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A Study of the Homogeneous Reaction Between a Vinyl Sulfone Reactive Dye and Methyl-α-D-glucoside. Part I: A Kinetic Study

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ABSTRACT

The reaction between a vinyl sulfone dye and methyl-α-D-glucoside is studied in H_2O–dioxan solution. The attacking site of different OH groups in methyl-α-D-glucoside is determined by AM 400 ^1H-NMR spectroscopy, and the reaction products are separated by a TLC–double scanning method. It is shown that only the C_6 and C_4 hydroxyl groups are involved. The relative rates of reaction (k_6/k_4) were determined and found to be 6·087 at 50°C and 6·015 at 60°C.

1 INTRODUCTION

The mechanism of the reaction between vinyl sulfone reactive dyes and cellulose is still not completely understood. We have used methyl alcohol, *n*-propyl alcohol and isopropyl alcohol as model cellulose compounds, but several questions remained unsettled.[1,2]

Venkataraman and coworkers have previously used methyl-α-D-glucoside as a model cellulose compound[3,4] and 60 MHz ^1H-NMR spectroscopy to study the NMR spectra of the acetates of vinylsulfonyl-methyl-α-D-glucoside in D_2O solution. The chemical shifts of various ^1H signals in the —CHO-dye system were used to identify the site of reaction only indirectly. The peak shapes obtained were not well defined due to splitting. The reaction was carried out in DMSO, and NaOH was used as the

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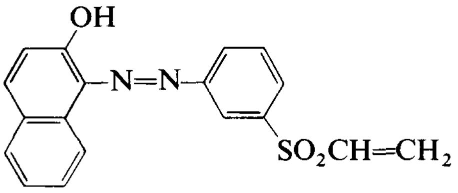
alkaline medium. These reaction conditions were very severe compared to the practical dyeing process. We have now carried out the reaction in water–dioxan solution with NaOH as alkali. The products of the reaction between the vinyl sulfone dye and methyl-α-D-glucoside were separated using thin-layer chromatography (TLC) techniques. The structures of the reaction products, i.e. the attaching sites of the glucosidic OH, were determined using a 400 Mz ^{1}H-NMR technique, both before and after the reaction. Two-dimensional ^{1}H-NMR was also used in some cases to confirm the structure of the reaction products. The constituents of the final reaction products were further identified by mass spectrometry, elemental analyses and other means.

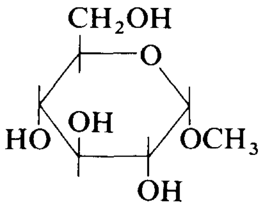
2 GENERAL DERIVATION OF RATE EQUATIONS

The structures of the vinyl sulfone reactive dye, methyl-α-D-glucoside and the reaction products concerned in the reaction are abbreviated to the following symbols:

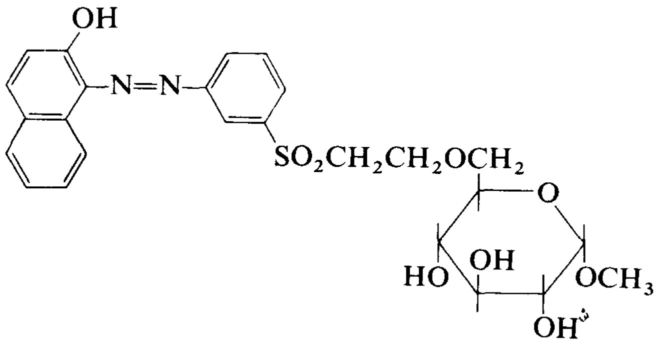
D:



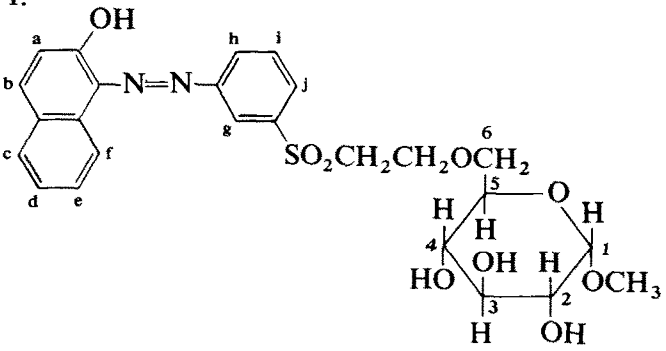
MOH:



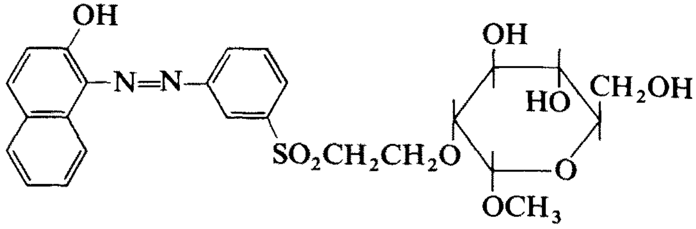
D$_6$:



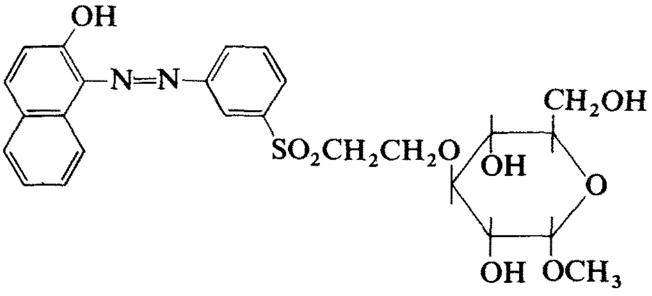
For spot 1:



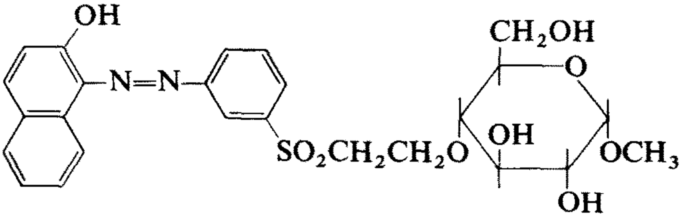
D$_2$:



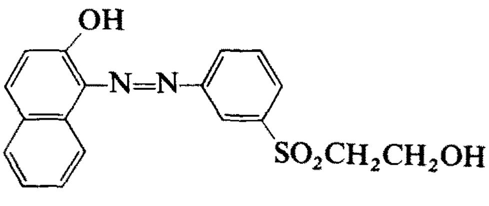
D$_3$:



D$_4$:



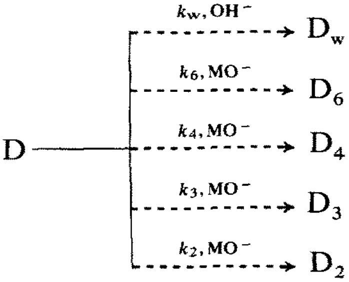
D$_w$:



The reactions between methyl-α-D-glucoside and the vinyl sulfone reactive dye in alkaline solution may be represented by the following equations:

$$\mathrm{MOH} + \mathrm{OH}^- \rightleftharpoons \mathrm{MO}^- + \mathrm{H_2O}$$

$$K_{\mathrm{eq}} = \frac{[\mathrm{MO}^-]}{[\mathrm{MOH}][\mathrm{OH}^-]} \quad \text{or } [\mathrm{MO}^-] = K_{\mathrm{eq}}[\mathrm{MOH}][\mathrm{OH}^-]$$



Therefore

$$\frac{-\mathrm{d}[\mathrm{D}]}{\mathrm{d}t} = k_w[\mathrm{D}][\mathrm{OH}^-] + k_6[\mathrm{D}][\mathrm{MO}^-] + k_4[\mathrm{D}][\mathrm{MO}^-] + k_3[\mathrm{D}][\mathrm{MO}^-] + k_2[\mathrm{D}][\mathrm{MO}^-]$$

