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MOMILACTONES, GROWTH INHIBITORS FROM RICE, ORYZA SATIVA L.

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As a part of searches concerning the growth regulating substances in higher plants[1], we have examined the active components from the seed husk (Japanese name, Momi) of Oryza sativa L., cv. Koshihikari, and isolated two compounds, named momilactone-A, and -B, which inhibit the growth of root of rice at less than 100 ppm. This paper describes the structure of momilactones.

Momilactone A (I), dp 235-236° (from CH_2Cl_2 + EtOH), $[\alpha]_D^{CHCl_3}$ -277° has molecular formula $C_{20}H_{26}O_3$ (M^+ 314.1891; mol wt 314.1880, Found C, 76.47; H, 8.37%), ν max (Laser Raman) 1770, 1700, 1665, 1640 cm^{-1}. Although the presence of a ketone function was not infered certainly by IR spectrum due to the weak absorption at 1700 cm^{-1}, C-13 NMR (CMR) spectrum clearly exhibits the presence of a ketone as well as a lactone groups at 205.00 and 174.25 ppm, respectively.

Due to the limited amounts of the compound (ca 150 mg from 200 Kg of dried husk) and formation of the complicated products by usual reactions, i.e., methanolic KOH, catalytic and metal hydride reductions, the structure was unequivocally determined by direct x-ray crystallographic analysis[2].

Crystals of this compound are orthorohombic, space group $P2_12_12_1$, with a = 7.625, b = 22.066, c = 10.201 Å and Z = 4. The phase problem was solved by

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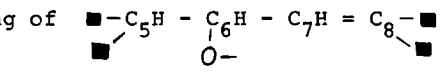
symbolic addition, and tangent refinement methods, the atomic parameters being refined by a block-diagonal least-squares method. Several cycles of refinement with anisotropic thermal parameters for 23 non-hydrogen atoms gave R factor of 0.11.

The molecular structure found in the crystal is shown in Figure 1.

The grouping of  was confirmed by decoupling experiments[3].

The absolute configuration was determined by positive cotton curves of CD and ORD of hydroxy ketone (II), isolated from the hydrolyzate of I with aq KOH in hot dioxane. II, mp 146°, $[\alpha]_D^{CHCl_3}$ -216°, $\nu_{max}^{CHCL_3}$ 3620, 1705 cm^{-1}, δ(ppm) two tert-methyls at 0.87 and 1.31, a sec-methyl at 1.15 (d,6), C_4-H at 2.85 (dq, 11, 6), C_5-H at ca 1.6, C_6-H at 4.15 (dd, 4.5, 5.5) and C_7-H at 5.60 (d, 5.5).

Momilactone-B (III), dp 242° (from CH_2Cl_2 + EtOH), $[\alpha]_D^{CHCl_3}$ -185° has molecular formula $C_{20}H_{26}O_4$ (M^+ 330.1834; mol wt 330.1830, Found C, 72.55; H, 8.01 %), $\nu_{max}^{CHCl_3}$ 3500, 1750, 1663, and 1638 cm^{-1}. Ca 100 mg of III was isolated from 200 Kg of dried husk and its structure was deduced mainly by comparison of physical data with those of I (Table 1 and 2).

Spectral data of III are alike with those of I excepting the following details. i) In IR spectrum of III, a hydroxyl group appeared instead of a ketone which was observed in I, and a lactone group of III showed a hydrogen bonding with the hydroxyl group. ii) One of the three tertiary methyl groups of I turned into a CH_2O-group in the NMR spectrum of III, and one proton of the CH_2O-group showed a W type coupling with C_5-H, which was confirmed by irradiation of C_5-H signals. iii) In the CMR spectra[4], C-3 and C-20 of I shifted largely in the spectrum of III, while the others appeared almost unchanged. In addition to these observations, the hydroxyl group of III was not acetylated under usual acetylation conditions, indicating the hindered nature of the group. Treatment of III with KOH afforded a mixture, the IR spectrum of which showed only a ketonic band near 1710 cm^{-1} in the carbonyl region.

