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The absolute configuration of angular 3′-acyloxypyranocoumarins by vibrational circular dichroism exciton chirality

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ABSTRACT

A complex mixture of lomatin C-3′ esters and (−)-*O*-angeloyllomatin **1** was isolated from the seeds of *Prionosciadium thapsoides*. Since a literature search revealed that some lomatin C-3′ monoesters have positive specific rotations, while others had negative values, the absolute configuration of all of the molecules was determined to be (*R*) by exciton chirality in the infrared region, and by chemical correlation. A single crystal X-ray study of acetyllomatin **3**, using the Flack and Hooft parameters, independently confirmed this absolute configuration.

1. Introduction

Since the very early isolation of coumarin from Nature in 1820,[1] hundreds of coumarin derivatives with a huge variety of substituents have been described,[2] from which pyranocoumarins constitute an important group.

Prionosciadium is a genus of herbaceous plants belonging to the Apiaceae family. It comprises thirty two species from which only twelve appear in the Missouri Botanical Garden plant list.[3] From this genus, angular-type pyranocoumarins such as lomatin **2** and chromones have typically been isolated.[4] Some lomatin esters have been evaluated as coronary vasodilatory and spasmolytic agents,[5] against lymphocyte H9 cells infected with HIV,[6] as phytotoxic compounds,[4b] and more recently against a specific antigen secreted by prostate cancer cells.[7]

(+)-Lomatin **2** was isolated from *Lomatium nuttallii* in 1964,[8e] and its absolute configuration was established by comparison of the specific rotation of (+)-(*R*)-3,5-dinitrobenzoyloxy-5,5-dimethyldihydrofuran-2(3*H*)-one, obtained after esterification of the ozonolysis product of (+)-**2**, with the respective derivative generated by ozonolysis of the angular dihydrofuranocoumarin (+)-(*S*)-8,9-dihydrooroselol **9** of known absolute configuration.[8b] Although the literature shows a wide range of specific rotations for **2**, with values measured in $CHCl_3$ of +7.6,[8d] +13.7,[8c] +14.0,[8a] and even +210;[4b] these specific rotations have been used to assign the absolute configuration of other lomatin ester derivatives such as (+)-(*S*)-*O*-angeloyllomatin **1**,[9] and (+)-(*R*)-*O*-dodecanoyllomatin **8**.[10] Compound **2** is also known as jatamansinol,[8d] and xanthogalol.[8c]

In turn, (+)-*O*-isobutyroyllomatin **4** was isolated as a natural product following a bioassay guided fractionation of the phytotoxic extracts of *Prionosciadium watsoni*,[4b] and its (*R*)-absolute configuration was assigned using Mosher esters. However, an *O*-isobutyroyllomatin sample in our hands, obtained after esterification of (+)-lomatin **2** with *i*-butyroyl chloride showed $[\alpha]_D = -9.1$. In addition, Murray in a classical review about naturally occurring coumarin[2] accounts nine lomatin C-3′ monoesters, from which two showed positive and three showed negative specific rotations when measured in $CHCl_3$. Although the specific rotation of an enantiomerically pure sample is frequently used to identify the absolute configuration of natural products, its dependence on temperature, concentration, solvent used for the measurement, and impurities in the sample has led to a literature with many examples of incorrect values for compounds considered to be enantiomerically pure.[11] Furthermore, the absolute configuration of (−)-(*R*)-4,5-dimethyl-3-hydroxy-2(5*H*)-furanone and (+)-(*R*)-5-ethyl-3-hydroxy-4-methyl-2(5*H*)-furanone was confirmed by VCD emphasizing the risk of assignments based on the comparison of the specific rotation sign of similar structures.[12] Therefore, in a continuation of our studies of natural compound structural analysis,[4a,13] we herein assign the absolute configuration of several