In our experiments, a large excess of MOH and OH$^-$ was used. The above equation can therefore be written as

$$\frac{-\mathrm{d}[\mathrm{D}]}{\mathrm{d}t} = (k_w + k_6' + k_4' + k_3' + k_2')[\mathrm{D}][\mathrm{OH}^-]$$

$$= k'[\mathrm{D}][\mathrm{OH}^-] = k[\mathrm{D}]$$

where $k_6' = k_6 K_{\mathrm{eq}}[\mathrm{MOH}]$
$k_4' = k_4 K_{\mathrm{eq}}[\mathrm{MOH}]$
$k_3' = k_3 K_{\mathrm{eq}}[\mathrm{MOH}]$
$k_2' = k_2' K_{\mathrm{eq}}[\mathrm{MOH}]$
$k' = k_w + k_6' + k_4' + k_3' + k_2'$
$k = k'[\mathrm{OH}^-]$

By integrating,

$$\ln\frac{\mathrm{D}_0}{\mathrm{D}_t} = kt$$

and

$$\frac{\mathrm{D}_w}{\mathrm{D}_6} = \frac{k_w}{k_6'} \qquad \frac{\mathrm{D}_w}{\mathrm{D}_4} = \frac{k_w}{k_4'} \qquad \frac{\mathrm{D}_w}{\mathrm{D}_3} = \frac{k_w}{k_3'} \qquad \frac{\mathrm{D}_w}{\mathrm{D}_2} = \frac{k_w}{k_2'}$$

Since excess of MOH is used, its concentration is not significantly changed during the reaction, i.e.

$$k_6:k_4:k_3:k_2 = k'_6:k'_4:k'_3:k'_2$$

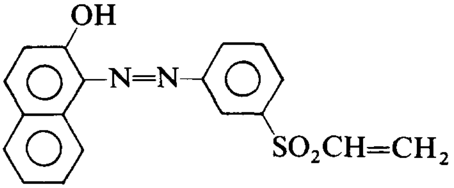
In the present case, we found that only D_4 and D_6 were actually formed, i.e.

$$k' = k_w + k'_6 + k'_4$$

Therefore, if the total rate constant k, and rate constants k'_6, k'_4 can be experimentally obtained, the relative rate constants k_6/k_4 may then be calculated using the above equations.

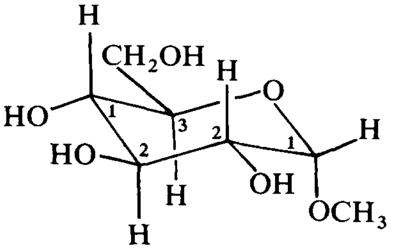
3 STARTING MATERIALS

The structure of the model vinyl sulfone reactive dye used is shown below. A dye structure in which the sulfonic acid group was not present was selected purely for convenience in its isolation and analysis.



m.p. 132°–134°C; $\lambda_{max} = 470$ nm (acetone); $m/z = 338$.
Analysis: found, C% 64·26 H% 4·20 N% 8·24
calc., 63·91 4·14 8·28

Methyl-α-D-glucoside was obtained from Janseen Chimica (Beerse, Belgium). This material was used without further purification.



The ^{1}H-NMR spectrum (Fig. 1) of this compound was determined in DMSO-d_6 with TMS as reference, using a Bruker AM 400. The data thus obtained was:

For methyl-α, D-glucopyranoside
^{1}*H*-NMR (400 MHz), DMSO-d_6/TMS: 3·26 (3H, S, OCH_3); 4·52 (1H, d, $J_{1,2} = 3{\cdot}6$ Hz, 1–H); 3·18 (1H, octa, $J_{1,2} = 3{\cdot}6$ Hz; $J_{2,3} = 9{\cdot}2$ Hz, $J_{2,2\text{-}OH} = 6{\cdot}1$ Hz,

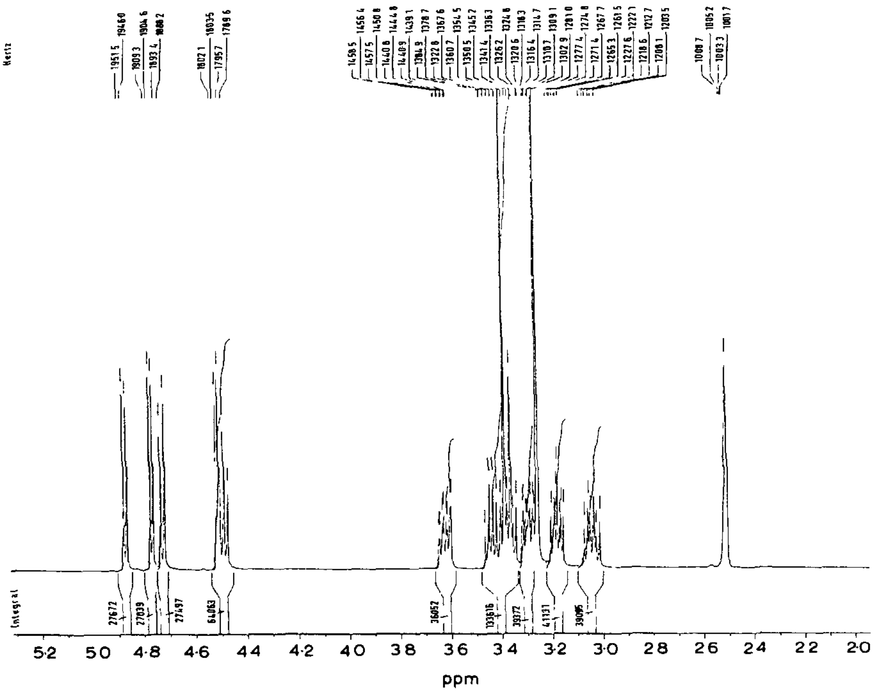


Fig. 1. ^{1}H-NMR spectrum of methyl-α-D-glucoside.

2–H); 4·73 (1H, d, $J_{2,2\text{-OH}} = 6{\cdot}1$ Hz, 2–OH); 3·38 (1H, hex, $J_{2,3} = 9{\cdot}2$ Hz, $J_{3,4} = 9{\cdot}2$ Hz, $J_{3,3\text{-OH}} = 5{\cdot}1$ Hz, 3–H); 4·77 (1H, d, $J_{3,3\text{-OH}} = 5{\cdot}1$ Hz, 3–OH); 3·05 (1H, hex, $J_{3,4} = 9{\cdot}2$ Hz, $J_{4,5} = 9{\cdot}2$ Hz, $J_{4,4\text{-OH}} = 5{\cdot}5$ Hz, 4–H); 4·87 (1H, d, $J_{4,4\text{-OH}} = 5{\cdot}5$ Hz, 4–OH); 3·29 (1H, octa, $J_{4,5} = 9{\cdot}2$ Hz, $J_{5,6a} = 6{\cdot}1$ Hz, $J_{5,6b} = 2{\cdot}0$ Hz, 5–H); 3·61 (1H, qua, $J_{5,6a} = 6{\cdot}1$ Hz, $J_{6a,6b} = 11{\cdot}6$ Hz, 6–H_a); 3·44 (1H, qua, $J_{5,6b} = 2{\cdot}0$ Hz, $J_{6a,6b} = 11{\cdot}6$ Hz, 6–H_b); 4·49 (1H, s, 6–OH).

4 RATE OF REACTION BETWEEN THE VINYL SULFONE REACTIVE DYE AND METHYL-α-D-GLUCOSIDE

A mixture of 0·02 g (0·059 mmol) of dye and 0·18 g (0·92 mmol) of methyl-α-D-glucoside (dye: glucoside = 1:15·6) in distilled water (2 ml) and dioxan (10 ml) was heated in a thermostat bath at 50 ± 1°C; 10% NaOH (0·0736 ml, 1·84 mmol) was similarly maintained at 50°C for 1 h. After addition of the NaOH to the dye solution, samples (0·05 ml) were removed at intervals, cooled immediately and the pH adjusted to 7 by addition of dilute HCl.

