Structure and Conformation of 5-Deoxy-5-hydroperoxy-5-epitelekin [†] and 5-Epitelekin [‡]

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The crystal and molecular structures of 5-deoxy-5-hydroperoxy-5-epitelekin (1) and 5-epitelekin (2) were determined by direct methods from 1 160 and 1 188 independent reflections, respectively, and refined to R 0.043 and 0.066. Both crystals are orthorhombic, space group $P2_12_12_1$. In both compounds the *cis*-decalin system shows a chair–chair conformation, of steroid-like type in (1) and of non-steroid type in (2), with the substituents at C(5) and C(10) in a β-orientation. A justification of the conformational preferences shown by the two derivatives is proposed. The γ-lactone ring, *cis*-fused at C(8), is puckered in both molecules, being of the *A*-type in (1) and of the *S*-type in (2).

cis-Decalin is a mobile system capable of adopting two double-chair conformations, traditionally referred to as steroid-like, *A*, and non-steroid, *B* (Figure 1).[1] In the field of sesquiterpenes, most of the conformational studies extant on *cis*-decalin derivatives refer to eremophillanes [2] or unlactonized eudesmanes.[3] Recently, however, *cis*-decalin derivatives of the C(8) *cis*-eudesmanolide class have been obtained in the course of studies of the constituents of *Artemisia umbelliformis* Lam. and their conformation has been established in solution by spectroscopic techniques (^{1}H n.m.r. and c.d.).[4] Whilst some eremophillanes studied by the same techniques were found to exist in solution at room temperature as mixtures of fast interconverting rotamers,[2] the present *cis*-decalin eudesmanolides instead showed a conformational equilibrium frozen in solution at room temperature, their conformation depending on the substituent at C(5).[4] This spectroscopic investigation showed that, in solution, 5-deoxy-5-hydroperoxy-5-epitelekin (1) adopts a steroid-like conformation and that its corresponding alcohol (2) adopts a non-steroid conformation instead. However, some anomalous values of the coupling constants in the ^{1}H n.m.r. spectrum of (2) made it difficult to establish the conformation of the fragment C(6)–C(7)–C(8)–C(9) for this compound; on the basis of the c.d. curve as well, this fragment seemed to approach planarity, most probably in order to accomodate the *cis*-fused lactone ring.[5]

Owing to the lack of precise knowledge of the geometry of (2), no attempt was made at justifying the conformational preferences shown by these products.[4] The *X*-ray analysis of (1) and (2) was therefore undertaken in order to obtain more details of their molecular geometry.

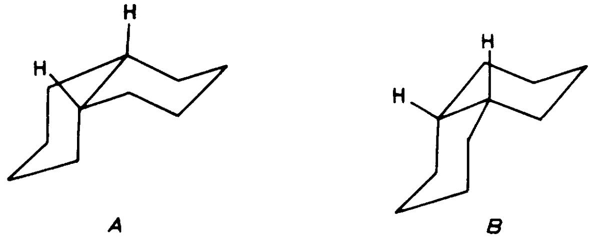
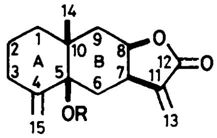


Figure 1. Representation of the steroid-like, *A*, and non-steroid, *B*, conformations of the *cis*-decalin system



(1) R = OH
(2) R = H

Results and Discussion

Tables 1 and 2 show the atomic parameters of the non-hydrogen atoms and Tables 3 and 4 list the bond distances and angles of molecules (1) and (2), respectively, illustrated in Figures 2 and 3.[6] On the basis of previous results,[4] these illustrations most probably represent the absolute configurations of the molecules. The conformation of both rings A and B is of the chair type in both molecules, with the substituents at C(5) and C(10) in the β-orientation, as revealed by the relative positions of C(3) and C(10) and of C(6) and C(9) with respect to the mean planes through the remaining atoms of rings A and B. These mean planes make, between each other, angles of 123.3(2) and 119.0(4)° in molecules (1) and (2), respectively, *i.e.* close to the value of 120° to be expected for an ideal *cis*-decalin system.

