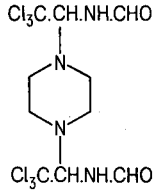
Table I. Chemicals

No.	Compound Structure II R	M.P.	Solvent	Formula	Analyses Found			Required		
					C	H	N	C	H	N
III	3-Pyridylamino	173	Benzene/petrol[a]	$C_8H_8Cl_3N_3O$	36.0	3.1	15.9	35.75	3.0	15.6
IV	2-Pyridylamino	190	Benzene	$C_8H_8Cl_3N_3O$	36.0	3.0	15.9	35.75	3.0	15.6
V	3-Quinolylamino	227 (dec.)	Benzene/chloroform	$C_{12}H_{10}Cl_3N_3O$	45.1	3.1	13.2	45.2	3.1	13.2
VI	2-Pyrimidylamino	174	Benzene/petrol[a]	$C_7H_7Cl_3N_4O$	30.9	2.8	20.6	31.2	2.6	20.8

[a] Petrol as solvent refers to fraction of b.p. 60–80°.

acetone there was added the appropriate aminopyridine (0.01 mol.) dissolved in acetone. The mixture was refluxed for 2–8 h and was then filtered. The solvent was partly evaporated and the residue poured onto crushed ice. An oil formed which soon solidified. The solid was washed with water, dried and crystallized. Yields were 50–75%.

The biological tests were carried out[11] by methods described previously[12,7]. In in vitro tests the compounds showed very low activity against the test organisms, *Alternaria brassicicola, Botrytis cinerea, Septoria nodorum* and *Uromyces fabae*. The concentration required to inhibit germination completely was above 1000 ppm in all cases. As protectant sprays for the control of wheat powdery mildew, *Erysiphe graminis*, only compound (III) showed



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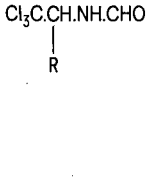
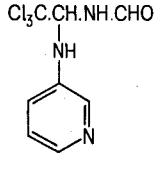


II



III

Table II. Systemic activity against *E. graminis* on sand-grown wheat seedlings 7 days after treatment

Compound number	Infection grade (% of control)				
	ppm 100	50	25	10	5
III	0+[a]	0	0	0	0
			0[b]	< 2[b]	< 2[b]
IV	14	43	93	–	–
V	75	96	100	–	–
VI	0+	7+	43	–	–
I	0	0	0	0	0
			0+[b]	8[b]	40[b]

[a] + Indicates phytotoxicity. [b] After 23 days.

much activity at an application rate of 100 ppm. It gave 47% disease control. The results of tests for systemic activity by root application against *E. graminis* on wheat growing in sand are given in Table II. It is evident that compound (III) is a very effective systemic fungicide for the control of wheat powdery mildew giving complete disease control at 5 ppm after 7 days and over 98% disease control after 23 days. Compounds (IV) and (VI) also show good systemic activity while compound (V) is slightly active. The compounds were much less effective by soil application presumably due to their absorption on soil constituents (cf.[7]).

The discovery of systemic activity in compounds (III)-(VI) considerably extends the range of compounds of type (II) now known to possess systemic fungicidal properties. It reinforces the belief[7,8] that the antifungal effects are associated with the chemical grouping CX_3–CH. NH.CHO(X=Br or Cl). Chemical modifications on the –NH.CHO grouping have so far resulted in substantial loss of systemic fungicidal activity[7,8]. It is interesting to note that like several of its systemically active relatives[7–9], compound (III) is a poor fungistat and has mediocre protectant activity. The reasons for this behaviour are not yet clear but it suggests that the systemic activity may be due to conversion in vivo to a more active entity or to some indirect mechanism.

Summary. The systemic fungicidal activity of a new formamide, *N*-[2, 2, 2-trichloro-1-(3-pyridylamino)ethyl]-formamide, is reported.

L. A. SUMMERS

Department of Chemistry, University of Newcastle, Newcastle 2308, (New South Wales, Australia), 22 January 1975.

