S = 1.962	$\Delta\rho_{max}$ = 0.29 e Å^{-3}
3256 reflections	$\Delta\rho_{min}$ = −0.14 e Å^{-3}
316 parameters	Extinction correction: none
H-atom parameters not refined	Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

O10—C1	1.233 (2)	N6—C5	1.470 (3)
N3—C2	1.467 (3)	N6—C7	1.466 (3)
N3—C4	1.443 (3)	C1—C2	1.519 (3)
N3—C19	1.360 (3)	C2—C11	1.544 (3)
N6—C1	1.342 (3)	C4—C5	1.508 (3)
C2—N3—C4	114.6 (2)	O10—C1—C2	118.2 (2)
C2—N3—C19	123.2 (2)	N6—C1—C2	120.4 (2)
C4—N3—C19	121.5 (2)	N3—C2—C1	111.1 (2)
C1—N6—C5	124.9 (2)	N3—C2—C11	112.3 (2)
C1—N6—C7	116.8 (2)	C1—C2—C11	110.3 (2)
C5—N6—C7	118.1 (2)	N3—C4—C5	109.9 (2)
O10—C1—N6	121.4 (2)	N6—C5—C4	110.2 (2)
O10—C1—N6—C5	177.5 (2)	C1—C2—N3—C4	42.8 (2)
O10—C1—N6—C7	−8.4 (3)	C1—C2—N3—C19	−127.7 (3)
O10—C1—C2—N3	170.3 (2)	C1—C2—C11—C12	166.5 (2)
O10—C1—C2—C11	−64.5 (3)	C2—N3—C4—C5	−64.1 (2)
O20—C19—N3—C2	171.6 (3)	C2—C1—N6—C5	−3.8 (3)
O20—C19—N3—C4	1.7 (4)	C2—C1—N6—C7	170.3 (2)
N3—C2—C1—N6	−8.5 (3)	C4—N3—C2—C11	−81.3 (4)
N3—C4—C5—N6	47.6 (2)	C4—C5—N6—C7	170.0 (2)
N6—C1—C2—C11	116.7 (2)	C5—N6—C7—C8	−132.4 (3)
C1—N6—C5—C4	−15.9 (3)	C5—C4—N3—C19	106.5 (2)
C1—N6—C7—C8	53.0 (3)	C11—C2—N3—C19	108.2 (3)

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O18—H13···O20^{i}	0.747	1.911	2.648 (2)	170
O33—H29···O18^{ii}	0.816	1.964	2.771 (3)	170

Symmetry codes: (i) $-x, y-\frac{1}{2}, -z$; (ii) $x-1, 1+y, z$.

All H atoms were fixed at geometrically favourable positions. The absolute configuration of the molecule is derived from the known (*S*)-configuration of the tyrosine moieties.

Data collection: *Rigaku/AFC Diffractometer Control Software* (Rigaku Corporation, 1988). Cell refinement: *Rigaku/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1995). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985) and *DIRDIF*94 (Beurskens *et al.*, 1994). Program(s) used to refine structure: *TEXSAN*. Software used to prepare material for publication: *TEXSAN*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: OB1005). Services for accessing these data are described at the back of the journal.

References

Beurskens, P. T., Admiraal, G., Beurskens, G., Bosman, W. P., de Gelder, R., Israel, R. & Smits, J. M. M. (1994). *The DIRDIF*94 *Program System*. Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands.

IUPAC–IUB Commission on Biochemical Nomenclature (1970). *Pure Appl. Chem.* **25**, 1273–1280.

Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

Kojima, Y., Ikeda, Y., Kumata, E., Maruo, J., Okamoto, A., Hirotsu, K., Shibata, K. & Ohsuka, A. (1991). *Int. J. Peptide Protein Res.* **37**, 468–475.

Kojima, Y., Miyake, H., Ikeda, Y., Shibata, K., Yamashita, T., Ohsuka, A. & Sugihara, A. (1992). *Polym. J.* **24**, 591–595.

Kojima, Y., Yamashita, T. & Miyake, H. (1995). *Chem. Lett.* pp. 201–202.

Miyake, H., Kojima, Y., Yamashita, T. & Ohsuka, A. (1993). *Makromol. Chem.* **194**, 1925–1933.

Miyake, H., Yamashita, T., Hirotsu, K. & Kojima, Y. (1996). *Acta Cryst.* C**52**, 681–684.

