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BUTANOLIDES AS A COMMON FEATURE OF *IRYANTHERA LANCIFOLIA* AND *VIROLA SURINAMENSIS*

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Key Word Index—*Virola surinamensis* ; *Iryanthera lancifolia* ; Myristicaceae ; butanolides ; aliphatic γ-lactones ; chemotaxonomy.

Abstract—A comparative phytochemical study between pericarps of *Iryanthera lancifolia* and *Virola surinamensis* showed that the first one contains a new pair of epimeric 2-alkenyl-γ-lactones, besides an aryltetralinic lignan and one tocotrienol, while the second species contains the lignans, galgravin and veraguensin, seven juruenolides : juruenolides C, D, F, G and *epi*-juruenolides D, F, G, together with three pairs of epimeric aliphatic 2-alkenyl-γ-lactones. Juruenolide F, *epi*-juruenolides D, F, G and the 2-alkenyl-γ-lactones are new natural compounds.

INTRODUCTION

The Myristicaceae is composed of 18 genera and its species are spread through Asian, African and American tropical forests [1]. Among the species occurring in the Amazon rain forest, 80% belong to *Virola* and *Iryanthera* genera [2]. Ethnopharmacological interest inspired the earlier phytochemical investigations on Myristicaceae, which made it possible to describe the occurrence of lignoids, alkaloids, γ-lactones and flavonoids in species of this family. The γ-lactone polyketides are widely distributed among *Iryanthera* species but restricted to trunk wood [3–7] and fruits [7, 8]. Phytochemical investigation on fruits and wood of *Virola* showed occurrence of lignoids, flavonoids and alkaloids [9] in different tissues, while γ-lactones have been found only in seeds and seedling leaves of *V. surinamensis* [10, 11]. The occurrence of butanolides in *Iryanthera* species and *V. surinamensis* is summarised in Table 1.

The present work deals with the comparative phytochemical investigation of pericarps from *I. lancifolia* and *V. surinamensis* and reports the isolation of one pair of epimeric 2-alkenyl-γ-lactones (**9a**, **10a**), besides lignan **12** and tocotrienol **11** from pericarps of *I. lancifolia* ; the dichloromethane extract of *V. surinamensis* pericarps afforded three pairs of epimeric 2-alkenyl-γ-lactones (**9a–c**, **10a–c**), juruenolides C (**1a**), D (**1b**), F (**1c**), G (**1d**) and *epi*-juruenolides D (**2a**), F (**2b**) and G (**2c**), besides two tetrahydrofuran lignans : veraguensin (**13**) and galgravin (**14**). The aliphatic γ-lactones **9a–c**, **10a–c**, and the juruenolides **1c** and **2a–c** are new natural compounds.

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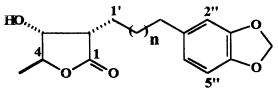
RESULTS AND DISCUSSION

Pericarps of *I. lancifolia* and *V.surinamensis* were collected near Belém, Pará State, Brazil. The isolation procedure for the pericarp constituents of *I. lancifolia* involved chromatographic fractionation on silica gel and successive fractionation by prep. TLC, which yielded **9a**, **10a**, **11** and **12**. The chlorophyll-free dichloromethane fraction from pericarps of *V. surinamensis* submitted to column chromatography and subsequent fractionation by TLC and HPLC afforded **1a–d**, **2a–c**, **9a–c**, **10a–c**, **13** and **14**. Compounds **1a, 1b, 1d**, **11–14** were identified by analyses of spectroscopic data and comparison with those reported in the literature [7, 8, 11].

