Dendryol A, B, C, and D, Four New Compounds Produced by a Weed Pathogenic Fungus *Dendryphiella* sp.

Masayasu Tanaka[a], Junko Ohra[a], Yasuko Tsujino[a], Takane Fujimori[a], Hideo Ago[b] and Hideaki Tsuge[b]

[a] Applied Plant Research Laboratory, Yokohama Center, Japan Tobacco Inc., 6–2, Umegaoka, Aoba-ku, Yokohama, Kanagawa 227, Japan
[b] Life Science Research Laboratory, Japan Tobacco Inc., 6–2, Umegaoka, Aoba-ku, Yokohama, Kanagawa 227, Japan

Z. Naturforsch. **50 c**, 751–756 (1995); received June 19/August 11, 1995

Dendryphiella sp., Phytopathogen, Anthraquinone, *Eleocharis kuroguwai*, Phytotoxic Activity

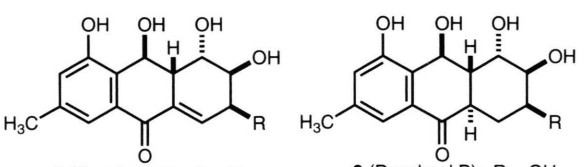
Four novel anthraquinone derivatives, named Dendryol A, B, C, and D, were isolated from the culture filtrate of *Dendryphiella* sp. Their structures were elucidated from spectral data and single-crystal X-ray diffraction analysis. The four compounds showed phytotoxic activity against barnyardgrass at more than 1 μl application of 5000 μg/ml.

Introduction

In the course of our continuing studies on herbicidal compounds from phytopathogenic fungi, we undertook an investigation of the culture filtrate of the weed pathogen, *Dendryphiella* sp., that was isolated from a diseased *Eleocharis kuroguwai* in Shimane Prefecture of Japan (Imaizumi, 1992). This led to the isolation of four new compounds depicted in Fig. 1, Dendryol A, B, C, and D, appearing to be related to hexa- and octa-hydroanthraquinones. In this paper we describe the isolation, structure determination, and phytotoxic activities of those compounds.

Results and Discussion

The four new compounds were obtained from the EtOAc extract of the culture filtrate of *Dendryphiella* sp. by reverse phase HPLC. Data from a $^1H-^1H$ COSY spectra, in conjunction with spin decoupling experiments of 1D-NMR data, enabled the formulation of partial structures. DEPT (Distortionless Enhancement by Polarization Transfer) experiments and C–H COSY spectra, which established the one-bond $^1H-^{13}C$ connectivities, facilitated the assignment of all the carbon signals. HMBC(Heteronuclear Multiple Bond Connectivity) experiments (Summers *et al.*, 1986), which established the two- and three-bond $^1H-^{13}C$ correlations, established the connectivities of partial structures and were helpful in assigning the NMR signals. NOESY (Nuclear Overhauser Effect Spectroscopy) experiments were also used to establish the stereochemistries.



1 (Dendryol A): R = H
4 (Dendryol D): R = OH
2 (Dendryol B): R = OH
3 (Dendryol C): R = H

Fig. 1. Structures of the anthraquinone derivatives produced by *Dendryphiella* sp.

Compound **1**, designated Dendryol A, was obtained as a pale yellow crystal with m.p. 190–192 °C and $[\alpha]_D^{25}$ −158° (MeOH, c 0.05). The molecular formula, $C_{15}H_{16}O_5$, was derived on the basis of its ^{13}C-NMR spectral data and HRFABMS (High Resolution Fast Atom Bombardment Mass spectrometry). The UV/VIS spectrum showed λ_{max} at 242, 285 and 336 nm. The ratio of carbons to hydrogens in the molecule indicated tricyclic nature since it has four olefins [^{13}C-NMR δ ppm 138.0, 120.5, 140.2, 123.4, 158.1, 133.4, 128.0, 131.9; ^1H-NMR δ ppm 7.15(1H), 7.38(1H), 6.89(1H)], a ketone [^{13}C-NMR δ ppm 186.6; IR ν_{max} cm^{-1} 1667] and three hydroxyl groups [^{13}C-NMR δ ppm 66.8, 67.6, 67.7; ^1H-NMR δ ppm

