se situent effectivement dans les cavités octaédriques de ce réseau (1 site sur 2 occupé).

La Fig. 4 décrit, dans ces conditions, l'empilement structural parallèlement au plan (*bc*).

A ce stade, deux hypothèses sont possibles:

– Existence d'un désordre total au niveau des atomes d'oxygène provenant des groupements OH^-, NO_3^- et H_2O. Cette possibilité est à rejeter, nous semble-t-il, car elle entraînerait une maille hexagonale (en pointillés sur la Fig. 3).

– Ordre au niveau des plans anioniques. La composition du plan médian de chaque séquence est nécessairement: OH^- et H_2O, les groupements nitrate ne pouvant intervenir que dans les plans extrêmes. La proportion, dans chaque maille élémentaire, doit être en accord avec la formule chimique, de 1 NO_3^- pour 1 OH^-, pour 1H_2O.

Discussion de la structure proposée

Dans la formulation générale utilisée lors de la systématique présentée dans l'article I, l'hydroxynitrate de zinc répond au cas $x=1$, $y=1$, $z=2$. C'est le premier exemple possible de sel hydraté appartenant au type structural I (Tableau 1, article I). La condition limite $x=y$ impliquant, nous l'avons vu, que les groupements nitrate interviennent dans les deux plans extrêmes à raison d'un oxygène sur deux leur appartenant (Fig. 4).

L'hypothèse de structure qui vient d'être présentée et dont nous résumons les caractéristiques ci-dessous, correspond bien au type I appliqué au composé 1,1,2 [Fig. 2(*b*), article I], c'est-à-dire:

– Empilement, le long de l'axe *a*, de trois plans compacts constitués par les groupements hydroxyle, les molécules d'eau et un atome d'oxygène de chaque groupement nitrate, ces derniers étant disposés de façon ordonnée.

– Taux d'occupation des sites octaédriques par les atomes de zinc: $T=\frac{1}{2}$.

– Paramètre le long de l'axe d'empilement:

Valeur théorique: $p=n\times 9{,}2$ Å (relation 5, article I).

Valeur expérimentale: $p=17{,}94$ Å proche de la valeur théorique (avec $n=2$).

Il semble difficile d'accorder une signification physique à la différence des distances entre les deux groupes de plans d'atomes de zinc: 2,33 et 2,68 Å (*cf.* Fig. 4), les coordonnées atomiques n'ayant été déterminées qu'approximativement. Cependant, si cette signification physique existait, l'explication pourrait être trouvée dans la composition des plans anioniques telle qu'elle est indiquée Fig. 4, et qui conduit bien aux proportions caractérisant la formule chimique. La répartition des charges négatives, homogène dans la séquence *A–B–A*, ne l'est plus dans la séquence *B–A–B* (une charge dans le plan médian contre deux dans les deux plans extrêmes). Les atomes de zinc seraient alors, dans ce dernier cas, davantage attirés vers les plans de charge négative plus élevée, ce qui entraînerait la distance supérieure de 2,68 Å. De plus, cette répartition expliquerait aussi $n=2$ dans le calcul du paramètre.

Ainsi, le nitrate basique $Zn(OH)_2.Zn(NO_3)_2.2H_2O$ et vraisemblablement aussi le sel isotype $Ni(OH)_2.Ni(NO_3)_2.2H_2O$, fournissent les premiers exemples de sels hydratés appartenant au type structural I dont toutes les caractéristiques sont vérifiées de façon satisfaisante.

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The Crystal Structure of the α-Bromonorketone of (+)-2,5-Diepi-β-cedrene

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A three-dimensional X-ray structure analysis of the 'equatorial' α-bromonorketone, $C_{14}H_{21}BrO$, of a new sesquiterpene, (+)-2,5-diepi-*β*-cedrene, has been performed. The crystals are orthorhombic, space group $P2_12_12_1$, $a=12·740$, $b=7·465$, $c=14·335$ Å, $Z=4$. Bromine was used as a phase-determining heavy atom. The value of the *R* index for the refined structure is 0·045. The structure contains two *trans*-fused five-membered rings with considerable internal strain.

