

Fig. 1. ORTEP drawing of the aglycone ethyl ether of jasminin with thermal ellipsoids at the 30% probability level. H atoms are shown as spheres of arbitrary radius.

(Inoue & Kuwashima, 1990). The absorption lines were similar among all compounds. This means these compounds have the same chemical ring structure. In Fig. 2, ^{13}C chemical shifts of these compounds are shown. Chemical-shift differences ($\Delta\delta$) between jasminin and the other compounds are shown against the chemical shift of jasminin. The chemical-shift values of jasminin (1) and its derivative (4) are quite similar. Larger chemical-shift differences between the aglycone ethyl ether and the other compounds are observed than those between jasminin and its derivative (4). This suggests that the three-dimensional conformation of the aglycone ethyl ether differs from natural jasminin derivatives although they have the same chemical structures.

Just one large chemical-shift difference between jasminin and jasminin β -D-glucoside (4) exists, for C(17). This suggests that (4) has a through-space interaction between C(17) and β -D-glucose.

The conformational difference based on ^{13}C NMR spectra suggests the possibility that jasminin has a different conformation from its aglycone ethyl ether. An X-ray analysis of jasminin would be interesting and would be expected to show the relationship

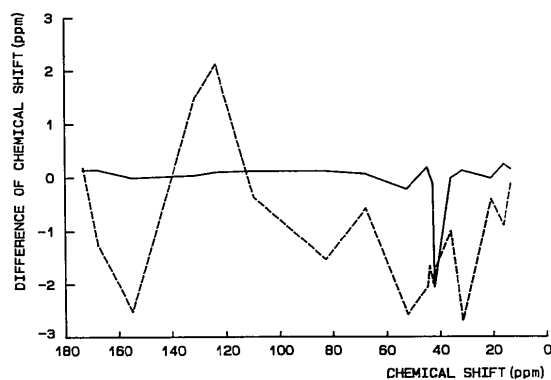


Fig. 2. ^{13}C NMR chemical-shift differences of jasminin derivatives against jasminin. The abscissa shows the chemical shift of jasminin. The ordinate shows the chemical shift difference $\Delta\delta$ between jasminin (1) and its derivatives: the aglycone ethyl ether of jasminin (2) (broken line), jasminin β -D-glucoside (4) (solid line).

between the chemical structure and the three-dimensional conformation. We are now trying to make good-quality single crystals of jasminin and related compounds.

References

- ASAKA, Y., KAMIKAWA, T. & KUBOTA, T. (1974). *Tetrahedron*, **30**, 3257–3262.
 DEBAERDEMAEKER, T., GERMAIN, G., MAIN, P., TATE, C. & WOOLFSON, M. M. (1987). *MULTAN87. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.
 FUKUYO, M. & SHIMADA, A. (1969). Abstr. 22nd Annu. Meet. Chem. Soc. Jpn, p. 66.
 INOUE, K. & KUWASHIMA, H. (1990). Private communication.
 JOHNSON, C. K. (1976). *ORTEPII*. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
 KAMIKAWA, T., INOUE, K. & KUBOTA, T. (1970). *Tetrahedron*, **26**, 4561–4587.

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Structure of 4,7-Diacetoxy-12,15-difluorohexacyclo-[8.6.0.0^{2,15}.0^{3,8}.0^{9,12}.0^{11,16}]hexadeca-3,5,7-triene-13,14-dicarboxylic Anhydride

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Abstract. $\text{C}_{22}\text{H}_{16}\text{F}_2\text{O}_7$, $M_r = 430.37$, m.p. = 511–514 K, orthorhombic, $Pcab$, $a = 14.364$ (1), $b = 29.662$ (3), $c = 8.7612$ (6) Å, $V = 3732.9$ (5) Å³, $Z =$

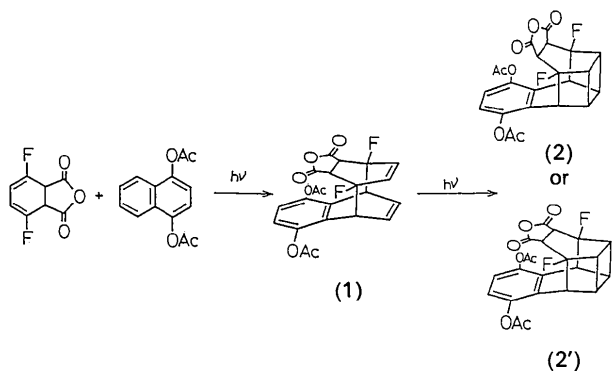
8, $D_x = 1.532$ Mg m⁻³, Cu $K\alpha$ ($\lambda = 1.54178$ Å), $\mu = 1.05$ mm⁻¹, $F(000) = 2224$, $T = 289$ K, $R = 0.050$ for 2852 non-zero reflections. The mirror symmetry of

