

Table 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters ($\text{\AA}^2 \times 10^4$)
$$U_{eq} = \frac{1}{3}(\text{trace of the orthogonalized } U_{ij} \text{ matrix}).$$

| | x | y | z | U_{eq} |
|-------|-----------|-----------|-----------|-------------|
| Si | 1633 (1) | 7815 (1) | 7324 (1) | 201 (2) |
| F | 4016 (3) | 7507 (2) | 7445 (2) | 357 (6) |
| O(1) | 153 (4) | 6962 (3) | 8274 (2) | 325 (7) |
| H(1) | 46 (100) | 6215 (67) | 8285 (53) | 1035 (217)* |
| C(1) | 1694 (5) | 7068 (3) | 6067 (2) | 271 (9) |
| C(2) | 2501 (6) | 5424 (4) | 6129 (3) | 406 (12) |
| C(3) | -492 (7) | 7192 (5) | 5843 (4) | 520 (15) |
| C(4) | 3189 (7) | 7842 (4) | 5178 (3) | 474 (13) |
| C(5) | 913 (5) | 9832 (3) | 7491 (2) | 273 (9) |
| C(6) | 2409 (10) | 10796 (5) | 6768 (4) | 737 (21) |
| C(7) | 983 (8) | 10106 (4) | 8590 (3) | 501 (15) |
| C(8) | -1315 (8) | 10271 (5) | 7370 (5) | 792 (24) |
| O(2) | -480 (3) | 4155 (2) | 8491 (2) | 376 (8) |
| N | -2423 (4) | 3819 (3) | 8858 (2) | 245 (7) |
| C(9) | -3034 (4) | 3321 (3) | 9849 (2) | 273 (9) |
| C(10) | -5035 (5) | 2929 (3) | 10234 (2) | 281 (9) |
| C(11) | -6447 (5) | 3048 (3) | 9610 (3) | 302 (10) |
| C(12) | -5804 (4) | 3573 (4) | 8600 (2) | 290 (9) |
| C(13) | -3782 (4) | 3957 (3) | 8232 (2) | 267 (9) |

* Isotropic.

Table 2. Bond lengths (\AA) and angles ($^\circ$)

| | | | |
|-------------------|------------|-------------------|-----------|
| Si-F | 1.606 (2) | Si-O(1) | 1.609 (2) |
| Si-C(1) | 1.877 (3) | Si-C(5) | 1.878 (3) |
| O(1)-H(1) | 0.695 (64) | C(1)-C(2) | 1.543 (4) |
| C(1)-C(3) | 1.529 (6) | C(1)-C(4) | 1.530 (5) |
| C(5)-C(6) | 1.508 (6) | C(5)-C(7) | 1.538 (5) |
| C(5)-C(8) | 1.519 (7) | O(2)-N | 1.316 (3) |
| N-C(9) | 1.351 (4) | N-C(13) | 1.358 (4) |
| C(9)-C(10) | 1.370 (4) | C(10)-C(11) | 1.385 (5) |
| C(11)-C(12) | 1.383 (4) | C(12)-C(13) | 1.377 (4) |
| O(1)...O(2) | 2.630 (6) | | |
| F-Si-O(1) | 108.2 (1) | F-Si-C(1) | 104.2 (1) |
| O(1)-Si-C(1) | 112.5 (1) | F-Si-C(5) | 105.5 (1) |
| O(1)-Si-C(5) | 106.3 (1) | C(1)-Si-C(5) | 119.5 (1) |
| Si-O(1)-H(1) | 122.2 (51) | Si-C(1)-C(2) | 107.8 (2) |
| Si-C(1)-C(3) | 111.8 (2) | C(2)-C(1)-C(3) | 108.2 (3) |
| Si-C(1)-C(4) | 111.8 (3) | C(2)-C(1)-C(4) | 108.0 (3) |
| C(3)-C(1)-C(4) | 109.1 (3) | Si-C(5)-C(6) | 113.2 (2) |
| Si-C(5)-C(7) | 107.5 (2) | C(6)-C(5)-C(7) | 107.8 (3) |
| Si-C(5)-C(8) | 110.5 (3) | C(6)-C(5)-C(8) | 109.8 (4) |
| C(7)-C(5)-C(8) | 107.8 (4) | O(2)-N-C(9) | 119.7 (3) |
| O(2)-N-C(13) | 119.5 (3) | C(9)-N-C(13) | 120.8 (2) |
| N-C(9)-C(10) | 120.3 (3) | C(9)-C(10)-C(11) | 120.0 (3) |
| C(10)-C(11)-C(12) | 118.9 (3) | C(11)-C(12)-C(13) | 119.8 (3) |
| N-C(13)-C(12) | 120.1 (3) | Si-O(1)...O(2) | 127.6 (4) |
| N-O(2)...O(1) | 117.2 (4) | | |