The γ-lactone moiety of compounds **1a–d**, **2a–c**, **9a–c** and **10a–c** was defined through analysis of their IR (carbonyl absorption at 1750 ± 3 cm^{-1}) and ^{1}H NMR spectra, which showed doublets at δ 1.28 (Me-4) for **1a–d** and **9a–c** and at δ 1.39 (Me-4) for **2a–c** and **10a–c** and a multiplet at δ 4.4 ± 0.8 (H-4). These absorptions, associated with intense peaks at m/z 116 and 129 in the mass spectra for **9a–c** and **10a–c**, indicated the presence of a lactone ring bearing one methyl group and one hydroxyl group. The relative stereochemistries of these five-membered ring lactones

Table 1. Butanolides isolated from different tissues of *Iryanthera* species and *V. surinamensis*

Species	Tissue	Butenolides	References
I. juruensis	Wood	**1d**, **1e**, **1f**, **5a**, **5b**, **6**, **7a**, **7b**, **7c**	3, 6, 7
I. ulei	Wood	**1f**	7
I. elliptica	Wood	**8**	4
I. paraensis	Fruit	**3a**, **3b**, **4a**, **4b**	8
I. grandis	Fruit	**4c**	7
V. surinamensis	Seedling leaf	**1a**	10
	Seed	**1a**, **1b**	11



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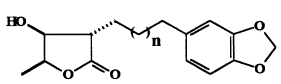
1b n = 7
1c n = 11
1d n = 13
1e n = 17
1f n = 19



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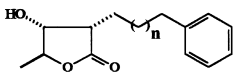

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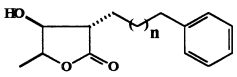

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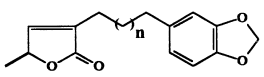

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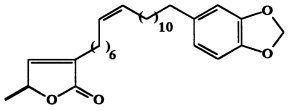

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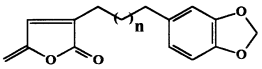

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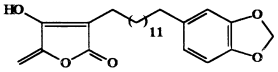

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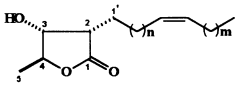

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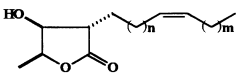
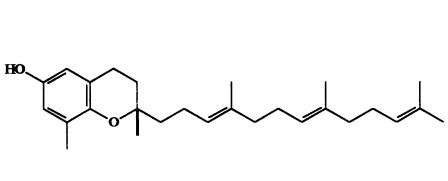
9b n = 7, m = 7
9c n = 9, m = 7



10a n = 5, m = 3
10b n = 7, m =7
10c n = 9, m = 7

determined by ^{13}C NMR analyses are reported in the literature [8, 12]. The chemical shift for the methyl group is δ 13.8 $\pm$ 0.2 when it is *cis* to the hydroxyl group on C-3, and δ 18.0 $\pm$ 0.2, when it is *trans*. The γ-protection of the hydroxyl group is also observable on the ^{13}C signals for C-1′ of the aliphatic chain, which appear at δ 23.2 $\pm$ 0.2 when they are *cis* to each other and at δ 27.8 $\pm$ 0.6 when they are *trans*. Lanthanide-induced shifts and NOE experiments are in agreement with these results [7, 8, 12]. The relative stereochemistries of the isolated lactones **1a–d**, **2a–c**, **9a–c** and **10a–c** were established based on the ^{13}C NMR data (Table 2). Moreover, the ^{1}H NMR and the ^{13}C NMR spectra for the rest of the molecule show absorptions for one piperonyl unit linked to the end of a methylene chain for juruenolides **1a–d** and **2a–**



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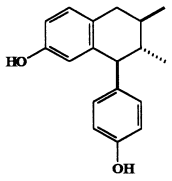

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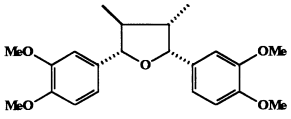

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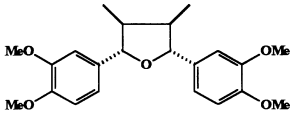

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Table 2. ^{13}C NMR data for juruenolides **1b–d** and **2a–c**, and aliphatic lactones **9a–c** and **10a–c**

