Crystal Structures and Conformations of Shiromodiol† 8-*O*-Angelate and of the Corresponding 6-Ketone‡

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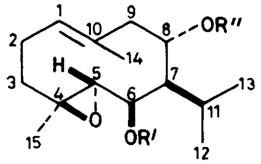
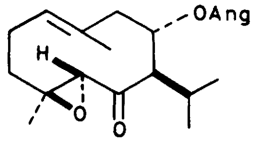
The *X*-ray crystal structures of shiromodiol 8-*O*-angelate (**3**) and of the corresponding 6-ketone (**4**) were determined by direct methods from 1 164 and 1 005 independent reflections respectively and refined to *R* 0.052 and 0.049. Both compounds are orthorhombic, space group $P2_12_12_1$. The results show that oxidation of the chair-boat germacrane alcohol (**3**) to the ketone (**4**) is accompanied by a conformational inversion of the molecular fragment C(5) ⋯ C(10), since compound (**4**) exists in the solid state as a double-chair rotamer with the methyls *syn*-oriented on the α-face of the molecule and the isopropyl side-chain β axial. This represents a previously unobserved conformational geometry for germacrane derivatives and it is present also in solution. The flipping from the chair-boat to the chair-chair conformation removes a transannular interaction between the protons β-H(5) and β-H(8) as well as the Pitzer strain and a non-bonded interaction between the oxo group and the isopropyl side-chain. All this overrides the effect of steric congestion, in the chair-chair conformation of (**4**), between the methyl group at C(10) and the oxygen atom at C(8), the separation of which is *ca*. 0.4 Å less than the sum of the van der Waals radii.

Investigation of the ripe fruits of *Laserpitium halleri* Crantz led to the isolation of a series of sesquiterpene alcohol esters, the more abundant of which have structures based on the germacrane shiromodiol (**1**) nucleus.[1] A spectroscopic study of the natural compounds (**2**) and (**3**), and of some derivatives, showed that their conformation is strongly affected by modifications of the oxygenated functions at C(6) and C(8). In particular, the alcohol (**3**) exists in solution mostly as an intramolecularly hydrogen-bonded chair-boat rotamer, with the methyl groups at C(4) and C(10) on the α-face of the molecule and with the isopropyl side-chain at C(7) in a β-equatorial orientation;[1] the corresponding 6-ketone (**4**) adopts a different conformation, which, according to spectral data and to the outcome of chemical reactions, can be formulated as a double-chair type with the methyl groups on the α-face and the isopropyl side-chain in a β-axial orientation.[1] This represents a previously unencountered conformational geometry for germacrane derivatives. In order to clarify the conformational details of (**4**), the present *X*-ray investigation was undertaken. An *X*-ray study of a diester of shiromodiol (6-*p*-bromobenzoate 8-acetate) has already been reported, albeit in abstract form only. [2,3] We have therefore also studied the structure of the monoester (**3**), both for reference and for establishing the influence of the intramolecular hydrogen bond on the conformation of the flexible ten-membered ring.



	R′	R″
(**1**)	H	H
(**2**)	Ac	Ang
(**3**)	H	Ang



(**4**)

Ang = angeloyl [(*Z*)-2-methylbut-2-enoyl]

Results and Discussion

Figures 1 and 2 are ORTEP II drawings[4] of views chosen to display the relevant conformational features of compounds (**3**) and (**4**), and represent their absolute configurations.[1] Bond lengths and valence angles are listed in Tables 3 and 4 and the relevant torsion angles in Table 5.