The mean C_{sp^3}–C_{sp^3} value over the bonds of rings A and B is 1.53 Å for both compounds, slightly shorter than expected. However, bonds C(1)–C(2) and C(2)–C(3) (Tables 3 and 4) are much shorter than expected; this trend was also noted in one related *trans*-decalin isomer,[7] in the eudesmanolide erivanin,[8] and in the eremophillane tetradymol.[9] The mean C–C_{sp^3}–C value is 113° in both the present molecules. The largest differences between (1) and (2), as regards both bond lengths and angles, occur at C(5) and C(7). It is difficult to envisage a reason for the general shortening of the above bonds, and for the differences between bond and angles of

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[†] (3a*R*,4a*S*,8a*R*,9a*R*)-Decahydro-4a-hydroperoxy-8a-methyl-3,5-dimethylenenaphtho[2,3-*b*]furan-2(3*H*)-one.

[‡] (3a*R*,4a*S*,8a*R*,9a*R*)-Decahydro-4a-hydroxy-8a-methyl-3,5-dimethylenenaphtho[2,3-*b*]furan-2(3*H*)-one.

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

Atom	*x*	*y*	*z*	*U* *
C(1)	5 632(5)	−1 091(3)	3 324(3)	57(1)
C(2)	5 342(5)	−160(4)	2 619(2)	60(1)
C(3)	6 483(5)	792(3)	2 831(2)	52(1)
C(4)	6 319(4)	1 170(3)	3 851(2)	41(1)
C(5)	6 591(4)	270(2)	4 605(2)	33(1)
C(6)	6 354(4)	651(2)	5 643(2)	37(1)
C(7)	4 586(4)	879(2)	5 954(2)	39(1)
C(8)	3 390(4)	4(3)	5 605(2)	42(1)
C(9)	3 732(4)	−479(3)	4 628(2)	41(1)
C(10)	5 515(4)	−765(3)	4 396(2)	39(1)
C(11)	4 441(4)	748(3)	7 026(2)	39(1)
C(12)	3 951(4)	−428(2)	7 186(2)	39(1)
C(13)	4 689(5)	1 447(3)	7 723(3)	53(1)
C(14)	6 080(5)	−1 776(3)	4 978(3)	57(1)
C(15)	5 988(6)	2 202(3)	4 071(3)	66(1)
O(1)	3 456(3)	−872(2)	6 352(1)	44(1)
O(2)	3 964(3)	−960(2)	7 915(2)	49(1)
O(3)	8 238(3)	−154(2)	4 495(2)	44(1)
O(4)	9 413(3)	736(2)	4 680(2)	58(1)

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

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

Atom	*x*	*y*	*z*	*U* *
O(1)	4 632(3)	9 339(3)	10 550(2)	70(1)
O(2)	2 547(4)	10 149(4)	10 744(3)	86(1)
O(3)	4 954(3)	9 816(2)	6 966(2)	56(1)
C(1)	7 892(5)	8 151(5)	8 220(4)	68(2)
C(2)	8 509(6)	7 633(5)	7 165(4)	80(2)
C(3)	7 378(6)	7 242(4)	6 378(4)	79(2)
C(4)	6 307(5)	8 191(4)	6 176(3)	57(1)
C(5)	5 725(4)	8 773(3)	7 217(3)	46(1)
C(6)	4 771(5)	7 866(3)	7 776(4)	57(1)
C(7)	4 318(5)	8 138(4)	8 953(4)	57(1)
C(8)	5 419(5)	8 726(4)	9 682(3)	62(1)
C(9)	6 265(5)	9 632(4)	9 076(3)	56(1)
C(10)	6 908(4)	9 176(4)	7 982(3)	48(1)
C(11)	3 084(5)	8 910(4)	9 152(4)	58(1)
C(12)	3 331(6)	9 533(5)	10 198(4)	65(2)
C(13)	1 933(5)	9 068(5)	8 560(5)	79(2)
C(14)	7 712(5)	10 194(4)	7 451(4)	62(2)
C(15)	5 889(6)	8 472(5)	5 179(4)	78(2)

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

Table 3. Bond lengths (Å) and angles (°) of compound (1)

