Dyes and Pigments 21 (1993) 173–183

A Homogeneous Reaction between a Water Soluble Vinyl Sulfonyl Reactive Dye and Methyl-α-D-Glucoside. Part 1—Synthesis, Purification and Identification of the Structures of Dye-Glucoside

Zhenghua Zhu & Yiaodong Zhang

East China University of Chemical Technology, Shanghai, 200237,
People's Republic of China

(Received 23 September 1992; accepted 6 November 1992)

ABSTRACT

A water soluble vinyl sulfonyl reactive dye containing a sulfonic acid group in the molecule was synthesized, purified and its structure confirmed. Its reaction products with methyl-α-D-glucoside were separated and structurally determined by 600 MHz NMR and elemental analysis. It was found that only D_6 *and* D_4 *were formed; no* D_2 *or* D_3 *was present. These results were similar to our previous report in which a model vinyl sulfonyl reactive dye without a sulfonic acid group in the molecule was reacted with methyl-α-D-glucoside.*

1 INTRODUCTION

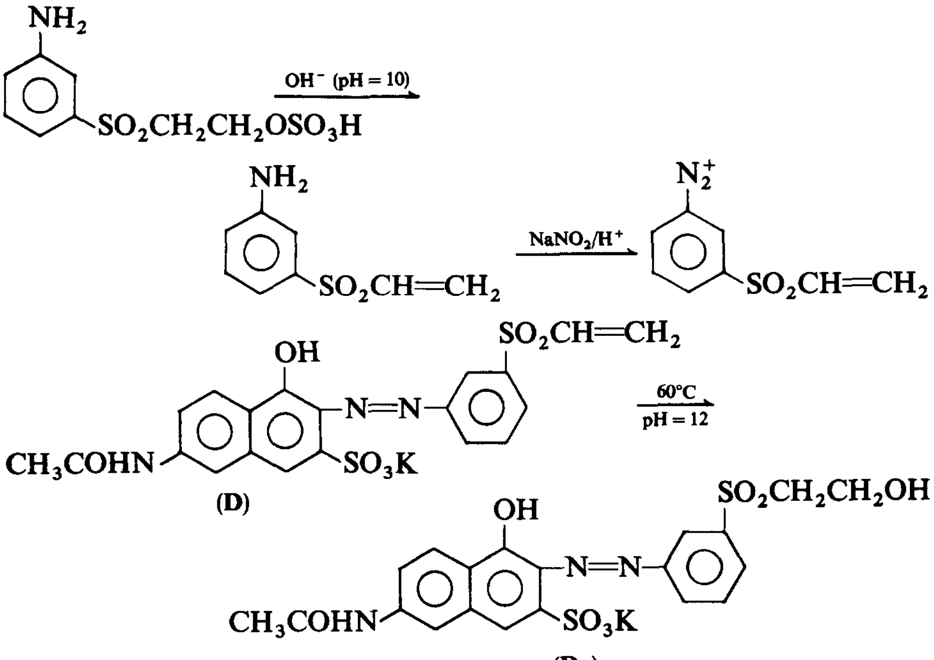
The reaction between vinyl sulfonyl reactive dyes and cellulose fiber is still not completely understood. We have used methyl-α-D-glucoside (MOH) as a model cellulose fiber and an insoluble vinyl sulfonyl compound as a model commercial dye.[1] The absence of a sulfonic acid group renders the purification, separation and structure determination of the vinyl sulfonyl dye and its reaction products with MOH much easier to handle. However, introduction of a sulfonic acid group also greatly changes the reaction parameters of the dye with MOH. In this paper, we prepare, separate and purify the dye and dye-glucosides and determine structures by column chromatography double scanning and 600 MHz ^{2}H NMR.

Dyes and Pigments 0143-7208/93/$06.00

2 SYNTHESIS AND CHARACTERISATION OF WATER-SOLUBLE VINYL SULFONYL REACTIVE DYES

2.1 Synthesis of water-soluble vinyl sulfonyl reactive dyes

The water-soluble vinyl sulfonyl reactive dye (**D**) and the hydrolysed dye (**D**$_w$) were synthesized by the following route.



