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METABOLITES OF *FUSARIUM SOLANI*

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Key Word Index—*Fusarium solani*; Deuteromycetes.

Abstract—Three metabolites and one derivative produced by *F. solani* have been identified as 5,10-dihydroxy-7-methoxy-3-methyl-1H-naphtho-[2,3-*c*]-pyran-1,6,9-trione (anhydrofusarubin lactone); 1,5,10-trihydroxy-7-methoxy-3-methyl-1-H-naphtho-[2,3-*c*]-pyran-6,9-dione; 5,10-dihydroxy-1,7-dimethoxy-3-methyl-1H-naphtho-[2,3-*c*]-pyran-6,9-dione and 2,3-dihydro-5-hydroxy-8-methoxy-2,4-dimethyl-naphtho-[1,2-*b*]-furan-6,9-dione.

INTRODUCTION

This is the last report in a series of publications on the production of metabolites from *Fusarium solani* [1–5]. *Fusarium solani* (Mart.) Appel and Wr. Emend. Snyd. and Hans., a common soil fungus in citrus groves, can be readily isolated from vascular tissue of fibrous roots from citrus trees affected with blight [1]. Vascular translocation of fungal secondary metabolites with phytotoxic properties could account for some of the foliar symptoms of blight. Large quantities of these metabolites were required for field and greenhouse testing. In this series of publications we have identified 18 metabolites produced by *F. solani*. Six of the 18 were new compounds and we prepared eight derivatives of some of the metabolites.

RESULTS AND DISCUSSION

In the large-scale production of metabolites of *F. solani* a number of runs were made under varying conditions [4]. Two very dark purple to black pigments were produced many times. There are three purple metabolites that have the same R_f in solvent systems A and B (see Exp.) on silica gel GF plates. They are compounds **1** and **2** and an unidentified metabolite **5**. Solvent system C will separate **1** and **2**, but not **2** and **5**. Solvent system D will separate **1**, **2** and **5** on silica gel GF. Use of silica gel HF 60 and solvent systems A or C, without acid, will separate compounds **1**, **2**, **3** and **5**. A minor purple constituent of these was 5,10-dihydroxy-7-methoxy-3-methyl-1H-naphtho-[2,3-*c*]-pyran-1,6,9-trione **1**. Compound **1** was first isolated from *Nectria haematococca* by Parisot *et al.* [6] and called anhydrofusarubin lactone. Our NMR and mass spectral data were in agreement with this reference, but in the UV/vis spectra we found absorption maxima at 255, 312, 330 inf., 508 inf., 536, 576, 612 nm, whereas ref. [6] reported values of 240, 285, 355, 500 nm. Parisot *et al.* [6] also reported a hydroxy absorption in the IR spectrum that we did not observe.

There are two possible tautomeric forms of **1**, and structure assignment is based on the resonance of H-8 in the ^{1}H NMR spectrum [7]. A major product from several runs was compound **2**. The proposed structure for **2** was based on the NMR and mass spectra. In $CDCl_3$ the H-1 peak is at δ6.73. When run in Me_2SO the H-1 peak is at 6.55 (*d*, $J = 6.2$) and the OH-1 peak is at 6.82 (*d*, $J = 6.2$). Addition of D_2O removes the signal at δ6.82 and a singlet for H-1 appears at 6.63. Treatment of **2** with acid in methanol gave compound **3**.

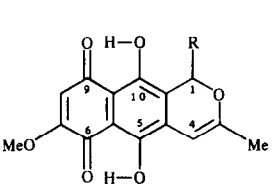
A trace metabolite which had previously been isolated from still cultures [1] was shown to be 2,3-dihydro-5-hydroxy-8-methoxy-2, 4-dimethyl-naphtho-[1,2-*b*]-furan-6,9-dione **4** by examination of spectral data and comparison with a similar compound which contained a hydroxymethyl group instead of a methyl at C-4 [4]. Compounds **2**, **3** and **4** are reported for the first time.