[11] Dr. G. A. CARTER of the Agricultural Research Council, Plant Growth Substance and Systemic Fungicide Unit, Wye College, University of London kindly carried out the biological tests. Prof. R. L. WAIN, Director of th ‹Unit, is warmly thanked for his help in arranging the tests and for research discussions.

[12] K. LEHTONEN, L. A. SUMMERS and G. A. CARTER, Pestic. Sci. *3*, 357 (1972).

The Oxindole Alkaloids of *Vinca elegantissima* Hort.[1]

The isolation of reserpinine and an oxindole alkaloid designated as elegantine was reported earlier[2] from *Vinca elegantissima* Hort. var. *Vinca major* Linn. (Apocynaceae). The compound elegantine has now been found to be identical with isomajdine (**1**)[3]. An authentic sample of the latter not being available, the identity was established by comparison of their physical and spectroscopic data and through isomerisation of elegantine to majdine (**2**)[3], which was identified by direct comparison.

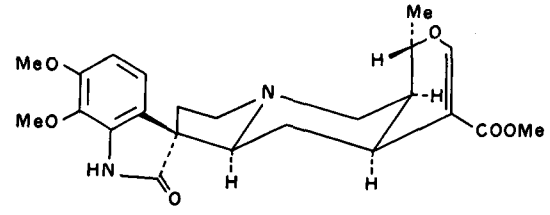
Further investigation of *V. elegantissima* has led to the isolation of majdine itself, vincamajoreine[4] and lochnerine[5]. In addition, two new oxindole bases named elegantissine (**3**), amorphous, $[\alpha]_D$ + 3.4° ($CHCl_3$) and isoelegantissine (**4**), m.p. 190°, $[\alpha]_D$ + 5.7° ($CHCl_3$) could be isolated in very low yields. The mass spectra (M^+ 428) of both of them were almost superimposable to that of **1** and their IR-spectra were very close to those of **1** and **2**; the 4 compounds exhibited almost identical UV-spectra. The

Compound	Configuration[a]	Equilibrium mixture[b] (%)	CD maxima[c] λnm ($[\theta]\times10^{-3}$)	Corresponding isomer	
				10,11-dimethoxy[7]	Ar-unsubstituted[8]
Majdine (**2**)	3S, 4R, 7R	20	290(+2.3)255(−30) 230(−46)	Carapanaubine	Uncarine C
Isomajdine (**1**)	3S, 4R, 7S	35	290(−10)252(−85) 222(+65)	Isocarapanaubine	Uncarine E
Elegantissine (**3**)	3R, 4S, 7R	10	290(+2.0)257(+26) 227(−16)	Rauvoxine	Uncarine F
Isoelegantissine (**4**)	3R, 4S, 7S	35	290(−3.5) 252sh(+32) 240(+43)220(−2.5)	Rauvoxinine	Uncarine D

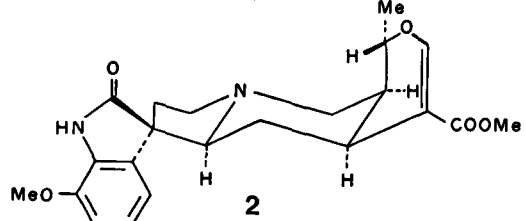
[a] The stereochemistry at other centres are 15S, 19S, 20S for all compounds. [b] Estimated from TLC. [c] In MeOH.

new compounds were therefore inferred to be stereoisomers of **1** and **2**.

Acid catalyzed equilibration[6] of isomajdine with 10% (v/v) aqueous acetic acid (100°, 3 h) yielded majdine and two other compounds (Table) identical with the natural products. The same mixture of the 4 compounds could be obtained from either **3** or **4** by similar treatment. Thus, elegantissine and isoelegantissine proved to be the 3β-isomers of majdine and isomajdine. The remaining stereochemistry at C–7 could be assigned unambiguously from their CD data (Table).



