C7	0.9436 (11)	0.1649 (2)	1.3496 (8)	0.0428 (15)
C8	0.7625 (11)	0.1856 (2)	1.3817 (10)	0.056 (2)
C9	0.7959 (14)	0.2110 (2)	1.5659 (12)	0.070 (2)
C10	1.0076 (16)	0.2163 (2)	1.7230 (11)	0.071 (2)
C11	1.1904 (13)	0.1957 (2)	1.6953 (10)	0.072 (2)
C12	1.1561 (11)	0.1707 (2)	1.5070 (9)	0.060 (2)
N13	0.7230 (7)	0.03502 (12)	0.9956 (6)	0.0322 (11)
C14	0.5177 (10)	0.01726 (15)	0.9234 (8)	0.0338 (13)
O15	0.3618 (6)	0.02756 (11)	0.7499 (5)	0.0433 (10)
C16	0.7866 (9)	0.0477 (2)	0.6417 (8)	0.0445 (15)
O17	0.8635 (6)	0.00442 (12)	0.6683 (5)	0.0501 (11)

Table 2. *Selected bond lengths (Å)*

Crystal	(I)	(I)	(II)
Molecule	(I*a*)	(I*b*)	(I*a*)
	n = *A*	*n* = *B*	*n* = –
O1*n*—C2*n*	1.407 (3)	1.409 (3)	1.419 (6)
O1*n*—C6*n*	1.434 (3)	1.439 (3)	1.431 (5)
C2*n*—O3*n*	1.414 (3)	1.417 (3)	1.410 (6)
C2*n*—C7*n*	1.506 (3)	1.507 (3)	1.495 (6)
O3*n*—C4*n*	1.435 (3)	1.423 (3)	1.425 (5)
C4*n*—C5*n*	1.522 (3)	1.520 (3)	1.530 (6)
C5*n*—C6*n*	1.514 (3)	1.539 (3)	1.533 (6)
C5*n*—N13*n*	1.471 (3)	1.473 (3)	1.458 (6)
C5*n*—C16*n*	1.521 (4)	1.520 (3)	1.524 (6)
N13*n*—C14*n*	1.324 (3)	1.319 (3)	1.331 (6)
C14*n*—C14*n*^{i}	1.538 (5)	1.530 (5)	1.523 (9)
C14*n*—O15*n*	1.233 (3)	1.206 (3)	1.236 (5)
C16*n*—O17*n*	1.415 (3)	1.420 (3)	1.424 (5)

Equivalent positions: for (I*a*) in (I) (i) = $2 - x, 2 - y, -z$; for (I*b*) in (I) (i) = $1 - x, 2 - y, -z$; for (I*a*) in (II) (i) = $1 - x, -y, 2 - z$.

Table 3. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
(I)				
N13*A*—H13*A*···O15*A*^{i}	0.86	2.28	2.695 (3)	109
N13*B*—H13*B*···O15*B*^{ii}	0.86	2.28	2.679 (3)	108
O17*A*—H17*A*···O15*A*^{iii}	0.82	2.00	2.778 (3)	158
O17*B*—H17*B*···O3*A*^{iv}	0.82	2.06	2.831 (3)	157
(II)				
N13—H13···O17^{v}	0.86	2.23	2.995 (5)	149
O17—H17···O15^{vi}	0.82	1.93	2.731 (5)	166

Symmetry codes: (i) $2 - x, 2 - y, -z$; (ii) $1 - x, 2 - y, -z$; (iii) $2 - x, 1 - y, -z$; (iv) $x - 1, y, z$; (v) $2 - x, -y, 2 - z$; (vi) $1 - x, -y, 1 - z$.

Data collection was terminated at a θ value of 22° for (I) and 24° for (II) because of the absence of observable data. The diagrams were prepared using *ORTEP*II (Johnson, 1976) as implemented in *PLATON* (Spek, 1995*a*). Examination of the structures with the *SOLV* option in *PLATON* showed that there were no solvent-accessible voids in the crystal lattices. For all three stereoisomers, H atoms were refined as riding [default in *SHELXL*93 (Sheldrick, 1993) C—H 0.93–0.98, N—H 0.86 and O—H 0.82 Å].

For both compounds, data collection: *CAD*-4 *Software* (Enraf–Nonius 1992); cell refinement: *SET*4 and *CELDIM* (*CAD*-4 Software); data reduction: *DATRD*2 (*NRCVAX*94; Gabe, Le Page, Charland, Lee & White, 1989); program(s) used to solve structures: *SOLVER* (*NRCVAX*94); program(s) used to refine structures: *NRCVAX*94; *SHELXL*93 (Sheldrick, 1993); molecular graphics: *NRCVAX*94; *PLATON* (Spek, 1995*a*); *PLUTON* (Spek 1995*b*); software used to prepare material for publication: *NRCVAX*94; *SHELXL*93 and *WordPerfect*.

