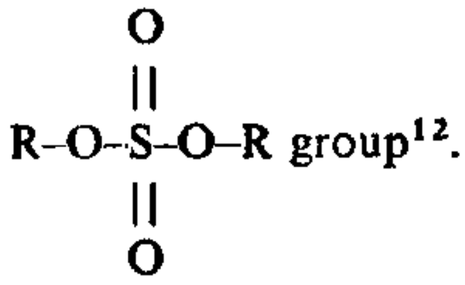
C=25.53%, H=1.50%, Cl=50.15%; and calculated for $C_9H_6Cl_6O_4S$, C=25.53%, H=1.41%, Cl=50.35%. Further, the endosulfan and the photoproduct were hydrolysed with alkali and the hydrolysed solutions gave positive test for sulphite and sulphate ions respectively[11]. The bromo derivatives of endosulfan and its photoproduct were prepared; the m.p.'s were 85 and 55°C, respectively. New bands were seen in the IR spectra of the photoproduct at 1445, 1230 and 645 cm^{-1}, which are characteristic of



R–O–S–O–R group[12].

However, the NMR spectra of endosulfan and its photoproduct are almost identical. The product of photo-sensitized oxidation of endosulfan was the same as that of oxidation carried out in the dark using H_2O_2 + NaOCl mixture as the oxidant.

It was confirmed that the C=C bond remained unattacked during oxidation[13] and therefore the site of attack in endosulfan is the sulphur atom. The participation of singlet oxygen as the active oxidizing species in the photo-oxidation was confirmed by using singlet oxygen scavengers, where the yield was considerably reduced[14].

The experimental data suggest the mechanism shown in scheme 1. The primary process of the photo-chemical reaction involves the absorption of radiation while the secondary reactions lead to the transformation of the various electronically excited states to give chemical products.

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SYNTHESIS OF SOME 2-AMINO-3-CYANO-4, 6-DISUBSTITUTED PYRIDINE DERIVATIVES AND THEIR ANTIBACTERIAL ACTIVITY

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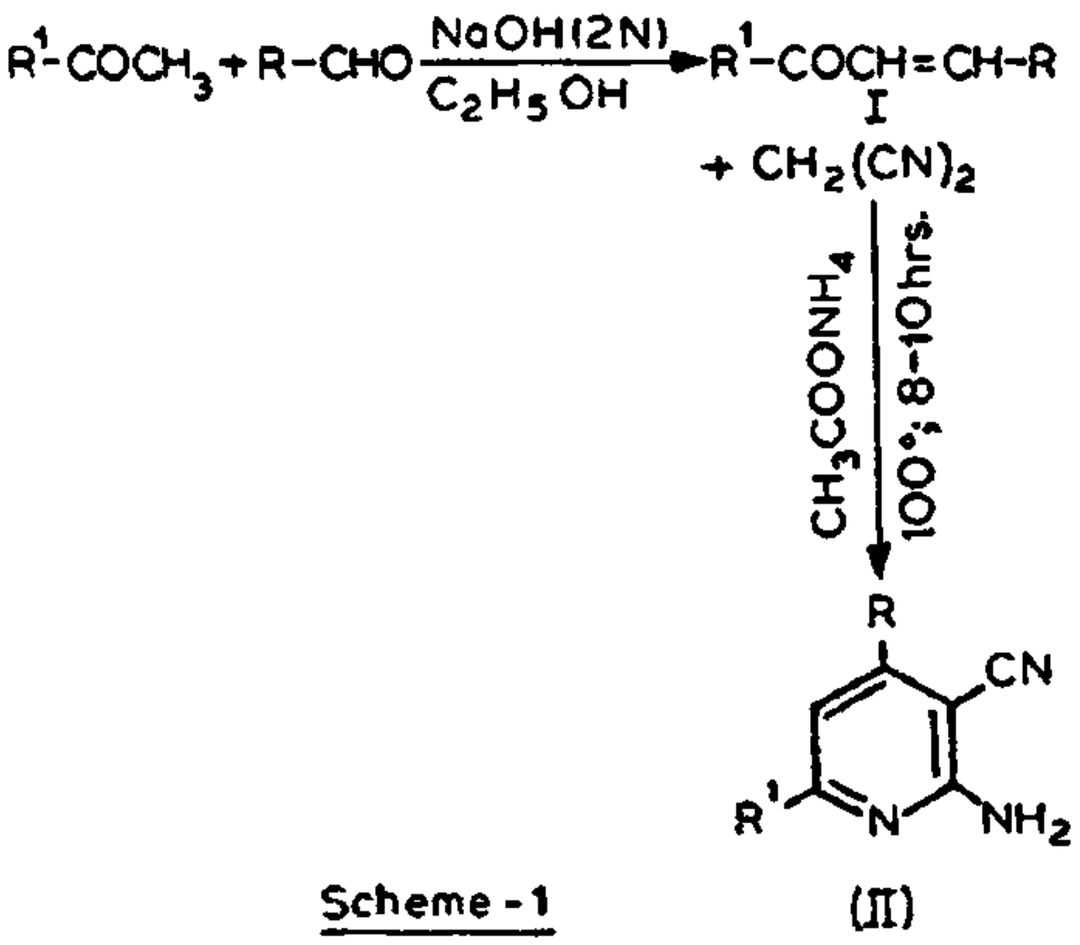
CYCLIZATION of chalcones with dicyanomethane in 1:1 molar ratio in the presence of ammonium acetate gives 2-amino-3-cyano-4, 6-disubstituted pyridines through Michael reaction.

