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SESQUITERPENOID EMMOTINS FROM TWO *PORAQUEIBA* SPECIES*

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Key Word Index—*Poraqueiba guianensis*; *P. paraensis*; Icacinaceae; secoiridoids; sesquiterpenes; triterpenes; lignans; structure elucidation.

Abstract—The phytochemical examination of the trunkwood of *Poraqueiba guianensis* afforded two novel emmotins, emmotin-Z [(2*R*, 3*S*)-2,6-dihydroxy-3-(2′-hydroxyisopropyl)-5-formyl-8-methyl-1,2,3,4-tetrahydronaphthalene] and its 6-*O*-methyl ether, two known seco-iridoids, secologanoside and its methyl ester, both of them obtained as natural products in their pure form, a new triterpenoid acid, icacinic acid reported elsewhere, and a rare lignan, 1-hydroxypinoresional, along with sitosterol, its 3-*O*-β-D-glucoside and glucose. Emmotin-Z was also isolated from *P. paraensis*, besides pinoresinol.

INTRODUCTION

The systematic position of the family Icacinaceae is controversial, having been placed in different positions by different authors [1]. It is a pantropical family and its centre of distribution in the New World is in the upper Amazon basin of Brazil. In the course of a systematic investigation of the Brazilian Icacinaceae, we have examined the trunkwood composition of *Emmotum nitens* (Benth.) Miers [2–6], *E. fagifolium* Desv. [7], *E. orbiculatum* (Benth.) Miers and *E. glabrum* Bentham ex. Miers [8]. Rearranged eudesmane sesquiterpenes with a 1,4-dimethyl-7-isopropyl decalin skeleton, named emmotins, were consistently found in all the analysed species. *Emmotum* Desv. and *Poraqueiba* Aubl. are botanically recognized as closely related genera [9, 10].

In addition to the previously reported triterpene, icacinic acid [11], the present paper deals with the chemical examination of the trunkwoods of two Brazilian *Poraqueiba* species, *P. guianensis* Aubl. and *P. paraensis* Ducke and the structure elucidation of two novel emmotins.

RESULTS AND DISCUSSION

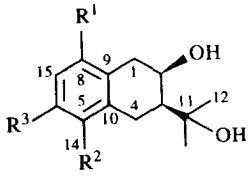
Extensive fractionation of the trunkwood ethanolic extract of *P. guianensis* afforded as major constituents two seco-iridoids: secologanoside and its methyl ester, both obtained in their pure forms from a different natural source, to that described in the previous report [12]. Their identification relied on comparison of their physical and spectral data with those previously reported [12], as well as with authentic samples. NMR data with complete assignment of the protons and carbons are presented. The two seco-iridoids, and the other known compounds, sitosterol, its 3-*O*-β-D-glucoside, glucose and two lignans, pinoresinol and its rare 1-hydroxy derivative, were obtained, together with two novel sesquiterpenoid emmotins (**1** and **2**). The benzene extract of *P. paraensis* furnished pinoresinol and emmotin Z (**1**).

1-Hydroxypinoresinol (**3**) ($[M]^+$ *m/z* 374, $C_{20}H_{22}O_7$) was characterized by its 100 MHz ^{1}H NMR spectrum, which showed a pattern of signals related to that described for α, α-3, 7-dioxobicycle-[3, 3, 0]-octane lignans [13], exhibiting oxygenation at C-1 [δ 3.0–3.3 (*m*, H-5), 3.7–4.0, (*m*, H-4α), 4.10 (*d*, *J* = 9.0 Hz, H-8β), 4.23 (*d*, *J* = 9.0 Hz, H-8α), 4.50 (*t*, *J* = 8.0 Hz, H-4β), 4.88, (*s*, H-2), 4.90, (*d*, *J* = 4.0 Hz, H-6)]. A negative Gibbs test confirmed the location of the hydroxyl groups at the *para*-positions of the aromatic rings [14–16].

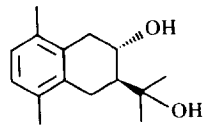
A close structural relationship between the sesquiterpenes **1** and **2** was revealed by UV and IR spectra which indicated the presence of an aryl carbonyl moiety (**1**; ν_{max} 1630 cm^{-1}, λ_{max}: 261, 353 nm; **2** ν_{max} 1670 cm^{-1}, λ_{max}: 274, 334 nm). The molecular formulae (**1**: $C_{15}H_{20}O_4$; **2**: $C_{16}H_{22}O_4$) were deduced from HRMS and EIMS, respectively, showing a difference of one CH_2 unit between them. A combination of one- and two-dimensional ^{1}H and ^{13}C NMR spectra was used for structure determination.

