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Austrocortinin: Crystal structure of a natural anthraquinone pigment from fungi

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Abstract

A natural anthraquininoid pigment, austrocortinin (1,4-dihydroxy-2-methoxy-7-methylanthracene-9,10-dione, $C_{16}H_{12}O_5$), was isolated from Fungi K_BK5, a novel endophytic fungus of *Lagerstroemia speciosa*. The pigment is monoclinic in $P2_1/c$ with $a = 8.6758(2)$ Å, $b = 7.9050(2)$ Å, $c = 18.6415$ Å, $\beta = 97.099(1)^\circ$, $V = 1268.67(6)$ Å^3, and $Z = 4$.

Keywords: Anthraquinone; Crystal structure; Hydrogen bonding; Fungi K_BK5

1. Introduction

9,10-Anthraquinone and its derivatives are important compounds used in the field of dyes and pigments [1,2]. The relationship between molecular conformation and visible spectra of some amino derivatives of anthraquinone has been reported [3,4]. This kind of compounds can have more than one polymorphs that exhibit interconversion of polymorphic forms when they are induced thermally [5]. They are also potentially useful in the field of organic semiconductors because they offer intriguing properties for low cost organic electronics [6–8]. These dyeing and organic semiconducting properties are affected by the intermolecular interactions, for example, hydrogen bonding, π–π interactions and C–H interactions. These kinds of intermolecular interactions are helpful in the effective three dimensional molecular stacking of anthraquinone dyes. Especially, the property of being hydrogen donors and acceptors in their structure make them possible to be an interesting charge transfer complex.

Fungal endophyte K_BK5 is a novel endophytic fungus of *Lagerstroemia speciosa*, Queen flower. It can produce pigments when grown in Sabouraud's Dextrose Broth medium. We have unexpectedly found that this kind of fungus can produce an anthraquininoid, austrocortinin (1,4-dihydroxy-2-methoxy-7-methylanthracene-9,10-dione, $C_{16}H_{12}O_5$). Usually, this compound is one among the series of anthraquinone metabolites often isolated from *Cortinarius* sp. and *Dermocybe splendida* [9].

In this paper, single X-ray structure determination and crystal packing analysis of austrocortinin have been investigated to determine its structure and the important intermolecular interactions in the solid state.

2. Experimental

Austrocortinin was isolated from the organic extract phase of the liquid culture of fungal endophyte K_B5. Selected

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endophytic fungal K_BK5 was chosen for the study of metabolites and cultivated on SDA at room temperature for 1 week. The agar culture was cut with flamed cork borer (diameter 7 mm). Five disks were inoculated into 250 ml Erlenmeyer flasks containing 100 ml of Sabouraud's Dextrose Broth (SDB) medium. The cultures were incubated at room temperature for 14 days.

The culture broth of selected endophytic fungal K_BK5 (4 l) was filtered through 4 layers of cotton gauze and exhaustively pressed. The filtrate was extracted with an equal volume of ethyl acetate for 5 times. The organic extracted layers were combined and dried on anhydrous sodium sulfate. The solvent was evaporated using a rotary evaporator and the crude extract of broth was collected.

The fungal mycelia were blended and extracted 10 times with ethyl acetate in ultrasonic bath and filtered. The combined filtrate was dried on sodium sulfate and evaporated until dryness. The crude extract of mycelium was collected.

The broth and mycelium crude extracts of isolate K_BK5 were purified by column chromatography.

The single crystals suitable for X-ray structure analysis were recrystallized by slow evaporation method from chloroform as transparent red rod crystals. X-ray diffraction data were collected at 293(2) K on a Bruker SMART diffractometer with graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). A total of 3567 unique ($R_{int} = 0.0205$) reflections were collected in the range of $2.37^\circ < 2\theta < 30.42^\circ$ with ω scan mode. The crystal structure was solved by direct methods and refined by full-matrix least squares against F^2 using SHELXL-97 package software [10,11]. Non-hydrogen atoms were refined with anisotropic thermal parameters. All hydrogen atoms were found from difference Fourier maps and were refined isotropically. Crystal data and experimental details are given in Table 1 and the atomic coordinates are listed in Table 2. A final refinement of 292 parameters with no restraints gave $R = 0.0497$ for observed reflections. The bond lengths and angles of the title compound are given in Table 3. Crystallographic data for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre and can be obtained on quoting the deposit number CCDC 659510.

