Indian Journal of Chemistry
Vol. 48B, September 2009, pp. 1324-1328

Note

Molecular and crystal structure of an isoflavonoid, 5, 7, 4′-trihydroxy-6, 3′-diprenylisoflavone from *Cudrania javanensis*

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Received 9 January 2008; accepted (revised) 8 May 2009

The title compound belongs to isoflavone group and non ionic in nature. All the exocylic oxygen atoms are bonded covalently with the parent carbon atoms. The oxygen atoms are planar with the respective rings to which they are attached. The average C-O bond lengths are found to be 1.33Å. The crystal structure is stabilized by the network of hydrogen bonding in their crystalline assembly.

Keywords: *Cudrania javanensis*, Moraceae, isoflavonoids, crystal structure

Phytochemical investigation of Moraceae family has revealed the occurrence of isoflavonoids and flavonoids. One of the most important species of this family is *Cudrania javanensis*[1]. The fruits of this plant contain an important prenylated isoflavonoid, 5,7,4′-trihydroxy 6,3′-diprenylisoflavonoid[2] having neuroprotective[3] activity. It has been reported that prenylated isoflavonoids have more antioxidative property than non-prenylated isoflavones[4]. The chemical structure assigned to this compound on the basis of IR, NMR, and mass spectral data, is shown in **Figure 1**. To the best of the knowledge there has been no crystallographic study on this molecule yet. In this article molecular and crystal structure of compound **1** has been described.

Materials and Methods

Powdered fruits of the plant *Cudrania javanensis* were extracted in methanol in soxhlet apparatus, which gave a mixture of compounds. One compound from the mixture was isolated by usual chromatographic techniques. On crystallization with toluene and a few drops of ethyl acetate, pale-yellow crystalline solid was obtained, having a m.p. 165°C. The compound was identified as 5,7,4′-trihydroxy-6,3′-diprenylisoflavone by comparison of its physical and spectroscopic (IR, NMR, and MS) data with the reported values as well as by comparing with authentic samples.

Experimental Section

Single crystals of the title compound **1** were allowed to grow from toluene by slow evaporation method. The X-ray data of the single crystal ($0.50 \times 0.15 \times 0.08$ mm^3) of the title compound **1** were collected at RT with MoK_α radiation (λ=0.71073Å) using a Bruker Nonius SMART CCD diffractometer, equipped with graphite monochromator. Lattice parameters were determined from least square refinement of 25 well-centered reflections in the range $1.61 < \theta < 26.66$. SAINT software[5] was used for the integration of data. Bruker SMART software[6] was used for the data collection and also for indexing reflections and the unit cell parameters. The structure of the title compound **1**, was solved by Direct Methods procedure using SHELXL97 and refined by full matrix least squares technique on F^2 using SHELXL97 software[7,8]. A total of 11,024 reflections were recorded of which 3,900 reflections were found unique. Absorption corrections were not applied.

The positions of the hydrogen atoms in the title compound were calculated from different synthesis maps and were allowed to ride on the corresponding non-hydrogen atoms. The hydrogen attached to hetero atoms were located from different Fourier maps and refined with isotropic displacement co-efficient. The final refinement cycle converged R=0.0817 and wR (F^2) = 0.2623. Atomic scattering factors were taken from International Tables of X-ray crystallography.

The chemical structure and ORTEP view[9] of the reported compound were shown in **Figure 1** and **Figure 2** respectively. The crystal data, refinement parameters and details of structure analysis were summarized in **Table I**. Relevant geometrical parameters (selected bond distances and bond angles) are given in the **Table II** and **Table III**. The thermal parameters and atomic coordinates are shown in **Table IV** and **Table V** respectively.

