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## Note

# Preparation of crystalline octa-*O*-(trimethylsilyl)sucrose

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In 1957, Henglein *et al.*[1] reported the preparation of octa-*O*-(trimethylsilyl)-sucrose; sucrose was treated for 5 h at 40° with chlorotrimethylsilane in hexane in the presence of pyridine and formamide. The product was vacuum distilled, $\text{b.p.}_{0.07\,\text{mm}}$ 208–210°. A little later, Chang and Hass[2] prepared the same derivative by reaction of sucrose and excess chlorotrimethylsilane in pyridine solution. Again, vacuum distillation yielded a viscous, colorless oil. Prophetically, these authors noted a potential use for this derivative in the separation of sucrose by vapor-phase chromatography. The trimethylsilyl derivative was also said to exhibit "a marked tendency to hydrolyze", a statement apparently based on its conversion to sucrose when heated under reflux in water. In another early work, Hedgley and Overend[3] prepared octa-*O*-(trimethylsilyl)maltose as a distillable material, forming a colorless glass.

During our early work[4,5] on the gas chromatography of carbohydrate *O*-trimethylsilyl derivatives, we had remained unaware of Chang and Hass's preparation and of their suggestion. However, we carried out a preparative-scale synthesis of octa-*O*-(trimethylsilyl)sucrose under conditions different from those of the earlier workers. The compound, distilled in vacuum, was initially a colorless oil. After being kept for two days, spontaneous crystallization took place; those crystals, which formed in a thin layer, were feather-like. When a chloroform solution of the compound was evaporated to an oil in a stream of nitrogen and seeded, a mass of rhombic crystals was obtained. Although a number of crystalline *O*-trimethylsilyl carbohydrate derivatives are known, they all contain other substituents or functional groups, or both, as well as the trimethylsilyl substituents. The octa-*O*-trimethylsilyl derivative of sucrose is, therefore, particularly interesting, since crystallinity arises with only the trimethylsilyl substituents.

The material prepared originally in October 1964 has been kept in a rubber stoppered flask since that time (with no special precautions) and has shown no deterioration; clearly, the rate of hydrolytic decomposition is minimal.

The mass spectrum of our material did not show a peak corresponding to the molecular ion ($M^{+\cdot}$) for octa-*O*-(trimethylsilyl)sucrose (*m/e* 918). Kochetkov *et al.*[7] have examined a series of octa-*O*-(trimethylsilyl) derivatives of various D-glucosyl-

D-glucoses. They noted that the peak at *m/e* 918 was either very small or completely missing. With octa-*O*-(trimethylsilyl)sucrose and the mass spectrometer operated under high-gain conditions, it was, however, possible to detect small peaks at *m/e* 903 (M −15, loss of Me), 828 (M−90, loss of $Me_3SiOH$), and 738 ($M^+ - 2 \times 90$). The fragment having the highest *m/e* value that gave an easily visible peak under normal gain conditions was at *m/e* 451; this was attributed to $C_6H_7O(OSiMe_3)_4$ derived from either half of the molecule. A similar fragment has been noted, for example, in the m.s. of octa-*O*-(trimethylsilyl)maltose[7]. The loss of $Me_3SiOH$ from the fragment at *m/e* 451 gave another large peak at *m/e* 361.

It seems likely that the crystalline product could have considerable potential value as an internal standard in gas-chromatographic applications. Noncrystalline material has already been used in this fashion by Walker and Jeanloz[6] in connection with the synthesis of di-*N*-acetylisochitobiose-L-asparagine.

## EXPERIMENTAL

A mixture of sucrose (5 g), pyridine (50 ml), hexamethyldisilazane (15 g), and chlorotrimethylsilane (5 g) was shaken overnight in a room at 29°. The pyridine and volatile materials were then removed in vacuum. The whitish residue was treated with ether (50 ml), and the solid removed by filtration, and washed with further portions of ether. The ether extracts were evaporated, and the residual oil was distilled in vacuum. The fraction with b.p.$_{\sim 0.01\,mm}$ 195–200° was collected. After two days at room temperature, crystallization had occurred, m.p. 63–65°, $[\alpha]_D^{22}$ +35.9° (*c* 5.8, chloroform); m.s. (LKB 9000, 70 eV; trap current, 60 μA; probe temperature 45°): *m/e* 451 (6.5), 437 (6.3), 361 (31.3), 319 (4.7), 271 (8.0), 243 (7.0), 217 (25.0), 169 (10.0), 147 (25.0), 129 (12.5), 117 (6.7), 103 (19.2), and 73 (base peak). For the noncrystalline material, Henglein *et al.*[1] reported $[\alpha]_D^{20}$ +32.15° (*c* 5.0, benzene); Chang and Hass[2], presumably in error, reported $[\alpha]_D^{20}$ +3.47° (*c* 50 (w/w), benzene).

*Anal.* Calc. for $C_{36}H_{86}O_{11}Si_8$: C, 47.01; H, 9.42. Found: C, 46,59, 46.79; H, 9.42, 9.31.

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