



2-(5-Q-benzoyl-2,3-Q-isopropylidene- $\beta$ -D-ribofuranosyl)succinates (2)<sup>15</sup> (62% yield), the rearranged product, 5-Q-benzoyl-2,3-Q-isopropylidene-1-S-(methylthio)carbonyl-1-thio- $\beta$ -D-ribofuranose (3)<sup>16</sup> (10% yield), and 1 (2% recovery yield). In this reaction, 2.2 equivalents of Bu<sub>3</sub>SnH was needed for the disappearance of 1 ( t.l.c. examination): addition of Bu<sub>3</sub>Sn• to dimethyl maleate occurs competitively. Thus the reactivity of 1 with Bu<sub>3</sub>Sn• was decided to be rather low and comparable to that of dimethyl maleate.

In the similar reactions of 1 with methyl vinyl ketone and methyl acrylate, more reactive than dimethyl maleate<sup>4,8</sup>, it is necessary to reduce the amount of olefin and/or to increase the amount of Bu<sub>3</sub>SnH in order to minimize the competitive addition of Bu<sub>3</sub>Sn• to olefin. Thus, by the use of 5 equivalents of methyl vinyl ketone and 7 equivalents of Bu<sub>3</sub>SnH, the corresponding C-glycosyl compound, 4-(5-Q-benzoyl-2,3-Q-isopropylidene- $\beta$ -D-ribofuranosyl)-2-butanone (4)<sup>16</sup> (49% yield), 3 (3% yield), and the reduced product, 1,4-anhydro-5-Q-benzoyl-2,3-Q-isopropylidene-D-ribitol (5)<sup>16</sup> (9% yield) were obtained; and by the use of 4 equivalents of methyl acrylate and 2 equivalents of Bu<sub>3</sub>SnH, methyl 3-(5-Q-benzoyl-2,3-Q-isopropylidene- $\beta$ -D-ribofuranosyl)propionate (6)<sup>16</sup> (34% yield), a diastereomeric mixture of methyl 5-(5-Q-benzoyl-2,3-Q-isopropylidene- $\beta$ -D-ribofuranosyl)-4-methoxycarbonylpentanoate (7) (14% yield), and 3 (5% yield) were obtained.

Treatment of 1 with 5 equivalents of dimethyl acetylenedicarboxylate and 2.7 equivalents of Bu<sub>3</sub>SnH gave no C-glycosyl compounds (almost all of 1 remained unchanged : t.l.c. examination), whereas treatment of 1 with 1 equivalent of dimethyl acetylenedicarboxylate and 2.7 equivalents of Bu<sub>3</sub>SnH gave a diastereomeric mixture of 2 (34% yield), 3 (5% yield), and 5 (23% yield). It is clear that dimethyl acetylenedicarboxylate reacted first with Bu<sub>3</sub>Sn• and then with ribofuranosyl radical to give 2 after the normal working up.

Vinylene carbonate, maleimide, maleic anhydride, N-ethylmaleimide, and furan were also applied as olefin derivatives to the reaction under several conditions. Among these olefins vinylene carbonate and N-ethylmaleimide gave the corresponding C-ribofuranosyl compounds, 4-(5-Q-benzoyl-2,3-Q-isopropylidene-D-ribofuranosyl)-1,3-dioxolan-2-one (8)<sup>17</sup> (20% yield) and 2-(5-Q-benzoyl-2,3-Q-isopropylidene-D-ribofuranosyl)-N-ethylmaleimide (9)<sup>17</sup> (28% yield), respectively. It was thus concluded that ribofuranosyl radical additions to olefins has potential utilities for the construction of various types of C-ribofuranosyl compounds.

Then, the diastereomeric mixture of 2 was converted to 2-(5-Q-t-butyldi-phenylsilyl-2,3-Q-isopropylidene- $\beta$ -D-ribofuranosyl)succinimide (12 and 13) straightforward by 6 steps in a 25.4 % overall yield as shown in Scheme 1. The  $\beta$ -configurations at 1'-positions of 12 and 13 were confirmed at the stage of the corresponding 5'-OH derivatives (10 and 11), which were partly isolated and proved to be identical with authentic specimen<sup>18</sup>, respectively. The mixture of DL-12 and -13 had been converted to DL-showdomycin (DL-14) by the



sequential treatments with LICA, PhSeCl, NaIO<sub>4</sub>, and TFA<sup>19</sup>. Therefore the synthesis of showdomycin (14) was achieved formally. This synthesis is the third example of showdomycin synthesis via C - C bond formation between ribofuranosyl moiety and C<sub>4</sub>-aglycone moiety<sup>20,21</sup>.

