PART II

EXPERIMENTAL

2.1 Resins :

Resins used were sulfonated styrene divinylbenzene copolymer type sulfonic acid Dowex 50W cation exchange resins (Dow Chemical Co.) of 100/200 mesh, with X suffixes of 4, 8, 12 and 16 respectively. (X denotes the per cent of combined divinylbenzene in the styrene copolymer used as the resin matrix for preparing the sulfonate). These are further referred to as resins X4, X8, X12 (100/200) and X16 (20/50).

Moisture and capacity of resins :

The resins were washed, cycled between sodium chloride and hydrochloric acid, regenerated with a large excess of hydrochloric acid, washed free of acid, filtered, air dried and stored in well stoppered containers.

Moisture content was determined by heating weighed samples ($\sim$0.5 g.) of air dry resin in clean, dry weighing bottles, in an oven ($\sim$100 to 103°C.) to a constant weight and per cent moisture content was then calculated.

For the estimation of capacity of the resins weighed samples ($\sim$0.5 g.) of air dry resins were contacted with 50 ml. of 1N barium chloride solution in well stoppered flasks with frequent shaking. Next day, the liberated acid was estimated by titrating the aliquots with standard sodium hydroxide solution and the capacity was then calculated. Preliminary work had indicated that increase in contact time did not increase the amount of acid liberated. Table (2.1) gives the values of per cent moisture content and capacity of the different resins.

Different organic forms of the resin :

Organic amine (∽ 30-35 ml.) was dissolved in 10 % aqueous (by volume) acetone (∽ 1 litre), the resin (∽ 30 g.) was added, stirred well and kept over night. The contents of the beaker were transfered to the glass column fitted with a sintered glass disc at the bottom, Washed with 10 % aqueous acetone and then with excess of water. The resin was then filtered, air dried, moisture content determined and the capacity of air dry form of the resin calculated from capacity of the oven dry resin in the hydrogen form.

The ammonium form of the resin was prepared by passing excess of 0.5N ammonia solution through the resin in a column and then washing it with excess of water till free from ammonia.

Table 2.1

Moisture and capacity of the resin in hydrogen form.

Resin	Mesh	% moisture content	capacity in meq./g. Air dry	capacity in meq./g. Oven dry
X4	100/200	23.1	3.78	4.91
X8	100/200	27.6	3.47	4.79
X12	100/200	31.1	3.30	4.80
X16	20/50	19.6	3.80	4.72

2.2 Chemicals :

A.R. or C.P. grade chemicals were used.

7-Hydroxy-4-methylcoumarin (185) :

Resorcinol (50 g.) and ethylacetoacetate (62 g.) were mixed in a beaker to an uniform paste and H_2SO_4 (75 %, ~ 450 ml.) was added to it. The paste dissolved slowly with evolution of heat producing a dark red solution, which was kept (for 30 minutes) at 80-85° in a water bath. The solution was cooled to room temperature and added to 2 litres of ice water. The light yellow precipitate was washed free from acid with cold water. It crystallised from alcohol in needles, m.p. 185°.

7-Methoxy-4-methylcoumarin (186) :

7-Hydroxy-4-methylcoumarin (1 g.) in acetone (75 ml.) was refluxed with anhydrous potassium carbonate (2 g.) and dimethyl sulfate (1 ml.) for 6 hrs.. The acetone was removed by distillation and potassium carbonate dissolved in water. The residue crystallised from alcohol, m.p. 159°.

7-Hydroxy-5-methylcoumarin (187) :

Equimolar quantities of orcinol and malic acid were treated in a long neck round bottom flask with double the quantity of concentrated H_2SO_4. The mixture was heated on a low flame till effervescence ceased (occasionally flame had to be removed to control effervescence). The reaction mixture was then poured in ice water and the solid that separated on standing, crystallised from hot water, m.p. 248°.

7-Methoxy-5-methylcoumarin :

7-Hydroxy-5-methylcoumarin was methylated and crystallised from aqueous alcohol, m.p. 136°.