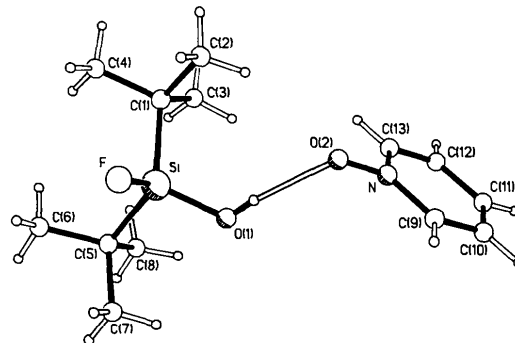


Fig. 1. Structure of the adduct, showing the atom-labelling scheme.

shorter than in other hydrogen-bonded silanols (Clegg, 1983; Graalman, Klingebiel, Clegg, Haase & Sheldrick, 1983). This can be ascribed to the electron-withdrawing fluoro substituent, which has also been observed to shorten adjacent Si-N bonds in silazanes (Clegg, Sheldrick & Stalke, 1984).

We thank the Fonds der Chemischen Industrie for financial support.

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Structure of Sucrose Octaacetate, $C_{28}H_{38}O_{19}$, at 173 K

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(Received 6 October 1983; accepted 13 December 1983)

Abstract. $M_r = 678.60$, orthorhombic, $P2_12_12_1$, $a = 18.350$ (7), $b = 21.441$ (6), $c = 8.350$ (5) \AA , $V = 3285.2$ \AA^3 , $Z = 4$, $D_x = 1.372$ g cm^{-3} , $\lambda(\text{Mo K}\alpha) = 0.71073$ \AA , $\mu = 1.1$ cm^{-1} , $F(000) = 1432$. Final R

$= 0.053$ for 2156 unique observed reflections. The pyranose and furanose rings are in chair (4C_1) and twist (4T_1) conformations respectively. The conformations about the glycosidic bonds differ by 14 and 23° from

the conformations observed in sucrose. The conformations of the pyranose and furanose rings are also different from those observed for sucrose.

Introduction. A class of sucrose octa- and heptaesters of long-chain fatty acids, collectively termed sucrose polyester (SPE), has been investigated by the Procter and Gamble Company as a non-absorbable dietary fat substitute (Fallat, Glueck & Mattson, 1976; Mattson, Jandacek & Webb, 1976). As SPE passes through the intestinal tract, it absorbs dietary and enterohepatic cholesterol with a resultant decrease in plasma low-density lipoprotein cholesterol, a risk factor in coronary artery disease. SPE thus potentially offers both dietary and cardiovascular benefits. The crystal-structure determination of sucrose octaacetate, hereafter referred to as SUOA, was undertaken to serve as a prototypical sucrose polyester.

Experimental. Clear needles grown from aqueous ethanol at room temperature, $0.10 \times 0.17 \times 0.50$ mm; Syntex P2₁ four-circle diffractometer, Syntex LT-1 low-temperature device, graphite-monochromatized Mo K α ; cell constants from setting angles of 15 reflections; corrections for Lorentz and polarization effects, no absorption correction applied; $\theta_{\max} = 25^\circ$; $h = 0$ to 22, $k = 0$ to 26, $l = 0$ to 10; standard reflections (400, 041, 002, 210) measured every 100 reflections showed random variations (<2%) from mean intensities; 3323 unique reflections, 2156 observed with $|F_o| > 4.0\sigma(|F_o|)$; direct methods; refinement on F ; 102 reflection removed due to a large $\Delta(F)/\sigma(F)$; methine H atoms located but not refined, methyl and methylene H atoms idealized 0.96 Å from parent atoms; $R = 0.053$, $R_w = 0.047$, $S = 1.41$; $w = (\sigma^2|F_o| + 0.00025|F_o|^2)^{-1}$; scattering factors those of Ibers & Hamilton (1974); mean (max.) shift: σ in final refinement cycle = 0.083 (0.272); final difference electron density map revealed a featureless background below $\pm 0.25 e \text{ \AA}^{-3}$; Data General Eclipse S-250 computer using *SHELXTL* (Sheldrick, 1981) programs.

Discussion. A listing of final atomic parameters for the non-H atoms is presented in Table 1.* A drawing of the molecule illustrating the atom-labeling scheme is shown in Fig. 1. Bond lengths and bond angles are listed in Table 2. The structure consists of individual molecules separated by normal van der Waals contacts. A stereoscopic drawing of the packing within the unit cell is shown in Fig. 2.