4.1 Separation of reaction products

Shimadzu CS-910 TLC–double scanning was used. Using a microinjector, 1 ml of reaction solution was dropped onto a chromatographic plate, made from silica gel G with 5% carboxymethylcellulose solution.

The spots were air-dried and the chromatogram was developed with chloroform–benzene–absolute ethyl alcohol (1:1:0·25).

Four spots were apparent, the mean R_F values of these being $R_{F1} = 0{\cdot}339$, $R_{F2} = 0{\cdot}425$, $R_{F3} = 0{\cdot}776$ and $R_{F4} = 0{\cdot}860$. The absorption maxima of these were $\lambda_{max}(1) = 469{\cdot}8$ nm, $\lambda_{max}(2) = 469{\cdot}2$ nm, $\lambda_{max}(3) = 470{\cdot}2$ nm and $\lambda_{max}(4) = 469{\cdot}4$ nm. The spots were provisionally identified as:

spot 1	reaction product 1 (in larger amount)
spot 2	reaction product 2 (in lesser amount)
spot 3	hydrolysed dye
spot 4	unreacted dye

4.2 Structural indentification of the reaction products

Spots 1 and 2 are the reaction products formed from interaction of the dye and the glucoside. These two spots were identified by elemental analyses, mass spectra and ^{1}H-NMR.

4.2.1 Elemental analysis

Spot 1	C%	H%	N%
Calc.	56·28	5·25	5·25
Found	56·35	5·27	5·14
Spot 2			
Calc.	56·28	5·25	5·25
Found	56·31	5·67	5·74

4.2.2 Mass spectra

Mass spectra showed a parent ion at *m/z* 533. Spots 1 and 2 may thus correspond to pure D_6, D_4, D_3 or D_2.

4.2.3 Melting point

Spot 1: m.p. 90·7–92·2°C; spot 2: m.p. 129–130°C.

4.3 Identification of reaction products by ^{1}H-NMR

The ^{1}H-NMR spectra of the constituents of spots 1 and 2 are shown in Figs 2 and 3. Parts of the ^{1}H-NMR spectra of spots 1 and 2 are shown enlarged in

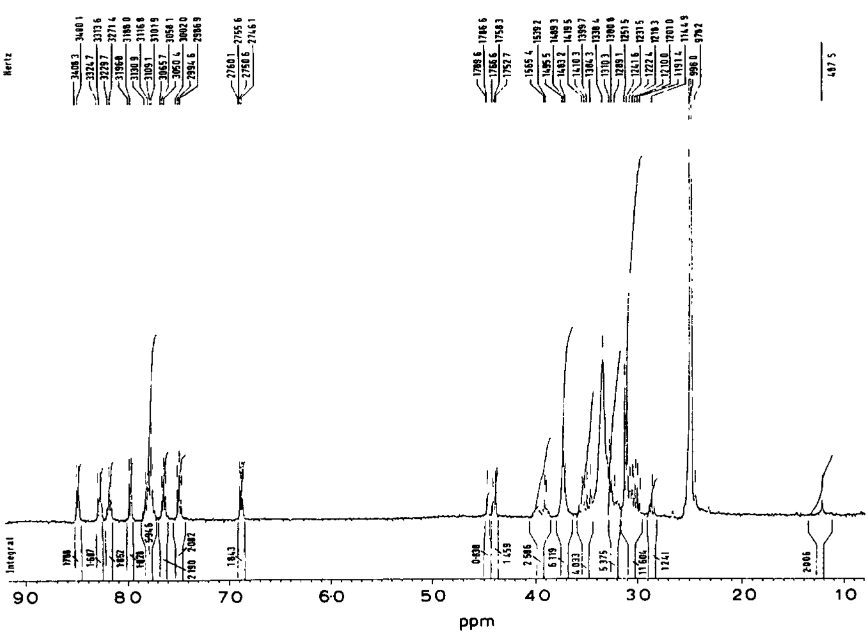


Fig. 2. ^{1}H-NMR spectrum of spot 1.

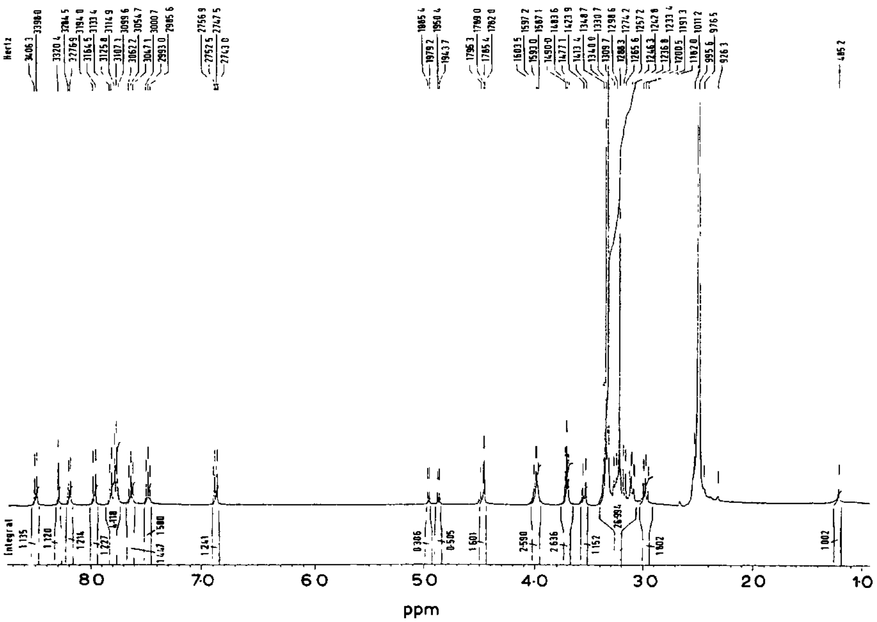


Fig. 3. ^{1}H-NMR spectrum of spot 2.

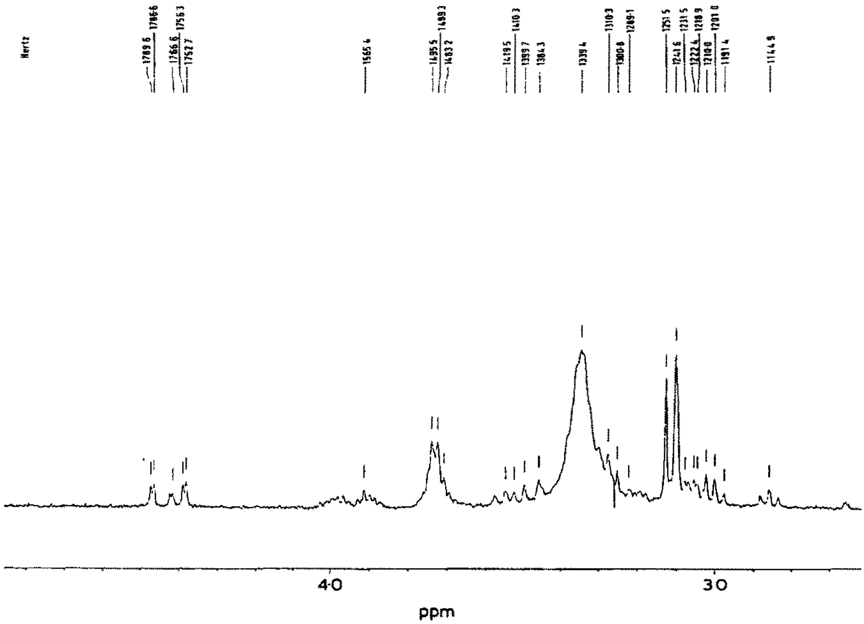


Fig. 4. ^{1}H-NMR spectrum of spot 1, partly enlarged.

Figs 4 and 5. The ^{1}H-NMR spectrum of spot 1 in D_2O is shown in Figs 6 and 7, and the ^{1}H-NMR spectrum of spot 2 in D_2O is shown in Fig. 8.