Analysis : Found : C = 69.23; H = 4.97.

$C_{11}H_{10}O_3$ Requires : C = 69.47; H = 5.20 %.

Hoesch (188) reported m.p. 146°.

7-Hydroxy-8-methylcoumarin (189) :

2-Methylresorcinol (1 g.) and malic acid (1.2 g.) were treated in a long neck round bottom flask with double the quantity of concentrated H_2SO_4. The mixture was heated on a low flame till effervescence ceased (occasionally flame had to be removed to control effervescence). The reaction mixture was then poured in ice water and the solid that separated was crystallised from water, m.p. 242°.

Analysis : Found : C = 68.00; H = 4.20.

$C_{10}H_8O_3$ Requires : C = 68.19; H = 4.55 %.

Seshadri and Venkateswarlu (189) reported m.p. 231-32°.

7-Methoxy-8-methylcoumarin :

7-Hydroxy-8-methylcoumarin was methylated. It crystallised from water, m.p. 122°.

7,8-Dimethoxy-4-methylcoumarin :

7,8-Dihydroxy-4-methylcoumarin was methylated. m.p. 132-33°.

5-Hydroxy-4,7-dimethylcoumarin (190) :

To a mixture of dry orcinol (5 g.) and ethylacetoacetate (5 g.), cooled in ice, P_2O_5 (18 g.) is added gradually. A vigorous reaction takes place with evolution of much heat. When the reaction ceased, the cold mass is treated with water. The precipitate is washed with water and crystallised from dilute ethanol (charcoal). It forms colourless needles, m.p. 248°.

5-Methoxy-4,7-dimethylcoumarin :

5-Hydroxy-4,7-dimethylcoumarin was methylated. It crystallised from dilute alcohol, m.p. 146°.

7-Methoxy-4,8-dimethylcoumarin :

7-Hydroxy-4,8-dimethylcoumarin was methylated. It crystallised from dilute alcohol, m.p. 153°.

Analysis : Found : C = 70.50; H = 5.46.
$C_{12}H_{12}O_3$ Requires : C = 70.60; H = 5.88 %.

5,7-Dihydroxy-4-methylcoumarin (191) :

Phosphoric acid (5 g.) was added with stirring to a mixture of phloroglucinol (2 g.) and ethylacetoacetate (2 g.) and the vigorous reaction moderated by occasional cooling in tap water. When the reaction ceased, the solid mixture was ground under water, and the product was collected and washed with water, crystallised from acetic acid, the coumarin separated in flat prisms, m.p. 293°.

5,7-Dimethoxy-4-methylcoumarin:

5,7-Dihydroxy-4-methylcoumarin was methylated. It crystallised from methanol, m.p. 171°.

4-Hydroxy-3-methylcoumarin (192) :

Methyl propionylsalicylate (50 g.) (prepared by heating methylsalicylate (50 g.) with propionic anhydride (40 g.) for 48 hrs. and purified by pouring in water, dissolving the oil in ether and washing with water and sodium bicarbonate solution) was treated with sodium (12 g.) and heated for one hour (170-175°). After cooling, a little methyl alcohol was added, then 250 ml. of water. The solution filtered and filtrate acidified with hydrochloric acid and separated compound crystallised from dilute alcohol, m.p. 230°.

4,7-Dihydroxy-3-methylcoumarin (192) :

Resorcinol (5 g.) and ethyl-methylmalonate (10 g.) with diphenylether (25 ml.) were refluxed for 8 hrs.. The solution on cooling was extracted with petroleum ether and the compound separated washed repeatedly with petroleum ether till free from diphenylether and crystallised from dilute alcohol to colourless needles, m.p. 302-304°.

4,5,7-Trihydroxy-3-methylcoumarin (193) :

A mixture of phloroglucinol (3.2 g.) and diethyl-methylmalonate (4.4 g.) in diphenylether (25 ml.) was refluxed for 3 hrs.. The product separated on cooling, washed repeatedly with petroleum ether, crystallised from hot water in needles, m.p. 291°.

