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The Crystal Structure of Chanootin, a Bicyclic C_{15}-Tropolone

By Bengt Karlsson, Anne-Marie Pilotti and Anne-Charlotte Wiehager

Institute of Inorganic and Physical Chemistry, University of Stockholm, S-104 05 Stockholm, Sweden

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Chanootin, $C_{15}H_{18}O_3$, is a bicyclic C_{15}-tropolone isolated from the heartwood of *Chamaecyparis nootkatensis* (Lamb.) Spach. (Cupressales, Cupressaceae). From o.r.d. data the compound appears to be optically inactive although it contains asymmetric carbon atoms. Chanootin crystallizes in space group $P2_1/c$, with $Z=4$, $a=9{\cdot}158$, $b=8{\cdot}372$, $c=18{\cdot}627$ Å, $\beta=112{\cdot}26°$; *i.e.* it must exist as a racemate. Three-dimensional intensity data were recorded with an automatic diffractometer and scintillation counter. The structure was determined by the application of direct methods and refined by full-matrix least-squares calculations to a final R index of 0·049. The carbon–carbon bond lengths of the tropolone ring exhibit bond alternation, as reported for tropone derivatives and the ring is only approximately a planar heptagon.

Introduction

Chanootin, $C_{15}H_{18}O_3$, is a bicyclic C_{15}-tropolone isolated from the heartwood of *Chamaecyparis nootkatensis* (Lamb.) Spach. (Cupressales, Cupressaceae) (Norin, 1964). The Cupressaceae tropolones are all modified terpenes and the three isoprene units in chanootin are connected 'head-to-tail' (Simonsen, 1952).

Chanootin possesses two asymmetric carbon atoms but appears to be optically inactive. Owing to lack of material the configuration of chanootin could not be subjected to detailed chemical study (Norin, 1964). The present X-ray analysis was undertaken in order to remove the remaining uncertainties.

Experimental

Oscillation and Weissenberg photographs indicated a monoclinic unit cell (Table 1). Extinctions are consistent with the space group $P2_1/c$. Three-dimensional intensity data were collected on a Siemens four-circle automatic diffractometer to a 2θ limit of 130° with monochromatized Cu $K\alpha$ radiation and the θ–2θ scan mode at a scan speed of 1° min^{-1}. A crystal with an approximate volume of 0·012 mm^3 was mounted with the b axis coincident with the φ axis. Altogether 2440 independent reflexions were collected of which 2016 were considered to be observed. Three standard reflexions were used as monitors.

Table 1. *Crystal data*

Lattice constants	$a=$ 9·158 (3) Å
	$b=$ 8·372 (2)
	$c=$18·627 (5)
	$\beta=$112·26° (2)
Cell volume	$V=$1321·75 Å^3
Density (X-ray)	$d=$1·236 g cm^{-3}
Molecules per unit cell	$Z=4$
Space group	$P2_1/c$

Lorentz and polarization corrections were applied, but no absorption corrections were made. Preliminary scale and temperature factors were derived from a Wilson plot. The structure factors were then reduced to normalized structure factor magnitudes, $|E(hkl)|$.

Solution and refinement

The structure was solved by a modified version of the *MULTAN* direct phase determination procedure (Germain, Main & Woolfson, 1970).

The reflexions with the highest $|E|$ values were used in the process. The convergence elimination algorithm was performed on a set of 164 reflexions having $|E|>1{\cdot}45$. The starting set obtained is given in Table 2. It comprises three origin-specifying reflexions and three variables. Thus eight sets of signs were generated. An $|E|$ map computed with the signs of the most reliable set showed 15 of the 18 non-hydrogen atoms of the molecule. The remaining 3 atoms were located from a difference Fourier synthesis.

