Dyes and Pigments **24** (1994) 281–294

Studies on Structural Effects in the Reaction between Model Vinylsulfone Reactive Dyes and Methyl-α-D-glucoside. Part I: Synthesis and Identification of Model 'Dye–Fiber' Compounds

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(Received 12 November 1993; accepted 20 December 1993)

ABSTRACT

Four different model vinylsufone reactive dyes were synthesized. Model 'dye–fiber' compounds were obtained during the reaction between these dyes and methyl-α-D-glucoside as a 'model' cellulose. The structures of the products were established by MS, ^{1}H-NMR and elemental analysis.

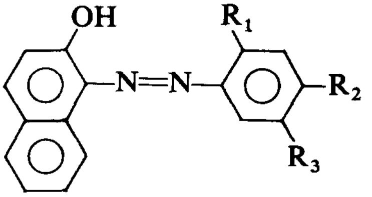
1 INTRODUCTION

The reactivity and fastness to hydrolysis of the dye–fiber bond are important properties of reactive dyes and some previous studies of these properties have been carried out.[1–3] The reaction of vinylsulfone reactive dye with model cellulose (methyl-α-D-glucoside) has been shown to occur predominantly (86%) at the primary OH group on C-6, and only 14% occurs at the secondary OH group on C-4.[4,5] The kinetics of the alkaline hydrolysis of the model 'dye–fiber' compounds indicate that the primary model 'dye–fiber' compound $\mathbf{D}_6$ is hydrolyzed faster than the secondary model 'dye–fiber' compound $\mathbf{D}_4$. Thus, the predominantly existing $\mathbf{D}_6$ is more easily hydrolyzed than $\mathbf{D}_4$ which exists only in minor amount.

In this present paper, vinylsulfone reactive dyes of different structures are used to study their general reactions towards methyl-α-D-glucoside. The objective is to investigate the structural effects of vinylsulfone reactive dyes on the reactions with methyl-α-D-glucoside, and also to evaluate the structural effects of dye-glucosides on the rates of alkaline hydrolysis.

2 SYNTHESIS OF MODEL VINYLSULFONE REACTIVE DYES

Four model vinylsulfone reactive dyes were synthesized by known methods; their structures are as shown below:



Dye	R_1	R_2	R_3
A	H	OMe	$SO_2CH{=}CH_2$
B	H	H	$SO_2CH{=}CH_2$
C	OMe	H	$SO_2CH{=}CH_2$
D	H	$SO_2CH{=}CH_2$	H
E	OMe	$SO_2CH{=}CH_2$	OMe

The melting points, absorption wavelengths and elemental analyses of dyes A–E are given in Table 1; ^{1}H-NMR (600 MHz) spectra were recorded on a Spectrospin AMX-600.

TABLE 1
Melting Points, Absorption Wavelengths, and Elemental Analyses of Dyes A–B

Dye	*mp (°C)*	*λ_{max} (nm)*		*Elemental analysis (%)*		
				C	*H*	*N*
A	207–209	472	Calcd:	61·96	4·35	7·16
			Found:	61·77	4·44	7·64
B	132–134	470	Calcd:	63·91	4·14	8·28
			Found:	63·92	4·14	8·12
C	243–245	483	Calcd:	61·96	4·35	7·61
			Found:	61·73	4·42	7·60
D	197–199	470	Calcd:	63·91	4·14	8·28
			Found:	63·56	4·22	8·31
E	—	—	Calcd:	60·30	4·52	7·04
			Found:	59·78	4·60	7·08

3 PREPARATION OF MODEL 'DYE–FIBER' COMPOUNDS

3.1 Synthesis

A mixture of the dye (0·059 mmol) and methyl-α-D-glucoside (0·18 g, 0·92 mmol) in distilled water (2 ml) and dioxane (10 ml) was maintained at 50 ± 1°C for 1 h. Aqueous sodium hydroxide (10%, 0·0738 ml), preheated to 60°C, was added and stirring continued for 30 min. The reaction solution was cooled to room temperature and then poured on to ice water and neutralized to pH 5–6 with dilute hydrochloric acid. The resultant precipitate was filtered to give the crude product.

3.2 Purification of the reaction products

The crude products were separated by TLC. Four spots were present; the developing solution used was chloroform–benzene–ethyl alcohol (1 : 1 : 0·4). The R_f values of the components are given in Table 2.

The four spots were assigned as: spot 1, reaction product in large amount; spot 2, reaction product in minor amount; spot 3, hydrolyzed dye; spot 4, unreacted dye.

Although spot 1 had a very similar R_f value to spot 2, the reaction products were readily separated by column chromatography; analytical data are given in Table 3.

The data in Table 3 indicate that spot 1 and spot 2 are the expected products derived from the dyes and methyl-α-D-glucoside.

Methyl-α-D-glucoside used in this study was obtained from Janssen Chimica; mp: 169°C; (α): +158°. Its ^{1}H-NMR spectrum was measured on a Bruker-Spectrospin AMX-600, using DMSO-d_6 as solvent and TMS as reference. The data obtained were as follows.

^{1}H-NMR (DMSO-d_6, TMS)

δ: 4·85 (1H, d, $J_{4,4\text{-OH}}$ = 5·6 Hz, 4-OH); 4·74 (1H, d, $J_{3,3\text{-OH}}$ = 4·9 Hz, 3-OH); 4·69 (1H, d, $J_{2,2\text{-OH}}$ = 6·4 Hz, 2-OH); 4·51 (1H, d, $J_{1,2}$ =

TABLE 2
R_f Values of the Components in the Reaction Products

Dye	*Spot 1*	*Spot 2*	*Spot 3*	*Spot 4*
A	0·36	0·44	0·67	0·81
B	0·34	0·43	0·78	0·68
C	0·40	0·49	0·67	0·74
D	0·39	0·51	0·68	0·90
E	0·13	0·22	0·44	0·76

TABLE 3
Analytical Data of the Components Derived from Dyes A–E and Methyl-α-D-glucoside