Cyanopyridines with different alkyl and aryl groups have been found to have antimicrobial[1,2], fungicidal[3-5], antihypertensive[6-8], cardiovascular[9], and other activities. Only a few cyanopyridines have been synthesized by Michael reaction[10], and by other methods[11-15], during the past few years. Keeping in view the biological activity of the cyanopyridine derivatives, we have synthesized some new cyanopyridine derivatives.

The condensation of acetophenone (1 mol) with benzaldehyde (1 mol) in the presence of sodium hydroxide and ethanol resulted in the formation of

chalcone (I). Dicyanomethane and chalcone reacted in 1:1 molar ratio in the presence of ammonium acetate to give 2-amino-3-cyano-4,6-disubstituted pyridine (II) through Michael reaction with the elimination of 1 mol each of water and hydrogen (scheme 1). All the newly synthesized compounds (II) are yellow and are soluble in chloroform, DMSO and TFA.

IR spectra (KBr pellets) were recorded on a Perkin–Elmer 577 grating infrared spectrophotometer. All the synthesized 2-amino-3-cyano-4,6-disubstituted pyridines showed three characteristic bands in the region 3470–3020 cm^{-1}, which are due to $-NH_2$ group, and a strong band due to $-C\equiv N$ group in the region 2220–2200 cm^{-1} (table 1).



Scheme - 1

^1H NMR spectra were recorded on an FX 90Q JEOL spectrometer (90 mHz) in $CDCl_3$ and in DMSO-d_6 using TMS as an internal standard. The chemical shifts are given in ppm downfield from TMS (table 1).

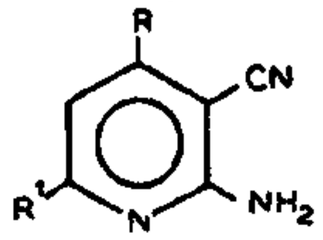
The chalcones were synthesized according to Vogel's method[16].

Synthesis of 2-amino-3-cyano-4,6-disubstituted pyridines

A mixture of dicyanomethane (1 mol), chalcone (1 mol) and ammonium acetate (8 mol) in ethanol (150 ml) was refluxed on a water bath for about 8–10 h. The contents of the flask were poured into crushed ice with constant stirring to obtain a solid yellow mass, which was washed with water and ethanol. the residue was recrystallized from ethanol–dimethylformamide (2:1). The prepared compounds are listed in table 2.

