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Structure of the Aglycone Ethyl Ether of Jasminin

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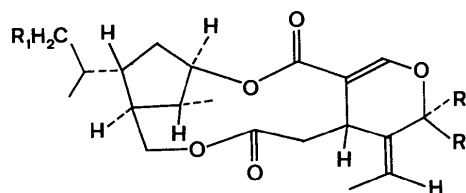
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Abstract. *rel-(7S,14S,15S,17S)-7-Ethoxy-8-(E)-ethylidene-17-methyl-15-[(1S)-1-methyl-2-hydroxyethyl]-2,6,12-trioxatricyclo[12.2.1.0^{4,9}]heptadec-4-ene-3,11-dione*, C₂₂H₃₂O₇, *M_r* = 408.49, orthorhombic, *P*₂₁₂₁, *a* = 25.773 (15), *b* = 10.540 (3), *c* = 8.087 (5) Å, *V* = 2196.8 (2) Å³, *Z* = 4, *D_x* = 1.24 g cm⁻³, λ(Cu Kα) = 1.5418 Å, μ = 7.14 cm⁻¹, *F*(000) = 880, *T* = 299 K, *R* = 0.043 for 2294 observed reflections. The molecular structure of the aglycone ethyl ether of jasminin is consistent with the structure of jasminin proposed from the results of chemical and spectroscopic methods.

Introduction. The structure of jasminin (1), the bitter principle of *Jasminum mesnyi* (*unnan oubai*) has been extensively studied by chemical and spectroscopic methods (Kamikawa, Inoue & Kubota, 1970; Asaka, Kamikawa & Kubota, 1974). The hydrolysis of jasminin by *p*-toluenesulfonic acid in ethanol gives the title compound, the aglycone ethyl ether (2), in which the β-D-glucose unit of jasminin is replaced with ethyl ether by *S*N₂ substitution. The bromination of the aglycone ethyl ether gives the bromide derivative (3). Preliminary X-ray analysis of (3)

has been performed by the Patterson method (Fukuyo & Shimada, 1969). Crystallographic data for (3) are *a* = 26.54, *b* = 10.14, *c* = 8.43 Å, *P*₂₁₂₁, *R* = 0.16. The structure of jasminin has been uncertain because of the possibility of skeletal transformation by ethanolysis.



- (1): *R*₁ = OH, *R*₂ = β-D-glucoside, *R*₃ = H
 (2): *R*₁ = OH, *R*₂ = H, *R*₃ = OCH₂CH₃
 (3): *R*₁ = Br, *R*₂ = H, *R*₃ = OCH₂CH₃
 (4): *R*₁, *R*₂ = β-D-glucoside, *R*₃ = H

Recently, ¹³C NMR spectra of aglycone ethyl ether (2) and jasminin (1) were recorded (Inoue & Kuwashima, 1990). The ¹³C NMR spectrum of jasminin is similar to that of its aglycone ethyl ether: corresponding chemical shifts and peak splittings

Table 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic temperature factors ($\text{\AA}^2 \times 10^3$) with e.s.d.'s in parentheses

	x	y	z	U_{eq}
O(1)	3898 (2)	3999 (6)	-591 (8)	61 (2)
O(2)	4087 (2)	5029 (6)	2652 (7)	56 (2)
O(3)	4500 (2)	3880 (6)	4568 (8)	60 (2)
O(4)	3104 (2)	2089 (6)	5582 (9)	72 (3)
O(5)	2885 (3)	775 (6)	3454 (8)	77 (3)
O(6)	4269 (3)	2182 (7)	48 (12)	101 (3)
O(7)	4094 (5)	9892 (10)	-1974 (12)	147 (5)
C(8)	4127 (3)	4080 (8)	3772 (11)	48 (3)
C(9)	2736 (4)	2976 (10)	3106 (14)	64 (4)
C(10)	4396 (4)	6983 (9)	1584 (13)	66 (4)
C(11)	3245 (3)	3410 (9)	2413 (12)	60 (4)
C(12)	2742 (4)	1857 (10)	4190 (14)	72 (4)
C(13)	3540 (4)	2739 (10)	5239 (11)	62 (4)
C(14)	3639 (3)	3312 (9)	3839 (12)	58 (4)
C(15)	4886 (3)	5097 (8)	1075 (11)	49 (3)
C(16)	3909 (4)	2855 (9)	73 (13)	65 (4)
C(17)	4286 (3)	6674 (8)	-199 (11)	50 (3)
C(18)	4558 (3)	5741 (8)	2356 (13)	56 (4)
C(19)	5446 (4)	5513 (10)	1197 (14)	71 (4)
C(20)	4640 (3)	5508 (9)	-558 (13)	58 (3)
C(21)	2277 (4)	3550 (12)	2773 (17)	87 (5)
C(22)	4260 (4)	7375 (10)	-3172 (12)	68 (4)
C(23)	4358 (4)	7751 (9)	-1417 (13)	70 (4)
C(24)	3412 (4)	2577 (8)	904 (12)	61 (4)
C(25)	4361 (4)	4421 (9)	-1539 (12)	61 (4)
C(26)	3993 (6)	8886 (11)	-895 (15)	102 (5)
C(27)	2204 (4)	4678 (12)	1807 (18)	104 (6)
C(28)	3046 (5)	-1386 (12)	3569 (15)	107 (6)
C(29)	2853 (5)	-367 (12)	4484 (17)	105 (5)

