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Note

Molecular and crystal structure of 6α-acetoxy azadirone

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The crystal structure of the title compound, **1** has been determined by X-ray crystallographic techniques. The compound crystallizes in orthorhombic space group $P2_12_12_1$ with unit cell parameters: a=10.699(3) Å, b=15.510(4) Å, c=16.626(4) Å, Z=4. The structure has been solved by direct methods and refined to R = 0.0585 for 6681 independent reflections.

Keywords: *Chisocheton paniculatus,* Meliaceae, limonoids, 6α-acetoxy azadirone, crystal structure

Limonoids have attracted much attention because of their marked and notable insect antifeedant[1,2] activity. They are found in the plants of Meliaceae[3] family as secondary metabolites[4,5]. One of the most important limonoid found in the plant *Chisocheton paniculatus*[6] Hiern of Meliaceae family is 6α-acetoxy azadirone[7] **1**. This compound exists as α- as well as β-isomer. The crystal structure of β-isomer is already known[8]. Herein is reported the molecular and crystal structure of its α-isomer.

Materials and Methods

Powdered fruits of the plant *Chisocheton paniculatus* were extracted with petroleum ether (60-80°C) using a soxhlet apparatus, which gave a mixture of several compounds. One compound was isolated by usual chromatographic technique. On purification by crystallization from toluene, a white crystalline solid was obtained having a melting point of 192°C. The compound was identified as 6α-acetoxy azadirone **1** by a comparison of its physical (*e.g.* m.p.) and spectroscopic (IR, NMR, and MS) data with the reported values[7] as well as by comparing with authentic samples.

Experimental Section

Single crystals of the title compound **1** were grown from toluene by slow evaporation technique. The XRD data for a good quality single crystal (0.40 × 0.34 × 0.22 mm^3) was collected at 296K temperature with a Bruker 3-circle diffractometer (Bruker Nonius SMART APEX 2) equipped with CCD area detector [using graphite monochromated MoK_α radiation (λ = 0.71073 Å)]. Bruker SMART software[9] was used for data collection and also for indexing reflections and the unit cell parameters. The data were integrated using SAINT software[10]. The structures were solved by direct methods and refined by full-matrix least-squares calculation using SHELXL software[11,12]. Lattice parameters were determined from θ values in the range $3.81<\theta < 28.40$. A total of 20488 reflections were recorded of which 6681 reflections were found unique. Absorption correction was not applied.

All the non-H atoms were refined in the anisotropic approximation against F^2 of all reflections. The H-atoms except those attached to N, O and F were placed at their calculated positions and refined in the isotropic approximations. The hydrogens attached to heteroatoms (N, O and F) were located from the difference Fourier maps and refined with isotropic displacement co-efficients. The final refinement cycle converged at R=0.0501 and wR (F^2) = 0.1464. Atomic scattering factors were taken from International Tables for X-ray crystallography.

The chemical structure of **1** is given in the **Figure 1** and its ORTEP view[13] in **Figure 2**. Crystal data and other experimental details are given in the **Table I**.

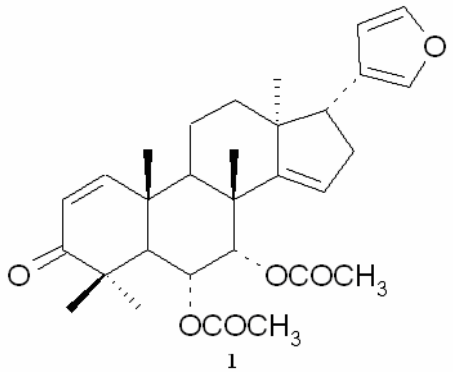

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Figure 1 — Structure of 6α-acetoxy azadirone

