Isolation of compound **2**. The *n*-butanol fraction on subsequent column chromatography over silica gel (EtOAc–MeOH 7:3) furnished compound **2** as a viscous light yellow solid (100 mg).

Acetylation of **2**. Compound **2** (50 mg) on acetylation with Ac_2O/pyridine afforded heptaacetate **2a** (40 mg); IR ν_{max}^{neat} cm^{-1}: 2980, 2940, (Me), 1750 (OAc), 1650, 1440, 1370, 1230 (ester), 1040, 910, 920, 760, 600; ^1H NMR ($CDCl_3$): δ 1.15 (6H, *d*, $J = 8$ Hz, 2 × Me), 1.95 (21H, *brs*, 7 × Ac), 3.55 (1H, *m*, methine proton), 4.70 (2H, *d*, $J = 8$ Hz, Ar–CH_2) 4.0–4.2, 4.7–5.0 (12H, *m*, sugar protons), 4.98 (1H, *d*, $J = 7$ Hz, glycosyl H-1), 5.20 (1H, *d*, $J = 7$ Hz, galactosyl H-1), 6.70, 7.65 (2H each *d*, $J = 9$ Hz, Ar–H); ^{13}C NMR ($CDCl_3$); δ 15.0 (C-8, 9), 20.2 (7 × MeCO), 38 (C-7), 40(C-10), 62.1 (C-6′), 64.1 (C-6″), 65.8 (C-5′), 67.1 (C-3″), 69(C-4′), 73.0(C-2″), 75.9 (C-4″), 77.3, 77.5 (C-2′, 3′), 79(C-5″), 94.3, 94.8 (C-1′, 1″), 127 (C-3, 5), 128.5 (C-2, 6), 137(C-1), 145 (C-4), 170 (7 × MeCO).

Mild hydrolysis of **2**. Compound **2** (30 mg) was dissolved in 2% H_2SO_4 with addition of a few drops of MeOH and heated gently on a water bath for 1 hr. The hydrolysates were examined for sugars after each interval of 5 min. by co-PC (Whatman No. 1, *n*-BuOH–C_6H_6–pyridine–H_2O = 5:1:3:3, 48 hr) along with authentic samples of glucose and galactose. It was observed that the first sugar obtained during hydrolysis was glucose (hrf 35.0) while galactose (hrf. 30.5) was detected later.

Compound **3**. Obtained as light yellow oil by hydrolysis of compound **2** with dil. HCl on extraction with ether. ^1H NMR and MS data identical to those of cuminyl alcohol.

Acknowledgements—The authors thank Dr A. Husain (Director, CIMAP, Lucknow) and CSIR, New Delhi, for awarding a Research Associateship to one of us (BA).

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Phytochemistry, Vol. 27, No. 10, pp. 3310–3311, 1988.
Printed in Great Britain.

0031–9422/88 $3.00 + 0.00

FUSALANIPYRONE, A MONOTERPENOID FROM *FUSARIUM SOLANI*

WOLF-RAINER ABRAHAM and HANS-ADOLF ARFMANN

GBF-Gesellschaft für Biotechnologische Forschung mbH, Mascheroder Weg 1, D-3300 Braunschweig, F.R.G.

(*Received* 10 *February* 1988)

Key Word Index—*Fusarium solani*; Deuteromycetes; Moniliales; fungal metabolite; monoterpenoid; α-pyrone; fusalanipyrone.

Abstract—6-(2′*Z*-butenyl)-3-Methyl-α-pyrone was isolated from the fungus *Fusarium solani* strain DSM 62416 and named fusalanipyrone. This monoterpenoid was not present in *F. solani* strain DSM 62413.

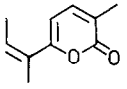
INTRODUCTION

Some species of the genus *Fusarium* are known to produce sesquiterpenes. While some strains produce sesquiterpenoids with the trichothecane skeleton, *F. culmorum* (W. G. Smith) Sacc. produces culmorin, a longicamphandiol. Up to now, no monoterpenoids have been reported from this genus.

