Crystal structure of kakkalidone, $C_{23}H_{24}O_{11}$

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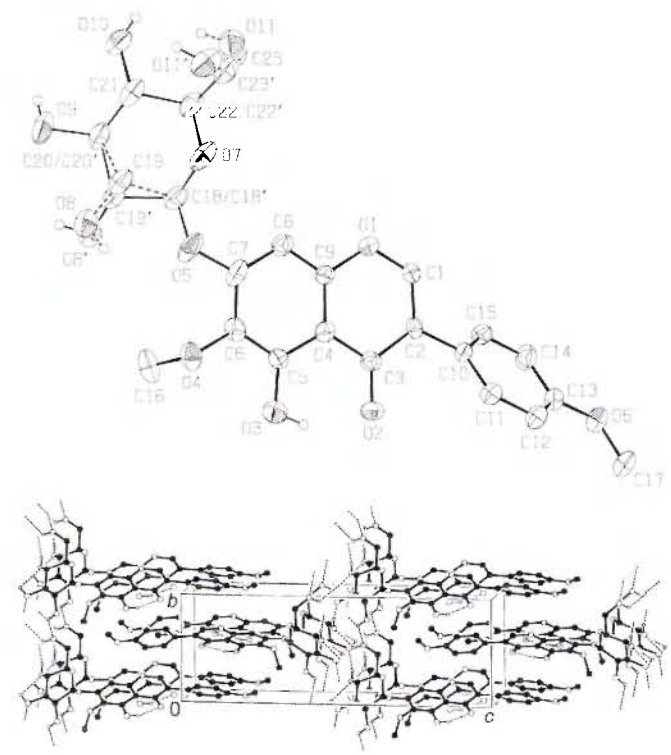

Abstract

$C_{23}H_{24}O_{11}$, monoclinic, $P12_11$ (no. 4), a = 6.081(3) Å, b = 7.838(3) Å, c = 22.60(1) Å, β = 92.127(7)°, V = 1076.4 Å^3, Z = 2, $R_{gt}(F)$ = 0.072, $wR_{ref}(F^2)$ = 0.226, T = 298 K.

Source of material

The flowers of *Pueraia lobata* were collected from the Taibai Mountains of Shaanxi province in July, 2005. All commercially available reagents were used as supplied. The dry powders (100 g) of the flowers of *Pueraia lobata* were refluxed for 1 h with 70 % ethanol (700 mL) three times. The ethanol-soluble portion of the extraction mixture was dried on a rotary evaporator under reduced pressure and subjected to silica-gel column chromatography (6×100 cm). Kakkalidone was eluted from the column with $CHCl_3/CH_3OH$ (6:1, *v/v*) and colorless crystals suitable for X-ray diffraction analysis were obtained by slow evaporation from 95 % ethanol solution after two weeks at room temperature.

Discussion

In traditional Chinese medicine, the flowers of *Pueraia lobata* are used in therapy to counteract problems associated with alcohol drinking [1]. Kakkalide, kakkalidone and irisolidone are the three main active components of the flowers of *Pueraia lobata*. Kakkalide is the largest part among them. Irisolidone (5,7-dihydroxy-6,4′-dimethoxyisoflavone), a kind of flavonoid, had the most potent inhibitory activity against *Helicobacter pylori* (HP) [2] and reduced the ethanol-induced mortality as well as serum alanine aminotransferase (ALT) and aspartate aminotransferase (AST) activities [3-5]. Animal experiments indicated that kakkalidone is an important intermediate in the biotransformation reactions in which kakkalide is metabolized to irisolidone occurring in intestinal bacteria [3].

