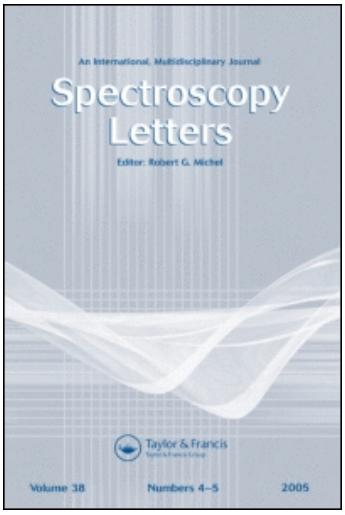

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Structural Elucidation of Novel Derivatives of Pyranobisquinolines ^{1}H-NMR, ^{13}C-NMR and Mass Spectroscopic Study of (7H)-6,8-Dichloro-7-methyl-pyrano(3,2-c:5,6-c')bisquinoline and (7H)-6,8-dichloro-7-methyl-pyrano (3,2-c:5,6-b')bisquinoline

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STRUCTURAL ELUCIDATION OF NOVEL DERIVATIVES OF PYRANOBISQUINOLINES ^{1}H-NMR, ^{13}C-NMR AND MASS SPECTROSCOPIC STUDY OF (7H)-6,8-DICHLORO-7-METHYL-PYRANO(3,2-c:5,6-c')BIS-QUINOLINE AND (7H)-6,8-DICHLORO-7-METHYL-PYRANO (3,2-c:5,6-b')BISQUINOLINE

KEYWORDS: (7H)-6,8-Dichloro-7-methyl-pyrano(3,2-c:5,6-c') bisquinoline,(7H)-6,8-Dichloro-7-methyl-pyrano (3,2-c:5,6-b')bisquinoline-derivatives, structural elucidation, ^{1}H-NMR, ^{13}C-NMR, Mass Spectroscopy.

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ABSTRACT

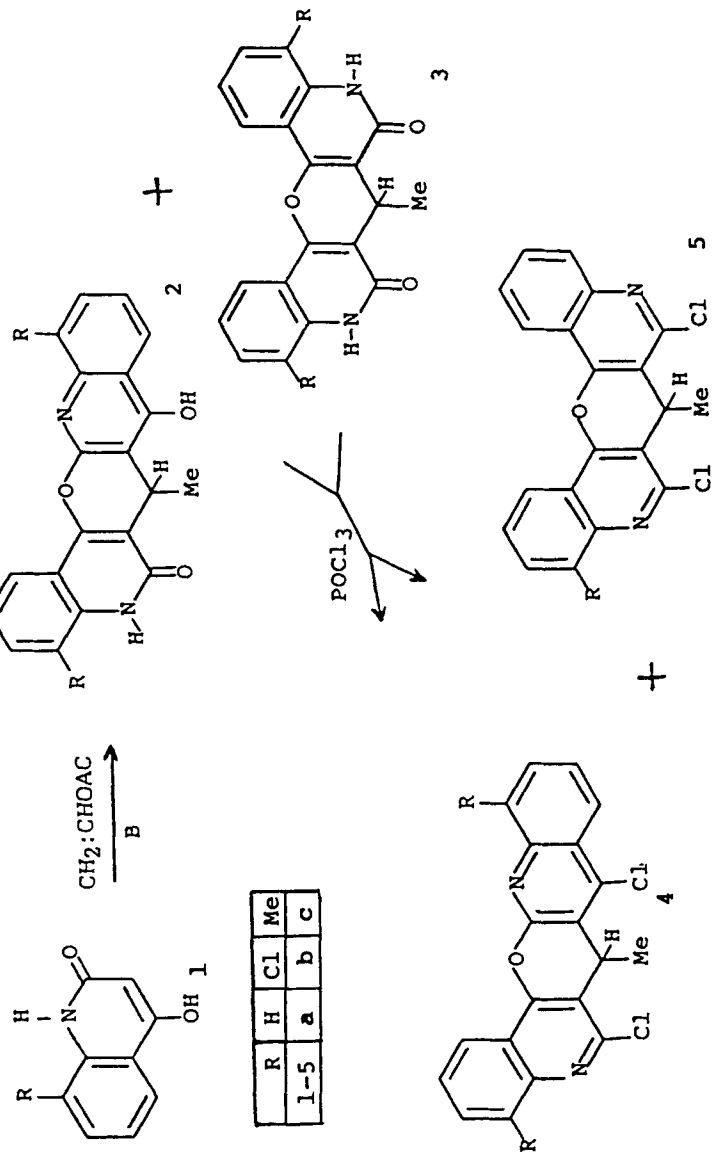
Elucidation of the structure of hitherto unknown novel pyranobisquinoline derivatives, (7H)-6,8-Dichloro-7-methyl -pyrano(3,2-c;5,6-c')bisquinoline **5** and (7H)-6,8-Dichloro-7-methyl-pyrano(3,2-c:5,6-b')bisquinoline **4** obtained as unexpected products[1] in the Michael type reaction of vinylacetate on 4-hydroxyquinoline-2(1H)-one **1** by NMR methods is reported.