Reprint requests to M. Tanaka.
Telefax: 045(972)4312

0939–5075/95/1100–0751 $ 06.00

4.28(1H), 4.06(1H),5.35(1H); IR ν_{max} cm^{-1} 3352]. In addition to the above mentioned functionalities, there was a methyl [^{13}C-NMR δ ppm 21.1; ^{1}H-NMR δ ppm 2.32(3H)], a methine [^{13}C-NMR δ ppm 43.8; ^{1}H-NMR δ ppm 3.09(1H)] and a methylene [^{13}C-NMR δ ppm 31.1; ^{1}H-NMR δ ppm 2.34(1H), 2.76(1H)].

The partial structures were elucidated as follows: the chemical shift of C-9 (δ 67.7) and H-9 (δ 5.35) indicated the attachment of this methine carbon to oxygen. The very low field shift of H-9 is considered C-9 neighboring to a aromatic ring. In the COSY spectrum, H-13 showed coupling to the two methines of H-9 and H-1 (δ 4.28). The chemical shifts of H-1 (δ 4.28), C-1 (δ 66.8), H-2 (δ 4.06) and C-2 (δ 67.6) indicated the attachment of the methine carbons to oxygen. The COSY spectrum also showed coupling of H-2 to H-1 and each proton of a methylene at δ 2.34 and 2.76 (Ha,b-3). Additional coupling was observed from the H-3 methylene protons to a olefinic proton H-4 (δ 7.15), which was also coupled to a deshielded methine proton (H-13).

By the HMBC experiments the correlations were observed between the H-4–C-2 and H-2–C-4. The HMBC experiment also revealed a correlation between H-1 and a signal of δ 131.9 which was assigned to C-14. These observations indicated C-13 attached to C-14 resulted in forming a dihydroxycyclohexene ring. Detailed analysis of proton decoupling experiments revealed the coupling constants of H-13 and Ha,b-3, which are homoallylic relationships, are an abnormally large value; H-13–Ha-3 (J = 4.0 Hz), H-13–Hb-3 (J = 2.0 Hz). Furthermore, Ha-3 coupled to Hb-3 with large value (J = 20.0 Hz) indicated C-3 are neighboring to sp^2 carbon (Barfield *et al.*, 1963).

The combination of these relationships provided evidence for partial structure **A** (Fig. 2).

The remaining six olefinic carbons (δ 120.5, 140.2, 123.4, 158.1, 133.4, 128.0) were assigned to aromatic carbons. The coupling constants of the aromatic protons appeared at δ 6.89 (J = 2.5) and δ 7.38 (J = 2.5) indicated presence of a 1,2,4,6-tetra-substituted aromatic structure. The chemical shift of a methyl [^{13}C-NMR 21.1; ^{1}H-NMR 2.32(3H)] and C-8 (δ 158.1) indicated the existence of a methyl attached to aromatic ring and phenolic hydroxyl group, respectively. The ^{13}C-NMR signal resonated at δ 186.6 assigned a carbonyl group which was attached to C-11 from the HMBC correlation between H-5 and the carbonyl signal. The IR spectrum absorbed at 1667cm^{-1} also revealed the presence of an aryl carbonyl group. The construction of substitution patterns of the aromatic ring and exact assignment of the ^{13}C-NMR signals were established by the HMBC experiment. The correlations were shown in the partial structure **B** (Fig. 2).

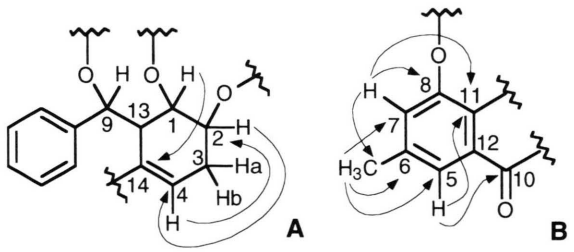


Fig. 2. Partial structures A and B. The arrows indicate HMBC correlations.