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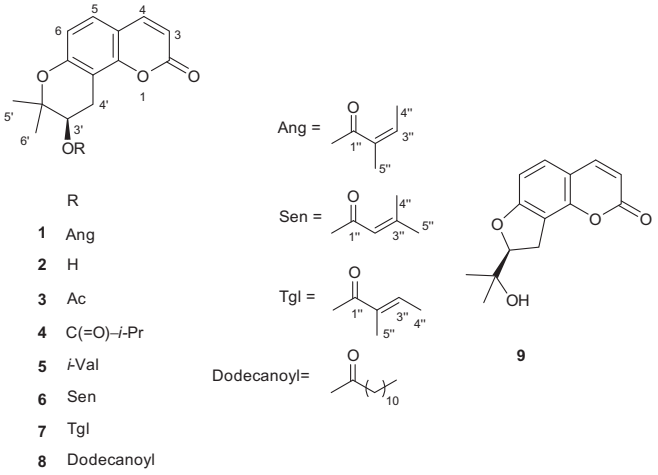
3′-acyloxypyranocoumarins using an independent and reliable methodology.

The method of choice was vibrational circular dichroism exciton chirality (VCDEC)[14] for which it has been shown that the Harada–Nakanishi rule holds. Similar to the well-established electronic circular dichroism chirality methodology,[15] VCDEC is based on the through-space interaction of two or more IR chromophores, which yield a pair of VCD signals with opposite signs around the absorption region of the chromophores. The sign of this split-type VCD signal reflects the absolute configuration of the molecule.[14c] Thus, when the interacting chromophores are counterclockwise oriented, the long-wavelength component of the associated exciton couplet can be expected to exhibit a negative Cotton effect, while when they are clockwise oriented, the long-wavelength Cotton effect is positive.



2. Results and discussion

After column chromatography of the EtOAc extract of the seeds of *Prionosciadium thapsoides*, (−)-*O*-angeloyllomatin **1**[8c,d,16] was isolated along with a complex mixture of lomatin derivatives in which **1** and *O*-isobutyroyllomatin **4** could be identified. Compound **1** showed $[\alpha]_D = -7.6$ and its ^1H and ^{13}C NMR spectra were in agreement with those described for the (*S*)-enantiomer isolated from *Selinum cryptotaenium*,[9] whose specific rotation was $[\alpha]_D = +6.2$.

A portion of the lomatin ester mixture was subjected to alkaline hydrolysis to afford (+)-**2** ($[\alpha]_D = +12.4$), whose ^1H and ^{13}C NMR data were essentially the same as those described.[8d,17] A solution of (+)-**2** was treated at room temperature with acetyl, isobutyroyl, isovaleroyl, senecioyl, and dodecanoyl chlorides to afford the (−)-**3**,[7,5a,8c,d,18] (−)-**4**,[4] (+)-**5**,[19] (+)-**6**,[8a,19,20] and (+)-**8**[10] esters, respectively. Treatment of (+)-**2** with angeloyl chloride only afforded (+)-*O*-tigloyllomatin **7**. The identity of (+)-**2** and the lomatin C-3′ esters was confirmed by 1D and 2D NMR, including COSY, HSQC, and HMBC experiments, and by comparison of their spectroscopic properties with those described. It is important to note that the specific rotation for **4** of −10.6 (*c* 0.16, $CHCl_3$), measured herein using two different instruments, was opposite to that described for the (*R*)-enantiomer ($[\alpha]_D = +20.0$).[4b] A sample of (−)-**4** was subjected to alkaline hydrolysis to afford (+)-**2** ($[\alpha]_D = +11.5$).

The C-3′ lomatin esters, which contain two carbonyl groups, are ideal candidates to be studied by vibrational circular dichroism exciton chirality (VCDEC) to determine their absolute configuration.

The VCD spectra of (−)-**1**, (−)-**3**, (−)-**4**, (+)-**5**, (+)-**6**, (+)-**7**, and (+)-**8** showed a strong bisignate VCD signal in the carbonyl stretching region, with a negative–positive couplet from lower to higher frequencies. The amplitudes given in Table 1 correspond to a counterclockwise orientation of the two carbonyl groups, and therefore we can conclude that the absolute configuration of all these molecules is (*R*).

