

3-methyl-octacosan-1,3-diol, has also been isolated in the present investigation.

Thus, while the alkanes of *F. indica* consist of a mixture of C_{27} , C_{28} and C_{29} *n*-alkanes with C_{27} and C_{29} predominating, the alkanol and alkane diol consist of mass spectrometrically homogeneous branched C_{29} components not apparently derived, in this species, from reduction of the corresponding carboxylic acid according to the tenets of biogenesis⁸ of C_{27} and C_{29} *n*-alkanes.

The co-occurrence of the alkanol, $C_{29}H_{60}O$, and the alkane diol, $C_{29}H_{60}O_2$, in *F. indica* having methyl substituents at different positions, is an example of non-specific methylation pattern in plant species involving carbonyl centres (instead of carbanion centres) of the corresponding C_{28} -poly β -keto chain. These two compounds would act as markers in chemotaxonomic studies of plants belonging to the sub-family *Fumariaceae*, as these are stable secondary end products.

Microanalyses were done by C.D.R.I., Lucknow and by Dr. F. B. Strauss, Oxford, IR (nujol), NMR ($CDCl_3$) and mass spectra were recorded in National Chemical Laboratory, Poona.

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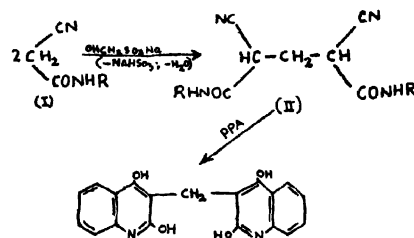
Synthesis of Methylene Bis-(2,4-Dihydroxy Quinolines)

J. M. TRIVEDI & C. M. MEHTA

Department of Chemistry, Faculty of Science, M.S. University of Baroda, Baroda

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THE interaction study of hydroxymethane sulphonate with cyanacet anilides was undertaken to prepare methylene bisderivatives, with a view to synthesis diquinolylmethanes. In earlier communications methylene bis-derivatives¹ of acetoacet anilides and their cyclised products² were reported. In the present investigation cyanacetanilides (I) are allowed to react with sodium hydroxy methane sulphonate, forming the corresponding methylene bis-derivatives (II), which undergo, simultaneous partial hydrolysis and cyclisation with PPA. (3,4,5), giving 3-3'-methylene bis-(2,4-quinolinediols) (III), the course of reaction is expressed as :



(where, R = phenyl, tolyl, xylyl or naphthyl group).

Experimental

The required methylene bis-derivatives of the substituted amides of cyanacetic acid are prepared as under :

(I) *Methylene bis(cyanacetanilide)* : Cyanacetanilide (0.02M) dissolved in 90% methanol to which was added solution of sodium hydroxymethane sulphonate

TABLE I—METHYLENE BIS-(HYDROXYQUINOLINES)

T = (2,2', 4,4'-Tetrahydroxy-)

Q = (-3,3'-Diquinolylmethane)

B = (-3,3'-Dibenzoquinolylmethane)

Sr. No.	Compound	Molecular formula	M.P. °C	Yield %	Nitrogen %		Carbon %		Hydrogen %	
					Found	Reqd.	Found	Reqd.	Found	Reqd.
1.	T-Q	$C_{19}H_{14}O_4N_2$	400	41.6	8.59	8.38	68.03	68.25	4.32	4.22
2.	T-8,8'-dichloro-Q	$C_{19}H_{12}O_4N_2Cl_2$	400	48.7	6.93	6.95	—	—	—	—
3.	T-6,6'-dichloro-Q	$C_{19}H_{12}O_4N_2Cl_2$	400	52.5	6.44	6.95	59.11	59.55	2.66	2.97
4.	T-7,7'-dimethyl-Q	$C_{21}H_{18}O_4N_2$	400	36.1	7.81	7.73	69.25	69.60	5.42	5.00
5.	T-6,6'-dimethyl-Q	$C_{21}H_{18}O_4N_2$	400	41.7	8.10	7.73	—	—	—	—
6.	T-6,6',8,8'-tetramethyl-Q	$C_{23}H_{22}O_4N_2$	400	48.0	7.54	7.18	—	—	—	—
7.	T-6,6',7,7'-tetramethyl-Q	$C_{23}H_{22}O_4N_2$	400	50.9	7.33	7.18	70.28	70.75	5.62	5.68
8.	T-B-(7 : 8)	$C_{27}H_{18}O_7N_2$	400	48.6	6.31	6.45	—	—	—	—
9.	T-B-(5 : 6)	$C_{27}H_{18}O_4N_2$	400	46.3	6.11	6.45	—	—	—	—

(0.01M) in 5 ml of water. The reaction mixture was refluxed on a sand-bath for 3 hr and 50 ml of water was added to it at room temperature. The resulting product was then filtered and crystallised from acetic acid in white fine crystals. In the same way other bis-derivatives required for the synthesis of diquinolyl methanes are obtained.