In the crystal structure of kakkalidone, the atoms of benzopyranone moiety are nearly coplanar, the dihedral angle between ring A (C4-C9) and ring C (O1,C1-C4,C9) is 1.5° (figure, top). To avoid steric hindrance, the two rigid ring systems, phenyl ring B (C10-C15) and benzopyranone moiety, are rotated by 50.1° with respect to each other. The methoxy group at C13 atom is almost coplanar with phenyl ring with the C17–O6–C13–C12 torsion angle of 0.6°. Furthermore, the methoxy group at atom C6 is perpendicular to the benzopyranone moiety, indicative by the C16–O4–C6–C7 torsion angle of 89.8°, as the result of the disubstitution on C5 atom and C7 atom of the isoflavone moiety [6]. The six-membered ring of β-glucose located on C7 is formed by O7, C18 to C22 and shows chair conformation. Atoms C18 (C18′), C19 (C19′), C20 (C20′), C22 (C22′), C23 (C23′), O8 (O8′) and O11(O11′) show positional disorder, which is probably the origin of the rather high final R values. Bond lengths and angles are in expected ranges. The hydrogen bond interactions O–H···O and C–H···O play crucial roles in making supramolecular assemblies. O11–H11···O10, O11′–HI1′···O10, O8′–H8′···O11′ and O10–H10···O9 link the molecules to form an 1D infinite structure along b axis (figure, bottom). Weak interactions which include C18–H18···O4, C18′–H18′···O4 and C16–H16A···O11 are co-responsible for the conformation of these constituents. Both O10 and O4 act as hydrogen donors to form bifurcated hydrogen bonds. The H···O distances fall in the range of 1.94 Å – 2.49 A. Furthermore, the molecules are stacked along the b axis through aromatic π-π interactions. Ring C at (x,y,z) stacks with ring B at (2–x,½+y,–z), meanwhile, ring B at (x,y,z) stacks with ring C at (2–x,–½+y,–z). The centroid-to-centroid distance between B and C rings is 3.725 Å with the dihedral angle of 8.3°, indicating significant intermolecular π-π interactions. Hydrogen bonds and aromatic π-π stacking interactions assemble the molecules into a three-dimensional framework (figure, bottom).

Table 1. Data collection and handling.

Crystal:	colorless needle, size 0.12 × 0.43 × 0.45 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	1.18 cm^{-1}
Diffractometer, scan mode:	Bruker SMART CCD, φ/ω
$2\theta_{max}$:	50°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	5491, 3281
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 1894
$N(param)_{refined}$:	349
Program:	SHELXTL [7]

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Table 2. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	Occ.	x	y	z	U_{iso}
H(3)	2a		−0.4845	−0.0856	0.8793	0.096
H(8)	2a	0.46	−0.1462	−0.1243	0.6058	0.123
H(8′)	2a	0.54	−0.0070	−0.2634	0.5703	0.107
H(9)	2a		0.2347	0.0002	0.4704	0.163
H(10)	2a		0.6020	0.2477	0.5248	0.113
H(11)	2a	0.46	0.4102	0.5254	0.5612	0.112
H(11′)	2a	0.54	0.3213	0.4901	0.5416	0.133
H(1)	2a		0.3052	0.2387	0.9452	0.053
H(8A)	2a		0.1594	0.1972	0.7549	0.064
H(11A)	2a		−0.2483	0.1963	1.0369	0.064
H(12)	2a		−0.2137	0.1713	1.1393	0.076
H(14)	2a		0.3946	−0.0178	1.1237	0.072
H(15)	2a		0.3576	0.0071	1.0235	0.059
H(16A)	2a		−0.5863	−0.2563	0.6802	0.114
H(16B)	2a		−0.4501	−0.2976	0.7387	0.114
H(16C)	2a		−0.3301	−0.2329	0.6827	0.114

Table 2. Continued.

Atom	Site	Occ.	x	y	z	U_{iso}
H(17A)	2a		−0.0129	0.0799	1.2786	0.121
H(17B)	2a		−0.1799	0.0326	1.2267	0.121
H(17C)	2a		−0.0860	0.2185	1.2319	0.121
H(18)	2a	0.46	0.1648	−0.0101	0.6637	0.076
H(19)	2a	0.46	−0.0442	0.1580	0.5612	0.084
H(20)	2a	0.46	0.3178	−0.0837	0.5788	0.083
H(18′)	2a	0.54	0.1625	0.0115	0.6734	0.076
H(19′)	2a	0.54	−0.0985	0.0110	0.5681	0.071
H(20′)	2a	0.54	0.3500	−0.0777	0.5706	0.083
H(21)	2a		0.2401	0.2463	0.5285	0.078
H(22)	2a	0.46	0.4367	0.1433	0.6359	0.080
H(23A)	2a	0.46	0.5256	0.4159	0.6688	0.076
H(23B)	2a	0.46	0.6575	0.3712	0.6124	0.076
H(22′)	2a	0.54	0.4689	0.1716	0.6385	0.080
H(23C)	2a	0.54	0.3698	0.4679	0.6546	0.084
H(23D)	2a	0.54	0.5593	0.4427	0.6106	0.084

Table 3. Atomic coordinates and displacement parameters (in Å^2).