C(1)–C(2)	1.514(6)	C(1)–C(10)	1.554(5)
C(2)–C(3)	1.509(6)	C(3)–C(4)	1.504(4)
C(4)–C(5)	1.531(4)	C(4)–C(15)	1.313(5)
C(5)–C(6)	1.535(4)	C(5)–C(10)	1.557(4)
C(5)–O(3)	1.448(4)	C(6)–C(7)	1.532(4)
C(7)–C(8)	1.520(4)	C(7)–C(11)	1.513(4)
C(8)–C(9)	1.512(4)	C(8)–O(1)	1.488(4)
C(9)–C(10)	1.532(4)	C(10)–C(14)	1.539(5)
C(11)–C(12)	1.492(4)	C(11)–C(13)	1.306(5)
C(12)–O(1)	1.347(4)	C(12)–O(2)	1.207(4)
O(3)–O(4)	1.464(3)		
C(2)–C(1)–C(10)	115.5(3)	C(1)–C(2)–C(3)	110.0(3)
C(2)–C(3)–C(4)	111.3(3)	C(3)–C(4)–C(5)	115.1(3)
C(3)–C(4)–C(15)	122.0(3)	C(5)–C(4)–C(15)	122.9(3)
C(4)–C(5)–C(6)	114.9(2)	C(4)–C(5)–C(10)	111.1(2)
C(6)–C(5)–C(10)	110.3(2)	C(4)–C(5)–O(3)	108.2(2)
C(6)–C(5)–O(3)	108.9(2)	C(10)–C(5)–O(3)	102.7(2)
C(5)–C(6)–C(7)	116.2(2)	C(6)–C(7)–C(8)	112.9(2)
C(6)–C(7)–C(11)	109.7(3)	C(8)–C(7)–C(11)	101.3(2)
C(7)–C(8)–C(9)	116.1(3)	C(7)–C(8)–O(1)	104.3(2)
C(9)–C(8)–O(1)	110.7(2)	C(8)–C(9)–C(10)	117.1(3)
C(1)–C(10)–C(5)	110.6(3)	C(1)–C(10)–C(9)	108.7(3)
C(5)–C(10)–C(9)	108.3(2)	C(1)–C(10)–C(14)	107.0(3)
C(5)–C(10)–C(14)	111.7(3)	C(9)–C(10)–C(14)	110.6(3)
C(7)–C(11)–C(12)	105.6(2)	C(7)–C(11)–C(13)	131.3(3)
C(12)–C(11)–C(13)	123.1(3)	C(11)–C(12)–O(1)	109.3(3)
C(11)–C(12)–O(2)	129.1(3)	O(1)–C(12)–O(2)	121.5(3)
C(8)–O(1)–C(12)	109.6(2)	C(5)–O(3)–O(4)	109.2(2)

Table 4. Bond lengths (Å) and angles (°) of compound (2)

O(1)–C(8)	1.474(6)	C(11)–C(13)	1.336(7)
O(2)–C(12)	1.226(7)	O(1)–C(12)	1.347(6)
O(3)–C(5)	1.433(5)	C(1)–C(2)	1.529(7)
C(1)–C(10)	1.531(7)	C(2)–C(3)	1.517(8)
C(3)–C(4)	1.516(7)	C(4)–C(5)	1.531(6)
C(4)–C(15)	1.313(6)	C(5)–C(6)	1.540(6)
C(5)–C(10)	1.542(6)	C(6)–C(7)	1.523(6)
C(7)–C(8)	1.536(7)	C(7)–C(11)	1.501(7)
C(8)–C(9)	1.506(7)	C(9)–C(10)	1.552(6)
C(10)–C(14)	1.536(6)	C(11)–C(12)	1.471(7)
C(8)–O(1)–C(12)	109.5(3)	C(1)–C(2)–C(3)	110.8(4)
C(2)–C(1)–C(10)	112.3(4)	C(3)–C(4)–C(5)	115.2(4)
C(2)–C(3)–C(4)	112.7(4)	C(5)–C(4)–C(15)	122.6(4)
C(3)–C(4)–C(15)	122.1(4)	O(3)–C(5)–C(6)	109.5(3)
O(3)–C(5)–C(4)	112.0(3)	O(3)–C(5)–C(10)	105.6(3)
C(4)–C(5)–C(6)	107.1(3)	C(6)–C(5)–C(10)	112.3(3)
C(4)–C(5)–C(10)	110.5(4)	C(6)–C(7)–C(8)	115.2(4)
C(5)–C(6)–C(7)	116.6(3)	C(8)–C(7)–C(11)	101.9(4)
C(6)–C(7)–C(11)	119.8(4)	O(1)–C(8)–C(9)	107.8(4)
O(1)–C(8)–C(7)	104.9(4)	C(8)–C(9)–C(10)	113.9(4)
C(7)–C(8)–C(9)	113.2(4)	C(1)–C(10)–C(9)	110.1(3)
C(1)–C(10)–C(5)	110.4(3)	C(1)–C(10)–C(14)	109.6(4)
C(5)–C(10)–C(9)	108.3(3)	C(9)–C(10)–C(14)	108.0(3)
C(5)–C(10)–C(14)	110.4(3)	C(7)–C(11)–C(13)	131.0(4)
C(7)–C(11)–C(12)	106.9(4)	O(1)–C(12)–O(2)	120.0(4)
C(12)–C(11)–C(13)	122.1(5)	O(2)–C(12)–C(11)	129.7(5)
O(1)–C(12)–C(11)	110.2(4)		

