Papers published by the candidate dealing with the work other than that described in this thesis.

1. Bromination of Coumarins. Part III. Bromination of some 5-hydroxycoumarin derivatives and their methyl ethers. By Lele, Parikh and Sethna (J. Indian Chem. Soc., 1953, Vol. 30, 610)

2. Condensation of some aromatic aldehydes with orcacetophenone and its monomethyl ether. By Mahajani, Lele and Sethna (J. M. S. University of Baroda, India, 1954, 3, 41)

3. Bromination of ethyl-7-hydroxycoumarin-3-carboxylate and some dihydroxycoumarin derivatives. By Lele and Sethna (J. Sci. Ind. Research, India, 1955, 14B, 101)

4. Studies in the hydroxyanthracene series, Part I, Some reactions of 1-anthrol. By Lele, Shah and Sethna (J. Org. Chem., 1956, 21, 1293)

5. Pigment of Raphanus caudatus Linn. By Lele (J. Sci. Ind. Research, India, 1959, 18B, 243)

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BROMINATION OF COUMARINS. PART III. BROMINATION OF SOME 5-HYDROXYCOUMARIN DERIVATIVES AND THEIR METHYL ETHERS

By S. S. Lele, R. J. Parikh and Suresh Sethna

5-Hydroxy-4-methyl- and 5-hydroxy-4 : 7-dimethyl-coumarin and their methyl ethers have been brominated with one mole, two moles and with excess of bromine. The first bromine atom is found to enter the 8-position in all cases. Ths second bromine atom has been found to enter the 6-position in the case of the hydroxycoumarins and the 3-position in the case of the methoxycoumarins. With excess of bromine the 3 : 6 : 8-tribromocoumarins have been obtained.

In the bromination of 7-hydroxy- and 6-hydroxycoumarin derivatives the first bromine atom has been found to enter the 3-position (Dalvi and Sethna, this *Journal*, 1949, **26**, 359, 467). It has, however, been found by Dey and Kutti (*Proc. Nat. Inst. Sci. India*, 1940, **6**, 641) that in the bromination of 8-methoxycoumarin the first bromine atom enters the 5-position. In view of this it was thought of interest to study the bromination of 5-hydroxycoumarins and their methyl ethers.

5-Hydroxy-4-methylcoumarin on bromination with one mole of bromine gave a product the methyl ether of which did not give a coumarilic acid derivative on heating with alkali, indicating that the first bromine atom had not entered the 3-position. The methyl ether was subjected to Elbs persulphate oxidation when the oxidation product was obtained in good yield This indicated that the 6-position must be free, for the Elbs persulphate oxidation of 6-substituted coumarins is very difficult (Dalvi, Desai and Sethna, this *Journal*, 1951, **28**, 366). Moreover, the oxidation product gives an orange-yellow colour with alkali which appears to be characteristic of the bromo derivatives of 6-hydroxycoumarins (Dalvi and Sethna, *loc. cit.*). The monobromo product has therefore been assigned the structure of 5-hydroxy-8-bromo-4-methylcoumarin. 5-Methoxy-4-methylcoumarin gave on bromination with one mole of bromine the same monobromo product as the methyl ether of the 5-hydroxy-8-bromo-4-methylcoumarin.

An attempt was made to seek further confirmation of this structure by the synthesis of 5-hydroxy-8-bromo-4-methylcoumarin by another method. Methyl 5-hydroxy-4-methylcoumarin-6-carboxylate was brominated with one mole of bromine when a monobromo product was obtained, the methyl ether of which did not give a coumarilic acid, thus indicating that the bromine had entered the 8-position. The bromo-ester was hydrolysed to the corresponding acid. Attempts to decarboxylate the acid in a sealed tube, and by the quinoline-copper powder method, however, failed to give the required bromocoumarin, the bromine being knocked off during the decarboxylation.

Bromination of Methyl 5-Hydroxy-4-methylcoumarin-6-carboxylate and its Methyl Ether with one mole of Bromine

Methyl 5-Hydroxy-8-bromo-4-methylcoumarin-6-carboxylate.—The coumarin ester (0.4 g.) was dissolved in hot acetic acid (10 c.c.) and the solution while hot was treated with bromine (0.27 g.) in acetic acid (2.7 c.c.). The product which separated on cooling crystallised from dilute alcohol in yellow needles (0.3 g.), m.p. 214°. (Found : Br, 25.2. $C_{12}H_9O_5Br$ requires Br, 25.6 per cent).

5-Hydroxy-8-bromo-4-methylcoumarin-6-carboxylic Acid.—The coumarin acid (0.5 g.) was dissolved in hot acetic acid (15 c.c.) and the solution while hot was treated with bromine (0.36 g.) in acetic acid (3.6 c.c.). The product separating on cooling was crystallised from acetic acid in needles, m.p. 266°. (Found : Br, 26.3. $C_{11}H_7O_5Br$ requires Br, 26.8 per cent).

The same acid was obtained by hydrolysing the ester described above by keeping in contact with cold sodium hydroxide (10%, 20 c.c.) for 48 hours.

The *methyl ether* of methyl 5-hydroxy-8-bromo-4-methylcoumarin-6-carboxylate was prepared by dissolving the compound (0.5 g.) in acetone (20 c.c.) and refluxing with methyl iodide (1 c.c.) and anhydrous potassium carbonate (1 g.) for 20 hours. A pasty mass was obtained on working up as usual. This was washed with petroleum ether and crystallised from alcohol in needles, m.p. 100-102°. (Found : Br, 24.2. $C_{13}H_{11}O_5Br$ requires Br, 24.5 per cent).

5-Methoxy-8-bromo-4-methylcoumarin-6-carboxylic Acid.—Methyl 5-hydroxy-8-bromo-4-methylcoumarin-6-carboxylate (0.5 g.) was refluxed with NaOH (10%, 20 c.c.) for 2 hours. The product obtained on acidification was crystallised from alcohol in needles, m.p. 144°. (Found : Br, 25.1. $C_{12}H_9O_5Br$ requires Br, 25.6 per cent).

Bromination of 5-Hydroxy-4 : 7-dimethylcoumarin and its Methyl Ether.

5-Hydroxy-4 : 7-dimethylcoumarin was prepared according to Pechmann and Cohen (*Ber.*, 1884, **17**, 2187), and was methylated in acetone solution with methyl iodide as usual, m.p. 147°. Collie and Crystall (*J. Chem. Soc.*, 1907, **91**, 1805) give m.p. 146°.

(i) Bromination with one mole of Bromine : 5-Hydroxy-8-bromo-4 : 7-dimethylcoumarin.—5-Hydroxy-4 : 7-dimethylcoumarin (1.9 g.) in acetic acid (40 c.c.) was treated with bromine (1.6 g.) in acetic acid (16 c.c.) in hot. The product separating on cooling was crystallised from acetic acid in shining needles (1.g), m.p. 257-58° (decomp.). (Found : Br, 29.3. $C_{11}H_6O_3Br$ requires Br, 29.7 per cent). It formed a yellow salt with alkali.

5-Methoxy-8-bromo-4 : 7-dimethylcoumarin.—The monobromo product (0.5 g.) was dissolved in acetone (50 c.c.) and refluxed with dimethyl sulphate (1 c.c.) and anhydrous K_2CO_3 (1 g.) for 20 hours. The product obtained on working up as usual was crystallised from acetic acid in tiny needles (0.5 g.), m.p. 190°. (Found : Br, 28.6. $C_{12}H_{11}O_3Br$ requires Br, 28.3 per cent).

on cooling crystallised from dilute alcohol in needles (0.25 g.), m.p. 227°. (Found : Br, 47.5. $C_{10}H_6O_3Br_2$ requires Br, 47.9 per cent).

The *methyl ether*, prepared by the dimethyl sulphate-acetone-potassium carbonate method as usual, crystallised from dilute acetic acid in needles, m.p. 214-15°. (Found : Br, 45.9. $C_{11}H_8O_3Br_2$ requires Br, 46.0 per cent).

5-Methoxy-6 : 8-dibromo-4-methylcoumarin (0.5 g.) was refluxed with NaOH (10%, 20 c.c.) for 2 hours. The resulting solution on acidification gave the original methyl ether.

5-*Methoxy*-3 : 8-*dibromo*-4-*methylcoumarin*.—5-Methoxy-4-methylcoumarin (0.5 g.) in acetic acid (15 c.c.) was treated with bromine (1.6 g., 4 moles) in acetic acid (16 c.c.). The reaction mixture was then heated on a steam-bath for 2 hours. The product obtained on dilution was crystallised from dilute acetic acid in yellow needles (0.6 g.), m.p. 168°. (Found : Br, 45.9. $C_{11}H_8O_3Br_2$ requires Br, 46.0 per cent).

4-*Methoxy*-7-*bromo*-3-*methylcoumarilic Acid*.—The above dibromocoumarin (0.5 g.) was refluxed with NaOH solution (10%, 20 c.c.) for 2 hours. The product obtained on acidification was crystallised from acetic acid in needles (0.2 g.), m.p. 270°. It gave a green colour with hot concentrated sulphuric acid. (Found : C, 46.9 ; H, 3.6. $C_{11}H_9O_4Br$ requires C, 46.3 ; H, 3.2 per cent).

(*iii*) *Bromination with excess of Liquid Bromine* : 5-*Hydroxy*-3 : 6 : 8-*tribromo*-4-*methylcoumarin*.—5-Hydroxy-4-methylcoumarin (0.3 g.) in acetic acid (20 c.c.) was treated with excess of liquid bromine (2 g.). The reaction mixture was then refluxed on a steam-bath for 1 hour. The product separating on cooling crystallised from acetic acid in yellow needles (0.5 g.), m.p. 238°. (Found : Br, 58.8. $C_{10}H_5O_3Br_3$ requires Br, 58.1 per cent). On boiling with alcohol and acetone the tribromo derivative gave a black product. On extracting this with acetic acid a dark brown product was obtained which did not melt till 290° but left no residue on heating on a spatula. This product has not been worked up further.