Consideration of all the evidence presented so far leads to postulation of structure III for momilactone-B, with the exception of the absolute configuration which was assumed by the fact that ORD curves of both compounds showed a

Table 1

PMR of Momilactone-A (I) and B (III)

Proton	Chemical shift, multiplicity, and coupling constants (Hz)	Chemical shift, multiplicity, and coupling constants (Hz)
5-H	2.32, d, (5.0)	2.20, dd, (7.1 and 2.1)*
6-H*	4.83, t, (5.0)*	4.94, dd, (7.1 and 4.5)*
7-H*	5.70, d, (5.0)*	5.68, d, (4.5)*
14-H_2	2.03 and 2.22, d, (12.5)	overlapped with others
15-H	5.85, dd, (17 and 10.8)	5.83, dd, (17.6 and 10.5)
16-H	4.93, dd, (10.8 and 1.2)	4.92, dd, (10 5 and 1.2)
16-H	4.95, dd, (17 and 1.2)	4.95, dd, (17.6 and 1.2)
17-H_3	0.90, S	0.87, S
18-H_3	1.52, S	1.40, S
20-H_3	1.00, S	3.55, dd, (9.0 and 2.1) 4.07, bd, (9.0)*

* assignments were confirmed by decoupling.

Table 2

CMR[a] of Momilactone-A (I) and B (III)

carbon number	Momilactone-A (I)	Momilactone-B (III)	carbon number	Momilactone-A (I)	Momilactone-B (III)
1	34.89[b]	28.82[b]	11	24.03	24.81[b]
2	31.25[b]	26.45[b]	12	37.25	37.25
3	205.00	96.59	13	40.16	39.98
4	53.57	50.36	14	47.57	47.44
5	46.67[c]	43.02[c]	15	148.95	148.83
6	73.17	73.78	16	110.12	110.18
7	114.06	114.00	17	21.97[d]	21.90
8	147.98	146.70	18	21.42[d]	18.99
9	50.24[c]	44.65[c]	19	174.25	180.52
10	32.52	30.76	20	21.78[d]	72.74

a : Spectra in $CDCl_3$ taken at 15.359 MHz on a JNM-TFT-100 spectrometer of JEOL Co. Ltd.; chemical shifts in parts per million down field from TMS.

b,c and d : Values in each vertical column may be reversed.

similar slope and sign, as well as from biogenetical point of view. The rice husk contains some other inhibitors which will be discussed elsewhere.

References

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1. Previous papers, H. Yanagawa, T. Kato, Y. Kitahara, N. Takahashi, Y. Kato, Tetrahedron Letts., 2549 (1972); ibid., 1073 (1973)

2. A total of 2215 independent reflections were measured by a Rigaku automatically controlled four circle diffractiometer using Mo-Kα radiation.

3. Proton NMR spectra (PMR) were measured with a Varian HA-100. Chemical shifts are in ppm from TMS; coupling constants (J'S) are in Hz and were obtained by first order analyses. The symbol ■ refers to a carbon bearing no hydrogen.

4. For an example, E. Wenkert, B. L. Buckwalter, J. Am. Chem. Soc., 94, 4367 (1972) and references therein.

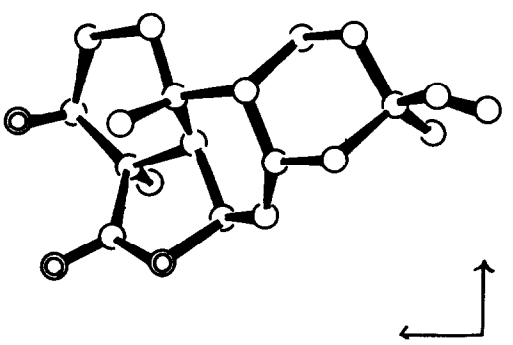
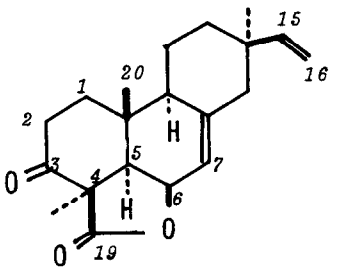
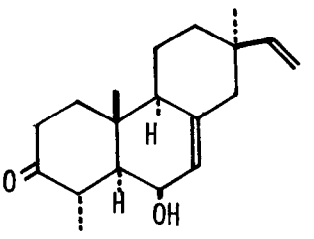


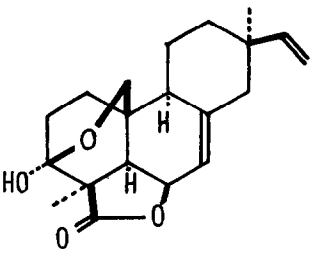
Figure 1
Molecular structure of (I) viewed along the b axis. Carbon and oxygen atoms are indicated by single and double circles, respectively.



(I)



(II)



(III)