Introduction

An extract from the wood of *Sciadopitys verticillata* Sieb. et Zucc. (Cupressales, Taxodiaceae) has been found to contain, besides the common Cupressales sesquiterpenes α-cedrene and *β*-cedrene, a new sesquiterpene, $C_{15}H_{24}$ (Norin *et al.*, 1973). Detailed spectroscopic studies and chemical degradation indicated that the latter must be of a new tricyclic type but closely related to (+)-β-cedrene. We have determined its structure by an X-ray single-crystal analysis of its 'equatorial' α-bromonorketone.

Experimental

Weissenberg photographs of this compound exhibited axial extinctions only, consistent with the requirements of space group $P2_12_12_1$. Data for the crystal unit cell are given in Table 1. The X-ray intensity data were collected on a Siemens automatic four-circle diffractometer up to a 2θ limit of 110° with monochromatized Cu $K\alpha$ radiation. A crystal of irregular shape with an approximate volume of 0·020 mm^3 was mounted with the b axis coincident with the φ axis of the diffractometer. The intensities of 1039 independent reflexions were measured twice (five-points measuring procedure) by scanning in the θ–2θ mode at a speed of 2·5° min^{-1}. Background measurements were made at each end of the scan. The net intensities, I_{net}, and their estimated standard deviations, $\sigma(I_{\text{net}})$, based on counter statistics, were calculated. Lorentz–polarization and absorption corrections (μ=43·90 cm^{-1}) were applied. Only the 985 most significant reflexions with $\sigma(I_{\text{net}})/I_{\text{net}} \leq 0{\cdot}25$ were used in the subsequent calculations. During the alignment of the crystal the intensity of some monitor reflexions decreased by about 7%.

Table 1. *Crystal unit-cell data*

Figures in parentheses are calculated standard deviations.

Lattice constants	a = 12.740 (3) Å
	b = 7.465 (1)
	c = 14.335 (3)
Cell volume	V= 1363.3 Å^3
Density (X-ray)	d = 1.388 g cm^{-3}
Molecules per unit cell	Z= 4
Space group	$P2_12_12_1$

However during the period of data collection three monitor reflexions measured at intervals of 40 reflexions showed a deviation of only 3% in intensity. Individual reflexions were corrected for this loss by fitting a linear function of time to the intensity of the monitor reflexions.

Structure determination and refinement

The structure was solved by the heavy-atom technique. The position of the bromine atom was determined from a three-dimensional Patterson synthesis and the complete structure was then obtained from a series of Fourier syntheses.

A modified version of the full-matrix least-squares program *LALS* (Gantzel, Sparks & Trueblood, 1961) was used for parameter refinement. The weighting scheme of Hughes (1941) was used throughout with $F_{o,\min}$=3·0. The scattering factors for carbon and oxygen are those of Freeman (1959), for bromine that of Hanson, Herman, Lea & Skillman (1964) and for hydrogen that of Stewart, Davidson & Simpson (1965). After refinement with isotropic temperature factors the R value was 0·15. Conversion to anisotropic temperature factors and refinement gave R=0·072. A subsequent three-dimensional difference Fourier synthesis displayed well defined peaks for 18 of the 21 hydrogen atoms in the molecule. The three hydrogen atoms not resolved belong to one CH_3 group. The hydrogen positional and thermal parameters were held constant throughout further refinement cycles. The isotropic thermal parameters for the hydrogen atoms were chosen to be equal to those of the final isotropic value of their parent atoms. The final R index calculated for 984 reflexions is 0·045.

Table 2 contains the final fractional coordinates and anisotropic thermal parameters for the non-hydrogen atoms, Table 3 the positional and isotropic thermal