GF thanks NSERC (Canada) for research grants.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AB1322). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Enraf–Nonius (1992). *CAD-4/PC Software*. Version 1.1. Enraf–Nonius, Delft, The Netherlands

Gabe, E. J., Le Page, Y., Charland, J.-P., Lee, F. L. & White, P. S. (1989). *J. Appl. Cryst.* **22**, 384–387.

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

Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.

Spek, A. L. (1995*a*). *PLATON. Molecular Geometry Program.* July 1995 version. University of Utrecht, Utrecht, Holland.

Spek, A. L. (1995*b*). *PLUTON. Molecular Graphics Program.* July 1995 version. University of Utrecht, Utrecht, Holland.

Acta Cryst. (1996). C**52**, 231–235

Molecular Co-Crystals of Carboxylic Acids. 23.† The 1:1 Adducts of 3-Amino-1*H*-1,2,4-triazole with 5-Nitrosalicylic Acid and 3,5-Dinitrosalicylic Acid

GRAHAM SMITH,[a]* DANIEL E. LYNCH,[a] KARL A. BYRIEL[b] AND COLIN H. L. KENNARD[b]

[a]*School of Chemistry, Queensland University of Technology, PO Box 2434, Brisbane 4001, Australia, and* [b]*Department of Chemistry, The University of Queensland, Brisbane 4072, Australia*

(*Received 24 October 1994; accepted 26 July 1995*)

Abstract

The structures of the 1:1 molecular adducts of the herbicide 3-amino-1*H*-1,2,4-triazole (amitrole, 3-AT) with 5-nitrosalicylic acid (5-NSA), 3-amino-$2H,4H^+$-1,2,4-triazolium 5-nitrosalicylate, $C_2H_5N_4^+.C_7H_4NO_5^-$, (1), and 3,5-dinitrosalicylic acid (DNSA), 3-amino-$2H,4H^+$-1,2,4-triazolium 3,5-dinitrosalicylate, $C_2H_5N_4^+.C_7H_3N_2O_7^-$, (2), have been determined by X-ray diffraction and refined to residuals R = 0.035 and 0.037 for 1355 and 826 observed reflections, respectively. In both adducts, the acid protonates the hetero N atom of the amitrole ring. For (1), both molecules are involved in a network structure in which all available proton-donor and acceptor atoms, including the nitro O atoms, participate in hydrogen bonding. For (2), the two-dimensional sheet

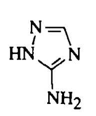
---

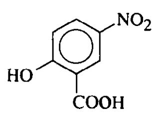
† Part 22: Smith, Lynch, Byriel & Kennard (1995*a*).

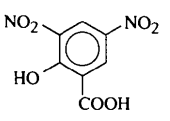
structure involves those atoms comprising the proximal sites of the interacting molecules, with limited interaction through the nitro O atoms.

Comment

The commercial herbicide amitrole [3-amino-1*H*-1,2,4-triazole or 3-AT, (I)] has proved to be a useful Lewis base for molecular adduct formation, with both good stereochemical features and suitable proton-donor and acceptor sites in its amine and hetero N atom functional groups. The structures of the 1:1 amitrole adducts with the nitro-substituted benzoic acids 3-nitrobenzoic acid $[(3\text{-AT})^+(3\text{-NBA})^-]$ (Lynch, Smith, Byriel & Kennard, 1994), 4-nitrobenzoic acid $[(3\text{-AT})^+(4\text{-NBA})^-]$ (Byriel, Kennard, Lynch, Smith & Thompson, 1992) and 3,5-dinitrobenzoic acid $[(3\text{-AT})^+(\text{DNBA})^-.2H_2O]$ (Lynch, Smith, Byriel & Kennard, 1992) have been determined. 5-Nitrosalicylic acid [5-NSA, (II)] and 3,5-dinitrosalicylic acid [DNSA, (III)] have the potential for formation of proton-transfer heteroadducts because of their acid strength [pK_a = 2.14 and 2.18 for (I) and (II), respectively]. Although a large number of adducts of Lewis bases with DNSA, together with their IR spectra, appear in the chemical literature (Hindawey, Nasser, Issa & Issa, 1980; Issa, Hindawey, El-Kholy & Issa, 1981), no crystal structures were known until those of both the parent acid hydrate, DNSA.H_2O, and the adducts with the three isomeric monoaminobenzoic acids were completed by our group (Smith, Lynch, Byriel & Kennard, 1995*b*). However, adduct formation with 5-NSA has been less encouraging, the 1:1 adduct with amitrole reported here, *i.e.* $[(3\text{-AT})^+(5\text{-NSA})^-]$, (1), being the only one for which crystals suitable for single-crystal X-ray analysis have been prepared. Also reported here is the 1:1 adduct of amitrole with DNSA, $[(3\text{-AT})^+(\text{DNSA})^-]$, (2).