The 250 and 600 MHz ^{1}H NMR spectra of **1** and **2** showed signals corresponding to one aromatic proton [**1**: δ 6.68, (*s*) **2**: δ 6.72, (*s*)]; one aldehydic proton [**1**: δ 10.42,

*Part 2 in the series 'Chemistry of Brazilian Icacinaceae'. For Part 1, see ref. [1].



	R^1	R^2	R^3
1	Me	CHO	OH
2	Me	CHO	OMe
4	Me	Me	H
6	Me	Me	OH



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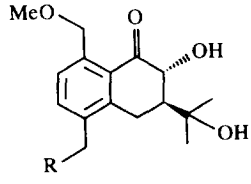
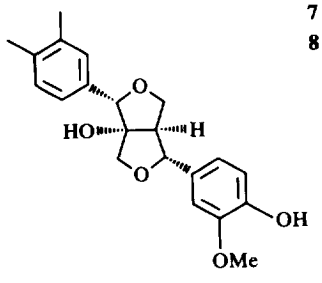


	R
7	H
8	OH



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(*s*): **2**: 10.64, (*s*)]; one methyl group in an aromatic ring [**1**: δ2.24, (*s*), **2**: 2.29, (*s*)] and one 2-hydroxyisopropyl group [**1**: δ1.38 (3H, *s*), 1.49 (3H, *s*); **2**: 1.40 (3H, *s*), 1.46 (3H, *s*)]. A chelated hydroxyl proton singlet (δ12.12) for **1** was replaced in the spectrum of **2** by a single (δ3.88) due to a methoxyl group, clearly showing that **2** was the *O*-methyl ether of **1**. The other signals, besides those of three hydroxyls, exchanged in the presence of D_2O, and were represented by three double doublets, two doublets and one broad signal (see Experimental). ^{13}C-{^1H} and DEPT NMR spectra confirmed the presence of six quaternary, three tertiary and two secondary carbons and three methyl groups (see Experimental). The chemical shifts and coupling patterns, close to those described for (+)-rishitinol (**4**) [δ_{H-2} 4.75 (1H, *br s*, $W_{1/2}$ = 8 Hz); δ_{H-1} 2.5–3.0 (2H, *m*); δ_{H-3} 1.55–1.87 (1H, *m*)] [17], led to the location of the hydroxyl and 2-hydroxyisopropyl groups in emmotin-Z, at positions C-2 and C-3, respectively, in a *cis*-relative configuration. COSY experiments clearly showed couplings between H-2, 2 H-1 and H-3, that were not evident in the first-order analysis of the ^1H NMR spectrum [δ_{H-2} 4.76 (1H, *br s*, $W_{1/2}$ = 7.6 Hz); δ_{H-1} 2.69, (*d*, $J_{1\alpha,1\beta}$ = 17.0 Hz), 2.84 (*d*, $J_{1\beta,1\alpha}$ = 17.0 Hz); δ_{H-3} 1.67, (*dd*, $J_{3,4\beta1}$ = 12.5 Hz, $J_{3,4\alpha}$ = 6.0 Hz)]. In the *trans*-configuration, in 2-epi-rishitinol (**5**) δ_{H-2} 4.12, (1H, *td*, *J* = 10.0, 10.0, 6.0 Hz); δ_{H-1} 2.1–2.8 (*m*), 2.60, (*dd*, $J_{1\alpha,1\beta}$ = 16.0 Hz, $J_{1\alpha,2\beta}$ = 6.0 Hz); δ_{H-3} 1.94, (*ddd*, $J_{3\alpha,4\beta}$ = 12.0 Hz, $J_{3\alpha,4\alpha}$ = 6.0 Hz, $J_{3\alpha,2\beta}$ = 10.0 Hz)] [3], the H-2 signal appeared as a *ddd*, as shown, with much larger $W_{1/2}$. The benzenoid ring substituents (CHO, Me, OH), in **1**, were located initially on the assumption that it should have the typical skeleton of the emmotins, previously described from other Icacinaceous species of the genus *Emmotum* [2–8] and, secondly, on the first-order analysis of the signals due to the two groups of methylene benzylic protons at C-1 and C-4. Of these two groups, the one that produced signals at lower δ values [δ2.69 and 2.84 (*d*, *J* = 17.0 Hz)] did not show any coupling, a feature that is indicative of equatorially located vicinal protons. Clearly this equatorial methine proton was the one at C-2, since in a more stable *cis*-conformation, the hydroxyl group must be axial, leaving the hydroxyisopropyl group at C-3 in an equatorial position. This less deshielded methylene group corresponds, then, to protons at C-1. Therefore, the aromatic methyl group must be located at C-8 and the formyl group at C-5. Moreover, the C-4 methylene proton signal [δ3.27 (*dd*, *J* = 17.0 and 6.0 Hz), 3.39, (*dd*, *J* = 17.0 and 12.5 Hz)] revealed the expected deshielding effect of the CHO group at C-5 and showed coupling constants that confirmed the axial position of the vicinal H-3. Additional data confirming the above observations were obtained from the NOESY spectrum (600.13 MHz), which indicated the following inter-proton contacts: δ4.76 (H-2) → 1.38 (Me), 1.67 (H-3), 2.69 (H-1) and 2.84 (H-1); δ3.27 (H-4) and 3.39 (H-4) → 1.38 (Me), δ1.67 (H-3); δ2.24 (Me-15) → 2.69 (H-1), 2.84 (H-1) and 6.68 (H-7); and finally δ1.67 (H-3) → δ2.69 (H-1).

