Reaction of Methyl 2,3-*O*-Isopropylidene-α-L-rhamnopyranoside with Triphenyl Phosphite Methiodide

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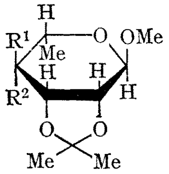
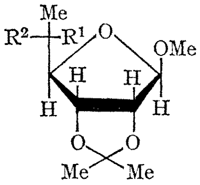
THE reaction of the triphenyl phosphite methiodide complex[1] with suitably substituted sugar derivatives has been used[2] to prepare iodo-derivatives and hence, deoxy-derivatives. Thus, from methyl 2,3-*O*-isopropylidene-α-L-rhamnopyranoside (I) a mixture of methyl 4,6-dideoxy-4-iodo-2,3-*O*-isopropylidene-α-L-talopyranoside [(II), m.p. 55°, $[\alpha]_D^{20}$ −65° ($CHCl_3$)] and methyl 4,6-dideoxy-4-iodo-2,3-*O*-isopropylidene-α-L-mannopyranoside [(III) m.p. 81°, $[\alpha]_D^{20}$ 0° ($CHCl_3$)] was obtained. The iodides (II) and (III) were reduced to methyl 4,6-dideoxy-2,3-*O*-isopropylidene-α-L-*lyxo*-hexopyranoside (IV), the structure and configuration of which was established[3] by chemical and n.m.r. methods. The configuration at C-4 of the isomeric iodides (II) and (III) was assigned[3] on the basis of their different reactivity with sodium azide; (II) undergoes nucleophilic displacement whereas (III) does not.

An attempt to reproduce the above synthesis of the iodides (II) and (III), which were required for further syntheses, gave different results. Reaction of triphenyl phosphite methiodide and the rhamnoside (I) in benzene gave a crude mixture (50%), m.p. 40—45°, which could not be separated by t.l.c. on alumina or silica gel. Recrystallization from light petroleum gave predominantly methyl 5,6-dideoxy-5-iodo-2,3-*O*-isopropylidene-β-D-allofuranoside [(VI), m.p. 54·5—55·5°, $[\alpha]_D^{21}$ −68·6° ($CHCl_3$)]. A syrup, isolated from the mother liquor, on treatment with sodium azide yielded methyl 5-azido-5,6-dideoxy-2,3-*O*-isopropylidene-α-L-talofuranoside (VII) and the iodide (III) [m.p. 79—80°, $[\alpha]_D^{21}$ −11·7° ($CHCl_3$)], which were separated on alumina. Reduction followed by *N*-acetylation of the azido-derivative (VII) gave the known[4,5] methyl 5-acetamido-5,6-dideoxy-2,3-*O*-isopropylidene-α-L-talofuranoside [(VIII), $[\alpha]_D^{21}$

−84·6° (EtOH)]. Iodides (III) and (VI) were hydrogenated over Raney nickel in the presence of trimethylamine (1 equiv.). The iodide (III) yielded (85%) methyl 4,6-dideoxy-2,3-*O*-isopropylidene-α-L-*lyxo*-hexopyranoside [(V), $[\alpha]_D^{21}$ −43·1° ($CHCl_3$)] and isomer (VI) afforded (84%) methyl 5,6-dideoxy-2,3-*O*-isopropylidene-β-D-*ribo*-hexo-furanoside [(IX), $[\alpha]_D^{21}$ −72·9° ($CHCl_3$)]. The structures of the iodides (III) and (VI) and of the corresponding deoxy-derivatives (IV) and (IX) were established by n.m.r.† The spectrum of (III) exhibited signals at τ 5·07 (s, H-1, $J_{1,2}$ 0·75, $J_{1,3}$ and $J_{1,5} \neq 0$ Hz), 5·49, (q, H-3, $J_{1,3} \neq 0$, $J_{2,3}$ 5·25, $J_{3,4}$ 8·75 Hz), 6·03 (d q, H-5, $J_{4,5}$ 11, $J_{5,6}$ 6 Hz), 6·13, (q H-2, $J_{1,2}$ 0·75, $J_{2,3}$ 5·25 Hz) 6·34 (q, H-4, $J_{3,4}$ 8·75, $J_{4,5}$ 11 Hz), 6·64 (s, –OMe), 8·50 and 8·67 (s, CMe_2), and 8·57 (d, 6-H, $J_{5\cdot 6}$ 6 Hz). The assignments‡ were verified by means of frequency-sweep tickling and INDOR experiments, and unambiguously confirm the structure of the α-L-mannopyranoside (III) with the equatorial iodine at C-4 (1*C* conformation). The spectrum of the compound (VI), similarly assigned, contained signals at τ 4·96 (s, H-1, $J_{1,2}$ 0, $J_{1,3} \neq 0$ Hz), 5·10 (q, H-3, $J_{1,3} \neq 0$, $J_{2,3}$ 6, $J_{3,4}$ 1·2 Hz), 5·46 (d, H-2, $J_{1,2}$ 0, $J_{2,3}$ 6 Hz), 5·73, (q, $J_{3,4}$ 1·2, $J_{4,5}$ 11·6 Hz), 6·05 (dq, (H-5; $J_{4,5}$ 11·6, $J_{5,6}$ 7 Hz), 6·65 (s, OMe), 8·54 and 8·70 (s, CMe_2) and 8·02 (d, 6-H, $J_{5,6}$ 7 Hz), C-6. This assignment (*cf.* ref. 8) confirms the furanoid structure of compound (VI), and on the basis of the magnitude of $J_{4,5}$ (11·6 Hz) the *allo*-configuration is assigned. The parameters of n.m.r. spectra of the deoxy-derivatives (IV) and (IX) are consistent with previous data,[3,7] and a detailed discussion will be presented elsewhere.





(I) R^1 = OH, R^2 = H
(II) R^1 = H, R^2 = I
(III) R^1 = I, R^2 = H
(IV) R^1 = R^2 = H
(V) R^1 = N_3, R^2 = H

(VI) R^1 = H, R^2 = I
(VII) R^1 = N_3, R^2 = H
(VIII) R^1 = NHAc ,R^2 = H
(IX) R^1 = R^2 = H

The compound, m.p. 55°, described by Adamjanc, Kochetkov, and Usov[3] is probably the furanoside (VI). Together with published[5,6,8] studies concerning the nucleophilic substitution of 4-*O*-methane- and toluene-*p*-sulphonates of (I), these results constitute a further case of S_N2 substitution at C-4 of compound (I), with simultaneous contraction of the pyranose ring.

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† N.m.r. spectra were obtained with a Varian HA-100 spectrometer for solutions in deuteriochloroform with hexamethyldisiloxane (HMDS) as internal reference (τ_{HMDS} 9·95). All data presented are from first-order analysis.

‡ In the work of Adamjanc, Kochetkov, and Usov (ref. 3) only the position of the quartet at τ 5·49 was recorded and wrongly assigned to H-4.

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