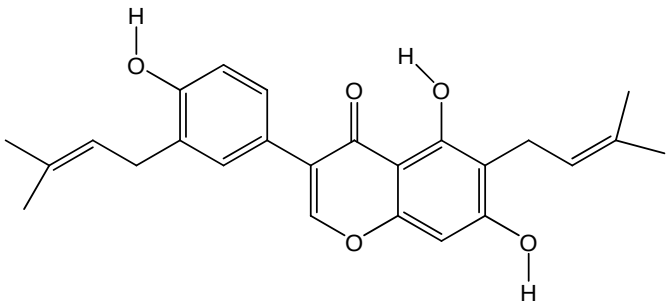

Figure 1 — Structure of 5,7,4′-trihydroxy-6,3′-diprenylisoflavone

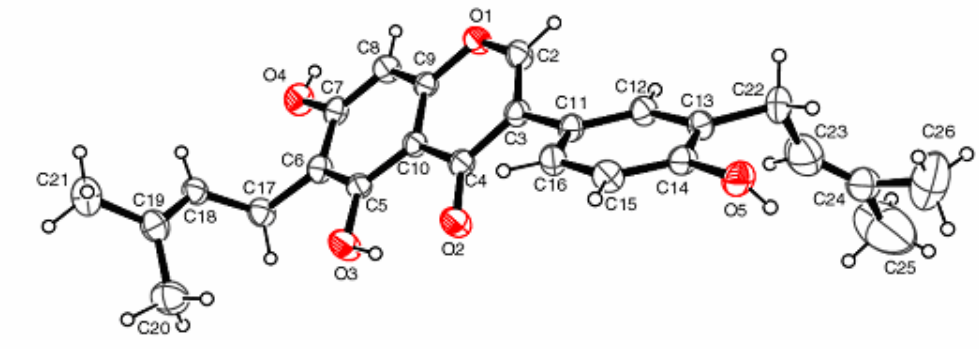

Figure 2 — An ORTEP view of **1** in 30% probability

Table I — Crystal data and structure refinement for **1**

Empirical formula	$C_{25}H_{26}O_5$	
Formula weight	406.46	
Temperature	293(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C_2/c	
Unit cell dimensions	a = 25.2732(12) Å	α= 90°.
	b = 7.4414(3) Å	β= 93.063(3)°.
	c = 22.3113(9) Å	γ = 90°.
Volume	4190.0(3) $Å^3$	
Z	8	
Density (calculated)	1.289 Mg/m^3	
Absorption coefficient	0.089 mm^{-1}	
F(000)	1728	
Crystal size	0.50 × 0.15 × 0.08 mm^3	
Theta range for data collection	1.61 to 26.66°	
Index ranges	-31<=h<=27, -9<=k<=9, -28<=l<=27	
Reflections collected	11024	
Independent reflections	3900 [R(int) = 0.0509]	
Completeness to theta = 26.66°	95.1%	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	3900 / 0 / 280	
Goodness-of-fit on F^2	0.988	
Final R indices [I>2sigma (I)]	R1 = 0.0817, wR2 = 0.2209	
R indices (all data)	R1 = 0.1589, wR2 = 0.2623	
Extinction coefficient	0.0002(4)	
Largest diff. peak and hole	0.897 and -0.283 e.$Å^{-3}$	

Table II — Bond lengths [Å] for **1**

O(1)-C(2)	1.342(4)	C(9)-C(10)	1.401(5)
O(1)-C(9)	1.372(4)	C(11)-C(16)	1.388(5)
O(2)-C(4)	1.270(5)	C(11)-C(12)	1.398(5)
O(3)-C(5)	1.347(5)	C(12)-C(13)	1.397(5)
O(4)-C(7)	1.345(4)	C(13)-C(14)	1.386(5)
O(5)-C(14)	1.385(4)	C(13)-C(22)	1.517(5)
C(2)-C(3)	1.341(6)	C(14)-C(15)	1.380(5)
C(3)-C(4)	1.456(5)	C(15)-C(16)	1.377(5)
C(3)-C(11)	1.479(5)	C(17)-C(18)	1.499(6)
C(4)-C(10)	1.424(5)	C(18)-C(19)	1.315(6)
C(5)-C(6)	1.375(5)	C(19)-C(20)	1.501(7)
C(5)-C(10)	1.427(5)	C(19)-C(21)	1.510(6)
C(6)-C(7)	1.403(6)	C(22)-C(23)	1.531(9)
C(6)-C(17)	1.518(5)	C(24)-C(23)	1.245(8)
C(7)-C(8)	1.385(5)	C(24)-C(25)	1.434(12)
C(8)-C(9)	1.383(5)	C(24)-C(26)	1.481(9)