Atom	Site	Occ.	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
O(1)	2a		0.1894(7)	0.2059(5)	0.8640(2)	0.048(3)	0.057(3)	0.044(2)	−0.010(2)	0.011(2)	−0.004(2)
O(2)	2a		−0.3204(7)	−0.0177(6)	0.9460(2)	0.047(3)	0.070(3)	0.053(3)	−0.014(2)	0.009(2)	0.004(2)
O(3)	2a		−0.4970(7)	−0.0876(6)	0.8431(2)	0.052(3)	0.070(3)	0.069(3)	−0.006(3)	0.003(2)	−0.003(3)
O(4)	2a		−0.4877(8)	−0.0509(7)	0.7241(2)	0.054(3)	0.072(4)	0.063(3)	0.012(2)	−0.015(2)	−0.014(2)
O(5)	2a		−0.1387(7)	0.086(1)	0.6738(2)	0.041(3)	0.174(6)	0.048(3)	0.027(3)	0.006(2)	−0.025(3)
O(6)	2a		0.1268(9)	0.0524(7)	1.2017(2)	0.084(3)	0.087(4)	0.041(3)	−0.012(3)	0.008(2)	−0.007(2)
O(7)	2a		0.1510(9)	0.2401(7)	0.6410(2)	0.105(4)	0.068(3)	0.050(2)	0.032(3)	0.031(2)	0.006(2)
O(8)	2a	0.46(1)	−0.114(2)	−0.088(2)	0.5731(6)	0.087(8)	0.087(8)	0.073(7)	−0.003(7)	0.010(6)	−0.024(7)
O(8′)	2a	0.54	−0.033(2)	−0.207(2)	0.5998(4)	0.077(6)	0.077(7)	0.061(6)	−0.013(5)	0.015(5)	−0.009(5)
O(9)	2a		0.196(1)	−0.070(1)	0.4947(3)	0.119(4)	0.145(5)	0.064(3)	−0.008(4)	0.020(3)	−0.050(3)
O(10)	2a		0.5434(9)	0.1536(7)	0.5262(2)	0.080(3)	0.096(4)	0.051(3)	0.006(3)	0.019(2)	0.002(3)
O(11)	2a	0.46	0.422(3)	0.544(2)	0.5969(6)	0.097(9)	0.066(8)	0.062(7)	−0.006(8)	0.004(7)	0.008(6)
O(11′)	2a	0.54	0.292(3)	0.522(2)	0.5749(7)	0.13(1)	0.052(6)	0.089(8)	0.012(7)	0.040(7)	0.011(6)
C(1)	2a		0.188(1)	0.1919(8)	0.9234(3)	0.044(4)	0.044(4)	0.044(4)	−0.009(3)	0.004(3)	−0.010(3)
C(2)	2a		0.0278(9)	0.1152(7)	0.9534(2)	0.035(3)	0.037(4)	0.039(3)	0.006(3)	−0.005(3)	−0.009(3)
C(3)	2a		−0.162(1)	0.0470(8)	0.9214(3)	0.043(3)	0.038(4)	0.049(3)	−0.001(3)	0.005(3)	−0.001(3)
C(4)	2a		−0.156(1)	0.0594(8)	0.8577(3)	0.046(4)	0.034(3)	0.049(3)	0.008(3)	0.008(3)	−0.004(3)
C(5)	2a		−0.327(1)	−0.0057(8)	0.8202(3)	0.033(3)	0.045(4)	0.055(4)	0.003(3)	0.003(3)	−0.012(3)
C(6)	2a		−0.315(1)	0.0062(9)	0.7601(3)	0.034(3)	0.065(4)	0.055(4)	0.009(3)	−0.011(3)	−0.010(3)
C(7)	2a		−0.136(1)	0.083(1)	0.7353(3)	0.059(4)	0.087(5)	0.038(4)	0.021(4)	0.003(3)	−0.008(4)