Table 1
VCDEC couplet data for the two carbonyl groups of **1** and **3**–**8**

Compd	*M*	$\Delta\varepsilon_1$[a] (ν[cm^{-1}])	$\Delta\varepsilon_2$[a] (ν[cm^{-1}])	*A*[b]
1	0.08	−0.07 (1722)	+0.04 (1734)	−0.11
3	0.09	−0.07 (1724)	+0.05 (1745)	−0.12
4	0.06	−0.10 (1722)	+0.07 (1740)	−0.17
5	0.06	−0.10 (1724)	+0.06 (1742)	−0.16
6	0.08	−0.09 (1715)	+0.05 (1724)	−0.14
7	0.08	−0.09 (1703)	+0.05 (1730)	−0.14
8	0.06	−0.09 (1720)	+0.05 (1744)	−0.14

[a] In M^{-1} cm^{-1}.
[b] $\Delta\varepsilon_1 - \Delta\varepsilon_2$.

Although VCDEC does not require quantum chemistry calculations, we carried out the VCD calculation[21] of (*R*)-**3** in order to confirm the absolute configuration. After Monte Carlo conformational searching at the MMFF94 level of theory, two conformers with a 0.55 kcal/mol energy difference, accounting for the total conformational population were observed, since the third conformer was 7.6 kcal/mol less stable. The two conformers were submitted to single point energy calculations using density functional theory (DFT) with the B3LYP/6-31G(d) functional and basis set, followed by complete geometry optimization at the DFT B3LYP/DGDZVP level, whereby they converged into the single conformation shown in Figure 1. This most stable conformation showed H–C3′–C4′–Hα

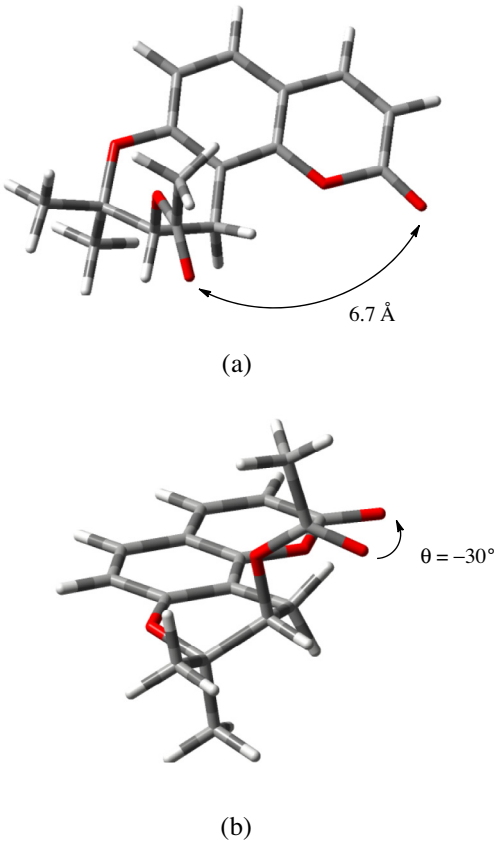


Figure 1. DFT B3LYP/DGDZVP most stable conformer of (*R*)-**3** showing (a) the *syn*-relationship of the ester carbonyl group and H3′, and (b) the counterclockwise twist of the two carbonyl groups' orientation. The through space intercarbonyl distance is calculated from the center of the carbonyl groups.

and H–C3′–C4′–Hβ dihedral angles of −71.8 and +43.2 degrees, respectively. Furthermore, the ester carbonyl group is *syn*-oriented with H3′; the interchromophoric distance, measured from the center of the carbonyl groups, is 6.7 Å (**a** in Fig. 1), and the dihedral angle between the carbonyl groups is −30° (**b** in Fig. 1). The thermochemical parameters and the IR and VCD frequencies at 298 K and 1 atm were calculated, and compared with the experimental VCD frequencies (Fig. 2), and showed excellent similarity. Numerical comparison of the experimental and calculated VCD spectra of (*R*)-**3**, using the Compare*VOA* software,[22] gave a similarity index (S_{IR}) value of 95.2. The calculated spectra for (*R*)-**3** were compared with the experimental spectra of (−)-**1**, (−)-**4**, (+)-**5**, (+)-**6**, (+)-**7**, and (+)-**8**, providing S_{IR} values of 86.0, 76.9, 81.4, 80.1, 83.9, and 39.7, respectively (Table 2).

