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NEOLIGNANS FROM *NECTANDRA PUBERULA**

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Key Word Index—*Nectandra puberula*; Lauraceae; geranylgeranodioic acid; neolignans; diaryldimethyl-*n*-butanones.

Abstract—The trunk wood of *Nectandra puberula* was found to contain 1,6-geranylgeranodioic acid besides five neolignans, the known veraguensin and the novel 7-hydroxy- and 7-oxo-3,4,3′,4′-tetraoxy-8.8′-neolignans, all with the (8*S*,8′*R*)-absolute configuration.

INTRODUCTION

Although numerous *Nectandra* species are widely distributed all over Brazil, relatively few chemical analyses have been reported. One of the possible explanations for the neglect of this genus may be due to the difficulty in classifying plant material in the *Ocotea–Nectandra* group of the family Lauraceae. Professor Klaus Kubitzki, Universität, Hamburg, is working towards this goal and kindly identified the species analysed in the present paper as *Nectandra puberula* (Schott.) Nees. A sample of trunk wood of this plant was found to contain a diterpenoid (**1a**), sitosterol (**2**), sitostenone (**3**), as well as the neolignans **4** (veraguensin [2, 3]), **5**, **6a**, **6b** and **6c**. Compound **5** has already been described [4, 5], although with the wrong 8′*S*-configuration. Compounds **1a**, **6a**, **6b** and **6c** have not been reported previously.

In order to facilitate comparisons among different neolignans, the numbering of these compounds follows the biogenetic rules outlined in ref. [6].

RESULTS

The number of carbons and hydrogens in the elementary formula ($C_{20}H_{30}O_4$) of **1a** was established by NMR counts. The mass spectrum contained a $[M - H_2O]^+$ peak (*m/z* 316) but no $[M]^+$ peak. Diazomethane methylation produced a diester (**1b**), in agreement with the presence of two carboxyl groups, both of which (ν_{max} 1691, 1656 cm^{-1}) must be α,β-unsaturated. This fact, together with NMR evidence for four methyls linked to double bonds, six allylic methylenes and four olefinic protons, led to **1a** as one of the possible structures. This proposal was confirmed by detailed analysis of the ^{1}H NMR and ^{13}C NMR spectra.

The central methyls are equivalent. The corresponding chemical shift of δ1.64 is closely comparable with the value of 1.62 for the central methyls of geranylgeraniol [7]. Thus compound **1a** must possess an analogous all-*trans* geometry, at least in its central part. The two peripheral methyls are not equivalent. As indicated by their chemical shifts, one must be situated at the α-position (α-Me, δ1.81, *d*, J = 1.5 Hz; β-H, δ6.77, *tq*, J = 7.0, 1.5 Hz) and the other at the β-position (β-Me, δ2.15, *d*, J = 1.5 Hz; α-H, δ5.69, *q*, J = 1.5 Hz) of α,β-unsaturated carboxyl systems. These assignments were confirmed by double resonance experiments and are closely comparable with the analogous data for the two model compounds **7** (α-Me, δ1.88; β-H, δ7.00) and **8** (β-Me, δ2.18; α-H, δ5.72). If the model compounds **7**-**9** [8, 9] are numbered according to the corresponding positions of **1**, the following ^{13}C NMR comparisons (δ values) again favour the proposed structure for this compound: **1b**/**7** 167.23/168.90 (C-1), 127.55/128.40 (C-2), 12.39/11.50 (C-17); **1b**/**8** 115.37/115.60 (C-15), 168.62/169.00 (C-16); **1b**/**9** 136.07/136.06 (C-10), 125.11/125.56 (C-11), 16.03/15.40 (C-19).

The elementary formula ($C_{22}H_{30}O_5$) for **5** was determined by a combination of low-resolution mass spectrometry and NMR counts. The constitutional formula was established by trivial NMR assignments. Proof of the structure and of the absolute configuration relied on the acid-catalysed transformation of **5** into (−)-galbulin (**10**) [10], a tetralin-type neolignan of known absolute stereochemistry.

