four atoms, C(1), C(2), C(3), C(4) and C(3), C(4), C(5), C(6), form planar zigzag chains (planes *J* and *K*). These chains are twisted against each other by 43° around C(3)–C(4).

The planes *G* and *I* (phenyl rings) are almost parallel to each other with an angular deviation of 10°; and although the planes *G* and *H* can be regarded as equivalent, the latter is twisted along the boronic acid–phenyl ring axis. The angles included here are 39° (*H–G*) and 44° (*H–I*). This configuration affects the symmetry of the molecule significantly. If one assumes a similar configuration for the molecule in solution, then at least at elevated temperatures a degenerative transition caused by rotation of the phenyl rings *G* and *I* should be possible. Without this knowledge, a structure analysis of the compound by ^{13}C NMR spectroscopy based on the equivalence of C(1), C(2) and C(5), C(6) in the mannitol chain and the C atoms of the phenyl rings of planes *G* and *H* could have led to wrong conclusions. The results of ^{13}C NMR spectroscopic analysis will be reported elsewhere (Wulff, Zabrocki, Gupta, Kirfel & Will, 1977).

A stereoscopic view of the arrangement of the molecules in the unit cell, approximately along [001], is shown in Fig. 3.

References

GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* A**27**, 368–376.

JEFFREY, G. A. & KIM, H. S. (1970). *Carbohydr. Res.* **14**, 207–216.

JOHNSON, C. K. (1965). *ORTEP.* Oak Ridge National Laboratory Report ORNL-3794.

KUIVILLA, H. G., KEOUGH, A. E. & SOBOCZENSKI, E. J. (1954). *J. Org. Chem.* **19**, 780–783.

SUGIHARA, J. M. & BOWMAN, C. M. (1958). *J. Amer. Chem. Soc.* **80**, 2443–2446.

WULFF, G., ZABROCKI, A., GUPTA, A., KIRFEL, A. & WILL, G. (1977). In preparation.

ZABROCKI, K. (1971). Diplom Thesis, Univ. of Bonn.

ZACHARIASEN, W. H. (1963). *Acta Cryst.* **16**, 1139–1144.

Acta Cryst. (1977). B**33**, 641–649

The Crystal Structure of the Triterpene Oxide Campanulin. A Comparative Study on a Strained Hydrocarbon Ring System

BY FRODE MO

Department of Biological Structure, University of Washington, Seattle, Washington 98195, *USA and Institutt for røntgenteknikk,* Universitetet i Trondheim-NTH, N*-7034 *Trondheim-NTH, Norway*

(*Received* 24 *June* 1976; *accepted* 30 *July* 1976)

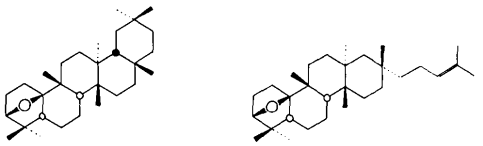
The structure of campanulin, $C_{30}H_{50}O$, was solved by a tangent-refinement procedure and refined by full-matrix least squares. The final *R* based on 2290 F_o corrected for absorption was 0·039; R_w was 0·046. Campanulin is a friedelan-type triterpene with *cis*-fused rings *D* and *E* in the chair form. The conformation of this part of the molecule is highly strained, as borne out by a number of long C–C bonds, large valency angles and small torsion angles. The electronic structure of rings *A*, *B* and *C* is in close agreement with that of baccharis oxide [Mo, *Acta Cryst.* (1973), B**29**, 1796–1807]. R.m.s. and maximum differences over 21 pairs of C–C and C–O bonds in the two structures are only 0·004 and 0·010 Å; corresponding figures for 37 pairs of valency angles are 0·69 and 1·6° respectively. The results indicate that the e.s.d.'s from the least-squares refinement are realistic estimates. Since packing forces appear to be of minor significance for the molecular conformation, it is also suggested that the parameters obtained in these studies are good approximations to those of the isolated molecules.

Introduction

A triterpene oxide isolated from various *Rhododendron* species (Rangaswami & Sambamurthy, 1961*a*; Arthur & Hui, 1961) and *Dendropanax trifidus* Makino (Kimura, Hashimoto & Agata, 1960) has been varyingly named campanulin, epoxyglutinane and dendropanoxide. Rangaswami & Sambamurthy (1961*b*) showed that campanulin and epoxyglutinane are identical compounds. From chemical and spectro-

* Present address.

scopic studies they proposed (I) or *D:B-friedo*-3β,10-epoxy-10β-oleanane for the correct structure of campanulin.



(I) (II)

The existence of a 3,10-oxide bridge in a triterpenoid molecule was first demonstrated in the structure analysis of baccharis oxide (II) (Mo, Anthonsen & Bruun, 1972). Mass spectra of baccharis oxide and campanulin indicated closely similar structures in the vicinity of the oxide bridge (Bruun & Anthonsen, 1973), thus lending support to formula I for campanulin. The conformation of baccharis oxide is largely determined by strong intramolecular, non-polar forces, in particular by a number of close contacts involving 1,3-diaxial methyl groups (Mo, 1973). Assuming (I) to be the correct formula for campanulin, a crystallographic study would provide valuable, independent evidence that the conformation and electronic structure of that part of the strained fused-ring system are negligibly or very little affected by differences in substitution at ring *D*.

During this work, White, Fayos & Clardy (1973) reported briefly on an X-ray study of campanulin. They establish (I) as its structure but give no bond lengths or angles. The present investigation, being based on more than twice their number of observations, was aimed primarily at a detailed study of the molecular structure and it was therefore carried through.

Experimental

Campanulin was isolated from *Rhododendron campanulatum* Don. Crystals grown from a mixture of methanol and chloroform were kindly supplied by Dr T. Bruun of the Organic Chemistry Laboratories of this University. Crystallographic data are: campanulin, $C_{30}H_{50}O$, F.W. 426·73, m.p. 206–207 °C; $a = 6{\cdot}302\,(4)$, $b = 13{\cdot}943\,(9)$, $c = 28{\cdot}925\,(6)$ Å at $21{\cdot}5 \pm 1$ °C; $D_x = 1{\cdot}115$ g cm^{-3} for $Z = 4$, λ(Cu $K\alpha_1$) = 1·5405 Å, μ(Cu $K\bar{\alpha}$) = 4·9 cm^{-1}; space group $P2_12_12_1$.

Lattice constants were determined from the setting angles of 12 high-angle reflexions and the determination was repeated once during data collection and once at the end. All cell axes increased significantly during the exposure, from 0·009 for *a* to 0·017 Å for *b*. The parameters given are mean values, and the errors reflect the observed changes. The standard deviations in any single measurement of cell axes were about 1:10^4.