In addition to the observed strong bisignate VCD couplet, some vibrational modes were identified for **3**. Thus, the negative band at 1280 cm^{-1} is mainly due to an asymmetric H–C3′–C4′–H_2 bending along with asymmetric O3′–C1″ and C1″–C2″ stretchings. In the absorption centered at 1259 cm^{-1}, three positive vibrations can be identified: a band at 1269 cm^{-1} due to asymmetric O1′–C2′ and C2′–C3′ stretchings, along with a symmetric H–C3′–C4′–H_2 bending; a band at 1259 cm^{-1} due to asymmetric O3′–C1″ and C1″–C2″ stretching, along with a symmetric H–C3′–C4′–H_2 bending; and a band at 1256 cm^{-1} due to asymmetric O3′–C1″ and C1″–C2″ stretchings, along with a small asymmetric H–C3′–C4′–H_2 bending; and an asymmetric coumarin ring stretching. The observed vibration at 1052 cm^{-1} arises mainly from asymmetric H–C3′–C4′–H_2 bending and C3′–O stretching. These calculated vibrational modes for **3** also show good similarity with the experimental VCD frequencies (Fig. 3) for (−)-**1**, (−)-**4**, (+)-**5**, (+)-**6**, (+)-**7**,

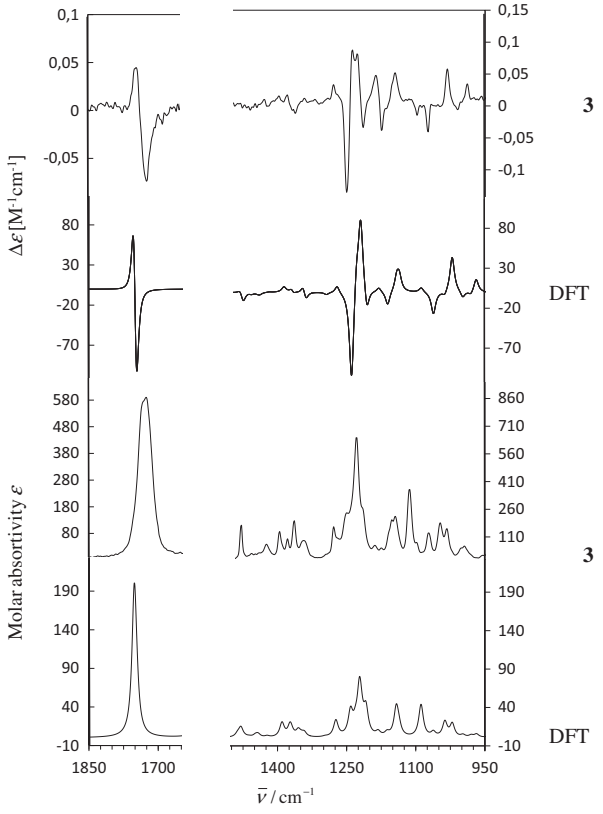


Figure 2. Comparison of the experimental IR and VCD spectra for (−)-**3** with the DFT B3LYP/DGDZVP calculated IR and VCD spectra for (*R*)-**3**.

Table 2
Confidence level data comparison of the experimental spectra with the calculated IR and VCD spectra of (3′*R*)-**3** at the B3LYP/DGDZVP level of theory

Compd	[a]*anH*	[b]S_{IR}	[c]S_E	[d]S_{-E}	[e]*ESI*	[f]*C*
1	0.981	86.0	79.2	18.2	61.0	100
3	0.982	95.2	91.4	19.8	71.6	100
4	0.977	76.9	70.1	14.7	55.4	100
5	0.981	81.4	72.5	17.0	55.6	100
6	0.978	80.1	69.4	17.6	51.8	98
7	0.986	83.9	77.2	19.2	57.9	100
8	0.980	39.7	73.0	15.7	57.3	100

[a] Anharmonicity factor.
[b] IR spectral similarity.
[c] VCD spectral similarity for the correct enantiomer.
[d] VCD spectral similarity for the incorrect enantiomer.
[e] Enantiomer similarity index, calculated as the $S_E - S_{-E}$ difference.
[f] Confidence level for the stereochemical assignments.