(D)

(D$_w$)

The crude dyes **D** and **D**$_w$ were separated and purified by column chromatography and by precipitation with potassium acetate; Their purities were examined by thin layer chromatography with double scanning CS-930 fixed phase used was silica gel G + 0·2% CMC and the moving phase *n*-butanol: ethanol: acetic acid: water = 60:10:0·5:20; both products gave single spots.

Both **D** and **D**$_w$ contain water of crystallization. Before analysis, **D** and **D**$_w$ were kept in a vacuum desiccator with P_2O_5 and silica gel.

2.2 Elemental analysis and ¹H nmr spectrum of dye

Dye D		C	H	N
$C_{20}H_{16}N_3S_2O_7K$ 3/2 H_2O				
514 + 27	Calc. %	44·36	3·51	7·76
	Found %	44·52	3·58	7·84
		44·58	3·82	7·88

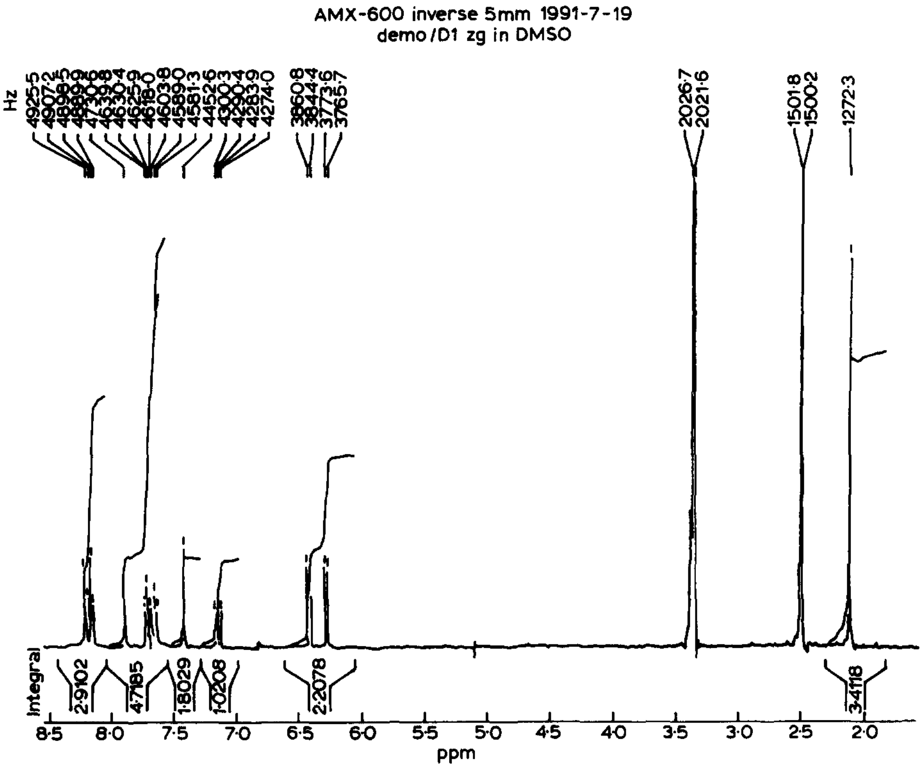


Fig. 1. 600 MHz spectrum of vinyl sulfone reactive dye **D**.