INTRODUCTION

The formation and reactivities of the quinone-methide are of particular interest since many reactions involving the intermediate invariably yielded new heterocyclic ring system[2-5]. A cycloaddition reaction leading to a dihydropyrano(3,2-c)quinoline system, wherein the ^{1}H-NMR assignments and Mass fragmentations were categorised, was reported[3] from our Laboratory. Contribution of L. Jurd[6] et al to ^{13}C- and ^{1}H-NMR spectroscopic study of bisquinoline alkaloids are outstanding. Vander Donckt[7] et al have shown the deshielding of ortho, para, peri- and 'angular' protons and shielding of meta protons of 10 aza-aromatic derivatives. We here report the study of the structure of **4** and **5** by NMR spectroscopy. At this juncture,it is pertinent to mention that the results of a pre-screening[8] performed on compound **5a** (NSC 646479-c/1) by National Cancer Institute (NCI) on a panel of 60 human tumor cell lines show that a few selectivity parameters are significant,namely the percentage growth rate reduces to 8% in case of Leukemia HL-60 (TB) cell line. Hence the structural elucidation of **5a** and its derivatives / isomers should gain importance.

EXPERIMENTAL

Reagent grade aniline, diethylmalonate, phosphorous pentoxide, phosphoric acid, phosphoryl chloride and vinylacetate were used after usual purification methods. The solvents, petroleum ether, ethylacetate and methanol were purified by standard procedure. The reactions were performed under free atmosphere. ^{1}H-NMR spectra were recorded in $CDCl_3$ either at 300



Scheme 1.

MHZ on a Varian XL-300 spectrophotometer or at 400 MHZ on a Jeol GSX-400 spectrophotometer using tetramethylsilane (TMS) as internal standard. The ^{13}C-NMR experiments were conducted on a Varian XL-90 spectrophotometer with TMS as internal standard. The Mass spectra were recorded on a Jeol Jms-D 300 Mass spectrometer.

RESULTS AND DISCUSSION

4 and **5** have been characterised by ^{1} H-NMR and ^{13}C-NMR and Mass spectroscopies. TABLE 1 lists the ^{1}H-NMR spectral data of **4** and **5** with the assignment of chemical shifts. Figure 1 & 2 shows the ^{1}H- and ^{13}C-NMR of **5** in $CDCl_3$. The following are the chemical shifts (δ,ppm) assigned:

Ar-CH_3	:	20.979
CH_2	:	32.212
C_6-Cl & C_8-Cl	:	155.681
Aryl	:	145.751, 141.783, 128.685, 126.496, 123.885, & 119.621
Pyran carbons		
[C_6,C_5,C_3 &C_2]	:	125.056, 128.226 & 130.768.

Twelve carbon signals (Fig 2) against eight proton count (along with methine and methyl proton signals-Fig 1) of **5a** predicts a pyrano fused bisquinoline structure. Mass spectrum of **5a** registered a molecular ion peak at m/e 366(2%),base peak at m/e 351 (100%) and fragment ions at m/e 206 and 281 well attests our assignment. ^{1}H- NMR spectra of **4** & **5** distinguish themselves from

