PART IV

DISCUSSION

4A....... COUMARINS

4B... NITROTOLUENES

4 A.1

ULTRAVIOLET ABSORPTION SPECTRA

Table U 4.01

Values of λ and log ∈ for maxima for the ultraviolet absorption spectra of 7-hydroxy and 7-methoxy monomethylcoumarins.

Solvent :	Methanol		10% Methanol			Methanol		10% Methanol	
Compound	λm	log∈	λm	log∈	Compound	λm	log∈	λm	log∈
* I	274	4.03	278	4.03	-	-	-	-	-
	311	3.74	300-12	3.79	-	-	-	-	-
**7-OHI	254	3.41	252	3.38	**7-MeOI	318-22	4.16	322-25	4.16
	325	4.16	325	4.13		-	-	-	-
* 7-OH-4-MeI	322	4.14	322	4.11	7-MeO-4-MeI	320	4.19	320	4.18
7-OH-5-MeI	328	4.17	326-30	4.12	7-MeO-5-MeI	254	3.54	-	-
	-	-	-	-		326-28	4.15	326-28	4.13
7-OH-8-MeI	258	3.63	254-56	3.64	7-MeO-8-MeI	256	3.60	254	3.63
	326-28	4.11	326-28	4.08		322-24	4.17	324-26	4.15

* Dr.R.A.Bhatt, Ph.D.Thesis (1968), Baroda.

** Dr.M.J.Mehta, Ph.D.Thesis (1968), Baroda.

Table U 4.02

Values of λ and logϵ for maxima for the ultraviolet absorption spectra of trisubstituted hydroxy and methoxycoumarins.

Solvent :	Methanol		10% Methanol			Methanol		10% Methanol	
Compound	λm	logϵ	λm	logϵ	Compound	λm	logϵ	λm	logϵ
*5-OH-4-MeI	250	3.91	250	3.90	-	-	-	-	-
	296	4.08	296	4.05		-	-	-	-
**5-OH-4,7-diMeI	302-4	4.13	304-6	4.13	5-MeO-4,7-diMeI	304-6	4.16	308-10	4.14
**5,7-diOH-4-MeI	256-58	3.82	256	3.77	5,7-diMeO-4-MeI	254	3.67	254	3.87
	322-24	4.10	320	4.06		320	4.17	320	4.18
7-OH-4-MeI	322	4.14	322	4.11	7-MeO-4-MeI	320	4.19	320	4.18
**7-OH-4,8-diMeI	324	4.15	322	4.12	7-MeO-4,8-diMeI	254	3.07	254	3.66
	-	-	-	-		320	4.16	320	4.16
***7,8-diOH-4-MeI	260-62	3.95	258-60	3.90	7,8-diMeO-4-MeI	-	-	-	-
	322	4.08	320-22	4.05		314-18	4.17	318	4.17

* Dr.R.A.Bhatt, Ph.D.Thesis (1968), Baroda.

** Dr.R.S.Hegde, Ph.D.Thesis (1969), Baroda.

*** Dr.D.J.Patel, Ph.D.Thesis (1965), Baroda.

Table U 4.03

Values of λ and log ϵ for maxima for the ultraviolet absorption spectra of coumarin carboxylic acids.

Compound	Solvent	pH	λm	log ϵ	λm	log ϵ
*7-OH-4-MeI	M	-	-	-	322	4.14
	TM	7-1	-	-	322	4.11
7-OH-4-MeI-6-COOH	w	7-3	-	-	326-28	4.17
		2-0.5	-	-	326	4.14
7-OH-4-MeI-8-COOH	w	7-4	266	3.83	330	4.11
		2	266	3.84	328	4.09
		1-0.5	266	3.86	326-28	4.08

I : coumarin

M : methanol

TM : 10 % aqueous methanol

w : water

* Dr. R.A.Bhatt, Ph.D.Thesis (1968) Baroda.

Table U 4.04

Values of λ and $\log \epsilon$ for maxima in ultraviolet absorption of 4-hydroxy and 4-methoxycoumarins.

Compound	Solvent	pH	λ_m	$\log \epsilon$	λ_m	$\log \epsilon$	λ_m	$\log \epsilon$
*4-OHI	M	-	270	3.93	280	4.01	302	3.96
	TM	7-6	-	-	286	4.11	294	4.08
		5	-	-	282-83	4.11	292-98	4.06
		4	270	4.00	280	4.09	300	3.96
		3-1	270	4.00	280	4.09	300	3.70
**4-MeOI	M	-	264	4.04	275	4.03	300	3.83
	TM	7-1	267	4.07	276	4.07	300	3.87
4,5-diOHI	M	-	-	-	292	4.05	-	-
	TM	7	-	-	292	4.11	-	-
		3-1	-	-	294	4.10	-	-
4-OH-5-MeOI	M	-	-	-	294	4.07	-	-
	TM	7	-	-	296	4.08	-	-
		4	-	-	296	4.14	-	-
		2	-	-	294-98	4.13	-	-
		1	-	-	292	4.14	-	-
4,5-diMeOI	M	-	-	-	286	4.09	-	-
	TM	7-1	-	-	292	4.11	-	-
4,6-diOHI	M	-	276	3.98	286	3.76	320	3.52
	TM	7	-	-	296	4.12	-	-
		4	276	4.07	286	4.01	322	3.74
		2	276	4.08	-	-	326	3.72
		1	276	4.09	-	-	326	3.73

Table U 4.04 (contd.)

4-OH-6-MeOI	M	-	-	-	286	4.00	316	3.84
	TM	7	-	-	296	4.12	-	-
		3	274	4.08	-	-	324	3.77
		2.6-1	274	4.10	-	-	324	3.77
4,6-diMeOI	M	-	270	3.99	280	3.86	326	3.69
	TM	7-1	270	4.07	-	-	324	3.70
*4,7-diOHI	M	-	-	-	284	3.97	304	4.16
	TM	7-4	-	-	284	3.99	302	4.14
		3-1	-	-	282	3.87	308	4.13
*4-OH-7-MeOI	M	-	-	-	284	4.05	303	4.21
	TM	7-4	-	-	284	4.07	302	4.23
		3-1	-	-	282	3.93	308	4.22
**4,7-diMeOI	M	-	-	-	280	3.92	305	4.19
	TM	7-1	-	-	280	3.92	306	4.20

* Dr. R.S.Hegde, Ph.D. Thesis (1969) Baroda.