In both compounds the endocyclic bond lengths are generally shorter, and the bond angles larger, than the normal values, as customary for germacrane derivatives with endocyclic *trans*-double bonds or *trans*-epoxy groups.[3-5] The means of the $C(sp^3)$–$C(sp^3)$ bond lengths, taken over the endocyclic bonds except C(4)–C(5), belonging to the oxirane ring, are 1.531(2) and 1.528(3) Å for (**3**) and (**4**) respectively. The largest angular deviations from the ideal $C(sp^3)$ geometry occur, as expected, at the epoxide function;[3] the other endocyclic C–$C(sp^3)$–C angles range from 109 to 120° (Tables 3 and 4), the mean values being 112.3(2) and 115.3(3)° for (**3**) and (**4**), respectively. The former value is identical with that of tanacetols,[6] which also adopt the chair-boat conformation of (**3**). Both bond-length

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† Shiromodiol is (4*S*,5*S*,6*R*,7*R*,8*S*)(*E*)-4,5-epoxygermacr-1(10)-ene-6,8-diol

‡ *Supplementary data available* (SUP 56388, 8 pp.): H-atom co-ordinates and anisotropic temperature factors for compounds (3) and (4). For details of Supplementary Publications see Instructions for Authors, *J. Chem. Soc., Perkin Trans. 2*, Issue no. 1, 1986. Structure factor tables are available on request from the editorial office.

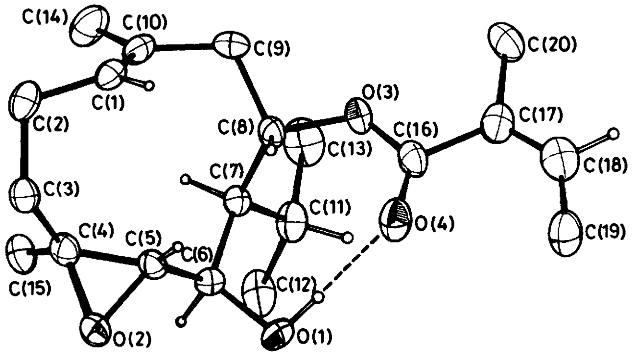

Figure 1. ORTEP II drawing of one molecule of derivative (**3**) with the thermal ellipsoids of non-hydrogen atoms at the 20% probability level.

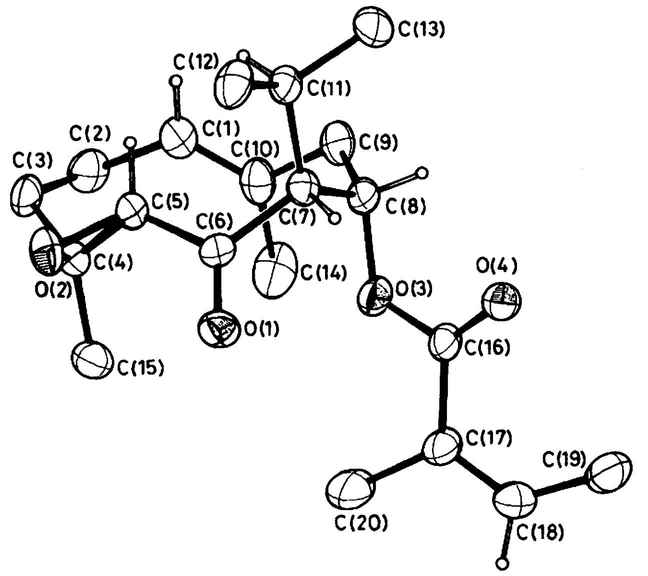

Figure 2. ORTEP II drawing of one molecule of derivative (**4**) with the thermal ellipsoids of non-hydrogen atoms at the 20% probability level.

Table 1. Atomic co-ordinates (× 10^4) and temperature factors (Å^2 × 10^3) of compound (**3**)