* Lists of powder diffraction data (hkl assignments, d -spacings, intensities and lattice constants), structure factors, anisotropic thermal parameters, and H-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39122 (17 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. Atom coordinates ($\times 10^4$) and equivalent isotropic temperature factors ($\text{\AA}^2 \times 10^3$) with e.s.d.'s in parentheses

| | x | y | z | U_{eq}^* |
|--------|----------|----------|-----------|------------|
| O(1) | 3536 (2) | 2296 (2) | 2978 (4) | 26 (1) |
| O(2) | 2807 (2) | 2922 (1) | 452 (4) | 26 (1) |
| O(3) | 1849 (2) | 1914 (2) | -66 (4) | 29 (1) |
| O(4) | 2225 (2) | 775 (1) | 1338 (4) | 27 (1) |
| O(5) | 4002 (2) | 1570 (1) | 1153 (4) | 26 (1) |
| O(6) | 4457 (2) | 421 (2) | 2390 (4) | 33 (1) |
| O(7) | 3760 (2) | 3243 (2) | -1043 (5) | 42 (1) |
| O(9) | 1169 (2) | 1976 (2) | 2192 (4) | 47 (1) |
| O(11) | 2325 (2) | 156 (2) | -820 (5) | 65 (2) |
| O(13) | 4411 (2) | -613 (2) | 2053 (6) | 60 (2) |
| O(1') | 4453 (2) | 3475 (2) | 5245 (4) | 39 (1) |
| O(2') | 4773 (2) | 2430 (2) | 3549 (4) | 29 (1) |
| O(3') | 3361 (2) | 1798 (2) | 5799 (4) | 28 (1) |
| O(4') | 4918 (2) | 1767 (2) | 7457 (4) | 29 (1) |
| O(6') | 6220 (2) | 1510 (2) | 5223 (4) | 39 (1) |
| O(7') | 3951 (2) | 4423 (2) | 5035 (6) | 59 (2) |
| O(9') | 2601 (2) | 2612 (2) | 6125 (5) | 49 (1) |
| O(11') | 5096 (3) | 736 (2) | 7155 (5) | 64 (2) |
| O(13') | 6765 (2) | 901 (2) | 3418 (5) | 65 (2) |
| C(1) | 3758 (3) | 2189 (2) | 1370 (6) | 25 (2) |
| C(2) | 3086 (3) | 2294 (2) | 322 (6) | 26 (2) |
| C(3) | 2487 (3) | 1850 (2) | 905 (6) | 23 (2) |
| C(4) | 2780 (3) | 1186 (2) | 702 (5) | 24 (2) |
| C(5) | 3483 (3) | 1103 (2) | 1654 (6) | 27 (2) |
| C(6) | 3822 (3) | 482 (2) | 1338 (7) | 33 (2) |
| C(7) | 3190 (3) | 3358 (2) | -379 (6) | 28 (2) |
| C(8) | 2838 (3) | 3982 (3) | -353 (8) | 49 (2) |
| C(9) | 1204 (3) | 1951 (2) | 758 (6) | 31 (2) |
| C(10) | 574 (3) | 1951 (3) | -386 (7) | 43 (2) |
| C(11) | 2046 (3) | 278 (2) | 437 (7) | 32 (2) |
| C(12) | 1462 (3) | -99 (3) | 1242 (7) | 42 (2) |
| C(13) | 4705 (3) | -167 (3) | 2637 (7) | 37 (2) |
| C(14) | 5372 (3) | -164 (3) | 3651 (7) | 47 (2) |
| C(1') | 3932 (3) | 3241 (2) | 4144 (6) | 35 (2) |
| C(2') | 4056 (3) | 2542 (2) | 4070 (6) | 25 (2) |
| C(3') | 3981 (3) | 2211 (2) | 5730 (6) | 23 (2) |
| C(4') | 4667 (3) | 1814 (2) | 5817 (6) | 29 (2) |
| C(5') | 5207 (3) | 2165 (2) | 4801 (6) | 28 (2) |
| C(6') | 5770 (3) | 1765 (3) | 3973 (7) | 39 (2) |
| C(7') | 4401 (3) | 4091 (2) | 5617 (7) | 39 (2) |
| C(8') | 4977 (4) | 4258 (3) | 6819 (7) | 57 (2) |
| C(9') | 2684 (3) | 2056 (2) | 5929 (6) | 30 (2) |
| C(10') | 2101 (3) | 1576 (3) | 5813 (7) | 47 (2) |
| C(11') | 5175 (3) | 1198 (2) | 7913 (6) | 34 (2) |
| C(12') | 5578 (3) | 1253 (3) | 9488 (6) | 42 (2) |
| C(13') | 6708 (3) | 1071 (3) | 4774 (7) | 44 (2) |
| C(14') | 7124 (4) | 833 (3) | 6211 (9) | 67 (3) |

* U_{eq} defined as one third of the trace of the orthogonalized U_{ij} tensor.

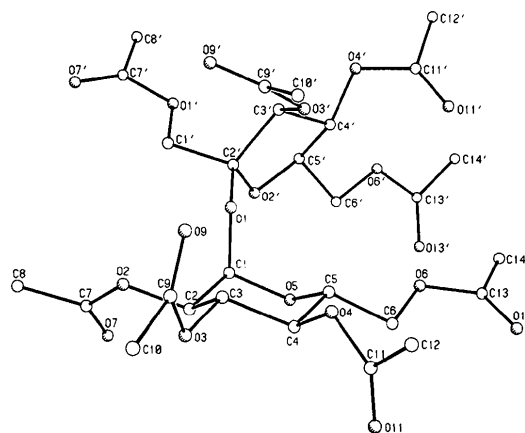


Fig. 1. Perspective drawing of SUOA. H atoms have been omitted for the sake of clarity.