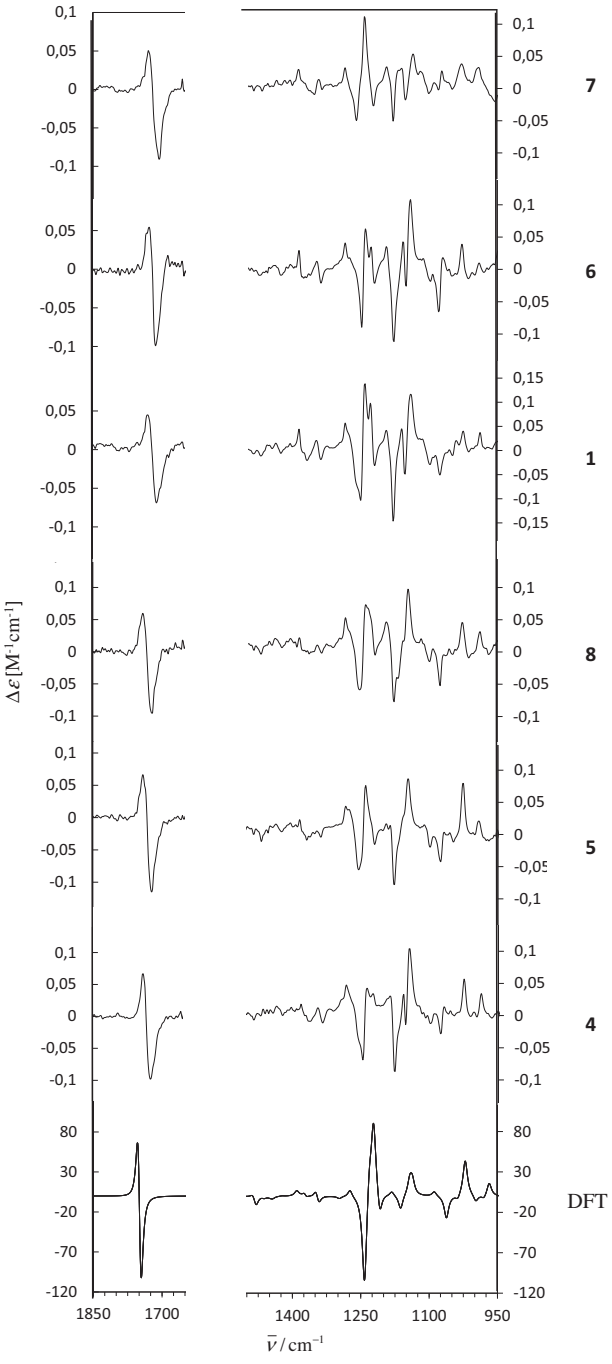


Figure 3. Comparison of the VCD spectra of **1** and **4**–**8** with the calculated spectrum of **3** (bottom). Carbonyl couplets were measured from less concentrated solutions.

and (+)-**8**, thus corroborating the validity of the conclusion based on VCDEC.

In an independent and complementary approach for determining the absolute configuration of **3**, a single crystal X-ray diffraction study was undertaken. A crystal was mounted on a diffractometer equipped with Cu $K\alpha$ graphite monochromated radiation and a large charge coupled device detector. Compound **3** crystallized in the monoclinic system, space group $P2_1$. The molecular structure (Fig. 4) was solved by direct methods and refined to a discrepancy index of 3.4%. The complete sphere data set was used to calculate the Flack parameter,[23] which for the (*R*)-enantiomer was $x = 0.0$ (2), and the Hooft parameter,[24] which was $y = 0.03$ (9). The Flack and Hooft parameters for the (*S*)-enantiomer were $x = 1.0$ (2) and $y = 0.97$ (9), respectively, which again indicates that the absolute configuration of (−)-acetyllomatin is (*R*), which is in agreement with the VCDEC results.