Atom	*x*	*y*	*z*	*U**
O(1)	2 625(4)	1 548(3)	8 717(2)	73(1)
O(2)	2 970(4)	2 970(2)	10 259(2)	69(1)
O(3)	−125(3)	−522(2)	9 039(2)	64(1)
O(4)	−37(4)	852(3)	8 214(2)	83(1)
C(1)	−13(5)	1 130(4)	11 309(3)	61(2)
C(2)	611(6)	1 879(4)	11 917(3)	75(2)
C(3)	1 470(5)	2 734(3)	11 477(3)	63(2)
C(4)	2 542(5)	2 272(3)	10 905(3)	58(2)
C(5)	2 099(5)	2 058(3)	10 078(2)	51(1)
C(6)	2 714(5)	1 219(3)	9 544(3)	55(2)
C(7)	2 119(4)	109(3)	9 705(2)	51(2)
C(8)	468(5)	85(3)	9 695(3)	53(2)
C(9)	−187(6)	−420(4)	10 447(3)	72(2)
C(10)	282(5)	126(4)	11 209(2)	64(2)
C(11)	2 836(6)	−738(4)	9 174(3)	70(2)
C(12)	4 427(5)	−645(5)	9 150(4)	92(2)
C(13)	2 420(7)	−1 858(4)	9 459(4)	100(2)
C(14)	1 124(8)	−556(5)	11 781(3)	102(3)
C(15)	3 732(5)	1 677(4)	11 296(3)	74(2)
C(16)	−410(5)	−38(5)	8 361(3)	65(2)
C(17)	−1 227(5)	−746(5)	7 804(3)	76(2)
C(20)	−1 645(7)	−1 863(4)	8 137(4)	96(2)
C(18)	−1 552(6)	−436(5)	7 103(4)	94(2)
C(19)	−1 266(7)	547(5)	6 687(3)	101(3)

* Equivalent isotropic *U* defined as one third of the trace of the orthogonalised U_{ij} tensor.

Table 2. Atomic co-ordinates (× 10^4) and temperature factors (Å^2 × 10^3) of compound (**4**)

Atom	*x*	*y*	*z*	*U**
O(1)	2 190(3)	10 398(3)	7 688(3)	81(2)
O(2)	3 032(4)	12 100(2)	6 759(3)	82(2)
O(3)	3 291(4)	8 483(2)	6 994(2)	72(1)
O(4)	3 236(4)	7 491(3)	8 234(3)	87(2)
C(1)	5 369(6)	10 324(5)	5 343(4)	73(2)
C(2)	4 839(6)	11 039(5)	4 644(4)	86(3)
C(3)	4 174(6)	11 872(4)	5 194(4)	74(2)
C(4)	3 236(5)	11 510(4)	5 930(4)	63(2)
C(5)	3 816(5)	11 253(4)	6 859(4)	58(2)
C(6)	3 329(5)	10 459(3)	7 490(3)	56(2)
C(7)	4 328(5)	9 745(4)	7 892(3)	57(2)
C(8)	4 563(5)	8 853(4)	7 273(4)	59(2)
C(9)	5 452(6)	8 919(4)	6 391(4)	73(2)
C(10)	4 936(6)	9 457(4)	5 540(4)	71(2)
C(11)	5 581(5)	10 216(4)	8 280(4)	63(2)
C(12)	5 238(8)	11 024(4)	8 972(4)	95(3)
C(13)	6 479(7)	9 505(2)	8 777(5)	93(3)
C(14)	3 928(9)	8 929(5)	4 942(4)	112(3)
C(15)	2 010(6)	11 039(5)	5 558(4)	84(3)
C(16)	2 703(6)	7 837(4)	7 564(4)	63(2)
C(17)	1 332(6)	7 618(4)	7 263(4)	80(2)
C(20)	640(8)	8 384(7)	6 706(8)	165(5)
C(18)	738(5)	6 831(5)	7 524(5)	89(2)
C(19)	1 225(7)	6 013(5)	8 079(6)	112(3)

* Equivalent isotropic *U* defined as one third of the trace of the orthogonalised U_{ij} tensor.

shortening and bond-angle widening are more marked in (**4**) than in (**3**); also, the C(1) ••• C(5) transannular separation is shorter in (**4**) than in (**3**) (Table 6). The sequence of torsion angles around the ten-membered ring (Table 5) shows that this ring adopts a chair-boat conformation in (**3**) and a chair-chair conformation in (**4**). The torsion angles around C(1)=C(10) are notably different from 180°, as usual with this kind of derivative.[3]

A fairly strong intramolecular hydrogen bond occurs in the alcohol (**3**), with the ester carbonyl oxygen as acceptor (Figure 1): O(1)–H is 0.95(2), O(1) ••• O(4) 2.796(3), and O(4) ••• H 1.85(3) Å, and O(1)–H ••• O(4) is 177(3)°. This linear hydrogen bond leads to the formation of an eight-membered ring instead of the more common six-membered ring. The endocyclic torsion angles (Table 5) of the monoester (**3**) are close to those of the previously reported diester;[2,3] hence, in spite of the conformational mobility of these compounds in solution,[1] the intramolecular hydrogen bond affects the chair-boat geometry to a very small extent only.

