

STRUCTURES OF A NOVEL BINAPHTHYL AND THREE NOVEL BENZOPHENONE DERIVATIVES WITH PLANT-GROWTH INHIBITORY ACTIVITY FROM THE FUNGUS *DALDINIA CONCENTRICA*

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A novel binaphthyl (**1**) and three novel benzophenone derivatives (**2-4**) have been isolated from the fungus (Ascomycetes) *Daldinia concentrica*. Their structures have been established by a combination of high resolution NMR spectra, X-ray crystallographic analysis and chemical degradation. Compounds **2** and **3** possess plant-growth inhibitory activity.

KEYWORDS fungus; Ascomycetes; *Daldinia concentrica*; binaphthyl; benzophenone derivative; X-ray crystallographic analysis

In our previous paper, we reported on the isolation and structure elucidation of seven novel drimane-type sesquiterpenoid ethers of isocitric acid, cryptoporin acids A-G having strong superoxide release inhibitory and anti-tumour-promoting activities, from the fungus *Cryptoporus volvatus* belonging to Polyporaceae.¹ In the course of the investigation of the biologically active substances from the fungus, we isolated a novel binaphthyl (**1**) and three novel benzophenone derivatives (**2-4**) from the AcOEt extract of *Daldinia concentrica* belonging to the Xylariaceae, together with a known binaphthyl (**5**).² Here we wish to report the isolation and structure elucidation of **1-4**.

The AcOEt extract (26.7g) of the dry material (424 g) of *D. concentrica* collected in Tokushima in 1993 was subjected repeatedly to column chromatography on Sephadex LH-20 (CHCl₃: MeOH = 1:1) and on silica gel (CHCl₃-AcOEt gradient) to afford **1**³ (1.67 g), **2**⁴ (2.58 g), **3**⁵ (1.67 g), **4**⁶ (0.13 g) as well as a known binaphthyl (**5**) (67mg).

The IR and ¹H NMR spectra of **1** (C₂₂H₁₈O₄) indicated the presence of a hydrogen-bonded phenolic hydroxyl [3360 cm⁻¹; δ_H 9.53 (s)] and a methoxy [δ_H 4.10 (s)] group. As **1** showed only half carbon signals of molecular formula in the ¹³C NMR spectrum, **1** might be a symmetrical dimer. Acetylation (Ac₂O, pyridine) of **1** afforded a diacetate (**6**) [1760 cm⁻¹; δ_H 2.68 (3H, s, -OAc)] indicating the presence of two phenolic hydroxyl groups. Compound **1** was treated with BBr₃ in CH₂Cl₂ at -78°C to give **5**, followed by acetylation to afford a tetraacetate (**7**); these were identical with the authentic data on **5** and **7**,² respectively. The structure of **1** was finally established as 1, 1'-dihydroxy-8, 8'-dimethoxybinaphthyl by NOE difference spectrum of diethyl ether (**8**) [δ_H 1.58 (t), 4.22 (q), each J=6.8 Hz, 2xOEt] of **1**.

The IR and ¹H NMR (acetone-d₆) spectra of **2** (C₁₇H₁₆O₆) indicated the presence of two phenolic hydroxyl [3350 cm⁻¹; δ_H 10.06, 11.94 (each 1H, s)], two methoxy [δ_H 3.85, 4.00 (each 3H, s)], and one hydrogen bonded conjugated formyl [1650 cm⁻¹; δ_H 10.16 (1H, s)] groups. Methylation (MeI/ NaH/DMF) gave a dimethyl ether (**9**), indicating the presence of two phenolic hydroxyl groups. Acetylation of **2** afforded a monoacetate (**10**) and a diacetate (**11**). Ethylation (EtI/K₂CO₃/

acetone, reflux) of **2** gave a diethyl ether (**12**) [$C_{24}H_{28}O_6$; EI-MS: m/z 412 (M^+); 1H NMR ($CDCl_3$): δ 2.16 (s, -COMe)] by aldol condensation. Compound **2** was treated with *p*-TsOH/MeOH to afford an acetal derivative (**13**) [δ_H 6.51 (1H, s, H-8)]. Compound **9** was reduced with $LiAlH_4$, followed by acetylation to afford **14**. Hydrogenolysis ($H_2/20\%Pd-C$) of **14** afforded a diphenyl methane derivative (**15**). The structure of **2** was determined as 2-formyl-2', 5-dihydroxy-5'-methyl-3, 3'-dimethoxybenzophenone from the above results and NOE difference spectra of **2**, **12**, **14** and **15**, as shown in Fig. 1.