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the molecule is slightly distorted by a packing effect. Short 1,4 contacts, C...C 3.154 (3) and 3.044 (3) Å, are found in the cage of the molecule. Both acetyl groups are in a similar conformation formed by intramolecular C—H...O=C interactions.

Introduction. The title compound (2) was synthesized by a similar method to that developed recently (Kimura, Kura, Nukada, Okamoto, Satake & Morosawa, 1988; Kimura, Okamoto, Kura, Okazaki, Nagayasu, Satake & Morosawa, 1988): (1) was prepared by the [4πs + 4πs] photoaddition of 1,4-diacetoxynaphthalene and *cis*-3,6-difluoro-1,2-dihydrophthalic anhydride. The [2πs + 2πs] intramolecular photocycloaddition of (1) afforded a product (2) which is an important precursor in the synthesis of hexaprismane derivatives. In principle, there are two possible structures, (2) and (2'), for the product. The structure has been confirmed as (2) by X-ray diffraction analysis.



Experimental. Crystals were grown from an ethyl acetate solution. Colourless plates with developed {010} faces; 0.30 × 0.14 × 0.40 mm. Rigaku AFC-5 four-circle diffractometer equipped with rotating anode (40 kV, 200 mA), Ni-filtered Cu Kα. 20 reflections within 44 < 2θ < 46° used to determine the lattice parameters. Intensity data collected within 2θ_{max} = 125° (0 ≤ h ≤ 16, 0 ≤ k ≤ 34, 0 ≤ l ≤ 10), ω-2θ scan method [scan speed 4° min⁻¹ in ω, scan range (1.2 + 0.15tanθ)° in ω], background measured for 4 s on either side of the peak, three standard reflections recorded after every 97 reflections, fluctuations within 1.5% in *F*. Lorentz and polarization corrections, no absorption correction. 2980 unique reflections measured; 2852 non-zero reflections used in the structure analysis. Structure solved by *MULTAN78* and refined by block-diagonal least squares (non-H atoms anisotropically). H atoms were found from a difference Fourier map and refined isotropically; $\sum w(|F_o| - |F_c|)^2$ minimized with $w = 1.0/[\sigma(F_o)^2 - 0.0777|F_o| + 0.0047|F_o|^2]$. Final *R* = 0.050, *wR* = 0.053, *S* = 1.95, (Δ/σ)_{max} =

Table 1. Final atomic coordinates and equivalent isotropic thermal parameters with e.s.d.'s in parentheses

