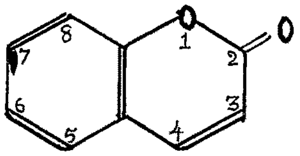
# Part II : STUDIES WITH COUMARINS

5. Coumarins
6. Ultraviolet absorption spectra of coumarins
7. Sorption studies with coumarins
8. Separation of coumarins

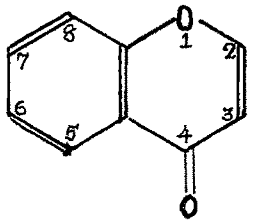
5.

## COUMARINS (1,2)

The fusion of a pyrone ring with a benzene nucleus gives rise to a class of heterocyclic compounds known as benzopyrones, of which two distinct types are recognized : (1) benzo-α-pyrones commanly called coumarins and (2) benzo-γ-pyrones, called chromones, the latter differing from the former only in position of the carbonyl group in the heterocyclic ring.



Benzo-α-Pyrone



Benzo-γ-Pyrone

Representatives of three groups of compounds are found to occur in the vegetable kingdom, either in the free or in the combined state. Coumarin, the parent substance of the benzo-α-pyrone group, was first isolated from tonkabeans in 1820. Several coumarin derivatives have been found to be widely distributed in the plant kingdom. Particularly the plant belonging to the natural orders of orchidaceae, Leguminoceae, Rutaceae, Umbelliferae and Labiatae are rich sources of naturally occuring coumarins.

Coumarin and its derivatives are substances of potential value for synthetic purposes. Their easy accessibility opens the way through suitable reactions to the synthetic preparation of other heterocyclic compounds, such as coumarones, furanocoumarins ( or furocoumarins ) chromons-α-pyrone, flavano-α-pyrones and chromones as well as natural products containing such ring systems.

Coumarins have been found to be physiologically effective for animals as well as man. It has been observed that coumarin acts as a narcotic for rabbits, frogs, earthworms and many other animals. It is a sedative and hypnotic for mice. It has toxic effect on man as well as dog.

Some hydroxycoumarins possessing the power of absorbing ultraviolet light are extensively used as medicinals in skin diseases. Some coumarins in the plant play the important role of protecting the plant from harmful effect of the shortwave rediation.

References :

1. Sethna, S.M. and Shah, N.M., Chem.Rev., 36, 1 (1945).
2. Sethna, S.M. and Phadke, R., Organic reaction, Roger Adams, 7, 1 (1953).

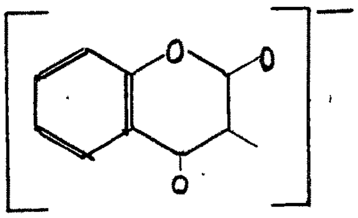
# ULTRAVIOLET ABSORPTION SPECTRA OF COUMARINS

## Introduction :

Tasaki (1) studied the absorption spectra of the substituted coumarins in alcoholic solution. Coumarin, hydroxy-and methoxycoumarins, dihydroxycoumarin, esculin, esculetin, acetylcoumarin, diacetylesculatin and methylenedihydroxyphenyl coumarin were studied. Coumarin showed two absorption maxima. When one or two hydroxy groups were introduced into the benzene nucleus of coumarin the substance showed only one absorption maximum.

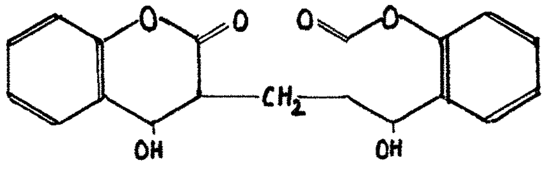
Mangini and Passerini (2) have reported the ultraviolet absorption maxima and log $\epsilon$ for coumarin (I) its 3-,4-,5-,6-,7-,8-Me, 3-, 4-, 6-, 7-Cl and 3-, 4-, 6-, 7-MeO derivatives in ethanol, $C_6H_{14}$, 60 % $HClO_4$ or $H_2SO_4$ ( 1 : $10^5$). I and the 3-, 5-, 6-, 7- and 8Me derivatives showed maxima at 282-86 mμ, log $\epsilon$ 3.95-4.02 ; the 4-Me derivative at 287 mμ log $\epsilon$ 3.55.

Examination of ultraviolet spectra by Chmielewska and Ciecierska (3) showed that the three substituted derivatives of 4-hydroxycoumarin in 96 % ethanol were completely ionized with the formation of an

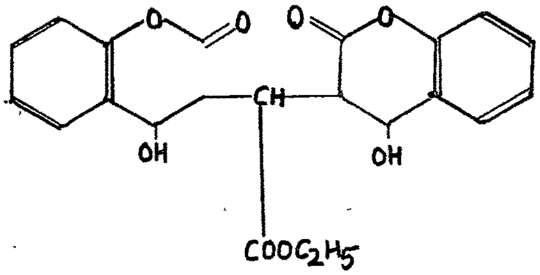


ion, Dicoumarol (I)

and pelentan (II) under similar conditions did not form ions of this type. The results, though not sufficient to prove the ketal structure of I and II, were considered to show that in ethanol both I and II given below, must occur in tautomeric form.



(I)



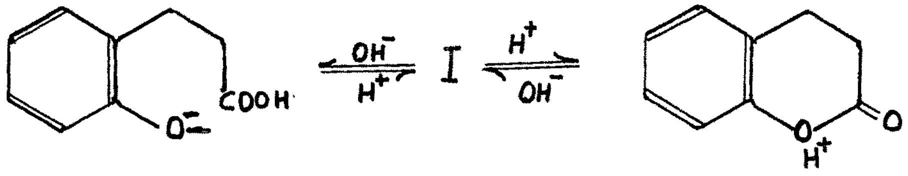
(II)

5-, 6- and 7-hydroxy (I), methoxy-(II), methyl-(III) and acetoxycoumarins (IV) and 5,7-, 6,7- and 7,8-dihydroxy(V), dimethoxy (VI), dimethyl (VII), and diacetoxy (VIII) coumarins were prepared by Nakabayashi, Tokoroyama, Miyazaki and Isono(4) and the ultraviolet absorption spectra were determined in 95 % ethanol (III), (IV), (VII) and (VIII) showed spectra similar to that of coumarin, irrespective of the position or number of the substitutents ; (I), (II), (IV) and (VI) on the other hand showed complicated spectra according to the position and number of substitutents present. On the assumption that the two absorption bands of coumarin at 270 and 312 mμ, were those of benzene around 200 and 240-260 mμ that had shifted to these regions the ultraviolet absorption spectra of these coumarin derivatives were qualitatively explained according to the latest theory regarding light absorption.

Jacobson and Amstutz (5) recorded ultraviolet absorption spectra of a series of thirteen new coumarins and concluded that neither addition of the 4-methyl group nor of the 6-alkyl groups have significant effect on the spectra.

Goodwin and Pollock (6) studied the ultraviolet absorption spectra of a series of coumarin derivatives for use as a clue to the identification of unknown fractions isolated from the roots. They concluded that saturation of the double bond at the 3,4-position in the coumarin nucleus grately reduces absorption at wavelength larger than 300 mμ, secondly 4-Me substitution has very little effect upon the absorption and thirdly there is a great similarity between the absorption spectra of hydroxy derivatives and their ethers.

Cingolani (7) studied the ultraviolet absorption spectra in ethanol, 0.1 NaOH and 60 % $HClO_4$ solution of coumarin (I), and its following derivatives, 3-Me, 3-Me-6-MeO, 3-Me-7-MeO, 3-Me-8-MeO, 3-Me-6,7-diMeO, 3-Me-6, 8-diMeO, 4-Me, 4-Me-6-MeO, 7-MeO, 4-Me-5,7-diMeO,4-Me-6,7-diMeO and 4-Me-7,8-diMeO and have given interpretation in terms of electronic structures. Variations of spectra in acid and alkaline solutions agree with the possibility that coumarins could ionise as bases or acids (by ring opening). Spectra in alcoholic solution were attributed to I, in 0.1 N NaOH to II and 60 % $HClO_4$ to III. I,3-Me-I and 4-Me-I gave similar spectra in alcohol with a strong band at 265-275, and a weak band at 325-75 mμ. The position of MeO in the ring influences the spectra. 6-MeO derivatives caused bathochromic shifts in the 1st band below 250 mμ. ; 8-MeO derivatives caused hypsochromic shifts. The maxima band of all 3-Me-I derivatives were shifted to greater λ in contrast with 4-Me-I derivatives. The position of the Me caused a shift to



(II) (III)

greater λ. This was evident when with the lactone form of 3-Me-I derivatives and explained by admitting that the equilibrium for 3-Me-I is shifted toward quinoid form, where as with 4-Me-I it was shifted to nonquinoid form.

Cingolani (8) examined the ultraviolet absorption spectra in ethanol, in 0.1 N NaOH, and after acidification of alkaline solution for coumarin and the following derivatives: -4-Me-8-OH, 8-OH, 4-Me-5, 8-$(OH)_2$, 3-Me, 4-Me, 4-Me-6-OH-5, 7-$(MeO)_2$ and 4-Me-5-OH. The curves are characteristic enough for any of these compounds to be identified in an unknown solution, especially if the behaviour in alkaline solution is examined, since the lactone ring opens and the hydroxy cinnamic acid formed isomerizes at different rates according to structures. After isomerization the original lactone can only be recovered by acidification if a 5-OH group is present. In ethanol the 275 and 310 mµ. bands of coumarin were shifted to longer λ by 6-OH or 6-Me, and to shorter λ by 5-or 8-OH or Me alone. Both 5 and 8 substituents together give bands for Me at 228, 293 and 343 mµ. 7-OH or Me gives a single band at 310-30 mµ.

Ganguly and Bagchi (9) studied the ultraviolet absorption maxima and log $\epsilon$ for coumarin (I), 3-Me(I), 3,4-diMe(I), 4,8-diMe(I) and 4,6-diMe(I) in 95 % ethanol solution. Absorption measurement in region 220-340 mμ showed that it is possible to distinguish between them on the basis of absorption characteristics. A methyl group present either in the benzene or in the pyrone ring fails to show any significant change in the absorption properties of the parent compound.

Sen and Bagchi (10) studied the ultraviolet absorption spectra of coumarin (I), 7-OH(I), 7-OH-4-Me(I), 6-OH-4-Me(I), 4-OH(I), 4-OH-3-Me(I), 3-OH(I) and 5-OH-4-Me(I) in ethanol. Absorption spectra of coumarin substituted by hydroxy groups in the aromatic as well as in the heterocyclic nucleus in different positions showed bathochromic shift in the position of one or more of the principal bands.

The above data on the ultraviolet absorption spectra seem to be in rather largely, in not easily accessible literature and mutually not quite in agreement. The ultraviolet absorption spectra reported by Bagchi and coworkers could be useful in distinguishing between coumarins and chromones ; they, however, did not think that isomeric methylcoumarins could be distinguished by their data.

This chapter gives comparative survey of the published data on ultraviolet absorption spectra of coumarins and also reinvestigation of some coumarins with a view to assessing the usefulness of ultraviolet absorption spectra in distinguishing substituted isomeric coumarins and their estimation in dilute solution.

## Experimental :

**Chemicals :** The substituted coumarins except 6-hydroxy-4-methylcoumarin, 7-hydroxy-4-methylcoumarin, 5,7-dihydroxy-4-methylcoumarin and 5,7-dimethoxy-4-methylcoumarin were obtained from Prof. S.M.Sethna's laboratory and were recrystallised and checked for melting point. Distilled water, ethanol (95 % ) and distilled methanol (B.D.H.) were used.

### 6-Hydroxy-4-methylcoumarin : (11)

Hydroquinone (5 g.) mixed with ethyl acetoacetate (5 g.) and sulphuric acid (25.0 ml., 80 % ) was added slowly to it. The reaction mixture on keeping over night was poured in ice-cold water. The product which separated out crystallised from alcohol, m.p. 244°C.

### 7-Hydroxy-4-methylcoumarin : (12)

Resorcinol (5 g.) was condensed with ethyl acetoacetate (5 g.) in presence of sulphuric acid (25 ml. 80 % ) and kept overnight. The reaction mixture was poured in icecold water. The product obtained was crystallised from alcohol,m.p. 185°C.

### 5,7-Dihydroxy-4-methylcoumarin : (13)

Phloroglucinol (12 g.), ethyl acetoacetate (12.5 g.) and sulphuric acid (60.0 ml., 80 % ) were kept overnight. The next day the reaction mixture was poured in icecold water and yellow product obtained was crystallised from alcohol, m.p. 290-91°C. Pechmann and Cohen (13) give m.p. 282-84°C.

<u>5,7-Dimethoxy-4-methylcoumarin</u> : (14)

5,7-Dihydroxy-4-methylcoumarin (1 g,) was dissolved in acetone (70 ml.) and refluxed with dimethyl sulphate (0.8 ml.) and anhydrous potassium carbonate (3.0 g.) for 9 hrs. The reaction mixture was filtered and the acetone recovered. The solid obtained was crystallised from alcohol, m.p. 174°C. Canter, Curd and Robertson (14) give the same melting point.

<u>Procedure</u> : The stock solution of coumarins were first prepared by dissolving known weights of coumarins in solvents and the concentrations weee calculated from weights. The stock solutions were then suitably diluted with solvent.The ultraviolet absorption spectra were studied with a Beckman Model DU Spectrophotometer using 10 mm. quartz cells in the range 240 mµ-370 mµ. The values of the extinction coefficients, $\epsilon$ , were calculated by dividing the observed optical density, D, by the concentration of coumarins in gram moles per litre.

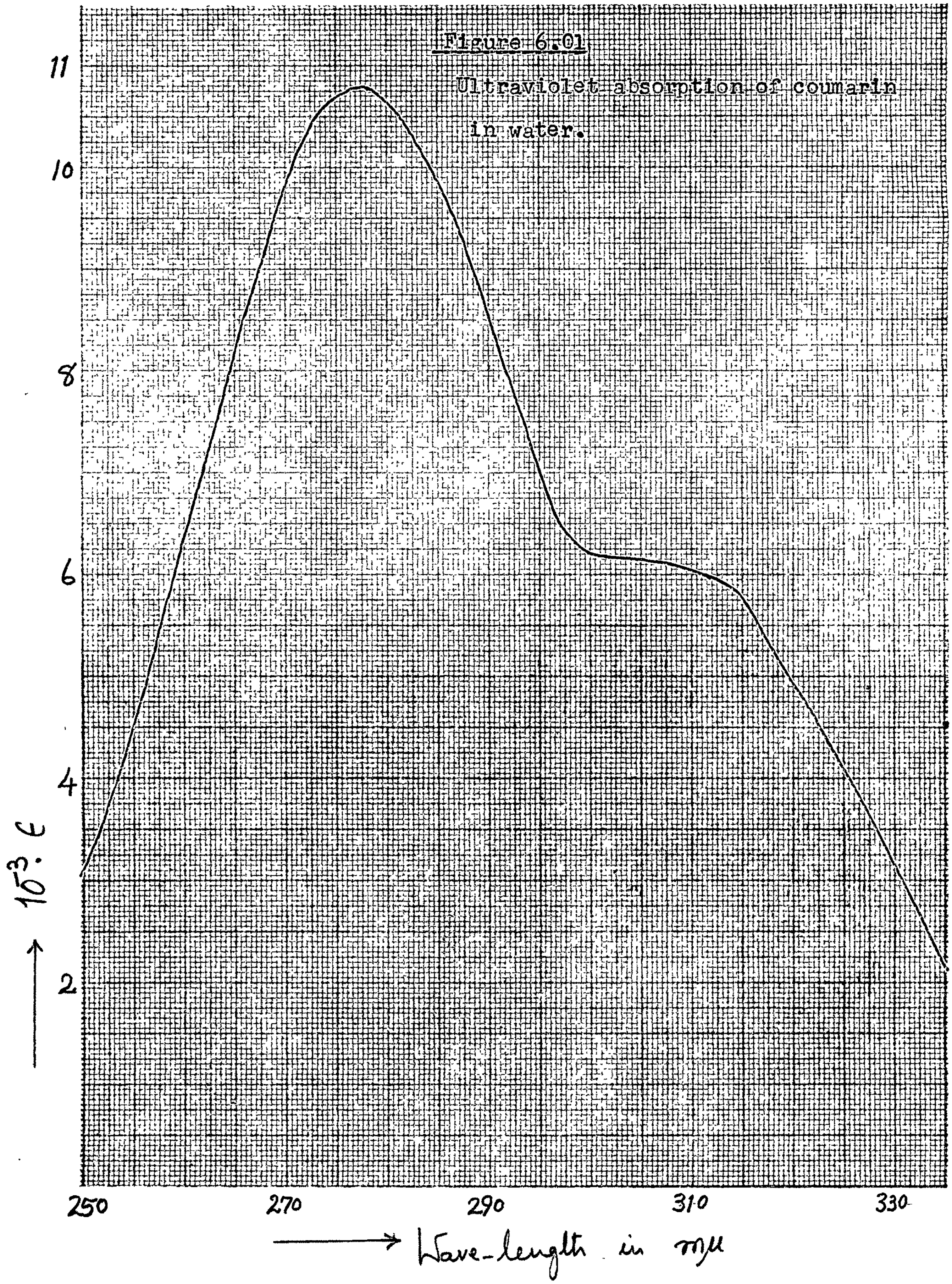


Figure 6.01
Ultraviolet absorption of coumarin in water.
11
10
8
6
4
2
$10^{-3}.\epsilon$
250
270
290
310
330
Wave-length in mμ

**Results :**

### Table 6.01

Ultraviolet absorption of coumarin in water

| Wave length (mμ) | ε | Wave length (mμ) | ε |
|---|---|---|---|
| 250 | 3008 | 280 | 10530 |
| 252 | 3548 | 284 | 10000 |
| 254 | 4191 | 286 | 9506 |
| 256 | 4804 | 296 | 6615 |
| 258 | 5549 | 298 | 6353 |
| 260 | 6220 | 300 | 6176 |
| 264 | 7739 | 305 | 6132 |
| 266 | 8468 | 310 | 6059 |
| 268 | 9082 | 312 | 5987 |
| 270 | 9668 | 314 | 5855 |
| 272 | 10210 | 316 | 5593 |
| 274 | 10460 | 325 | 4235 |
| 276 | 10640 | 340 | 1139 |
| 278 | 10680 | 350 | 219.1 |

