Short Communication

Structure of Aszonapyrone
A Monomethyl Ether-1,
a Derivative of Aszonapyrone
A, Produced by
Aspergillus zonatus

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In the previous communication,¹⁾ we reported the isolation of aszonapyrone A, which showed antibacterial activity from dry mycelial mats of *Aspergillus zonatus* IFO 8817, and its chemical structure indicated in **1** based upon chemical and spectroscopic data. In order to obtain the validity of this structure, we carried out an X-ray analysis on aszonapyrone A monomethyl ether-1 (**2**), a derivative of aszonapyrone A. The structure of **2** was determined as depicted in structural formula **2**.

To obtain crystals for the X-ray analysis, **1** was treated with diazomethane in ether. The reaction mixture showed two UV-quenching spots on a silica gel TLC plate (benzene-ethyl acetate, 9:1, v/v). The mixture was separated by preparative TLC (silica gel GF₂₅₄; benzene-acetone, 9:1, v/v) and each component was recrystallized from benzene-acetone to afford pure aszonapyrone A monomethyl ethers -1 (**2**) and -2 (**3**).

2: mp 276~278°C. IR $\nu_{\text{max}}^{\text{KBr}}$ cm⁻¹: 1740, 1700, 1690 (sh), 1650, 1560, 1460, 1440, 1240,

910. UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm (ϵ): 298 (8600). ¹H-NMR $\delta_{\text{TMS}}^{\text{CDCl}_3}$: 0.76 (3H, s), 0.84 (9H, s), 1.00~2.80 (17H, m), 2.04 (3H, s), 2.23 (3H, s), 3.92 (3H, s), 4.54 (1H, dd, $J=4, 12$ Hz), 4.72 (1H, s), 4.88 (1H, s), 6.06 (1H, s). ¹³C-NMR $\delta_{\text{TMS}}^{\text{CDCl}_3}$: 15.2 (q), 16.4 (q), 16.5 (q), 19.0 (t), 19.3 (q), 20.1 (q), 21.1 (q), 23.7 (t), 23.9 (t), 28.1 (q), 37.7 (s), 38.0 (s), 38.4 (t), 38.5 (t), 40.3 (s), 40.3 (t), 54.2 (d), 55.6 (d), 56.0 (q), 60.1 (d), 81.1 (d), 95.1 (d), 105.9 (s), 106.2 (t), 149.0 (s), 160.7 (s), 165.1 (s), 165.5 (s), 170.6 (s). MS m/z : 470 (M^+), 455, 411, 395, 154, 153.

3: mp 201~203°C. IR $\nu_{\text{max}}^{\text{KBr}}$ cm⁻¹: 1740, 1680, 1630, 1600, 1460, 1400, 1250, 908. UV $\lambda_{\text{max}}^{\text{EtOH}}$ nm (ϵ): 262 (8200).

Since it is well known that the methylation of 4-hydroxy α -pyrone with diazomethane in ether affords two compounds, 4-methoxy α -pyrone and 2-methoxy γ -pyrone,^{2,3)} the compounds **2** and **3** were expected to be one of the compounds consisting of either an α -pyrone or γ -pyrone moiety. In the UV spectrum of **3**, absorption maximum at 262 nm indicated the presence of a γ -pyrone moiety.^{2,4)} On the other

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hand, the UV absorption maximum of **2** was similar to that of **1**. The presence of a 4-methoxy α -pyrone moiety in **2** was supported by IR absorption bands and the UV maximum,⁵⁾ together with the proton signal at δ 3.92 due to $-\text{OCH}_3$ and the carbon signal at δ 56.2 due to $-\text{OCH}_3$.

Crystals of the compound **2** are monoclinic, space group $P2_1$, with $a = 14.539(4)$, $b = 13.662(4)$, $c = 6.661(3)$ Å, $\beta = 103.14(5)^\circ$ and $Z = 2$.