Table 2. *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}
Br	2663 (1)	1357 (2)	7688 (1)	113 (1)	319 (3)	65 (1)	−21 (2)	−57 (1)	−51 (2)
C(1)	4229 (5)	2547 (9)	10259 (5)	68 (5)	152 (12)	50 (4)	−27 (13)	−2 (7)	18 (11)
C(2)	3954 (6)	1732 (9)	11223 (5)	105 (6)	209 (14)	44 (4)	−73 (16)	−9 (7)	31 (12)
C(3)	3097 (7)	3061 (14)	11598 (6)	116 (7)	386 (24)	61 (5)	−72 (22)	41 (10)	17 (17)
C(4)	3107 (7)	4751 (11)	10991 (6)	116 (7)	257 (17)	69 (5)	15 (18)	60 (10)	−56 (15)
C(5)	4154 (5)	4560 (9)	10475 (5)	71 (5)	195 (12)	40 (3)	−40 (13)	13 (6)	−10 (11)
C(6)	4505 (6)	5570 (9)	9577 (5)	98 (5)	151 (11)	53 (4)	−36 (14)	0 (8)	−1 (12)
C(7)	5153 (5)	4005 (9)	9060 (5)	75 (4)	194 (14)	60 (4)	−30 (14)	31 (7)	−27 (12)
C(8)	4497 (6)	3294 (10)	8285 (5)	97 (5)	204 (15)	53 (4)	−20 (15)	38 (8)	−14 (13)
C(9)	3799 (5)	1765 (8)	8558 (5)	77 (5)	158 (12)	49 (4)	5 (12)	−1 (7)	−8 (11)
C(10)	3379 (5)	1921 (8)	9552 (5)	68 (4)	133 (11)	55 (4)	−4 (11)	2 (7)	−4 (10)
C(11)	5286 (5)	2528 (11)	9809 (6)	57 (4)	204 (14)	72 (5)	−1 (13)	9 (8)	−16 (14)
C(12)	4896 (8)	1585 (15)	11890 (6)	133 (8)	382 (25)	77 (5)	−48 (26)	−56 (11)	94 (22)
C(13)	5308 (9)	7023 (11)	9845 (6)	163 (9)	215 (16)	66 (5)	−178 (22)	9 (11)	21 (14)
C(14)	3618 (7)	6351 (10)	9005 (6)	139 (8)	198 (15)	79 (5)	24 (20)	−36 (10)	40 (17)
O(15)	4533 (5)	3868 (8)	7473 (3)	180 (6)	309 (13)	44 (3)	−145 (15)	52 (7)	−4 (11)

Table 3. *Positional and isotropic thermal parameters of the hydrogen atoms*

	10^3x	10^3y	10^3z	10^2B
H(C2)	373	51	1110	598 Å^2
H1(C3)	250	232	1158	863
H2(C3)	326	313	1225	863
H1(C4)	230	474	1086	569
H2(C4)	322	587	1147	569
H(C5)	469	448	1083	498
H(C7)	596	448	880	432
H(C9)	935	438	1144	403
H1(C10)	280	282	952	420
H2(C10)	346	89	974	420
H1(C11)	553	147	955	601
H2(C11)	584	292	1045	601
H1(C12)	552	99	1183	730
H2(C12)	506	302	1218	730
H3(C12)	456	96	1249	730
H1(C13)	595	643	1020	606
H2(C13)	483	758	1028	606
H3(C13)	548	757	944	606

Table 4. *Observed and calculated structure amplitudes*

The columns contain the index k, $10|F_o|$ and $10|F_c|$. The reflexion marked with an asterisk was not included in the refinement.

[illegible]

parameters for the hydrogen atoms, and Table 4 the observed and calculated structure factor amplitudes.