** Dr. M.J.Mehta, Ph.D.Thesis (1968) Baroda.

Table U 4.05

Invariant wavelengths and log ϵ for 4-hydroxycoumarins.

Compound	λ mμ	log ϵ
*4-OHI	315	3.79
4,5-diOHI	304	4.05
4,6-diOHI	280	4.03
*4,7-diOHI	306	4.12
4-OH-5-MeOI	306	4.13
4-OH-6-MeOI	280	4.04
*4-OH-7-MeOI	307	4.21

* Dr.R.S.Hegde, Ph.D.Thesis (1969), Baroda.

Table U 4.06

Values of λ and log ϵ for maxima for the ultraviolet absorption spectra of ortho-, meta- and para-nitrotoluenes.

Compound :	ortho		meta		para	
Solvent:	λm	log ϵ	λm	log ϵ	λm	log ϵ
Water	265	3.69	273	3.84	285	3.94
10% methanol	265	3.71	272.5	3.85	284	3.95
20% "	264	3.72	272	3.86	283	3.97
40% "	264	3.75	272	3.88	282	3.99
60% "	262	3.72	270	3.87	281	3.97
80% "	261	3.71	268	3.87	279	3.97
100% "	258	3.78	265	3.88	273.5	3.98

4 A.1 Ultraviolet absorption spectra of coumarins :

I Methyl substituted 7-hydroxy and 7-methoxycoumarins :

Tables (U 3.01 - U 3.07) give ultraviolet absorption data for coumarin, 7-hydroxy and 7-methoxycoumarins and methyl substituted 7-hydroxy and 7-methoxycoumarins in methanol and aqueous methanol and Table (U 4.01) summarises the values of λ m and log ϵ .

Coumarin in methanol solution has two maxima, the first at 274 mμ, , the second at 311 mμ. In 10 % aqueous methanol and in water over pH range 7-1 the first maximum is shifted slightly towards lenger wavelength side to 278 mμ, the value of log ϵ is essentially same. The second maximum is over the range 300-312 mμ, the value of log ϵ is some what higher.

When the -OH group is substituted in 7 position in coumarin nucleus, in methanol solution the first maximum of coumarin is shifted from 274 to 254 mμ and the value of log ϵ is decreased from 4.03 to 3.41, while the value of second maximum is increased from 311 to 325 mμ and the value of log ϵ is increased from 3.74 to 4.16. This suggests that substitution of -OH group in coumarin nucleus markedly changes the ultraviolet absorption values.

When methyl group is substituted in 7-hydroxycoumarin nucleus the value of λm, the observed maximum is decreased by small amount when the substitution is in 4 position and increased by a small amount when the substitution is in 5 or 8 position. The value of log ϵ is also changed only by an a small amount.

It appears that the substitution of methyl group causes only a small change in the value of λm and $\log \epsilon$. The results given in table (U 4.01) also suggest that when the hydroxy group is converted to methoxy group the value of λm is decreased only by a small amount (about 4 mμ) and the value of $\log \epsilon$ is altered by small amount only. When the solvent is changed from methanol to 10 % methanol, the values of λm and $\log \epsilon$ are either almost same or changed by a small amount.

It appears that the change in solvent-solute interaction accompanying the change in dielectric constant of the medium, when the solvent is changed from methanol to 10 % methanol, has relatively small effect on ultraviolet absorption of the coumarins studied.

II <u>Trisubstituted hydroxy and methoxycoumarins</u> :

Tables(U 3.08 - U 3.12) give ultraviolet absorption data for trisubstituted hydroxy and methoxycoumarins and table (U 4.02) summarises the values of λm and $\log \epsilon$.

In methanol solution of 5-hydroxy-4-methylcoumarin, the first maximum of coumarin is shifted from 270 to 250 mμ and the second maximum is shifted from 311 to 296 mμ. On a substitution of methyl group in 7 position in 5-hydroxy-4-methylcoumarin, the first maximum is not observed and the value of second maximum is increased by small amount to 302 - 304 mμ.

If a -OH group is substituted in 7 position of 5-hydroxy-4-methylcoumarin nucleus, the first maximum appeared at 256 mμ and second is shifted to 322 mμ. The substitution of methyl or hydroxy group in 7 position in 5-hydroxy-4-methylcoumarin does not change the value of log ϵ significantly.

For 7-hydroxy-4-methylcoumarin the first maximum of coumarin is not observed, the second maximum is shifted to 322 mμ. When a methyl or hydroxy group is substituted in 8 position, the value of second maximum is practically same and the value of log ϵ is also changed by small amount. In 7,8-dihydroxy-4-methylcoumarin the first maximum is observed at 260 mμ, but for 7-hydroxy-4,8-dimethylcoumarin the first maximum is not observed within the range studied.

On conversion of hydroxy group into corresponding methoxy group for these hydroxycoumarins, the value of λm is either essentially same or decreased by a small amount (4-6 mμ) and the value of log ϵ is also changed by a small amount.

The change of solvent from methanol to 10 % methanol either makes no change or changes by a small amount in the values of λm and log ϵ .

The change of pH from 7-1 has not measurable effect on the ultraviolet absorption of the coumarins mentioned in this and the previous section.

The ultraviolet absorption data provide a convenient and reliable method for the estimation of coumarins in dilute solution and this procedure was used for the estimation in further work.

III Coumarine - carboxylic acids :

Tables (U 3.13 and U 3.14) give the ultraviolet absorption data for 7-hydroxy-4-methylcoumarin-6-carboxylic acid and 7-hydroxy-4-methylcoumarin-8-carboxylic acid and table (U 4.03) summarises the values of λm and logϵ .

In methanol solution of 7-hydroxy-4-methylcoumarin the two maxima of coumarin are replaced by one maximum which occurs at 322 mμ and the value of log ϵ is 4.14. The results in 10 % methanol over pH range 7-1 are not significantly different.

