

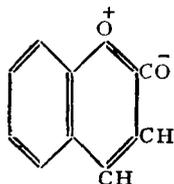
# FIXATION OF THE AROMATIC DOUBLE BONDS IN THE COUMARIN RING SYSTEM.

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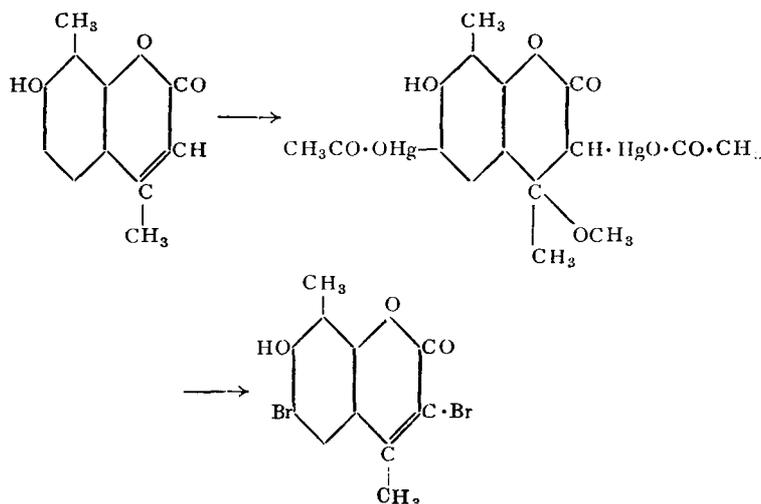
THE idea that the double bonds of aromatic ring systems are not always capable of oscillation as originally conceived by Kekule and that in several cases they have a tendency to get fixed in certain favourable positions has been gaining increased acceptance during recent years. The factor producing this fixation seems to be the fusion with a second ring.<sup>1</sup> Naphthalene seems to exist only in the symmetrical form possessing a double bond common to the two rings and seems to be incapable of assuming the alternative structure.<sup>2</sup> That even the formation of chelate rings produces bond fixation has been shown by Baker.<sup>3</sup> A number of evidences indicate the existence of such a fixation in the coumarin molecule. A double bond seems to exist in common to the two rings and in this respect it seems to resemble naphthalene. From many chemical and physical considerations coumarin has been frequently given the following structure in which the two rings are aromatic.



Though in coumarin itself substitution invariably takes place in the sixth position, in 7-hydroxy-coumarin it is exclusively in the eighth position. When the hydroxyl group is involved in the formation of fresh rings such as the furan and the pyrone, almost invariably the angular variety is produced. The migration of the allyl group from the allyl ether of 4-methyl-7-hydroxycoumarin has been shown to be to the eighth position,<sup>3</sup> thus showing conclusively that there exists a double bond between the 7 and 8 positions. However in the pyrogenic conversion of the acetyl derivative (Fries) of the hydroxy compound<sup>4</sup> and in the formation of a fresh  $\alpha$ -pyrone ring<sup>5</sup> it has been realised that the position 6 is to a small extent reactive. With a view to let in more definite evidence as to how far the double bonds of the benzene ring can assume the alternative positions, the method of Fieser<sup>2&6</sup> is here adopted.

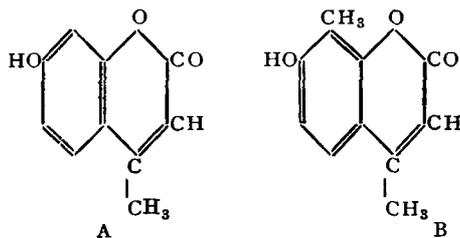
The position 8 is blocked by means of a methyl group and the reactivity of 7-hydroxy-4 : 8-dimethylcoumarin examined.

7-Hydroxy-4 : 8 dimethylcoumarin forms an acetyl derivative which undergoes the Fries rearrangement on heating with aluminium chloride to give a fair yield of 7-hydroxy-4 : 8-dimethyl-6-acetylcoumarin. The constitution of this and of several others described in this paper are deduced from well-known analogies and there exist no alternatives. 7-hydroxy-4 : 8-dimethylcoumarin reacts fairly easily with mercuric acetate in methyl alcoholic solution to produce a product in which addition at the double bond and mercuration in the benzene ring have taken place according to the general behaviour of coumarins already elucidated.<sup>7</sup> On treatment with bromine this mercury compound forms 7-hydroxy-4 : 8-dimethyl-3 : 6-dibromocoumarin.



The reaction of diazonium salts on the coumarin was examined in acetic acid medium since in an alkaline solution the pyrone ring will be opened out. The most reliable evidence is that obtained from the migration of the allyl group (Claisen's transformation). The allyloxycompound readily undergoes change on being heated to produce an allylhydroxydimethylcoumarin in good yield. The product is obviously 7-hydroxy-6-allyl-4 : 8-dimethylcoumarin.

From these and from results already recorded it is concluded that though coumarins react predominantly in the form (A) possessing a double bond between the two rings and consequently another between the 7 and 8 positions, reactivity in the isomeric form (B) is also possible and if the eighth position is blocked up by a methyl group reaction takes place fairly easily in the 6th position, the necessary shift in the double bonds having taken place.

*Experimental.*

*7-Hydroxy-4 : 8-dimethylcoumarin*<sup>5</sup> was prepared by condensing 2-methyl-resorcinol with ethylacetoacetate in the presence of sulphuric acid. On recrystallisation from alcohol it was obtained as thin plates melting at 258°.

