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Artigo

AROMATIC COMPOUNDS FROM THREE BRAZILIAN LAURACEAE SPECIES

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Phytochemical investigations on three Brazilian Lauraceae species from the Cerrado region of São Paulo State, *Ocotea corymbosa* (Meins) Mez., *O. elegans* Mez. and *Persea pyrifolia* Nees & Mart. ex Nees resulted in the isolation of flavonoids, an ester of the 4-*O*-*E*-caffeoylquinic acid, an aromatic sesquiterpene besides furofuran lignans. This is the first chemical study on the leaves of *Ocotea elegans and O. corymbosa* as well as the first report of non-volatile compounds from *Persea pyrifolia*.

Keywords: Lauraceae; *Ocotea*; *Persea*.

INTRODUCTION

The Lauraceae family comprises 52 genera and approximately 3000 species, mostly from tropical and warm subtropical regions of the world.[1] Lauraceae species present several groups of secondary metabolites, most of them aromatic, which seem to be relevant for chemotaxonomic classification in Lauraceae.[2]

The genus *Ocotea* comprises ca. 350 species. Previous phytochemical studies have revealed the presence of neolignans, benzylisoquinoline alkaloids, phenylpropanoids, flavonoids and sesquiterpenes,[3] besides a variety of volatile components from its essential oils.[1] *Ocotea elegans* is known as *canela de ferro* or *canela preta* in Brazil where it is widespread. Despite its huge distribution, the only study performed on *O. elegans* reports the isolation of neolignans from the stems by using countercurrent chromatography.[4] *Ocotea corymbosa* is popularly known as *canela de corvo* or *canela fedorenta* in Brazil and its wood is employed in the civil construction industry.[5] Only two studies were performed on *O. corymbosa*; monoterpenes and sesquiterpenes as well as phytosterols were isolated from the unripe fruits[3] and sesquiterpenes with calamenene skeleton were characterized from its bark.[6] No previous studies have been performed on leaves of *O. corymbosa*.

Persea is a genus that comprises ca. 200 species, the most well studied of these being *P. americana* Mill, known as "avocado fruit". Previous phytochemical studies on avocado seeds identified various classes of natural products such as phytosterols, triterpenes,[7] fatty acids with olefinic and acetylenic bonds,[8] alkylfurans,[9] dimers of flavanols,[10] oligomeric proanthocyanidins[11] and glucosylated abscisic acids.[12] *Persea pyrifolia* is popularly known as *maçaranduba* and it is frequently employed in the furniture manufacturing industry.[13] The only study carried out on *P. pyrifolia* dealt with volatile compounds from the leaves.[14]

As part of our on-going program devoted to phytochemical investigations on Brazilian Lauraceae species, in this work we report the isolation of an ester of the 4-*O*-*E*-caffeoylquinic acid (**1**) and three flavonoids (**2**-**4**) from *O. corymbosa*, an aromatic sesquiterpene (**5**) and a flavonoid (**6**) from *O. elegans* as well as four furofuran lignans (**7**-**10**) from *P. pyrifolia*. This is the first chemical study on the leaves of *O. elegans and O. corymbosa* as well as the first report of non-volatile compounds from *P. pyrifolia*.

