Crystal and molecular structure of lancerodiol–*p*–hydroxybenzoate

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ABSTRACT

Lancerodiol–*p*–hydroxybenzoate was isolated from the leaves of *Ferula sinaica* L. (Apiaceae) as light needle crystals. This work reports for the first time the molecular structure and relative configuration of compound **1**, established by X–ray analysis.

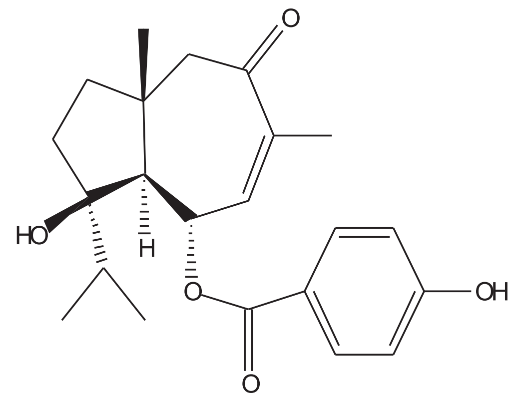
Key words: Crystal structure, *Ferula sinaica*, lancerodiol, sesquiterpene

INTRODUCTION

The genus *Ferula* presents interesting phytochemical features. *Ferula sinaica* L. (Apiaceae) is widespread in Sinai peninsula, Egypt. The gum resins of the genus *Ferula* have been used in folklore medicine for treatment of various diseases.[1] Thus, *Ferula communis* L., its subspecies and varieties have been used as agents against hysteria and to treat dysentery,[2] *Ferula jaeschkeana* vatke has been applied to wounds and bruises,[3] and *Ferula tingitana* L. has proved to be a good source of ammoniac, an oleo-gum resin used in medicine.[4] The widespread sesquiterpene compounds in this genus are characteristic daucanes, humulanes, himachalanes, germacranes, eudesmanes, and guainanes.[5] Chemically, the resin of the species is characterized by the presence of sesquiterpenes,[5–8] sesquiterpene coumarines,[7–9] and monoterpenes.[9–12] Investigation of the CH_2Cl_2:MeOH (1:1) extract of the leaves of *F. sinaica* led to the isolation of lancerodiol–*p*–hydroxybenzoate **1**. Herein, we describe the relative stereochemistry and the molecular structure of **1** by X–ray diffraction.

MATERIALS AND METHODS

General



1

Figure 1: Symmetry transformations used to generate equivalent atoms

Compound **1** [Figure 1], with a molecular formula $C_{22}H_{28}O_5$, was isolated from CH_2Cl_2:MeOH (1:1) extract of the leaves of *F. sinaica* and was recrystallized from $CDCl_3$. A colorless needle was mounted on glass fiber at room temperature. Preliminary examination and data collection were performed on Siemens P4 (oriented graphite monochromator; Mo–Kα radiation) at 293 K. Cell parameters were calculated from the least–squares fitting for 25 high angle reflections (2θ > 15). Omega scans for several intense reflections indicated acceptable crystal quality. Crystallographic data for the structural analysis [Figure 2] have been deposited with the Cambridge Crystallographic data center (CCDC) and allocated the deposition number CCDC 207262. These data can be obtained free of charge through the website www.ccdc.Cam.ac.uk/cants/retrieving html/or from the CCDC, 12 union Road, Cambridge CB2 1 EZ, UK; fax: +44–1223–336033; email: deposit@ccdc.cam.ac.uk.

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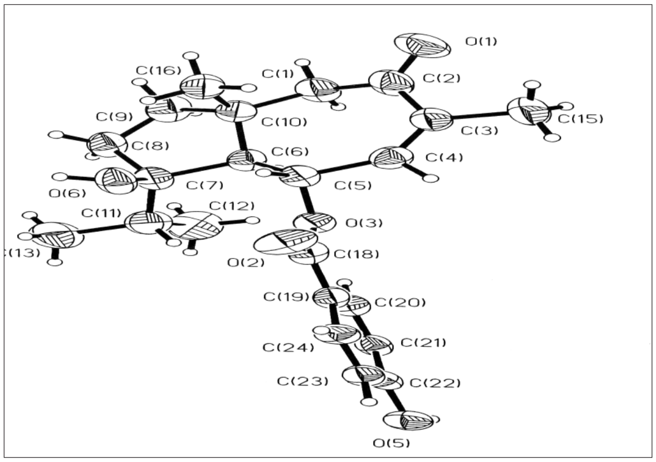

Figure 2 : X-ray structure of compound **1**

Table 1: Crystal data and structure refinement for lancerodiol *p*–hydroxybenzoate