Dye	*Component*	*MS (m/z)*	*mp (°C)*		*Elemental analysis (%)*		
					C	*H*	*N*
A	Spot 1	562	96·1–98·5	Calcd:	55·52	5·34	4·98
				Found:	55·21	5·18	4·70
	Spot 2	562	208·5–210·3	Calcd:	55·52	5·34	4·98
				Found:	55·70	5·13	5·12
B	Spot 1	533	90·7–92·2	Calcd:	56·28	5·25	5·26
				Found:	56·35	5·27	5·14
	Spot 2	533	129–130	Calcd:	56·28	5·25	5·26
				Found:	56·31	5·67	5·74
C	Spot 1	562	117·4–120·1	Calcd:	55·52	5·34	4·98
				Found:	55·31	5·43	4·78
	Spot 2	562	216·3–218·2	Calcd:	55·52	5·34	4·98
				Found:	55·70	5·20	5·16
D	Spot 1	533	107·4–110·3	Calcd:	56·28	5·25	5·26
				Found:	56·09	5·76	5·70
	Spot 2	533	217·7–219·0	Calcd:	56·28	5·25	5·26
				Found:	56·15	5·27	5·10
E	Spot 1	593	—	Calcd:	60·30	4·52	7·04
				Found:	59·78	4·60	7·11
	Spot 2	593	—	Calcd:	60·30	4·52	7·04
				Found:	59·55	4·67	7·08

3·6 Hz, 1-H); 4·47 (1H, t, $J_{6a,6\text{-}OH} = J_{6b,6\text{-}OH}$ = 6·4 Hz, 6-OH); 3·18 (1H, octet, $J_{1,2}$ = 3·6 Hz, $J_{2,3}$ = 9·3 Hz, $J_{2,2\text{-}OH}$ = 6·3 Hz, 2-H); 3·36, 1H, sextet, $J_{2,3}$ = 9·4 Hz, $J_{3,4}$ = 9·2 Hz, $J_{3,3\text{-}OH}$ = 4·9 Hz, 3-H); 3·04 (1H, sextet, $J_{3,4}$ = 9·2 Hz, $J_{4,5}$ = 9·2 Hz, $J_{4,4\text{-}OH}$ = 5·6 Hz, 4-H); 3·29 (1H, octet, $J_{4,5}$ = 9·2 Hz, $J_{5,6a}$ = 6·1 Hz, $J_{5,6b}$ = 2·0 Hz, 5-H); 3·62 (1H, q, $J_{5,6a}$ = 6·1 Hz, $J_{6a,6b}$ = 11·5 Hz, 6-Ha); 3·44 (1H, q, $J_{5,6b}$ = 2·0 Hz, $J_{6a,6b}$ = 11·5 Hz, 6-Hb). (These data from 600 MHz spectra may be compared with those from 400 MHz.[1])

4 ^{1}H-NMR (600 MHz) DETERMINATION OF THE STRUCTURE OF THE MODEL 'DYE–FIBER' COMPOUNDS

4.1 Identification of the reaction products derived from dye A

The ^{1}H-NMR spectra of spot 1 and spot 2 derived from Dye A are shown in Figs 1 and 2; enlargements of parts of the spectra of spots 1

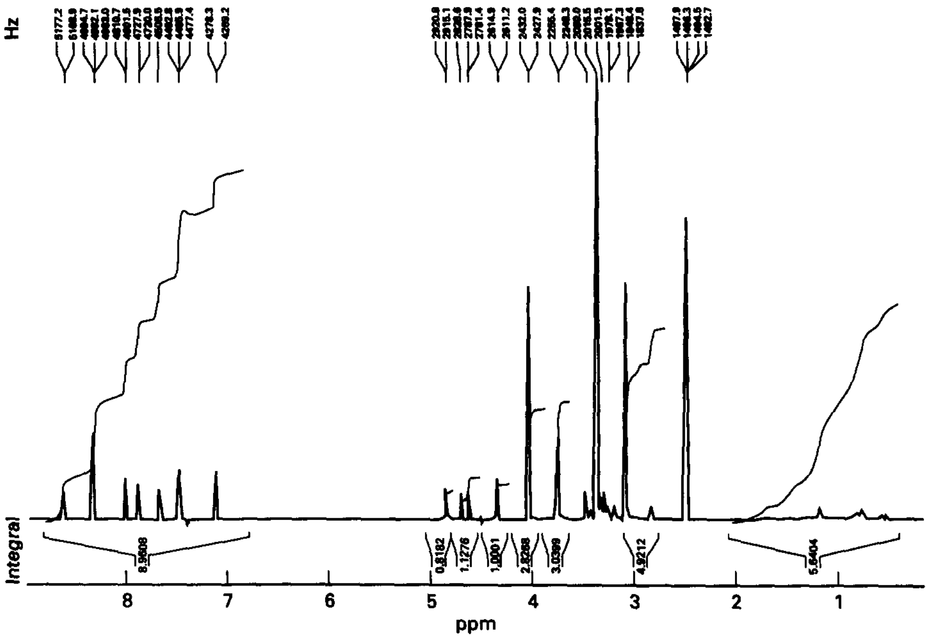


Fig. 1. ^{1}H-NMR spectrum of DGA-6.

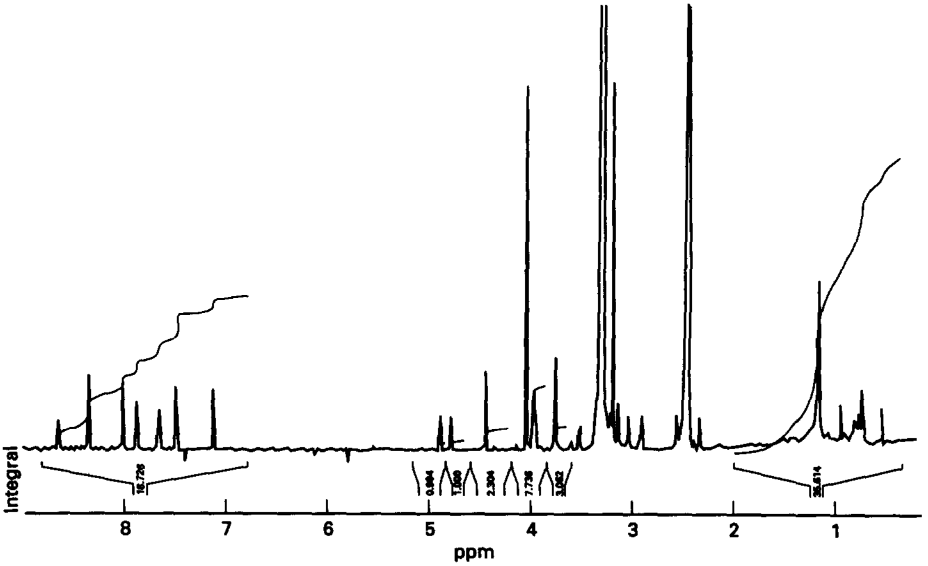


Fig. 2. ^{1}H-NMR spectrum of DGA-4.