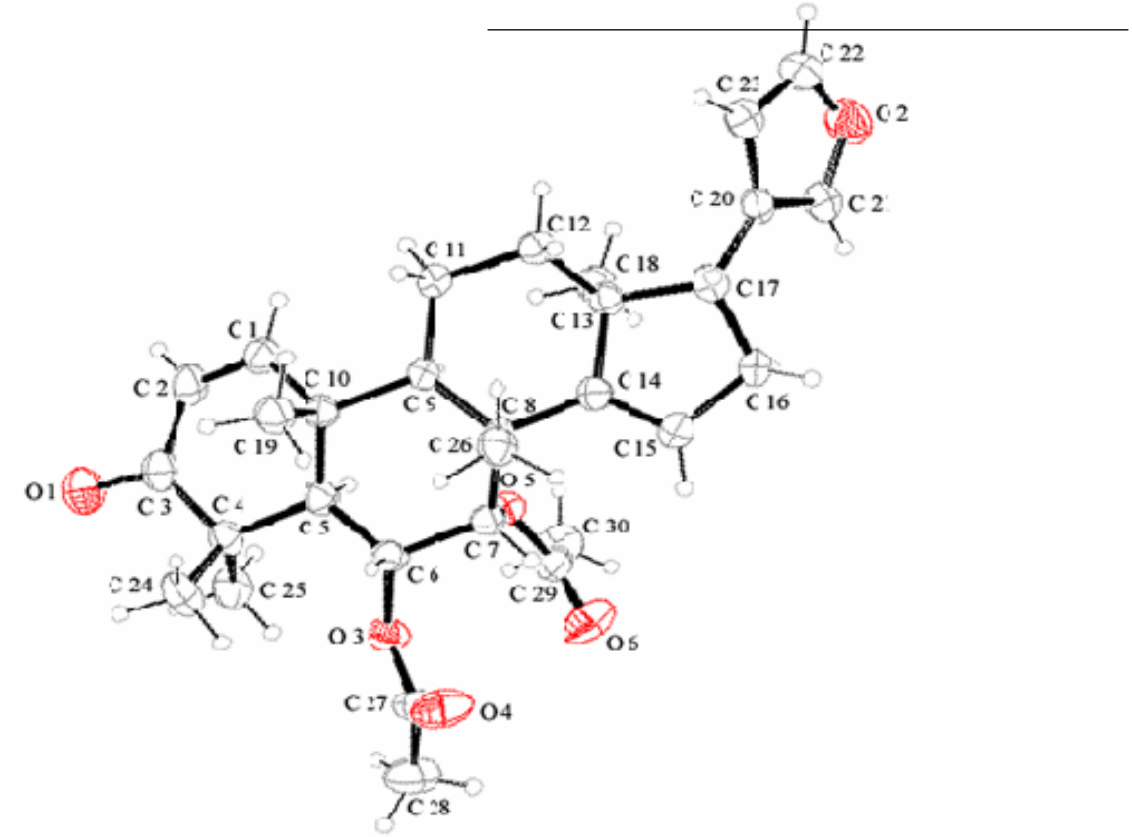

Figure 2 — An ORTEP view of **1** in 30% probability

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

Empirical formula	:	$C_{30}H_{38}O_6$
Formula weight	:	494.60
Temperature	:	296(2) K
Wavelength	:	0.71073 Å
Crystal system	:	Orthorhombic
Space group	:	$P2_12_12_1$
Unit cell dimensions	:	a = 10.699(3) Å α= 90° b = 15.510(4) Å β= 90° c = 16.626(4) Å. γ = 90°
Volume	:	2759.0(12) $Å^3$
Z	:	4
Density (calculated)	:	1.191 Kg/m^3
Absorption coefficient	:	0.082 mm^{-1}
F(000)	:	1064
Crystal size	:	0.48 × 0.34 × 0.22 mm^3
Theta range for data collection	:	3.81 to 28.40°.
Index ranges	:	-11<=h<=14, -20<=k<=20, -22<=l<=21
Reflections collected	:	20488
Independent reflections	:	6681 [R(int) = 0.0585]

Contd

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

Completeness to theta = 28.40°	:	98.1%
Absorption correction	:	None
Refinement method	:	Full-matrix least-squares on F^2
Data / restraints / parameters	:	6681 / 0 / 332
Goodness-of-fit on F^2	:	0.998
Final R indices [I>2sigma(I)]	:	R1 = 0.0501, wR2 = 0.1200
R indices (all data)	:	R1 = 0.0876, wR2 = 0.1464
Absolute structure parameter	:	0.0(11)
Largest diff. peak and hole	:	0.174 and -0.180 $e.Å^{-3}$

