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Structure and absolute configuration of a visamminol derivative using IR and vibrational circular dichroism

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ABSTRACT

The aerial parts of *Arracacia tolucensis* (Kunth) Hemsl. (Apiaceae) provided the new visamminol derivative (*S*)-(+)-4′-*O*-angeloylvisamminol (**1**), along with the known angular pyranocoumarin **2**. Analysis of HMBC NMR correlations did not allow distinction of the linear dihydrofurochromone **1** from pyranochromone **5**. The structure and *S* absolute configuration of (+)-**1** was therefore established by comparison of the IR and vibrational circular dichroism spectra of the natural product with the DFT B3LYP/DGDZVP calculated spectra for (*S*)-**1** and (*S*)-**5**. Structural verification followed by single crystal X-ray diffraction of (+)-**1** and chemical correlation.

1. Introduction

The genus *Arracacia* (Apiaceae) contains around 50 species (Pimenov and Leonov, 1993) from which only three have been the subject of chemical and biological studies (Calderón and Ríos, 1975; Delgado and Garduño, 1987; Figueroa et al., 2007). The fruits and aerial parts of *Arracacia tolucensis* (Kunth) Hemsl. are used in the northeastern state of Tamaulipas, Mexico, as carminative, digestive stimulant agent, and to treat diabetes. The crude plant extract has shown no toxic or mutagenic effect in mice (Déciga-Campos et al., 2007), and from an antimicrobacterial guided fractionation seven simple coumarins and four furocoumarins were isolated (Figueroa et al., 2007).

We herein describe the structure and absolute configuration assignment, using IR and vibrational circular dichroism, of the dihydrofurochromone **1** from the EtOAc extracts of the aerial parts of *A. tolucensis* (Kunth) Hemsl. (*S*)-(+)-4′-*O*-angeloylvisamminol (**1**) belongs to the rare group of dihydrofurochromones bearing a hydroxy group at C-5.

2. Results and discussion

(*S*)-(+)-4′-*O*-Angeloylvisamminol (**1**) was obtained as colorless very small crystals, m.p. 134–135 °C from the aerial parts of *A. tolucensis*. The $C_{20}H_{22}O_6$ molecular composition of **1** was determined by HR-EIMS (*m/z* 358.1414, calc 358.1416). The ^{1}H NMR spectrum exhibited the typical signals of an angeloyl group at δ 5.97 (qq, J = 7.3, 1.5 Hz, H-3″), 1.90 (dq, J = 7.3, 1.5 Hz, Me-4″) and 1.71 (quint, J = 1.5 Hz, Me-5″). It also showed a hydrogen-bonded hydroxy group singlet at δ 12.90, that in the HMBC experiment showed correlations with the carbon atoms at δ 156.6, 108.4, and 105.4. In addition there is a vinyl proton signal at δ 6.03 (q, J = 0.7 Hz, H-3) coupled to a methyl group at δ 2.34 (d, J = 0.7 Hz, Me-9). Furthermore, an aromatic proton at δ 6.30 (s, H-8), is showing HMBC correlations with two aromatic sp^2 carbon atoms (δ 166.1 and 158.4) bearing an oxygen atom, and with a carbon atom (δ 108.6) bearing a methylene group. In turn, this methylene group, as part of an ABX system (δ 5.08, dd, J = 9.6, 7.3 Hz, H-2′; 3.22, dd, J = 15.8, 9.6 Hz, H-3′a; and 3.16, dd, J = 15.8, 7.3 Hz, H-3′b), presented long-range correlations with the carbon atom bearing the hydroxy group (δ 156.6) and the sp^3 carbon atom bearing an oxygen atom (δ 89.6). Two methyl singlets at δ 1.62 and 1.60 (Me-5′ and Me-6′) complete the ^{1}H NMR spectrum. The combined NMR data suggest either structure **1** or **5**.

