Structures of a new type of yellow pigments, falconensones A and B, from *Emericella falconensis*

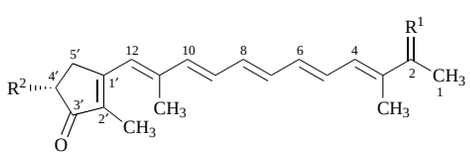
Nobuko Ogasawara, Reiko Mizuno and Ken-ichi Kawai

Faculty of Pharmaceutical Sciences, Hoshi University, Ebara 2-4-41, Shinagawa-ku, Tokyo 142, Japan

Two new yellow pigments designated falconensones A 1 and B 2 have been isolated from the mycelium of *Emericella falconensis* and/or *E. fruticulosa* along with new azaphilone derivatives, falconensins A–H, and hopane-type triterpenes, zeorin, hopane-7β,22-diol, and hopane-6α,7β,22-triol. The structures of 1 and 2 have been determined by spectroscopic investigations and an X-ray analysis of the *p*-bromophenylhydrazone of 1 acetone solvate. Compounds 1 and 2 have a novel carbon skeleton: namely, they are cyclopent-2-enone derivatives connected to an extensively conjugated methyl ketone at C-3.

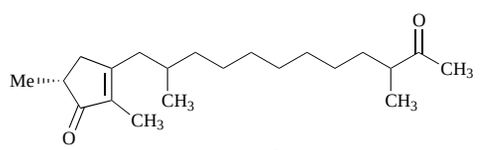
Recently we isolated seven new hydrogenated azaphilones, falconensins A–G,[1,2] a new azaphilone, falconensin H,[3] and three hopane-type triterpenes, zeorin (hopane-6α,22-diol), hopane-7β,22-diol and hopane-6α,7β,22-triol,[2] from the mycelial extract of ascomycetous fungi, *Emericella falconensis* Horie, Miyaji, Nishimura and Udagawa, strain NHL 2999 (=ATCC 76117)[4] and *E. fruticulosa* (Raper and Fennell) Malloch and Cain, strain IFO 30841. We now report the isolation of two new cyclopentenone pigments from the same source which we name falconensones A **1** and B **2**.

Falconensone A **1**, $C_{21}H_{26}O_2$, *m/z* 310, was isolated by chromatography as an orange coloured solid. The ^{13}C NMR spectrum of **1** (Table 1) showed the presence of five methyl groups, one methylene, one methine, six double bonds (12 sp^2 carbons), and two carbonyl groups, whilst the ^1H NMR spectrum in $CDCl_3$ showed the presence of five methyl groups [δ 1.21 (d), 1.80, 1.93, 2.12 and 2.36], one methylene [δ 2.47 (br d) and 3.16 (dd)], one methine [δ 2.45 (br qd)], and eight olefinic protons

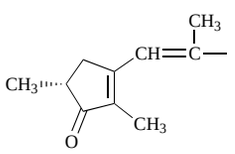


1 R^1 = O, R^2 = CH_3
2 R^1 = O, R^2 = H
4 R^1 = NNH–C$_6$H$_4$–Br, R^2 = CH_3

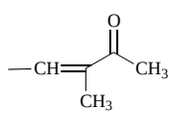
[δ 6.50–6.54 (5H), 6.55–6.62 (2H) and 7.10 (1H, br d)]. On the basis of this evidence, together with its molecular formula, compound **1** was assigned a monocyclic structure. The partial structure of the fragment $CH(CH_3)CH_2$ was identified by proton decoupling of the signals at δ 1.13 (3H, d), 2.37 (1H, qdd), 2.57 (1H, br d) and 3.21 (1H, br dd), measured in $(CD_3)_2CO$ (Table 1). Hydrogenation of **1** in the presence of Pd–charcoal (10%) gave decahydrofalconensone A **3**, $C_{21}H_{36}O_2$, still possessing one double bond. This double bond was thought to be tetrasubstituted, since the signals associated with it were not observed below δ 3 in the ^1H NMR spectrum. The fragment $CH(CH_3)CH_2$ was identified by proton decoupling of the signals at δ 1.09 (3H, d), 2.30 (1H, br qd), 2.02 (1H, br d) and 2.63 (1H, br dd). The maximum at 239 and 301 nm in the UV spectrum of **3** showed the presence of an α,β-unsaturated ketone. From a detailed analysis of the ^1H-detected heteronuclear multiple-quantum coherence *via* direct coupling (HMQC) and heteronuclear multiple bond connectivity by 2D multiple quantum NMR (HMBC) spectra of **3** (Fig. 2), it was confirmed decahydrofalconensone A had a 2,4-dimethyl-3-oxocyclopent-1-enyl residue and a methyl ketone. These results suggested the presence of fragments **A** and **B** in the molecule of **3**. The UV



