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SYNTHESIS AND TERMITICIDAL ACTIVITY OF N¹-ISONICOTINOYL-5,5-DIMETHYL CYCLOHEXANE-4-(SULPHA/SUBSTITUTED PHENYL AZO)-1,2-DIAZOLES

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A novel series of heterocyclic compounds namely N¹-isonicotinoyl 5,5′-dimethyl cyclohexane-4-(sulpha/substituted phenylazo)-1,2-diazoles have been synthesized. The structures of the synthesized compounds were supported by elemental analysis, IR and NMR spectra data. They were screened for termiticidal activity against termites *(Microcerotermes beesoni)* at different concentrations. It was compared with Endosulfan and explained through regression equation, $Y_{p,c}=mX + C$.

Diazole derivatives possess various types of biological activities viz., antimicrobial, antiprotozoal, antifungal, pesticidal, orthopodicidal, nematocidal, etc[1-8]. In view of the biological importance of such compounds we have synthesized bicyclic sulpha/substituted phenyl azo-1,2-diazoles of isonicotinic acid hydrazide, by linking of two heterocycles.

The present communication describes the synthesis of N¹-isonicotinoyl-5,5′-dimethyl-cyclohexane-4-(sulpha/substituted phenylazo)-1,2-diazoles by condensation of sulpha/substituted phenylazo-5,5′-dimethylcyclohexane 1,3-dione with isonicotinic acid hydrazide using gl acetic acid as the condensing agent (Scheme-1). They were tested for termiticidal activity.

Biological assay

All the synthesized compounds were screened for their termiticidal activity against *Microcerotermes beesoni* at different concentrations. It was compared with standard pesticide Endosulfan at various concentrations. The mortality of *Microcerotermes beesoni* was determined graphically using regression equation[11] (Table-2). The study revealed that the compounds III, VII, IX, XII, XVII, XXIII and XXVIII showed effective mortality against termites. The standard compound Endosulfan showed 100% mortality against termites in 10 hr., 7½ hr and 6 hr at 0.25%, 0.50% and 1.0% concentrations. The newly synthesized bicyclic heterocyclic-1,2-diazoles namely N¹-isonicotinoyl-5,5′-dimethyl cyclohexane-4-(3-chlorophenylazo), (2-chloro-4-nitrophenylazo), (3-nitrophenylazo), (2-methylphenylazo), (1-naphthylazo), (N¹-2-pryridyl sulphanilamidobenzeneazo), (N¹-2-acetyl sulphanilamidobenzeneazo)-1,2-diazoles showed 100% mortality in 9 to 10 hr, 6 to 71/2 hr, and 5 to 6 hr, at 1%, 2% and 2.5% concentrations respectively.

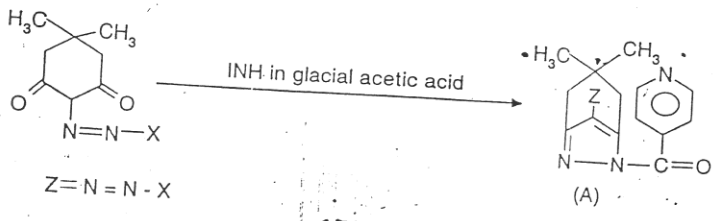
These compounds have therefore good potential for use as pesticides for soil treatment to control termites.

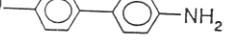
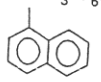
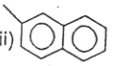
Experimental

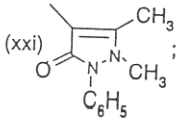
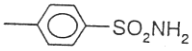
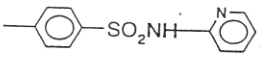
The melting points of the synthesized compounds were determined in open capillaries in a GANSON electrical melting apparatus and are uncorrected. The homogeneity and purity of the compounds were checked over thin layer chromatoplates coated with silica Gel-G (thickness 0.5 mm), developing solvent acetone/DMF (3:1), nonsaturated chamber at room temp. (20 ± 1°). Infrared spectra (in cm^{-1}) were determined in KBr on a Perkin Elmer 577 Spectrophotometer and ^1H NMR spectra were recorded on Bruker WM-400 spectrometer at 200 MHz in $CDCl_3$ + DMSO-d_6 using TMS as in internal reference (chemical shift in δ ppm).