TABLE 1 : ^{1}H-NMR Spectra Data of Compounds **4** and **5**

Compound	Chemical Shift, δ ppm (J, Hz)						
4a	C_7-CH_3	C_7-H	C_1-H	C_{12}-H	C_4 & C_9-2H	C_3 & C_{10}-2H	C_2 & C_{11}-2H
	1.60 d, J=6.9	4.96 q, J=6.9	8.26 d, J=7.2	8.53 d, J=7.2	7.79 m	7.67 m	8.04 m
4b	C_7-CH_3	C_7-H	C_1-H	C_{11}-H	C_2 & C_{10}-2H	C_3 & C_9-2H	
	1.63 d, J=7.2	4.98 q, J=7.2	8.20 d, J=7.0	8.50 d, J=7.0	7.90 m	7.56 m	
4c	C_7-CH_3	C_7-H	C_1-H	C_9-H	C_4 & C_{12} -2CH_3	C_2,C_3,C_{10} & C_{11}-4H	
	1.60 d, J=7.0	4.93 q, J=7.0	8.44 d, J=7.4	8.08 d, J=7.4	2.80 S	7.45 - 7.64 envelop	
5a	C_7-CH_3	C_7-H	C_4 & C_{10}-2H	C_1 & C_{13}-2H	C_3 & C_{11}-2H	C_2 & C_{12}-2H	
	1.54 d, J=7.2	5.08 q, J=7.2	8.0 d, J=7.2	8.16 d, J=7.2	7.54 m	7.70 m	
5b	C_7-CH_3	C_7-H	C_1 & C_{13}-2H	C_3 & C_{11}-2H	C_2 & C_{12}-2H		
	1.62 d, J=6.9	5.17 q, J=6.9	8.19 d, J=7.5	7.90 d, J=7.5	7.56 m		

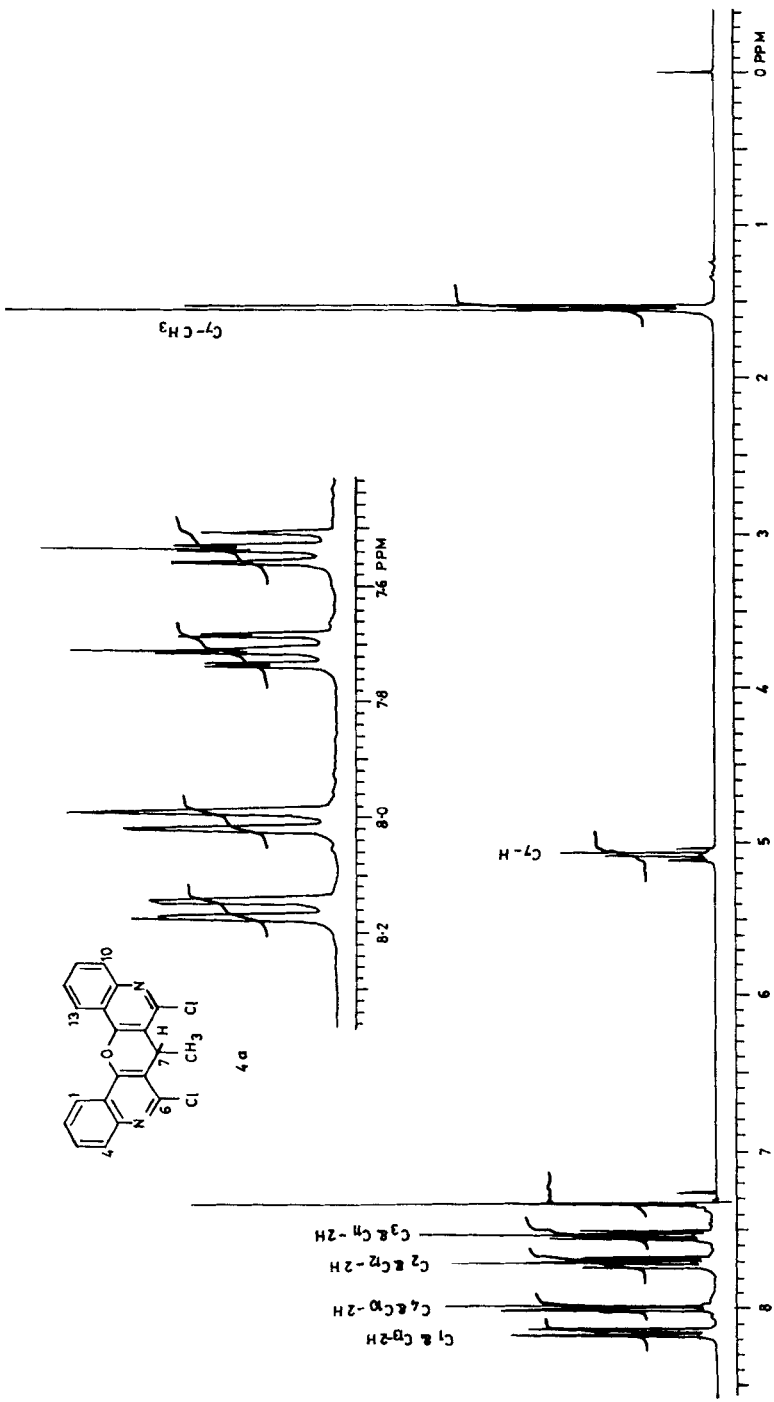


Fig. 1. ^{1}H-NMR Spectrum of (7H)-6,8-Dichloro-7-methyl-pyrano (3,2-C:5,6-C') Bisquinoline (300 MHz)

