Tetrahedron Letters,Vol.23,No.24,pp 2479-2480,1982 0040-4039/82/242479-02$03.00/0
Printed in Great Britain

STRUCTURAL INVESTIGATION OF AN ANTIBIOTIC SPORAVIRIDIN IV. STRUCTURAL REVISION OF VIRIDOPENTAOSES

Ken-ichi Harada, Susumu Ito and Makoto Suzuki*

Faculty of Pharmacy, Meijo University, Tempaku, Nagoya 468, Japan

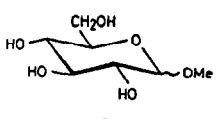
Summary: Structures of viridopentaose A, B and C are revised as 4A, 4B and 4C, respectively, by ^{1}H-NMR (360 MHz) spectra and chemical degradations.

Sporaviridin(SVD) is a basic antibiotic produced by *Streptosporangium viridogriseum*, and considered to be a glycosidic compound containing amino sugars.[1] In this communication we report the structural revision of the constituent heteropentasaccharides of SVD, viridopentaoses.

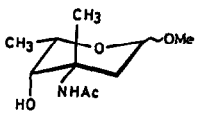
N-Acetylsporaviridin(SVD-N-Ac), a derivative obtained by treatment of SVD with acetic anhydride in MeOH, consists mainly of three components(SVD-N-Ac-A, B and C). Each component was degradated smoothly to a common glycosylated moiety and an oligosaccharide under basic condition [e.g. 7% NH_4OH, 5% NaOMe or 1% NaOH(aq)-MeOH]. Methanolysis of the common compound yielded two methyl glycosides, methyl D-glucoside(1) and methyl N-acetylvancosaminide(2).[2,3]

As to the oligosaccharide mentioned above, SVD-N-Ac-A, B and C liberated three pentasaccharides, viridopentaose A, B and C, respectively, whose structures were determined incorrectly as 3A, 3B and 3C on the basis of analysis of the ^{13}C-NMR spectra.[4,5] Afterward we found that treatment of each pentasaccharide with 5% NaOH(aq)-MeOH released readily an N-acetylacosamine(6) to give unsaturated tetrasaccharides, 5A, 5B and 5C, respectively.[6]

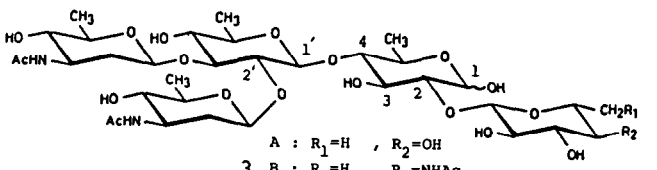
The formation of these degradation products suggests that the original positions for one of two N-acetylacosamines in viridopentaoses are not C-2′ but C-3. Full assignments of the ^{1}H-NMR (360 MHz)[7] spectra in $CDCl_3$, recently applied, for peracetylated viridopentaoses(7A, 7B, 7C)[8] resolve definitively the above problem. The chemical shifts of H-3 in reducing quinovose unit[9] and H-2 in non-reducing quinovose unit[10] for 7A, 7B and 7C show that the hydroxy group at C-3 is linked with an N-acetylacosamine unit, whereas the hydroxy group at C-2′ is acetylated.
In addition, methanolysis of permethylated viridopentaose A, B and C afforded the methyl glycosides, 8, 9 and 10 in common and 11A, 11B and 11C, respectively. These results establish that the structures of viridopentaose A, B and C should be revised as 4A, 4B and 4C, respectively.



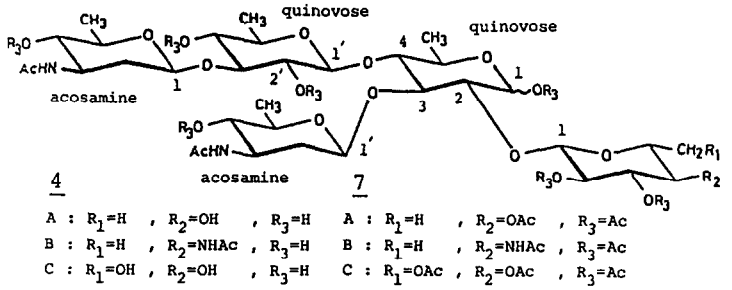
1



2



3 A : R_1=H , R_2=OH
B : R_1=H , R_2=NHAc
C : R_1=OH , R_2=OH

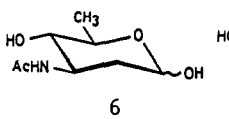


4

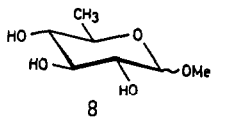
A : R_1=H , R_2=OH , R_3=H
B : R_1=H , R_2=NHAc , R_3=H
C : R_1=OH , R_2=OH , R_3=H