Table 2. *Starting phase sets obtained from the convergence map*

The correct phase values are those without parentheses.

h			$\varphi_{\mathbf{h}}$	$\lvert E_{\mathbf{h}}\rvert$
5	0	6	0	2·36
0	2	1	0	2·51
2	1	−4	0	2·91
4	1	10	0, (π)	2·08
4	2	−8	0, (π)	2·57
0	8	1	(0), π	2·70

After isotropic full-matrix least-squares refinement the R value was 0·15. Anisotropic thermal parameters were then assigned to all non-hydrogen atoms and a further 2 cycles of least-squares calculations lowered R to 0·092. A subsequent difference Fourier synthesis revealed the positions of all the hydrogen atoms.

Table 3. *Positional and anisotropic thermal parameters of the non-hydrogen atoms*

The β values refer to the temperature factor expression $\exp\left[-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+hk\beta_{12}+hl\beta_{13}+kl\beta_{23})\right]$. Estimated standard deviations are given in parentheses. Values are $\times 10^4$.

	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(1)	3213 (2)	5355 (2)	3014 (1)	68 (3)	90 (3)	23 (1)	−12 (4)	28 (2)	3 (2)
C(2)	2147 (2)	6571 (3)	2787 (1)	66 (3)	95 (3)	26 (1)	−13 (4)	16 (2)	−5 (2)
C(3)	2222 (2)	8166 (3)	3079 (1)	72 (3)	92 (3)	30 (1)	0 (4)	33 (2)	2 (2)
C(4)	3560 (2)	8772 (3)	3742 (1)	98 (3)	91 (3)	28 (1)	−22 (4)	40 (2)	−12 (2)
C(5)	4896 (3)	7981 (3)	4213 (1)	98 (3)	121 (3)	25 (1)	−22 (5)	14 (2)	−25 (3)
C(6)	5412 (2)	6429 (3)	4170 (1)	79 (3)	132 (3)	24 (1)	11 (5)	11 (2)	−4 (3)
C(7)	4705 (2)	5260 (2)	3635 (1)	72 (3)	101 (3)	22 (1)	5 (4)	27 (2)	6 (2)
C(8)	5458 (2)	3635 (3)	3646 (1)	72 (3)	105 (3)	27 (1)	22 (4)	26 (2)	12 (2)
C(9)	4473 (3)	2959 (3)	2844 (2)	83 (3)	107 (3)	33 (1)	20 (5)	27 (3)	−20 (3)
C(10)	2341 (2)	3731 (2)	2596 (1)	76 (3)	89 (3)	28 (1)	4 (4)	19 (2)	−9 (2)
C(11)	2012 (3)	3830 (3)	1721 (2)	129 (4)	156 (4)	28 (1)	51 (6)	6 (3)	−31 (3)
O(12)	1932 (2)	2825 (2)	2931 (1)	79 (2)	98 (2)	48 (1)	6 (3)	32 (2)	26 (2)
O(13)	1112 (2)	9122 (2)	2770 (1)	90 (2)	96 (2)	49 (1)	28 (3)	18 (2)	−12 (2)
O(14)	3419 (2)	10302 (2)	3920 (1)	147 (3)	98 (3)	35 (1)	9 (4)	19 (2)	−20 (2)
C(15)	7186 (2)	3733 (3)	3784 (2)	76 (3)	124 (3)	31 (1)	10 (5)	29 (3)	−6 (3)
C(16)	8381 (3)	3004 (3)	4327 (2)	83 (3)	177 (4)	29 (1)	55 (5)	16 (3)	−22 (3)
C(17)	10042 (3)	3214 (5)	4370 (2)	82 (4)	276 (7)	53 (2)	47 (7)	30 (3)	−51 (5)
C(18)	8203 (4)	1879 (6)	4921 (2)	161 (5)	334 (9)	40 (1)	172 (10)	38 (4)	76 (5)

These, given fixed isotropic thermal parameters equal to those of their parent atoms, were included in the refinement. At this point 15 reflexions with very large structure factor amplitudes were removed from the data because they appeared to be affected by secondary extinction. These are marked with asterisks in Table 5. The final agreement index calculated for 2001 reflexions is 0·049. The final positional and thermal parameters of the non-hydrogen atoms, together with their standard deviations, are listed in Table 3 and those for the hydrogen atoms in Table 4. The final calculated structure factors are compared with the observed values in Table 5. Hughes's (1941) weighting scheme was used throughout with an $F_{0,\min}$ of 1·5. The scattering factors of Freeman (1959) were used for carbon and oxygen and that of Stewart, Davidson & Simpson (1965) for hydrogen.