Antibacterial activity: The antibacterial activity of all the compounds was determined according to the method of Varma and Nobles[17]. The test organisms were *Escherichia coli* and *Staphylococcus aureus*. Sterile filter paper discs (5 mm diam.) saturated with the solution of the test compounds were placed on inoculated plates 0.5% NaCl, 0.5% glucose, 2.5% peptone, pH 6.8–7.0, 1.5% agar after allowing solvent to evaporate. The plates were incubated at 37°C for 24 h. Zones of inhibition around the discs were measured. All the compounds exhibited significant activity against *S. aureus* but showed no activity against *E. coli* (table 3).

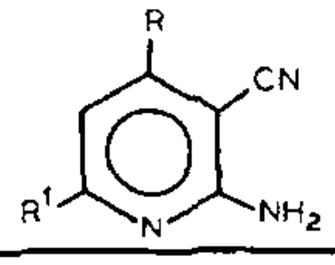
Table 1 *IR and ^1H NMR spectroscopic data for 2-amino-3-cyano-4,6-disubstituted pyridines*



Compound	IR (KBr: ν, cm^{-1}) $-NH_2$			$-C\equiv N$ (conj.)	$-OCH_3$	NMR ($CDCl_3$: δ ppm from TMS) $\cong CH$ (aromatic)	$-NH_2$	Aromatic protons (R^1)	Aromatic protons (R)
1	3430,	3370,	3040	2210 *s*	—	7.14 *s*	7.30–7.6 *bs*	7.77–8.26	6.5–7.0
2	3430,	3270,	3150	2200 *s*	3.82 *s*	7.37 *s*	7.51–7.78 *bs*	7.79–8.25	6.86–7.26
3	3470,	3330,	3200	2220 *s*	—	7.35 *s*	7.38–7.69 *bs*	7.74–8.19	6.80–7.30
4	3420,	3320,	3020	2200 *s*	—	7.89 *s*	7.91–8.20 *bs*	8.27–8.60	6.90–7.80
5	3460,	3350,	3080	2210 *s*	—	7.35 *s*	7.40–7.74 *bs*	7.76–8.21	6.84–7.11
6	3470,	3330,	3150	2220 *s*	—	7.24 *s*	7.37–7.76 *bs*	7.77–8.11	6.7–7.10
7	3465,	3365,	3155	2220 *s*	3.82 *s*	7.14 *s*	8.30–8.57 *bs*	8.58–8.70	6.97–7.10
8	3450,	3350,	3145	2220 *s*	3.82 *s*	7.03 *s*	7.24–7.70 *bs*	7.71–8.10	6.36–6.9
9	3470,	3365,	3140	2220 *s*	3.82 *s*	7.50 *s*	8.04–8.51 *bs*	8.53–8.70	6.56–7.16
10	3400,	3310,	3150	2180 *s*	—	7.56 *s*	7.78–8.21 *bs*	8.25–8.48	6.75–7.33

s, Strong, *s*, Singlet; *bs*, broad singlet.

Table 2 *Physical and chemical data for 2-amino-3-cyano-4,6-disubstituted pyridines*



Compound	R	R¹	Mol. formula	mp* (°C)	Yield (%)	Analysis, % found (calcd) C	H	N
1	*m*.ClC_6H_4	C_6H_5	$C_{18}H_{12}ClN_3$	226	30	70.90 (70.70)	4.05 (3.93)	14.00 (13.75)
2	*p*.$OCH_3C_6H_4$	C_6H_5	$C_{19}H_{15}N_3O$	165	36	75.89 (75.75)	5.13 (4.98)	13.92 (13.95)
3	*o*.ClC_6H_4	C_6H_5	$C_{18}H_{12}ClN_3$	190	30	71.10 (70.70)	4.13 (3.93)	13.50 (13.75)
4	*m*.BrC_6H_4	C_6H_5	$C_{18}H_{12}BrN_3$	248	32	62.03 (61.71)	3.66 (3.43)	12.40 (12.00)
5	*p*.BrC_6H_4	C_6H_5	$C_{18}H_{12}BrN_3$	175	34	61.86 (61.71)	3.30 (3.43)	11.66 (12.00)
6	*p*.FC_6H_4	C_6H_5	$C_{18}H_{12}FN_3$	140	50	74.61 (74.74)	4.36 (4.15)	14.93 (14.53)
7	*p*.$OCH_3C_6H_4$	*p*.ClC_6H_4	$C_{19}H_{14}ClN_3O$	170	35	68.10 (67.96)	4.31 (4.17)	12.27 (12.52)
8	*p*.$OCH_3C_6H_4$	*p*.BrC_6H_4	$C_{19}H_{14}BrN_3O$	140	34	60.40 (60.00)	3.56 (3.68)	11.37 (11.05)
9	*p*.$OCH_3C_6H_4$	*p*.$NO_2C_6H_4$	$C_{19}H_{14}{}_4O_3$	220	30	66.21 (65.89)	4.20 (4.05)	16.38 (16.18)
10	C_6H_5	*p*.$NH_2C_6H_4$	$C_{18}H_{14}N_4$	260	34	75.38 (75.52)	4.80 (4.90)	19.90 (19.58)