4-Hydroxy-5-methoxycoumarin (194) :

2-Hydroxy-6-methoxyacetophenone (195) (1 g.) was mixed with ethylcarbonate (10 ml.) in the presence of pulverized sodium (1.5 g.). After the initial vigorous reaction had subsided the reaction mixture was heated on a steam bath for an hour. Alcohol was then added to destroy the excess of sodium and the excess of ethylcarbonate was removed with ether. The product obtained on acidification, crystallised from dilute alcohol in colourless needles, m.p. 155°.

4,5-Dimethoxycoumarin (194) :

4-Hydroxy-5-methoxycoumarin was methylated. It crystallised from dilute alcohol, m.p. 179-180°.

4,5-Dihydroxycoumarin (194) :

A mixture of 4-hydroxy-5-methoxycoumarin (0.5 g.) and anhydrous aluminium chloride (1 g.) was heated at 145-150° for three hrs.. Ice and hydrochloric acid were then added and the product obtained crystallised from dilute alcohol in colourless needles, m.p. 221°.(dec.).

4-Hydroxy-6-methoxycoumarin (196) :

Finely powdered anhydrous aluminium chloride (13.5 g.) was added in portions during 20 minutes to a mixture of quinol dimethylether (17 g.) and malonyl chloride (7 g.) in dry CS_2 (50 ml.). The mixture was set aside for 24 hrs. and then refluxed in a water bath for 2 hrs.. After removal of the solvent, the complex was decomposed with water (100 ml.) and concentrated HCl (50 ml.), warmed to 80° and cooled and the precipitates collected. The product was purified through sodium hydroxide solution. It crystallised from aqueous acetic acid as needles, m.p. 270°.

4,6-Dimethoxycoumarin :

4-Hydroxy-6-methoxycoumarin was methylated. It crystallised from aqueous acetic acid, m.p. 138°.

4,6-Dihydroxycoumarin :

4-Hydroxy-6-methoxycoumarin was demethylated with fused aluminium chloride - sodium chloride at 180°. It crystallised from aqueous acetic acid in plates m.p. 290°.

4,7-Dihydroxycoumarin (197) :

Resorcinol (22 g.), cyanoacetic acid (17 g.) and zinc chloride (10 g.) are mixed in dry ether (60 ml.) and saturated with hydrogen chloride, when 4-imino-7-hydroxy-3,4-dihydro-1:2-benzopyrone is obtained. The imide is hydrolysed by dilute acid to 4,7-dihydroxycoumarin. This crystallises from water in long silky needles, m.p. 265°.

7-Hydroxy-4-methylcoumarin-6-carboxylic acid (198) :

Concentrated H_2SO_4 (20 ml.) was added to a mixture of β-resorcylic acid (5 g.) and ethylacetoacetate (5 g.), when heat was evolved and the mixture turned brownish. After keeping over night, the mixture was heated on water bath for 2 hrs., cooled and poured into water. The precipitated solid was treated with saturated $NaHCO_3$ solution when most of it dissolved, leaving a small amount of residue, which when crystallised from alcohol had m.p. 185-86° and was found to be 7-hydroxy-4-methylcoumarin. The $NaHCO_3$ extracts on acidification with conc. HCl, gave a yellowish coloured precipitate which was collected and recrystallised from glacial acetic acid in colourless needles, m.p. 284-85°. This is 7-hydroxy-4-methylcoumarin-6-carboxylic acid.

7-Hydroxy-4-methylcoumarin-8-carboxylic acid (199) :

γ-Resorcylic acid (10 g.) and ethylacetoacetate (10 ml.)

were condensed in presence of conc. H_2SO_4 (15 ml.). The product recrystallised from acetic acid, m.p. 263° (dec.).

4-Hydroxy-, 7-hydroxy-, 4-methoxy-, 7-methoxy-, 4,7-dimethoxy-, 4-hydroxy-7-methoxy-, 4-hydroxy-6-methyl-, 5-hydroxy-4-methyl-, 6-hydroxy-4-methyl-, 6-methoxy-4-methyl-, 4,6-dimethyl-, 4,7-dimethyl-, 7-hydroxy-4,5-dimethyl-, and 7-hydroxy-4,8-dimethylcoumarins were obtained from Prof. S.M. Sethna's laboratory, crystallised and melting points checked.