Table 2. Bond lengths (Å) and angles (°)

| | | | |
|---------------|-----------|---------------|-----------|
| O(1)—C(1) | 1.421 (6) | O(1)—C(2') | 1.422 (6) |
| O(2)—C(2) | 1.445 (6) | O(2)—C(7) | 1.361 (6) |
| O(3)—C(3) | 1.431 (6) | O(3)—C(9) | 1.371 (6) |
| O(4)—C(4) | 1.449 (6) | O(4)—C(11) | 1.346 (6) |
| O(5)—C(1) | 1.411 (6) | O(5)—C(5) | 1.445 (6) |
| O(6)—C(6) | 1.466 (7) | O(6)—C(13) | 1.356 (6) |
| O(7)—C(7) | 1.209 (6) | O(9)—C(9) | 1.200 (6) |
| O(11)—C(11) | 1.196 (7) | O(13)—C(13) | 1.201 (7) |
| O(1')—C(1') | 1.419 (7) | O(1')—C(7') | 1.361 (6) |
| O(2')—C(2') | 1.406 (6) | O(2')—C(5') | 1.432 (6) |
| O(3')—C(3') | 1.444 (6) | O(3')—C(9') | 1.364 (6) |
| O(4')—C(4') | 1.448 (6) | O(4')—C(11') | 1.360 (6) |
| O(6')—C(6') | 1.438 (7) | O(6')—C(13') | 1.354 (7) |
| O(7')—C(7') | 1.193 (7) | O(9')—C(9') | 1.211 (6) |
| O(11')—C(11') | 1.185 (6) | O(13')—C(13') | 1.194 (8) |
| C(1)—C(2) | 1.528 (7) | C(2)—C(3) | 1.533 (7) |
| C(3)—C(4) | 1.531 (7) | C(4)—C(5) | 1.526 (7) |
| C(5)—C(6) | 1.492 (7) | C(7)—C(8) | 1.485 (7) |
| C(9)—C(10) | 1.501 (8) | C(11)—C(12) | 1.501 (7) |
| C(13)—C(14) | 1.489 (8) | C(1')—C(2') | 1.515 (7) |
| C(2')—C(3') | 1.563 (7) | C(3')—C(4') | 1.523 (7) |
| C(4')—C(5') | 1.506 (7) | C(5')—C(6') | 1.511 (7) |
| C(7')—C(8') | 1.500 (9) | C(9')—C(10') | 1.487 (8) |
| C(11')—C(12') | 1.514 (7) | C(13')—C(14') | 1.511 (9) |

| | | | |
|----------------------|-----------|----------------------|-----------|
| C(1)—O(1)—C(2') | 118.3 (4) | C(2)—O(2)—C(7) | 114.8 (4) |
| C(3)—O(3)—C(9) | 115.3 (4) | C(4)—O(4)—C(11) | 116.6 (4) |
| C(1)—O(5)—C(5) | 113.9 (3) | C(6)—O(6)—C(13) | 116.2 (4) |
| C(1')—O(1')—C(7') | 116.4 (4) | C(2')—O(2')—C(5') | 111.2 (3) |
| C(3')—O(3')—C(9') | 118.1 (4) | C(4')—O(4')—C(11') | 115.9 (4) |
| C(6')—O(6')—C(13') | 116.3 (4) | O(1)—C(1)—O(5) | 111.3 (4) |
| O(1)—C(1)—C(2) | 106.7 (4) | O(5)—C(1)—C(2) | 108.7 (4) |
| O(2)—C(2)—C(1) | 112.4 (4) | O(2)—C(2)—C(3) | 107.5 (4) |
| C(1)—C(2)—C(3) | 107.7 (4) | O(3)—C(3)—C(2) | 110.4 (4) |
| O(3)—C(3)—C(4) | 108.2 (4) | C(2)—C(3)—C(4) | 106.9 (4) |
| O(4)—C(4)—C(3) | 106.2 (4) | O(4)—C(4)—C(5) | 109.4 (4) |
| C(3)—C(4)—C(5) | 110.4 (4) | O(5)—C(5)—C(4) | 109.0 (4) |
| O(5)—C(5)—C(6) | 107.0 (4) | C(4)—C(5)—C(6) | 111.4 (4) |
| O(6)—C(6)—C(5) | 107.8 (4) | O(2)—C(7)—O(7) | 122.7 (4) |
| O(2)—C(7)—C(8) | 112.7 (4) | O(7)—C(7)—C(8) | 124.5 (5) |
| O(3)—C(9)—O(9) | 123.3 (5) | O(3)—C(9)—C(10) | 110.2 (4) |
| O(9)—C(9)—C(10) | 126.5 (5) | O(4)—C(11)—O(11) | 124.0 (5) |
| O(4)—C(11)—C(12) | 110.4 (4) | O(11)—C(11)—C(12) | 125.6 (5) |
| O(6)—C(13)—O(13) | 121.8 (5) | O(6)—C(13)—C(14) | 111.0 (4) |
| O(13)—C(13)—C(14) | 127.1 (5) | O(1')—C(1')—C(2') | 106.0 (4) |
| O(1)—C(2')—O(2') | 111.4 (4) | O(1')—C(2')—C(1') | 107.0 (4) |
| O(2')—C(2')—C(1') | 108.8 (4) | O(1')—C(2')—C(3') | 109.9 (4) |
| O(2')—C(2')—C(3') | 106.2 (4) | C(1')—C(2')—C(3') | 113.6 (4) |
| O(3')—C(3')—C(2') | 112.5 (4) | O(3')—C(3')—C(4') | 107.9 (4) |
| C(2')—C(3')—C(4') | 102.9 (4) | O(4')—C(4')—C(3') | 110.3 (4) |
| O(4')—C(4')—C(5') | 111.0 (4) | C(3')—C(4')—C(5') | 103.7 (4) |
| O(2')—C(5')—C(4') | 104.2 (4) | O(2')—C(5')—C(6') | 105.8 (4) |
| C(4')—C(5')—C(6') | 115.0 (4) | O(6')—C(6')—C(5') | 106.1 (4) |
| O(1')—C(7')—O(7') | 122.3 (5) | O(1')—C(7')—C(8') | 109.5 (5) |
| O(7')—C(7')—C(8') | 128.2 (5) | O(3')—C(9')—O(9') | 121.6 (4) |
| O(3')—C(9')—C(10') | 111.6 (4) | O(9')—C(9')—C(10') | 126.7 (5) |
| O(4')—C(11')—O(11') | 123.9 (5) | O(4')—C(11')—C(12') | 110.1 (4) |
| O(11')—C(11')—C(12') | 126.0 (5) | O(6')—C(13')—O(13') | 122.2 (5) |
| O(6')—C(13')—C(14') | 110.4 (5) | O(13')—C(13')—C(14') | 127.3 (5) |