The assignments of the carbon signals were based on DEPT 90 and 135 spectra as well as by comparison with data for tetralins [18, 19]. The following two features deserve comments. Overlapping of signals due to one methyl (C-15, δ20.8) and one methylene (δ20.9) group was clarified by the DEPT 135 spectrum. Of the two benzylic methylene groups, the deshielded one (δ35.0) was assigned to C-1 due to the β-effect of the hydroxyl group, while the shielding of C-4 (δ20.9) was due almost exclusively to its *ortho*-relationship to the formyl group, as can be deduced from comparison with the δ values in emmotin-A (**7**) (δ_{C-4}; 29.0) and emmotin-B (**8**) (δ_{C-4}: 26.9) [2].

Upon catalytic reduction conditions, (+)-emmotin-Z (**1**) underwent hydrogenolysis, giving (+)-6-hydroxyrishitinol (**6**) which possessed ^1H NMR data similar to those reported for (+)-rishitinol (**4**) [17]. The diamagnetic shift observed for the methylene protons at C-4 was approximately 0.5 ppm.

The absolute configuration of the emmotins was not established. It is reasonable to assume that **1** and **2** have, at C-3, the absolute configuration that is common to the tetralin emmotins [2, 3], corresponding to *S* in the case of the 2-hydroxytetralins. If the configuration at C-3 is assumed, and taking into account the *cis*-relationship between the substituents at C-2 and C-3, as revealed by the ^1H NMR data, the configuration at C-2 must therefore be *R*.

This phytochemical examination of *Poraqueiba* species may provide additional support for Dalghren's systematic allocation of Icacinaceae in Cornales [20], since

it revealed the occurrence of monoterpenoid iridoids, a biogenetic group used as chemical markers for this superorder and previously found in other species of this family [1].

Another significant piece of chemosystematic information arising from this study is support for the close botanical relationship between the two genera *Poraqueiba* and *Emmotum*, with the finding of the rearranged eudesmane sesquiterpenoid emmotins exclusively in them, out of the 10 chemically investigated genera of the Icacinaceae [1].

EXPERIMENTAL

General. ^{1}H NMR were recorded at 100, 250 and 600.13 MHz at the University of Paris-Sud (Orsay-France) and ULIRS (Queen Mary and Westfield College, London, U.K.). The measurements were made in $CDCl_3$, using Bruker AM 250 and Bruker AMX 600 instruments, with ^{13}C measurements obtained at 150.92 MHz. TMS was used in most of the cases as int. standard. TLC spots were visualized by 25% ceric sulphate soln in H_2SO_4 and heating at 100°. UV spectra were recorded in EtOH $-H_2O$ (9:1) and IR in KBr discs. All the Sephadex LH-20 columns were run by MeOH.

Plant material. Poraqueiba guianensis and *P. paraensis* were collected near Manaus, Amazon State and Belém, Pará State, respectively. Voucher specimens are deposited at the INPA herbarium, Manaus, under the registry numbers 9586 and 259, respectively.