3-AT (I)


5-NSA (II)


DNSA (III)

Both adducts involve proton transfer from the carboxylic acid group of the acid to a hetero N atom of amitrole. The network structure of (1) comprises 5-NSA molecules and hetero-ring-protonated 3-AT molecules involved in hydrogen-bonding interactions, with all available proton-donor and acceptor groups participating. The result is a convoluted ribbon structure linked laterally into a network polymer (Fig. 2). The 5-NSA molecules are almost planar [torsion angles C(21)—C(11)—C(111)—O(121) 176.0 (3) and C(41)—C(51)—N(511)—O(521) 176.6 (3)°], while the phenolic proton participates in an intramolecular hydrogen bond with the carboxylic acid O atom [O···O 2.500 (3) Å]. This is similar to the situation found for both salicylic acid (O···O 2.640 Å; Sundaralingam & Jensen, 1965) and for 3,5-dinitrosalicylic acid (O···O 2.566 Å; Smith *et al.*, 1995*b*). Although this distance in (1) is shorter than for these acids, it is longer than the value for (2) [2.452 (5) Å] and more comparable with the other known adducts of DNSA (range 2.452–2.460 Å; Smith *et al.*, 1995*b*).

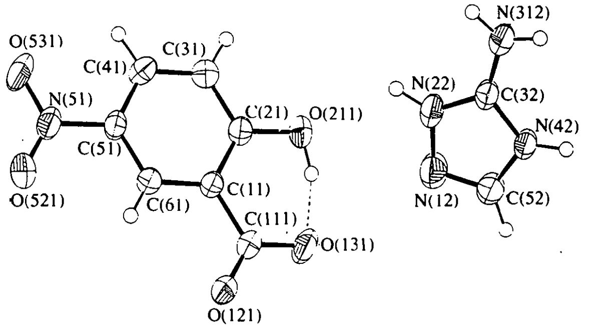


Fig. 1. The molecular conformation and atom-numbering scheme of the individual molecules of amitrole and 5-nitrosalicylic acid in the adduct $[(3\text{-AT})^+(5\text{-NSA})^-]$, (1). Atoms are shown as 30% probability ellipsoids.

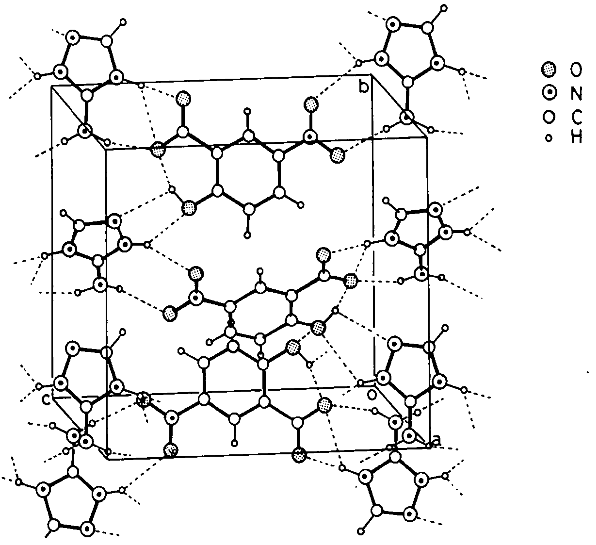


Fig. 2. Perspective view of the packing of (1) in the unit cell.

With (2), the primary interaction between 3-AT and DNSA involves the protonated hetero N atom of 3-AT and the proximal sites of DNSA [the phenolic O(211) atom and a nitro O(311) atom]. Other intermolecular interactions *via* both the amine and hetero N atoms of 3-AT result in an essentially two-dimensional sheet structure lying approximately perpendicular to the *b* axis (Fig. 4), which makes this example different from both (1) and the other known 3-AT adducts. The intramolecular O—H···O hydro-

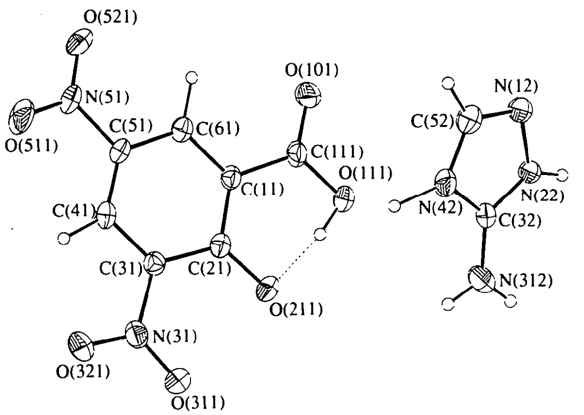


Fig. 3. The molecular conformation and atom-numbering scheme of the individual molecules of amitrole and 3,5-dinitrosalicylic acid in the adduct [(3-AT)$^+$(DNSA)$^-$], (2). Atoms are shown as 30% probability ellipsoids.