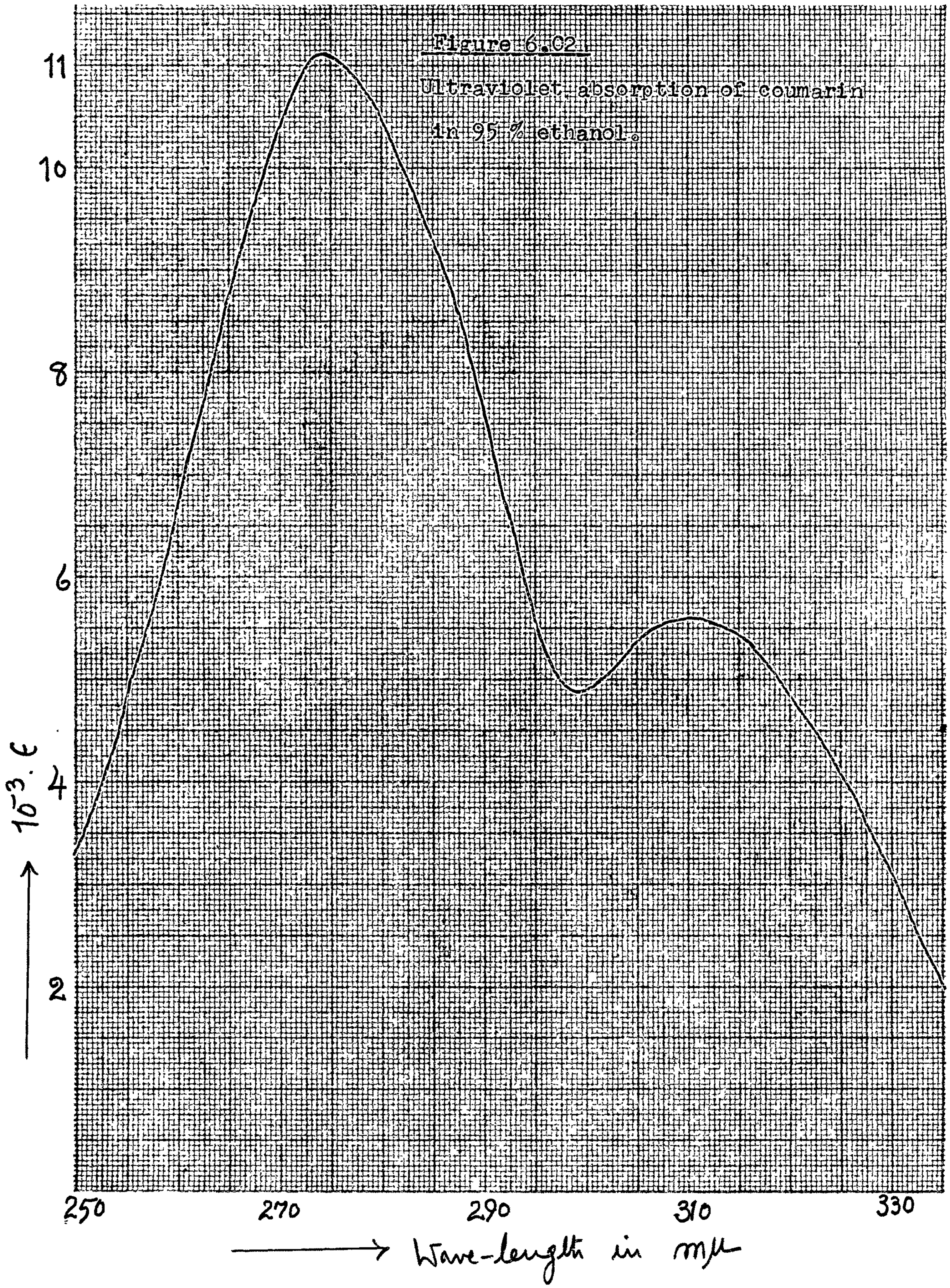


Figure 6.02.

Ultraviolet absorption of coumarin in 95 % ethanol.

## Table 6.02

Ultraviolet absorption of coumarin in ethanol

| Wave length (mμ) | ϵ | Wave length (mμ) | ϵ |
|---|---|---|---|
| 250 | 3242 | 276 | 10810 |
| 252 | 3825 | 278 | 10630 |
| 254 | 4512 | 280 | 10290 |
| 256 | 5228 | 286 | 9024 |
| 260 | 6805 | 296 | 5125 |
| 264 | 8324 | 305 | 5330 |
| 266 | 9038 | 310 | 5504 |
| 268 | 9709 | 315 | 5359 |
| 270 | 10320 | 325 | 3967 |
| 272 | 10760 | 340 | 935 |
| 274 | 11010 | 350 | 102 |

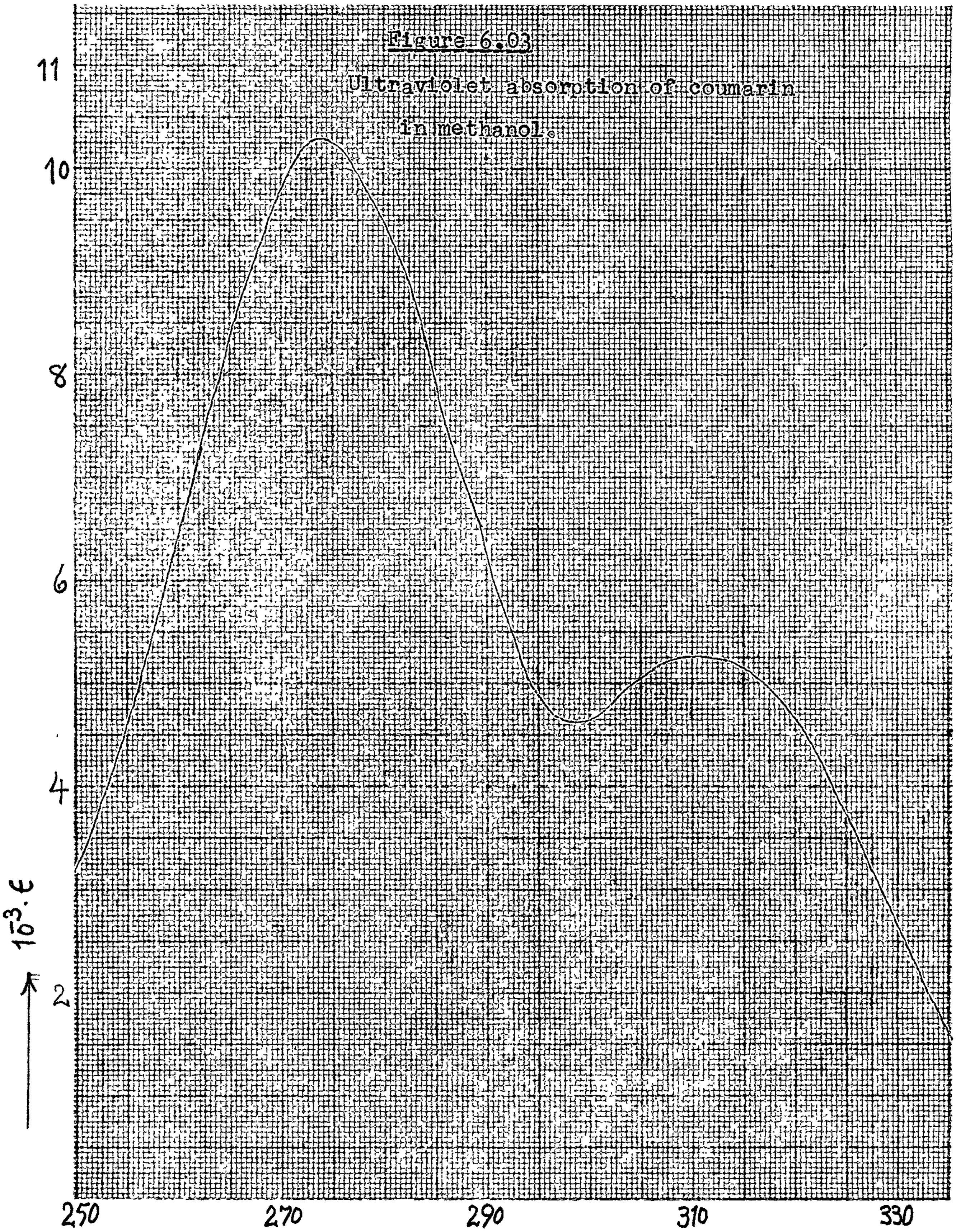


Figure 6.03
Ultraviolet absorption of coumarin in methanol.
11
10
8
6
4
2
$10^{-3}.\epsilon$
250
270
290
310
330
Wave-lenght in mμ

Table 6.03

Ultraviolet absorption of coumarin in methanol

| Wave length (mμ) | ε | Wave length (mμ) | ε |
|---|---|---|---|
| 250 | 3212 | 278 | 9754 |
| 252 | 3782 | 280 | 9419 |
| 254 | 4410 | 286 | 7856 |
| 256 | 5111 | 296 | 4717 |
| 258 | 5884 | 305 | 5140 |
| 260 | 6643 | 310 | 5228 |
| 264 | 8032 | 312 | 5242 |
| 266 | 8660 | 314 | 5183 |
| 268 | 9258 | 316 | 5053 |
| 270 | 9813 | 325 | 3650 |
| 272 | 10120 | 340 | 832 |
| 274 | 10200 | 350 | 102 |
| 276 | 9959 | | |

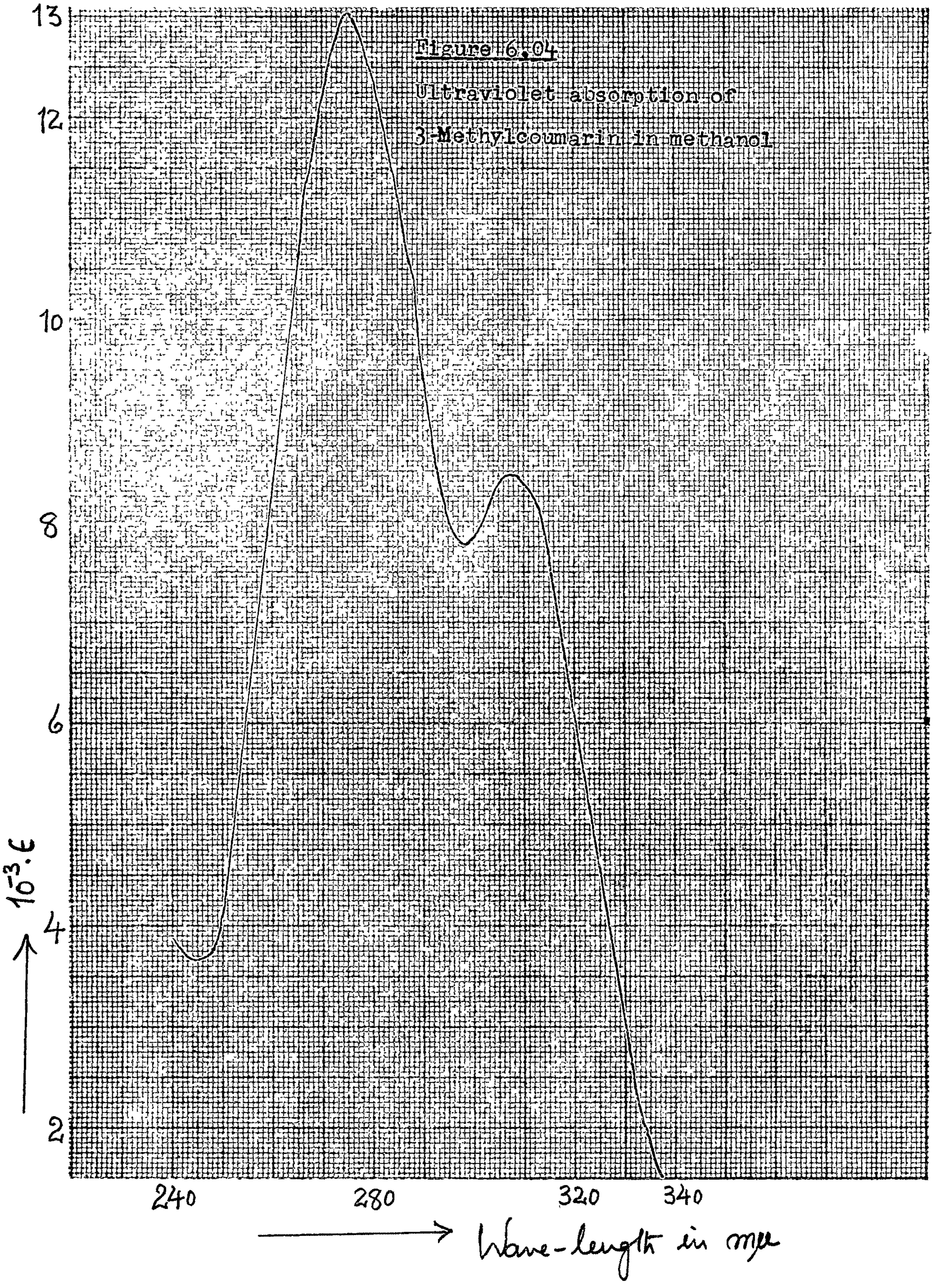


Figure 6.04

Ultraviolet absorption of 3-Methylcoumarin in methanol

## Table 6.04

Ultraviolet absorption of 3-methylcoumarin in methanol

| Wave length (mμ) | ε | Wave length (mμ) | ε |
|---|---|---|---|
| 240 | 3885 | 286 | 11060 |
| 242 | 3752 | 290 | 9313 |
| 244 | 3664 | 296 | 7902 |
| 246 | 3730 | 298 | 7767 |
| 248 | 3752 | 300 | 7945 |
| 250 | 4414 | 305 | 8364 |
| 252 | 4988 | 310 | 8320 |
| 254 | 5584 | 315 | 7681 |
| 256 | 6555 | 320 | 6223 |
| 260 | 8299 | 325 | 4591 |
| 264 | 9913 | 330 | 3311 |
| 268 | 11460 | 335 | 1832 |
| 270 | 12290 | 340 | 905 |
| 274 | 13020 | 345 | 574 |
| 278 | 12470 | 350 | 375 |
| 282 | 11940 | 360 | 265 |

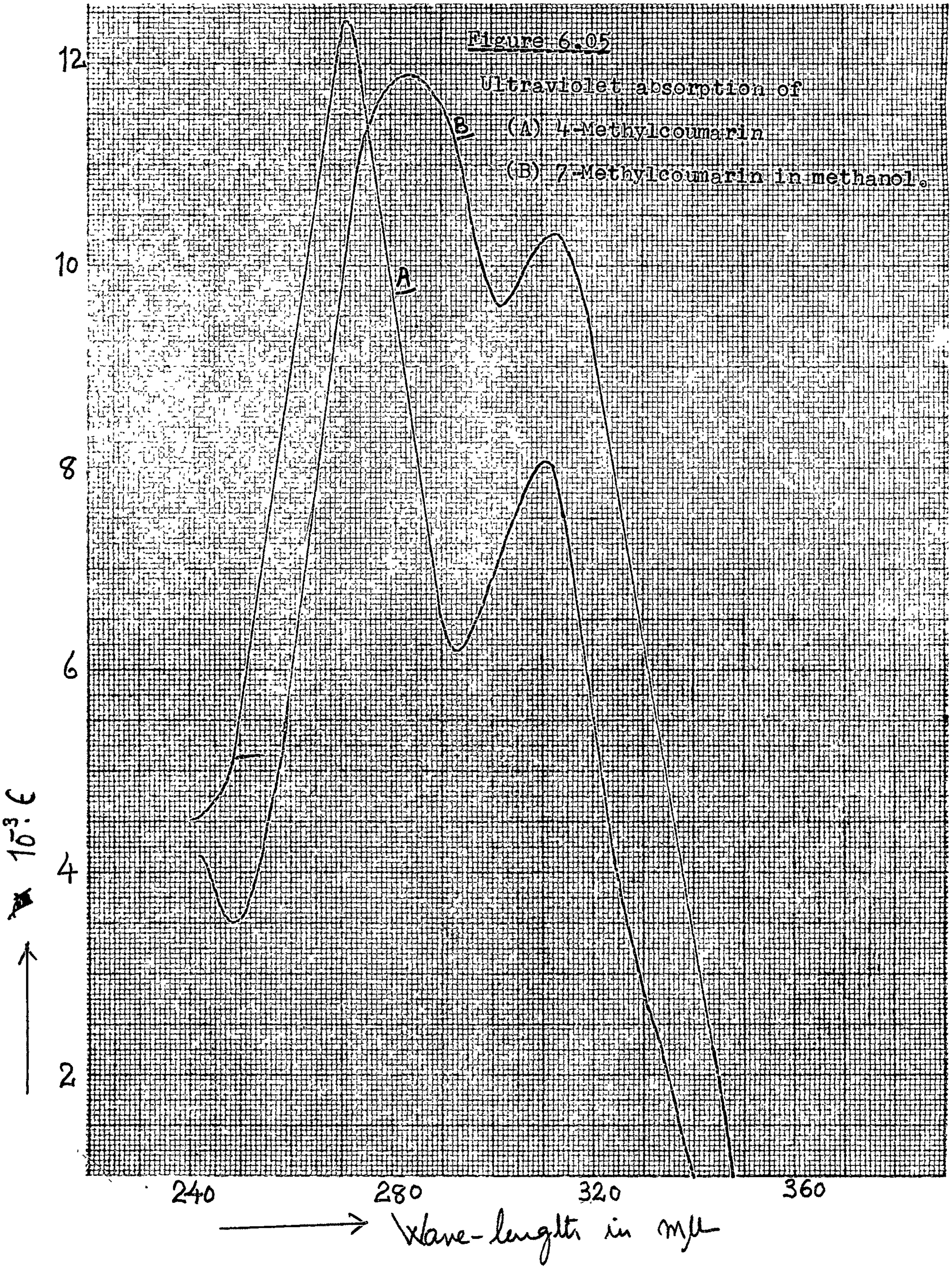


Figure 6.05

Ultraviolet absorption of
(A) 4-Methylcoumarin
(B) 7-Methylcoumarin in methanol.

