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Isolation and Structure of a New Diprenyl Phenol, Colletorin B Produced by Cephalosporium diospyri

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Cephalosporium diospyri causes the wilt disease of American persimmon. 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 aschochlorin and 3 with LL-Z, 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) K₂HPO₄ (1.3), KH₂PO₄ (1.0), (NH₄)₂SO₄ (0.5), MgSO₄ · 7H₂O (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 C₉H₂₄O₃ from the high resolution mass spectrum (HR-MS) m/z 288.1736 (M+, 288.1726 calcd. for C₉H₂₄O₃). Its spectral data are as follows. IR νmax cm⁻¹: 3130, 1600, 1250. UV λmax nm (ε): 207 (15200), 223 (11600), 238 (8860), 300 (18700), 340sh (5930). ¹H NMR δ DCl: 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, 6'), 5.26 (1H, br. t, J=7.3 Hz, 2'), 6.21 (1H, s, 5), 6.22 (1H, br. s, 4-0H), 10.07 (1H, s, 1-CHO), 12.77 (1H, s, 2-0H).

Since the 1 H 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 phenolic proton (δ 6.21) and a diprenyl group (the other proton), and the UV spectrum revealed the maxima at λmax 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 (C₉H₂₃O₃Cl), except that 1 possesses a phenylic proton and no chlorin, whereas colletochlorin B possesses a chlorine but no phenylic proton. Therefore, the structure of 1 was elucidated to be that shown in the figure. The ¹³C-NMR spectrum described as follows offers additional evidence for this structure.

UV λmax nm (ε): 207 (15200), 223 (11600), 238 (8860), 300 (18700), 340sh (5930). ¹H NMR δ DCl: 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, 6'), 5.26 (1H, br. t, J=7.3 Hz, 2'), 6.21 (1H, s, 5), 6.22 (1H, br. s, 4-0H), 10.07 (1H, s, 1-CHO), 12.77 (1H, s, 2-0H).

Therefore, the structure of 1 was elucidated to be that shown in the figure. The ¹³C-NMR spectrum described as follows offers additional evidence for this structure. δ DCl: 16.2 (q, 3'-CH₃), 17.7 (q, 7'-CH₃ or 8'), 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'), 131.2 (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 Colletotrichium nicotianae. According to their nomenclature, 1 is named colletorin B.

Compound (2), mp 167-170°C. HR-MS m/z: 404.1728 (M⁺); calcd. for C₂₃H₂₉O₄Cl, 404.1753. IR νmax cm⁻¹: 3350, 1700, 1620, 1240. UV λmax nm (ε): 238 (22200), 265sh (10600), 353 (24800). ¹H NMR δ DCl: 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), 2.46 (2H, m, 7'), 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'), 3.57 (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, 4-0H), 10.14 (1H, s, 1-CHO), 12.70 (1H, s, 2-0H). All the spectral data for 2 are in agreement with those of ascochlorin which has been isolated from several fungi. This antibiotics shows inhibitory activities against some viruses and fungi in vitro. Compound (3), mp 168~171°C, C₂₃H₃₂O₄. IR νmax cm⁻¹: 3380, 1690, 1630. UV λmax nm (ε): 209 (20200),...
$^1$H-NMR $\delta^{(CDCl_3)}$: 0.58 (3H, s, 6'-CH$_3$), 0.88 (3H, d, $J=3.8$ Hz, 7'-CH$_3$ or 11'-CH$_3$), 0.95 (3H, d, $J=3.8$ Hz, 11'-CH$_3$ or 7'-CH$_3$), 1.30 ~ 1.70 (3H, m, 5' and 7'), 1.84 (3H, s, 3'-CH$_3$), 1.80 ~ 2.15 (4H, m, 4' and 8'), 2.24 ~ 2.50 (3H, m, 9' and 11'), 2.49 (3H, s, 6-CH$_3$), 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 which had been obtained from *Tetrahyena 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.

REFERENCES