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EXPERIMENTAL

General

Analytical and preparative HPLC separations were performed by using stainless-steel Phenomenex Luna phenyl-hexyl (250 x 4.6 mm and 250 x 22 mm, 5 and 10 μm particle size, respectively) and Phenomenex Luna C-18 (250 x 4.6 mm and 250 x 22 mm, 5 and 10 μm particle size, respectively). Mobile phases for chromatography were prepared from HPLC grade solvents. Methanol and acetonitrile were obtained from J.T. Baker (Phillipsburg, NJ, USA) and Tedia (Fairfield, OH, USA), respectively. Water was purified in-house with a Millipore Milli-Q system (Billerica, MA, USA). The analytical HPLC separations were carried out using a Shimadzu (Kyoto, Japan) LC-10Ai pump system, a Shimadzu SIL-10Ai auto injector and a Shimadzu SPD-10Avp UV-Vis detector. The HPLC system used for preparative separations was a Varian (Walnut Creek, CA, USA) PrepStar SD-1 equipped with a Rheodyne (Cotati, CA, USA) injector with a 2 mL sample loop and a ProStar UV-Vis detector. NMR spectra were recorded on a Varian Inova 500 FT-NMR (Palo Alto, CA, USA) spectrometer operating at 500 MHz (^{1}H) and 125 MHz (^{13}C). Chemical shifts were referenced relative to TMS or the corresponding residual solvent signals. Deuterated solvents ($CDCl_3$ and DMSO-d_6) were purchased from Cambridge Isotope Laboratories, Inc. (Andover, MA, USA). DCCC separations were performed using an EYELA D.C.C. - 300 (Tokyo Rikakikai CO LTD). All solvents used for column chromatography (CC) as well as for DCCC were from analytical grade. Silica gel for CC (60-200 μm) was purchased from Acros Organics (New Jersey, NJ, USA).

Plant material

The specimens *O. elegans* Mez. and *P. pyrifolia* Nees & Mart. ex Nees were collected at Fazenda Campininha, Mogi-Guaçu, SP;

O. corymbosa (Meins) Mez. was collected in Araraquara, SP, Brazil. Voucher specimens of *O. elegans* (Moraes 06), *O. corymbosa* (deLuca 001) and *P. pyrifolia* (Lima 136) are deposited at the Herbarium of Instituto de Botânica, SP, Brazil.

Extraction and isolation of chemical constituents

In order to delineate this work, our selection criterion for the elected fractions was based on monitoring the occurrence of signals in the region of aromatic chemical shifts in the ^{1}H NMR spectra. For each studied species, only fractions showing aromatic signals were selected for further chromatographic separations.

The dried and powdered leaves (200 g) of *O. corymbosa* were sequentially extracted with hexane and methanol at room temperature (3 x 1000 mL, 3 days). The solvents were evaporated under reduced pressure. The methanolic residue (13.6 g) was suspended with methanol:water (9:1, v/v, 300 mL) and then partitioned successively with hexane, ethyl acetate and *n*-butanol (3 x 100 mL). The *n*-butanolic residue (2.0 g) was submitted to DCCC in descendent mode yielding 33 fractions (180 mL). The solvent system employed was a mixture of chloroform:methanol:water (43:37:20, v/v/v). Fractions 30 (60.0 mg) and 31 (85.0 mg) were subsequently purified by preparative HPLC, using as eluent an isocratic mixture of methanol:water (47:53, v/v), 5 mL min^{-1}, column: Phenomenex Luna phenyl-hexyl (250 x 22 mm, 10 µm particle size) and UV detection at λ 254 nm. This procedure yielded the compounds **1** (12.0 mg, t_R = 21.28 min), **2+3** (20.0 mg, t_R = 28.61 min) and **4** (5.0 mg, t_R = 31.53 min).

The dried and powdered leaves (50.0 g) of *O. elegans* were submitted to extraction with ethanol at room temperature (3 x 200 mL, 3 days). The solvent was evaporated under reduced pressure. The residue (1.23 g) was suspended with methanol:water (9:1, v/v, 50 mL) and then washed with hexane. The hydroalcoholic residue (1.0 g) was submitted to silica gel (60-200 µm) CC, eluted with a gradient of hexane, ethyl acetate and methanol affording 17 fractions (50 mL). The fraction 2 afforded compound **5** (8.0 mg). The fraction 15 (200 mg) was further purified by preparative HPLC yielding compound **6** (120 mg, t_R = 32.51 min). As eluent was used an isocratic mixture of water:acetonitrile (8:2, v/v), 12 mL min^{-1}, column: Phenomenex Luna phenyl-hexyl (250 x 22 mm, 10 µm particle size) and UV detection at λ 254 nm.