For spot 1

^{1}H-NMR (400 MHz), DMSO–d_6/TMS: 8·51 (1H, d, $J_{a,b}$ = 8·2 Hz, H_a); 7·66 (1H, d, $J_{b,c}$ = 8·2 Hz, H_b); 7·64 (1H, d, $J_{e,f}$ = 7·7 Hz, H_f); 7·77 (2H, t, $J_{c,d}$ = 7·5 Hz, $J_{d,e}$ = 7·5 Hz, H_c, H_e); 6·88 (1H, t, $J_{c,d}$ = $J_{d,e}$ = 7·5 Hz, H_d); 8·30 (1H, S, H_g); 8·19 (1H, d, $J_{f,g}$ = 8·3 Hz, H_h); 7·49 (1H, t, $J_{f,g}$ = $J_{g,h}$ = 7·6 Hz; H_i); 7·98 (1H, d, $J_{i,j}$ = 8·8 Hz, H_j); 3·53 (2H, t, J = 9·9 Hz, C—CH_2O); 3·72 (2H, t, J = 6·2 Hz, S—CH_2—C); 4·52 (1H, d, $J_{1,2}$ = 3·6 Hz, 1–H); 3·26 (3H, S, OCH_3); 3·18 (1H, octa, $J_{1,2}$ = 3·6 Hz, $J_{2,3}$ = 9·2 Hz, $J_{2,2\text{-}OH}$ = 6·1 Hz; 2–H); 4·73 (1H, d, $J_{2,2\text{-}OH}$ = 6·1 Hz; 2–OH); 3·38 (1H, hex, $J_{2,3}$ = 9·2 Hz, $J_{3,4}$ = 9·2 Hz, $J_{3,3\text{-}OH}$ = 5·1 Hz; 3–H); 4·77 (1H, d, $J_{3,3\text{-}OH}$ = 5·1 Hz; 3–OH); 3·05 (1H, hex, $J_{3,4}$ = 9·2 Hz, $J_{4,5}$ = 9·2 Hz, $J_{4,4\text{-}OH}$ = 5·5 Hz, 4–H); 4·87 (1H, d, $J_{4,4\text{-}OH}$ = 5·5 Hz, 4–OH); 3·29 (1H, octa, $J_{4,5}$ = 9·2 Hz, $J_{5,6a}$ = 6·1 Hz, $J_{5,6b}$ = 2·0 Hz, 5–H); 3·61 (1H, qua, $J_{5,6a}$ = 6·1 Hz, $J_{6a,6b}$ = 11·6 Hz, 6–H_a); 3·44 (1H, qua, $J_{5,6b}$ = 2·0 Hz, $J_{6a,6b}$ = 11·6 Hz, 6–H_b).

For spot 2

^{1}H-NMR (400 MHz), DMSO–d_6/TMS: 8·51 (1H, d, $J_{a,b}$ = 8·3 Hz, H_a); 7·65 (1H, d, $J_{b,c}$ = 8·3 Hz, H_b); 7·63 (1H, d, $J_{e,f}$ = 7·6 Hz, H_f); 7·77 (2H, t, $J_{c,d}$ = 7·6 Hz, $J_{d,e}$ = 7·7 Hz, H_b, H_e); 6·88 (1H, t, $J_{c,d}$ = $J_{d,e}$ = 7·5 Hz, H_d); 8·30 (1H, S, H_g); 8·20

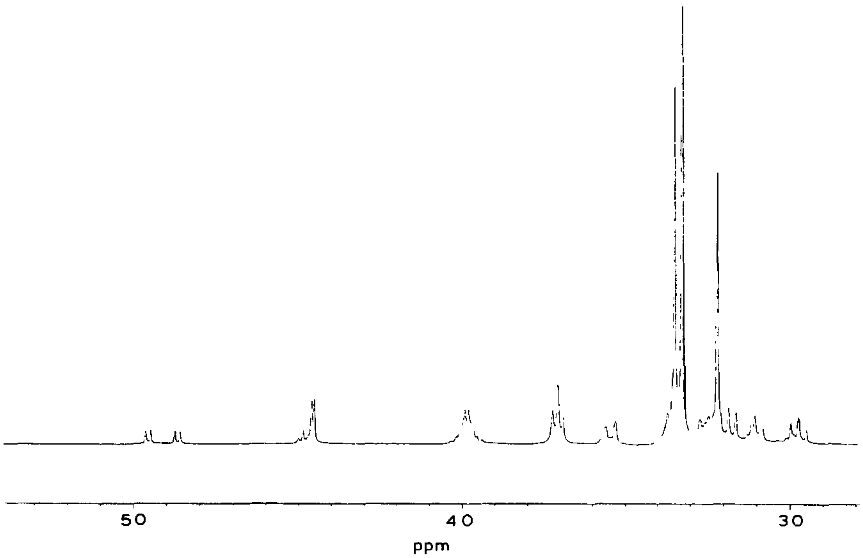


Fig. 5. ^{1}H-NMR spectrum of spot 2, partly enlarged.

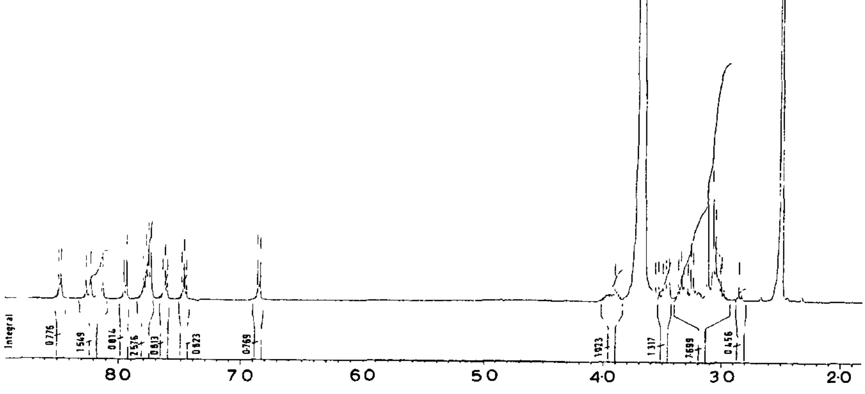


Fig. 6. ^{1}H-NMR spectrum of spot 1 with addition of D_2O.

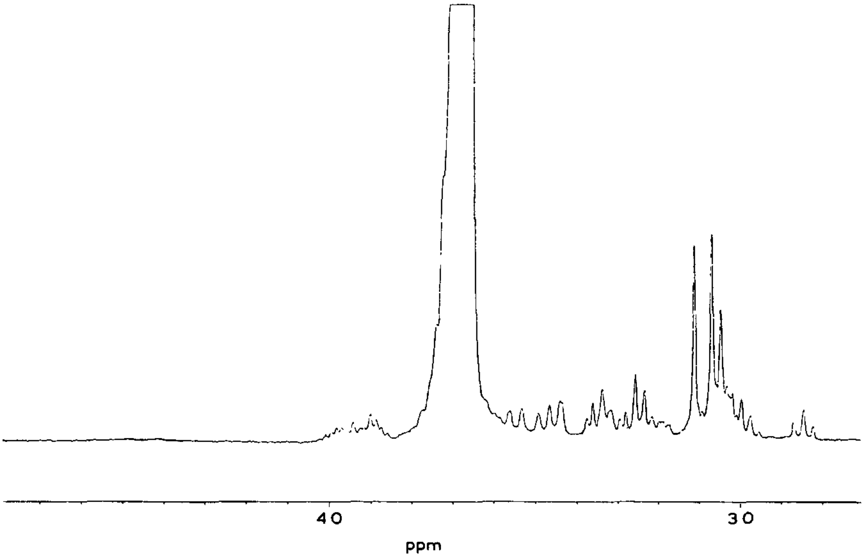


Fig. 7. ^{1}H-NMR spectrum of spot 1 with addition of D_2O, partly enlarged.