Table 4. *Positional* ($\times 10^3$) *and isotropic thermal parameters of the hydrogen atoms, with estimated standard deviations in parentheses*

	x	y	z	B
H(C2)	114 (3)	636 (3)	236 (2)	2·57 Å^2
H(C5)	557 (3)	856 (3)	460 (2)	3·11
H(C6)	644 (3)	616 (3)	458 (2)	3·02
H(C8)	532 (3)	306 (3)	406 (2)	2·68
H1(C9)	438 (3)	183 (3)	284 (2)	3·22
H2(C9)	491 (3)	342 (3)	247 (2)	3·22
H1(C11)	192 (3)	275 (4)	151 (2)	4·22
H2(C11)	99 (4)	434 (4)	158 (2)	4·22
H3(C11)	259 (4)	450 (3)	148 (2)	4·22
H(O12)	98 (3)	326 (3)	274 (2)	3·53
H(O14)	267 (4)	1078 (3)	352 (2)	3·86
H(C15)	739 (3)	441 (3)	344 (2)	3·11
H1(C17)	1079 (4)	364 (4)	494 (2)	5·57
H2(C17)	1042 (4)	219 (4)	429 (2)	5·57
H3(C17)	1012 (4)	397 (4)	399 (2)	5·57
H1(C18)	847 (4)	269 (4)	530 (2)	6·09
H2(C18)	705 (4)	158 (4)	482 (2)	6·09
H3(C18)	886 (4)	91 (4)	500 (2)	6·09

Results and discussion

From o.r.d. data chanootin appears to be optically inactive although it contains asymmetric carbon atoms. The compound crystallizes in space group $P2_1/c$, *i.e.* it must exist as a racemate, which is rather unusual for isolated natural products. On the basis of chemical and spectroscopic analyses it is clear that chanootin is a bicyclic tropolone. These studies also reveal the functional groups but not the way in which the isobutenyl group is attached to the five-membered ring relative to the hydroxyl group, nor the way in which the five-membered ring is attached to the tropolone system.

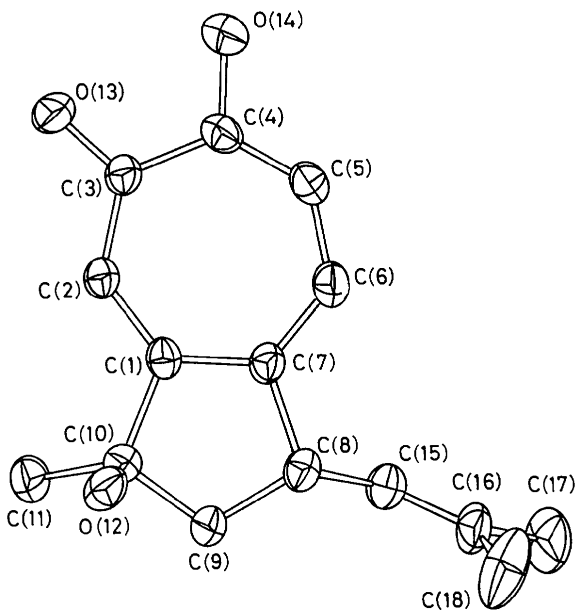

Fig. 1. A perspective view of the molecule.