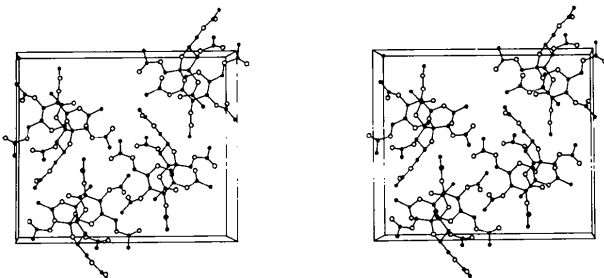


Fig. 2. Stereoview of the molecular packing of SUOA. The O atoms are represented as open circles. The view direction is approximately down the *b* axis.

Table 3. Carbohydrate backbone and glycosidic linkage comparisons

| | Sucrose | SUOA |
|---------------------------------|---------|-----------|
| Pyranose ring | | |
| q_2 (Å) | 0.050 | 0.055 |
| ϕ_2 (°) | 183.7 | 132.5 |
| q_3 (Å) | 0.554 | 0.611 |
| θ_2 (°) | 5.2 | 5.2 |
| Q (Å) | 0.556 | 0.613 |
| Furanose ring | | |
| q_2 (Å) | 0.353 | 0.329 |
| ϕ_2 (°) | 265.1 | 302.8 |
| Torsion angles ^a (°) | | |
| ω_1 | 107.8 | 93.4 (4) |
| ω_2 | -44.7 | -21.9 (5) |
| ω_3 | 171.4 | -59.7 (5) |
| ω_4 | -69.6 | 178.4 (4) |
| ω_5 | -56.4 | 65.3 (5) |

(a) The torsion angles are defined as $\omega_1 = \omega[\text{O}(5)\text{—C}(1)\text{—O}(1)\text{—C}(2')]$, $\omega_2 = \omega[\text{C}(1)\text{—O}(1)\text{—C}(2')\text{—O}(2')]$, $\omega_3 = \omega[\text{O}(2')\text{—C}(2')\text{—C}(1')\text{—O}(1')]$, $\omega_4 = \omega[\text{O}(2')\text{—C}(5')\text{—C}(6')\text{—O}(6')]$, $\omega_5 = \omega[\text{O}(5)\text{—C}(5)\text{—C}(6)\text{—O}(6)]$.