the present derivatives; all we may note is that shorter bonds attend larger angles as expected.

Compounds (1) and (2) also adopt different conformations in the solid state as shown by the endocyclic torsion angles whose signs are regularly opposite, excepting the angle C(8)O(1)C(12)C(11) (Table 5). The two conformations nicely fit the steroid-like and non-steroid patterns,[1] respectively, as in solution.†

The γ-lactone ring, *cis*-fused at C(8), is puckered both in (1) and (2) and shows an envelope conformation. The lactone ring shows an appreciable degree of π-delocalization in (2) (Table 4) which is compatible with the smaller overall deviation from planarity. The values of the torsion angle H(7)C(7)C(11)C(13) show that the ring is of the *A*-type in (1) and of the *S*-type in (2), approaching the pseudo-rotational extremes in both cases.[10] These values of dihedral angles are in agreement with the allylic coupling constants ${}^4J_{7,13}$ observed in the ^{1}H n.m.r. spectra.[4] The axial substituent in the lactone

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† To our knowledge the only other *cis*-decalin eudesmanolide studied by *X*-ray diffractometry is a C(6) *trans*-eudesmanolide obtained from a guaianolide 1(10)-epoxide, and found to adopt a non-steroid conformation in the solid state (N. H. Fischer, Yung-Fung Wu-Shih, G. Chiari, F. R. Fronczek, and S. F. Watkins, *J. Nat. Prod.*, 1981, **44**, 104).

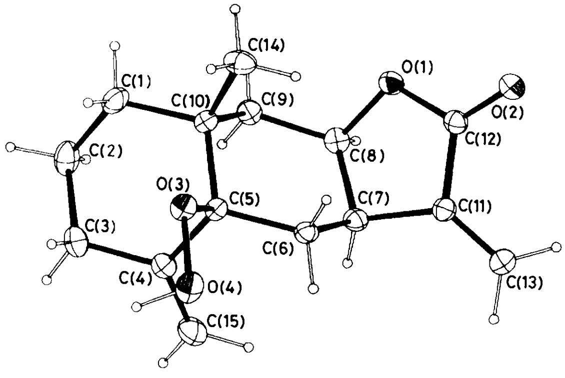

Figure 2. ORTEP II drawing[6] of the molecule of 5-deoxy-5-hydroperoxy-5-epitelekin (1), with the thermal ellipsoids at the 20% probability level

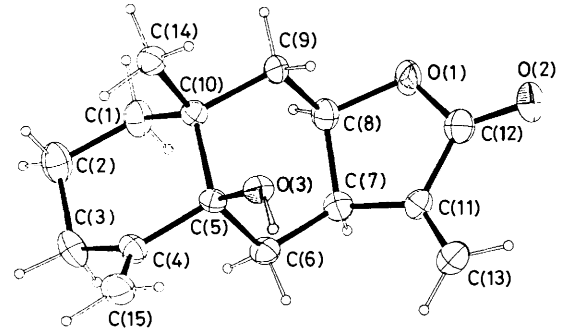

Figure 3. ORTEP II drawing of the molecule of 5-epitelekin (2) with the thermal ellipsoids at the 20% probability level

Table 5. Pertinent torsion angles (°); e.s.d.s 0.3—0.4° unless given in parentheses