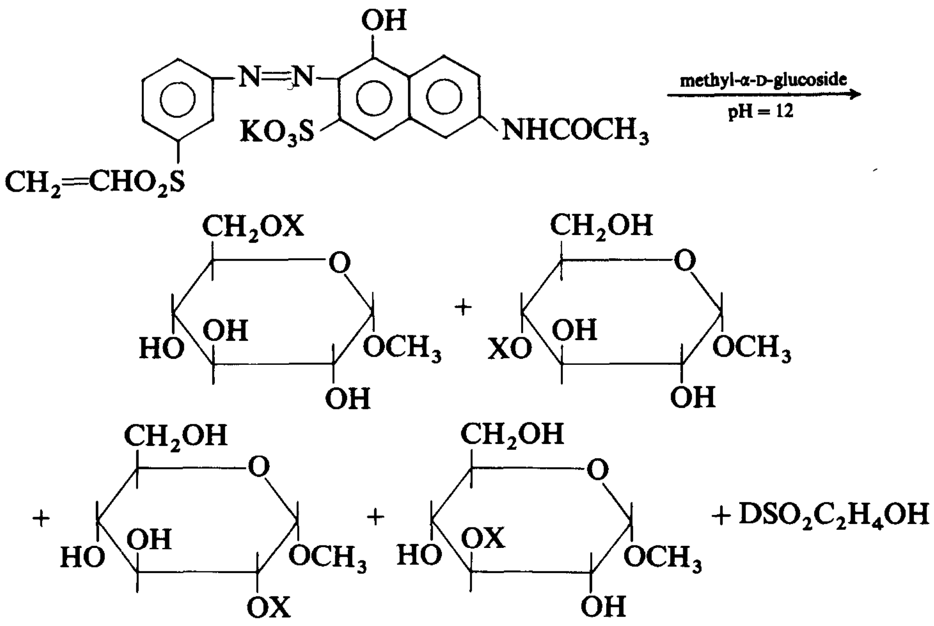
		C	H	N
Hydrolyzed dye $\mathbf{D}_w$				
$C_{20}H_{18}N_{33}S_2O_8K$ 3/2 H_2O				
532 + 27	Calc. %	42·93	3·55	7·57
	Found %	43·12	3·84	7·50
		43·28	3·68	7·63

The ^2H NMR spectrum (obtained on a Brucker Spectrospin AM × 600) shows Fig. 1 the characteristic double bond peaks of $—CH{=}CH_2$ at $\delta = 6{\cdot}5$ ppm; this confirms that the additional water is water of crystallization and that the water molecule has not reacted at the double bond.

3 SYNTHESES, SEPARATION, PURIFICATION AND STRUCTURE DETERMINATION OF DYE-GLUCOSIDES

3.1 Syntheses of dye-glucosides

The possible reactions between vinyl sulfonyl reactive dye **D** MOH may be represented by the following schemes:



where X denotes $—CH_2CH_2—SO_2—D$.

The reaction products were initially separated and examined by TLC. Only four spots were observed: spot 1 was unreacted dye, spot 2 hydrolysed dye and spots 3 and 4 were reacted dyes. The structures of these reacted dyes were then determined by chromatography. The fixed phase used was silica gel G + 0·2% CMC and the moving phase isobutylalcohol: methyl alcohol: acetic acid: water = 60:10:1:20.

The reaction solution was cooled to 0–5°C, acidified with concentrated hydrochloric acid and extracted by *n*-butyl alcohol. The butyl alcohol layer was separated and neutralized by adding 1 N KOH at 0–5°C. The layers were combined and extracted with chloroform to remove excess MOH. The potassium salts of the reaction products in the aqueous layer were then separated by column chromatography. The column (6·5 cm × 100 cm) was composed of 10–40 μm silica gel G and was eluted by mixed solvents isobutyl alcohol: methyl alcohol: acetic acid: H_2O = 60:10:1:20 at 15–18°C. The bands which were obtained were collected and examined by TLC. The first band was unreacted dye and the second hydrolysed dye. The third and fourth bands were dye-glucosides and were eluted with methyl alcohol and collected separately. The alcoholic solutions were concentrated, diluted with large amount of acetone and filtered to remove any precipitate formed, e.g. MOH, silica gel, calcium sulfate. Potassium acetate was added to the above filtrate to obtain the reaction product.

The R_{fs} values of dye **D**, hydrolysed dye $\mathbf{D}_w$ and the reaction products were obtained from TLC.

TABLE 1
R_{fs} Values of Spots 3 and 4

	R_{f1}	R_{f2}	R_{f3}	R_{f4}
A	0·57	0·519	0·41	0·33
B	0·65	0·556	0·43	0·34
C	0·267	0·3	0·15	0·10
D	0·51	0·49	0·37	0·31

The fixed phase used was silica gel G + 0·2% CMC and different mobile phases A, B. C and D were used, viz.

A *n*-butyl alcohol:ethyl alcohol:acetic acid:H_2O = 60:10:1:20
B isobutyl alcohol:methyl alcohol:acetic acid:H_2O = 60:10:1:20
C isobutyl alcohol:ethyl acetate:ammonia water = 6:6:4
D *n*-butyl alcohol:ethyl acetate:H_2O:ammonia water = 60:330:10:2.

