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Structural Analysis of Substituted 3-Arylazo-2-hydroxy-6-pyridones

A. Cee, B. Horáková & A. Lyčka

Research Institute of Organic Syntheses, 532 18 Pardubice-Rybitví,
Czechoslovakia

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ABSTRACT

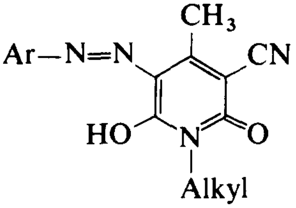
A structural analysis of substituted 3-arylazo-2-hydroxy-6-pyridones was based on the detection of the 2-hydroxy-6-pyridone coupling component by reaction of the dye with zinc and resorcinol in dilute ammonia, when a blue-coloured air oxidation product is formed. Identification of the 2-hydroxy-6-pyridone component was made using chromatographic comparison of the coloured product of the indophenol reaction with an authentic product and by fragmentation of the 2-hydroxy-6-pyridone component by the action of stannous chloride in concentrated hydrochloric acid, in conjunction with chromatographic identification of the characteristic products and also with data from IR, ^{1}H-NMR, ^{13}C-NMR and mass spectra. These techniques afforded a useful overall method for the identification of the structure of dyes of this type.

1 INTRODUCTION

There have been described a series of azo dyes using 1-alkyl-5-cyano-2-hydroxy-4-methyl-6-pyridones as coupling components.[1–3] These dyes have excellent colouration properties and give very bright greenish-yellow hues. The dyes are typified by the general formula **I** and were initially introduced for the colouration of synthetic-polymer fibres.

Further structural modifications, yielding pigments, acid dyes and reactive dyes, involved hydrolysis of the nitrile group to carboxamido or its replacement by other substituents.

The detection and confirmation of the presence of the 2-hydroxy-6-pyridone part of the dye molecule are complicated since, subsequent to



I

reductive fission of the dye, less stable compounds are formed on exposure to air. For this reason, various characteristic colour reactions of the reduction products have been used, e.g. with resorcinol, followed by air oxidation in presence of ammonia, and such colour reactions have been reviewed in the literature.[4]

We report here the applicability of similar colour reactions, in conjunction with other analytical techniques, to the identification of dyes of structure I.

2 EXPERIMENTAL

2.1 Model compounds, purification, control of identity and purity

Azo dyes prepared by coupling of diazotised aniline or sulphanilic acid with a coupling component of the 2-hydroxy-6-pyridone type were used as model compounds (Table 1).

Purification of these model dyes without solubilising groups was carried out by crystallization from acetone–water or ethanol–water mixtures. The dyes soluble in water,viz. those with sulphonic or phosphonic groups, were washed with dilute hydrochloric acid to remove inorganic salts and other impurities from the coupling reaction and were then crystallised from aqueous ethanol.

The purity of model dyes and their identity were assessed by chromatography on Silufole plates (Glasswork Kavalier, n.p. Votice), developed by the systems S_1–S_3:

S_1: 1-propanol–ammonia, 2:1;
S_2: heptane–acetone, 2:1;
S_3: benzene–acetone, 2:1.

Paper chromatography on Whatman No. 3 paper using, as eluant, systems S_4–S_7:

S_4: 1-propanol–water, 2:1;
S_5: 1-propanol–ammonia, 2:1;
S_6: 1-butanol saturated by 10% HCl (upper layer);[5]
S_7: 1-butanol–acetic acid–water, 4:1:5 (upper layer);