### Table 6.05

Ultraviolet absorption of 4-methylcoumarin in methanol

| Wave length (mμ) | $\epsilon$ | Wave length (mμ) | $\epsilon$ |
|---|---|---|---|
| 240 | 4524 | 278 | 9860 |
| 242 | 4583 | 282 | 8686 |
| 244 | 4644 | 286 | 7268 |
| 246 | 4945 | 290 | 6273 |
| 248 | 5368 | 292 | 6152 |
| 250 | 5880 | 296 | 6454 |
| 252 | 6454 | 300 | 7117 |
| 254 | 7147 | 305 | 7690 |
| 256 | 7962 | 310 | 8052 |
| 258 | 8746 | 315 | 7087 |
| 260 | 9380 | 320 | 5126 |
| 262 | 9922 | 325 | 3680 |
| 266 | 11100 | 330 | 2745 |
| 270 | 12300 | 335 | 1659 |
| 272 | 12250 | 340 | 814 |
| 274 | 11640 | 345 | 573 |

Table 6.06

Ultraviolet absorption of 7-methylcoumarin in methanol

| Wave length (mμ) | ε | Wave length (mμ) | ε |
|---|---|---|---|
| 242 | 4147 | 286 | 11800 |
| 244 | 3992 | 288 | 11700 |
| 246 | 3585 | 290 | 11410 |
| 248 | 3430 | 294 | 10470 |
| 250 | 3623 | 296 | 9979 |
| 252 | 3953 | 300 | 9535 |
| 254 | 4360 | 305 | 9883 |
| 256 | 4825 | 310 | 10230 |
| 260 | 6124 | 315 | 9845 |
| 264 | 7558 | 320 | 8778 |
| 268 | 9126 | 325 | 7207 |
| 272 | 10950 | 330 | 5658 |
| 276 | 11450 | 335 | 4225 |
| 280 | 11620 | 340 | 2635 |
| 282 | 11690 | 350 | 775 |
| 284 | 11760 | 360 | 504 |

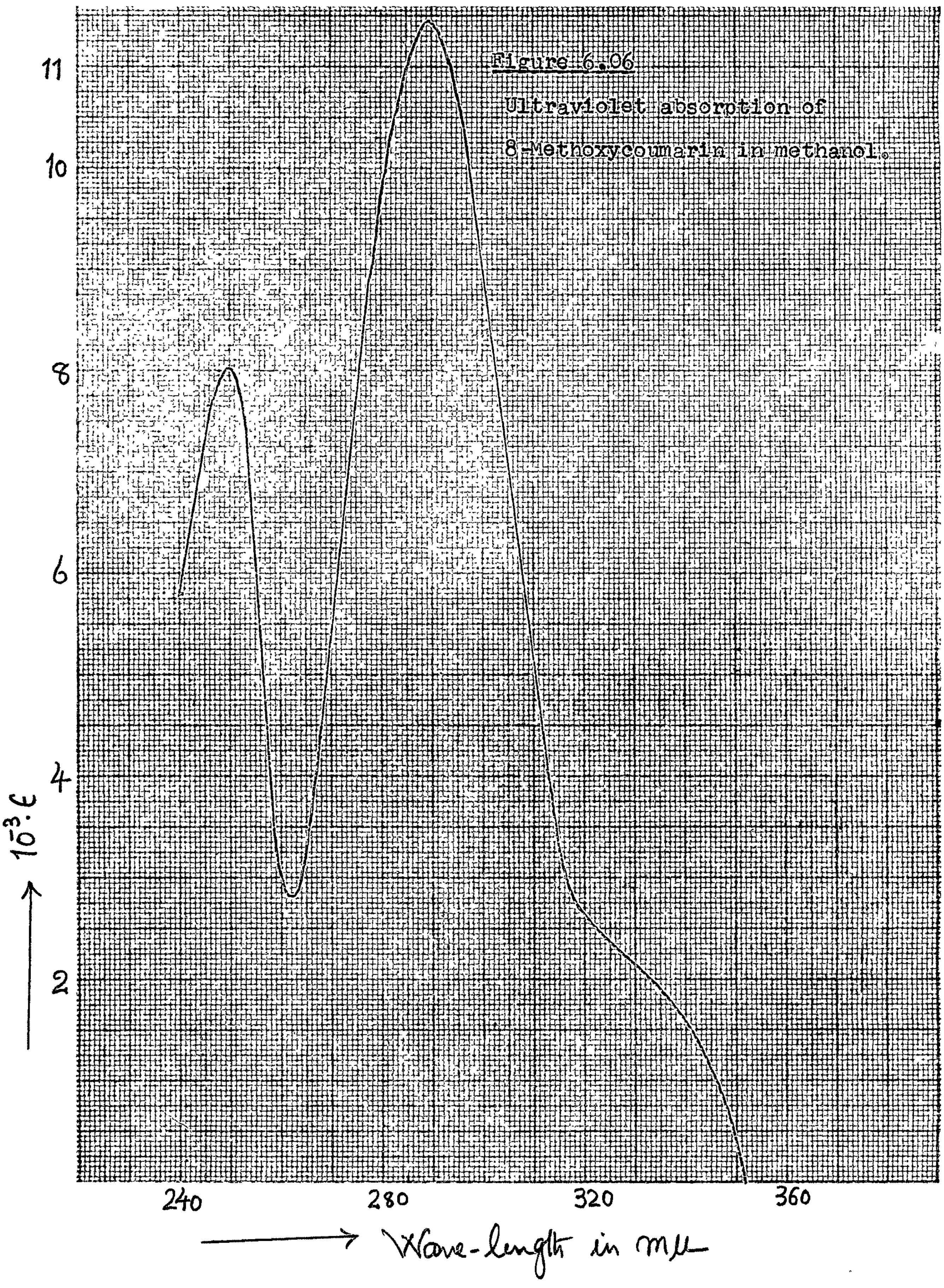


Figure 6.06

Ultraviolet absorption of 8-Methoxycoumarin in methanol.

### Table 6.07

Ultraviolet absorption of 8-methoxycoumarin in methanol

| Wave length (mμ) | ε | Wave length (mμ) | ε |
|---|---|---|---|
| 240 | 5737 | 276 | 8137 |
| 242 | 6449 | 280 | 9674 |
| 246 | 7499 | 284 | 10730 |
| 248 | 7800 | 290 | 11320 |
| 250 | 7949 | 294 | 10800 |
| 252 | 7725 | 296 | 10310 |
| 254 | 7060 | 300 | 9036 |
| 256 | 5438 | 305 | 6974 |
| 258 | 3938 | 310 | 4762 |
| 260 | 3075 | 320 | 2550 |
| 262 | 2813 | 330 | 2063 |
| 266 | 3750 | 340 | 1500 |
| 268 | 4537 | 350 | 975 |
| 272 | 6412 | 360 | 600 |
| 274 | 7311 | | |

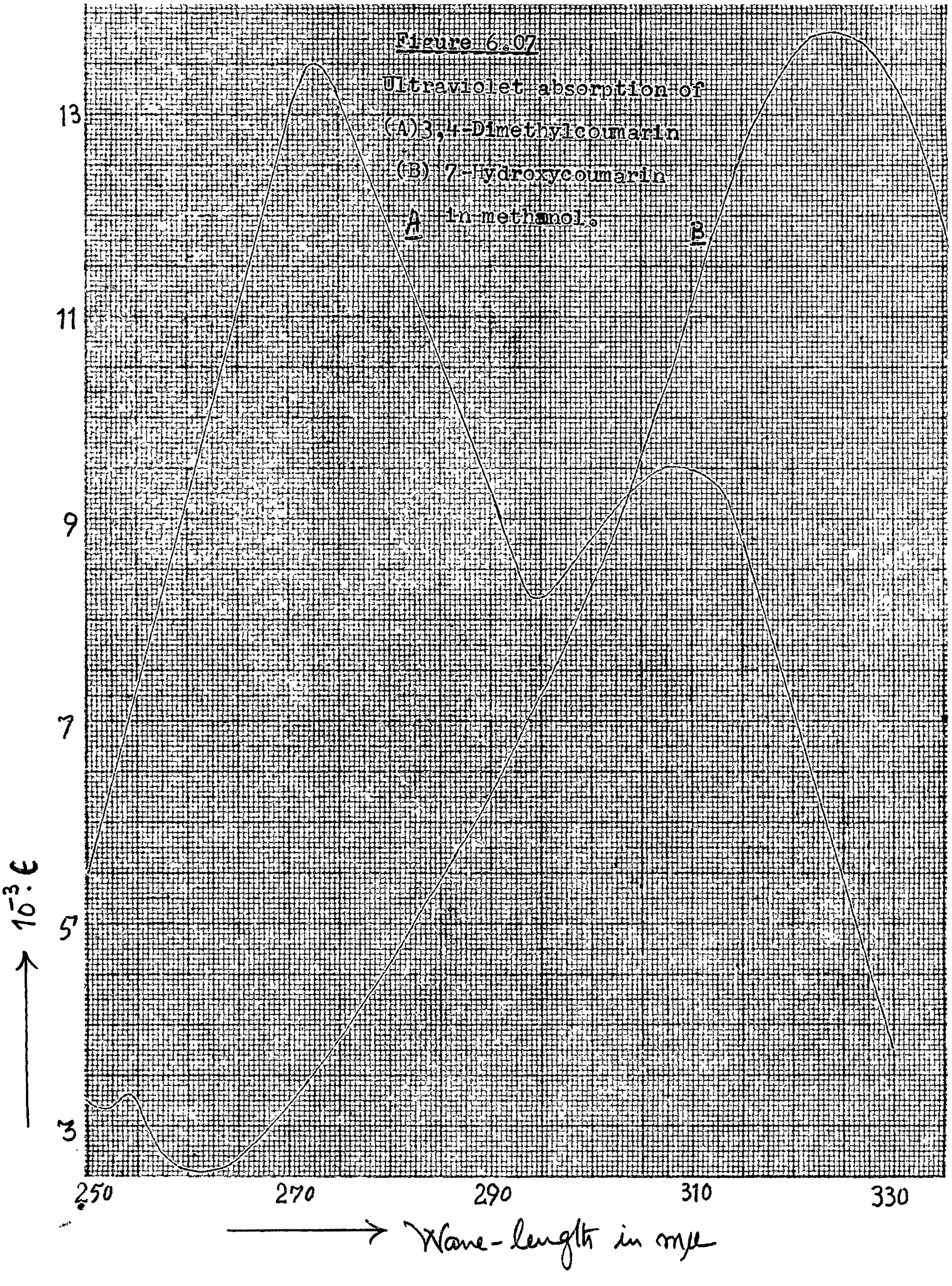


Figure 6.07

Ultraviolet absorption of
(A) 3,4-Dimethylcoumarin
(B) 7-Hydroxycoumarin
in methanol.

Table 6.08

Ultraviolet absorption of 7-hydroxycoumarin in methanol

| Wave length (mμ) | ε | Wave length (mμ) | ε |
|---|---|---|---|
| 250 | 3272 | 284 | 5378 |
| 252 | 3240 | 290 | 6448 |
| 253 | 3207 | 294 | 6965 |
| 254 | 3336 | 298 | 7839 |
| 255 | 3013 | 302 | 8584 |
| 256 | 2851 | 306 | 9815 |
| 258 | 2818 | 310 | 11240 |
| 260 | 2592 | 314 | 12440 |
| 262 | 2657 | 318 | 13280 |
| 264 | 2689 | 322 | 13600 |
| 266 | 2851 | 324 | 13710 |
| 268 | 3240 | 326 | 13680 |
| 270 | 3466 | 330 | 13220 |
| 272 | 3661 | 334 | 11920 |
| 274 | 3823 | 338 | 10530 |
| 276 | 4083 | 342 | 9005 |
| 278 | 4373 | 348 | 6253 |
| 279 | 4406 | 355 | 3240 |
| 280 | 4731 | 360 | 2138 |
| 282 | 5087 | 370 | 1652 |

## Table 6.09

Ultraviolet absorption of 3,4-dimethylcoumarin in methanol

| Wave length (mμ) | $\epsilon$ | Wave length (mμ) | $\epsilon$ |
|---|---|---|---|
| 240 | 4591 | 276 | 12630 |
| 242 | 4412 | 278 | 12330 |
| 244 | 4366 | 280 | 11640 |
| 246 | 4658 | 284 | 10880 |
| 248 | 5150 | 288 | 9539 |
| 250 | 5665 | 292 | 8420 |
| 252 | 6338 | 296 | 8330 |
| 254 | 7099 | 298 | 8598 |
| 256 | 7881 | 300 | 8867 |
| 258 | 8688 | 305 | 9361 |
| 260 | 9539 | 310 | 9404 |
| 262 | 10350 | 315 | 8598 |
| 264 | 11060 | 320 | 6539 |
| 266 | 11730 | 325 | 5218 |
| 268 | 12410 | 330 | 3493 |
| 270 | 12990 | 335 | 1792 |
| 272 | 13390 | 340 | 940 |
| 274 | 13210 | 345 | 582 |

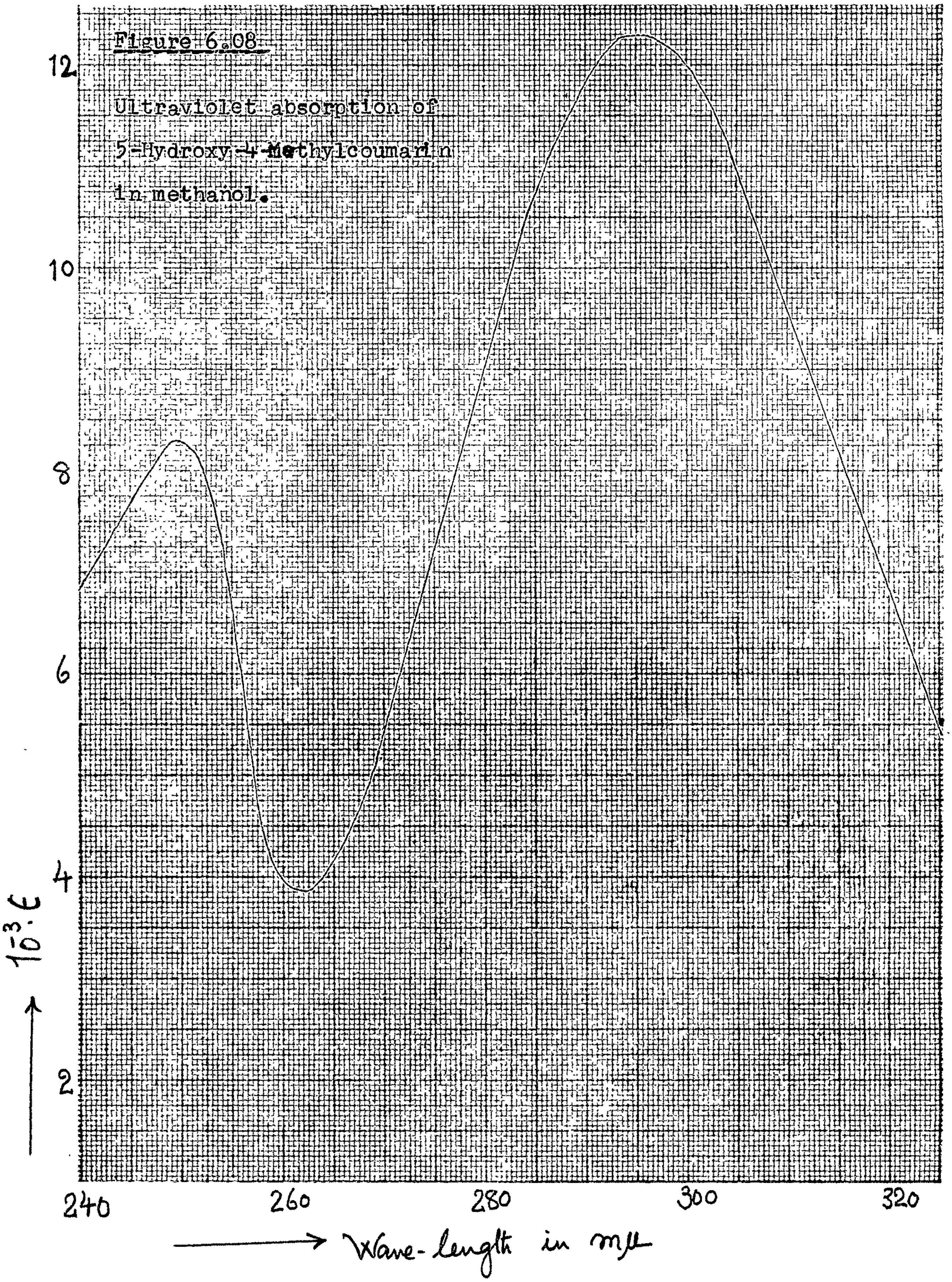


**Figure 6.08**

Ultraviolet absorption of 5-Hydroxy-4-Methylcoumarin in methanol.