The different R_f values for spot 1 (**D**), spot 2 (**D**$_w$) spot 3 and spot 4 are as given in Table 1.

The results of elemental analyses of spots 1, 2, 3 and 4 were as follows:

		C	H	N
Spot 1 (**D**)	$C_{20}H_{16}N_3O_7S_2K \cdot 3/2\ H_2O$			
	Calc. %	44·36	3·51	7·76
	Found %	44·55	3·70	7·86
Spot 2 (**D**$_w$)	$C_{20}H_{18}N_3O_8S_2K \cdot 3/2\ H_2O$			
	Calc. %	42·93	3·55	7·57
	Found %	43·20	3·75	7·65
Spot 3	$C_{27}H_{30}N_3O_{13}S_2K \cdot 2\ H_2O$			
	Calc. %	43·66	4·55	5·66
	Found %	43·67	4·45	5·57
		43·55	4·49	5·54
Spot 4	$C_{27}H_{30}N_3O_{13}S_2K \cdot 2\ H_2O$			
	Calc. %	43·66	4·55	5·66
	Found %	43·64	4·50	5·61
		43·77	4·47	5·66

3.2 Confirmation of structures of spots 3 and 4 by ^{1}H NMR

By comparison of the chemical shifts of the OH hydrogen atoms in methyl-α-D-glucoside and the dye-glucosides, the sites of reaction between **D** and MOH were determined.

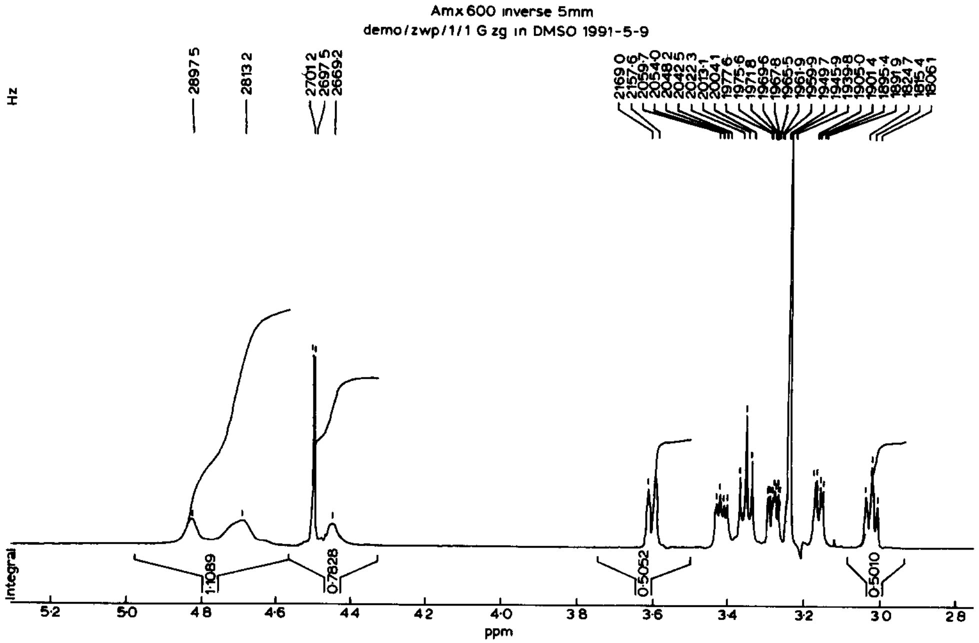


Fig. 2. 'H-NMR spectrum of methyl-α-D-glucoside (600 MHz).