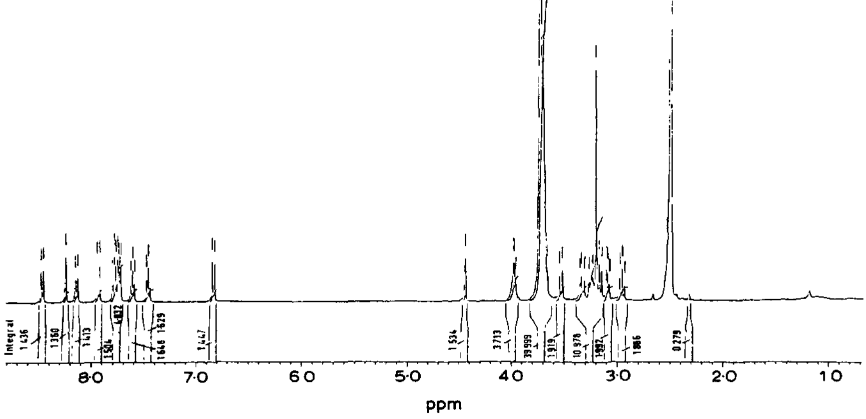


Fig. 8. ^{1}H-NMR spectrum of spot 2 with addition of D_2O.

(1H, d, $J_{f,g}$ = 8·3 Hz, H_h); 7·48 (1H, t, $J_{f,g} = J_{g,h}$ = 7·6 Hz; H_i); 7·97 (1H, d, $J_{i,j}$ = 9·0 Hz, H_j); 3·35 (2H, t, J = 9·0 Hz, C—CH_2O); 3·69 (2H, t, J = 6·5 Hz, S—CH_2—C); 4·52 (1H, d, $J_{1,2}$ = 3·6 Hz, 1–H); 3·26 (3H, S, OCH_3); 3·18 (1H, octa, $J_{1,2}$ = 3·6 Hz, $J_{2,3}$ = 9·2 Hz, $J_{2,\text{-OH}}$ = 6·1 Hz, 2–H); 4·87 (1H, d, $J_{2,2\text{-OH}}$ = 6·1 Hz; 2–OH); 3·38 (1H, hex, $J_{2,3}$ = 9·2 Hz, $J_{3,4}$ = 9·2 Hz, $J_{3,3\text{-OH}}$ = 5·1 Hz, 3–H); 4·96 (1H, d, $J_{3,3\text{-OH}}$ = 5·1 Hz, 3–OH); 3·05 (1H, qua, $J_{3,4}$ = 9·2 Hz, $J_{4,5}$ = 9·2 Hz, 4–H); 3·29 (1H, octa, $J_{4,5}$ = 9·2 Hz, $J_{5,6a}$ = 6·2 Hz, $J_{5,6b}$ = 2·0 Hz, 5–H); 3·61 (1H, qua, $J_{5,6a}$ = 6·2 Hz, $J_{6a,6b}$ = 11·6 Hz, 6–H_a); 3·44 (1H, qua, $J_{5,6b}$ = 2·0 Hz, $J_{6a,6b}$ = 11·6 Hz, 6–H_b); 4·46 (1H, s, 6–OH).

The ^{1}H-NMR of methyl-α-D-glucoside (Fig. 1) shows 6–OH to be at δ4·49, and in the ^{1}H-NMR spectrum of the 6–OH reaction product 1, this peak 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 4·73 to 4·39, for 3–OH from 4·77 to 4·42 and for 4–OH, from 4·87 to 4·47. Figure 6 shows the ^{1}H-NMR spectrum with D_2O added; the peaks

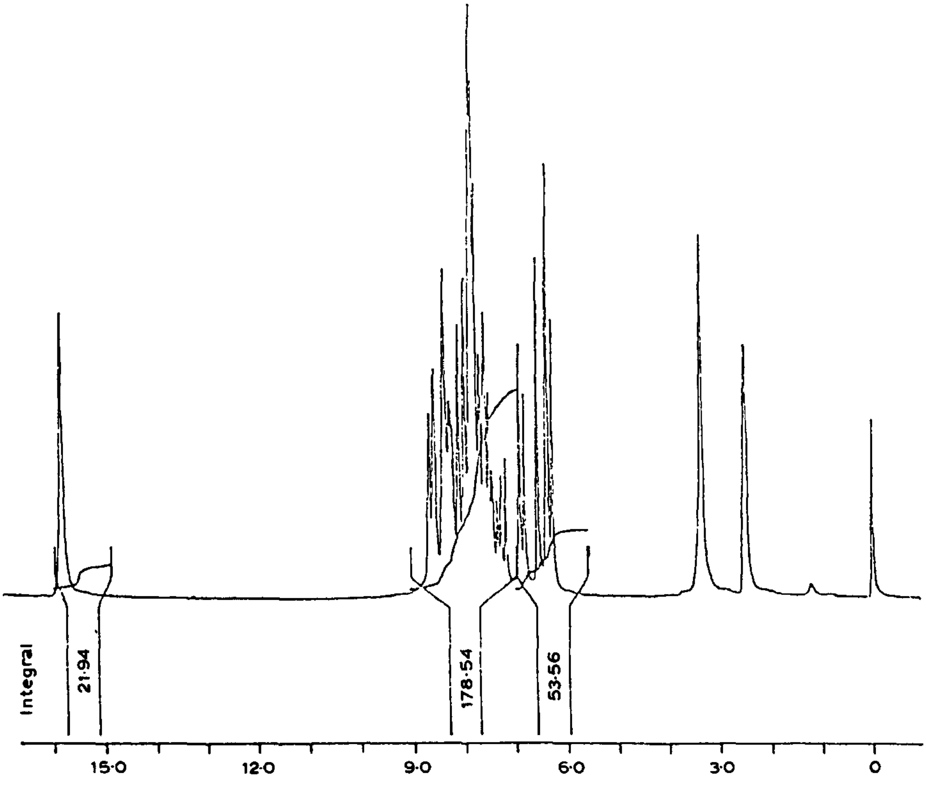
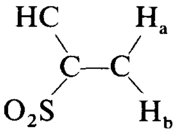


Fig. 9. ^{1}H-NMR spectrum of vinyl sulfone dye.

for 2–OH, 3–OH and 4–OH are absent. From Fig. 9, compared to the starting dye, the doublet ethylenic hydrogen



δ_a (6·23), δ_b (6·43) and δ_c (6·86) are absent, and a peak at $\delta = 3{\cdot}525$, is present, indicating the presence of ethanic H. Thus, the reaction product (spot 1) can be identified as D_6.

In the ^{1}H-NMR spectrum of reaction product 2 (spot 2), the doublet at $\delta = 4{\cdot}87$ has disappeared, but the doublets of 2–OH and 3–OH, and the triplet of 6–OH at $\delta = 4{\cdot}46$ still remain. Because of the attachment of the dye molecule, the bond angles of the six-membered ring cause shifts of 2–OH from $\delta = 4{\cdot}725$ to $\delta = 4{\cdot}87$, and of 3–OH from $\delta = 4{\cdot}77$ to 4·87. 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. Therefore, the structure of the reaction product 2 (spot 2) can be assigned to D_4.

Using ^{1}H-NMR at 60 MHz, it was impossible to differentiate the various OH groups in the methyl-α-D-glucoside molecule. The structural identification can only be done by indirect prediction of the chemical shift changes of the ring H atoms, and the structure cannot be precisely determined.