The dried and powdered leaves (250 g) of *P. pyrifolia* were sequentially extracted with hexane and methanol at room temperature (3 x 1000 mL, 3 days). The solvents were evaporated under reduced pressure. The hexanic residue (8.0 g) was suspended with methanol:water (9:1, v/v, 200 mL) and then washed with hexane. The hydroalcoholic residue (1.0 g) was submitted to silica gel (60-200 µm) CC, eluted with a gradient of hexane, ethyl acetate and methanol yielding 30 fractions (25 mL). The fractions 4-7 were pooled together and furnished compound **7** (37.0 mg). Fractions 10 (90.0 mg) and 18 (80.0 mg) were purified by preparative HPLC. As eluent was used an isocratic mixture of methanol:water (55:45, v/v), 12.0 mL min^{-1}, column: Phenomenex Luna C-18 (250 x 22 mm, 10 µm particle size) and UV detection at λ 254 nm. This procedure afforded the compounds **8** (11.0 mg, t_R = 35.05 min), **9** (3.0 mg, t_R = 25.43 min) and **10** (3.0 mg, t_R = 52.86 min).

By a combination of spectroscopic methods (^{1}H and ^{13}C NMR spectra) and comparison with the literature data, the compounds were identified as follows: 4-*O*-*E*-caffeoylquinic acid methyl ester (**1**),[15] quercetin-3-*O*-β-D-glucoside (**2**),[16] quercetin-3-*O*- β-D-galactoside (**3**),[16] quercetin-3-*O*-β-D-xyloside (**4**),[16] *rel*-(1*R*, 4*S*)-7-hydroxycalamenene (**5**),[6] *rel*-(2*R*, 3*R*)-dihydroquercetin-3-*O*-α-L-rhamnoside (astilbin) (**6**),[17] *rel*-(7*S*, 7'*S*, 8*R*, 8'*R*)-sesamin (**7**),[18] *rel*-(7*S*, 7'*S*, 8*R*, 8'*R*)-methylpiperitol (**8**),[18] *rel*-(7*S*, 7'*S*, 8*R*, 8'*R*)-eudesmin (**9**)[18] and *rel*-(7*S*, 7'*S*, 8*R*, 8'*R*)-magnolin (**10**).[19]