Table III — Bond angles [°] for **1**

C(2)-O(1)-C(9)	118.8(3)	C(16)-C(11)-C(12)	117.5(3)
O(1)-C(2)-C(3)	126.6(3)	C(16)-C(11)-C(3)	122.4(3)
C(2)-C(3)-C(4)	116.9(3)	C(12)-C(11)-C(3)	120.2(3)
C(2)-C(3)-C(11)	122.2(3)	C(13)-C(12)-C(11)	122.9(4)
C(4)-C(3)-C(11)	120.9(4)	C(14)-C(13)-C(12)	117.0(3)
O(2)-C(4)-C(10)	120.9(3)	C(14)-C(13)-C(22)	123.5(3)
O(2)-C(4)-C(3)	121.8(3)	C(12)-C(13)-C(22)	119.5(4)
C(10)-C(4)-C(3)	117.3(3)	C(15)-C(14)-O(5)	117.5(3)
O(3)-C(5)-C(6)	118.6(3)	C(15)-C(14)-C(13)	121.2(3)
O(3)-C(5)-C(10)	119.3(3)	O(5)-C(14)-C(13)	121.3(3)
C(6)-C(5)-C(10)	122.2(3)	C(16)-C(15)-C(14)	120.6(4)
C(5)-C(6)-C(7)	118.0(3)	C(15)-C(16)-C(11)	120.7(3)
C(5)-C(6)-C(17)	120.6(4)	C(18)-C(17)-C(6)	111.7(3)
C(7)-C(6)-C(17)	121.3(3)	C(19)-C(18)-C(17)	127.5(5)
O(4)-C(7)-C(8)	122.0(4)	C(18)-C(19)-C(20)	124.2(4)
O(4)-C(7)-C(6)	115.8(3)	C(18)-C(19)-C(21)	121.4(4)
C(8)-C(7)-C(6)	122.1(3)	C(20)-C(19)-C(21)	114.4(4)
C(7)-C(8)-C(9)	118.5(4)	C(13)-C(22)-C(23)	110.1(4)
O(1)-C(9)-C(10)	119.9(3)	C(23)-C(24)-C(25)	130.1(8)
C(8)-C(9)-C(10)	122.3(3)	C(23)-C(24)-C(26)	126.1(6)
C(9)-C(10)-C(4)	120.4(3)	C(25)-C(24)-C(26)	103.9(7)
C(9)-C(10)-C(5)	116.8(3)	C(24)-C(23)-C(22)	130.7(6)
C(4)-C(10)-C(5)	122.8(3)		

Results and Discussion

The torsion angles through C8-C9-C10-C4 = 174.92(35) and O1-C9-C10-C5 =177.92(.31), which indicate that the two planes of the isoflavone are nearly co-planar. The planarity of these two planes are also confirmed by the study of dihedral angle between the least square planes passing through C5-C6-C7-C8-C9-C10 and O1-C2-C3-C4-C10-C9, which is found to be 3.51(2)°. The planarity is presumed due to the effect of conjugation. The torsion angles through C2-C3-C11-C12 =-39.46(54)° and C4-C3-C11-C16 = 140.40(40)°, which demonstrated that the phenolic ring is not coplanar with the isoflavone and deviates with an angle approximately of 40° from the isoflavone. The non-planarity is presumed due to the effect of substituion. In the molecule 5,7,4′-trihydroxy-6,3′-diprenylisoflavone, the C—C bond lengths are normal and are in good agreement with the standard value 1.326(2)Å[10]. However, the bond angle C11—C12—C13 in the molecule is slightly lower than the normal value as also found in other molecules. These torsion angles are shown in **Table VI**.

