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# Duclauxin Ethyl Acetate Solvate, $2C_{29}H_{22}O_{11}.C_4H_8O_2$

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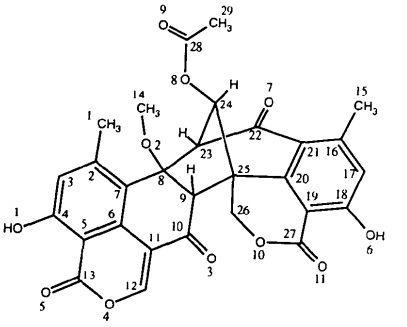
## Abstract

Duclauxin, [8*R*-(8$\alpha$,8a$\beta$,15a$\beta$,15b$\alpha$,16*S**)]-16-(acetyloxy)-8a,15a-dihydro-4,11-dihydroxy-8a-methoxy-6,9-dimethyl-7*H*-8,15b-methano-1*H*,3*H*,12*H*-benzo-[*de*]cyclohepta[1,2-*g*:3,4,5-*d'e'*]bis[2]benzopyran-3,7,-12,15(8*H*)-tetrone, cocrystallized with ethyl acetate solvent (2:1). Duclauxin, an antitumor agent, when isolated from *Penicillium herquei* displays an unusually low melting point (469–471 K) compared with duclauxin from *P. duclauxii* or *P. stipitatum* (503 and 508–509 K, respectively), even though all spectral characterizations of duclauxin from these three sources indicate identical substances. The X-ray structural analysis of duclauxin from *P. herquei* reveals the presence of an ethyl acetate molecule, which is a likely explanation for the abnormal melting point. The duclauxin molecular structure consists of two largely planar halves which are held by the remaining atoms into an approximate open clam-shell configuration. Significant intramolecular hydrogen bonding is observed between the phenolic hydroxyl groups and lactonic carbonyl O atoms; the only significant intermolecular hydrogen bonding is between the ketonic O(3) atom of one duclauxin molecule to the phenolic O(6) atom in the other. There are no especially close intermolecular contacts between ethyl acetate and either of the duclauxin molecules.

## Comment

Duclauxin is a heptacyclic molecule containing an isocoumarin and a dihydroisocoumarin group. The compound is produced by several *Penicillium* species (Shibata, Ogihara, Tokutake & Tanaka, 1965; Kuhr *et al.*, 1973; Bryant, Cutler & Jacyno, 1993*a*) and it is an effective agent against numerous tumor cell types (Fuskova, Proksa & Fuska, 1977; Kawai & Nozawa, 1982; Shiojiri, Kawai, Kato, Ogihara & Nozawa, 1983; Kovac, Bohmerova & Fuska, 1978; Kawai *et al.*, 1985; Bryant, Cutler & Jacyno, 1993*b*). Duclauxin prevents ATP synthesis by inhibiting mitochondrial respiration. Consequently, duclauxin may eventually prove to be an antitumor agent for clinical practice.



Regardless of the source of duclauxin (*Penicillium duclauxii*, *P. stipitatum* or *P. herquei*), all characterization data (IR, $^1$H and $^{13}$C NMR, TLC analysis, GC-MS) are equivalent with the exception of the melting point temperatures (Shibata *et al.*, 1965; Kuhr *et al.*, 1973; Bryant, Cutler & Jacyno, 1993*a*). The melting point temperatures of duclauxin from *P. duclauxii* and *P. stipitatum* are 503 and 508–509 K, respectively, while that of duclauxin from *P. herquei* is 469–471 K. This apparent anomaly prompted an X-ray analysis of duclauxin from *P. herquei*.

Initial attempts to solve the structure using *SIR*88 (Burla *et al.*, 1989) were unsuccessful. A solution was found using *SIR*92 (Altomare *et al.*, 1994), which gave starting coordinates for the 80 non-H atoms in both duclauxin molecules and five of the six non-H atoms in ethyl acetate. The successful structure solution attests to the improved features in the *SIR*92 program.