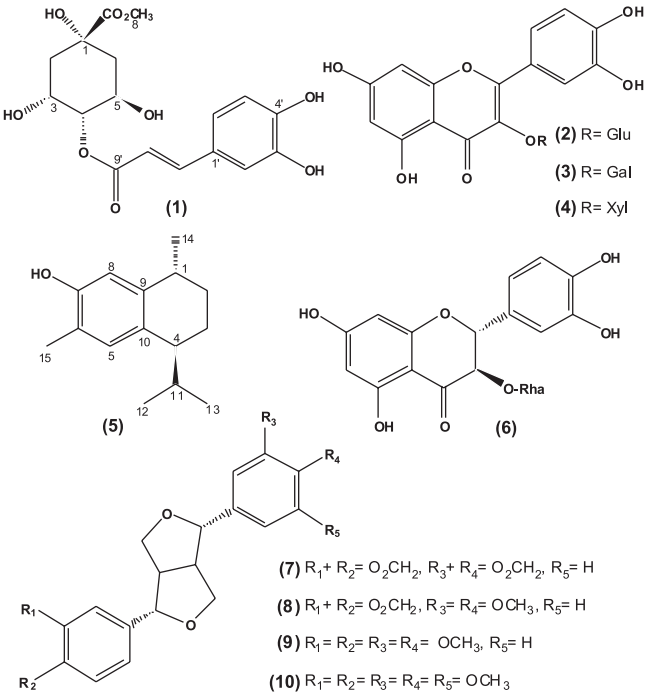

Figure 1. *Structure of the isolated compounds*

RESULTS AND DISCUSSION

The present study reports the isolation of one ester of the 4-*O*-*E*-caffeoylquinic acid (**1**), four flavonoids (**2-4** and **6**), one aromatic sesquiterpene (**5**) and four furofuran lignans (**7-10**) from the leaves of three Lauraceae species from the Cerrado region of São Paulo state, Brazil (Figure 1). This is the first time that an aromatic sesquiterpene and flavonoids are reported for *O. elegans*, flavonoids and an ester of the 4-*O*-*E*-caffeoylquinic acid for *O. corymbosa* as well as furofuran lignans for *P. pyrifolia*.

The sesquiterpene *rel*-(1*R*, 4*S*)-7-hydroxycalamenene (**5**) isolated from *O. elegans*, has already been isolated from *O.* corymbosa.[6] However, there are no reports regarding this compound on other Lauraceae genera.

All the flavonoids isolated are derived from quercetin (**2-4**) and dihydroquercetin (**6**) aglycones. This feature seems to be common to other Lauraceae species likewise *O. elegans* and *O. corymbosa*.

The furofuran lignans (**7-10**) isolated from *P. pirifolia* were reported previously from *Nectandra, Licaria,* and *Litsea* species.[20] This finding corroborates the importance of lignans and neolignans as phytochemical constituents in Lauraceae species.

The genera studied in this work encompass many species, which are difficult to identify based just on morphological features.[21] Mistakes in botanical identification could be prevented by using the information obtained from a comprehensive analysis of the chemical profiles of the putative species.

SUPPLEMENTARY MATERIAL

NMR (^{1}H and ^{13}C) data for the isolated compounds **1**-**10** are available at http://www.quimicanova.sbq.org.br, in PDF format with free access.

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Material Suplementar

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NMR (^{1}H and ^{13}C) data for the isolated compounds 1-10.

4-*O*-*E*-caffeoylquinic acid methyl ester (**1**): ^{1}H NMR (DMSO-d_6, 500 MHz) δ: 1.92 (1H, dd, *J* = 3.5 and 13.5 Hz, H-2ax.), 2.10 (2H, m, H-2eq. and H-6eq.), 3.57 (1H, m, H-3), 5.01 (1H, dd, *J* = 5.0 and 8.5 Hz, H-4), 3.88 (1H, m, H-5), 1.76 (dd, *J* = 9.5 and 12,5, H-6ax.), 3.55 (1H, s, H-8), 7.02 (1H, d, *J* = 2.0 Hz, H-2´), 6.76 (1H, d, *J* = 8.5 Hz, H-5´), 6.96 (1H, dd, *J* = 2.0 and 8.5 Hz, H-6´), 7.37 (1H, d, *J* = 16.0 Hz, H-7´), 6.10 (1H, d, *J* = 16.0 Hz, H-8´). ^{13}C NMR (DMSO-d_6, 125 MHz) δ : 73.0 (C-1), 35.0 (C-2), 69.3 (C-3), 71.0 (C-4), 67.2 (C-5), 37.2 (C-6), 173.6 (C-7), 51.8 (C-8), 125.3 (C-1'), 114.6 (C-2'), 148.5 (C-3'), 145.6 (C-4'), 115.8 (C-5'), 121.3 (C-6'), 145.1 (C-7'), 113.8 (C-8´), 165.3 (C-9´).