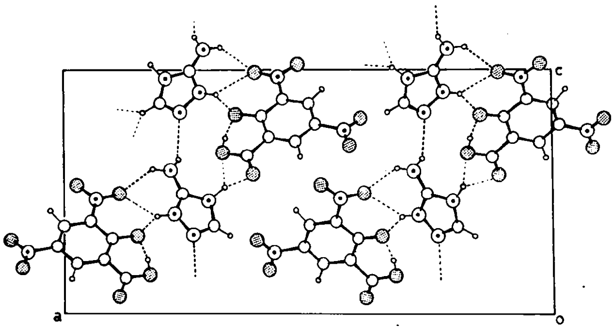


Fig. 4. Perspective view of the packing of (2) in the unit cell.

gen bond is also present in the DNSA molecule, but with the proton located on the carboxyl O atom [O···O 2.452 (5) Å], contributing to its planarity [torsion angles C(21)—C(11)—C(111)—O(101) 178.2 (4), C(21)—C(31)—N(31)—O(321) 177.8 (4) and C(41)—C(51)—N(51)—O(521) −170.0 (4)°].

The situation whereby the proton is located on the carboxyl O atom rather than the phenolic group {as found with (2) and the isomeric monoaminobenzoic acid adducts of DNSA, [(3-ABA)(DNSA)] and [(4-ABA)$_2$(DNSA)] (Smith *et al.*, 1995*b*)} contrasts with that found in adduct (1) and in the third member of the aminobenzoic acid–DNSA adduct series, [(2-ABA)(DNSA)] (Smith *et al.*, 1995*b*). The contention by Hindawey *et al.* (1980) that the phenolic group is involved in the primary proton transfer has been refuted on the basis of the relative pK_a values for the carboxyl and phenol groups (2.14 and 7.29, respectively), despite the observation that in some adducts the proton is located on the carboxylic acid group. It is considered that relocation of the proton on the carboxyl group follows primary proton transfer *via* the carboxyl group and occurs in those examples where the hydroxyl group is involved in extensive hydrogen bonding in adduct formation. This is supported by the structural evidence from the compounds discussed here and reported previously (Smith *et al.*, 1995*b*).

Experimental

Adduct (1) was prepared by refluxing equimolar amounts of 5-nitrosalicylic acid and 3-amino-1*H*-1,2,4-triazole in 95% aqueous ethanol for 20 min at 383 K. Pale-yellow prisms (m.p. 479–481 K) formed upon total evaporation of the solvent at room temperature. Adduct (2) was prepared by refluxing equimolar amounts of 3,5-dinitrosalicylic acid and 3-amino-1*H*-1,2,4-triazole in 95% aqueous ethanol for 20 min at 383 K. Yellow prisms (m.p. 501–503 K) formed upon total evaporation of the solvent at room temperature.

Adduct (1)

Crystal data

$C_2H_5N_4^+.C_7H_4NO_5^-$
$M_r = 267.2$
Monoclinic
$P2_1/a$
$a = 7.307\,(2)$ Å
$b = 12.327\,(1)$ Å
$c = 12.330\,(3)$ Å
$\beta = 100.12\,(1)°$
$V = 1093.3\,(4)$ Å^3
$Z = 4$
$D_x = 1.623$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 25 reflections
$\theta = 6–14°$
$\mu = 0.135$ mm^{-1}
$T = 298\,(2)$ K
Prismatic
0.21 × 0.21 × 0.16 mm
Yellow

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (Fair, 1990)
$T_{\min} = 0.99$, $T_{\max} = 1.00$
2104 measured reflections
1937 independent reflections
1355 observed reflections [$I > 2.0\sigma(I)$]

$R_{\rm int} = 0.016$
$\theta_{\max} = 25°$
$h = 0 \rightarrow 8$
$k = 0 \rightarrow 14$
$l = -14 \rightarrow 14$
3 standard reflections monitored every 200 reflections
intensity decay: 1.0%

Refinement

Refinement on F^2
$R(F) = 0.035$
$wR(F^2) = 0.091$
$S = 1.05$
1355 reflections
209 parameters
All H-atom parameters refined

$w = 1/[\sigma^2(F_o)^2 + (0.045P)^2 + 0.37P]$ where $P = [\max(F_o^2,0) + 2F_c^2]/3$
$(\Delta/\sigma)_{\max} = 0.1$
$\Delta\rho_{\max} = 0.19$ e Å^{-3}
$\Delta\rho_{\min} = -0.22$ e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Adduct (2)