The crystal structure of duclauxin recrystallized from ethyl acetate was found to contain a 2/1 ratio of duclauxin/ethyl acetate. The presence of a solvent molecule of ethyl acetate is surely the cause of the lower melting point for duclauxin recrystallized from ethyl acetate; the higher melting duclauxin was recrystallized from benzene and cannot contain ethyl acetate. Both molecules of duclauxin in the title compound have the same configuration and both structures are nearly identical. The largest structural difference was found in the orientation of the acetate units. In molecule 1, the torsion angle C(23)—C(24)—O(8)—C(28) was found to be $-97.6$; in molecule 2 it is $-67.8°$. The absolute configuration was not determined in this study but was assumed to be the same as the configuration in monobromoduclauxin (Ogihara, Iitaka & Shibata, 1968). Two

related structural analogs of duclauxin, gilmaniellin and dechlorogilmaniellin, have been reported (Chexal, Tamm, Hirotsu & Clardy, 1979).

There are strong intramolecular hydrogen-bonding interactions between the phenolic OH and the lactonic C=O groups: O(106)···O(111) 2.604 (5), O(206)···O(211) 2.589 (5), O(101)···O(105) 2.630 (5) and O(201)···O(205) 2.625 (4) Å. The only significant intermolecular hydrogen-bonding contact between the two independent molecules is O(103)···O(206) [3.011 (5) Å]. Close contacts are also found between one of the lactonic groups in molecule 1 and the carbonyl O atom of the acetate group in molecule 2: O(209)···P(110) 3.086 (5), O(209)···C(127) 2.824 (6) and O(209)···O(111) 3.215 (5) Å. There are no especially close contacts from either of the duclauxin molecules to ethyl acetate; the closest approach is between the duclauxin acetate carbonyl O atom and the carbonyl O atom in ethyl acetate [O(109)···O(302) 3.341 (7) Å]. The ethyl acetate conformation about the $CH_3$—$CH_2$—O—C(=O) bonds is unexpected; the C(306)—C(305)—O(301)—C(303) torsion angle is −85.9 (7)°.

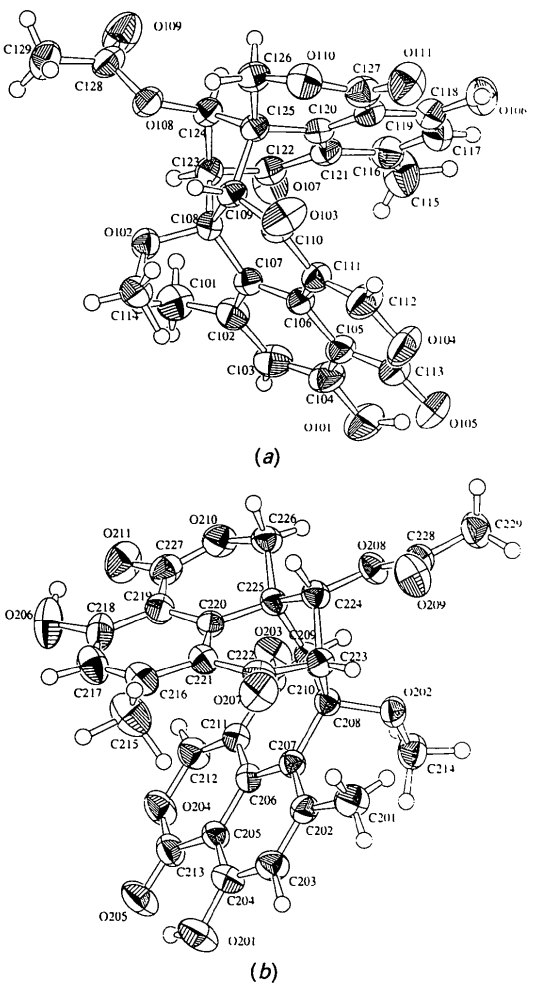



Fig. 1. *ORTEP* (Johnson, 1976) plot of (*a*) molecule 1 and (*b*) molecule 2 of the title compound. Displacement ellipsoids are drawn at the 50% probability level.