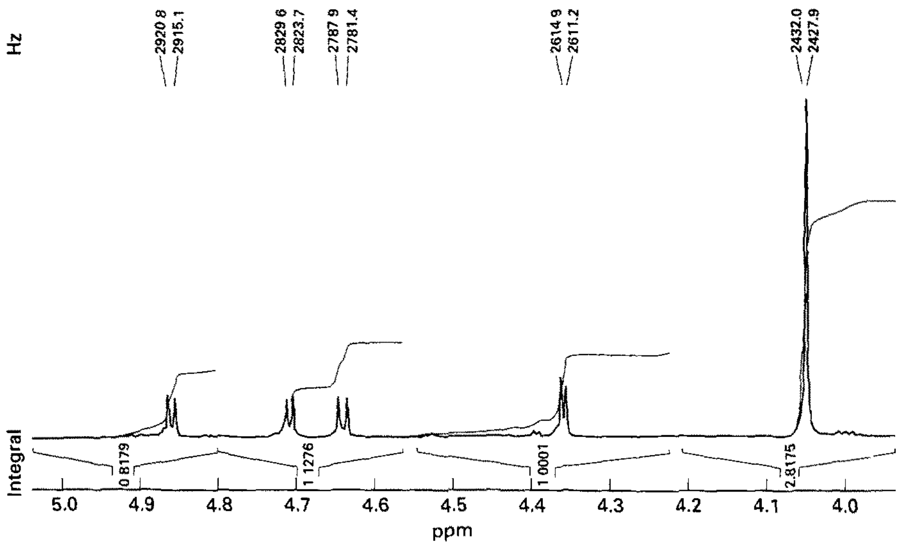


Fig. 3. ^{1}H-NMR spectrum of DGA-6, partly enlarged.

and 2 are shown in Figs 3 and 4. The D_2O-exchanged spectra of spots 1 and 2 are shown in Figs 5 and 6.

For spot 1: ^{1}H-NMR (DMSO-d_6, TMS)
δ: 8·62 (1H, d, $J_{a,b}$ = 8·3 Hz, Ha); 8·33 (1H, s, Hg); 8·31 (1H, d, $J_{h,j}$ = 9·2 Hz, Hh); 8·01 (1H, d, $J_{h,j}$ = 9·2 Hz, Hj); 7·87 (2H, t, $J_{c,d}$ = $J_{d,e}$ = 7·9 Hz, Hc, He); 7·68 (1H, d, $J_{b,c}$ = 8·6 Hz, Hb); 7·66 (1H, d, $J_{e,f}$ = 8·2 Hz, Hf); 7·12 (1H, t, $J_{c,d}$ = $J_{d,e}$ = 9·1 Hz, Hd); 4·86 (1H, d,

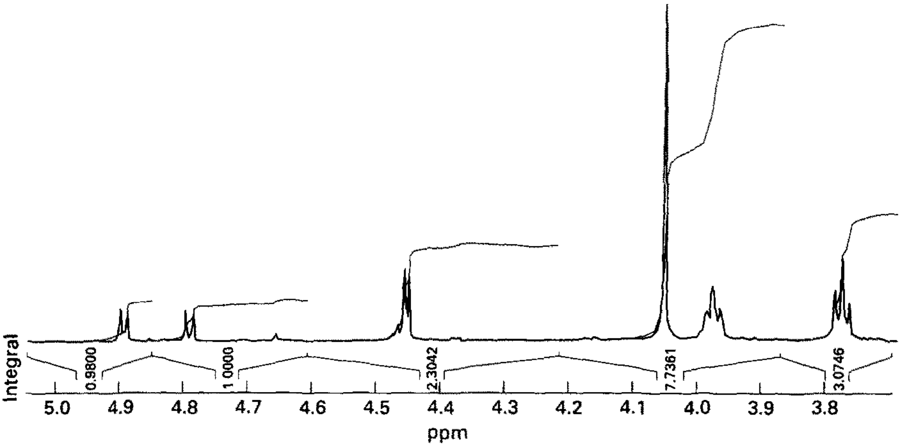


Fig. 4. ^{1}H-NMR spectrum of DGA-4, partly enlarged.

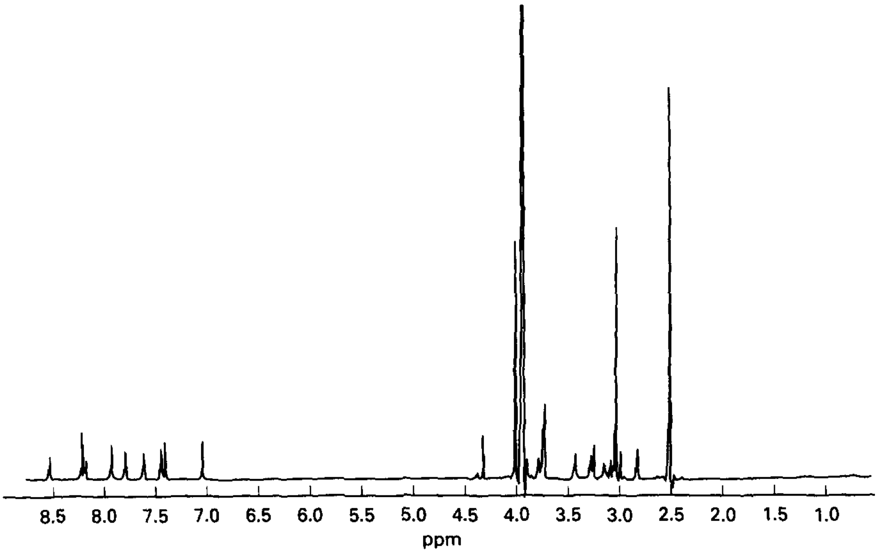


Fig. 5. ^{1}H-NMR spectrum of DGA-6 (D_2O-exchanged).

