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THE REVISED STRUCTURE OF PSEUDOANISATIN BY X-RAY CRYSTAL STRUCTURE DETERMINATION

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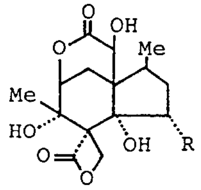
Abstract: *The structure of pseudoanisatin, a non-toxic constituent of Japanese star anise has been revised from* 3 *to* 5 *by an X-ray crystallographic analysis.*

Japanese star anise (*Illicium anisatum* L.) is well known for potent convulsant constituents, anisatin (1) and neoanisatin (2).[1-3] Pseudoanisatin,[4] $C_{15}H_{22}O_6$ is a non-toxic constituent of the same plant. One of us (N.K.) previously suggested[5] a structure (3) for pseudoanisatin. Recently, we found that ^{13}C-NMR spectrum of pseudoanisatin was not consistent with the previous structure (3) because of two singlets assignable to carbonyl carbons at 206 and 174 ppm (in d_5-pyridine with tetramethylsilane as an internal standard), although pseudoanisatin showed a strong carbonyl band at 1710 cm^{-1}. Presence of a ketonic group was chemically confirmed by the formation of an oxime (4). In order to obtain the correct structure of pseudoanisatin, we carried out an X-ray crystallographic analysis.

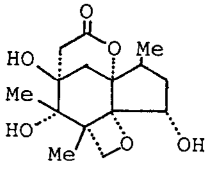
Pseudoanisatin forms monoclinic prisms from ethyl acetate, space group C2, Z=4, a=18.424, b=7.828, and c=10.279 Å, β=97.60°, U=1469.4 $Å^3$, D_O=1.357 g/cm^3. The cell dimensions and intensities were measured on a micro-computer controlled four-circle diffractometer[6] with Cu-Kα radiation (λ=1.5418 Å) in the 2θ-θ scan mode for $2\theta \leq 120°$. Of the 1169 independent reflections measured, 1141 having $|F_o| \geq 3\sigma|F_o|$ were used for the structure analysis. The structure was solved by the direct method using MULTAN,[7] and was refined by the block diagonal least-squares method. In the final refinement, anisotropic thermal parameters were used for the non-hydrogen atoms. The all hydrogen atoms except hydroxy group were introduced at culculated positions with an isotropic thermal vibration parameter of B=4.5 but not refined (Fig. 1). The final R value was 0.070 (see reference 8 for crystallographic details).[8] Computations for refinement were performed with an FACOM M-200 computer using the program UNICS II.[9]

The carbon skeleton of the revised structure (5) of pseudoanisatin is the same with that

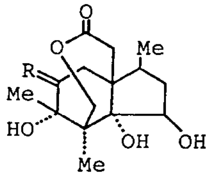


1 R=OH

2 R=H



3



4 R=NOH

5 R=O

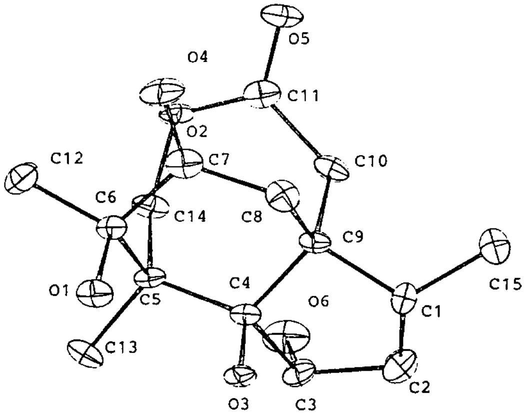


Fig. 1. The ORTEP drawing of pseudoanisatin

of anisatin (1) and neoanisatin (2). 360 MHz ^{1}H-NMR spectrum data[10] (in d_5-pyridine) are also compatible with the structure (5): a proton-proton coupling (J=2.5 Hz) through 4σ-bonds was observed at two signals of δ 3.24 (dd, H-8) and δ 3.88 (dd, H-10), indicating "W" arrangement formed by three carbons of C-8, C-9, and C-10. Signals due to three hydroxy groups were observed in another ^{1}H-NMR spectrum (in d_6-DMSO) at δ 5.77 (1H, d, J=6), δ 6.23 (1H, s), and δ 6.62 (1H, s).

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References and notes

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8) Final crystallographic coordinates have been deposited with the Cambridge Crystallographic Data Centre.

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10) Chemical shifts expressed by δ values (J values in Hz) are as follows:0.88 (3H, d, J=7), 1.43 - 1.55 (1H, m, H-1), 1.63 (3H, s), 1.74 (3H, s), 2.55 - 2.80 (2H, m, H-2), 2.74 (1H, d, J=15, H-10), 2.80 (1H, d, J=16, H-8), 3.24 (1H, dd, J=16 & 2.5, H-8), 3.88 (1H, dd, J=15 & 2.5, H-10), 3.96 (1H, d, J=14, H-14), 4.75 - 4.80 (1H, m, H-3), and 6.03 (1H, d, J=14, H-14)

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