### Table 6.10

Ultraviolet absorption of 5-hydroxy-4-methylcoumarin in methanol.

| Wave length (mμ) | $\epsilon$ | Wave length (mμ) | $\epsilon$ |
|---|---|---|---|
| 240 | 6754 | 278 | 8377 |
| 242 | 7207 | 282 | 9654 |
| 246 | 7815 | 286 | 10690 |
| 248 | 8009 | 290 | 11730 |
| 250 | 8226 | 292 | 11990 |
| 252 | 8074 | 294 | 12130 |
| 254 | 7425 | 296 | 12080 |
| 256 | 5758 | 298 | 11930 |
| 258 | 4720 | 300 | 11800 |
| 260 | 4005 | 305 | 11040 |
| 262 | 3832 | 310 | 9439 |
| 266 | 4438 | 320 | 6537 |
| 270 | 5585 | 330 | 4200 |
| 272 | 6234 | 340 | 2706 |
| 274 | 6926 | 350 | 1429 |
| 276 | 7663 | 360 | 823 |

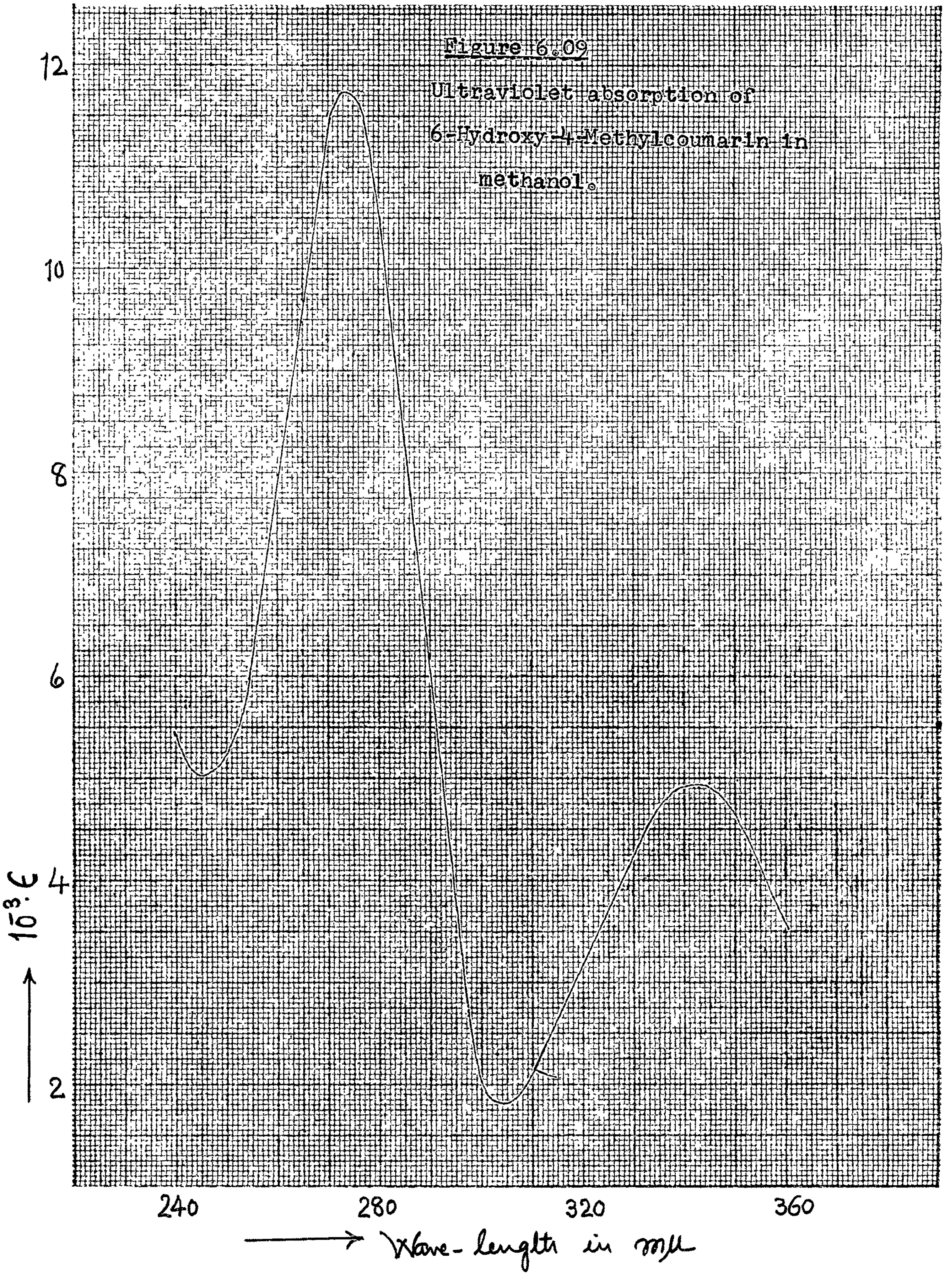


**Figure 6.09**

Ultraviolet absorption of 6-Hydroxy-4-Methylcoumarin in methanol.

### Table 6.11

Ultraviolet absorption of 6-hydroxy-4-methylcoumarin in methanol.

| Wave length (mμ) | ϵ | Wave length (mμ) | ϵ |
|---|---|---|---|
| 240 | 5507 | 290 | 6045 |
| 242 | 5202 | 295 | 3468 |
| 246 | 5086 | 300 | 2038 |
| 248 | 5248 | 305 | 1875 |
| 250 | 5389 | 310 | 2203 |
| 252 | 5670 | 315 | 2695 |
| 254 | 6092 | 320 | 3280 |
| 256 | 6631 | 325 | 3819 |
| 258 | 7333 | 330 | 4265 |
| 260 | 8013 | 335 | 4686 |
| 262 | 8694 | 340 | 4920 |
| 266 | 10310 | 342 | 4944 |
| 272 | 11620 | 345 | 4920 |
| 274 | 11670 | 350 | 4593 |
| 276 | 11570 | 355 | 4171 |
| 280 | 10420 | 360 | 3468 |
| 284 | 8622 | | |

## Figure 6.10

Ultraviolet absorption of 7-Hydroxy-4-Methylcoumarin in methanol.

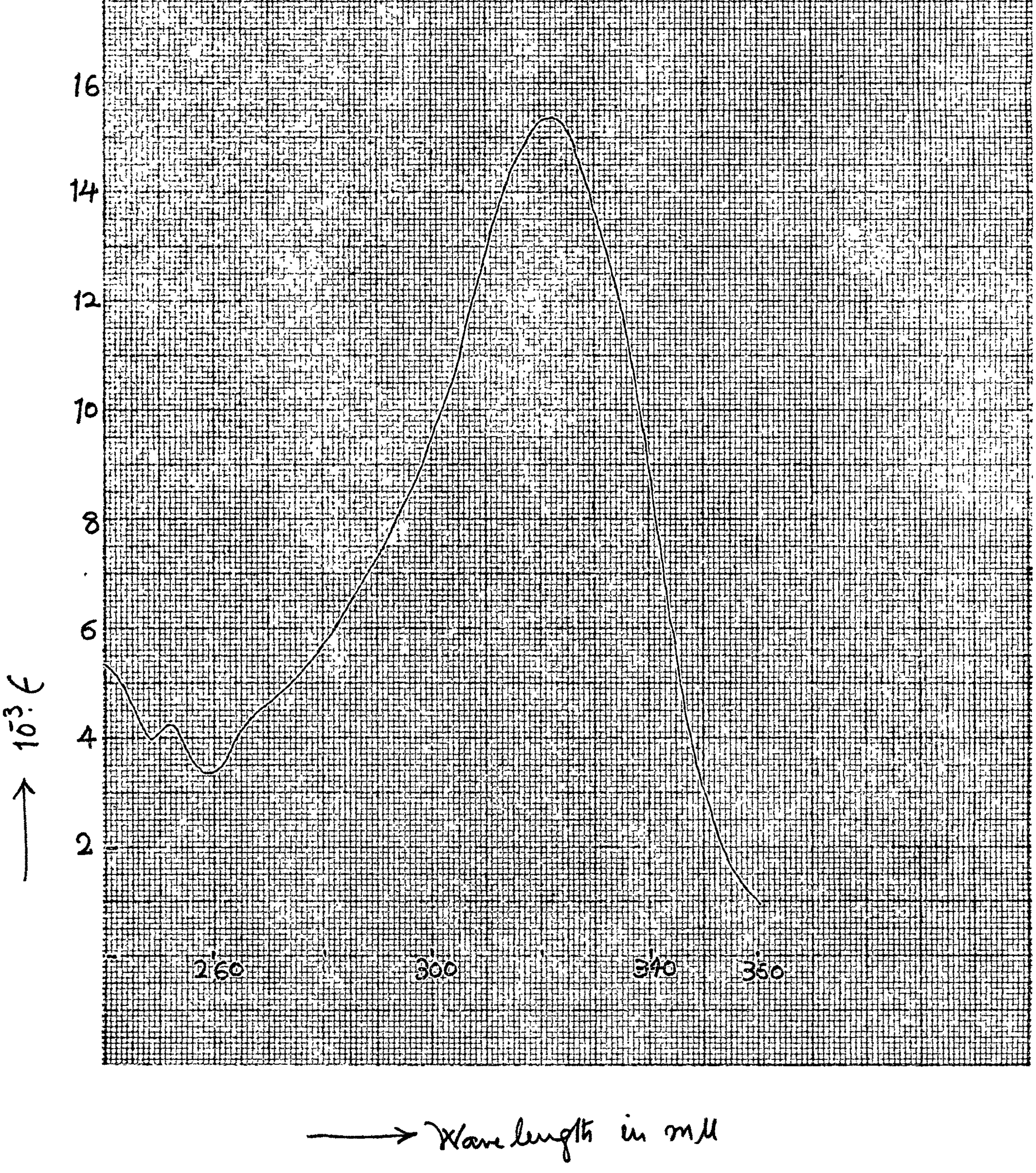


Table 6.12

Ultraviolet absorption of 7-hydroxy-4-methylcoumarin in methanol.

| Wave length (mμ) | ε | Wave length (mμ) | ε |
|---|---|---|---|
| 240 | 5248 | 310 | 12880 |
| 242 | 5042 | 315 | 14220 |
| 248 | 4075 | 320 | 15230 |
| 252 | 4213 | 325 | 15020 |
| 254 | 3868 | 328 | 14270 |
| 258 | 3384 | 330 | 13400 |
| 262 | 3522 | 335 | 11630 |
| 266 | 4385 | 340 | 9736 |
| 272 | 4834 | 345 | 6042 |
| 278 | 5352 | 350 | 3350 |
| 284 | 6492 | 355 | 1589 |
| 290 | 7423 | 360 | 967 |
| 300 | 9149 | | |

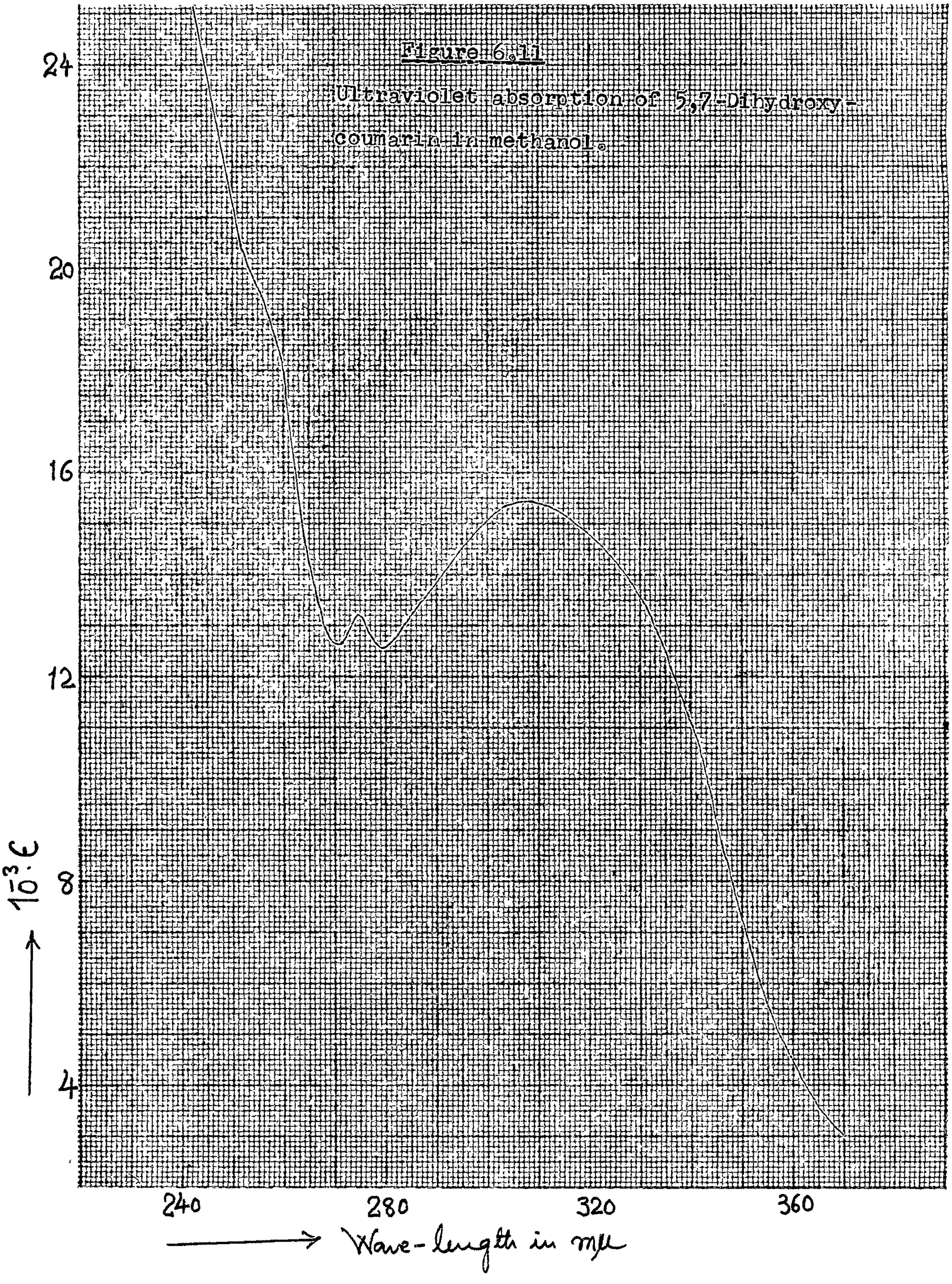


Figure 6.11

Ultraviolet absorption of 5,7-Dihydroxy-coumarin in methanol.

## Table 6.13

Ultraviolet absorption of 5,7-dihydroxycoumarin in methanol.

| Wave length (mμ) | ε | Wave length (mμ) | ε |
|---|---|---|---|
| 240 | 25770 | 290 | 13740 |
| 242 | 24630 | 294 | 14090 |
| 246 | 22630 | 296 | 14450 |
| 248 | 21780 | 300 | 14950 |
| 250 | 21140 | 305 | 15310 |
| 252 | 20290 | 310 | 15170 |
| 254 | 19510 | 315 | 14950 |
| 256 | 19070 | 320 | 14520 |
| 258 | 18150 | 325 | 14030 |
| 260 | 17230 | 330 | 13310 |
| 262 | 15590 | 335 | 11890 |
| 266 | 13460 | 340 | 10600 |
| 268 | 12960 | 345 | 8898 |
| 272 | 12670 | 350 | 7190 |
| 274 | 13110 | 355 | 5482 |
| 276 | 12390 | 360 | 4414 |
| 280 | 12750 | 370 | 3203 |
| 284 | 12880 | | |

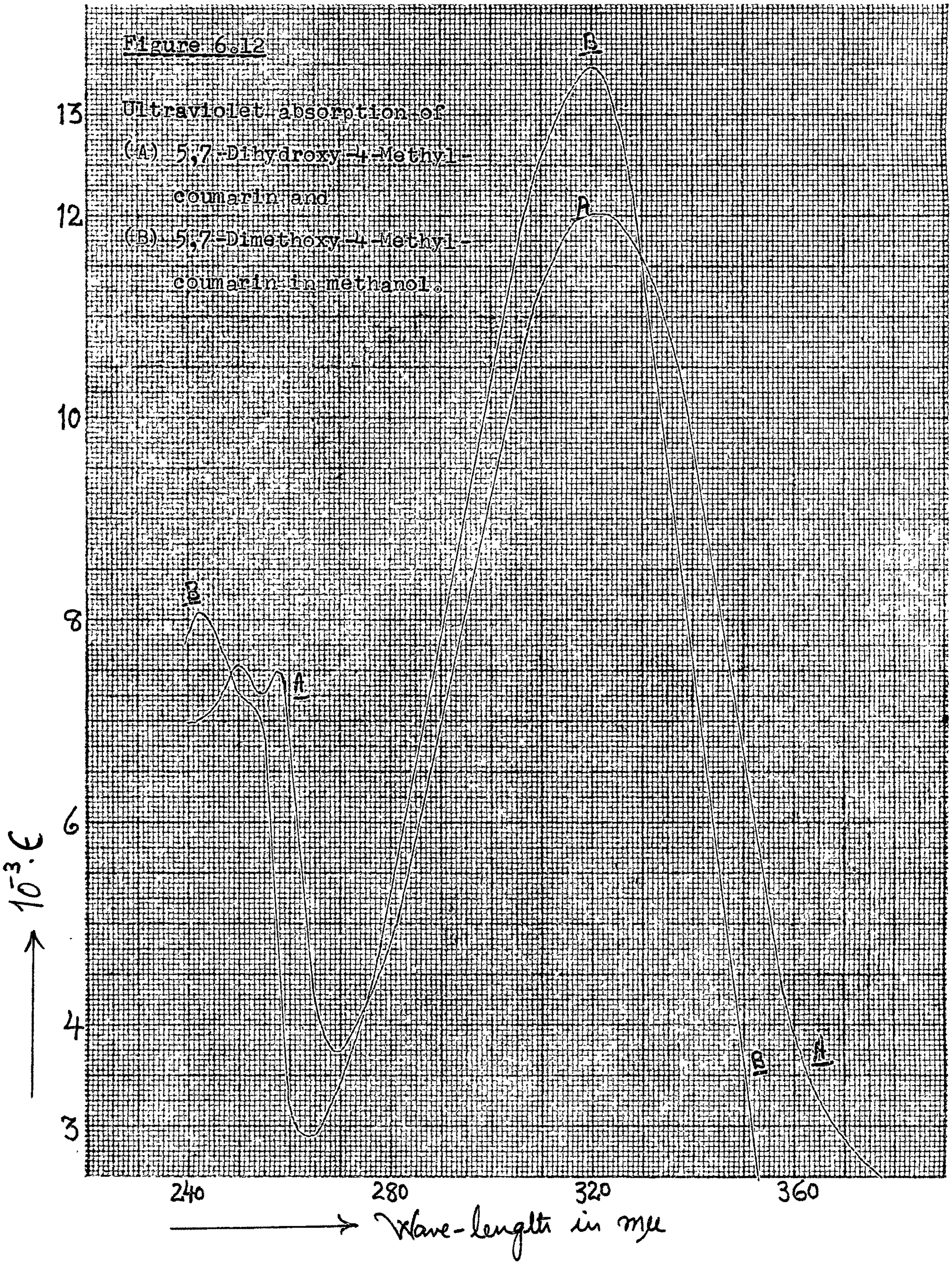


**Figure 6.12**

Ultraviolet absorption of
(A) 5,7-Dihydroxy-4-Methyl-coumarin and
(B) 5,7-Dimethoxy-4-Methyl-coumarin in methanol.