	(1)	(2)
C(10)C(1)C(2)C(3)	54.5	−56.4
C(1)C(2)C(3)C(4)	−55.0	50.9
C(2)C(3)C(4)C(5)	56.1	−49.5
C(3)C(4)C(5)C(6)	−177.6	−72.4
C(4)C(5)C(6)C(7)	71.8	167.0
C(5)C(6)C(7)C(8)	43.2	−37.1
C(6)C(7)C(8)C(9)	−35.7	39.5
C(7)C(8)C(9)C(10)	42.9	−52.0
C(8)C(9)C(10)C(1)	−172.3	−61.3
C(2)C(1)C(10)C(9)	68.3	177.6
C(2)C(1)C(10)C(5)	−50.5	58.0
C(3)C(4)C(5)C(10)	−51.5	50.2
C(10)C(5)C(6)C(7)	−54.6	45.6
C(4)C(5)C(10)C(1)	46.4	−53.3
C(4)C(5)C(10)C(9)	−72.6	−173.9
C(6)C(5)C(10)C(1)	175.0	66.1
C(6)C(5)C(10)C(9)	56.0	−54.4
(ω_1)C(8)O(1)C(12)C(11)	6.7	8.8
(ω_2)C(13)C(11)C(12)O(2)	−13.2	8.8
(ω_3)C(11)C(7)C(8)O(1)	−30.9	25.3
(ω_4)C(9)C(8)C(7)C(6)	35.7	−39.5
C(5)O(3)O(4)HO(4)	−97(2)	
H(7)C(7)C(11)C(13)	−39(2)	−89(4)
H(7)C(7)C(8)H(8)	−37(3)	33(3)
C(15)C(4)C(5)O(3)	−118.7	−13.9

ring [O(1) in (1) and C(11) in (2)] deviates from the ideal arrangement to the same extent in both derivatives as seen from the torsion angle H(7)C(7)C(8)H(8) (Table 5) which, ideally, should be ±60°. This partially contrasts with the results obtained from the analysis of the ^{1}H n.m.r. spectra: the value of $J_{7,8}$ is in fact 4.8 Hz for (1) and 7.8 Hz for (2). Only the former value is in agreement with the experimental torsion angle (Table 5) found in the solid state, but the latter value would require a smaller torsion angle and is closer to the value predicted for a lactone ring of the *P*(*S*) pseudo-rotational type (*e.g.* $J_{7,8}$ 9.0 Hz in umbellifolide[5] where the ring is of the *P*-type †). Therefore the conformation of (2) in solution is slightly different than in the solid state. The relative values of the moduli and signs of ω_2 and ω_3 (Table 5) satisfy the general relationships found to hold between these angles[11,12] and with the deviation from planarity of the present γ-lactones. From the above values a negative Cotton effect in the zone for the $n \longrightarrow \pi^*$ transition of the lactone chromophore can be predicted for (1) and a positive effect for (2).[13] In point of fact, compound (1) has Θ_{260} $-2\,000°$, but compound (2) does not display a maximum in that zone, which agrees with a possible greater planarity of this lactone ring in solution.[4]

The length of the O(3)–O(4) bond in the peroxy-function of (1) appears normal[14] and so does the torsion angle around this bond (Tables 3 and 5). As regards the packing of the two structures, it is worth noting that, in both, a spiral of intermolecular hydrogen bonds twines along the *z*-axis as displayed in Figure 4: in (1), O(4) · · · O(2)′ ($1.5 - x, \bar{y}, 0.5 - z$) = 2.815(2) Å; in (2), O(3) · · · O(2)′ ($0.5 - x, 2 - y, z - 0.5$) = 2.819(2) Å.

The conformational preferences shown by derivatives (1) and (2) can be justified as follows. On the one hand, in ring B of both (1) and (2) a 1,3-diaxial destabilizing interaction occurs, far more pronounced in the steroid-like system of (1), where C(14) · · · O(1) = 3.078(5) Å, than in the non-steroid system of (2), where C(11) · · · O(3) = 3.367(5) Å; besides, the non-steroid conformation, with an equatorial methyl group at C(10) and an axial hydroxy-group at C(5), seems more stable than the steroid form, where the former is axial and the latter equatorial, since a methyl group displays a higher conformational energy than an oxygenated function.[15] On the other hand, ' long ' groups at C(5) would be in a fairly crowded medium in the non-steroid conformation, owing to steric hindrance caused ' in front ' by the *exo*-methylene groups at C(4) and C(11) and ' in the rear ' by the methyl group at C(10) and by the lactone ether oxygen O(1) (see Figures 2 and 3). Even though this interaction is small for the ' short ' O–H group, on account of its short bond length and of the small van der Waals radius of the proton, models show that it becomes important for an O–O–H group. Furthermore, the steroid conformation seems to be preferable for (1) on considering electronic effects. In fact it has been reported that in compounds of the methylene-cyclohexane series, some polar groups, α to the double bond, tend to assume an axial orientation.[16,17] This has been accounted for in terms of orbital interaction, either of the $n \longrightarrow \pi^*$ and of the $\sigma \longrightarrow \pi^*$ type (A, and ' antianomeric