Table IV — Anisotropic displacement parameters ($Å^2 \times 10^3$) for MN-02. The anisotropic displacement factor exponent takes the form: $-2\pi^2[h^2a^{*2}U^{11} + ... + 2h\,ka^*\,b^*\,U^{12}]$

	U^{11}	U^{22}	U^{33}	U^{23}	U^{13}	U^{12}
O(1)	35(2)	70(2)	41(2)	-2(1)	-1(1)	5(1)
O(2)	36(2)	96(2)	45(2)	-7(1)	0(1)	7(1)
O(3)	41(2)	110(2)	47(2)	-10(2)	1(1)	11(2)
O(4)	36(2)	78(2)	68(2)	0(1)	6(1)	13(1)
O(5)	36(2)	72(2)	73(2)	-7(1)	5(1)	3(1)
C(2)	40(2)	60(2)	49(2)	-3(2)	7(2)	7(2)
C(3)	32(2)	48(2)	45(2)	3(2)	2(2)	2(2)
C(4)	35(2)	51(2)	46(2)	-1(2)	2(2)	1(2)
C(5)	34(2)	54(2)	40(2)	0(2)	-2(2)	-2(2)
C(6)	38(2)	46(2)	52(2)	2(2)	6(2)	6(2)
C(7)	31(2)	48(2)	56(2)	7(2)	5(2)	5(2)
C(8)	35(2)	59(2)	49(2)	2(2)	-3(2)	8(2)
C(9)	34(2)	46(2)	43(2)	-2(2)	2(2)	-1(2)
C(10)	31(2)	48(2)	42(2)	0(2)	4(2)	1(2)
C(11)	33(2)	47(2)	47(2)	-2(2)	5(2)	2(2)
C(12)	38(2)	53(2)	48(2)	2(2)	3(2)	6(2)
C(13)	42(2)	51(2)	48(2)	-5(2)	10(2)	2(2)
C(14)	30(2)	52(2)	54(2)	-6(2)	2(2)	7(2)
C(15)	41(2)	58(2)	50(2)	2(2)	-1(2)	14(2)
C(16)	44(2)	58(2)	45(2)	7(2)	6(2)	0(2)
C(17)	46(2)	59(2)	52(2)	-5(2)	9(2)	7(2)
C(18)	38(2)	65(3)	43(2)	-5(2)	7(2)	1(2)
C(19)	55(3)	65(3)	56(3)	-3(2)	15(2)	9(2)
C(20)	76(4)	103(4)	71(3)	4(3)	-13(3)	2(3)
C(21)	82(4)	86(3)	73(3)	14(3)	19(3)	-1(3)
C(22)	51(3)	64(3)	66(3)	8(2)	21(2)	2(2)
C(24)	83(4)	73(3)	67(3)	1(2)	5(3)	-10(3)
C(23)	131(6)	115(5)	80(4)	8(3)	17(4)	-10(4)
C(26)	104(6)	179(8)	162(8)	61(6)	22(5)	-20(5)
C(25)	640(40)	176(12)	163(11)	-47(8)	130(16)	-245(17)