quercetin-3-*O*-β-D-glucoside (**2**): ^{1}H NMR (DMSO-d_6, 500 MHz) δ : 6.20 (1H, bs, H-6), 6.41 (1H, bs, H-8), 7.58 (1H, d, *J* = 2.0 Hz, H-2'), 6.84 (1H, d, *J* = 8.5 Hz, H-5'), 7.57 (1H, dd, *J* = 2.0 and 8.5 Hz, H-6'), 5.46 (1H, d, *J* = 7.0 Hz, H-1''), 3.58 - 3.24 (sugar H). ^{13}C NMR (DMSO-d_6, 125 MHz) δ : 156.2 (C-2), 133.3 (C-3), 177.4 (C-4), 161.2 (C-5), 98.7 (C-6), 164.2 (C-7), 93.5 (C-8), 156.3 (C-9), 104.0 (C-10), 121.1 (C-1'), 115.2 (C-2'), 144.8 (C-3'), 148.4 (C-4'), 116.2 (C-5'), 121.6 (C-6'), 100.8 (C-1''), 74.1 (C-2''), 76.5 (C-3''), 69.9 (C-4''), 77.5 (C-5''), 60.9 (C-6'').

quercetin-3-*O*-β-D-galactoside (**3**): ^{1}H NMR (DMSO-d_6, 500 MHz) δ : 6.20 (1H, bs, H-6), 6.41 (1H, bs, H-8), 7.53 (1H, d, *J* = 2.0 Hz, H-2'), 6.81 (1H, d, *J* = 8.5 Hz, H-5'), 7.66 (1H, dd, *J* = 2.0 and 8.5 Hz, H-6'), 5.37 (1H, d, *J* = 7.0 Hz, H-1''), 3.56 - 3.28 (sugar H). ^{13}C NMR (DMSO-d_6, 125 MHz) δ : 156.1 (C-2), 133.4 (C-3), 177.4 (C-4), 161.2 (C-5), 98.7 (C-6), 164.2 (C-7), 93.5 (C-8), 156.2 (C-9), 103.9 (C-10), 121.1 (C-1'), 115.2 (C-2'), 144.8 (C-3'), 148.5 (C-4'), 115.9 (C-5'), 121.9 (C-6'), 101.8 (C-1''), 71.2 (C-2''), 73.4 (C-3''), 67.9 (C-4''), 75.8 (C-5''), 60.1 (C-6'').

quercetin-3-*O*-β-D-xyloside (**4**): ^{1}H NMR (DMSO-d_6, 500 MHz) δ : 6.16 (1H, bs, H-6), 6.36 (1H, bs, H-8), 7.56 (1H, d, *J* = 2.0 Hz, H-2'), 6.84 (1H, d, *J* = 8.5 Hz, H-5'), 7.53 (1H, dd, *J* = 2.0 and 8.5 Hz, H-6'), 5.33 (1H, d, *J* = 7.0 Hz, H-1''), 3.31 - 2.96 (sugar H). ^{13}C NMR (DMSO-d_6, 125 MHz) δ : 156.2 (C-2), 133.1 (C-3), 177.2 (C-4), 162.5 (C-5), 99.1 (C-6), 164.1 (C-7), 94.0 (C-8), 156.2 (C-9), 104.3 (C-10), 121.0 (C-1'), 116.2 (C-2'), 146.2 (C-3'), 150.1 (C-4'), 116.5 (C-5'), 121.9 (C-6'), 102.3 (C-1''), 74.5 (C-2''), 76.8 (C-3''), 70.2 (C-4''), 66.0 (C-5'').

rel-(1*R*, 4*S*)-7-hydroxycalamenene (**5**): ^{1}H NMR ($CDCl_3$, 500 MHz) δ : 2.64 (1H, m, H-1), 1.25 (1H, m, H-2a), 1.18 (1H, m, H-2b), 1.49 (1H, m, H-3a), 1.74 (1H, m, H-3b), 2.56 (1H, m, H-4), 6.86 (1H, s, H-5), 6.57 (1H, s, H-8), 2.12 (1H, m, H-11), 0.64 (3H, d, *J* = 6.5 Hz, H-12), 0.91 (3H, d, *J* = 6.5 Hz, H-13), 1.16 (3H, d, *J* = 7.0 Hz, H-14), 2.13 (3H, s, H-15). ^{13}C NMR ($CDCl_3$, 125 MHz) δ : 32.6 (C-1), 30,8 (C-2), 21.6 (C-3), 43.1 (C-4), 130.5 (C-5), 120.6 (C-6), 151.4 (C-7), 113.0 (C-8), 142.1 (C-9), 132.2 (C-10), 31.9 (C-11), 17.3 (C-12), 21.2 (C-13), 22.2 (C-14), 15.5 (C-15).

