molecules in cages formed between the two nearest layers related by translation along **b**. These guest molecules show four different coplanar orientations in the cage in which they are hydrogen bonded to the host O(8)—H(80) hydroxyl. In gossypol/salicylaldehyde, channels accommodating guest molecules A are formed between the two nearest layers related by an n-glide plane. The guest molecules located in the channels are hydrogen bonded to the host O(8)—H(80). The best plane C(1A)–C(6A) forms a dihedral angle of 15·7° with the naphthyl moiety C(11)–C(20), and the local stacks consisting of six aromatic rings can be distinguished in this structure.

The inclusion compounds of gossypol with benzaldehyde and salicylaldehyde are examples of inclusion compounds with guest:host ratio exceeding 1. In this case one of the solvent molecules and gossypol are used to build 'an inclusion aggregate' (a layer), stabilized by hydrogen bonds and stacking interactions, with the solvent molecule enclosed within a cage formed by gossypol molecules. However, because these aggregates are not able to form a close-packed crystal, an additional solvent molecule is included on crystallization. In this case the inclusion aggregate plays the role of host. It can be expected that a lattice inclusion compound with a structure similar to gossypol/benzaldehyde or gossypol/salicylaldehyde can be obtained with two different guest species: guest A will be accommodated in voids formed between the inclusion aggregates of gossypol and guest B.

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Structure of D-*glycero*-L-*galacto*-Heptitol

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Abstract. $C_7H_{16}O_7$, $M_r = 212·20$, monoclinic, $P2_1$, $a = 4·748$ (3), $b = 8·362$ (6), $c = 11·428$ (7) Å, $\beta = 92·01$ (3)°, $V = 453·4$ (5) Å^3, $Z = 2$, $D_x = 1·554$ g cm^{-3}, $\lambda(Cu\ K\alpha_1) = 1·54051$ Å, $\mu = 11·7$ cm^{-1}, $F(000) = 228$, $T = 293$ K, final $R = 0·049$ for 993 unique observed data. The molecules adopt a

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Table 1. *Final fractional coordinates of* C *and* O *atoms with equivalent isotropic thermal parameters* (Å²) *and of* H *atoms with isotropic thermal parameters* (Å²); *e.s.d.'s are given in parentheses*

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

	x	y	z	U_{eq}
O(1)	0·7218 (7)	0·8530 (4)	0·4237 (2)	0·0350 (8)
O(2)	0·5053 (5)	0·65100 (0)	0·2410 (2)	0·0281 (7)
O(3)	1·0076 (5)	0·4757 (4)	0·2135 (1)	0·0258 (6)
O(4)	0·4710 (5)	0·2500 (4)	0·3617 (2)	0·0300 (7)
O(5)	0·9772 (5)	0·0955 (4)	0·3010 (2)	0·0293 (7)
O(6)	0·7727 (6)	−0·1046 (4)	0·1290 (2)	0·0318 (7)
O(7)	0·2473 (6)	−0·0377 (5)	0·0053 (2)	0·0369 (8)
C(1)	0·8586 (8)	0·7105 (5)	0·3889 (3)	0·0286 (9)
C(2)	0·6544 (8)	0·5839 (5)	0·3400 (3)	0·0244 (9)
C(3)	0·8178 (8)	0·4353 (5)	0·3033 (3)	0·0231 (9)
C(4)	0·6228 (8)	0·2987 (5)	0·2625 (3)	0·0231 (9)
C(5)	0·7850 (7)	0·1586 (5)	0·2133 (3)	0·0226 (8)
C(6)	0·5957 (8)	0·0250 (5)	0·1608 (3)	0·0250 (9)
C(7)	0·4320 (8)	0·0832 (5)	0·0523 (3)	0·031 (1)
H(11)	1·00 (1)	0·746 (7)	0·323 (4)	0·04 (1)
H(12)	0·950 (8)	0·660 (5)	0·456 (3)	0·03 (1)
H(2)	0·53 (1)	0·558 (7)	0·400 (4)	0·05 (1)
H(3)	0·93 (1)	0·398 (7)	0·373 (4)	0·05 (1)
H(4)	0·50 (1)	0·343 (9)	0·209 (5)	0·08 (1)
H(5)	0·90 (1)	0·220 (7)	0·149 (5)	0·03 (1)
H(6)	0·454 (9)	−0·025 (5)	0·220 (3)	0·023 (9)
H(71)	0·58 (1)	0·112 (8)	−0·015 (5)	0·07 (1)
H(72)	0·348 (9)	0·192 (6)	0·061 (4)	0·02 (1)
H(10)	0·61 (1)	0·85 (1)	0·492 (6)	0·13 (2)
H(20)	0·339 (9)	0·614 (5)	0·230 (3)	0·03 (1)
H(30)	0·94 91)	0·472 (9)	0·140 (6)	0·12 (2)
H(40)	0·33 (1)	0·208 (7)	0·352 (4)	0·05 (1)
H(50)	0·91 (1)	0·025 (7)	0·343 (5)	0·04 (1)
H(60)	0·69 (1)	−0·193 (7)	0·158 (4)	0·03 (1)
H(70)	0·14 (1)	−0·06 (1)	0·047 (5)	0·17 (2)

