Table 3. *Torsion angles*

The convention used is that of the IUPAC–IUB Commission on Biochemical Nomenclature (1970).

[C(2)′–N(1)–C(1)$^\alpha$–C(1)′]	φ_1	26·4°
[C(1)′–N(2)–C(2)$^\alpha$–C(2)′]	φ_2	30·4
[N(1)–C(1)$^\alpha$–C(1)′–N(2)]	ψ_1	−18·6
[N(2)–C(2)$^\alpha$–C(2)′–N(1)]	ψ_2	−22·6
[C(1)$^\alpha$–C(1)′–N(2)–C(2)$^\alpha$]	ω_1	−9·3
[C(2)$^\alpha$–C(2)′–N(1)–C(1)$^\alpha$]	ω_2	−5·3

As with c-Sar-Val, the molecules are held together by a linear array of hydrogen bonds of length 2·90 (1) Å, each molecule having one donor site [N(1)–H] and one acceptor site [C(1)′=O(1)] with the second carbonyl group [C(2)′=O(2)] not being hydrogen bonded. The closest H···H contacts are 2·14 Å for H(1)···H(10) (intramolecular) and 2·41 Å for H(5)···H(7) (intermolecular, related by 2_1 screw parallel to **a**).

References

ALLEN, F. H., ROGERS, D. & TROUGHTON, P. G. H. (1971). *Acta Cryst.* B31, 2561–2565.
DAVIES, D. B. & KHALED, M. A. (1976). *J. Chem. Soc. Perkin* II. In the press.
GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1971). *Acta Cryst.* A27, 368–376.
GROTH, P. (1969). *Acta Chem. Scand.* 23, 3155–3162.
International Tables for X-ray Crystallography (1968). Vol. III, 2nd ed., pp. 201–209. Birmingham: Kynoch Press.
IUPAC–IUB COMMISSION ON BIOCHEMICAL NOMENCLATURE (1970). *Biochemistry*, 9, 3471–3479.
SLETTEN, E. (1970). *J. Amer. Chem. Soc.* 92, 172–177.
STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* 42, 3175–3187.
TIMMINS, P. A. (1975). *Acta Cryst.* B31, 2561–2565.

Utahin, a Ditropolonofuran

BY BENGT KARLSSON, ANNE-MARIE PILOTTI AND ANNE-CHARLOTTE WIEHAGER

Department of Structural Chemistry, Arrhenius Laboratory, University of Stockholm, S-104 05 Stockholm, Sweden

Abstract. $C_{20}H_{20}O_5$, isolated from *Juniperus utahensis* Lemm, triclinic, space group $P\bar{1}$, with $Z=2$, $a=13·106$ (3), $b=10·724$ (2), $c=7·640$ (2) Å, $\alpha=98·45$ (2), $\beta=125·03$ (3), $\gamma=99·33$ (4)°, $V=828·4$ Å^3, $D_c=1·356$ g cm^{-3}. The structure was determined by the application of direct methods and refined by full-matrix least squares to a final R of 0·041 for the 1257 observed intensities collected with a Philips PW 1100 computer-controlled diffractometer. The tropolone systems are only approximately planar and exhibit bond-length alternations indicating some double-bond fixation both for C–C and C–O bonds. Each part of the ditropolonoid is involved in intramolecular hydrogen bonds; only one of the parts is involved in intermolecular hydrogen bonds. The latter hold together dimers of centrosymmetrically related molecules.

Introduction. $C_{20}H_{20}O_5$ has been isolated from *Juniperus utahensis* Lemm, and from spectral data and chemical properties was established to be a symmetrical diisopropylditropolonofuran (Baggaley & Norin, 1968). An investigation was undertaken to determine the complete structure and to study the delocalization of the π-electron system of this ditropolonoid.