A prismatic crystal 0·07 × 0·23 × 0·40 mm mounted with *a* tilted *ca* 2° from the diffractometer φ axis, was used for the X-ray measurements. The intensities of 2464 $\bar{h}kl$ reflexions (excluding space-group extinctions) were measured with Ni-filtered Cu $K\alpha$ radiation on a Picker FACS-1 diffractometer to a 2θ limit of 128°. The scan mode was $\omega/2\theta$ at 1° min^{-1} in 2θ and the basic scan range was 1·3°. Backgrounds were measured for 40 s at each end of the scan.

Two standard reflexions were measured at intervals of 30 reflexions. The intensities decreased by *ca* 3·4 and 7·7% and the data were scaled with a third-degree-polynomial fit to the average standard decay. Absorption coefficients were in the range 1·119 to 1·033 and the intensities were corrected before conversion to structure factors. Standard deviations were calculated as: $\sigma(F) = [\sigma_s^2(F) + cF^2]^{1/2}$ and $\sigma_s(F) = \frac{1}{2}F[\sigma(I)/I]$, where $\sigma(I)$ is based on counting statistics (Mo, 1973). The value $4{\cdot}5 \times 10^{-4}$ was used for *c*.

Structure determination and refinement

The structure was solved by the multisolution tangent-refinement method in a modified version of *TANNY* (Mo, 1972), designed to develop and refine phases within a set of reflexions with $|E|$ larger than some preset value by means of a weighted tangent formula. No limit is used for the number of Σ_2 triples to be generated.

In several applications of this program, refined phases for groups of reflexions shifted considerably when the number of $|E|$'s in the data was changed. These instabilities during phase development were traced back in many cases to 2-D reflexions in the starting set, obtained from Σ_1 relations, or accepted in the first phasing cycles. 2-D reflexions of the same zone frequently interact in Σ_2 triples, some of which may be grossly in error, probably because of increased overlap in projections. Phases from single relations of this kind should therefore be avoided (*e.g.* Karle, 1970*a*); however, single relations often have to be used in the early cycles. In general, only triples involving the largest $|E|$'s should be employed at this critical stage, a strategy which is corroborated by theoretical arguments (Hauptman, 1970; Karle, 1970*b*).

The tangent-refinement program was therefore modified to proceed in two steps. In the first, involving *m* cycles, only reflexions of $|E| \geq E_{\text{start}}$ (1·9–2·0) are considered and some 50 to 80 phases developed and added to the unrefined set of starting phases. In the second step the limit in $|E|$ is reduced to E_{stop} (1·6–1·7) and *n* more cycles of generation and refinement of *all* phases are carried through. Starting sets are examined by checking every Σ_2 relation in preliminary runs. If zonal

Table 1. *Final atomic parameters*

Thermal parameters, $U_{ij}(\times 10^4)$, are defined by: $\exp[-2\pi^2(U_{11}a^{*2}h^2 + U_{22}b^{*2}k^2 + U_{33}c^{*2}l^2 + 2U_{12}a^*b^*hk + 2U_{13}a^*c^*hl + 2U_{23}b^*c^*kl)]$. E.s.d.'s of the parameters appear in parentheses. The H atoms are identified by the number of the attached C atom.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O	0·4924 (3)	0·5676 (1)	0·4532 (1)	578 (10)	567 (10)	613 (10)	−217 (10)	−21 (9)	−106 (8)
C(1)	0·1887 (5)	0·5735 (2)	0·4089 (1)	798 (19)	400 (11)	498 (13)	69 (14)	−28 (14)	30 (11)
C(2)	0·1939 (6)	0·6618 (2)	0·4412 (1)	1237 (28)	425 (13)	609 (15)	103 (18)	−58 (19)	12 (12)
C(3)	0·3497 (5)	0·6287 (2)	0·4787 (1)	854 (20)	440 (12)	643 (15)	−127 (16)	−80 (16)	−129 (12)
C(4)	0·2461 (5)	0·5577 (2)	0·5128 (1)	698 (17)	512 (13)	446 (13)	10 (14)	−83 (13)	−89 (11)
C(5)	0·2048 (4)	0·4726 (2)	0·4788 (1)	400 (12)	448 (11)	413 (11)	−6 (11)	−24 (10)	−27 (10)
C(6)	0·2559 (4)	0·3726 (2)	0·4956 (1)	599 (15)	491 (12)	364 (11)	−15 (13)	57 (12)	49 (10)
C(7)	0·2209 (4)	0·2985 (2)	0·4571 (1)	547 (14)	419 (11)	397 (11)	−27 (12)	108 (11)	36 (9)
C(8)	0·2618 (3)	0·3375 (1)	0·4076 (1)	318 (11)	327 (9)	358 (10)	−6 (9)	18 (9)	47 (9)
C(9)	0·4367 (3)	0·4172 (2)	0·4079 (1)	325 (11)	407 (11)	394 (11)	−72 (10)	−2 (9)	26 (9)
C(10)	0·3328 (4)	0·5026 (2)	0·4349 (1)	435 (12)	391 (11)	421 (11)	−95 (11)	−47 (11)	−6 (9)
C(11)	0·4974 (4)	0·4463 (2)	0·3581 (1)	488 (13)	456 (12)	469 (12)	−180 (12)	40 (11)	30 (10)
C(12)	0·5244 (4)	0·3630 (2)	0·3249 (1)	456 (13)	493 (13)	429 (11)	−95 (12)	107 (11)	72 (11)
C(13)	0·3241 (3)	0·3009 (1)	0·3216 (1)	328 (10)	340 (9)	375 (10)	29 (10)	34 (9)	33 (8)
C(14)	0·2878 (3)	0·2563 (1)	0·3709 (1)	315 (10)	326 (9)	403 (10)	−19 (9)	61 (9)	32 (8)
C(15)	0·0829 (4)	0·1962 (2)	0·3680 (1)	417 (12)	420 (11)	482 (12)	−79 (11)	134 (11)	−12 (10)
C(16)	0·1065 (4)	0·1112 (2)	0·3352 (1)	641 (16)	420 (12)	649 (15)	−157 (13)	192 (14)	−90 (11)
C(17)	0·1989 (4)	0·1328 (2)	0·2866 (1)	569 (14)	430 (12)	561 (13)	−52 (12)	120 (12)	−137 (11)
C(18)	0·3581 (4)	0·2199 (1)	0·2851 (1)	380 (11)	392 (11)	440 (11)	43 (10)	81 (10)	−6 (9)
C(19)	0·3989 (4)	0·2531 (2)	0·2342 (1)	582 (15)	471 (12)	448 (12)	49 (13)	124 (11)	−46 (10)
C(20)	0·2218 (5)	0·2496 (2)	0·1962 (1)	849 (20)	711 (16)	403 (12)	199 (18)	−29 (14)	−93 (12)
C(21)	0·0785 (6)	0·1631 (2)	0·2032 (1)	839 (22)	866 (19)	612 (15)	−28 (19)	−102 (16)	−296 (15)
C(22)	0·0114 (5)	0·1463 (2)	0·2529 (1)	620 (16)	745 (18)	669 (15)	−157 (16)	6 (14)	−252 (14)
C(23)	0·3368 (6)	0·2413 (2)	0·1495 (1)	1228 (27)	876 (19)	469 (14)	145 (24)	41 (18)	−85 (15)
C(24)	0·0828 (7)	0·3400 (2)	0·1946 (1)	1315 (32)	909 (20)	589 (15)	428 (24)	−279 (21)	−160 (16)
C(25)	0·3265 (6)	0·0435 (2)	0·2715 (1)	945 (22)	423 (12)	901 (20)	−16 (16)	348 (19)	−138 (14)
C(26)	0·1386 (4)	0·3668 (1)	0·3073 (1)	450 (13)	433 (11)	405 (10)	104 (12)	−13 (10)	−13 (9)
C(27)	0·4677 (4)	0·1874 (2)	0·3847 (1)	473 (13)	460 (12)	488 (12)	103 (12)	5 (11)	51 (10)
C(28)	0·6446 (4)	0·3857 (2)	0·4318 (1)	361 (12)	723 (16)	604 (14)	3 (13)	−31 (11)	−42 (13)
C(29)	0·0422 (6)	0·5934 (2)	0·5355 (1)	956 (24)	724 (18)	705 (17)	171 (19)	91 (18)	−184 (15)
C(30)	0·4092 (6)	0·5344 (2)	0·5504 (1)	987 (24)	729 (17)	606 (16)	−30 (19)	−286 (18)	−127 (14)