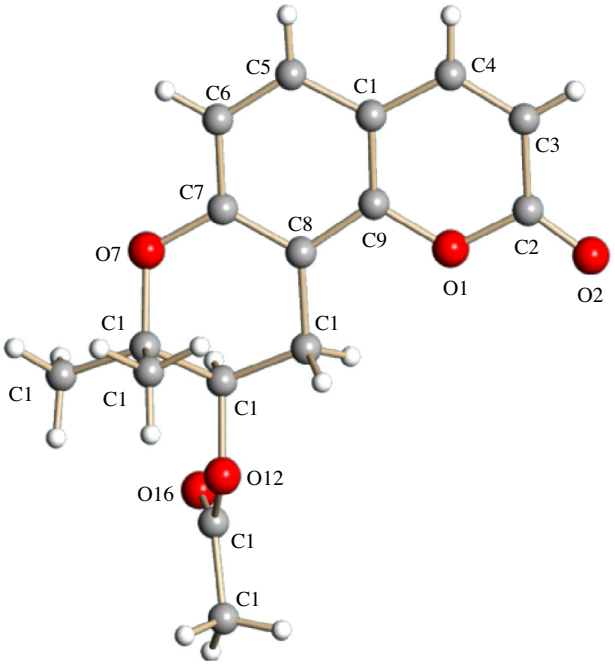


Figure 4. Perspective view of the X-ray crystal structure of **3**.

3. Conclusion

The (*R*)-absolute configuration of (−)-**1**, (−)-**3**, (−)-**4**, (+)-**5**, (+)-**6**, (+)-**7**, and (+)-**8**, was assigned using vibrational circular dichroism exciton chirality, and confirmed both by VCD DFT B3LYP/DGDZVP calculations, and by X-ray Flack and Hooft parameter determination for (*R*)-**3**.

4. Experimental

4.1. General

The ^{1}H, ^{13}C, and 2D NMR spectra were acquired in $CDCl_3$ solutions on a Varian System 500 (125 MHz for ^{13}C) spectrometer at 298 K. Chemical shifts are expressed in ppm (δ) relative to TMS as the internal reference and *J* values are given in Hz. High resolution mass spectra were obtained in the electron impact mode at 70 eV on a Jeol GCMateII spectrometer. Optical rotations were determined in $CHCl_3$ using Perkin Elmer 341 and Jasco DIP-370 polarimeters. Column chromatography separations were carried out on Natland silica gel 60 (200–300 Mesh ASTM). Column chromatography separations and reactions were monitored with Merck silica gel 60 F_{254} TLC plates. Visualization was achieved with the UV light (254 nm) and by a ceric sulfate reagent followed by heating.

4.2. Plant material

Seeds of *Prionosciadium thapsoides* were collected from Chiquihuite hill, México City, during September 2009. A whole plant was authenticated by Professor M. González Ledesma at Herbario del Centro de Investigaciones Biológicas, UAEH, Pachuca, Hidalgo, Mexico (Voucher number 1836).

4.3. Isolation of natural compounds

The air-dried seeds of *Prionosciadium thapsoides* (600 g) were extracted with EtOAc at room temperature for three weeks to give a pale orange viscous oil, which was dissolved in acetone, kept at 4 °C for 12 h, and filtered to remove fatty materials. The filtrate was evaporated under vacuum to afford 32 g of the defatted extract. A portion of 16 g of this extract was chromatographed over silica-gel (mesh 300–400) using hexanes, hexanes/EtOAc gradient (9:1, 4:1, 7:3, 1:1), and EtOAc as eluents. Fractions of 1 L of each polarity were collected, monitored by TLC, and identified as A (0.29 g), B (0.24 g), C (1.41 g), D (1.83 g), E (0.2 g), and F (0.41 g). ^{1}H NMR spectra of fractions A and B showed fatty material. Re-chromatography of fraction C gave (−)-**1** (90 mg), and a complex mixture of esters whose ^{1}H NMR analysis allowed us to identify *O*-angeloyllomatin **1**, and *O*-isobutyroyllomatin **4** as the major components. Fraction D also showed this inseparable mixture of lomatin esters.

4.4. Preparation of acyllomatin derivatives

A solution of fraction C (0.5 g) in EtOH (5 mL), was treated with KOH/EtOH (5%) and stirred at room temperature for 48 h, and then neutralized with HCl (5%). The EtOH was evaporated, the residue was extracted with EtOAc, and then washed with water. The organic layer was subjected to column chromatography to afford 0.26 g of (+)-**2**.

To a solution of 25 mg (0.1 mmol) of lomatin in CH_2Cl_2 (3 mL) and 6.1 mg of dimethylaminopyridine (0.05 mmol), the corresponding acyl chloride (0.12 mmol) was added. Each reaction mixture was stirred at room temperature for 3 h, after which water was added (5 mL), and the organic layer was extracted with EtOAc (3 × 5 mL), washed with water (3 × 5 mL), and dried over anhydrous Na_2SO_4. The solvent was evaporated, and the residue was purified by column chromatography to afford 23.7 mg (81.7%) of (−)-**3**, 25.0 mg (77.9%) of (−)-**4**, 30.5 mg (91.1%) of (+)-**5**, 28.0 mg (84.8%) of (+)-**6**, 26.0 mg (80.0%) of (+)-**7**, and 40.3 mg (92.6%) of (+)-**8**.

