Larvicidal Activity of some Carbazoles

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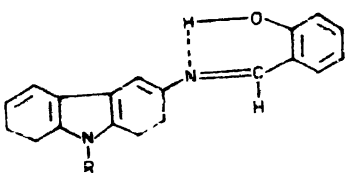
Manuscript received 29 May 1990, revised 8 October 1990, accepted 28 November 1990

IN consideration of the biological properties of carbazoles[1] and our interest in the pesticidal and larvicidal activities[2-4] of carbazoles, we report here the preparation of some new carbazole derivatives with a view to examine their larvicidal activities. We also report the biological activities of these compounds as well as some carbazoles of known structures.

3-Aminocarbazole and its *N*-methyl derivative were condensed with salicyl aldehyde to give the Schiff bases, *o*-hydroxy phenyl-*N*-(3-carbazolyl)azomethine (**1**) and *o*-hydroxyphenyl-*N*-(3-*N*-methylcarbazolyl)azomethine (**2**). The new Schiff bases were characterised by elemental analysis, mass spectral and ir data. The molecular ion peaks for **1** and **2** were found to be *m/z* 286 and 300 respectively. The mass fragmentation pattern of **1** showed other characteristic peaks at *m/z* 262 (*M*−17), 193 (*M*−93) and 167 (*M*−119). Similarly, some characteristic peaks of **2** are *m/z* 283 (*M*−17), 268 (283−15), 207 (*M*−93), 180 (*M*−120) and 120 (*M*−180). The values of *m/z* 269 for **1** and 283 for **2** are for the same type of fragmentation giving $C_{19}H_{12}\overset{+}{N}_2R$ (R=H or CH_3); similarly, *m/z* 193 for **1** and 207 for **2** are also for the same type $C_{13}H_8\overset{+}{N}_2R$ (R=H or CH_3). Also *m/z* 166 for **1** and 180 for **2** are for the same type of fragmentation pattern giving $C_{12}H_7\overset{+}{N}R$ (R=H or CH_3). These show that some fragmentation patterns are of similar type. On the basis of the above data structures of **1** and **2** are shown as



1; R=H **2**; R=CH_3

For the preparation of *N*-cinnamoylcarbazole[5], cinnamic acid is converted to cinnamoyl chloride by $SOCl_2$, which when refluxed with carbazole in dry benzene gave the corresponding carboximide, i.e. *N*-cinnamoylcarbazole.

Experimental

All the melting points were determined in sulphuric acid bath and are uncorrected. Purity of the compounds was checked by tlc. Infrared spectra were recorded in KBr.

The known carbazoles, viz. nitro[6], amino[7] and cinnamoyl[5] derivatives were prepared using the reported methods and characterised.

o-Hydroxyphenyl-N-(3-carbazolyl)azomethine (**1**): 3-Aminocarbazole (1.82 g) dissolved in ethanol (50 ml) was refluxed for 8 h with salicyl aldehyde (1.2 ml). It was then cooled and the resulting solid was crystallised from ethanol, (75%), m.p. 229−30° (Found: C, 79.69; H, 4.78; N, 9.80. $C_{19}H_{14}N_2O$ calcd. for: C, 79.72; H, 4.89; N, 9.79%): M^+ 285; ν_{max} 3 600−3 200br (hydrogen bonded OH), 3 410 (NH), 3 050, 2 930 (CH), 1 640 (C=N) and 1 610 cm^{-1} (Ar).

o-Hydroxyphenyl-N-(3-N-methylcarbazolyl)azomethine (**2**): To a solution of 3-amino-9-methylcarbazole (1.96 g) in ethanol (50 ml), salicyl aldehyde (1.2 ml) was added and the mixture refluxed for 10 h. On cooling, the resulting solid was crystallised from ethanol, (80%), m.p. 138° (Found: C, 79.89; H, 5.25; N, 9.21. $C_{20}H_{16}N_2O$ calcd. for: C, 80.0; H, 5.33; N, 9.21%); M^+ 300; ν_{max} 3 600−3 350br (hydrogen bonded OH), 3 050, 2 925 (CH), 1 625 (C=N) and 1 600 cm^{-1} (Ar).

Biological activity: Toxicity tests to third inster mosquito larvae[3] (*Culex fatigans*) were carried out by dissolving each compound (5 mg) in acetone (A.R.; 1 ml). The solution was added in thin stream to mosquito larvae in water so that the ultimate volume was kept to 50 ml after proper stirring. Control was also run. Five replications (30 larvae each) were taken for each compound at 27±2° and percentage of mortality was counted after 24 h (Table 1). Toxicity were determined from critical value. Comparison of mortality in *N*-methylcarbazole and *N*-methyl-3-aminocarbazole at different concentration are presented in Table 2.

Results and Discussion

It is evident from Table 1 that 3-nitrocarbazole is toxic, but *N*-methyl-3-nitrocarbazole is non-toxic. 3-Aminocarbazole is inactive, while 3-amino-*N*-methylcarbazole is toxic. The Schiff base from 3-aminocarbazole and salicyl aldehyde has some toxicity, while that from 3-amino-*N*-methylcarbazole is non-toxic. *N*-Cinnamoylcarbazole and 1-nitro-

TABLE 1—PERCENTAGE OF MORTALITY OF MOSQUITO LARVAE (*Culex fatigans*) AFTER 24 h INTERVAL BY DIFFERENT CARBAZOLES

Compd.*	%Mortality** (mean)
Carbazole	6.60(14.89)
9-Methylcarbazole	100.00(90.00)
3-Nitrocarbazole	81.99(64.82)
3-Nitro-9-methylcarbazole	(–)
1-Nitrocarbazole	6.18(14.42)
3-Aminocarbazole	7.64(16 00)
3-Amino-9-methylcarbazole	100 00(90 00)
o-Hydroxyphenyl-*N*-(carbazoyl)azomethine (**1**)	58 95(50.13)
m-Hydroxyphenyl-*N*-(3-*N*-methylcarbazolyl)azomethine (**2**)	(–)
N-Cinnamoylcarbazole	(–)
Acetone	(–)
F value (above degree of freedom)	606 61 (Significant at 1% level)
CD (critical difference)	at 1% 18.61 at 5% 13.91

*Concentration=100 ppm. **Figure in parenthesis represents angular transformation ; (–)=no mortality.

TABLE 2—VARIATION OF PERCENTAGE OF MORTALITY OF MOSQUITO LARVAE (*Culex fatigans*) AFTER 24 h INTERVAL AT DIFFERENT CONCENTRATION OF *N*-METHYLCARBAZOLE AND *N*-METHYL-3-AMINOCARBAZOLE

Conc. ppm	*N*-Methylcarbazole	3-Amino-*N*-methylcarbazole
5	(–)	(–)
10	12.58	(–)
20	50.83[a]	27 37
30	51.21[a]	60.70[a]
40	76.92[a]	80.38[a]
50	78.20[a]	87.90[a]
60	87.97[a]	100.00[a]
70	100.00[a]	

(–)=No mortality. [a]Values significantly different from control ($P>0.01$).

carbazole are found to be non-toxic during 24 h. Table 2 shows that LC_{50} of *N*-methylcarbazole and *N*-methyl-3-aminocarbazole are 23.5 and 24.0 respectively.

Acknowledgement

The authors express their thanks to U.G.C., New Delhi, for financial assistance. Thanks are also due to Dr. A. Banerji, Head, Bio-organic Division, Bhabha Atomic Research Centre for the spectra. The help extended during the research work by Visva-Bharati authorities and the Principal, Durgapur Women's College, is also gratefully acknowledged.

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