serve, à ces niveaux, des distances respectives de 3,41 et 3,18 Å bien plus courtes que les distances de van der Waals correspondantes 3,80 et 3,57 Å.

Lorsqu'une molécule est en orientation anormale, (Fig. 6), les contacts les plus courts restent de même nature, Br$\cdots$S et Br$\cdots$C(5) deviennent respectivement 3,35 et 3,41 Å, le contact van der Waals S$\cdots$CH$_3$ est remplacé par un contact de van der Waals CH$\cdots$CH$_3$. Les analogies de contact, dans le cas d'une molécule en orientation normale et d'une molécule retournée, justifient le désordre moléculaire observé.

Il est à remarquer, pour le dérivé diisopropylé, les interactions importantes sont analogues à celles observées ici. Les distances Br$\cdots$S et Br$\cdots$C(5) valent respectivement 3,53 et 3,51 Å, cela explique que, malgré une pseudosymétrie moins grande des molécules, ce désordre soit encore observé.

Conclusion

De nombreux composés organiques présentent un désordre moléculaire à l'état cristallin. Nos résultats montrent qu'une étude poussée des séries de Fourier différence permet d'une part, de déterminer le degré de désordre et, d'autre part, d'atteindre une géométrie moléculaire acceptable. Il a été important de pouvoir émettre une hypothèse de départ raisonnable sur le désordre, et ensuite de trouver le processus d'affinement qui permet d'obtenir ce résultat. Nous pensons que ce processus peut être appliqué plus généralement dans le cas de structures où il existe un désordre statique et où le nombre de paramètres d'affinement n'est pas prohibitif.

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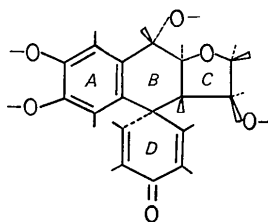# The Crystal Structure of Athrotaxin

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The crystal structure of athrotaxin has been solved by a non-centrosymmetric direct method and refined to an R index of 0·044. The space group is $P2_12_12_1$ with four formula units of $C_{17}H_{16}O_6.H_2O$ per unit cell, and lattice parameters $a = 15·263$, $b = 6·960$, $c = 14·529$ Å. Athrotaxin is a naturally occurring phenol isolated from the heartwood of the Tasmanian conifer *Athrotaxis selaginoides* Don. (Cupressales, Taxodiaceae)

Ring B is in the *trans* configuration with respect to ring C, and rings B and D are connected in a *spiro* junction. All the hydrogen atoms are drawn to indicate the stereochemistry.

Introduction

A number of related, easily oxidizable phenols have been isolated from the heartwood of the Tasmanian Conifer *Athrotaxis selaginoides* Don. (Cupressales, Taxodiaceae) (Erdtman & Vorbrüggen, 1960). All these compounds belong to a new family of natural products called conioids (Daniels, Erdtman, Nishimura, Norin, Kierkegaard & Pilotti, 1971). One of these phenolic substances, a strongly levorotatory compound called athrotaxin, has the composition $C_{17}H_{16}O_6.H_2O$. Structural studies of this compound by spectroscopic and chemical methods had been carried out but all attempts to determine a complete skeletal

structure had been unsuccessful. An X-ray analysis of athrotaxin was therefore undertaken.

Experimental

Weissenberg photographs of this compound exhibited axial extinctions only, consistent with the requirements of space group $P2_12_12_1$.

The X-ray intensity data were collected on a Siemens Automatic four-circle diffractometer. A crystal of irregular shape with approximate dimensions $0.309 \times 0.248 \times 0.027$ mm (along the cell axes a, b and c) was mounted with the b axis coincident with the φ axis of the diffractometer. The intensities of 1792 independent reflexions with $\sin \theta/\lambda < 0.61$ were measured by the θ–2θ scanning technique with monochromated Cu $K\alpha$ radiation. Each reflexion was measured twice and stationary background measurements were made at both ends of the scan range of $1.5°$. The diffractometer automatically selects a measuring time up to a preset maximum or inserts attenuators (nickel) if appropriate so as to achieve similar counting statistics for all but the weakest reflexions.

The intensities were corrected for Lorentz–polarization and absorption ($\mu = 9.79$ cm^{-1}), and were approximately scaled to the absolute values by means of a Wilson plot. Normalized structure factor magnitudes were derived.