The oxirane moiety is symmetric in both molecules and shows bond and angle values (Tables 3—5) typical of this ring.[3,7] In compound (**4**) the oxirane ring is almost orthogonal to the plane through the C(5)–C(6)–C(7)–O(1) carbonyl group, the torsion angle being 76°. This geometry allows a maximum overlapping of the bent orbitals of the ring with the π-carbonyl orbitals.[8] Oxirane rings conjugated to oxo groups are known[8] to make contributions to the Cotton effect opposite to those of alkyl groups; in compound (**4**), however, the three-membered ring is likely to make only a small contribution to the Cotton effect since it is distributed almost symmetrically between the back left-hand upper and lower quadrants. The

Table 3. Bond lengths (Å) and bond angles (°) of compound (3)

O(1)–C(6)	1.444(5)	O(2)–C(4)	1.452(5)
O(2)–C(5)	1.452(5)	O(3)–C(8)	1.450(5)
O(3)–C(16)	1.316(6)	O(4)–C(16)	1.207(7)
C(1)–C(2)	1.508(7)	C(1)–C(10)	1.314(7)
C(2)–C(3)	1.540(7)	C(3)–C(4)	1.510(6)
C(4)–C(5)	1.468(6)	C(4)–C(15)	1.503(7)
C(5)–C(6)	1.504(6)	C(6)–C(7)	1.538(6)
C(7)–C(8)	1.563(6)	C(7)–C(11)	1.548(6)
C(8)–C(9)	1.538(7)	C(9)–C(10)	1.513(7)
C(10)–C(14)	1.514(8)	C(11)–C(12)	1.511(7)
C(11)–C(13)	1.548(7)	C(16)–C(17)	1.504(8)
C(17)–C(20)	1.571(8)	C(17)–C(18)	1.271(8)
C(18)–C(19)	1.450(8)		

C(4)–O(2)–C(5)	60.7(3)	C(8)–O(3)–C(16)	118.8(4)
C(2)–C(1)–C(10)	127.7(4)	C(1)–C(2)–C(3)	109.2(4)
C(2)–C(3)–C(4)	112.5(4)	O(2)–C(4)–C(3)	114.8(3)
O(2)–C(4)–C(5)	59.6(3)	C(3)–C(4)–C(5)	118.2(4)
O(2)–C(4)–C(15)	114.7(4)	C(3)–C(4)–C(15)	115.1(4)
C(5)–C(4)–C(15)	121.9(4)	O(2)–C(5)–C(4)	59.6(3)
O(2)–C(5)–C(6)	117.8(4)	C(4)–C(5)–C(6)	125.2(4)
O(1)–C(6)–C(5)	109.8(3)	O(1)–C(6)–C(7)	114.1(3)
C(5)–C(6)–C(7)	113.6(3)	C(6)–C(7)–C(8)	112.5(3)
C(6)–C(7)–C(11)	111.9(3)	C(8)–C(7)–C(11)	114.8(4)
O(3)–C(8)–C(7)	113.9(3)	O(3)–C(8)–C(9)	103.8(3)
C(7)–C(8)–C(9)	113.8(4)	C(8)–C(9)–C(10)	112.1(4)
C(1)–C(10)–C(9)	119.2(4)	C(1)–C(10)–C(14)	125.7(4)
C(9)–C(10)–C(14)	115.0(4)	C(7)–C(11)–C(12)	113.4(4)
C(7)–C(11)–C(13)	110.4(4)	C(12)–C(11)–C(13)	109.4(5)
O(3)–C(16)–O(4)	123.3(5)	O(3)–C(16)–C(17)	111.1(5)
O(4)–C(16)–C(17)	125.6(5)	C(16)–C(17)–C(20)	116.6(4)
C(16)–C(17)–C(18)	120.5(5)	C(20)–C(17)–C(18)	122.8(5)
C(17)–C(18)–C(19)	131.3(6)		