	x	y	z	B (Å^2)		x	y	z	B (Å^2)
H(11)	0·250 (4)	0·587 (2)	0·379 (1)	4·7 (6)	H(222)	−0·061 (5)	0·084 (2)	0·258 (1)	5·9 (7)
H(12)	0·020 (5)	0·548 (2)	0·405 (1)	5·3 (6)	H(231)	0·458 (6)	0·293 (2)	0·146 (1)	8·1 (9)
H(21)	0·193 (5)	0·727 (2)	0·423 (1)	8·0 (8)	H(232)	0·215 (6)	0·243 (2)	0·126 (1)	9·1 (9)
H(22)	0·046 (5)	0·677 (2)	0·456 (1)	6·4 (7)	H(233)	0·453 (5)	0·191 (2)	0·151 (1)	6·4 (7)
H(31)	0·440 (5)	0·673 (2)	0·497 (1)	5·2 (6)	H(241)	0·158 (5)	0·390 (2)	0·197 (1)	6·1 (7)
H(51)	0·042 (4)	0·472 (2)	0·472 (1)	3·0 (4)	H(242)	0·001 (6)	0·344 (2)	0·163 (1)	8·1 (9)
H(61)	0·416 (5)	0·371 (2)	0·506 (1)	5·6 (6)	H(243)	−0·025 (5)	0·341 (2)	0·227 (1)	6·3 (7)
H(62)	0·146 (5)	0·365 (2)	0·523 (1)	5·1 (6)	H(251)	0·416 (5)	0·055 (2)	0·243 (1)	7·5 (8)
H(71)	0·332 (4)	0·252 (2)	0·465 (1)	5·0 (6)	H(252)	0·464 (6)	0·031 (2)	0·295 (1)	8·1 (9)
H(72)	0·064 (4)	0·274 (2)	0·457 (1)	3·7 (5)	H(253)	0·238 (6)	0·000 (2)	0·271 (1)	7·8 (8)
H(81)	0·121 (3)	0·371 (1)	0·398 (1)	1·8 (4)	H(261)	0·175 (4)	0·407 (2)	0·280 (1)	5·0 (6)
H(111)	0·619 (4)	0·482 (2)	0·359 (1)	4·3 (5)	H(262)	0·004 (4)	0·333 (2)	0·299 (1)	4·4 (5)
H(112)	0·396 (3)	0·485 (1)	0·346 (1)	2·2 (4)	H(263)	0·077 (4)	0·416 (2)	0·331 (1)	3·9 (5)
H(121)	0·558 (4)	0·395 (2)	0·293 (1)	4·7 (6)	H(271)	0·514 (4)	0·149 (2)	0·361 (1)	4·8 (6)
H(122)	0·638 (5)	0·314 (2)	0·334 (1)	6·0 (7)	H(272)	0·576 (4)	0·216 (2)	0·396 (1)	4·9 (6)
H(151)	−0·036 (3)	0·237 (1)	0·357 (1)	3·2 (4)	H(273)	0·430 (4)	0·147 (2)	0·414 (1)	4·6 (6)
H(152)	0·038 (4)	0·173 (2)	0·398 (1)	4·1 (5)	H(281)	0·736 (5)	0·359 (2)	0·409 (1)	5·8 (7)
H(161)	0·188 (6)	0·064 (2)	0·348 (1)	7·8 (8)	H(282)	0·697 (6)	0·444 (2)	0·443 (1)	8·5 (9)
H(162)	−0·025 (4)	0·078 (2)	0·333 (1)	3·9 (5)	H(283)	0·611 (5)	0·332 (2)	0·456 (1)	6·0 (7)
H(181)	0·504 (4)	0·196 (1)	0·294 (1)	3·5 (5)	H(291)	−0·061 (5)	0·608 (2)	0·512 (1)	7·6 (8)
H(191)	0·474 (5)	0·313 (2)	0·234 (1)	5·2 (6)	H(292)	0·046 (5)	0·658 (2)	0·549 (1)	5·3 (6)
H(192)	0·514 (4)	0·210 (2)	0·221 (1)	3·7 (5)	H(293)	−0·002 (6)	0·544 (2)	0·564 (1)	8·5 (9)
H(211)	−0·052 (5)	0·164 (2)	0·183 (1)	5·8 (7)	H(301)	0·547 (5)	0·498 (2)	0·533 (1)	6·6 (7)
H(212)	0·120 (5)	0·111 (2)	0·194 (1)	4·7 (6)	H(302)	0·465 (5)	0·593 (2)	0·567 (1)	6·4 (7)
H(221)	−0·061 (5)	0·200 (2)	0·265 (1)	5·6 (6)	H(303)	0·368 (5)	0·486 (2)	0·570 (1)	5·9 (7)

reflexions enter in the first few cycles *via* single Σ_2 relations confined to one zone, their $|E|$'s are set at a value below E_{start}. If still being phased from single relations in the second step, these reflexions are excluded from the data set. In actual runs values of $m = 6$–7 and $n = 4$–5 proved adequate for selecting one or a very small number of phase models based on their figures of merit. Only the corresponding starting sets need be tested finally with an E_{stop} of, *e.g.*, 1·4–1·5, m and n being increased as required. Figures of merit for the correct model tend to improve when the set of E's is increased.