These results indicate that for 7-hydroxy-4-methylcoumarin the effect of change of pH from 7-1 in 10 % aqueous methanol solution is negligible. Also there is little effect of solvent change from methanol to 10 % methanol.

When a -COOH group is substituted in 7-hydroxy-4-methylcoumarin in 6 position, the value of λm is shifted to the right by a small amount, the value of logϵ is practically same.

Change of pH from 0.5 - 7 makes relatively small difference in the value of λm and logϵ .

When a -COOH group is substituted in 7-hydroxy-4-methylcoumarin in 8 position the first maximum appears at 266 mμ and the second at 330 mμ. In aqueous medium at lower pH the value is practically same, when -COOH is substituted in 8 position. There is no effect on first maximum on change of pH from 0.5 - 7. Value of second maximum is slightly increased from 326 - 330-32 mμ.

One possible explaination for the observation that change of pH from 0.5 - 7 has little effect on ultraviolet absorption of 7-hydroxy-4-methylcoumarin-6-carboxylic acid and 7-hydroxy-4-methylcoumarin-8-carboxylic acid may be that the ultraviolet absorption of the acid molecule and acid anion may differ by a small amount only.

IV 4-Hydroxy and 4-methoxycoumarins :

Tables (U 3.15 - U 3.25) give the ultraviolet absorption spectra of 4-hydroxycoumarin, 4,5 ; 4,6 and 4,7-dihydroxycoumarins and their corresponding methoxycoumarins in methanol and 10 % aqueous methanol at different pH. The table (U 4.04) gives the values of wavelength and extinction coefficients for maxima for the ultraviolet absorption spectra of these coumarins.

Effect of subsituent :

(a) In methanol :

In methanol solution for 4-hydroxycoumarin the two maxima of coumarin at 274 $m\mu$ and 311 $m\mu$ are replaced by three maxima at 270 $m\mu$, 280 $m\mu$ and 302 $m\mu$.

When a -OH group is substituted in 4-hydroxycoumarin in 5 position, the three maxima of 4-hydroxycoumarin are replaced by one maximum at 292 $m\mu$. When a -OH group is substituted in 6 position in 4-hydroxycoumarin, the first and second maxima of 4-hydroxycoumarin at 270 $m\mu$ and 280 $m\mu$ are slightly shifted towards right (about 6 $m\mu$), whereas the third maximum at 302 $m\mu$ is shifted to 320 $m\mu$ and the value of log ϵ for this maximum is markedly reduced by about 0.4. When -OH group is substituted in 7 position in 4-hydroxycoumarin, the first maximum is not observed and the second and third maxima are increased by small amount to 284 $m\mu$ and 304 $m\mu$. The value of log ϵ at third maximum is higher than that for 4-hydroxycoumarin.

(b) In 10 % methanol at low pH :

In 10 % methanol at low pH, the value of λm are either same or are increased by small amount (about 6 $m\mu$) as compared to those in methanol. The value of log ϵ is changed in some cases.

For 4,6-dihydroxycoumarin at the second maximum there is a shoulder at about 282 to 286 $m\mu$.

The observation that the values of λm is lower in methanol than that in 10 % methanol at low pH in some cases may be attributed to the decrease in solvent-solute interaction due to decrease in dielectric constant.

(c) In 10 % methanol at high pH :

When pH of the aqueous methanol solution is changed from lower to higher value the first maximum is not observed, the second and thrid maxima are shifted quite markedly.

In 4,5- and 4,7-dihydroxycoumarins, the maxima are decreased by a small amount. In case of 4,6-dihydroxycoumarin the first maximum is not observed, the average wavelength of the shoulder replacing the second maximum of 4-hydroxycoumarin is somewhat increased. The λm at the third maximum is markedly decreased from 326 $m\mu$ to 296 $m\mu$ and corresponding value of log ϵ is increased about 0.3.

On comparing the values at high pH in aqueous methanol, 4-hydroxycoumarin has two maxima at 286 and 294 mμ. When -OH group is substituted in 5,6 or 7 position the wavelength of maximum is changed by a small amount by about 4 to 8 mμ, except that for 4,5-dihydroxycoumarin the maximum at 286 is not observed. The value of log ϵ is almost same or changed by small amount.

Effect of conversion from hydroxy to methoxy :

(a) Dihydroxy to dimethoxy :

When 4-hydroxycoumarin is converted to 4-methoxycoumarin in methanol solution and 10 % methanol all the three maxima are shifted slightly ($\sim$ 4-5 mμ) towards left and the log ϵ values are higher than that of 4-hydroxycoumarin by a small amount.

When 4,5-dihydroxycoumarin is converted to 4,5-dimethoxycoumarin, in methanol the maximum is shifted from 294 to 286 mμ, but in 10 % methanol the maximum is 292 mμ, log ϵ value remaining almost unaffected or slightly higher. In case of 4,6- and 4,7--dimethoxycoumarins also, there is little shift of maxima towards left as compared to the dihydroxycoumarins.

In all the methoxy and dimethoxycoumarins there is no effect of pH.

(b) One group conversion :

When second -OH group in 5 and 7 position in 4-hydroxycoumarin is converted to methoxy group, the value of λm is not significantly changed in methanol solution, log ϵ is either same or changed very slightly. When the 6-hydroxy group in 4-hydroxycoumarin is changed to methoxy, the first maximum is not observed in methanol solution, the second and third maxima are same or slightly decreased, the logϵ values at these maxima are slightly higher than those of 4,6-dihydroxycoumarin.

In 10 % methanol at relatively low pH the conversion of hydroxy group in the benzene ring to methoxy group does not appear to alter value of λm significantly and the same is valid for values of λm in 10 % methanol at relatively high pH.

Table (U 4.05) gives the values of invarient wavelength of 4-hydroxycoumarins. At these wavelengths the ultraviolet absorption is independent of pH over the range 7-1. 4-Hydroxycoumarin has invarient wavelength at 315 mμ and this reduced to 304 and 306 mμ for 4,5- and 4,7-dihydroxycoumarin and is further reduced to 280 mμ for 4,6-dihydroxycoumarin.