Molecular Structure Corporation (1995). *TEXSAN. Single Crystal Structure Analysis Software*. Version 1.7-2. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Ramachandran, G. N. & Sasisekharan, V. (1968). *Adv. Protein Chem.* **23**, 283–437.

Rigaku Corporation (1988). *Rigaku/AFC Diffractometer Control Software*. Rigaku Corporation, Tokyo, Japan.

Sheldrick, G. M. (1985). *SHELXS*86. *Program for the Solution of Crystal Structures*. University of Göttingen, Germany.

Takenaka, H., Miyake, H., Kojima, Y., Yasuda, M., Gemba, M. & Yamashita, T. (1993). *J. Chem. Soc. Perkin Trans.* 1, pp. 933–937.

Toniolo, C. (1990). *Int. J. Peptide Protein Res.* **35**, 287–300.

Yamashita, T., Kojima, Y., Hirotsu, K. & Ohsuka, A. (1989). *Int. J. Peptide Protein Res.* **33**, 110–114.

Yamashita, T., Takenaka, H. & Kojima, Y. (1993). *Amino Acids*, **4**, 187–192.

Yamashita, T., Tsuru, E., Banjyo, E., Doe, M., Shibata, K., Yasuda, M. & Gemba, M. (1997). *Chem. Pharm. Bull.* **45**, 1940–1944.

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Absolute configuration of the active stereoisomer of new rice fungicide Carpropamid

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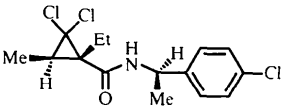
Abstract

The absolute configuration of the active component of fungicide Carpropamid of a diastereoisomeric mixture was determined to be (1*S*,3*R*)-*N*-[(*R*)-1-(4-chlorophenyl)ethyl]-2,2-dichloro-1-ethyl-3-methylcyclopropanecarboxamide, $C_{15}H_{18}Cl_3NO$. Two molecules are tightly coupled in the crystal. The intermolecular hydrogen bonding between C=O and H—N is responsible for this assembly.

Comment

New fungicide Carpropamid, *N*-[(*R*)-1-(4-chlorophenyl)-ethyl]-2,2-dichloro-1-ethyl-3-methylcyclopropanecarboxamide, (I), was launched successfully on the market in 1997 (Kagabu & Kurahashi, 1998). It controls rice blast disease caused by pathogenic *Pyricularia oryzae* by inhibiting the biosynthesis of melanin of this fungus (Kurahashi *et al.*, 1996, 1997). The commercial product is a mixture of two diastereoisomers composed of (1*S*,3*R*) and (1*R*,3*S*) configurations on the cyclopropane part, and it has been reported that the isomer of the larger dextrorotation is superior in biological activity (Kagabu & Kurahashi, 1998). We separated the component of $[\alpha]$ = +87.9 from the other of $[\alpha]$ = +40.5 by repeating preparative thin-layer chromatography (TLC) and determined its absolute configuration to be (1*S*, 3*R*).



(I)

The crystal structure of the biologically preferable isomer is mapped as two independent molecules (Fig. 1). The N1—C9 and N2—C24 bond lengths, 1.337 (6) and 1.328 (7) Å, are close to that of C=N (imine) (1.33 Å) (Sasada, 1984). The double-bond character is obviously brought about by the transfer of the lone-pair electrons on the N atom. The torsion angles O1—C9—N1—C7 −4.4 (8) and O2—C24—N2—C22 2.9 (9)° give further evidence for the sp^2 nature of the N atoms. The interatomic distances between the carbonyl-O atom of one molecule and the amine-N atom of the associated half are 2.933 (4) and 2.879 (6) Å for O1···N2 and O2···N1($-1-x$, $\frac{1}{2}+y$, $-\frac{3}{2}-z$), respectively, suggesting the existence of an intermolecular hydrogen bond between the amide moieties. This hydrogen-bonded molecular stacking compares well with the twined segments of proteins (Baker & Hubbard, 1984; Jeffrey & Saenger, 1991; Allen *et al.*, 1998).