The structural and conformational features of the chanootin molecule are illustrated in Fig. 1. Bond distances and angles for the structure are listed in Tables 6 and 7. No corrections for thermal vibrations have been made. The standard deviations, calculated from the least-squares matrix alone, are 0·003 and 0·002 Å in the C–C and C–O bonds respectively and the deviation in the bond angles not involving hydrogen is about 0·2°.

In the tropolone ring two types of C–C bonds with different bond lengths appear, showing the tropone-type bond alternation (Shimanouchi *et al.*, 1967). The tropone system, 2,4,6-cycloheptatrienone, has double-bond fixation for C–C and C–O bonds. Similar bond alternation has been found previously (Ito & Fukazawa, 1972). A significant difference between the C–O bond lengths is also observed. The average value of the shorter carbon–carbon bonds C(1)–C(2), C(4)–C(5) and C(6)–C(7) is 1·370 Å. This mean value is in between the normal carbon–carbon double bond distance, and the aromatic carbon–carbon bond length. The average value of the longer bonds [C(1)–C(7), C(2)–C(3), C(3)–C(4) and C(5)–C(6)] is 1·427 Å, which is longer than the aromatic carbon–carbon bond length but shorter than the sp^2–sp^2 carbon–carbon single bond length. The C(3)–O(13) and C(4)–O(14) bond lengths are 1·250 Å and 1·341 Å, respectively. The intramolecular distance O(13)–O(14) is 2·569 Å. A hydrogen atom is found at the normal bond distance (0·89 Å) from O(14) and at 2·10 Å from O(13).

Table 5. *Observed and calculated structure amplitudes*

The columns use the running index k, $10|F_o|$ and $10|F_c|$ respectively.

[illegible]		

Table 6. *Bond distances between non-hydrogen atoms, with estimated standard deviations in parentheses*

C(1)–C(2)	1·362 (2) Å	C(7)—C(8)	1·523 (3) Å
C(1)–C(7)	1·419 (2)	C(8)—C(9)	1·532 (3)
C(1)–C(10)	1·540 (2)	C(8)—C(15)	1·506 (2)
C(2)–C(3)	1·434 (3)	C(9)—C(10)	1·530 (3)
C(3)–C(4)	1·461 (3)	C(10)–C(11)	1·517 (3)
C(3)–O(13)	1·250 (2)	C(10)–O(12)	1·433 (2)
C(4)–C(5)	1·376 (3)	C(15)–C(16)	1·325 (3)
C(4)–O(14)	1·341 (2)	C(16)–C(17)	1·503 (3)
C(5)–C(6)	1·395 (3)	C(16)–C(18)	1·508 (4)
C(6)–C(7)	1·371 (3)		

The angle O(14)–H(14)···O(13) is 111·8°. The bond angles around C(3) indicate a greater sp^2 character for this atom than for C(4). Thus the observed alternation in bond lengths probably indicates some double-bond fixation both for C–C and C–O bonds with concomitantly decreased π-electron delocalization. Other bond lengths agree very well with values usually observed (Sutton, 1965).

The equations of various least-squares planes and deviations from these planes are listed in Table 8. The tropolone system is not strictly planar. The atoms are out of the mean plane by amounts that are large relative to the positional standard deviations. Accordingly the seven-membered ring is only approximately a planar heptagon. The interior angles of the tropolone ring vary from 123·2 to 130·7°. The average value is 128·5°, however, in good agreement with that in a regular heptagon. In the five-membered ring the four atoms [C(1), C(7), C(8), C(10)] which form the planar part are coplanar within about ±0·017 Å and the fifth atom is displaced by about 0·449 Å. The isobutenyl group is attached to the ring in a *trans* configuration relative to the hydroxyl group O(12).