(II) 2,2', 4,4'-Tetrahydroxy-3,3'-diquinolyl methane : Methylene bis(cyanacetanilide) (3.329; 0.1M) was dissolved in a clear solution of polyphosphoric acid prepared by dissolving phosphorous pentoxide (20.0 g) in phosphoric acid (12.0 ml, d. 1.75), and the reaction mixture was heated in an oil bath at 140° for 3 hr with a calcium chloride guard tube. After cooling, hydrochloric acid (60 ml, 1N) was added and the mixture was neutralized with sodium hydroxide solution (pH 4), when the crude product was precipitated. It was then filtered and crystallised from glacial acetic acid. The diquinolyl methane derivatives listed in table 2 are accordingly synthesised.

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Stabilities of some Heterocyclic Amine Complexes : Part II.

R. C. SHARMA & P. K. BHATTACHARYA

Chemistry Department, Faculty of Science, M.S. University, Baroda-2

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IN the previous communication¹ formation constants of Ni(II), Cd(II) and Mg(II) complexes with pyridine and monomethyl pyridines have been discussed. Structure of nickel complexes has also

been studied². In the present work the reactions between Ni(II) and di- and tri-methyl pyridines (2:4-lutidine, 2:6-lutidine and 2:4:6-collidine) have been studied in aqueous solution. Ni(II) complexes of lutidine in non-aqueous solvents have been studied earlier³.

Materials and Methods : The inorganic compounds were all BDH(A.R.) or Fluka pure quality. The ligands were, however, purified by fractional distillation and the purity was tested by finding out the boiling points. Double distilled water was used for preparing all the solutions.

A Metrohm pH meter model E 350A was used which reads up to the accuracy of ± 0.05 . A constant temperature bath was used to maintain constant temperature, its accuracy being $\pm 0.1^\circ$.

The proton ligand and metal ligand formation constants at 35° and 45° ($\pm 0.1^\circ$) have been determined by Irving-Rossotti's two titration techniques⁴ as detailed in the previous paper¹. Log K_1 and log K_2 values obtained from the formation curves have been improved by use of successive approximation method⁵. The values have been tabulated in Table 1 and have an accuracy of ± 0.05 .

Discussion

The experimental data reveals that the stabilities of the complexes are in the order of 2:4-lutidine complex < 2:6-lutidine complex < 2:4:6-collidine complex which is in accordance with the basicities of the ligands (2:4-lutidine < 2:6-lutidine < 2:4:6-collidine). Exact linear relationship⁵, however, does not hold good. This may be attributed to the difference in $M-N\pi$ interaction, entropy and enthalpy changes in the formation of different complexes. Nickel(II), being a transition metal ion with d^8 configuration, has filled $d\pi$ orbitals and can affect interaction with the $p\pi$ orbital over the nitrogen atom of the tertiary base molecule. The extent of $M-L\pi$ interaction differs depending on the number and position of the $-CH_3$ group introduced in the ring. Lutidine complexes are more stable than pyridine and picoline complexes as expected from higher basicities of the lutidines. With the increase in temperature the basicities of the ligands go down and there is corresponding decrease in the formation constants as seen in Table 1.

TABLE 1

	PK^H		log K_1		log K_2		$\Delta \log PK^H$	$\Delta \log \beta_2$
	35°	45°	35°	45°	35°	45°		
Diaquo bis 2:4 lutidine Nickel (II)	6.44	6.32	3.26	3.14	2.67	2.56	0.12	0.23
Diaquo bis 2:6 lutidine Nickel (II)	6.61	6.53	3.32	3.25	2.77	2.70	0.07	0.14
Diaquo bis 2:4:6 collidine Nickel (II)	6.93	6.80	3.56	3.43	2.99	2.88	0.13	0.24