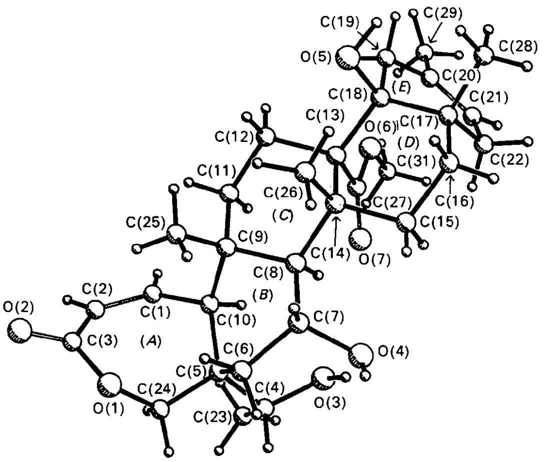

Fig. 1. Perspective view of galphimine B.

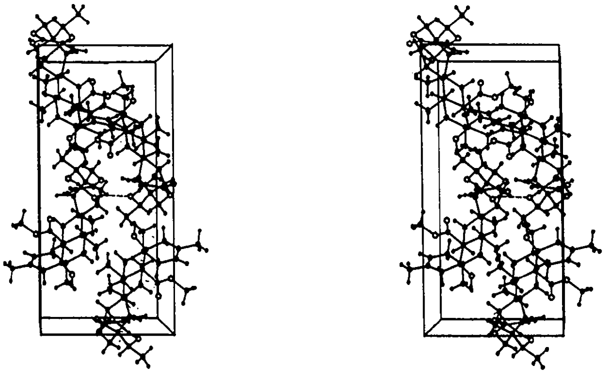

Fig. 2. Stereoscopic view of a unit cell of galphimine B viewed along the *b* axis.

isomer could be rejected at the 0.005 significance level [$\mathcal{R}_{(3,1623,0.005)} = 1.004$]. Accordingly, all coordinates reported herein refer to the statistically favored configuration: the 4*R*-enantiomer. In addition to the statistical disorder of the methylene chloride solvent molecule, an orientational disorder was also observed and modeled by splitting the position of one Cl atom [Cl(1)] into two major positions.

Atomic parameters are listed in Table 1. Distances and angles are listed in Table 2.* A perspective view of the molecule showing the atomic numbering and the stereochemistry is given in Fig. 1. Fig 2 shows the molecular packing.

Related literature. A galphimine B closely related *nor*, *seco*-triterpenoid has been isolated from *Lophanthera lactescens* (Dos S., Braz, Gottlieb & Shoolery, 1990).

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* Lists of structure factors, anisotropic thermal parameters, torsion angles and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55659 (14 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HH0595]

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Structure of a Coupled Carbohydrate and Terpene

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Abstract. (1*S*-{1α,1[3*R**,5*R**(*R**)],2α,5β})-5-[1,2-Bis(benzyloxy)ethyl]-4,5-dihydro-3-[1-hydroxy-2-methyl-5-(1-methylvinyl)cyclohexyl]-2(3*H*)-furanone, $C_{30}H_{34}O_7$, $M_r = 506.3$, monoclinic, $P2_1$, $a = 12.780\,(1)$, $b = 6.478\,(1)$, $c = 16.832\,(2)$ Å, $\beta = 93.00\,(1)°$, $V = 1391.6\,(3)$ Å^3, $Z = 2$, $D_x = 1.209$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 0.9$ cm^{-1}, $F(000) = 540$, $T = 298$ K, $R = 0.0504$ and $wR = 0.0584$ for 2177 reflections [$I \geq 2\sigma(I)$]. Crystal chirality was assigned on the basis of the two components coupled to form the title compound. The carbohydrate lactone, L-gulonic-γ-lactone, was utilized as a precursor to the tetrahydrofuran ring and the dibenzoate appendage. In a similar manner, the terpene ketone (+)-dihydrocarvone was the precursor to the cyclohexanol ring. The absolute stereoche-

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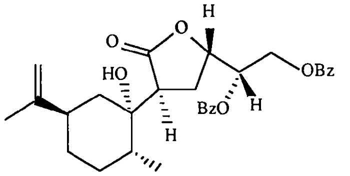
mistry of the molecule was established from the fixed C atoms C4 and C15 of the tetrahydrofuran and appendage, and C atoms C6 and C9 bearing the methyl and isopropene groups, respectively, on the cyclohexanol ring. It is worth noting that the two rings are coupled with the least sterically hindered faces of each ring. The X-ray studies shown herein establish the stereochemistry of the C2—O5 bond. O5—H5, the only hydroxyl group present, is involved in one intramolecular hydrogen bond with O1: O5—H5 = 0.76 (8), O5···O1 = 2.819 (5), H5···O1 = 2.28 (7) Å, O5—H5···O1 = 129 (7)°.