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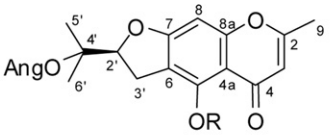
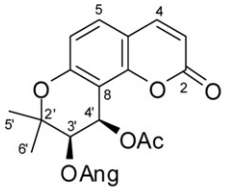
Since vibrational circular dichroism (VCD) has been used to determine the absolute configuration (AC) of chiral natural products (Nafie, 2008; He et al., 2011; Polavarapu, 2012) and its use along with IR analysis to differentiate structural isomers is limited to two cases (Stephens et al., 2005; Min et al., 2007) a VCD study using density functional theory (DFT) at the B3LYP/DGDZVP level of theory was undertaken for (*S*)-**1** and (*S*)-**5**. After geometric optimization of (*S*)-**1**, nine conformers in a 2.03 kcal/mol window accounting for 98.7% of the total conformational population were found, and used to calculate the thermochemical parameters (Table S1), IR and VCD frequencies. The most stable conformer is shown in Fig. 1. The nine conformers were used to generate the final IR (top trace, Fig. 2) and VCD (top trace, Fig. 3) curves obtained according to their Boltzmann population. A similar protocol was followed for (*S*)-**5**. After optimization only two conformers in an 1.80 kcal/mol energy window (Table S1) were found, the third conformer is 5.7 kcal mol^{-1} less stable and its contribution to the conformational population is meaningless. The most stable conformer is shown in Fig. 1. The final weighted IR and VCD curves for (*S*)-**1** and (*S*)-**5** are shown in Figs. 2 and 3, respectively. Comparison of experimental and calculated IR and VCD spectra for (*S*)-(**1**) and (*S*)-(**5**) reveals the structure and AC of the natural product is (*S*)-**1**.

After many attempts to obtain independent confirmation for the (*S*)-**1** structure, we were fortunate enough to grow a little prism suitable for single crystal X-ray diffraction. Fig. 4 shows the molecular perspective, from which a *syn* periplanar orientation between the carbonyl group and the Me-4″ group of the angeloyl moiety was observed, in agreement to the most stable calculated conformation.

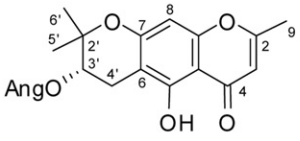
We could further confirm the (*S*)-**1** structure by chemical correlation with (+)-4′-*O*-angeloyl-5-*O*-methylvisamminol (**3**) by



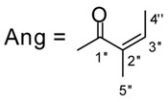
	R
1	H
3	Me
4	Ac

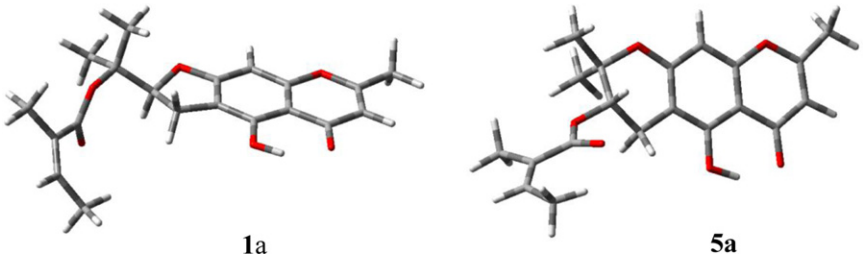


2



5





1a **5a**

Fig. 1. DFT B3LYP/DGDZVP calculated most stable conformer of (*S*)-**1** and (*S*)-**5**.

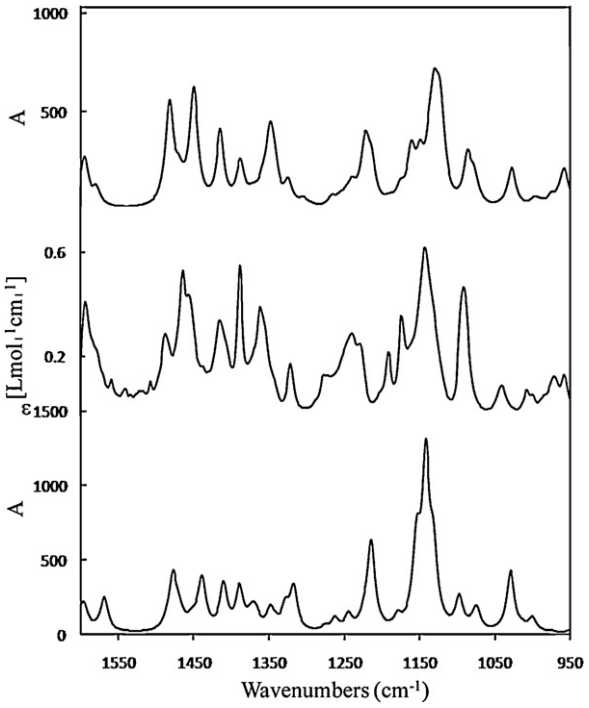


Fig. 2. Comparison of the experimental IR spectrum (center) of dihydrofurochromone (*S*)-**1** and the calculated IR spectra for (*S*)-**1** (top) and pyranochromone (*S*)-**5** (bottom).