Table 1
Crystal data and experimental details

Empirical formula	$C_{16}H_{12}O_5$
Formula weight	284.27
CCDC No.	659510
Color/shape	Red/prismatic
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	$a = 8.6758(2)$ Å
	$b = 7.9050(2)$ Å
	$c = 18.6415(5)$ Å
	$\beta = 97.0990(10)^\circ$
Volume, Å^3	1268.67(6)
Z	4
Calculated density, g/cm^3	1.488
Temperature, K	293(2)
Absorption coefficient (Mo Kα), cm^{-1}	1.12
$F(000)$	592
θ range for data collection	2.37–30.42°
Reflections collected/unique	8920/3576 [R(int) = 0.0205]
Data/restraints/parameters	3576/0/238
Goodness-of-fit on F^2	1.066
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0445$, $wR2 = 0.1331$
R indices (all data)	$R1 = 0.0628$, $wR2 = 0.1458$
Largest diff. peak and hole	0.326 and −0.161 e$^-$/Å^3

Table 2
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å$^2 \times 10^3$)

Atom	x	y	z	$U_{(eq)}$
C(1)	1750(1)	1979(1)	−275(1)	36(1)
C(2)	2080(1)	2782(1)	−957(1)	36(1)
C(3)	1431(1)	4361(2)	−1151(1)	42(1)
C(4)	1703(1)	5143(2)	−1793(1)	44(1)
C(5)	2679(1)	4338(2)	−2232(1)	48(1)
C(6)	3338(2)	2782(2)	−2045(1)	45(1)
C(7)	3033(1)	1967(1)	−1410(1)	38(1)
C(8)	3698(1)	281(1)	−1224(1)	40(1)
C(9)	3339(1)	−534(1)	−568(1)	36(1)
C(10)	3926(1)	−2146(1)	−380(1)	40(1)
C(11)	3578(1)	−2961(1)	252(1)	42(1)
C(12)	2666(1)	−2161(1)	706(1)	40(1)
C(13)	2071(1)	−500(1)	532(1)	37(1)
C(14)	2393(1)	295(1)	−97(1)	35(1)
C(15)	2747(2)	−4491(2)	1518(1)	53(1)
C(16)	964(2)	6818(2)	−2018(1)	61(1)
O(1)	941(1)	2721(1)	137(1)	47(1)
O(2)	4543(1)	−430(1)	−1635(1)	55(1)
O(3)	4853(1)	−2971(1)	−792(1)	53(1)
O(4)	1188(1)	201(1)	999(1)	48(1)
O(5)	2267(1)	−2795(1)	1325(1)	50(1)

3. Results and discussion

3.1. Description of crystal structure

An ORTEP view of the molecule is shown in Fig. 1. Austrocortinin is a planar molecule which was distorted from the mean plane with the mean deviation of total 22 atoms being 0.056.

Crystal packing scheme is shown in Figs. 2 and 3. The compound is arranged in a herringbone packing motif without any heteroatom interactions. The anthraquinone rings form an

Table 3
Bond lengths (Å)

	Distance		Distance
C(1)–O(1)	1.2484(12)	C(8)–C(9)	1.4503(15)
C(1)–C(14)	1.4654(15)	C(9)–C(10)	1.4008(16)
C(1)–C(2)	1.4800(15)	C(9)–C(14)	1.4330(14)
C(2)–C(3)	1.3982(16)	C(10)–O(3)	1.3475(13)
C(2)–C(7)	1.4095(14)	C(10)–C(11)	1.4072(17)
C(3)–C(4)	1.3932(16)	C(11)–C(12)	1.3808(15)
C(4)–C(5)	1.4012(17)	C(12)–O(5)	1.3433(14)
C(4)–C(16)	1.5074(19)	C(12)–C(13)	1.4334(15)
C(5)–C(6)	1.3825(19)	C(13)–O(4)	1.3473(12)
C(6)–C(7)	1.4010(16)	C(13)–C(14)	1.3882(15)
C(7)–C(8)	1.4770(16)	C(15)–O(5)	1.4362(15)
C(8)–O(2)	1.2561(13)		

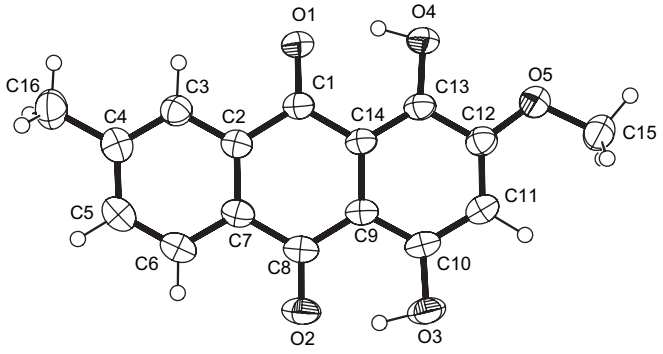

Fig. 1. Molecular structure and atomic numbering of austrocortinin.

anthraquinone column through a face-to-face slip stacking motif along the *a*-axis. The quinone ring of one molecule is stacked over the ring containing the dihydroxy groups of the other neighboring molecule with the distance between the centers of the adjacent anthraquinone ring of approximately 3.768 Å. The stacking distance between the nearest atoms of two adjacent planes is 3.4634(14) Å. The intermolecular closet O···O′ distance is 3.7511(13) Å, indicating no interaction between the oxygen atoms.

The molecule presents the intramolecular hydrogen bonds between the quinone oxygen atom and the hydroxyl oxygen atom with the distances of O3···O2 and O4···O1 being 2.5447(14) Å and 2.5520(12) Å, respectively. The geometry of the hydrogen bondings is given in Table 4.

The C–H···O short contacts have been found between the atom at the aromatic hydrogen carbon and the hydroxyl oxygen atom of the other molecule. The distance of C5–H···O4 (x, $-y+1/2$, $z+1/2$) and C11–H···O3 ($-x+1$, $-y-1$, $-z$) are 3.41(1) Å and 3.59(1) Å, respectively.

