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MOMILACTONE-C, A MINOR CONSTITUENT OF GROWTH INHIBITORS IN RICE HUSK

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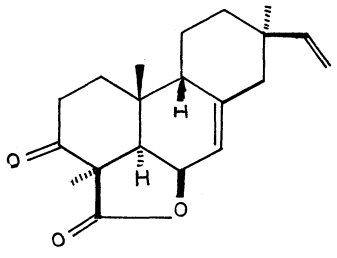
Structure of momilactone-C (M-C), a minor constituent of growth inhibitors in rice husk, was determined by X-ray analysis, which revealed that C_9-C_{10} of M-C was unusual cis configuration having a boat conformation of A ring. The stereochemistry of C_9 of previously reported momilactone-A and B (I and II) has been erroneously written and should now be revised to β-configuration with respect to hydrogen atom as in M-C.

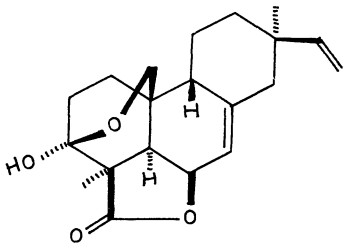
Previously we reported the isolation and structural elucidation of momilactone-A (I) and -B (II)[2] which showed the inhibitory activities toward the germination of lettuce seeds and growth of root of rice. This paper deals with the structural elucidation of momilactone-C, a minor constituent of growth inhibitors in husk of *Oryza sativa* L. CV. *Koshihikari*[3].

Momilactone-C (III), isolated in ca 3 mg from 300 kg of dried rice husk, mp 227 - 228° (accompanied with sublimation), has molecular formula $C_{20}H_{28}O_3$ (M^+ 316.2037; mol wt 316.2038), ν_{max} ($CHCl_3$) 3610 (sharp) (OH), 1760 (γ-lactone), 1660, 1635, and 915 cm^{-1}. PMR spectrum ($CDCl_3$) revealed the following groupings: ■-$CH=CH_2$ [5.86 (dd, 10.7 and 18.0 Hz), 4.96 (dd, 18.0 and 1.2 Hz), and 4.91 ppm (dd, 10.7 and 1.2 Hz)]; C_7-H, 5.65 ppm (bd, 5 Hz); C_6-H, 4.88 ppm (bt, 5 Hz); C_2-H, ca 3.8 ppm (m); C_{13}-Me, 0.87 ppm (s); C_4-Me, 1.38 ppm (s); C_{10}-Me, 1.15 ppm (s)[4]. Although physical evidence described above suggests that III has the same skeleton with those of I and II, the compound was submitted to direct X-ray crystallographic analysis due to the limited amounts of the material.

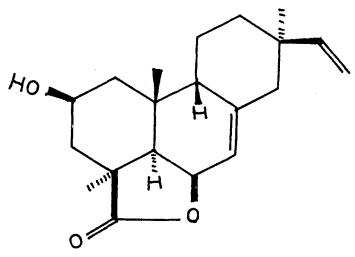
The crystals of momilactone-C (III) belong to orthorhombic space group $P2_12_12_1$: a=10.284, b=7.895, c=21.672 Å, Dx=1.20 g/cm^3 (z=4). A total of 1874 reflections were measured on a four circle diffractometer using CuKα-radiation (2θ<140°). The structure was solved by the symbolic addition and multi-solution tangent formula



(I)



(II)



(III)

refinement method[5]. One correct solution was finally determined by applying the quartet invariant approach[6]. The E-map based on the phases revealed the partial structure of momilactone-C, which was confirmed by the least-squares refinement. The remaining six carbon atoms of the ring C were found by the difference Fourier synthesis. When the anisotropic temperature factors were applied for non-hydrogen atoms and the isotropic temperature factors for all hydrogen atoms which were located by the difference Fourier synthesis, the refinement terminated to give an R-factor of 0.056.

The structural and conformational features of momilactone-C (III) are shown in Fig. 1. The bond lengths and angles are almost normal for the assigned structure. It is noteworthy that C_9-C_{10} is unusual cis configuration[7] having a skew boat conformation of A ring, resulting that OH group at C_2 is equatorial to avoid the strong 1,3-non-bonded interaction with the axial methyl group at C_{10}-position.

Momilactone-C shows a weak but clear inhibitory activity toward the germination of lettuce seeds (50% inhibition at 1000 ppm).

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3. T. Kato, M. Tsunakawa, N. Sasaki, H. Aizawa, K. Fujita, Y. Kitahara and N. Takahashi, Phytochem., in press.
4. PMR were measured with Varian HA-100. Coupling constants were obtained by first order analysis. ■ refers a carbon bearing no hydrogen.
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6. G. T. Detitta, J. E. Edmonds, D. A. Langs, and H. Hauptman, ibid., A31, 472 (1975).
7. By careless miskate, stereochemistry at C_9 of momilactones A and B were erroneously reproduced from molecular structure solved by X-ray analysis[2]. The stereochemistry of M-A, M-B, and hydroxy ketone should be revised to β-configuration with respect to hydrogen atom as in M-C.

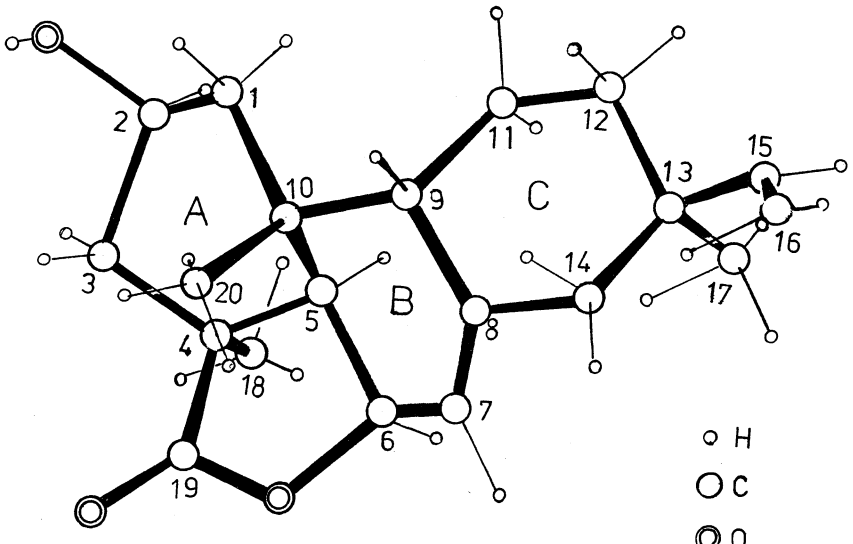

Fig. 1

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