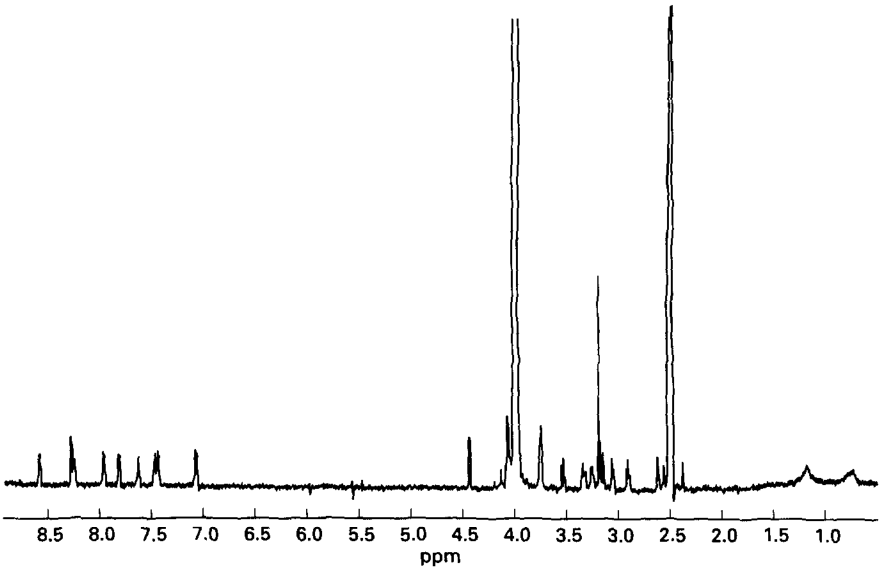
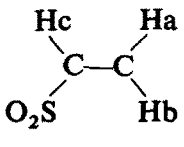


Fig. 6. ^{1}H-NMR spectrum of DGA-4 (D_2O-exchanged).

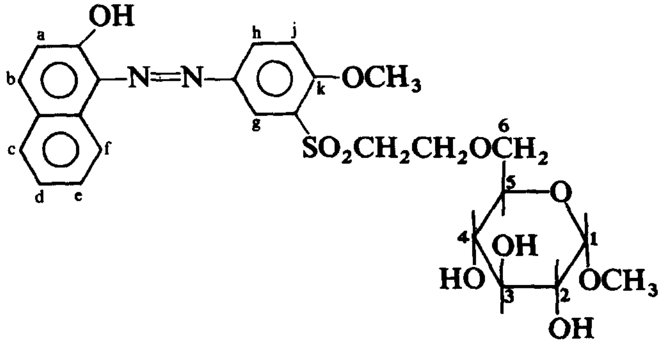
$J_{4,4\text{-OH}}$ = 5·7 Hz, 4-OH); 4·71 (1H, d, $J_{3,3\text{-OH}}$ = 4·9 Hz, 3-OH); 4·64 (1H, d, $J_{2,2\text{-OH}}$ = 6·5 Hz, 2-OH); 4·36 (1H, d, $J_{1,2}$ = 3·7 Hz, 1-H); 4·05 (3H, s, k-OMe); 3·75 (2H, t, J = 7·1 Hz, SO_2—CH_2—C); 3·47 (2H, t, J = 10·2 Hz, C—CH_2O); 3·18 (1H, octet, $J_{1,2}$ = 3·7 Hz, $J_{2,3}$ = 9·3 Hz, $J_{2,2\text{-OH}}$ = 6·3 Hz, 2-H); 3·36 (1H, sextet, $J_{2,3}$ = 9·4 Hz, $J_{3,4}$ = 9·2 Hz, $J_{3,3\text{-OH}}$ = 4·9 Hz, 3-H); 3·04 (1H, sextet, $J_{3,4}$ = 9·2 Hz, $J_{4,5}$ = 9·2 Hz, $J_{4,4\text{-OH}}$ = 5·6 Hz, 4-H); 3·29 (1H, octet, $J_{4,5}$ = 9·2 Hz, $J_{5,6a}$ = 6·1 Hz, $J_{5,6b}$ = 2·0 Hz, 5-H); 3·62 (1H, q, $J_{5,6a}$ = 6·1 Hz, $J_{6a,6b}$ = 11·5 Hz, 6-Ha); 3·44 (1H, q, $J_{5,6b}$ = 2·0 Hz, $J_{6a,6b}$ = 11·5 Hz, 6-Hb).