Table 6.14

Ultraviolet absorption of 5,7-dihydroxy-4-methylcoumarin in methanol

| Wave length (mμ) | ϵ | Wave length (mμ) | ϵ |
|---|---|---|---|
| 240 | 6971 | 296 | 8580 |
| 242 | 7044 | 300 | 9367 |
| 246 | 7223 | 305 | 10470 |
| 248 | 7471 | 310 | 11300 |
| 250 | 7508 | 315 | 11730 |
| 252 | 7365 | 320 | 11940 |
| 254 | 7223 | 325 | 11800 |
| 256 | 7330 | 330 | 11400 |
| 258 | 7437 | 335 | 10620 |
| 260 | 6794 | 340 | 9510 |
| 262 | 5434 | 345 | 8007 |
| 266 | 3896 | 350 | 6436 |
| 268 | 3718 | 355 | 5077 |
| 272 | 3968 | 360 | 3968 |
| 276 | 4183 | 365 | 3290 |
| 280 | 4826 | 370 | 2932 |
| 284 | 5649 | 380 | 2502 |
| 290 | 7079 | | |

Table 6.15

Ultraviolet absorption of 5,7-dimethoxy-4-methylcoumarin in methanol.

| Wave length (mμ) | ε | Wave length (mμ) | ε |
|---|---|---|---|
| 240 | 7736 | 290 | 7561 |
| 242 | 8041 | 294 | 8736 |
| 246 | 7780 | 296 | 9344 |
| 248 | 7518 | 300 | 10430 |
| 250 | 7214 | 305 | 11610 |
| 252 | 7214 | 310 | 12470 |
| 254 | 7041 | 315 | 13120 |
| 256 | 6433 | 320 | 13390 |
| 258 | 4911 | 325 | 12690 |
| 260 | 3694 | 330 | 11480 |
| 262 | 3042 | 335 | 9933 |
| 266 | 2998 | 340 | 8042 |
| 268 | 3173 | 345 | 5476 |
| 272 | 3651 | 350 | 3303 |
| 274 | 3868 | 355 | 1999 |
| 276 | 4216 | 360 | 1217 |
| 280 | 5042 | 370 | 782 |
| 284 | 5998 | 380 | 652 |

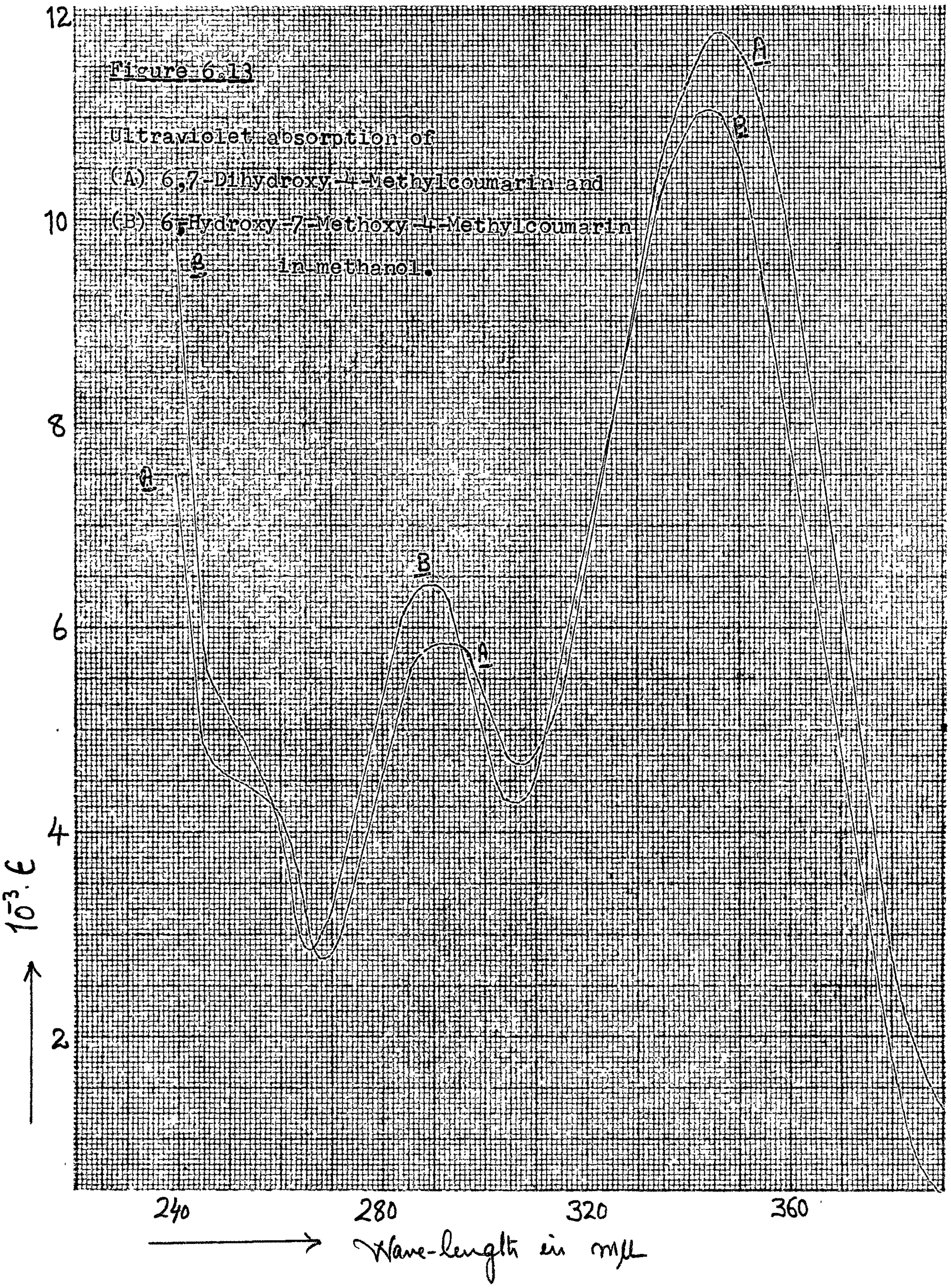


Figure 6.13

Ultraviolet absorption of
(A) 6,7-Dihydroxy-4-Methylcoumarin and
(B) 6-Hydroxy-7-Methoxy-4-Methylcoumarin
in methanol.

Table 6.16

Ultraviolet absorption of 6,7-dihydroxy-4-methylcoumarin in methanol.

| Wave length (mμ) | ϵ | Wave length (mμ) | ϵ |
|---|---|---|---|
| 240 | 7464 | 290 | 5782 |
| 242 | 6236 | 294 | 5801 |
| 244 | 5367 | 296 | 5782 |
| 246 | 4780 | 300 | 5328 |
| 248 | 4612 | 305 | 4780 |
| 250 | 4516 | 310 | 4780 |
| 252 | 4516 | 315 | 5499 |
| 254 | 4441 | 320 | 6671 |
| 256 | 4403 | 325 | 7936 |
| 258 | 4252 | 330 | 9279 |
| 260 | 4102 | 335 | 10580 |
| 262 | 3836 | 340 | 11340 |
| 266 | 2967 | 345 | 11760 |
| 268 | 2777 | 350 | 11570 |
| 272 | 3024 | 355 | 10770 |
| 274 | 3307 | 360 | 9618 |
| 276 | 3648 | 370 | 6331 |
| 280 | 4460 | 380 | 2929 |
| 284 | 5367 | 390 | 1323 |

## Table 6.17

Ultraviolet absorption of 7-methoxy-6-hydroxy-4-methylcoumarin in methanol.

| Wave length (mμ) | ϵ | Wave length (mμ) | ϵ |
|---|---|---|---|
| 240 | 9687 | 290 | 6356 |
| 242 | 7802 | 294 | 6049 |
| 244 | 6531 | 296 | 5720 |
| 246 | 5676 | 300 | 4909 |
| 248 | 5326 | 305 | 4296 |
| 250 | 5129 | 310 | 4559 |
| 252 | 4975 | 315 | 5501 |
| 254 | 4756 | 320 | 6774 |
| 256 | 4625 | 325 | 8110 |
| 258 | 4406 | 330 | 9294 |
| 260 | 4012 | 335 | 10280 |
| 262 | 3442 | 340 | 10890 |
| 266 | 2849 | 345 | 10980 |
| 268 | 2981 | 350 | 10500 |
| 272 | 3594 | 355 | 9491 |
| 274 | 4033 | 360 | 8110 |
| 276 | 4406 | 370 | 4690 |
| 280 | 5370 | 380 | 1644 |
| 284 | 6049 | 390 | 0504 |

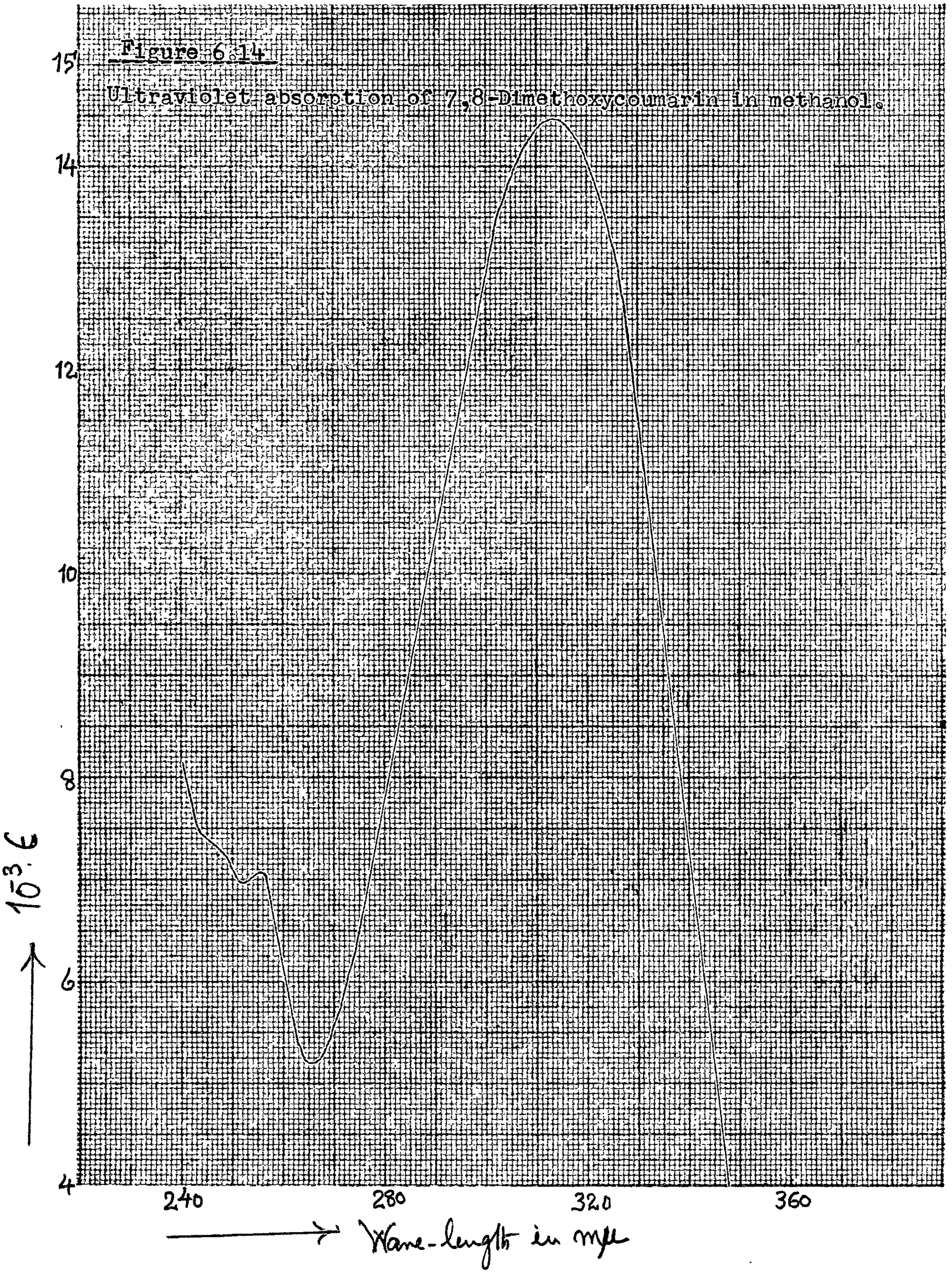


Figure 6.14

Ultraviolet absorption of 7,8-Dimethoxycoumarin in methanol.

Table 6.18

Ultraviolet absorption of 7,8-dimethoxycoumarin in methanol.

| Wave length (mμ) | ε | Wave length (mμ) | ε |
|---|---|---|---|
| 240 | 8164 | 280 | 7856 |
| 242 | 7764 | 284 | 8997 |
| 244 | 7395 | 288 | 10160 |
| 246 | 7271 | 292 | 11280 |
| 248 | 7206 | 296 | 12390 |
| 250 | 7055 | 300 | 13090 |
| 252 | 6963 | 305 | 13930 |
| 254 | 7025 | 310 | 14350 |
| 256 | 7055 | 315 | 14270 |
| 258 | 6717 | 320 | 13870 |
| 260 | 6255 | 325 | 12880 |
| 262 | 5669 | 330 | 11190 |
| 264 | 5299 | 335 | 9243 |
| 266 | 5207 | 340 | 7086 |
| 268 | 5330 | 345 | 4622 |
| 270 | 5669 | 350 | 2558 |
| 272 | 6070 | 360 | 0863 |
| 274 | 6471 | 370 | 493 |
| 276 | 6933 | | |

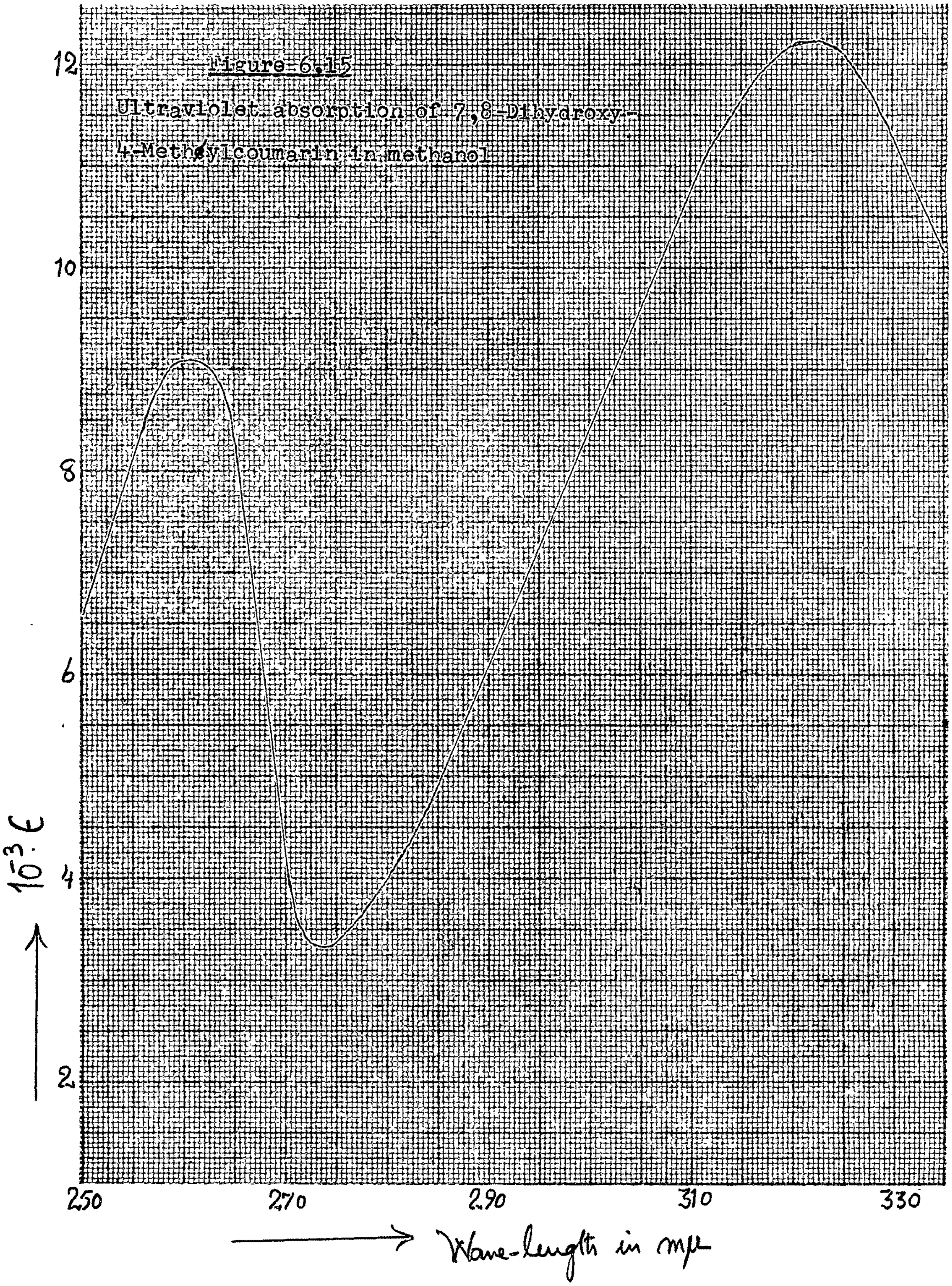


Figure-6.15

Ultraviolet absorption of 7,8-Dihydroxy-4-Methylcoumarin in methanol

Table 6.19

Ultraviolet absorption of 7,8-dihydroxy-4-methylcoumarin in methanol.