TABLE 1
Summary of the Model Dyes

Compound	*Diazo component*	*Coupling component*
1	Aniline-4-sulphonic acid	2-Hydroxy-4-methyl-6-pyridone
2	Aniline-4-sulphonic acid	1,4-Dimethyl-2-hydroxy-6-pyridone
3	Aniline-4-sulphonic acid	5-Cyano-2-hydroxy-4-methyl-6-pyridone
4	Aniline	5-Cyano-1,4-dimethyl-2-hydroxy-6-pyridone
5	Aniline-4-sulphonic acid	5-Carboxy-2-hydroxy-4-methyl-6-pyridone
6	Aniline-4-sulphonic acid	5-Carbamoyl-1,4-dimethyl-2-hydroxy-6-pyridone
7	2-Methyl-4-nitroaniline	5-Cyano-2-hydroxy-4-methyl-6-pyridone
8	4-Amino-4′-isopropylbenzophenone	5-Cyano-2-hydroxy-4-methyl-6-pyridone
9	3-Aminophenyl benzenesulphonate	5-Cyano-2-hydroxy-4-methyl-6-pyridone
10	2-Nitroaniline	5-Cyano-1-ethyl-2-hydroxy-4-methyl-6-pyridone
11	2-(2-Methoxyethoxy)ethyl-4-aminobenzoate	5-Cyano-1-ethyl-2-hydroxy-4-methyl-6-pyridone
12	4-(*N*,*N*-dibutyl)sulphamidoaniline	1-Butyl-5-cyano-2-hydroxy-4-methyl-6-pyridone
13	Benzyl *p*-aminobenzoate	1-Butyl-5-cyano-2-hydroxy-4-methyl-6-pyridone
14	4-Methoxy-2-nitroaniline	5-Cyano-1-(2′-ethylhexyl)-2-hydroxy-4-methyl-6-pyridone
15	1-(4,6-Dichloro-1,3,5-triazine-2-yl)amino-3′-amino-4′,6′-benzenedisulphonic acid	5-Carbamoyl-1-ethyl-2-hydroxy-4-methyl-6-pyridone
16	3-Sulpho-4-aminobenzene-1,1′-azobenzene-3′-phosphonic acid	5-Carbamoyl-1-(1′-ethylene-4′-sulphobenzene)-2-hydroxy-4-methyl-6-pyridone
17	Aniline	1-Ethyl-2-hydroxy-4-methyl-5-sulphomethano-6-pyridone

which was used to identify the products of the colour reactions and also the products of fission.

Further, chromatography on Silufole was employed, using as mobile phase

S_8: 1-propanol–water, 2:1.

The following processes were used for the detection of the chromatographic spots:

D_1: ninhydrin (0·2 g) dissolved in 100 ml ethanol and 1 ml pyridine;
D_2: Ehrlich agent (1 g *p*-dimethylaminobenzaldehyde dissolved in 100 ml ethanol and 5 ml HCl);
D_3: diazotisation in the vapour phase and coupling with R-salt (1 g sodium 2-naphthol-3,6-disulphonate dissolved in 100 ml 5% solution of sodium carbonate).

2.2 Detection of the 2-hydroxy-6-pyridone components in azo dyes using colour reactions

2.2.1 Water-soluble dyes

Dye (10 mg) was dissolved in 1 ml of dilute ammonia (1:1) and 1 g of powdered zinc and 50 mg of resorcinol were then added. After decolourisation, a spot of the reaction liquor was applied to filter paper and subjected to air oxidation.

2.2.2 Water-insoluble dyes

Dye (10 mg) was dissolved in 1 ml of dimethylformamide; several drops of dilute ammonia were added and then 1 g of powdered zinc and 50 mg of resorcinol. After decolourisation, a drop of the reaction liquor was applied to filter paper and subjected to air oxidation. The characteristic blue-coloured air oxidation product was formed after several seconds.

2.3 Identification of the 2-hydroxy-6-pyridone component

(a) Identification of the coloured product in the reaction mixture was carried out by comparison with the standard by paper chromatography using the S_4 system.

(b) Identification of the characteristic products from the chemical splitting was carried out using the following procedure.

A 50 mg sample of dye was heated in a sealed tube for 30 min at 180°C with 1 ml of a solution of stannous chloride (40 g $SnCl_2 . 2\,H_2O$ dissolved in

140 ml conc. HCl). Fission products were identified chromatographically using systems S_5, S_6 and S_7 and by the reagents D_1–D_3.

The resulting amino acid was also identified by formation of a derivative: viz., the solution after fission by stannous chloride was neutralised with solid KOH and after addition of 5 ml water containing 0·5 g $NaHCO_3$, a solution of 0·25 ml 2,4-dinitrofluorobenzene in 3 ml ethanol was added. After stirring for 30 min, the 2,4-dinitrophenyl derivative was extracted with ether and identified by mass spectrometry. The preparation of the standards for the identification of the coloured reaction products was carried out using 1-alkyl-5-cyano-2-hydroxy-4-methyl-6-pyridone according to the literature and the resultant 3-amino derivative converted by reaction with resorcinol to the indophenol. The sample of 5-cyano-1,4-dimethyl-2-hydroxy-6-pyridone was prepared by Ing. F. Vyskočil, C.Sc., at the Organic Technology Laboratory of the Research Institute of Organic Syntheses.