For spot 2: ^{1}H-NMR (DMSO-d_6, TMS)
δ: 8·62 (1H, d, $J_{a,b}$ = 8·3 Hz, Ha); 8·33 (1H, s, Hg); 8·31 (1H, d, $J_{h,j}$ = 9·1 Hz, Hh); 8·01 (1H, d, $J_{h,j}$ = 9·2 Hz, Hj); 7·87 (2H, t, $J_{c,d}$ = $J_{d,e}$ = 7·9 Hz, Hc, He); 7·68 (1H, d, $J_{b,c}$ = 8·6 Hz, Hb); 7·66 (1H, d, $J_{e,f}$ = 8·2 Hz, Hf); 7·12 (1H, t, $J_{c,d}$ = $J_{d,e}$ = 9·1 Hz, Hd); 4·90 (1H, d, $J_{3,3\text{-OH}}$ = 4·9 Hz, 3-OH); 4·80 (1H, d, $J_{2,2\text{-OH}}$ = 6·5 Hz, 2-OH); 4·46 (1H, t, $J_{6a,6\text{-OH}}$ = $J_{6b,6\text{-OH}}$ = 6·4 Hz, 6-OH); 4·05 (3H, s, k-OMe); 3·75 (2H, t, J = 7·1 Hz, SO_2—CH_2—C); 3·47 (2H, t, J = 10·2 Hz, C—CH_2—O); 3·18 (1H, octet, $J_{1,2}$ = 3·7 Hz, $J_{2,3}$ = 9·3 Hz, $J_{2,2\text{-OH}}$ = 6·3 Hz, 2-H); 3·36 (1H, sextet, $J_{2,3}$ = 9·4 Hz, $J_{3,4}$ = 9·2 Hz, $J_{3,3\text{-OH}}$ = 4·9 Hz, 3-H); 3·04 (1H, sextet, $J_{3,4}$ = 9·2 Hz, $J_{4,5}$ = 9·2 Hz, $J_{4,4\text{-OH}}$ = 5·6 Hz, 4-H); 3·29 (1H, octet, $J_{4,5}$ = 9·2 Hz, $J_{5,6a}$ = 6·1 Hz, $J_{5,6b}$ = 2·0 Hz, 5-H); 3·62 (1H, q, $J_{5,6a}$ = 6·1 Hz, $J_{6a,6b}$ = 11·5 Hz, 6-Ha); 3·44 (1H, q, $J_{5,6b}$ = 2·0 Hz, $J_{6a,6b}$ = 11·5 Hz, 6-Hb).

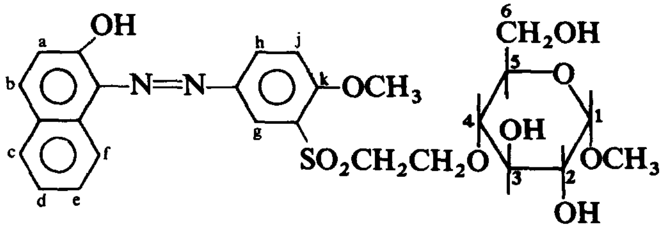
The ^{1}H-NMR spectrum of methyl-α-D-glucoside shows the signal for 6-OH at 4·47 ppm, while in the ^{1}H-NMR spectrum of the spot 1 reaction product the 6-OH signal is not present. Because of small changes in the bond angles of the six-membered ring caused by the attachment of the dye to the 6-OH, δ for 2-OH shifts from 4·69 to 4·64 ppm, δ for 3-OH shifts from 4·74 to 4·71 ppm, and δ for 4-OH shifts from 4·85 to 4·86 ppm. Figure 5 shows the 1H-NMR spectrum of DGA-6 with D_2O added; the peaks for 2-OH, 3-OH, and 4-OH are absent. From Fig. 1, compared to the starting dye, the doublet ethylenic hydrogen signals δ_a (6·31 ppm), δ_b (6·43 ppm), δ_c (6·76 ppm) are absent, and two peaks at δ 3·75 ppm and δ 3·47 ppm are present, indicating the presence of ethanic H. Thus, the spot 1 reaction product can be identified as DGA-6.



In the ^{1}H-NMR spectrum of the spot 2 reaction product, the doublet at δ 4·85 ppm disappears but the doublets for 2-OH and 3-OH, and the triplet for 6-OH remain. Because of the attachment of the dye molecule, the bond angles of the six-membered ring cause shifts of the δ value for 2-OH from 4·69 to 4·80, and the δ value for 3-OH shifts from 4·74 to 4·90 ppm; 6-OH remains unchanged. The doublet of the ethylenic hydrogen is not present. When D_2O is added, the original peaks of 2-OH, 3-OH, and 6-OH disappear (Fig. 6). Therefore, the structure of the spot 2 reaction product can be assigned as DGA-4.



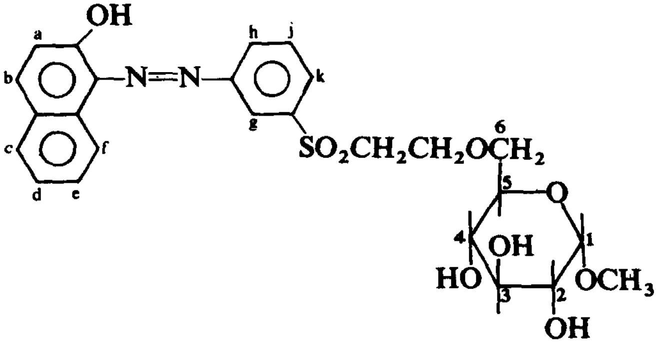
DGA-6



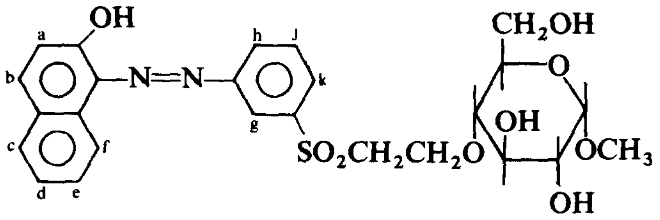
DGA-4

4.2 Identification of reaction products derived from dye B

The identification by ^{1}H-NMR of the reaction products derived from dye B has been previously reported.[1] The structures of DGB-6 and DGB-4 are shown.



DGB-6



DGB-4

4.3 Identification of the reaction products derived from dye C

Using ^{1}H-NMR techniques, as above, data pertinent to the reaction products from dye C are as follows.