3



fragment **A**

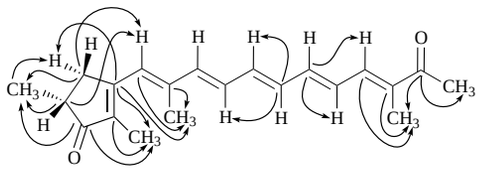


fragment **B**

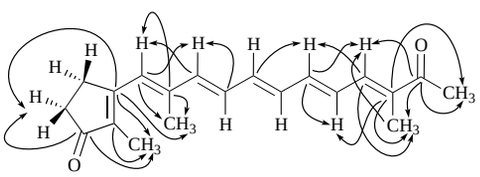
maximum at 239 nm was reasonable for the presence of the above five-membered unsaturated ketone in **3**.

Since seven olefinic protons still severely overlapped in the ^1H NMR measured made in $(CD_3)_2CO$, the ^1H NMR spectrum of **1** was measured in C_6D_6. A direct correlation between the carbons and the protons was confirmed from the analysis of the HMQC spectrum of **1**. The presence of fragments **A** and **B** was also established as being present in **1** from the result of **3** and by the analysis of the HMBC spectrum (Fig. 1). From the remaining unassigned signals of **1**, six sp^2 carbons and six protons, it is clear that fragments **A** and **B** are connected by three double bonds (CH=CHCH=CHCH=CH). The structure of falconensone A was, therefore, assumed to be as shown in **1**.

In order to confirm the above structure and the stereochemistry of the double bonds of falconensone A **1**, an X-ray crystallographic analysis of a derivative of **1** was attempted. Falconensone A **1** was treated with *p*-bromophenylhydrazinium chloride to afford falconensone *p*-bromophenylhydrazone **4**. Crystals of **4** acetone solvate were grown in acetone as dark red prisms, which were suitable for X-ray analysis. The absolute crystal structure of falconensone A *p*-bromophenylhydrazone **4** acetone solvate was determined, using Bijoet's inequality relationship in the anomalous dispersion for bromine atoms (see Fig. 3). Two molecules of **4** and acetone were present in an asymmetric unit. Each molecule of **4** and acetone were mainly packed by hydrogen bonding between the carbonyl oxygen and NH [N(2)–H···O(4): 3.10 Å, N(4)–H···O(2): 3.10 Å]. The bond lengths and angles are not significantly different from the expected values.[5] The absolute structure of falconensone A was consequently established as (*R*)-(3*E*,5*E*,7*E*,9*E*,11*E*)-3,11-

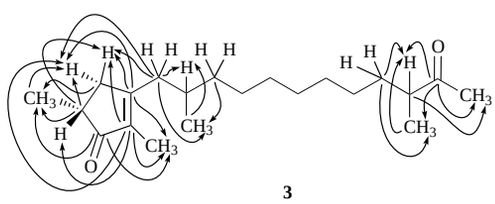


1



2

Fig. 1 Correlations in the HMBC spectrum of falconensones A **1** and B **2**. Arrow indicates the correlation from carbon (C_A) to proton (H_B): $C_A \longrightarrow H_B$.



3

Fig. 2 Correlations in the HMBC spectrum of decahydrofalconensone A **3**. Arrow indicates the correlation from carbon (C_A) to proton (H_B): $C_A \longrightarrow H_B$.

dimethyl-12-(2,4-dimethyl-3-oxocyclopent-1-enyl)dodeca-3,5,7,9,11-pentaen-2-one. The absolute configuration of the methyl group in the cyclopentenone ring is *R*. The assignments of the ^{1}H and ^{13}C NMR signals of **1** are summarized in Table 1.