Extraction and isolation. Dried, bark free, ground trunkwoods of *P. guianensis* (13 kg) and *P. paraensis* (6.7 kg) were exhaustively extracted with EtOH and C_6H_6, respectively and the extracts evapd to dryness under red. pres. The residue obtained from *P. guianensis* was then extracted, exhaustively with EtOAc, yielding an extract (85.7 g) that was chromatographed on a silica gel column. Elution employed mixts of solvents of increasing polarity: C_6H_6, C_6H_6–$CHCl_3$, $CHCl_3$, $CHCl_3$–EtOAc, EtOAc and EtOAC–MeOH in different proportions and gave 8 main frs: F-1 (7.55 g, C_6H_6, C_6H_6–$CHCl_3$); F-2 (1.16 g, $CHCl_3$); F-3 (2.66 g, $CHCl_3$–EtOAc, 4:1); F-4 (1.51 g, $CHCl_3$–EtOAc, 3:7); F-5 (36.26 g, EtOAc); F-6 (5.70 g, EtOAC); F-7 (15.03 g, EtOAc–MeOH, 19:1); F-8 (7.39 g, MeOH). Extended purification gave sitosterol (0.590 g) from F-1, a mixture of olean-12-en-28-oic acid hydroxyl derivatives (0.074 g) from F-2; the emmotins **1** (0.073 g) (Sephadex LH-20 column, crystallized from Me_2CO) and **2** (0.015 g, Sephadex LH-20 column) along with 1-hydroxypinoresinol (0.027 g, Sephadex LH-20 column) from F-3. F-5 was rechromatographed on silica gel column ($CHCl_3$–EtOAc, EtOAC, MeOH) and afforded 3 compounds, eluted by EtOAc, in the following order: sitosterol-β-D-glucoside (0.05 g, recrystallization from MeOH), seco-loganoside methyl ester (Sephadex LH-20 column) and seco-loganoside (Sephadex LH-20, crystallization from EtOAc). From F-6, after rechromatography on silica gel, followed by gel filtration on Sephadex LH-20 column, the two last compounds were again isolated, with a total amount of 0.9 and 15.0 g (0.1% in the trunkwood and 4.1% in the ethanolic extract), respectively. Icacinic acid [11] (0.150 g) was also obtained from F-6. The more polar fr. (F-8) was rechromatographed on silica gel and D-(+)-glucose (1.50 g) was isolated, after elution with EtOAc–MeOH (49:1) and successive washings with $CHCl_3$.

The benzene extract of *P. paraensis* (42.0 g) was chromatographed on a silica gel column, employing C_6H_6, $CHCl_3$ and MeOH in mixts of increasing polarity. After gel permeation of Sephadex LH-20 column, two compounds were obtained: pinoresinol (0.029 g, C_6H_6–$CHCl_3$, 9:1) and emmotin-Z (0.026 g, C_6H_6–$CHCl_3$, 1:1).

Secologanoside or secoxyloganin. Amorphous powder, mp 143–144° (dry Me_2CO–Et_2O); IR ν_{max} cm^{-1}: 3480, 3320, 2930, 1720, 1700, 1640, 1260, 1100, 1080, 1035, 1010, 960, 935, 910, 895, 870, 815, 795, 770. UV λ_{max} nm (log ε): 238 (4.00). CIMS-(isobutane): *m/z*: 458, 447, 433, 419, 405 $[M + 1]^+$. ^{1}H NMR (400 MHz, D_2O): δ2.46 (1H, *dd*, J = 16.0 and 7.3 Hz, H-6), 2.66 (1H, *dd*, J = 16.0 and 6.3 Hz, H-6), 2.76–2.81 (1H, *m*, H-9), 3.14–3.34 (1H, *m*, H-5), 3.31 (1H, *dd*, J = 8.0 and 9.5 Hz, H-2'), 3.40 (1H, *t*, J = 9.5 Hz, H-3' or H-4'), 3.47–3.51 (1H, *m*, H-5'), 3.50 (1H, *t*, J = 9.5 Hz, H-3' or H-4'), 3.71 (3H, *s*, OMe), 3,73 (1H, *dd*, J = 12.5 and 6.0 Hz, H-6'), 3.92 (1H, *dd*, J = 12.5 and 2.2 Hz, H-6'), 4.83 (1H, *d*, J = 8.2 Hz, H-1'), 5.30 (1H, *dd*, J = 10.6 and 1.5 Hz, H-10), 5.34 (1H, *dd*, J = 17.2 and 0.8 Hz, H-10), 5.53 (1H, *d*, J = 5.0 Hz, H-1), 5.69 (1H, *ddd*, J = 17.3, 10.3 and 9.4 Hz, H-8), 7.54 (1H, *d*, J = 1.5 Hz, H-3); ^{13}C NMR (25.2 MHz, D_2O): δ30.4 (*d*, C-5), 37.2 (*t*, C-6), 46.0 (*d*, C-9), 54.1 (*q*, OMe), 63.1 (*t*, C-6'), 71.8 (*d*, C-4'), 74.9 (*d*, C-2'), 77.9 (*d*, C-3' or C-5'), 78.5 (*d*, C-3' or C-5'), 99.0 (*d*, C-1' or C-1), 100.8 (*d*, C-1 or C-1'), 111.0 (*s*, C-4), 123.0 (*t*, C-10), 134.6 (*d*, C-1 or C-1'), 155.2 (*d*, C-3), 171.2 (*s*, C-11), 178.8 (*s*, C-7).