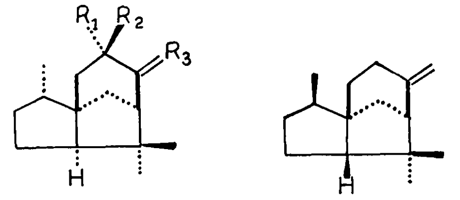
Discussion of the structure

The structure revealed by this analysis is the α-bromonorketone of (+)-2,5-diepi-β-cedrene [Fig. 1(*a*)] with the two five-membered rings *trans*-fused.* In β-cedrene [Fig. 1(*b*)], however, the five-membered rings are *cis*-fused. Fig. 2, a perspective view of the molecule (Johnson, 1965), gives the atom numbering scheme. Bond distances and angles together with their standard deviations are given in Tables 5 and 6. The standard deviations for the bond lengths based on the results of the least-squares refinement range from 0·007 to 0·013 Å. No attempt has been made to correct bond lengths for the effect of thermal motion. Most bond lengths (Fig. 3) in this structure are quite normal (Sutton, 1965), but a few require comment. C(6)–C(7) (1·61 Å) is significantly ($>7\sigma$) longer than the average value of the other $C(sp^3)$–$C(sp^3)$ bonds in the structure. This effect is probably due to the considerable internal strain involved in the *trans*-configuration of the two five-membered rings. Naturally occurring molecules containing *trans*-fused five-membered rings have not been reported before. The C(1)–C(11) bond is about 5σ shorter than the mean $C(sp^3)$–$C(sp^3)$ value, 1·54 Å. The two $C(sp^3)$–$C(sp^2)$ bonds have bond distances of 1·49 and 1·50 Å, in good agreement with usually observed values (Lide, 1962). The departure from the ordinary envelope form (Table 7) of the five-membered rings is presumably an effect of the molecular strain. Among the possible four-atom planes for the five-membered ring A (Fig. 3) the two sets C(1), C(2), C(3), C(4) and C(2), C(3), C(4), C(5) exhibit the smallest deviation from their respective mean planes. C(5) and C(1) have deviations of 0·665 and 0·666 Å respectively. The atoms C(5), C(6), C(7)

Table 5. *Bond distances between non-hydrogen atoms with estimated standard deviations in parentheses*

C(1)–C(2)	1·550 (10) Å
C(1)–C(5)	1·537 (10)
C(1)–C(10)	1·556 (10)
C(1)–C(11)	1·493 (9)
C(2)–C(3)	1·570 (12)
C(2)–C(12)	1·539 (12)
C(3)–C(4)	1·533 (13)
C(4)–C(5)	1·531 (11)
C(5)–C(6)	1·558 (10)
C(6)–C(7)	1·611 (10)
C(6)–C(13)	1·540 (12)
C(6)–C(14)	1·512 (11)
C(7)–C(8)	1·488 (10)
C(7)–C(11)	1·547 (11)
C(8)–C(9)	1·499 (10)
C(8)–O(15)	1·241 (9)
C(9)–C(10)	1·526 (10)
C(9)–Br	1·934 (7)

* The absolute configuration of the sesquiterpene follows from ORD and CD data of the norketone (Norin *et al.*, 1973).



(*a*) (*b*)

Fig. 1. (*a*) The stereochemistry of (I) the α-bromonorketone of 2,5-diepi-β-cedrene, $R_1 = H$, $R_2 = Br$, $R_3 = O$; (II) 2,5-diepi-β-cedrene, $R_1 = R_2 = H$, $R_3 = CH_2$. (*b*) The stereochemistry of β-cedrene.

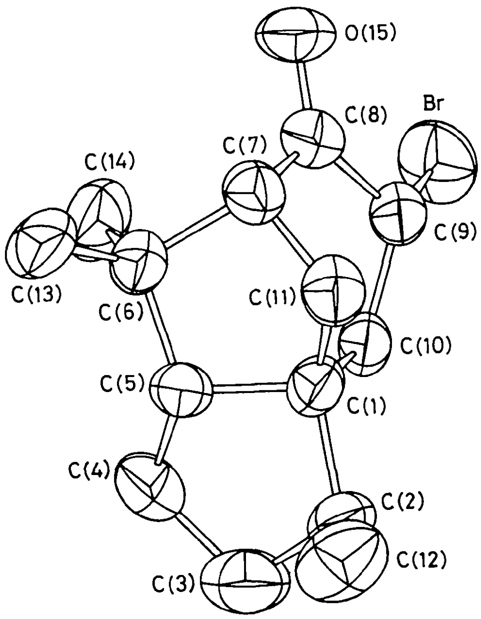


Fig. 2. A perspective view of the α-bromonorketone of (+)-2,5-diepi-β-cedrene.