Table 2. *Bond distances* (Å), *bond angles* (°) *and selected torsion angles* (°); *e.s.d.'s are given in parentheses*

O(1)—C(1)	1·421 (5)	O(2)—C(2)	1·428 (4)
O(3)—C(3)	1·430 (4)	O(4)—C(4)	1·424 (4)
O(5)—C(5)	1·432 (4)	O(6)—C(6)	1·426 (5)
O(7)—C(7)	1·431 (5)	C(1)—C(2)	1·528 (6)
C(2)—C(3)	1·531 (6)	C(3)—C(4)	1·533 (6)
C(4)—C(5)	1·521 (6)	C(5)—C(6)	1·542 (6)
C(6)—C(7)	1·520 (5)		

O(1)—C(1)—C(2)	113·1 (3)	O(2)—C(2)—C(1)	107·9 (3)
O(2)—C(2)—C(3)	110·1 (3)	C(1)—C(2)—C(3)	110·0 (3)
O(3)—C(3)—C(2)	110·1 (3)	O(3)—C(3)—C(4)	110·3 (3)
C(2)—C(3)—C(4)	112·4 (3)	O(4)—C(4)—C(3)	106·7 (3)
O(4)—C(4)—C(5)	110·6 (3)	C(3)—C(4)—C(5)	112·2 (3)
O(5)—C(5)—C(4)	110·1 (3)	O(5)—C(5)—C(6)	110·7 (3)
C(4)—C(5)—C(6)	114·0 (3)	O(6)—C(6)—C(5)	108·0 (3)
O(6)—C(6)—C(7)	108·9 (3)	C(5)—C(6)—C(7)	111·1 (3)
O(7)—C(7)—C(6)	111·7 (3)		

Angles in the chain

O(1)—C(1)—C(2)—C(3)	179·3 (3)	C(4)—C(5)—C(6)—O(6)	−174·3 (3)
C(1)—C(2)—C(3)—C(4)	175·5 (3)	C(4)—C(5)—C(6)—C(7)	66·3 (4)
C(2)—C(3)—C(4)—C(5)	173·5 (3)	C(5)—C(6)—C(7)—O(7)	−177·7 (3)
C(3)—C(4)—C(5)—C(6)	−174·7 (3)		

Angles between vicinal O atoms

O(1)—C(1)—C(2)—O(2)	59·2 (4)	O(4)—C(4)—C(5)—O(5)	−58·8 (4)
O(2)—C(2)—C(3)—O(3)	57·7 (4)	O(5)—C(5)—C(6)—O(6)	−49·5 (3)
O(3)—C(3)—C(4)—O(4)	171·5 (3)	O(6)—C(6)—C(7)—O(7)	63·4 (4)