1



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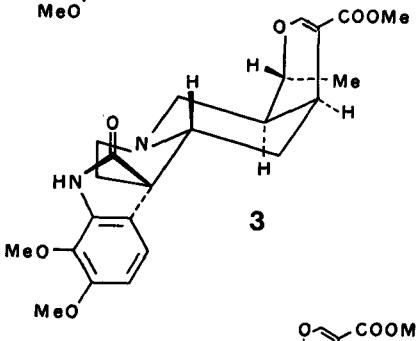

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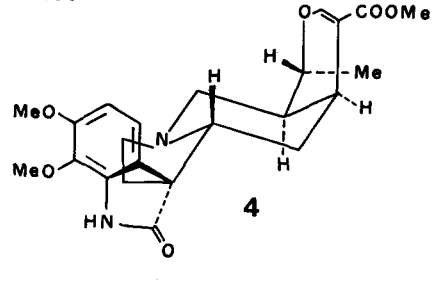

4

It has been shown[7,8] in case of both 10,11-dimethoxy and Ar-unsubstituted heteroyohimbine type oxindoles with *cis* D/E ring fusion that the sign of the Cotton effects of 250 nm and 290 nm bands are related respectively to the stereochemistry at C–3 and C–7. As expected, both **3** and **4** showed positive Cotton effects around 250 nm confirming their 3β-stereochemistry, while negative effects were observed in this region for majdine and isomajdine. On the other hand, the positive Cotton effect at 290 nm allowed the assignment of 7R configuration to elegantissine (**3**) as in rauvoxine and uncarine F while the negative effect was in accord with the 7S stereochemistry in isoelegantissine (**4**).

Zusammenfassung. Aus *Vinca elegantissima* Hort. var. *V. major* wurden zwei neue Oxindolalkaloide, Elegantissin (**3**) und Isoelegantissin (**4**) isoliert und ihre Konstitution aus den spektralen Eigenschaften und der Isomerisierung zu den bekannten Alkaloiden Majdin (**2**) und Isomajdin (**1**) abgeleitet.

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Indian Institute of Experimental Medicine, 4, R.S.C. Mullick Road, Calcutta-700032 (India),
3 April 1975.

[1] Part XXXV in the series 'Studies on Indian Medicinal Plants'. For Part XXXIV see S. Chattopadhyay and S. C. Pakrashi, J. Indian chem. Soc., in press.

[2] J. Bhattacharyya and S. C. Pakrashi, Tetrahedron Lett. *1972*, 159.

[3] I. Ognyanov, B. Pyuskyulev, I. Kompiš, T. Sticzay, G. Spitteller, M. Shamma and R. J. Shine, Tetrahedron *24*, 4641 (1968) and the references cited therein.

[4] M. Plat, R. Lemay, J. le Men, M. M. Janot, C. Djerassi and H. Budzikiewicz, Bull. Soc. chim. Fr. *1965*, 2497. – J. L. Kaul, J. Trojánek and A. K. Bose, Chemy Ind. *1966*, 853.

[5] M. M. Janot and J. le Men, C. r. hebd. Séanc. Acad. Sci., Paris *243*, 1789 (1956). – W. B. Mors, P. Zaltzman, J. J. Beereboom, S. C. Pakrashi and C. Djerassi, Chemy Ind. *1956*, 173.

[6] M. Shamma, R. J. Shine, I. Kompiš, T. Sticzay, F. Morsingh, J. Poisson and J. L. Pousset, J. Am. chem. Soc. *89*, 1739 (1967).

[7] J. L. Pousset, J. Poisson and M. Legrand, Tetrahedron Lett. *1966*, 6283. – J. Poisson and J. L. Pousset, Tetrahedron Lett. *1967*, 1919. – J. L. Pousset, J. Poisson, R. J. Shine and M. Shamma, Bull. Soc. chim. Fr. *1967*, 2766.

[8] A. F. Beecham, N. K. Hart, I. R. Johns and J. A. Lamberton, Aust. J. Chem. *21*, 491 (1968).

[9] Acknowledgement: The authors are grateful to Prof. Howard Smith of Vanderbilt University, Nashville, Tenn. for the CD-spectra and to Dr. J. Trojánek, Pharmaceutical and Biochemical Research Institute, Prague for an authentic sample of majdine.

[10] To whom correspondences should be addressed.