EXPERIMENTAL

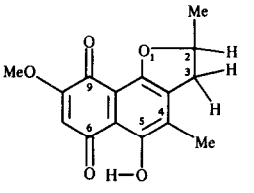
^{1}H NMR (270 MHz, TMS as internal standard) in $CDCl_3$ or $(CD_3)_2$ SO and MS were obtained through the Chemistry Department of Florida State University. Mps: uncorr.

TLC solvent systems. (A) C_6H_6–$MeNO_2$–HOAc (75:25:2), (B) C_6H_6–Me_2CO–HOAc (40:10:1), (C) $CHCl_3$–HOAc (200:1), (D) $CHCl_3$–CH_3NO_2 (9:1). TLC plates were 250 μm silica gel GF and 1 mm silica gel HF 60. Column chromatography: Kieselgel 60 reinst (70–230 mesh ASTM) E. Merck Dramstadt, 5 × 20 cm. The silica was deactivated with HOAc and H_2O, washed with Me_2CO and then $CHCl_3$, then eluted with $CHCl_3$, $CHCl_3$–Me_2CO, 2, 5, 10 and 15%.

5,10-*Dihydroxy*-7-*methoxy*-3-*methyl*-1H-*naphtho*-[2,3-c]-*pyran*-1,6,9-*trione* (**1**). MS *m/z* 302, (100%), 287, (14.5%); dark crystals from $CHCl_3$ mp 300°; IR ν_{max}^{KBr} cm^{-1}: 1745, 1650sh, 1610, 1582, 1532, 1470, 1435, 1400, 1375sh, 1350, 1300, 1275sh,



1 R = O
2 R = H,OH
3 R = H, MeO



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1260, 1230, 1190, 1175, 1155, 1135, 1115, 1060, 1025w, 980, 955, 935w, 875, 865sh, 845sh, 800, 780, 725, 710; ^{1}H NMR: δ2.38 (3H, *s*, Me-3), 3.97 (3H, *s*, MeO-7), 6.30 (1H, *s*, H-8), 6.84 (1H, *s*, H-4), 12.75 (1H, *s*, OH-5), 14.28 (1H, *s*, OH-10), addition of D_2O removes the OH signals at δ12.75 and 14.75; UV λ_{max}^{MeOH} nm (log ε): 255 (4.25), 312 (3.55), 330 inf. (3.46), 508 inf. (3.72), 536 (3.77), 576 (3.72), 612 (3.49).

1,5,10-*Trihydroxy*-7-*methoxy*-3-*methyl*-1H-*naphtho*-[2-3-c]-*pyran*-6,9-*dione* (**2**). MS *m/z* 304 (31.4%), 289 (11%), 261 (100%), $C_{15}H_{12}O_7$ requires 304.0581, found 304.0590; deep purple crystals (Me_2CO) mp 245° on a preheated block; IR ν_{max}^{KBr} cm^{-1}: 3425*s*, 1600, 1580, 1440, 1400, 1385sh, 1280sh, 1250, 1225sh, 1190w, 1155, 1110w, 1070, 1040, 990, 955, 890, 860*br*, 805; ^{1}H NMR $CDCl_3$: δ2.18 (3H, *s*, Me-3), 3.94 (3H, *s*, MeO-7), 6.26 (1H, *s*, H-8), 6.45 (1H, *s*, H-4), 6.73 (1H, *s*, H-1), 12.85 (1H, *s*, OH-5), 13.25 (1H, *s*, H-10), addition of D_2O removes the OH signals at δ12.85 and 13.25; $(CD_3)_2$SO: δ2.04 (3H, *s*, Me-3), 3.84 (3H, *s*, MeO-7), 6.10 (1H, *s*, H-8), 6.20 (1H, *s*, H-4), 6.55 (1H, *d*, J = 6, H-1), 6.82 (1H, *d*, J = 6, OH-1), 12.76 (1H, *s*, OH-5), 13.22 (1H, *s*, OH-10). Addition of D_2O removes the OH signals at δ6.82, 12.76, 13.22, and the doublet at 6.55 appears as a singlet at 6.63; UV λ_{max}^{MeOH} nm (log ε): 228 (4.06), 263 (4.05), 278sh (4.01), 343 (3.23), 509 (3.80), 535 (3.87), 572 (3.71).