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† The difference noted between the $^{3}J_{7,8}$ values shown by (1) and (2) may be partially ascribed to the approximately antiperiplanar disposition of H(7) and O(1) in compound (1): this disposition is expected to result in a maximum decreasing effect of the electronegative oxygen atom on $^{3}J_{7,8}$. On the other hand, O(1) is synclinal to H(7) in (2) and therefore a smaller substituent effect is predicted (K. G. R. Pachler, *Tetrahedron*, 1971, **27**, 187).

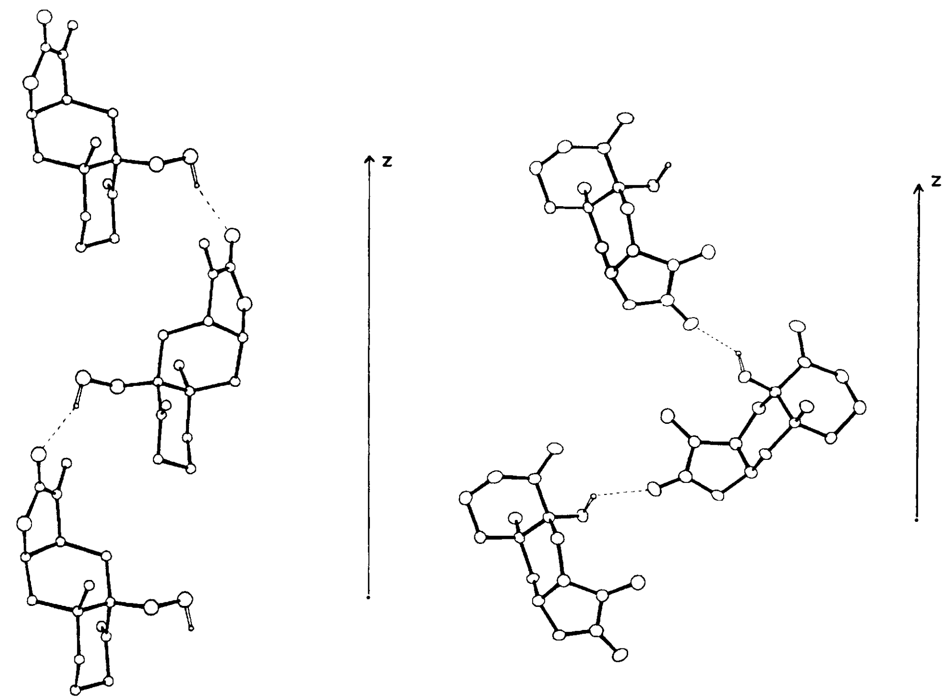

Figure 4. (a) Hydrogen bonding in the structure of 5-deoxy-5-hydroperoxy-5-epitelekin (1). (b) Hydrogen bonding in the structure of 5-epitelekin (2)

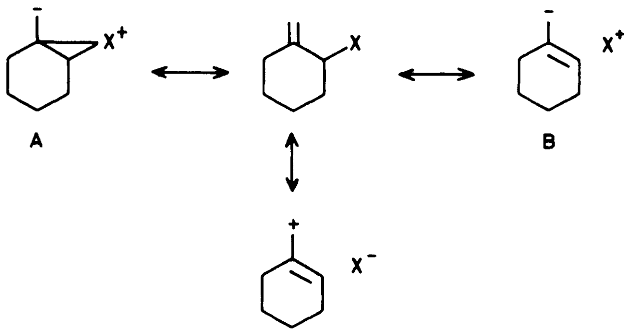

Figure 5. Possible resonance representation of the interaction between an exocyclic double bond and an α axial polar group

resonance ' [18] B in the valence-bond scheme of Figure 5) or of the $\pi \longrightarrow \sigma^*$ type (' anomeric resonance ' [18] C of Figure 5). Even though when X = OCH_3 or Br the interaction can be rationalized only in terms of anomeric resonance,[18] the general picture is not completely satisfactory and some results are apparently consistent only with species A and B. Whatever the mechanism, this interaction requires an anticlinal relationship between the double bond and the polar group and, by ^{13}C n.m.r. spectroscopy, it has been found to be larger for a hydroperoxy-group than for a hydroxy-group.[19] As the anticlinal orientation is possible only with the steroid conformation [*cf.* the values of the angle C(15)C(4)C(5)O(3) in Table 5], the hydroperoxy-group is therefore likely to favour this conformation over the non-steroid one much more than a hydroxy-group. This interaction, however, does not seem to influence the bond distances involved [7] (Tables 3 and 4).