The hydroxycoumarins may be considered as very weak acids, such as phenols, but the 4-hydroxycoumarins are relatively more acidic than the other hydroxycoumarins; the former may be considered practically unionised in the pH range 7 to 1, but the latter may be considered to be ionised to some extent in aqueous alcohol used as solvent (141). The decrease in the pH of the solution will decrease the degree of dissociation and hence the ultraviolet absorption depending on the pK of the acid and the difference in the ultraviolet absorption of the acid anion and the undissociated acid molecule. Hence, when the pH is reduced from 7 to 1, the values of λ and logϵ for maxima for ultraviolet absorption may vary measurably at first and then at low pH depending on the pK of the acid the ultraviolet absorption should become practically constant. At the invarient wavelength, the value of log ϵ for ultraviolet absorption is not affected by pH in the range 7 to 1. These data provides a convenient method for the estimation of 4-hydroxy substituted coumarins in dilute solutions of pH in the range 7 to 1.

4 A.2

SORPTION EQUILIBRIUM STUDIES

Table E 4.01

Values of B for methyl-substituted 7-hydroxy and 7-methoxycoumarins with resin in H^+ form in 10 % aqueous methanol.

Resin = Compound	X4	X8	X12	Compound	X4	X8	X12
*7-OHI	5.0	-	-	7-MeOI	11.5	9.1	7.5
7-OH-4-MeI	11.1	5.7	4.0	7-MeO-4-MeI	15.0	14.3	7.1
7-OH-5-MeI	9.0	7.5	6.1	7-MeO-5-MeI	16.6	16.0	13.1
7-OH-8-MeI	10.7	10.0	6.6	7-MeO-8-MeI	20.0	19.9	15.8

* Dr.D.J.Patel, Ph.D.Thesis (1965), Baroda.

Table E 4.02

Values of B for trisubstituted hydroxy and methoxycoumarins with resin in H^+ form in 10 % aqueous methanol.

Resin = Compound	X4	X8	X12	Compound	X4	X8	X12
4-Me-7-OHI	11.1	5.7	4.0	4-Me-7-MeOI	15.0	14.3	7.1
*4-Me-5,7-diOHI	14.2	-	-	4-Me-5,7-diMeOI	37.5	37.5	30.7
***4-Me-7,8-diOHI	4.8	-	-	4-Me-7,8-diMeOI	11.2	9.3	7.1
*4,8-diMe-7-OHI	19.4	-	-	4,8-diMe-7-MeOI	36.0	35.0	25.0
**4,5-diMe-7-OHI	41.7	-	-	-	-	-	-

* Dr.R.S.Hegde, Ph.D.Thesis (1969), Baroda.

** Dr.R.A.Bhatt, Ph.D.Thesis (1968), Baroda.

*** Dr.D.J.Patel, Ph.D.Thesis (1965), Baroda.

Table E 4.03

Effect of crosslinking on B for coumarin carboxylic acids with resin in H^+ form.

	Resin =	X4	X8	X12	X16
Compound	Solvent				
7-OH-4-MeI	10% MeOH	11.1	5.7	4.0	2.9
7-OH-4-MeI-6-COOH	N/100 HCl	8.2	6.5	6.1	5.8
7-OH-4-MeI-8-COOH	"	5.0	3.6	2.9	2.4
7-OH-4-MeI-6-COOH	N/10 HCl	9.0	8.3	8.1	6.0
7-OH-4-MeI-8-COOH	"	7.5	5.4	4.0	3.1

Table E 4.04

Values of B for methoxycoumarins in 10 % aqueous methanol.

Resin = Compound	X4	X8	X12
*4-MeOI	11.0	-	-
4,5-diMeOI	11.7	10.6	8.5
4,6-diMeOI	16.0	20.0	13.0
*4,7-diMeOI	20.2	-	-

* Dr.M.J.Mehta, Ph.D.Thesis (1968), Baroda.

Table E 4.05

Values of B for 4-methylcoumarins with resin in H^+ form in 10 % aqueous methanol.

Resin = Compound	X4	X8	X12	X16
*4-MeI	9.4	-	-	-
4-Me-5-OHI	12.8	6.6	5.3	5.0
4-Me-6-OHI	8.0	4.7	3.6	4.0
4-Me-7-OHI	11.1	5.7	4.0	2.9
4-Me-6-MeOI	14.0	9.6	7.1	6.3
4-Me-7-MeOI	15.0	14.3	12.0	-
4,6-diMeI	17.7	11.7	9.3	8.2
4,7-diMeI	20.0	15.0	10.9	9.4

* Dr.M.J.Mehta, Ph.D.Thesis (1968), Baroda.

Table E 4.06

Values of B for some substituted coumarins with resin X4 with different counter ions in 10 % aqueous methanol.

Compound : Counter ion	5-OH-4-MeI	6-OH-4-MeI	7-OH-4-MeI
H^+	12.8	8.0	11.1
Anilinium	17.1	7.7	16.0
Me-Anilinium	15.0	13.3	13.3
DiMe-Anilinium	26.6	11.2	16.0
Et-Anilinium	21.6	13.1	17.1
DiEt-Ammonium	18.3	10.0	12.0
TriEt-Ammonium	13.7	9.0	10.0

Table E 4.07

Values of B for 4-hydroxy-3-methylcoumarin and 4-hydroxy-6-methylcoumarin with resin in H^+ form.