*Melting points are uncorrected.

Table 3 *Antibacterial activity*

Compound	*S. aureus*	*E. coli*
1	+ + +	−
2	+ +	−
3	+	−
4	+ +	−
5	+	−
6	+ + +	−
7	+ + +	−
8	+ +	−
9	+ + +	−
10	+ +	−
Gentamycin	+ + + +	+ + + +

−, No inhibition; +, inhibition zone 6–7 mm; + +, 7–8 mm; + + +, 9–11 mm; + + + +, 20–22 mm.

The bacterial cultures were obtained from the Microbiology Laboratories, S.M.S. Medical College, Jaipur.

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5 September 1988

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A NEW SPECIES OF *CHRYSOSPORIUM*

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THE genus *Chrysosporium* Corda has been reviewed earlier[1-3]. Presently 22 species of this genus have been enumerated[3]. *C. tropicum*, *C. lucknowense*, *C. indicum*, *C. evolceanui*, *C. crassitunicatum*, *C. carmichaeli*, *C. queenslandicum* and *C. sulfureum*[4-8] were isolated from Indian soil. The present communication deals with a new species of *Chrysosporium* not described earlier.

Chrysosporium geophilum Kushwaha and Shrivastava sp. nov. (figure 1).

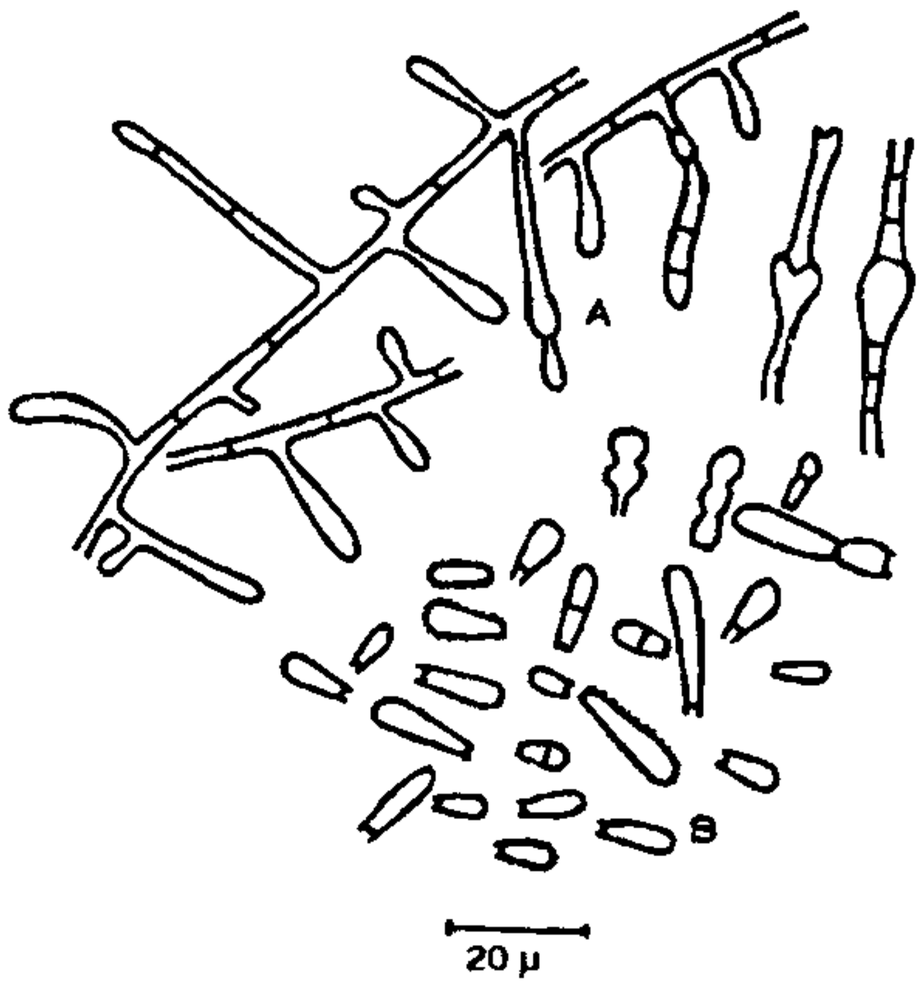

Figure 1. *Chrysosporium geophilum.* **A**, Hyphae, with conidiogenous cells; **B**, conidia.

Colonies in agaro Sabouraudii cum dextroso composite per viginti dies crescentes diametrum 60–70 mm attingentes, albee, subtus pallide cremeobrunneae, densae definito, aequali. Hyphae sepatatae, hyalinae, tenuiter tunicatae, 1–4 µm crassae, frequenter celluas condioigenas inflates, hyellnas, leviter et cresse tunicatas, subglobosas wel aliquantum anormes, 8 µm crassas producentes. Hyphae spatuliformes productae. Conidia terminalia lateraliaque sessilia vel in prominentiis brevibus gests, subhyaline, levia vel aspara, tenuiter tunicatae, abovoidea vel clavata, continus vel raro bicellularia, 2–4 × 4–20 µm, cicatrice basali lato notata 4–10 × 2–4 µm intercalaria rariora, subhyalina, levia vel aspera, doliiformia vel allipsoidea, 2–4 µm.