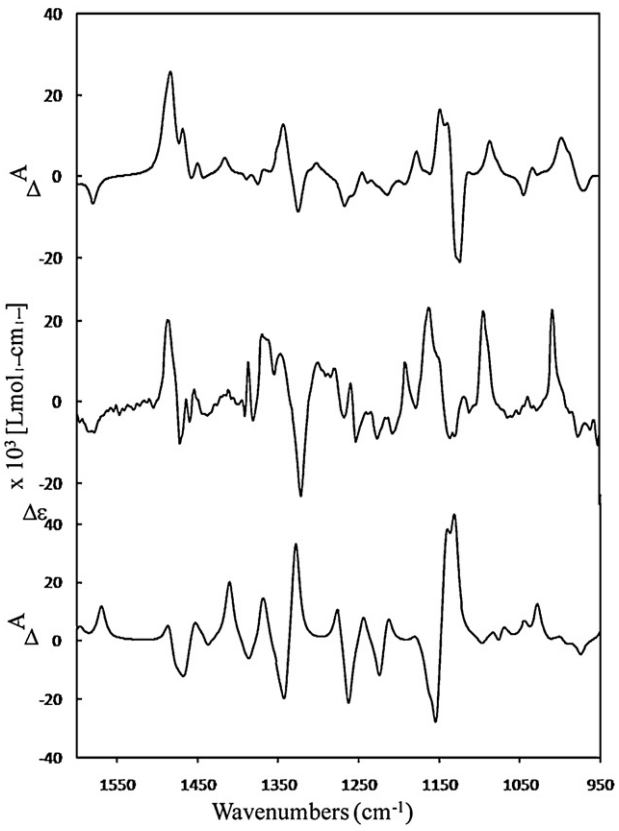


Fig. 3. Comparison of the experimental VCD spectrum (center) of dihydrofurochromone (*S*)-**1** and the calculated VCD spectra for (*S*)-**1** (top) and pyranochromone (*S*)-**5** (bottom).

treatment of **1** with dimethyl sulfate in acetone. ^{1}H and ^{13}C NMR data of **3** obtained in this work were identical to those described (Torres-Valencia et al., 2008), while the $[\alpha]_D$ +75 value was higher than the reported value of +59.

The *O*-acetyl derivative **4** was generated by treatment of a solution of **1** with pyridine and acetic anhydride. The ^{1}H NMR spectrum showed no hydrogen-bonded hydroxy proton, and the signal of the acetyl methyl group was observed at δ 2.43 as a singlet. ^{1}H and ^{13}C NMR data are shown in Table 1.

The second natural product isolated from the EtOAc extract was identified as (3′*R*, 4′*R*)-(−)-4′-*O*-acetyl-3′-*O*-angeloylkhellactone (**2**) by comparison of its NMR data with those described (Okuyama and Shibata, 1981; Bellino et al., 1986). The AC was assigned by comparison of the specific rotation ($[\alpha]_D$ −41.2, EtOH) with that described for the (3′*S*, 4′*S*) enantiomer of +48.2 (MeOH) (Lou et al., 2004).

