AZO DYE FORMATION IN 5-HYDROXYCOUMARINS

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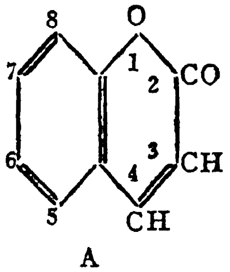
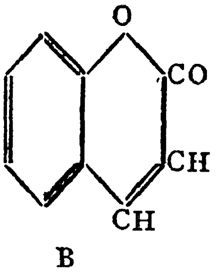
FROM a study of the reactivity of 7-hydroxy-coumarins[1] and -chromones[2] it was concluded that though these compounds normally exhibited great reactivity in position 8 indicating that a double bond was fixed between the 7 and 8 positions as in (A) and (C), reactivity in the alternative structures (B) and (D) was not altogether precluded. The coupling of phenolic compounds with diazonium salts to form azo dyes is a very facile reaction taking place energetically even at low temperatures, and even feeble reactivity of a nuclear position would suffice to direct a diazo group to that position. Hence in order to get more information on the subject of bond fixation, the behaviour of certain 7-hydroxy-chromones and -coumarins towards diazotised *p*-nitraniline was studied in detail.[3] The results indicated that the factors controlling the composition of the azo dye are rather complex and that, whether a mono- or a bis-azo dye is formed may depend not only on the disposition of aromatic double bonds and the quantity of the reagent employed, but on various other factors such as the solubility of the mono-azo dye that may be produced first, and its capacity to react further to form the bis-azo dye.



A



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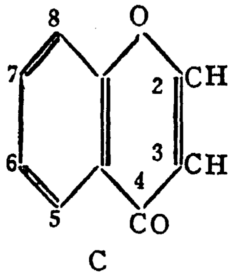

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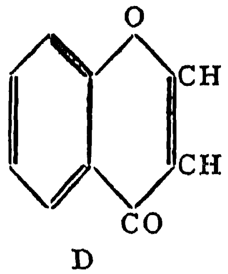

D

With a view to see how far the above conclusion regarding the factors that control azo dye formation is valid, the reactivity of 5-hydroxy-7-methylcoumarin[4] (I) and 5-hydroxy-4 : 7-dimethyl-coumarin[5] (II) has now been investigated. In these two compounds the question of bond fixation does not come in as in the case of 7-hydroxy-coumarins, and both the 6 and 8 positions, which are respectively ortho and para to the 5-hydroxy, may be expected to react, resulting in the formation of bis-azo dyes, provided of course, there are no other interfering factors. The reactivity of 7-hydroxy-5-methylcoumarin[6,7] (III) has also been studied for purposes of comparison with 5-hydroxy-7-methylcoumarin, and also with the object of seeing if the introduction of an alkyl substituent in the benzene part of the coumarin ring system has any influence on azo dye formation.

The diazo-coupling reactions were carried out in a manner essentially the same as that employed for the chromones and coumarins previously studied.[8] In the case of (III) the reaction was carried out in sodium carbonate medium but this could not be done with (I) and (II) as these 5-hydroxy-coumarins were very sparingly soluble in sodium carbonate. The use of sodium hydroxide was also precluded as this would result in the possible opening of the α-pyrone ring. Hence dilute ammonium hydroxide was employed in conjunction with alcohol to get them into solution. The diazonium salt solution was prepared by diazotising *p*-nitraniline and making up the solution to known volume, the temperature being kept near 0° throughout the process. Calculated quantities of this solution were added to the ice-cold solutions of the coumarins to give just one molecular proportion of the reagent in one set of experiments and slightly more than two molecular proportions in another set. After allowing the mixture to stand in the refrigerator for two days, the dye was filtered, crystallised from glacial acetic acid and washed with a large volume of water and then with a little alcohol. The air-dry dye was then examined for its composition by analysing for nitrogen.

	Phenolic compound	Medium employed	No. of molecular proportions of diazotised *p*-nitraniline	% N found in dye	% N calculated for		Colour of dye
					Mono-azo dye	Bis-azo dye	
I	5-Hydroxy-7-methyl-coumarin	Ammonia and alcohol	1 >2	12·5 14·7	12·9	17·7	Brown Dark brown
II	5-Hydroxy-4 : 7-dimethyl-coumarin	Ammonia and alcohol	1 >2	12·1 13·6	12·4	17·2	Red Dark brown
III	7-Hydroxy-5-methyl-coumarin	Sodium carbonate	1 >2	12·7 15·7	12·9	17·7	Red brown Red brown

The results recorded in the above table show that in all the three cases only mono-azo dyes were formed when one molecular proportion of the diazonium salt was employed, and a mixture of the mono- and bis-azo dyes with more than two molecular proportions of the reagent. In the case of the 5-hydroxy-coumarins, though both the ortho and para (6 and 8) positions are free and may be expected to react with the diazonium salt to give bis-azo dyes, this has not happened even when excess of the reagent was available. The present findings thus confirm the opinion already expressed[3a] that bis-azo dye formation is not controlled only by the disposition of nuclear double bonds and the reactivity of positions in the original compound, but is subject to various other factors, such as solubility related to the mono-azo dye and its reactivity.

The results obtained with 7-hydroxy-5-methylcoumarin were not very different from those with 7-hydroxycoumarin, thus showing that the introduction of an alkyl substituent in the benzene part has not changed the reactivity of 7-hydroxycoumarin to any degree.

Summary

The 5-hydroxycoumarins behave very similar to 7-hydroxycoumarins in regard to azo-dye formation with one and more than two molecular proportions of diazotised *p*-nitraniline. The significance of these results is discussed.

The authors desire to express their grateful thanks to Prof. T. R. Seshadri for his kind interest in this work.

REFERENCES

1.	Rangaswami and Seshadri ..	*Proc. Ind. Acad. Sci.*, A, 1938, **7**, 8.
2.	———— ..	*Ibid.*, A, 1939, **9**, 1.
3.	———— ..	*Ibid.*, A, 1939, **9**, 526.
3*a*.	———— ..	*Ibid.*, A, 1941, **14**, **565**.
4.	Sastry and Seshadri ..	*Ibid.*, A, 1940, **12**, 498.
5.	Dey ..	*J. C. S.*, 1915, 1614.
6.	Pechmann and Welsh ..	*Ber.*, 1884, **17**, 1649.
7.	Rao and Seshadri ..	*Proc. Ind. Acad. Sci.*, A, 1941, **13**, 255.

A Correction.—In the paper entitled " Fixation of Aromatic Double Bonds " by Rangaswami and Seshadri (*Proc. Ind. Acad. Sci.*, A, 1941, **14**, 547–71), the inclusion of the word " 7-hydroxy-4-methylcoumarin " in the first line on page 565 is a mistake. This compound gives a bis-azo dye with one molecular proportion of diazonium salt, only in sodium hydroxide medium (*vide* reference 3 in the present paper) and under these circumstances there is the possibility of the pyrone ring opening out.