3.2.1 ^{1}H NMR spectrum of methyl-α-D-glucoside (Fig. 2)

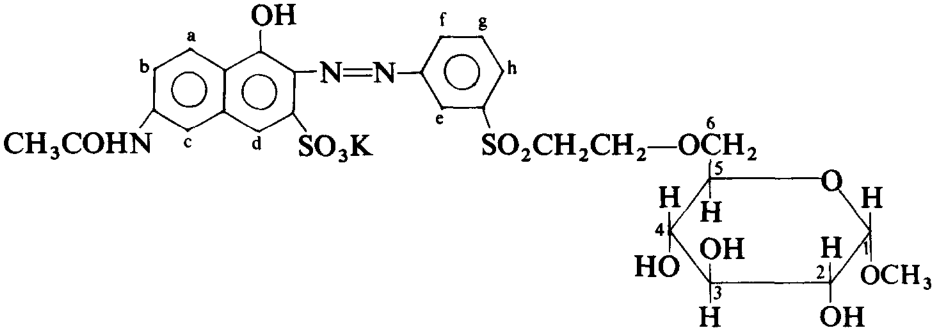
^{1}H-NMR e (600 MHz), DMSO-d/TMS: 3·24 (OCH_3s)
4·516(H_1, JH_1H_2 = 3·6 Hz d) 3·184(H_2, JH_2H_3 = 9·20 Hz,
JH_1H_2 = 3·6 Hz, $JH_2OH'_2$ = 6·10 H_2, octa)
4·725 (OH'_2, JH_2OH_2 = 6·10 Hz, d) 3·375 (H_3,
$JH_3OCH'_3$ = 5·10 Hz, JH_2H_3 = 9·20 Hz, JH_3H_4 = 9·20 Hz,
octa), 3·046 (H_4, JH_3H_4 = 9·20 Hz, JH_4H_5 = 9·20 Hz,
$JH_4OH'_4$ = 5·50 Hz, octa) 4·767 (OH_3, JH_3OH_3 = 5·10 Hz d)
4·871(OH_4, JOH_4H_4 = 5·50 Hz, d) 3·294 (H_5, JH_4H_5 = 9·20 Hz
JH_5H_{6a} = 3·0 Hz, JH_5H_{6b} = 11·0 Hz, octa)
3·614(H_{6a}, $JH_{6a}OH_6$ = 6·10 Hz, $JH_{6a}H_5$ = 11·64 Hz,
$JH_{6a}H_{6b}$ = 2·0 Hz, octa) 3·439(H_{6b}, $JH_{6b}H_{6a}$ = 6·2 Hz
$JH_{6b}H_5$ = 11·64 Hz qua) 4·489(OH'_6, JH_6HO_6 = 6·20 Hz

In summary, the chemical shifts in ppm of hydrogen in the four hydroxy groups in methyl-α-D-glucoside are:

No.	*Chemical shift*	*Shape*
OH'6	4·489	Triplet
OH'4	4·871	Doublet
OH'3	4·767	Doublet
OH'2	4·725	Doublet
H'	4·516	Doublet

3.1.2 'H NMR spectrum of spot 4

'H-NMR (600 MHz), DMSO-d6/TMS 7·82 (Ha), 7·80 (Hb) 8·08(Hc), 7·67(Hd), 8·298(He, J = 11·1 Hz), 8·198(H_f, J_{fg} = 8·3 Hz 7·487(Hg, J_{fg} = 7·55 Hz), 7·981 (Hh, J_{gh} = 8·8 Hz) 3·525 (C—CH_2O, J = 9·9 Hz), 3·723 (S—CH_2—C, J = 6·15 Hz), 4·516 (H_1, JH_1H_2 = 3·60 Hz), 3·257(OCH_3), 3·184 (H_2, JH_1H_2 = 3·60 Hz, JH_2H_3 = 9·20 Hz, JH_2OH_2 = 6·10 Hz), 4·386 (OH'_2, JH_2OH_2 = 6·10 Hz) 3·375(H_3, JH_2H_3 = 9·20 Hz, JH_3H_4 = 9·20 Hz, JH_3OH_2 = 5·10 Hz) 4·417(OH_3, JH_3OH_3 = 5·10 Hz) 3·046(H_4, JH_3H_4 = 9·20 Hz, JH_4H_5 = 9·20 Hz, JH_4OH_4 = 5·50 Hz), 4·470 (OH'_4, JH_4OH_4 = 5·50 Hz), 3·294(H_5, JH_5H_4 = 9·20 Hz, JH_5H_{6a} = 11·0 Hz JH_5H_{6b} = 3·0 Hz) 3·614(H_{6a}, JH_5H_{6a} = 11·64, $JH_{6a}H_{6b}$ = 2·0 Hz), 3·439(H_{6b}, JH_5H_{6b} = 11·64 Hz, $JH_{6a}H_{6b}$ = 6·2 Hz)



D$_6$

The 'H NMR spectrum of spot 4 and the same spectrum with the addition of D_2O are shown in Figs 3 and 4.