5,10-*dihydroxy*-1,7-*dimethoxy*-3-*methyl*-1H-*naphtho*-[2,3-c]-*pyran*-6,9-*dione* (**3**). MS *m/z* (rel. int.): 318 (34.7), 287 (88.9), 286 (100); $C_{16}H_{14}O_7$ requires 318.0738, found 318.0764; purple crystals (C_6H_6) mp 190° on a preheated block; IR ν_{max}^{KBr} cm^{-1}: 1605, 1585, 1430, 1380, 1310w, 1250, 1220, 1185, 1150, 1080, 1050, 1015, 955, 885w, 865w, 815, 790sh; ^{1}H NMR $CDCl_3$: δ2.15 (3H, *s*, Me-3), 3.62 (3H, *s*, MeO-1), 3.93 (3H, *s*, MeO-7), 6.24 (1H, *s*), 6.25 (1H, *s*), 6.29 (1H, *s*), 12.80 (1H, *s*, OH-5), 13.24 (1H, *s*, OH-10), addition of D_2O removes signals at δ12.80 and 13.24; UV λ_{max}^{MeOH} nm (log ε): 228 (4.01), 263 (3.98), 278sh (3.96), 342 (3.15), 507 (3.68), 535 (3.75), 572 (3.63).

2,3-*Dihydro*-5-*hydroxy*-8-*methoxy*-2,4-*dimethyl*-*naphtho*-[1,2-b]-*furan*-6,9-*dione* (**4**). MS *m/z* (rel. int.): 274 (100), 259 (23), 245 (53), $C_{15}H_{14}O_5$ requires 274.084, found 274.087; red crystals (EtOAc) mp 220–224°; IR ν_{max}^{KBr} cm^{-1}: 1665, 1625, 1585, 1460, 1435, 1405, 1380sh, 1350w, 1270w, 1240, 1210, 1190, 1160, 1105w, 1085, 1045, 1025, 1010sh, 960, 935, 875, 860, 810, 790, 760, 725; ^{1}H NMR: δ1.59 (3H, *d*, J = 6, Me-2), 2.25 (3H, *s*, Me-4), 2.75 (1H, *dd*, J = 17, 6.5, H-3), 3.30 (1H, *dd*, J = 17, 9, H-3), 3.88 (3H, *s*, MeO-8), 5.20 (1H, *m*, H-2), 6.06 (1H, *s*, H-7), 13.50 (1H, *s*, OH-5) addition of D_2O removes the OH signal at δ13.50; UV λ_{max}^{MeOH} nm (log ε): 225 (4.70), 299 (4.03), 480 (3.99), 500 (3.97), 532 (3.63).

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A BIANTHRONE *C*-GLYCOSIDE FROM *ASPHODELUS RAMOSUS* TUBERS

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Key Word Index—*Asphodelus ramosus*; Liliaceae; *C*-glycosides; bianthrones; ^{13}C NMR.

Abstract—Ramosin, the first member of the new class of bianthrone *C*-glycosides, has been isolated from tubers of *Asphodelus ramosus*. On the basis of spectral evidence, its structure was established as (−)-10′-*C*-[β-D-glucopyranosyl]-1,1′,8,8′,10,10′-hexahydroxy-3,3′-dimethyl-10,7′-bianthracene-9-9′-dione. The complete ^{13}C chemical shift assignment of the compound is reported.

INTRODUCTION

In connection with our studies [1, 2] on Liliaceae metabolites we have investigated the components of *Asphodelus ramosus* tubers. From the ethereal extract of these tubers we isolated several bianthrone *C*-glycosides. In this paper we describe the isolation and structural determination, obtained only on the basis of spectroscopic evidence, of the major metabolite **1**, named ramosin.

RESULTS AND DISCUSSION

The negative-ion FAB-mass spectrum of **1** showed a pseudomolecular ion peak at *m/z* 671 $[M-H]^-$ that,