Oxidation of **5** led to the ketone **6d**. The IR (ν_{max} 1670 cm^{-1}) and UV (λ_{max} 304 nm, ε 7700) data for this oxidation product and for the three compounds **6a** ($C_{20}H_{22}O_5$), **6b** ($C_{20}H_{20}O_5$) and **6c** ($C_{21}H_{24}O_5$) are closely comparable. The problem in this series concerns the relative localization of the benzylic methylene and the benzylic carbonyl groups. The ^{1}H NMR spectrum of **6b** shows two signals for methylenedioxyls, one at δ5.94 and one at δ6.02. The latter signal, revealing conjugation with the benzylic carbonyl, must be assigned here, and in the spectra of **6a** and **6c** (Table 1), to a piperonyloyl unit.

An additional compound of the diaryl-butanone type (**6e**) was recently described and characterized by spectral means (Table 2) including mass spectrometry. The base peak, *m/z* 194, corresponds to **11e**. The veratryl and not the

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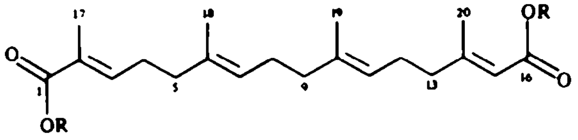
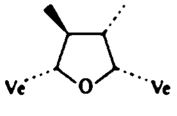
*Part LXXIX in the series "The Chemistry of Brazilian Lauraceae". For Part LXXVIII, see ref. [1]. Based on the M.Sc. thesis presented by J.C.M. to the Universidade Federal de São Carlos (1985).



1a R = H
1b R = Me



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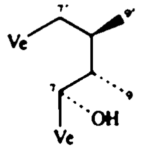

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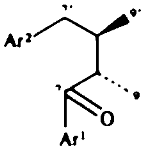
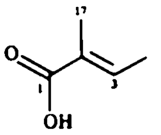


6a Ar¹ = Pi, Ar² = Gu
6b Ar¹ = Ar² = Pi
6c Ar¹ = Pi, Ar² = Ve
6d Ar¹ = Ar² = Ve
6e Ar¹ = Ve, Ar² = Pi



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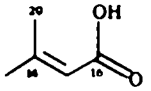

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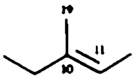

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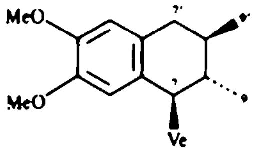
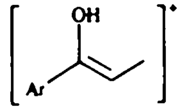
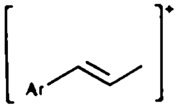


10

Pi = piperonyl
Ve = veratryl
Gu = guaiacyl



11a Ar = Pi
11b Ar = Pi
11c Ar = Pi
11d Ar = Ve
11e Ar = Ve



12a Ar = Gu
12b Ar = Pi
12c Ar = Ve
12d Ar = Ve
12e Ar = Pi

piperonyl group must thus be linked to the carbonyl group. Strangely, the mass spectrum of **6e** lacks another intense peak for **12e** at *m/z* 162 [11]. In our mass spectra the fragmentation ions **11** and **12** gave rise to intense peaks: **6a** *m/z* (rel. int.) 178 (100), 164 (97); **6b** 178 (100), 162 (91); **6c** 178 (100); **6d** 194 (100), 178 (99). Clearly the three new compounds possess a piperonyloyl residue and guaiacyl (**6a**), piperonyl (**6b**) and veratryl (**6c**) moieties, respectively.

The absolute configuration of (−)-galbulin (**10**) is known [12]. Since **10** can be obtained by acid-catalysed cyclization of **5** and **5** can be converted by oxidation into **6d**, **5** and **6d** must have the same chiralities at C-8 and C-8' as those known to occur in **10**. The ORD and CD curves of **6d** and of all the other representatives of series **6** show comparable Cotton effects and all these compounds thus have identical absolute configurations.

EXPERIMENTAL

Isolation of the constituents. A sample of the trunk of *N. puberula* was collected from Cardoso Island (close to the southern littoral of São Paulo State) by Dr. Mario Motidome (Universidade de São Paulo). Identification of the species was done by Prof. Klaus Kubitzki (Universitat Hamburg). The sample was dried at room temp. and separated into bark and wood. Powdered bark (263 g) was extracted with $CHCl_3$ in a Soxhlet apparatus. The solvent was evaporated and the residue (5.97 g) was subjected to dry CC (190 g Merck silica gel 60; $CHCl_3$–EtOAc, 9:1). The column was cut into 25 parts of equal