Negative cosine invariants in violation of the tangent formula may be identified and the knowledge used with advantage in the phase-determination process (Hauptman, 1972). The modification of the usual multi-solution techniques employed in the present work is a defensive approach in that one seeks to avoid single phase indications from triples having a higher probability of being aberrant. This is especially desirable in the early stage during expansion of the starting set. The method has worked well with a number of structures of similar complexity.

The E map for the best phase model showed all 31 C and O atoms in the structure. Least-squares isotropic refinement of these atoms was based on all 2464 F with unit weights. At an R of 0·146, coordinates of the H atoms were determined from a ΔF map. All 50 H atoms were included with isotropic, and heavier atoms with anisotropic temperature factors. In the subsequent full-matrix least-squares refinement the variables were separated into three overlapping blocks; blocking was varied throughout the refinement. 163 reflexions with $\sigma(F) > F/2$ were given zero weight; later, another 11 very weak reflexions for which $F_c < F_o$ were also weighted zero. At the end of the refinement, average and maximum parameter shifts of C and O atoms were less than 0·01 and 0·15 of the e.s.d. respectively; corresponding figures for H are 0·04 and 0·30. The final R was 0·039 and $R_w\{=[\Sigma w(|F_o| - K|F_c|)^2/\Sigma wF_o^2]^{1/2}\}$ was 0·046, based on 2290 F_o with weights $w = 1/\sigma^2(F)$.* Positional and thermal parameters of the atoms are given in Table 1. Atomic form factors for C and O were those of Doyle & Turner (1968); the values of Stewart, Davidson & Simpson (1965) were used for H.

Results and discussion

Identical views of the structures of campanulin and baccharis oxide are presented in Fig. 1; the labelling of the atoms and rings in campanulin corresponds to the system used for baccharis oxide (Mo, 1973).

Molecular structure

The short unsaturated chain attached to C(17) in baccharis oxide is bent back in campanulin to form a chair-ring *cis*-fused to ring D about 17–18. Fig. 1 indicates that the conformation of the common ring structure is closely similar in the two molecules; the largest differences appear in the D rings, as expected. Endocyclic torsion angles, φ, of both structures are compared in Table 2. Fig. 2 is a collection of Newman projections along some of the bonds.

As in baccharis oxide, ring a is nearly a C_3(O) envelope and ring b with the *gem* dimethyl group at C(4) is more distorted toward the half-chair. The conformation about 4–5 is twisted by an average of about +16°

Table 2. *Endocyclic torsion angles* (°)

The torsion angle about a bond y–z, $\varphi(y,z)$, is calculated for the atomic sequence x–y–z–u, where x and u belong to the ring in question. The sign convention for φ is that of Klyne & Prelog (1960). Torsion angles of campanulin are in column I, corresponding values of baccharis oxide (Mo, 1973) in column II.

	Ring *a*			Ring *b*	
	I	II		I	II
1, 2	+3·1	+1·6	4, 5	+11·1	+9·7
2, 3	+32·1	+33·6	5,10	+23·8	+25·5
3, O	−56·2	−57·2	10, O	−51·0	−52·4
O,10	+57·7	+57·0	O, 3	+59·9	+60·5
10, 1	−37·0	−35·7	3, 4	−43·5	−42·8

	Ring *A*			Ring *B*	
	I	II		I	II
1, 2	+3·1	+1·6	5, 6	−56·1	−57·2
2, 3	−76·8	−75·5	6, 7	+31·0	+32·5
3, 4	+65·4	+66·7	7, 8	+30·9	+28·0
4, 5	+11·1	+9·7	8, 9	−67·1	−63·5
5,10	−81·4	−79·0	9,10	+42·2	+39·1
10, 1	+70·0	+70·3	10, 5	+17·2	+19·2

	Ring *C*			Ring *D*	
	I	II		I	II
8, 9	+41·3	+44·2	13,14	−62·5	−62·9
9,11	−43·4	−46·5	14,15	+64·9	+62·5
11,12	+57·5	+57·6	15,16	−49·4	−48·7
12,13	−63·5	−61·5	16,17	+29·8	+32·7
13,14	+58·9	+57·3	17,18	−29·0	−35·3
14, 8	−50·7	−51·3	18,13	+46·2	+52·0

	Ring *E*
	I
17,18	−42·3
18,19	+34·6
19,20	−35·2
20,21	+44·4
21,22	−58·0
22,17	+56·0

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32081 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

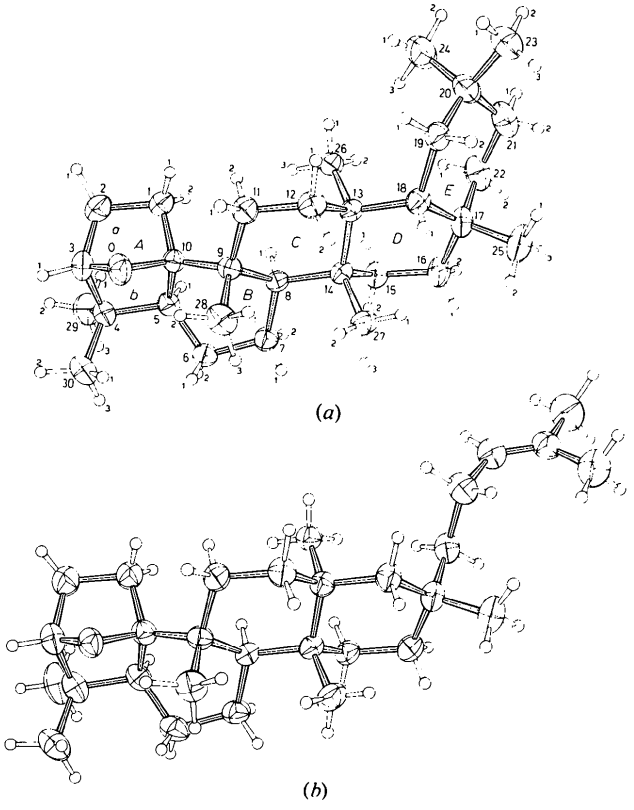


Fig. 1. Identical views of (*a*) campanulin and (*b*) baccharis oxide molecules with respect to a plane defined by atoms 2, 6 and 8. The numbering of H atoms in small numerals corresponds to the system used in Table 1.