2.4 Spectral measurements

The measurement of the model compounds in the IR region was carried out on a Perkin–Elmer 621 using suspensions in nujol.

^1H- and ^{13}C-NMR spectra were measured by standard methods on a JNM-FX 100 (JEOL) at 99·602 or 25·047 MHz, respectively, in pulse mode with Fourier transformation. The spectra were measured in deuterium chloride or deuterium oxide. Chemical shifts are given on the δ scale.

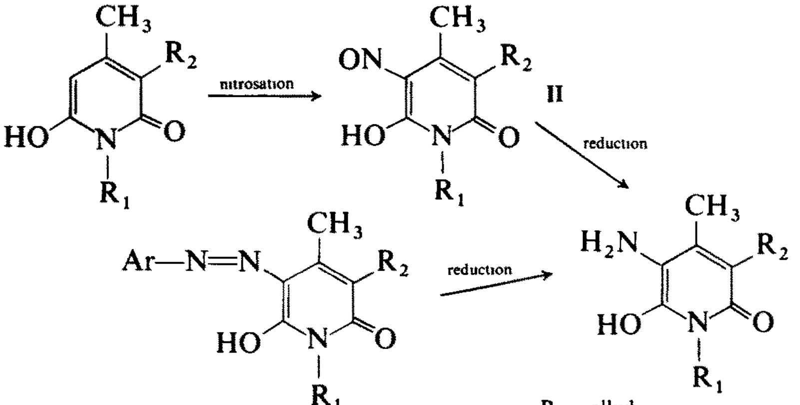
The mass spectra of dyes without solubilising groups were recorded on a JMS-01 SG-Z (JEOL).

3 RESULTS AND DISCUSSION

3.1 Detection and identification of the 2-hydroxy-6-pyridone coupling components by the indophenol reaction

The reduction of the azo dyes with powdered zinc in aqueous ammonia in presence of resorcinol gives a reaction mixture which gives a blue colouration on air oxidation on paper. The blue colouration is characteristic and sufficiently stable for this configuration and was formed by all the model compounds of the hydroxypyridone type.[6]

This colour reaction is analogous to that observed with pyrazolone dyes, which under the same conditions give an indophenol reaction with the colour of the oxidation product being red to violet.[7] The blue product (**IV**) is also formed from the corresponding 3-aminopyridone (**III**), which is itself obtained from the nitroso derivative (**II**).[8]

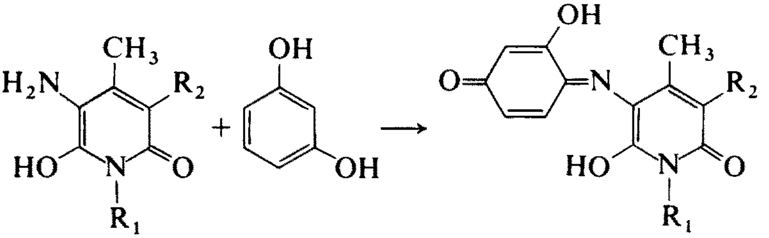


II

III

R_1 = alkyl
R_2 = —H, —CN, —CO·NH$_2$, —COOH

The reaction with resorcinol proceeds according to the following scheme.



IV

The identity of the products was compared by paper chromatography using the S_4 solvent system and the results are shown in Table 2, from which it is apparent that the method is convenient for the identification of the hydroxypyridone component in that the hue of colouration is influenced by the substituent in the 5-position in the following way:

—CN	Violet blue
—CO.NH$_2$	Dark blue
—CH$_2$.SO$_3$H	Light blue

and that the substitution on the hetero nitrogen atom influences the R_f value.

3.2 Splitting of the pyridone ring and identification of fragments

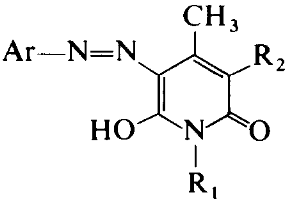
Whilst the reagents used for the azo dye degradation above cause the azo dye molecules to degrade to amines, under other conditions the decomposition proceeds even further, so that the pyridone part of the coupling component also degrades. In the resultant complex reaction mixture can be found characteristic fragments, the formation of which can contribute to the clarification of the structure of this part of the dye molecule. Heating in

TABLE 2

Paper Chromatography of the Colouration Products (System S_4)