Compound :	4-OH-3-MeI				4-OH-6-MeI			
Resin =	X4	X8	X12	X16	X4	X8	X12	X16
Solvent								
10 % MeOH	8.8	6.2	4.6	5.2	12.0	9.2	7.1	5.0
10 % MeOH in N/100 HCl	8.9	5.7	4.5	3.6	12.4	9.1	7.6	6.6
10 % MeOH in N/10 HCl	9.8	7.9	6.4	5.6	14.3	11.7	9.0	5.7

4 A.2 Sorption equilibrium studies of coumarins :

The synthetic ion exchange resin consists of an irregular, macromolecular, three dimensional network of hydrocarbon chains to which ionogenic groups are attached and the surplus electric charge is balanced by mobile counter ions. The hydrocarbon network is hydrophobic, but the ionogenic groups are hydrophilic. Hence, when the resin particle is placed in water, it sorbs water and swells to limited extent. The amount of water sorbed and the extent of swelling depend on the degree of crosslinking, X and the counter ions. If the external solvent contains a non-electrolyte, it is also sorbed to a certain extent and after some time a state of equilibrium is reached. The amount sorbed will depend on several factors, which include the London (dispersion) interactions, the dipole-dipole interactions, the relative solubility of the solute in the medium inside and outside the resin particle, the solvent uptake and the volume of the swollen particle, the equilibrium concentration of the solute in the external solution and the temperature. Besides these, there may be specific interactions in a particular system.

A sorption equilibrium study involves three substances; the resin, the solvent and the solute. For the resin, the variable may include the matrix structure, the relative degree of crosslinking, the type and the acid or base strength of the ionogenic group, and the charged, shape, size and the hydration of the counter ions. The solvent may be aqueous, mixed or organic; it may be polar or non-polar and have different dielectric constant and the solvation of ionogenic groups and the solute molecules. For the solute, the variable may include the shape, size, polarity and the relative solubility in the medium inside and outside the resin particle.

The amount of solute sorbed per unit capacity of the resin at a given temperature, will hence, be determined by the overall effect of the variables on the sorption and a complex behaviour is to be expected. Hence, a study of one variable at a time may provide towards better understanding of the phenomena.

The sorption equilibria of coumarin and substituted coumarins with sulfonic acid cation exchange resin of degree of crosslinking from 4 to 16 in aqueous and aqueous methanol solution with or without hydrochloric acid were studied. The resin Dowex 50W is styrene divinylbenzene copolymer based sulfonic acid cation exchange resin in hydrogen form.

The sorption equilibrium studies of coumarins were carried out at room temperature, since the small variation in temperature did not make substantial change. From the initial concentration Co and equilibrium concentration Ce (in moles/litre), the values of S, the moles of the organic solute sorbed per equivalent of the resin, were calculated from the equation

$$S = \frac{(Co - Ce)}{Cr}$$

Cr is the capacity of the air dried resin in equivalents per litre of solution. The plots of S against Ce were linear, fig. (E 3.01) gives some illustrative plots and the slope of these plots is defined as B. Tables (E 4.01 - E 4.07) give the values of B obtained in this way from data of tables (E 3.01 - E 3.10).

The data indicate that in most cases the sorption of organic solutes as well as the slope of the plot of B against X decreases as the degree of crosslinking increases. This may be attributed to the decrease in the water sorption of the resin with increase in degree of crosslinking. The extent of decrease in the value of B with increase in degree of crosslinking may be considered to depend mainly on relative contribution of two effects : the decrease in the water sorption of the resin and an increase in the interaction of the hydrocarbon network of the resin and the organic solute with increase in degree of crosslinking of the resin. It appears that the first effect is relatively more pronounced than the second, leading to overall decrease in the sorption of the coumarins with increase in degree of crosslinking. The actual extent however may vary in some cases.

It is indicated that the value of B for the sorption decreases with increase in per cent (by volume) of methanol in the solvent. This may be attributed to the decrease in the dipole-dipole interactions with decrease in the dielectric constant of the solvent medium.

In the case of some of 4-hydroxycoumarins and coumarin carboxylic acids the value of B increases as the pH of the solvent is reduced by the presence of hydrochloric acid.

The hydroxycoumarins in general, may be considered as very weak acids, some 4-hydroxycoumarins and coumarin carboxylic acids are relatively stronger acids than the other and for these, the increase in the value of B may be attributed to the decrease in the degree of dissociation at low pH. The very weak acid coumarin should be almost undissociated in 10 % methanol and hence, decrease in the pH of solvent should have little effect on the value of B. The extent of increase in value of B when pH is decreased and the value of pH below which there is no further significant increase in the value of B, should depend on the relative pK value of the organic acids. However, the possibility that other factors affecting sorption may also be operative to some extent in some cases should not be ruled out.

In general, it is also observed that the conversion of the hydroxycoumarin to the corresponding methoxycoumarin increases the value of B by about one and half to two times, which implies that the separation of the mixtures of hydroxycoumarins and corresponding methoxycoumarins may be feasible.

Since relative contribution of the interaction leading to sorption should depends on the nature and/or position of group or groups, substituted in the coumarin nucleus, it is likely that the substituted coumarins may exhibit relatively different sorption which may enable separation of mixtures under suitable conditions.

Tables (E 3.01 and E 3.02) give the sorption data of 7-hydroxycoumarin, 7-hydfoxy-5-methylcoumarin, 7-hydroxy-8-methylcoumarin and corresponding methoxycoumarins in 10 % aqueous methanol on resins X4, X8 and X12 in H^+ form and the value of B are summarised in table (E 4.01).

The substitution of methyl group in 4,5 and 8 position in 7-hydroxycoumarin increases the value of B to about one and half to two times. The same is valid for the corresponding methyl substituted 7-methoxycoumarin. The position of a methyl group has some effect on the value of B, but this is relatively small.

Values of B in table (E 4.02) indicates that when a hydroxy group is substituted in 5 position in 7-hydroxy-4-methylcoumarin nucleus, the value of B is increased by about one and half times, but when -OH group is substituted in 8 position the value is decreased to about half. The value of B for 5,7-dihydroxy-4-methylcoumarin is about three times that of 7,8-dihydroxy-4-methylcoumarin. When a methyl group is substituted in 7-hydroxy-4-methylcoumarin in 5 position the value of B is increased about four times and when the methyl group is substituted in 8 position the value is increased by about two times. The value of B for 7-hydroxy-4,5-dimethylcoumarin is about twice that of 7-hydroxy-4,8-dimethylcoumarin.