rel-(2*R*, 3*R*)-astilbin (**6**): ^{1}H NMR (DMSO-d_6, 500 MHz) δ : 5.25 (1H, d, *J* = 10.0 Hz, H-2), 4.65 (1H, d, *J* = 10.0 Hz, H-3), 5.90 (1H, d, *J* = 2.0 Hz, H-6), 5.88 (1H, d, *J* = 2.0 Hz, H-8), 6.89 (1H, s, H-2'), 6.74 (2H, s, H-5' and H-6'), 4.04 (1H, d, *J* = 1.5 Hz, H-1''), 3.90 - 3.10 (sugar H), 1.05 (1H, d, *J* = 6.0 Hz, H-6''). ^{13}C NMR (DMSO-d_6, 125 MHz) δ : 81.6 (C-2), 75.7 (C-3), 194.5 (C-4), 163.5 (C-5), 96.1 (C-6), 167.2 (C-7), 95.1 (C-8), 162.2 (C-9), 101.0 (C-10), 127.0 (C-1'), 114.8 (C-2'), 145.2 (C-3'), 145.9 (C-4'), 115.4 (C-5'), 119.0 (C-6'), 100.1 (C-1''), 70.1 (C-2''), 70.4 (C-3''), 71.7 (C-4''), 69.0 (C-5''), 17.8 (C-6'').

rel-(7*S*, 7'*S*, 8*R*, 8'*R*)-sesamin (**7**): ^{1}H NMR ($CDCl_3$, 500 MHz) δ : 6.77 (2H, d, *J* = 1.5 Hz, H-2 and H-2´), 6.71 (2H, d, *J* = 8.0 Hz, H-5 and H-5´), 6.70 (2H, dd, *J* = 1.5 and 8.0 Hz, H-6 and H-6´), 4.64 (2H, d, *J* = 4.0 Hz, H-7 and H-7´), 2.97 (2H, m, H-8 and H-8´), 4.15 (2H, dd, *J* = 7.0 and 9.0 Hz, H-9eq. and H-9´eq.), 3.78 (2H, dd, *J* = 4.0 and 9.0 Hz, H-9ax. and H-9´ax.), 5.87 (4H, s, O-CH_2-O). ^{13}C NMR ($CDCl_3$, 125 MHz) δ : 135.0 (C-1 and C-1´), 106.4 (C-2 and C-2´), 147.0 (C-3 and C-3´), 147.9 (C-4 and C-4´), 108.1 (C-5 and C-5´), 119.2 (C-6 and C-6´), 85.7 (C-7 and C-7´), 54.3 (C-8 and C-8´), 71.6 (C-9 and C-9´), 101.0 (O-CH_2-O).

rel-(7*S*, 7'*S*, 8*R*, 8'*R*)-methylpiperitol (**8**): ^{1}H NMR ($CDCl_3$, 500 MHz) δ : 6.78 (1H, m, H-2), 6.70 (1H, dd, *J* = 0.5 and 8.0 Hz, H-5), 6.73 (1H, m, H-6), 4.66 (2H, m, H-7 and H-7´), 3.00 (2H, m, H-8 and H-8´), 4.17 (2H, m, H-9eq. and H-9´eq.), 3.81 (2H, m, H-9ax. and H-9´ax.), 6.83 (1H, d, *J* = 2.0 Hz, H-2´), 6.78 (2H, m, H-5´ and H-6´), 5.87 (2H, s, O-CH_2-O), 3.80 (3H, s, OMe-3´), 3.82 (3H, s, OMe-4´). ^{13}C NMR ($CDCl_3$, 125 MHz) δ : 135.1 (C-1), 106.4 (C-2), 147.1 (C-3), 147.9 (C-4), 108.1 (C-5), 119.3 (C-6), 85.7 (C-7 and C-7´), 54.1 (C-8 and C-8´), 71.7 (C-9 and C-9´), 133.5 (C-1´), 109.3 (C-2´), 148.7 (C-3´), 149.2 (C-4´), 111.3 (C-5´), 118.2 (C-6´), 101.0 (O-CH_2-O), 55.9 (OMe-3´ and OMe-4´).