RESULTS AND DISCUSSION

When grown on a medium containing 1% glucose, 1% universalpeptone (Merck), 2% malt extract and 0.3% yeast extract, *F. solani* (Martins) Saccardo DSM 62416 excreted an UV absorbing compound into the medium. Extraction of the medium and chromatography of the extract gave a viscous oil. The mass spectrum gave a

molecular ion of the composition $C_{10}H_{12}O_2$. The ^1H NMR spectrum displays a broad doublet at δ 1.81 of three protons. This methyl group is coupled to a double quartet at δ 6.62 of one proton which has a long range coupling to a methyl group at δ 1.84. This coupling system belongs to a 2-butenyl moiety. Irradiation at δ 6.62 caused an NOE of the resonance at δ 1.84 which pointed to a *Z*-configuration of the 2-butenyl side chain. Another group of protons contains a doublet at δ 6.04 of one proton which is coupled with a doublet at δ 7.12 (1H). This doublet at lowfield displayed a small coupling to a methyl group at δ 2.09. The absorption in the IR spectrum at 1720 cm^{-1} together with the shifts of the protons in the NMR spectrum is only in agreement with a 3,6-disubstituted α-pyrone. Taking all the information together the metabolite produced by *F. solani* DSM 62416 is 6-(2′*Z*-butenyl)-3-methyl-α-pyrone (**1**) which we named fusalanipyrone.



1

To the best of our knowledge this compound has never been described as a natural product. The 3′*E*-stereoisomer was synthesized in 1970 by Dreiding and coworkers [1]. A closely related compound, nectriapyrone (4-methoxy-fusalanipyrone), was isolated in 1975 by Nair and Carey from *Thyronectria missouriensis* (Ell et Ev) Seaver [2]. Nectriapyrone displays antibacterial activity against *Staphylococcus aureus*, fusalanipyrone in contrast is not active against *Staphylococcus* and *Escherichia coli*, but is a weak antibiotic against *Candida albicans*, *Mucor* and *Trichoderma koningii*.

The occurrence of monoterpenoids in fungi is very rare and has only been reported for *Thyronectria missouriensis*, *Pleurotus euosmus* [3], *Kluyveromyces lactis* [4], *Ambrosiozyma monospora* v. d. Walt [5], *Phellinus* spp. [6], *Eremothecium ashbyii* [7], *Ceratocystis* spp. [8], *Trametes odorata* [9], *Gloeophyllum odoratum* [10], and *Cystostereum muraii* [11]. The fact that *F. solani* strain DSM 62413 does not produce fusalanipyrone underlines the observation that relatively few strains posses the ability of monoterpenoid biosynthesis.

EXPERIMENTAL

The fungus was precultivated at 27° and 100 rpm in 5 × 100 ml EM flasks containing 20 ml of the following medium: 1% glucose, 1% universalpeptone (Merck), 2% malt extract and 0.3% yeast extract. After 48 hr the cultures were transfered to five 1 l flasks filled with 200 ml of the medium and incubated for another period of 24 hr. Then after 1, 3, and 7 days samples were taken and analysed as follows: to 1 ml of culture broth 0.2 ml EtOAc were added and shaken for 2 min prior to centrifugation. 10 μl of the EtOAc extract were subjected to HPTLC (CH_2Cl_2). The spots were visualized by UV absorption at 254 nm or by spraying with anisaldehyde–H_2SO_4 in HOAc and heating to 140° for 1 min.

Extraction and purification. Culture medium and mycelia were separated by filtration and both extracted (× 3) with EtOAc. The solvent was evapd and the crude extract separated on silica gel-60 columns with a *n*-hexane–EtOAc acetate gradient (changing from 19:1 to 1:1). When necessary the collected fractions were purified further by prep. TLC. Under these conditions *Fusarium solani* DSM 62416 produced 30 mg/l 2-phenylethanol and 4 mg/l fusalanipyrone.

Spectral measurements. NMR; ^1H at 400 MHz, ^{13}C at 75.5 MHz, $CDCl_3$ was solvent and TMS int. standard; IR: $CHCl_3$; MS: 70 eV.

Fusalanipyrone (**1**). Colourless, viscous oil. IR: 1720 cm^{-1}. ^1H NMR: δ 1.81 (3H, *br d*, $J = 7$ Hz, 4′-H), 1.84 (3H, *br s*, 1′-H, 2.09 (3H, *br s*, 5′-H), 6.04 (1H, *d*, $J = 7$ Hz, 5-H), 6.62 (1H, *br q*, 3′-H), 7.12 (1H, *br d*, $J = 7$ Hz, 4-H).

Acknowledgement—We are indebted to Dr E. Forche and Dr F. Sasse for testing the biological activity of fusalanipyrone.

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