Summing up, compound (2), with a hydroxy-group at C(5) and in a non-steroid conformation, displays a 1,3-diaxial interaction involving groups of smaller steric requirement. Nonetheless when ' sterically long ' groups are present at C(5), capable of stronger interactions with the exocyclic double bond at C(4), the steroid conformation may be favoured owing to both steric and electronic effects: this is the case of compound (1) in which a hydroperoxy-group replaces the hydroxy-group at C(5).

Experimental

Crystal Data.—*5-Deoxy-5-hydroperoxy-5-epitelekin* (1). $C_{15}H_{21}O_4$, $M = 266.3$, no m.p.,[4] $[\alpha]_D^{25}$ −21° ($CHCl_3$, c 7 g dm^{-3}), orthorhombic, space group $P2_12_12_1$, $a = 8.165(3)$, $b = 12.082(5)$, $c = 13.991(4)$ Å, $U = 1\,380.3(8)$ Å^3, $Z = 4$, $D_c = 1.28$ Mg m^{-3}, $F(000) = 572$, μ(Mo-K_α) = 0.10 mm^{-1}, room temperature. The cell parameters were obtained and refined from 16 diffractometric reflections, $16° \leqslant 2\theta \leqslant 25°$ (Mo-K_α radiation, $\lambda = 0.710\,69$ Å).

5-Epitelekin (2). $C_{15}H_{20}O_3$, $M = 248.3$, m.p. 145 °C, $[\alpha]_D^{25}$ 76° ($CHCl_3$, c 5 g dm^{-3}), orthorhombic, space group $P2_12_12_1$, $a = 9.677(1)$, $b = 11.365(1)$, $c = 12.109(1)$ Å, $U = 1\,331.7(2)$ Å^3, $Z = 4$, $D_c = 1.24$ Mg m^{-3}, $F(000) = 536$, μ(Cu-K_α) = 0.69 mm^{-1}, room temperature. The cell parameters were obtained and refined from 25 diffractometric reflections, $63° \leqslant 2\theta \leqslant 110°$, (Cu-$K_\alpha$ radiation, $\lambda = 1.541\,78$ Å).

Data Collection.—For both crystals the intensities were measured on a Nicolet R3 diffractometer, remeasuring periodically a standard reflection which showed no decay in the *X*-ray beam, using the ω-scan technique at variable speed, from 1.5° min^{-1} for the weakest to 10° min^{-1} for the strongest reflections; scan range 1.4°. For (1) 1 484 independent reflections were measured, 1 160 of which, with $I \geqslant 2\sigma(I)$, were corrected for background and for the Lorentz-polarization effect and placed on an approximate absolute scale by statistical methods using the Nicolet[20] system of programs. For (2) 1 338 independent reflections were measured, 1 193 of which, with $I \geqslant 2\sigma(I)$, were similarly treated. An empirical absorption correction, based on the ψ-scan method,[21] was applied to both sets of data.