C(8)	2a		0.037(1)	0.1473(9)	0.7714(3)	0.043(4)	0.069(5)	0.049(4)	0.007(3)	0.007(3)	−0.007(3)
C(9)	2a		0.023(1)	0.1347(7)	0.8309(3)	0.040(4)	0.037(4)	0.046(4)	0.002(3)	0.010(3)	−0.006(3)
C(10)	2a		0.053(1)	0.1023(8)	1.0193(2)	0.051(4)	0.043(4)	0.036(3)	−0.007(3)	0.009(3)	−0.006(3)
C(11)	2a		−0.119(1)	0.1527(9)	1.0545(3)	0.054(4)	0.056(4)	0.051(4)	0.000(3)	0.007(3)	−0.005(3)
C(12)	2a		−0.098(1)	0.1379(9)	1.1161(3)	0.064(5)	0.068(5)	0.058(4)	0.003(4)	0.018(4)	−0.017(4)
C(13)	2a		0.093(1)	0.074(1)	1.1426(3)	0.068(5)	0.061(4)	0.045(4)	−0.015(4)	0.006(4)	−0.012(3)
C(14)	2a		0.265(1)	0.025(1)	1.1066(3)	0.064(4)	0.072(5)	0.043(4)	0.000(4)	−0.005(3)	−0.004(3)
C(15)	2a		0.242(1)	0.0400(8)	1.0466(3)	0.046(4)	0.051(4)	0.052(4)	−0.001(3)	0.013(3)	−0.007(3)
C(16)	2a		−0.461(2)	−0.224(1)	0.7048(4)	0.080(6)	0.063(5)	0.082(5)	0.007(4)	−0.033(4)	−0.023(4)
C(17)	2a		−0.053(2)	0.100(1)	1.2377(3)	0.103(6)	0.101(7)	0.040(4)	−0.018(5)	0.021(4)	−0.010(4)
C(18)	2a	0.46	0.063(1)	0.074(1)	0.6462(3)	0.059(3)	0.080(4)	0.052(3)	0.012(3)	0.015(3)	−0.006(3)
C(19)	2a	0.46	0.019(2)	0.055(3)	0.5800(6)	0.071(6)	0.086(6)	0.053(5)	0.013(6)	0.020(5)	−0.008(6)
C(20)	2a	0.46	0.235(1)	−0.004(1)	0.5529(3)	0.067(3)	0.094(4)	0.047(3)	0.010(3)	0.009(3)	−0.017(3)
C(18′)	2a	0.54	0.063(1)	0.074(1)	0.6462(3)	0.059(3)	0.080(4)	0.052(3)	0.012(3)	0.015(3)	−0.006(3)
C(19′)	2a	0.54	0.026(2)	−0.040(2)	0.5906(5)	0.064(6)	0.076(6)	0.040(5)	0.004(6)	0.012(5)	0.002(5)
C(20′)	2a	0.54	0.235(1)	−0.004(1)	0.5529(3)	0.067(3)	0.094(4)	0.047(3)	0.010(3)	0.009(3)	−0.017(3)
C(21)	2a		0.335(1)	0.169(1)	0.5523(3)	0.077(4)	0.078(4)	0.041(3)	0.030(4)	0.012(3)	0.003(3)
C(22)	2a	0.46	0.359(1)	0.236(1)	0.6146(3)	0.089(4)	0.065(4)	0.047(3)	0.005(4)	0.020(3)	0.005(3)
C(23)	2a	0.46	0.512(3)	0.395(2)	0.6266(8)	0.079(7)	0.063(7)	0.049(6)	0.004(7)	0.022(6)	0.016(6)
C(22′)	2a	0.54	0.359(1)	0.236(1)	0.6146(3)	0.089(4)	0.065(4)	0.047(3)	0.005(4)	0.020(3)	0.005(3)
C(23′)	2a	0.54	0.403(3)	0.425(3)	0.6156(8)	0.084(6)	0.071(6)	0.056(6)	0.003(6)	0.022(6)	−0.006(5)

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