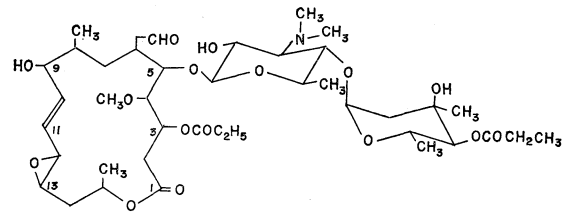
THE STRUCTURES OF ANTIBIOTICS YL-704 C_1, C_2 AND W_1

Sir:

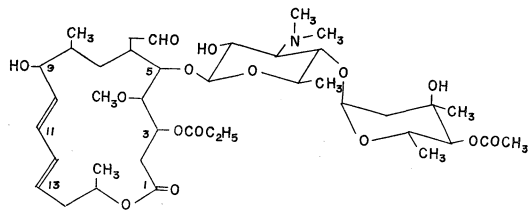
Recently, we have reported the structures of new macrolide antibiotics YL-704 A_1 and B_1[1].* They were isolated as the main products of *Streptomyces platensis* MCRL-0388, but, in fact, they were accompanied with three minor antibiotics, YL-704 C_1, C_2 and W_1. Now, we wish to communicate on the structure elucidation of these three minor antibiotics**.

Physicochemical properties of these antibiotics were summarized in Table 1. From the data of NMR spectra, it was apparent that YL-704 C_1, C_2 and W_1 contained an aldehyde function. This was also supported by the absorption at 2730~2750 cm^{-1} of IR spectra.

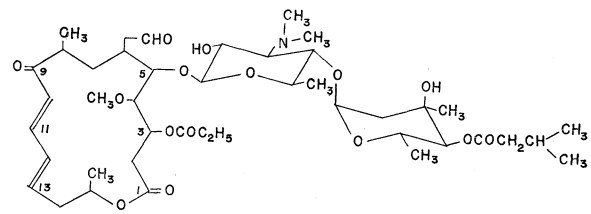
The characteristic property to each of the three antibiotics was observed in



YL - 704 C_1



YL - 704 C_2



YL - 704 W_1

Table 1. Physicochemical properties

	YL-704 C_1	YL-704 C_2	YL-704 W_1
	colorless needle	colorless small prism	colorless plate
m.p.	125~127°C	116~118°C	159~161°C
Formula	$C_{41}H_{67}NO_{16}$	$C_{40}H_{65}NO_{15}$	$C_{43}H_{69}NO_{15}$
M.W.	829	799	839
Elem. Anal. (%)	obsd. / calcd.	obsd. / calcd.	obsd. / calcd.
C	59.45 / 59.35	60.21 / 60.08	61.71 / 61.50
H	8.03 / 8.08	8.20 / 8.14	8.13 / 8.22
N	1.75 / 1.69	1.68 / 1.75	1.70 / 1.67
UV (EtOH, nm)	end absorption	232.5 (log ε 4.43)	280 (log ε 4.37)
IR (nujol, cm^{-1})	3460, 2730, 1740, 1730, 1640	3500, 2740, 1740, 1725, 1640	3550, 3410, 2750, 1748, 1737, 1690, 1640, 1603
NMR ($CDCl_3$, ppm) (100 MHz)	1.00—1.35, 2.55, 3.30, 3.95, 4.08, 4.48, 4.67, 5.18, 5.74, 6.14, 9.63	0.90—1.30, 2.16, 2.54, 3.28, 3.55, 3.91, 4.12, 4.44, 4.65, 5.17, 5.55—6.30, 6.69, 9.63	0.90—1.35, 2.53, 3.30, 3.57, 3.87, 4.42, 4.64, 5.12, 6.05—6.43, 9.54
$[\alpha]_D^{22}$ (c 1, $CHCl_3$)	−69°	−42°	−32°
pKa′ (50% EtOH)	7.00	7.01	6.95

* These antibiotics were previously named as YL-704 A and B respectively[1].

** YL-704 C_1 was found to be identical with maridomycin III reported in the 11th ICAAC (Oct. 1971).

their respective UV absorption: YL-704 C_2 showed the absorption maximum at 232.5 nm like the major products A_1 and B_1. The maximum of component W_1 was shifted to a longer wave length (280 nm) indicating the presence of the $\alpha, \beta, \gamma, \delta$-dienone chromophore might be concerned. However, no such characteristic absorption maximum was observed in the spectrum of YL-704 C_1.

YL-704 C_1 and C_2 afforded the diacetates of m.p. 102~104°C and m.p. 105~107°C respectively, by the usual acetylation precedure, while W_1 gave the monoacetate of m.p. 188~189°C. The mass spectra of these three acetates presented fragmentation patterns which were important to their structure elucidation as in the case of the diacetates of YL-704 A_1 and B_1*. Among many diagnostic fragments, those due to the two aglycone ions (AGL^+, $AGL\text{-}CO^+$) and the acyl-disaccharide ion (ADS^+) were listed in Table 2. From these fragmentation patterns and the above physicochemical data, the structures of the three antibiotics were deduced as follows:

YL-704 C_1: This component has one more oxygen atom in the aglycone portion in addtion to those present in A_1 and B_1, and has the same terminal acyl group as B_1. The γ, δ-epoxy-α, β-en-ol system is present as an aglycone-chromophore.

YL-704 C_2: The aglycone structure of this component is the same as in A_1 and B_1, but the terminal acyl group is one methylene unit less than B_1.

