethanolic HCl			
	λ_{\max} .	$\log \epsilon$	λ_{\min} .	$\log \epsilon$	λ_{\max} .	$\log \epsilon$	λ_{\min} .	$\log \epsilon$	λ_{\max} .	$\log \epsilon$	λ_{\min} .	$\log \epsilon$
Ia	245	4.35	230—232	4.31	240	3.60	265	4.17	235—240	4.48	260—265	4.33
	—	—	265	4.16	285—290	4.23	350—353	3.88	270—280	4.35	355	4.09
	295—300	4.29	385	3.72	430	4.23	450	4.21	420—430	4.39	—	—
	520—530	4.57	—	—	—	—	—	—	—	—	—	—
Ib	230	4.47	266—270	4.16	228	4.57	255—266	4.12	225—228	4.57	255—265	4.12
	290—292	4.28	380—390	3.75	275—286	4.15	300	4.10	280—282	4.16	300	4.10
	—	—	—	—	310—315	4.14	—	—	310—315	4.14	345	3.86
	470—480	4.28	—	—	480—490	4.36	345—350	3.86	—	—	—	—
Ic	—	—	230	4.00	260	4.37	295—300	3.74	265	4.48	295	3.70
	255—260	4.24	365	3.48	395—400	4.40	—	—	380—385	4.37	—	—
	500	4.52	—	—	—	—	—	—	—	—	—	—

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