## NOTES AND REFERENCES

- 1 Present address : Research Institute for Polymers and Textiles, Yatabe-Higashi, Tsukuba, Ibaraki 305, Japan.
- 2 G. E. Keck and J. B. Yates, J. Am. Chem. Soc., 104, 5829 - 5831 (1982).
- 3 B. Giese and J. Dupuis, Angew. Chem. Int. Ed. Engl., 22, 622 - 623 (1983).
- 4 R. M. Adlington, J. E. Baldwin, A. Basak, and R. P. Kozyrod, J. Chem. Soc., Chem. Commun., 944 - 945 (1983).
- 5 G. E. Keck, E. J. Enholm, and D. F. Kachensky, Tetrahedron Lett., 25, 1867 - 1870 (1984).
- 6 G. E. Keck, E. J. Enholm, J. B. Yates, and M. R. Wiley, Tetrahedron, 41, 4079 - 4094 (1985).
- 7 J. Dupuis, B. Giese, J. Hartung, M. Leising, H.-G. Korth, and R. Sustmann, J. Am. Chem. Soc., 107, 4332 - 4333 (1985).
- 8 Y. Araki, T. Endo, M. Tanji, J. Nagasawa, Y. Ishido, Tetrahedron Lett., in press.
- 9 Only one example of ribofuranosyl radical additions is known (ref. 5,6) : photochemically induced additions of phenyl 5-O-t-butyl-diphenylsilyl-2,3-O-isopropylidene-1-thio- $\alpha$ -D-ribofuranoside with allyltributyltin and methallyltributyltin.
- 10 R. S. Klein, H. Ohru, and J. J. Fox, J. Carbohydr. Nucleosides Nucleotides, 1, 265 - 269 (1974).
- 11 This ribofuranosyl bromide was synthesized from 1,2,3,5-tetra-O-acetyl- $\beta$ -D-ribofuranose and bromotrimethylsilane according to the method of Israel and used without purification : J. W. Gillard and M. Israel, Tetrahedron Lett., 22, 513 - 516 (1981).
- 12 The chloride was much less reactive than dimethyl maleate with Bu<sub>3</sub>Sn $\cdot$  : Bu<sub>3</sub>Sn $\cdot$  mainly added to dimethyl maleate rather than abstracted a chlorine atom from the sugar, whereas the crude bromide (note 11) was extremely unstable : hydrolyzed much faster than abstracted of a bromine atom.
- 13 This compound was synthesized from 5-O-benzoyl-2,3-O-isopropylidene-D-ribofuranose by the application of Gross's method with a slight modification : P. D. Cesare and B. Gross, Synthesis, 714 - 715 (1950).
- 14 The methylthiothiocarbonate 1 was smoothly reduced to 5 by Bu<sub>3</sub>SnH - AIBN, though 2,3,4,6-tetra-O-acetyl-1-O-methylthiothiocarbonyl- $\beta$ -glucopyranose had been reduced very slowly (ref. 8) : ribofuranosyl radical was formed more easily than glucopyranosyl radical from the corresponding compounds bearing the same anomeric substituent.
- 15 About 3 : 4 mixture of the corresponding diastereomers. The nmr spectrum and the micro-elemental analysis data of this mixture agree well with its structure.
- 16 The structures of these compounds were confirmed by their ir and nmr spectra, and by their micro-elemental analyses.
- 17 Ratios of the diastereomers of these compounds couldn't be estimated. However, their nmr spectra and micro-elemental analyses data agree well with the desired C-ribofuranosyl structures.
- 18 A. Rosenthal and J. Chow, J. Carbohydr. Nucleosides Nucleotides, 7, 77 - 92 (1980).
- 19 A. P. Kozikowski and A. Ames, J. Am. Chem. Soc., 103, 3923 - 3924 (1981).
- 20 T. Inoue and I. Kuwajima, J. Chem. Soc., Chem. Commun., 251 - 253 (1980).
- 21 A. G. M. Barrett and H. B. Broughton, J. Org. Chem., 49, 3673 - 3674 (1984).

(Received in Japan 9 November 1987)