Experimental. Compound (I) was first purified by gravity column chromatography over silica gel to produce a thick colorless oil. Next, the oil was dissolved in the hot solvent mixture of hexanes–dichloromethane (20:1) which produced fine white needles on cooling. An additional recrystallization from ethyl acetate at 296 K over 10 d gave thick colorless needles. The crystals had an m.p. of 418–419 K (uncorrected). The crystal used in the X-ray analysis was obtained by slow evaporation from methanol and had dimensions of 0.26 × 0.40 × 0.55 mm. Data were collected at 298 K on a Siemens *P*3*m*/*V* diffractometer equipped with a graphite monochromator utilizing Mo *Kα* radiation. 50 reflections with $20 \leq 2\theta \leq 22°$ were used to refine the cell parameters. 2840 reflections were collected using the ω-scan method (h 0→15, k 0→7, l −20→20; 2θ range 3→50°; 1.2° ω scan at 2–4° $\min^{-1}$ depending on intensity). 2708 reflections were unique; $R_{int} = 0.0134$. Four reflections (317, $30\bar{3}$, $\bar{1}0\bar{2}$, $\bar{4}\bar{2}5$) were measured every 96 reflections to monitor instrument and crystal stability (maximum correction on I was < 2.5%). Absorption corrections were applied based on measured crystal faces using *SHELXTL-Plus* (Sheldrick, 1990); absorption coefficient $\mu = 0.9\ \mathrm{cm}^{-1}$ (minimum and maximum transmission factors 0.965 and 0.978, respectively).



(I)

Table 1. *Fractional coordinates and equivalent isotropic thermal parameters* (Å^2) *for the non-*H *atoms of compound* (I)

$U_{eq} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{A}_{ij}$, where $\mathbf{A}_{ij}$ is the dot product of the ith and jth direct-space unit-cell vectors

	x	y	z	U_{eq}
O1	0.2741 (3)	1.17379†	0.7067 (2)	0.0896 (13)
O4	0.3205 (2)	0.9921 (7)	0.8144 (2)	0.0651 (10)
O5	0.1432 (3)	0.9545 (7)	0.5962 (2)	0.0722 (13)
O15	0.4755 (2)	0.7058 (7)	0.7714 (2)	0.0654 (10)
O16	0.5954 (2)	0.7268 (8)	0.9228 (2)	0.0788 (11)
O17	0.6537 (3)	0.9819 (9)	1.0012 (2)	0.0976 (14)
O24	0.5384 (3)	0.3860 (9)	0.7868 (3)	0.113 (2)
C1	0.2787 (3)	1.0096 (8)	0.7400 (3)	0.0599 (14)
C2	0.2422 (3)	0.8032 (8)	0.7079 (2)	0.0551 (14)
C3	0.2516 (4)	0.6615 (9)	0.7795 (2)	0.0579 (14)
C4	0.3215 (3)	0.7799 (8)	0.8402 (3)	0.0574 (14)
C5	0.1335 (3)	0.8184 (8)	0.6623 (2)	0.0553 (13)
C6	0.1005 (4)	0.6084 (8)	0.6273 (3)	0.065 (2)
C7	−0.0097 (5)	0.6210 (12)	0.5876 (3)	0.088 (2)
C8	−0.0900 (5)	0.7042 (12)	0.6414 (4)	0.094 (2)
C9	−0.0595 (3)	0.9137 (10)	0.6761 (3)	0.073 (2)
C10	0.0509 (3)	0.8998 (10)	0.7165 (3)	0.0625 (15)
C11	−0.1371 (4)	1.0006 (12)	0.7322 (3)	0.089 (2)
C12	−0.1593 (8)	1.197 (2)	0.7296 (6)	0.218 (6)
C13	−0.1826 (5)	0.872 (2)	0.7887 (4)	0.152 (4)
C14	0.1765 (6)	0.5215 (11)	0.5697 (3)	0.084 (3)
C15	0.4339 (3)	0.7045 (10)	0.8497 (2)	0.0619 (15)
C16	0.5012 (4)	0.8425 (10)	0.9037 (3)	0.075 (2)
C17	0.6646 (3)	0.8121 (10)	0.9741 (2)	0.068 (2)
C18	0.7539 (3)	0.6731 (10)	0.9949 (2)	0.065 (2)
C19	0.7650 (3)	0.4827 (11)	0.9586 (3)	0.079 (2)
C20	0.8483 (4)	0.3568 (13)	0.9802 (4)	0.096 (2)
C21	0.9204 (5)	0.416 (2)	1.0380 (4)	0.100 (3)
C22	0.9103 (5)	0.602 (2)	1.0743 (3)	0.106 (3)
C23	0.8282 (4)	0.7343 (13)	1.0539 (3)	0.084 (2)
C24	0.5257 (3)	0.5373 (9)	0.7473 (3)	0.073 (2)
C25	0.5628 (3)	0.5685 (11)	0.6653 (3)	0.084 (2)
C26	0.5559 (5)	0.7546 (14)	0.6264 (4)	0.107 (3)
C27	0.5938 (5)	0.769 (2)	0.5510 (4)	0.132 (4)
C28	0.6364 (6)	0.614 (2)	0.5166 (6)	0.147 (4)
C29	0.6472 (7)	0.430 (2)	0.5522 (6)	0.152 (4)
C30	0.6085 (5)	0.4014 (14)	0.6298 (4)	0.128 (3)

