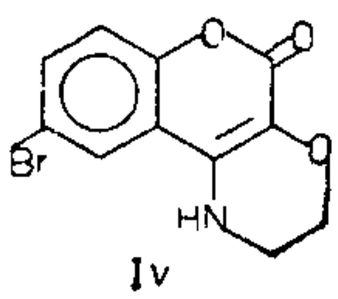
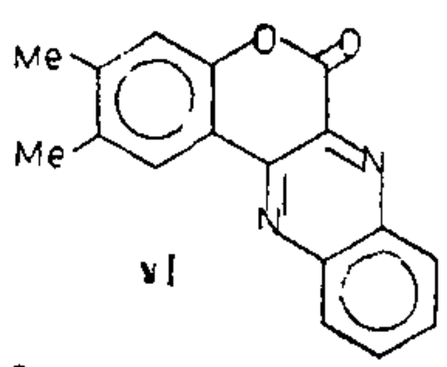
It was observed that dichlorocoumarins having groups with –I effect such as chlroine, bromine, etc., in the benzene ring reacted with Grignard reagents easily, whereas electron donating substituents present in the dichlorocoumarin derivatives hindered the formation of 3-chloroflavones. Thus, it was observed that (I) did not react with phenyl magnesium bromide, even under different experimental conditions. However, (II) reacted with this reagent to afford 3-chloro-6-bromoflavone in 40% yield. The structure (VII) assigned toit was consistent with spectral data showing a keto band in the i.r. at 1680 cm^{-1} and $M^+ = 335$.

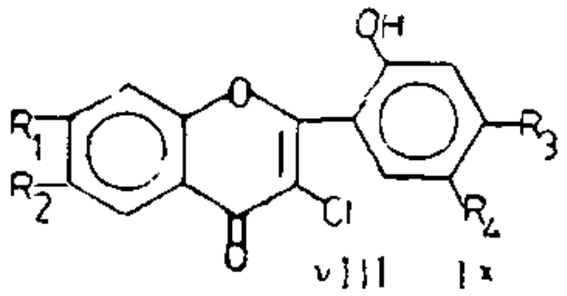
Wihle working on 3-chloroflavones, our attention was drawn to a recent publication by Gerg *et al.*,[3] who have described the synthesis of 3-chloroflavones which are the key intermediates in the preparation of some physiologically active compounds. Some 3-chloroflavone derivatives synthesised earlier by us pertaining to our work are described here.



Iv



vI



vIII IX

VIII: $R_1 = R_2 = R_3 = R_4 =$ Me.
IX: $R_1 = R_3 =$ H; $R_2 = R_4 =$ Br.

3, 4-Dimethylphenol (0·01 mole), anhydrous aluminium chloride (0·011 mole) and hexachloropropene (0·01 mole) in carbon disulphide were reacted in the usual manner. The chloroaluminium salt (prepared from 0·01 mole, 3, 4-dimethyl phenol and 0·011 mole anhydrous aluminium chloride in carbon disulphide) was added to the above solution and the mixture stirred for 24 hr. The solvent was removed under reduced pressure and the dark tarry mass was decomposed with ice and dilute sulphuric acid. The brown residue was filtered and triturated with methanol ard again filtered. The filtrate on concentration gave a colourless compound which on repeated crystallisations from benzene-petrol ether (40-60°) yielded the pure sarnple which was found to be 6, 7-dimethyl-3, 4-dichlorocoumarin (*I*), (confirmed by mixed m.p. with authentic sample). The residue on repeated crystallisations from benzene-acetone gave a pink compound (TLC single spot) which showed molecular ion peak M^+ at 329 indicating the molecular formula to be $C_{19}H_{17}O_3Cl$. The i.r. spectrum showed a bard at 1680 cm^{-1} ( ) C = 0) in addition to the usual aromatic bands at 1600, 1500 and 900 cm^{-1}. From the above data, the compound was assigned the structure 3-chloro-6, 7, 4′, 5′-tetramethyl-2′-hydroxyflavone (VIII).

Similarly, *p*-bromophenol gave 6-bromo-3, 4-dichlorocoumarin (II) (confirmed by mixed m.p. with the authentic sample) and 3-chloro-6, 5′-dibromo-2′-hydroxyflavone (IX). They were separated by the fractional crystallisations. The i.r. spectrum of the flavone showned the ketonic band at 1680 cm^{-1} while the mass spectrum showed molecular ion peak M^+ and 431, confirming the assigned structure.

All the compounds gave satisfactory elemental analyses.

The authors are indebted to Ciba-Geigy Research Centre, Bombay, for spectra and Mrs. J. A. Patankar and Mr. D. S. More for microanalyses. We also thank Dr. Nitya Nand, C.D.R.I., Lucknow, for the pharmacological screening of our compounds and to CSIR for a JRF to ARD.

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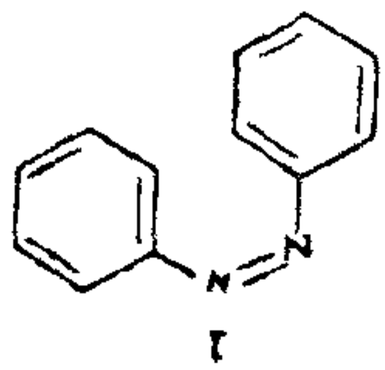
PHOTOCYCLIZATION OF 2-PHENYLAZOPYRIDINE : FORMATION OF 4-PYRIDO [*c*] CINNOLINE

PHOTOCHEMICAL cyclodehydrogenation of azobenzene (I) to benzo [*c*] cinnoline (II) occurs on irradiation of azobenzene in presence of proton acids[1] or in presence of Lewis acids[2,3]. As this reaction is of technological importance in connection with the photochemical fading of azo-dyes[4], it was thought of interest to examine similar reactions in the case of 2-phenylazopyridine (*III*). *This communication describes the* results of the irradiations of 2-phenylazopyridine under different conditions. The formation of the photocyclized product, 4-pyrido [*c*] cinnoline (IV), accounts for the fading observed in all these cases.