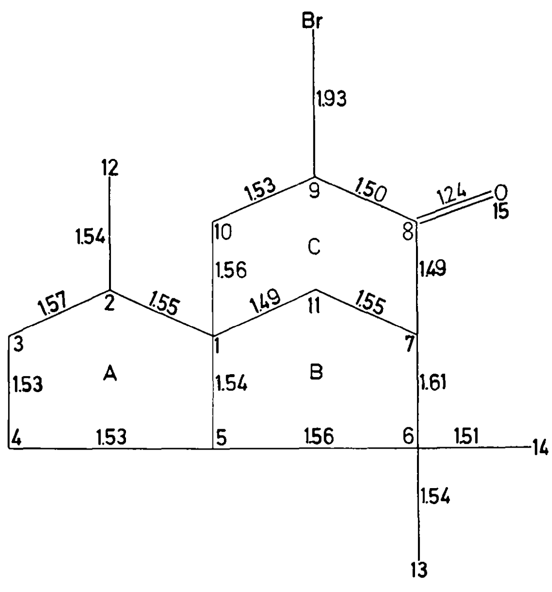


Fig. 3. Interatomic distances in $C_{14}H_{21}BrO$.

and C(11) of ring *B* are coplanar within ±0·069 Å and C(1) deviates by 0·763 Å from the mean plane. The six-membered ring *C* has a distorted boat conformation with atoms C(8), C(9) and C(11) displaced below the plane of the other three atoms. The intermolecular packing arrangement is shown projected along the *c* axis in Fig. 4. The intermolecular distances given in Tables 8 and 9 are normal van der Waals contacts. No suitable hydrogen donors for hydrogen bond formation are available.

Table 6. *Interatomic angles with estimated standard deviations in parentheses*

C(2)—C(1)—C(5)	101·0 (6)°
C(2)—C(1)—C(10)	107·8 (6)
C(2)—C(1)—C(11)	125·9 (6)
C(5)—C(1)—C(10)	112·4 (6)
C(5)—C(1)—C(11)	98·8 (6)
C(10)-C(1)—C(11)	110·0 (6)
C(1)—C(2)—C(3)	102·4 (6)
C(1)—C(2)—C(12)	113·9 (7)
C(3)—C(2)—C(12)	112·0 (7)
C(2)—C(3)—C(4)	108·7 (7)
C(3)—C(4)—C(5)	101·8 (7)
C(1)—C(5)—C(6)	106·8 (6)
C(4)—C(5)—C(1)	104·0 (6)
C(4)—C(5)—C(6)	127·2 (6)
C(5)—C(6)—C(7)	100·1 (5)
C(5)—C(6)—C(13)	109·0 (6)
C(5)—C(6)—C(14)	114·8 (7)
C(7)—C(6)—C(13)	106·6 (7)
C(7)—C(6)—C(14)	114·4 (6)
C(13)-C(6)—C(14)	111·1 (7)
C(6)—C(7)—C(8)	108·3 (6)
C(6)—C(7)—C(11)	104·7 (6)
C(8)—C(7)—C(11)	109·0 (6)
C(7)—C(8)—C(9)	114·2 (6)
C(7)—C(8)—O(15)	123·8 (7)
C(9)—C(8)—O(15)	122·0 (7)
C(8)—C(9)—C(10)	113·2 (6)
C(8)—C(9)—Br	113·3 (5)
C(10)-C(9)—Br	110·6 (5)
C(9)—C(10)-C(1)	112·8 (6)
C(1)—C(11)-C(7)	101·2 (6)

Table 7. *Least-squares planes and deviations*

The planes are described in terms of axes (m,n,p) having $m\|\mathbf{a}$, $n\|\mathbf{b}$ and $p\|\mathbf{c}$. The atoms indicated with asterisks were omitted from the calculations of the least-squares plane.

Plane *A*(1)	$0·7687m+0·4268n+0·4763p=12·0087$
Plane *A*(2)	$0·5612m+0·3643n+0·7432p=15·3125$
Plane *B*	$0·8052m+0·4232n+0·4153p=12·0145$
Plane *C*	$-0·5216m+0·8357n+0·1720p=1·3077$

Plane *A*(1)		Plane *A*(2)	
C(1)	−0·050 Å	C(1)*	−0·666 Å
C(2)	0·079	C(2)	−0·058
C(3)	−0·081	C(3)	0·090
C(4)	0·053	C(4)	−0·090
C(5)*	0·665	C(5)	0·057

