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CHRYSANTHONE, A BIOACTIVE ALKALOID FROM *ASCOCHYTA CHRYSANTHEMI**

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Key Word Index—*Ascochyta chrysanthemi*; Ascomycetes; isoquinoline alkaloid; structural elucidation; X-ray analysis.

Abstract—The structure and relative configuration of chrysanthone, a new isoquinoline alkaloid isolated from a culture of *Ascochyta chrysanthemi*, have been elucidated on the basis of X-ray analysis and NMR evidence.

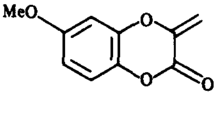
INTRODUCTION

In the screening of the fungal genus *Mycosphaerella* [1–3] for secondary and possible phytotoxic metabolites, we have investigated *M. ligulicola* [4, 5]. This fungus, which belongs to the Ascomycetes and is often described as *Ascochyta chrysanthemi* (conidial stage), is the causal agent of a well-described ray blight disease on chrysanthemum florets, for which phytotoxin production has been proposed [6, 7]. In previous papers [4, 5], investigations on *M. ligulicola* Baker (CBS 367.67, DSM 6254, and DSM 63133) for the production of secondary metabolites resulted in the isolation and characterization of the known phytotoxin (+)-epoxydon [8], already isolated from *Phoma* and *Phyllosticta* species, its natural monoacetyl derivative and two other compounds **1** and **2**.

Our investigation of a strain of *A. chrysanthemi* [6, 7] has led to the isolation and characterization of a new major metabolite **3** for which we propose the name chrysanthone. This paper deals with the isolation and the structural elucidation of this alkaloid using X-ray crystallography and NMR spectroscopy.

RESULTS AND DISCUSSION

The strain of *A. chrysanthemi* was grown on potato-dextrose broth in stationary culture for two weeks. Ethyl acetate extracts of the mycelium were evaporated and subjected to CC on silica gel containing 2% KH_2PO_4 to give chrysanthone **3** as white crystals, mp 193°; $[\alpha]_D = -37.2°$ (pyridine; *c* 0.1). The high-resolution mass spectrum established the molecular formula of **3** as $C_{15}H_{15}NO_4$. Two prominent peaks at *m/z* 215 $[C_{12}H_9NO_3]^+$ and 187 $[C_{11}H_9NO_2]^+$ could be rationalized as being due to sequential loss of methylvinyl ether (α-cleavage) and CO from ring C. The IR spectrum (KBr) showed a carbonyl band at $1650\ cm^{-1}$ and the UV spectrum bands at λ_{max} (EtOH) 263 and 357 nm (ε 47 000 and 9000).



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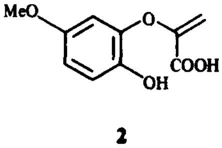

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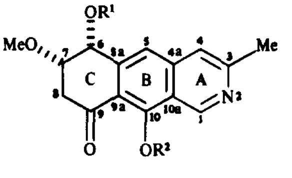

3 R¹ = R² = H
3a R¹ = R² = Ac
3b R¹ = Ac, R² = H

The ^{13}C NMR spectrum (Table 1) exhibited signals due to a carbonyl (δ_C 203.16), two methyls, one of them oxygen bearing, one methylene, and two oxygen-bearing methine carbon atoms; nine aromatic resonances (δ_C 161.73–110.48) which completed the spectrum may be compatible with the presence of a tetrasubstituted isoquinoline moiety. First-order analysis of the signals displayed by the ^1H NMR spectrum (Table 1), as corroborated by extensive $^1H-\{^1H\}$ selective decoupling experiments, indicated the presence of a CHOH–CH(OMe)–CH_2 fragment, a phenolic hydroxyl proton (δ_H 14.10) chelated with the above carbonyl group, three aromatic protons at δ_H 9.44, 7.62 and 7.39, the lowest field one presenting long-range couplings of 1.0 and 0.9 Hz with the other two protons, and an aromatic methyl group benzylically coupled ($J = 0.8$ Hz) to the proton resonating at δ_H 7.62.