The *methyl ether* was prepared by dissolving the above product (0.3 g.) in benzene (70 c.c.) and refluxing with anhydrous potassium carbonate and dimethyl sulphate (0.3 g.) for 20 hours. The product, obtained on working up as usual, crystallised from acetic acid in shining needles (0.2 g.), m.p. 183-84°. (Found : Br, 55.8. $C_{11}H_7O_3Br_3$ requires Br, 55.2 per cent).

The same product was obtained when 5-methoxy-4-methylcoumarin (0.5 g.) in acetic acid (20 c.c.) was treated with bromine (3 g.) in acetic acid (30 c.c.).

4-*Methoxy*-5 : 7-*dibromo*-3-*methylcoumarilic Acid*.—5-Methoxy-3 : 6 : 8-tribromo-4-methylcoumarin (0.5 g.) was refluxed with NaOH (10%, 20 c.c.) for 2 hours. The solid obtained on acidification was crystallised from acetic acid in needles (0.2 g.), m.p. 286°. (Found : C, 36.4 ; H, 2.2. $C_{11}H_8O_4Br_2$ requires C, 36.3 ; H, 2.2 per cent). The acid gave a greenish coloration with hot concentrated sulphuric acid.

EXPERIMENTAL

5-Hydroxy-4-methylcoumarin-6-carboxylic acid and its methyl ester and 5-hydroxy-4-methylcoumarin and its methyl ether were prepared according to the method of Sethna, Shah and Shah (*J. Chem. Soc.*, 1938, 228).

Bromination of 5-Hydroxy-4-methylcoumarin and its Methyl Ether

(*i*) *Bromination with one mole of Bromine* : *5-Hydroxy-8-bromo-4-methylcoumarin.*—5-Hydroxy-4-methylcoumarin (0.5 g.) was dissolved in hot acetic acid (10.0 c.c.) and the solution while hot was treated with bromine (0.45 g.) in acetic acid (4.5 c.c.). After an hour a brown crystalline mass separated which crystallised from dilute acetic acid in needles (0.2 g.), m.p. 256°. (Found : Br, 30.7. $C_{10}H_7O_3Br$ requires Br, 31.4 per cent).

The *methyl ether* was prepared by dissolving the above product (0.3 g.) in acetone (20 c.c.) and refluxing with dimethyl sulphate (0.25 g.) and anhydrous potassium carbonate (1 g.) for 20 hours. The potassium carbonate was filtered and acetone evaporated. The residue obtained was crystallised from dilute alcohol, m.p. 223° (Found : Br, 29.7. $C_{11}H_9O_3Br$ requires Br, 29.7 per cent).

The same product was obtained when 5-methoxy-4-methylcoumarin (0.5 g.) in acetic acid (10 c.c.) was treated with bromine (0.4 g.) in acetic acid (4 c.c.). The methoxybromocoumarin (0.3 g.) was refluxed with sodium hydroxide (10%, 20 c.c.) for 2 hours. The resulting solution on acidification gave back the starting material.

Elbs Persulphate Oxidation of 5-Methoxy-8-bromo-4-methylcoumarin : 5-Methoxy-6-hydroxy-8-bromo-4-methylcoumarin.—The methoxybromocoumarin (1 g.) was dissolved in sodium hydroxide solution (40 c.c., 10%) by warming on a steam-bath. The solution was then cooled and potassium persulphate (1.1 g. in 25 c.c. of water) was added gradually from a separating funnel during 2 hours. The solution was mechanically stirred and the temperature was not allowed to rise above 10°. The reaction mixture was then kept overnight. The next day it was just acidified with concentrated hydrochloric acid when the original substance (0.3 g.) was obtained. This was filtered and the filtrate was extracted with ether and the aqueous layer was heated on a boiling water-bath with concentrated hydrochloric acid (25 c.c.) for 40 minutes. The product which separated on cooling crystallised from rectified spirit in needles (0.3 g.), m.p. 230°. It dissolves in alkali with an orange colour. (Found : C, 45.6 ; H, 3.6. $C_{11}H_9O_4Br$ requires C, 46.3 ; H, 3.2 per cent).

(*ii*) *Bromination with two moles of Bromine* : *5-Hydroxy-6 : 8-dibromo-4-methylcoumarin.*—5-Hydroxy-4-methylcoumarin (0.3 g.) in acetic acid (10 c.c.) was treated with bromine (0.5 g.) in acetic acid (5 c.c.) in hot. The product which separated

5-Hydroxy-4-methylcoumarin on bromination with two moles of bromine gave a dibromo product, the methyl ether of which did not give a coumarilic acid on heating with alkali. It is therefore assigned the structure of 5-hydroxy-6 : 8-dibromo-4-methylcoumarin. 5-Methoxy-4-methylcoumarin on bromination with two moles of bromine did not give a pure product but with 4 moles of bromine a dibromo product was obtained which gave a bromocoumarilic acid and was found to be different from the methyl ether of 5-hydroxy-6 : 8-dibromo-4-methylcoumarin. Hence, the structure of 5-methoxy-3 : 8-dibromo-4-methylcoumarin is assigned to this product.

The bromination of 5-hydroxy-4-methylcoumarin with excess of liquid bromine gave a tribromo derivative, the methyl ether of which was identical with the tribromo derivative obtained from 5-methoxy-4-methylcoumarin. This product gave a coumarilic acid derivative. The 3 : 6 : 8-tribromo structures have therefore been assigned to these products. The hydroxy-tribromo compound gave a black, very high melting product, immediately, on heating with alcohol or acetone.

The bromination of 5-hydroxy-4 : 7-dimethylcoumarin and its methyl ether was carried out to see whether it followed the same pattern. The results were found to be similar. The monobromo product obtained by the bromination of the hydroxycoumarin was methylated and was found to be identical with the monobromo product of the methyl ether. The methylated product did not give any coumarilic acid on boiling with alkali. It gave on Elbs persulphate oxidation, the oxidation product in good yield, thus indicating that the first bromine atom had entered the 8-position. Further, the hydroxy-monobromo product has a m. p. of 257-58° and is distinctly different from the product of m. p. 217° obtained on Pechmann condensation of 4-bromo-orcinol with ethyl acetoacetate which has been assigned the structure of 5-hydroxy-6-bromo-4 : 7-dimethylcoumarin (Chakravarti and Mazumdar, this *Journal*, 1937, **14**, 725). It may be mentioned here that Desai and Gaitonde (*Proc. Ind. Acad. Sci.*, 1947, **25A**, 366) have arbitrarily assigned the structure of 5-hydroxy-3-bromo-4 : 7-dimethylcoumarin to the compound obtained on bromination of 5-hydroxy-4 : 7-dimethylcoumarin. They used more than 1.5 moles of bromine. On careful repetition of the work under their conditions the substance of m.p. 217°, as stated by them, could not be obtained.

The hydroxycoumarin on bromination with two moles of bromine gave a product to which the structure of 5-hydroxy-6 : 8-dibromo-4 : 7-dimethylcoumarin has been assigned as its methyl ether did not give any coumarilic acid. 5-Methoxy-4 : 7-dimethylcoumarin on bromination with two moles of bromine gave a product which gave a bromocoumarilic acid and was found to be different from the above methyl ether. Hence, the structure of 5-methoxy-3 : 8-dibromo-4 : 7-dimethylcoumarin has been assigned to this product.

With excess of liquid bromine both the hydroxy and the methylated coumarins gave the tribromo derivatives to which 3 : 6 : 8-tribromocoumarin structures have been assigned.

The same product was obtained when 5-methoxy-4 : 7-dimethylcoumarin (2 g.) in hot acetic acid (20 c.c.) was treated with bromine (1.6 g.) in acetic acid (16 c.c.).

The methyoxybromocoumarin (0.5 g.) was refluxed with sodium hydroxide (10% ; 10 c.c.) for 4 hours. The resulting solution on acidification gave the starting material.

Elbs Persulphate Oxidation of 5-Methoxy-8-bromo-4 : 7-dimethylcoumarin : 5-Methoxy-6-hydroxy-8-bromo-4 : 7-dimethylcoumarin.—The methoxybromocoumarin (1 g.) was dissolved NaOH (3 g. in 30 c.c. water) by warming on a steam-bath. The solution was then cooled and oxidised with potassium persulphate (1.1 g. in 25 c.c. water) during 2 hours. On working up as usual 6-hydroxy-5-methoxy-8-bromo-4 : 7-dimethylcoumarin was obtained. It was crystallised from rectified spirit in long needles, m.p. 199-200°. (Found : C, 47.6 ; H, 3.5. $C_{12}H_{11}O_4Br$ requires C, 48.2 ; H, 3.7 per cent). The product formed an orange-yellow coloured sodium salt with 10% NaOH solution.

(*ii*) *Bromination with two moles Bromine : 5-Hydroxy-6 : 8-dibromo-4 : 7-dimethylcoumarin.*—5-Hydroxy-4 : 7-dimethylcoumarin (1.9 g.) in acetic acid (40 c.c.) was treated with bromine (3.2 g.) in acetic acid (32 c.c.) by heating on a steam-bath for 2 hours. The solid separating on cooling was crystallised from acetic acid in shining prisms (1.5 g.), m.p. 238-39° (decomp.). (Found : Br, 45.7. $C_{11}H_8O_3Br_2$ requires Br, 46.0 per cent). It gave a yellow sodium salt with alkali.

The *methyl ether* was prepared as usual by the dimethyl sulphate-acetone-K_2CO_3 method and crystallised from acetic acid in white shining needles (0.4 g.), m.p. 216°. (Found : Br, 44.1. $C_{12}H_{10}O_3Br_2$ requires Br, 44.2 per cent). This product on heating with 10% sodium hydroxide solution gave the original product back.