Crystal data

$C_2H_5N_4^+.C_7H_3N_2O_7^-$
$M_r = 312.2$

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å

Orthorhombic
$Pna2_1$
$a = 24.070$ (5) Å
$b = 4.332$ (3) Å
$c = 11.8298$ (5) Å
$V = 1233.5$ (8) Å^3
$Z = 4$
$D_x = 1.676$ Mg m^{-3}

Cell parameters from 25 reflections
$\theta = 6–14°$
$\mu = 0.147$ mm^{-1}
$T = 298$ (2) K
Prismatic
0.40 × 0.16 × 0.12 mm
Yellow

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: ψ scan (Fair, 1990)
$T_{\rm min} = 0.98$, $T_{\rm max} = 1.00$
1135 measured reflections
1135 independent reflections
826 observed reflections [$I > 2.0\sigma(I)$]

$\theta_{\rm max} = 25°$
$h = 0 \rightarrow 28$
$k = 0 \rightarrow 5$
$l = 0 \rightarrow 14$
3 standard reflections monitored every 200 reflections
intensity decay: 3%

Refinement

Refinement on F^2
$R(F) = 0.037$
$wR(F^2) = 0.087$
$S = 0.98$
826 reflections
231 parameters
All H-atom parameters refined

$w = 1/[\sigma^2(F_o)^2 + (0.137P)^2]$ where $P = [\max(F_o^2,0) + 2F_c^2]/3$
$(\Delta/\sigma)_{\rm max} = 0.15$
$\Delta\rho_{\rm max} = 0.17$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.27$ e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Adduct (1)				
C(11)	0.1826 (3)	0.0595 (2)	0.3749 (2)	0.032 (1)
C(111)	0.2134 (3)	−0.0058 (2)	0.2772 (2)	0.040 (1)
O(121)	0.3030 (2)	−0.0915 (1)	0.2911 (1)	0.050 (1)
O(131)	0.1414 (3)	0.0309 (2)	0.1833 (1)	0.062 (1)
C(21)	0.0916 (3)	0.1601 (2)	0.3604 (2)	0.035 (1)
O(211)	0.0284 (2)	0.2008 (1)	0.2604 (1)	0.049 (1)
C(31)	0.0659 (3)	0.2210 (2)	0.4522 (2)	0.040 (1)
C(41)	0.1252 (3)	0.1821 (2)	0.5567 (2)	0.041 (1)
C(51)	0.2106 (3)	0.0815 (2)	0.5695 (2)	0.034 (1)
N(51)	0.2631 (3)	0.0376 (2)	0.6796 (1)	0.042 (1)
O(521)	0.3306 (3)	−0.0529 (1)	0.6924 (1)	0.057 (1)
O(531)	0.2344 (3)	0.0934 (2)	0.7578 (1)	0.061 (1)
C(61)	0.2409 (3)	0.0208 (2)	0.4805 (2)	0.033 (1)
N(12)	0.0257 (3)	0.2379 (2)	1.0237 (2)	0.053 (1)
N(22)	0.1067 (3)	0.3295 (2)	1.0733 (2)	0.045 (1)
C(32)	0.1645 (3)	0.3954 (2)	1.0009 (2)	0.036 (1)
N(312)	0.2446 (3)	0.4907 (2)	1.0192 (2)	0.048 (1)
N(42)	0.1191 (2)	0.3465 (2)	0.9026 (1)	0.037 (1)
C(52)	0.0367 (3)	0.2521 (2)	0.9214 (2)	0.046 (1)
Adduct (2)				
C(11)	0.9173 (2)	0.4584 (10)	0.2205 (4)	0.035 (1)
C(21)	0.9013 (2)	0.2509 (10)	0.3069 (3)	0.035 (1)
O(211)	0.8501 (1)	0.1719 (8)	0.3182 (3)	0.051 (1)
C(31)	0.9455 (2)	0.1406 (9)	0.3781 (3)	0.036 (1)
N(31)	0.9350 (2)	−0.0739 (8)	0.4697 (3)	0.045 (1)
O(311)	0.8874 (1)	−0.1598 (10)	0.4901 (3)	0.072 (1)
O(321)	0.9745 (2)	−0.1658 (10)	0.5248 (3)	0.067 (1)
C(41)	1.0001 (2)	0.2233 (11)	0.3597 (4)	0.039 (1)
C(51)	1.0124 (2)	0.4187 (10)	0.2735 (4)	0.038 (1)
N(51)	1.0704 (1)	0.4940 (10)	0.2505 (3)	0.047 (1)
O(511)	1.1062 (1)	0.3463 (10)	0.2999 (4)	0.078 (1)
O(521)	1.0814 (1)	0.6997 (10)	0.1841 (4)	0.067 (1)
C(61)	0.9722 (2)	0.5439 (10)	0.2033 (4)	0.036 (1)
C(111)	0.8749 (2)	0.5905 (11)	0.1433 (4)	0.044 (1)
O(101)	0.8861 (1)	0.7748 (9)	0.0697 (3)	0.063 (1)
O(111)	0.8234 (1)	0.4990 (9)	0.1580 (3)	0.053 (1)
N(12)	0.7367 (1)	−0.2029 (10)	0.3224 (4)	0.053 (1)
N(22)	0.7755 (1)	−0.2282 (10)	0.4072 (3)	0.044 (1)
C(32)	0.7575 (2)	−0.3992 (12)	0.4915 (4)	0.046 (1)
N(312)	0.7842 (2)	−0.4703 (15)	0.5841 (4)	0.081 (2)
N(42)	0.7051 (2)	−0.4847 (10)	0.4618 (4)	0.051 (1)
C(52)	0.6954 (2)	−0.3601 (13)	0.3595 (4)	0.055 (1)