2.3 Solvents :

The solvents used were water (distilled), aqueous methanol, methanol, aqueous methanol at different pH, 10 % methanol in N/100 n-caproic acid, 10 % tertiary butanol.

The aqueous methanols were prepared by volume, for example : 10 % methanol was prepared by diluting 100 ml. methanol to 1 litre with distilled water. 10 % methanol in 0.01N HCl was prepared by adding calculated amount of hydrochloric acid to 100 ml. of methanol and diluting to 1 litre with distilled water in volumetric flask. 10 % methanol in N/100 n-caproic acid was prepared in the same manner, 10 % tertiary butanol was prepared by volume.

2.4 Procedure :

Solutions :

The solutions of the substituted coumarins and nitro toluenes were prepared by dissolving weighed amount in particular solvent in standard measuring flask and then suitably diluting.

pH measurements :

The pH of the solution was adjusted by adding hydrochloric acid or sodium hydroxide and measured with either Beckman model H-2 or Leeds and Northrup pH-meter.

Ultraviolet measurements :

The ultraviolet absorption measurements were carried out with a Beckman model DU spectrophotometer, using 10 mm. quartz cells in the range 250-350 $m\mu$.. The values of extinction coefficient, ϵ were calculated by dividing the measured optical density, D by the concentration of the compound in gram moles per litre.

Sorption equilibrium studies :

Coumarin solutions of different concentrations and known volume were placed in contact with weighed amounts (1.0 g.) of air dry resin, in well stoppered flasks, with frequent shaking at room temperature ($\sim$ 30°C.) for 24 hrs.. After the equilibrium was reached, the initial and the equilibrium concentrations were determined by ultraviolet absorption.

A similar procedure was adopted for the sorption study of nitro toluene.

Preliminary work indicated, that increase in contact time or small variation in room temperature did not change the amount of solute sorbed measurably.

When the resin in organic cationic forms was placed in the solvent, it was observed that there was hydrolysis to a small extent and so, correction was made in the measured ultraviolet absorption in obtaining the values of 'S' by carrying out the blank.

Column studies :

Column elution of coumarins using different solvents and eluants was studied. Resin 50WX4 in hydrogen form was used.

Two columns, A and B were set up. Column data are summarized in table (2.2).

Table 2.2

Column data

Column	A	B
Resin 50WX4 in hydrogen form	mesh 100/200	100/200
Bed length	54 cms.	94 cms.
Bed volume	131 ml.	220 ml.
Capacity of the resin in the column	163 meq.	283 meq.
Flow rate of effluent	5 ml./min.	5 ml./min.

For carrying out a run, the column was first washed with several bed volumes of the solvent, back washed and the resin was allowed to settle under gravity and the liquid level was brought to the resin bed level and 100 ml. of the coumarin solution were added. When the liquid level was again at resin bed level, 25 ml. of the eluant were added and the column was connected to an overhead reservoir of eluant. The first sample collected was equal to void volume and was numbered as sample No. v.v.. After that effluent was collected in 100 ml. measuring flasks and numbered as 1, 2 and so on. The solute content for each sample was estimated by ultraviolet absorption.

When the run was over, the column was conditioned with the solvent to be used for the next run to be carried out.

W_s, denotes the solute content in millimoles in 100 ml. effluent sample, W denotes the solute content in millimoles in 100 ml. of the solution initially sorbed on the resin bed.

For the runs with nitro toluenes a similar procedure was followed, except that instead of 100 ml. of the solution 25 ml. of the solution was sorbed on the resin and the samples were collected in 25 ml. measuring flasks.

U_s, denotes the solute content in millimoles in 25 ml. effluent sample, U denotes the solute content in millimoles in 25 ml. of the solution initially sorbed on the resin bed.