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[2α(2*S*,3*S*,4*R*,6*R*),3β,5α]-14-Hydroxy-19-oxo-3,2-[(tetrahydro-3,4-dihydroxy-6-methyl-2*H*-pyran-2,3-diyl)bis(oxy)]card-20(22)-enolide Dihydrate (Calactin), $C_{29}H_{39}O_9.2H_2O$, a Cardenolide from *Asclepias linaria*

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Abstract

This X-ray diffraction study establishes the molecular structure of the title compound. The asymmetric unit comprises two independent molecules (*A* and *B*). Both molecules are closely similar with regard to bond lengths and angles. In both molecules, the six-membered rings all adopt chair conformations. The *D* ring of the steroid moiety has an envelope conformation and the lactone ring is almost flat. The *A*/*B*, *B*/*C* and *A*/*F* ring junctions are *trans* and the *C*/*D* and *F*/*G* ring junctions are *cis*. The crystal structure is stabilized by a three-dimensional network of hyrogen bonds and C—H···O interactions.

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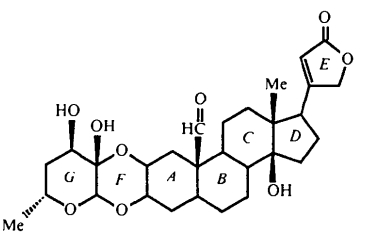
Comment

Cardenolides constitute one of several groups of plant secondary compounds that are sequestered by phytophagous insects for defense against predation. Most members of the genus *Asclepias* (*Asclepiadaceae*) produce the cardiactive steroids at varying concentrations. Plants of *Asclepias* have also been studied for high proteolytic enzyme content (Brockbank & Lynn, 1979; Barragan, Cruz, Del Castillo & Castañeda-Agulló, 1985). These enzymes are named asclepains.

Calactin (I) is a naturally occurring cardenolide which was isolated from extracts of the aerial parts of the plant *Asclepias linaria*. The sample was collected in the southeast of the State of Durango, Mexico. The chemical and spectroscopic studies led to the proposal of the chemical structure of calactin (Brüschweiler, Stöckel & Reichstein, 1969).



(I)

The molecular packing diagram viewed along the *b* axis is presented in Fig. 2, showing the hydrogen-bonding scheme. The water molecules are hydrogen bonded to hydroxyl O atoms. The molecules in the crystal are stabilized by a three-dimensional network of hydrogen bonds: O(2)···O(1) 2.960 (13), O(8*B*)···O(7*B*) 2.728 (7) and O(1*A*)···O(3*B*)(2 − *x*, 1 − *y*, *z*), 2.898 (7), O(1)···O(8*B*)(0.5 + *x*, 0.5 + *y*, 2 − *z*) 2.856 (8), O(2)···O(7*A*)(1.5 − *x*, −0.5 + *y*, 1 − *z*) 2.740 (10), O(1*B*)···O(3*A*)(2 − *x*, 1 − *y*, 1 + *z*) 2.768 (6) Å; and five intermolecular C—H···O interactions < 3.4 Å: C(12*A*)···O(5*A*)(1.5 − *x*, −0.5 + *y*, 1 − *z*) 3.304 (7), C(23*A*)···O(8*A*)(0.5 + *x*, 1.5 − *y*, 1 − *z*) 3.112 (9), C(26*A*)···O(3*B*)(1.5 − *x*, 0.5 + *y*, 1 − *z*)

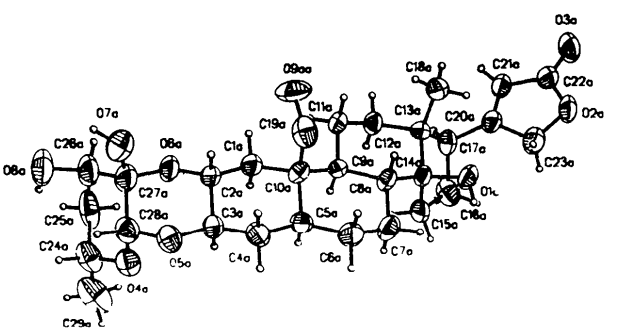


Fig. 1. The molecular structure of the title compound with numbering scheme.

3.370 (9), C(12*B*)···O(5*B*)(1.5 − *x*, −0.5 + *y*, 2 − *z*)
3.347 (6), C(23*B*)···O(8*B*)(0.5 + *x*, 0.5 − *y*, 2 − *z*)
3.233 (9) Å.