Falconensone B **2**, $C_{20}H_{24}O_2$, *m*/*z* 296 (M^+), is closely related to **1**. In this compound, the ^{1}H NMR signals assigned to $CH(CH_3)CH_2$ are replaced by two new signals at δ 2.39 (2H) and 2.82 (2H) indicative of the fragment CH_2CH_2. This result assumed that **2** is a 4′-nor-methyl derivative of **1**. The analyses of the HMQC and HMBC (Fig. 1) spectra of **2** led us to confirm the structure of falconensone B as shown in **2**. The stereochemistry of the double bonds in **2** were not determined, but it is presumed that all, except that in the cyclopentenone ring, would have an *E*-configuration, taking into account the similarity of the chemical shifts of the ^{1}H and ^{13}C NMR signals (Table 1).

Falconensones A **1** and B **2** have the novel cyclopent-2-en-1-one skeleton with the methyl ketone residue connected through a conjugated pentaene moiety. It is likely that these compounds would be biosynthesized from the nonaketide, derived through the acetate–malonate pathway, followed by the methylation at the three positions C-3, C-11 and C-4′. The biological activity of falconensones A **1** and B **2** will be investigated in the near future.

Experimental

Mps were determined on a Yanagimoto micro-melting point apparatus and are uncorrected. Optical rotations were measured with a JASCO DIP-1000 spectrometer and are recorded as 10^{-1} deg cm^2 g^{-1}. Mass spectra (MS) were taken with a JEOL JMS-D-300 spectrometer. UV and IR spectra were recorded on a Hitachi U-3210 spectrophotometer and a JASCO IR-810 spectrophotometer, respectively. ^{1}H and ^{13}C NMR were recorded on a JEOL Lambda-500 spectrometer at 500.00 and 126.65 MHz, respectively, using tetramethylsilane as an internal standard. Coupling patterns are indicated as follows: singlet = s, doublet = d, triplet = t, quartet = q, multiplet = m and broad = br. *J* Values are in Hz. CD curves were determined on a JASCO J-600 spectropolarimeter. Column chromatography was performed using Kieselgel 60 (Art. 7734; Merck). Low pressure liquid chromatography (LPLC) was performed on a Chemco Low-Prep 81-M-2 pump and a glass column (200 × 10 mm) packed with silica gel CQ-3 (30–50 μm; Wako) with the flow rate of 6 ml min^{-1}. High-performance liquid chromatography (HPLC) was performed with a Senshu SSC-3160 pump with the flow rate of 5 ml min^{-1} using a Senshu Pak PEGASIL Silica 60-5 (10 i.d. × 250 mm) pre-packed column, equipped with a Shimamura YRU-883 RI-UV monitor. TLC was conducted on pre-coated Kieselgel 60 F_{254} plates (Art. 5715; Merck). Spots on TLC were detected on the basis of their colouration and absorption under UV light.

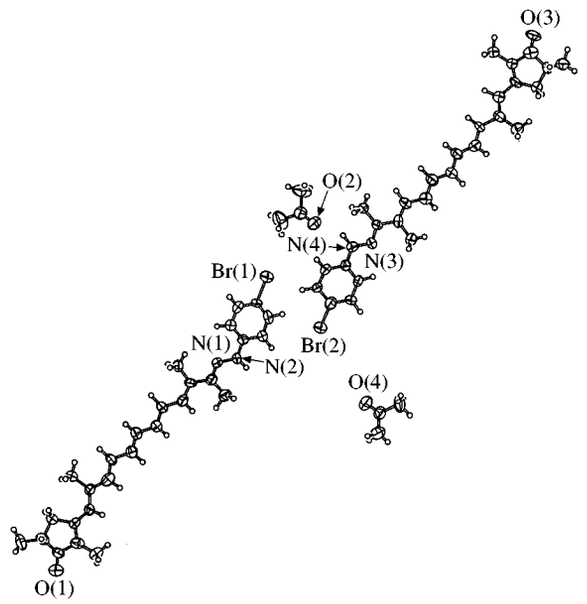


Fig. 3 Crystal structure of falconensone A *p*-bromophenylhydrazone **4** acetone solvate with thermal ellipsoids of 50% probability