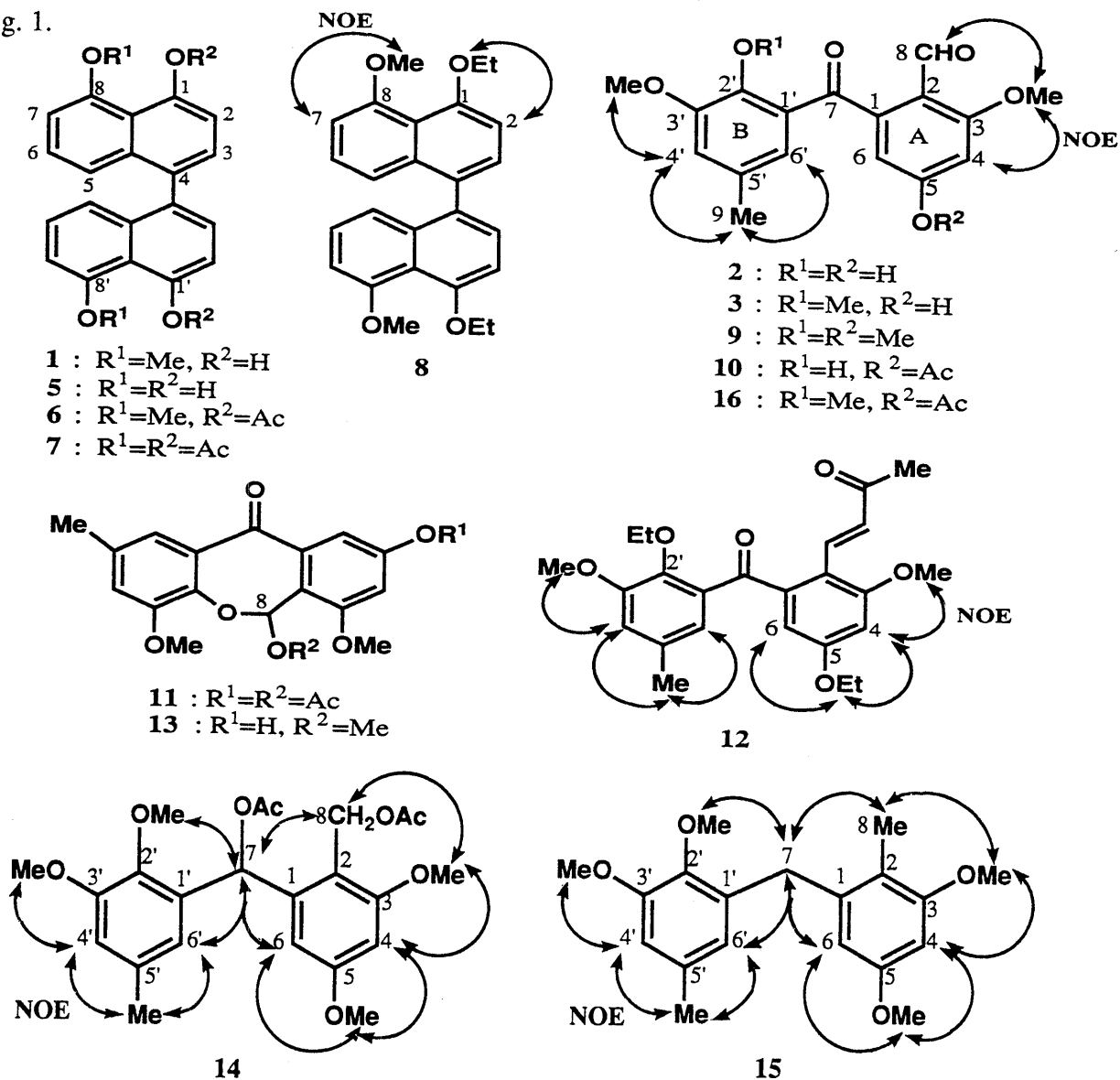


Fig. 1.

The 1H and ^{13}C NMR spectra of **3** ($C_{18}H_{18}O_6$) were similar to those of **2**, except for the presence of three methoxy [δ_H 3.40, 3.83 and 3.97 (each 3H, s)] in place of a hydrogen-bonded phenolic hydroxyl group [δ_H 11.94 (1H, s)]. Methylation of **3** gave a monomethyl ether (**9**), and the acetylation gave a monoacetate (**16**), indicating the presence of one phenolic hydroxyl group. The structure of **3** was finally established as C-2' methyl ether of **2** by X-ray crystallography⁷⁾, as shown in Fig. 2. In the 1H NMR spectrum of **3**, C₂-OMe appeared at remarkably high field (δ_H 3.40). This chemical shift is caused by the paramagnetic effect of the benzene ring A, as shown in Fig. 2.