Table V — Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters ($Å^2$ × 10^3)for MN-02. U(eq) is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	Y	z	U(eq)		x	Y	z	U(eq)
O(1)	2457(1)	5528(4)	765(1)	49(1)	C(12)	769(1)	5677(5)	930(2)	46(1)
O(2)	1433(1)	5135(4)	-703(1)	59(1)	C(13)	235(2)	5977(5)	1028(2)	47(1)
O(3)	2222(1)	4440(4)	-1349(1)	66(1)	C(14)	-61(1)	6876(5)	582(2)	45(1)
O(4)	3883(1)	3578(4)	-374(1)	61(1)	C(15)	169(2)	7521(5)	78(2)	50(1)
O(5)	-595(1)	7230(4)	636(1)	60(1)	C(16)	698(2)	7217(5)	-6(2)	49(1)
C(2)	1942(2)	5939(5)	789(2)	49(1)	C(17)	3290(2)	3603(5)	-1460(2)	52(1)
C(3)	1574(1)	5863(5)	333(2)	42(1)	C(18)	3509(2)	5236(6)	-1753(2)	48(1)
C(4)	1753(1)	5314(5)	-248(2)	44(1)	C(19)	3340(2)	5983(6)	-2262(2)	58(1)
C(5)	2531(1)	4482(5)	-838(2)	43(1)	C(20)	2891(2)	5265(8)	-2661(2)	84(2)
C(6)	3059(2)	4055(5)	-865(2)	45(1)	C(21)	3595(2)	7660(7)	-2495(2)	80(2)
C(7)	3374(1)	4063(5)	-328(2)	45(1)	C(22)	7(2)	5293(6)	1600(2)	60(1)
C(8)	3175(1)	4555(5)	215(2)	48(1)	C(24)	-405(2)	2234(7)	1729(2)	74(1)
C(9)	2646(1)	5013(4)	226(2)	41(1)	C(23)	-41(3)	3243(10)	1581(3)	108(2)
C(10)	2304(1)	4971(5)	-290(2)	41(1)	C(26)	-915(3)	2809(12)	1965(4)	148(3)
C(11)	1009(1)	6262(5)	415(2)	42(1)	C(25)	-440(7)	311(15)	1719(5)	323(15)

Table VI — Torsion angles (deg) for MN-02

C9	-O1	-C2	-C3	1.68	0.56	O4	-C7	-C8	-C9	-179.16	0.34
C2	-O1	-C9	-C8	-178.51	0.33	C6	-C7	-C8	-C9	1.49	0.56
C2	-O1	-C9	-C10	1.71	0.48	C7	-C8	-C9	-O1	-178.88	0.32
O1	-C2	-C3	-C4	-1.28	0.58	C7	-C8	-C9	-C10	0.90	0.56
O1	-C2	-C3	-C11	176.93	0.34	O1	-C9	-C10	-C4	-5.30	0.52
C2	-C3	-C4	-O2	177.37	0.35	O1	-C9	-C10	-C5	177.92	0.31
C2	-C3	-C4	-C10	-2.34	0.51	C8	-C9	-C10	-C4	174.92	0.35
C11	-C3	-C4	-O2	-0.86	0.55	C8	-C9	-C10	-C5	-1.86	0.53
C11	-C3	-C4	-C10	179.43	0.33	C3	-C11	-C12	-C13	-178.60	0.34
C2	-C3	-C11	-C12	-39.46	0.54	C16	-C11	-C12	-C13	1.54	0.55
C2	-C3	-C11	-C16	140.40	0.40	C3	-C11	-C16	-C15	178.24	0.35
C4	-C3	-C11	-C12	138.67	0.37	C12	-C11	-C16	-C15	-1.90	0.55
C4	-C3	-C11	-C16	-41.47	0.53	C11	-C12	-C13	-C14	0.91	0.55
O2	-C4	-C10	-C5	2.41	0.56	C11	-C12	-C13	-C22	179.91	0.35
O2	-C4	-C10	-C9	-174.17	0.34	C12	-C13	-C14	-O5	179.73	0.33
C3	-C4	-C10	-C5	-177.88	0.33	C12	-C13	-C14	-C15	-3.08	0.55
C3	-C4	-C10	-C9	5.53	0.51	C22	-C13	-C14	-O5	0.77	0.58
O3	-C5	-C6	-C7	-178.50	0.33	C22	-C13	-C14	-C15	177.96	0.37
O3	-C5	-C6	-C17	1.88	0.54	C12	-C13	-C22	-C23	-71.67	0.51
C10	-C5	-C6	-C7	1.69	0.55	C14	-C13	-C22	-C23	107.27	0.49
C10	-C5	-C6	-C17	-177.92	0.34	O5	-C14	-C15	-C16	-179.91	0.34
O3	-C5	-C10	-C4	4.02	0.54	C13	-C14	-C15	-C16	2.80	0.59
O3	-C5	-C10	-C9	-179.28	0.33	C14	-C15	-C16	-C11	-0.19	0.59
C6	-C5	-C10	-C4	-176.18	0.35	C6	-C17	-C18	-C19	-115.26	0.48
C6	-C5	-C10	-C9	0.52	0.53	C17	-C18	-C19	-C20	-1.91	0.74
C5	-C6	-C7	-O4	177.86	0.33	C17	-C18	-C19	-C21	178.75	0.41
C5	-C6	-C7	-C8	-2.75	0.56	C13	-C22	-C23	-C24	-137.02	0.71
C17	-C6	-C7	-O4	-2.52	0.52	C13	-C22	-C23	-H23	42.99	0.76
C17	-C6	-C7	-C8	176.87	0.35	C26	-C24	-C23	-C22	1.09	1.18
C5	-C6	-C17	-C18	91.69	0.44	C25	-C24	-C23	-C22	-178.59	0.87
C7	-C6	-C17	-C18	-87.92	0.44						