Isolation of metabolites from *Emericella falconensis*

E. falconensis, strain NHL 2999, was cultivated in Czapek medium supplemented with 0.2% yeast extract (30 l) using 120 Roux flasks at 25 °C for 28 days. The dried mycelium was extracted with CH_2Cl_2 and the organic layer was dried (Na_2SO_4) and then evaporated *in vacuo*. The extract (36.2 g) obtained was dissolved in $CHCl_3$ and the filtrate was concentrated by evaporation. The residue (30.4 g) was chromatographed on silica gel with $CHCl_3$–acetone (60:1) after the elution with $CHCl_3$ to give the **1** and **2** rich fraction (16.9 g). After the re-chromatography on silica gel of this fraction, two fractions were obtained: the first eluted with benzene–acetone (15:1) and the second with benzene–acetone (10:1). The former fraction was further purified by the repeated LPLC with cyclohexane–acetone (10:1) and benzene–EtOAc (8:1) followed by the HPLC purification with the solvent system of hexane–acetone (10:1) (t_r 10 min) to afford falconensone A **1** (303 mg), whereas the latter fraction was purified by the repeated LPLC with benzene–acetone (15:1) and toluene–acetone (12:1), and then finally purified by HPLC with hexane–acetone (10:1) (t_r 14 min) to afford falconensone B **2** (3 mg).

Falconensone A **1**: orange prisms, $C_{21}H_{26}O_2$, mp 195–197 °C (from acetone); $[\alpha]_D^{20}$ +149 (*c* 0.45, $CHCl_3$) (Found: C, 81.06; H, 8.41. Calc. for $C_{21}H_{26}O_2$: C, 81.25; H, 8.44%); EI-MS *m*/*z* (%) 310.1919 (M^+, 310.1931 for $C_{21}H_{26}O_2$, 100), 295 [$(M - Me)^+$, 6], 267 [$(M - Ac)^+$, 13], 109 [$(C_7H_9O)^+$, 58] and 43 [$(Ac)^+$, 45]; CI-MS (isobutane) *m*/*z* (%) 311 [$(M + H)^+$, 100]; λ_{max}(MeOH)/nm (log ε) 249 (4.09), 310 (4.13), 389 (4.79), 408 (4.87) and 431 (4.76); ν_{max}(KBr)/cm^{-1} 1680 and 1647 (conjugated C=O) and 1587; ^{1}H NMR ($CDCl_3$) δ 1.21 (3H, d, *J* 7.3), 1.80 (3H, br s),

Table 1 ^{13}C and ^{1}H NMR assignments for falconensones A **1** and B **2**

	1[a]		**1**[b]		**2**[c]	
Position	δ_C	δ_H	δ_C	δ_H	δ_C	δ_H
1 (Me)	25.33	2.07	26.09	2.31	25.60	2.29
2	197.47		198.98		199.23	
3	137.12		137.29		136.64	
3-Me	11.86	1.91	12.10	1.87	11.66	1.86
4	138.08	6.83	139.97	7.24	138.87	7.03
5	129.62	6.45	130.52	6.62–6.81	129.24	6.53–6.62
6	139.29	6.34	141.12	6.62–6.81	139.64	6.53–6.62
7	136.36	6.38	137.87	6.62–6.81	134.01	6.41–6.48
8	140.26	6.33	141.27	6.62–6.81	140.01	6.41–6.48
9	134.24	6.23	135.44	6.62–6.81	136.48	6.41–6.48
10	130.97	6.37	132.55	6.62–6.81	131.16	6.41–6.48
11	140.96		143.00		141.69	
11-Me	14.45	1.78	15.21	2.15	14.64	2.05
12	128.48	6.31	128.51	6.62	127.49	6.41–6.48
1′	160.72		162.75		164.00	
2′	138.14		138.17		138.82	
2′-Me	9.23	1.80	9.51	1.73	8.92	1.73
3′	209.45		210.68		208.97	
4′	39.65	2.16	40.53	2.37	29.67	2.82
						2.82
4′-Me	16.82	1.11	17.37	1.13		
5′	38.80	2.04	39.68	2.57	34.30	2.39
		2.62		3.21		2.39

[a] Measured in C_6D_6. [b] Measured in $(CD_3)_2CO$. [c] Measured in $CDCl_3$.