Empirical formula	$C_{22}H_{28}O_5$
Color/shape	Colorless/plate
Formula weight	372.44
Space group	$P2_12_12_1$
Temperature (K)	293(3)
Cell constants (Å)[a]	*a* = 8.179(2), *b* = 14.615(3), *c* = 17.408(3)
Formula units/unit cell	4
Absorption coefficient	0.083/mm
Diffractometer	Siemens P4/adaptive omega
Structure solution	SHELXS[6]
Refinement method	Full–matrix least–squares on F^2
Weights	$\sigma^2(F_o^2) + (0.1184P)^2 + 2.3288P$ where $P = (F_o^2 + 2F_c^2)/3$
Goodness–of–fitb on F2	1.068
R indices [$I \geq 2\sigma(I)$]	$R(F)^b = 0.0725$
R indices (all data)	$R(F)^b = 0.0968$
Flack parameter[c]	0(4)
Largest diff. peak and hole	0.458 and 0.204 e.Å^3
Crystal size (mm)	0.4 × 0.4 × 0.1
Scan width	Ka separation
Standard reflections	2,0,0;0,4,0;0,0,2
Decay of standards	<1%
Reflections measured	2193
2θ range	$4° \leq 2\theta \leq 50°$
Range h,k,l	+9, +17, +20
Reflections unique[b]	2102
Cell volume	2080.9 (8)
Dcal g/CM^3	1.189
Λ	0.71073 Å
Structure refinement[d]	SHELXL–93[7]
F(000)	800
wR(F^2)[b]	0.1934
wR(F^2)[b]	0.2349
Extinction coefficient[e]	0.012(4)

[a] Least–squares refinements of $(\sin\vartheta/\lambda)^2$ for 50 reflections with $2\vartheta > 15°$, [b] $R(F) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$:$wR(F^2) = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$. Goodness-of-fit $[S(F^2)] = [\Sigma w(F_o^2 - F_c^2)^2/(No_{data} - No_{parameters})]^{1/2}$, [c] Flac, H.D. Acta Cryst. 1983, A39, 876, [d] Neutral scattering factors and anomalous dispersion correction taken from international tables for crystallography volume C, [e] Larson, A.C. Acta Cryst. 1976, 23, 664.; Zachariasen, W.H. Acta Cryst. 1963, 1139, [f] Lorentz and polarization correction applied. No absorption correction

Table 2: Functional atomic coordination and equivalent isotropic displacement parameters (Å × 10^3)

	x	*y*	*z*	*U* (eq)
O(1)	−4652(9)	−8788(4)	−8678(3)	86(2)
O(2)	−2070(6)	−4532(3)	−9412(3)	60(1)
O(3)	−802(5)	−5574(3)	−8679(2)	39(1)
O(5)	5376(6)	−3438(3)	−9809(3)	50(1)
O(6)	−3553(6)	−4823(3)	−7495(3)	54(1)
C(1)	−3414(11)	−7935(4)	−7700(4)	56(1)
C(2)	−3726(11)	−8161(4)	−8527(4)	60(2)
C(3)	−2944(9)	−7658(4)	−9159(4)	49(2)
C(4)	−2389(8)	−6796(4)	−9138(3)	46(2)
C(5)	−2346(8)	−6057(4)	−8541(3)	42(1)
C(6)	−2357(8)	−6303(4)	−7698(3)	42(1)
C(7)	−2459(9)	−5466(4)	−7142(3)	47(2)
C(8)	−3230(10)	−5873(4)	−6411(3)	52(2)
C(9)	−3614(11)	−6875(5)	−6579(4)	59(2)
C(10)	−3735(8)	−6944(4)	−7459(4)	44(2)
C(11)	−816(10)	−4962(5)	−6986(4)	62(2)
C(12)	553(11)	−5575(7)	−6751(5)	86(3)
C(13)	−1058(13)	−4190(6)	−6395(5)	85(3)
C(15)	−2850(13)	−8179(6)	−9911(4)	78(3)
C(16)	−5442(9)	−6659(5)	−7725(4)	58(2)
C(18)	−803(9)	−4832(4)	−9134(3)	42(2)
C(19)	813(8)	−4459(4)	−9262(3)	38(1)
C(20)	2186(8)	−4805(4)	−8902(3)	41(1)
C(21)	3716(8)	−4472(4)	−9067(3)	41(1)
C(22)	3901(8)	−3789(4)	−9613(3)	38(1)
C(23)	2539(8)	−3421(4)	−9955(3)	42(1)
C(24)	1021(8)	−3745(4)	−9787(3)	43(1)

U (eq) is defined as one–third of the trace of the orthogonalized *U*ij tensor

Plant material

F. sinaica was collected in 2005 from El-Minia, Egypt. A voucher specimen of the collection was identified by Prof. Mohamed Jaber and was deposited at the Department of Botany, Aswan–Faculty of Science, Egypt.

