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Preliminary communication

Reaction of lithium dimethyl cuprate with methyl 2,3-anhydro-5-deoxy-α-D-ribofuranoside. A new, convenient route for preparation of 2,5-dideoxy-2-*C*-methyl-D-arabinofuranose derivatives

HIROSHI YAMAMOTO*, HIROSHI SASAKI, and SABURO INOKAWA
Department of Chemistry, Faculty of Science, Okayama University, Okayama 700 (Japan)

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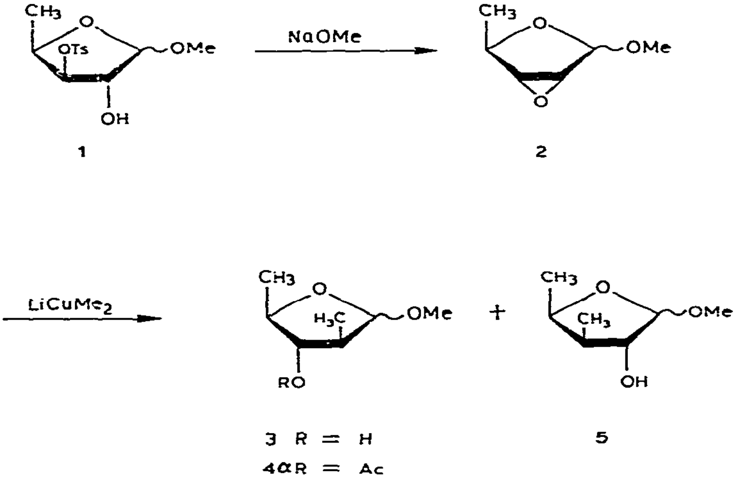
The use of sugars as chiral synthons in synthesizing a wide variety of complex natural products is of increasing interest[1]. Nucleophilic reaction of 2,3-anhydro-D-ribofuranosides is known to take place at C-2 or C-3, or both, depending upon steric and polar effects[2]. We here describe a new, convenient route for preparation of the hitherto unreported 2,5-dideoxy-2-*C*-methyl-α-D-arabinofuranose derivatives (3α and 4α) as potential building blocks in the synthesis of macrolides and other natural products.



1 2

3 R = H
4αR = Ac
5

Methyl 2,3-anhydro-5-deoxy-α-D-ribofuranoside (2α) was prepared in 85% yield from methyl 5-deoxy-3-*O*-*p*-tolylsulfonyl-α-D-xylofuranoside (1α), which was readily derived from D-xylose[2,3]. Treatment of 2α with lithium dimethyl cuprate (2.0 equiv.) in ether for 3 h at 0°, followed by the usual processing, gave a mixture of two sugars, separable in a column of silica gel with 1:49 (v/v) methanol–chloroform as the eluant.

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*To whom correspondence should be addressed.

The structures of the products were established, by their spectra, as methyl 2,5-dideoxy-2-*C*-methyl-α-D-arabinofuranoside (3α) {a colorless oil; 54% yield; $[\alpha]_D^{15}$ +102° (*c* 1.29, $CHCl_3$); $\nu_{max}^{CHCl_3}$ 3500 cm^{-1} (OH); *m/z* 146 (M^+)}, and methyl 3,5-dideoxy-3-*C*-methyl-α-D-xylofuranoside (5α) {a colorless oil; 10% yield; $[\alpha]_D^{15}$ +148° (*c* 1.35, $CHCl_3$); $\nu_{max}^{CHCl_3}$ 3540 cm^{-1} (OH); *m/z* 146 (M^+)}; the assignments for the ^{1}H-n.m.r. spectra of both compounds are recorded in Table I.

TABLE I

^{1}H-N.M.R. PARAMETERS[a] FOR THE DIDEOXY-*C*-METHYL-PENTOFURANOSIDES IN $CDCl_3$

Compound	*MeO-1* *H-1*	*Me-2* *(HO-2)* *H-2*	*Me-3* *(RO-3)* *H-3*	*H-4*	H_3-5	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	J_{Me-CH}	J_{HO-CH}
3α	3.36 s	1.09 d	(2.8 brs)								
	4.62 d	2.14 qdd	3.40 dd	3.98 qd	1.31 d	1.8	3.5	4.8	6.5	7.0	
4α	3.35 s	1.15 d	(2.07 s)								
	4.59 d	2.1 qdd	4.41 dd	4.12 qd	1.34 d	1.0	3.2	5.5	6.1	7.6	–
5α	3.48 s	(2.55 d)	0.98 d								
	4.84 d	3.79 ddd	2.28 qdd	4.36 dq	1.10 d	4.5	6.5	7.0	6.2	7.5	8.0

[a] Chemical shifts (δ values) in p.p.m. from Me_4Si. Coupling constants (*J*) in Hz.

The major product was treated with acetic anhydride in pyridine, to give the acetyl derivative 4α {a colorless oil; 80% yield; $[\alpha]_D^{15}$ +101° (*c* 1.15, $CHCl_3$); $\nu_{max}^{CHCl_3}$ 1730 cm^{-1} (ester); *m/z* 188 (M^+); ^{1}H-n.m.r. data, see Table I}, further confirming the structure of 3α.

On the other hand, the reaction of $LiCuMe_2$ with the β anomer 2β, obtained from 1β in 50% yield, did not produce the expected β isomer, 3β, or 5β. As 1α and 1β were equilibrated in acidic methanol (~9 : 11, respectively, based on the n.m.r. data) and were chromatographically separable, the 2-*C*-methyl-D-arabinofuranoses (3α and 4α) are more effectively prepared *via* 1α and 2α.

REFERENCES

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