| Wave length (mμ) | ϵ | Wave length (mμ) | ϵ |
|---|---|---|---|
| 250 | 6377 | 290 | 5848 |
| 252 | 7099 | 292 | 6306 |
| 254 | 7839 | 294 | 6834 |
| 256 | 8333 | 296 | 7311 |
| 258 | 8684 | 300 | 8368 |
| 260 | 8966 | 305 | 9690 |
| 262 | 8984 | 310 | 10800 |
| 264 | 8620 | 315 | 11530 |
| 266 | 7450 | 320 | 12070 |
| 268 | 5865 | 325 | 11940 |
| 270 | 4422 | 330 | 11110 |
| 272 | 3612 | 335 | 9970 |
| 274 | 3294 | 340 | 8403 |
| 276 | 3418 | 345 | 6290 |
| 278 | 3593 | 350 | 4298 |
| 280 | 3893 | 355 | 2766 |
| 282 | 4263 | 360 | 1726 |
| 284 | 4615 | 370 | 652 |
| 286 | 4967 | 380 | 352 |
| 288 | 5426 | | |

Table 6.20

Ultraviolet absorption maxima and extinction coefficients for coumarins

| Sl. No.<br>1. | Solvent<br>2. | Substance<br>3. | $\lambda_1$ mμ<br>4. | $\lambda_2$ mμ<br>5. | log $\epsilon_1$<br>6. | log $\epsilon_2$<br>7. |
|---|---|---|---|---|---|---|
| 1 | Water | (1) | 277 | 305 | 4.03 | 3.73 |
| 2 | A | (1) | 274 | 311 | 4.03 | 3.74 |
| 3 | C | (1) | 274 | 311 | 4.01 | 3.72 |
| 4 | C | 3-Me ( I) | 274 | 307 | 4.11 | 3.92 |
| 5 | C | 4-Me ( I) | 271 | 310 | 4.10 | 3.90 |
| 6 | B | 5-Me ( I) | 275 | 315 | 4.04 | 3.84 |
| 7 | A | 6-Me ( I) | 278 | 320 | 4.07 | 3.74 |
| 8 | C | 7-Me ( I) | 284 | 312 | 4.10 | 4.01 |
| 9 | A | 7-Me ( I) |  | 315 |  | 3.95 |
| 10 | A | 7-Me ( I) | 283 | 313 | 4.03 | 3.92 |
| 11 | A | 8-Me ( I) | 281 | 310 | 4.07 | 3.65 |
| 12 | A | 5-MeO ( I) |  | 298 |  | 4.11 |
| 13 | A | 6-MeO ( I) | 278 | 342 | 4.06 | 3.69 |
| 14 | A | 7-MeO ( I) |  | 323 |  | 4.33 |
| 15 | A | 7-MeO ( I) | 252 | 318-23 | 3.32 | 4.17 |

Tabla 6.20 ( Continued)

| 1 | 2 | 3 | 4 | 5 | 6 | 7 |
|---|---|---|---|---|---|---|
| 16 | C | 8-MeO ( I) | 250 | 292 | 3.9 | 4.05 |
| 17 | A | 5-OH ( I) | 250 | 298 | 3.79 | 4.01 |
| 18 | A | 6-OH ( I) | 280 | 345 | 4.03 | 3.65 |
| 19 | C | 7-OH ( I) | 254 | 324 | 3.52 | 4.14 |
| 20 | B | 8-OH ( I) | 253 | 292 | 3.92 | 4.00 |
| 21 | B | 3-Me-6-MeO ( I) |  | 337 |  | 3.73 |
| 22 | B | 3-Me-7-MeO ( I) |  | 320 |  | 4.20 |
| 23 | B | 3-Me-8-MeO ( I) | 252 | 287 | 3.95 | 4.11 |
| 24 | C | 4,3-di-Me ( I) | 272 | 308 | 4.13 | 3.97 |
| 25 | B | 4,6-di-Me ( I) | 273-3.5 | 317-23 | 4.01 | 3.69 |
| 26 | B | 4,7-di-Me ( I) | 277-8.5 | 314-15 | 4.03 | 3.95 |
| 27 | B | 4,8-di-Me ( I) | 276.5-8 | 311 | 4.09 | - |
| 28 | C | 4-Me-5-OH ( I) | 250 | 294 | 3.91 | 4.08 |
| 29 | C | 4-Me-6-OH ( I) | 274 | 342 | 4.07 | 3.69 |
| 30 | C | 4-Me-7-OH ( I) | 252 | 322 | 3.62 | 4.18 |
| 31 | B | 4-Me-6-MeO ( I) | 273 | 340 | 4.05 | 3.70 |

(Continued on next page )

Table 6.20 ( Continued )

| 1. | 2. | 3. | 4. | 5. | 6. | 7. |
|---|---|---|---|---|---|---|
| 32 | C | 5,7-$(OH)_2$ ( I) | | 306 | | 4.18 |
| 33 | C | 4-Me-5,7-diOH ( I) | 258 | 320 | 3.87 | 4.08 |
| 34 | C | 4-Me-5,7-diMeO ( I) | 252 | 320 | 3.86 | 4.13 |
| 35 | C | 4-Me-6,7-diOH ( I) | 294 | 346 | 3.76 | 4.07 |
| 36 | C | 4-Me-6-OH-7-MeO( I) | 290 | 345 | 3.80 | 4.04 |
| 37 | B | 4-Me-6,7-diMeo ( I) | 290 | 342 | 3.72 | 4.06 |
| 38 | B | 3-Me-6,7-diMeo ( I) | 295 | 340 | 3.76 | 4.10 |
| 39 | C | 7,8-diMeo ( I) | 255 | 312 | 3.85 | 4.16 |
| 40 | C | 4-Me-7,8-diOH ( I) | 261 | 322 | 3.95 | 4.08 |

(I) indicates coumarin. A = 95 % ethanol ; B = ethanol ; and C = methanol.

Data for compound Nos. 1-5, 8,16,19,24,28-30,32-36,39 and 40 reported by (15); data for Nos 6 reported by (1) ; for Nos. 7,9,12-14, 17 and 18 reported by (2) ; for Nos. 10,11,15,20-23 31,37 and 38 reported by (3) ; and for Nos. 25-27 reported by (7).

Table 6.21

Effect of substitution on the ultraviolet absorption maxima of coumarin

| Position | Substituent | | | | | |
|---|---|---|---|---|---|---|
| | Me | | MeO | | OH | |
| | $\Delta\lambda_1$ | $\Delta\lambda_2$ | $\Delta\lambda_1$ | $\Delta\lambda_2$ | $\Delta\lambda_1$ | $\Delta\lambda_2$ |
| 3 | + 0 | - 4 | - | - | - | - |
| 4 | - 4 | + 0 | - | - | - | - |
| 5 | + 0 | + 4 | - | - 16 | - 22 | - 16 |
| 6 | + 4 | + 8 | + 4 | + 32 | + 4 | + 32 |
| 7 | + 8 | + 4 | - 22 | + 12 | - 22 | + 12 |
| 8 | + 8 | + 0 | - 22 | - 18 | - 22 | - 18 |

$\Delta\lambda_1$ indicates the shift from the first ultraviolet absorption maxima, 274 mμ, of coumarin when the H in the position indicated is substituted by methyl, methoxy or hydroxy groups.

$\Delta\lambda_2$ indicates the shift from the second ultraviolet absorption maxima, 311 mμ, of coumarin when H in the position indicated is substituted by methyl, methoxy or hydroxy groups.

## Discussion :

Table 6.20 gives the values for ultraviolet absorption maxima and log of extinction coefficients for coumarins. Coumarin shows one principal maximum at 274 mμ and second maximum at 311 mμ. In almost all cases the principal maxima are sharp and well defined but ~~is~~ the second maxima except in few cases are in general broad . Table 6.21 gives the shifts from these maxima when one H in coumarin is substituted by methyl, hydroxy or methoxy group.

Methyl-substituted coumarins : The data presented in tables 6.21 indicate that when one H in coumarin is substituted by a methyl group, the shifts in the two maxima of coumarin are small, but significant and characteristic for the position of substitution. A study of results presented in table 6.20 also indicates that for dimethylcoumarins, the shifts in the two maxima of coumarin are in fair agreement with those calculated from algebric addition of the shifts for the maxima for the two groups from table 6.21. Thus the shifts given in table 6.21 should be useful in distinguishing between different monomethyl- and dimethylcoumarins.

5,6,7 and 8-monohydroxy- and / or methoxycoumarins : The results in table 6.21 ~~is~~ also indicate that the substitution of hydroxy or methoxy groups substantially shifts the maxima of coumarin. These could be used, however, for mono-substituted coumarins, the substituent being OH or MeO, to distinguish between (5 or 8 ), 6 or 7 positions of substitutions. However, the shifts could not be used to decide whether the substituent is OH or MeO. Also, the shifts are not additive for di(OH and / or MeO ) substituted coumarins, as calculated from table 6.20 ; : (15).

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7

## SORPTION STUDIES WITH COUMARINS

Sorption of weak nonelectrolytes on ionexchange resins has been investigated by several workers (1-20); no study with coumarins is, however, available. So the column sorption-desorption of coumarin with water and methanol as solvents and the comparative sorption of coumarin and twelve substituted coumarins in 10 % methanol (by volume) on a strongly basic anion-exchange resin, Amberlite IRA-400, are described in this chapter (21).

### Experimental :

Resin : The resin used was Amberlite IRA-400 (Rohm and Haas Co.). This is a strongly basic anion exchange resin, obtained by introducing strongly basic quaternary ammonium groups, as ionogenic groups, into a styrene divinylbenzene copolymer. The resin was air-dried and -40,+60 mesh fraction was used in this work.

The resin was cycled thrice between sodium chloride and sodium hydroxide, finally regenerated with a large excess of sodium hydroxide, washed free of alkali, air-dried, and stored. The moisture content was estimated by drying samples (~ 0.5 g.) to a constant weight at 105°C. For capacity estimation, weighed samples ( ~ 0.5 g.) were placed in contact with 50 cc. of standard hydrochloric acid (~ 0.1 N ) with intermittent shaking and the acid sorbed was estimated: Moisture content = 21.15 % ; capacity per g. of air-dried and oven dried resin = 2.035 meq. and 2.58 meq. respectively.

Chemicals : 8-Hydroxycoumarin, 7,8-dihydroxy-4-methylcoumarin and 7,8-dimethoxycoumarin ~~were~~ obtained from Prof.S.M.Sethna's laboratory, were recrystallised and checked for melting points. Coumarin and rest of substituted coumarins were from samples used in chapter 6. Hydrochloric acid and sodium hydroxide of A.R. quality, distilled water and distilled methanol(B.D.H.)were used.

Procedure : Coumarin and substituted coumarins were estimated in column effluent samples by ultraviolet absorption(21)with Beckman Model DU spectrophotometer, using 10 mm. quartz cells.

Results and Discussion :

Run one : A resin column of the following column data was set up : capacity of the resin in the column = 92 meq. bed volume = 123 ml. bed length = 53.5 cm, void-volume = 30 ml. An aqueous coumarin solution ($5.49 \times 10^{-4}$ M ) was passed downflow in the column at the rate of 10 ml./min. and 36 samples ( each of 100 ml.) were collected. The first sample included 30 ml. of water from void-volume. The first sample and then even numbered samples were estimated for coumarin. Let 'a' and 'b' denote for the sorption run the concentration (in g. moles/litre) of solute in the influent solution and effluent samples respectively ; then 100(a-b) / a is denoted by x. The sorption curve is obtained by plotting x against the effluent sample number. The sorption curve obtained in this way is shown in Fig. 7.1. Plot 1 A.

After 36th sample, the column was drained, backwashed with distilled water, resin allowed to settle, and then distilled water was passed downflow at the rate of 10 ml./min.; 36 samples (each of 100 ml.) were collected. The first and then the even numbered samples were estimated for coumarin. Let b denote the concentration of solute (in g.moles./litre)

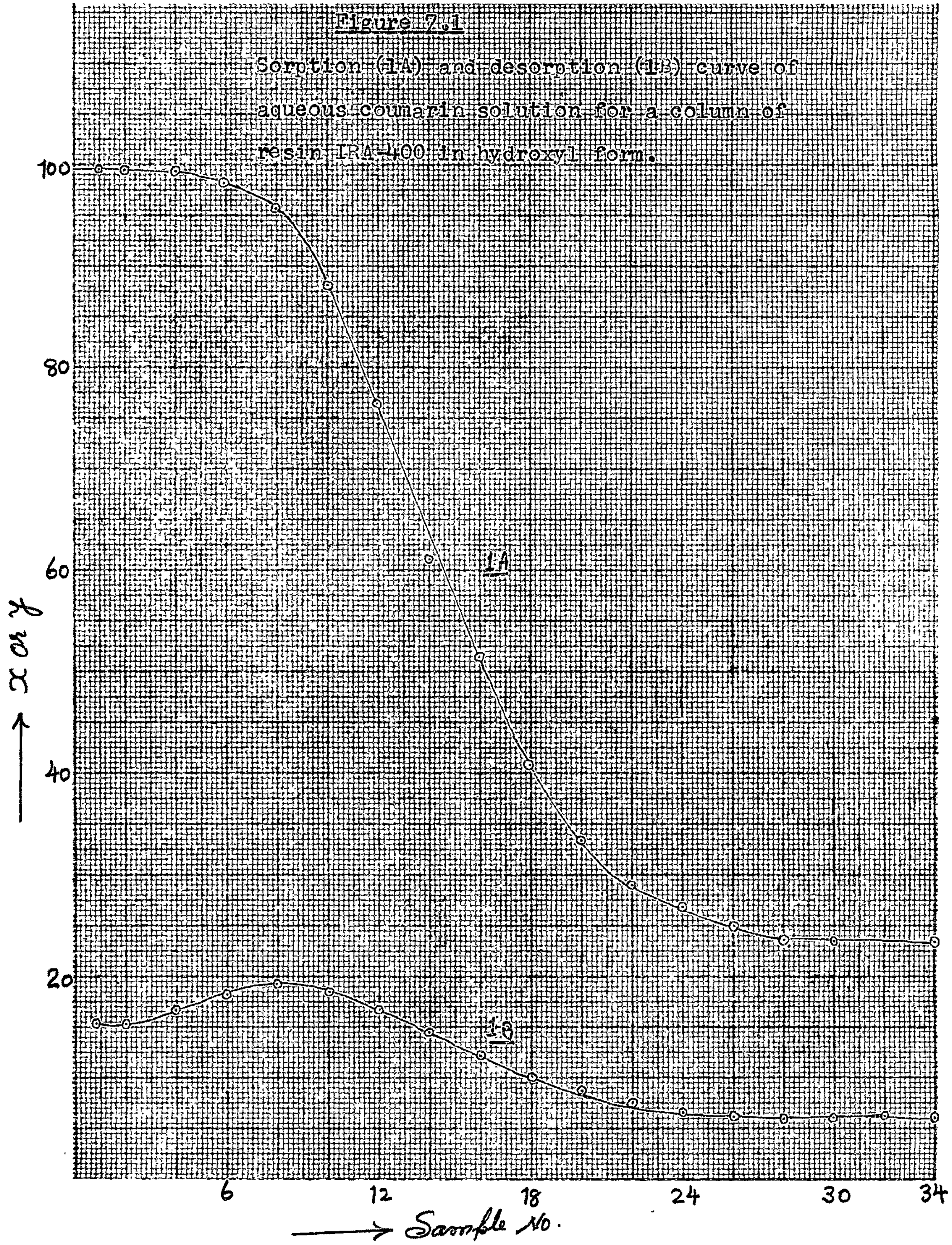


Figure 7.1

Sorption (1A) and desorption (1B) curve of aqueous coumarin solution for a column of resin IRA-400 in hydroxyl form.

### Table 7.01 a

Sorption of coumarin from solution ~~with~~ in water on Amberlite IRA-400 in hydroxyl form

| Sample No. | x | Sample No. | x | Sample No. | x |
|---|---|---|---|---|---|
| 1 | 100 | 14 | 61.5 | 26 | 25.8 |
| 2 | 100 | 16 | 50.2 | 28 | 24.4 |
| 4 | 100 | 18 | 42.2 | 30 | 24.0 |
| 6 | 100 | 20 | 34.0 | 32 | 24.0 |
| 8 | 95.9 | 22 | 29.7 | 34 | 24.0 |
| 10 | 88.3 | 24 | 27.8 | 36 | 24.0 |
| 12 | 76.8 | | | | |

### Table 7.01 b

Elution of coumarin after the above run with water

| Sample No. | y | Sample No. | y | Sample No. | y |
|---|---|---|---|---|---|
| 1 | 15.7 | 14 | 14.9 | 28 | 6.0 |
| 2 | 15.9 | 16 | 12.6 | 30 | 5.9 |
| 4 | 16.9 | 18 | 10.6 | 32 | 5.8 |
| 6 | 18.4 | 20 | 9.0 | 34 | 5.8 |
| 8 | 19.5 | 22 | 7.8 | 36 | 5.8 |
| 10 | 18.8 | 24 | 7.1 | 38 | 5.8 |
| 12 | 17.1 | 26 | 6.4 | | |

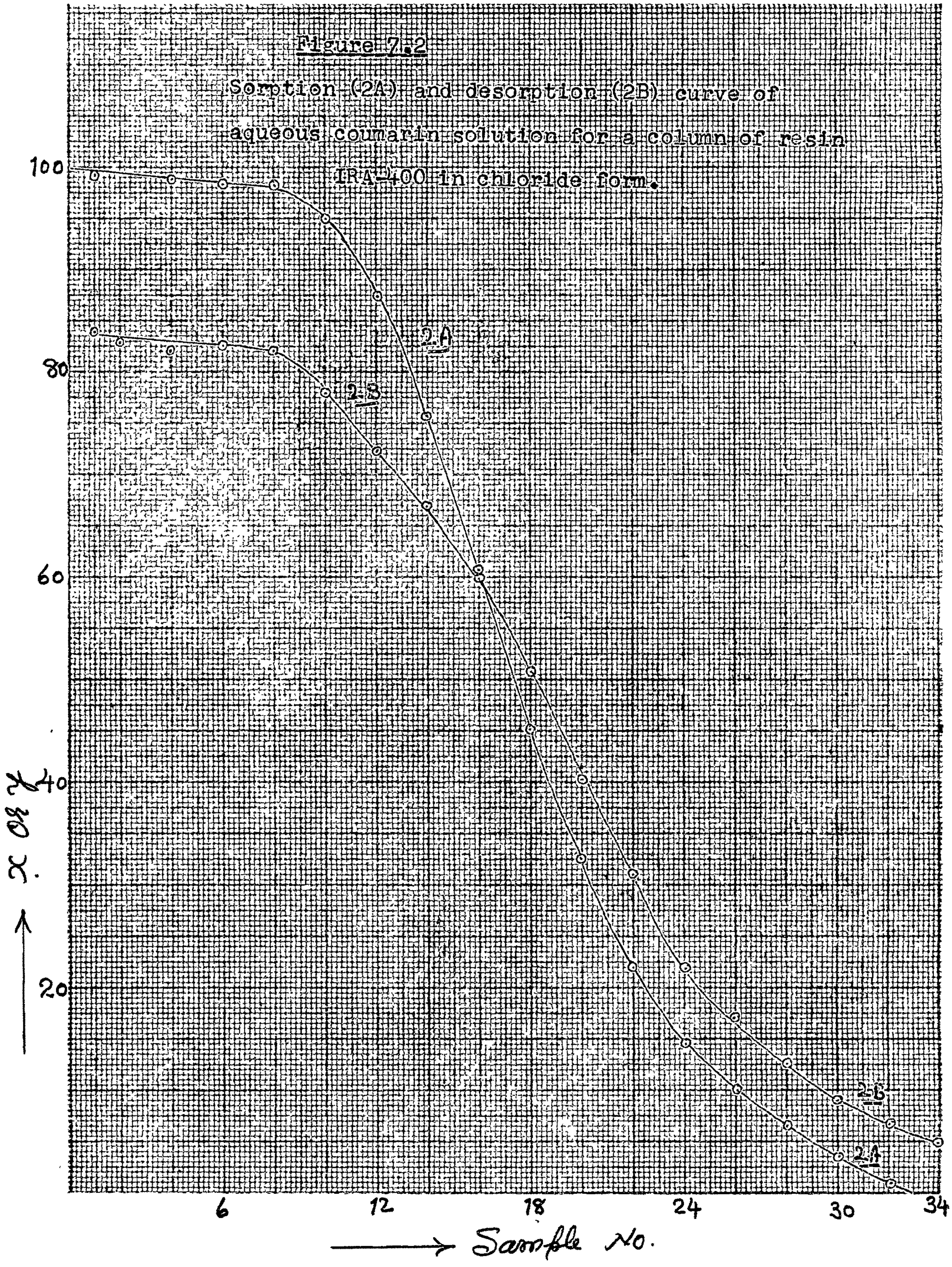


**Figure 7.2**

Sorption (2A) and desorption (2B) curve of aqueous coumarin solution for a column of resin IRA-400 in chloride form.