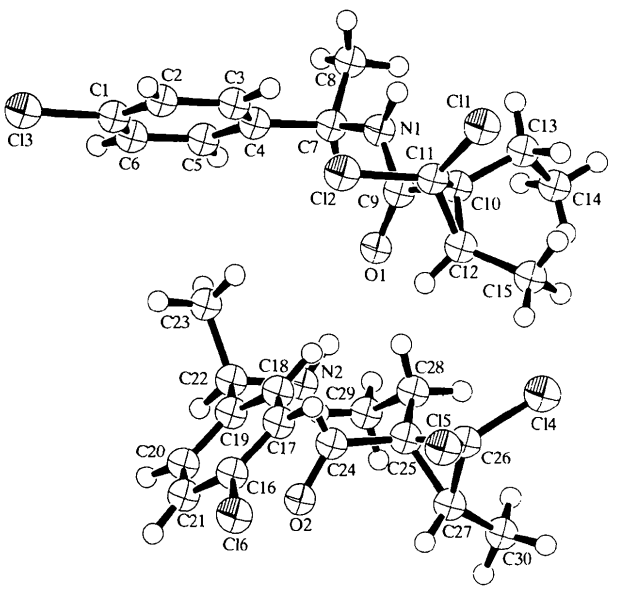


Fig. 1. *ORTEP* drawing (Johnson, 1965) of the two independent molecules of (I) with the atomic numbering scheme. Displacement ellipsoids of non-H atoms are shown at the 50% probability level. H atoms are shown as spheres of an arbitrary radius.

Experimental

Carpropamid was subjected to preparative TLC (SiO_2) with hexane/ethyl acetate (5:1) as the eluant. The component of specific rotation $[\alpha]$ = +87.9 (MeOH) was recrystallized from methanol [m.p. 409 K; ^{1}H NMR (400 MHz, $CDCl_3$, p.p.m.): δ = 0.99 (3H, *t*, *J* = 7.3 Hz, CH_3), 1.20 (3H, *d*, *J* = 6.6 Hz, CH_3), 1.53 (3H, *d*, *J* = 4.6 Hz, CH_3), 1.56 (1H, *dt*, *J* = 7.56 Hz, CH_2a), 1.93 (1H, *dt*, *J* = 7.56 Hz, CH_2b), 2.20 (1H, *q*, *J* = 6.6 Hz, CH), 5.85 (1H, *br. s*, NH), 7.30 (4H, *m*, Ar)].

Crystal data

$C_{15}H_{18}Cl_3NO$
M_r = 334.67
Orthorhombic
$P2_12_12_1$
a = 13.6977 (5) Å
b = 19.8307 (8) Å
c = 12.7594 (8) Å
V = 3465.9 (2) Å^3
Z = 8
D_x = 1.283 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.7107 Å
Cell parameters from 25 reflections
θ = 10.2–12.4°
μ = 0.523 mm^{-1}
T = 296.2 K
Prismatic
0.68 × 0.47 × 0.39 mm
Colorless

Data collection

Rigaku AFC-7*R* diffractometer
ω–2θ scans
Absorption correction: none
4430 measured reflections
4429 independent reflections
3488 reflections with $I > 2.0\sigma(I)$

R_{int} = 0.01
θ_{max} = 27.5°
h = 0 → 17
k = 0 → 25
l = 0 → 16
3 standard reflections every 150 reflections
intensity decay: 1.91%

Refinement

Refinement on *F*
R = 0.055
wR = 0.067
S = 1.484
3488 reflections
362 parameters
H-atom parameters not refined
$w = 1/[\sigma^2(F_o) + 0.0004|F_o|^2]$

$(\Delta/\sigma)_{max}$ = 0.033
$\Delta\rho_{max}$ = 0.39 e Å^{-3}
$\Delta\rho_{min}$ = −0.45 e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute structure: Flack (1983)
Flack parameter = −0.2 (1)

Table 1. *Selected geometric parameters (°)*

N1—C7—C4	112.8 (5)	N2—C22—C19	110.9 (5)
N1—C7—C8	108.7 (5)	N2—C22—C23	108.8 (5)
O1—C9—N1	123.4 (5)	O2—C24—N2	121.2 (5)
O1—C9—C10	121.5 (5)	O2—C24—C25	122.7 (5)
N1—C9—C10	115.1 (4)	N2—C24—C25	116.0 (5)
C11—C10—C12	58.6 (4)	C26—C25—C27	58.4 (4)
C10—C11—C12	60.2 (4)	C25—C26—C27	61.0 (4)
C10—C12—C11	61.2 (4)	C25—C27—C26	60.6 (4)
O1—C9—N1—C7	−4.4 (8)	C7—N1—C9—C10	173.3 (5)
O2—C24—N2—C22	2.9 (9)	C8—C7—N1—C9	−148.3 (5)
N1—C7—C4—C3	20.8 (8)	C17—C18—C19—C22	−178.4 (6)
N1—C7—C4—C5	−161.4 (5)	C18—C19—C22—C23	−70.4 (8)
N2—C22—C19—C18	52.4 (8)	C19—C22—N2—C24	70.4 (7)
N2—C22—C19—C20	−127.6 (6)	C20—C19—C22—C23	109.5 (6)
C3—C4—C7—C8	−101.5 (7)	C21—C20—C19—C22	178.2 (6)
C5—C4—C7—C8	76.2 (7)	C22—N2—C24—C25	−178.0 (5)
C6—C5—C4—C7	−178.2 (7)	C23—C22—N2—C24	−164.1 (6)