	(+)-epimers						(−)-epimers					
δ	**1b**	**1c**	**1d**	**9a**	**9b**	**9c**	**2a**	**2b**	**2c**	**10a**	**10b**	**10c**
C-1	177.4	177.1	177.6	177.1	177.5	178.3	—	177.3	177.4	177.5	177.7	178.7
C-2	43.7	43.7	43.7	43.7	43.7	43.8	49.2	49.2	49.2	49.2	49.3	49.2
C-3	73.7	73.9	73.7	73.9	73.7	73.2	74.1	74.1	74.0	74.1	73.9	73.5
C-4	82.4	82.3	82.5	82.3	82.5	83.0	78.0	78.0	78.3	78.1	78.3	78.9
C-5	18.0	18.0	18.0	18.1	18.0	17.8	13.9	13.8	13.8	13.8	14.0	13.7
C-1′	23.2	23.3	23.2	23.3	23.2	23.1	27.2	27.2	28.4	28.4	28.4	28.3

c; while compounds **9a–c** and **10a–c** lack aromatic absorptions in their ^1H and ^{13}C NMR spectra. Finally, **9a–c** and **10a–c** show, in contradistinction to **1a–d** and **2a–c**, one triplet at δ 5.33 in the ^1H NMR spectra and two peaks at ca δ 129 in the ^{13}C NMR spectra, due to olefinic protons and carbons, respectively, suggesting the presence of an unsaturated aliphatic chain. Analysis of $[M]^+$ peaks in the mass spectra of juruenolides defined the length of the methylene chain (Table 3). The absolute configuration of juruenolides was established by comparison of the $[\alpha]_D$ signals with those reported in the literature [7, 8]. Compound **1c** showed positive values of $[\alpha]_D$ thus the structure is (2*S*,3*R*,4*S*)-3-hydroxy-4-methyl-2-(13′-piperonyl-*n*-tridecyl)-γ-lactone. Compounds **2a–c** showed negative values, thus the structures are (2*S*,3*S*,4*S*)-3-hydroxy-4-methyl-2-(15′-piperonyl-*n*-pentadecyl)-γ-lactone, (2*S*,3*S*,4*S*)-3-hydroxy-4-methyl-2-(13′-piperonyl-*n*-tridecyl)-γ-lactone and (2*S*,3*S*,4*S*)-3-hydroxy-4-methyl-2-(9′-piperonyl-*n*-nonyl)-γ-lactone, respectively. The position of the double bond on the aliphatic chain was determined through analyses of *m*/*z* fragment ions in the mass spectra of epoxidized derivatives, as presented in Fig. 1 and Table 4, and confirm that the structures of **9a–10a**, **9b–10b** and **9c–10c** are derivatives of 9-tetradecenoic acid, 11-eicosenoic acid and 13-docosenoic acid, respectively.

Table 3. Mass spectral data (*m*/*z*) of juruenolides

Juruenolides	$[M]^+$	$[M]^+$-H_2O	$[ArCH_2]^+$
1c ($n = 11$)	418 (30)	—	135 (100)
2a ($n = 7$)	362 (25)	344 (5)	135 (100)
2b ($n = 11$)	418 (25)	400 (3)	135 (100)
2c ($n = 13$)	446 (27)	428 (3)	135 (100)

The biosynthetic proposal for γ-lactone polyketide formation involves condensation of a pyruvoyl unit with the α-methylene of a saturated or unsaturated fatty acid, followed by cyclization to give rise to the lactone ring. The involvement of cinnamyl-CoA during the biosynthetic process leads alternatively to formation of ω-cinnamyl-2-alkyl-γ-lactones (juruenolides), which are the common feature normally found in Myristicaceous species.

Aliphatic γ-lactones are known to occur in species of the Annonaceae [12] and the Lauraceae [13, 14], which are taxonomically closely related to Myristicaceae. Lactones **9a–c** and **10a–c** constitute the first report of aliphatic γ-lactones in a neotropical Myristicaceous species. Earlier studies with pollen morphology of the American Myristicaceous genera had proposed the evolutionary sequence: *Otoba*, *Virola*, *Osteophloeum*, *Compsoneura* and *Iryanthera* [15]. Recent analyses based on pollen morphology suggested that *Virola* and *Compsoneura* are more