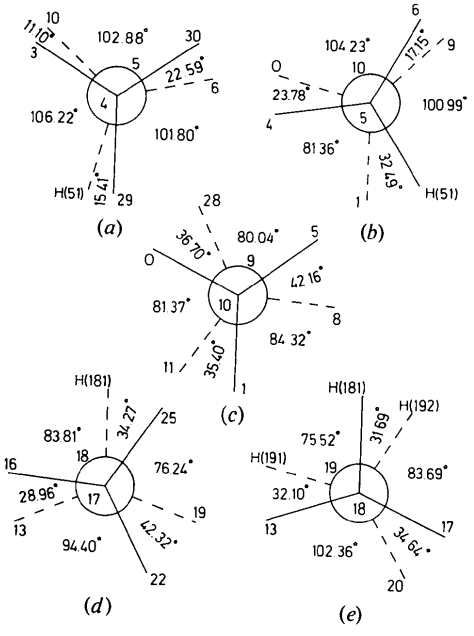


Fig. 2. Newman projections along the bonds (*a*) 4–5, (*b*) 5–10, (*c*) 10–9, (*d*) 17–18 and (*e*) 18–19.

from fully eclipsed in both structures [Fig. 2(*a*)]. The average and maximum differences in endocyclic torsion angles of rings *a*, *b* and *A* in the two triterpenes are only 1·2 and 2·4° respectively.

Endocyclic torsion angles $\varphi[7–8]$, $\varphi[8–9]$ and $\varphi[9–10]$ in ring *B* are increased by 3–3·5° compared to baccharis oxide. The changes correspond to a small left-handed rotation of C(6), C(7) and C(9) about $\overrightarrow{14–8}$ causing a slightly larger distortion of the twist-boat conformation of this ring. The average torsion angle $\langle\varphi\rangle$ about 5–10 is +24·5, *cf.* +25·6° in baccharis oxide. The conformation of ring *C* is very little affected by the change in substitution at ring *D*, the largest difference from baccharis oxide being a closure of *ca* 3·0° of endocyclic angles $\varphi[8–9]$ and $\varphi[9–11]$. The enhanced flattening of the ring at these bonds implies opening of the dihedral angle $\varphi[1–10–9–11]$; $\langle\varphi\rangle$ about 10–9 is +38·1 or 4·4° larger than in baccharis oxide. We interpret the changes in rings *B* and *C* of campanulin as minor local adjustments near one well-defined minimum-energy conformation. The overall effect seems to be a slight relief of strain in this part of the molecule.

Additional strain from the *cis* fusion to ring *E* is clearly involved in the marked flattening of ring *D* near the *D*/*E* junction. This ring is severely distorted from the regular chair form (Table 2). Repulsion between the axial methyl groups $C(26)H_3$ and $C(24)H_3$ is in part offset by reduced endocyclic angles $\varphi[18–19]$ and $\varphi[19–20]$ in ring *E*. According to the predictions of Bucourt & Hainaut (1965), the opposing torsion angles $\varphi[21–22]$ and $\varphi[22–17]$ should then open up above

Table 3. *Intramolecular contacts*

(*a*) Shortest intramolecular C···H contacts involving methyl groups

i	*j*	D_{ij}	*i*	*j*	D_{ij}
C(24)	H(261)	2·70 Å	C(27)	H(122)	2·53 Å
C(25)	H(212)	2·76	C(27)	H(161)	2·69
C(26)	H(81)	2·64	C(27)	H(181)	2·63
C(26)	H(112)	2·57	C(28)	H(61)	2·60
C(26)	H(151)	2·57	C(28)	H(272)	2·62
C(26)	H(243)	2·58	C(29)	H(22)	2·58
C(27)	H(71)	2·63	C(30)	H(61)	2·61

(*b*) Shortest intramolecular H···H contacts (<2·30 Å)

i	*j*	D_{ij}	*i*	*j*	D_{ij}
H(11)	H(112)	1·94 Å	H(262)	H(243)	2·10 Å
H(22)	H(291)	2·00	H(263)	H(81)	2·06
H(61)	H(301)	2·11	H(263)	H(112)	2·27
H(72)	H(152)	2·23	H(271)	H(181)	2·03
H(121)	H(191)	2·13	H(272)	H(122)	2·28
H(243)	H(221)	2·26	H(272)	H(281)	2·26
H(261)	H(243)	2·19	H(273)	H(71)	2·17
H(262)	H(151)	2·17	H(283)	H(61)	1·97
H(262)	H(221)	2·14	H(283)	H(71)	2·10

normal values, but close contacts to both methyl groups 24 and 26 (Table 3) prevent further movement of C(22) towards the α side of the molecule. As a result, ring E has the smallest mean magnitude of endocyclic torsion angles among the six-membered chair-rings: 45·1°. The extreme flattening at the D/E junction is illustrated in Fig. 3 and in the Newman projections of Fig. 2(*d*) and (*e*).

The shortest diaxial C···C distance involving C(26) is 3·301 (4) Å to C(24). The angle between axial bonds 13–26 and 20–24 is 21·7° with C(26) and C(24) pointing towards the apex. The corresponding angle between diaxial bonds 14–27 and 9–28 in ring C is 23·3°, the C(27)···C(28) distance being 3·278 (4) Å. The significance of axial substituents for the molecular conformation is brought out in Table 3(*b*). As in baccharis oxide, the central axial methyl groups 26, 27 and 28 are embedded in short intramolecular contacts. Of the 18 shortest H···H contacts, 13 involve H bonded to C atoms 24, 26, 27 and 28. The small conformational change of ring B of campanulin has brought $C(28)H_3$ closer to the methylene group $C(7)H_2$ and there are short H···H distances in a triangle formed by $C(7)H_2$, $C(27)H_3$ and $C(28)H_3$. A similar triangle of short H···H distances involves $C(22)H_3$, $C(24)H_3$ and $C(26)H_3$.

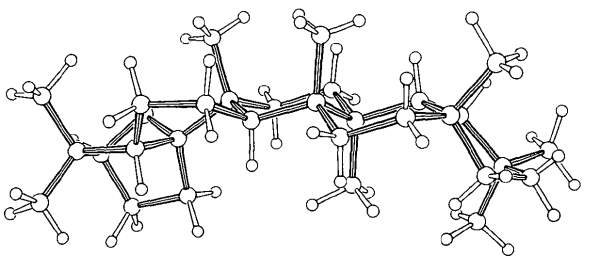


Fig. 3. Perspective view approximately along the main molecular plane of campanulin.

Table 4. *Mean values of endocyclic valency angles* $\langle\theta\rangle$ *and magnitudes of torsion angles* $\langle|\varphi|\rangle$ *in some cyclohexane rings*

		$\langle\theta\rangle$	$\langle\|\varphi\|\rangle$
Cyclohexane, calc.*		111·0°	56·1°
	obs.†	111·4	54·9
Ring C	Campanulin	111·85	52·6
	Baccharis oxide‡	111·8	53·1
Ring D	Campanulin	112·8	47·0
	Baccharis oxide‡	112·5	49·0
Ring E	Campanulin	114·1	45·1

* Calculated semi-empirically by Altona & Sundaralingam (1970).
† Electron diffraction, Bastiansen *et al.* (1973).
‡ X-ray diffraction, Mo (1973).