Cell dimensions and intensities were measured from a crystal of approximate volume 0·0005 mm^3 on the

Philips PW 1100 computer-controlled diffractometer with graphite-monochromatized Cu $K\alpha$ radiation. The lattice constants were determined by least-squares refinement of the setting angles of 25 accurately centred reflexions. The ω–2θ scan technique was employed to measure reflexions out to $\theta=65°$ at a scan speed of 0·016° s^{-1}. Backgrounds were estimated by stationary counting at $\pm0·75$ 2θ from the peak maxima. Three reference reflexions were measured approximately every 90 min. No systematic variation was detected. 2836 unique reflexions were measured. Of these, the 1255 satisfying the condition $\sigma(I)/I \le 0·25$ were selected for subsequent refinement. Lorentz and polarization factors were applied but no correction for absorption was made.

The absolute scale and overall temperature factor for the calculation of normalized structure factor magnitudes were estimated by Wilson's (1942) method. The structure was solved by a modified version of the *MULTAN* direct phase-determination procedure (Germain, Main & Woolfson, 1970) from the 344 reflexions with $|E|\ge1·45$. An E map computed from well phased reflexions displayed 20 of the non-H atoms as prominent peaks. The structure was refined by the full-matrix least-squares method. When the R value reached 0·072 with anisotropic temperature factors, a
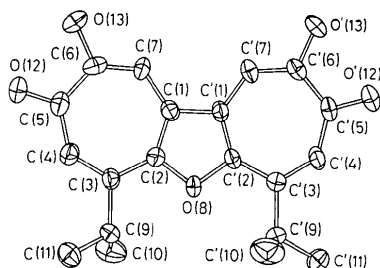
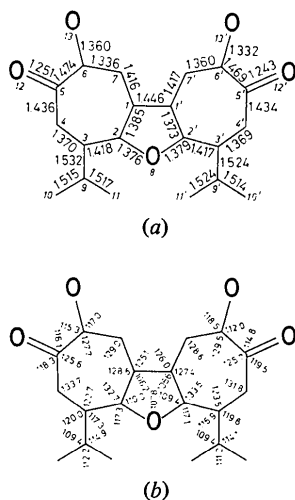Fig. 1. A perspective view of the molecule.

(a)

(b)

Fig. 2. (a) Bond distances in the molecule. (b) Bond angles in the molecule.

difference synthesis revealed all the H atoms. The H atoms were given the final isotropic thermal parameters of the atoms to which they are attached and only the positional parameters were included in further refinement. R fell to 0·041 after two cycles of refinement for 1255 reflexions.* The Freeman (1959) scattering fac-

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31882 (3 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. Positional ($\times 10^3$) and isotropic ($\times 10^2$) thermal parameters of the hydrogen atoms, with estimated standard deviations in parentheses

	x	y	z	B (Å^2)
H(C4)	915 (4)	867 (4)	−30 (6)	278
H(C'4)	693 (4)	98 (4)	106 (6)	264
H(C7)	1179 (3)	601 (3)	417 (5)	229
H(C'7)	1124 (4)	398 (4)	453 (6)	242
H(C9)	654 (4)	619 (4)	−150 (6)	273
H(C'9)	575 (4)	292 (4)	−212 (7)	297
H1(C10)	693 (4)	665 (5)	−463 (7)	457
H2(C10)	665 (4)	520 (5)	−428 (7)	457
H3(C10)	550 (5)	596 (4)	−524 (7)	457
H1(C'10)	546 (5)	276 (5)	118 (8)	544
H2(C'10)	610 (5)	420 (5)	105 (8)	544
H3(C'10)	462 (5)	332 (5)	−60 (8)	544
H1(C11)	572 (4)	787 (4)	−272 (7)	390
H2(C11)	712 (4)	862 (5)	−228 (7)	390
H3(C11)	704 (4)	855 (5)	−29 (7)	390
H1(C'11)	392 (5)	121 (4)	−340 (7)	467
H2(C'11)	511 (4)	60 (5)	−317 (8)	467
H3(C'11)	489 (4)	83 (5)	−120 (8)	467
H(O13)	1292 (4)	871 (5)	386 (7)	378
H(O'13)	1087 (4)	123 (5)	541 (7)	355

