Note

Isolation and Structure of
a New Diprenyl Phenol,
Colletorin B Produced by
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Cephalosporium diospyri causes the wilt disease of American persimmon.¹⁾ In the course of our researches on the metabolites produced by this fungus, one new diprenyl phenol (**1**) and two known compounds, **2** which was identified with aschochlorin²⁾ and **3** with LL-Z 1272 *e*,³⁾ were obtained. This note describes the isolation and structural elucidation of these compounds.

Cephalosporium diospyri IFO 6118 was shake-cultured on 100 ml of a medium containing (g per 1 liter of water) K_2HPO_4 (1.3), KH_2PO_4 (1.0), $(NH_4)_2SO_4$ (0.5), $MgSO_4 \cdot 7H_2O$ (0.5) and dextrose (50) in a 500 ml flask at 25°C for 40 days. The culture filtrate (about 17 liters) was concentrated *in vacuo* to one-tenth of its original value and extracted with ethyl acetate. The residue (467 mg) obtained after removing the ethyl acetate was chromatographed on the column of silica gel (Malincrodt 100 mesh, eluted with chloroform) and further purified by the use of preparative TLC (developed with chloroform-methanol, 25:1, v/v). Three compounds, **1**, **2** and **3**, were isolated as crystals; these yields were 52, 22 and 26 mg respectively.

Compound (**1**), mp 124~126°C has the molecular formula $C_{18}H_{24}O_3$ from the high resolution mass spectrum (HR-MS) m/z 288.1736 (M^+ , 288.1726 calcd. for $C_{18}H_{24}O_3$). Its spectral data are as follows. IR ν_{max}^{KBr} cm^{-1} : 3130, 1600, 1250. UV λ_{max}^{EtOH} (e): 207 (15200), 223 (11600),

238 (8860), 300 (18700), 340sh (5930). 1H NMR $\delta_{TMS}^{CDCl_3}$: 1.59 (3H, s, 7'-CH₃ or 8'), 1.68 (3H, s, 8' or 7'-CH₃), 1.81 (3H, d, $J=0.8$ Hz, 3'-CH₃), 2.08 (4H, m, 4' and 5'), 2.49 (3H, s, 6-CH₃), 3.41 (2H, d, $J=7.3$ Hz, 1'), 5.05 (1H, m, 6'), 5.26 (1H, br. t, $J=7.3$ Hz, 2'), 6.21 (1H, s, 5), 6.22 (1H, br. s, 4-OH), 10.07 (1H, s, 1-CHO), 12.77 (1H, s, 2-OH). Since the 1H NMR spectrum showed the presence of an aldehyde group (δ 10.07), a hydrogen-bonded OH group (δ 12.77), another phenolic OH group (δ 6.22), a phenylic methyl group (δ 2.49), a phenylic proton (δ 6.21) and a diprenyl group (the other proton), and the UV spectrum revealed the maxima at λ_{max}^{EtOH} 300 nm and 340 nm, it is suggested that **1** is an orsellinaldehyde derivative containing a diprenyl side-chain. These data are quite similar to those reported for colletochlorin B ($C_{18}H_{23}O_3Cl$), except that **1** possesses a phenylic proton and no chlorin, whereas colletochlorin B possesses a chlorine but no phenylic proton.⁴⁾ Therefore, the structure of **1** was elucidated to be that shown in the figure. The ^{13}C -NMR spectrum described as follows offers additional evidence for this structure. $\delta_{TMS}^{CDCl_3}$: 16.2 (q, 3'-CH₃), 17.7 (q, 7'-CH₃), 18.0 (q, 6-CH₃), 21.2 (t, 1'), 25.7 (q, 8'), 26.4 (t, 5'), 39.7 (t, 4'), 110.9 (d, 5), 111.5 (s, 3'), 113.3 (s, 1), 121.0 (d, 2'), 123.7 (d, 6'), 132.1 (s, 7'), 139.9 (s, 3'), 141.9 (s, 6), 162.6 (s, 2), 163.6 (s, 4), 192.9 (d, 1-CHO). Such diprenyl phenols as **1** and colletochlorin B had been isolated from *Colletotrichum nicotianae*.^{4,5)} According to their nomenclature, **1** is named colletorin B.

Compound (**2**), mp 167~170°C. HR-MS m/z : 404.1728 (M^+ ; calcd. for $C_{23}H_{29}O_4Cl$, 404.1753. IR ν_{max}^{KBr} cm^{-1} : 3350, 1700, 1620, 1240. UV λ_{max}^{EtOH} nm (e): 238 (22200), 265sh (10600), 353 (24800). 1H -NMR $\delta_{TMS}^{CDCl_3}$: 0.69 (3H, s, 6'-CH₃), 0.80 (3H, d, $J=4.9$ Hz, 7'-CH₃ or 11'-CH₃), 0.83 (3H, d, $J=4.9$ Hz, 11-CH₃ or 7'-CH₃), 1.62 (1H, m, 7'), 1.92 (3H, d, $J=1.0$ Hz, 3'-CH₃), 1.95 (2H, m, 8'), 2.38 (3H, m, 9' and 11'), 2.60 (3H, s, 6-CH₃), 3.53 (2H, d, $J=7.5$ Hz, 1'), 5.37 (1H, d, $J=16.1$ Hz, 4'), 5.53 (1H, br. t, $J=7.5$ Hz, 2'), 5.90 (1H, d, $J=16.1$ Hz, 5'), 6.50 (1H, br. s, 4-OH), 10.14 (1H, s, 1-CHO), 12.70 (1H, s, 2-OH). $[\alpha]_D^{25} - 30^\circ$ ($c=0.18$, methanol). All the spectral data for **2** are in agreement with those of aschochlorin which has been isolated from several fungi.^{3,6,7)} This antibiotics shows inhibitory activities against some viruses and fungi *in vitro*.²⁾

Compound (**3**), mp 168~171°C, $C_{23}H_{32}O_4$, IR ν_{max}^{KBr} cm^{-1} : 3380, 1690, 1630. UV λ_{max}^{EtOH} nm (e): 209 (20200),

223 (21900), 238 (18600), 299 (28500), 340sh (10900). ^1H -NMR $\delta_{\text{TMS}}^{\text{CDCl}_3}$: 0.58 (3H, s, 6'-CH₃), 0.88 (3H, d, $J=3.8$ Hz, 7'-CH₃ or 11'-CH₃), 0.95 (3H, d, $J=3.8$ Hz, 11'-CH₃ or 7'-CH₃), 1.30~1.70 (3H, m, 5' and 7'), 1.84 (3H, s, 3'-CH₃), 1.80~2.15 (4H, m, 4' and 8'), 2.24~2.50 (3H, m, 9' and 11'), 2.49 (3H, s, 6-CH₃), 3.47 (2H, d, $J=6.6$ Hz, 1'), 5.27 (1H, t, $J=6.6$ Hz, 2'), 6.20 (1H, s, 5), 6.78 (1H, m, 4-OH), 10.11 (1H, s, 1-CHO), 12.65 (1H, s, 2-OH). On the basis of the above data, **3** was identified with LL-Z 1272 ϵ which had been obtained from *Tetrahymena pyriformis*.³⁾

Recently, colletorin B (1) has also been obtained from the mutant of *C. gregatum* type A which causes brown stem rot of azuki beans. The details of this finding will be reported in the future.

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