4.4 Determination of the quantitative yields of the reaction products by TLC–double scanning

A standard solution of the dye in acetone, at a concentration of 0·005 g/ml was prepared. Aliquot portions of this solution were further diluted to give a series of solutions of concentration a_n ($n = 1$–6). The samples were applied to chromatographic plates, developed and scanned. The peak areas of the spots

TABLE 1
Peak Areas and Dosage Weights of Vinyl Sulfonyl Dye

Sample	*Dosage weights, a* ($\times 10^{-8}$ *g*)	*Peak area,* A_1 (*relative units*)
a_1	60	462·53
a_2	30	25 130
a_3	15	11 567
a_4	7·5	5 264
a_5	3·75	3 292
a_6	1·875	1 168

TABLE 2
Peak Area and Dosage Weights of Hydrolysed Vinyl Sulfonyl Dye

Sample	*Dosage weight, b* ($\times 10^{-8}$ g)	*Peak areas A_2* (*relative units*)
b_1	60	68 579
b_2	30	29 865
b_3	15	15 314
b_4	7·5	6 288
b_5	3·75	3 029
b_6	1·875	1 875

TABLE 3
Peak Areas and Dosage Weights of Vinyl Sulfone Dye–Methylglucoside-6

Sample	*Dosage weight, c* ($\times 10^{-9}$ g)	*Peak area A_3* (*relative units*)
c_1	200	21 704
c_2	100	10 135
c_3	50	5 108
c_4	25	2 145
c_5	12·5	994
c_6	6·25	506

TABLE 4
Peak Areas and Dosage Weight of Vinyl Sulfone Dye–Methylglucoside-4

Sample	*Dosage weight, d* ($\times 10^{-9}$ g)	*Peak area A_4* (*relative units*)
d_1	200	20 258
d_2	100	10 026
d_3	50	4 983
d_4	25	2 021
d_5	12·5	852
d_6	6·25	501

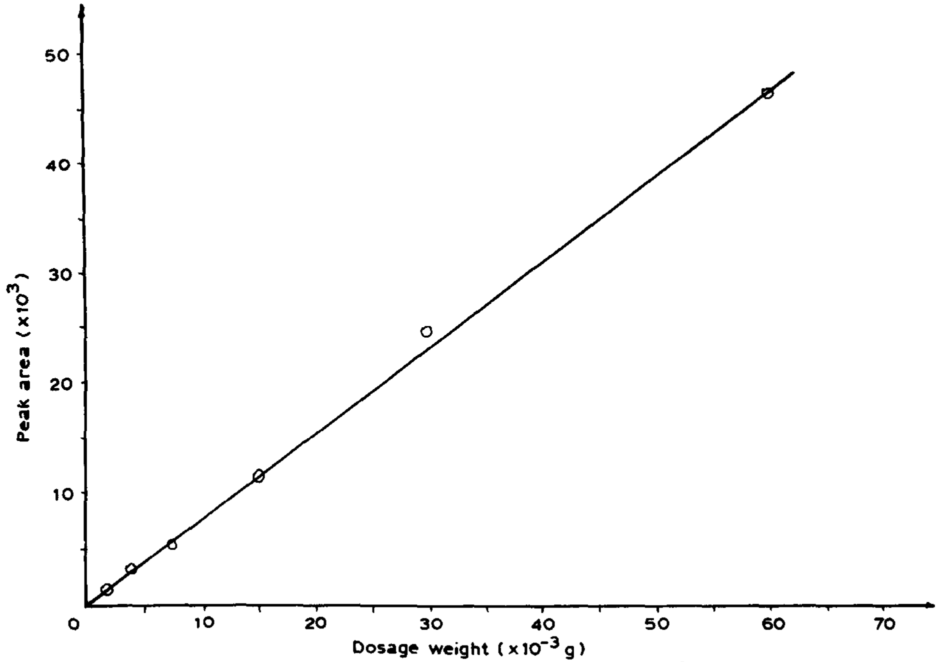


Fig. 10. Standard curve of vinyl sulfone dye: $A_1 = 7{\cdot}812 \times 10^{10}\ a + 66{\cdot}184$; $r = 0{\cdot}9987$; $k_1 = 7{\cdot}812 \times 10$.

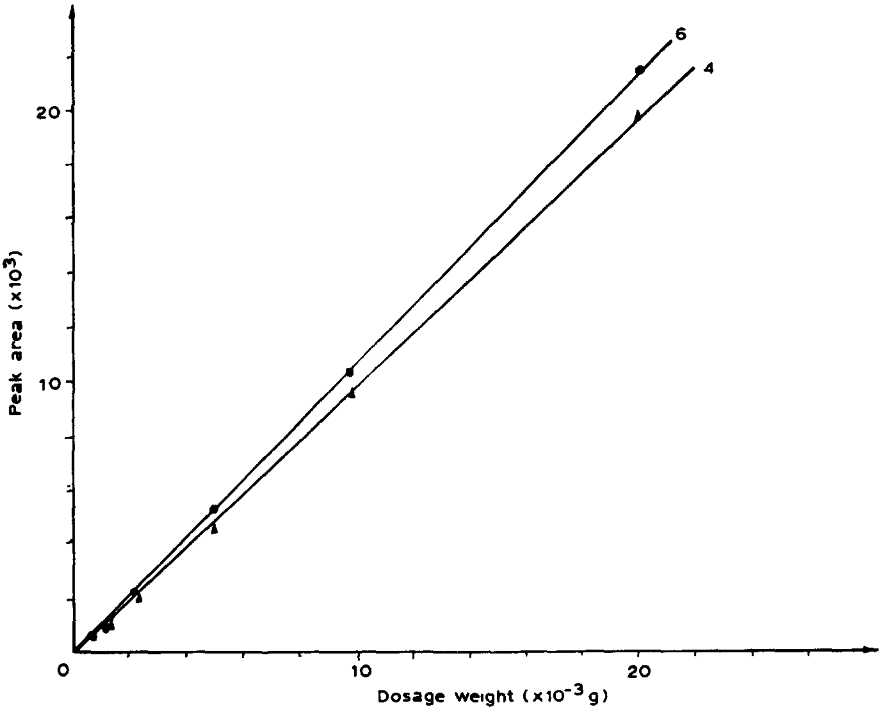


Fig. 11. Standard curve of dye-glucoside-4 and dye-glucoside-6: $A_3 = 1{\cdot}097 \times 10^{11}\ c - 434{\cdot}74$; $r_3 = 0{\cdot}9996$; $k_3 = 1{\cdot}097 \times 10$; $A_4 = 1{\cdot}0305 \times 10^{11}\ d - 322{\cdot}3$; $r_4 = 0{\cdot}9764$; $k_4 = 1{\cdot}0305 \times 10$.

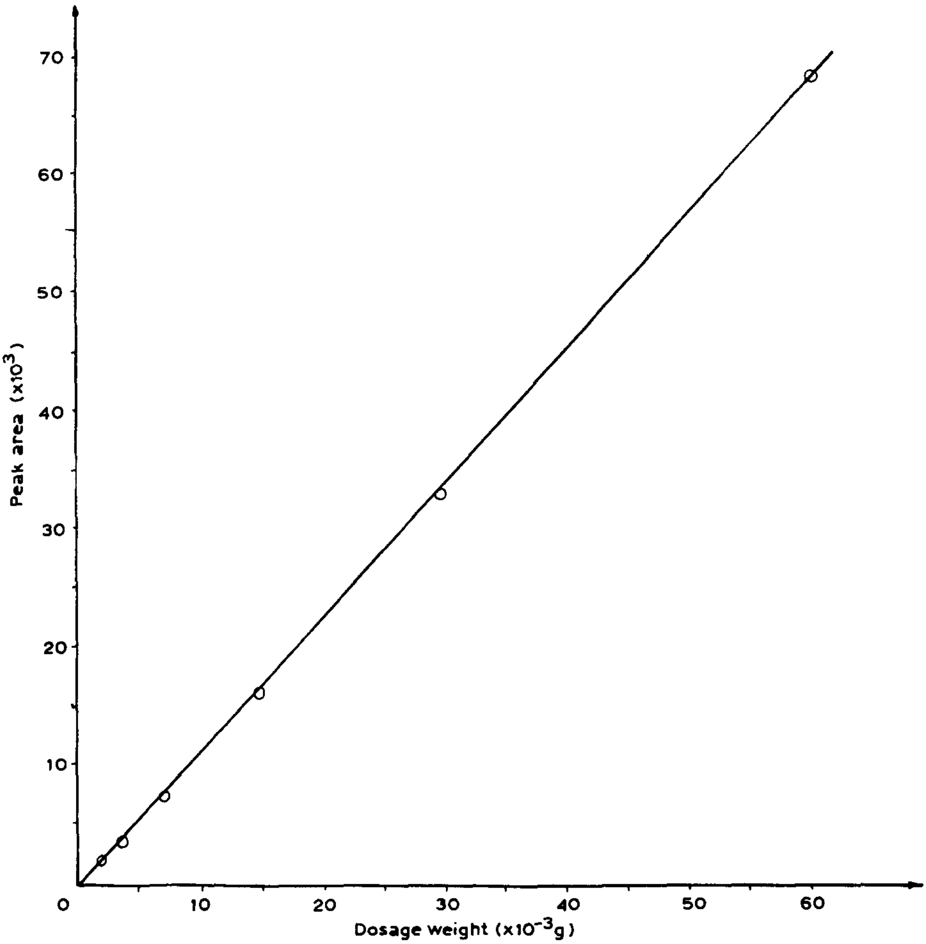


Fig. 12. Standard curve of hydrolyzed dye: $A_2 = 11{\cdot}493 \times 10^{10} b - 1801{\cdot}57$; $r_2 = 0{\cdot}9980$; $k_2 = 11{\cdot}4930$.