Table 7. *Interatomic angles with estimated standard deviations in parentheses*

C(2)—C(1)—C(7)	130·5 (2)°
C(2)—C(1)—C(10)	120·5 (2)
C(7)—C(1)—C(10)	108·9 (2)
C(1)—C(2)—C(3)	130·7 (2)
C(2)—C(3)—C(4)	123·2 (2)
C(2)—C(3)—O(13)	120·5 (2)
C(4)—C(3)—O(13)	116·3 (2)
C(3)—C(4)—C(5)	129·1 (2)
C(3)—C(4)—O(14)	114·3 (2)
C(5)—C(4)—O(14)	116·6 (2)
C(4)—C(5)—C(6)	130·6 (2)
C(5)—C(6)—C(7)	128·9 (2)
C(1)—C(7)—C(6)	126·6 (2)
C(1)—C(7)—C(8)	110·6 (2)
C(6)—C(7)—C(8)	122·7 (2)
C(7)—C(8)—C(9)	102·7 (2)
C(7)—C(8)—C(15)	113·3 (2)
C(9)—C(8)—C(15)	112·3 (2)
C(8)—C(9)—C(10)	106·6 (2)
C(1)—C(10)–C(9)	102·5 (2)
C(1)—C(10)–C(11)	114·8 (2)
C(1)—C(10)–O(12)	107·5 (2)
C(9)—C(10)–C(11)	112·4 (2)
C(9)—C(10)–O(12)	107·9 (2)
C(11)–C(10)–O(12)	111·1 (2)
C(8)—C(15)–C(16)	128·0 (2)
C(15)–C(16)–C(17)	120·9 (2)
C(15)–C(16)–C(18)	124·0 (2)
C(17)–C(16)–C(18)	115·0 (3)

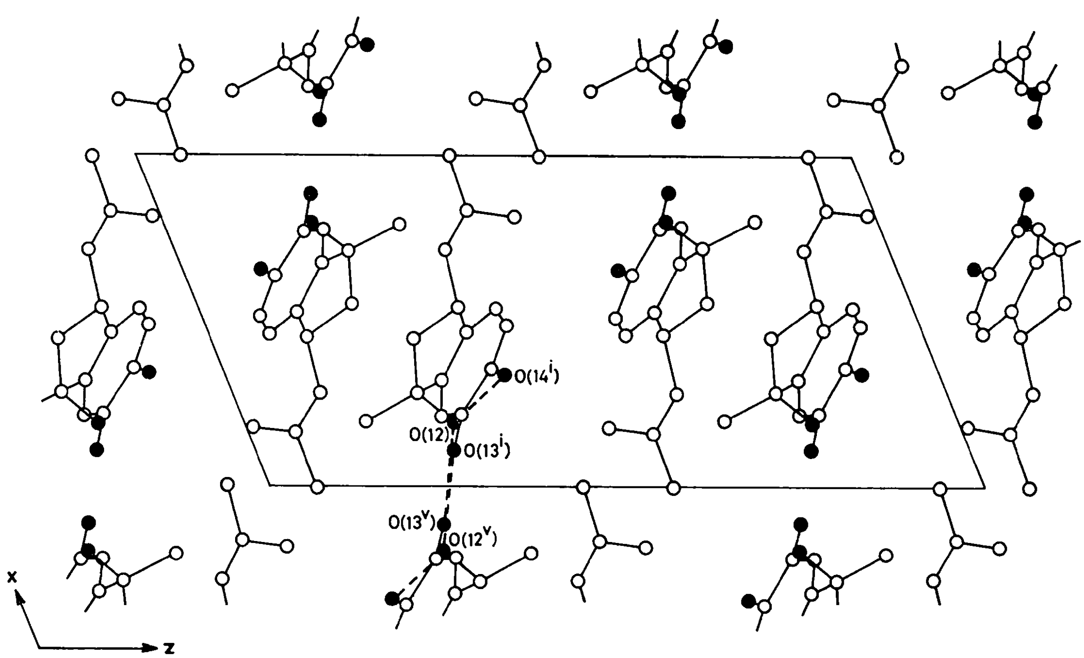

Fig. 2. The structure projected along the *b* axis. Hydrogen bonds, which are marked with broken lines, are observed between molecules related by the screw axes intersecting, the *ac* plane at 0,0,¼; 0,0,¾; 1,0,¼ and 1,0,¾. These hydrogen bonds form an extended network in the **b** direction. ○ carbon, ● oxygen.