Table 2. Diagnostic fragments in mass spectra of the acetyl derivatives

Acetates	M^+ m/e	AGL^+ m/e	$[AGL\text{-}CO]^+$ m/e	ADS^+ m/e
YL-704 A_1 $C_{47}H_{75}NO_{17}$	925	465	437	444
YL-704 B_1 $C_{45}H_{71}NO_{17}$	897	465	437	416
YL-704 C_1 $C_{45}H_{71}NO_{18}$	913	481	453	416
YL-704 C_2 $C_{44}H_{69}NO_{17}$	883	465	437	402
YL-704 W_1 $C_{45}H_{71}NO_{16}$	881	421	393	444

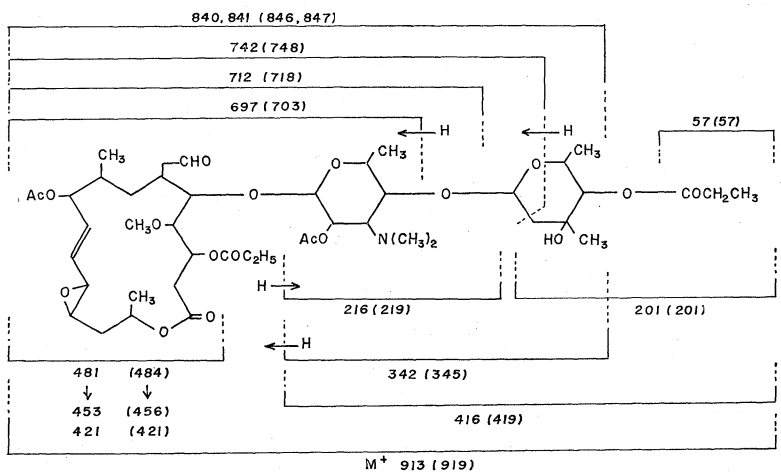
YL-704 W_1: The $\alpha,\beta,\gamma,\delta$-dienone chromophore is present in the aglycone portion. The acyldisaccharide structure is the same as in A_1.

In accordance with the above deduction, YL-704 C_1 was oxidized by MnO_2 to give the dehydro-compound $C_{41}H_{65}NO_{16}$, m.p. 128~130°C, λ_{max}^{EtOH} 239 nm (log ε, 4.13).

This substance was very similar to carbomycin A[2,3] in various physicochemical properties including mass-spectral fragmentation patterns of their acetates.

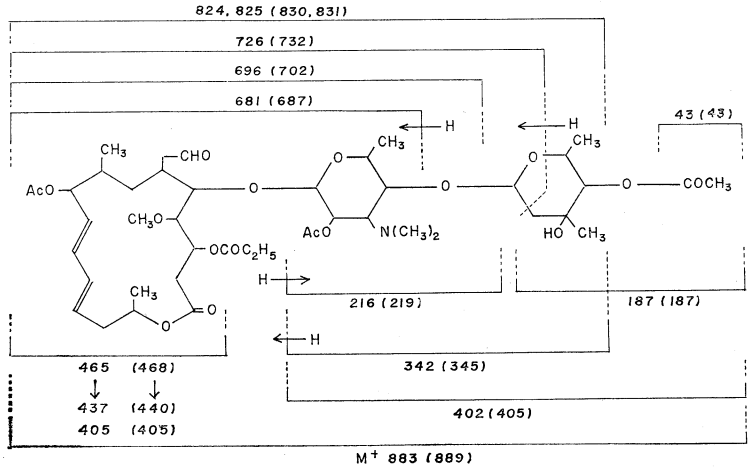
YL-704 W_1 was determined to be identical with the dehydro-compound of YL-704 A_1, which was derived by MnO_2-oxidation. Besides, the mass-spectral fragmentation patterns of these compounds were quite similar to that of carbomycin B[3,4] except only in the moiety of the ester group sub-

Scheme 1. Diagnostic fragmentations of diacetyl YL-704 C_1

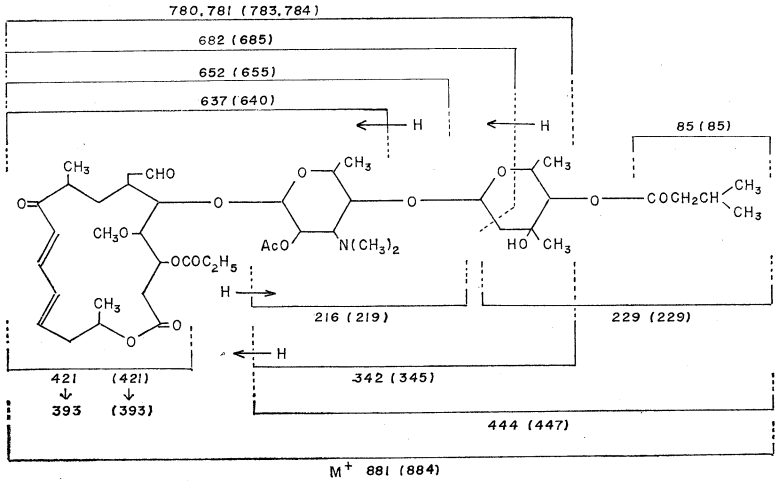


* The assignment made on the acetates was fully reconfirmed by the mass spectra of the corresponding trideuteroacetates.

Scheme 2. Diagnostic fragmentations of diacetyl YL-704 C_2



Scheme 3. Diagnostic fragmentations of acetyl YL-704 W_1



stituted at C_3 of the aglycone portion.

Thus, the structures of the acetates of YL-704 C_1, C_2 and W_1 were determined as described in Scheme 1, 2 and 3 respectively. In these schemes, assignments of the other mass-spectral fragmentation patterns of the acetates and the corresponding trideutero-acetates (in the parentheses) were also given. The present experimental results were further supported by mass spectrometry of other sixteen-membered macrolide antibiotics which will be reported elsewhere in detail.

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