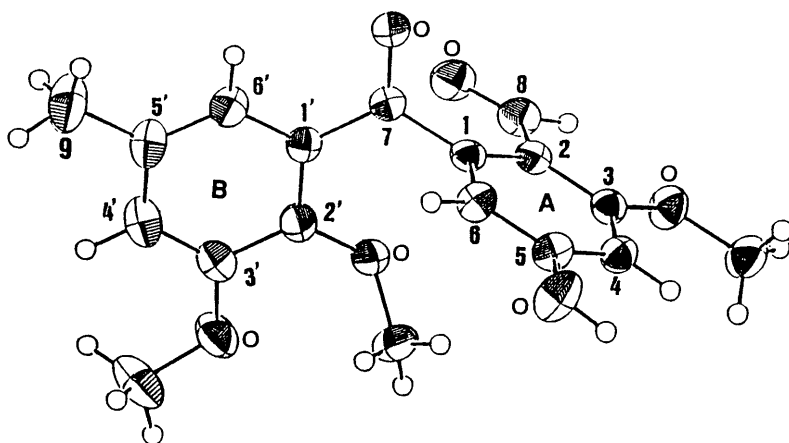


Fig. 2. ORTEP Drawing of 3

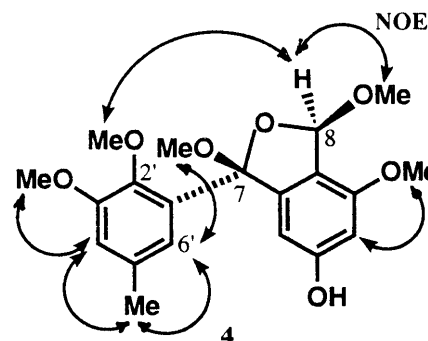


Fig. 3. NOE Difference Spectra of 4

The ^1H and ^{13}C NMR spectra of **4** ($\text{C}_{20}\text{H}_{24}\text{O}_7$) indicated the presence of five methoxy [δ_{H} 3.22, 3.43, 3.60, 3.63, and 3.76 (each 3H, s)], an acetal [δ_{H} 6.11 (IH, s, H-8); δ_{C} 99.6 (d, C-8)] and a ketal [δ_{C} 109.3 (s, C-7)] signal. The stereostructure of **4** was deduced from careful analysis of NOE difference spectra as shown in Fig. 3. Compound **4** may be racemate since the optical rotation is $[\alpha]_{\text{D}} \pm 0^\circ (\text{CHCl}_3)$. Compound **3** was treated with *p*-TsOH/MeOH to afford **4** easily. As MeOH was used in the process of isolation, compound **4** might be an artifact arising from **3**.

Compounds **2** and **3** completely inhibited germination of the root of rice in husk at 5 ppm, and other bioassays of the new compounds are in progress.

ACKNOWLEDGEMENT This work was partly supported by a Grant-in-Aid for Cancer Research from the Ministry of Health and Welfare, Japan.

REFERENCES AND NOTES

- 1) Y. Asakawa, T. Hashimoto, Y. Mizuno, M. Tori, Y. Fukazawa, *Phytochemistry*, **30**, 1555 (1991).
- 2) J. M. Anderson, J. Murray, *Chem. and Ind.*, **1956**, 376.
- 3) HR-MS: m/z 346.1201, $\text{C}_{22}\text{H}_{18}\text{O}_4$ requires 346.1205 ; EI-MS: m/z 346 (M^+ , 100%), 331, 316, 299 ; FT-IR (KBr) cm^{-1} : 3360 (OH), 1610; 1590, 1080 ; UV (EtOH) λ_{max} nm (log ϵ): 226 (4.42), 322 (3.72).
- 4) HR-MS: m/z 316.0945, $\text{C}_{17}\text{H}_{16}\text{O}_6$ requires 316.0951 ; EI-MS: m/z 316 (M^+ , 100%), 301, 287 , FT-IR (KBr) cm^{-1} : 3350 (OH), 1640; 1020 ; UV (EtOH) λ_{max} nm (log ϵ): 214 (4.43), 272 (4.21), 323 (4.05).
- 5) HR-MS: m/z 330.1077, $\text{C}_{18}\text{H}_{18}\text{O}_6$ requires 330.1104 ; EI-MS: m/z 330 (M^+ , 100%), 315, 299, 284 , FT-IR(KBr) cm^{-1} : 3180 (OH), 1670; 1030 ; UV (EtOH) λ_{max} nm (log ϵ): 213 (4.39), 262 (4.02), 321 (3.96).
- 6) $[\alpha]_{\text{D}}^{20} \pm 0^\circ$ (c1.0, CHCl_3); HR-MS: m/z 376.1537, $\text{C}_{20}\text{H}_{24}\text{O}_7$ requires 376.1522 ; EI-MS: m/z 376 (M^+), 345, 195 (100%); FT-IR (KBr) cm^{-1} : 3430 (OH), 1620; 1070 ; UV (EtOH) λ_{max} nm (log ϵ): 210 (4.56), 284(3.76).
- 7) The crystal data for **3** are as follows : monoclinic; space group $\text{P } 2_1/c$ with $a=13.222$ (5), $b=11.982$ (4), $c=11.205$ (4) Å, $\beta=111.83$ (3)°, $V=1648$ (1)Å³, $Z=4$, and Cu K- α ($\lambda=1.54178$) by Mac Science MXC 18 instrument. Final R value was 0.059 for 3105 reflections.

(Received May 2, 1994; accepted June 3, 1994)