Table 4. Bond lengths (Å) and bond angles (°) of compound (4)

O(1)–C(6)	1.200(6)	O(2)–C(4)	1.443(7)
O(2)–C(5)	1.438(7)	O(3)–C(8)	1.453(6)
O(3)–C(16)	1.349(7)	O(4)–C(16)	1.189(7)
C(1)–C(2)	1.502(9)	C(1)–C(10)	1.321(9)
C(2)–C(3)	1.554(9)	C(3)–C(4)	1.497(8)
C(4)–C(5)	1.477(8)	C(4)–C(15)	1.509(8)
C(5)–C(6)	1.506(7)	C(6)–C(7)	1.536(7)
C(7)–C(8)	1.540(7)	C(7)–C(11)	1.540(7)
C(8)–C(9)	1.538(8)	C(9)–C(10)	1.508(8)
C(10)–C(14)	1.520(10)	C(11)–C(12)	1.532(8)
C(11)–C(13)	1.523(9)	C(16)–C(17)	1.495(9)
C(17)–C(20)	1.504(11)	C(17)–C(18)	1.311(9)
C(18)–C(19)	1.471(10)		

C(4)–O(2)–C(5)	61.7(3)	C(8)–O(3)–C(16)	118.5(4)
C(2)–C(1)–C(10)	128.9(6)	C(1)–C(2)–C(3)	109.5(5)
C(2)–C(3)–C(4)	111.7(5)	O(2)–C(4)–C(3)	117.1(4)
O(2)–C(4)–C(5)	59.0(3)	C(3)–C(4)–C(5)	115.7(5)
O(2)–C(4)–C(15)	114.1(5)	C(3)–C(4)–C(15)	116.2(5)
C(5)–C(4)–C(15)	122.1(5)	O(2)–C(5)–C(4)	59.3(3)
O(2)–C(5)–C(6)	118.8(5)	C(4)–C(5)–C(6)	124.5(5)
O(1)–C(6)–C(5)	120.7(5)	O(1)–C(6)–C(7)	120.8(4)
C(5)–C(6)–C(7)	118.5(4)	C(6)–C(7)–C(8)	115.1(4)
C(6)–C(7)–C(11)	113.8(4)	C(8)–C(7)–C(11)	114.6(4)
O(3)–C(8)–C(7)	107.5(4)	O(3)–C(8)–C(9)	109.4(4)
C(7)–C(8)–C(9)	119.8(4)	C(8)–C(9)–C(10)	117.5(5)
C(1)–C(10)–C(9)	120.6(5)	C(1)–C(10)–C(14)	123.9(5)
C(9)–C(10)–C(14)	115.5(5)	C(7)–C(11)–C(12)	110.4(5)
C(7)–C(11)–C(13)	112.5(5)	C(12)–C(11)–C(13)	109.2(5)
O(3)–C(16)–O(4)	122.5(5)	O(3)–C(16)–C(17)	112.8(5)
O(4)–C(16)–C(17)	124.7(5)	C(16)–C(17)–C(20)	116.2(6)
C(16)–C(17)–C(18)	121.9(5)	C(20)–C(17)–C(18)	121.8(6)
C(17)–C(18)–C(19)	130.2(6)		