Table 2. *Selected geometric parameters (Å, °)*

Adduct (1)			
C(11)—C(61)	1.382 (3)	C(51)—N(51)	1.449 (3)
C(11)—C(21)	1.403 (3)	N(51)—O(521)	1.219 (2)
C(11)—C(111)	1.499 (3)	N(51)—O(531)	1.232 (2)
C(111)—O(121)	1.240 (3)	N(12)—C(52)	1.290 (3)
C(111)—O(131)	1.268 (3)	N(12)—N(22)	1.368 (3)
C(21)—O(211)	1.336 (2)	N(22)—C(32)	1.329 (3)
C(21)—C(31)	1.398 (3)	C(32)—N(312)	1.314 (3)
C(31)—C(41)	1.372 (3)	C(32)—N(42)	1.342 (3)
C(41)—C(51)	1.385 (3)	N(42)—C(52)	1.349 (3)
C(51)—C(61)	1.378 (3)		
C(61)—C(11)—C(21)	119.1 (2)	C(41)—C(51)—N(51)	118.8 (2)
C(61)—C(11)—C(111)	120.4 (2)	O(521)—N(51)—O(531)	122.0 (2)
C(21)—C(11)—C(111)	120.5 (2)	O(521)—N(51)—C(51)	119.8 (2)
O(121)—C(111)—O(131)	123.7 (2)	O(531)—N(51)—C(51)	118.1 (2)
O(121)—C(111)—C(11)	119.8 (2)	C(51)—C(61)—C(11)	119.8 (2)
O(131)—C(111)—C(11)	116.4 (2)	C(52)—N(12)—N(22)	103.2 (2)
O(211)—C(21)—C(31)	118.1 (2)	C(32)—N(22)—N(12)	111.6 (2)
O(211)—C(21)—C(11)	121.9 (2)	N(312)—C(32)—N(22)	128.0 (2)
C(31)—C(21)—C(11)	120.0 (2)	N(312)—C(32)—N(42)	126.0 (2)
C(41)—C(31)—C(21)	120.5 (2)	N(22)—C(32)—N(42)	106.0 (2)
C(31)—C(41)—C(51)	118.9 (2)	C(32)—N(42)—C(52)	106.2 (2)
C(61)—C(51)—C(41)	121.8 (2)	N(12)—C(52)—N(42)	113.0 (2)
C(61)—C(51)—N(51)	119.4 (2)		
Adduct (2)			
C(11)—C(61)	1.389 (5)	C(51)—N(51)	1.460 (5)
C(11)—C(21)	1.415 (6)	N(51)—O(521)	1.217 (5)
C(11)—C(111)	1.484 (6)	N(51)—O(511)	1.221 (5)
C(21)—O(211)	1.286 (4)	C(111)—O(101)	1.212 (5)
C(21)—C(31)	1.440 (6)	C(111)—O(111)	1.311 (5)
C(31)—C(41)	1.380 (6)	N(12)—C(52)	1.281 (6)
C(31)—N(31)	1.450 (5)	N(12)—N(22)	1.376 (5)
N(31)—O(321)	1.219 (5)	N(22)—C(32)	1.315 (6)
N(31)—O(311)	1.229 (5)	C(32)—N(312)	1.306 (7)
C(41)—C(51)	1.358 (7)	C(32)—N(42)	1.361 (6)
C(51)—C(61)	1.385 (6)		
C(61)—C(11)—C(21)	122.3 (4)	C(41)—C(51)—N(51)	119.2 (4)
C(61)—C(11)—C(111)	117.6 (4)	C(61)—C(51)—N(51)	118.0 (4)
C(21)—C(11)—C(111)	120.1 (3)	O(521)—N(51)—O(511)	122.7 (4)
O(211)—C(21)—C(11)	120.3 (3)	O(511)—N(51)—C(51)	117.9 (4)
O(211)—C(21)—C(31)	124.1 (4)	C(51)—C(61)—C(11)	118.2 (4)
C(11)—C(21)—C(31)	115.6 (3)	O(101)—C(111)—O(111)	120.3 (4)
C(41)—C(31)—C(21)	121.8 (4)	O(101)—C(111)—C(11)	122.8 (4)
C(41)—C(31)—N(31)	116.8 (4)	O(111)—C(111)—C(11)	116.8 (4)
C(21)—C(31)—N(31)	121.3 (3)	C(52)—N(12)—N(22)	103.6 (4)
O(321)—N(31)—O(311)	121.5 (4)	C(32)—N(22)—N(12)	112.0 (3)
O(321)—N(31)—C(31)	118.2 (4)	N(312)—C(32)—N(22)	127.4 (4)
O(311)—N(31)—C(31)	120.3 (4)	N(312)—C(32)—N(42)	127.4 (5)
C(51)—C(41)—C(31)	119.2 (4)	N(22)—C(32)—N(42)	105.2 (4)
C(41)—C(51)—C(61)	122.8 (4)	C(52)—N(42)—C(32)	106.5 (4)