$$B_{eq} = (4/3)\sum\beta_{ii}/a_i^{*2}$$

	x	y	z	B _{eq} (Å ²)
C(1)	0.4352 (1)	0.12153 (6)	-0.1960 (2)	3.55 (8)
C(2)	0.4523 (1)	0.16246 (6)	-0.0893 (2)	3.23 (7)
C(3)	0.4046 (1)	0.16183 (6)	0.0624 (2)	3.22 (8)
C(4)	0.3695 (1)	0.20114 (6)	0.1284 (2)	3.58 (8)
C(5)	0.3189 (1)	0.20023 (7)	0.2624 (2)	4.50 (9)
C(6)	0.3040 (1)	0.15906 (8)	0.3341 (2)	4.61 (9)
C(7)	0.3396 (1)	0.12035 (6)	0.2710 (2)	3.89 (9)
C(8)	0.3897 (1)	0.12052 (6)	0.1353 (2)	3.33 (8)
C(9)	0.4268 (1)	0.07861 (6)	0.0632 (2)	3.54 (8)
C(10)	0.4239 (1)	0.07590 (6)	-0.1146 (2)	3.81 (9)
C(11)	0.5308 (1)	0.06836 (6)	-0.1209 (2)	3.61 (8)
C(12)	0.5349 (1)	0.07104 (6)	0.0551 (2)	3.35 (8)
C(13)	0.5992 (1)	0.10516 (6)	0.1340 (2)	3.13 (7)
C(14)	0.6213 (1)	0.14674 (6)	0.0351 (2)	3.16 (7)
C(15)	0.5595 (1)	0.15415 (6)	-0.1033 (2)	3.13 (7)
C(16)	0.5419 (1)	0.11379 (6)	-0.2072 (2)	3.50 (8)
O(17)	0.38019 (8)	0.24240 (4)	0.0537 (1)	3.94 (6)
C(18)	0.4668 (1)	0.26184 (7)	0.0576 (2)	3.77 (8)
O(19)	0.53055 (9)	0.24457 (5)	0.1231 (2)	4.57 (6)
C(20)	0.4684 (1)	0.30459 (7)	-0.0289 (2)	4.65 (10)
O(21)	0.31818 (9)	0.07900 (5)	0.3422 (2)	4.84 (7)
C(22)	0.3860 (2)	0.05958 (7)	0.4286 (2)	4.89 (11)
C(23)	0.3525 (2)	0.0165 (1)	0.4960 (3)	7.73 (15)
O(24)	0.4611 (1)	0.07606 (6)	0.4436 (2)	6.21 (9)
C(25)	0.6942 (1)	0.08475 (7)	0.1630 (2)	3.90 (9)
O(26)	0.7178 (1)	0.05679 (6)	0.2511 (2)	5.69 (8)
O(27)	0.75903 (9)	0.10421 (5)	0.0677 (2)	4.49 (7)
C(28)	0.7201 (1)	0.13881 (7)	-0.0157 (2)	4.04 (9)
O(29)	0.7648 (1)	0.15655 (6)	-0.1131 (2)	6.01 (8)
F(30)	0.55450 (8)	0.02857 (3)	0.1161 (1)	4.46 (6)
F(31)	0.59748 (7)	0.19056 (3)	-0.1839 (1)	4.03 (5)

0.2 for non-H atoms and 1.1 for H atoms. The residual electron density in the final difference map was within ±0.25 e Å⁻³.

Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV). Programs: *MULTAN78* (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). *HBL5-V* and *DAPH* (Ashida, 1973), *MOLCON* (Fujii, 1979) and *ORTEP* (Johnson, 1971). Computations carried out at the Research Center for Protein Engineering, Institute for Protein Research, Osaka University and at the Okayama University Computer Center.

Discussion. The final atomic parameters are listed in Table 1.* Thermal ellipsoids of the molecule are shown in Fig. 1 with atomic numbering. Bond lengths and angles are listed in Table 2.

The molecule has approximately mirror symmetry in the crystal. The bond lengths and angles for the chemically equivalent parts are similar. A slight distortion from the symmetry, found around C(12) and C(15) [C(8)—C(9)—C(12)—C(13) 5.2 (3), C(3)—C(2)—C(15)—C(14) -2.3 (3)°], is caused by a

* Lists of structure factors, anisotropic thermal parameters, H-atom parameters, bond lengths and angles involving H atoms and selected torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53398 (13 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. Bond lengths (Å) and angles (°) with e.s.d.'s in parentheses