The structure and relative stereochemistry of chrysanthone **3** were determined by single-crystal X-ray analysis. A PLUTO view of chrysanthone **3**, is shown in Fig. 1. Final positional parameters are given in Table 2, while in

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*Part 26 in the series 'Secondary Mould Metabolites'. For part 25 see Arnone, A., Assante, G., Camarda, L., and Nasini, G. (1989) *Gazz. Chim. Ital.* (in press).

Table 1. ^{13}C and ^{1}H NMR data for chrysanthane **3** in DMSO-d_6

C	δ_C^*/ppm	^1J(CH)/Hz	$^{>1}J$(C,H)/Hz	δ_H/ppm	J(H,H)/Hz
1	147.76 *Ds*	181.5		9.44	1.0 (H-4), 0.9 (H-5)
3	156.21 *Sddq*		12.5 (H-1), 2.5 (H-4), 6 (H_3-11)		
4	118.03 *Dddq*	163.5	2 (H-1), 4.5 (H-5), 4 (H_3-11)	7.62	1.0 (H-1), 0.8 (H_3-11)
4a	140.27 *Sm*				
5	113.95 *Dm*	166		7.39	0.9 (H-1), 1.3 (H-6)
5a	144.49 *Sm*				
6	68.87 *Dm*	141.5		5.04	1.3 (H-5), 2.5 (H-7), 6.4 (OH-6)
7	78.99 *Dm*	147		3.95	2.5 (H-6), 3.3 (H-8a), 5.0 (H-8b)
8a	40.74 *Tm*	130		3.09	3.3 (H-7), 17.6 (H-8b)
8b				3.03	5.0 (H-7), 17.6 (H-8a)
9	203.16 *Sdt*		6.5 (H-7), 6.5 (H_2-8)		
9a	110.48 *Sm*				
10	161.73 *Sm*				
10a	116.63 *Sm*				
11	24.02 *Qd*	127	3 (H-4)	2.62	0.8 (H-4)
12	59.94 *Qd*	141.5	4 (H-7)	3.34	
OH-6				5.88	6.4 (H-6)
OH-10				14.10	

*Capital letters refer to the pattern resulting from directly bonded (C, H) couplings [^1J(CH)] and small letters to that from (C, H) couplings over more than one-bond [$^{>1}J$(CH)].

Table 3 bond lengths and selected bond angles are reported. The geometry of the isoquinoline fragment (rings A and B) compares well with analogous structures [9, 10], the only significant differences occurring at the junction with the non-aromatic ring C. The C(5a)–C(9a) bond length [1.444(5) Å] in chrysanthone **3** is slightly longer than the value of 1.399(4) Å in 1-isoquinolyl (phenyl) methanol [8] and 1.389(5) Å found in the ethyl carbonate derivative of 1-isoquinolyl(phenyl) methanol [10]. The stereochemistry of the B-C ring junction is similar to that reported in the analogous derivative of 1-methylene-6-methoxy-1,2,3,4,-tetrahydronaphthalene [11]; all other C ring bond lengths and angles are in the normal range.

The angle between the least-squares planes defined by rings being planar [maximum deviations from the correspondent least-squares plane 0.006(4) Å in both cases].
spondent least-squares plane 0.006(4) Å in both cases).
The aliphatic ring C is a slightly twisted half-boat which can be described in terms of the parameters $\phi_2 = 12.5$ (5)°, $Q_T = 0.517$ (3) and $\theta = 125.4(4)°$ [12]. The sp^2 hybridized carbons C(5a), C(9a) and C(9) and the sp^3 C(8) and C(5) are roughly coplanar [maximum deviation from correspondent least-squares plane 0.054(4) Å], while C(7) is at 0.699(3) Å from the same least-squares plane. The angle formed by this plane with the B ring plane measures 4.4(1)°.