5-Methoxy-3 : 8-dibromo-4 : 7-dimethylcoumarin.—5-Methoxy-4 : 7-dimethylcoumarin (2 g.) in acetic acid (20 c.c.) was treated with bromine (3.2 g.) in acetic acid (32 c.c.) on a steam-bath for 2 hours. Product obtained was crystallised from acetic acid in shining needles (2 g.), m.p. 245-46°. (Found : Br, 44.1. $C_{12}H_{10}O_3Br_2$ requires Br, 44.2 per cent).

The same product was obtained when 5-methoxy-8-bromo-4 : 7-dimethylcoumarin (1.4 g) was brominated with one mole of bromine (0.8 g. in 8 c.c. of acetic acid) in hot.

4-Methoxy-7-bromo-3 : 6-dimethylcoumarilic Acid.—The above dibromocoumarin (0.6 g.) was refluxed with EtOH–NaOH (10%, 15 c.c.) for 3 hours. The product obtained on working up as usual was crystallised from acetic acid in small plates (0.2 g.), m.p. 269-70° (decomp.). (Found : C, 48.0, H, 3.4. $C_{12}H_{11}O_4Br$ requires C, 48.2 ; H, 3.7 per cent.). It dissolves in cold sulphuric acid to give a yellow solution which turns dark green on warming.

(*iii*) *Bromination with excess of Liquid Bromine : 5-Hydroxy-3 : 6 : 8-tribromo--4 : 7-dimethylcoumarin.*—5-Hydroxy-4 : 7-dimethylcoumarin (1.9 g.) was treated with liquid bromine (4 c.c.) and the reaction mixture was kept overnight. The excess of bromine was removed with sodium bisulphite and the product obtained was

crystallised from acetic acid in shining flakes (2.2 g.), m.p. 262-63°. (Found : Br, 56.5. $C_{11}H_7O_3Br_3$ requires Br. 56.1 per cent).

The *methyl ether*, prepared as usual by the dimethyl sulphate-K_2CO_3 method, was crystallised from acetic acid in shining faint yellow plates, m.p. 232-33°. (Found : Br, 54.5. $C_{12}H_9O_3Br_3$ requires Br, 54.4 per cent).

The same product (1.5 g.) was obtained when 5-methoxy-4 : 7-dimethylcoumarin (2 g.) was brominated with liquid bromine (5 c.c.) by heating on a steam-bath at 60°-70° for 2 hours.

4-*Methoxy*-5 : 7-*dibromo*-3 : 6-*dimethylcoumarilic Acid.*—The above coumarin (0.5 g.) was refluxed with EtOH–NaOH (10%, 20 c.c.) for 4 hours. The solid obtained on working up as usual was crystallised from acetic acid in tiny plates, (0.2 g.), m.p. 294-95°. (Found ; C, 38.0 ; H, 2.8. $C_{12}H_{10}O_4Br_2$ requires C, 38.1 ; H, 2.7 per cent). It dissolves in sulphuric acid in cold to give a yellow solution which turns dark green on warming.

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CONDENSATION OF SOME AROMATIC ALDEHYDES WITH ORCACETOPHENONE AND ITS MONOMETHYL ETHER

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A number of polyhydroxy ketones like resacetophenone, quinacetophenone, phloracetophenone and gallacetophenone have been condensed with many aromatic aldehydes in presence of alkali, and chalkone, flavanone or a mixture of both obtained.[1,2,3,4] Orcacetophenone, however, has not been condensed so far with aromatic aldehydes. Orcacetophenone behaves abnormally in some reactions, for example, in the Kostanecki-Robinson acetylation of orcacetophenone, 7-acetoxy-4-acetomethyl-5-methylcoumarin, instead of the corresponding chromone, was obtained.[5] It was therefore thought of interest to study the condensation of orcacetophenone and its monomethyl ether with some aromatic aldehydes such as benzaldehyde, *p*-anisaldehyde and *p*-hydroxybenzaldehyde.

Orcacetophenone on condensation with benzaldehyde in presence of alkali gave a white product to which the structure of 7-hydroxy-5-methylflavanone has been assigned as it gave a pink colour with magnesium and hydrochloric acid and did not give any colour with alcoholic ferric chloride. No chalkone could be isolated. The monomethyl ether of orcacetophenone on similar condensation with benzaldehyde gave a mixture of two products A and B. The structure of 2-hydroxy-4-methoxy-6-methylchalkone has been assigned to the product A as it gave a deep red colour with concentrated sulphuric acid and reddish brown colouration with alcoholic ferric chloride. With boric acid-citric acid reagent it gave a deep yellow colour. The product A was isomerised to B by refluxing with dilute sulphuric acid in alcoholic solution. The compound B was found to be the same as the methyl ether of 7-hydroxy-5-methylflavanone. 7-Methoxy-5-methylflavanone was converted into 7-methoxy-5-methylflavanol with amyl nitrite and hydrochloric acid.

Orcacetophenone on condensation with *p*-anisaldehyde gave a product to which the structure of 7-hydroxy-4'-methoxy-5-methylflavanone has been assigned on the basis of its colour reactions. The monomethyl

ether of orcacetophenone on similar condensation with *p*-anisaldehyde gave 7:4'-dimethoxy-5-methylflavanone as the main product of the reaction. The corresponding chalkone, 2-hydroxy-4:4'-dimethoxy-6-methylchalkone, was obtained in a very small quantity. The chalkone was isomerised to 7:4'-dimethoxy-5-methylflavanone and this flavanone was converted into 7:4'dimethoxy-5-methylflavanol as usual.

The condensation of orcacetophenone with *p*-hydroxybenzaldehyde gave 7 : 4'-dihydroxy-5-methylflavanone but orcacetophenone monomethyl ether gave only 2 : 4'-dihydroxy-4-methoxy-6-methylchalkone. This chalkone was isomerised to the corresponding flavanone with dilute sulphuric acid.

EXPERIMENTAL

7-Hydroxy-5-methylflavanone : To a solution of orcacetophenone[6] (1.7 g.) and benzaldehyde (1.1 g.) in ethyl alcohol (15 ml.) was added potassium hydroxide (40 g. in 40 ml. water) at room temperature. The mixture became deep red in colour. After keeping the reaction mixture for 48 hours at room temperature it was diluted with water, extracted with ether to remove unreacted benzaldehyde and acidified with dilute hydrochloric acid. The separated solid was filtered and washed repeatedly with sodium bicarbonate solution (5%) to remove benzoic acid. The flavanone was obtained as colourless plates after two crystallisations from alcohol, m. p. 218°. (Found : C, 75.2 ; H, 5.4 . $C_{16}H_{14}O_3$ requires C, 75.6 ; H, 5.5 per cent) The product gave yellow colour with concentrated sulphuric acid and no colour with alcoholic ferric chloride. Boric acid-citric acid test was also negative.

7-Methoxy-5-methylflavanone : Monomethyl ether of orcacetophenone (1.8 g.) and benzaldehyde (1.1 g.) were dissolved in sufficient alcohol and to the solution potassium hydroxide (30 g. in 50 ml. water) was added at room temperature and the mixture kept for 48 hours. It was then diluted with water and extracted with ether. The alkaline layer was treated as described later. The substance obtained on removing the ether crystallised from dilute alcohol in white needles (0.6 g.), m. p. 99°. Mixed melting point with the methyl ether of 7-hydroxy-5-methylflavanone, prepared by refluxing the hydroxyflavanone (0.5 g.) in acetone (20 ml.) with methyl iodide (2 ml.) and anhydrous potassium carbonate for 15 hours, was not depressed. (Found : C, 76.4 ; H, 5.5 . $C_{17}H_{16}O_3$ requires C, 76.1 ; H, 6.0 per cent)

2-Hydroxy-4-methoxy-6-methylchalkone: The alkaline solution from the above condensation after ether extraction was acidified with dilute hydrochloric acid. The solid obtained was washed with sodium bicarbonate solution and crystallised from alcohol in clusters of yellow needles (0.8 g.), m.p. 88°. (Found: C, 75.8; H, 5 7. $C_{17}H_{16}O_3$ requires C, 76.1; H, 6.0 per cent) It gave a red colouration with concentrated sulphuric acid and reddish brown colouration with alcoholic ferric chloride. Its solution in dry acetone gave deep yellow colour with boric acid—citric acid reagent.

The chalkone was converted into the corresponding flavanone by refluxing in alcohol (50 ml.) with concentrated sulphuric acid (2 ml.) on a steam bath for 24 hours. The flavanone crystallised from dilute alcohol in clusters of needles (0.3 g.), m.p. 99°. Mixed melting point with 7-methoxy-5-methylflavanone was not depressed.

7-Methoxy-5-methylflavanol: 7-Methoxy-5-methylflavanone (0.5 g.) and amyl nitrite (3 g.) were dissolved in ether (100 ml.) and hydrogen chloride was passed through it for two hours. The mixture was left overnight and the next day run into dilute sodium hydroxide solution. The ethereal layer was repeatedly washed with more of sodium hydroxide solution. The product obtained on acidification crystallised from dilute alcohol in needles (0.2 g.) m.p. 206°. (Found: C, 72.5; H, 5.4, after drying the sample at 120° under reduced pressure for two hours. $C_{17}H_{14}O_4$ requires C, 72.3; H, 5.0 per cent).

7-Hydroxy-4'-methoxy-5-methylflavanone: Orcacetophenone (1.6 g.) and *p*-anisaldehyde (1.36 g.) were dissolved in alcohol and to the solution potassium hydroxide (40 g. in 40 ml. water) was added at room temperature. The mixture was kept in a stoppered flask for 48 hours. The product obtained on working up the reaction mixture as usual crystallised from dilute alcohol in white plates (1.2 g.), m.p. 202°. (Found: C, 71.5; H, 5.8. $C_{17}H_{16}O_4$ requires C, 71.9; H, 5.6 per cent). It gave a pink colour with magnesium and hydrochloric acid and a yellow colour with concentrated sulphuric acid. With alcoholic ferric chloride no colour was obtained.