Table 1. Positional and anisotropic thermal parameters of the non-hydrogen atoms

The β values refer to the temperature-factor expression: exp $[-(h^2\beta_{11}+k^2\beta_{22}+l^2\beta_{33}+hk\beta_{12}+hl\beta_{13}+kl\beta_{23})]$. 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)	9880 (4)	5495 (4)	2132 (7)	66 (4)	56 (4)	179 (12)	30 (7)	134 (12)	62 (12)
C'(1)	9505 (4)	4214 (4)	2343 (7)	67 (4)	50 (4)	189 (12)	42 (7)	138 (12)	57 (11)
C(2)	8731 (4)	5773 (4)	663 (7)	61 (4)	57 (5)	194 (13)	40 (7)	131 (12)	70 (12)
C'(2)	8161 (4)	3796 (4)	980 (7)	75 (5)	58 (5)	182 (12)	57 (7)	140 (13)	98 (12)
C(3)	8455 (4)	6868 (4)	−173 (7)	71 (5)	61 (5)	199 (13)	45 (7)	152 (13)	94 (12)
C'(3)	7237 (4)	2640 (4)	500 (7)	64 (4)	53 (4)	188 (13)	28 (7)	124 (12)	74 (11)
C(4)	9401 (4)	7962 (5)	378 (8)	82 (5)	63 (4)	243 (13)	41 (7)	169 (13)	130 (12)
C'(4)	7594 (4)	1635 (4)	1409 (7)	73 (5)	55 (5)	249 (15)	23 (7)	156 (14)	96 (13)
C(5)	10802 (4)	8289 (4)	1770 (7)	87 (5)	67 (5)	231 (14)	22 (7)	171 (13)	85 (13)
C'(5)	8830 (4)	1434 (4)	2953 (7)	92 (5)	55 (5)	247 (14)	57 (7)	178 (14)	118 (13)
C(6)	11578 (4)	7483 (4)	3102 (7)	62 (5)	77 (5)	189 (13)	15 (7)	115 (13)	46 (13)
C'(6)	10119 (4)	2348 (4)	3955 (7)	86 (5)	65 (5)	199 (13)	66 (8)	154 (13)	118 (13)
C(7)	11176 (4)	6298 (4)	3236 (7)	66 (5)	65 (5)	170 (12)	46 (7)	109 (12)	81 (12)
C'(7)	10385 (4)	3555 (4)	3691 (7)	70 (5)	75 (6)	204 (14)	53 (8)	141 (13)	108 (13)
O(8)	7681 (3)	4737 (3)	−49 (5)	65 (3)	55 (3)	241 (9)	34 (5)	129 (8)	118 (8)
C(9)	7009 (4)	6767 (4)	−1845 (8)	65 (5)	65 (5)	288 (16)	50 (7)	161 (14)	148 (14)
C'(9)	5798 (4)	2563 (4)	−1043 (8)	66 (5)	74 (5)	286 (15)	35 (7)	146 (14)	160 (14)
C(10)	6513 (5)	6079 (6)	−4191 (9)	91 (6)	153 (8)	304 (19)	107 (10)	141 (17)	143 (19)
C'(10)	5475 (6)	3374 (7)	270 (12)	88 (6)	175 (9)	558 (28)	117 (12)	288 (23)	210 (25)
C(11)	6728 (6)	8082 (5)	−1715 (11)	101 (6)	85 (6)	506 (23)	90 (9)	278 (21)	191 (18)
C'(11)	4848 (5)	1164 (6)	−2331 (11)	73 (6)	101 (6)	448 (24)	−2 (9)	67 (18)	167 (19)
O(12)	11461 (3)	9360 (3)	1970 (6)	94 (4)	91 (4)	459 (13)	13 (6)	208 (11)	219 (11)
O'(12)	8833 (3)	409 (3)	3532 (5)	114 (4)	83 (4)	415 (13)	75 (6)	200 (12)	251 (11)
O(13)	12885 (3)	8078 (3)	4317 (6)	66 (4)	97 (4)	387 (12)	−4 (6)	132 (10)	141 (11)
O'(13)	11136 (3)	1947 (3)	5320 (6)	97 (4)	89 (4)	384 (12)	94 (6)	189 (11)	246 (11)

Table 3. *Comparison of bond lengths* (Å)

The atoms are numbered according to the tropolone molecule, *i.e.* C(1) is the carbonyl C atom and C(2) the C atom to which the hydroxyl group is attached.