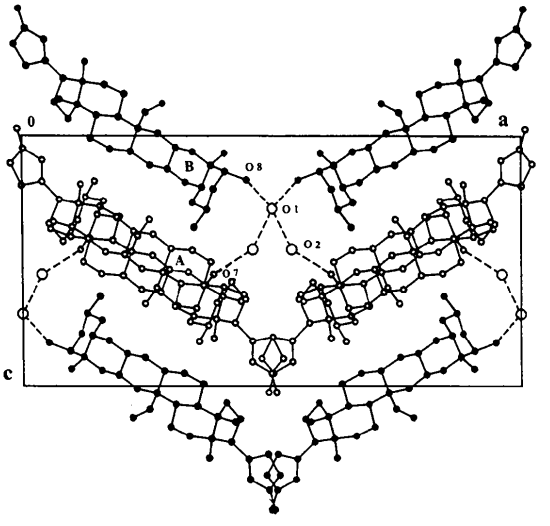


Fig. 2. The packing arrangement as viewed along **b**. Hydrogen bonds are shown by dashed lines.

Experimental

Crystal data

$C_{29}H_{39}O_9.2H_2O$
M_r = 567.6
Orthorhombic
$P2_12_12$
a = 29.868 (7) Å
b = 12.567 (4) Å
c = 14.705 (5) Å
V = 5519 (3) Å^3
Z = 8
D_x = 1.37 Mg m^{-3}
Cu $K\alpha$ radiation
λ = 1.5418 Å
Cell parameters from 25 reflections
θ = 4.9-18.1°
μ = 0.825 mm^{-1}
T = 293 K
Needle
0.64 × 0.4 × 0.10 mm
Colourless
Crystal source: recrystallized from diethyl ether

Data collection

Nicolet *P3/F* diffractometer
$2\theta/\theta$ scans
Absorption correction: none
3962 measured reflections
3942 independent reflections
3262 observed reflections [$I > 2.5\sigma(I)$]
R_{int} = 0.040
θ_{max} = 55°
$h = 0 \rightarrow 31$
$k = 0 \rightarrow 13$
$l = 0 \rightarrow 15$
2 standard reflections monitored every 50 reflections
intensity variation: <3%

Refinement

Refinement on F
R = 0.064
wR = 0.081
S = 1.21
3262 reflections
734 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o) + 0.0031(F_o)^2]$
$(\Delta/\sigma)_{max}$ = 0.28
$\Delta\rho_{max}$ = 0.21 e Å^{-3}
$\Delta\rho_{min}$ = −0.27 e Å^{-3}
Extinction correction: empirical (*SHELXTL*; Sheldrick, 1985)
Extinction coefficient: χ = 0.00024 (12)
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$