For spot 1: ^{1}H-NMR (DMSO-d_6, TMS)

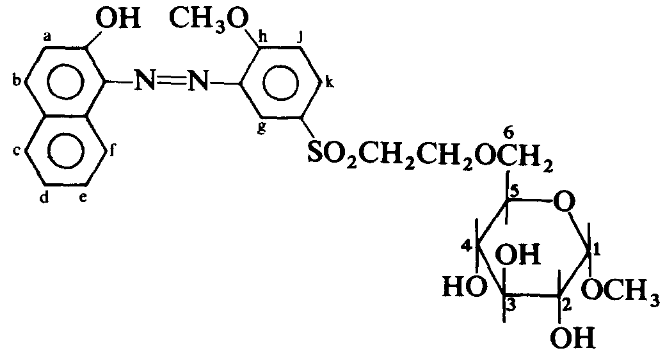
δ: 8·54 (1H, d, $J_{a,b}$ = 8·1 Hz, Ha); 8·35 (1H, s, Hg); 8·33 (1H, d, $J_{j,k}$ = 9·4 Hz, Hk); 8·02 (1H, d, $J_{j,k}$ = 9·2 Hz, Hj); 7·85 (2H, t, $J_{c,d}$ = $J_{d,e}$ = 7·9 Hz, Hc, He); 7·76 (1H, d, $J_{b,c}$ = 8·3 Hz, Hb); 7·66 (1H, d, $J_{e,f}$ = 8·2 Hz, Hf); 7·5 (1H, t, $J_{c,d}$ = $J_{d,e}$ = 9·1 Hz, Hd); 4·53 (1H, d, $J_{3,3\text{-OH}}$ = 4·9 Hz, 4-OH); 4·43 (1H, d, $J_{2,2\text{-OH}}$ = 6·6 Hz, 3-OH); 4·39 (1H, d, $J_{6a,6\text{-OH}}$ = $J_{6b,6\text{-OH}}$ = 6·4 Hz, 2-OH); 4·47 (1H, d, $J_{1,2}$ = 3·6 Hz, 1-H); 3·70 (2H, t, J = 7·1 Hz, SO_2—CH_2—C); 3·47 (2H, t, J = 10·2 Hz, C—CH_2—O); 4·10 (3H, s, h-OCH_3); 3·18 (1H, octet, $J_{1,2}$ = 3·7 Hz, $J_{2,3}$ = 9·3 Hz, $J_{2,2\text{-OH}}$ = 6·3 Hz, 2-H); 3·36 (1H, sextet, $J_{2,3}$ = 9·4 Hz, $J_{3,4}$ = 9·2 Hz, $J_{3,3\text{-OH}}$ = 4·9 Hz, 3-H); 3·05 (1H, sextet, $J_{3,4}$ = 9·2 Hz, $J_{4,5}$ = 9·2 Hz, $J_{4,4\text{-OH}}$ = 5·6 Hz, 4-H); 3·29 (1H, octet, $J_{4,5}$ = 9·2 Hz, $J_{5,6a}$ = 6·1 Hz, $J_{5,6b}$ = 2·0 Hz, 5-H); 3·62 (1H, q, $J_{5,6a}$ = 5·9 Hz, $J_{6a,6b}$ = 11·5 Hz, 6-Ha); 3·44 (1H, q, $J_{5,6b}$ = 2·0 Hz, $J_{6a,6b}$ = 11·5 Hz, 6-Hb).

For spot 2: ^{1}H-NMR (DMSO-d_6, TMS)

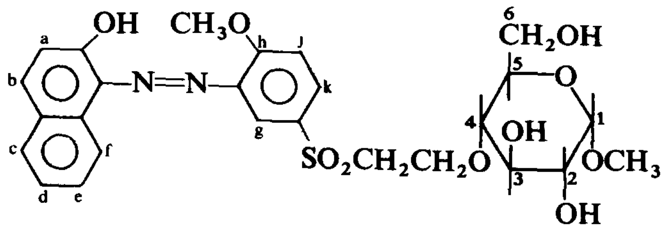
δ: 8·40 (1H, d, $J_{a,b}$ = 8·1 Hz, Ha); 8·31 (1H, s, Hg); 7·95 (1H, d, $J_{j,k}$ = 9·6 Hz, Hk); 7·87 (1H, d, $J_{j,k}$ = 9·2 Hz, Hj); 7·80 (2H, t, $J_{c,d}$ = $J_{d,e}$ = 7·8 Hz, Hc, He); 7·73 (1H, d, $J_{b,c}$ = 8·4 Hz, Hb); 7·64 (1H, d, $J_{e,f}$ = 8·2 Hz, Hf); 7·48 (1H, t, $J_{c,d}$ = $J_{d,e}$ = 9·2 Hz, Hd); 4·94 (1H, d, $J_{3,3\text{-OH}}$ = 4·8 Hz, 3-OH); 4·86 (1H, d, $J_{2,2\text{-OH}}$ = 6·6 Hz, 2-OH); 4·56 (1H, t, $J_{6a,6\text{-OH}}$ = $J_{6b,6\text{-OH}}$ = 6·4 Hz, 6-OH); 4·47 (1H, d, $J_{1,2}$ = 3·6 Hz, 1-H); 4·10 (3H, s, h-OCH); 3·72 (2H, t, J = 7·0 Hz, SO_2—CH_2—C); 3·48 (2H, t, J = 10·2 Hz, C—CH_2O); 3·18 (1H, octet, $J_{1,2}$ = 3·7 Hz, $J_{2,3}$ = 9·3 Hz, $J_{2,2\text{-OH}}$ = 6·3 Hz, 2-H); 3·36 (1H, sextet, $J_{2,3}$ = 9·4 Hz, $J_{3,4}$ = 9·2 Hz, $J_{3,3\text{-OH}}$ = 4·9 Hz, 3-H); 3·05 (1H, sextet, $J_{3,4}$ = 9·2 Hz, $J_{4,5}$ = 9·2 Hz, $J_{4,4\text{-OH}}$ = 5·6 Hz, 4-H); 3·29 (1H, octet, $J_{4,5}$ = 9·2 Hz, $J_{5.6a}$ = 6·1 Hz, $J_{5,6b}$ = 2·0 Hz, 5-H); 3·60 (1H, q, $J_{5,6a}$ = 6·1 Hz, $J_{6a,6b}$ = 11·5 Hz, 6-Ha); 3·44 (1H, q, $J_{5,5b}$ = 2·0 Hz, $J_{6a,6b}$ = 11·5 Hz, 6-Hb).