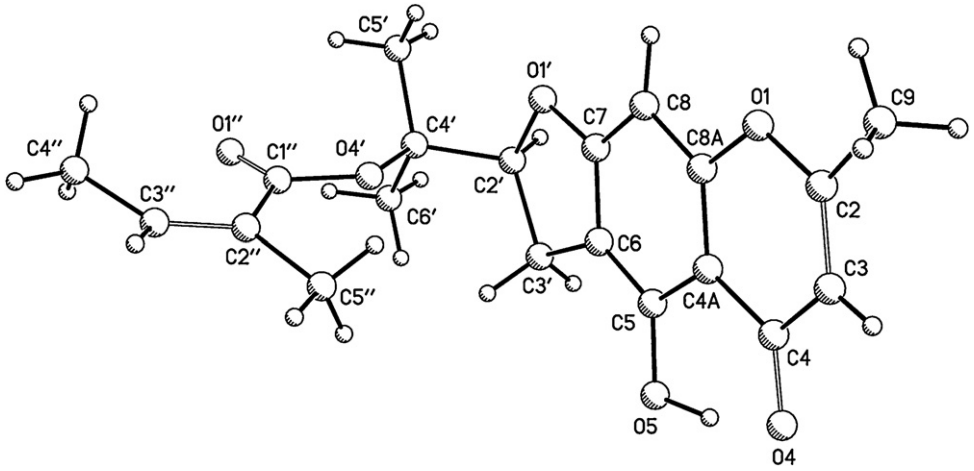


Fig. 4. Perspective view of the X-ray crystal structure of **1**.

Table 1
NMR data of **1** and **4**.[a]

Position	1			4		
	δ_C	δ_H (*J* Hz)	HMBC	δ_C	δ_H (*J* Hz)	HMBC
2	166.5			164.3		
3	108.4	6.03 q (0.7)	2, 4a	111.1	5.96 q (0.7)	2, 4a
4	182.6			176.9		
4a	105.4			110.8		
5	156.6			145.3		
6	108.6			118.7		
7	166.1			164.2		
8	88.6	6.30 s	4a, 6, 7, 8a	95.5	6.65 s	4a, 6, 7, 8a
8a	158.4			159.2		
9	20.4	2.34 d (0.7)	2, 3			
2'	89.6	5.08 dd (9.6, 7.3)	6′	89.7	5.06 dd (9.4, 7.4)	
3'	26.8	3.22 dd (15.8, 9.6)	5, 6, 7, 2′, 4′	27.3	3.22 dd (16.3, 9.4)	5, 6, 7, 2′
		3.16 dd (15.8, 7.3)	5, 6, 7, 2′, 4′		3.17 dd (16.3, 7.4)	5, 6, 7, 2′
4'	82.1			81.7		
5'	22.2	1.62 s	2′, 3′, 6′	21.5	1.61 s	2′, 4′, 6′
6'	21.3	1.60 s	2′, 3′, 5′	22.1	1.60 s	2′, 4′,5′
5OH		12.90	3, 4a, 5		-	

1: OAng; ^{1}H NMR, δ 5.97 qq(7.3, 1.5, H-2″), 1.90 dq(7.3, 1.5, Me-4″), 1.71 quint(1.5, Me-5″); ^{13}C NMR, δ 167.1(C1″), 137.5 (C3″), 128.8 (C2″), 20.5 (C5″), 15.6 (C4″). **4**: OAng, ^{1}H NMR, δ 5.98 qq(7.3, 1.5, H-2″), 1.89 dq(7.3, 1.5, Me-4″), 1.68 quint(1.5, Me-5″); ^{13}C NMR, δ 167.0(C1″), 137.9 (C3″), 128.6 (C2″), 20.6 (C4″), 15.6 (C5″). **4**: Ac; ^{1}H NMR, δ 2.43 (Me-2‴); ^{13}C NMR, δ 169.0 (C1‴), 21.1 (C2‴).
[a] ^{1}H at 500 MHz, and ^{13}C at 125 MHz, in $CDCl_3$ using TMS as the internal standard.

3. Concluding remarks

The structure and *S* absolute configuration of (+)-**1** were assigned by comparison of the experimental IR and VCD spectra with DFT B3LYP/DGDZVP calculated spectra for (*S*)-**1** and (*S*)-**5**, confirming the capability of the IR and VCD combination for the simultaneous determination of the structure and absolute configuration of a new natural product. Confirming evidence was obtained from X-ray analysis of **1** and chemical correlation.