7: 4'-Dimethoxy-5-methylflavanone: Monomethyl ether of orcacetophenone (1.8 g.) and *p*-anisaldehyde (1.36 g.) were dissolved in alcohol and to the solution sodium hydroxide (50 g. in 40 ml. water) was added at room temperature. The mixture was kept in a stoppered flask for 48

hours. It was then diluted with water to about 400 ml. and cooled in an ice bath. The separated solid was filtered and the filtrate was treated as described later. The residue crystallised from dilute alcohol in tiny needles (1.8 g.), m.p. 101-102°. Mixed melting point with 7:4'-dimethoxy-5-methylflavanone prepared from 7-hydroxy-4'-methoxy-5-methylflavanone by the methyl iodide-potassium carbonate method was not depressed.

2-Hydroxy-4:4'-dimethoxy-6-methylchalkone: The alkaline filtrate from the above experiment was acidified with dilute hydrochloric acid and the solid obtained washed with sodium bicarbonate solution. It crystallised from dilute alcohol in shining plates, m.p. 101°. (Found: C, 72.4; H, 5.8. $C_{18}H_{18}O_4$ requires C, 72.4; H, 5.8 per cent.) It gave red colour with concentrated sulphuric acid and reddish brown colouration with alcoholic ferric chloride. Its solution in dry acetone gave orange colour with boric acid-citric acid reagent.

Isomerisation of the above chalkone was carried out using dilute sulphuric acid in alcoholic solution as usual. The product did not depress the melting point of 7:4'-dimethoxy-5-methylflavanone obtained above.

7:4'-Dihydroxy-5-methylflavanone: Orcacetophenone (1.6 g.) and *p*-hydroxybenzaldehyde (1.2 g.) were dissolved in alcohol and potassium hydroxide (25 g. in 25 ml. water) added at room temperature. The mixture was kept in a stoppered flask for 48 hours. The product obtained on working up the reaction mixture as usual crystallised from dilute alcohol in colourless shining needles (1.2 g.), m.p. 279°. (Found: C, 71.5; H, 5.4. $C_{16}H_{14}O_4$ requires C, 71.1; H, 5.2 per cent.) It gave pink colour with magnesium and hydrochloric acid, a pale yellow colour with concentrated sulphuric acid and no colour with alcoholic ferric chloride. Citric acid-boric acid test was also negative.

The *dimethyl ether* prepared by the methyl iodide-potassium carbonate method as usual crystallised from dilute alcohol in needles, m.p. 101°. Mixed melting point with 7:4'-dimethoxy-5-methylflavanone, described earlier, was not depressed.

7:4'-Dimethoxy-5-methylflavanol: 7:4'-Dimethoxy-5-methylflavanone (0.5 g.) and amyl nitrite (3.0 g.) were dissolved in ether (100 ml.) and hydrogen chloride passed through it for two hours. The mixture was left over-night and the next day run into dilute solution of sodium hydroxide. The ethereal layer was washed with more of sodium hydroxide

solution. The alkaline extracts on acidification gave a product which crystallised from alcohol in needles (0.2 g.), m.p. 217°. (Found : C, 69.2 ; H, 5.6. $C_{18}H_{16}O_5$ requires C, 69.2 ; H, 5.7 per cent.)

2:4'-Dihydroxy-4-methoxy-6-methylchalkone : Monomethyl ether of orcacetophenone (1.8 g.) and *p*-hydroxybenzaldehyde (1.2 g.) were dissolved in alcohol and to the solution potassium hydroxide (40 g. in 40 ml. water) was added at room temperature and the mixture was kept in a stoppered flask for 48 hours. The product obtained on working up the reaction mixture as usual was crystallised first from benzene and then from dilute alcohol in short yellow needles (1.0 g.), m.p. 168°. (Found : C, 71.3 ; H, 5.3. $C_{17}H_{16}O_4$ requires C, 71.8 ; H, 5.6 per cent.) It gave red colouration with concentrated sulphuric acid and a reddish brown colouration with alcoholic ferric chloride. Its solution in dry acetone gave deep yellow colour with boric acid-citric acid reagent.

7-Methoxy-4'-hydroxy-5-methylflavanone : Isomerisation of the above chalkone was carried out using dilute sulphuric acid in alcoholic solution as usual. Tne product crystallised from dilute alcohol in colourless shining plates, m. p. 182°. (Found : C, 71.5 H, 5.8. $C_{17}H_{16}O_4$ requires C, 71.8; H, 5·7 per cent.) It gave pale yellow colour with concentrated sulphuric acid and no colour with alcoholic ferric chloride. It gave pink colour with magnesium and hydrochloric acid.

SUMMARY

Orcacetophenone condenses with benzaldehyde, *p*-anisaldehyde and *p*-hydroxybenzaldehyde in presence of caustic potash to give 7-hydroxy-5-methyl-,7-hydroxy-4'-methoxy-5-methyl-, and 7:4'-dihydroxy-5-methylflavanone respectively. Orcacetophenone monomethyl ether with benzaldehyde gave a mixture of 2-hydroxy-4-methoxy-6-methylchalkone and 7-methoxy-5-methylflavanone in almost equal proportions. With *p*-anisaldehyde it gave 7:4'-dimethoxy-5-methylflavanone as the main product and 2-hydroxy-4:4'-dimethoxy-6-methylchalkone in a very small quantity. With *p*-hydroxybenzaldehyde, however, only 2:4'-dihydroxy-4-methoxy-6-methylchalkone was obtained. The chalkones have been isomerised to the corresponding flavanones. The methoxyflavanones have been converted into the corresponding flavanols.

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Bromination of Ethyl-7-hydroxy-coumarin-3-carboxylate & Some Dihydroxycoumarin Derivatives

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The bromination of some mono and dihydroxycoumarins has been studied. Ethyl-7-hydroxycoumarin-3-carboxylate gives a mixture of 6- and 8-bromo compounds with one molecule of bromine, the 6:8-dibromo compound with two moles of bromine and the 4(?):6:8-tribromo compound with excess of bromine. With one mole of bromine, 4:7-dihydroxycoumarin gives the 3-bromo compound and not the 8-bromo compound as reported by earlier workers. Similarly, with two moles of bromine 7:8-dihydroxy-4-methylcoumarin gives the 3:6-dibromo and not the 3:4-dibromo compound. With different quantities of bromine, 5:7-dihydroxy-4-methylcoumarin gives only the 3:6:8-tribromo compound and 5:7-dimethoxy-4-methylcoumarin gives only the 3:8-dibromo compound.

EARLIER studies[1-3] on the bromination of some 7-hydroxycoumarin derivatives and their methyl ethers have shown that the first bromine atom in all cases enters the 3-position and the subsequent bromine atoms enter the benzene ring. It was, therefore, thought of interest to study systematically the bromination of a 3-substituted coumarin. Ethyl-7-hydroxycoumarin-3-carboxylate was selected for this study and ethyl-7-hydroxy-6-bromocoumarin-3-carboxylate. With one mole of bromine this compound gave two products which were found to be ethyl-7-hydroxy-8-bromocoumarin-3-carboxylate. With two moles of bromine the 6:8-dibromo compound was obtained. With excess of bromine a tribromo derivative was obtained which on hydrolysis with cold sodium hydroxide gave the tribromo acid. On oxidation with alkaline potassium permanganate the tribromo compound gave a thick syrupy mass, which did not crystallize. This compound was found to be 2:4-dibromoresorcinol. On Pechmann condensation with ethyl acetoacetate it gave 7-hydroxy-6:8-dibromo-4-methylcoumarin. The tribromo compound has, therefore, been tentatively assigned the structure ethyl-7-hydroxy-4:6:8-tribromocoumarin-3-carboxylate.

While the present work was in progress Seshadri and Varadarajan[3] reported their results on the bromination of 7-hydroxy-3-phenylcoumarin. They also obtained a mixture of 6-bromo and 8-bromo isomers with one molecule of bromine, 6:8-dibromo compound with two moles of bromine and 7-hydroxy-3-(*p*-bromophenyl)-6:8-dibromocoumarin with excess of bromine.

The bromination of several monohydroxycoumarin derivatives has been studied by Sethna *et al.*[1,4]. This work has now been extended and the bromination of some dihydroxy coumarin derivatives has been studied. Baüer and Schoder carried out the bromination of 4:7-dihydroxycoumarin with one mole of bromine in carbon tetrachloride solution and obtained a compound melting at 127°. They suggested the structure 4:7-dihydroxy-8-bromocoumarin for this product. The monobromo product obtained on bromination of 4:7-dihydroxycoumarin in acetic acid in the present study has melting point 212°. The dimethyl ether of this product gives a bromine-free coumarilic acid derivative on heating with alkali and so the monobromo product must be the 3-bromo compound.

The bromination of 7:8-dihydroxy-4-methylcoumarin and its dimethyl ether with one and two moles of bromine has been carried out by Sakai and Kato[6]. With one mole of bromine the present authors obtained the same 3-bromo derivative as obtained by Sakai and Kato. Sakai and Kato assigned the structure 7:8-dihydroxy-3:4-dibromo-4-methylcoumarin to the dibromo product. This product has now been found to be 7:8-

dihydroxy-3:6-dibromo-4-methylcoumarin as its dimethyl ether gave bromocoumarilic acid on hydrolysis with alkali indicating the presence of a bromine atom in the 3-position. The dimethyl ether of the dibromocoumarin could not be oxidized by Elbs persulphate oxidation method indicating that the 6-position was also substituted[7]. This structure has been confirmed by direct comparison of the product with 7: 8-dihydroxy-3: 6-dibromo-4-methylcoumarin obtained by the Pechmann condensation of 4-bromopyrogallol with ethyl acetoacetate and subsequent bromination of the 7: 8-dihydroxy-6-bromo-4-methylcoumarin so obtained with one mole of bromine.