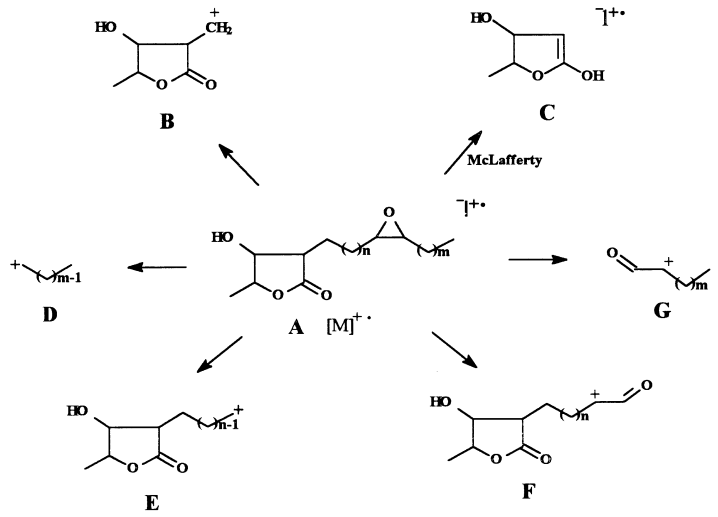

Fig. 1. Proposed fragmentation for the aliphatic γ-lactones.

Table 4. Mass spectral data for epoxidized derivatives of aliphatic γ-lactones

	9a/**10a** *m/z* (rel. int.)	**9b**/**10b** *m/z* (rel. int)	**9c**/**10c** *m/z* (rel. int.)
A	298 (2)	382 (1)	410 (1)
B	129 (73)	129 (96)	129 (90)
C	116 (100)	116 (80)	116 (82)
D	57 (100)	113 (7)	113 (5)
E	199 (3)	227 (2)	255 (2)
F	241 (2)	269 (2)	297 (3)
G	99 (27)	155 (12)	155 (11)

closely related than the other genera [16, 17]. The most recent evolutionary sequence based on the wood anatomy and phylogeny resulted in the sequence: *Compsoneura*, *Otoba*, *Iryanthera*, *Virola* and *Osteophloeum* [18]. Analyses of the chemical composition of *Iryanthera* species often revealed the presence of γ-lactones in different species. The similarity between *Iryanthera* and *Virola* based on the occurrence of γ-lactones is in agreement with the observations on wood anatomy.

EXPERIMENTAL

General

Prep. TLC was carried out on silica gel PF-254 (Merck) and CC on silica gel 60 (40–63 μm) (Merck). ^{1}H (200 MHz) and ^{13}C (50 MHz) NMR were recorded in $CDCl_3$ with TMS as int. standard. EI-MS were obtained at 70 or 20 eV.

Plant material

Pericarps of *I. lancifolia* were collected at Reserva do Gavião (WWF-INPA), near Manaus-AM, Brazil, in 1989 (voucher 141860 MG, Herbarium João Murça Pires, Museu Paraense Emílio Goeldi, Belém-PA). Pericarps of *V surinamensis* (Rol.) Warb. were collected at Combu Island, near Belém-PA, Brazil, in February of 1995 (voucher Lopes-037, SPF-Herbarium of Instituto de Biociências, Universidade de São Paulo, São Paulo-SP).