Both the intermolecular hydrogen bond and the π–π interplanar interaction contribute to the orientation of molecular aggregation in the crystal.

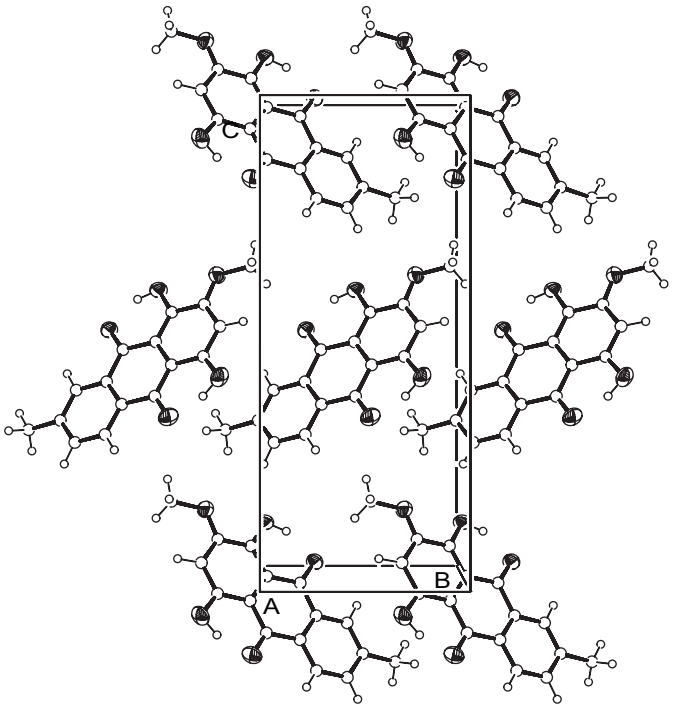

Fig. 2. Crystal packing scheme of austrocortinin along *a*-axis.

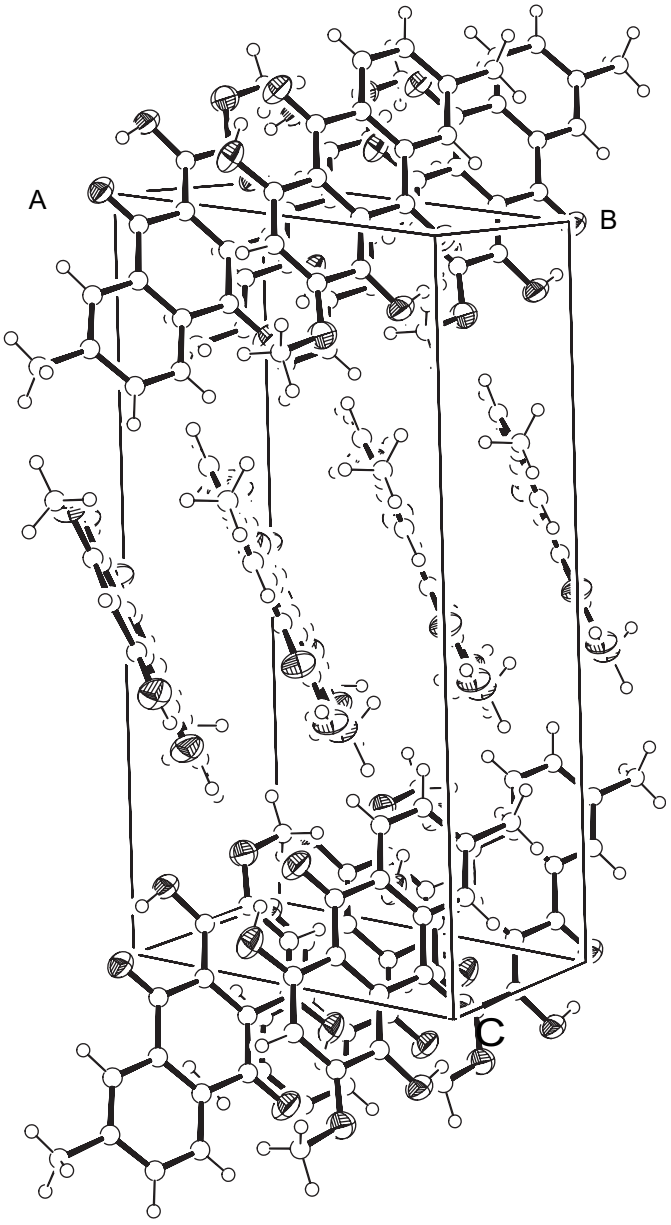

Fig. 3. Crystal packing scheme of austrocortinin along *ab*-axes.

Table 4
Hydrogen bonding geometry

D–H···A	*d*(D–H), Å	*d*(H···A), Å	*d*(D···A), Å	∠(DHA), °
O(3)–H···O(2)	0.99(2)	1.60(2)	2.5447(14)	157.2(18)
O(4)–H···O(1)	0.94(2)	1.68(2)	2.5520(12)	152.6(18)

Acknowledgements

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