Tilden and Burrows[8] brominated 5: 7-dimethoxycoumarin with excess of bromine and obtained 5: 7-dimethoxy-3: 8-dibromocoumarin. With excess of bromine in a sealed tube, however, they obtained 5: 7-dihydroxy-3: 6: 8-tribromocoumarin. The bromination of 5: 7-dihydroxy-4-methylcoumarin has not been studied before. 5: 7-Dihydroxy-4-methylcoumarin was brominated with one mole of bromine in acetic acid under different conditions, but the monobromo product could not be isolated; only mixtures of the tribromo derivative and the original compound were obtained. Bromination with two moles and excess of bromine gave better yields of the tribromo product, but no other product could be isolated. 5: 7-Dimethoxy-4-methylcoumarin on bromination with one mole of bromine in acetic acid at room temperature gave a dibromo compound. Attempts to get a monobromo derivative were not successful. The dibromo product on hydrolysis with hot alcoholic potassium hydroxide gave a bromocoumarilic acid derivative. This showed that one of the two bromine atoms was in 3-position. To decide the position of the second bromine atom the dimethyl ether was subjected to Elbs persulphate oxidation when a good yield of the oxidation product was obtained. This indicated that the 6-position in the methyl ether must be free[7] and that the product is 5:7-dimethoxy-3: 8-dibromo-4-methyl coumarin. With excess of bromine the same 3: 8-dibromo derivative was obtained. The tribromo compound could not be obtained.

Experimental procedure

Ethyl-7-hydroxy-8-bromocoumarin-3-carboxylate — Ethyl-7-hydroxycoumarin-3-carboxylate[9] (0·3 g.) was dissolved in acetic acid (5·0 cc.) by heating and bromine (0·2 g.) in acetic acid (2·0 cc.) was added gradually to the hot solution. On cooling, a yellow crystalline mass separated which was filtered and crystallized from alcohol in needles (0·15 g.), m.p. 264°. (Found: Br, 25·3. $C_{12}H_9O_5Br$ requires Br, 25·6%.) Mixed melting point with an authentic sample of ethyl-7-hydroxy-8-bromocoumarin-3-carboxylate, prepared by the condensation of 2: 4-dihydroxy-3-bromobenzaldehyde with diethyl malonate in the presence of piperidine, was not depressed.

Ethyl-7-hydroxy-6-bromocoumarin-3-carboxylate — The filtrate obtained from the above experiment after separation of the precipitate was diluted with water and the precipitate which separated crystallized from dilute alcohol in small needles, m.p. 274°. (Found: Br, 25·1. $C_{12}H_9O_5Br$ requires Br, 25·6%.) Mixed melting point with an authentic sample of ethyl-7-hydroxy-6-bromocoumarin-3-carboxylate, prepared by the condensation of 2: 4-dihydroxy-5-bromobenzaldehyde[3] with diethyl malonate in the presence of piperidine, was not depressed.

2 : 4 - *Dihydroxy - 3 - bromobenzaldehyde* — 2-Bromoresorcinol[10] (10 g.) was dissolved in sodium-dried ether (100 cc.) in a three-necked flask provided with a mercury-sealed stirrer, and zinc cyanide (20 g.) added. Rapid stream of hydrogen chloride was then passed for 2 hr. and the reaction mixture left overnight. The next day the ether was decanted off, water (100 cc.) added and the precipitate obtained crystallized from hot water (charcoal) in plates, m.p. 169°. (Found: Br, 36·4. $C_7H_5O_3Br$ requires Br, 36·8%.)

Ethyl-7-hydroxy-6: 8-dibromocoumarin-3-carboxylate — Ethyl-7-hydroxycoumarin-3-carboxylate (0·3 g.) was dissolved in hot acetic acid (5·0 cc.) and bromine (0·4 g.) in acetic acid (4 cc.) added gradually to the hot solution. The yellow product which separated crystallized from acetic acid in colourless needles (0·3 g.), m.p. 238°. (Found: Br, 40·4. $C_{12}H_8O_5Br_2$ requires Br, 40·8%.) Mixed melting point with an authentic sample of ethyl-7-hydroxy-6: 8-dibromocoumarin-3-carboxylate, prepared by the condensation of 2: 4-dihydroxy-3: 5-dibromobenzaldehyde[3] with diethyl malonate in the presence of piperidine, was not depressed.

The same product was obtained by brominating ethyl-7-hydroxy-6-bromocoumarin-3-carboxylate with one mole of bromine.

7-Hydroxy-6: 8-dibromocoumarin-3-carboxylic acid — To the above ester (0·3 g.) sodium hydroxide solution (10%, 20 cc.) was added and the solution kept at room temperature for 48 hr. The product obtained on acidification crystallized from alcohol in needles, m.p. 258°. (Found: Br, 46·0. $C_{10}H_4O_5Br_2$ requires Br, 45·5%.)

Ethyl-7-hydroxy-4(?): 6: 8-tribromocoumarin-3-carboxylate — To ethyl-7-hydroxycoumarin-3-carboxylate (0·5 g.) liquid bromine (4 cc.) was added and the reaction mixture kept at room temperature for 24 hr. Excess of bromine was then removed by adding a concentrated solution of sodium bisulphite. The separated solid crystallized from dilute alcohol in plates (0·8 g.), m.p. 198°-200°. (Found: Br, 51·6. $C_{12}H_7O_5Br_3$ requires Br, 50·9%.)

7-Hydroxy-4(?): 6: 8-tribromocoumarin-3-carboxylic acid — The tribromo ester (0·3 g.) was dissolved in sodium hydroxide solution (10%, 20 cc.) and the reaction mixture kept at room temperature for 48 hr. The product obtained on acidification crystallized from alcohol in needles, m.p. 282°. (Found: Br, 54·4. $C_{10}H_3O_5Br_3$ requires Br, 54·2%.)

Oxidation of ethyl-7-hydroxy-4(?): 6: 8-tribromocoumarin-3-carboxylate — The tribromo ester (0·3 g.) was dissolved in sodium hydroxide solution (10%, 20 cc.) and the solution refluxed. Saturated solution of potassium permanganate in water was added to the reaction mixture in 1 cc. lots at intervals of 10 min. till there was permanent pink colour and heating continued for 1 hr. The solution was then cooled, saturated with sulphur dioxide and extracted with ether. A syrupy mass was obtained which could not be crystallized and so was subjected to Pechmann condensation with ethyl acetoacetate.

7-Hydroxy-6: 8-dibromo-4-methylcoumarin — The syrupy mass (0·5 g.) obtained in the above experiment was condensed with ethyl acetoacetate (0·8 g.) in the presence of sulphuric acid (80%, 2 cc.) as usual and the product obtained crystallized from acetic acid in shining needles, m.p. 229°-30°. (Found: Br, 47·4. $C_{10}H_6O_3Br_2$ requires Br, 47·9%.) Mixed melting point with an authentic sample of 7-hydroxy-6: 8-dibromo-4-methylcoumarin obtained by the condensation of 2: 4-dibromoresorcinol[11] with ethyl acetoacetate in the presence of sulphuric acid was not depressed.

4: 7-Dihydroxy-3-bromocoumarin — 4:7-Dihydroxycoumarin (0·5 g.) was dissolved in hot acetic acid (10 cc.) and bromine (0·45 g.) in acetic acid (4·5 cc.) added to the hot solution. The mixture, after cooling, was diluted with water and then extracted with ether. The product obtained from the ethereal extract crystallized from benzene in colourless plates, m.p. 212°. (Found: Br, 31·4. $C_9H_5O_4Br$ requires Br, 31·1%.)

The dimethyl ether of the above compound prepared by refluxing an acetone solution of the compound with methyl iodide and potassium carbonate crystallized from dilute alcohol in clusters of needles, m.p. 131°-32°. (Found: Br, 28·3. $C_{11}H_9O_4Br$ requires Br, 28·1%.) The same product was obtained on treating 4: 7-dimethoxycoumarin (0·5 g.) in acetic acid (10 cc.) with bromine (0·39 g.) in acetic acid (3·9 cc.).

3: 6-Dimethoxycoumarilic acid — 4: 7-Dimethoxy-3-bromocoumarin (0·5 g.) was refluxed with sodium hydroxide solution (10%, 20 cc.) for 4 hr. The resulting solution on acidification gave a product which crystallized from alcohol in needles, m.p. 208°. (Found: C, 60·0, H, 5·1. $C_{11}H_{10}O_5$ requires C, 59·5; H, 4·5%.)

7: 8-Dihydroxy-3: 6-dibromo-4-methylcoumarin — 7: 8-Dihydroxy-4-methylcoumarin[12] (1·0 g.) was dissolved in hot acetic acid (20 cc.) and bromine (1·6 g.) in acetic acid (16 cc.) added to the hot solution. On cooling, a white mass separated which crystallized from dilute acetic acid in tiny needles, m.p. 264°. Sakai and Kato[6], who assigned the 3: 4-dibromo structure to this product, reported the same melting point. Mixed melting point with an authentic sample of 7: 8-dihydroxy-3: 6-dibromo-4-methylcoumarin was not lowered.

6: 7-Dimethoxy-5-bromo-3-methylcoumarilic acid — The dimethyl ether (1 g.) of the above compound was refluxed with sodium hydroxide solution (10%, 20 cc.) for 4 hr. The product obtained on acidification crystallized from dilute alcohol in needles, m.p. 248°. Sakai and Kato reported the same melting point.

7: 8-Dihydroxy-3: 6-dibromo-4-methylcoumarin — 4-Bromopyrogallol[13] (1 g.), ethyl acetoacetate (0·6 g.) and sulphuric acid (80%, 5 cc.) were mixed and the reaction

mixture kept overnight. The dark product (7:8-dihydroxy-6-bromo-4-methylcoumarin) which separated on pouring the reaction mixture in water crystallized from dilute acetic acid (charcoal) in colourless plates (0·6 g.), m.p. 254°. (Found: Br, 29·1. $C_{11}H_7O_4Br$ requires Br, 29·5%.)