Table 1. Crystal data

Lattice constants	$a =$ 15·263 (5) Å
	$b =$ 6·960 (5)
	$c =$ 14·529 (5)
Cell volume	$V = 1543·4$ Å^3
Density (X-ray)	$d =$ 1.437 g.cm^{-3}
Molecules per unit cell	$Z =$ 4
Space group	$P2_12_12_1$

Solution and refinement

The phase determination was carried out by application of the $\sum_1$, $\sum_2$ and 'weighted sum' formulae (Karle & Karle, 1966). To implement the sum-of-angles formula, four phases were assigned to specify the origin and enantiomorph (Hauptman & Karle, 1956). It was necessary to assign phases to some other reflexions in order to proceed with the phase determination. One general reflexion, treated as a variable, was given all the trial values: 0, π, $\pm \pi/4$, $\pm \pi/2$, $\pm 3\pi/4$. Another starting phase was evaluated with the $\sum_1$ relation. This reflexion had a sign probability of 0·97.

The six phases listed in Table 2 were extended and refined by use of the $\sum_2$ and 'weighted sum' formulae. This was accomplished by using a program, written by R. Norrestam (1971), for the IBM 1800 computer.

$$\varphi_h \simeq \langle \varphi_k + \varphi_{h-k} \rangle_{k_r} \tag{1}$$

$$\varphi_h \simeq \frac{\sum_{k_r} |E_k E_{h-k}| \, (\varphi_k + \varphi_{h-k})}{\sum_{k_r} |E_k E_{h-k}|} \tag{2}$$

Table 2. Phase assignments for specifying the origin and implementing equation (1)

h	φ_h	E_h	
11 3 0	$\pi/2$	3·68	origin and enantiomorph
0 4 9	0	3·30	
0 1 3	$\pi/2$	2·96	
14 0 5	$\pi/2$	3·00	
0 6 4	π	2·65	Σ_1
12 2 5	$\begin{cases} 0, \pi \\ \pm \pi/2, \pm \pi/4, \pm 3\pi/4 \end{cases}$	2·82	variable

Only reflexions with $|E_h| > 1.5$ and strong triple-phase relationships were used in the formulae (1) and (2). A phase was not accepted unless it entered into at least three combinations per formula (1) and had a standard deviation less than $\pi/6$ radians.

Since eight trial phase values were given to a general reflexion, the phase determining procedure yielded eight possible solutions. For the correct set of phases a total of 138 phases were determined. An E map based on these phases revealed the positions of 15 atoms. The remainder of the structure was obtained from difference syntheses. The number of phase values determined in the correct set was larger than in any other. Moreover, the largest number of triple-phase relationships was used in the solution which gave the correct set of phases. The reflexion 12,2,5 (Table 2) had a phase value of $-\pi/4$ in the correct solution.

The atomic parameters were refined by the full-matrix least-squares technique (Gantzel, Sparks & Trueblood, 1966) with isotropic temperature factors for the non-hydrogen atoms. The scattering factor curves used for oxygen and carbon are those given by Freeman (1959). 1542 reflexions were used in the refinement and Hughes's (1941) weighting procedure with $F_o$min $= 1.63$ was applied. The R index fell to 0·118. Anisotropic refinement of the non-hydrogen atoms resulted in an R index of 0·07. A difference map was computed and 16 of the 18 hydrogen atoms were located. After introduction of the hydrogen atoms into the least-squares analysis with fixed isotropic temperature factors ($B = 3.5$ Å^2), R was reduced to 0·044. The scattering factors used for hydrogen were those given by Stewart, Davidson & Simpson (1965).

The refinement of the structure was continued until changes in coordinates of non-hydrogen atoms upon successive least-squares cycles were less than five per cent of their standard deviations. Observed and calculated structure factors are given in Table 3.

Results and discussion of the structure

The bond lengths and bond angles, uncorrected for thermal motion, were computed from the refined coordinates given in Tables 4(a) and 5, and are listed in Tables 6 and 7. The bond distances for the molecule are displayed in Fig. 1. The standard deviations for the bond lengths based on the results of the least-squares refinement range from 0·003 to 0·004 Å. The

mean C–C distance in the benzene ring is 1·394 Å, which is in good agreement with accepted values. The two C–O single bond lengths between an oxygen atom and an sp^2-hybridized carbon atom agree well with the value $1·34 \pm 0·02$ Å suggested by Lide (1962) for such bonds. The mean value of 1·426 Å for the $C(sp^3)$–O single bond lengths is in accordance with the average

