Fig. 2. Stereoview of the packing of the molecules. The origin is at
the lower left-hand corner, a is vertical, b is horizontal and c
towards the viewer.

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Structure of the Melampolide Sesquiterpene Lactone Alloschkuhriolide, C₁₅H₁₈O₄

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Abstract. M_r = 262.3, orthorhombic, P2_12_12_1, a =
5.7993 (6), b = 14.945 (1), c = 15.730 (2) Å, U =
1363.3 (3) Å³, Z = 4, D_m = 1.26, D_x = 1.28 Mg m⁻³,
Cu Kα, λ = 1.54184 Å, μ = 0.67 mm⁻¹, F(000) = 560,
T = 295 K, R = 0.058 for 1049 observed reflections.
Alloschkuhriolide (I) is the C(6), C(7) trans-fused product of relactonization of schkuhriolide (II), a
naturally occurring C(7),C(8) cis-fused sesquiterpene
lactone. The relactonization does not alter the gross
conformation of the cyclodecadiene skeleton. It seems,
however, that it results in a certain release of strain in
the molecule.

Introduction. Recently we have reported the crystal
structure of schkuhriolide monohydrate, a naturally
occurring sesquiterpene lactone of the melampolide
type, which is exceptional among melampolides in
possessing a cis lactone ring closed at C(8)
(Rychlewska, 1982). Comparison of this structure with
other melampolides studied by X-ray methods has
revealed considerable conformational similarity in these
compounds. The conformation of the ten-membered ring

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Experimental. Crystals grown from mixture of chloroform and diisopropyl ether, $D_m$ by flotation. Weissenberg photographs indicated orthorhombic symmetry, space group $P2_12_12_1$, cell parameters by least-squares refinement of setting angles of 15 reflections centered on Enraf-Nonius diffractometer; crystal 0-3 x 0-4 x 0-45 mm, $\theta$-2$\theta$ scan, variable scan rate, graphite-monochromated Cu $K\alpha$ radiation, 1107 reflections, 28$\leq115^\circ$, h 0-6, k 0-16, l 0-13, background and integrated intensity for each reflection evaluated from profile analysis according to the Lehmann & Larsen (1974) method using PRADA program (Jask61ski, 1981), no absorption correction, 1056 reflections with $I \geq 1.96 \sigma(I)$ considered significant, seven additional reflections omitted because of secondary extinction, structure solved with MULTAN (Germain, Main & Woolfson, 1971), refined with SHELX76 (Sheldrick, 1976); anisotropic refinement of nonhydrogen atoms followed by difference syntheses led to location of all the H atoms [except those attached to C(1) and C(15) which were placed by calculation]; most H atoms included in the refinement as fixed contributions, but positional parameters of hydroxyl hydrogen allowed to which were placed by calculation; most H atoms included in the refinement as fixed contributions, but positional parameters of hydroxyl hydrogen allowed to refine freely, and methyl H atoms refined as rigid methyl group; all hydrogen atoms given fixed isotropic temperature factor ($U = 0.06 \text{Å}^2$); function minimized $\sum w(F_o - F_c)^2$, w = $k/(\sigma_F^2 + g F^2)$, $g$ refined, $R = 0.056$ ($R_w = 0.089$) with $k = 1.0$ and $g = 0.0126$; $S = 0.85$ for $m = 1049$ observations and $n = 178$ refined parameters; in final cycle of refinement average and maximum shift/error were 0-04 and 0-68, respectively, maximum shift corresponded to rotation of methyl group; residual fluctuations in the difference map within the range $\pm 0.2 \text{e Å}^{-3}$; atomic scattering factors of SHELX76 used.

Discussion. Final atomic coordinates are given in Table 1.* The absolute configuration of alloschkuhriolide (I), assigned by comparison with that of schkuhriolide (II) (Rychlewksa, 1982), is illustrated in Fig. 1 together with the atom numbering (PLUTO78, Motherwell & Clegg, 1978). Bond lengths and angles are given in Table 2 and torsional angles in Table 3.

The basic skeleton of alloschkuhriolide comprises a macrocyclic cis-1(10)-trans-4-cyclodecanediene, trans-fused at C(6)-C(7) with a five-membered $\gamma$-lactone. The hydroxyl group at C(8) is $\beta$-oriented.

The ten-membered ring adopts a distorted chair-boat conformation. The lactone ring has a conformation intermediate between 7$\alpha$,6$\beta$-half-chair and 7$\alpha$-envelope.

* Lists of structure factors, anisotropic thermal parameters and hydrogen-atom coordinates have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38652 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
The sum of the five endocyclic torsion-angle moduli is 91.9° and the asymmetry parameters (Daux & Norton, 1975) are $\Delta C^2 = 5.2$, $\Delta C^3 = 6.6$, $\Delta C^5 = 13.7^\circ$.

A comparison of the torsion angles observed in alloschkuhriolide with the values found in schkuhriolide is shown in Table 3. Both cyclodecadiene and lactone rings exhibit almost the same type of deformation and the two molecules are very much alike. Some differences in the molecular conformation appear at the ring fusion; in order to accommodate a cis-fused lactone, the junction torsion angles in both rings should have nearly identical values and should ideally lie in the vicinity of 20°, corresponding to the torsion angle in the minimum-energy conformation of an isolated $\alpha$-glycololactone (Guy, Sim & White, 1976). This would, however, introduce a significant amount of distortion in the ten-membered macrocycle. In schkuhriolide, a compromise is achieved in that the required flattening of the ten-membered ring is minimized by the simultaneous puckering of the $\gamma$-lactone. The necessary flattening of the cyclodecadiene ring is accomplished by closing of the junction torsion angle $[-38.2 (5)^\circ]$ and by the valence-angle deformation $[C(7)\cdots C(8)\cdots C(9) 124.8 (4)^\circ]$. trans annelation of the lactone ring in alloschkuhriolide affects the ten-membered-ring conformation to a much lesser extent. The cyclodecadiene conformation is more closely related to those of other melampolides (Watkins, Fisher & Bernal, 1973; Kartha, Go & Joshi, 1972), and the lactone ring adopts a conformation more closely resembling the minimum-energy form (Guy, Sim & White, 1976). It may thus be concluded that the formation of alloschkuhriolide via the lactone rearrangement in its parent lactone, schkuhriolide, results in a certain relief of strain in the molecule without affecting the general topology of the macrocyclic skeleton.

In spite of the conformational similarities of the two molecules, their crystal packing arrangements are somewhat different. In alloschkuhriolide (Fig. 2) the hydroxyl substituent at C(8) forms an intermolecular hydrogen bond with the aldehyde oxygen atom O(3) at $x-\frac{1}{2}$, $-y+\frac{1}{2}$, $-z$. The O(4)…O(3) and H(O4)…O(3) distances are 2.973 (4) and 2.55 (5) Å, respectively, and the O(4)–H(O4)…O(3) angle is 140 (3)^°. The atom H(O4) lies 0.91 (5) Å from O(4). These interactions link the molecules into helices with the long axis parallel to the crystallographic a axis. In schkuhriolide, the water of hydration participates in hydrogen bonds running along the a axis and the hydrogen-bonding network is more extensive.

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