## Experimental

Duclauxin was obtained from *P. herquei* grown for 21d on gostar medium (Bryant, Cutler & Jacyno, 1993*a*). A total of 54 2.8 l Fernabach flasks were harvested and duclauxin extracted as described previously. Pure duclauxin was precipitated from ethyl acetate at 277 K. The crystals were dried under a stream of nitrogen for 4 h.

*Crystal data*

$2C_{29}H_{22}O_{11}.C_4H_8O_2$
$M_r$ = 1181.08
Monoclinic
$P2_1$
$a$ = 13.179 (1) Å
$b$ = 12.075 (1) Å
$c$ = 17.963 (1) Å
$\beta$ = 109.100 (7)°
$V$ = 2701.0 (4) Å$^3$
$Z$ = 2
$D_x$ = 1.452 Mg m$^{-3}$
Cu $K\alpha$ radiation
$\lambda$ = 1.54178 Å
Cell parameters from 25 reflections
$\theta$ = 8–16°
$\mu$ = 0.958 mm$^{-1}$
$T$ = 296 (1) K
Thin plate
0.30 × 0.30 × 0.04 mm
Colorless

*Data collection*

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical (North, Phillips & Mathews, 1968)
$T_{min}$ = 0.80, $T_{max}$ = 1.00
6858 measured reflections
5833 independent reflections
4675 observed reflections [$I > 3\sigma(I)$]
$R_{int}$ = 0.03
$\theta_{max}$ = 75°
$h$ = 0 → 16
$k$ = 0 → 15
$l$ = −22 → 22
3 standard reflections
frequency: 120 min
intensity decay: 0.22%

*Refinement*

Refinement on $F$
$R$ = 0.038
$wR$ = 0.042
$S$ = 3.130
4675 reflections
775 parameters
H-atom parameters not refined
$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{max}$ = 0.00
$\Delta\rho_{max}$ = 0.21 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.19 e Å$^{-3}$
Extinction correction: Zachariasen (1967) type 2 Gaussian isotropic
Extinction coefficient: 0.54 × 10$^{-6}$
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV) for C and O, and Stewart, Davidson & Simpson (1965) for H

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

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

| | $x$ | $y$ | $z$ | $U_{eq}$ |
|---|---|---|---|---|
| Molecule 1 | | | | |
| O(101) | 0.3429 (3) | −0.1965 | 0.3566 (2) | 0.0768 |
| O(102) | 0.8112 (2) | −0.1790 (4) | 0.3200 (2) | 0.0444 |
| O(103) | 0.6195 (2) | −0.0522 (4) | 0.0860 (2) | 0.0669 |
| O(104) | 0.3367 (2) | −0.1024 (4) | 0.1294 (2) | 0.0753 |