Extraction and isolation

Air-dried and powdered leaves (200 g) of *F. sinaica* were extracted with CH_2Cl_2: MeOH (1:1) at room temperature for 24 h. The extract was concentrated *in vacuo* to give a residue (15 g) that was chromatographed by using flash column chromatography on a silica gel eluted with *n*–hexane–CH_2Cl_2 step–gradient up to CH_2Cl_2 and CH_2Cl_2–MeOH up to 15% MeOH (2 l each of the solvent mixture). The *n*–hexane–CH_2Cl_2 fraction (1:3) was carefully chromatographed on a Sephadex LH–20 column eluted with *n*–hexane–CH_2Cl_2–MeOH (7:4:0.25) with increasing polarity to give compound **1** (21 mg).

RESULTS AND DISCUSSION

Colorless needle crystals suitable for X–ray diffraction were grown by slow evaporation of $CDCl_3$ solution. The crystal data [Tables 1-3] for lancerodiol–*p*–hydroxybenzoate were as follows: orthorhombic, space group $P2_12_12_1$ with a = 8.179 (2) Å, b = 14.165 (3) Å, c = 17.408 (3) Å, V = 2080.9 (8) Å, Z = 4. The structure refined to $R(F) = 0.0\,725$ [$I > 2\sigma(I)$] and $wR(F^2) = 0.1934$ [$I > 2\sigma(I)$] for 2102 observed reflections with Mo–Kα radiation (λ = 0.71073 Å). The scanning speed was varied according to the intensity, from a minimum of 1 to a maximum of 11/min.

Table 3: Bond lengths (Å) and angles (°) of compound 1

O(1)–C(2)	1.2219	O(3)–C(5)–C(6)	106.25
O(2)–C(18)	1.2258	C(4)–C(5)–C(6)	120.15
O(3)–C(18)	1.3436	C(5)–C(6)–C(10)	114.65
O(3)–C(5)	1.4667	C(5)–C(6)–C(7)	114.65
O(5)–C(22)	1.3547	C(10)–C(6)–C(7)	105.85
O(6)–C(7)	1.4358	O(6)–C(7)–C(8)	110.56
C(1)–C(2)	1.49910	O(6)–C(7)–C(11)	107.65
C(1)–C(10)	1.5329	C(8)–C(7)–C(11)	113.05
C(2)–C(3)	1.47010	O(8)–C(7)–C(6)	106.45
C(3)–C(4)	1.3409	C(8)–C(7)–C(6)	103.45
C(3)–C(15)	1.5179	C(11)–C(7)–C(6)	115.76
C(4)–C(5)	1.4998	C(9)–C(8)–C(7)	107.35
C(5)–C(6)	1.5118	C(8)–C(9)–C(10)	105.55
C(6)–C(10)	1.5249	C(6)–C(10)–C(16)	115.25
C(6)–C(7)	1.5628	C(6)–C(10)–C(1)	112.35
C(7)–C(8)	1.5409	C(16)–C(10)–C(1)	109.36
C(7)–C(11)	1.55710	C(6)–C(10)–C(9)	100.75
C(8)–C(9)	1.52510	C(16)–C(10)–C(9)	110.06
C(9)–C(10)	1.5389	C(1)–C(10)–C(9)	108.95
C(10)–C(16)	1.52910	C(12)–C(11)–C(13)	110.77
C(11)–C(12)	1.49112	C(12)–C(11)–C(7)	114.36
C(11)–C(13)	1.53910	C(13)–C(11)–C(7)	110.76
C(18)–C(19)	1.4469	O(2)–C(18)–O(3)	121.56
C(19)–C(20)	1.3828	O(2)–C(18)–O(19)	125.25
C(19)–C(24)	1.3978	O(3)–C(18)–C(19)	113.25
C(20)–C(21)	1.3749	C(20)–C(19)–C(24)	118.16
C(21)–C(22)	1.3868	C(20)–C(19)–C(18)	122.35
C(22)–C(23)	1.3739	C(24)–C(19)–C(18)	119.96
C(23)–C(24)	1.3619	C(21)–C(20)–C(19)	121.05
C(18)–O(3)–C(5)	119.05	C(20)–C(21)–C(22)	119.96
C(2)–C(1)–C(10)	116.36	O(5)–C(22)–C(23)	117.75
O(1)–C(2)–C(3)	118.37	O(5)–C(22)–C(21)	122.85
O(1)–C(2)–C(1)	119.47	C(23)–C(22)–C(21)	119.46
C(3)–C(2)–C(1)	122.36	C(24)–C(23)–C(22)	120.75
C(4)–C(3)–C(2)	126.76	C(23)–C(24)–C(19)	120.86
C(4)–C(3)–C(15)	118.66		
O(1)–C(2)–C(1)	119.47		
C(3)–C(2)–C(1)	122.36		
C(4)–C(3)–C(2)	126.76		
C(4)–C(3)–C(15)	118.66		
C(2)–C(3)–C(15)	114.76		
C(3)–C(4)–C(5)	134.86		
O(3)–C(5)–C(4)	104.75		

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