The formulation of **A** and **B** was established by HMBC experiment showing the correlations of H-9–C-11, H-9–C-12 and H-9–C-8. The combination of the above data allowed the formulation of the structure **1**.

In order to confirm the structure **1** and establish its relative stereochemistry, a single-crystal X-ray diffraction analysis of **1** was carried out. The X-ray molecular model of this compound confirmed all the above deductions on its structure and established the relative configuration of **1** depicted in Fig. 1.

Compound **2**, designated Dendryol B, was obtained as a pale yellow oil with $[\alpha]_D^{25}$ −33.2° (MeOH, c 0.06). The molecular formula, $C_{15}H_{18}O_6$, was derived on the basis of its ^{13}C-NMR spectral data and HRFABMS. The UV/VIS spectrum showed λ_{max} at 220, 262 and 317 nm. The ratio of carbons to hydrogens in the molecule indicated tricyclic nature since it has three olefins [^{13}C-NMR δ ppm 119.3, 140.1, 122.9, 158.0 , 133.1, 128.8; ^{1}H-NMR δ ppm 6.92(1H), 7.29(1H)], a ketone [^{13}C-NMR δ ppm 201.0; IR ν_{max} cm^{-1} 1673] and four hydroxyl groups [^{13}C-NMR δ ppm 69.6, 73.0, 68.2, 67.6; ^{1}H-NMR δ ppm 4.39(1H), 3.94(1H), 4.03(1H), 5.31(1H); IR ν_{max} cm^{-1} 3361]. In addition to the above mentioned functionalities, there was a methyl [^{13}C-NMR δ ppm 21.1; ^{1}H-NMR δ ppm 2.32(3H)], two methines [^{13}C-NMR

δ ppm 46.0, 43.1; ^{1}H-NMR δ ppm 2.29(1H), 2.66(1H)] and a methylene [^{13}C-NMR δ ppm 28.8; ^{1}H-NMR δ ppm 1.71(1H), 2.22(1H)].

These spectral data were similar to that of **1**, except the olefinic signals of α,β-unsaturated part [^{13}C-NMR δ ppm 131.9(C), 138.0(CH); ^{1}H-NMR δ ppm 7.15(1H)] was replaced by sp^3 carbon signals [^{13}C-NMR δ ppm 43.1(CH), 28.8(CH_2); ^{1}H-NMR δ ppm 2.66(1H), 1.71(1H), 2.22(1H)], and a methylene of cyclohexene ring [^{13}C-NMR δ ppm 31.1 (CH_2); ^{1}H-NMR δ ppm 2.34(1H), 2.76(1H)] was replaced by a hydroxylated methine [^{13}C-NMR δ ppm 68.2; ^{1}H-NMR δ ppm 4.03(1H)].

The partial structures and stereochemistry were elucidated as follows: In the COSY spectrum, H-13 (δ 2.29) showed coupling to H-14 (δ 2.66) in addition to H-9 (δ 5.31) and H-1 (δ 4.39). The coupling constants of H-13–H-14 (J = 13.8 Hz) and H-13–H-9 (J = 10.0 Hz) indicated the *trans*-diaxial relationship of these protons (Jackman *et al.*, 1969). The COSY spectrum also showed coupling of H-2 (δ 3.94) to H-1 (δ 4.39) and H-3 (δ 4.03) with the coupling constants of J = 3.8 and J = 2.6, respectively. The axial proton (δ 1.71) of the C-4 showed the same coupling constant of J = 12.0 with H-3 and H-14, respectively, indicating the *trans*-diaxal relationships of these protons. The preceding correlations were summarized in partial structure **C** (Fig. 3), including the relative stereochemistry. The stereochemistry was also supported by a NOESY experiment showing cross peaks of H-9–H-14 and H-14–H-3.

The remaining carbon and proton signals were assignable to the partial structure **B**. The assignments (Table I) were confirmed by HMBC experiment. The structure **2** was constructed by HMBC experiment showing the correlations between H-9–C-12 and H-9–C-11 and H-5–C-10.