4.4.1. *O*-Angeloyllomatin 1

$[\alpha]_D^{22} = -7.6$ (*c* 0.07, $CHCl_3$), ($[\alpha]_D = -24.1$).[8d] ^{1}H and ^{13}C NMR data were essentially the same as those of the (*S*)-enantiomer ($[\alpha]_D = +6.2$).[9]

4.4.2. Lomatin 2

$[\alpha]_D^{22} = +12.4$ (*c* 0.10, $CHCl_3$), [($[\alpha]_D = +7.6$),[8d] ($[\alpha]_D = +13.7$),[8c] ($[\alpha]_D = +14.0$),[8a] ($[\alpha]_D = +210$)[4b]]. ^{1}H and ^{13}C NMR data were identical to those reported.[8c,d]

4.4.3. *O*-Acetyllomatin 3

$[\alpha]_D^{22} = -6.2$ (*c* 0.15, $CHCl_3$), ($[\alpha]_D = -6.8$).[8d] ^{1}H NMR data were essentially the same as reported;[5a] ^{13}C NMR δ 161.1 (C-2), 112.6 (C-3), 143.3 (C-4), 112.2 (C-4a), 126.7 (C-5), 114.3 (C-6), 156.2

(C-7), 106.9 (C-8), 153.4 (C-8a), 76.5 (C-2′), 69.4 (C-3′), 23.1 (C-4′), 23.0 and 24.6 (C-5′, C-6′), 170.2 (C-1″), 21.0 (C-2″).

4.4.4. *O*-Isobutyroyllomatin 4

$[\alpha]_D^{22} = -10.6$ (*c* 1.7, $CHCl_3$), ($[\alpha]_D = +20.0$).[4] ^1H and ^{13}C NMR data were essentially the same as reported.[4a]

4.4.5. *O*-Isovaleroyllomatin 5

$[\alpha]_D^{22} = +28.0$ (*c* 0.91, $CHCl_3$), ($[\alpha]_D = +30.0$).[19] ^1H NMR data were essentially the same as those reported.[19] ^{13}C NMR δ 161.1 (C-2), 112.6 (C-3), 143.0 (C-4), 112.1 (C-4a), 126.7 (C-5), 114.3 (C-6), 156.3 (C-7), 107.0 (C-8), 153.4 (C-8a), 76.5 (C-2′), 69.2 (C-3′), 23.1 (C-4′), 22.7 and 24.1 (C-5′ and C-6′), 172.2 (C-1″), 43.4 (C-2″), 25.7 (C-3″), 22.4 (C-4″), 22.3 (C-5″).

4.4.6. *O*-Senecioyllomatin 6

$[\alpha]_D^{22} = +69.3$ (*c* 0.84, $CHCl_3$), ($[\alpha]_D = +71.8$).[8a] ^1H NMR data were essentially the same as those reported;[8a] ^{13}C NMR δ 161.1 (C-2), 112.5 (C-3), 143.8 (C-4), 112.1 (C-4a), 126.6 (C-5), 143.8 (C-6), 156.4 (C-7), 107.2 (C-8), 153.4 (C-8a), 76.7 (C-2′), 68.3 (C-3′), 23.1 (C-4′), 22.9 and 24.6 (C-5′ and C-6′), 165.3 (C-1″), 115.5 (C-2″), 158.3 (C-3″), 20.3 (C-4″), 27.4 (C-5″).