† Coordinate fixed to define origin for structure with non-centrosymmetric space group.

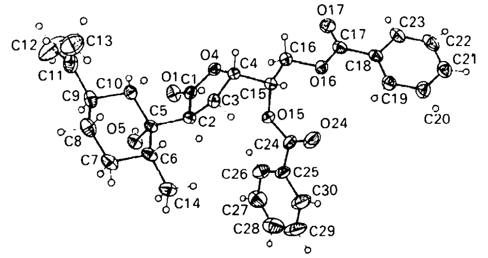


Fig. 1. Molecular structure of (I), with 50% probability ellipsoids, showing the atom-numbering scheme.

The structure was solved by direct methods in *SHELXTL-Plus* from which the locations of all non-H atoms were obtained. The structure was refined (*SHELX*76; Sheldrick, 1976) using full-matrix least squares and the positions of all non-methyl H atoms were determined from a difference Fourier map. The non-H atoms were treated anisotropically, whereas most of the H atoms were refined with isotropic thermal parameters; H atoms on C12, C13 and C26–C30 were calculated in idealized positions and their isotropic thermal parameters were fixed. 429 parameters were refined and $\sum w(|F_o| - |F_c|)^2$ was minimized; $w = 1/(\sigma|F_o|)^2$, $\sigma(F_o) = 0.5\,kI^{-1/2}\{[\sigma(I)]^2 + (0.02I)^2\}^{1/2}$, I(intensity) = $(I_{peak} - I_{background}) \times$ (scan rate), and $\sigma(I) = (I_{peak} + I_{background})^{1/2} \times$ (scan rate), k is the correction for decay and Lp effects, 0.02 is a factor used to down-

Table. 2. *Bond lengths* (Å) *and angles* (°) *for the non-*H *atoms of compound* (I)