value of $1·426 \pm 0·005$ Å (Sutton, 1965). Effects of conjugation are apparent in the C(9)–C(10) and C(10)–
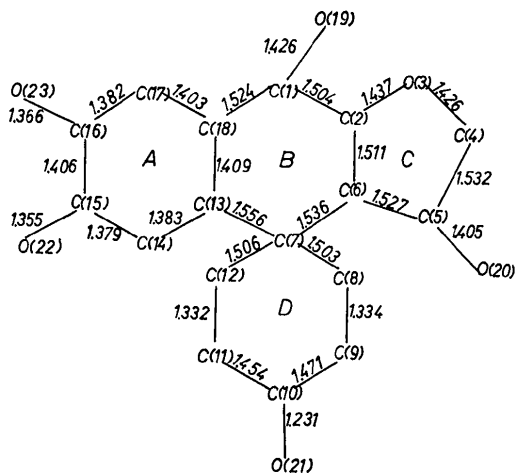

Fig. 1. Interatomic distances (in Å).

Table 4. *Atomic coordinates and thermal parameters*

(a) Fractional atomic coordinates ($\times 10^4$) for non-hydrogen atoms with their standard deviations

	x	y	z
C(1)	3948 (2)	2686 (4)	2801 (2)
C(2)	3460 (2)	4541 (4)	2663 (2)
O(3)	3826 (2)	5688 (3)	1936 (2)
C(4)	3143 (3)	6911 (6)	1614 (3)
C(5)	2261 (2)	5999 (4)	1867 (2)
C(6)	2544 (2)	4122 (4)	2323 (2)
C(7)	1958 (2)	3213 (4)	3064 (2)
C(8)	1668 (2)	4625 (4)	3784 (2)
C(9)	841 (2)	4815 (4)	4067 (2)
C(10)	136 (2)	3647 (4)	3662 (2)
C(11)	367 (2)	2426 (5)	2888 (2)
C(12)	1194 (2)	2229 (4)	2608 (2)
C(13)	2502 (2)	1643 (4)	3569 (2)
C(14)	2062 (2)	503 (4)	4197 (2)
C(15)	2481 (2)	−910 (4)	4697 (2)
C(16)	3377 (2)	−1237 (4)	4537 (2)
C(17)	3824 (2)	−83 (4)	3921 (2)
C(18)	3410 (2)	1407 (4)	3437 (2)
O(19)	4793 (1)	3110 (3)	3168 (2)
O(20)	1722 (2)	5628 (4)	1104 (2)
O(21)	−617 (2)	3738 (4)	3962 (2)
O(22)	2080 (2)	−2016 (3)	5339 (2)
O(23)	3815 (2)	−2662 (3)	4992 (2)
O(24)	4580 (2)	757 (4)	550 (2)

Table 3. *Structure factors*

Each group of three columns contains k, $10|F_o|$ and $10|F_c|$, and is headed by the values of h and l common to the group.

Table 4 (cont.)

(b) Thermal parameters.

The β values refer to the temperature factor expression

$$\exp\left[-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+hk\beta_{12}+hl\beta_{13}+kl\beta_{23})10^{-5}\right]$$

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
C(1)	180	1404	363	−71	21	−157
C(2)	204	1302	384	−178	36	−22
O(3)	223	1977	570	−280	35	588
C(4)	298	2385	717	−217	−143	1256
C(5)	251	1411	384	24	−22	−64
C(6)	197	1232	342	−60	−5	−156
C(7)	179	1176	313	−95	5	−140
C(8)	236	1370	354	−65	−23	−307
C(9)	280	1351	416	76	86	−335
C(10)	214	1347	466	−17	39	37
C(11)	210	1559	417	−239	−69	−240
C(12)	244	1320	343	−157	−66	−223
C(13)	189	1326	281	50	1	−165
C(14)	194	1584	371	72	45	−3
C(15) ·	240	1398	298	3	−5	−150
C(16)	266	1332	333	235	−34	−99
C(17)	197	1579	377	165	62	−110
C(18)	190	1229	321	35	−3	−201
O(19)	176	1604	584	−20	−85	−206
O(20)	358	1660	535	174	−325	−123
O(21)	250	2172	693	123	246	460
O(22)	266	1785	425	70	−76	−299
O(23)	286	1795	568	379	−150	−567
O(24)	249	2670	689	−65	−92	876