### Table 7.02 a

Sorption of coumarin from solution ~~with~~ in water on IRA-400 in chloride form.

| Sample No. | x | Sample No. | x | Sample No. | x |
|---|---|---|---|---|---|
| 1 | 100 | 12 | 87.4 | 24 | 15.2 |
| 2 | 100 | 14 | 75.9 | 26 | 10.0 |
| 4 | 100 | 16 | 61.2 | 28 | 5.2 |
| 6 | 100 | 18 | 45.7 | 30 | 3.0 |
| 8 | 100 | 20 | 33.3 | 32 | 1.5 |
| 10 | 95 | 22 | 22.8 | 34 | 0.0 |

### Table 7.02 b

Elution of coumarin after the above run with water

| Sample No. | y | sample No. | y | sample No. | y |
|---|---|---|---|---|---|
| 1 | 84.0 | 14 | 67.1 | 28 | 10.0 |
| 2 | 82.8 | 16 | 60.9 | 30 | 6.8 |
| 4 | 81.9 | 18 | 56.0 | 32 | 4.5 |
| 6 | 82.8 | 20 | 38.5 | 34 | 2.6 |
| 8 | 82.2 | 22 | 29.9 | 36 | 1.3 |
| 10 | 77.6 | 24 | 19.9 | 38 | 0.4 |
| 12 | 70.5 | 26 | 15.6 | 40 | 0.1 |

Figure 7.3

Desorption (3) of coumarin by methanol for the chloride form of the resin IRA-400.

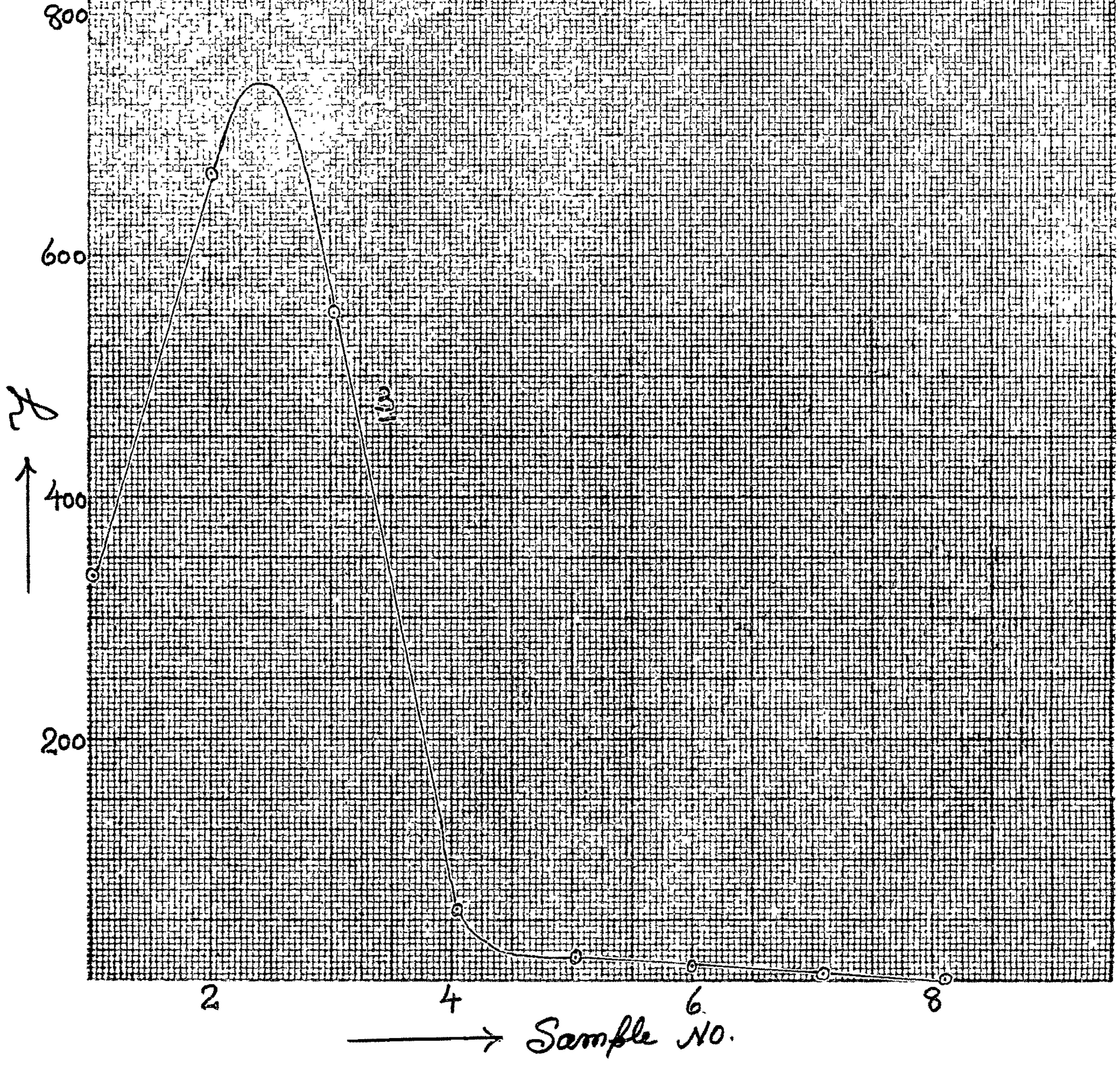


Table 7.03 b

Elution of coumarin after the absorption of aqueous solution of coumarin with methanol

| Sample No. | y | Sample No. | y |
|---|---|---|---|
| 1 | 344 | 6 | 10.5 |
| 2 | 669 | 7 | 8.0 |
| 3 | 551 | 8 | 4.0 |
| 4 | 63 | 9 | 1.5 |
| 5 | 22.5 | 10 | 0.0 |

## Table 7.04

Sorption of coumarin from solution in 10 % methanol on IRA-400 in chloride form.

| Sample No. | x | Sample No. | x | Sample No. | x |
|---|---|---|---|---|---|
| 1 | 62.3 | 6 | 1.57 | 12 | 0.5 |
| 2 | 19.4 | 8 | 0.87 | 14 | 0.17 |
| 4 | 4.4 | 10 | 0.7 | - | - |

## Table 7.05

Sorption of 7,8-dimethoxycoumarin from solution in 10 % methanol on IRA-400 in chloride form.

| Sample No. | x | Sample No. | x | Sample No. | x |
|---|---|---|---|---|---|
| 1 | 53.9 | 6 | 5.4 | 12 | 2.0 |
| 2 | 18.9 | 8 | 3.5 | 14 | 1.2 |
| 4 | 8.3 | 10 | 2.9 | 16 | - |

## Table 7.06

Sorption of 6,7-dimethoxy-4-methylcoumarin from solution in 10 % methanol on IRA-400 in chloride form.

| Sample No | x | Sample No | x | Sample No | x |
|---|---|---|---|---|---|
| 1 | 55.0 | 6 | 8.6 | 12 | 3.7 |
| 2 | 22.2 | 8 | 5.4 | 14 | 2.1 |
| 4 | 11.4 | 10 | 4.6 | 15 | 0.8 |

## Table 7.07

Sorption of 8-methoxycoumarin from solution in 10 % methanol on IRA-400 in chloride form.

| Sample No. | x | Sample No. | x | Sample No. | x |
|---|---|---|---|---|---|
| 1 | 72.2 | 6 | 5.8 | 12 | 0.3 |
| 2 | 33.6 | 8 | 2.5 | 14 | - |
| 4 | 12.5 | 10 | 1.1 | 16 | - |

## Table 7.08

Sorption of 3-methylcoumarin from solution in 10 % methanol on IRA-400 in chloride form.

| Sample No. | x | Sample No. | x | Sample No. | x |
|---|---|---|---|---|---|
| 1 | 75.8 | 6 | 5.6 | 12 | 0.7 |
| 2 | 35.71 | 8 | 3.1 | 14 | 0.7 |
| 4 | 14.2 | 10 | 1.1 | 16 | 0.5 |

## Table 7.09

Sorption of 7-methylcoumarin from solution in 10 % methanol on IRA-400 in chloride form.

| Sample No. | x | Sample No. | x | Sample No. | x |
|---|---|---|---|---|---|
| 1 | 79.2 | 6 | 8.7 | 12 | 2.9 |
| 2 | 38.9 | 8 | 5.3 | 14 | 2.2 |
| 4 | 16.6 | 10 | 4.1 | 16 | - |

## Table 7.10

Sorption of 8-hydroxycoumarin from solution in 10 % methanol on IRA-400 in chloride form.

| Sample No. | x | Sample No. | x | Sample No. | x |
|---|---|---|---|---|---|
| 1 | 92.9 | 8 | 18.7 | 16 | 8.6 |
| 2 | 79.5 | 10 | 13.5 | 18 | 8.3 |
| 4 | 46.8 | 12 | 11.2 | 19 | - |
| 6 | 28.7 | 14 | 9.0 | 20 | - |

## Table 7.11

Sorption of 6-hydroxy-4-methylcoumarin from solution in 10 % methanol on IRA-400 in chloride form.

| Sample No. | x | Sample No. | x | Sample No. | x |
|---|---|---|---|---|---|
| 1 | 96.0 | 8 | 22.4 | 16 | 7.6 |
| 2 | 80.0 | 10 | 19.2 | 18 | 3.3 |
| 4 | 49.3 | 12 | 17.2 | 19 | 2.8 |
| 6 | 34.3 | 14 | 14.2 | 20 | - |

### Table 7.12

Sorption of 7-hydroxycoumarin from solution in 10 % methanol on IRA-400 in chloride form.

| Sample No. | x | Sample No. | x | Sample No. | x |
|---|---|---|---|---|---|
| 1 | 100.0 | 8 | 46.8 | 16 | 25.6 |
| 2 | 98.0 | 10 | 36.6 | 18 | 24.5 |
| 4 | 90.0 | 12 | 32.0 | 19 | 22.8 |
| 6 | 74.8 | 14 | 28.7 | 20 | - |

### Table 7.13

Sorption of 7-hydroxy-4-methylcoumarin from solution in 10 % methanol on IRA-400 in chloride form.

| Sample No. | x | Sample No. | x | Sample No. | x |
|---|---|---|---|---|---|
| 1 | 100.0 | 8 | 56.7 | 16 | 32.9 |
| 2 | 98.0 | 10 | 49.0 | 18 | 29.8 |
| 4 | 86.3 | 12 | 41.9 | 19 | 28.5 |
| 6 | 71.6 | 14 | 37.0 | 20 | - |

## Table 7.14

Sorption of 5-hydroxy-4-methylcoumarin from solution in 10 % methanol on IRA-400 in chloride form.

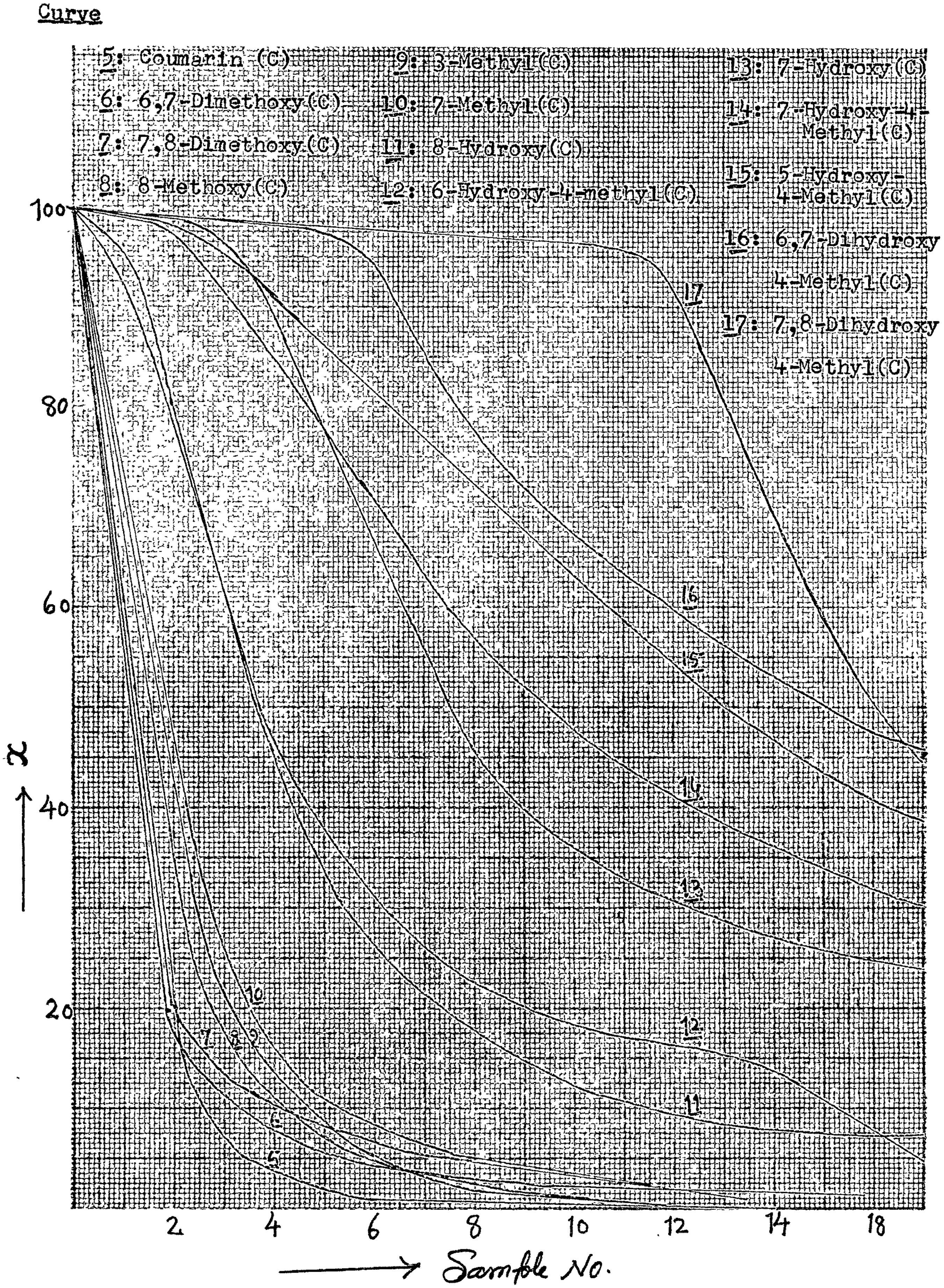
| Sample No. | x | Sample No. | x | Sample No. | x |
|---|---|---|---|---|---|
| 1 | 100.0 | 8 | 72.8 | 16 | 40.9 |
| 2 | ~~100.0~~ 98.0 | 10 | 62.1 | 18 | 38.9 |
| 4 | 91.2 | 12 | 54.7 | 19 | 38.0 |
| 6 | 82.4 | 14 | 47.8 | 20 | - |

## Table 7.15

Sorption of 6,7-dihydroxy-4-methylcoumarin from solution in 10 % methanol on IRA-400 in chloride form.

| Sample No. | x | Sample No. | x | Sample No. | x |
|---|---|---|---|---|---|
| 1 | 100.0 | 8 | 78.2 | 16 | 49.6 |
| 2 | 100.0 | 10 | 67.8 | 18 | 44.2 |
| 4 | ~~100.0~~ 98.5 | 12 | 60.3 | 19 | 43.7 |
| 6 | 93.6 | 14 | 54.0 | 20 | - |

Figure 7.4


Curve
5: Coumarin (C)
6: 6,7-Dimethoxy(C)
7: 7,8-Dimethoxy(C)
8: 8-Methoxy(C)
9: 3-Methyl(C)
10: 7-Methyl(C)
11: 8-Hydroxy(C)
12: 6-Hydroxy-4-methyl(C)
13: 7-Hydroxy(C)
14: 7-Hydroxy-4-Methyl(C)
15: 5-Hydroxy-4-Methyl(C)
16: 6,7-Dihydroxy 4-Methyl(C)
17: 7,8-Dihydroxy 4-Methyl(C)
100
80
60
40
20
α
2
4
6
8
10
12
14
18
Sample No.
17
16
15
14
13
12
11
10
7
8
9
6
5

## Table 7.16.

Sorption of 7,8-dihydroxy-4-methylcoumarin from solution in 10 % methanol on IRA-400 in chloride form.

| Sample No. | x | Sample No. | x |
|---|---|---|---|
| 1 | 100.0 | 12 | 90.1 |
| 2 | 100.0 | 14 | 72.1 |
| 4 | 99.5 | 16 | 50.3 |
| 6 | 98.1 | 18 | 39.7 |
| 8 | 97.4 | 19 | 36.9 |
| 10 | 96.7 | 20 | - |

for the desorption run in the effluent samples. Then 100 b/a is denoted by y and the plot of y against effluent sample number provides the desorption curve. The plot 1 B in Fig. 7.1 is the desorption curve obtained in this way. Fig. 7.1 indicates that, on the hydroxy form of the resin used, the break-through for the sorption curve 1A is not sharp and the elution (1B) is slow.