Table 5. Relevant endocyclic and exocyclic torsion angles (°); e.s.d.s 0.2—0.4°

	(3)	(4)
C(1)–C(2)–C(3)–C(4)	−52.6	−49.6
C(2)–C(3)–C(4)–C(5)	89.0	84.5
C(3)–C(4)–C(5)–C(6)	−151.9	−146.8
C(4)–C(5)–C(6)–C(7)	80.7	131.5
C(5)–C(6)–C(7)–C(8)	52.0	−90.9
C(6)–C(7)–C(8)–C(9)	−127.6	78.7
C(7)–C(8)–C(9)–C(10)	57.0	−71.6
C(8)–C(9)–C(10)–C(1)	60.7	104.2
C(9)–C(10)–C(1)–C(2)	−163.5	−168.7
C(10)–C(1)–C(2)–C(3)	114.3	108.1
C(7)–C(8)–O(3)–C(16)	−90.7	−89.7
C(8)–O(3)–C(16)–C(17)	−170.8	172.3
C(8)–O(3)–C(16)–O(4)	10.1	−7.6
C(9)–C(8)–O(3)–C(16)	145.1	138.7
O(3)–C(16)–C(17)–C(18)	−177.0	159.1
O(4)–C(16)–C(17)–C(18)	2.1	−21.1

strong Cotton effect at 310 nm observed[1] in the c.d. spectrum of (**4**) is probably the result of negative contributions from the isopropyl side-chain and from the C(4) ··· C(2) fragment, lying in the negative back octants, as well as from the angelate function, lying in one negative front octant.

In both structures the packing is determined by van der Waals forces only, as revealed by the low density values (*cf.* Experimental section). Models show that the chair-boat conformation of germacradienes presents an intramolecular non-bonded interaction between the 'flagpole' β-H(5) and β-H(8). The experimental results of Table 6 reveal that the H(5) ··· H(8) distance is shorter than the sum of the van der Waals radii[9,10] in all compounds of this type that we have studied so far. The shortening of the H(5) ··· H(8) separation seems to be approximately correlated with a narrowing of the endocyclic torsion angle around C(6)–C(7) (Table 6). Even though this contact is not particularly accentuated in (**3**), models show that the change in hybridization of C(6), when passing from (**3**) to (**4**), would cause β-H(5) and β-H(8) to come closer if the conformation of the C(5) ··· C(10) molecular fragment were to be maintained in the course of the oxidative reaction. The flipping of this fragment from the boat to the chair conformation relieves the molecule of this interaction and of the torsional strain intrinsically present in a chair-boat conformation. Furthermore, in the latter conformation a strain arises due to a non-bonded interaction between the carbonyl group and the equatorial isopropyl side-chain. In the chair-chair conformation the strain associated with all these factors is removed; steric congestion between the 1,3-diaxially oriented methyl group at C(10) and the oxygen at C(8) is however present, with a transannular separation O(3) ··· C(14) of only 3.018(7) Å, *ca.* 0.4 Å shorter than the sum of standard van der Waals radii.[9,10]* Short intramolecular distances between hydrogen atoms and proton acceptors have been assumed to imply hydrogen bonding;[11] however, they occur mainly in heterocycles and involve C–H groups 'activated' by bonding to

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[*] Conjugation with the carbonyl group should make the shape of O(3) anisotropic, with a shorter radius in the direction of the C(16)–O(3) bond and a longer radius in the orthogonal direction. In the case of the carbonyl oxygen atoms, for instance, these values are *ca.* 1.40 and 1.60—1.70 Å respectively.[10] Since C(14) (Figure 2) is not aligned with the C(16)–O(3) bond, the transannular interaction between O(3) and C(14) is probably even stronger than that inferrable from standard van der Waals radii.

Table 6. Distances (Å) and angles (°) regarding relevant transannular separations in some germacrane derivatives; e.s.d.s in parentheses

	(3)[a]	(4)[a]	Methyl-hallerin[b]	Tanacetol B acetate[c]	Spiciformin[b] acetate
β-H(5) ··· β-H(8)	2.30(1)	>3.3	2.13(1)	2.28(3)	2.23(2)
C(5)–C(6)–C(7)–C(8)	52.0(5)	−90.9(5)	25.7(3)	64.3(4)	59.5(4)
C(1) ··· C(5)	3.096(7)	2.954(8)	2.993(5)	3.158(5)	3.150(2)

[a] Present work. [b] Results to be published. [c] Ref. 6.