1.93 (3H, br s), 2.12 (3H, br s), 2.36 (3H, s), 2.45 (1H, br qd, *J* 7.3, 6.5), 2.47 (1H, br d, *J* 17.9), 3.16 (1H, dd, *J* 17.9 and 6.5), 6.50–6.54 (5H, m), 6.55–6.62 (2H, m) and 7.10 (1H, br d, *J* 10.4); ^{1}H NMR [$(CD_3)_2CO$] δ 1.13 (3H, d, *J* 7.3), 1.73 (3H, t, *J* 2.0), 1.87 (3H, d, *J* 1.2), 2.15 (3H, br s), 2.31 (3H, s), 2.37 (1H, qdd, *J* 7, 3, 7.2 and 2.8), 2.57 (1H, br d, *J* 17.4), 3.21 (1H, br dd, *J* 17.4 and 7.2), 6.62–6.81 (7H, m) and 7.24 (1H, dd, *J* 10.5 and 1.5); ^{1}H NMR (C_6D_6) δ 1.11 (3H, d, *J* 7.3), 1.78 (3H, br s), 1.80 (3H, t, *J* 1.8), 1.91 (3H, d, *J* 1.5), 2.04 (1H, br d, *J* 17.8), 2.07 (3H, s), 2.16 (1H, qdd, *J* 7, 3, 6.3 and 2.7), 2.62 (1H, br dd, *J* 17.8 and 6.4), 6.23 (1H, dd, *J* 14.0 and 10.8), 6.31 (1H, br s), 6.33 (1H, m), 6.34 (1H, m), 6.37 (1H, m), 6.38 (1H, m), 6.45 (1H, br dd, *J* 14.8 and 11.2) and 6.83 (1H, dq, *J* 11.2, 1.5); and CD (*c* 1.3 × 10^{-5}, dioxane) $\Delta\varepsilon^{20}$ (nm): +1.6 (304), +3.0 (401) and +2.0 (427).

Falconensone B **2**: orange microcrystalline powder, $C_{20}H_{24}O_2$, mp 196–198 °C; EI-MS *m*/*z* (%) 296.1775 (M^+, 296.1776 for $C_{20}H_{24}O_2$, 46), 253 [$(M - Ac)^+$, 8] 204 (14), 109 [$(C_7H_9O)^+$, 44] and 43 [$(Ac)^+$, 100]; λ_{max}(MeOH)/nm (log ε) 213 sh (3.46), 248 (3.59), 299 (3.65), 310 (3.65), 386 sh (4.49), 4.07 (4.58) and 430 (4.47); ν_{max}(KBr)/cm^{-1} 1680 and 1650 (conjugated CO); and ^{1}H NMR ($CDCl_3$) δ 1.73 (3H, br s), 1.86 (3H, br s), 2.05 (3H, br s), 2.29 (3H, s), 2.39 (2H, m), 2.82 (2H, m), 6.41–6.48 (5H, m), 6.53–6.62 (2H, m) and 7.03 (1H, br d, *J* 9.2).

Hydrogenation of falconensone A 1 with 10% Pd–C

10% Pd–C (14 mg) was suspended to a solution of falconensone A **1** (10 mg) in CH_2Cl_2 (3 ml) and the mixture was stirred at room temperature under a hydrogen atmosphere for 2 h. After the catalyst had been filtered off, the filtrate was evaporated *in vacuo*. The residue was purified by LPLC using the solvent system of benzene–acetone (5:1) followed by repeated HPLC [hexane–acetone (10:1) and/or benzene–acetone (40:1)] to afford decahydrofalconensone A **3** (7 mg).