	C(1)–O(1)	C(2)–O(2)	C(1)–C(2)	C(2)–C(3)	C(3)–C(4)	C(4)–C(5)	C(5)–C(6)	C(6)–C(7)	C(7)–C(1)
β-Thujaplicin	1·261 (5)	1·349 (5)	1·469 (6)	1·367 (5)	1·422 (6)	1·355 (6)	1·413 (6)	1·364 (4)	1·413 (7)
γ-Thujaplicin	1·247 (4)	1·338 (4)	1·458 (4)	1·362 (4)	1·408 (4)	1·374 (4)	1·414 (4)	1·352 (4)	1·431 (4)
Tropolone	1·261 (3)	1·333 (3)	1·454 (4)	1·379 (4)	1·393 (4)	1·341 (4)	1·410 (4)	1·373 (4)	1·410 (3)
Chanootin	1·250 (2)	1·341 (2)	1·461 (3)	1·376 (3)	1·395 (3)	1·371 (3)	1·419 (2)	1·362 (2)	1·434 (3)
Utahin (non-primed part)	1·251 (5)	1·360 (5)	1·474 (6)	1·366 (6)	1·416 (5)	1·385 (5)	1·418 (5)	1·370 (5)	1·436 (6)
Utahin (primed part)	1·243 (5)	1·332 (5)	1·469 (5)	1·360 (5)	1·417 (5)	1·373 (5)	1·417 (5)	1·369 (5)	1·434 (6)
Tropolone (MO calculation)	1·258	1·389	1·462	1·355	1·452	1·357	1·452	1·355	1·462

tors for O and C and those of Stewart, Davidson & Simpson (1965) for H were used throughout the analysis. Hughes's (1941) weighting scheme was used throughout with an $F_{o,\min}$ of 4·5. The final positional and thermal parameters of the non-H atoms, together with their standard deviations, are listed in Table 1 and those of the H atoms in Table 2.

Discussion. The structural and conformational features of the utahin molecule are illustrated in Fig. 1. The bond lengths and angles are shown in Fig. 2. Standard deviations are estimated to be 0·005 Å and 0·4° respectively. Somewhat larger values, about 0·007 Å, are observed for the bond lengths involving atoms C(9), C'(9), C(10), C'(10), C(11) and C'(11). No corrections for thermal vibrations have been made.

The tropolone rings exhibit bond-length alternation in accordance with those in the crystal structures of β-thujaplicin (Derry & Hamor, 1972), γ-thujaplicin (Berg, Karlsson, Pilotti & Wiehager, 1976), tropolone (Shimanouchi & Sasada, 1973) and chanootin (Karlsson, Pilotti & Wiehager, 1973). Bond lengths from these studies together with the results of a molecular orbital treatment of tropolone (Dewar & Trinajstic, 1970) are listed in Table 3.

The C(5)–C(6) and C'(5)–C'(6) bonds are 1·469 and 1·474 Å respectively, close to the $C(sp^2)$–$C(sp^2)$ single-bond value. The other C–C 'single' bonds are, however, significantly shorter. The mean value of these bonds is 1·423 Å. The mean 'double' bond value is 1·365 Å. The C–O bonds are also involved in the electron delocalization. The average values of bonds involving carbonyl O and hydroxyl O are 1·247 and 1·346 Å respectively.