In the ^{1}H-NMR spectrum of the spot 1 reaction product, the triplet at δ 4·47 ppm is absent, but the doublets for 2-OH, 3-OH, and 4-OH remain. Because of small changes in the bond angles of the six-membered ring caused by the attachment of the dye to the 6-OH, the δ value for 2-OH shifts from 4·69 ppm to 4·39 ppm, that for 3-OH from 4·74 ppm to 4·43 ppm, and that for 4-OH from 4·85 ppm to 4·53 ppm; in the D_2O exchange spectrum the peaks for 2-OH, 3-OH, and 4-OH disappear. Compared to the dye C, the doublet ethylenic hydrogen signals δ_a (6·25 ppm), δ_b (6·43 ppm), and δ_c (6·81 ppm) are absent, while two peaks at δ 3·70 and 3·47 ppm are present, indicating the presence of ethanic H. Thus, the spot 1 reaction product can be identified as DGC-6.

In the ^{1}H-NMR spectrum of the spot 2 reaction product, the doublet at δ 4·85 ppm disappears, but the doublets for 2-OH and 3-OH, and the triplet for 6-OH remain. Because of the attachment of the dye molecule, the bond angles of the six-membered ring cause shifts of the 2-OH signal from 4·69 ppm to 4·86 ppm, and the 3-OH signal from 4·70 ppm to 4·90 ppm; the 6-OH signal remains unchanged. The doublet for the ethylenic hydrogen is not present. In the D_2O-exchanged spectrum, the peaks for 2-OH, 3-OH, and 6-OH disappear. The structure of the spot 2 reaction product can therefore be assigned as DGC-4.



DGC-6



DGC-4

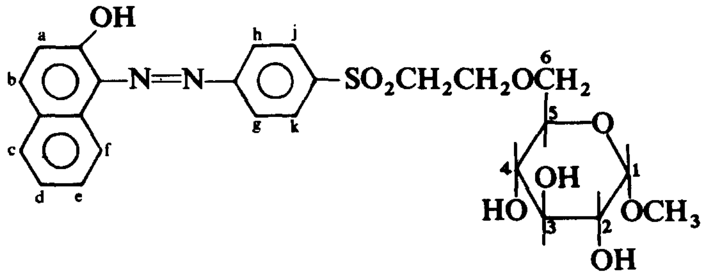
4.4 Identification of the reaction products derived from dye D

For spot 1: ^{1}H-NMR (DMSO-d_6, TMS)
δ: 8·44 (1H, d, $J_{a,b}$ = 8·1 Hz, Ha); 8·03 (1H, d, $J_{g,k}$ = 8·6 Hz, Hg); 7·97 (1H, d, $J_{h,j}$ = 8·2 Hz, Hh); 7·95 (1H, d, $J_{h,j}$ = 8·2 Hz, Hj); 7·86 (1H, d, $J_{g,k}$ = 8·6 Hz, Hk); 7·76 (2H, t, $J_{c,d}$ = $J_{d,e}$ = 7·6 Hz, Hc, He); 7·64 (1H, t, $J_{b,c}$ = 7·8 Hz, Hb); 7·55 (1H, t, $J_{e,f}$ = 7·4 Hz, Hf); 7·20 (1H, q, $J_{c,d}$ = $J_{d,e}$ = 9·8 Hz, Hd); 4·52 (1H, d, $J_{4,4\text{-OH}}$ = 5·4 Hz, 4-OH); 4·47 (1H, d, $J_{3,3\text{-OH}}$ = 5·2 Hz, 3-OH); 4·45 (1H, d, $J_{2,2\text{-OH}}$ = 6·1 Hz, 2-OH); 3·73 (2H, t, 7·2 Hz, SO_2—CH_2—C); 3·49 (2H, t, J = 10·2 Hz, C—CH_2—O); 3·18 (1H, octet, $J_{1,2}$ = 3·7 Hz, $J_{2,3}$ = 9·3 Hz, $J_{2,2\text{-OH}}$ = 6·3 Hz, 2-H); 3·36 (1H, sextet, $J_{2,3}$ = 9·4 Hz, $J_{3,4}$ = 9·2 Hz, $J_{3,3\text{-OH}}$ = 4·9 Hz, 3-H); 3·04 (1H, sextet, $J_{3,4}$ = 9·2 Hz, $J_{4,5}$ = 9·2 Hz, $J_{4,4\text{-OH}}$ = 5·6 Hz, 4-H); 3·29 (1H, octet, $J_{4,5}$ = 9·2 Hz, $J_{5,6a}$ = 6·1 Hz, $J_{5,6b}$ = 2·0 Hz, 5-H); 3·62 (1H, q, $J_{5,6a}$ = 5·9 Hz, $J_{6a,6b}$ = 11·5 Hz, 6-Ha); 3·44 (1H, q, $J_{5,6b}$ = 2·0 Hz, $J_{6a,6b}$ = 11·5 Hz, 6-Hb).