The conformation of the equatorial methoxy substituent can be described in terms of torsion angles C(6)–C(7)–O(7)–C(12) = −155.1(3)° and C(8)–C(7)–O(7)–C(12) = 82.2(4)°. It may be noted, while methyl hydrogens are all very near to the staggered positions, H(010) is nearly eclipsed with respect to C(9) allowing for the formation of a strong intramolecular hydrogen bond [H(010) . . . O(9) 1.81 (5) Å, O(10) . . . O(9) 2.540 (4) Å, O(10) . . . H(010) . . . O(9) 150 (5)°]. The hydrogen bonding of chrysanthone **3** in the crystal is completed by the three-centre bonding [13] involving H(012): a weak intra-

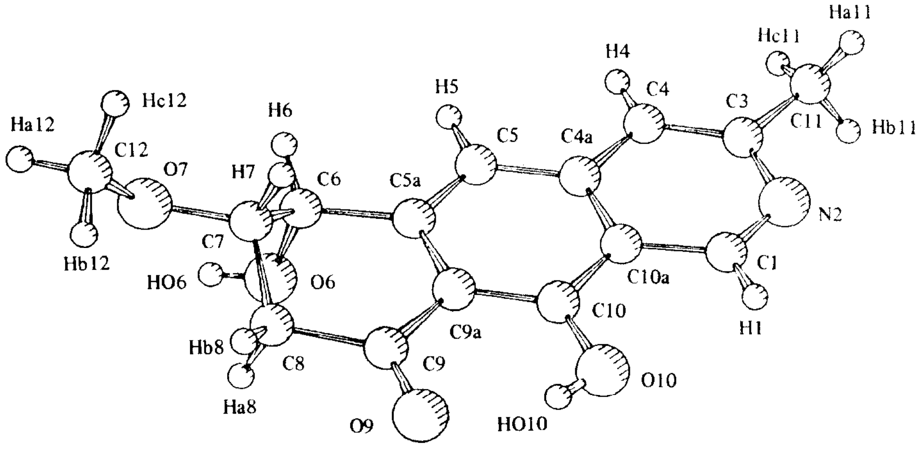


Fig. 1.

Table 2. Final positional parameters (× 10^4) of chrysanthone with e.s.d on last significant figure in parentheses (equivalent isotropic temperature factors Beq (Å^2)

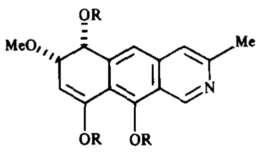
Atom	X	Y	Z	Beq
C-1	5054 (7)	8788 (2)	−211 (9)	3.3 (3)
N-2	3617 (5)	9080 (2)	782 (7)	3.4 (2)
C-3	2680 (6)	8682 (2)	2338 (8)	3.0 (3)
C-4	3221 (6)	7999 (2)	2898 (8)	2.9 (3)
C-4A	4753 (5)	7680 (0)	1862 (7)	2.5 (2)
C-5	5404 (5)	6977 (2)	2369 (7)	2.6 (2)
C-5A	6901 (5)	6700 (2)	1301 (7)	2.3 (2)
C-6	7565 (5)	5948 (2)	1789 (7)	2.6 (2)
O-6	6368 (4)	5564 (2)	−457 (6)	3.5 (2)
C-7	9887 (5)	5892 (2)	2042 (7)	2.6 (2)
O-7	10462 (4)	5190 (1)	2694 (5)	3.3 (2)
C-8	10382 (6)	6114 (2)	−553 (8)	2.7 (2)
C-9	9587 (5)	6837 (2)	−1395 (7)	2.6 (2)
O-9	10387 (4)	7182 (1)	−2899 (5)	3.6 (2)
C-9A	7894 (5)	7114 (2)	−363 (7)	2.4 (2)
C-10	7266 (5)	7800 (2)	−894 (7)	2.6 (2)
O-10	8106 (5)	8211 (2)	−2433 (6)	3.7 (2)
C-10A	5700 (5)	8088 (2)	221 (7)	2.5 (2)
C-11	1044 (8)	9040 (3)	3394 (12)	4.3 (4)
C-12	12584 (6)	5103 (3)	4062 (11)	4.1 (3)

molecular interaction with O(7) [H(06) . . . O(7) 2.59(4) Å, O(6) . . . O(7) 2.877(3) Å] and intermolecularly with the N-2 atom of the molecule related by symmetry operator (-*x*, *y* − 1/2, *z*), [H(06) . . . N(2) 2.08(4) Å, O(6) . . . N(2) 2.863(4) Å, O(6) . . . H(06) . . . N(2) 159(4)°].