Table 1. ^{1}H NMR spectral data for diaryldimethyl-*n*-butanone neolignans ($CDCl_3$, 270 MHz)

H	Multiplicity	*J* (Hz)	**6a**	**6b**	**6c**
2	*d*	*	7.27	7.26	7.27
5	*d*	8	6.76	6.75	6.76
6	*dd*	2, 8	7.29	7.32	7.29
8	*dq*	5, 7	3.27	3.29	3.27
9	*d*	7	1.12	1.12	1.12
2′	*d*	1.5	6.67†	6.67	6.70
5′	*d*	8	6.86	6.78	6.82
6′	*dd*	1.5, 8	6.67†	6.62	6.72
7′	*dd*	7, 13.5	2.58	2.56	2.60
7′	*dd*	7, 13.5	2.42	2.41	2.44
8′	*dqt*	5, 6.5, 7	2.22	2.19	2.24
9′	*d*	6.5	0.84	0.82	0.84
3′-OMe	*s*		3.86		3.86‡
4′-OMe	*s*	–			3.88‡
3,4-O_2CH_2	*s*		6.02	6.02†	6.02†
3′,4′-O_2CH_2	*s*			5.94	

*Covered by $CHCl_3$ peak.
†Multiplet.
‡Interchangeable assignments.

Table 2. ^{13}C NMR chemical shifts (δ) for diaryldimethyl-*n*-butanone neolignans ($CDCl_3$, 20 MHz)

C	**6a**	**6b**	**6c**	**6e**
1	129.5	128.9	128.1	129.7
2	107.9	107.9	107.7	110.5
3	148.7	148.3	148.1	148.9
4	152.8	151.1	151.5	152.9
5	108.4	108.4	108.3	109.9
6	124.4	124.4	124.2	122.4
7	202.5	201.7	202.0	202.4
8	43.3	43.4	43.0	42.8
9	15.3	15.2	15.2	14.8
1′	132.6	134.7	133.2	134.5
2′	111.8	108.2	111.3	108.0
3′	146.7	147.5	149.0	147.4
4′	144.2	145.9	147.5	145.6
5′	114.4	109.7	112.4	109.4
6′	122.1	122.2	122.6	121.9
7′	37.8	37.9	37.5	37.4
8′	41.5	41.6	41.3	41.2
9′	11.4	11.6	11.2	11.2
OMe	56.0		55.8	55.7
OMe			55.9	55.8
O_2CH_2	101.9	100.9	101.8	100.5
O_2CH_2		101.9		–

length, each of which was extracted with CH_2Cl_2 MeOH. The solvents were evaporated. Residues 1, 2 and 3 were composed of fats. Residues 4, 5 and 6 were submitted separately to prep. TLC on silica gel developed with hexane Me_2CO (9:1) followed by silica gel developed with C_6H_6 EtOAc (4:1) to give **6b** (33 mg), **6c** (34 mg) and **6a** (11 mg). Residue 4 was crystallized from Et_2O to give **4** (65 mg). Residue 8 was purified by prep. TLC (silica gel; C_6H_6-EtOAc, 4:1) to give **5** (98 mg). Residues 9, 10 and 11 were submitted separately to prep. TLC on silica gel developed with $CHCl_3$ Me_2CO (9:1) followed by silica gel developed with C_6H_6 EtOAc (4:1) to give **5** (98 mg) and **1a** (80 mg). Powdered wood (3 kg) was extracted with $CHCl_3$ in a Soxhlet apparatus. The solvent was evaporated. The residue (1.4 g), treated as above, gave **2** (38 mg) and **3** (27 mg).