Secologanoside methyl ester. White amorphous solid, mp 142–144°. Acetylation gave the tetra-acetyl derivative, identical to authentic sample obtained from *Mentzelia lindley* [12]. ^{13}C NMR (25.2 MHz, $CDCl_3$): δ27.2 (C-5), 34.0 (C-6), 43.7 (C-9), 51.4 (OMe), 51.7 (OMe), 61.3 (C-6'), 69.3 (C-4'), 72.9 (C-2'), 75.2 and 75.6 (C-3' and C-5'), 96.1 and 98.3 (C-1' and C-1), 108.7 (C-4), 120.4 (C-10), 132.8 (C-8), 152.1 (C-3), 167.3 (C-11), 173.6 (C-7).

1-Hydroxypinoresinol (**3**) [14–16]. Light yellow amorphous powder, mp 106–108°; IR ν_{max} cm^{-1}: 3420, 2940, 1660, 1600, 1520, 1465, 1455, 1380, 1275, 1240, 1210, 1160, 1135, 1060, 1035. UV λ_{max} nm (log ε): 235 (4.40), 286 (4.04), 338 (3.79). $\lambda_{max}^{EtOH+NaOH}$ nm (log ε): 225 (4.57); 229 (4.25); 357 (4.04). EIMS *m/z* (rel. int.): 374 $[M^+]$ (56), 222(26), 207(41), 193(24), 165(51), 164(10), 163(40), 152(74), 151(100), 137(80). ^{1}H NMR (100 MHz, $CDCl_3$): δ1.6–1.9 (1H, *b s*, disappear with D_2O), 3.0–33 (1H, *m*, H-5), 3.7–4.0 (1H, *m*, H-4β), 3.95 (6H, *s*, OMe), 4.10 (1H, *d*, J = 9.0 Hz, H-8β), 4.23 (1H, *d*, J = 9.0 Hz, H-8α), 4.50 (1H, *t*, J = 8.0 Hz, H-4α), 4.88 (1H, *s*, H-2), 4.90 (1H, *d*, J = 4 Hz, H-6), 5.72 (1H, *b s*, disappear with D_2O), 6.8–7.1 (6H, *m*, ArH).

Emmotin-Z (**1**). (2*R*,3*S*)-2, 6-Dihydroxy-3-(2'-hydroxyisopropyl)-5-formyl-8-methyl-1,2,3,4-tetrahydronaphthalene, light yellow needles, mp 190–192°, $[\alpha]^{23}$ = + 44 ($CHCl_3$; c = 0.35); IR ν_{max} cm^{-1}: 3480, 3430, 2980, 1630, 1600, 1575, 1465, 1445, 1315, 1210, 1130. UV λ_{max}