	x	y	z	U_{eq}
O(1)	1	1/2	0.7091 (7)	0.133 (4)
O(2)	0.9608 (3)	0.3914 (8)	0.5492 (7)	0.136 (5)
O(1*A*)	0.9379 (1)	0.8072 (3)	0.3419 (3)	0.054 (1)
O(2*A*)	1.0220 (1)	0.6990 (5)	0.1113 (3)	0.078 (2)
O(3*A*)	1.0083 (2)	0.6439 (7)	−0.0273 (3)	0.134 (3)
O(4*A*)	0.6634 (1)	0.7241 (3)	0.7394 (3)	0.055 (1)
O(5*A*)	0.6889 (1)	0.8763 (3)	0.6758 (3)	0.053 (1)
O(6*A*)	0.6668 (1)	0.7280 (4)	0.5395 (3)	0.058 (1)
O(7*A*)	0.6168 (2)	0.8709 (5)	0.5486 (3)	0.086 (1)
O(8*A*)	0.5565 (2)	0.7450 (6)	0.6306 (4)	0.103 (2)
O(9*A*)	0.7458 (3)	0.8916 (8)	0.3332 (6)	0.078 (4)
O(9′)	0.7747 (5)	0.9777 (12)	0.4025 (10)	0.099 (6)
C(1*A*)	0.7392 (2)	0.7372 (5)	0.4738 (4)	0.046 (2)
C(2*A*)	0.7047 (2)	0.7955 (5)	0.5294 (3)	0.044 (2)
C(3*A*)	0.7231 (2)	0.8260 (5)	0.6211 (4)	0.044 (2)
C(4*A*)	0.7619 (2)	0.9003 (5)	0.6094 (4)	0.049 (2)
C(5*A*)	0.7984 (2)	0.8453 (5)	0.5531 (4)	0.043 (2)
C(6*A*)	0.8416 (2)	0.9105 (5)	0.5459 (4)	0.055 (2)
C(7*A*)	0.8780 (2)	0.8461 (5)	0.4995 (4)	0.054 (2)
C(8*A*)	0.8637 (2)	0.8006 (4)	0.4070 (4)	0.041 (2)
C(9*A*)	0.8188 (2)	0.7380 (4)	0.4144 (3)	0.035 (2)
C(10*A*)	0.7813 (2)	0.8053 (4)	0.4595 (4)	0.039 (2)
C(11*A*)	0.8058 (2)	0.6916 (4)	0.3223 (4)	0.043 (2)
C(12*A*)	0.8437 (2)	0.6229 (5)	0.2831 (4)	0.045 (2)
C(13*A*)	0.8880 (2)	0.6861 (4)	0.2706 (3)	0.040 (2)
C(14*A*)	0.9015 (2)	0.7365 (4)	0.3627 (4)	0.041 (2)
C(15*A*)	0.9192 (2)	0.6420 (5)	0.4188 (4)	0.052 (2)
C(16*A*)	0.9466 (2)	0.5786 (5)	0.3501 (4)	0.064 (2)
C(17*A*)	0.9261 (2)	0.5995 (5)	0.2553 (4)	0.048 (2)
C(18*A*)	0.8833 (2)	0.7647 (5)	0.1937 (4)	0.052 (2)
C(19*A*)	0.7691 (2)	0.8959 (5)	0.3972 (4)	0.058 (2)
C(20*A*)	0.9600 (2)	0.6280 (5)	0.1828 (4)	0.049 (2)
C(21*A*)	0.9597 (2)	0.6016 (7)	0.0979 (4)	0.075 (3)
C(22*A*)	0.9977 (2)	0.6457 (7)	0.0519 (4)	0.078 (3)
C(23*A*)	1.0009 (2)	0.6917 (7)	0.1988 (4)	0.077 (3)
C(24*A*)	0.6275 (2)	0.6512 (5)	0.7547 (4)	0.066 (2)
C(25*A*)	0.6104 (2)	0.6069 (6)	0.6642 (5)	0.082 (3)
C(26*A*)	0.5965 (2)	0.6948 (7)	0.5997 (5)	0.079 (3)
C(27*A*)	0.6324 (2)	0.7764 (6)	0.5922 (4)	0.066 (2)
C(28*A*)	0.6509 (2)	0.8113 (5)	0.6859 (4)	0.053 (2)
C(29*A*)	0.6458 (3)	0.5661 (6)	0.8190 (5)	0.101 (4)
O(1*B*)	0.9248 (1)	0.2945 (3)	0.8536 (2)	0.052 (1)
O(2*B*)	1.0139 (1)	0.1956 (4)	0.6324 (3)	0.076 (2)
O(3*B*)	1.0039 (2)	0.1354 (5)	0.4918 (3)	0.091 (2)
O(4*B*)	0.6589 (1)	0.1916 (3)	1.2670 (2)	0.053 (1)
O(5*B*)	0.6724 (1)	0.3383 (3)	1.1850 (3)	0.060 (1)
O(6*B*)	0.6580 (1)	0.1690 (3)	1.0637 (2)	0.052 (1)
O(7*B*)	0.5952 (2)	0.2806 (4)	1.0694 (3)	0.083 (2)
O(8*B*)	0.5513 (1)	0.1367 (4)	1.1759 (3)	0.078 (2)
O(9*B*)	0.7186 (3)	0.3727 (8)	0.8707 (7)	0.108 (4)
O(9″)	0.7530 (8)	0.4432 (18)	0.9086 (16)	0.183 (8)
C(1*B*)	0.7279 (2)	0.1991 (5)	0.9889 (4)	0.050 (2)
C(2*B*)	0.6915 (2)	0.2496 (5)	1.0460 (4)	0.047 (2)
C(3*B*)	0.7088 (2)	0.2920 (4)	1.1321 (4)	0.049 (2)
C(4*B*)	0.7445 (2)	0.3757 (5)	1.1163 (4)	0.057 (2)
C(5*B*)	0.7832 (2)	0.3226 (4)	1.0620 (3)	0.043 (2)
C(6*B*)	0.8241 (2)	0.3930 (5)	1.0524 (4)	0.055 (2)
C(7*B*)	0.8623 (2)	0.3314 (5)	1.0093 (4)	0.052 (2)
C(8*B*)	0.8500 (2)	0.2820 (4)	0.9174 (4)	0.040 (2)