1,6-Geranylgeranodioic acid (**1a**). Mp 109–112° (MeOH). IR ν_{max}^{KBr} cm^{-1}: 3352–2742 (OH), 1691 (CO), 1656 (C=C); UV λ_{max}^{MeOH} nm: 217 (ε 16 800); ^{1}H NMR (270 MHz, $(CD_3)_2CO$): δ6.77 (*tq*, *J* = 7.0, 1.5 Hz, H-3), 2.32 (*q* (*br*), *J* = 7.5 Hz, 2H-4), 2.05–2.21 (*m*, 2H-5, 2H-8, 2H-9, 2H-12, 2H-13), 5.16 (*m*, H-7, H-11), 5.69 (*q*, *J* = 1.5 Hz, H-15), 1.81 (*d*, *J* = 1.5 Hz, 3H-17), 1.64 (*s*(*br*), 3H-18, 3H-19), 2.15 (*d*, *J* = 1.5 Hz, 3H-20), 2.83 (*s*(*br*), $2CO_2H$); MS *m/z* (rel. int.): $[M]^+$ (absent), 316 (1) $[M - H_2O]^+$, 298 (1) $[316 - H_2O]^+$, 288 (2) $[316 - CO]^+$, 270 (1) $[298 - CO]^+$, 235 (2), 217 (3), 213 (1), 189 (4), 181 (3), 178 (45), 164 (11), 163 (5), 162 (28), 161 (5), 150 (8), 149 (35), 135 (19), 122 (11), 121 (41), 107 (16), 105 (9), 95 (29), 93 (61). Methylation of **1** with diazomethane, followed by purification (silica gel column; C_6H_6 Me_2CO, 17:3) of the reaction product gave the *dimethyl ester* **1b**, oil. IR ν_{max}^{KBr} cm^{-1}: 1720 (CO), 1653 (C=C). ^{1}H NMR (270 MHz, $CDCl_3$): δ6.73 (*t*(*br*) *J* = 6.5 Hz, H-3), 2.25 (*q*, *J* = 7.5 Hz, 2H-4), 2.13 2.05 (*m*, 2H-5, 2H-8, 2H-9, 2H-12, 2H-13), 5.13 (*m*, H-7), 5.10 (*m*, H-11), 5.67 (*s*(*br*), H-15), 1.83 (*d*, *J* = 1.5 Hz, 3H-17), 1.60 (*s*(*br*), 3H-18, 3H-19), 2.16 (*d*, *J* = 1.5 Hz, 3H-20), 3.37 (*s*, OMe), 3.68 (*s*, OMe); ^{13}C NMR (20 MHz, $CDCl_3$): δ 168.62 (C-16), 167, 23 (C-1), 159.91 (C-14), 142.21 (C-3), 136.07 (C-10), 133.91 (C-6), 127.55 (C-2), 125.11 (C-11), 123.06 (C-7), 115.37 (C-15), 51.57 (MeO-1) 50.67 (MeO-16), 40.95 (C-9), 39.61 (C-5), 38.26 (C-13), 27.40 (C-8), 27.40 (C-12), 26.62 (C-4), 26.03 (C-20), 18.79 (C-18), 16.03 (C-19), 12.39 (C-17); MS *m/z* (rel. int.): $[M]^+$ (absent), 330 (5) $[M - MeOH]^+$, 302 (3) $[330 - CO]^+$, 298 (4), 270 (2), 249 (4), 217 (9), 213 (13), 189 (15), 167 (37), 164 (6), 163 (10), 149 (100), 135 (10), 122 (19), 121 (89), 107 (30), 105 (22), 95 (34), 93 (62), 67 (30).

(7R,8S,8′R)-*7-Hydroxy-3,4,3′,4′-tetramethoxy-8.8′-neolignan* (**5**). For IR, ^{1}H NMR and ^{13}C NMR and MS, see compound **2** in ref. [4]. Additional data: $[\alpha]_D^{22} - 15°$ (*c* 0.704; $CHCl_3$); CD (*c*

0.704; MeOH): $[\theta]^{max}_{290}$ − 1500, $[\theta]^{max}_{275}$ + 2350, $[\theta]^{max}_{252}$ − 150, $[\theta]^{max}_{240}$ + 950.