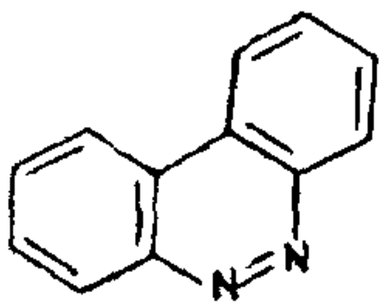
2-Phenylazopyridine was prepared by the condensation of 2-aminopyridine with freshly sublimed nitrosobenzene in presence of pyridine and sodium hydroxide[5].

When a very dilute solution of 2-phenylazopyridine (0·0001 M) in petroleum ether was exposed to sunlight, a gradual bleaching of the colour of the solution from deep red to pale yellow was observed. The reaction was followed spectrophotometrically by the reduction in the intensity of the peak at 450 nm and appearance

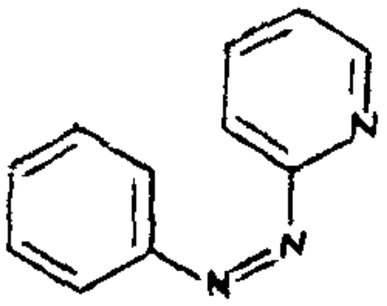
of a new peak around 380 nm characteristic of the cyclized product[1]. Bleaching occurred more rapidly when an ethanolic sulphuric acid solution of 2-phenylazopyridine was kept exposed to light.



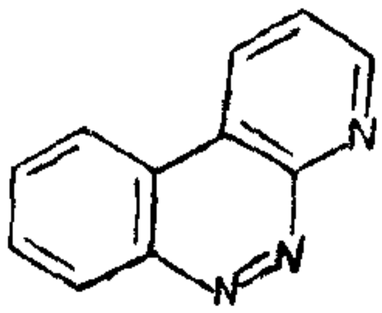
I



II



III



IV

A solution of 2-phenylazopyridine (500 mg) in ethanol (800 ml) containing concentrated sulphuric acid (50 ml) was irradiated in an Engelhard-Hanovia one-litre photochemical reactor with a Philips HPK 125 W high-pressure mercury-quartz lamp for 20 hr. Working-up and chromatography of the reaction mixture on a neutral alumina column afforded a greenish yellow fluorescent solid (120 mg), m.p. 193°, identified as 4-pyrido [*c*] cinnoline from elemental analysis and spectra.

4-Pyrido [*c*] cinnoline was also obtained by the irradiation of 2-phenylazopyridine in presence of anhydrous aluminium chloride in dichloromethane.

The mechanism of the cyclization appears essentially the same as that of azobenzene to benzo [*c*] cinnoline[3]. Azobenzene is known to undergo photocyclization only in presence of acids. In the case of 2-phenylazopyridine, there are evidences of cyclization to some extent even in neutral medium. This suggests some differences in certain aspects of the mechanism. This is being investigated in detail by studying the nature of the excited states involved.

Prof. S. S. Moosath is thanked for encouragement and the University of Calicut for facilities.

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NEW COLORIMETRIC ESTIMATION OF UREA WITH *p*-DIMETHYLAMINOBENZALDEHYDE

METHODS available for the determination of urea are either time-consuming and cumbersome[1,2] or not applicable to samples containing high percentage of the diamide[3–7]. *para*-Dimethylaminobenzaldehyde has been found to give a bright greenish yellow colour with urea. The reaction is specific to urea and not affected by acetamide and biuret. No interference is observed with the common ions such as NH_4^+, Na^+, K^+, Ca^{++}, Cl^-, $SO_4^=$, NO_3^- and $H_2PO_4^-$ found in NK fertilizers. Hence the method finds application in the determination of urea in fertilizers. However, the final acid concentration in the colour-developed solution should be less than 0·13 N. Blank corrections are needed if HPO_4^{--} is present.

To an aliquot of urea solution containing 10–60 mg urea, 5 ml of 0·6% para-dimethylamirobenzaldehyde in 0·25–0·30 N HCl is added and the solution is made up to 25 ml with distilled water. The bright greenish colour- developed is read at 420 nm. The colour is stable for quite few hours. The method is comparable to the conventional methods within ± 1·0%. The coefficient of variability of the method is 0·81% with repeatability of 2·2% of the urea present in the sample at the concentrations suggested elsewhere.

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SONUSIDE—A NEW GLYCOSIDE FROM *ACACIA CONCINNA* D.C. BEANS WITHOUT SEEDS

DURING the search of natural glycosides of anti-tumour, anti-fertility, anti-cancer, and anti-cough and anti-rheumatism properties, it was found[1] that triterpenic as well as steroidal saponins with more than one sugar chain are the real glycosides found in nature which undergo partial hydrolysis or decomposition by heat, bacteria, enzymes and mild acids to give saponins of one sugar chain only. *Acacia concinna* D.C. (family