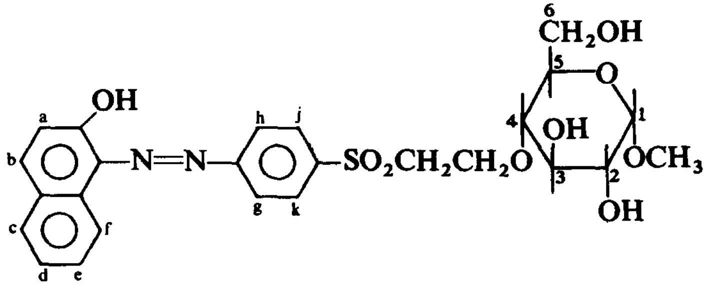
For spot 2: ^{1}H-NMR (DMSO-d_6, TMS)
δ: 8·44 (1H, d, $J_{a,b}$ = 8·1 Hz, Ha); 8·00 (1H, d, $J_{j,k}$ = 8·6 Hz, Hg); 7·97 (1H, d, $J_{k,j}$ = 8·2 Hz, Hh); 7·95 (1H, d, $J_{h,j}$ = 8·2 Hz, Hj); 7·93 (1H, d, $J_{g,k}$ = 8·6 Hz, Hk); 7·73 (2H, t, $J_{c,d}$ = $J_{d,e}$ = 7·6 Hz, Hc, He); 7·62 (1H, t, $J_{b,c}$ = 7·8 Hz, Hb); 7·50 (1H, t, $J_{e,f}$ = 7·4 Hz, Hf); 7·17 (1H, $J_{c,d}$ = $J_{d,e}$ = 9·8 Hz, Hd); 4·97 (1H, d, $J_{3,3\text{—OH}}$ = 5·9 Hz, 3-OH); 4·87 (1H, d, $J_{2,2\text{-OH}}$ = 6·5 Hz, 2-OH); 4·46 (1H, t, $J_{6a,6\text{-OH}}$ = $J_{6b,6\text{-OH}}$ = 6·4 Hz, 6-OCH); 4·50 (1H, d, $J_{1,2}$ = 3·4 Hz, 1-H); 3·63 (2H, t, J = 6·7 Hz, SO_2—CH_2—C); 3·35 (2H, t, J = 9·0 Hz, C—CH_2—O); 3·18 (1H, octet, $J_{1,2}$ = 3·7 Hz, $J_{2,3}$ = 9·3 Hz, $J_{2,2\text{-OH}}$ = 6·3 Hz, 2-H); 3·36 (1H, sextet, $J_{2,3}$ = 9·4 Hz, $J_{3,4}$ = 9·2 Hz, $J_{3,3\text{-OH}}$ = 4·9 Hz, 3-H); 3·04 (1H, sextet, $J_{3,4}$ = 9·2 Hz, $J_{4,5}$ = 9·2 Hz, $J_{4,4\text{-OH}}$ = 5·6 Hz, 4-H); 3·29 (1H, octet, $J_{4,5}$ = 9·2 Hz, $J_{5.6a}$ = 6·1 Hz, $J_{5,6b}$ = 2·0 Hz, 5-H); 3·59 (1H, q, $J_{5,6a}$ = 5·9 Hz, $J_{6a,6b}$ = 11·5 Hz, 6-Ha); 3·42 (1H, q, $J_{5,6b}$ = 2·0 Hz, $J_{6a,6b}$ = 11·5 Hz, 6-Hb).

In the ^{1}H-NMR spectrum of the spot 1 reaction product, the triplet at δ 4·47 ppm is not present, but the doublets for 2-OH, 3-OH, and 4-OH remain. Because of small changes in the bond angles of the six-membered ring caused by the attachment of the dye to the 6-OH, the δ value for 2-OH shifts from 4·69 to 4·45 ppm, that for 3-OH from 4·74 to 4·47 ppm, and that for 4-OH from 4·85 ppm to 4·52 ppm. In the D_2O exchanged spectrum, the peaks for 2-OH, 3-OH, and 4-OH disappear. On comparing the spectrum of DGD-6 with that of dye D, the doublet ethylenic hydrogen δ_a (6·22 ppm), δ_b (6·36 ppm), and δ_c (6·75 ppm) were absent, and two peaks at δ 3·73 and 3·49 ppm are present, indicating the presence of ethanic H. Thus, the spot 1 reaction product can be identified as DGD-6.

In the ^{1}H-NMR spectrum of the spot 2 reaction product, the doublet at δ 4·85 ppm disappears, but the doublets for 2-OH and 3-OH, and the triplet for 6-OH remain. Because of the attachment of the dye molecule, the bond angles of the six-membered ring cause shifts of the δ value for 2-OH from 4·69 to 4·87 ppm, and for 3-OH from 4·74 to 4·97 ppm; 6-OH remains unchanged. Therefore, the structure of the spot 2 reaction product can be assigned as DGD-4.



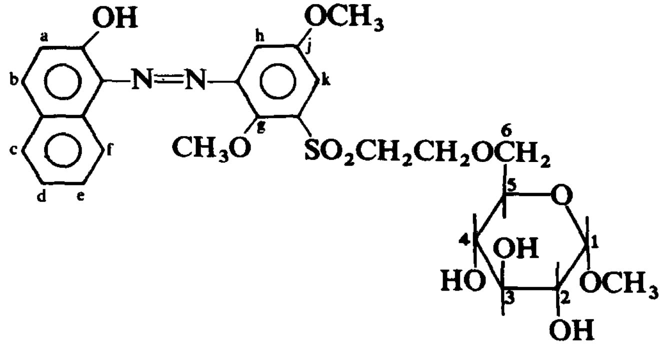
DGD-6



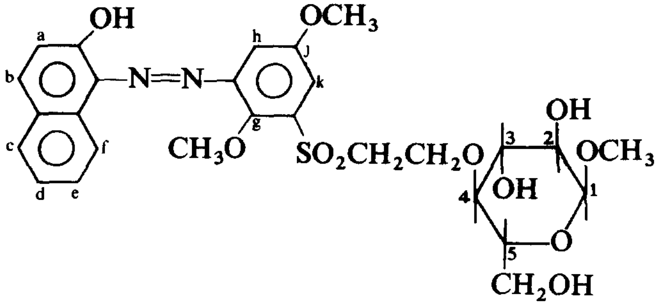
DGD-4

4.5 Identification of the reaction products derived from dye E

This identification of the reaction products derived from dye E by 600 ^{1}H-NMR has been carried out.[6] This (unpublished) work shows 4·94 ppm due to the δ of 3-OH, 4·84 ppm due to the δ of 2-OH, 4·48 ppm is due to the δ of 6-OH, and 4·52 ppm due to the δ of 1-H. The structures of DGE-6 and DGE-4 are therefore as shown.



DGE-6



DGE-4

5 CONCLUSIONS

During the reaction between model vinylsulfone reactive dye and model cellulose, (methyl-α-D-glucoside) two reaction products were obtained. Of these two products, the primary product was in larger amount than the secondary product. Their structures were established by mass spectra, ^{1}H-NMR spectra (600 MHz), R_f and elemental analyses. Neither $\mathbf{D}_2$ nor $\mathbf{D}_3$ was found to be present.

ACKNOWLEDGMENTS

The authors are indebted to Dr Tappe and Dr Russ (Farbwerke Hoechst) for their helpful discussions.

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