Decahydrofalconensone A **3**: colourless amorphous powder; $[\alpha]_{435}^{20}$ −33 (*c* 0.52, MeOH); EI-MS *m*/*z* (%) 320.2710 (M^+, 320.2713 for $C_{21}H_{36}O_2$, 13), 305 [$(M - Me)^+$, 2] 277 [$(M - Ac)^+$, 2], 249 (16), 151 (84) and 124 (100); λ_{max}(MeOH)/nm (log *e*) 239 (4.10) and 301 (1.91); ν_{max}(KBr)/cm^{-1} 1710 (C=O) and 1680 (conjugated C=O); ^{1}H NMR ($CDCl_3$) δ 0.79 (3H, d, *J* 6.4, 11-Me), 1.01 (3H, d, *J* 7.0, 3-Me), 1.09 (3H, d, *J* 7.3, 4′-Me), 1.12–1.30 (13H, m), 1.57 (1H, m, 4-H), 1.61 (3H, br s, 2′-Me), 1.68 (1H, m, 11-H), 2.02 (1H, br d, *J* 18.0, 5′-H), 2.06 [3H, s, 1-H_3 (Me)], 2.16 (1H, dd, *J* 13.3 and 9.0, 12-H), 2.28 (1H, m, 12-H), 2.30 (1H, br dq, *J* 7.3 and 6.0, 4′-H), 2.42 (1H, qt, *J* 7.0, 6.7, 3-H) and 2.63 (1H, dd, *J* 18.0 and 12.0, 5′-H); ^{13}C NMR ($CDCl_3$) δ 8.3 (2′-Me), 16.2 (3-Me), 16.7 (4′-Me), 19.7 (11-Me), 27.0 (CH_2), 27.2 (CH_2), 27.9 [C-1 (Me)], 29.4 (CH_2), 29.6 (CH_2), 29.7 (CH_2), 31.9 (C-11), 32.9 (C-4), 37.2 (C-10), 38.8 (C-12), 38.8 (C-5′), 39.4 (C-4′), 47.2 (C-3), 135.7 (C-2′), 171.3 (C-1′), 212.6 (C-3′) and 212.9 (C-2); and CD (*c* 8.8 × 10^{-5}, dioxane) $\Delta\varepsilon^{20}$ (nm) −25.0 (236) and −0.2 (331).

Synthesis of the *p*-bromophenylhydrazone of falconensone A 1

p-Bromophenylhydrazinium chloride (400 mg) was added to a solution of sodium acetate (250 mg) in EtOH (10 ml) followed by a solution of falconensone A **1** (80 mg) in $CHCl_3$ (5 ml) added dropwise. The mixture was warmed at 75 °C for 2.5 h after which it was poured into ice–water and extracted with $CHCl_3$. The extract was washed with 0.5 M aqueous HCl and then water and then evaporated *in vacuo*. The residue was purified by LPLC with benzene–acetone (40:1) and then recrystallized from acetone to afford falconensone A *p*-bromophenylhydrazone **4** (72 mg).

Falconensone A *p*-bromophenylhydrazone **4**: dark red crystalline powder, mp 183 °C; $[\alpha]_{435}^{20}$ −134 (*c* 0.58, $CHCl_3$) (Found: C, 66.88; H, 6.86; N, 5.33. Calc. for $C_{27}H_{31}N_2OBr{\cdot}C_3H_6O$: C, 67.03; H, 6.94; N, 5.21%); EI-MS *m*/*z* (%) 478.1358 (M^+, 478.1336 for $C_{27}H_{31}ON_2{}^{79}Br$, 16), 480.1328 ($M^+$, 480.1290 for $C_{27}H_{31}ON_2{}^{81}Br$, 15), 463, 461 [$(M - Me)^+$, 6], 173 [$(^{81}BrC_6H_5NH_2)^+$, 92] and 171 [$^{79}BrC_6H_5NH_2)^+$, 98]; λ_{max}(MeOH)/nm (log ε) 228 (4.43), 274 (4.29) and 440 (4.72); ν_{max}(KBr)/cm^{-1} 3320 (NH) and 1670 (conjugated C=O); ^{1}H NMR ($CDCl_3$) δ 1.21 (3H, d, *J* 7.4), 1.79 (3H, br s), 2.03 (3H, s), 2.13 (3H, s), 2.15 (3H, s), 2.44 (1H, br qd, *J* 7.4 and 6.5), 2.47 (1H, br d, *J* 17.1), 3.16 (1H, dd, *J* 17.1 and 6.5), 6.30–6.60 (7H, m), 6.77 (1H, br dd, *J* 13.5 and 11.0), 7.00 (2H, d, *J* 8.9), 7.35 (2H, d, *J* 8.9) and 7.38 (1H, br s, NH); CD (*c* 3.8 × 10^{-5}, dioxane) $\Delta\varepsilon^{20}$ (nm) +1.2 (285) and +1.0 (408).