$$U_{\text{eq}} = 1/3(U_{11} + U_{22} + U_{33}).$$

Table 2. Bond lengths (\AA) and angles ($^\circ$) of the aglycone ethyl ether of jasminin with e.s.d.'s in parentheses

O(1)—C(16)	1.321 (12)	O(1)—C(25)	1.486 (12)
O(2)—C(8)	1.353 (11)	O(2)—C(18)	1.447 (12)
O(3)—C(8)	1.176 (11)	O(4)—C(12)	1.482 (13)
O(4)—C(13)	1.345 (13)	O(5)—C(12)	1.338 (14)
O(5)—C(29)	1.467 (16)	O(6)—C(16)	1.168 (14)
O(7)—C(26)	1.398 (20)	C(8)—C(14)	1.497 (13)
C(9)—C(11)	1.498 (15)	C(9)—C(12)	1.470 (16)
C(9)—C(21)	1.356 (18)	C(10)—C(17)	1.506 (14)
C(10)—C(18)	1.509 (15)	C(11)—C(14)	1.540 (14)
C(11)—C(24)	1.564 (14)	C(13)—C(14)	1.308 (14)
C(15)—C(18)	1.500 (14)	C(15)—C(19)	1.512 (14)
C(15)—C(20)	1.528 (14)	C(16)—C(24)	1.476 (15)
C(17)—C(20)	1.558 (14)	C(17)—C(23)	1.514 (14)
C(20)—C(25)	1.568 (15)	C(21)—C(27)	1.435 (20)
C(22)—C(23)	1.495 (15)	C(23)—C(26)	1.579 (19)
C(28)—C(29)	1.396 (19)		
C(16)—O(1)—C(25)	117.8 (8)	C(8)—O(2)—C(18)	115.5 (7)
C(12)—O(4)—C(13)	117.0 (8)	C(12)—O(5)—C(29)	115.6 (9)
O(2)—C(8)—O(3)	124.1 (8)	O(2)—C(8)—C(14)	111.1 (7)
O(3)—C(8)—C(14)	124.8 (8)	C(11)—C(9)—C(12)	117.3 (9)
C(11)—C(9)—C(21)	123.6 (11)	C(12)—C(9)—C(21)	119.1 (11)
C(17)—C(10)—C(18)	105.1 (8)	C(9)—C(11)—C(14)	106.1 (8)
C(9)—C(11)—C(24)	111.2 (8)	C(14)—C(11)—C(24)	111.4 (8)
O(4)—C(12)—O(5)	107.8 (9)	O(4)—C(12)—C(9)	109.1 (9)
O(4)—C(12)—C(9)	114.9 (10)	O(4)—C(13)—C(14)	125.2 (10)
C(8)—C(14)—C(11)	119.4 (8)	C(8)—C(14)—C(13)	116.4 (9)
C(11)—C(14)—C(13)	123.4 (9)	C(18)—C(15)—C(19)	111.2 (8)
C(18)—C(15)—C(20)	103.6 (8)	C(19)—C(15)—C(20)	111.7 (8)
O(1)—C(16)—O(6)	124.4 (10)	O(1)—C(16)—C(24)	110.4 (9)
O(6)—C(16)—C(24)	125.2 (10)	C(10)—C(17)—C(20)	103.8 (8)
C(10)—C(17)—C(23)	116.0 (8)	C(20)—C(17)—C(23)	113.5 (8)
O(2)—C(18)—C(10)	106.6 (8)	O(2)—C(18)—C(15)	110.6 (8)
C(10)—C(18)—C(15)	105.2 (8)	C(15)—C(20)—C(17)	107.8 (8)
C(15)—C(20)—C(25)	114.9 (8)	C(17)—C(20)—C(25)	113.7 (8)
C(9)—C(21)—C(27)	126.3 (13)	C(17)—C(23)—C(22)	113.5 (9)
C(17)—C(23)—C(26)	108.7 (9)	C(22)—C(23)—C(26)	110.7 (9)
C(11)—C(24)—C(16)	118.9 (9)	O(1)—C(25)—C(20)	109.0 (8)
O(7)—C(26)—C(23)	107.3 (12)	O(5)—C(29)—C(28)	108.1 (11)

were observed. This encouraged us to determine the X-ray structure of aglycone ethyl ether of jasminin as a check of the jasminin structure based on chemical methods.