*7-Acetoxy-4 : 8-dimethylcoumarin* was obtained by heating the hydroxy compound with acetic anhydride and sodium acetate for 4–5 hours. It crystallises from alcohol as thin plates and needles melting at 135–36°. It is insoluble in cold dilute ammonia and in sodium bicarbonate solution and gives no colouration with ferric chloride. (Found : C 67.0, H 5.2 ;  $C_{13}H_{12}O_4$  requires C 67.2, H 5.2%.)

*Fries rearrangement : 7-hydroxy-6-acetyl-4 : 8-dimethylcoumarin.*— The above compound (0.2 g.) was intimately mixed with powdered anhydrous aluminium chloride (1 g.) and baked in an oil bath at 160° for one hour. After cooling the product was decomposed with dilute hydrochloric acid and the solid filtered. It was macerated with cold dilute ammonia which removed a small amount of impurity. The undissolved residue crystallised from alcohol as colourless fine needles melting at 192–93°. (Found : C 67.4, H 5.3 ;  $C_{13}H_{12}O_4$  requires C 67.2 H 5.2%.) The yield was 0.1 g. and the compound gave a reddish violet colouration with alcoholic ferric chloride solution.

*Action of mercuric acetate.*—A solution of the hydroxydimethylcoumarin (0.5 g.) in methanol (50 c.c.) was mixed with a solution of mercuric acetate (2 g.) in methanol (15 c.c.) containing a few drops of acetic acid. A small precipitate was formed immediately. This was filtered and the clear filtrate heated under reflux for 6 hours. The solid that had separated was filtered while the mixture was hot and washed repeatedly with hot methanol and air dried—(yield 0.6 g.). By boiling the filtrate again more of the product could be obtained ; but it was not quite pure. The compound had no definite crystalline structure and decomposed slowly above 260°. It had no melting point. It was sparingly soluble in cold aqueous alkali, but dissolved completely on warming (Found : Hg 55.1 ; C 25.4% ;  $C_{16}H_{18}O_8Hg_2$  requires Hg 54.3, C 26.0%).

*7-Hydroxy-4 : 8 -dimethyl-3 : 6-dibromocoumarin.*—The mercury compound (1.6 g.) was suspended in glacial acetic acid (50 c.c.), and a solution of bromine in acetic acid added with shaking until the colour of bromine persisted. The solid rapidly went into solution as the bromination proceeded and a clear solution was eventually obtained from which a crystalline pale yellow solid deposited slowly. After shaking for about half an hour the mixture was left overnight, poured into ice water (500 c.c.) and the solid filtered off after about 2 hours. It was then macerated with potassium bromide solution to remove mercuric bromide, filtered, washed with water and crystallised repeatedly from glacial acetic acid. The dibromo compound was thus obtained as rectangular rods melting above 300°. (Found : Br 38.8 ;  $C_{11}H_8O_3Br_2$ ,  $C_2H_4O_2$  requires Br 39.2%.)

*Coupling with Diazocompounds.*—The hydroxy-dimethylcoumarin (0.1 g.) was dissolved in excess of glacial acetic acid and the solution divided into two halves. To one of these was added an ice cold solution of diazotised paranitraniline containing sodium acetate. There was no formation of colour or precipitate immediately. When enough of the solution of the diazo salt was added to cause a slight turbidity and the mixture left overnight, a deep red solid was deposited by the morning. To the other half water was added to cause slight turbidity. On leaving overnight it formed a small precipitate which was practically colourless thus showing that an azo-dye was formed in the first case as a result of coupling.

*7-Allyloxy-4 : 8-dimethylcoumarin.*—The hydroxy-coumarin (0.6 g.) in acetone solution was heated with allylbromide (2 g.) and anhydrous potassium carbonate (2 g.) for 7 hours on a water bath. The solvent was then evaporated, the residue treated with cold water (100 c.c.) and allowed to stand overnight. The solid that had separated was filtered, macerated with cold dilute ammonia in order to remove unchanged hydroxy-coumarin, filtered and washed. On recrystallisation from dilute alcohol the allyl ether was obtained as long thin rectangular plates melting at 108°. (Found : C 72.9, H 6.1 ;  $C_{14}H_{14}O_3$ , requires C 73.1, H 6.1 %.) Yield was good being 0.6 g.

*Claisen rearrangement. 7-hydroxy-4 : 8-dimethyl-6-allylcoumarin.*—The allyl ether (0.5 g.) was heated in a test tube at about 220° by means of an oil bath for 2½ hours. Care was taken that at no time the temperature exceeded 230°. After cooling, the mass was extracted with alcohol and filtered. On adding excess of water to the alcoholic solution a pale yellow solid was obtained melting at 150–160° (yield 0.4 g.). Treatment with dilute ammonia did not bring about any improvement. After repeated crystallisation from alcohol it was obtained in the form of star-like clusters of short needles and

rectangular plates melting at 168–70°. (Found : C 73·1, H 6·0 ;  $C_{14}H_{14}O_3$  requires C 73·1, H 6·1%.) The substance had a marked tendency to form supersaturated solutions in alcohol from which hard big crystals separated slowly after prolonged standing. If on the other hand water was added to the hot solution until turbidity appeared, almost all the substance came down on cooling.

*Summary.*

The behaviour of 7-hydroxy-coumarin indicates that there exists a double bond between 7 and 8 positions. But 7-hydroxy-4 : 8-dimethyl-coumarin couples with diazocompounds and undergoes mercuration in the benzene nucleus. Its acetyl derivative undergoes the Fries migration and its allyl ether the Claisen transformation. It is therefore concluded that the nuclear double bonds are not fixed and are capable of assuming alternative positions.

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