Colonies on Sabou.raud's dextrose agar white, 60–70 mm in diameter, reverse pale creamy brown, dense and fluffy at centre, thinner outwards, raised centrally, margin defined. Hyphae septate, hyaline, thin-walled, 1–4 µm wide, frequently producing swollen conidiogenous cells, hyaline, smooth and thick-walled, subglobose or irregular in shape, up to 8 µm wide. Racquet hyphae present. Lateral conidia sessile on short protrusions, subhyaline, initially echinulate and some becoming smooth-walled on maturity, thick-walled, obovoid to elavate, 1-celled, 4–20 × 2–4 µm. Two-celled conidia rare, 4–10 × 2–4 µm. Intercalary conidia less abundant, subhyaline, smooth or rough, thick-walled, barrel-shaped to ellipsoid 2–4 µm.

This fungus was isolated from human hair buried in soil collected from the L.L.R. Hospital Campus, Kanpur, India, in May 1982 and its specific epithet refers to its habitat.

Subcultures were deposited in the culture collection of the Department of Botany, Christ Church College, Kanpur (CC/534); CMI, Kew, England (IMI 276183); and ITCC, New Delhi, India (ITCC 3345).

This fungus bears some similarities to *C. indicum*, *C. tropicum* and *C. pannicola* in its morphology. However, the present fungus can be differentiated from *C. indicum* and *C. tropicum* on the basis of presence of 2-celled and larger conidia borne on swollen conidiogenous cells. The large conidia of *C. geophilum* which are initially echinulate and become smooth-walled on maturity further differ from those of *C. pannicola*.

Two-celled conidia of *C. carmichaeli* and *Chrysosporium* anamorph of *Arthoderma curreyi* also resemble those of the new species, but on the basis of colony colour, larger conidia and swollen conidio-