Structure Analysis.—For all subsequent computations use was made of the SHELXTL system.[22] The solution of both structures was attained by the program RANTAN[23] which permitted the location of all the non-hydrogen atoms from *E*-maps showing the best figures of merit. The refinement was by standard least-squares methods and all hydrogen atoms were located on difference Fourier maps at an advanced stage of the anisotropic refinement. In the case of (1) the co-ordinates of the hydrogen atoms were refined under the initial constraints[22] C–H or O–H = 0.96 ± 0.02 Å; two variable isotropic parameters were also refined, one for the hydrogen atoms of the *cis*-decalin system and the other for the hydrogen atoms of the exocyclic functions, which converged to 0.053(3) and 0.072(5) $Å^2$, respectively. Unit weights proved satisfactory. At convergence (mean shift/e.s.d. = 0.08), $R = 0.043$ for 1 160 reflections and 234 parameters. In the case of (2) the co-ordinates of the hydrogen atom of the O(3)–H group were refined under the initial constraint O–H = 1.00 ± 0.04 Å, but the other hydrogen atoms were forced to ride on the bonded carbon atoms by introducing adequate AFIX[22] instructions. Two variable isotropic parameters were refined as for compound (1) and they converged to 0.088(5) and 0.106(7) $Å^2$ respectively. In the closing cycles the following weighting scheme was introduced: $w = 1/[\sigma(F_0) + G\,F_0^2]$, where σ is the standard deviation of F_0 and G is a variable to be adjusted after each cycle. At convergence (mean shift/e.s.d. = 0.010), $R = 0.066$, $wR = 0.069$, and $G = 0.000\,16$ for 1 188 reflections and 174 parameters. Five reflections had to be discarded in the course of the refinement because they were probably affected by the secondary extinction effect.

Tables of observed and calculated structure factors, anisotropic thermal parameters of the non-hydrogen atoms, and hydrogen atoms parameters, are deposited as Supplementary Publication No. SUP 23859 (18 pp.).*

References

1 C. Djerassi, in ' Optical Rotatory Dispersion,' McGraw-Hill, New York, 1960, p. 76.

2 M. Toda, T. Sato, T. Tokahashi, K. Tori, I. Horibe, and K. Kuriyama, *J. Chem. Soc.*, *Perkin Trans. 1*, 1981, 2695.

3 A. G. Hartmann and J. B. De Roos, *J. Org. Chem.*, 1969, **34**, 736.

4 G. Appendino, P. Gariboldi, and G. M. Nano, *Phytochemistry*, 1983, **22**, 2767.

5 G. Appendino, P. Gariboldi, M. Calleri, G. Chiari, and D. Viterbo, *J. Chem. Soc.*, *Perkin Trans. 1*, 1983, 2705.

6 C. K. Johnson. ORTEP II. Report ORNL-3794, 1970. Oak Ridge Laboratory, Tennessee.

7 G. Appendino, M. Calleri, G. Chiari, and D. Viterbo, *Acta Crystallogr. C*, 1984, in the press.

8 U. Rychlewska, M. Holub, E. Bloszyk, and B. Droždž, *Collect. Czech. Chem. Commun.*, 1982, **47**, 88.

9 P. W. Jennings, J. C. Hurley, S. K. Reeder, A. Holian, P. Lee, C. N. Coughlan, and R. D. Larsen, *Org. Chem.*, 1976, **41**, 4077.

10 Z. Samek, *Collect. Czech. Chem. Commun.*, 1979, **44**, 558.

11 A. T. McPhail and G. A. Sim, *Tetrahedron*, 1973, **29**, 1751.

12 P. J. Cox and G. A. Sim, *J. Chem. Soc.*, *Perkin Trans. 2*, 1977, 255.

13 A. F. Beecham, *Tetrahedron*, 1972, **28**, 5543.

14 C. J. Fritchie and R. K. McMullan, *Acta Crystallogr. B*, 1981, **27**, 1086 and references therein.

15 E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, ' Conformational Analysis,' Interscience, New York, 1965, pp. 436—438.

16 N. S. Zefirov and I. V. Baranenkov, *Zh. Org. Khim.*, 1981, **17**, 2364.

17 Minh Tan Phan Viet, J. Lessard, and J. K. Saunders, *Tetrahedron Lett.*, 1979, 317.

18 N. S. Zefirov and I. V. Baranenkov, *Tetrahedron*, 1983, **39**, 1769.

19 F. S. El-Feraly, Y. N. Chan, G. A. Capiton, R. W. Dosckotch, and R. W. Fairchild, *J. Org. Chem.*, 1979, **44**, 3952.

20 NICOLET, Nicolet XTL Operation Manual, Nicolet Analytical Instruments Inc., Cupertino. 1981.

21 A. C. T. North, D. C. Phillips, and F. S. Mathews, *Acta Crystallogr. A*, 1968, **24**, 351.

22 G. M. Sheldrick, SHELXTL, revision 3. An Integrated System for Solving, Refining and Displaying Crystal Structures from Diffraction Data, Univ. of Göttingen, 1981.

23 Yao Jia-Xing, *Acta Crystallogr. A*, 1981, **37**, 642.

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