7

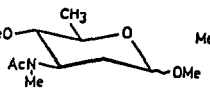
A : R_1=H , R_2=OAc , R_3=Ac
B : R_1=H , R_2=NHAc , R_3=Ac
C : R_1=OAc , R_2=OAc , R_3=Ac



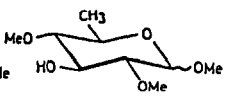
6



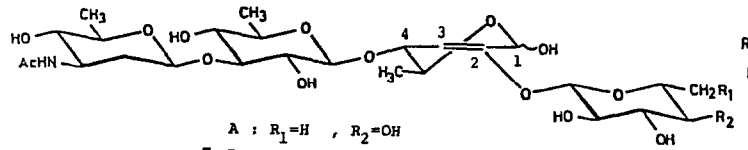
8



9

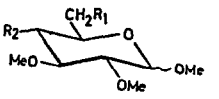


10



5

A : R_1=H , R_2=OH
B : R_1=H , R_2=NHAc
C : R_1=OH , R_2=OH



11

A : R_1=H , R_2=OMe
B : R_1=H , R_2=N(Me)Ac
C : R_1=OMe , R_2=OMe

Acknowledgement

The authors wish to thank Dr. T. Iwashita, Suntory Institute for Bioorganic Research, for obtaining the ^{1}H-NMR (360 MHz) spectra and helpful discussions.

References and notes

1. T. Okuda, Y. Ito, T. Yamaguchi, T. Furumai, M. Suzuki and M. Tsuruoka, J. Antibiotics, Ser. A., 19, 85 (1966).
2. W. D. Weringa, D. H. Williams, T. Feeney, J. P. Brown and R. W. King, J. C. S. Perkin I, 1972, 443.
3. A. W. Johnson, R. M. Smith and R. D. Guthrie, J. C. S. Perkin I, 1972, 2153.
4. K. I. Harada, S. Ito, T. Murase and M. Suzuki, Heterocycles, 13, 145 (1979).
5. K. I. Harada, S. Ito and M. Suzuki, Tetrahedron Letters, 1979, 3965.
6. A : mp 224-226°C, $[\alpha]_D$ -42.0°(c 0.3, MeOH), SIMS : m/z 610(MH^+). B : mp 209-212°C, $[\alpha]_D$ -46.7° (c 0.3, MeOH), SIMS : m/z 651(MH^+). C : mp 175-180°C, $[\alpha]_D$ -35.7°(c 0.3, MeOH), SIMS : m/z 626(MH^+).
7. A Nicolet NT 360 spectrometer was used for ^{1}H-NMR measurements.
8. Each acetate (7A, 7B and 7C) is mainly α-anomer. A : mp 160-163°C, $[\alpha]_D$ +9.7°(c 0.3, MeOH), FDMS : m/z 1157(M+Na)$^+$, 1135(MH^+). B : mp 175-177°C, $[\alpha]_D$ +18.3°(c 0.3, MeOH), FDMS : m/z 1156(M+Na)$^+$, 1134(MH^+). C : mp 152-157°C, $[\alpha]_D$ +11.6°(c 0.3, MeOH), FDMS : m/z 1215(M+Na), 1193(MH^+).
9. 7A : 3.96 ppm(t), $J_{2,3}$ = 9.5, $J_{3,4}$ = 9.5 Hz. 7B : 3.98 ppm(t), $J_{2,3}$ = 9.0, $J_{3,4}$ = 9.0 Hz. 7C : 3.94 ppm(t), $J_{2,3}$ = 9.9, $J_{3,4}$ = 9.9 Hz.
10. 7A : 4.93 ppm(dd), $J_{1,2}$ = 8.1, $J_{2,3}$ = 9.9 Hz. 7B : 4.93 ppm(dd), $J_{1,2}$ = 8.1, $J_{3,4}$ = 9.5 Hz. 7C : 4.93 ppm(dd), $J_{1,2}$ = 8.0, $J_{2,3}$ = 9.5 Hz.

(Received in Japan 5 March 1982)