Acetylation of chrysanthone **3** with pyridine–acetic anhydride gave the expected diacetate **3a** together with the triacetates **4** and **5**, arising from successive acetylation of the enolic OH at C-9 and loss of methanol, while acetylation with H_2SO_4–Ac_2O afforded the monoacetate **3b**.

Chrysanthone **3** is phytotoxic causing yellowing of the leaves above and below the introduction point of the toxin solution and extensive asymmetrical necrosis on the terminal part of the vicinal leaves; metabolite **3** is also active in inhibiting growth of bacteria and it has a weak antifungal activity on *Cladosporium cucumerinum* (see Experimental).

It is possible to observe the similarity of compound **3** with the 2-aza-anthraquinones **6** and **7**; although anthraquinones represent a large class of natural products, their aza-analogues are rarely found in nature. So far, only bostrycoidin **6** [14] and its 6-*O*-methylderivative **7** [15] have been isolated; bostrycoidin has been isolated from *Fusarium bostrycoides* and *F. solani* and shown to possess antibiotic activity against the tubercle bacillus *in vitro*. From a biogenetic point of view, it is interesting to



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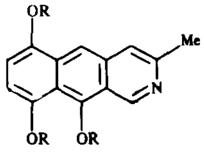
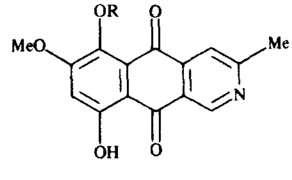


5 R = Ac

Table 3. Bond distances (Å) and angles (°) of chrysanthone, with e.s.d on last significant figure in parentheses

	Bond lengths
N-2—C-1	1.314 (6)
C-10A—C-1	1.414 (5)
C-3—N-2	1.365 (6)
C-4—C-3	1.374 (5)
C-11—C-3	1.496 (7)
C-4A—C-4	1.400 (5)
C-5—C-4A	1.424 (4)
C-10A—C-4A	1.411 (5)
C-5A—C-5	1.358 (5)
C-9A—C-5A	1.444 (5)
C-6—C-5A	1.517 (5)
C-10—C-9A	1.391 (5)
C-9—C-9A	1.457 (5)
O-10—C-10	1.335 (5)
C-10A—C-10	1.418 (5)
O-6—C-6	1.430 (4)
C-7—C-6	1.514 (5)
O-7—C-7	1.421 (4)
C-8—C-7	1.513 (6)
C-12—O-7	1.414 (5)
C-9—C-8	1.511 (5)
O-9—C-9	1.236 (5)
HO-6—O-6	0.82 (4)
HO-10—O-10	0.81 (5)
C-10A—C-1—N-2	124.5 (4)
C-3—N-2—C-1	117.9 (3)
C-4—C-3—N-2	121.8 (4)
C-11—C-3—N-2	115.6 (4)
C-11—C-3—C-4	122.6 (4)
C-4A—C-4—C-3	121.0 (4)
C-5—C-4A—C-4	124.2 (3)
C-10A—C-4A—C-4	117.2 (2)
C-10A—C-4A—C-5	118.6 (3)
C-5A—C-5—C-4A	121.2 (4)
C-9A—C-5A—C-5	120.7 (3)
C-6—C-5A—C-5	121.3 (3)
C-6—C-5A—C-9A	118.0 (3)
C-10—C-9A—C-5A	118.8 (3)
C-9—C-9A—C-5A	121.3 (3)
C-9—C-9A—C-10	119.8 (3)
O-10—C-10—C-9A	122.0 (4)
C-10A—C-10—C-9A	120.3 (3)
C-10A—C-10—O-10	117.7 (3)
C-4A—C-10A—C-1	117.6 (3)
C-10—C-10A—C-1	122.1 (4)
C-10—C-10A—C-4A	120.3 (3)
O-6—C-6—C-5A	106.4 (3)
C-7—C-6—C-5A	109.1 (3)
C-7—C-6—O-6	112.1 (3)
O-7—C-7—C-6	107.1 (3)
C-8—C-7—C-6	110.2 (3)
C-8—C-7—O-7	111.9 (3)
C-12—O-7—C-7	113.8 (3)
C-9—C-8—C-7	112.1 (3)
C-8—C-9—C-9A	118.5 (3)
O-9—C-9—C-9A	121.4 (3)
O-9—C-9—C-8	120.1 (3)
HO-6—O-6—C-6	110 (3)
HO-10—O-10—C-10	108 (4)



6 R = H
7 R = Me

observe that chrysanthone is a member of the fusarubin-javanacin family [16] but ring C is in reduced form.