Model Compound	*Coupling component of the model compound*	R_f	*Coloration of the spot*
1	2-Hydroxy-4-methyl-6-pyridone	0·32	Blue–violet
2	2-Hydroxy-1,4-dimethyl-6-pyridone	0·35	Blue–violet
4	5-Cyano-1,4-dimethyl-2-hydroxy-6-pyridone	0·49	Blue–violet
5	5-Carboxy-2-hydroxy-4-methyl-6-pyridone	0·50	Blue–violet
6	5-Carbamoyl-1,4-dimethyl-2-hydroxy-6-pyridone	0·39	Dark blue
10	5-Cyano-1-ethyl-2-hydroxy-4-methyl-6-pyridone	0·67	Blue–violet
12	1-Butyl-5-cyano-2-hydroxy-4-methyl-6-pyridone	0·88	Blue–violet
14	5-Cyano-1-(2′-ethylhexyl)-2-hydroxy-4-methyl-6-pyridone	0·90	Blue–violet
15	5-Carbamoyl-1-ethyl-2-hydroxy-4-methyl-6-pyridone	0·58	Dark blue
16	5-Carbamoyl-1-(1′-ethylene-4′-sulphobenzene)-2-hydroxy-4-methyl-6-pyridone	0·35	Dark blue
17	1-Ethyl-2-hydroxy-4-methyl-5-sulphomethano-6-pyridone	0·23	Light blue

stannous chloride in hydrochoric acid at 180°C for 30 min[9] proved to be a satisfactory technique for this hydrolytic fission.



V

$R_1 = \text{—alkyl}$
$R_2 = \text{—H, —COOH, —CO·NH}_2\text{, —CN}$

The following fragments were formed from azo dye molecules of the type V: aromatic amine, aliphatic amine and 2-amino-3-methylglutaric acid (Table 3).

The aromatic amines were identified by paper chromatography using system S_6 and reagents D_2 and D_3. Aliphatic amines were identified using systems S_6 and S_7 in the same way and 2-amino-3-methylglutaric acid using systems S_5, S_6 and S_7. The solution of ninhydrin in ethanol (D_1), giving red–violet spots after heating the chromatogram, was used for the detection of characteristic products.

2-Amino-3-methylglutaric acid was identified after conversion to the 2,4-dinitrophenyl derivative by reaction with Sanger reagent.[10] The mass

TABLE 3

Model compound	*Coupling component of model dye*	*Aliphatic amine*	*Amino acid*
1	2-Hydroxy-4-methyl-6-pyridone	—	2-Amino-3-methylglutaric acid
2	1,4-Dimethyl-2-hydroxy-6-pyridone	Methylamine	2-Amino-3-methylglutaric acid
3	5-Cyano-2-hydroxy-4-methyl-6-pyridone	—	2-Amino-3-methylglutaric acid
4	5-Cyano-1,4-dimethyl-2-hydroxy-6-pyridone	Methylamine	2-Amino-3-methylglutaric acid
5	5-Carboxy-2-hydroxy-4-methyl-6-pyridone	—	2-Amino-3-methylglutaric acid
6	5-Carbamoyl-1,4-dimethyl-2-hydroxy-6-pyridone	Methylamine	2-Amino-3-methylglutaric acid
10	5-Cyano-1-ethyl-2-hydroxy-4-methyl-6-pyridone	Ethylamine	2-Amino-3-methylglutaric acid
12	1-Butyl-5-cyano-2-hydroxy-4-methyl-6-pyridone	Butylamine	2-Amino-3-methylglutaric acid
14	5-Cyano-1-(2′-ethylhexyl)-2-hydroxy-4-methyl-6-pyridone	2-Ethylhexylamine	2-Amino-3-methylglutaric acid
16	5-Carbamoyl-1-(1′-ethylene-4′-sulphobenzene)-2-hydroxy-4-methyl-6-pyridone	2-Amino-1-(4′-sulphobenzene-1)-ethane	2-Amino-3-methylglutaric acid
17	1-Ethyl-2-hydroxy-4-methyl-5-sulphomethano-6-pyridone	Ethylamine	Unidentified product

TABLE 4
Wavenumbers (cm^{-1}) of Valence Vibration Bands

Model compound	ν_{-C-O}	$\nu_{-C\equiv N}$	ν_{-NH-}
7	1655 1688	2228	3385
10	1644 1688	2230	
13	1627 1678	2228	
14	1629 1678	2228	

spectrum of the purified derivative showed *m/e* 327, and on the basis of identical fragmentation and relative intensities in the spectrum compared with that of an authentic sample, the presence of 2-amino-3-methylglutaric acid was confirmed.