Table 2. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H27···O1	0.91	2.03	2.933 (4)	172
N1—H9···O2^{i}	1.00	1.96	2.879 (6)	151

Symmetry code: (i) $-1-x, y-\frac{1}{2}, -\frac{3}{2}-z$.

H atoms were found in electron-density difference maps, but were replaced in calculated positions and allowed to refine as riding models on their appropriate C atoms.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1996). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1998). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1985). Program(s) used to refine structure: *TEXSAN*. Software used to prepare material for publication: *TEXSAN*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1401). Services for accessing these data are described at the back of the journal.

References

Allen, F. H., Raithby, P. R., Shields, G. P. & Taylor, R. (1998). *Chem. Commun.* pp. 1043–1044.

Baker, E. N. & Hubbard, R. E. (1984). *Prog. Biophys. Mol. Biol.* **44**, 97–179.

Flack, H. D. (1983). *Acta Cryst.* A**39**, 876–881.

Jeffrey, G. A. & Saenger, W. (1991). *Hydrogen Bonding in Biological Structures*, ch. 19. Berlin: Springer-Verlag.

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

Kagabu, S. & Kurahashi, Y. (1998). *J. Pestic. Sci.* **23**, 145–147.

Kurahashi, Y., Hattori, Y., Kagabu, S. & Ponzen, R. (1996). *Pestic. Sci.* **47**, 199–202.

Kurahashi, Y., Sakawa, S., Kinbara, T., Tanaka, K. & Kagabu, S. (1997). *J. Pestic. Sci.* **22**, 108–112.

Molecular Structure Corporation (1998). *TEXSAN. Single Crystal Structure Analysis Software*. Version 1.9. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Molecular Structure Corporation (1996). *MSC/AFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Sasada, Y. (1984). *Chemistry Handbook*, 3rd ed., edited by the Chemical Society of Japan, ch. 15. Tokyo: Maruzen. (In Japanese.)

Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures*. University of Göttingen, Germany.

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3-Ethyl-5-(5,6,7,8-tetrahydro-5,5,8,8-tetramethyl-2-naphthylmethylene)thiazolidine-2,4-dione

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Abstract

The title compound, $C_{20}H_{25}NO_2S$, is under investigation for potential retinoid-receptor activity. The molecular conformation is approximately planar, with five methyl groups projecting from the mean plane. Twofold disorder of the methylene groups of the tetrahydrotetramethyl residue was detected and satisfactorily modelled.

Comment

Retinoic acid and its biological isosteres play important roles in a variety of biological processes including regulation of cell growth/differentiation and lipid peroxidase inhibition (Hiramatsu & Packer, 1990). The physiological effects of retinoids have emerged in their application in chemotherapy in several cancer treatments (Smith *et al.*, 1992; Vokes *et al.*, 1993) although they have significant side effects, due in part to their high hydrophobicity (Shimasaki *et al.*, 1995) and their ability to activate multiple retinoid receptors (Orfanos *et al.*, 1987). As part of our search for new antioxidant drugs, we have been studying retinoidal compounds bearing the 5,6,7,8-tetrahydro-5,5,8,8-tetramethyl moiety as potential inhibitors of cytochrome P450 isozymes and we have reported a potent antioxidant activity of a tetrahydrotetramethylbenzimidazol compound (Ates *et al.*, 1997). On the other hand, the thiazole moiety is found in many anticancer compounds as well as antioxidants (Schumaker *et al.*, 1997; Herbert *et al.*, 1993). Previously, it was reported that inclusion of the thiazolidine ring into the retinoic acid side-chain led to good retinoidal activity towards human promyelocytic leukaemia HL-60 cells (Tashima *et al.*, 1997).

It is apparent that specificity for binding at the active sites of different retinoid receptors must eventually depend on the conformational properties of the individual molecules. The size and conformational flexibility of the retinoid molecules obtained from X-ray studies are important factors for the future design of retinoid-type