

## Note

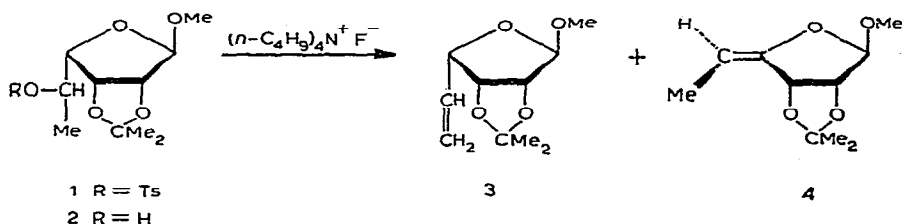
# Synthesis of methyl 5,6-dideoxy-2,3-*O*-isopropylidene- $\alpha$ -L-lyxo-hex-5-enofuranoside\*

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Treatment of methyl 2,3-*O*-isopropylidene-5-*O*-tosyl- $\alpha$ -L-rhamnofuranoside (1) with aqueous, methanolic potassium hydroxide was reported<sup>1,2</sup> to yield an olefin and a little of the parent alcohol 2. The olefin was not completely identified and was assumed<sup>2</sup> to be the terminal olefin 3. More recently, Arzoumanian and his co-



workers<sup>3</sup>, reasoning by analogy with the conversion of methyl 6-deoxy-2,3-*O*-isopropylidene-5-*O*-tosyl- $\beta$ -D-allofuranoside into methyl 5,6-dideoxy-2,3-*O*-isopropylidene- $\beta$ -D-erythro-hex-4-enofuranoside (4), suggested that the unsaturated product obtained from sulphonate 1 in the original work<sup>1,2</sup> was, in fact, the olefin 4. As supporting evidence, the similarity of the optical rotations of the products from the two reactions was cited. In spite of the fact that the experimental value for the rotation of olefin 4 was almost immediately corrected<sup>4</sup>, the suggested formation of 4 through the treatment of sulphonate 1 with base has been reiterated in at least two review articles<sup>5,6</sup>. We now describe the preparation and characterization of the hitherto unknown methyl 5,6-dideoxy-2,3-*O*-isopropylidene- $\alpha$ -L-lyxo-hex-5-enofuranoside (3) and supporting data on the properties of olefin 4. Their specific rotations suggest that the product previously obtained<sup>1,2</sup> from 1 was a mixture of olefins rather than a single isomer.

In an attempt to replace, with inversion, the tosyloxy group in 1 by fluoride, utilising tetra-*n*-butylammonium fluoride<sup>7</sup>, we observed the formation (83%) of two

\*Dedicated to Professor M. Stacey, C.B.E., F.R.S., in honour of his 65th birthday.

unsaturated products in the ratio of 2.2 to 1. The compounds were purified by p.l.c. and distillation.

The major component had  $[\alpha]_D^{20} +65.3^\circ$  (chloroform) in agreement with the value of  $[\alpha]_D^{25} +65.9^\circ$  reported<sup>4</sup> for an "improved" sample of 4. Its i.r. spectrum showed characteristic absorptions at 1700 and 830  $\text{cm}^{-1}$ , and its n.m.r. spectrum\* confirmed its structure as olefin 4. Thus, the resonance of the three protons at C-6 was split by H-5 at  $\tau$  4.91 into a doublet ( $J_{5,6}$  7 Hz). The assignment of the resonances at  $\tau$  4.81 and 5.52 to H-3 and H-2 (rather than H-2 and H-3), respectively, was made on the basis of the greater peak widths of the low-field doublet, most reasonably rationalised as arising from homoallylic coupling of the protons at C-6 to H-3. The available evidence does not unequivocally define the stereochemistry of 4, since its geometrical isomer (C-5 substituents interchanged) should have similar spectral properties. However, the stereochemical requirements of an E2 elimination would ensure that the isomer formed from 1 has the *E*-configuration<sup>8</sup> about the double bond as shown.

The minor component had  $[\alpha]_D^{20} -23.5^\circ$ , and its i.r. spectrum had absorptions at 3090, 1650 (weak), 1430, and 990  $\text{cm}^{-1}$ , in accord with the presence of a vinyl group. Conclusive structural evidence came from its n.m.r. spectrum. A modified ABX pattern for H-5, H-6 and H-6' occurred between  $\tau$  3.7 and 4.8, the X (H-5) resonances being further split by coupling to H-4 ( $J_{4,5}$  7 Hz), and the AB resonances showing fine splitting ( $\sim 1$  Hz) due to long-range coupling to H-4. Since the chemical shift between H-5 ( $\tau$  4.01) and H-4 ( $\tau$  5.63) is large compared to  $J_{4,5}$ , this part of the spectrum may be analysed\*\*, to a reasonable approximation, as an ABX system, after allowance is made for  $J_{4,5}$ . The magnitudes of the coupling constants obtained are typical of those found in similar vinylic systems<sup>9</sup>.

Assuming the specific rotation of olefins 3 and 4 in methanol are similar to their values in chloroform, the material obtained previously<sup>1,2</sup> from 1, with  $[\alpha]_D^{25} +14^\circ$  (methanol), appears to contain a high proportion of terminal olefin 3 (ratio of 4 to 3, 0.7:1). It is noteworthy that fluoride-induced formation of 1- and 2-butenes from 2-butyl toluene-*p*-sulphonate leads to a much lower proportion of the terminal olefin than when alkoxide is used as base<sup>10</sup>.