4. Experimental

4.1. General procedures

Melting points were determined on an electrothermal capillary melting point apparatus and are uncorrected. Optical rotations were determined in $CHCl_3$ using a Perkin Elmer 341 polarimeter. IR spectra were measured in $CHCl_3$ on a Perkin Elmer 2000 FT-IR spectrophotometer. ^{1}H, ^{13}C, and 2D NMR spectra were recorded in $CDCl_3$ solutions on a Varian System 500 (125 MHz for ^{13}C) spectrometer at 298 K. High resolution mass spectra were measured in the electron impact mode (70 eV) on a Jeol GCmateII spectrometer. Column chromatography was carried out on Merck Silica gel (100–200 mesh ASTM). VCD measurements were achieved on a dual PEM BioTools Chiral*IR* FT-VCD spectrophotometer operated at a resolution of 4 cm^{-1}.

4.2. Plant material

Aerial parts of *A. tolucensis* (Kunth) Hemsl. were collected from Alta Cima, Tamaulipas, México, during September 2009. A voucher specimen (No. 1769) is deposited at Herbarium of Facultad de Estudios Superiores Iztacala-UNAM.

4.3. Extraction and isolation

Air-dried powdered aerial parts of *A. tolucensis* (200 g) were extracted at room temperature with 3 L EtOAc for five days (×3). After solvent evaporation, the crude extract was dissolved in acetone, kept for 12 h at 4 °C, and filtered to remove fatty materials. The filtrate was evaporated under vacuum to afford 7.2 g (3.6%) of dark viscous oil, which was chromatographed over silica gel (200 g) using hexanes–EtOAc (up to 100% EtOAc) as eluents. After TLC evaluation, seven main fractions A–G were obtained. ^{1}H NMR analysis of fractions A–C showed the presence of fatty materials. Fraction D (276 mg) gave a solid which was recrystallized from EtOAc–hexanes to give 45 mg of **1** as a white powder. The mother liquor of **1** was purified by silica gel column chromatography employing hexanes and mixtures of hexanes–EtOAc (9:1–7:3) to afford white solids which after recrystallization from EtOAc–hexanes gave additional 155 mg of **1**. Fraction E (960 mg) was repeatedly subjected to CC using hexanes–EtOAc (9:1–7:3) as eluents to give **2** (656 mg) as a white solid. NMR data of **2** were identical to those described by Okuyama and Shibata (1981), and Bellino et al. (1986) for isopteryxin.

4.4. (*S*)-(+)-4′-*O*-Angeloylvisamminol (**1**)

White prisms, m.p. 134–135 °C; $[\alpha]_{589}^{20}$ + 78.0, $[\alpha]_{578}^{20}$ + 81.8, $[\alpha]_{546}^{20}$ + 94.5, $[\alpha]_{436}^{20}$ + 176.6, (*c* 0.98, $CHCl_3$). UV (EtOH) λ_{max} (log ε): 214 (4.70), 230 (4.49), 250 (4.33), 256 (4.23), 296 (4.10); IR ($CHCl_3$) ν_{max}: 3644, 1709, 1668, and 1634 cm^{-1}. For ^{1}H and ^{13}C NMR data see Table 1. EIMS *m/z* 358 [M]$^+$, 305 (22), 259 (16), 258 (26), 243 (100), 232 (57), 217 (24), 91 (11); HR-EIMS *m/z* 358.1414 (calcd for $C_{20}H_{22}O_6$ 358.1416).

4.5. (3′R, 4′R)-(−)-4′-O-*acetyl*-3′-O-*angeloylkhellactone* (**2**)

White solid, m.p. 132–133 °C (Lou et al., 2004; 136–137 °C); $[\alpha]_{589}^{22}$ − 41.2, (*c* 1.6, EtOH), $[\alpha]_{589}^{22}$ − 29.7, (*c* 1.6, MeOH), $[\alpha]_{589}^{22}$ − 47.9, (*c* 1.1, $CHCl_3$) [Lou et al., 2004; +48.2 (MeOH) for the (3′*S*, 4′*S*) enantiomer].

4.6. (*S*)-(+)-4′-*O*-Angeloyl-5-*O*-methylvisamminol (**3**)

To a solution of **1** (20 mg) in acetone (2 mL) was added anh. K_2CO_3 (15 mg), and Me_2SO_4 (0.1 mL). The reaction mixture was stirred under reflux for 3 h. The acetone was evaporated and the residue was extracted with EtOAc. The organic layer was washed with aq. NaOH and water, dried over anh. Na_2SO_4, filtered, and the solvent evaporated under vacuum. The residue was chromatographed over silica gel to yield **3** (14.3 mg, 65%) as colorless oil. $[\alpha]_D$ +74.9 (c 0.67, $CHCl_3$). ^{1}H and ^{13}C NMR data were identical to those described (Torres-Valencia et al., 2008).