| | | | | |
|---|---|---|---|---|
| O(105) | 0.2452 (2) | −0.1447 (4) | 0.2080 (2) | 0.0754 |
| O(106) | 0.4580 (2) | 0.3447 (4) | 0.1328 (2) | 0.0654 |
| O(107) | 0.7015 (3) | 0.0750 (4) | 0.4480 (2) | 0.0606 |
| O(108) | 0.9377 (2) | 0.0280 (4) | 0.3075 (2) | 0.0473 |
| O(109) | 1.0442 (2) | 0.1254 (5) | 0.4089 (2) | 0.0796 |
| O(110) | 0.7167 (2) | 0.1714 (4) | 0.1043 (1) | 0.0550 |
| O(111) | 0.5665 (3) | 0.2612 (5) | 0.0484 (2) | 0.0736 |
| C(101) | 0.7285 (4) | −0.1977 (5) | 0.4557 (3) | 0.0605 |
| C(102) | 0.6299 (3) | −0.1701 (5) | 0.3874 (2) | 0.0466 |
| C(103) | 0.5314 (4) | −0.1927 (5) | 0.3989 (3) | 0.0564 |
| C(104) | 0.4350 (3) | −0.1743 (5) | 0.3401 (3) | 0.0564 |
| C(105) | 0.4346 (3) | −0.1385 (5) | 0.2668 (2) | 0.0460 |
| C(106) | 0.5340 (3) | −0.1141 (4) | 0.2546 (2) | 0.0393 |
| C(107) | 0.6308 (3) | −0.1258 (4) | 0.3154 (2) | 0.0377 |
| C(108) | 0.7360 (3) | −0.0892 (4) | 0.3040 (2) | 0.0372 |
| C(109) | 0.7261 (3) | −0.0395 (4) | 0.2209 (2) | 0.0381 |
| C(110) | 0.6236 (3) | −0.0581 (5) | 0.1542 (2) | 0.0433 |
| C(111) | 0.5263 (3) | −0.0836 (4) | 0.1756 (2) | 0.0425 |
| C(112) | 0.4323 (3) | −0.0824 (5) | 0.1179 (3) | 0.0646 |
| C(113) | 0.3345 (3) | −0.1290 (5) | 0.2033 (3) | 0.0593 |
| C(114) | 0.7760 (3) | −0.2717 (5) | 0.2696 (3) | 0.0553 |
| C(115) | 0.5228 (4) | 0.2160 (6) | 0.3976 (3) | 0.0799 |
| C(116) | 0.5543 (3) | 0.2130 (5) | 0.3239 (2) | 0.0500 |
| C(117) | 0.4974 (4) | 0.2776 (5) | 0.2610 (3) | 0.0584 |
| C(118) | 0.5188 (3) | 0.2800 (5) | 0.1909 (3) | 0.0504 |
| C(119) | 0.6041 (3) | 0.2157 (5) | 0.1834 (2) | 0.0424 |
| C(120) | 0.6640 (3) | 0.1518 (4) | 0.2464 (2) | 0.0384 |
| C(121) | 0.6408 (3) | 0.1477 (4) | 0.3177 (2) | 0.0407 |
| C(122) | 0.7081 (3) | 0.0772 (5) | 0.3818 (2) | 0.0423 |
| C(123) | 0.7917 (3) | 0.0056 (5) | 0.3623 (2) | 0.0394 |
| C(124) | 0.8444 (3) | 0.0796 (4) | 0.3173 (2) | 0.0400 |
| C(125) | 0.7563 (3) | 0.0857 (4) | 0.2365 (2) | 0.0383 |
| C(126) | 0.7991 (3) | 0.1432 (5) | 0.1778 (2) | 0.0474 |
| C(127) | 0.6264 (3) | 0.2191 (5) | 0.1086 (2) | 0.0528 |
| C(128) | 1.0333 (3) | 0.0579 (5) | 0.3598 (2) | 0.0510 |
| C(129) | 1.1220 (4) | −0.0088 (6) | 0.3463 (3) | 0.0708 |
| Molecule 2 | | | | |
| O(201) | 0.5168 (2) | 0.0216 (4) | −0.3783 (2) | 0.0669 |
| O(202) | 1.0142 (2) | 0.1230 (4) | −0.2184 (1) | 0.0432 |
| O(203) | 0.9127 (2) | 0.1719 (4) | −0.0130 (2) | 0.0543 |
| O(204) | 0.5961 (2) | 0.1106 (4) | −0.1393 (2) | 0.0547 |
| O(205) | 0.4700 (2) | 0.0783 (4) | −0.2522 (2) | 0.0659 |