The value of B when a methyl group is substituted in 5 position in 7-hydroxy-4-methylcoumarin is about three times the value of B that when -OH group is substituted in the 5 position. When this substitution position is 8 the ratio is about four. When a methoxy group is substituted in this position in 7-methoxy-4-methylcoumarin, the value is decreased significantly. Hence, a substitution of -OH group in 7-hydroxy-4-methylcoumarin nucleus in 5 position increases, but in 8 position decreases the sorption. The substitution of methyl group in 7-hydroxy-4-methylcoumarin nucleus in 5 or 8 position increases the sorption, but the increase is less for 8 position than that for 5 position.

The value of B for 7-hydroxy-4-methylcoumarin-6-carboxylic acid and 7-hydroxy-4-methylcoumarin-8-carboxylic acid are summarised in table (E 4.03). The values were too low to be measured in water solution. The value of B for 7-hydroxy-4-methylcoumarin in 10 % aqueous methanol is 11.1 and it should be higher if the solvent could be water. Hence, the substitution of a -COOH group in 6 or 8 position decreases the sorption, but the decrease is relatively less when the positon of substitution is 6 than when it is 8. Thus the sorption of 7-hydroxy-4-methylcoumarin-8-carboxylic acid is lower than that of 7-hydroxy-4-methylcoumarin-6-carboxylic acid.

When a methoxy group is substituted in 4-methoxycoumarin nucleus (table E 4.04), the value of B increases by about one and half, two and three times when position of substitutions are 5,6 and 7 respectively. The order of sorption is

4-MeO < 4,5-diMeO < 4,6-diMeO < 4,7-diMeO

When a -OH group is substituted in 4-methylcoumarin the value of B (table E 4.05) of 4-methylcoumarin is increased some what when the substitution is in 5 or 7 position and some what decreased when the substitution position is 6.

The value of 5-hydroxy-4-methylcoumarin is somewhat higher than that of 7-hydroxy-4-methylcoumarin. It appears that the substitution of hydroxy group in 4-methylcoumarin in 5,6 or 7 position makes relatively more difference in the value of B . The value of B for 4-methyl-7-methoxycoumarin is somewhat higher than that of 4-methyl-6-methoxycoumarin.

The substitution of a methyl group in 4-methylcoumarin in 6 or 7 position increases the value of B to about one and half to two times. The value for substitution in 7 position is higher than that for substitution in 6 position. When the hydroxyl group in 4-methylcoumarin is replaced by methyl group the value of B becomes almost twice. When there is substitution in 6 or 7 position in 4-methylcoumarin nucleus the value of B for methoxy is some-what less than that for methyl.

The difference in sorption as indicated by the values of B suggests that separation of mixtures including some of position isomers should be feasible under suitable conditions.

Table (E 3.06) gives the data for the sorption of 5-hydroxy-4-methylcoumarin, 6-hydroxy-4-methylcoumarin and 7-hydroxy-4-methylcoumarin with resin X4 with different organic counter ions, in 10 % aqueous methanol solution. The data indicate that the sorption is significantly increased in some cases as compared to that for resin in H^+ form. The order of sorption is

5-OH-4-MeI $\geqslant$ 7-OH-4-MeI $\geqslant$ 6-OH-4-MeI

The extent of increase in the sorption depends on both the organic solute in solution and organic counter ion of the resin. In some cases a difference in the sorption of the isomers as indicated by B value is significant and is of interest.

Table (E 4.07) gives the results for 4-hydroxy-3-methylcoumarin and 4-hydroxy-6-methylcoumarin with resins X4, X8, X12 and X16 in 10 % aqueous methanol, 10 % methanol in N/100 hydrochloric acid and 10 % methanol in N/10 hydrochloric acid as solvent.

It is observed that the sorption is higher when the methyl group is substituted in 6 position than when it is substituted in 3 position in 4-hydroxycoumarin. The sorption of both isomers is higher than that of coumarin. The relative values suggest that separation of these two isomers should be feasible.

4 A.3

COLUMN STUDIES

Table R 4.01

Column elution of substituted coumarins on column A using 10 % aqueous methanol as solvent and eluent.

Compound	Elution Range	Vmax	Ratio	B_1
1. 7-OH-4-MeI	14-22	17	1.5	11.1
2. 7-OH-5-MeI	17-26	20.5	2.3	9.01
3. 7-OH-8-MeI	16-25	20.5	1.9	10.7
4. 7,8-diOH-4-MeI	8-13	10.3	2.1	4.9
5. 5,7-diOH-4-MeI	21-35	27	[illegible]	14.2
6. 7-OH-4,8-diMeI	24-40	31	1.6	18.5
7. 7-MeO-4-MeI	28-44	35	2.3	15.0
8. 7-MeO-5-MeI	32-46	39	2.3	13.7
9. 7-MeO-8-MeI	35-51	43	2.1	20.2
10. 7,8-diMeO-4-MeI	18-31	24.5	2.2	11.2
11. 5,7-diMeO-4-MeI	68-97	79	2.2	36.5
12. 7-MeO-4,8-diMeI	53-74	62	1.8	35.
13. 7-OH-4,5-diMeI	71-95	~80	1.9	42.5
14. 6-OH-4-MeI	11-18	14	1.75	8.8
15. 4,6-diMeI	21-35	27.5	1.8	17.7
16. 4,6-diMeOI	31-53	42.5	2.6	16.0
17. 4,5-diMeOI	20-37	28.5	2.4	11.7

Table R 4.02

Column elution of some coumarins on column A.

