The Formation of Several Products from the Trimethylsilylation of D-*altro*-3-Heptulose ("Coriose")

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Summary Upon trimethylsilylation, D-*alto*-3-heptulose initially yields pentakistrimethylsilylfuranose, which is transformed on further trimethylsilylation to a mixture of hexakistrimethylsilylfuranose and the hexakistrimethylsilyl ether of the keto-form.

CARBOHYDRATES undergoing trimethylsilylation usually retain the original ring structure.[1] Two-step trimethylsilylation of 2-ketoses gives a final product which retains the ring structure of the ketose.[2] However, D-*altro*-3-heptulose ("coriose") (I)[3] has been found to undergo a two-step trimethylsilylation in which the initial product is converted into a mixture of two trimethylsilyl ethers, one of which is that of the keto-form.

Upon g.l.c.† of coriose a few minutes after the reagent† is added to the crystals, a peak due to the initial trimethylsilyl ether (II) (retention time relative to α-D-glucose: 1·72) is observed. Two other peaks whose retention time relative to α-D-glucose is 1·99 (III) and 2·28 (IV), in addition to (II), appear after prolonged trimethylsilylation with an excess of the reagent. Growth of (III) and (IV) at the expense of (II) is observed, until finally (II) disappears.

The first trimethylsilyl ether (II), which is best prepared by trimethylsilylation at a lower temperature, or with a limited amount of the reagent, was purified by vacuum distillation (bath temp. 180°, at 1·4 mm.Hg.). This product, $[\alpha]_D^{20}$ + 15·3° (*c* 0·369, n-hexane), was analysed as $C_{22}H_{54}O_7Si_5$, which is supported by the M — 18 peak in

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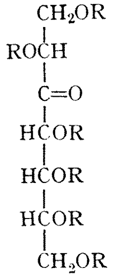
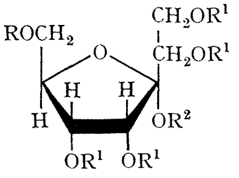
† Trimethylsilylation and g.l.c. were carried out as described for 2-ketoses.[2]

the mass spectrum. The hydroxy-group is indicated by the absorption at 3400 cm.$^{-1}$ in the i.r. spectrum. The n.m.r. spectrum in dimethyl sulphoxide exhibits a hydroxy-proton as a singlet at around τ 5, which disappears on treatment with D_2O, indicating that the hemiacetal hydroxy-group is free in (II). One of the final products, (III), was isolated by elution chromatography on a silicic acid column (petroleum–benzene) after trimethylsilylation overnight. This product, $[\alpha]^{20}_{D} + 51{\cdot}7°$ (c 0·405, n-hexane), was analysed as $C_{25}H_{62}O_7Si_6$, which is supported by the mass spectrum. Absence of hydroxy- and carbonyl groups is shown by the i.r. spectrum. The m/e 204 fragment in the mass spectrum, which has been reported to be small in furanoid compounds,[1] is smaller than 4% of the base peak (m/e 73) both in (II) and (III). No peak or spot which could be regarded as due to the anomers of (II) and (III) was detected on g.l.c. or t.l.c. Therefore, based on the structure of crystalline coriose (V),[4] compound (II) is presumed to be 1,2,4,5,7-pentakis-O-trimethylsilyl-α-coriofuranose, and (III) is regarded as 1,2,3,4,5,7-hexakis-O-trimethylsilyl-α-coriofuranose.



(I) R=H
(IV) R=Me$_3$Si



(II) R^1=Me$_3$Si;R^2=H
(III) R^1=R^2=Me$_3$Si
(V) R^1=R^2=H

The product (IV) was isolated by extracting the silicic acid column with methylene chloride. This trimethylsilyl ether, $[\alpha]^{20}_{D} - 17{\cdot}6°$ (c 0·691, n-hexane), $C_{25}H_{62}O_7Si_6$, shows no OH absorption in the i.r. spectrum, but shows a carbonyl absorption peak at 1722 cm.$^{-1}$, u.v. absorption at 282 nm (ϵ 102), and a negative Cotton effect in the o.r.d. spectrum, $[\Phi]^{20}_{316} + 2680°$, $[\Phi]^{20}_{262} - 3480°$ (c 0·691, n-hexane) Accordingly (IV) is 1,2,4,5,6,7-hexakis-O-trimethylsilyl-*keto*-coriose.

The ratio of (III) to (IV) varies between *ca.* 1 : 1 and *ca.* 1 : 3 from experiment to experiment. These three g.l.c. peaks are useful for identification of coriose, since the appearance of these peaks and the growth of peaks due to (III) and (IV) are also observed on trimethylsilylation of coriose-containing syrup, although equilibrated coriose shows the peak due to (IV), and other peaks, on g.l.c. immediately after addition of the reagent.

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[1] C. C. Sweeley, R. Bentley, M. Makita, and W. W. Wells, *J. Amer. Chem. Soc.*, 1963, **85**, 2497; H.-Ch. Curtius, M. Müller, and J. A. Völlmin, *J. Chromatog.*, 1968, **37**, 216; D. C. DeJongh, T. Radford, J. D. Hribar, S. Hanessian, M. Bieber, G. Dawson, and C. C. Sweeley, *J. Amer. Chem. Soc.*, 1969, **91**, 1728.

[2] T. Okuda and K. Konishi, *Chem. Comm.*, 1969, 796.

[3] T. Okuda and K. Konishi, *Chem. Comm.*, 1968, 553; 1968, 671; *J. Pharm. Soc. Japan*, 1968, **88**, 1329; *Tetrahedron*, 1968, **24**, 6907; *Chem. and Pharm. Bull.* (*Japan*), 1969, **17**, 735.

[4] T. Okuda, K. Osaki, and T. Taga, *Chem. Comm.*, 1969, 851.