C(9*B*)	0.8069 (2)	0.2162 (4)	0.9252 (4)	0.041 (2)
C(10*B*)	0.7674 (2)	0.2769 (4)	0.9704 (3)	0.041 (2)
C(11*B*)	0.7952 (2)	0.1696 (5)	0.8316 (4)	0.048 (2)
C(12*B*)	0.8337 (2)	0.1031 (4)	0.7943 (4)	0.046 (2)
C(13*B*)	0.8774 (2)	0.1674 (4)	0.7829 (4)	0.042 (2)
C(14*B*)	0.8890 (2)	0.2207 (4)	0.8745 (4)	0.041 (2)
C(15*B*)	0.9075 (2)	0.1285 (5)	0.9314 (4)	0.052 (2)
C(16*B*)	0.9350 (2)	0.0621 (5)	0.8651 (4)	0.064 (2)
C(17*B*)	0.9168 (2)	0.0853 (5)	0.7690 (4)	0.049 (2)
C(18*B*)	0.8725 (2)	0.2447 (4)	0.7036 (4)	0.048 (2)
C(19*B*)	0.7527 (2)	0.3641 (5)	0.9056 (4)	0.060 (2)
C(20*B*)	0.9512 (2)	0.1152 (5)	0.6996 (4)	0.049 (2)
C(21*B*)	0.9538 (2)	0.0864 (5)	0.6145 (4)	0.055 (2)
C(22*B*)	0.9915 (2)	0.1366 (6)	0.5707 (4)	0.068 (2)
C(23*B*)	0.9899 (2)	0.1909 (7)	0.7189 (4)	0.078 (3)
C(24*B*)	0.6301 (2)	0.1061 (4)	1.2939 (4)	0.055 (2)
C(25*B*)	0.6173 (2)	0.0414 (5)	1.2117 (4)	0.059 (2)
C(26*B*)	0.5942 (2)	0.1062 (5)	1.1418 (4)	0.057 (2)
C(27*B*)	0.6220 (2)	0.2069 (5)	1.1180 (4)	0.059 (2)
C(28*B*)	0.6398 (2)	0.2624 (5)	1.2046 (4)	0.057 (2)
C(29*B*)	0.6557 (3)	0.0408 (5)	1.3632 (4)	0.078 (3)

Table 2. *Selected geometric parameters* (Å, °)