were obtained and plots were made for the peak areas versus corresponding dosage weights. Standard curves for the model vinyl sulfone dye, hydrolysed dye, vinyl sulfone dye–methylglucoside-6 and vinyl sulfone dye–methyl glucoside-4 were obtained (see Tables 1–4).

The standard curves are shown in Figs 10, 11 and 12, which also give the pertinent regression equation, correlation coefficients and slopes of the plots.

4.5 Determination of rate constants of the reaction between the dye and methylglucoside

From the standard curves of vinyl sulfonyl dye–methyl glucoside-6 and vinyl sulfone dye–methyl glucoside-4 (abbreviated as D_6 and D_4), the

TABLE 5
Experimental Data and Calculated Results of the Reaction Between the Dye and Methylglucoside at 50 ± 1°C

Time (min)	A_6	A_4	A_w	A_D	D_t/D_w	D_4/D_w	ln D_0/D_t
0	—	—	—	16485	—	—	—
4	5982	881	1000	13633	6·115	0·968	0·190
5	7158	937	1090	8095	6·71	0·980	0·712
6	7258	1015	1144	6250	6·47	0·975	0·970
8	8377	1192	1347	4862	6·35	0·973	1·221
10	10518	1427	1619	4165	6·67	0·969	1.376
mean	—	—	—	—	6·46	0·973	—

quantities of D_6 and D_4 after various reaction times (in minutes), can thus be determined:

$$A_w = r_w D_w \qquad A_6 = r_6 D_6 \qquad A_4 = r_4 D_4$$

$$\frac{D_6}{D_w} = \frac{A_6 r_w}{A_w r_6} \qquad \frac{D_4}{D_w} = \frac{A_4 r_w}{A_w r_4} \qquad \frac{D_0}{D_t} = \frac{A_0}{A_t}$$

When the reaction is proceeding over a period of 10 min, D_6/D_w and D_4/D_w may be considered as constant because within this time limit, the dye–methylglucoside product is not undergoing any hydrolysis, i.e. $D_6/D_w = C_1$ = constant, $D_4/D_w = C_2$ = constant, and $D_0/D_t = A_0/A_t$.

The experimental and calculated results at 50 ± 1°C are shown in Table 5.

On plotting ln D_0/D_t against time t in minutes at 50 ± 1°C, a straight line is obtained (Fig. 13); the regression equation and the correlation coefficient at 50 ± 1°C are: $y = 0·1411x - 0·25235$, and $r = 0·9748$. The slope of the line k, i.e. total rate constant of the reaction at 50 ± 1°C, is 0·1411.

TABLE 6
Experimental Data and Calculated Results of Reaction Between Dye and Methylglucoside at 60 ± 1°C

Time (min)	A_6	A_4	A_w	A_D	D_6/D_w	D_4/D_w	ln D_0/D_t
1	—	—	—	8041	—	—	—
2	786·5	138·8	260·9	6651·2	3·082	0·544	0·338
2·5	1400	233·4	452·6	6270·1	3·162	0·527	0·392
3	1912	333·1	648·5	5940·2	3·015	0·523	0·453
3·5	2195	388·9	728·6	5360 3	3·080	0·546	0·556
4	2092	421·1	834·7	5638·7	2·632	0·543	0·562
4·5	2000	773·3	1031·8	4067·6	—	—	—
mean					3·085	0·535	—

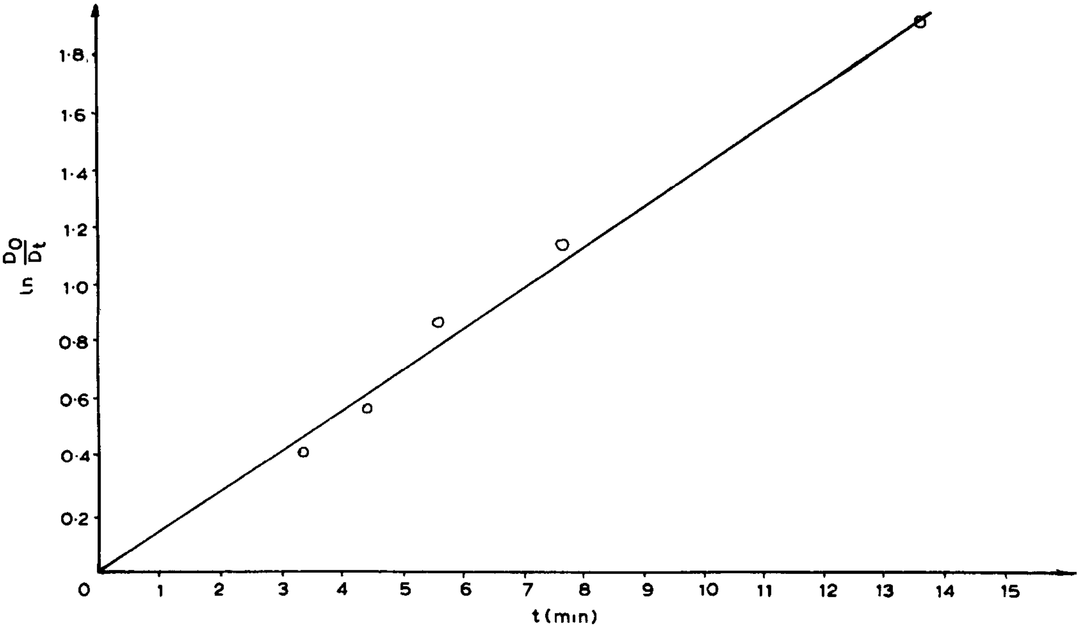


Fig. 13. A plot of $\ln D_0/D_t$ versus time (t) at 50 ± 1°C.

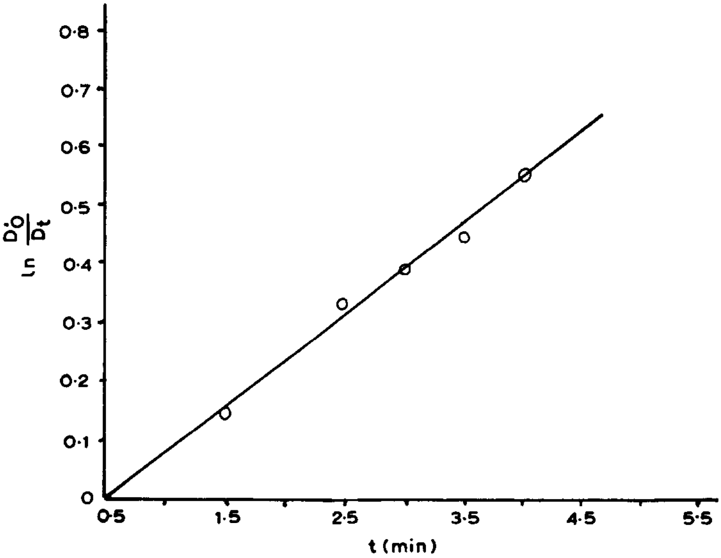


Fig. 14. A plot of $\ln D'_0/D_t$ versus time (t) at 60 ± 1°C.