4.7. (S)-(+)-5-O-Acetyl-4′-O-angeloylvisamminol (**4**)

A solution of **1** (105 mg) in pyridine (3.0 mL) was treated with Ac_2O (3.0 mL) at room temperature overnight, poured over ice-H_2O, and extracted with EtOAc. The organic layer was washed with 10% HCl, H_2O, aqueous $NaHCO_3$, and H_2O, dried over anh. Na_2SO_4, filtered, and evaporated under vacuum. The residue was subjected to column chromatography using hexanes–EtOAc (9:1–3:2) mixtures as eluent. Fractions eluted with hexanes–EtOAc (4:1), yielded (*S*)-(+)-5-*O*-acetyl-4′-*O*-angeloylvisamminol (18.5 mg) as a colorless oil; $[\alpha]_{589}^{20} + 77.6$, (*c* 0.8, $CHCl_3$); UV (EtOH) λ_{max} (log ε): 217 (4.49), 240 (4.30), 250 (4.24), 283 (4.10), 295 (4.07), 304 (4.05); IR ($CHCl_3$) ν_{max}: 1775, 1715, 1652, and 1623 cm^{-1}; EIMS $[M]^+$ 400 (12), 358 (20), 258 (85), 243 (100), 217 (60), 83 (35); EIHRMS *m/z*: 400.1519 (calc for $C_{22}H_{24}O_7$ 400.1522). For ^1H and ^{13}C NMR data see Table 1.

4.8. VCD measurement

A sample of 7.7 mg of **1** was dissolved in 150 μL of 100% $CDCl_3$ and placed in a BaF_2 cell with a pathlength of 100 μm. Seven data blocks, 1 h each, were added and the baseline was provided by subtracting the spectrum of the solvent acquired under the same conditions.

4.9. DFT calculations

Geometry optimization for (*S*)-**1** and (*S*)-**5** models was carried out using Monte Carlo searches and the MMFF94 molecular mechanic force field as implemented in the Spartan '08 program (Wave-Function, Irvine, CA, USA). Considering an initial energy cutoff of 10 kcal/mol above the global minimum value, 17 and six structures for **1** and **5**, respectively, were found. All obtained structures were subject to single point calculations using DFT and the B3LYP functional and 6-31G(d) basis set, followed by geometric optimization at the B3LYP/DGDZVP level of theory using the Gaussian '03 software (Gaussian, Inc. Wallingford, CT, USA). IR and VCD frequencies were calculated at the same level of theory. Computed IR and VCD spectra were generated by weighting the individual IR and VCD spectra according to a Boltzmann distribution using free energies derived from the energy minimization calculations. The frequencies were scaled using an anharmonicity factor of 0.97 for the B3LYP data, and the bandshapes were calculated with Lorentzian functions and a bandwidth of 6 cm^{-1}.

4.10. Single-crystal X-ray analysis of **1**

A crystal measuring 0.38 × 0.28 × 0.12 mm was mounted on an Enraf-Nonius CAD4 diffractometer equipped with Cu *K*α radiation (λ = 1.54184 Å) and data were acquired at 293(2) K in the ω-2θ scan mode. Unit cell refinements using 25 machine centered reflections were obtained using the CAD4 Express V2.0 software. The crystal was monoclinic, space group $P2_1$, with cell dimensions a = 12.820(3) Å, b = 5.687(1) Å, c = 13.710(3) Å, β = 117.63(3)°, V = 885.5(3) $Å^3$, ρ_{calcd} = 1.34 g/cm^3 for Z = 2, $C_{20}H_{22}O_6$, MW = 358.38, and F(000) 380e. A total of 1562 reflections were collected within the θ range 3.64–59.94° for $-14 \le h \le 12$, $0 \le k \le 6$, $0 \le l \le 15$ over a period of 19 h. The data were corrected for background, Lorentz polarization, and absorption (μ = 0.821 mm^{-1}), while crystal decay was negligible. The structure was solved by direct methods using the SIR2004 program. For the structural refinement, the non-hydrogen atoms were treated anisotropically, and the hydrogen atoms were refined isotropically. The unique reflections were 1441, the observed reflections were 1410, and final discrepancy indices, refining 256 parameters, were R_F = 3.9% and R_w = 11.2%. The final difference Fourier map was essentially featureless, the highest residual peak having a density of 0.230 e/A^3. Crystallographic data are deposited with the Cambridge Crystallographic Data Centre. The CCDC deposition number is 898416. Free copies of the data can be obtained via http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK; Fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk).