3.3 Spectroscopy methods

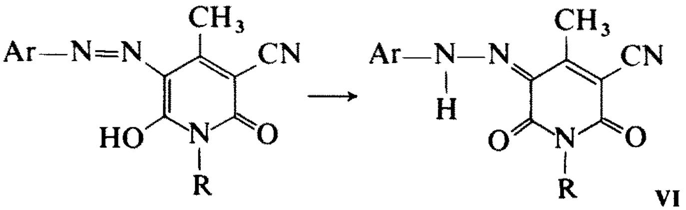
3.3.1 IR spectroscopy

The IR spectra of the model compounds without sulphonic groups were measured in nujol and the results are shown in Table 4.

It is clear from the results that the hydroxypyridone part of the molecule shows two characteristic vibrations, viz. the carbonyl group within the region $\nu_{-C\ O}$ 1627–1655 cm^{-1} and the nitrile groups on the hydroxypyridone configuration $\nu_{-C\equiv N}$ 2228–2230 cm^{-1}.

Where the heterocyclic nitrogen atom is not substituted, the vibration of the imino group appears in the spectrum at ν_{-NH-} 3385–3388 cm^{-1}.

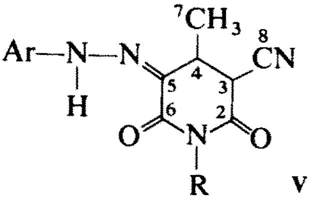
Shift of the equilibrium to pyridine-2,6-dione configuration (**VI**) can be concluded on the basis of the two carbonyl vibrations that appear in all the spectra of the model dyes in nujol.



VI

3.3.2 NMR spectroscopy

Interpretation of the ^1H- and ^{13}C-NMR spectra ($CDCl_3$, 330 K) of model compounds of type **VII** is given in Table 5.



VII

It can be argued that the nucleus of the hydroxypyridone coupling component gives a characteristic spectrum. The ^{1}H-NMR spectrum shows a characteristic singlet for the CH_3 group at the 4-position, and the spectrum also clearly shows that this component does not occur in the 2-hydroxypyridone configuration, but as the pyridine-2,6-dione one. This confirms the results of the IR spectra. The model dyes exist in the hydrazo form, with a characteristic wide singlet for the —NH-hydrogen bond.

3.3.3 Mass spectroscopy

The elemental composition of the compounds and of the characteristic ions arising from the 2-hydroxy-6-pyridone type of compounds were derived using high-resolution mass measurement and results are shown in Table 6.

Dyes of the pyridone type show molecular ions the relative intensity of which depends on the nature of substituents, on the size of molecule and on the general structure of the compounds. The molecular ion undergoes fragmentation partly by elimination of characteristic groups (alkyl, halogen, nitro, etc.) and by the formation of fragments typical for the diazo and coupling residues. The coupling component shows characteristic fragmentation. From the results obtained with the model compounds used, it is

TABLE 5

Chemical Shifts from ^{1}H- and ^{13}C-NMR

	Dye 4	*Dye 8*	*Dye 14*	*Dye 1*	*Dye 13*	*Dye 16*
Hδ(^{1}H)						
CH_3	2·62	2·56	2·62	2·50	2·62	2·22
NH	15·0	12·9	15·9	15·0	15·0	—
Cδ(^{13}C)						
2[a]	161·8	161·3	160·7			
3	101·5	102·2	104·1			
4	158·5	160·2	157·9			
5	122·8	124·9	125·5			
6[a]	160·1	160·6	160·0			
7	16·5	16·6	16·7			
8	114·3	114·8	113·9			

[a] Assignation can be to the opposite C atom.