(8S,8′R)-4′-*Hydroxy-3′-methoxy-3,4-methylenedioxy-7-oxo-8.8′-neolignan* (**6a**). Viscous oil; IR ν^{film}_{max} cm^{-1}: 3447 (OH), 1668 (CO), 1600, 1500, 1456 (Ar); UV λ^{MeOH}_{max} nm: 228, 276, 304 (ε 31 300, 18 250, 7600); ^{1}H NMR: see Table 1; ^{13}C NMR: see Table 2; MS *m/z* (rel. int.): 342 (8) $[M]^+$, 178 (100), 164 (97), 149 (20), 137 (26), 135 (7), 121 (16), 91 (14). $[\alpha]^{22}_D$ − 111° (*c* 0.79; MeOH); ORD (*c* 0.79; MeOH): $[\phi]^{pk}_{305}$ + 13 200, $[\phi]^{infl}_{304}$ + 4250, $[\phi]^{pk}_{283}$ + 6650, $[\theta]_{265}$ 0, $[\phi]^{tr}_{245}$ − 4400, $[\phi]^{infl}_{235}$ − 2750, $[\phi]^{tr}_{228}$ − 7900, $[\phi]_{217}$ 0, CD (*c* 0.79; MeOH): $[\theta]^{max}_{303}$ + 4100, $[\theta]^{infl}_{290}$ + 1300, $[\theta]^{max}_{276}$ + 6000, $[\theta]^{max}_{245}$ − 7600, $[\theta]^{infl}_{235}$ − 2000, $[\theta]^{max}_{225}$ − 4900.

(8S,8′R)-3,4,3′,4′-*Dimethylenedioxy-7-oxo-8.8′-neolignan* (**6b**). Viscous oil; IR ν^{film}_{max} cm^{-1}: 1682 (CO), 1609, 1489, 1445 (Ar); UV $\lambda\nu^{MeOH}_{max}$ nm: 229, 276, 305 (ε 33 500, 17 550, 7050); ^{1}H NMR: see Table 1; ^{13}C NMR: see Table 2; MS *m/z* (rel. int.): 340 (2) $[M]^+$, 178 (100), 162 (91), 149 (17), 135 (26), 121 (10), 91 (6); $[\alpha]^{22}_D$ + 88 (*c* 0.82; MeOH); ORD (*c* 0.82; MeOH): $[\phi]^{pk}_{306}$ + 12 400, $[\phi]^{infl}_{294}$ + 6900, $[\phi]^{pk}_{285}$ + 8250, $[\phi]_{260}$ 0, $[\phi]^{tr}_{242}$ − 6600, $[\phi]^{infl}_{234}$ 1800, $[\phi]^{tr}_{228}$ − 4400, $[\phi]_{218}$ 0. CD (*c* 0.82; MeOH): $[\theta]^{max}_{305}$ + 5600, $[\theta]^{infl}_{288}$ + 1200, $[\theta]^{max}_{276}$ + 5950, $[\theta]^{max}_{242}$ − 6700, $[\theta]^{infl}_{236}$ − 2050, $[\theta]^{max}_{225}$ − 5950.

(8S,8′R)-3′,4′-*Dimethoxy-3,4-methylenedioxy-7-oxo-8.8′-neolignan* (**6c**). Viscous oil; IR ν^{film}_{max} cm^{-1}: 1672 (CO), 1607, 1503, 1459 (Ar); UV λ^{MeOH}_{max} nm: 229, 275, 304 (ε 33 350, 19 950, 7950); ^{1}H NMR: see Table 1; ^{13}C NMR: see Table 2; MS *m/z* (rel. int.): 356 (2) $[M]^+$, 178 (100), 151 (19), 149 (18), 135 (6), 121 (12), 91 (8); $[\alpha]^{22}_D$ + 118 (*c* 0.53; MeOH); ORD (*c* 0.53; MeOH): $[\phi]^{pk}_{305}$ + 9400, $[\phi]^{infl}_{295}$ + 8350, $[\phi]^{pk}_{287}$ + 8750, $[\phi]_{266}$ 0, $[\phi]^{tr}_{245}$ − 5800, $[\phi]^{infl}_{233}$ − 3350, $[\phi]^{tr}_{227}$ − 5800, $[\phi]_{217}$ 0. CD (*c* 0.53; MeOH): $[\theta]^{max}_{301}$ + 5050, $[\theta]^{infl}_{290}$ + 4200, $[\theta]^{max}_{276}$ + 5900, $[\theta]^{max}_{245}$ − 5450, $[\theta]^{infl}_{235}$ − 2000, $[\theta]^{max}_{226}$ − 9700.