Selected bond distances and bond angles are given in **Table II**. The furan ring in the molecule at the position 17 shows normal geometry and lies in the same plane with those of the two-acetyl groups at position 6 and 7. Both the acetyl groups lying in the same side represent a specific geometry to the molecule (α-isomer). The furan ring at the position 17 is found to be twisted with respect to the D ring of the

steroidal structure. The existence of the two acetyl groups at positions 6 and 7 in the molecule is expected to stabilize the three dimensional assembly of the molecules in the solid state through C-H···O weak

Table II — Bond lengths [Å] and angles [°] for **1**

O(5)-C(29)	1.347(3)
O(5)-C(7)	1.447(3)
O(3)-C(27)	1.341(3)
O(3)-C(6)	1.462(3)
O(2)-C(21)	1.360(3)
O(2)-C(22)	1.363(4)
O(1)-C(3)	1.217(3)
O(4)-C(27)	1.199(3)
O(6)-C(29)	1.198(3)
C(10)-C(1)	1.511(3)
C(10)-C(19)	1.541(3)
C(10)-C(5)	1.563(3)
C(10)-C(9)	1.571(3)
C(7)-C(6)	1.529(3)
C(7)-C(8)	1.537(3)
C(8)-C(14)	1.529(3)
C(8)-C(26)	1.541(3)
C(8)-C(9)	1.545(3)
C(5)-C(6)	1.523(3)
C(5)-C(4)	1.564(3)
C(13)-C(12)	1.513(3)
C(13)-C(14)	1.521(3)
C(13)-C(18)	1.542(3)
C(13)-C(17)	1.568(3)
C(17)-C(20)	1.498(3)
C(17)-C(16)	1.529(4)
C(14)-C(15)	1.314(3)
C(9)-C(11)	1.542(3)
C(1)-C(2)	1.327(3)
C(11)-C(12)	1.539(3)
C(3)-C(2)	1.454(4)
C(3)-C(4)	1.525(3)
C(29)-C(30)	1.482(4)
C(15)-C(16)	1.511(3)
C(4)-C(25)	1.523(4)
C(4)-C(24)	1.553(4)
C(27)-C(28)	1.483(4)
C(23)-C(22)	1.336(4)
C(23)-C(20)	1.410(4)
C(20)-C(21)	1.362(4)
C(29)-O(5)-C(7)	119.51(17)
C(27)-O(3)-C(6)	116.4(2)
C(21)-O(2)-C(22)	105.9(2)
C(1)-C(10)-C(19)	105.25(19)
C(1)-C(10)-C(5)	106.24(19)
C(19)-C(10)-C(5)	114.11(17)
C(1)-C(10)-C(9)	108.56(17)
C(19)-C(10)-C(9)	114.50(18)
C(5)-C(10)-C(9)	107.73(17)
O(5)-C(7)-C(6)	107.45(17)
O(5)-C(7)-C(8)	109.28(16)
C(6)-C(7)-C(8)	111.88(19)
C(14)-C(8)-C(7)	109.58(19)
C(14)-C(8)-C(26)	106.29(17)
C(7)-C(8)-C(26)	108.36(18)
C(14)-C(8)-C(9)	108.62(17)
C(7)-C(8)-C(9)	108.97(16)
C(26)-C(8)-C(9)	114.92(19)
C(6)-C(5)-C(10)	108.96(18)
C(6)-C(5)-C(4)	114.77(17)
C(10)-C(5)-C(4)	115.97(19)
C(12)-C(13)-C(14)	109.80(19)
C(12)-C(13)-C(18)	112.01(18)
C(14)-C(13)-C(18)	110.85(19)
C(12)-C(13)-C(17)	114.04(18)
C(14)-C(13)-C(17)	99.93(16)
C(18)-C(13)-C(17)	109.60(18)
C(20)-C(17)-C(16)	116.1(2)
C(20)-C(17)-C(13)	117.09(18)
C(16)-C(17)-C(13)	103.43(17)
C(15)-C(14)-C(13)	111.03(19)
C(15)-C(14)-C(8)	127.7(2)
C(13)-C(14)-C(8)	120.80(19)
C(11)-C(9)-C(8)	112.28(18)
C(11)-C(9)-C(10)	113.81(18)
C(8)-C(9)-C(10)	114.54(16)
C(2)-C(1)-C(10)	122.0(2)
C(12)-C(11)-C(9)	115.38(19)
O(1)-C(3)-C(2)	120.4(2)
O(1)-C(3)-C(4)	119.9(2)
C(2)-C(3)-C(4)	119.76(18)
O(3)-C(6)-C(5)	108.98(18)
O(3)-C(6)-C(7)	106.88(19)
C(5)-C(6)-C(7)	111.60(16)
O(6)-C(29)-O(5)	122.4(3)
O(6)-C(29)-C(30)	125.5(3)
O(5)-C(29)-C(30)	112.1(2)
C(13)-C(12)-C(11)	113.85(18)
C(14)-C(15)-C(16)	112.2(2)
C(25)-C(4)-C(3)	108.5(2)
C(25)-C(4)-C(24)	109.5(2)
C(3)-C(4)-C(24)	103.59(19)
C(25)-C(4)-C(5)	114.62(19)
C(3)-C(4)-C(5)	110.17(18)
C(24)-C(4)-C(5)	109.9(2)
O(4)-C(27)-O(3)	123.4(2)
O(4)-C(27)-C(28)	126.0(3)
O(3)-C(27)-C(28)	110.6(3)
C(22)-C(23)-C(20)	107.8(3)
C(21)-C(20)-C(23)	105.1(2)
C(21)-C(20)-C(17)	128.0(2)
C(23)-C(20)-C(17)	126.9(2)
C(1)-C(2)-C(3)	123.0(2)
C(15)-C(16)-C(17)	101.13(19)
C(23)-C(22)-O(2)	110.4(3)
O(2)-C(21)-C(20)	110.8(3)