Table 4 gives mean values of endocyclic valency angles $\langle\theta\rangle$ and magnitudes of torsion angles $\langle|\varphi|\rangle$ for the chair-rings in campanulin and baccharis oxide. The table shows the close correspondence in structure of the two C rings and the more pronounced flattening of ring D of campanulin; $\langle|\varphi|\rangle$ values for rings C, D and E are increasingly reduced below the revised value of 54·9° for cyclohexane (Bastiansen, Fernholt, Seip, Kambara & Kuchitsu, 1973).

The structure of campanulin in which D and E are *cis*-fused chairs corroborates previous suggestions by Corey & Ursprung (1956) on the most stable conformation of friedelan-type triterpenes. In two related structures, one with a substituent in β at C(16) (Masaki, Niwa & Kikuchi, 1975) and the other with an O bridge between C(27) and C(28) (Rogers, Williams, Joshi, Kamat & Viswanathan, 1974), the conformation of both rings D and E was changed to boat with atoms 13, 16 and 19, 22 at bow and stern.

Bond lengths and angles

Bond lengths and angles are given in Tables 5 and 6. Mean values of the e.s.d.'s in lengths and angles not involving H are 0·0033 Å and 0·19° respectively. Corresponding values for baccharis oxide were 0·0041 Å and 0·23°.

Bond angles and in particular bond lengths of the tricyclic system and rings B and C are strikingly similar in the two triterpenes. The present analysis confirms the results obtained for the two C—O bonds in baccharis oxide. Average lengths of these bonds are 1·456 to the quaternary and 1·445 Å to the tertiary C atoms, and the C—O—C angle is 97·1°. Other details, for instance

Table 5. *Bond lengths* (Å)

Bond lengths of campanulin are in column I, some relevant bond lengths of baccharis oxide (Mo, 1973) in column II. E.s.d.'s of the bonds are in parentheses.

	I	II		I	II
O— 3	1·443 (3)	1·448 (4)	14— 8	1·562 (3)	1·557 (4)
O—10	1·454 (3)	1·459 (3)	14—15	1·541 (3)	1·542 (4)
1— 2	1·546 (3)	1·550 (5)	15—16	1·525 (3)	1·526 (4)
1—10	1·539 (3)	1·537 (5)	16—17	1·553 (3)	1·551 (4)
2— 3	1·533 (4)	1·515 (5)	17—18	1·576 (3)	
3— 4	1·543 (4)	1·539 (4)	18—19	1·565 (3)	
4— 5	1·564 (3)	1·568 (4)	19—20	1·567 (4)	
5— 6	1·511 (3)	1·511 (5)	20—21	1·520 (5)	
5—10	1·561 (3)	1·551 (4)	21—22	1·517 (4)	
6— 7	1·534 (3)	1·533 (4)	22—17	1·544 (4)	
7— 8	1·554 (3)	1·551 (4)	4—29	1·526 (5)	1·522 (5)
8— 9	1·565 (3)	1·565 (4)	4—30	1·532 (4)	1·531 (5)
9—10	1·566 (3)	1·561 (4)	9—28	1·545 (3)	1·561 (4)
9—11	1·545 (3)	1·551 (4)	13—26	1·543 (3)	
11—12	1·517 (3)	1·517 (4)	14—27	1·539 (3)	
12—13	1·533 (3)	1·538 (4)	17—25	1·544 (4)	
13—14	1·572 (3)		20—23	1·540 (4)	
13—18	1·561 (3)		20—24	1·535 (5)	

the large variation in C—C lengths at C(5) in baccharis oxide, are well reproduced in the present analysis. 23 C—C or C—O bonds, including three in ring *D*, are compared in Table 5. Only two of these are different: 2–3 and 9–28 (the 5–10 bonds are possibly significantly different). The difference in the 9–28 bonds, at least, may be related to observed changes in the environments of the $C(28)H_3$ groups. Whether the discrepancy in the 2–3 lengths is real or a statistical effect must remain an open question. Excluding 2–3 and 9–28, the r.m.s. and maximum differences between corresponding bonds are 0·004 and 0·010 Å respectively. The results suggest that the standard deviations in bond lengths from the least-squares refinement are realistic estimates. As expected, somewhat larger differences appear in pairs of valency angles. Of 37 pairs in Table 6, 15 are different, the r.m.s. and maximum differences over all 37 pairs being 0·69 and 1·6° respectively.

Large individual variations in bond lengths and angles in the *D* and *E* rings emphasize the high degree of strain in this part of the molecule. There are three consecutive C—C bonds 17–18–19–20 in the range 1·565–1·576 Å, and the angle θ[18–19–20] of 122·2° is unusually large for a cyclohexane ring. Increased angles θ[13–18–19] and θ[19–20–24] also serve to increase the $C(26)H_3 \cdots C(24)H_3$ distance. The observed values of bond lengths and angles and their standard

Table 6. *Valency angles* (°)

Valency angles of campanulin are in column I, some relevant angles of baccharis oxide (Mo, 1973) in column II. E.s.d.'s of the angles are in parentheses.