A comparison of the geometries of the carbohydrate backbones of sucrose (Brown & Levy, 1973; Hanson, Sieker & Jensen, 1973) and SUOA is presented in Table 3. The conformations of the furanoid and pyranoid rings have been described by using generalized puckering coordinates of Cremer & Pople (1975). The total puckering amplitude (Q) for the pyranoid ring of SUOA (0.613 Å) is slightly larger than the value (0.556 Å) for sucrose. Thus, the pyranose ring of SUOA is slightly more puckered than that of sucrose. The average endocyclic bond angle of each atom in sucrose is larger than that of the corresponding atom of SUOA by 1.7° . The phase angle (ϕ_2) of the furanoid ring of sucrose reveals that the ring is a *T* form with the twist axis through O(2'). For SUOA the phase angle indicates the furanoid ring is also a *T* form but with the twist axis through C(2'). The differences in the endocyclic bond angles of the structures differ as much as 1.7° but do not define a clear trend. The torsion angles ω_1 and ω_2 about the glycosidic linkage for SUOA are 14.4° smaller and 22.8° larger, respectively, than the corresponding values in sucrose. The C(1)—O(1)—C(2') bond angle, $118.3(4)^\circ$, for SUOA is 4.0° larger than the corresponding angle, $114.30(8)^\circ$, found for sucrose. The torsion angles ω_3 , ω_4 and ω_5 reveal that both structures contain two *gauche* conformers and one *trans* conformer for the primary groups. For both compounds the primary group on the pyranose ring is *gauche*, but the identities of the *trans* and *gauche* primary groups on the furanose rings are reversed for the two structures.

The metrical details of SUOA bear an interesting relationship to the 'anomeric effect' (Jeffrey, 1979). The bond angles C(1)—O(5)—C(5) and O(1)—C(1)—O(5) are $113.9(3)$ and $111.3(4)^\circ$ respectively. These values agree favorably with the expected values of 113.8 and 111.5° , respectively, for α -pyranoses according to

Table 4. Conformations observed in acetylated carbohydrate structures

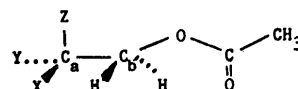
| Primary acetates ^a . $\omega(X)$ represents torsion angle ($^{\circ}$) $X-C_a-C_b-O$, $\omega(Y)$ $Y-C_a-C_b-O$, $\omega(Z)$ $Z-C_a-C_b-O$, $\omega(C_a)$ C_a-C_b-O-C , $\omega(C_b)$ $C_b-O-C=O$, $\omega(H)$ $H-C-C-O$. | C_a label | $\omega(X)^b$ | $\omega(Y)^b$ | $\omega(Z)^b$ | $\omega(C_a)^b$ | $\omega(C_b)^b$ | $\omega(H)^b$ |
|---|-------------|------------------------|---------------|---------------|-----------------|-----------------|---------------|
| This work | | | | | | | |
| C(2') | 180[O(1)] | -60[O(2')] | 59[C(3')] | -175 | -1 | 5 | |
| C(5') | 178[O(2')] | -68[C(4')] | 69[H(2')] | 172 | 0 | 17 | |
| C(5) | 176[C(4)] | -59[H(5)] | 65[O(5)] | 161 | -1 | -17 | |
| Galactosylgalactose octaacetate ^d | | | | | | | |
| C(5) | 176[O(5)] | -65[C(4)] | 62[H(5)] | 157 | -6 | | |
| C(5') | -164[C(4')] | -38[H(5')] | 75[O(5')] | -132 | 3 | | |
| Talopyranose pentaacetate ^e | | | | | | | |
| C(5) | 160[O(5)] | -78[C(4)] | 37[H(5)] | 109 | -5 | | |
| Ribose tetraacetate ^f | | | | | | | |
| C(4) | 174[H(4)] | -63[O(4)] | 56[C(3)] | -162 | 0 | -3 | |
| 2,5-O-Methylenemannitol tetraacetate ^g | | | | | | | |
| C(1) | 177[C(2)] | -65[O(1)] | 52[H(1)] | 148 | 1 | -38 | |
| C(4) | 175[C(3)] | -69[O(2)] | 68[H(4)] | 179 | 0 | 10 | |
| 6'-O-Tritylcellobiose heptaacetate ^h | | | | | | | |
| C(5) | 165[C(4)] | -74[H(5)] | 46[O(5)] | 67 | -2 | | |
| Cellotriose undecaacetate ⁱ | | | | | | | |
| C(5) | -166[H(5)] | -52[O(5)] | 64[C(4)] | 160 | 3 | | |
| C(5') | 165[H(5')] | -64[O(5')] | 52[C(4')] | 168 | 6 | | |
| C(5'') | 176[C(4'')] | -56[H(5'')] | 60[O(5'')] | 88 | 3 | | |
| Di-O-isopropylidenesucrose tetraacetate ^j | | | | | | | |
| C(5') | -177[C(4')] | 65[O(2')] | | -176 | 2 | | |
| Mannose-1,2-methylorthoacetate triacetate ^k | | | | | | | |
| C(5) | 168[H(5)] | -71[O(5)] ^l | 46[C(4)] | -171 | -9 | 20 | |