The acid or its biological equivalent **8**, derived by the acetate-mevalonate pathway, may undergo stepwise reduction yielding the intermediate aldehyde **9** and successively chrysanthone **3** (Scheme 1).

EXPERIMENTAL

Mps: uncorr. Flash CC was performed with Merck silica gel (0.040–0.063 mm) and TLC with Merck HF_{254} silica gel. UV spectra were measured in 95% EtOH. MS were recorded at 70 eV. ^1H and ^{13}C NMR were measured at 300 and 75 MHz, respectively. Chemical shifts are in ppm (δ) from TMS as int. std.

Cultivation of fungus and isolation of chrysanthone **3**. *Ascochyta chrysanthemi* was kindly supplied by Prof. Schadler, as strain L.I.1. Fifty Roux flasks in stationary culture of potato-dextrose-broth (Difco) were inoculated with a mycelium suspension. After two weeks the fungal felt was sepd from the culture filtrates and both extracted separately. Mycelium dried *in vacuo* (40°) was ground and extracted with hexane and successively with EtOAc in a Soxhlet apparatus. The EtOAc extracts were evapd and chromatographed on silica gel column (containing 2% KH_2PO_4) with hexane–EtOAc (1:1) as eluant. Crystallization from EtOAc of the frs containing **3** (0.5 g), allowed us to obtain a sample which could be analysed by crystallographic methods.

Chrysanthone **3**. 3-Methyl, 10-hydroxy, [6-hydroxy, 7-methoxy, 6,7,8-trihydro-benzen-9-one] [*g*]-isoquinoline. MS *m/z* 273 $[M]^+$ (67%), 239 (20), 215 (37), 187 $[M-C_4H_6O_2]^+$ (100); (found: *m/z* 273.0992; $C_{15}H_{15}NO_4$; calc. 273.1001; *m/z* 187.0621; $C_{11}H_9NO_2$; calc. 187.0633); (found: C, 66.13; H, 5.59; N, 4.98%; $C_{15}H_{15}NO_4$ requires C, 65.92; H, 5.53; N, 5.13%).

Acetylation of **3** *with pyridine and* Ac_2O. Compound **3** (100 mg) was dissolved in dry pyridine (2 ml) and Ac_2O (4 ml) and left for 20 hr at room temp. Standard work-up yielded a mixt. of derivatives **3a**, **4** and **5**; prep. TLC (silica gel; EtOAc–hexane, 2:1) of the residue gave a few mg of the pure compounds. The monoacetate **3a** was the main product.

3a, isolated as a glassy solid, mp 60–63°; MS *m/z* 357 $[M]^+$, 315 $[M-42]^+$, 255 $[M-102]^+$, 241, 225, and 215. ^1H NMR ($CDCl_3$): δ2.17 and 2.56 (6H, *s*, 2 OAc), 2.70 (3H, *br s*, H_3-11), 2.93 and 3.06 (2H, *m*, H_2-8), 3.46 (3H, *s*, H_3-12), 4.02 (1H, *m*, H-7), 6.45 (1H, *br d*, *J* = 2.7 Hz, H-6), 7.46 and 7.75 (2H, *br s*, H-4 and/or H-5), 9.40 (1H, *br s*, H-1).