The equations of various least-squares planes and deviations from these planes are listed in Table 4. The two seven-membered rings deviate only slightly from planarity, maximally 0·021 and 0·013 Å. The whole molecule, excluding atoms C(10), C'(10), C(11) and

C'(11), is planar within ±0·038 Å. The conformations of the isopropyl groups are such that atoms C(10) and C(11) deviate from the non-primed tropolone ring by 1·480 and −0·717 Å respectively, and atoms C'(10) and C'(11) deviate from the primed tropolone ring by −1·481 and 0·546 Å respectively. Relevant torsion angles for these groups are given in Table 5.

Table 4. *Least-squares planes and deviations* (Å)

The planes are described in terms of normalized equations in the orthogonal coordinate system (m,n,p) having $p\|c$, n in the bc plane, and m in the a,b,c octant.

Plane A $-0\cdot0348m - 0\cdot4540n - 0\cdot8903p = 4\cdot4080$
Plane B $-0\cdot0363m - 0\cdot4523n - 0\cdot8911p = 4\cdot3966$
Plane C $-0\cdot0303m - 0\cdot4521n - 0\cdot8914p = 4\cdot4635$

Deviations of atoms from the planes

Plane A					
C(1)	−0·002	C'(4)	0·018	C(6)	−0·006
C(2)	0·003	C'(5)	0·004	C(7)	−0·009
C(3)	−0·019	C'(6)	0·019	O(12)*	0·037
C(4)	−0·026	C'(7)	−0·005	O(13)*	−0·014
C(5)	0·012	C'(9)	−0·037		
C(6)	−0·012	O'(12)	−0·038	Plane C	
C(7)	−0·014	O'(13)	0·023	C'(1)	−0·005
O(8)	0·019			C'(2)	0·007
C(9)	0·022	Plane B		C'(3)	−0·002
O(12)	0·026	C(1)	0·003	C'(4)	0·001
O(13)	−0·019	C(2)	0·012	C'(5)	−0·009
C'(1)	−0·002	C(3)	−0·007	C'(6)	0·013
C'(2)	0·016	C(4)	−0·014	C'(7)	−0·006
C'(3)	0·014	C(5)	0·021	O'(12)*	−0·054
				O'(13)*	0·001

* Atom not included in the least-squares plane

The interior angles of the seven-membered rings range from 122·7 to 133·7 and 123·5 to 133·5° for the unprimed and primed units respectively. In both ring systems the smallest angle is at the C atom to which the isopropyl group is attached. The angles at the carbonyl C atoms, 125·6 and 125·7° respectively, are the next smallest here; however, in all the related structures these are the smallest angles.

Table 5. *Torsion angles* (°) *of the isopropyl groups*

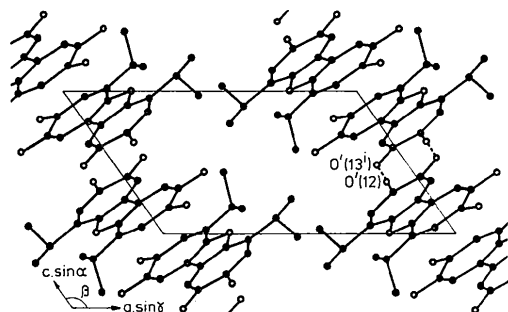| C(10)–C(9)–C(3)–C(2)	−86·8	C'(10)–C'(9)–C'(3)–C'(2)	−79·2
C(10)–C(9)–C(3)–C(4)	90·9	C'(10)–C'(9)–C'(3)–C'(4)	99·0
C(11)–C(9)–C(3)–C(2)	147·8	C'(11)–C'(9)–C'(3)–C'(2)	153·6
C(11)–C(9)–C(3)–C(4)	−34·5	C'(11)–C'(9)–C'(3)–C'(4)	−28·1

Fig. 3. The unit cell in projection along the b axis. Intermolecular hydrogen bonds are marked with dotted lines. ● Carbon. ○ Oxygen.

