

## Mercuration of Coumarins (A Note).

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Naik and Patel (*J. Chem. Soc.*, 1934, 1048) have mercurated coumarin derivatives 'with mercuric acetate in aqueous solution through the neutral sodium salt.' They have not made any reference to the work of Sen and Chakravarti (*J. Indian Chem. Soc.*, 1929, 6, 847; 1930, 7, 247) probably through oversight, though the method of preparation is exactly the same. We described the mercuration of coumarin, 7-hydroxy-4-methylcoumarin, 4:7-dimethylcoumarin, 6-aminocoumarin, 7:8-dihydroxy-4-methylcoumarin 4:6-dimethylcoumarin and also studied with interesting results the influence of substituents on the coumarins in mercuration by two different methods, (a) with yellow mercuric oxide and, (b) with mercuric acetate. Some of the compounds described by Naik and Patel are widely different from our compounds and as this work negatives in some cases the conclusions reached by us, it is necessary to record the following facts.

(1) 6:8-Bisacetoxymmercuricoumarin (decomp. 248°) has been obtained by Naik and Patel by the mercuration of coumarin, whereas it was found by Sen and Chakravarti (*loc. cit.*) that the mercury compound, thus obtained, is diacetoxymmercuri-*o*-coumaric acid (decomp. 215°), as it gives *o*-coumaric acid (m. p. 207-9°) and as the same mercury compound of *o*-coumaric acid (decomp. 215°) is obtained by mercuration of *o*-coumaric acid.

This is a convenient method for the preparation of *o*-coumaric acid and this has been admitted by Dey, Rao and Seshadri (*J. Indian Chem. Soc.*, 1934, 11, 745). It is also significant to note that Naik and Patel's compound is 'soluble in dilute sodium hydroxide solution.'

(2) According to Naik and Patel the effect of substituents on the mercuration of coumarins by mercuric acetate is extraordinary since in 6 nitrocoumarin the nitro group is knocked off and 6:8-diacetoxymmercuricoumarin is obtained. It has been found by us that 6-nitrocoumarin gives 5-nitro-*o*-coumaric acid, identical with the nitro-*o*-coumaric acid, prepared by Dey and Row (*J. Chem. Soc.*, 1924,

125, 561). This observation has also been supported by Dey, Rao and Seshadri (*loc. cit.*), who record "though the use of mercuric acetate resulted in a better yield (of 5-nitrocoumaric acid) the product obtained was rather impure and required several crystallisations."

Incidentally it may also be noted that whereas 6-aminocoumarin produces 6-acetoxymercuriaminocoumarin with mercuric acetate where the mercury atom replaces the hydrogen in the amino group (Sen and Chakravarti, *loc. cit.*) Naik and Patel have obtained 7-amino-6:8-bisacetoxymercuri-4-methylcoumarin from 7-amino-4-methylcoumarin and have given no experimental evidence that the compound possesses a free  $\text{NH}_2$  group.

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## Geometrical Inversion in the Acids Derived from Coumarins (A Note).

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In connection with the paper on the above subject (*J. Indian Chem. Soc.*, 1934, 11, 743) it was found necessary to give fuller details of certain experiments and to correct certain errors that had crept in during the course of publication.

7-Methoxycoumarin was obtained in a rather poor yield (1.5 g.) from umbelliferone (4 g.) by methylation in the ordinary way with dimethylsulphate in the presence of caustic alkali. A better yield (2.8 g.) was produced when the methylation was effected in benzene solution (boiling for 2 to 3 hours) in the presence of excess of anhydrous potassium carbonate. The decanted solution was distilled to remove the solvent and the residue was crystallised from methanol, m.p. 117-18°. But the easiest method for preparing the methoxycoumarin was from monomethylresorcinol which was itself made as below: