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THE BRANCHING POINT IN THE PENTASACCHARIDES VIRIDOPENTAOSES A, B AND C

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Summary: The branching point in the viridopentaoses has been determined by a three step sequence, permethylation/methanolysis/benzoylation, followed by CD measurements, a method which can be scaled down to microgram quantities.

We have determined the branching point in the viridopentaoses A, B and C, the oligosaccharide moiety of the antibiotic sporaviridin produced by Streptosporangium viridogrisium [1] by a recently developed micromethod.[2] The results are in agreement with structures 1, 7 and 8, as revised by Harada, et. al.[3]

Viridopentaose C 1 (50 μg) was methylated by Hakamori's method (NaH/DMSO; CH_3I)[4] to the permethylate which was refluxed for 4 hours in 4% HCl in methanol. After removal of solvent, the residue was p-bromobenzoylated by adding excess p-bromobenzoyl chloride[5] to a solution in pyridine, keeping the mixture at 60° for 12 hours, and quenching the reaction with methanol from a microsyringe. The solvent was removed after addition of a few drops of benzene or toluene to assist in removal of the pyridine. The acylated mixture was submitted to high performance liquid chromatography, μ-Porasil, MeOH: $CHCl_3$ (2:98)[6]; in the present case only the two UV absorbing peaks need be collected since all terminal units become permethylated methyl glycosides and hence are "UV transparent."

CI-MS (CH_4 carrier gas) showed the two products to be a monobenzoate 2 and a tribenzoate 3. Estimation of the sample weights from standard UV ε values[2,7] enabled us to measure the amplitudes[8] of CD curves which were 0 for 2, a non-branching quinovose unit,[9] and -6 for 3, the branching sugar. The value of -6 for 3 checks with the expected 0 value for 1e,2e,3e-tribenzoates,[10] and accordingly the branching point in viridopentaose C should be as shown in 1. If 4 were the structure (partial) of the viridopentaoses, as originally proposed,[11] it would have given the two dibenzoates 5 and 6, for which amplitudes of +62 and 0, respectively, would have been expected.[8]

Similar treatment of viridopentaose A 7 and B 8 gave the same tribenzoate 3.

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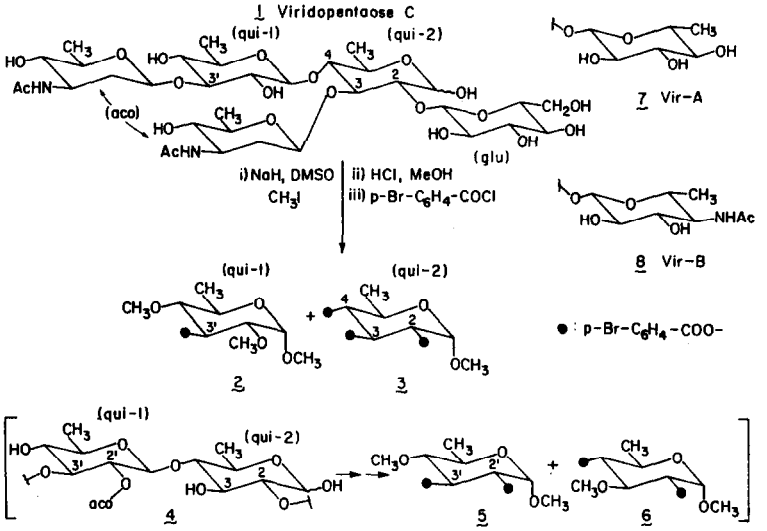

References and Notes

1. T. Okuda, Y. Ito, T. Yagamuchi, T. Furumai, M. Suzuki and M. Tsuruoka, J. Antibiotics, Ser A, 19, 85 (1966).
2. H.w. Liu and K. Nakanishi J. Am. Chem. Soc., 103, 7005 (1981).
3. K. Harada et. al., preceding communication.
4. S.I. Hakomori, J. Biochem., 55, 205 (1964).
5. p-Bromobenzoyl chloride was prepurified by dissolving in petroleum ether, filtering to remove acid and concentrating to yield crystalline material.
6. The sugar derivative can also be separated by application to silica precoated aluminum sheets; E. Merck, Darmstadt, G.F.R. ($MeOH:CHCl_3$, 6:94).
7. Standard ε values of p-bromobenzoates (in MeOH): mono,19,500; di, 38,200; tri, 57,200; tetra, 76,400.[8]
8. H.w. Liu and K. Nakanishi, J. Am. Chem. Soc., 103, 5591 (1981); idem, ibid, in press.
9. A nanogram scale method for characterization of sugars has been developed; to be published.
10. A 1e,2e,3e-tribenzoate should exhibit no exciton split CD; however,the fact that they frequently do, albeit small, is attributable to the distortion of the pyranose ring from an idealized chair form and other factors.[8]
11. K.I. Harada, S. Ito, T. Murase and M. Suzuki, Heterocycles, 13, 145, (1979); K.I. Harada, S. Ito, and M. Suzuki, Tetrahedron. Lett., 3965, (1979).

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