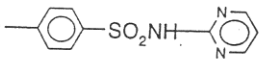
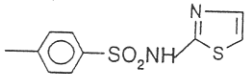
N¹-Isonicotinoyl-5,5′-dimethyl cyclohexane-4-(sulpha/substituted phenylazo)-1,2-diazoles

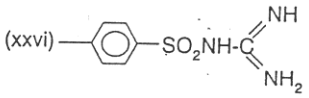
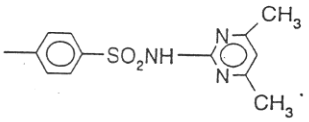
A mixture of sulpha/substituted phenylazo 5,5′-dimethyl cyclohexane-1,3-dione (0.05 mol) and isonicotinic acid hydrazide (0.05 mol) was refluxed in gl acetic acid for 4 hr. and contents were left over night. The coloured solid mass was filtered, washed with water and dried. It was recrystallized form gl acetic acid to furnish shining crystals of N¹-isonicotinoyl-5,5′-dimethyl cyclohexane-4-(sulpha/substituted phenylazo)-1,2-

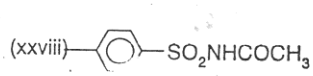
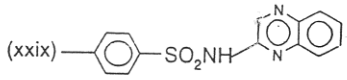


X= (i) C_6H_5; (ii), 2-Cl-C_6H_4; (iii) 3-Cl-C_6H_4; (iv) 4-Cl-C_6H_4;
(v) 2,4,6-$(Br)_3$-3-C_6H_2; (vi) 3-F-C_6H_4; (vii) 2-Cl-4-NO_2-C_6H_3;
(viii) 2-NO_2-C_6H_4; (ix) 3-NO_2-C_6H_4; (x) 4-NO_2-C_6H_4;
(xi) 3-NO_2-4-CH_3-C_6H_3; (xii) 2-CH_3-C_6H_4; (xiii) 4-CH_3-C_6H_4;
(xiv) 2-OCH_3-C_6H_4; (xv) 4-OCH_3-C_6H_4, (xvi)  ; (xvii)  ; (xviii)  ; (xix) 4-COOH-C_6H_4; (xx) 4-OH-C_6H_4;

(xxi)  ; (xxii)  (xxiii) 

(xxiv)  ; (xxv) 

(xxvi)  ; (xxvii) 

(xxviii)  ; (xxix) 

(SCHEME-1)

diazoles. By analogous procedure, several substituted-1,2-diazoles have been synthesized. Their characteristics are recorded in Table-1.

The structures of the synthesized compounds were supported by IR spectra. In their IR spectra the parent compound showed a peak at 780 cm^{-1} (aromatic ring) and a sharp peak at 1360 as the [-C-$(CH_3)_2$] group is present. A number of peaks were obtained at 1550, 1570, 1600, 1610 which indicate the presence of N=N heterocyclic pyridine ring, C=C and C=N respectively. A characteristic peak at 1710 due to bicyclic ring and a peak at 1740 as C=O of tert. amide having N in diazole ring, helped in establishing the structure. The above structures were confirmed by NMR spectra as follows :

N¹-isonicotinoyl-5,5'-dimethyl cyclohexane-4-(2-chlorophenylazo)-1,2-diazole (ii)

1.10 (s, 6H, $C(CH_3)_2$); 2.12 (s, 4H, 2xCH_2); 7.20-7.76 (d, ArH, C_6H_4Cl, J=8Hz); 7.12 (dd, 2,4-pyridine

Table-1

Characterization data of N'-isonicotinoyl-5,5'-dimethyl cyclohexane-4-(X) azo-1,2-diazoles