Compound **3**, designated Dendryol C, was obtained as a pale yellow oil with $[\alpha]_D^{25}$ +10.3° (MeOH, c 0.12). The molecular formula $C_{15}H_{18}O_5$ was determined on the basis of its ^{13}C-NMR spectral data and HRFABMAS. The UV/VIS spectrum showed λ_{max} at 222, 261 and 319, indicated the similarity of the chromophore to that of **2**. The mole weight of **3** was 16 mass units lower than that of **2**, suggesting lack of a hydroxyl group in **2**. The ^{13}C-NMR and ^{1}H-NMR spectrum were similar to that of **2**, except the hydroxyl methine [^{13}C-NMR δ ppm 68.2; ^{1}H-NMR δ ppm 4.03] was replaced by a methylene [^{13}C-NMR δ ppm 26.6; ^{1}H-NMR δ ppm 1.71(1H), 1.95(1H)]. The above data indicated **3** possess the structure described in the figure.

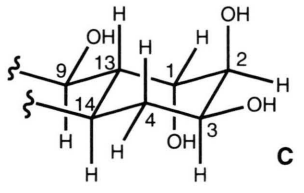


Fig. 3. Partial structure C.

The relative stereochemistry was determined as follows: the vicinal coupling constants of J = 2.8 Hz between H-2 (δ 3.92) and the methylene at C-3 at once precludes any *trans*-diaxal relationship and places the hydroxyl group at C-2 in an axial configuration (Gill *et al.*, 1990). The hydroxyl methine proton H-9 coupled with J = 10.0 Hz to a methine proton H-13, which was in turn coupled to methine proton H-14 with J = 14.0 Hz indicated the *trans*-diaxal relationship of H-9–H-13 and H-13–H-14, respectively. The axial configuration of H-14 also supported by the coupling constants of a neighboring methylene protons Ha,b-4 (J = 3.8 and 11.3 Hz). The coupling constant between H-13 and hydroxyl methine proton H-1 (J = 2.8 Hz) indicated the axial configuration of the hydroxyl group of H-1. The combination of these relationships proved evidence for the structure **3**.

Compound **4**, designated Dendryol D, was obtained as a pale red crystal with m.p. 209–212°C and $[\alpha]_D^{25}$ −120° (MeOH, c 0.25). The molecular formula $C_{15}H_{16}O_6$ was determined on the basis of its ^{13}C-NMR spectral data and HRFABMAS. The mole weight was 16 mass units higher than that of **1** suggesting one more hydroxyl group in **1**. The UV/VIS spectrum showed λ_{max} at 241, 285 and 337 indicated the similarity of the chromophore to that of **1**. The ^{13}C-NMR and ^{1}H-NMR spectrum were similar to that of **1**, except the allyl methylene signals [^{13}C-NMR δ ppm 31.1; ^{1}H-NMR δ ppm 2.34(1H), 2.76(1H)] was replaced by a hydroxyl methine [^{13}C-NMR δ ppm 70.7; ^{1}H-NMR δ ppm 4.15]. This methine proton was coupled with the hydroxyl methine H-2 (δ 4.02) and the vinyl proton H-4 (δ 6.96). The above data indicated **4** possess the structure described in the figure.

Table I. ^{1}H-NMR (300 MHz), ^{13}C-NMR (75 MHz) and HMBC data for **1–4**[a].