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.phytol.2012.09.006.

References

Bellino, A., Venturella, P., Marino, M.L., Servettaz, O., Venturella, G., 1986. Coumarins from *Sesseli bocconi*. Phytochemistry 25, 1195–1199.
Calderón, J., Ríos, T., 1975. Isolation and identification of some constituents of *Arracacia vaginata*. Lloydia 38, 174–175.
Déciga-Campos, M., Rivero-Cruz, I., Arriaga-Alba, M., Castañeda-Corral, G., Ángeles-López, G.E., Navarrete, A., Mata, R., 2007. Acute toxicity and mutagenic activity of Mexican plants used in traditional medicine. J. Ethnopharmacol. 110, 334–342.
Delgado, G., Garduño, J., 1987. Pyranocoumarins from *Arracacia nelsonii*. Phytochemistry 26, 1139–1141.
Figueroa, M., Rivero-Cruz, I., Rivero-Cruz, B., Bye, R., Navarrete, A., Mata, R., 2007. Constituents, biological activities and quality control parameters of the crude extract and essential oil from *Arracacia tolucensis* var. *multifida*. J. Ethnopharm. 113, 125–131.
He, Y., Wang, B., Dukor, R.K., Nafie, L.A., 2011. Determination of absolute configuration of chiral molecules using vibrational optical activity: a review. Appl. Spect. 65, 699–723.
Lou, H.-X., Sun, L.-R., Yu, W.-T., Fan, P.-H., Cui, L., Gao, Y.-H., Ma, B., Ren, D.-M., Ji, M., 2004. Absolute configuration determination of angular dihydrocoumarins from *Peucedanum praeruptorum*. J. Asian Nat. Prod. Res. 6, 177–184.
Min, H.M., Aye, M., Taniguchi, T., Miura, N., Monde, K., Ohzawa, K., Nikai, T., Niwa, M., Takaya, Y., 2007. A structure and an absolute configuration of (+)-alternamin, a new coumarin from *Murraya alternans* having antidote activity against snake venom. Tetrahedron Lett. 48, 6155–6158.
Nafie, L.A., 2008. Vibrational circular dichroism: a new tool for the solution-state determination of the structure and absolute configuration of chiral natural product molecules. Nat. Prod. Comm. 3, 451–466.
Okuyama, T., Shibata, S., 1981. Studies on coumarins of a Chinese drug "Qian-Hu". Planta Med. 42, 89–96.
Pimenov, M.G., Leonov, M.V., 1993. The Genera of the Umbelliferae: A Nomenclator. Royal Botanic Gardens, Kew, UK.
Polavarapu, P.L., 2012. Determination of the structures of chiral natural products using vibrational circular dichroism. In: Berova, N., Polavarapu, P.L., Nakanishi, K., Woody, R.W. (Eds.), Comprehensive Chiroptical Spectroscopy. Stereochemical Analysis of Synthetic Compounds, Natural Products, and Biomolecules, vol. 2, Wiley, New York, pp. 387–420 (chapter 11).
Stephens, P.J., McCann, D.M., Devlin, F.J., Flood, T.C., Butkus, E., Stončius, S., Cheeseman, J.R., 2005. Determination of molecular structure using vibrational circular dichroism spectroscopy: the keto-lactone product of Baeyer–Villiger oxidation of (+)-(1*R*,5*S*)-bicyclo[3.3.1]nonane-2,7-dione. J. Org. Chem. 70, 3903–3913.
Torres-Valencia, J.M., Chávez-Ríos, O.E., Cerda-García-Rojas, C.M., Burgueño-Tapia, E., Joseph-Nathan, P., 2008. Dihydrofurochromones from *Prionosciadium thapsoides*. J. Nat. Prod. 71, 1956–1960.