Run two : Another resin column (capacity of the resin in the column = 81.4 meq.) was set up, a large excess of sodium chloride solution was passed ,and then washed free of chloride ions with distilled water. The resin was then in chloride form and the column data were : bed volume = 112 ml, bed length = 47 cm, void volume = 30 ml. An aqueous solution of coumarin ($5.571 \times 10^{-4}$ M ) was passed downflow in the column at the rate of 10 cc./min. and 36 samples ( each of 100 ml.) were collected. The first sample included 30 ml. of water from void-volume. The first and the even numbered samples were estimated for coumarin. In figure 7.2, plot 2 A shows the sorption curve, obtained by the procedure noted above. The column was then drained, backwashed with distilled water, resin bed allowed to settle, and then distilled water passed downflow at the rate of 10 ml./min., 36 samples, each of 100 ml, were collected. The first and then even numbered samples were estimated for coumarin and the desorption curve 2B in figure 7.2 was obtained by the procedure detailed above.

Comparison of figures 7.1 and 7.2 indicates that the chloride form of resin used is more suitable for sorption-desorption of coumarin from aqueous solution than the hydroxyl form of the resin. From plot 2A (Fig.7.2), the amount of coumarin sorbed per 100 meq. of resin is calculated to be equal to $12.14 \times 10^{-4}$ g. moles,

Run three : After run two, the same resin column was further washed with a large excess of distilled water, backwashed, and the resin allowed to settle. 3.6 litres of aqueous coumarin solution ( $5.30 \times 10^{-4}$ M ) were passed downflow at the rate of 10 ml./min. The column was then drained, backwashed with methanol and resin bed allowed to settle. Then methanol was passed in the column downflow at the rate of 5 ml./min. 10 samples ( each of 100 ml.) were collected and estimated for coumarin. The desorption curve obtained is given in figure 7.3. Comparision of figure 7.3 and curve 2B in figure 7.2 indicates that methanol is more suitable for desorption of coumarin for the chloride form of the resin used than water.

Run four : After run three, the resin column was further washed with excess of methanol, backwashed with methanol and resin bed allowed to settle. A solution of coumarin in methanol ( $55.0 \times 10^{-4}$ M ) was passed downflow in the column at the rate of 5 ml./min. The samples ( 100 ml. each) were collected and estimated for coumarin. The first sample included 30 ml. of solvent from void-volume. The values of x for first three effluent samples were 75.5, 4.2 and 0.0. The coumarin sorbed per 100 meq. of resin is calculated equal to $3.85 \times 10^{-4}$ g. moles. A comparison with sorption run in run two indicates that though the ratio of coumarin concentrations in influent solution is 9.87, the ratio of amounts of coumarin sorbed per 100 meq. of resin is only 0.317. This supports that methanol is less suitable for sorption and more suitable for desorption of coumarin on the chloride form of the resin.

Run five : Another column of the resin ( capacity of the resin in the column = 6.1 meq.) was set up and the resin converted into chloride form. Excess of 10 % methanol ( by volume ) was then passed in the column. The column data were : bed-volume = 7.3 ml. ; bed-length = 15.2 cms. A solution of coumarin in 10 % methanol ( $5.55 \times 10^{-4}$ M ) was passed in the column downflow at the rate of 10 ml./min. and samples (100 ml. each ) were collected. Curve 5 in figure 7.4 shows the sorption curve obtained by plotting x against sample number. The column was then washed with excess of each of the following: methanol, methanolic hydrochlorid acid, distilled water, aqueous sodium hydroxide, distilled water, aqueous sodium chloride, distilled water and 10 % methanol. The column was then backwashed with 10 % methanol and resin bed allowed to settle.

Run 6 to 17 : Runs were repeated, using the procedure set for run five, with solutions ($5.55 \times 10^{-4}$ M ) in 10 % methanol for each of the following : 7,8-diMeO (I), 6,7-diMeO (I), 8-MeO (I), 3-Me(I), 7-Me(I),8-OH(I), 6-OH-4Me(I), 7-OH(I), 7-OH-4-Me(I), 5-OH-4-Me(I),6,7-di OH-4-Me(I) and 7,8-di OH-4-Me(I). The sorption curves (6 to 17) are shown in figure 7.4. (I) denotes coumarin.

The family of 13 sorption curves (5 to 17 ) in figure 7.4 indicates that coumarin and methoxy-,methyl-, and hydroxycoumarins are sorbed on the chloride form of strongly basic anion-exchange resin used in 10 % methanol. The sorption increases in the order : Coumarin< methoxycoumarins < methylcoumarins < hydroxycoumarins. For methoxycoumarins, the sorption study indicates that sorption increases in the order : dimethoxy < monomethoxy and 8-methoxy < 6-methoxy. On the other hand, the sorption for hydroxycoumarins increases in the order : monohydroxy < dihydroxy and 6-hydroxy < 8-hydroxy < 7-hydroxy < 5-hydroxy.

In chapter 6, it was observed that from the ultraviolet absorption maxima, hydroxy and methoxy substitution, when the substitution was in 5,6,7, or 8 position in the benzene ring of coumarin, could not be distinguished ; also, the same was true for 5- and 8-hydroxycoumarins. Figure 7.4 indicates that such cases could be distinguished from their sorption curves.

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8

## SEPARATION OF COUMARINS

In this chapter, the separation of mixtures of some coumarins (1), at room temperature ( ~ 30 °C) is described.

Experimental :

Resin and Chemicals : The resin used was a strongly basic anion exchanger, Amberlite IRA-400 ( Rohm and Hass ); this and the chemicals used were from the samples used in the earlier work (1,2).

Procedure : A column of the resin Amberlite IRA-400 in the hydroxyl form was set up. The column data were : moisture content of the air-dry resin = 21.15 % ; capacity of the air-dry resin per gm = 2.035 meq. ; capacity of the resin in the column = 20.37 meq. ; bedvolume = 25.0 ml. ; bedlength = 49.0 cms. The resin was converted into the chloride form by passing a large excess of sodium chloride solution. The column was then washed free of chloride ions, backwashed and allowed to settle under gravity. Then several bedvolumes of 10 % methanol (100 ml. of methanol made to a litre with distilled water) were passed to replace the water in the column. Then the solvent level was brought to the resin bed level and 50 ml. of the solution of coumarin in 10 % methanol were passed. The flow rate used in all the runs was 5 ml./minute. When the solution level was again at resin bed level, 10 ml. of the proper eluent were added and then the column was connected to an overhead reservoir of the eluent. The effluent was collected in samples. The first sample, numbered as v.v., was equal to the void volume. After this

100 ml. samples were collected and numbered as 1,2,3 and so on. The solute content in the effluent was estimated by ultraviolet absorption (3) using Beckman Model DU spectrophotometer and 10 mm. quartz cells. When the run was discontinued, the eluent was further passed, (without collecting the samples) to remove all the sorbed solute. The column was then washed free of the eluent with distilled water, backwashed, allowed to settle under gravity and 10 % methanol was passed to replace water in the column. The column was then ready for the next run, and the run was repeated for another compound.

In the separation studies, 50 ml. of the mixture in 10 % methanol were passed. When the solution level was at resin bedlevel, 10 ml. of the first eluent were added and the column was connected to an overhead reservoir of the first eluent. The eluent was passed to elute the first component. Then the eluent was changed to the second eluent to elute the second component. In ~~the~~ case of ternary mixtures, the eluent was then changed to the third eluent to elute the third component. Then the column was washed free of the eluent, backwashed, allowed to settle and water replaced by passing 10 % methanol. Then the procedure was repeated with the next mixture.

Nomenclature :

$w$ = the m.mols, of the solute in 50 ml. of solution in 10 % methanol, and initially sorbed on the column.

$P_w$ = 100 ·(m.mols, of the solute in effluent sample of 100 ml.) / w

## Table 8.1 a

Column elution data of coumarins.

| Compound = | Coumarin | 3-Me(I) | 3,4-diMe(I) | 7-Me(I) |
|---|---|---|---|---|
| $10^2.w$ = | 2.82 | 2.92 | 2.88 | 2.93 |
| Eluent = | a | a | a | a |
| Sample No. | $P_w$ = | $P_w$ = | $P_w$ = | $P_w$ = |
| v. v. | - | - | - | - |
| 1 | - | - | - | - |
| 2 | 20.80 | 6.43 | 3.38 | 1.60 |
| 3 | 28.05 | 14.40 | 8.45 | 10.10 |
| 4 | 21.45 | 16.08 | 11.82 | 16.85 |
| 5 | 14.90 | 16.08 | 12.16 | 15.10 |
| 6 | 6.11 | 12.85 | 11.50 | 13.50 |
| 7 | 4.95 | 11.26 | 10.15 | 11.80 |
| 8 | 1.65 | 8.03 | 9.50 | 9.20 |
| 9 | R. D. | 6.40 | 7.60 | 8.40 |
| 10 | | 4.82 | 6.75 | 6.75 |
| 11 | | 3.05 | 5.92 | 5.00 |
| 12 | | R. D. | 5.10 | R. D. |
| 13 | | | 4.40 | |
| 14 | | | 3.38 | |
| 15 | | | R. D. | |

## Table 8.1 b

Column elution data of coumarins.

| Compound = | 7-OH(I) | 7-OH(I) | 7-OH(I) | 7-OH(I) | 7-OH(I) |
|---|---|---|---|---|---|
| $10^2 . w$ = | 2.82 | 2.82 | 2.90 | 2.87 | 2.89 |
| Eluent = | a | b | $c_1$ | c | $c_2$ |
| Sample No. 1. | $P_w$ = 2. | $P_w$ = 3. | $P_w$ = 4. | $P_w$ = 5. | $P_w$ = 6. |
| v. v. | - | - | - | - | - |
| 1 | - | - | 24.27 | 58.32 | 94.13 |
| 2 | - | - | 6.13 | 34.54 | 4.02 |
| 3 | - | - | 4.12 | 3.88 | 1.81 |
| 4 | - | - | 2.34 | 2.03 | R. D. |
| 5 | - | - | 2.10 | 0.73 | |
| 6 | - | - | R. D. | R. D. | |
| 7 | - | 0.22 | | | |
| 8 | - | 0.53 | | | |
| 9 | - | 1.15 | | | |
| 10 | - | 1.97 | | | |
| 11 | - | 3.00 | | | |
| 12 | - | 3.90 | | | |

( Continued on next page )

Table 8.1 b (Continued)

| 1. | 2. | 3. | 4. | 5. | 6. |
|---|---|---|---|---|---|
| 13 | - | 4.50 | | | |
| 14 | - | 5.20 | | | |
| 15 | - | 5.61 | | | |
| 16 | - | 5.85 | | | |
| 17 | - | 5.98 | | | |
| 18 | - | 6.10 | | | |
| 19 | - | 5.80 | | | |
| 20 | - | 5.10 | | | |
| 21 | R. D. | 5.08 | | | |
| 22 | | 4.99 | | | |
| 23 | | 4.98 | | | |
| 24 | | 4.60 | | | |
| 25 | | 4.31 | | | |
| 26 | | R. D. | | | |

## Table 8.1 c

Column elution data of coumarins.

| Compound = | 6,7-diMeO-4-Me(I) | 7,8-diMeO(I) | 8-OH(I) | 8-OH(I) |
|---|---|---|---|---|
| $10^2.w$ = | 2.70 | 2.77 | 2.75 | 2.81 |
| Eluent = | a | a | b | c |
| Sample No. | $P_w$ = | $P_w$ = | $P_w$ = | $P_w$ = |
| v. v. | - | - | - | - |
| 1 | - | - | - | 70.21 |
| 22 | 8.57 | 3.20 | - | 24.60 |
| 3 | 15.60 | 11.16 | - | 2.95 |
| 4 | 14.00 | 16.90 | 1.03 | 1.91 |
| 5 | 11.00 | 15.95 | 3.07 | R. D. |
| 6 | 9.35 | 12.70 | 5.60 | |
| 7 | 7.80 | 9.75 | 7.32 | |
| 8 | 7.00 | 7.50 | 8.43 | |
| 9 | 6.25 | 6.00 | 8.90 | |
| 10 | 5.45 | 4.30 | 8.80 | |
| 11 | 4.69 | 3.50 | 8.00 | |
| 12 | 3.90 | 2.50 | 7.23 | |
| 13 | 3.12 | 2.25 | 6.14 | |
| 14 | R. D. | R. D. | 5.27 | |
| 15 | | | 4.56 | |
| 16 | | | 4.03 | |
| 17 | | | 3.00 | |
| 18 | | | R. D. | |

## Table 8.1 d

Column elution data of coumarins.

| Compound = | 6,7-diOH-4-Me(I) | 6,7-diOH--4-Me(I) | 7,8-diOH-4-Me(I) | 7,8-diOH-4-Me(I) |
|---|---|---|---|---|
| $10^2.w$ = | 2.87 | 2.90 | 2.85 | 2.85 |
| Eluent = | b | c | b | c |
| Sample No. | $P_W$ = | $P_W$ = | $P_W$ = | $P_W$ = |
| v. v. | - | - | - | - |
| 1 | - | 44.64 | - | 43.94 |
| 2 | - | 42.78 | - | 49.40 |
| 3 | - | 9.19 | - | 5.36 |
| 4 | - | 3.10 | - | 1.34 |
| 5 | - | 0.12 | - | R. D. |
| 6 | - | R. D. | - | |
| 7 | - | | - | |
| 8 | - | | - | |
| 9 | - | | - | |
| 10 | - | | - | |
| 11 | - | | - | |
| 12 | - | | - | |
| 13 | - | | - | |
| 14 | - | | - | |
| 15 | - | | - | |
| 16 | - | | - | |
| 17 | - | | - | |
| 18 | - | | R. D. | |
| 19 | R. D. | | | |

Table 8.2

Separation of some mixtures of coumarins.

| Mixture No.<br>1. | First component<br>2. | Second component<br>3. | Third component<br>4. | First component eluted with<br>5. | After elution of first component, second component eluted with<br>6. | After elution of second component, third component eluted with<br>7. |
|---|---|---|---|---|---|---|
| 1. Components = | 7-Me(I) + | 8-OH(I) | - | a | c | - |
| $10^{2}.w$ = | 1.45 | 1.41 | | | | |
| 2. Components = | 7-Me(I) + | 7,8-diOH-4-Me(I) | - | a | c | - |
| $10^{2}.w$ = | 1.48 | 1.42 | | | | |
| 3. Components = | 6,7-diMeO-+<br>4-Me(I) | 8-OH(I) | - | a | c | - |
| $10^{2}.w$ = | 1.43 | 1.41 | | | | |

(Continued on next page )

Table 8.2 (Continued)

| 1. | 2. | 3. | 4. | 5. | 6. | 7. |
|---|---|---|---|---|---|---|
| 4. Components | = 6,7-diMeO-4-Me(I) | + 7,8-diOH-4-Me(I) | - | a | c | - |
| $10^2$.w | = 1.43 | 1.42 | | | | |
| 5. Components | = 8-OH(I) | + 7,8-diOH-4-Me(I) | - | b | c | - |
| $10^2$.w | = 1.40 | 1.42 | | | | |
| 6. Components | = 7-Me(I) | + 8-OH(I) | + 7,8-diOH-4-Me(I) | a | b | c |
| $10^2$.w | = 0.872 | 0.838 | 1.14 | | | |
| 7. Components | = 6,7-diMeO-4-Me(I) | + 7-OH(I) | + 6,7-diOH-4-Me(I) | a | b | c |
| $10^2$.w | = 0.872 | 0.845 | 1.13 | | | |

R.D. = run discontinued.

a = 10 % methanol (prepared by diluting 100 ml. of methanol to one litre with distilled water).

b = N/10 HCl in 10 % methanol.

c = N/100 HCl in methanol.

$c_1$ = methanol.

$c_2$ = 1 N HCl in methanol.

Results and discussion :

Table 8.1 gives the column elution data for coumarin and the substituted coumarins studied. From these data, it is observed that the compounds studied may be broadly divided into three groups : group A includes coumarin, 3-Me(I), 7-Me(I), 3,4-diMe(I), 6,7-diMeO-4-Me(I) and 7,8-diMeO(I); group B includes 7-OH(I) and 8-OH(I) and group C includes 6,7-diOH-4-Me(I) and 7,8-diOH-4-Me(I). It is observed that group A compounds are eluted with 10 % methanol, group B compounds are not eluted with 10 % methanol but are slowly eluted with N/10 HCl in 10 % methanol and also eluted with N/100 HCl in methanol and group C compounds are not eluted with 10 % methanol or with N/10 HCl in 10 % methanol but are eluted with N/100 HCl in methanol. Hence it should be possible to separate the binary and ternary mixtures containing not more than one compound from each group.

Table 8.2 gives the binary and ternary mixtures which were studied to illustrate the validity of this procedure.

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