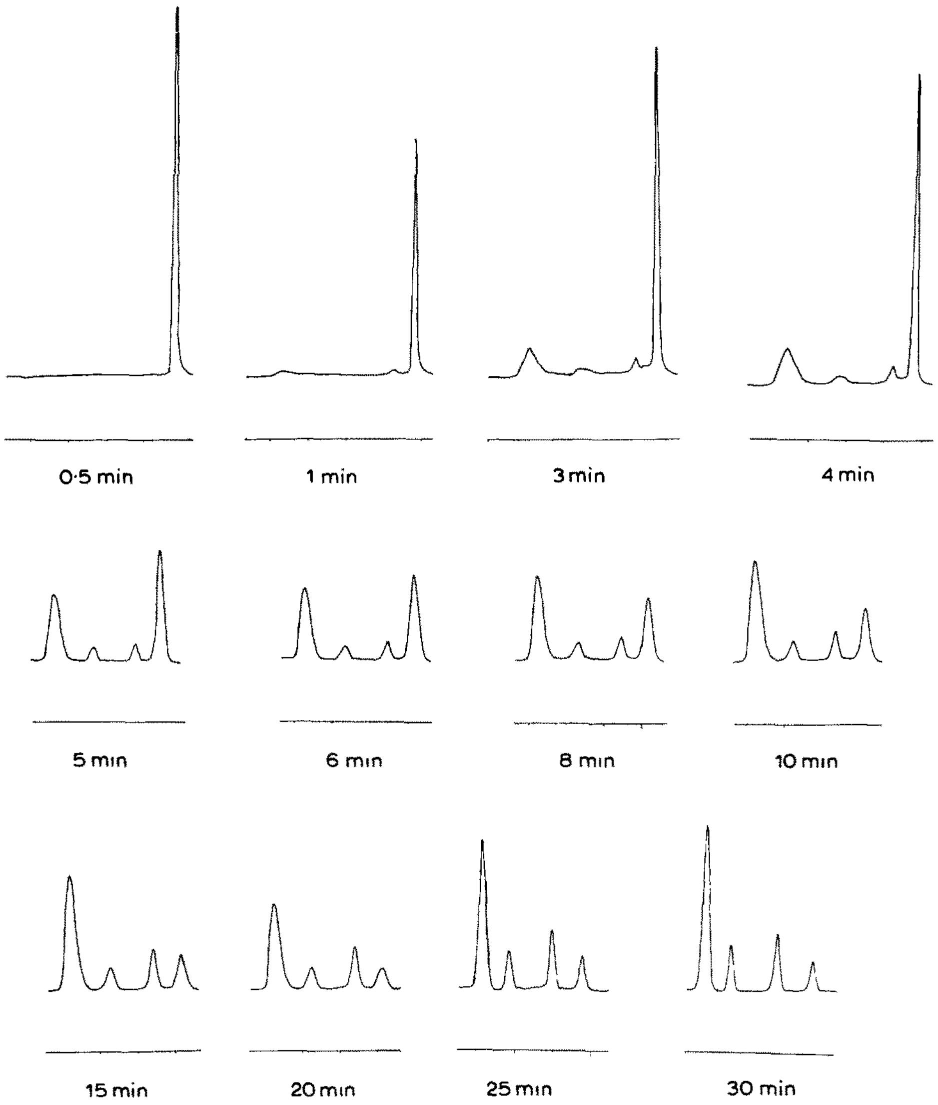


Fig. 15. The formation of reaction product plots by TLC–double scanning at 50 ± 1°C.

Similarly, the total rate constant of the reaction at 60 ± 1°C was obtained. The experimental and calculated results at 60 ± 1°C are shown in Table 6; the regression equation and the correlation coefficient at 60 ± 1°C are: $y = 0{\cdot}1603x - 0{\cdot}34981$, and $r = 0{\cdot}9873$. The slope of the line k, i.e. the total rate constant of the reaction at 60 ± 1°C, is 0·1603 (see Fig. 14).

The course of reaction between the vinyl sulfone reactive dye with methyl-α-D-glucoside at 50 ± 1°C and 60 ± 1°C is clearly shown by TLC–double scanning plots (see Fig. 15).

TABLE 7

The Formation of D_6, D_4 and D_w after Different Times (t) at 50 ± 1°C

Time (min)	D_6 (%)	D_4 (%)	D_w (%)	D (%)
0	—	—	—	100
4	26·2	4·29	5·6	64·01
5	41·4	6·53	6·7	54·63
6	46·3	7·38	7·5	38·82
8	52·7	9·31	9·4	28·59
10	58·0	9·50	10·3	22·20

TABLE 8

The Formation of D_6, D_4 and D_w after Different Times (t) at 60 ± 1°C

Time (min)	D_6 (%)	D_4 (%)	D_w (%)	D (%)
2	10·4	1·81	2·7	85·09
2·5	16·6	2·69	4·7	76·00
3	21·6	3·68	9·7	65·02
3·5	23·8	3·82	10·1	62·28

TABLE 9

The Relative Amounts of D_6 and D_4 After Different Times (t) at 50 ± 1°C

Time (min)	D_6 (%)	D_4 (%)
0	—	—
4	85·89	14·11
5	86·38	13·62
6	86·25	13·75
8	84·99	15·01
10	85·93	14·07
mean	85·89	14·11

TABLE 10

The Relative Amounts D_6 and D_4 after Different Times (t) at 60 ± 1°C

Time (min)	D_6 (%)	D_4 (%)
2	85·21	14·79
2·5	86·05	13·95
3	85·44	14·56
3·5	86·16	13·84
mean	85·72	14·28

4.6 Calculation of the reaction amounts of D_6 and D_4

The relative reactivities of —$CH_2OH(6)$ and —CHOH(4) at 50 ± 1°C and 60 ± 1°C were calculated as shown in Tables 7 and 8. The relative amounts of D_6 and D_4 after different times (t) at 50 ± 1°C and 60 ± 1°C are given in Tables 9 and 10.

From Tables 9 and 10, it is apparent that the relative amounts of D_6 and D_4 formed at 50 or 60°C are the same. As far as methylglucoside is concerned, the relative reactivities of 6–OH to 4–OH are:

$$k_6/k_4 = k'_6/k'_4 = 85{\cdot}89/14{\cdot}11 = 6{\cdot}087, \quad \text{at } 50 \pm 1^\circ\text{C}$$
$$k_6/k_4 = k'_6/k'_4 = 85{\cdot}72/14{\cdot}25 = 6{\cdot}015, \quad \text{at } 60 \pm 1^\circ\text{C}$$

i.e. the reactivity of —$CH_2OH(6)$ is equal to 6·087 times that of —CH(OH) (4) at 50°C, and 6·015 times that of —CHOH (4) at 60°C.

5 CONCLUSIONS

The competitive reactions of different OH groups of methyl-α-D-glucoside, reacted homogeneously with a model vinyl sulfone reactive dye, have been studied at 50 and 60°C. The reaction was carried out in water–dioxan in the presence of NaOH. The reaction products were separated by TLC–double scanning methods. Only D_6 and D_4 were found to be present. The relative amounts of D_6 to D_4 were 85·89%: 14·11% at 50°C and 85·72: 14·25 at 60°C.

The reaction products D_6 and D_4 were identified by 400 MHz ^{1}H-NMR, mass spectrometry and elemental analyses. The structure of methyl-α-D-glucoside was also studied by 400 MHz ^{1}H-NMR.

The reactivity of —$CH_2OH(6)$ in methyl-α-D-glucoside was found to be 6·087 times that of —CHOH(4) at 50°C, and 6·015 times that of —CHOH(4) at 60°C for the same glucoside molecule with the model vinyl sulfone reactive dye.

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