Compd	Yield (%)	M.P. (°C)	Mol formula	Nitrogen % Found	(Calcd)	R_f
I	78	115	$C_{20}H_{19}N_3O$	13.20	(13.24)	0.8172
II	71	130	$C_{20}H_{18}ClN_3O$	11.90	(11.94)	0.9156
iii	73	126	$C_{20}H_{18}ClN_3O$	11.91	(11.94)	0.5432
iv	70	205	$C_{20}H_{18}ClN_3O$	11.92	(11.94)	0.7615
v	72	180	$C_{20}H_{16}Br_3N_3O$	07.53	(07.58)	0.6943
vi	72	179	$C_{20}H_{18}N_3OF$	12.51	(12.53)	0.7925
vii	68	157	$C_{20}H_{17}ClN_4O_5$	13.00	(13.06)	0.8321
viii	73	167	$C_{20}H_{18}N_4O_3$	15.10	(15.46)	0.7925
ix	69	181	$C_{20}H_{18}N_4O_3$	15.32	(15.46)	0.8235
x	76	143	$C_{20}H_{18}N_4O_3$	15.40	(15.46)	0.9321
xi	75	215	$C_{21}H_{20}N_4O_3$	14.76	(14.89)	0.5641
xii	71	207	$C_{21}H_{21}N_3O$	12.62	(12.68)	0.5932
xiii	68	198	$C_{21}H_{21}N_3O$	12.63	(12.68)	0.7321
xiv	67	167	$C_{21}H_{21}N_3O_2$	12.00	(12.10)	0.8231
xv	77	181	$C_{21}H_{21}N_3O_2$	12.00	(12.10)	0.8651
xvi	78	183	$C_{26}H_{24}N_4O$	13.70	(13.72)	0.9631
xvii	65	175	$C_{24}H_{21}N_3O$	11.34	(11.44)	0.7251
xviii	72	198	$C_{24}H_{21}N_3O$	11.35	(11.44)	0.6932
xix	71	200	$C_{21}H_{19}N_3O_3$	11.51	(11.63)	0.7251
xx	68	169	$C_{20}H_{19}N_3O_2$	12.50	(12.61)	0.8235
xxi	76	159	$C_{25}H_{25}N_5O_2$	16.32	(16.39)	0.9211
xxii	68	172	$C_{20}H_{20}N_4O_3S$	14.10	(14.14)	0.8235
xxiii	75	177	$C_{25}H_{23}N_5O_3S$	14.72	(14.79)	0.7321
xxiv	67	189	$C_{24}H_{22}N_6O_3S$	17.71	(17.72)	0.7641
xxv	72	180	$C_{23}H_{21}N_5O_3S_2$	14.51	(14.61)	0.8251
xxvi	75	179	$C_{21}H_{22}N_6O_3S$	19.10	(19.17)	0.6931
xxvii	70	175	$C_{26}H_{26}N_6O_3S$	16.56	(16.73)	0.7321
xxviii	72	164	$C_{22}H_{22}N_4O_4S$	12.72	(12.78)	0.8235
xxix	70	201	$C_{28}H_{24}N_6O_3S$	16.00	(16.03)	0.7521

Table-2
Determination of Regression equation for termiticidal activity against *Microcorotermos beesoni*

Comp	Concentration (%)	Regression Equation*
iii	1.5	$Y_{1.5,III}$=0.0342X +1.4476
	2.0	$Y_{2.0,III}$=0.0877X+0.4380
	2.5	$Y_{2.5,III}$=0.0816X+2.7428
vii	1.5	$Y_{1.5,VII}$=0.0367X +1.2462
	2.0	$Y_{2.0,VII}$=0.0729X+0.6470
	2.5	$Y_{2.5,VII}$=0.0805X+2.7809
ix	1.5	$Y_{1.5,IX}$=0.0515X -1.8177
	2.0	$Y_{2.0,IX}$=0.0594X+4.0263
	2.5	$Y_{2.5,IX}$=0.0680X+5.05
xii	1.5	$Y_{1.5,XII}$=0.0448X - 0.7103
	2.0	$Y_{2.0,XII}$=0.0558X+1.0790
	2.5	$Y_{2.5,XII}$=0.0668X+3.4052
xvii	1.5	$Y_{1.5,XVII}$=0.0440X -1.0552
	2.0	$Y_{2.0,XVII}$=0.515X+3.0790
	2.5	$Y_{2.5,XVII}$=0.0575X+4.2052
xxiii	1.5	$Y_{1.5,XXIII}$=0.0367X +1.7651
	2.0	$Y_{2.0,XXIII}$=0.0812X+2.2
	2.5	$Y_{2.5,XXIII}$=0.0782X+5.1208
xxviii	1.5	$Y_{1.5,XXVIII}$=0.0434X +0.9678
	2.0	$Y_{2.0,XXVIII}$=0.0731X -1.3922
	2.5	$Y_{2.5,XXVIII}$= 0.0795X-0.8857
Endosulfan	1.5	$Y_{1.5,Endo}$=0.0464X -3.2528
	2.0	$Y_{2.0,Endo}$=0.0598X -1.4150
	2.5	$Y_{2.5,Endo}$=0.885X-3.9047