Table 5. *Fractional coordinates for hydrogen atoms* $(\times 10^3)$

	Bonded to	x	y	z
H(1)	C(1)	406	214	217
H(2)	C(2)	344	526	320
H(3)	C(4)	324	685	82
H(4)	C(5)	199	694	225
H(5)	O(20)	136	522	92
H(6)	C(6)	259	305	184
H(7)	C(8)	216	543	406
H(8)	C(9)	65	567	465
H(9)	C(11)	−11	186	252
H(10)	C(12)	139	150	204
H(11)	C(14)	152	78	428
H(12)	O(22)	155	−170	541
H(13)	O(23)	346	−333	531
H(14)	C(17)	444	−28	384
H(15)	O(24)	479	−19	96
H(16)	O(24)	494	153	31

Table 6. *Bond distances with standard deviations*

C(1)—C(2)	1·504 (4) Å
C(2)—O(3)	1·437 (3)
O(3)—C(4)	1·426 (4)
C(4)—C(5)	1·532 (4)
C(5)—C(6)	1·527 (4)
C(6)—C(2)	1·511 (3)
C(6)—C(7)	1·536 (3)
C(7)—C(8)	1·503 (3)
C(8)—C(9)	1·334 (4)
C(9)—C(10)	1·471 (4)
C(10)-C(11)	1·454 (4)
C(11)-C(12)	1·332 (4)
C(12)-C(7)	1·506 (3)
C(7)—C(13)	1·556 (3)
C(13)-C(14)	1·383 (3)
C(14)-C(15)	1·379 (4)
C(15)-C(16)	1·406 (3)
C(16)-C(17)	1·382 (4)
C(17)-C(18)	1·403 (2)
C(18)-C(1)	1·524 (3)
C(13)-C(18)	1·409 (3)
C(1)—O(19)	1·426 (3)
C(5)—O(20)	1·405 (3)
C(10)-O(21)	1·231 (3)
C(15)-O(22)	1·355 (3)
C(16)-O(23)	1·366 (3)

Table 7. *Interatomic angles with standard deviations*

C(1)—C(2)—O(3)	112·5 (0·2)°
C(1)—C(2)—C(6)	109·7 (0·2)
C(2)—O(3)—C(4)	106·8 (0·3)
O(3)—C(4)—C(5)	108·5 (0·3)
C(4)—C(5)—C(6)	102·2 (0·3)
C(5)—C(6)—C(2)	103·8 (0·2)
C(6)—C(2)—C(3)	103·1 (0·2)
C(2)—C(6)—C(7)	112·9 (0·2)
C(5)—C(6)—C(7)	119·5 (0·2)
C(6)—C(7)—C(8)	113·0 (0·2)
C(6)—C(7)—C(12)	109·3 (0·2)
C(7)—C(8)—C(9)	123·9 (0·3)
C(8)—C(9)—C(10)	121·0 (0·3)
C(9)—C(10)-C(11)	117·1 (0·3)
C(10)-C(11)-C(12)	121·8 (0·3)
C(11)-C(12)-C(7)	123·5 (0·3)
C(12)-C(7)—C(13)	107·6 (0·2)
C(12)-C(7)—C(8)	112·1 (0·2)
C(6)—C(7)—C(13)	108·0 (0·2)
C(7)—C(13)-C(18)	122·9 (0·2)
C(7)—C(13)-C(14)	117·1 (0·2)
C(13)-C(7)—C(8)	106·7 (0·2)
C(13)-C(14)-C(15)	122·1 (0·3)
C(14)-C(15)-C(16)	118·6 (0·3)
C(15)-C(16)-C(17)	119·6 (0·3)
C(16)-C(17)-C(18)	122·1 (0·3)
C(17)-C(18)-C(13)	117·5 (0·3)
C(17)-C(18)-C(1)	119·5 (0·2)
C(13)-C(18)-C(1)	123·0 (0·2)
C(18)-C(1)—C(2)	108·4 (0·2)
C(18)-C(1)—O(19)	112·5 (0·2)
O(19)-C(1)—C(2)	108·7 (0·2)
C(4)—C(5)—O(20)	113·7 (0·3)
O(20)-C(5)—C(6)	110·5 (0·3)
C(9)—C(10)-O(21)	120·9 (0·3)
O(21)-C(10)-C(11)	122·1 (0·3)
C(14)-C(15)-O(22)	123·9 (0·3)
O(22)-C(15)-C(16)	117·5 (0·3)
C(15)-C(16)-O(23)	120·9 (0·3)
O(23)-C(16)-C(17)	119·6 (0·3)