Angles between vicinal H atoms

H(11)—C(1)—C(2)—H(2)	−179 (5)	H(4)—C(4)—C(5)—H(5)	64 (6)
H(12)—C(1)—C(2)—H(2)	58 (4)	H(5)—C(5)—C(6)—H(6)	−170 (4)
H(2)—C(2)—C(3)—H(3)	−61 (5)	H(6)—C(6)—C(7)—H(71)	−169 (4)
H(3)—C(3)—C(4)—H(4)	169 (5)	H(6)—C(6)—C(7)—H(72)	83 (4)

Fig. 1. *SCHAKAL* (Keller, 1980) drawing of the title compound.

bent 'sickle' conformation, thus avoiding 1,3-parallel interactions between O(4) and O(6). All seven hydroxyl groups are involved as donors and acceptors in a complex pattern of intermolecular hydrogen bonds.

Introduction. Heptitols (sugar alcohols with a central carbon chain of seven C atoms) can occur as ten diastereomers, of which four are *meso* forms. Thus, 16 stereoisomers are possible and most of them have been synthesized or isolated from plants.

So far only the crystal structures of *meso-glycero-gulo*-heptitol (Nimgirawath, James & Mills, 1976), of D-*glycero*-L-*allo*-heptitol (Angyal, Saunders, Grainger, Le Fur & Williams, 1986) and of 'D-perseitol', D-*glycero*-D-*galacto*-heptitol (Kanters, Schouten, van der Sluis & Duisenberg, 1990), are known. We now report the crystal structure of D-*glycero*-L-*galacto*-heptitol.

Experimental. Crystals suitable for X-ray analysis were obtained from a sample of D-*glycero*-L-*galacto*-heptitol prepared following known literature procedures (Sowden & Strobach, 1960) by crystallization from ethanol. A colorless transparent crystal of dimensions 0·7 × 0·4 × 0·2 mm was used for data collection on an Enraf–Nonius CAD-4 diffractometer with graphite-monochromated Cu $K\alpha$ radiation. Cell parameters were determined by least-squares
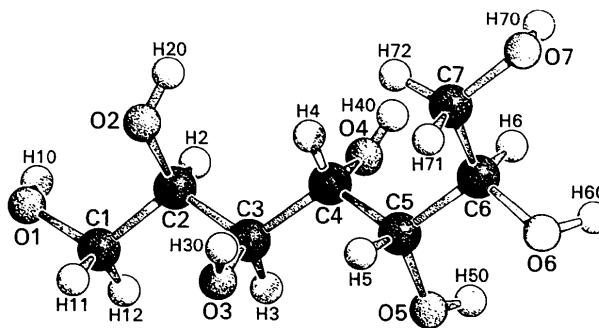
refinement of the setting angles of 25 reflexions within $75·2 \leq 2\theta \leq 93·5°$. Intensity data were measured by $\theta/2\theta$ scans ($4·5 \leq 2\theta \leq 153°$; $0 \leq h \leq 5$, $0 \leq k \leq 10$, $-14 \leq l \leq 14$). No significant decay in the intensity for three standards monitored every 2 h. 1163 data were measured, of which 1009 were symmetry independent ($R_{int} = 0·0156$). 993 intensities were considered observed $[F_o > 3\sigma(F_o)]$. Data were corrected for Lorentz and polarization effects but not for absorption.