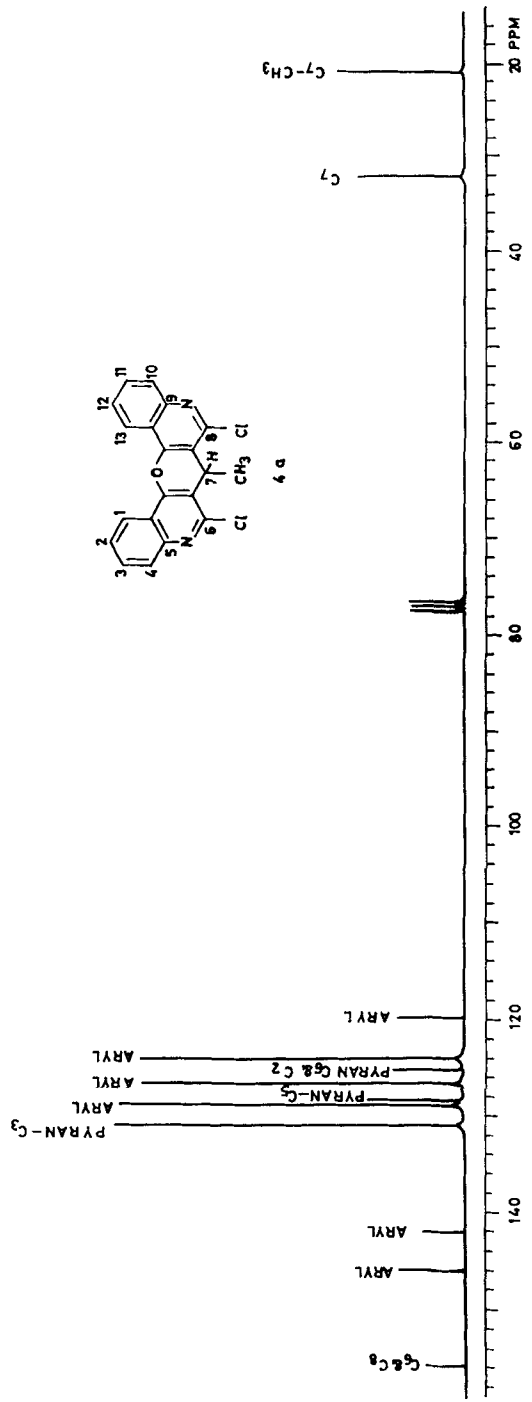


Fig. 2. ^{13}C-NMR Spectrum of (7H)-6,8-Dichloro-7-methyl-pyrano (3,2-C:5,6-C') Bisquinoline (300 MHz)

each other inaccordance with the loss of symmetry in **4**. Furtherly, aromatic absorptions of **4** extended upto δ 8.54 ppm consisting of five distinct signals. However, the pyran methine proton was shifted upfield by 0.1 ppm in case of **4**.

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REFERENCES

1. C. Balasubramanian, K. Kumaraswami and P.S. Mohan, *Indian J Chem.*, In Press.
2. L.D. Boger and N.S. Weinreb, Hetero-Diels Alder methodology in Organic Chemistry, **47** London: Academic Press, 1987.
3. K. Kumaraswami and P. Shanmugam, *Tetrahedron Lett*, **29**, 2235, 1988.
4. M.A. Chauncey and M.F. Grundon, *Synthesis*, **11**, 1005, 1990.
5. L.J. Asherson and D.W. Young, *J. Chem. Soc., Perkin Trans., 1*, 522, 1980.
6. Leonard jurd, Mabry Benson and Rosalind Y. Wong., *Aus. J. Chem.*, **36**, 759, 1983.
7. E. Vander Donekt, R.H. Martin et F. Geerts-Evrard, *Tetrahedron*, **20**, 1495, 1964.
8. C. Balasubramanian and P.S. Mohan, Manuscript under preparation.

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