Structure determination of falconensone A *p*-bromophenylhydrazone 4 acetone solvate by X-ray diffraction

The crystals of falconensone A *p*-bromophenylhydrazone **4** acetone solvate were grown from acetone as dark red prisms.

Diffraction intensities were collected from a crystal of dimensions 0.50 × 0.30 × 0.10 mm on a Rigaku AFC-7 four-circle diffractometer. Of the total 4238 unique reflections (complete for $2\theta < 120°$), 3727 satisfied the criterion $F > 3\sigma(F)$ and only these were used in the solution and refinement of the structure.

Crystal data. $C_{27}H_{31}BrN_2O\cdot C_3H_6O$, $M = 537.34$, triclinic, space group $P1$, $a = 11.528(2)$, $b = 16.327(1)$, $c = 8.427(2)$ Å, $\alpha = 100.78(1)$, $\beta = 106.47(2)$, $\gamma = 70.110(8)°$, $V = 1423.1(4)$ Å^3, $Z = 2$, $D_c = 1.254$ g cm^{-3}, $F(000) = 564$, Cu-Kα X-radiation (graphite monochromator) and $\lambda = 1.541\,78$ Å.

The structure was solved by direct methods using SAPI91[6] and expanded using Fourier techniques (DIRDIF 92[7]). The final refinement was done by the full-matrix least-squares method. Anisotropic thermal parameters were used for all non-hydrogen atoms and the hydrogen atoms were fixed. The refinement converged to R (R_w) 0.047 (0.040).[5]

Absolute structure determination of falconensone A *p*-bromophenylhydrazone 4 acetone solvate. The absolute structure was determined by comparison of the observed intensity ratios of the Bijvoet pairs with those of the calculated ones. The results were incorrect when the initial structure was chosen. Moreover, the R (R_w) value was 5.5 (4.9)% after a least-squares calculation was done for 7369 reflections when the initial structure was chosen, but this value was reduced to 5.2 (4.5)% when the antipodal (correct) structure was chosen.

Acknowledgements

We thank Prof. Makoto Miyaji of the Research Center for Pathogenic Fungi and Microbial Toxicoses, Chiba University, and Dr Shun-ichi Udagawa of Tokyo University of Agriculture, for their kind advice. We are grateful to Mrs T. Ogata, Mrs Y. Kawada and Mr H. Komiya of Hoshi University for elemental analysis and NMR and mass measurements. This work was supported in part by a Grant-in-Aid for Scientific Research (No. 07672296) from the Ministry of Education, Science, Sport and Culture, Japan.

References

1 T. Itabashi, K. Nozawa, M. Miyaji, S. Udagawa, S. Nakajima and K. Kawai, *Chem. Pharm. Bull.*, 1992, **40**, 3142.
2 T. Itabashi, N. Ogasawara, K. Nozawa and K. Kawai, *Chem. Pharm. Bull.*, 1996, **44**, 2213.
3 T. Itabashi, K. Nozawa, S. Nakajima and K. Kawai, *Chem. Pharm. Bull.*, 1993, **41**, 2040.
4 Y. Horie, M. Miyaji, K. Nishimura and S. Udagawa, *Trans. Mycol. Soc. Jpn.*, 1989, **30**, 257.
5 Lists of atomic parameters, bond lengths and bond angles are available on request from the Cambridge Crystallographic Data Centre. Requests for such data should be accompanied by a full bibliographic reference for this work together with the reference number 207/130.†
6 F. Hai-Fu, Structure Analysis Programs with Intelligent Control, Rigaku Corporation, Tokyo, Japan (1991).
7 P. T. Beurkens, G. Admiraal, G. Beurkens, W. P. Bosman, S. Garcia-Granda, R. O. Gould, J. M. M. Smits and C. Smykalla, The DIRDIF program system, Technical Report of the Crystallography Laboratory, University of Nijmegan, The Netherlands (1992).

† For details of these schemes, see Instructions for Authors (1997), *J. Chem. Soc., Perkin Trans. 1*, 1997, Issue 1.

Paper 7/01277B
Received 24*th February* 1997
Accepted 3*rd June* 1997