The structure was solved by direct methods. The solution with the highest figure of merit showed all non-H atoms. The structure obtained was in accordance with the known chirality (Sowden & Strobach,

Table 3. *Geometry of the hydrogen bonds* (Å,°)

D—H···A	D—H	D···A	H···A	D—H···A	Symmetry operation on A
O(1)—H(10)···O(4^I)	0·97 (7)	2·784 (4)	1·90 (7)	150 (6)	$-x+1, \frac{1}{2}+y, -z+1$
O(2)—H(20)···O(3^{II})	0·85 (4)	2·789 (4)	1·96 (4)	165 (4)	$x-1, y, z$
O(3)—H(30)···O(7^{III})	0·89 (7)	2·742 (4)	1·85 (7)	174 (7)	$-x+1, \frac{1}{2}+y, -z$
O(4)—H(40)···O(5^{II})	0·76 (5)	2·745 (4)	1·99 (5)	171 (5)	$x-1, y, z$
O(5)—H(50)···O(1^{IV})	0·83 (6)	2·769 (5)	1·95 (6)	172 (6)	$x, y-1, z$
O(6)—H(60)···O(2^{IV})	0·91 (6)	2·746 (4)	1·85 (6)	169 (5)	$x, y-1, z$
O(7)—H(70)···O(6^{II})	0·74 (6)	2·759 (4)	2·03 (7)	167 (6)	$x-1, y, z$

1960). All aliphatic H atoms were localized in theoretical positions (sp^3 hybridization) with C—H 0·96 Å. The hydroxyl-group H atoms were taken from a difference map. Full-matrix refinement on F of 191 parameters including scale factor, positional and anisotropic thermal parameters for all non-H atoms, and positional and isotropic parameters for all H atoms resulted in $R = 0·049$ and $wR = 0·058$. The ratio of observations to number of variables is 5·2. The function minimized was $\sum w(|F_o| - |F_c|)^2$ with weights $w = 1/\sigma^2(|F_o|)$. Max. shift/e.s.d. was 0·43 in the final cycle; max. and min. heights in final $\Delta\rho$ map 0·31 and $-0·32$ e Å^{-3}. Complex neutral-atom scattering factors were taken from *SHELX*76. Programs used were *SHELXS*86 (Sheldrick, 1990), *SHELX*76 (Sheldrick, 1976) and *PLATON*88 (Spek, 1982) on MicroVAX II and VAX 3200 computers.

Discussion. The final fractional coordinates and isotropic or equivalent isotropic thermal parameters of C, O and H atoms are listed in Table 1.* Bond distances and angles and some torsion angles in the title compound are given in Table 2. A perspective view of the molecule is shown in Fig. 1 which also gives the atom numbering. It can be seen that the carbon chain is planar up to C(6) and also that O(1) and O(6) are involved in this extended 'zig zag' arrangement. Nevertheless, bending of the carbon chain involving C(7) occurs at C(6) by rotation around the C(5)/C(6) bond, thus producing an overall 'sickle' geometry. This situation was predicted (Mills, 1974) because of unfavourable 1,3-parallel interactions between O(4) and O(6) in an extended conformation. This conformation is also dominant in solution (Lewis, 1986).

That the influence of such 1,3-parallel interactions between C and O atoms (designated as C//O and O//O, respectively) in crystal structure geometries could have been overestimated formerly as summarized by G. A. Jeffrey (Jeffrey & Kim, 1970), was first pointed out by one of us (Angyal, Saunders, Grainger, Le Fur & Williams, 1986) in connection

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* Lists of structure factors, anisotropic thermal parameters, and bond lengths and angles involving H atoms have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53795 (13 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

with the structure determination of D-*glycero*-L-*allo*-heptitol. Also, the structure of D-altritol is bent, but accepts a C//O interaction as well, which could be avoided easily by rotating 60° around the C(4)—C(5) bond (Kopf, Bischoff & Köll, 1991). Meanwhile in nitroalditols four examples were found where a planar 'zig zag' conformation is adopted, despite the fact that in these cases O//O interactions have to be tolerated (Kopf, Brandenburg, Seelhorst & Köll, 1990; Köll, Malzahn & Kopf, 1990). For instance, the 7-deoxy-7-nitro derivative of the title compound shows overall planar geometry in the crystal with a 1,3-parallel arrangement between O(4) and O(6) (Köll, Malzahn & Kopf, 1990). Therefore, the conformation of D-*glycero*-L-*galacto*-heptitol has to be considered as a 'classical' one, but this result was not 'predictable' from earlier studies.