Intramolecular hydrogen bonds are observed in each tropolone moiety in utahin. The distances $O(12)$–$O(13)$ and $O'(12)$–$O'(13)$ are 2·510 and 2·586 Å respectively. H atoms are found at normal X-ray-measured bond distances (0·82 and 0·82 Å) from $O(13)$ and $O'(13)$ and at 1·94 and 2·11 Å, respectively, from $O(12)$ and $O'(12)$. The angles $O(13)$–$H(O13)\cdots O(12)$ and $O'(13)$–$H(O'13)\cdots O'(12)$ are 126 and 117° respectively. However, only the primed parts of the molecules are involved in intermolecular hydrogen bonding to form hydrogen-bonded dimers of centrosymmetrically related molecules. The intermolecular distance $H(O'13)\cdots O'(12^i)$ ($i \equiv 2-x, -y, 1-z$) is 2·04 Å and the angle $O'(13)$–$H(O'13)\cdots O'(12^i)$ is 152°. The distance $O'(13)\cdots O'(12^i)$ is 2·793 Å. Other intermolecular contacts

are normal van der Waals distances. The crystal packing projected along the b axis is shown in Fig. 3.

References

BAGGALEY, K. H. & NORIN, T. (1968). *Chem Commun.* pp. 233–234.

BERG, J.-E., KARLSSON, B., PILOTTI, A.-M. & WIEHAGER, A.-C. (1976). *Acta Cryst.* B32, 3121–3123.

DERRY, J. E. & HAMOR, T. A. (1972). *J. Chem. Soc.* pp. 694–697.

DEWAR, M. J. S. & TRINAJSTIC, N. (1970). *Croat. Chem. Acta*, 42, 1–12.

FREEMAN, A. J. (1959). *Acta Cryst.* 12, 261–271.

GERMAIN, G., MAIN, P. & WOOLFSON, M. M. (1970). *Acta Cryst.* B26, 274–285.

HUGHES, E. W. (1941). *J. Amer. Chem. Soc.* 63, 1737–1752.

KARLSSON, B., PILOTTI, A.-M. & WIEHAGER, A.-C. (1973). *Acta Cryst.* B29, 1209–1213.

SHIMANOUCHI, H. & SASADA, Y. (1973). *Acta Cryst.* B29, 81–90.

STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* 42, 3175–3187.

WILSON, A. J. C. (1942). *Nature, Lond.* 150, 151–152.

5-Isopropyltropolone, γ-Thujaplicin

By JAN-ERIC BERG, BENGT KARLSSON, ANNE-MARIE PILOTTI AND ANNE-CHARLOTTE WIEHAGER

Department of Structural Chemistry, Arrhenius Laboratory, University of Stockholm, S-104 05 Stockholm, Sweden

Abstract. $C_{10}H_{12}O_2$, monoclinic, $P2_1/n$, $a = 7\cdot573$ (2), $b = 18\cdot311$ (5), $c = 6\cdot632$ (2) Å, $\beta = 105\cdot1$ (2)°, $Z = 4$, $V = 887\cdot9$ Å³, $D_c = 1\cdot227$ g cm⁻³. The final R value is 0·064 for 1078 observed independent reflexions. The π-electron system in the tropolone moiety is only partially delocalized with some double-bond localization both for C–C and C–O bonds. The hydroxyl H participates in a bifurcated hydrogen bond, of which one branch is intramolecular and the other intermolecular.

Introduction. Intensities were obtained from two crystals with approximate volumes 0·0045 and 0·002 mm³ on a computer-controlled diffractometer (Philips PW 1100, graphite monochromator, Cu $K\alpha$ radiation, $\omega/2\theta$

scan, stationary background measurements at the beginning and end of each scan). 1695 unique reflexions up to $\theta = 70°$ were measured. Of these, the 1078 satisfying the condition $\sigma(I)/I \le 0\cdot25$ were used for subsequent refinement. During the data collection three monitor reflexions measured at intervals of approximately 1·5 h showed a decrease in intensity of 10–15%, from both crystals. Individual reflexions were corrected for this loss by fitting a linear function of time to the intensities of the monitor reflexions.

The cell constants were refined by least squares from diffractometer-measured settings of 25 reflexions. The structure was solved by the multisolution tangent-formula refinement (Germain, Main & Woolfson, 1971)