Position	Compound **1** δC	δH	*J* [Hz]	HMBC ^{13}C with ^{1}H	Compound **2** δC	δH	*J* [Hz]	HMBC ^{13}C with ^{1}H
1	66.8	4.28 dd	3.4, 4.6	9, 2	69.6	4.39 dd	2.7, 3.8	9
2	67.6	4.06 ddd	2.2, 4.2, 4.6	1, 4	73.0	3.94 dd	2.6, 3.8	
3	31.1	2.34 ax dddd 2.76 eq dddd	2.0, 2.2, 4.8, 20.0 2.6, 4.0, 4.8, 20.0	1	68.2	4.03 ddd	2.6, 4.6, 12.0	4 eq, 4 ax
4	138.0	7.15 ddd	2.6, 4.0, 4.8	2	28.8	1.71 ax q 2.22 eq ddd	12.0 3.7, 4.6, 12.0	
5	120.5	7.38 d	2.5	7, 6-CH_3	119.3	7.29 br. s		6-CH_3
6	140.2			6-CH_3	140.1			
7	123.4	6.89 d	2.5	5, 6-CH_3	122.9	6.92 br. s		6-CH_3
8	158.1			7, 9	158.0			7
9	67.7	5.35 d	10.0		67.6	5.31 d	10.0	13
10	186.6			5	201.0			5
11	133.4			9	133.1			9
12	128.0			5, 7, 9	128.8			5, 7, 9
13	43.8	3.09 dddt	2.0, 3.4, 10.0, 4.0	2, 4, 9	46.0	2.29 ddd	2.7, 10.0, 13.8	9
14	131.9			1	43.1	2.66 ddd	3.7, 12.0, 13.8	4 eq, 4 ax
6-CH_3	21.1	2.32 s		5, 7	21.1	2.32 s		

Position	Compound **3** δC	δH	*J* [Hz]	Compound **4** δC	δH	*J* [Hz]
1	67.9	4.23 dd	2.8, 3.2	69.0	4.32 dd	4.7, 6.2
2	69.6	3.92 dt	3.2, 2.8	72.4	4.02 dd	3.4, 6.2
3	26.6	ax, 1.71 m eq, 1.95 m		70.7	4.15 dd	2.4, 3.4
4	20.4	ax, 1.67 m eq, 2.00 m		136.7	6.96 dd	1.2, 3.4
5	119.4	7.28 d	1.7	120.3	7.41 br. s	
6	140.1			140.3		
7	123.0	6.90 d	1.8	123.9	6.94 br. s	
8	158.2			158.2		
9	67.7	5.33 d	10.1	69.3	5.43 d	10.4
10	202.0			186.9		
11	133.2			133.6		
12	129.0			128.0		
13	46.7	2.34 ddd	2.8, 10.0, 14.0	45.5	3.18 ddd	2.4, 4.7, 10.4
14	43.8	2.58 ddd	3.8, 11.3, 14.0	134.8		
6-CH_3	21.2	2.33 s		21.1	2.35 s	

[a] Chemical shifts are given in ppm on the δ scale, referenced to the solvent peak CHD_2OD at 3.35 ppm for ^{1}H-NMR and at 49.5 ppm for ^{13}C-NMR in CD_3OD.

The relative stereochemistry was determined as follows: the hydroxyl methine H-9 was coupled with J = 10.4 Hz to the methine H-13, which was in turn coupled to a hydroxyl methine proton H-1 with J = 4.7 Hz indicated the *trans*-diaxal relationship of H-9–H-13 and axial-equatorial relationship of H-13–H-1. The stereochemistry at the cyclohexene ring was assumed to be the same as in **2** and the related compounds **1** and **3**. The combination of these relationships provided the evidence for the structure **4**.

Phytotoxic activity of the four compounds were tested on seven plants listed in Table II by the leaf-puncture assay using the previously reported method (Tanaka *et al.*, 1994). Kuroguwai, the host plant of the fungi, showed no symptoms against applications of these compounds. But, of the tested plants, barnyardgrass was sensitive to the four compounds at the dose tested. No effect appeared when the samples were applied to not wounded intact leaves in droplets. When the compounds were applied to wounds of barnyardgrass,

Table II. Necrotic effect of compounds **1–4** in the leaf-puncture assay on various plants.