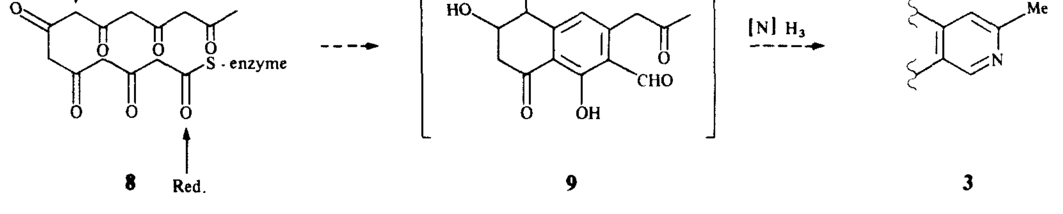
4. Yellow crystals (CH_2Cl_2–hexane), mp 70–75°; MS *m/z* 399 $[M]^+$. ^1H NMR ($CDCl_3$): δ2.20, 2.28, and 2.35 (9H, *s*, 3 OAc), 2.66 (3H, *br s*, H_3-11), 3.37 (3H, *s*, H_3-12), 4.30 (1H, *dd*, *J* = 5 and 4 Hz, H-7), 5.92 (1H, *d*, *J* = 5 Hz, H-8 or H-6), 6.20 (1H, *d*, *J* = 4 Hz, H-6 or H-8), 7.44 and 7.70 (2H, *br s*, H-4 and/or H-5), 9.45 (1H, *br s*, H-1).

5. White crystals (EtOAc), mp 160–165°; MS *m/z* 367 $[M]^+$. ^1H NMR ($CDCl_3$): δ2.45, 2.51, and 2.57 (9H, *s*, 3 OAc), 2.71 (3H, *d*, *J* = 1.0 Hz, H_3-11), 7.08 and 7.28 (2H, *d*, *J* = 8.0 Hz, H-7 and/or H-8), 7.55 (1H, *dq*, *J* = 1.5 Hz and 1.0 Hz, H-4), 8.22 (1H, *d*, *J* = 0.8 Hz, H-5), and 9.38 (1H, *dd*, *J* = 1.5 and 0.8 Hz, H-1); ^{13}C NMR ($CDCl_3$): δ20.85, 21.16, 21.22 and 168.82, 169.07, 169.32 (*q* and *s*, ^1J = 130 Hz, 3 OAc), 24.10 (*q*, ^1J = 127.5 Hz, C-11), 117.19 (*d*, ^1J = 164.5 Hz, C-5), 117.23 (*d*, ^1J = 163 Hz, C-4), 118.32 and 119.21 (*d*, ^1J = 167 and 166 Hz, C-7 and/or C-8), 118.78 and 119.55 (*s*, C-9a and/or C-10a), 130.05 and 133.35 (*s*, C-4a and/or C-5a), 143.25 and 143.46 (*s*, C-9 and/or C-10), 144.35 (*s*, C-6), 148.11 (*d*, ^1J = 182 Hz, C-1), and 150.79 (*s*, C-3).

Acetylation with Ac_2O and H_2SO_4. Compound **3** (50 mg) was reacted with Ac_2O (3 ml) and a drop of H_2SO_4. The reaction was stopped after 30 min; dil and extn with CH_2Cl_2 gave after prep. TLC in CH_2Cl_2–MeOH (30:1) 30 mg of the diacetate **3b**, mp 225–230°; MS *m/z* 315 $[M]^+$; ^1H NMR ($CDCl_3$): δ2.19 (3H, *s*, OAc-6), 2.69 (3H, *d*, *J* = 0.8 Hz, H_3-11), 2.98 (1H, *ddd*, *J* = 17.8, 4.3, and 0.9 Hz, H-8b), 3.17 (1H, *dd*, *J* = 17.8 and 8.9 Hz, H-8a), 3.49 (3H, *s*, H_3-12), 4.01 (1H, *ddd*, *J* = 8.9, 4.3, and 2.7 Hz, H-7), 6.39 (1H, *ddd*, *J* = 2.7, 0.9 and 0.9, H-6), 7.20 (1H, *dd*, *J* = 0.9 and 0.8 Hz, H-5), 7.36 (1H, *dq*, *J* = 1.2 and 0.8 Hz, H-4), 9.57 (1H, *dd*, *J* = 1.2 and 0.8 Hz, H-1), and 14.05 (1H, *s*, OH-10); ^{13}C NMR ($CDCl_3$): δ21.11 and 170.30 (*q* and *s*, ^1J = 130 Hz, OAc), 24.55 (*q*, ^1J = 127 Hz, C-11), 39.75 (*t*, ^1J = 131 Hz, C-8), 57.31 (*q*, ^1J = 142 Hz, C-12), 69.42 (*d*, ^1J = 151 Hz, C-6), 75.83 (*d*, ^1J = 144 Hz, C-7), 110.49 (*s*, C-9a), 116.57 (*d*, ^1J = 166 Hz, C-5), 118.12 (*s*, C-10a), 118.56 (*d*, ^1J = 162 Hz, C-4), 137.24 and 140.76 (*s*, C-4a and/or C-5a), 148.99 (*d*, ^1J = 183 Hz, C-1), 157.26 (*s*, C-3), 164.07 (*s*, C-10), and 201.24 (*s*, C-9).