O(1*A*)—C(14*A*)	1.438 (6)	O(1*B*)—C(14*B*)	1.447 (6)
O(2*A*)—C(22*A*)	1.318 (8)	O(2*B*)—C(22*B*)	1.349 (8)
O(2*A*)—C(23*A*)	1.434 (7)	O(2*B*)—C(23*B*)	1.462 (8)
O(3*A*)—C(22*A*)	1.207 (7)	O(3*B*)—C(22*B*)	1.218 (8)
O(4*A*)—C(24*A*)	1.430 (8)	O(4*B*)—C(24*B*)	1.433 (7)
O(4*A*)—C(28*A*)	1.400 (7)	O(4*B*)—C(28*B*)	1.399 (7)
O(5*A*)—C(3*A*)	1.447 (6)	O(5*B*)—C(3*B*)	1.458 (7)
O(5*A*)—C(28*A*)	1.406 (7)	O(5*B*)—C(28*B*)	1.393 (7)
O(6*A*)—C(2*A*)	1.422 (7)	O(6*B*)—C(2*B*)	1.447 (7)
O(6*A*)—C(27*A*)	1.424 (7)	O(6*B*)—C(27*B*)	1.422 (7)
O(7*A*)—C(27*A*)	1.428 (9)	O(7*B*)—C(27*B*)	1.417 (8)
O(8*A*)—C(26*A*)	1.424 (9)	O(8*B*)—C(26*B*)	1.427 (7)
O(9*A*)—O(9′)	1.720 (17)	O(9*B*)—O(9″)	1.465 (25)
O(9*A*)—C(19*A*)	1.173 (11)	O(9*B*)—C(19*B*)	1.144 (11)
O(9′)—C(19*A*)	1.044 (17)	O(9″)—C(19*B*)	0.995 (23)
C(1*A*)—C(2*A*)	1.506 (7)	C(1*B*)—C(2*B*)	1.513 (8)
C(1*A*)—C(10*A*)	1.536 (7)	C(1*B*)—C(10*B*)	1.557 (8)
C(2*A*)—C(3*A*)	1.506 (7)	C(2*B*)—C(3*B*)	1.469 (8)
C(3*A*)—C(4*A*)	1.498 (8)	C(3*B*)—C(4*B*)	1.517 (8)
C(4*A*)—C(5*A*)	1.532 (8)	C(4*B*)—C(5*B*)	1.555 (8)
C(5*A*)—C(6*A*)	1.533 (8)	C(5*B*)—C(6*B*)	1.516 (8)
C(5*A*)—C(10*A*)	1.552 (7)	C(5*B*)—C(10*B*)	1.537 (7)
C(6*A*)—C(7*A*)	1.516 (8)	C(6*B*)—C(7*B*)	1.517 (8)
C(7*A*)—C(8*A*)	1.536 (8)	C(7*B*)—C(8*B*)	1.531 (8)
C(8*A*)—C(9*A*)	1.560 (7)	C(8*B*)—C(9*B*)	1.536 (7)
C(8*A*)—C(14*A*)	1.532 (7)	C(8*B*)—C(14*B*)	1.532 (7)
C(9*A*)—C(10*A*)	1.551 (7)	C(9*B*)—C(10*B*)	1.555 (7)
C(9*A*)—C(11*A*)	1.525 (7)	C(9*B*)—C(11*B*)	1.536 (8)
C(10*A*)—C(19*A*)	1.506 (8)	C(10*B*)—C(19*B*)	1.516 (8)
C(11*A*)—C(12*A*)	1.534 (7)	C(11*B*)—C(12*B*)	1.525 (8)
C(12*A*)—C(13*A*)	1.556 (7)	C(12*B*)—C(13*B*)	1.544 (7)
C(13*A*)—C(14*A*)	1.549 (7)	C(13*B*)—C(14*B*)	1.544 (7)
C(13*A*)—C(17*A*)	1.590 (8)	C(13*B*)—C(17*B*)	1.578 (8)
C(13*A*)—C(18*A*)	1.508 (8)	C(13*B*)—C(18*B*)	1.524 (8)
C(14*A*)—C(15*A*)	1.539 (8)	C(14*B*)—C(15*B*)	1.532 (8)
C(15*A*)—C(16*A*)	1.525 (9)	C(15*B*)—C(16*B*)	1.524 (8)
C(16*A*)—C(17*A*)	1.546 (8)	C(16*B*)—C(17*B*)	1.543 (8)
C(17*A*)—C(20*A*)	1.512 (8)	C(17*B*)—C(20*B*)	1.496 (8)
C(20*A*)—C(21*A*)	1.291 (9)	C(20*B*)—C(21*B*)	1.305 (9)
C(20*A*)—C(23*A*)	1.481 (9)	C(20*B*)—C(23*B*)	1.523 (9)
C(21*A*)—C(22*A*)	1.434 (9)	C(21*B*)—C(22*B*)	1.441 (9)
C(24*A*)—C(25*A*)	1.531 (10)	C(24*B*)—C(25*B*)	1.506 (8)
C(24*A*)—C(29*A*)	1.529 (10)	C(24*B*)—C(29*B*)	1.516 (9)
C(25*A*)—C(26*A*)	1.515 (11)	C(25*B*)—C(26*B*)	1.483 (9)
C(26*A*)—C(27*A*)	1.487 (10)	C(26*B*)—C(27*B*)	1.554 (9)
C(27*A*)—C(28*A*)	1.548 (9)	C(27*B*)—C(28*B*)	1.546 (9)
C(22*A*)—O(2*A*)—C(23*A*)	108.6 (5)	C(22*B*)—O(2*B*)—C(23*B*)	108.7 (5)
C(24*A*)—O(4*A*)—C(28*A*)	112.9 (4)	C(24*B*)—O(4*B*)—C(28*B*)	114.4 (4)