Table 3. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	H···*A*	*D*···*A*	*D*—H···*A*
Adduct (1)			
O(211)—H(211)···O(131)	1.66 (4)	2.500 (3)	156 (3)
O(211)—H(211)···N(12$^{\rm i}$)	2.61 (3)	2.951 (3)	103 (2)
N(312)—H(312)···O(131$^{\rm ii}$)	1.97 (3)	2.811 (3)	158 (3)
N(42)—H(42)···O(121$^{\rm ii}$)	1.73 (3)	2.663 (2)	177 (3)
N(42)—H(42)···O(131$^{\rm ii}$)	2.55 (3)	3.163 (2)	124 (2)

N(22)—H(22)···O(211^{iii})	2.36 (3)	2.938 (3)	123 (2)
N(312)—H(322)···O(531^{iv})	2.18 (3)	3.006 (3)	159 (3)
N(22)—H(22)···O(521^{iv})	2.39 (3)	3.193 (3)	151 (3)
N(312)—H(322)···O(131^{v})	2.75 (3)	3.242 (3)	117 (3)
C(41)—H(41)···O(121^{ii})	2.61 (2)	3.353 (3)	138 (2)
Adduct (2)			
O(111)—H(111)···O(211)	1.57 (6)	2.452 (5)	169 (6)
N(22)—H(22)···O(211)	1.90 (5)	2.709 (5)	149 (5)
N(22)—H(22)···O(311)	2.21 (5)	2.882 (4)	131 (4)
N(312)—H(312)···O(311)	2.43 (7)	3.036 (7)	131 (6)
N(312)—H(311)···N(12^{vi})	2.26 (6)	3.036 (7)	152 (5)
N(42)—H(42)···O(101^{vii})	1.58 (8)	2.745 (6)	155 (7)
N(42)—H(42)···O(111^{vii})	2.27 (8)	3.295 (6)	138 (5)
C(52)—H(52)···O(511^{viii})	2.40 (7)	3.089 (7)	126 (5)
C(52)—H(52)···O(511^{ix})	2.66 (7)	3.172 (7)	112 (5)

Symmetry codes: (i) $x, y, z-1$; (ii) $\frac{1}{2}-x, \frac{1}{2}+y, 1-z$; (iii) $x, y, 1+z$; (iv) $\frac{1}{2}-x, \frac{1}{2}+y, 2-z$; (v) $\frac{1}{2}+x, \frac{1}{2}-y, 1+z$; (vi) $\frac{3}{2}-x, y-\frac{1}{2}, \frac{1}{2}+z$; (vii) $\frac{3}{2}-x, y-\frac{3}{2}, \frac{1}{2}+z$; (viii) $x-\frac{1}{2}, -\frac{1}{2}-y, z$; (ix) $x-\frac{1}{2}, \frac{1}{2}-y, z$.

The structures were solved by direct methods using *SHELXS*86 (Sheldrick, 1985) and refined by full-matrix least squares (*SHELXL*93; Sheldrick, 1993) with anisotropic displacement parameters for all non-H atoms. H atoms were located by difference methods.

For both compounds, data collection: *MolEN* (Fair, 1990); cell refinement: *MolEN*; data reduction: *Xtal*3.2 (Hall, Flack & Stewart, 1992); molecular graphics: *PLATON*92 (Spek, 1990).