The orientation of both terminal hydroxyl groups is g,t. Deviations from planarity of the central spine [O(1) to O(6)] are small as can be concluded from the torsion angles in the chain, which ideally should be 180°. As in all free carbohydrates, molecules in the crystal are held together by a complex pattern of intermolecular hydrogen bonds, which involves all O atoms as donors and acceptors. This pattern, which is given in Table 3, not only determines the observed dense packing of molecules ($D_x = 1·554$ g cm^{-3}) but should also influence the selection of a preferred conformation during crystallization. No intramolecular or bifurcated hydrogen bonds were observed.

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Structure of Bufothionin

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Abstract. (1,3,4,5-Tetrahydro-5,5-dimethylpyrrolo-[4,3,2-*de*]quinolinio)-6-sulfate (bufothionin), $C_{12}H_{14}N_2O_4S$, $M_r = 282.32$, monoclinic, $P2_1/c$, $a = 7.000$ (1), $b = 9.709$ (1), $c = 18.238$ (5) Å, $\beta = 95.51$ (4)°, $V = 1233.7$ (4) Å³, $Z = 4$, $D_m = 1.52$, $D_x = 1.520$ Mg m⁻³, Cu $K\alpha_1$, $\lambda = 1.5406$ Å, $\mu = 2.415$ mm⁻¹, $F(000) = 592$, $T = 295$ K, final $R = 0.047$ for 2267 unique reflections. The molecule has a positive and a negative charge in a single structure. Intermolecular hydrogen bonds link the centrosymmetrical molecules to form a dimeric structure.

Introduction. The title compound is one of the major components of the extract of the skin of *Bufo marinus* (L.). The molecular structure has not been determined by means of nuclear magnetic resonance (NMR) or mass spectrometry (MS) because of the difficulty of interpreting the spectra. This study was therefore performed in order to clarify the structure.

Experimental. Bufothionin was purified from an extract of the toad skins (purchased from National Reagents, Bridgeport, Connecticut, USA) by using high-performance liquid chromatography (Akizawa, Ohtani, Kasai, Goto & Yoshioka, 1990). Colorless needle crystals were grown from the eluate (water–acetonitrile, 9:1 *v/v*) by slow evaporation at room temperature. The proposed chemical formula is consistent with that estimated by NMR, MS and X-ray fluorescence spectrometry.

Crystal size $0.65 \times 0.18 \times 0.15$ mm. D_m by flotation in $CHCl_3$–CCl_4. Data collection on an Enraf–Nonius CAD-4 diffractometer, graphite-monochromated Cu $K\alpha_1$ radiation, cell dimensions refined using 20 reflections having $25 < \theta < 30°$, intensity data $1.5 \leq \theta \leq 75°$; ω–2θ scans; $\Delta\omega = (0.5 + 0.15\tan\theta)°$; horizontal detector aperture $(1.0 + 0.5\tan\theta)$ mm; $-8 \leq h \leq 8$, $0 \leq k \leq 12$, $0 \leq l \leq 22$. Three standard reflections ($0\bar{1}2$, 111, $2\bar{1}0$) showed no significant intensity variation during X-ray exposure time. Corrections for Lorentz and polarization, and an empirical absorption correction using ψ scans (transmission factors 0.892–0.997). 2581 reflections collected, 2349 were above the significance level of $3\sigma(F_o)$ and 2267 were unique ($R_{int} = 0.016$). Structure solved by direct methods using *MULTAN*11/82 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1982). Ten H atoms introduced from difference Fourier maps. Refinement on F by full-matrix least squares with anisotropic temperature factors for non-H atoms and isotropic ones for H atoms. Among the remaining four H atoms, three [H(C9), H'(C9) and H''(C12)] were placed at the calculated positions. With H(N1) attached in a correct position, N(1) and O(3)($1 - x$, $-y$, $-z$) are linked *via* a hydrogen bond. All H atoms fixed with

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