| Secondary acetates ^c . $\omega(HC)$ represents torsion angle ($^{\circ}$) $H-C_a-O-C$, $\omega(X)$ $X-C_a-O-C$, $\omega(Y)$ $Y-C_a-O-C$, $\omega(C_a)$ $C_a-O-C=O$, $\omega(HO)$ $H-C-C=O$. | C_a label | $\omega(HC)$ | $\omega(X)$ | $\omega(Y)$ | $\omega(C_a)$ | $\omega(HO)$ | d (Å) |
|---|-------------|--------------|-------------|-------------|---------------|--------------|---------|
| This work | | | | | | | |
| C(2) | -42 | -164 | 78 | -7 | 24 | | 2.24 |
| C(3) | -11 | -134 | 109 | 5 | -3 | | 2.15 |
| C(4) | 21 | -108 | 133 | 2 | 15 | | 2.29 |
| C(3') | 53 | -74 | 173 | -7 | -8 | | 2.55 |
| C(4') | 32 | -105 | 140 | -12 | -4 | | 2.41 |
| Galactosylgalactose octaacetate ^d | | | | | | | |
| C(2) | -19 | -141 | 101 | -2 | | | 2.26 |
| C(3) | -31 | -146 | 93 | 4 | | | 2.22 |
| C(4) | 10 | -109 | 131 | -4 | | | 2.40 |
| C(1') | 9 | -117 | 122 | 6 | | | 2.25 |
| C(2') | -5 | -132 | 107 | -3 | | | 2.30 |
| C(3') | -4 | -119 | 122 | -6 | | | 2.24 |
| Methylxylose triacetate ^e | | | | | | | |
| C(2) | 2 | -118 | 123 | -3 | | | 2.29 |
| C(3) | 37 | -85 | 155 | 5 | | | 2.40 |
| C(4) | 5 | -115 | 126 | 0 | | | 2.24 |
| Talopyranose pentaacetate ^e | | | | | | | |
| C(1) | -33 | -155 | 84 | -1 | | | 2.38 |
| C(2) | 5 | -116 | 124 | -3 | | | 2.35 |
| C(3) | -29 | -148 | 85 | -12 | | | 2.33 |
| C(4) | 21 | -99 | 143 | 6 | | | 2.32 |
| Ribose tetraacetate ^f | | | | | | | |
| C(1) | 40 | -82 | 165 | 2 | 48 | | 2.43 |
| C(2) | -37 | -161 | 87 | 2 | 60 | | 2.29 |
| C(3) | -50 | -176 | 69 | -4 | 6 | | 2.47 |
| 2,5-O-Methylenemannitol tetraacetate ^g | | | | | | | |
| C(2) | -15 | -127 | 108 | -3 | 80 | | 2.19 |
| C(3) | -11 | -125 | 110 | -6 | -37 | | 2.41 |
| 6'-O-Tritylcellobiose heptaacetate ^h | | | | | | | |
| C(2) | 18 | -105 | 135 | 5 | | | 2.36 |
| C(3) | -16 | -132 | 108 | -1 | | | 2.45 |
| C(4) | -9 | -126 | 115 | -8 | | | 2.34 |
| C(1') | 3 | -57 | 123 | 10 | | | 2.33 |
| C(2') | -24 | -148 | 93 | -7 | | | 2.36 |
| C(3') | -2 | -121 | 119 | 1 | | | 2.30 |

Table 4 (cont.)

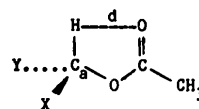
| C_a label | $\omega(HC)$ | $\omega(X)$ | $\omega(Y)$ | $\omega(C_a)$ | $\omega(HO)$ | d (Å) |
|--|--------------|-------------|-------------|---------------|--------------|---------|
| Cellotriose undecaacetate ⁱ | | | | | | |
| C(2) | 12 | -101 | 141 | -10 | | 2.37 |
| C(3) | -7 | -119 | 123 | 1 | | 2.32 |
| C(4) | -13 | -134 | 112 | -1 | | 2.18 |
| C(2') | 7 | -110 | 130 | 7 | | 2.46 |
| C(3') | 14 | -105 | 138 | -9 | | 2.38 |
| C(1'') | 33 | -96 | 145 | -14 | | 2.34 |
| C(2'') | -1 | -123 | 116 | -5 | | 2.41 |
| C(3'') | -8 | -132 | 110 | 3 | | 2.28 |
| Di-O-isopropylidenesucrose tetraacetate ^j | | | | | | |
| C(3) | | -129 | 115 | 4 | | |
| C(3') | | -84 | 160 | -8 | | |
| C(4') | | -80 | 167 | 2 | | |
| Mannose-1,2-methylorthoacetate triacetate ^k | | | | | | |
| C(3) | -30 | -134 | 101 | 7 | 19 | |
| C(4) | -27 | -134 | 111 | -7 | 55 | |
| Levoglucozan triacetate ^m | | | | | | |
| C(2) | 42 | -87 | 154 | -1 | 0 | 2.42 |
| C(3) | -28 | -156 | 82 | 2 | -52 | 2.27 |
| C(4) | 27 | -95 | 145 | 1 | 39 | 2.32 |
| Xylobiose hexaacetate ⁿ | | | | | | |
| C(2) | 6 | -123 | 119 | 9 | -25 | 2.30 |
| C(3) | 4 | -121 | 120 | 6 | 28 | 2.19 |
| C(4) | 13 | -105 | 135 | 5 | -13 | 2.24 |
| C(1') | 30 | -90 | 150 | 2 | -56 | 2.20 |
| C(2') | 13 | -104 | 136 | 0 | 31 | 2.27 |
| C(3') | 9 | -105 | 132 | -1 | -2 | 2.23 |

(a) Metrical details are defined schematically according to:



(b) The atom label in square brackets identifies atom X, atom Y, or atom Z.