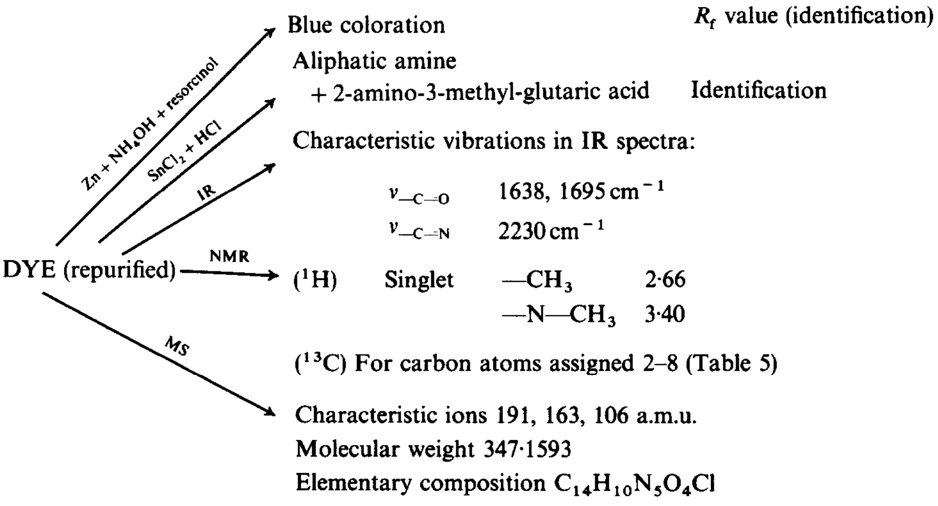
TABLE 6
Mass Spectra Data for Some 2-Hydroxy-6-pyridone Dyes

Model compound	*Mol wt*	*Elemental composition*	*Characteristic ions m/z*
7	313·0820	$C_{14}H_{11}N_5O_4$	177, 149, 106
8	400·1505	$C_{23}H_{20}N_4O_3$	—
10	424·0842	$C_{20}H_{16}N_4O_5S$	191, 163, 106
11	327·0982	$C_{15}H_{13}N_5O_4$	177, 149, 106
13	501·2419	$C_{25}H_{35}N_5O_4S$	177, 149, 106
14	144·1839	$C_{25}H_{24}N_4O_4$	177, 149, 106

evident that there are two routes leading to the same fragment. The relative intensity of individual ions depends on a number of factors and it cannot be estimated in advance. Where the characteristic fragments shown in Table 6 are observed in the spectrum, the hydroxypyridone component can be assumed to be present, although the absence of such fragments in the spectrum does not preclude the possibility of such a structure.

4 CONCLUSION

Application of the above analytical techniques for the identification of coupling components of the hydroxypyridone type is illustrated with respect to the analysis of the yellow dye 2-chloro-4-nitroaniline → 1-methyl-3-cyano-4-methyl-2-hydroxy-6-pyridone as a typical model for dyes of this



Blue coloration — R_f value (identification)
Aliphatic amine + 2-amino-3-methyl-glutaric acid — Identification

Characteristic vibrations in IR spectra:

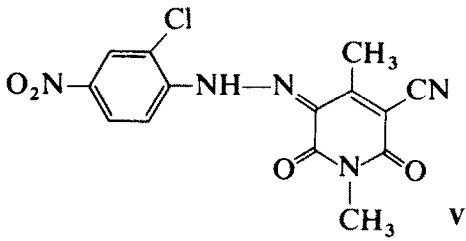
$\nu_{\text{—C=O}}$	1638, 1695 cm^{-1}
$\nu_{\text{—C}\equiv\text{N}}$	2230 cm^{-1}

(^1H)	Singlet	$—CH_3$	2·66
		$—N—CH_3$	3·40

(^{13}C) For carbon atoms assigned 2–8 (Table 5)

Characteristic ions 191, 163, 106 a.m.u.
Molecular weight 347·1593
Elementary composition $C_{14}H_{10}N_5O_4Cl$

Fig. 1.



VIII

series. The dye (**VIII**) was synthesised by procedures described in the relevant patent literature.[11-15] The crude dye was purified by acetone extraction and recrystallisation from aqueous ethanol. Application of the analysis methods described above are a satisfactory structural elucidation: thus, the diazo component was identified by reduction, thermal dissociation and thin-layer chromatography as 2-chloro-4-nitroaniline.

Identification of the coupling component was made according to the data set out in Fig. 1.

The overall conclusion from the individual results shown above is that the coupling component is of the 2-hydroxy-6-pyridone type with substitution in positions 1 and 4 by methyl groups, in position 3 by a nitrile group and in position 5 by the azo group. The dye exists in the hydrazone form.These results are fully in accord with the dye structure **VIII** and thus show that the techniques described in this study are satisfactory and enable the structural determination of azo dyes of the hydroxypyridone type to be readily carried out.

ACKNOWLEDGEMENTS

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