Table 8. *Least-squares planes and deviations for (a) the tropolone system, (b) the tropolone ring, (c) the five-membered ring and (d) the isobutenyl group*

The planes are described in terms of a vector basis $\mathbf{m}\|\mathbf{a}^*$, $\mathbf{n}\|\mathbf{b}$ and $\mathbf{p}\|\mathbf{c}$.

Plane (*a*): $-0{\cdot}4473m-0{\cdot}3117n+0{\cdot}8383p=1{\cdot}1809$
Plane (*b*): $-0{\cdot}4506m-0{\cdot}3203n+0{\cdot}8332p=1{\cdot}0970$
Plane (*c*): $-0{\cdot}4208m-0{\cdot}3270n+0{\cdot}8462p=1{\cdot}2127$
Plane (*d*): $+0{\cdot}1068m+0{\cdot}7740n+0{\cdot}6242p=5{\cdot}9199$.

Plane (*a*)		Plane (*b*)	
C(1)	−0·024 Å	C(1)	−0·011 Å
C(2)	0·018	C(2)	0·026
C(3)	0·008	C(3)	0·002
C(4)	−0·012	C(4)	−0·031
C(5)	0·035	C(5)	0·016
C(6)	0·028	C(6)	0·020
C(7)	−0·030	C(7)	−0·023
O(13)	0·018		
O(14)	−0·040		

Plane (*c*)		Plane (*d*)	
C(1)	−0·017 Å	C(8)	−0·007 Å
C(7)	0·017	C(15)	0·005
C(8)	−0·010	C(16)	0·014
C(9)*	−0·449	C(17)	−0·009
C(10)	0·010	C(18)	−0·003

* This atom is not included in the least-squares plane.

Fig. 2 gives the molecular packing and hydrogen bonding viewed down the *b* axis. Short intermolecular distances are listed in Table 9. Hydrogen bonds are observed between molecules related by the screw axes intersecting the *ac* plane at $0,0,\frac{1}{4}$; $0,0,\frac{3}{4}$; $1,0,\frac{1}{4}$ and $1,0,\frac{3}{4}$. These hydrogen bonds form an extended network in the **b** direction. However, there are no hydrogen bonds connecting molecules in the **c** direction.

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Table 9. *Intermolecular distances less than* 3·8 Å

Code for symmetry related atoms

Superscript	Coordinates *x*	*y*	*z*
None	x	y	z
i	x	$-1+y$	z
ii	$-1+x$	y	z
iii	$1-x$	$1-y$	$1-z$
iv	$1-x$	$2-y$	$1-z$
v	$-x$	$-\frac{1}{2}+y$	$\frac{1}{2}-z$
vi	$1-x$	$-\frac{1}{2}+y$	$\frac{1}{2}-z$

C(8)—O(14^{i})	3·501 Å	C(2)—O(13^{v})	3·441 Å
C(9)—O(14^{i})	3·371	C(10)–O(13^{v})	3·437
C(10)–O(14^{i})	3·690	C(11)–O(13^{v})	3·347
O(12)–C(4^{i})	3·783	O(12)–C(2^{v})	3·614
O(12)–O(13^{i})	3·177	O(12)–C(3^{v})	3·559
O(12)–O(14^{i})	2·795	O(12)–O(13^{v})	2·810
O(12)–C(17^{ii})	3·716	C(9)—C(1^{vi})	3·790
C(4)—C(18^{iii})	3·486	C(15)–C(2^{vi})	3·684
C(5)—C(18^{iii})	3·760	C(15)–C(3^{vi})	3·741
O(14)–C(18^{iii})	3·555	C(15)–O(13^{vi})	3·786
O(14)–C(5^{iv})	3·533	C(17)–O(13^{vi})	3·794

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