Solvent =	20 % MeOH	30 % MeOH	40 % MeOH
Compound		Elution Range	
7-OH-4,5-diMeI	45-61	22-33	-
5-OH-4,7-diMeI	24-34	11-18	-
5-MeO-4,7-diMeI	37-50	15-26	7-12

Table R 4.03

Column elution of 4-hydroxycoumarins on column A

Compound	E.R.	10^2W	10^2W_F	P_F	K
Solvent : 10 % Methanol					
4,7-diOHI	8-18	4.73	4.03	85	0.17
4,6-diOHI	7-16	3.02	2.82	93	0.07
4-OH-7-MeOI	13-23	3.46	2.84	82	0.22
4-OH-6-MeOI	13-25	5.67	4.81	85	0.18
4-OH-5-MeOI	15-24	3.22	2.92	91	0.10
Solvent : 10 % Methanol in N/100 HCl					
4,7-diOHI	8-19	5.00	4.22	85	0.17
4,6-diOHI	12-24	3.16	2.92	92	0.08
4,5-diOHI	9-17	3.10	2.43	78	0.28
4-OH-7-MeOI	16-31	5.00	4.82	95	0.05
4-OH-6-MeOI	25-43	2.53	2.38	94	0.06
4-OH-5-MeOI	17-27	4.50	4.25	94	0.06
Solvent : 10 % Methanol in N/10 HCl					
4-OHI	12-19	3.94	3.54	90	0.14
4,7-diOHI	8-21	3.73	3.29	88	0.13
4,6-diOHI	12-27	3.12	3.06	98	0.02
4,5-diOHI	11-24	4.21	3.25	77	0.29
4-OH-7-MeOI	13-34	3.49	3.42	98	0.02
4-OH-6-MeOI	27-42	1.70	1.68	99	0.01
4-OH-5-MeOI	16-28	3.65	3.57	98	0.02

Table R 4.04

Column elution of 7-OH-4-MeI-6-COOH and 7-OH-4-MeI-8-COOH.

Column	Compound Solvent	7-OH-4-MeI-6-COOH	7-OH-4-MeI-8-COOH
		Elution Range	
A	N/100 HCl	9 - 18	15 - 25
A	N/10 HCl	14 - 22	21 - 34
A	N/2 HCl	15 - 22	23 - 32
B	N/100 HCl	14 - 21	26 - 34

Table R 4.05

Column elution of ortho-, meta-. and para-nitrotoluenes on column A.

Compound Solvent	ortho	meta	para
		Elution Range	
Resin : 50WX4 H^+ form.			
Water	45-79	53-91	50-74
10 % MeOH	37-55	41-63	39-59
10 % MeOH in N/100 HCl	38-58	43-65	40-60
10 % MeOH in N/10 HCl	39-60	42-65	40-61
40 % MeOH	13-19	14-20	13-20
10 % MeOH in N/100 n-caproic acid	34-53	37-60	34-54
10 % ter.butanol	41-58	45-65	42-58
Resin : 50WX4 NH_4^+ form.			
10 % MeOH	31-51	34-59	32-53

4 A.3 Column studies of coumarins :

I

Tables (R 3.01 - R 3.08) give column elution data for substituted coumarins in 10 % aqueous methanol and the results are summarised in table (R 4.01).

The results are in general, as may be expected from the values of B given earlier. As the value of B for a compound increases, in general, the break-through volume increases and the elution band becomes broader and reduced in height. The increase in the column lengths increases break-through volume and the number of samples containing the solute, but the relative separation is improved.

The results with aqueous methanol show that as the per cent content of methanol is increased the break-through volume and number of samples containing the solute is reduced, but the relative separation is adversely effected.

Results suggest that separation of mixtures including those of position isomers should be feasible and some separations are presented as illustrations. Tables (R 3.09 - R 3.16).

The result of this study provide a useful and convenient technique for separation of mixtures including those of position isomers.

II.

Tables (R 3.17 - R 3.20) give the column elution runs for 7-hydroxy-4-methylcoumarin-6-carboxylic acid and 7-hydroxy-4-methylcoumarin-8-carboxylic acid.

The results are in general, consistent with the remarks made above.

Tables (R 3.21 and R 3.22) give the runs illustrating the separation of 7-hydroxy-4-methylcoumarin-6-carboxylic acid and 7-hydroxy-4-methylcoumarin-8-carboxylic acid.

III.

4,7-dihydroxycoumarin was recrystallised three times and its melting point was checked.

Table (R 3.23a) gives the data for the run in water as solvent and eluant. After the elution of the first band from sample No. 32 the eluant was changed to 30 % aqueous methanol and the run was continued and the effluent was collected in one sample of 1200 ml.

The data indicate that unlike other coumarins studied earlier, the elution is in two bands. The first band is from sample No. 15 to 30 and contains 82 % of the coumarin sorbed, the second band was eluted with 30 % aqueous methanol containing rest of the coumarin. This implies that 4,7-dihydroxycoumarin is resolved into two components, the first containing 82 % of the compound.

Table (R 3.24) gives the data of elution run for 4,7-dihydroxycoumarin in 10 % aqueous methanol as solvent and eluant. In the first band 85 % of the material was eluted out, from sample No. 22 eluant was changed to 30 % aqueous methanol and the rest of the material was eluted out. Here again, the elution indicates that the elution is in two bands indicating that the compound is eluted in two components.

In the next run 100 ml. of sample Nos. (peak) from the previous run were taken and sorbed on the column as usual and the run was carried out with 10 % aqueous methanol. The elution pattern was similar to that given for above runs.

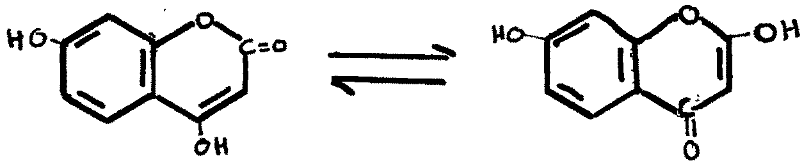
The pH of the original solution was reduced to a pH of approximately 0.5. The pH of a cut from the first band of the run given in table and of a cut of second band (table R 3.24) was reduced to approximate pH 0.5 by adding hydrochloric acid and the ultraviolet absorption was measured from 250 - 350 mμ and the spectra was found to be similar.

The run given in table (R 3.24) was repeated. 100 ml. of 4,7-dihydroxycoumarin was first sorbed on the column as usual and the column was allowed to stand for two days and then the elution was carried out with 10 % aqueous methanol. The result was similar to that given in table (R 3.24).

Table (R 3.23c) gives the elution run for 4,7-dihydroxycoumarin in 30 % aqueous methanol as solvent and eluant as follows. The run indicates two bands implying again that the elution is of two component system. The first may be considered to be between 4-10 containing about 89 % of the eluted material and the second to be between 9-18 containing rest of the material.