C(11) bonds which are adjacent to double bonds. Their bond lengths are appreciably shorter than single bond values. Furthermore the two C–C bonds adjacent to C=C have values ~1·504 Å, as compared with the mean value of 1·522 Å for C–C bonds adjacent to saturated carbon atoms. The two C–C single bonds next to an aromatic bond have values of 1·524 and 1·556 Å; the long bond is associated with a fully substituted carbon atom at C(7). As was pointed out by Hall & Maslen (1965), the C–C single bonds of fully substituted carbon atoms tend to be lengthened. The carbonyl distance C(10)–O(31) at 1·231 Å is in the range observed for ketones.

The ring systems, molecular configurations and the orientations and relative magnitudes of the thermal

ellipsoids [*cf.* Table 4(*b*)] are shown in Fig. 2. The planarity and conformation of each ring can be seen in Table 8.

Table 8. *Least-squares planes and deviations*

The planes are described in terms of axes (*m*, *n*, *p*) having $m\|a$, $n\|b$ and $p\|c$.

Plane *A*: $0.2068m + 0.6499n + 0.7314p = 5.3424$
Plane *B*: $0.1726m + 0.6322n + 0.7553p = 5.2940$
Plane *C*: $0.0033m + 0.4653n + 0.8851p = 4.3426$
Plane *D*: $-0.1354m + 0.7381n - 0.6610p = -1.6042$

Plane *A*		Plane *B*	
Atom	Deviation	Atom	Deviation
C(13)	−0·017 Å	C(1)	0·002 Å
C(14)	−0·004	C(2)*	0·538
C(15)	0·020	C(6)*	−0·261
C(16)	−0·015	C(7)	−0·002
C(17)	−0·006	C(13)	0·005
C(18)	0·022	C(18)	−0·005

Plane *C*		Plane *D*	
Atom	Deviation	Atom	Deviation
C(2)*	0·570 Å	C(7)*	−0·092 Å
O(3)	0·009	C(8)	0·002
C(4)	−0·013	C(9)	−0·002
C(5)	0·012	C(10)*	−0·067
C(6)	−0·008	C(11)	0·002
		C(12)	−0·002
		O(21)*	−0·153

* These atoms are not included in the least-squares planes.
Angles between planes: $B\wedge C$ 15·6°, $B\wedge D$ 86·8°

Ring *B* is in the *trans* configuration with respect to ring *C*. The five-membered ring *C* is in the shape of an envelope with four atoms coplanar within 0·013 Å and one atom deviating from this plane by 0·57 Å. Ring *B* is slightly puckered with two atoms significantly out of the plane of the other four. As required by the
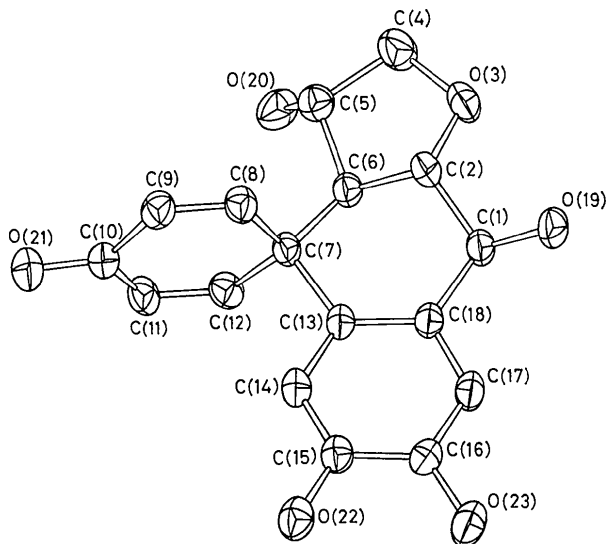
adjacent aromatic ring, C(18), C(13), C(1) and C(7) are coplanar. C(6) and C(2), however, deviate by 0·26 and 0·54 Å from this plane.

Rings *B* and *D* are connected in a *spiro* junction, *i.e.* the two rings have only one atom in common. Ring *D* is boat shaped and is bent towards the phenyl ring. The angle between *B* and *D* is 86·8°.

The molecular packing is determined by the hydrogen bonding network indicated by the dashed lines in Fig. 3. The hydrogen atom coordinates are given in Table 5 and a proposed hydrogen bonding scheme is given in Table 9.