Experimental. The aglycone ethyl ether of jasminin was obtained as described elsewhere (Asaka, Kamikawa & Kubota, 1974). A needle crystal $0.5 \times 0.2 \times 0.2$ mm, Rigaku AFC-6 diffractometer, graphite-monochromated Cu $K\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$), at $T = 299 \text{ K}$, cell parameters by least squares on setting angles of 20 reflections ($20 < 2\theta < 28^\circ$), 2294 unique reflections, of which 1153 were treated as observed in the refinement based on $I > 3\sigma(I)$, $2\theta_{\text{max}} = 135^\circ$ ($0 < h < 30$, $0 < k < 12$, $0 < l < 9$), $\omega/2\theta$ scan mode, scan speed 4° min^{-1} , scan width $(1.257 + 0.5 \tan \theta)^\circ$, background measured for 5 s on each side of the peaks, three standard reflections monitored every 200 reflections, no significant variation in intensity, no absorption correction, structure solved by *MULTAN87* (Debaerdemaeker, Germain, Main, Tate & Woolfson, 1987) on an INMOS T800 processor. In the final cycles of block-matrix least-squares refinement, all non-H atoms refined anisotropically, H atoms were placed at reasonable positions and refined isotropically, 261 parameters refined, $\sum w\Delta F^2$ minimized with $w = 1/[\sigma^2(F_o) + 0.00474F_o^2]$, $R = 0.043$, $wR = 0.053$, $S = 1.219$, $(\Delta/\sigma)_{\text{max}} = 0.1$, $\Delta\rho_{\text{max}} = 0.29$, $\Delta\rho_{\text{min}} = -0.35 \text{ e \AA}^{-3}$, scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV).

The coordinates and equivalent isotropic thermal parameters are given in Table 1. Bond lengths and angles are shown in Table 2. An *ORTEPII* (Johnson, 1976) drawing of the aglycone ethyl ether of jasminin is given in Fig. 1.* The alcoholic oxygen forms an intermolecular hydrogen bond to the carbonyl oxygen [O(3)] of one of the lactones.

Discussion. The structure of the aglycone ethyl ether of jasminin (2) is basically the same as that of the bromide derivative (3). The bromination does not cause any conformational deformation of the aglycone ethyl ether.

Bond lengths in the carbonyl moieties of lactones (1.176, 1.168 \AA) of the aglycone ethyl ether are shorter than the usual value for a carbonyl group.

^{13}C NMR spectra were measured for jasminin, its aglycone ethyl ether and the natural jasminin derivative, compound (4), which had the same ring structure as jasminin and another β -D-glucose at C(26)

* Lists of structure factors F_o and σ , anisotropic thermal parameters, H-atom coordinates, bond lengths, bond angles and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 53392 (15 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

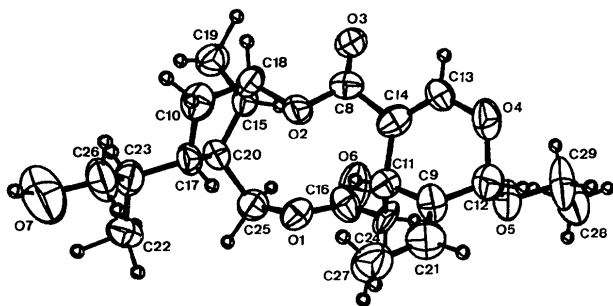


Fig. 1. ORTEP drawing of the aglycone ethyl ether of jasminin with thermal ellipsoids at the 30% probability level. H atoms are shown as spheres of arbitrary radius.

(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

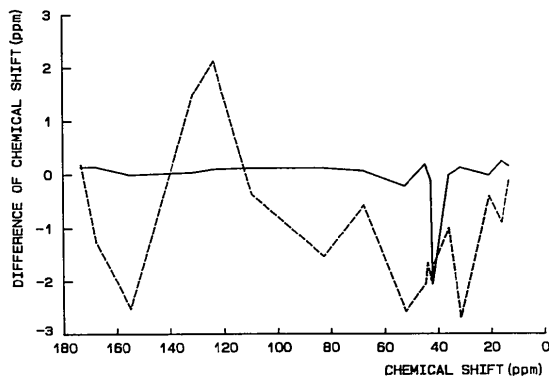


Fig. 2. ^{13}C NMR chemical-shift differences of jasminin derivatives against jasminin. The abscissa shows the chemical shift of jasminin. The ordinate shows the chemical shift difference $\Delta\delta$ between jasminin (1) and its derivatives: the aglycone ethyl ether of jasminin (2) (broken line),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

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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