#### EXPERIMENTAL

Preparative layer chromatography (p.l.c.) was carried out on Kieselgel PF<sub>254</sub>. N.m.r. spectra were measured on a Varian HA-100 instrument with tetramethylsilane as the internal reference, and chemical shifts are accurate to  $\tau \pm 0.02$ . Abbreviations used are d, doublet; dd, double doublet; m, multiplet; q, quartet; s, singlet. Tetra-*n*-butylammonium fluoride, prepared by triple decomposition of silver sulphate,

\*Our n.m.r. data are in good agreement with those reported in a less-detailed analysis<sup>3</sup>.

\*\*The agreement between the experimentally measured spectrum and a spectrum simulated by a computer, using the calculated coupling constants and chemical shifts, supported the correctness of the values obtained.

tetra-*n*-butylammonium iodide, and barium fluoride<sup>11</sup>, contained a small amount of residual barium fluoride. It was dried before use by the repeated addition and evaporation of benzene\*.

*Treatment of methyl 2,3-O-isopropylidene-5-O-tosyl- $\alpha$ -L-rhamnofuranoside (1) with tetra-*n*-butylammonium fluoride.* — Tetra-*n*-butylammonium fluoride (4 g) and **1** (1 g) in acetonitrile (22 ml) were heated under reflux for 22 h. The mixture was then concentrated and the residue dissolved in ether (100 ml). The organic solution was washed with water (4  $\times$  75 ml), dried (Na<sub>2</sub>SO<sub>4</sub>), and concentrated. T.l.c. (benzene-ether; 19:1 v/v) of the syrupy product showed two major components having *R<sub>F</sub>* 0.28 and 0.41. P.l.c. in the same solvent yielded the slow- and fast-running components as syrups (0.16 and 0.30 g, respectively). The material having *R<sub>F</sub>* 0.41 was distilled to yield methyl 5,6-dideoxy-2,3-*O*-isopropylidene- $\beta$ -D-erythro-hex-4-enofuranoside (**4**), b.p. 70–74° (bath)/2.8 mmHg,  $[\alpha]_D^{20} + 65.3^\circ$  (c 1.3, chloroform); lit.<sup>3</sup> b.p. 40–42°/0.1 mmHg,  $[\alpha]_D^{25} + 12.5^\circ$  (chloroform); lit.<sup>4</sup>  $[\alpha]_D^{25} + 65.9^\circ$  (chloroform);  $\nu_{\max}^{\text{film}}$  2820 (OMe), 1700 (enol ether), 1385, 1375 (CMe<sub>2</sub>), 830 cm<sup>-1</sup> (olefin C–H); n.m.r. data (CDCl<sub>3</sub>):  $\tau$  4.81 (d, H-3), 4.91 (q, H-5), 4.97 (s, H-1), 5.52 (d, H-2), 6.62 (s, OMe), 8.30 (d, H-6), 8.55 (s) and 8.64 (s) (CMe<sub>2</sub>); *J*<sub>1,2</sub> < 0.5, *J*<sub>2,3</sub> 6.2, *J*<sub>5,6</sub> 7.0 Hz.

*Anal.* Calc. for C<sub>10</sub>H<sub>16</sub>O<sub>4</sub>: C, 60.0; H, 8.0. Found: C, 60.3; H, 8.3.

The material having *R<sub>F</sub>* 0.28 was contaminated with sulphonate **1** (9% by n.m.r.) which showed similar chromatographic mobility. The material was purified by distillation to yield the analytical sample of methyl 5,6-dideoxy-2,3-*O*-isopropylidene- $\alpha$ -L-lyxo-hex-5-enofuranoside (**3**), b.p. 76°(bath)/3.2 mmHg,  $[\alpha]_D^{20} - 23.5^\circ$  (c 1.4, chloroform);  $\nu_{\max}^{\text{film}}$  3090 (olefin CH<sub>2</sub> str.), 2820 (OMe), 1650 (C=C, weak), 1430 (olefin CH<sub>2</sub> def.), 1385, 1375 (CMe<sub>2</sub>), 990 cm<sup>-1</sup> (olefin CH def.); n.m.r. data (CDCl<sub>3</sub>):  $\tau$  4.01 (m, H-5), 4.62 (m, H-6), 4.69 (m, H-6'), 5.09 (s, H-1), 5.33 (dd, H-3), 5.44 (d, H-2), 5.63 (dd, H-4), 6.65 (s, OMe), 8.54 (s) and 8.69 (s) (CMe<sub>2</sub>); *J*<sub>1,2</sub> < 1, *J*<sub>2,3</sub> 6, *J*<sub>3,4</sub> 3.5, *J*<sub>4,5</sub> 7, *J*<sub>4,6</sub> = *J*<sub>4,6'</sub> = ~1, *J*<sub>5,6</sub> 17.7, *J*<sub>5,6'</sub> 9.8, *J*<sub>6,6'</sub> 2 Hz.

*Anal.* Calc. for C<sub>10</sub>H<sub>16</sub>O<sub>4</sub>: C, 60.0; H, 8.0. Found: C, 60.12; H, 8.19.

*Mass spectra.* — The *m/e* values for parent ions and peaks > 50% relative abundance are recorded. Compound **3**: 200, 185, 85 (base peak), 83, 82, 81, 71, 69, 59, 58, 57, 55, 54, 43, 41, 39, 29, 28, 27. Compound **4**: 200, 127, 111, 85, 83, 59, 55, 43 (base peak), 28.

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