| O(206) | 0.7452 (3) | −0.2192 (4) | 0.0272 (2) | 0.0800 |
| O(207) | 0.9429 (3) | −0.2343 (4) | −0.2535 (2) | 0.0637 |
| O(208) | 1.1879 (2) | −0.0044 (4) | −0.0824 (1) | 0.0441 |
| O(209) | 1.2505 (2) | −0.0901 (4) | −0.1695 (2) | 0.0653 |
| O(210) | 1.0201 (2) | −0.0215 (4) | 0.0804 (1) | 0.0528 |
| O(211) | 0.8808 (3) | −0.0759 (4) | 0.1112 (2) | 0.0691 |
| C(201) | 0.8863 (3) | −0.0118 (5) | −0.3622 (2) | 0.0542 |
| C(202) | 0.8082 (3) | 0.0123 (5) | −0.3183 (2) | 0.0414 |
| C(203) | 0.6995 (3) | 0.0082 (5) | −0.3637 (2) | 0.0490 |
| C(204) | 0.6200 (3) | 0.0283 (5) | −0.3306 (2) | 0.0479 |
| C(205) | 0.6493 (3) | 0.0553 (4) | −0.2507 (2) | 0.0397 |
| C(206) | 0.7590 (3) | 0.0617 (4) | −0.2044 (2) | 0.0355 |
| C(207) | 0.8393 (3) | 0.0377 (4) | −0.2377 (2) | 0.0356 |
| C(208) | 0.9578 (3) | 0.0436 (4) | −0.1873 (2) | 0.0357 |
| C(209) | 0.9807 (3) | 0.0685 (4) | −0.0982 (2) | 0.0357 |
| C(210) | 0.8919 (3) | 0.1183 (4) | −0.0727 (2) | 0.0373 |
| C(211) | 0.7817 (3) | 0.0982 (4) | −0.1243 (2) | 0.0366 |
| C(212) | 0.7017 (3) | 0.1198 (5) | −0.0956 (2) | 0.0467 |
| C(213) | 0.5659 (3) | 0.0812 (5) | −0.2168 (2) | 0.0493 |
| C(214) | 0.9671 (3) | 0.2313 (5) | −0.2307 (3) | 0.0541 |
| C(215) | 0.7706 (4) | −0.3368 (6) | −0.2209 (3) | 0.0756 |
| C(216) | 0.8116 (3) | −0.2660 (5) | −0.1493 (3) | 0.0516 |
| C(217) | 0.7654 (3) | −0.2722 (5) | −0.0920 (3) | 0.0580 |
| C(218) | 0.7993 (3) | −0.2098 (5) | −0.0248 (3) | 0.0547 |
| C(219) | 0.8881 (3) | −0.1384 (4) | −0.0113 (2) | 0.0430 |
| C(220) | 0.9346 (3) | −0.1276 (4) | −0.0702 (2) | 0.0373 |
| C(221) | 0.8974 (3) | −0.1880 (4) | −0.1393 (2) | 0.0403 |
| C(222) | 0.9497 (3) | −0.1705 (5) | −0.1991 (2) | 0.0435 |
| C(223) | 1.0204 (3) | −0.0677 (4) | −0.1869 (2) | 0.0397 |
| C(224) | 1.0977 (3) | −0.0798 (4) | −0.1029 (2) | 0.0398 |
| C(225) | 1.0252 (3) | −0.0432 (4) | −0.0560 (2) | 0.0368 |
| C(226) | 1.0872 (3) | −0.0373 (5) | 0.0315 (2) | 0.0445 |
| C(227) | 0.9279 (3) | −0.0765 (5) | 0.0635 (2) | 0.0494 |
| C(228) | 1.2619 (3) | −0.0204 (5) | −0.1201 (2) | 0.0466 |
| C(229) | 1.3533 (3) | 0.0579 (5) | −0.0921 (3) | 0.0585 |
| Molecule 3 | | | | |
| O(301) | 0.8432 (3) | 0.3151 (5) | 0.4289 (2) | 0.0877 |
| O(302) | 0.9930 (4) | 0.4035 (5) | 0.4918 (3) | 0.1092 |
| C(303) | 0.9349 (4) | 0.3247 (6) | 0.4876 (3) | 0.0692 |
| C(304) | 0.9535 (4) | 0.2297 (6) | 0.5416 (3) | 0.0807 |
| C(305) | 0.8107 (6) | 0.4061 (7) | 0.3722 (4) | 0.1014 |
| C(306) | 0.7533 (6) | 0.4867 (8) | 0.4057 (5) | 0.1359 |