The above data indicate that 4,7-dihydroxycoumarin is resolved into two components during the elution. The major part of the solute being in the first band. The elution is faster with increase in per cent methanol content in solvent. The spectra of the two components eluted were similar when a cut from first band was rechromatographed, as in the above run, it again resolved into two similar bands.

The above observations are consistent with the suggestion that 4-hydroxycoumarins exist in solution as a mobile equilibrium between coumarin and corresponding chromones (164, 165). Accordingly, 4,7-dihydroxycoumarin in solution exists in mobile equilibrium, which is attained fairly rapidly between 4,7-dihydroxycoumarin (1) and 2,7-dihydroxychromone (2)



(1) (2)

The relative amounts of the two components in equilibrium may depend on the solvent medium and the temperature.

The similarity of the ultraviolet absorption spectra of samples from first and second bands and the resolution of a sample from first band again into two bands, when it was rechromatographed in the same way as in run (R 3.24) support the above suggestion.

IV.

Table (R 3.29) gives the elution run for 4,5-dihydroxycoumarin with 10 % methanol in N/100 hydrochloric acid as solvent and eluant. After the first band was eluted out the column was washed with 30 % aqueous methanol to elute the remaining material and then was conditioned with solvent to be used for next run and then next run was carried out.

The run carried out in this way are given in tables (R 3.28 - R 3.30). The table (R 4.03) summarises the values of E.R., P_F and K. It is observed that the amount eluted in the first band may depend on the pH of the solution and on the position and nature of the substituent in the coumarin nucleus. In some cases the value of P_F is almost 100.

When a methyl group is present in the 4-hydroxycoumarin nucleus, the value of P_F is almost about 100, but in case of some of the dihydroxy and hydroxy-methoxycoumarins the P_F may be as low as about 80. It appears feasible to regard the 4-hydroxycoumarins in solution to be present as 4-hydroxycoumarin in mobile equilibrium with corresponding 2-hydroxychromones. The equilibrium 4-OHcoumarin $\overset{K}{\rightleftharpoons}$ 2-OH-chromone being fairly rapidly attained. The equilibrium constant K is given by

$$K = \frac{W - W_F}{W_F}$$

The values of K calculated in this way are included in table (R 4.03).

The relative amounts of coumarin and corresponding chromone determining the equilibrium constant may vary with composition and pH of the solvent as well as the nature and position of the substituent in the 4-hydroxycoumarin nucleus.

The column run hence, should provide a reasonable value of the relative amounts of 4-hydroxycoumarins and corresponding 2-hydroxychromones in solution in equilibrium and thus provides some idea of equilibrium constant.

Some 4-hydroxycoumarins with P_F almost 100 and which form the component to be eluted out in the first band were tried for the separation and some of the mixtures are given in tables (R 3.31 and R 3.32) as illustration.

4 B.

NITROTOLUENES

4 B.1 Ultraviolet absorption spectra of nitrotoluenes :

Tables (U 3.26 - U 3.28) give ultraviolet absorption data for mono nitrotoluenes in water, aqueous methanols and methanol solution and the values of λm and log ϵ are summarised in table (U 4.06).

In water o-nitrotoluene has maximum at 265 mμ, the value of log ϵ is 3.68; for m-nitrotoluene the value of λm and log ϵ are increased to 273 mμ and 3.84 and for p-nitrotoluene the value is further increased to 285 mμ and 3.94. The values are in the order

ortho $<$ meta $<$ para

At relatively higher methanol content the value of λm is decreased and that of log ϵ is somewhat increased. In methanol the value of λm are reduced by about 8-12 mμ and log ϵ is increased by 0.04-0.1.

The decrease in the value of λm may be attributed to the decrease in dielectric constant of the solvent and hence decrease in solvent-solute interaction.

The values given are in agreement with those given in literature in water and alcohols table (1.1).

The literature values also support the observation done that the value of λm is lower in non-polar solvents than that in more polar solvents.

The ultraviolet absorption provides a convenient method for the estimation of nitrotoluene in dilute solution and was used in sorption studies.

4 B.2 Sorption equilibria of mono nitrotoluenes :

The sorption of three mono nitrotoluenes was studied with resin X4 in H^+ form in aqueous solution. The sorption isotherms obtained by plotting S vs Ce had a positive slope which increased with increasing value of Ce, the equilibrium concentration. This behaviour was rather different from that described earlier, where S vs Ce plots were linear.

Fig. (E 3.02) gives the illustration of the type of sorption isotherm obtained. The sorption of ortho and para isomers were practically same and that of meta only somewhat higher, indicating that the sorption of the three isomers were not significantly different.

In aqueous methanol solution the sorption decreased as the methanol content of the solvent increased, but here again the sorption of ortho and para isomers was almost same, and that of meta isomer was somewhat higher.

The sorption in 10 % aqueous methanol were almost same with or without the presence of hydrochloric acid (N/100, N/10), but the presence of n-caproic acid (N/100) reduced the sorption to a small extent. The sorption isotherms in 10 % ter. butanol (table E 4.07) were on the other hand linear and the value of B given by the slope of the plot of S vs Ce were : ortho = 8.2, para = 8.6 and meta = 10.0.

The sorption on the NH_4^+ form of the resin in 10 % aqueous methanol solution was somewhat less than that on H^+ form.

It appears that the mono nitrotoluenes can be sorbed in aqueous or aqueous alcoholic solution by the resin, but the relative sorption is not substantially different and the extent of sorption decreases with decrease in dielectric constant of the solvent implying that alcoholic or aqueous alcoholic medium should give fast elution.

4 B.3 Column studies of mono nitrotoluenes :

Tables (R 3.33 - R 3.40) give the elution curve for mono nitrotoluenes with resin X4.

In these runs 25 ml. of the nitrotoluene solution was sorbed on the column and then after initial sample equal to void volume the effluent was collected in 25 ml. samples.

Table (R 4.05) gives the summary of the column runs obtained. It is observed that the sorption of the meta is somewhat higher than that of ortho and para isomers, the sorption of ortho and para isomers is almost same.

The results indicate that the nitrotoluenes may be sorbed on resin column and eluted out, the elution being faster in higher per cent content of organic solvent in the eluant.