	I	II		I	II
3–O–10	97·1 (2)	97·0 (2)	11–12–13	112·3 (2)	111·6 (2)
2– 1–10	101·7 (2)	102·4 (3)	12–13–14	106·7 (2)	
1– 2– 3	101·7 (2)	101·3 (3)	12–13–18	109·7 (2)	
O– 3– 2	102·4 (2)	102·5 (2)	12–13–26	107·8 (2)	
O– 3– 4	102·3 (2)	101·8 (2)	14–13–18	110·2 (2)	
2– 3– 4	112·0 (3)	113·6 (3)	14–13–26	111·6 (2)	
3– 4– 5	98·9 (2)	98·8 (2)	18–13–26	110·8 (2)	
3– 4–29	114·9 (2)	115·4 (3)	8–14–13	110·2 (2)	
3– 4–30	107·9 (2)	108·6 (2)	8–14–15	110·0 (2)	
5– 4–29	112·2 (2)	112·6 (2)	8–14–27	110·7 (2)	
5– 4–30	113·4 (2)	113·5 (3)	13–14–15	106·8 (2)	106·4 (2)
29– 4–30	109·2 (2)	107·8 (3)	13–14–27	112·1 (2)	
4– 5– 6	117·5 (2)	116·7 (3)	15–14–27	107·0 (2)	
4– 5–10	102·9 (2)	103·4 (2)	14–15–16	112·0 (2)	112·7 (2)
6– 5–10	113·5 (2)	113·5 (2)	15–16–17	116·7 (2)	117·0 (2)
5– 6– 7	111·0 (2)	110·6 (2)	16–17–18	114·3 (2)	
6– 7– 8	114·1 (2)	114·4 (2)	16–17–22	108·0 (2)	
7– 8– 9	111·1 (2)	112·2 (2)	16–17–25	107·2 (2)	
7– 8–14	113·0 (2)	112·3 (2)	18–17–22	112·1 (2)	
9– 8–14	116·4 (2)	116·6 (2)	18–17–25	106·4 (2)	
8– 9–10	104·3 (2)	105·5 (2)	22–17–25	108·6 (2)	
8– 9–11	110·8 (2)	109·6 (2)	17–18–13	116·9 (2)	
8– 9–28	113·4 (2)	113·9 (2)	17–18–19	111·0 (2)	
10– 9–11	111·6 (2)	111·9 (2)	13–18–19	116·3 (2)	
10– 9–28	110·4 (2)	109·7 (2)	18–19–20	122·2 (2)	
11– 9–28	106·4 (2)	106·4 (2)	19–20–21	110·9 (2)	
O–10– 1	100·7 (2)	100·1 (2)	19–20–23	106·4 (3)	
O–10– 5	103·2 (2)	102·2 (2)	19–20–24	113·7 (2)	
O–10– 9	111·4 (2)	111·5 (2)	21–20–23	109·6 (2)	
1–10– 5	105·3 (2)	106·4 (3)	21–20–24	108·4 (3)	
1–10– 9	119·5 (2)	119·0 (3)	23–20–24	107·6 (2)	
5–10– 9	114·7 (2)	115·4 (2)	20–21–22	114·4 (2)	
9–11–12	114·7 (2)	114·7 (2)	21–22–17	113·9 (3)	

Angles involving H of campanulin (I) and baccharis oxide (II)

Type		Number	Range	Mean	$\sigma_{av.}$
X*CH	I	80	98·8–128·3	109·6	1·5
	II	79	103·2–117·2	109·4	1·7
HCH	I	35	87·2–125·4	107·3	2·3
	II	35	101·6–114·0	108·3	2·6

* X = C, O.

deviations are believed to be realistic figures in view of the good quantitative agreement in structure of rings *A–C* of the two triterpenes. Throughout the campanulin molecule from C(4) to C(20) there is an unbroken chain of long C—C bonds, 1·561–1·572 Å.

Of the 50 C—H bonds, 41 refined to lengths in the range 0·91–1·10 Å, four are 0·82–0·86 and five others are 1·11–1·15 Å. The mean value is 1·00 Å ($\sigma_{mean} \sim$ 0·04 Å). A survey of angles involving H is given in Table 6.

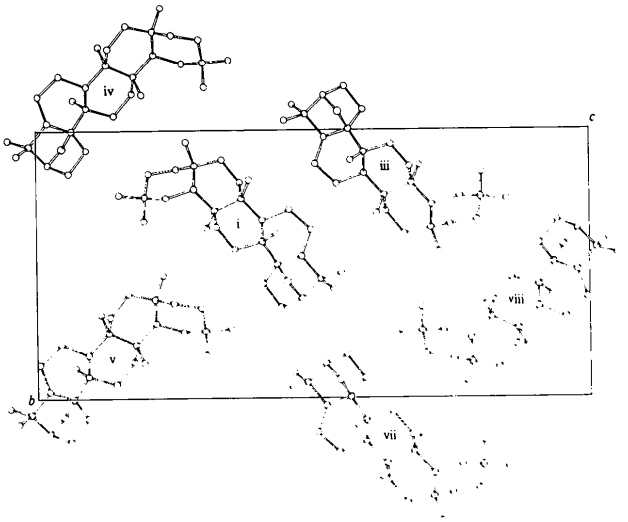


Fig. 4. Packing of molecules projected on (100). The symmetry code is explained in Table 7.

Table 7. *Intermolecular contacts*

Distances are included within a limit of 0·2 Å greater than the sum of corresponding van der Waals radii: $R_C = 1·80$, $R_O = 1·52$, $R_H = 1·17$ Å (Kitaigorodsky, 1973). A limit of 2·60 Å has been used for H···H contacts.

Symmetry code

i	x	y	z	v	$-x$	$\frac{1}{2}+y$	$\frac{1}{2}-z$
ii	$1+x$	y	z	vi	$1-x$	$-\frac{1}{2}+y$	$\frac{1}{2}-z$
iii	$\frac{1}{2}+x$	$\frac{1}{2}-y$	$1-z$	vii	$\frac{1}{2}+x$	$\frac{3}{2}-y$	$1-z$
iv	$-x$	$-\frac{1}{2}+y$	$\frac{1}{2}-z$	viii	$\frac{1}{2}-x$	$1-y$	$\frac{1}{2}+z$

i	j	j_{sc}	D_{ij}
C(12)	H(262)	ii	3·14 Å
C(28)	H(51)	ii	3·02
C(28)	H(72)	ii	3·16
C(28)	H(81)	ii	3·16
C(6)	H(72)	iii	3·13
C(27)	H(62)	iii	3·00
C(1)	H(211)	v	3·07
C(24)	H(253)	v	3·18
C(25)	H(121)	vi	2·89
H(122)	H(151)	ii	2·41
H(122)	H(262)	ii	2·54
H(281)	H(81)	ii	2·45
H(282)	H(51)	ii	2·37
H(61)	H(72)	iii	2·47
H(71)	H(62)	iii	2·59
H(273)	H(62)	iii	2·30
H(283)	C(7)	iii	3·17
H(11)	H(211)	v	2·45
H(233)	H(11)	vi	2·53
H(251)	H(121)	vi	2·47
H(31)	H(22)	vii	2·59

Packing of the molecules

The stacking is illustrated in Fig. 4; intermolecular contact distances are listed in Table 7. With reference to the limits cited in this table, there are 42 intermolecular van der Waals contacts of normal length involving most of the exposed parts of the molecule. The shortest distance is C(25)···H(121) at $1-x$, $-\frac{1}{2}+y$, $\frac{1}{2}-z$: 2·89 Å. Methylene groups $C(6)H_2$, $C(7)H_2$, $C(12)H_2$ and methyl $C(28)H_3$ participate in several contacts; however, the packing is relatively loose, inasmuch as the coordination number is only 10.

The molecular packing of campanulin is quite different from that of baccharis oxide, described in Fig. 4 and Table 9 of Mo (1973). The influence on molecular conformation of relatively weak intermolecular forces therefore must also be different in the two cases. In view of this, the results confirm that the stereochemistry is largely determined by intramolecular forces and the refined structure parameters should be good approximations to those of the isolated molecules.