The above coumarin (0·5 g.) in hot acetic acid (10 cc.) was treated with bromine (0·3 g.) in acetic acid (3 cc.). The 3:6-dibromo compound which separated on cooling, was crystallized from dilute acetic acid as tiny needles (0·3 g.), m.p. 264°.

5:7-*Dihydroxy*-3:6.8-*tribromo*-4-*methylcoumarin* — 5:7-Dihydroxy-4-methylcoumarin[14] (1 g.) was dissolved in hot acetic acid (30 cc.) and bromine (0·83 g.) in acetic acid (8·3 cc.) added to the hot solution. As no precipitate separated on cooling, the reaction mixture was diluted with water and cooled in an ice bath when a yellow product separated out. It was crystallized from acetic acid, m.p. 241°. (Found: Br, 55·6. $C_{10}H_5O_4Br_3$ requires Br, 55·9%.) The original compound was obtained on extraction of the mother liquor with ether.

The same tribromo derivative was obtained in good yield on treating 5:7-dihydroxy-4-methylcoumarin (2 g.) with excess of bromine (3 cc.) in acetic acid (30 cc.).

5:7-*Dimethoxy*-3:8-*dibromo*-4-*methylcoumarin* — 5:7-Dimethoxy-4-methylcoumarin[15] (1 g.) was dissolved in acetic acid (15 cc.) and bromine (0·73 g.) in acetic acid (7·3 cc.) added gradually to it at room temperature. The solid which separated crystallized from acetic acid in needles (0·7 g.), m.p. 284°. (Found: Br, 41·9. $C_{12}H_{10}O_4Br_2$ requires Br, 42·3%.)

4:6-*Dimethoxy*-7-*bromo*-3-*methylcoumarilic acid* — The above bromocoumarin (0·5 g.) was refluxed with alcoholic potassium hydroxide solution (10 per cent, 40 cc.) for 8 hr. on a steam bath. The product obtained on acidification crystallized from alcohol in small needles (0·2 g.), m.p. 225°. It gives effervescence with sodium bicarbonate solution and a violet colouration with concentrated sulphuric acid. (Found: Br, 24·9. $C_{12}H_{11}O_5Br$ requires Br, 25·4%.)

6-*Hydroxy*-5:7-*dimethoxy*-3:8-*dibromo*-4-*methylcoumarin* — 5:7-Dimethoxy-3:8-dibromo-4-methylcoumarin (1 g.) was dissolved in sodium hydroxide solution (10%, 30 cc.) with the help of pyridine and by warming on a steam bath. It was then oxidized with potassium persulphate (0·66 g. in 30 cc. water) according to the procedure described by Parikh and Sethna[16]. The product obtained crystallized from dilute alcohol in needles (0·2 g.), m.p. 201°. It dissolves in sodium hydroxide solution to give a deep yellow solution. (Found: Br, 40·1. $C_{12}H_{10}O_5Br_2$ requires Br, 40·6%.)

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Studies in the Hydroxyanthracene Series. Part I. Some Reactions of 1-Anthrol

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1-Anthrol takes part in the Gattermann reaction to give the 4-formyl derivative in good yield. Oxidation of the methyl ether of the 4-formyl derivative with alkaline permanganate gave 1-hydroxyanthraquinone-4-carboxylic acid. On Friedel-Crafts acetylation of 1-anthrol, both at room temperature and on the steam-bath, 2-acetyl-1-anthrol was formed. This latter product also resulted from the Nencki acetylation of 1-anthrol, as well as from the Fries rearrangement of 1-anthrolacetate at 140°. When carried out at room temperature, however, the Fries rearrangement gave a mixture of the 2-acetyl and 4-acetyl isomers.

1-Anthrol-2-carboxylic acid has been synthesized in good yield by a modified method. When 1-anthrol was condensed with ethyl acetoacetate and ethyl benzoylacetate in the presence of 80% sulfuric acid the corresponding anthra-α-pyrones were formed.

Among the hydroxyanthracene derivatives there has been very little work with 1-anthrol. It was therefore thought of interest to study the various reactions of 1-anthrol.

The Gattermann reaction on 1-anthrol gave a product in good yield which formed a 2,4-phenylhydrazone but which did not give any color with alcoholic ferric chloride. The structure of 4-formyl-1-anthrol has therefore been assigned to this product. Upon methylation and subsequent oxidation with alkaline potassium permanganate this product gave an acid which in turn gave a blood-red color with alkali and on decarboxylation with quinoline and copper powder yielded 1-hydroxyanthraquinone. The structure of 1-hydroxyanthraquinone-4-carboxylic acid has therefore been assigned to this acid. This acid had previously been synthesized by Birukoff[1] by the condensation of *p*-cresol with phthalic anhydride and subsequent oxidation of the 4-methyl-1-hydroxyanthraquinone formed to the acid. In addition 4-formyl-1-anthrol has been reduced by Clemmensen's method to 4-methyl-1-anthrol.

Upon Friedel and Crafts acetylation, both at room temperature as well as on the steam-bath, 1-anthrol yielded a ketone (A) which gave a bluish-violet coloration with alcoholic ferric chloride. This ketone was methylated and the methyl ether was oxidized with sodium hypochloride solution whereupon another ketone (B) was obtained. Ketone (B) gave a blood-red color with zinc and alkali and upon further oxidation with the same reagent it yielded the known 1-methoxyanthraquinone-2-carboxylic acid. This latter acid was identified by direct comparison with an authentic specimen which had been prepared by the nitration of 2-methylanthraquinone following the method of Roemer and Link[2] to yield 1-nitro-2-methylanthraquinone which then was oxidized with a mixture of chromic anhydride and concentrated nitric acid to 1-nitroanthraquinone-2-carboxylic acid.[3] This latter product was converted to 1-methoxyanthraquinone-2-carboxylic acid by boiling with potassium hydroxide in methyl alcohol.[4] From this it follows that the ketone (B) is 2-acetyl-1-methoxyanthraquinone and consequently product (A) is 2-acetyl-1-anthrol.

The Nencki acetylation of 1-anthrol also provided the same ketone (A) in good yield; in addition, the Fries rearrangement of 1-anthrolacetate at 140° gave ketone (A). At room temperature, however, the Fries rearrangement of 1-anthrolacetate gave 2-acetyl-1-anthrol and a second ketone in low yield. Since this latter ketone did not give a color with alcoholic ferric chloride it has been assigned the structure of 4-acetyl-1-anthrol.

Laska and Haller[5] prepared an acid of melting point 200° by heating the alkali salt of 1-anthrol at about 220° with carbon dioxide under pressure. They assigned the structure of 1-anthrol-2-carboxylic acid to this substance. Kranzlein and Corell[6] claim to have prepared the same acid by fusing a compound they believed to be 2-carboxy-1-anthracenesulfonic acid with alkali. For the 1-anthrol-2-carboxylic acid they reported a melting point of 268°.

Consequently it was thought of interest to prepare 1-anthrol-2-carboxylic acid and to establish its structure. When 1-anthrol was heated with potassium bicarbonate at 120° in glycerine for four hours an acid of melting point 200° was obtained. Upon methylation of this product with dimethyl sulfate in acetone in the presence of potassium carbonate a methoxy ester (X) was obtained which upon hydrolysis with 10% sodium hydroxide yielded a methoxy acid (Y). This acid upon oxidation with sodium hypochlorite solution gave the known 1-methoxyanthraquinone-2-carboxylic acid which had been prepared as described above. Therefore, (Y) is 1-methoxyanthracene-2-carboxylic

(1) Birukoff, *Ber.*, 20, 2438 (1887).
(2) Roemer and Link, *Ber.*, 16, 695 (1883).
(3) Terres, *Ber.*, 46, 1634 (1913).
(4) Eckert and Endler, *British Abstracts*, 120, i 871 (1921).
(5) Laska and Haller, German Patent 559,333, [*Chem. Abstr.*, 27, 735 (1933)].
(6) Kranzlein and Corell, German Patent 564,129, [*Chem. Abstr*; 27, 1000 (1933)].

acid and (X) is methyl 1-methoxyanthracene-2-carboxylate. These results confirm the structure of 1-hydroxyanthracene-2-carboxylic acid as assigned by Laska and Haller[5] to their product; in consequence the acid of Kranzlein and Corell[6] must have some other structure.

On the Pechmann condensation with ethyl acetoacetate and ethyl benzoylacetate in the presence of 80% sulfuric acid, 1-anthrol yielded products to which the structures of 4′-methyl-1,2-anthra-α-pyrone and 4′-phenyl-1,2-anthra-α-pyrone respectively have been assigned. These assignments were made since upon treatment with alkali and dimethyl sulfate the two products yielded acrylic acids; this is a characteristic test for coumarin derivatives.[7]

EXPERIMENTAL

All melting points are uncorrected.

4-Formyl-1-anthrol. 1-Anthrol (prepared according to Dienel)[8] (5 g.) in sodium-dried ether (200 ml.) and zinc cyanide (10 g.) were mixed in a three-necked flask provided with a mercury-sealed stirrer. A stream of hydrogen chloride gas then was passed into the mixture for two hours and it was left to stand overnight. The following day the ether was decanted and the product was refluxed with 50% alcohol for 30 minutes. The product which was obtained upon cooling was crystallized from benzene in yellow needles (5 g.), m.p. 206°. It did not give any color with an alcoholic ferric chloride solution.

Anal. Calc'd for $C_{15}H_{10}O_2$: C, 81.1; H, 4.5. Found: C, 81.0; H, 4.7.

The *2,4-dinitrophenylhydrazone* was prepared in the usual manner and had melting point 286°.

Anal. Calc'd for $C_{21}H_{14}N_4O_5$: N, 13.9. Found: N, 13.8.