	Compound							
	1		**2**		**3**		**4**	
Plant	1 µl[a]	2 µl	1 µl	2 µl	1 µl	2 µl	1 µl	2 µl
Kuroguwai	–[b]	–	–	–	–	–	–	–
Barnyardgrass	2×6[c]	1×8	1×6	1×6	1×1	1×5	1×6	1×7
Velvetleaf	2×2	2×2	–	–	–	–	–	–
Rice	–	–	–	–	–	–	–	–
Corn	–	–	–	–	–	–	–	–
Cowpea	–	–	–	–	–	–	–	–

[a] Concentration: 5000 µg/ml.
[b] No effect.
[c] Necrotic area (mm×mm).

a necrotic area spread from the applied point to the top of the leaf.

Experimental

General

Spectral data were recorded on the following instruments: ^{1}H and ^{13}C-NMR, Bruker AC-300 and AM-500; FABMS, Kratos concept-2H; FT-IR, Nicolet 800 FT-IR spectrometer; UV/VIS, Beckman DU 650 spectro-photometer. Optical rotation was recorded with a Jasco DIP-370 polarimeter. Melting point was measured by Yanagimoto Micro Melting Point Apparatus. For HPLC, Hitachi L-6000 pump, L-3300 RI monitor and L-4000 UV detector were used. For TLC, aluminium foils coated with silica gel Merck 60 F_{254} was used.

Isolation procedures

Dendryphiella sp. which was isolated from a diseased *Eleocharis kuroguwai* in our laboratory (Imaizumi *et al.*, 1992) was maintained in 10% glycerol at −80°C. The stocked culture was transferred to potato dextrose agar (Difco) slants and grown at 25 °C for 2 weeks. For the compounds production the fungus was cultured in a Czapek-Dox medium (1 liter) fortified by yeast extract (Difco) at 0.1% shaken at 200 rpm and 28 °C for a week. The culture filtrate was extracted with ethyl acetate(1 liter × 3). The combined organic layers were dried over anhydrous Na_2SO_4, then concentrated *in vacuo* to give gummy residue (180 mg). The residue was subjected to reverse-phase HPLC (YMC-AQ, 5 µm C18 column; 20 × 250 mm; 1:1 MeOH:H_2O at 5.0 ml/min) to afford 12 mg of **2** at t_R 22.5 min, 10 mg of **1** at t_R 24.4 min, 8 mg of **4** at t_R 28.0 min and 5 mg of **3** at t_R 32.0 min.

Phytotoxic activities

A puncture was made on leaves of intact plants for 10–14 days in a green house; the sample was then dissolved in 5000 µg/ml of 70% acetone and applied to the puncture wounded by a 10 µl syringe. After incubating for 5 days in the greenhouse, the extent of the lesion was assessed. The results were listed in Table II.

Physicochemical properties of the isolated compounds

Dendryol A. – $[\alpha]_D^{25}$ −158°(MeOH, c 0.05); m.p. 190–192 °C; HRFABMAS $[M+H]^+$ *m/z* 277.10694 (calcd for $C_{15}H_{17}O_5$, 277.10754); UV λ_{max} (log ε) nm 242(4.1), 285(4.3), 336(3.5); IR (neat) ν_{max} (cm^{-1}) 3352, 1667, 1324, 1020, 798, 741; NMR see Table I.

Dendryol B. – $[\alpha]_D^{25}$ −33.2° (MeOH, c 0.06); HRFABMAS $[M+H]^+$ *m/z* 295.11725 (calcd for $C_{15}H_{19}O_6$, 295.11815); UV λ_{max} (log ε) nm 220(4.2), 262(4.0), 317(3.5); IR (neat) ν_{max} (cm^{-1}) 3361, 1673, 1320, 1016, 859, 755; NMR see Table I.

Dendryol C. – $[\alpha]_D^{25}$ +10.3° (MeOH, c 0.12); HRFABMAS $[M+H]^+$ *m/z* 279.12252 (calcd for $C_{15}H_{19}O_5$, 279.12322); UV λ_{max} (log ε) nm 222(4.2), 261(3.8), 319(3.4); IR (neat) ν_{max} (cm^{-1}) 3320, 1672, 1325, 1018, 855, 760; NMR see Table I.