The authors acknowledge financial assistance from the Australian Research Council, The University of Queensland and the Centre for Instrumental and Developmental Chemistry of the Queensland University of Technology.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AS1156). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Byriel, K. A., Kennard, C. H. L., Lynch, D. E., Smith, G. & Thompson, J. G. (1992). *Aust. J. Chem.* **45**, 969–981.

Fair, C. K. (1990). *MolEN. An Interactive Intelligent System for Crystal Structure Analysis.* Enraf–Nonius, Delft, The Netherlands.

Hall, S. R., Flack, H. D. & Stewart, J. M. (1992). Editors. *Xtal*3.2 *Reference Manual.* Universities of Western Australia, Australia, Geneva, Switzerland, and Maryland, USA.

Hindawey, A. M., Nasser, A. M. G., Issa, R. M. & Issa, Y. M. (1980). *Indian J. Chem.* **19**A, 615–619.

Issa, Y. M., Hindawey, A. M., El-Kholy, A. E. & Issa, R. M. (1981). *Gazz. Chim. Ital.* **111**, 27–33.

Lynch, D. E., Smith, G., Byriel, K. A. & Kennard, C. H. L. (1992). *Acta Cryst.* C**48**, 1265–1267.

Lynch, D. E., Smith, G., Byriel, K. A. & Kennard, C. H. L. (1994). *Acta Cryst.* C**50**, 1291–1294.

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

Sheldrick, G. M. (1993). *SHELXL*93. *Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.

Smith, G., Lynch, D. E., Byriel, D. A. & Kennard, C. H. L. (1995*a*). *Acta Cryst.* C**51**, 2629–2633.

Smith, G., Lynch, D. E., Byriel, K. A. & Kennard, C. H. L. (1995*b*). *Aust. J. Chem.* **48**, 1133–1149.

Spek, A. L. (1990). *Acta Cryst.* A**46**, C-34.

Sundaralingam, M. & Jensen, L. H. (1965). *Acta Cryst.* **18**, 1053–1058.

Acta Cryst. (1996). C**52**, 235–237

5-*O*-Acetylcuauhtemonyl 6-*O*-2′,3′-Epoxy-2′-methylbutyrate

AHMED A. AHMED,[a] BASMA A. ALI,[a] MARIUSZ KRAWIEC[b] AND WILLIAM H. WATSON[b]

[a]*Department of Chemistry, Faculty of Science, El-Minia University, El-Minia 61519, Egypt, and* [b]*Department of Chemistry, Texas Christian University, Fort Worth TX 76129, USA*

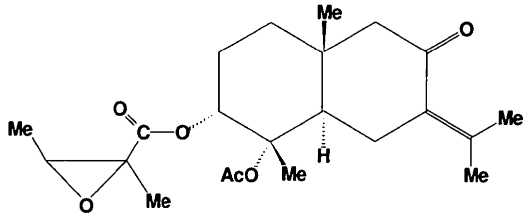
(*Received 4 April 1995; accepted 29 September 1995*)

Abstract

The title compound, $C_{22}H_{32}O_6$, is a sesquiterpene isolated from *Pluchea carolinensis* (*Compositae*). The X-ray structure is consistent with a compound isolated from other species of *Pluchea* and elucidated from spectroscopic data [Nakanishi, Crouch, Miura, Dominguez, Zamudio & Villarreal (1974). *J. Am. Chem. Soc.* **96**, 609–611].

Comment

As a part of our chemical study of the terpenoid constituents of *Compositae* plants, we investigated the CH_2Cl_2 extract of *Pluchea carolinensis*, (I). The genus *Pluchea* (tribe *Inuleae*, family *Compositae*) is traditionally placed in the subtribe *Plucheinae*. Several species of the genus have been studied chemically and it was shown that eudesmane derivatives are typical components (Ahmad, Farooqui, Sultana, Fizza & Khatoon, 1992; Uchiyama, Miyase, Ueno & Usmanghani, 1991; Ahmad, Farooqui, Fizza, Sultana & Khatoon, 1992; Ahmad, Fizza & Amber, 1989). Some *Pluchea* species are known for their medical properties (Mukhopadhyay *et al.*, 1983).



(I)

The two cyclohexane rings are *trans* fused, with both methyl groups (at C4 and C10) being axial (*cis* to one another). The acetoxy group is equatorial and located *cis* relative to the bulky axial (2,3-epoxy-2-methylbutyroyloxy) group. The methyl groups on the oxirane ring (at C19 and C20) are *trans* to one another. The dihedral angle between the oxirane ring and the carboxyl group (O5, C18, O4, C3) is 65.5 (7)°.

The torsion angle O4—C3—C4—O2 is −37.5 (7)° (*versus* −45.9° in cuauhtemone) which indicates a