C(3*A*)—O(5*A*)—C(28*A*)	112.1 (4)	C(3*B*)—O(5*B*)—C(28*B*)	111.0 (4)
C(2*A*)—O(6*A*)—C(27*A*)	112.1 (5)	C(2*B*)—O(6*B*)—C(27*B*)	112.9 (4)
O(9′)—O(9*A*)—C(19*A*)	36.5 (7)	O(9″)—O(9*B*)—C(19*B*)	42.7 (10)
O(9*A*)—O(9′)—C(19*A*)	41.9 (7)	O(9*B*)—O(9″)—C(19*B*)	51.2 (12)
C(2*A*)—C(1*A*)—C(10*A*)	111.3 (5)	C(2*B*)—C(1*B*)—C(10*B*)	112.1 (5)
O(6*A*)—C(2*A*)—C(1*A*)	108.1 (5)	O(6*B*)—C(2*B*)—C(1*B*)	107.6 (5)
O(6*A*)—C(2*A*)—C(3*A*)	110.5 (4)	O(6*B*)—C(2*B*)—C(3*B*)	110.0 (4)
C(1*A*)—C(2*A*)—C(3*A*)	111.2 (4)	C(1*B*)—C(2*B*)—C(3*B*)	112.2 (5)
O(5*A*)—C(3*A*)—C(2*A*)	110.5 (4)	O(5*B*)—C(3*B*)—C(2*B*)	110.0 (5)
O(5*A*)—C(3*A*)—C(4*A*)	109.8 (5)	O(5*B*)—C(3*B*)—C(4*B*)	109.2 (4)
C(2*A*)—C(3*A*)—C(4*A*)	109.8 (4)	C(2*B*)—C(3*B*)—C(4*B*)	111.5 (5)
C(3*A*)—C(4*A*)—C(5*A*)	109.3 (5)	C(3*B*)—C(4*B*)—C(5*B*)	107.6 (5)
C(4*A*)—C(5*A*)—C(6*A*)	113.3 (5)	C(4*B*)—C(5*B*)—C(6*B*)	113.3 (5)
C(4*A*)—C(5*A*)—C(10*A*)	113.0 (4)	C(4*B*)—C(5*B*)—C(10*B*)	112.4 (4)
C(6*A*)—C(5*A*)—C(10*A*)	112.9 (4)	C(6*B*)—C(5*B*)—C(10*B*)	112.6 (4)
C(5*A*)—C(6*A*)—C(7*A*)	110.4 (5)	C(5*B*)—C(6*B*)—C(7*B*)	110.3 (5)
C(6*A*)—C(7*A*)—C(8*A*)	113.5 (4)	C(6*B*)—C(7*B*)—C(8*B*)	113.4 (5)
C(7*A*)—C(8*A*)—C(9*A*)	111.3 (4)	C(7*B*)—C(8*B*)—C(9*B*)	110.6 (4)
C(7*A*)—C(8*A*)—C(14*A*)	111.6 (4)	C(7*B*)—C(8*B*)—C(14*B*)	112.7 (4)
C(9*A*)—C(8*A*)—C(14*A*)	113.5 (4)	C(9*B*)—C(8*B*)—C14*B*)	113.4 (4)
C(8*A*)—C(9*A*)—C(10*A*)	112.1 (4)	C(8*B*)—C(9*B*)—C(10*B*)	113.9 (4)
C(8*A*)—C(9*A*)—C(11*A*)	110.5 (4)	C(8*B*)—C(9*B*)—C(11*B*)	109.2 (4)
C(10*A*)—C(9*A*)—C(11*A*)	113.9 (4)	C(10*B*)—C(9*B*)—C(11*B*)	113.4 (4)
C(1*A*)—C(10*A*)—C(5*A*)	109.2 (4)	C(1*B*)—C(10*B*)—C(5*B*)	108.4 (4)
C(1*A*)—C(10*A*)—C(9*A*)	110.2 (4)	C(1*B*)—C(10*B*)—C(9*B*)	110.0 (4)
C(5*A*)—C(10*A*)—C(9*A*)	108.6 (4)	C(5*B*)—C(10*B*)—C(9*B*)	108.9 (4)
C(1*A*)—C(10*A*)—C(19*A*)	107.9 (4)	C(1*B*)—C(10*B*)—C(19*B*)	110.1 (4)
C(5*A*)—C(10*A*)—C(19*A*)	112.0 (5)	C(5*B*)—C(10*B*)—C(19*B*)	111.7 (4)
C(9*A*)—C(10*A*)—C(19*A*)	109.0 (4)	C(9*B*)—C(10*B*)—C(19*B*)	107.8 (4)
C(9*A*)—C(11*A*)—C(12*A*)	111.2 (4)	C(9*B*)—C(11*B*)—C(12*B*)	111.1 (4)
C(11*A*)—C(12*A*)—C(13*A*)	112.7 (5)	C(11*B*)—C(12*B*)—C(13*B*)	113.0 (5)
C(12*A*)—C(13*A*)—C(14*A*)	109.1 (4)	C(12*B*)—C(13*B*)—C(14*B*)	108.8 (4)
C(12*A*)—C(13*A*)—C(17*A*)	106.1 (4)	C(12*B*)—C(13*B*)—C(17*B*)	107.6 (4)
C(14*A*)—C(13*A*)—C(17*A*)	102.6 (4)	C(14*B*)—C(13*B*)—C(17*B*)	103.2 (4)
C(12*A*)—C(13*A*)—C(18*A*)	110.0 (4)	C(12*B*)—C(13*B*)—C(18*B*)	109.6 (4)
C(14*A*)—C(13*A*)—C(18*A*)	114.3 (5)	C(14*B*)—C(13*B*)—C(18*B*)	114.4 (4)
C(17*A*)—C(13*A*)—C(18*A*)	114.2 (4)	C(17*B*)—C(13*B*)—C(18*B*)	112.9 (4)
O(1*A*)—C(14*A*)—C(8*A*)	108.9 (4)	O(1*B*)—C(14*B*)—C(8*B*)	109.0 (4)