(c) Metrical details are defined schematically according to:



(d) Foces-Foces, Cano & Garcia-Blanco (1981). (e) Kopf & Köll (1981). (f) Czugler, Kálmán, Kovács & Pintér (1981). (g) Cameron, Cordes & Grindley (1977). (h) Taga, Sumiya, Osaki, Utamura & Koizumi (1981). (i) Pérez & Brisse (1977). (j) Drew, Lindseth & Khan (1979). (k) Flippen (1976). (l) James & Stevens (1981). (m) Leung & Marchessault (1974). (n) Leung & Marchessault (1973).

Jeffrey (1979). For α - and β -pyranoses the C—O bond lengths decrease according to C(5)—O(5) > O(5)—C(1) > C(1)—O(1). For SUOA the relative lengths of the latter two bonds in the pyranose ring are reversed so that C(5)—O(5) [1.445 (6) Å] > C(1)—O(1) [1.421 (6) Å] > O(5)—C(1) [1.411 (6) Å]. The bond lengths of the furanose ring are related similarly with C(5')—O(2') [1.432 (6) Å] > C(2')—O(1) [1.422 (6) Å] > C(2')—O(2') [1.406 (6) Å]. The same relationships among these bond lengths were observed in the sucrose structure (Brown & Levy, 1973; Hanson *et al.*, 1973).

The orientations of the acetate residues of SUOA and a wide variety of other carbohydrate polyacetate

molecules are described in Table 4. For each acetate group of SUOA the C—C(O)—O moiety is planar as expected. Although the structures are quite diverse, general trends are obvious. The conformation about the C(ring)—C(primary) bond of each primary acetate group tends to be staggered, *i.e.* one torsion angle is $\sim 180^\circ$ and the absolute magnitudes of the other two torsion angles are $\sim 60^\circ$. For ten of the fifteen examples in Table 4 the conformation about the C(primary)—O(acetate) bond is *trans* thereby minimizing steric effects. In each structure the C—O—C=O groups are planar in a *cis* conformation. A similar observation has been made for secondary acetate groups (Leung & Marchessault, 1973). This conformation is considerably more favorable energetically than the *trans* conformation where the H atoms of the methyl substituent of the acetate moiety and those of the primary C atom would be crowded. The H—C—C=O torsion angles show a tendency for the methyl group to be *cis* to the carbonyl rather than to be *gauche* to the carbonyl.

The orientations of the secondary acetate moieties follow the trend previously described by Leung & Marchessault (1973). The acetate groups are oriented so that the carbonyl O atoms almost eclipse the axial H atoms of corresponding ring C atoms. This conformation places the H atom of the secondary C atom and the carbonyl O atom close to each other. The average value [2.32 (9) Å] defined by the 46 non-bonded H...O distances in Table 4 is 0.28 Å shorter than the sum of the van der Waals radii of O and H and strengthens the suggestion of Taga *et al.* (1981) that weak CH...O hydrogen bonds occur that stabilize this conformation. For SUOA the C—H bonds of the acetates tend to be oriented *cis* to the carbonyl O atom as indicated by the H—C—C=O torsion angles. For the other secondary acetate groups in Table 4 the orientations of the methyl groups exhibit an array of H—C—C=O torsion angles ranging between the extremes of *cis* and *gauche* conformations.

The concept that the SPE molecules constitute an homologous structural series has been presented in a study of sucrose octaesters of long-chain fatty acids (Jandacek & Webb, 1978). A linear relation was found between the X-ray diffraction long spacing and the number of acyl C atoms of the fatty acid. In an effort to extend that comparison, we have collected the X-ray powder diffraction data of SUOA. A listing of Miller-index assignments, *d*-spacings, intensities and the least-squares lattice constants for SUOA has been deposited.* To determine if SUOA follows the structural trend defined by the four sucrose octaesters

analyzed by Jandacek & Webb (1978), we performed a linear regression analysis of their long spacing *vs* their number of acyl C atoms. The four long spacings obey the equation: long spacing (Å) = $3.35 + 2.665n$, where *n* is the number of acyl C atoms (correlation coefficient = 0.998). Based on this equation, the predicted long spacing for SUOA would be 8.68 Å. The larger observed long spacing for SUOA (14.13 Å) suggests that SUOA is not isostructural with the heavier SPE molecules examined by Jandacek & Webb (1978) or that the long-spacing relationship is non-linear over the interval from *n* = 2 to *n* = 10. In an effort to determine a long spacing within this interval, we analyzed sucrose octacaprylate. Although the experiment was performed at 193 K, no diffraction data were obtained. Thus an unambiguous interpretation of the X-ray long spacing of SUOA was not possible.

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* See previous footnote.