Dendryol D. – $[\alpha]_D^{25}$ −120° (MeOH, c 0.25); m.p. 209–212 °C; HRFABMAS $[M+H]^+$ *m/z* 293.10273 (calcd for $C_{15}H_{17}O_6$, 293.10293); UV λ_{max} (log ε) nm 241(3.9), 285(4.1), 337(3.3); IR (neat) ν_{max} (cm^{-1}) 3327, 1675, 1324, 1045, 751; NMR see Table I.

Single-crystal X-ray diffraction analysis of **1**

X-ray crystallographic data for **1.** – $C_{15}H_{16}O_5$, formula weight = 276.29, orthorhombic, space group: $P2_12_12_1$ (#19); a = 7.6632, b = 29.3374, c = 5.8038 Å; D_{calcd} = 1.41 g·cm^{-3}, µ(CuKα radiation λ = 1.54178 Å) = 8.85 cm^{-1}; Z = 4, 1307 independent reflections were measured out of $2\theta_{max}$ = 128.5 with a rotating anode diffractometer MacScience MXC 18 using CuKα radiation monochromator. The data were collected at 296 K from a

yellow prism (1.00×1.00×0.70 mm) using the ω-2θ scan technique.

The structure was solved by direct methods SAPI91 (Fan Hai-fu, 1991) and expanded using Fourier techniques DIRDIF92 (Beurskens *et al.*, 1992). The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included, but their positions were not refined; isotropic B values were refined. The final cycle of full-matrix least-squares refinement was based on 1307 observed reflections ($I > 3.00\sigma(I)$) and 198 variable parameters and converged (largest parameter was 0.68 times its esd) with unweighted and weighted agreement factors of: $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.050$, $R_w = [(\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o^2)]^{1/2} = 0.059$. All calculations were performed using the crystal structure analysis package teXsan crystallographic software package of Molecular Structure Corporation (1985 & 1992).

Acknowledgment

We thank Mr. Masashi Mizutani (Tobacco Science Research Laboratory of Japan Tobacco Inc.) for helpful measurement of the C-H COSY, NOESY and HMBC spectra. We also thank Dr. Masayoshi Kusama (Tobacco Science Research Laboratory of Japan Tobacco Inc.) for helpful measurement of the FABMAS spectra.

Barfield M. and Grant D. M. (1963), The effect of hyper conjugation on geminal spin-spin coupling constant. J. Am. Chem. Soc. **85**, 1899–1904.

Beurskens P. T., Admiraal G., Beurskens G., Bosman W. P., Garcia-Granda S., Gould R. O., Smits J. M. M. and Smykalla, C. (1992), The DIRDIF program system, Technical Report of the Crystallography Laboratory. University of Nijmegen, The Netherlands.

Fan Hai-Fu (1991), Structure Analysis Programs with Intelligent Control. Rigaku Corporation, Tokyo, Japan.

Gill M., Smrdel A. F. and Strauch R. J.(1990), Pigments of fungi. Part 12. Structure and absolute stereochemistry of antibiotic tetrahydroanthraqinones from the fungus *Dermocybe splendida* Hork. X-ray structure determination of Austrocortirubin phenylboronate and Austrocortilutein acetonide. J. Chem. Soc. Perkin Trans. 1, 1583–1592.

Imaizumi S., Tokumasu S., Nitta N., Fujimori T. and Yamada M., (1992), A new disease of paddy weed *Eleocharis kuroguwai* caused by *Dendryphiella* sp. Ann. Phytopath. Soc. Japan **58**, 158.

Jackman L. M. and Sternhell S. (1969,) Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry. Pergamon Press, London, pp. 290.

Summers M. F., Marzilli L. G. and A. Bax (1986), Complete ^1H and ^{13}C assignments of coenzyme B_{12} through the use of new two-dimensional NMR experiments. J. Am. Chem. Soc. **108**, 4285–4294.

Tanaka M., Ohra J., Tsujino Y., Sawaji M. and Fujimori T. (1994), Phytotoxin produced by *Nimbya scirpicola*. Biosci. Biotech. Biochem. **58**, 565–566.