4.4.7. *O*-Tigloyllomatin 7

$[\alpha]_D^{22} = +30.8$ (*c* 0.11, $CHCl_3$), ^1H NMR δ 7.62 (1H, d, *J* 9.5 Hz, H4), 7.26 (1H, d, *J* 8.5 Hz, H5), 6.80 (1H, d, *J* 8.5 Hz, H6), 6.80 (1H, qq, *J* 7.0, 1.5 Hz, H3″), 6.23 (1H, d, *J* 9.5 Hz, H3), 5.18 (1H, dd, *J* 5.2, 5.2 Hz, H3′), 3.23 (1H, dd, *J* 17.9, 5.2 Hz, H4′a), 2.99 (1H, dd, *J* 17.9, 5.2 Hz, H4′b), 1.80 (3H, dq, *J* 1.5, 1.5 Hz, H4″), 1.76 (3H, dq, *J* 7.0, 1.5 Hz, H5″), 1.38, 1.36 (3H each, s, Me-5′, Me-6′). ^{13}C NMR δ 161.1 (C-2), 112.6 (C-3), 143.8 (C-4), 112.1 (C-4a), 126.6 (C-5), 114.2 (C-6), 156.3 (C-7), 107.2 (C-8), 153.4 (C-8a), 77.2 (C-2′), 69.4 (C-3′), 23.1 (C-4′), 24.8 and 22.8 (C-5′ and C-6′), 167.0 (C-1″), 128.3 (C-2″), 138.2 (C-3″), 12.0 (C-4″), 14.4 (C-5″). EIHRMS *m*/*z* calcd for $C_{19}H_{20}O_5$ ($[M]^+$): 328.1311, found: 328.1310.

4.4.8. *O*-Dodecanoyllomatin 8

$[\alpha]_{589} = +22.8$ (*c* 1.71, $CHCl_3$), ($[\alpha]_{589} = +29.3$).[10] ^1H and ^{13}C NMR data were essentially the same as reported.[10]

4.5. VCD measurements

VCD spectra were measured on a dual PEM BioTools Chiral*IR* FT-VCD spectrophotometer operated at a resolution of 4 cm^{-1}. Deuterochloroform 0.08, 0.09, 0.06, 0.06, 0.08, 0.08, and 0.06 M solutions of **1**, **3**–**8**, respectively, were used for carbonyl couplet measurements; while 0.09, 0.10, 0.10, 0.10, 0.09, 0.10, and 0.07 M solutions of **1**, **3**–**8**, respectively, were used for 950–1650 cm^{-1} measurements. Each solution was placed in a BaF_2 cell with a pathlength of 100 μm. In all cases six 1 h blocks were added. The baseline was provided by subtracting the spectrum of the solvent acquired under the same conditions.

4.6. Single crystal structural determination of (*R*)-3′-*O*-acetyllomatin 3

Suitable crystals were obtained by slow evaporation of an EtOAc/hexane solution. The data were collected on an Agilent Xcalibur Atlas Gemini diffractometer using the enhanced CuKα X-ray source radiation (λ = 1.54184 Å) at 293 (2) K in the ω scan mode. Unit cell refinements using 3568 machine detected reflections were done with the CrysAlisPro, Agilent Technologies, Version 1.171.34.49 software. Crystal data were $C_{16}H_{16}O_5$, M = 288.29, monoclinic, space group $P2_1$, a = 5.4622(2) Å, b = 10.9387(4) Å, c = 11.6600(5) Å, β = 92.681(4)°, V = 695.92(5) Å, Z = 2, ρ = 1.38 mg/mm^3, μ(Cu $K\alpha$) = 0.853 mm^{-1}, total reflections = 9431, unique reflections 2902 (R_{int} 0.01%), observed reflections 2580. The structure was resolved by direct methods using the SHELXS-97 program included in the WingGX v1.70.01 crystallographic software package. For the structural refinement, the non-hydrogen atoms were treated anisotropically, and the hydrogen atoms, included in the structure factor calculation, were refined isotropically. The *R* indices were [$I > 2\sigma(I)$] R_1 = 3.4% and wR_2 = 8.6%. The largest difference peak and hole were 0.137 and −0.129 eÅ^3. The Olex2 v1.15 software allowed us to calculate the Flack parameter x = 0.0(2) and the Hooft parameter y = 0.97(9). For the inverted structure these parameters were x = 1.0(2) and y = 0.97(9), respectively. Crystallographic data (excluding structure factors) have been deposited at the Cambridge Crystallographic Data Centre CCDC number 1020904. Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 IEZ, UK. Fax: +44 (0)1223 336033 or e-mail: deposit@ccdc.cam.ac.ik.

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