Symmetry transformations used to generate equivalent atoms

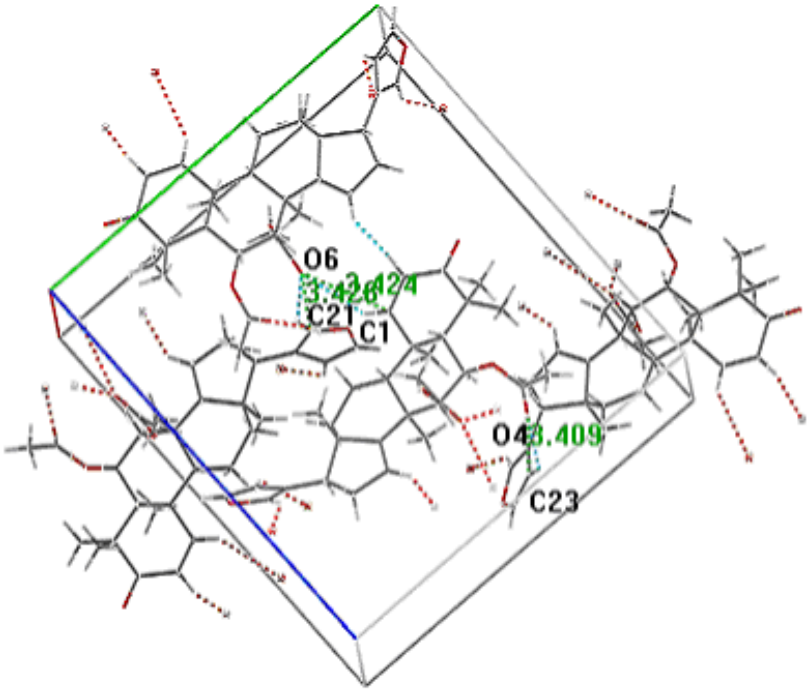

Figure 3 — Packing structure woth C-H···O interactions

interaction involving C_{23}-H···O_4, C_{21}-H···O_6 and C_1-H···O_6 interactions ($d_{C23\cdots O4}$ 3.40, $d_{C21\cdots O6}$ 3.42 Å and $d_{C1\cdots O6}$ 3.42 Å) respectively and van der Waals interactions as shown in the **Figure 3**. These distances are well within the reported range for C-H···O interaction[14]. The length of the double bond C3=O1 is slightly larger (1.217 Å) than the normal C=O double (1.20 Å) bond that could be attributed to the resonance caused by the α, β-unsaturated system present in the molecule.

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