Table VII — The details of the hydrogen bond geometry for **1** is as follows

D-H….A	D–H	D...A	H…A	D–H…A	
O3	-H3O...O2 (i)	0.811(3)	2.573(4)	1.852(3)	147.60(21)
C16	-H16…O2 (i)	0.930(4)	2.929(5)	2.541(3)	105.43(24)
C17	-H17... O4 (i)	0.970(4)	2.780(5)	2.453(3)	99.28(25)
C17	-H17...O3 (i)	0.970(4)	2.795(5)	2.442(3)	101.05(25)
C22	-H22...O5 (i)	0.970(5)	2.943(5)	2.534(3)	105.37(27)
O4	-H4O...O5 (ii)	0.793(3)	2.741(4)	1.984(3)	159.36(22)
O5	-H5O...O2 (iii)	0.829(3)	2.764(4)	2.005(3)	151.87(20)

Symmetry codes:

(i) x, y, z
(ii) x +1/2, +y-1/2, +z
(iii) -x,-y+1,-z

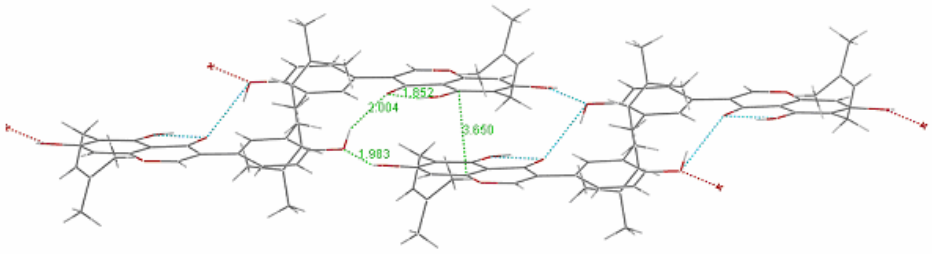

Figure 3 — The diagram shows that the compound **1** units self-assembly by intermolecular π-interactions along with inter and intra-molecular hydrogen bonding

The molecule contains four strong C–H···O interactions of C_{16}–H_{16}···O_2, C_{17}–H_{17}···O_4, C_{22}–H_{22}…O_5 and C_{17}–H_{17}···O_3. Besides these, some strong intermolecular D·····A interactions also observed inside the molecule with O_3·····O_2 = 2.573(4) Å, O_5·····O_2 = 2.764(4) Å and O_4·····O_5 = 2.741(4) Å. These interactions with symmetry are given in **Table VII**.

The packing pattern of the reported compound shows that alternate hydrogen bonded chains run in opposite directions and are stabilized by intermolecular π-stacking interactions (**Figure 3**). The perpendicular distance between the two planes of the Compound **1** is 3.650Å[11], which indicates that the molecular chains are strongly associated through π-interactions.

Acknowledgement

The authors are thankful to the Director, Institute of Advance Study in Science and Technology, Guwahati for providing laboratory facilities and Dr. Anil Saikia, Associate Professor, Department of Chemistry, IIT Guwahati for help in spectral data analysis. One of the authors (MK) is thankful to the UGC for financial support.

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