an electronegative heteroatom or to a conjugated double-bond system containing a heteroatom. (For a critical review of this subject see refs. 12 and 13.) In compound (**4**), C(14) is only allylic and, besides, the proton-acceptor character of O(3) is decreased by *p*–π conjugation with the ester carbonyl group. Hence it is unlikely that the short O(3) ··· C(14) distance implies the formation of a hydrogen bond, thus becoming a stabilizing factor for the double-chair conformation of (**4**). It is more likely instead that the release from Pitzer strain, from the strain due to the transannular β-H(5) ··· β-H(8) interaction, and from that due to a non-bonded interaction of the carbonyl group with the isopropyl side-chain, override the effect of the O(3) ··· C(14) interaction. In fact in solution too compound (**4**) exists only as a chair-chair rotamer, as evidenced by spectroscopic and chemical investigations.[1] No other interaction occurs between the axially oriented angelate function and the isopropyl chain which, as expected,[14] has the methyl groups oriented away from the ring (Figure 2). The axial orientation implies a higher molecular energy, but it is known, at least for compounds of the cyclohexane series, that the presence of an oxo group reduces the energy difference between the axial and the equatorial orientation of certain substituents (2-and 3-alkyl ketone effect[15]). In particular, for an isopropyl group α to an oxo group, the conformational energy drops from over 2 kcal mol^{-1} to 0.4—0.5 kcal mol^{-1}.

The angelate function is planar in derivative (**3**); r.m.s. deviation 0.0249 Å for the mean plane through the molecular fragment from O(3) to C(20) (Figure 1), which makes an angle of 51° with the mean plane through the ten-membered ring. In the oxo derivative (**4**) the absence of hydrogen bonding complies with a more marked thermal motion (Table 2) and with a larger deviation from planarity (r.m.s. deviation 0.209 Å) of the angelate group which is here almost orthogonal to the mean plane through the ten-membered ring (78°). The conformation is of the *s-cis* type in both derivatives (Table 5) as usual for angelate esters of sesquiterpene lactones, according to the results available in the literature. There are marked differences between some corresponding bonds of the two angelate functions (Tables 3 and 4) which are not simply attributable to the presence of the intramolecular hydrogen bond in (**3**) or to differences in the thermal motion. From the numerous results available in the literature (*e.g.* refs. 15 and 16), this moiety seemingly shows a fairly large range of bonds and angles difficult to rationalize.

Experimental

Crystals were prepared as described in ref. 1 and recrystallized from acetone in the case of (**3**) and from hexane–diethyl ether (1 : 1) in the case of (**4**).

Crystal Data.—Shiromodiol 8-angelate (**3**), $C_{20}H_{32}O_4$, m.p. 113—114 °C, $[\alpha]_D^{25}$ −57.1° ($CHCl_3$; *c* 1.00 g dm^{-3}), orthorhombic, $a = 9.465(2)$, $b = 12.668(5)$, $c = 16.679(4)$ Å (obtained and refined from 25 diffractometer reflections, $21° \leqslant 2\theta \leqslant 32°$, $\lambda = 0.710\,69$ Å), space group $P2_12_12_1$, $V = 2000(1)$ Å^3, $Z = 4$, $D_x = 1.12$ Mg m^{-3}, $F(000) = 736$. Colourless prismatic crystals; crystal dimensions 0.25 × 0.35 × 0.65 mm, μ(Mo-K_α) = 0.08 mm^{-1}.

6-Deoxy-6-oxoshiromodiol 8-angelate (**4**), $C_{20}H_{30}O_4$, m.p. 109—110 °C, $[\alpha]_D^{25}$ 15.6° ($CHCl_3$; *c* 2.2 g dm^{-3}), orthorhombic, $a = 10.220(4)$, $b = 13.996(7)$, $c = 14.034(6)$ Å (obtained and refined from 21 diffractometer reflections, $18° \leqslant 2\theta \leqslant 24°$, $\lambda = 0.710\,69$ Å), space group $P2_12_12_1$, $V = 2007(1)$ Å^3, $Z = 4$, $D_x = 1.11$ Mg m^{-3}, $F(000) = 728$. Colourless prismatic crystals; crystal dimensions: 0.20 × 0.45 × 0.65 mm, μ(Mo-K_α) = 0.08 mm^{-1}

Data Collection and Processing.[17]—Nicolet R3 four-circle diffractometer, graphite-monochromated Mo-K_α radiation, room temperature, ω-scan at variable speed, scan range 1.2°, backgrounds measured in stationary mode for 0.8 times the peak scan time. Periodic remeasurement of standard reflections did not show significant intensity variations for both crystals.