Phytotoxicity tests. Chrysanthemum plants of a commercial variety, 30–40 cm height, at flowering, were kept in a greenhouse at 24° and used as plant material. According to refs [6, 7], phytotoxicity tests were performed by cutting a leaf tongue maintaining the midvein and immersing it in a glass test tube filled with test soln and sealed with parafilm. Test soln was prepd by dissolving 4 mg of **3** in 200 μl of DMSO and dil to 20 ml with K-Pi buffer 1/15 M at pH 5.5. After 72 hr a yellowing of leaves above (7–8 cm) and below (3–4 cm) the insertion point appeared.

Antibacterial and antifungal tests. These were performed using paper disks (6 mm diam.) containing 250 μg of compound **3**. The disks were tested against *Bacillus cereus*, *B. subtilis*, *Escherichia coli*, *Aspergillus niger*, *Cladosporium cladosporioides*, *C. cucumer-*



Scheme 1.

inum, *C. herbarum*, and *Saccharomyces cerevisiae*. A 1×10^6 spore/ml concn was used for inoculating medium in Petri dishes. Inhibition of growth was evaluated from the 'halo' diam around the paper disks. Activity was shown against all bacteria (5 mm diam. inhibition halo) and against *C. cucumerinum*.

Crystal structure determination of **3**. *Crystal data*: $C_{15}O_4NH_{15}$, $M_r = 273.29$, monoclinic, $F(000) = 288$, $a = 6.620(2)$, $b = 19.257(4)$, $c = 5.142(1)$ Å, $\beta = 104.60(2)°$, from least-squares refinement of 25 reflections with $12.0 < \theta < 16.0°$, $V = 634.3(3)$ Å^3, $Z = 2$, D calc $= 1.431$ g/cm^3, μ (Mo-Kα radiation) $= 0.63$ cm^{-1}, space group $P2_1$, λ (MoK$\bar{\alpha}$) graphite monochromated 0.71069 Å, colourless transparent crystals, prismatic habit.

Data collection and structure analysis. A crystal of dimensions $0.25 \times 0.35 \times 0.30$ mm, mounted in general orientation on a glass fibre was used for all measurements. Data were collected on a PW 1100 diffractometer, 2 octants ($\pm h$, $+k$, $+l$), $\theta/2\theta$ scan mode, $2.5 < \theta < 30.0°$, three standard reflections monitored every 120 min, no perceptible decay. Of the 2065 independent reflections measured, 1289 with $I \geqslant 3\sigma(I)$ were considered as observed and used for all subsequent calculations; Lorentz and polarisation corrections were applied, but no absorption corrections were deemed necessary. The structure was solved using MULTAN [17] and refined by blocked full-matrix least-squares. All hydrogen atoms were located from Fourier difference maps and refined with isotropic temperature factors, while for non-hydrogen atoms anisotropic temperature factors were used. Reflections 001 and 100 were omitted in the final cycles, convergence being obtained for $R = \Sigma|(k|F_0| - |F_c|)|/\Sigma k|F_0| = 0.0430$ ($R_w = \Sigma w^{1/2}|(k|F_0| - |F_c|)|/\Sigma k w^{1/2}|F_0| = 0.0432$). Atomic scattering factors from the International Tables for X-Ray Crystallography [18] were used. The SHELX [19] program was used for the refinement while all geometrical calculations were performed with PARST [20]. Hydrogen atom final positional parameters, anisotropic temperature factors, bond lengths, bond and torsion angles, least-squares planes, and a complete list of observed and calculated structure factors have been deposited with the Cambridge Crystallographic Data Centre.

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