* Yp,c = mX + C
Where:p=Concenratin in percentage
C=Compound
Y= Mortality Rate, Nos. of Termites
X= Time, min.

carbonyl ortho to C=O, J=9 and 2 Hz); 8.04 (dd, 2,4-pyridine carbonyl, meta to C=O, J=9 and 2Hz).

N¹-Isonicotinoyl-5,5'-dimethyl cyclohexane-4-(2-nitorphenylazo)-1,2-diazole (viii)

1.11 (s, 6H, $C(CH_3)_2$); 2.14 (s, 4H, 2xCH_2); 7.72-8.20 (m, ArH, $C_6H_4NO_2$); 7.12 (dd, 2,4-pyridine carbonyl ortho to C=O, J=9 and 2 Hz); 8.04 (dd, 2,4-pyridine carbonyl, meta to C=O, J=9 and 2Hz).

N¹-Isonicotinoyl-5,5'-dimethyl cyclohexane-4-(4-nitrophenylazo)-1,2-diazole (x)

1.11 (s, 6H, $C(CH_3)_2$); 2.13 (s, 4H, 2xCH_2); 7.35 (d, 2, meta to NO_2 J=6Hz), 7.93(dd, 2, ortho to NO_2, J=9 and 3Hz); (dd, 2,4-pyridine carbonyl ortho to C=O, J=9 and 2 Hz); 8.04 (dd, 2,4-pyridine carbonyl, meta to C=O, J=9 and 2Hz).

N¹-isonicotinoyl-5,5'-dimethyl cyclohexane-4-(3-fluorophenylazo)-1,2-diazole (vi)

1.13 (s, 6H, $C(CH_3)_2$); 2.10 (s, 4H, 2xCH_2); 6.95-7.21 (m, ArH, C_6H_4F); 7.12 (dd, 2,4-pyridine carbonyl ortho to C=O, J=9 and 2 Hz); 8.04 (dd, 2,4-pyridine carbonyl, meta to C=O, J=9 and 2Hz).

N¹-isonicotinoyl-5,5'-dimethyl cyclohexane-4-(N¹-2-acetyl sulphanilamidobenzeneazo)-1,2-diazole (xxviii)

1.12 (s, 6H, $C(CH_3)_2$); 2.15 (s, 4H, 2xCH_2); 7.22-7.35 (m, 4H, ArH); 8.02 (br, s, 1H, NH); 2.38 (s, 3H, $COCH_3$); 7.12 (dd, 2,4-pyridine carbonyl ortho to C=O, J=9 and 2 Hz); 8.04 (dd, 2,4-pyridine carbonyl, meta to C=O, J-9 and 2 Hz).

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References

1. *Chem. Abstr.*, 96 (1982), 104425d.
2. *Chem. Abstr.*, 126 (1997), 238380u.
3. *Chem. Abstr.*, 126 (1997), 8113e.
4. *Chem. Abstr.*, 127 (1997), 121722m.
5. *Chem. Abstr.*, 127 (1997), 121723n.
6. *Chem. Abstr.*, 127 (1997), 81441k.
7. S.S. Nayal, Ph.D. Thesis, M.J.P.R. University, Bareilly, (1998).
8. Y. Singh and S.S. Nayal, *Pestology*, 22 (1998), 42.
9. *Dictionary of Organic Compounds*. Oxford, New York, 5 (1965), 2317.
10. E.C. Woodberg and V. Koppaka, *Cancer Chemotherapy Rep.*, *6* (1974), 58.
11. F. Matsumora, *Toxicology of Insecticides*, Second Edition, Plenum Press, New York (1985), 15.

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