Table 2. C—O *bond lengths* (Å)

| | Molecule 1 | Molecule 2 | Average |
|---|---|---|---|
| Ketonic C=O | | | |
| O(3)—C(10) | 1.211 (4) | 1.204 (4) | 1.215 |
| O(7)—C(22) | 1.220 (4) | 1.225 (5) | |
| Lactonic C=O | | | |
| O(5)—C(13) | 1.221 (5) | 1.215 (4) | 1.218 |
| O(11)—C(27) | 1.222 (5) | 1.212 (4) | |
| Ester C=O | | | |
| O(9)—C(28) | 1.175 (5) | 1.197 (5) | 1.186 |
| Lactonic O—C=O | | | |
| O(4)—C(13) | 1.376 (5) | 1.363 (5) | 1.354 |
| O(10)—C(27) | 1.347 (5) | 1.330 (5) | |
| Phenolic OH | | | |
| O(1)—C(4) | 1.366 (4) | 1.352 (4) | 1.352 |
| O(6)—C(18) | 1.339 (5) | 1.352 (5) | |
| Ester O—C(=OC) | | | |
| O(8)—C(28) | 1.351 (4) | 1.371 (4) | 1.361 |
| Ether O—$C_{sp^3}$ | | | |
| O(2)—C(14) | 1.418 (5) | 1.433 (5) | 1.429 |
| O(2)—C(8) | 1.433 (4) | 1.434 (4) | |
| Lactonic O—$C_{sp^3}$ | | | |
| O(4)—C(12) | 1.363 (5) | 1.360 (4) | 1.361 |
| Ester, lactone O—$C_{sp^3}$ | | | |
| O(10)—C(26) | 1.448 (5) | 1.448 (4) | 1.445 |
| O(8)—C(24) | 1.439 (4) | 1.447 (4) | |

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *MolEN* (Fair, 1990), *TEXSAN* (Molecular Structure Corporation, 1992). Program(s) used to solve structure: *SIR*92 (Altomare *et al.*, 1994). Program(s) used to refine structure: *TEXSAN*. Software used to prepare material for publication: *TEXSAN*.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: CD1037). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

## References


Altomare, A., Cascarano, M., Giacovazzo, C., Guagliardi, A., Burla, M. C., Polidori, G. & Camalli, M. (1994). *J. Appl. Cryst.* **27**, 435.

Bryant, F. O., Cutler, H. G. & Jacyno, J. M. (1993*a*). *J. Pharm. Sci.* **82**, 1214–1217.

Bryant, F. O., Cutler, H. G. & Jacyno, J. M. (1993*b*). *J. Natural Prod.* In the press.

Burla, M. C., Camalli, M., Cascarano, G., Giacovazzo, C., Polidori, G., Spagna, R. & Viterbo, D. (1989). *J. Appl. Cryst.* **22**, 389–393.

Chexal, K. K., Tamm, C., Hirotsu, K. & Clardy, J. (1979). *Helv. Chem. Acta*, **62**, 1785–1803.

Enraf–Nonius (1989). *CAD-4 Software*. Version 5.0, Enraf–Nonius, Delft, The Netherlands.
Fair, C. K. (1990). *MolEN. An Interactive Intelligent System for Crystal Structure Analysis*. Enraf–Nonius, Delft, The Netherlands.
Fuskova, A., Proksa, B. & Fuska, J. (1977). *Pharmazie*, **32**, 291–293.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Kawai, K. & Nozawa, Y. (1982). *Res. Commun. Chem. Pathol. Pharmacol.* **36**, 429–438.
Kawai, K., Shiojiri, H., Nakamaru, T., Nozawa, Y., Sugie, S., Mori, H., Kato, T. & Ogihara, Y. (1985). *Cell Biol. Toxicol.* **1**, 1–10.
Kovac, L., Bohmerova, E. & Fuska, J. (1978). *J. Antibiot.* **31**, 616–620.
Kuhr, I., Fuska, J., Sedmera, P., Podojil, M., Vokoun, J. & Vanek, Z. (1973). *J. Antibiot.* **26**, 535–536.
Molecular Structure Corporation (1992). *TEXSAN. TEXRAY Structure Analysis Package*, MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.
North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.
Ogihara, Y., Iitaka, Y. & Shibata, S. (1968). *Acta Cryst.* B**24**, 1037–1047.
Shibata, S., Ogihara, Y., Tokutake, N. & Tanaka, O. (1965). *Tetrahedron Lett.* **18**, 1287–1288.
Shiojiri, H., Kawai, K., Kato, T., Ogihara, Y. & Nozawa, Y. (1983). *Proc. Jpn. Assoc. Mycotoxicol.* **18**, 38–41.
Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.