From these figures, the chemical shifts (ppm) of various hydroxyl protons in spot 4 are:

OH'4	4·470	Doublet
OH'3	4·417	Doublet
OH'2	4·386	Doublet

In comparison with the chemical shifts of various hydroxyl protons in methyl-α-D-glucoside, these proton shifts are moved to higher fields due to the introduction of the bulky dye moiety. The chemical shift signal of the proton in the OH'-6 group which should be located at 4·0–4·15 ppm, is, for the same reason, not present.

The 'H NMR spectrum of spot 4 with D_2O added shows that the peaks for 2-OH', 3-OH' and 4-OH' are absent. Compared to the starting dye **D**, the doublet ethylenic hydrogen in the sulphonyl vinyl group δ a

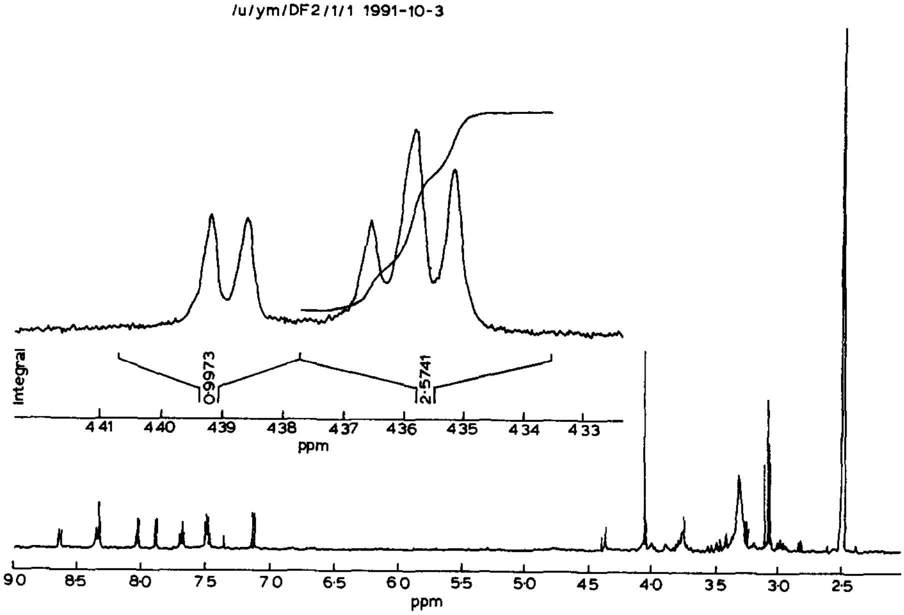


Fig. 3. 'H-NMR spectrum of spot 4.

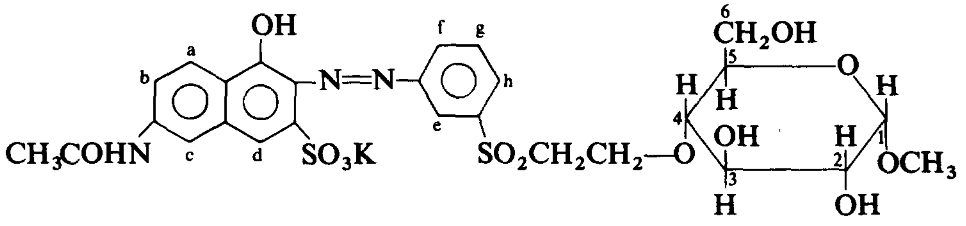
Fig. 4. 'H-NMR spectrum of spot 4 with addition of D_2O.

(6·23), δ b (6·34) and δ c (6·86) are absent, and a signal at δ = 3·723 ppm is apparent, indicating the presence of ethanic H.

All these factors indicate that the reaction product (spot 4) can be identified as $\mathbf{D}_6$.