Compound (**3**). Scan speed from 1° min^{-1} for the weakest to 10° min^{-1} for the strongest reflection; 1 475 independent reflections measured within $2\theta = 45°$; 1 167 with $I \geqslant 2\sigma(I)$ were considered as observed (*h*: 0,9; *k*: 0,13; *l*: 0,17). Three low-angle reflections, exceeding 60 000 counts s^{-1} at pre-scan,[17] were measured with the insertion of a copper attenuator, but had to be discarded in the course of the refinement because they were probably affected by the secondary extinction effect. Absorption correction was based on the ψ-scan method[18] using four high-χ reflections: the transmission coefficients ranged between 1.02 and 1.33.

Compound (**4**). Scan speed from 1.3 to 15° min^{-1}; 1 517 independent reflections measured within $2\theta = 45°$; 1 006 with $I \geqslant 2\sigma(I)$ were considered as observed (*h*: 0,10; *k*: 0,15; *l*: 0,15). Absorption correction was based on the ψ-scan method[18] using three high-χ reflections: transmission coefficients varied from 1.01 to 1.13.

Structure Solution and Refinement.—Programs and scattering factors (for neutral atoms) used are illustrated in ref. 19. The solution of both structures was attained by the program RANTAN, assigning random phases to the 247 $|E|$ values $\geqslant 1.65$ (2 852 triple-phase relationships and 226 negative quartets) in the case of (**3**) and 244 $|E|$ values $\geqslant 1.55$ (3 592 triple-phase relationships and 409 negative quartets) in the case of (**4**). The *E*-maps from the solutions with the best figures of merit allowed us to locate most of the non-hydrogen atoms; the missing atoms were found by subsequent least-squares and difference Fourier cycles. The refinement, by standard least-squares procedure, was based on F_0 values. All H atoms were located on difference Fourier maps in the course of the anisotropic refinement; however, for both molecules, the methyl H atoms (Figures 1 and 2) were placed in calculated positions and treated as rigid groups. The remaining H atoms were isotropically refined under the constraints C–H, O–H: 0.96 ± 0.02 Å. Two thermal parameters were refined for the H atoms, one assigned to the methyl hydrogen atoms and the other to the remaining hydrogen atoms; these parameters converged to 0.134(5) and

0.065(4) Å^2, respectively, in the case of (3) and to 0.136(6) and 0.067(4) Å^2 in the case of (4). Weighting scheme: $w = [\sigma^2(F_0) + GF_0^2]^{-1}$, where σ is the standard deviation of F_0 based on counting statistics and G is a variable to be refined. At convergence (mean shift over error $\leqslant$ 0.05) the agreement parameters were:

(3) $R = 0.052$, $wR = 0.055$, goodness of fit = 1.392 for 1 164 reflections and 279 least-squares parameters ($G = 0.001\ 35$; highest residual peaks in the final difference Fourier map $\leqslant$ 0.19 e Å^{-3}).

(4) $R = 0.049$, $wR = 0.052$, goodness of fit = 1.215 for 1 006 reflections and 273 least-squares parameters ($G = 0.001\ 14$; highest residual peaks in the final difference Fourier map $\leqslant$ 0.16 e Å^{-3}).

Tables 1 and 2 list the final parameters of compounds (3) and (4) respectively with reference to the numbering scheme of Figures 1 and 2.[4]

The overall thermal motion was higher in (4) than in (3), particularly as regards the angelate moiety (Tables 1 and 2); in-phase libration corrections,[19] however, did not yield bond lengthening greater than twice the standard deviations and therefore in Tables 3 and 4 we give the uncorrected values of bonds and angles.

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