Plane *B*		Plane *C*	
C(1)*	−0·763 Å	C(1)	0·000 Å
C(5)	−0·047	C(7)	0·000
C(6)	0·069	C(8)*	−0·199
C(7)	−0·069	C(9)*	−0·621
C(11)	0·047	C(10)	0·000
		C(11)*	−0·825

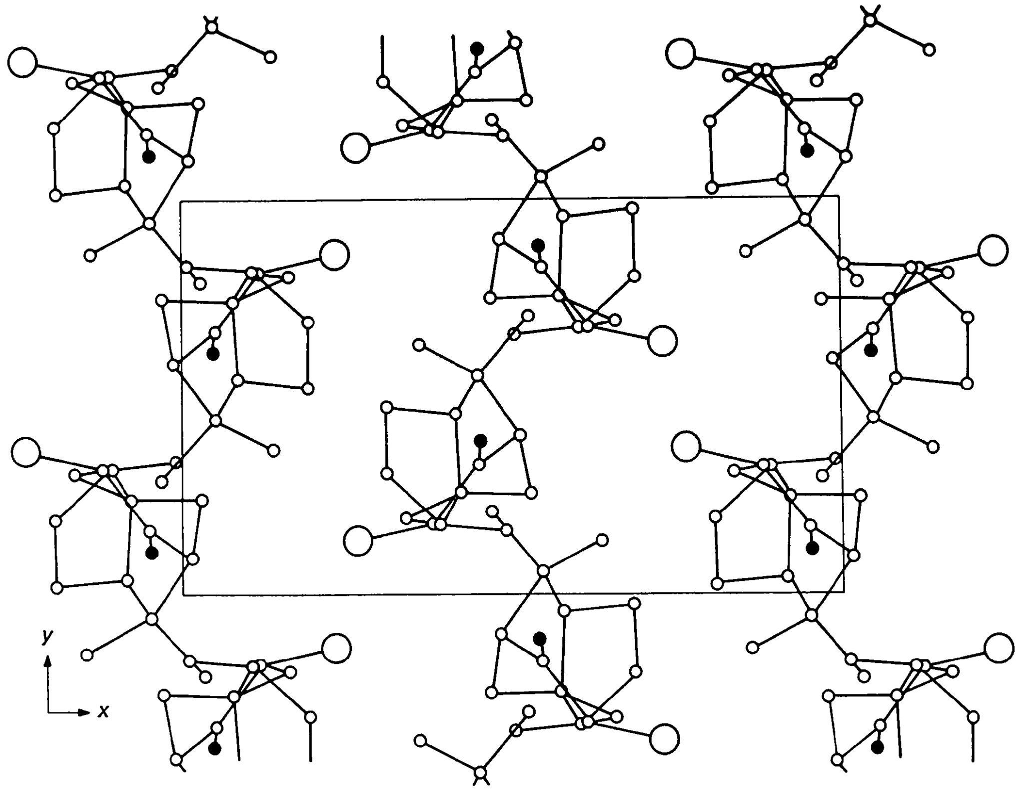


Fig. 4. The structure in projection along the c axis. ○ carbon ● oxygen ○ bromine

Table 8. *Intermolecular distances to the bromine atom*

Code for symmetry-related atoms.

Superscript		Superscript	
None	$x,\ y,\ z$	iii	$-\frac{1}{2}+x,\ \frac{1}{2}-y,\ 2-z$
i	$\frac{1}{2}-x,\ 1-y,\ -\frac{1}{2}+z$	iv	$1-x,\ -\frac{1}{2}+y,\ \frac{3}{2}-z$
ii	$\frac{1}{2}-x,\ -y,\ -\frac{1}{2}+z$		

Br···C(4^{i})	3·92 Å	Br···C(3^{ii})	3·78 Å
Br···C(2^{ii})	3·74	Br···C(12^{iii})	3·89

Table 9. *Intermolecular contacts involving carbon and oxygen*

C(8)···O(15^{iv})	3·69 Å	O(15)···C(13^{iv})	3·60 Å
C(9)···O(15^{iv})	3·37	O(15)···C(14^{iv})	3·68

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