C(1)—C(2)	1.552 (3)	C(12)—C(13)	1.535 (3)
C(1)—C(10)	1.538 (3)	C(12)—F(30)	1.397 (2)
C(1)—C(16)	1.553 (3)	C(13)—C(14)	1.540 (3)
C(2)—C(3)	1.495 (3)	C(13)—C(25)	1.514 (3)
C(2)—C(15)	1.564 (3)	C(14)—C(15)	1.519 (3)
C(3)—C(4)	1.396 (3)	C(14)—C(28)	1.506 (3)
C(3)—C(8)	1.398 (3)	C(15)—C(16)	1.525 (3)
C(4)—C(5)	1.381 (3)	C(15)—F(31)	1.401 (2)
C(4)—O(17)	1.396 (2)	O(17)—C(18)	1.372 (2)
C(5)—C(6)	1.390 (3)	C(18)—O(19)	1.196 (2)
C(6)—C(7)	1.373 (3)	C(18)—C(20)	1.477 (3)
C(7)—C(8)	1.390 (3)	O(21)—C(22)	1.362 (2)
C(7)—O(21)	1.410 (2)	C(22)—C(23)	1.488 (4)
C(8)—C(9)	1.493 (3)	C(22)—O(24)	1.192 (3)
C(9)—C(10)	1.560 (3)	C(25)—O(26)	1.183 (3)
C(9)—C(12)	1.571 (3)	C(25)—O(27)	1.377 (2)
C(10)—C(11)	1.553 (3)	O(27)—C(28)	1.378 (2)
C(11)—C(12)	1.545 (3)	C(28)—O(29)	1.191 (3)
C(11)—C(16)	1.553 (3)		
C(2)—C(1)—C(10)	115.2 (2)	C(11)—C(12)—F(30)	110.1 (2)
C(2)—C(1)—C(16)	89.9 (2)	C(13)—C(12)—F(30)	107.5 (2)
C(10)—C(1)—C(16)	90.2 (2)	C(12)—C(13)—C(14)	113.5 (2)
C(1)—C(2)—C(3)	116.9 (2)	C(12)—C(13)—C(25)	110.7 (2)
C(1)—C(2)—C(15)	89.2 (2)	C(14)—C(13)—C(25)	103.2 (2)
C(3)—C(2)—C(15)	121.3 (2)	C(13)—C(14)—C(15)	116.4 (2)
C(2)—C(3)—C(4)	121.6 (2)	C(13)—C(14)—C(28)	103.6 (2)
C(2)—C(3)—C(8)	119.1 (2)	C(15)—C(14)—C(28)	109.7 (2)
C(4)—C(3)—C(8)	119.2 (2)	C(2)—C(15)—C(14)	122.4 (2)
C(3)—C(4)—C(5)	121.7 (2)	C(2)—C(15)—C(16)	90.4 (2)
C(3)—C(4)—O(17)	119.9 (2)	C(2)—C(15)—F(31)	107.5 (2)
C(5)—C(4)—O(17)	118.3 (2)	C(14)—C(15)—C(16)	117.4 (2)
C(4)—C(5)—C(6)	118.8 (2)	C(14)—C(15)—F(31)	106.6 (2)
C(5)—C(6)—C(7)	119.7 (2)	C(16)—C(15)—F(31)	111.6 (2)
C(6)—C(7)—C(8)	122.3 (2)	C(1)—C(16)—C(11)	89.8 (2)
C(6)—C(7)—O(21)	117.9 (2)	C(1)—C(16)—C(15)	90.6 (2)
C(8)—C(7)—O(21)	119.6 (2)	C(11)—C(16)—C(15)	114.0 (2)
C(3)—C(8)—C(9)	118.2 (2)	C(4)—O(17)—C(18)	117.2 (1)
C(3)—C(8)—C(7)	118.8 (2)	O(17)—C(18)—O(19)	121.8 (2)
C(7)—C(8)—C(9)	122.9 (2)	O(17)—C(18)—C(20)	111.2 (2)
C(8)—C(9)—C(10)	117.1 (2)	O(19)—C(18)—C(20)	127.0 (2)
C(8)—C(9)—C(12)	119.4 (2)	C(7)—O(21)—C(22)	117.3 (2)
C(10)—C(9)—C(12)	88.5 (2)	O(21)—C(22)—C(23)	110.7 (2)
C(1)—C(10)—C(9)	114.5 (2)	O(21)—C(22)—O(24)	122.4 (2)
C(1)—C(10)—C(11)	90.3 (2)	C(23)—C(22)—O(24)	127.0 (2)
C(9)—C(10)—C(11)	90.9 (2)	C(13)—C(25)—O(26)	130.4 (2)
C(10)—C(11)—C(12)	89.7 (2)	C(13)—C(25)—O(27)	109.9 (2)
C(10)—C(11)—C(16)	89.7 (2)	O(26)—C(25)—O(27)	119.7 (2)
C(12)—C(11)—C(16)	115.9 (2)	C(25)—O(27)—C(28)	111.0 (1)
C(9)—C(12)—C(11)	90.8 (2)	C(14)—C(28)—O(27)	110.0 (2)
C(9)—C(12)—C(13)	118.7 (2)	C(14)—C(28)—O(29)	130.6 (2)
C(9)—C(12)—F(30)	108.1 (2)	O(27)—C(28)—O(29)	119.4 (2)
C(11)—C(12)—C(13)	120.4 (2)		

packing effect: there is a short contact C(18)⋯F(31) ($1-x, \frac{1}{2}-y, \frac{1}{2}+z$) 2.824 (2) Å, while no such short contact exists involving F(30). Similar conformations for the two acetyl groups [C(8)—C(7)—O(21)—C(22) 81.1 (2), C(7)—O(21)—C(22)—O(24) -0.8 (3), C(3)—C(4)—O(17)—C(18) -75.5 (2), C(4)—O(17)—C(18)—O(19) -0.6 (3)°] are favoured by intramolecular C—H⋯O=C interactions [O(19)⋯H(14) 2.53 (7) Å, O(19)⋯H(14)—C(14) 137 (2)°; O(24)⋯H(13) 2.64 (2) Å, O(24)⋯H(13)—C(13) 139 (2)°].