(8S,8′R)-3,4,3′,4′-*Tetramethoxy-7-oxo-8.8′-neolignan* (**6d**). To a soln of CrO_3 (2.7 g) in H_2O (10 ml) conc H_2SO_4 (2.3 ml) was added. The reagent was added dropwise to a soln of **5** (15 mg) in Me_2CO (max temp. 20°) until it took on a persistent yellow-brown colour. The reaction mixture was poured into H_2O and the mixture extracted with $CHCl_3$. The $CHCl_3$ layer was dried (anhydrous Na_2SO_4) and the solvent evaporated. The residue was purified by prep. TLC (silica gel; C_6H_6-EtOAc, 4:1) to give **6d** (11.7 mg), viscous oil. IR ν^{film}_{max} cm^{-1}: 1670, 1602, 1506, 1460, 1409, UV λ^{MeOH}_{max} nm: 229, 275, 304 (ε 33 600, 19 450, 7700); ^{1}H NMR (60 MHz, CCl_4): δ 6.85–7.25 (*m*, H-2, H-6), 6.27–6.55 (*m*, H-5, H-2′, H-5′, H-6′), 3.70 (*s*, 2 × OMe), 3.67 (*s*, 2 × OMe), 2.90–3.40 (*m*, H-8), 1.48–2.57 (*m*, 2H-7′, H-8′), 1.02 (*d*, *J* = 7 Hz, 3H-9), 0.78 (*d*, *J* = 6 Hz, 3H-9′); MS *m/z* (rel. int.): 372 (5) $[M]^+$, 194 (100), 178 (99), 165 (30), 151 (23), 137 (10), 135 (4), 121 (4), 107 (17), 91 (8); $[\alpha]^{22}_D$ + 83° (*c* 0.90; MeOH); ORD (*c* 0.90; MeOH): $[\phi]^{pk}_{305}$ + 8850, $[\phi]^{infl}_{295}$ + 8200, $[\phi]^{pk}_{285}$ + 8350, $[\phi]_{264}$ 0, $[\phi]^{tr}_{247}$ − 6750, $[\phi]^{infl}_{231}$ − 1900, $[\phi]^{tr}_{224}$ − 5200, $[\phi]_{215}$ 0. CD (*c* 0.90; MeOH): $[\theta]_{303}$ + 3400, $[\theta]^{infl}_{290}$ + 2550, $[\theta]^{max}_{278}$ + 5900, $[\theta]^{max}_{245}$ − 6300, $[\theta]^{infl}_{235}$ − 2100, $[\theta]^{max}_{225}$ − 5000.

(7S,8S,8′R)-3,4,3′,4′-*Tetramethoxy-7.6′,8.8′-neolignan* (**10**). To compound **5** (15 mg) in CH_2Cl_2 (3 ml), *p*-toluenesulphonic acid (1 mg) in CH_2Cl_2 was added. The soln was kept for 1 hr at room temp., and then, after the addition of more CH_2Cl_2, was neutralized with aq. $NaHCO_3$. The organic layer was dried ($MgSO_4$), filtered and evaporated. Recrystallization of the residue from Et_2O gave **10** (13.3 mg), mp 128–130°, lit. mp 132.8–133.6° [10]. IR ν^{KBr}_{max} cm^{-1}: 1593, 1474 (Ar), 774; UV λ^{MeOH}_{max} nm: 230, 281 (ε 19 650, 6920); MS: see ref. [13]; ^{1}H NMR (60 MHz, CCl_4): δ 6.47, 6.18, 5.89 (each *s*, respectively 2, 2 and 1 aromatic protons), 3.67, 3.63, 3.39 (each *s*, respectively 1, 2, 1 OMe), 3.25 (*d*, *J* = 9 Hz, H-7′), 1.65–1.30 (*m*, 2H-8, 8′), 2.63 (*d*, *J* = 7 Hz, 2H-7), 1.02 (*d*, *J* = 5 Hz, 3H-9), 0.80 (*d*, *J* = 5 Hz, 3H-9′); $[\alpha]^{22}_D$ − 15° (*c* 0.80; MeOH), lit. [10] − 8.5; ORD (*c* 0.80; MeOH): $[\phi]_{314}$ 0, $[\phi]^{tr}_{288}$ − 14 900, $[\phi]_{280}$ 0, $[\phi]^{pk}_{268}$ + 17 150, $[\phi]^{tr}_{246}$ + 5550, $[\phi]^{infl}_{240}$ − + 6250. CD (*c* 0.80; MeOH): $[\theta]^{max}_{282}$ − 8450, $[\theta]^{max}_{271}$ + 5550, $[\theta]^{max}_{247}$ − 1800, $[\theta]^{max}_{235}$ + 8700.

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