3.2.3 'H-NMR spectrum of spot 3

'H-NMR (600 MHz), DMSO-d6/TMS 'H-NMR (600 MHz), DMSO-d_6/TMS
7·832(H_a), 7·80(H_b), 8·08(H_c), 7·67(H_b), 8·037(H_e)
8·202(H_f, J_{fg} = 7·6 Hz), 7·483 H_g, J_{fg} = 7·55 Hz)
7·973(H_h, J_{gh} = 9·5 Hz), 3·350 (C—CHl$_2$O, J = 9·2 Hz)
3·692(S—CH$_2$C—, J = 6·45 Hz), 4·516 (H_1, JH_1H_2 = 3·60 Hz)
3·257(OCH$_3$), 3·184 (H_2, JH_1H_2 = 3·60 Hz,
JH_2H_3 = 9·20 Hz, JH_2OH_2 = 6·10 Hz), 4·868(OH'$_2$, JH_2OH_2 = 6·10 Hz),
3·375(H_3, JH_2H_3 = 9·20 Hz, JH_4H_3 = 9·20 Hz, JH_3OH_3 = 5·10 Hz),
4·965 (OH'$_3$, $JH_3OH'_3$ = 5·10 Hz), 3·046 (H_4, JH_3H_4 = 9·2 Hz,
JH_5H_4 = 9·2 Hz), 3·294 (H_5, JH_4H_5 = 9·20 Hz, JH_5H_{6a} = 11·0 Hz,
JH_5H_{6b} = 3·0 Hz), 3·614 (H_{6a}, JH_5H_{6a} = 11·64 Hz, $JH_{6a}H_{6b}$ = 2·0 Hz,
$JH_{6a}OH'_6$ = 6·10 Hz), 3·439 (H_{6b}, JH_5H_{6b} = 11·64 Hz, $JH_{6a}H_{6b}$ = 6·2 Hz),
4·464 (OH'$_6$, $JH_{6a}H_{6b}$ = 3·6 Hz, $JH_{6b}OH'_6$ = 3·4 Hz)



$\mathbf{D}_4$

The 'H-NMR spectrum of spot 3 and the same spectrum with the addition of D_2O are shown in Figs 5 and 6.

From these figures, the chemical shifts of various hydroxyl protons in spot 3 are:

OH'$_6$, 4·464 (triplet); OH'$_3$, 4·956 (doublet);
OH'$_2$, 4·868 (doublet).

In comparison with the chemical shifts of various hydroxyl protons in MOH, these hydroxyl proton shifts are moved to a lower field. The peak for the chemical shift in the OH'$_4$ group which should be present at 5·0 ppm, is absent. The 'H-NMR spectrum of spot 3, with D_2O added, shows that the peaks for 2-OH', 3-OH' and 6-'OH disappear. Compared to the starting dye **D**, the doublet ethylenic hydrogen in the vinyl sulfone

