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ABSOLUTE CONFIGURATION OF (-)-SOLANAPYRONE A

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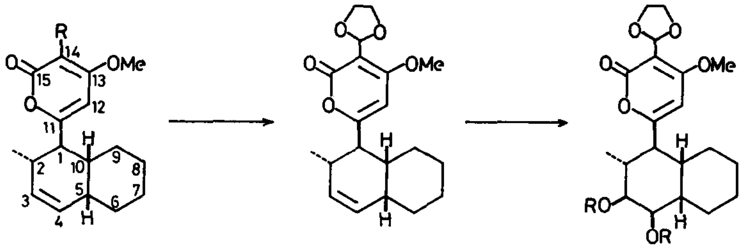
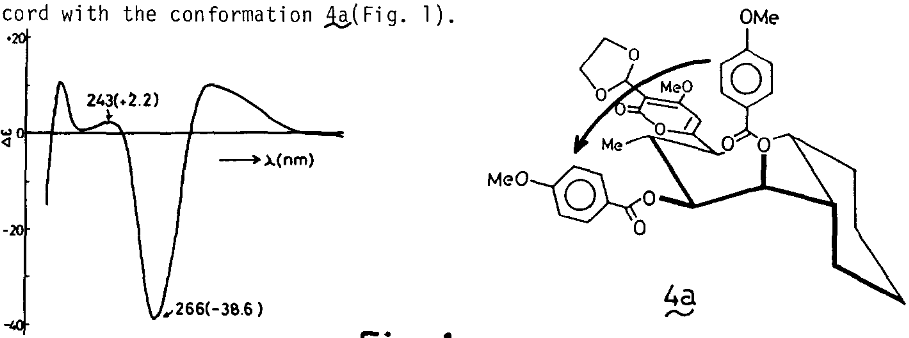
Abstract: Absolute configuration of (-)-solanapyrone A was confirmed by the application of CD exciton chirality method to the dibenzoate derivative.

Solanapyrone A(**1**)[1] is a phytotoxin isolated together with other toxic metabolites[1,2] from culture filtrate of <u>Alternaria solani</u> ASP-2, causal fungus of early blight disease of potato, and the structure and relative configuration of the phytotoxin have been elucidated. In this communication, we now describe the absolute configuration of (-)-solanapyrone A as **1** by the application of the CD exciton chirality method[3] to the dibenzoate derivative **4**.



1 R=-CHO
5 R=$-CH_2OH$
2
3 R=-H
4 R=$-CO\langle\bigcirc\rangle OMe$

Treatment of (-)-solanapyrone A(**1**) with ethylene glycol and TsOH in benzene at room temperature for 12 hr yielded an acetal **2**[4](55 %), $[\alpha]_D^{20}$ -51.7°(c=0.87, EtOH), molecular formula $C_{20}H_{26}O_5$ from high resolution MS m/z 346.1780(M^+, calcd. 346.1781). Oxidation of the acetal **2** with OsO_4 in pyridine gave a single product **3**[4](80 %), $[\alpha]_D^{20}$ -50°(c=1.1, EtOH), molecular formula $C_{20}H_{28}O_7$ from high resolution MS m/z 380.1820(M^+, calcd. 380.1835). The high stereoselectivity in the oxidation would be rationalized by the reason that the reagent (OsO_4) attacks from convex face of the molecule of the acetal **2**. The stereochemistry was confirmed by the ^1H NMR spectrum, in which a signal due to axial 3-H appeared as a double doublet(J=10.5 Hz and 3.0 Hz) at δ 3.35 ppm.[5,6] Treatment of the glycol **3** with p-methoxybenzoyl chloride in pyridine at room temperature for 12 hr afforded a dibenzoate **4**(97 %)[7], $[\alpha]_D^{20}$ -93°(c=1.15, EtOH), molecular formula $C_{36}H_{40}O_{11}$ from high resolution MS m/z 648.2574(M^+, calcd. 648.2571). No conformational change was observed in the transformation **3**→**4**, since the ^1H NMR spectrum exhibited the approptiate signals at δ 2.68(1H, dd, J=10.9, 10.9 Hz) due to axial 1-H, 5.16 (1H, dd, J=11.1, 3.0 Hz) due to axial 3-H, and 5.36(1H, dd, J=3.0, 2.6 Hz) due to equatorial 4-H in accord with the conformation 4a(Fig. 1).



CD spectrum of 4a

4a

Fig. 1

A straightforward application of the dibenzoate chirality method to 4 led to absolute configuration 4a, since the CD spectrum showed a negative first Cotton effect, λ^{EtOH}nm($\Delta\varepsilon$); 293(+9.3), 266(-38.6), 243(+2.2), 228(+0.5), 218(+9.8), which is expected for the stereostructure depicted in Fig. 1[8]. Therefore, (-)-solanapyrone A(1) has an absolute configuration, (1R, 2S, 5R, 10R), and having been chemically correlated with (-)-solanapyrone A(1), (-)-solanapyrone B(5) also has the same absolute stereochemistry as 1.

References and Footnotes

1. A. Ichihara, H. Tazaki, S. Sakamura, Tetrahedron Lett., 24, 5373(1983).
2. A. Ichihara, H. Tazaki, S. Sakamura, to be published.
3. N. Harada, K. Nakanishi 'Circular Dichroic Spectroscopy-Exciton Coupling in Organic Stereo-Chemistry', University Science Books, Mill Valley, CA, 1983.
4. Satisfactory spectral data(UV, IR and ^{1}H NMR) have been obtained for new compounds 2 and 3.
5. The CD spectrum of 3 showed only weak negative curve, λ^{EtOH}nm($\Delta\varepsilon$); 302(-0.8), 256(-0.23), 241(-0.37).
6. Any other possible diastereomers and conformers of 3 in the oxidation products are not compatible with the ^{1}H NMR data.
7. 4 UV $\lambda_{\max}^{\mathrm{EtOH}}$ nm(ε); 257(32100), 301(7800), IR $\nu_{\max}^{\mathrm{neat}}$ cm^{-1}; 1710, 1640, 1600, 1550, 1500, ^{1}H NMR(500 MH$_z$) $\delta_{\mathrm{TMS}}^{\mathrm{CDCl_3}}$ ppm; 0.89(3H, d, J=6.0 Hz, 2-CH$_3$), 1.31~1.81(8H, m, 6-~9-CH$_2$), 2.20(1H, dddd, J=13.3, 3.0, 2.9, 2.9 Hz, 5-H), 2.63(1H, br., 10-H), 2.68(1H, dd, J=10.9, 10.9 Hz, 1-H), 2.72(1H, br., 2-H), 3.81, 3.88, 3.94(each 3H, s, OCH$_3$), 3.97(2H, m, CHCH), 4.23(2H, m, CHCH), 5.16(1H, dd, J=11.1, 3.0 Hz, 3-H), 5.36(1H, dd, J=3.0, 2.6 Hz, 4-H), 6.08(1H, s, 12-H), 6.21(1H, s, -OCHO-), 6.81(2H, d, J=9.0 Hz, ArH), 6.99(2H, d, J=9.0 Hz, ArH), 7.83(2H, d, J=9.0 Hz, ArH), 8.07(2H, d, J=9.0 Hz, ArH).
8. Contribution of the pyrone ring in 4 to the CD spectrum was estimated to be small, since the chromophore is located in a rather remote position and almost lies in the same plane with two electric dipole transition moments of 3- and 4-benzoate groups.

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