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# A Lamotrigine Analogue: 3,5-Diamino-6-(2-fluorophenyl)-1,2,4-triazine Methanol Solvate

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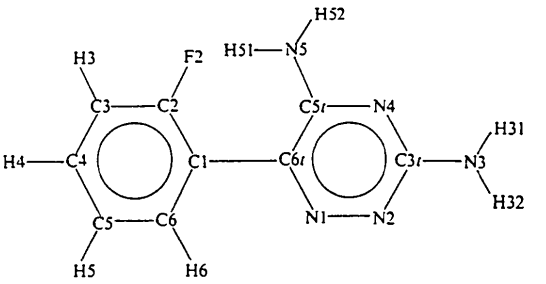
## Abstract

The crystal of the title compound, $C_9H_8FN_5.CH_3OH$, contains two conformers of the triazine molecule in the asymmetic unit, each with significantly distinct dihedral angles between their respective phenyl and triazine rings [50.8 (1) and 125.0 (1)°]. These two conformers exhibit significant differences in certain bond lengths and angles which may arise because of their different dihedral angles. An extensive hydrogen-bonding network maintains the crystal structure which also incorporates two solvent methanol molecules.

## Comment

The title compound is an analogue of the anticonvulsant 3,5-diamino-6-(2,3-dichlorophenyl)-1,2,4-triazine, known as lamotrigine (Janes, Lisgarten & Palmer, 1989), and was supplied by Wellcome Pharmaceuticals (UK). The structure determination was carried out as part of an ongoing investigation into structure–activity relationships of lamotrigine analogues.




(I)

Two conformations of the 2-fluorophenyl analogue exist in the asymmetric unit (the atoms of the second conformer are distinguished with a prime). The F atoms are coplanar with their respective phenyl rings. Atom N5 lies 0.144 (1) Å from its triazine ring plane, while the remaining amino N atoms are coplanar. The dihedral angles between the phenyl and triazine ring moieties of the conformers are 50.8 (1) and 125.0 (1)°, respectively. There is a significant difference in length between the related bonds C1—C2 [1.376 (3) Å] and C1′—C2′ [1.398 (3) Å], and between C2—F2 [1.363 (3) Å] and C2′—F2′ [1.332 (3) Å], which may arise from the difference in the dihedral angles of the two conformers. In the first conformer there is a marked distortion about the common axis of the phenyl and triazine rings, denoted by the atoms C3*t*, C6*t*, C1 and C4. Atom C4 is displaced 0.172 (1) Å from the triazine ring plane while the non-bonding angle given by C3*t*···C6*t*···C4 is 176.3 (1)°. In contrast, the second conformer shows no significant distortion about the common axis of its rings. These various larger distortions in the first conformer compared with the second, together with those given in Table 2, may well arise from steric hinderance between the F atom, the triazine ring $\pi$ electrons and the amino group on C5*t*.

There is an extensive hydrogen-bonding network within the crystal. The two conformers in the asymmetric unit are joined as a non-crystallographic dimer by hydrogen bonds between H52 and N4′, and H52′ and N4. An additional dimer union exists, from a *c*-glide plane, between the respective H31 and N2 atoms of the different conformers. The methanol O1*A* atom is linked to H51 and H32′, while H32 and H51′ are hydrogen bonded to O1*B*. In turn, the H1*A*