In the molecule the cage is composed of three four-membered rings, two six-membered rings and one eight-membered ring. Short 1,4 contacts, C(3)⋯C(14) 3.154 (3) and C(8)⋯C(13) 3.044 (3) Å, are found in the cage, the bonds C(2)—C(15) and C(9)—C(12) being lengthened as observed in some open-ended cage compounds (Watson, Nagl, Kashyap, Marchand & Zhao, 1989; Watson, Nagl, Marchand & Reddy, 1989). The bond lengths in the four-membered rings are comparable with those observed in related compounds (Watson, Nagl, Marchand, Reddy & Reddy, 1989; Watson, Nagl, Marchand & Deshpande, 1989; Iwamoto, Kashino & Haisa, 1989).

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References

- ASHIDA, T. (1973). *HBL5-V* and *DAPH*. *The Universal Crystallographic Computing System*, Osaka. The Computation Center, Osaka Univ., Japan.
- FUJII, S. (1979). *MOLCON*. *The Universal Crystallographic Computing System*, Osaka. The Computation Center, Osaka Univ., Japan.
- IWAMOTO, T., KASHINO, S. & HAISA, M. (1989). *Acta Cryst.* **C45**, 1753–1758.
- JOHNSON, C. K. (1971). *ORTEP*. Report ORNL-3794, revised. Oak Ridge National Laboratory, Tennessee, USA.
- KIMURA, M., KURA, H., NUKADA, K., OKAMOTO, H., SATAKE, K. & MOROSAWA, S. (1988). *J. Chem. Soc. Perkin Trans. 1*, pp. 3307–3310.
- KIMURA, M., OKAMOTO, H., KURA, H., OKAZAKI, A., NAGAYASU, E., SATAKE, K. & MOROSAWA, S. (1988). *J. Org. Chem.* **53**, 3908–3911.
- MAIN, P., HULL, S. E., LESSINGER, L., GERMAIN, G., DECLERCO, J.-P. & WOOLFSON, M. M. (1978). *MULTAN78*. *A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data*. Univs. of York, England, and Louvain, Belgium.
- WATSON, W. H., NAGL, A., KASHYAP, R. M., MARCHAND, A. P. & ZHAO, D. (1989). *Acta Cryst.* **C45**, 1342–1346.
- WATSON, W. H., NAGL, A., MARCHAND, A. P. & DESHPANDE, N. (1989). *Acta Cryst.* **C45**, 1339–1342.
- WATSON, W. H., NAGL, A., MARCHAND, A. P. & REDDY, G. M. (1989). *Acta Cryst.* **C45**, 1600–1602.
- WATSON, W. H., NAGL, A., MARCHAND, A. P., REDDY, G. M. & REDDY, S. P. (1989). *Acta Cryst.* **C45**, 659–661.

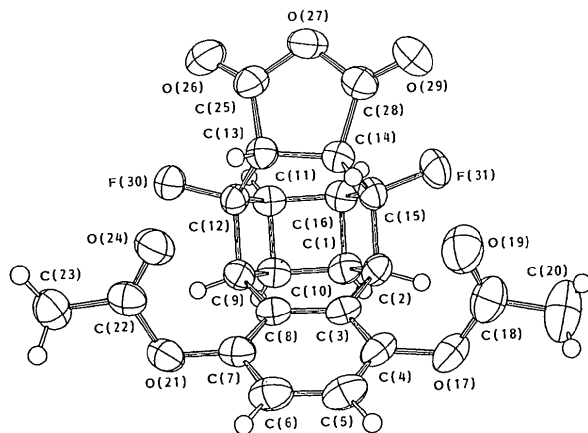


Fig. 1. Thermal ellipsoids with atomic numbering. Ellipsoids of 50% probability are drawn for the non-H atoms; the H atoms are represented as spheres equivalent to $B = 1.0 \text{ \AA}^2$.