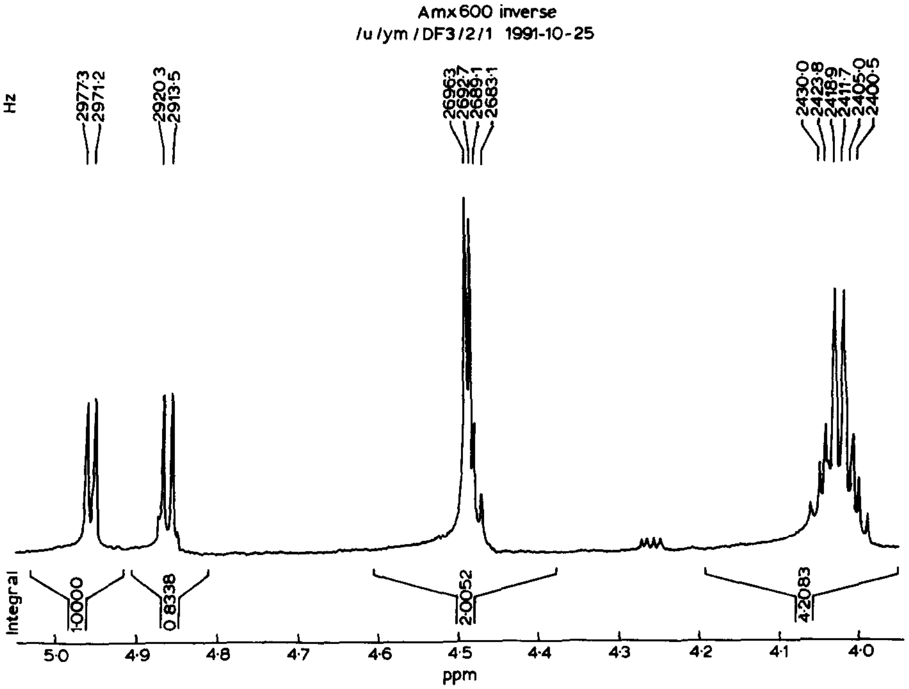


Fig. 5. 'H-NMR spectrum of spot 3.

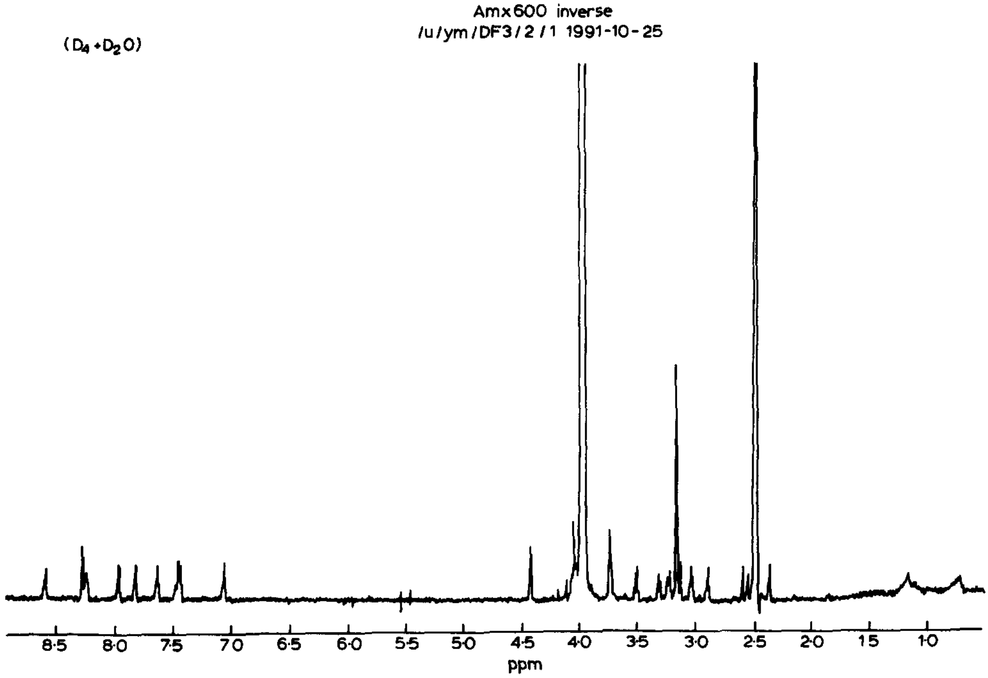


Fig. 6. 'H-NMR spectrum of spot 3 with addition of D_2O.

group is absent and a peak at $\delta = 3{\cdot}692$ ppm is present, indicating an ethanic proton.

These data indicate that the reaction product (spot 3) can be identified as $\mathbf{D}_4$.

4 CONCLUSION

Homogeneous reactions of a water-soluble vinyl sulfonyl reactive dye with methyl-α-D-glucoside have been studied. The presence of a sulfonic acid group in the dye molecule renders the separation, purification of the dye and reaction products more difficult. The reaction products are $\mathbf{D}_4$ and $\mathbf{D}_6$, which are identified by elemental analyses and by 600 MHz 'H-NMR. Neither $\mathbf{D}_2$ nor $\mathbf{D}_3$ was found to be present.

ACKNOWLEDGEMENTS

The authors express their thanks to Hoecht Aktiengesellschaft and Dr Tappe and Dr Russ for their cooperation in this study.

REFERENCE

1. Zhu Zhenghua, Xia Jian-Mei & Chen Kong-Chang, *Dyes and Pigments*, **17** (1991) 171–91.