The methyl ether of 4-formyl-1-anthrol was prepared by dissolving the 4-formyl-1-anthrol (1 g.) in 50 ml. of dry acetone and refluxing with 0.62 g. of dimethyl sulfate and 2 g. of anhydrous potassium carbonate for 20 hours. Upon removal of the acetone a product was obtained which, when recrystallized from dilute alcohol, formed yellow needles of m.p. 112°; yield 0.8 g.

Anal. Calc'd for $C_{16}H_{12}O_2$: C, 81.3; H, 5.1. Found: C, 81.1; H, 5.0.

1-Hydroxyanthraquinone-4-carboxylic acid. 4-Formyl-1-methoxyanthracene (0.5 g.) was suspended in 20 ml. of 20% sodium hydroxide solution and 0.5 g. of potassium permanganate was added. The flask was heated gently on a wire gauze for four hours; then the reaction mixture was filtered free of manganese dioxide and the filtrate was acidified. The product so obtained was purified through a sodium bicarbonate solution and then was recrystallized from dilute alcohol to form yellow needles, of m.p. 232–234°. (Birukoff[1] gives m.p. 236°).

Anal. Calc'd for $C_{15}H_8O_5$: C, 67.2; H, 3.0. Found: C, 67.0; H, 3.6.

This acid on decarboxylation in quinoline solution with copper powder gave a product of m.p. 190°. A mixture m.p. with 1-hydroxyanthraquinone prepared according to Ullmann[9] was not depressed.

4-Methyl-1-anthrol. A solution of 4-formyl-1-anthrol (0.5 g.) in acetic acid (20 ml.) was added drop by drop during 30 minutes to zinc amalgam (prepared from zinc dust, 5 g.) suspended in dilute hydrochloric acid (1:1, 8 ml.). Concentrated hydrochloric acid (1 ml.) then was added and the heating was continued one hour longer. The solution then was filtered hot and the filtrate was diluted with water. The product obtained was crystallized from dilute alcohol in needles (0.2 g.), m.p. 134–136°.

Anal. Calc'd for $C_{15}H_{12}O$: C, 86.5; H, 5.8. Found: C, 86.9; H, 5.9.

2-Acetyl-1-anthrol. A solution of 1-anthrol (1.9 g.) and acetic anhydride (1.3 g.; 1.2 moles) in nitrobenzene (10 ml.) was mixed with a solution of anhydrous aluminum chloride (2.7 g.; 2 moles) in nitrobenzene (20 ml.) and the reaction mixture, protected from moisture, was left for 72 hours at room temperature. It was then treated with ice and hydrochloric acid and the nitrobenzene was steam-distilled. The black product obtained was repeatedly extracted with alkali. The product obtained on acidification of the alkaline extracts crystallized from dilute acetic acid in brownish needles, m.p. 182°. It gave a bluish-violet coloration with alcoholic ferric chloride.

Anal. Calc'd for $C_{16}H_{12}O_2$: C, 81.4; H, 5.1. Found: C, 80.9; H, 4.6.

The same product was obtained (i) on heating the above reaction mixture on a steam-bath for 2 hours, (ii) in the Fries rearrangement of 1-anthrolacetate (2.4 g.) by heating in an oil-bath at 140° for 3 hours with anhydrous aluminum chloride (2.7 g.), and (iii) by heating 1-anthrol (1 g) for 2 minutes with acetic acid (1 ml.) and acetic anhydride (0.25 ml.) in the presence of zinc chloride (0.65 g.).

The *2,4-dinitrophenylhydrazone* prepared as usual gave m.p. 292°.

Anal. Calc'd for $C_{22}H_{16}N_4O_5$: N, 13.5. Found: N, 13.6.

The methyl ether. 2-Acetyl-1-anthrol (1 g.) was dissolved in dry acetone (50 ml.) and refluxed with dimethyl sulfate (0.6 g.) and anhydrous potassium carbonate (2 g.) for 20 hours. The product thus obtained was crystallized from dilute acetone in yellow needles, m.p. 126°.

Anal. Calc'd for $C_{17}H_{14}O_2$: C, 81.6; H, 5.6. Found: C, 81.9; H, 5.9.

2-Acetyl-1-methoxyanthraquinone. Sodium hydroxide (5.5 g.) in water (5.0 ml.) was added to crushed ice (50 g.) and chlorine was passed through the solution until the solution was neutral to litmus. Additional sodium hydroxide (2.5 g.) in water (10 ml.) was then added. To the resulting solution at 65°, 2-acetyl-1-methoxyanthracene (1 g.) was added portion-wise during half an hour. The temperature rose to 85° and was kept there for 3 hours. The separated product was filtered after cooling and was crystallized from dilute acetic acid in orange needles, m.p. 214°. It gave a red color with zinc and alkali.

Anal. Calc'd for $C_{17}H_{12}O_4$: C, 72.8; H, 4.3. Found: C, 72.7; H, 4.6.

1-Methoxyanthraquinone-2-carboxylic acid. 2-Acetyl-1-methoxyanthraquinone (1 g.) was suspended in sodium hypochlorite solution (prepared from 5 g. of sodium hydroxide as described above) and the mixture was refluxed in a water-bath at 85–90° for about 3 hours. After cooling an excess of sodium bisulphite was added to destroy the excess sodium hypochlorite and the solution was acidified with dilute hydrochloric acid. The product thus obtained was crystallized from glacial acetic acid in clusters of yellow needles, m.p. 254°. A mixture m.p. with an authentic sample, prepared as mentioned in the theoretical portion, was not depressed.

4-Acetyl-1-anthrol. A solution of 1-anthrolacetate (2.4 g.) in nitrobenzene (40 ml.) was mixed with a solution of anhydrous aluminum chloride (2.7 g.; 2 moles) in nitrobenzene (20 ml.) and the reaction mixture was left for 48 hours at room temperature. It then was treated with ice and hydrochloric acid and the nitrobenzene was steam-distilled. The black product thus obtained was repeatedly extracted with cold dilute alkali. On acidification of the combined alkaline extracts, a product was obtained which was dissolved in hot alcohol. On cooling, a small crop of crystals separated; these were found to be 2-acetyl-1-anthrol. The mother liquor on

(7) Canter and Robertson, *J. Chem. Soc.*, 1875 (1931).
(8) Dienel, *Ber.*, 2863 (1905).
(9) Ullmann, *Ber.*, **53**, 829 (1920).

dilution with water gave 4-acetyl-1-anthrol which was crystallized from alcohol in yellow shining plates, m.p. 260°.

Anal. Calc'd for $C_{16}H_{12}O_2$: C, 81.4; H, 5.1. Found: C, 81.6; H, 5.5.

The *2,4-dinitrophenylhydrazone* prepared as usual gave m.p. 274°.

Anal. Calc'd for $C_{22}H_{16}N_4O_6$: N, 13.5. Found: N, 13.1.

1-Anthrol-2-carboxylic acid. A mixture of 1-anthrol (1 g.), potassium bicarbonate (1.8 g.), and glycerine (5 ml.) was heated at 120° in an oil-bath for 4 hours. Carbon dioxide was bubbled through the solution during heating. The reaction mixture then was treated with water and the solution was filtered. The product obtained on acidifying the filtrate crystallized from dilute alcohol, m.p. 200° (decom.). Laska and Haller[6] give the same m.p.

Anal. Calc'd for $C_{15}H_{10}O_3$: C, 75.6; H, 4.2. Found: C, 75.4; H, 4.5.

Methyl-1-methoxyanthracene-2-carboxylate. 1-Anthrol-2-carboxylic acid (1 g.) was dissolved in dry acetone (50 ml.) and refluxed with dimethyl sulfate (1.1 g., 2.2 moles) and anhydrous potassium carbonate (2 g.) for 15 hours. The product thus obtained was crystallized from dilute alcohol in needles, m.p. 107°.

Anal. Calc'd for $C_{17}H_{14}O_3$: C, 76.7; H, 5.3. Found: C, 77.0; H, 5.5.

1-Methoxyanthracene-2-carboxylic acid. The above ester (0.5 g.) was heated on a steam-bath with 10% sodium hydroxide for 4 hours. The product obtained on acidification with dilute hydrochloric acid crystallized from benzene in shining plates, m.p. 207°.

Anal. Calc'd for $C_{16}H_{12}O_3$: C, 76.2; H, 4.8. Found: C, 76.7; H, 5.2.

1-Methoxyanthraquinone-2-carboxylic acid. The above acid (1 g.) was suspended in sodium hypochlorite solution (prepared from 5 g. of sodium hydroxide as described before) and the mixture was heated in a water-bath at 85–90° for about 3 hours. After cooling an excess of sodium bisulphite was added to destroy unreacted sodium hypochlorite and the solution was acidified with dilute hydrochloric acid. The product was crystallized from glacial acetic acid in clusters of yellow needles, m.p. 254°. A mixture melting point with an authentic sample, prepared as described before, was not depressed.

4'-Methyl-1,2-anthra-α-pyrone. A mixture of 1-anthrol (1.94 g.), ethyl acetoacetate (1.3 g.), and sulfuric acid (80%; 20 ml.) was kept at room temperature for 24 hours. The reaction mixture then was poured into ice-cold water. The separated solid on repeated crystallization from alcohol gave yellow shining needles (1 g.), m.p. 230°.

Anal. Calc'd for $C_{18}H_{12}O_2$: C, 83.1; H, 4.6. Found: C, 83.0; H, 4.7.

β-Methyl-β,2-(1-methoxyanthryl)-acrylic acid. 4'-Methyl-1,2-anthra-α-pyrone (1 g.) was dissolved in a boiling mixture of acetone (100 ml.) and sodium hydroxide (4%; 20 ml.) and to this solution dimethyl sulfate (2 ml.) was added with continuous vigorous shaking. More of the alkali and dimethyl sulfate were added with shaking and the mixture was heated on a steam-bath for a few minutes after making it distinctly alkaline. The product obtained on acidification with dilute hydrochloric acid, was crystallized from dilute alcohol in tiny yellow needles, m.p. 185°. It decolorized a dilute potassium permanganate solution.