The X-RAY 70 system (Stewart, Kundell & Baldwin, 1970) was used for structure refinement and analyses of molecular geometry. Drawings of molecules were made by *ORTEP* (Johnson, 1965).

A major part of this work was done during a visit to the Department of Biological Structure, University of Washington, Seattle, USA. The author thanks Professor L. H. Jensen and his co-workers at the University of Washington for their hospitality and for a generous amount of computer time. He is also indebted to Dr T. Bruun, Universitetet i Trondheim-NTH, for valuable discussions. Support by USPHS Grant GM-10828 from the National Institutes of Health and a grant from Norges Tekniske Høgskoles Fond are gratefully acknowledged.

References

ALTONA, C. & SUNDARALINGAM, M. (1970). *Tetrahedron*, **26**, 925–939.

ARTHUR, H. R. & HUI, W. H. (1961). *J. Chem. Soc.* pp. 551–554.

BASTIANSEN, O., FERNHOLT, L., SEIP, H. M., KAMBARA, H. & KUCHITSU, K. (1973). *J. Mol. Struct.* **18**, 163–168.

BRUUN, T. & ANTHONSEN, T. (1973). Private communication.

BUCOURT, R. & HAINAUT, D. (1965). *Bull. Soc. Chim. Fr.* pp. 1366–1378.

COREY, E. J. & URSPRUNG, J. J. (1956). *J. Amer. Chem. Soc.* **78**, 5041–5051.
DOYLE, P. A. & TURNER, P. S. (1968). *Acta Cryst.* A**24**, 390–397.
HAUPTMAN, H. (1970). *Crystallographic Computing*, edited by F. R. AHMED, S. R. HALL & C. P. HUBER, pp. 41–51. Copenhagen: Munksgaard.
HAUPTMAN, H. (1972). *Crystal Structure Determination. The Role of the Cosine Seminvariants*, pp. 187–209. New York: Plenum.
JOHNSON, C. K. (1965). *ORTEP*. Oak Ridge National Laboratory Report ORNL-3794.
KARLE, J. (1970*a*). *Crystallographic Computing*, edited by F. R. AHMED, S. R. HALL & C. P. HUBER, p. 18. Copenhagen: Munksgaard.
KARLE, J. (1970*b*). *Acta Cryst.* B**26**, 1614–1617.
KIMURA, K., HASHIMOTO, Y. & AGATA, I. (1960). *Chem. Pharm. Bull. (Tokyo)*, **8**, 1145–1146.
KITAIGORODSKY, A. I. (1973). *Molecular Crystals and Molecules*. New York: Academic Press.
KLYNE, W. & PRELOG, V. (1960). *Experientia*, **16**, 521–523.
MASAKI, N., NIWA, M. & KIKUCHI, T. (1975). *J. Chem. Soc. Perkin* II, pp. 610–614.
MO, F. (1972). Tekn. Rapport 17-RII-72. Inst. for røntgenteknikk, NTH, Trondheim.
MO, F. (1973). *Acta Cryst.* B**29**, 1796–1807.
MO, F., ANTHONSEN, T. & BRUUN, T. (1972). *Acta Chem. Scand.* **26**, 1287–1288.
RANGASWAMI, S. & SAMBAMURTHY, K. (1961*a*). *Proc. Indian Acad. Sci. Sect. A*, **53**, 98–104.
RANGASWAMI, S. & SAMBAMURTHY, K. (1961*b*). *Proc. Indian Acad. Sci. Sect. A*, **54**, 132–139.
ROGERS, D., WILLIAMS, D. J., JOSHI, B. S., KAMAT, V. N. & VISWANATHAN, N. (1974). *Tetrahedron Lett.* pp. 63–66.
STEWART, J. M., KUNDELL, F. A. & BALDWIN, J. C. (1970). X-RAY 70 system. Computer Science Center, Univ. of Maryland, College Park, Maryland.
STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
WHITE, J. D., FAYOS, J. & CLARDY, J. (1973). *Chem. Commun.* pp. 357–358.

Acta Cryst. (1977). B**33**, 649–654

Crystallography of Metal Picrates. I. General Survey. Crystal Structure of Red Thallium(I) Picrate $TlC_6H_2N_3O_7$

BY F. H. HERBSTEIN, M. KAPON AND S. WIELINSKI

Department of Chemistry, Technion–Israel Institute of Technology, Haifa, Israel

(*Received* 1 *July* 1976; *accepted* 30 *July* 1976)

The red polymorph of Tl^I picrate is monoclinic, $a = 10{\cdot}610\,(1)$, $b = 4{\cdot}548\,(5)$, $c = 19{\cdot}148\,(2)$ Å, $\beta = 101{\cdot}1\,(1)°$, $Z = 4$, space group $P2_1/c$. Intensities were measured on a Weissenberg diffractometer. The structure was refined to $R = 11{\cdot}7\%$. There are columns of Tl^+ ions along the [010] direction, each column being surrounded by four stacks of picrate ions. Each Tl^+ ion is surrounded by nine O atoms, six at the vertices of a distorted trigonal prism and three capped on the three rectangular faces (shortest $Tl^+ \cdots O = 2{\cdot}83$ Å). Similar (but not identical) coordination polyhedra have been reported in cryptate complexes of Tl^I and alkali-metal salts. We conclude that the $6s^2$ lone pair is not stereochemically active in red Tl^I picrate.

Introduction

Picric acid forms salts with many organic (Gartland, Freeman & Bugg, 1974) and metallic cations. Anhydrous picrates are formed with K^+, Rb^+, NH_4^+, Cs^+, Tl^+ and Ag^+ while picrates with various degrees of hydration are formed by other metals such as Li, Na, the alkaline earths, Zn, Cd, Hg, various transition metals, Al, Y, Sc, In and various rare-earth metals (Tucholski, 1932, 1933, 1934*a*,*b*,*c*). Crystal structures have been reported for the isomorphous NH_4 (Beukelman & Donnay, 1950; Maartman-Moe, 1969) and K picrates (Bettman & Hughes, 1954; Maartman-Moe, 1969; Palenik, 1972) and for some organic picrates [see, for example, Gartland *et al.* (1974), who give earlier references].

Tl^I picrate has two polymorphic forms, whose thermodynamic relation has been studied by solubility measurements (Rabe, 1901). The red polymorph, stable at 25 °C, has been reported, correctly, as monoclinic and the yellow polymorph, metastable at 25 °C, incorrectly, as triclinic (Stevanovic, 1903). The phase transformation has been studied by Cohen & Moesveld (1920) (see also Cohen, 1929). While the equilibrium temperature of red $\rightleftarrows$ yellow is 46 (Rabe, 1901) or 44 °C (Cohen, 1929), the transformation red $\rightarrow$ yellow proceeds very sluggishly below 120 °C. Study of the phase transformation must be based on knowledge of