(log ε): 227 s (4.11), 261 (4.27), 353 (3.71). HRMS *m/z* (rel. int.): 264.137 [M^+] (11) (calc. for $C_{15}H_{20}O_4$: 264.157), 246 (11), 211 (21), 203 (40), 189 (58), 188 (100). ^{1}H NMR (600.13 MHz, $CDCl_3$): δ 1.38 (3H, *s*, Me-12), 1.49 (3H, *s*, Me-13), 1.67 (1H, *dd*, *J* = 12.5 and 6.0 Hz, H-3), 2.24 (3H, *s*, Me-15), 2.41 (*br s*, 1H, OH), 2.69 (1H, *d*, *J* = 17.0 Hz, H-1α), 2.84 (1H, *d*, *J* = 17.0 Hz, H-1β), 3.19 (*br s*, 1H, OH), 3.27 (1H, *dd*, *J* = 17.0 and 6.0 Hz, H-4α), 3.39 (1H, *dd*, *J* = 17.0 and 12.5 Hz, H-4β), 4.76 (1H, *br s*, $W_{1/2}$ = 7.6 Hz, H-2), 6.68 (1H, *s*, H-7), 10.42 (1H, *s*, H-14), 12.12 (1H, *s*, ArOH); ^{13}C NMR (150.92 MHz, $CDCl_3$): δ 20.8 (*q*, C-15), 20.9 (*t*, C-4), 28.7 (*q*, C-12 or C-13), 29.3 (*q*, C-13 or C-12), 35.0 (*t*, C-1), 44.4 (*d*, C-3), 64.7 (*d*, C-2), 73.2 (*s*, C-11), 116.0 (*s*, C-5), 117.2 (*d*, C-7), 122.8 (*s*, C-9), 138.1 (*s*, C-8), 148.9 (*s*, C-10), 161.8 (*s*, C-6), 194.5 (*d*, C-14).

6-O-*Methylemmotin-Z* (**2**). (2*R*,3*S*)-2-hydroxy-6-methoxy-3-(2′-hydroxyisopropyl)-5-formyl-8-methyl-1,2,3,4-tetrahydronaphthalene, light yellow gum; IR ν_{max} cm^{-1}: 3400, 2980, 2930, 1670, 1595, 1465, 1415, 1405, 1380, 1365, 1300, 1270, 1260, 1210, 1150, 1105, 1070, 1045, 1030, 915, 880, 840, 805. UV λ_{max} nm (log ε): 223 (4.20), 274 (4.03), 334 (3.62). EIMS *m/z* (rel. int.): 260 [$M - H_2O$]$^+$ (39), 217 (98), 216 (35), 203 (36), 202 (100), 187 (64). ^{1}H NMR (250 MHz, $CDCl_3$): δ 1.40 (3H, *s*, Me-12), 1.46 (3H, *s*, Me-13), 1.58 (1H, *dd*, *J* = 12.5 and 6.0 Hz, H-3), 2.29 (3H, *s*, Me-15), 2.67 (1H, *dd*, *J* = 15.5 and 3.0 Hz, H-1α), 2.89 (1H, *dd*, *J* = 15.5 and 1.5 Hz, H-1β), 3.24 (1H, *dd*, *J* = 17.5 and 12.5 Hz, H-4β), 3.45 (1H, *dd*, *J* = 17.5 and 6.0 Hz, H-4α), 3.88 (3H, *s*, OMe), 5.27 (1H, *m*, $W_{1/2}$ = 9.0 Hz, H-2), 6.72 (1H, *s*, H-7), 10.64 (1H, *s*, H-14).

Catalytic reduction of emmotin-Z. Emmotin-Z (**1**) (0.011 g, 0.04 mmol) was dissolved in EtOH, and submitted to catalytic hydrogenation, in the presence of 10% Pd/C, affording 2,7-dihydroxy-3-(2′-hydroxyisopropyl)-5,8-dimethyl-1,2,3,4-tetrahydronaphthalene (**6**) (0.036 mmol, 90% yield). Amorphous solid, mp 185–187°; IR ν_{max} cm^{-1}: 3430, 2985, 1600, 1465, 1425, 1370, 1305, 1280, 1230, 1205, 1150, 1115, 1090, 1035, 925, 860. EIMS *m/z* (rel. int.): 250 [M]$^+$ (21), 232 (22), 217 (19), 190 (73), 189 (99), 176 (28), 174 (100), 173 (99), 162 (33), 161 (75), 160 (98), 159 (49), 148 (50), 115 (43), 105 (46). ^{1}H NMR (60 MHz, $CDCl_3$): δ 1.34 (3H, *s*, Me), 1.46 (3H, *s*, Me), 1.6–1.9 (1H, *m*, H-3), 2.13 (6H, *s*, Me-5 and Me-8), 2.64–3.00 (4H, *m*, 2 × H-1 and 2 × H-4), 4.6–4.9 (1H, *m*, H-2), 6.50 (1H, *s*, H-6).

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