O(1*A*)—C(14*A*)—C(13*A*)	105.2 (4)	O(1*B*)—C(14*B*)—C(13*B*)	105.0 (4)
C(8*A*)—C(14*A*)—C(13*A*)	113.3 (4)	C(8*B*)—C(14*B*)—C(13*B*)	114.0 (4)
O(1*A*)—C(14*A*)—C(15*A*)	109.3 (4)	O(1*B*)—C(14*B*)—C(15*B*)	109.5 (4)
C(8*A*)—C(14*A*)—C(15*A*)	115.6 (4)	C(8*B*)—C(14*B*)—C(15*B*)	115.4 (4)
C(13*A*)—C(14*A*)—C(15*A*)	104.0 (4)	C(13*B*)—C(14*B*)—C(15*B*)	103.3 (4)
C(14*A*)—C(15*A*)—C(16*A*)	103.5 (5)	C(14*B*)—C(15*B*)—C(16*B*)	105.0 (5)
C(15*A*)—C(16*A*)—C(17*A*)	107.2 (5)	C(15*B*)—C(16*B*)—C(17*B*)	107.0 (5)
C(13*A*)—C(17*A*)—C(16*A*)	105.8 (4)	C(13*B*)—C(17*B*)—C(16*B*)	105.6 (4)
C(13*A*)—C(17*A*)—C(20*A*)	114.6 (5)	C(13*B*)—C(17*B*)—C(20*B*)	115.9 (5)
C(16*A*)—C(17*A*)—C(20*A*)	114.3 (4)	C(16*B*)—C(17*B*)—C(20*B*)	115.5 (5)
O(9*A*)—C(19*A*)—O(9′)	101.5 (10)	O(9*B*)—C(19*B*)—O(9″)	86.1 (15)
O(9*A*)—C(19*A*)—C(10*A*)	126.7 (7)	O(9*B*)—C(19*B*)—C(10*B*)	127.4 (7)
O(9′)—C(19*A*)—C(10*A*)	131.3 (10)	O(9″)—C(19*B*)—C(10*B*)	133.7 (15)
C(17*A*)—C(20*A*)—C(21*A*)	128.0 (5)	C(17*B*)—C(20*B*)—C(21*B*)	128.8 (5)
C(17*A*)—C(20*A*)—C(23*A*)	124.7 (5)	C(17*B*)—C(20*B*)—C(23*B*)	123.4 (5)
C(21*A*)—C(20*A*)—C(23*A*)	107.3 (5)	C(21*B*)—C(20*B*)—C(23*B*)	107.8 (5)
C(20*A*)—C(21*A*)—C(22*A*)	110.5 (6)	C(20*B*)—C(21*B*)—C(22*B*)	110.8 (5)
O(2*A*)—C(22*A*)—O(3*A*)	120.3 (7)	O(2*B*)—C(22*B*)—O(3*B*)	119.8 (6)
O(2*A*)—C(22*A*)—C(21*A*)	108.7 (5)	O(2*B*)—C(22*B*)—C(21*B*)	109.1 (5)
O(3*A*)—C(22*A*)—C(21*A*)	130.9 (7)	O(3*B*)—C(22*B*)—C(21*B*)	131.1 (6)
O(2*A*)—C(23*A*)—C(20*A*)	104.8 (5)	O(2*B*)—C(23*B*)—C(20*B*)	103.6 (5)
O(4*A*)—C(24*A*)—C(25*A*)	110.2 (5)	O(4*B*)—C(24*B*)—C(25*B*)	109.6 (5)
O(4*A*)—C(24*A*)—C(29*A*)	106.1 (6)	O(4*B*)—C(24*B*)—C(29*B*)	106.8 (5)
C(25*A*)—C(24*A*)—C(29*A*)	113.7 (6)	C(25*B*)—C(24*B*)—C(29*B*)	112.0 (5)
C(24*A*)—C(25*A*)—C(26*A*)	111.7 (6)	C(24*B*)—C(25*B*)—C(26*B*)	112.2 (5)
O(8*A*)—C(26*A*)—C(25*A*)	110.7 (6)	O(8*B*)—C(26*B*)—C(25*B*)	108.7 (5)
O(8*A*)—C(26*A*)—C(27*A*)	108.8 (7)	O(8*B*)—C(26*B*)—C(27*B*)	109.9 (5)
C(25*A*)—C(26*A*)—C(27*A*)	110.6 (6)	C(25*B*)—C(26*B*)—C(27*B*)	110.7 (5)
O(6*A*)—C(27*A*)—O(7*A*)	110.3 (5)	O(6*B*)—C(27*B*)—O(7*B*)	111.2 (5)
O(6*A*)—C(27*A*)—C(26*A*)	105.4 (6)	O(6*B*)—C(27*B*)—C(26*B*)	105.0 (5)
O(7*A*)—C(27*A*)—C(26*A*)	111.8 (5)	O(7*B*)—C(27*B*)—C(26*B*)	110.1 (5)
O(6*A*)—C(27*A*)—C(28*A*)	110.3 (4)	O(6*B*)—C(27*B*)—C(28*B*)	110.7 (5)
O(7*A*)—C(27*A*)—C(28*A*)	106.3 (5)	O(7*B*)—C(27*B*)—C(28*B*)	108.4 (5)
C(26*A*)—C(27*A*)—C(28*A*)	112.8 (5)	C(26*B*)—C(27*B*)—C(28*B*)	111.5 (5)
O(4*A*)—C(28*A*)—O(5*A*)	107.4 (4)	O(4*B*)—C(28*B*)—O(5*B*)	106.6 (5)
O(4*A*)—C(28*A*)—C(27*A*)	111.9 (5)	O(4*B*)—C(28*B*)—C(27*B*)	113.2 (5)
O(5*A*)—C(28*A*)—C(27*A*)	111.0 (5)	O(5*B*)—C(2*B*)—C(27*B*)	112.2 (5)

