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A NOVEL BASE CATALYZED REARRANGEMENT OF PSEUDOANISATIN. X-RAY CRYSTALLOGRAPHIC ANALYSIS OF THE REARRANGEMENT PRODUCT

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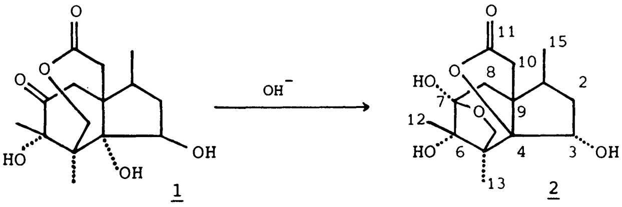
The structure of a base catalyzed rearrangement product of pseudoanisatin has been determined by an X-ray crystallographic analysis as the formula, indicating a novel stereoselective reaction which includes steric inversion at C-3 and C-4. The reaction mechanism is discussed.

Recently, on the basis of an X-ray crystallographic analysis, we reported[1)] the revised structure (1) of pseudoanisatin, $C_{15}H_{22}O_6$, a non-toxic constituent of Japanese star anise (*Illicium anisatum* L.). When treated with sodium methoxide in methanol, pseudoanisatin gave an isomer without notable by-products as reported previously.[2)] We now realized that the anhydrous condition is not necessarily required for the transformation reaction and the isomer is also obtainable in good yield by boiling a methanol solution with potassium carbonate. The IR spectrum of the isomer indicated the presence of a γ-lactone (1760 cm^{-1}) in place of ε-lactone (1710 cm^{-1}) of pseudoanisatin molecule. Its ^{13}C-NMR spectrum (in d_5-pyridine) showed one carbonyl carbon signal at 176 ppm and a singlet signal at 107 ppm, suggesting that the ketone group of pseudoanisatin was transformed into a hemiacetal group. The presence of three hydroxy groups was confirmed in its ^1H-NMR spectrum (in d_6-DMSO) at δ 5.98 (1H, s), δ 6.87 (1H, d, J=6 Hz), and δ 7.03 (1H, s). In another ^1H-NMR spectrum (in d_5-pyridine) the shape of a signal assigned to the proton of the secondary alcoholic group at C-3 was much changed in comparison with that of pseudoanisatin, suggesting stereochemical change at C-3.



In order to obtain the structure (2) of the isomer, we carried out an X-ray crystallographic analysis. The isomer crystallized from ethyl acetate as monohydrate and the crystal data are given in the Table 1. The cell dimensions and intensities were measured on a Rigaku RU-200-AFC-5 diffractometer with Cu Kα radiation (λ=1.5418 Å) in the 2θ-θ scan mode for 2$\theta \leq 120°$. 1332 independent reflections having $|F_o| \geq 2\sigma|F_o|$ were used for the structure analysis. The structure was solved by the direct method using MULTAN 78,$^{3)}$ 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 groups were introduced at calculated positions with an isotropic thermal vibration parameter of B=4.0 but not refined. The final R value was 0.050. The ORTEP drawing for non-hydrogen atoms are given in Fig. 1. Computations for refinement were performed with a FACOM-200 computer using the program UNICS II.$^{4)}$

Accordingly, the transformation of 1 into 2 with base involves unusual steric inversions at C-3 and C-4 besides translactonization into a stable γ-lactone from an ε-lactone and an acetal ring formation between ketone (C-7) and the generated primary alcoholic groups. Especially, the steric inversion at C-4 is of interest because it involves a conversion of ring juncture from *trans* into *cis* conformation. One of plausible reaction mechanisms for the transformation is shown in the Scheme 1. Strain by the octahydro-*trans*-indane system of pseudoanisatin might be a driving force for the transformation.

Table 1. Crystal Data of the Isomer.

Orthorhombic	M.p. 220-221°C
Space group $P2_12_12_1$	$C_{15}H_{22}O_6 \cdot H_2O$
a=19.229(12) Å	M.w.= 316.34
b=10.757(7)	D_c= 1.36 g/cm^3
c= 7.440(8)	D_m= 1.36
V=1538.9(21) Å^3	Z = 4

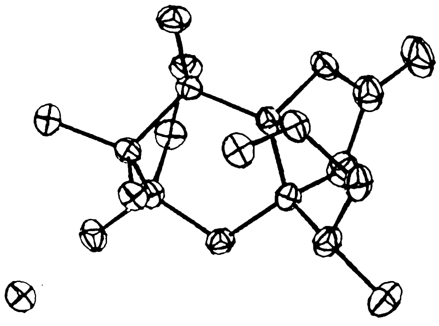
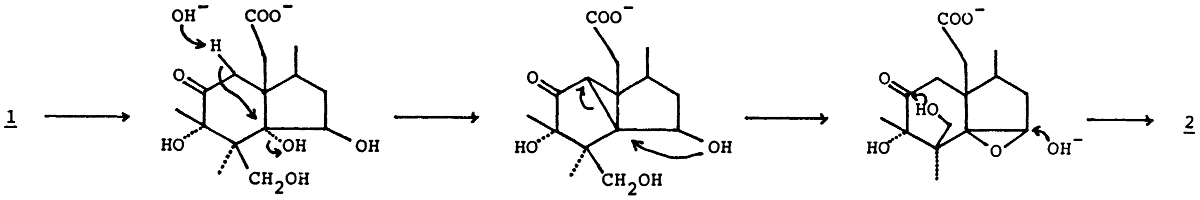


Fig. 1. ORTEP Drawing of 2.



Scheme 1. One of Plausible Reaction Mechanisms of the Transformation.

References

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3) P. Main, E. S. Hull, L. Lessinger, G. Germain, J. P. Declera, and M. M. Woolfson, "MULTAN 78, a System of Computer Programs for the Automatic Solution of Crystal Structure from X-Ray Diffraction Data," University of York, York, England.
4) The Universal Crystallographic Computation Program System (Riken Report, 50, 75 (1974)).

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