(1)	(2)	(3)	(1)—(2)	(1)—(2)—(3)
C1	O1		1,202 (5)	
C1	O4	C4	1.340 (5)	111.0 (4)
C4	O4		1.441 (7)	
C5	O5		1.430 (6)	
C15	O15	C24	1.446 (5)	118.4 (4)
C24	O15		1.340 (7)	
C16	O16	C17	1.441 (6)	116.8 (5)
C17	O16		1.324 (6)	
C17	O17		1.201 (8)	
C24	O24		1.190 (8)	
C2	C1	O1	1.507 (7)	127.6 (4)
C2	C1	O4		111.1 (4)
O1	C1	O4		121.2 (4)
C3	C2	C5	1.516 (6)	117.5 (4)
C3	C2	C1		104.0 (3)
C5	C2	C1	1.554 (6)	111.9 (4)
C4	C3	C2	1.527 (6)	104.3 (4)
C15	C4	O4	1.518 (6)	109.4 (4)
C15	C4	C3		115.2 (4)
O4	C4	C3		106.4 (3)
C6	C5	C10	1.533 (7)	110.6 (4)
C6	C5	O5		106.3 (3)
C6	C5	C2		110.8 (4)
C10	C5	O5	1.526 (6)	110.0 (4)
C10	C5	C2		110.8 (3)
O5	C5	C2		108.1 (3)
C7	C6	C14	1.528 (7)	110.3 (4)
C7	C6	C5		110.5 (4)
C14	C6	C5	1.516 (8)	113.7 (4)
C8	C7	C6	1.505 (9)	113.4 (5)
C9	C8	C7	1.521 (10)	112.4 (5)
C10	C9	C11	1.536 (6)	111.2 (4)
C10	C9	C8		109.2 (5)
C11	C9	C8	1.514 (8)	114.1 (5)
C5	C10	C9		113.8 (4)
C12	C11	C13	1.302 (14)	120.2 (7)
C12	C11	C9		119.3 (7)
C13	C11	C9	1.412 (10)	120.4 (7)
C16	C15	O15	1.511 (7)	108.7 (4)
C16	C15	C4		112.2 (4)
O15	C15	C4		107.0 (3)
O16	C16	C15		105.6 (5)
C18	C17	O16	1.481 (7)	112.4 (5)
C18	C17	O17		124.8 (4)
O16	C17	O17		122.9 (5)
C19	C18	C23	1.387 (9)	119.0 (5)
C19	C18	C17		122.1 (4)
C23	C18	C17	1.395 (6)	118.8 (5)
C20	C19	C18	1.375 (9)	120.4 (5)
C21	C20	C19	1.359 (9)	120.5 (7)
C22	C21	C20	1.362 (14)	119.7 (7)
C23	C22	C21	1.382 (10)	121.6 (6)
C18	C23	C22		118.7 (7)
C25	C24	O15	1.497 (7)	110.4 (5)
C25	C24	O24		125.9 (5)
O15	C24	O24		123.7 (5)
C26	C25	C30	1.373 (11)	120.1 (6)
C26	C25	C24		122.9 (6)
C30	C25	C24	1.381 (11)	117.0 (6)
C27	C26	C25	1.385 (9)	118.6 (8)
C28	C27	C26	1.29 (2)	122.3 (10)
C29	C28	C27	1.34 (2)	121.8 (9)
C30	C29	C28	1.434 (12)	119.5 (10)
C25	C30	C29		117.7 (8)

weight intense reflections and to account for instrument instability. Final $R = 0.0504$, $wR = 0.0584$ ($R_{\text{all}} = 0.0626$, $wR_{\text{all}} = 0.0605$) for 2177 reflections having $I > 2\sigma(I)$, and goodness of fit = 2.03. Maximum Δ/σ was 0.001 in the final refinement cycle and the minimum and maximum peaks in the ΔF map were -0.24 and $0.17\ \text{e}\ \text{Å}^{-3}$, respectively. The linear absorption coefficient was calculated using values from *International Tables for X-ray Crystallography* (1974, Vol. IV, p. 55). Scattering factors for non-H atoms were taken from Cromer & Mann (1968) with anomalous-dispersion corrections from Cromer & Liberman (1970), while those of H atoms were from Stewart, Davidson & Simpson (1965). The positional parameters and the equivalent isotropic thermal parameters of the non-H atoms are listed in Table 1,* bond lengths and angles are in Table 2. A thermal-ellipsoid drawing (*SHELXTL-Plus*) of the molecule with the atom-labelling scheme is given in Fig. 1.

Related literature. Simple methods of coupling achiral esters/lactones and ketones have been established (Enholm & Jiang, 1992*a*) which result in β-hydroxy esters. We have also studied several other examples of lactone carbohydrates such as δ-gluconolactone and γ-ribonolactone in couplings with the terpene ketone (−)-menthone (Enholm & Jiang, 1992*b*). The title structure shown in Fig. 1 can also be prepared with a cyclohexanol unit derived from (−)-menthone (Abboud, Jiang & Enholm, 1993).

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* Lists of the crystallographic data, anisotropic thermal parameters, H-atom positional parameters and bond lengths and angles, and structure-factor amplitudes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55698 (18 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: ST1029]

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