Anal. Calc'd for $C_{19}H_{16}O_3$: C, 78.1; H, 5.5. Found: C, 78.1; H, 5.5.

4'-Phenyl-1,2-anthra-α-pyrone. A mixture of 1-anthrol (1.94 g.), ethyl benzoylacetate (1.92 g.), and sulfuric acid (80%; 20 ml.) was kept at room temperature for 24 hours. The product obtained on working up the reaction mixture as before crystallized from ethyl acetate in needles (1 g.), m.p. 203°.

Anal. Calc'd for $C_{23}H_{14}O_2$: C, 85.7; H, 4.4. Found: C, 85.9; H, 4.8.

β-Phenyl-β,2-(1-methoxyanthryl)acrylic acid. 4'-Phenyl-1,2-anthra-α-pyrone (1 g.) in warm sodium hydroxide solution (10%; 20 ml.) was treated with dimethyl sulfate (2 ml.) as described above. The product obtained upon acidification, was crystallized from dilute alcohol as a yellow amorphous powder, m.p. 190°. It decolorized a dilute potassium permanganate solution.

Anal. Calc'd for $C_{24}H_{18}O_3$: C, 81.3; H, 5.1. Found: C, 81.2; H, 4.8.

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Pigment of *Raphanus caudatus* Linn.

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The pigment occurring in *Raphanus caudatus* has been examined and found to be malvin chloride. The anthocyanidin chloride has been prepared by hydrolysing the glucoside. Colour reactions, analysis and circular paper chromatography of the anthocyanidin chloride confirm it as malvidin chloride. Its acetyl derivative on oxidation with neutral potassium permanganate gives acetyl syringic acid.

SCHUDEL[1] isolated cyanin from the violet-red variety and pelargonin from the yellowish red variety of *Raphanus sativus*. No work seems to have been done so far on the colouring matter of *Raphanus caudatus* (Hindi: *Moongra*). The colouring matter of the whip-like, purple-coloured edible part of this plant, which is widely grown in this country, especially in Gujarat, has now been studied.

The pigment was readily extracted by ethanolic hydrochloric acid (1 per cent) and was purified through its lead salt.

The anthocyanin chloride left a residue of about 4 per cent. Ash-free anthocyanin could not be isolated even after repeated crystallizations. Anthocyanin is not at all extracted by amyl alcohol from 0·5 per cent hydrochloric acid indicating that it is not a monoglucoside. Its distribution number between isobutyl alcohol and 0·5 per cent hydrochloric acid was found to be 18·6 which is a little higher than what is observed for a diglucoside structure.

The anthocyanidin was obtained as dark red crystals when the glucoside was hydrolysed with boiling dilute hydrochloric acid. The carbon, hydrogen and methoxyl determinations and colour reactions indicated that it was malvidin chloride. Colour reactions in buffer solutions were directly compared with malvidin chloride isolated from *Clarkia elegans* and were found to be similar. Circular paper chromatography according to the method of Ponniah and Seshadri[2] gave a single curve which was identified as due to malvidin chloride by parallel spotting with malvidin chloride isolated from *C. elegans*. Sugar residue was identified as glucose by its osazone.

The anthocyanidin was fused with caustic potash in an atmosphere of nitrogen. Phloroglucinol was identified in the degradation products by paper partition chromatography.

The acetyl derivative of anthocyanidin was prepared and was oxidized in aqueous suspension with neutral potassium permanganate. The oxidation product was identified as acetyl derivative of syringic acid by direct comparison with an authentic sample prepared according to the method of Bogert and Coyne[3].

All the above observations indicate that the colouring matter of *R. caudatus* Linn. is malvin chloride.

Experimental procedure

Isolation of pigment — Sun-dried purple pods of *R. caudatus* (150 g.) were extracted with successive quantities of ethanolic hydrochloric acid (1 per cent). Saturated aqueous solution of lead acetate was then added to the combined extracts (3 litres) until the colour began to turn purple. Precipitated lead chloride was filtered and more lead acetate solution was added until all the anthocyanin lead salt was precipitated. The solution was then left overnight. Next day the dark blue precipitate was collected, washed with distilled water and finally with alcohol. The lead salt was purified by dissolving it in acetic acid and precipitating it by means of ether. The lead salt was then treated with methyl alcohol (100 ml.) containing hydrochloric acid (8 ml.). The separated lead chloride was removed and the red pigment precipitated with ether. This process was repeated until lead chloride no longer separated. The dark red amorphous powder was crystallized in the following manner. Anthocyanin chloride (200 mg.) was dissolved in methyl alcohol (13 ml.) and filtered. To the filtrate concentrated hydrochloric acid (1 ml.) was added. After 24 hr the crystals were filtered and washed with 12 per cent hydrochloric acid. Recrystallization yielded 90 mg. of air-dried material. This left about 4 per cent ash.

The anthocyanin was not extracted from a 0·5 per cent hydrochloric acid solution by isoamyl alcohol. It was also not extracted by ethyl acetate in presence of picric acid. It gave a bright bluish green colour with sodium carbonate which changed to green and

then yellow on addition of sodium hydroxide. The absorption curve was obtained with a Beckman DU spectrophotometer. The maximum occurs at 528 mμ.

Distribution number — The distribution ratio in mutually saturated *n*-butyl alcohol and 0·5 per cent hydrochloric acid was determined according to the modified method of Robinson and Todd[4]. The distribution numbers were 18·9 and 18·6 for 1·062 and 4·208 mg. respectively of the colouring matter.

Identification of the anthocyanidin and carbohydrate components — The anthocyanin chloride (200 mg.) was hydrolysed by boiling for 3 min. with water (11 ml.) and hydrochloric acid (9 ml.). The separated anthocyanidin chloride was filtered and washed with cold 1 per cent hydrochloric acid.

Carbohydrate — The filtrate from the above was extracted with isoamyl alcohol to remove the dissolved anthocyanidin chloride. The aqueous solution was neutralized with solid lead carbonate. The lead chloride precipitate was filtered and the excess of lead was removed from the filtrate by precipitation with hydrogen sulphide. The filtrate from the lead sulphide precipitate was concentrated on a water bath. Twenty ml. of this sugar solution was heated in a boiling water bath, with sodium acetate (3 g.) and phenylhydrazine hydrochloride (2 g.), for 30 min. The separated osazone was filtered and crystallized from hot 50 per cent alcohol, m.p. 208°. Mixed melting point with an authentic sample of glucosazone was not depressed.

Anthocyanidin — The anthocyanidin chloride was dissolved in alcohol, filtered and one-third volume of hydrochloric acid (12 per cent) was added. The solution was then kept in a refrigerator overnight. The separated crystals were filtered, washed with a little 10 per cent hydrochloric acid and dried in vacuum. (Found: C, 50·3; H, 4·2; MeO, 14·6. $C_{17}H_{15}O_7Cl.2H_2O$ requires C, 50·6; H, 4·7; MeO, 15·4%.) (Analysis obtained after drying the sample at 120° under vacuum: found: C, 56·4; H, 4·4; MeO, 16·1. $C_{17}H_{15}O_7Cl$ requires C, 55·5; H, 4·1; MeO, 16·91%.)

It was extracted by amyl alcohol from its solution in 0·5 per cent hydrochloric acid. When amyl alcohol layer was shaken with sodium acetate it became violet blue. The pigment was neither extracted by cyanidin reagent nor it imparted any colour to the reagent. It was not destroyed in the oxidation test.

For circular paper chromatography 1 per cent hydrochloric acid extract of the plant material was hydrolysed with 15 per cent hydrochloric acid and the anthocyanidin extracted with amyl alcohol, washed twice with 1 per cent hydrochloric acid and finally precipitated by means of petroleum ether into 1 per cent hydrochloric acid. This solution was transmitted to the centre of the filter paper to form the colour spot. The upper layer of butanol-acetic acid-water (4: 1: 5) was used as solvent. The chromatogram was allowed to develop for 40 min. at room temperature. A single red ring (R_f 0·52) was obtained. It was identified as due to malvidin chloride by parallel spotting with a sample obtained similarly from *C. elegans*.

Fusion with potassium hydroxide — Anthocyanidin (0·4 g.) was heated for 5 min. at 250° with potassium hydroxide (5 g.) and water (5 ml.) in an atmosphere of nitrogen. The mixture was cooled, diluted with water, acidified and extracted several times with ether. The acidic and phenolic degradation products were separated in the usual manner. Phenolic part was identified as phloroglucinol by paper partition chromatography. For development of chromatogram ascending method was used with Whatman No. 1. Upper layer of butanol-acetic acid-water mixture was used as solvent. Identification was carried out by parallel spotting with known sample of phloroglucinol and not through absolute R_f values.

Acetyl anthocyanidin — The anthocyanidin chloride (3 g.) was dissolved in pyridine (20 ml.) and the solution cooled. Acetyl chloride (5 ml.) was then added and the reaction mixture left overnight. The mixture was then poured into dilute hydrochloric acid. The acetyl derivative separated as an amorphous powder. It was filtered and directly oxidized by neutral potassium permanganate solution.

Oxidation of the acetyl derivative — The acetyl derivative (3 g.) was suspended in water (400 ml.) and magnesium sulphate (8 g.) was added. The mixture was stirred at room temperature and potassium permanganate (12 g.) was added during 3 hr and kept overnight. It was then acidified with concentrated sulphuric acid and manganese dioxide was dissolved by adding sodium bisulphite. The solution was filtered from the unreacted acetyl derivative and the filtrate extracted with ether. The product, left on evaporating ether, was purified through sodium bicarbonate and crystallized from hot water, m.p. 180°. Mixed melting point with the acetyl derivative of syringic acid[3] was not depressed.

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