In Tables 9 and 10, atoms belonging to different asymmetric units are labelled as follows:

Superscript	Coordinates
none	x, y, z
i	$x, y+1, z$
ii	$-x, y+\frac{1}{2}, \frac{1}{2}-z$
iii	$x+\frac{1}{2}, \frac{1}{2}-y, 1-z$
iv	$\frac{1}{2}-x, -y, z+\frac{1}{2}$
v	$1-x, y+\frac{1}{2}, \frac{1}{2}-z$

Table 9. *Proposed hydrogen bonding scheme*

O(23ᵛ) · · · H–O(24)	2·799 Å
O(24ⁱᵛ) · · · H–O(22)	2·699
O(20ⁱᵛ) · · · H–O(23)	2·747
O(21ⁱⁱ) · · · H–O(20)	2·746
O(19) · · · · H–O(24ᵛ)	2·789
O(3) · · · · · H–O(19ᵛ)	2·703

Table 10. *Intermolecular distances* < 3·8 Å *between non-hydrogen atoms*

C(4) · · · · · O(24ⁱ)	3·791 Å
C(8) · · · · · C(15ⁱ)	3·600
C(8) · · · · O(22ⁱ)	3·311
C(9) · · · · O(22ⁱ)	3·444
O(20) · · · C(11ⁱⁱ)	3·725
O(20) · · · C(10ⁱⁱ)	3·546
C(5) · · · · O(21ⁱⁱ)	3·374
O(20) · · · O(21ⁱⁱ)	2·746
C(10) · · · C(12ⁱⁱ)	3·706
O(21) · · · C(11ⁱⁱ)	3·736
C(10) · · · C(11ⁱⁱ)	3·546
O(21) · · · C(12ⁱⁱ)	3·447
O(20) · · · C(10ⁱⁱ)	3·546
C(17) · · · O(21ⁱⁱⁱ)	3·325
C(16) · · · O(21ⁱⁱⁱ)	3·183
O(23) · · · O(21ⁱⁱⁱ)	3·243
C(15) · · · O(24ⁱᵛ)	3·382
C(14) · · · O(24ⁱᵛ)	3·303
O(22) · · · C(5ⁱᵛ)	3·690
O(22) · · · O(20ⁱᵛ)	3·301
O(22) · · · O(3ⁱᵛ)	3·719
O(22) · · · C(6ⁱᵛ)	3·283
O(23) · · · O(20ⁱᵛ)	2·747
O(22) · · · O(24ⁱᵛ)	2·699
C(4) · · · · O(19ᵛ)	3·275
O(24) · · · O(23ᵛ)	2·799
O(19) · · · O(24ᵛ)	2·789
C(4) · · · · O(19ᵛ)	3·275
O(24) · · · C(16ᵛ)	3·757
O(3) · · · · C(1ᵛ)	3·690
O(3) · · · · O(19ᵛ)	2·703

Fig. 2. A perspective view of the molecule,

The intermolecular contacts less than 3·8 Å between pairs of non-hydrogen atoms are listed in Table 10. Some short C···O contacts are observed. [The normal van der Waals separation between a methyl carbon and an oxygen atom is 3·40 Å (Pauling, 1960).]

Fig. 3. The structure as seen in projection down the *b* axis.

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The Crystal Structure of Queen Substance, 9-Keto-*trans*-2-decenoic Acid, the Sex Pheromone of the Honeybee*

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The structure of 'queen substance', 9-keto-*trans*-2-decenoic acid, the sex pheromone of the honeybee, has been determined. The crystals are monoclinic, space group $P2_1/c$ with $a=9·584$ (9), $b=8·642$ (7), $c=13·371$ (12) Å, $\beta=96°58$ (4)', and $Z=4$. Intensities were measured with an automated diffractometer, using graphite monochromated Mo $K\alpha$ radiation. The structure was solved by the symbolic addition method. The atoms have unusually large anisotropic thermal parameters and possibly a small amount of disorder caused by occasional reversal of molecules. Bond length corrections are needed, because of the large thermal parameters, but could not be made for lack of a suitable model of correlated motion.

Introduction

Insect pheromones, or sex attractants, are an important class of biologically active substances currently

receiving intensive study. Most known pheromones are liquids at room temperature and thus are not easily studied by X-ray crystallography. The pheromone of the honeybee, 9-keto-*trans*-2-decenoic acid, however, is a solid at room temperature, and we have now determined its crystal structure. This compound is commonly referred to as 'queen substance'. The structural