Data were corrected for Lorentz and polarization. $R\sigma$ = 0.040. The structure was solved by direct methods (*SHELXTL*; Sheldrick, 1985). All non-H atoms were treated anisotropically in the least-squares refinement; O(1), O(2), O(2*A*), O(8*A*) and C(29*A*) show some disorder (see displacement parameters in Table 1); O(9*A*), O(9*B*), O(9′) and O(9″) have occupancy factors of

0.49 (2), 0.56 (2), 0.38 (2) and 0.38 (2), respectively, and were treated anisotropically, except for O(9″). The H-atom positions in the CH, CH_2 and CH_3 groups were generated, while those linked to O atoms were located in a difference Fourier map. Their positions were refined and included in the structure-factor calculations with a common isotropic temperature factor, U = 0.060 Å^2. Only one H atom for each water molecule was located. The high R value is due to the presence of disorder.

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Lists of structure factors, anisotropic displacement parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 71751 (24 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: CD1053]

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D-*glycero*-D-*gulo*-Heptono- (I) and 2,7-Ditosyl-D-*glycero*-D-*gulo*-heptono-1,4-lactone (II)

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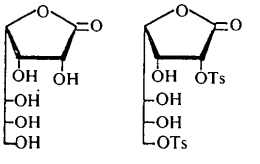
Abstract

The geometries of the lactone rings in the two structures are similar. Differences between $C_7H_{12}O_7$ (I) and $C_{21}H_{24}O_{11}S_2$ (II) occur in the conformation of the side chain with respect to the lactone ring, and in the crystal packing, with that of (I) being more influenced by hydrogen bonding. A weak intramolecular hydrogen bond of 2.718 (6) Å is present in (II).

Comment

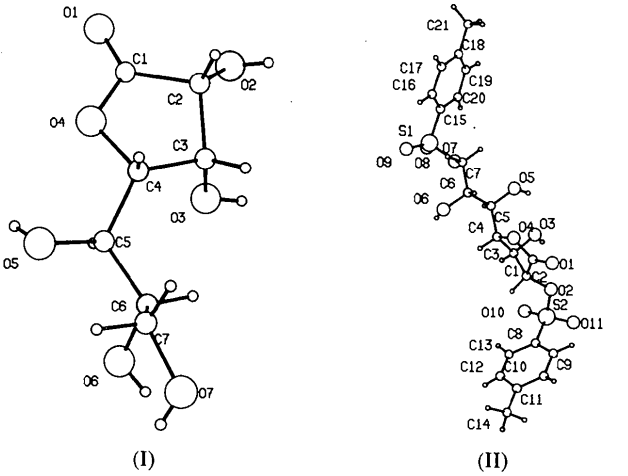
An investigation of the selective di-*O*-tosylation of aldonolactones and the selective di-*O*-mesylation of hexonolactones shows that the selectivity is good when the hydroxy groups at C(2) and C(3) are *cis* oriented. Furthermore, the selectivity is highest for the lactones which also have the side chain *cis* to the two hydroxy groups mentioned (Lundt & Madsen, 1992).

As tosyl and mesyl are good leaving groups the di-*O*-tosylates and di-*O*-mesylates can be used as substrates for nucleophilic substitution reactions. The ditosylation of D-*glycero*-D-*gulo*-heptono-1,4-lactone (I) gave the 2,7-di-*O*-tosylate (II) in good yield (64%). This yield is rather high considering that five O atoms are available for tosylation and could be a result of steric hindrance or intramolecular hydrogen bonding between some of the hydroxy groups. In order to see if a connection between conformation and yield could be found, the present structure investigations were carried out.



(I) (II)

The commercial compound (I) (Sigma) was recrystallized from ethanol at room temperature. Compound (II) was prepared by literature methods (Lundt & Madsen, 1992). The reflecting power of the crystals of (II) was rather poor. The bond lengths and angles listed in Table 2 agree well with those observed in related structures. The labelling of the atoms is shown in Fig. 1.



(I) (II)

Fig. 1. View of the molecules with atomic labelling.