rel-(7*S*, 7'*S*, 8*R*, 8'*R*)-eudesmin (**9**): ^{1}H NMR ($CDCl_3$, 500 MHz)

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δ : 6.83 (2H, d, *J* = 1.5 Hz, H-2 and H-2´), 6.77 (2H, d, *J* = 8.0 Hz, H-5 and H-5´), 6.79 (2H, dd, *J* = 1.5 and 8.0 Hz, H-6 and H-6´), 4.68 (2H, d, *J* = 4.0 Hz, H-7 and H-7´), 3.03 (2H, m, H-8 and H-8´), 4.18 (2H, dd, *J* = 7.0 and 9.0 Hz, H-9eq. and H-9´eq.), 3.81 (2H, m, H-9ax. and H-9´ax.), 3.80 (6H, s, OMe-3 and OMe-3´), 3.82 (6H, s, OMe-4 and OMe-4´). ^{13}C NMR ($CDCl_3$, 125 MHz) δ : 133.6 (C-1 and C-1´), 109.3 (C-2 and C-2´), 148.7 (C-3 and C-3´), 149.2 (C-4 and C-4´), 111.1 (C-5 and C-5´), 118.2 (C-6 and C-6´), 85.8 (C-7 and C-7´), 54.2 (C-8 and C-8´), 71.7 (C-9 and C-9´), 55.9 (OMe-3, OMe-3´, OMe-4 and OMe-4´).

rel-(7*S*, 7'*S*, 8*R*, 8'*R*)-magnolin (**10**): ^{1}H NMR ($CDCl_3$, 500 MHz) δ : 6.83 (1H, d, *J* = 2.0 Hz, H-2), 6.77 (1H, d, *J* = 8.0 Hz, H-5), 6.80 (1H, dd, *J* = 2.0 and 8.0 Hz, H-6), 4.69 (1H, d, *J* = 4.5 Hz, H-7), 3.03 (1H, m, H-8), 4.21 (1H, dd, *J* = 7.0 and 9.0 Hz, H-9eq.), 3.82 (1H, m, H-9ax.), 6.50 (1H, s, H-2' and H-6'), 4.67 (1H, d, *J* = 5.0 Hz, H-7'), 3.03 (1H, m, H-8'), 4.20 (1H, m, H-9´eq.), 3.84 (1H, m, H-9´ax.), 3.80 (3H, s, OMe-3), 3.82 (3H, s, OMe-4), 3.79 (3H, s, OMe-3' and OMe-5'), 3.76 (3H, s, OMe-4'). ^{13}C NMR ($CDCl_3$, 125 MHz) δ : 133.1 (C-1), 109.3 (C-2), 148.7 (C-3), 149.2 (C-4), 111.1 (C-5), 118.2 (C-6), 85.7 (C-7 and C-7´), 54.1 (C-8), 71.9 (C-9), 136.8 (C-1´), 102.9 (C-2´ and C-6´), 153.4 (C-3´ and C-5´), 137.6 (C-4´), 54.4 (C-8´), 71.7 (C-9´), 55.9 (OMe-3 and OMe-4), 56.2 (OMe-3´ and OMe-5´), 60.8 (OMe-4´).