A crystal with the dimensions $0.2 \times 0.3 \times 0.3$ mm was used during all diffraction measurements on a four circle diffractometer (Rigaku), which was controlled by microcomputer system designated by the authors. A θ - 2θ scanning mode with Ni-filtered $\text{CuK}\alpha$ was used to measure 2028 ($|F_o| > 3\sigma|F_o|$) independent reflections with 2θ values below 125° . The data were corrected for Lorentz and polarization effects, but no absorption correction was applied.

The structure was determined with a direct method using the multiple-solution program MULTAN. Twenty non-H atoms were located. The remaining non-H atoms and all H atoms except for those of the methyl groups were found in the Fourier and Fourier difference maps, respectively. The structure was refined with the block-diagonal least-squares method. The anisotropic refinement of the non-H atoms and isotropic refinement of the H atoms resulted in a final R value of 0.06. The

TABLE I. FRACTIONAL ATOMIC COORDINATES WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Atom	x	y	z
C1	0.0773 (4)	0.5273 (4)	0.7314 (6)
C2	0.0752 (4)	0.6267 (4)	0.6228 (6)
C3	0.1736 (5)	0.6667 (4)	0.6563 (8)
C4	0.2441 (5)	0.6018 (5)	0.5763 (7)
C5	0.2409 (4)	0.4990 (5)	0.6830 (7)
C6	0.3132 (5)	0.4256 (5)	0.6368 (8)
C7	0.3251 (4)	0.3404 (4)	0.7868 (6)
C8	0.2334 (4)	0.2855 (4)	0.7908 (6)
C9	0.1554 (4)	0.3618 (4)	0.8120 (6)
C10	0.1429 (4)	0.4511 (4)	0.6596 (7)
C11	0.0624 (4)	0.3106 (4)	0.8205 (6)
C12	0.0755 (4)	0.2353 (5)	0.9941 (7)
C13	0.1587 (4)	0.1669 (4)	0.9961 (7)
C14	0.2487 (4)	0.2187 (4)	0.9889 (6)
C15	0.3349 (5)	0.1497 (5)	1.0070 (7)
C16	0.1463 (4)	0.0682 (5)	1.0038 (7)
C17	0.2217 (6)	0.5984 (7)	0.3358 (8)
C18	0.3450 (5)	0.6464 (6)	0.6525 (8)
C19	0.0939 (5)	0.4202 (6)	0.4336 (7)
C20	0.2066 (5)	0.2181 (5)	0.5952 (6)
C21	0.1674 (6)	0.8420 (5)	0.6624 (8)
C22	0.1777 (7)	0.9318 (6)	0.5315 (10)
C23	0.3908 (6)	0.0134 (6)	1.2665 (7)
C24	0.3774 (4)	0.1109 (5)	1.2191 (6)
C25	0.4202 (5)	0.1824 (5)	1.3741 (7)
C26	0.4712 (5)	0.0471 (6)	1.6093 (8)
C27	0.4378 (5)	-0.0207 (5)	1.4668 (7)
C28	0.5283 (8)	0.0269 (9)	1.8287 (10)
C29	0.3744 (8)	-0.1560 (8)	1.1486 (11)
O1'	0.1726 (3)	0.7613 (3)	0.5525 (4)
O2'	0.4247 (3)	0.2684 (3)	1.3542 (4)
O3'	0.4618 (3)	0.1445 (3)	1.5712 (3)
O4'	0.3581 (3)	-0.0516 (3)	1.1143 (4)
O5'	0.1550 (4)	0.8386 (4)	0.8346 (6)

Stereoscopic View of Aszonapyrone A Monomethyl Ether-1.

The hydrogen atoms are omitted for clarity and no absolute configuration is implied.

final atomic coordinates are given in Table I. All rings were fused by consecutive equatorial bonds, the C-C bonds of the perhydrophenanthrene moiety being in the range 1.496 to 1.580 Å with an average value of 1.546(26) Å. The average value of the internal angle of the moiety was $111.1(3.4)^\circ$, and the bond distances of the α -pyrone ring were close to those of pyrenocine A.⁶⁾

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