Extraction and isolation

Air dried powdered pericarps (7 g) of *I. lancifolia* were extracted with $CHCl_3$–MeOH (2 : 1) at room temp. The extract (1 g) was submitted to flash CC over silica gel and afforded 6 pooled frs (A–F). Fr. B (52 mg) was submitted to prep. TLC (C_6H_6–Me_2CO, 4 : 1) and gave **10a** (14 mg) and **11** (3 mg). Prep. TLC (C_6H_6–Me_2CO, 4 : 1) of fr. C (23 mg) gave a mixt. of **9a** and **10a** (10 mg). Prep. TLC (C_6H_6–Me_2CO, 7 : 3) of fr. D (6 mg) gave **12** (4 mg). Air-dried powdered pericarps of *V. surinamensis* (118 g) were extracted with CH_2Cl_2 at room temp. The extract (4.5 g) suspended in 200 ml of MeOH–H_2O (7 : 3) was filtered through Celite. The filtered soln was extracted with hexane (3 × 50 ml), followed by CH_2Cl_2 (3 × 75 ml), and yielded 1.0 g and 1.4 g, respectively. The CH_2Cl_2 extract (700 mg) was submitted to CC on silica gel (150 g) eluted with hexane–EtOAc mixts of increasing polarities and gave 7 pooled frs. These were submitted to prep. TLC on silica gel (C_6H_6–Me_2CO, 9 : 1) and yielded the indicated mixts of diastereomers: fr. B (70 mg): **9a** + **10a** (5 mg), **9b** + **10b** (14 mg), **9c** + **10c** (20 mg); fr. C (190 mg): **1d** + **2c** (120 mg); fr. D (160 mg): **1c** + **2b** (90 mg); fr. E (60 mg): **1b** + **2a** (19 mg); fr. F (120 mg): **1a** (30 mg), **14** (20 mg), **15** (25 mg). Further analyses of these mixts of diastereomers from frs C and D by prep. HPLC (silica gel-60, 250 × 22mm column, hexane–EtOAc, 4 : 1) afforded **1c** (50 mg), **2b** (1 mg), **1d** (70 mg) and **2c** (4 mg). From fr. E, also after prep. HPLC (silica gel-60, 250 × 22 mm column,

hexane–EtOAc, 7 : 3), afforded **1b** (5 mg) and **2a** (2.5 mg).

(2S,3R,4S)-3-*Hydroxy*-4-*methyl*-2-(9′-*piperonyl*-n-*nonyl*)-*butanolide* (**1b**)

$[\alpha]_D = +12^\circ$ (MeOH, $c = 0.10$). ^{13}C NMR (50 MHz, $CDCl_3$): δ 177.4 (C-1), 43.7 (C-2), 73.7 (C-3), 82.4 (C-4), 18.0 (C-5), 23.2 (C-1′), 27.6 (C-2′), 29.1 (C-3′), 29.3, 29.4 (C-4′–C-7′), 31.7 (C-8′), 35.8 (C-9′), 136.9 (C-1″), 107.9 (C-2″), 147.3 (C-3″), 145.2 (C-4″), 108.8 (C-5″), 120.9 (C-6″), 100.6 (O—CH_2—O). For other data, see Ref. [11].

(2S,3R,4S)-3-*Hydroxy*-4-*methyl*-2-(13′-*piperonyl*-n-*tridecyl*)-*butanolide* (**1c**)

$[\alpha]_D = +25^\circ$ (MeOH, $c = 0.40$). EIMS 70 eV, m/z (rel. int.): 418 $[M]^+$ (30), 346 (3), 302 (8), 135 (100).^{1}H NMR (200 MHz, $CDCl_3$): δ 2.51–2.62 (1H, *m*, H-2), 4.12 (1H, *br d*, $J = 5.3$ Hz, H-3), 4.44 (1H, *br q*, $J = 6.6$ Hz, H-4), 1.27 (3H, *d*, $J = 6.6$ Hz, Me-4), 1.69 (2H, *m*, H-1′), 1.35 (22 H, *br*, H-2′–H-12′), 2.44 (2H, *t*, $J = 7.9$ Hz, H-13′), 6.60 (1H, *d*, $J = 1.4$ Hz, H-2″), 6.65 (1H, *d*, $J = 7.8$ Hz, H-5″), 6.53 (1H, *dd*, $J = 1.4$ and 7.8 Hz, H-6″), 5.84 (2H, *s*, O-CH_2-O). ^{13}C NMR (50 MHz, $CDCl_3$): δ 177.1 (C-1), 43.7 (C-2), 73.9 (C-3), 82.3 (C-4), 18.0 (C-5), 23.3 (C-1′), 27.6 (C-2′), 29.1 (C-3′), 29.4, 29.5 (C-4′—C-11′), 31.7 (C-12′), 35.6 (C-13′), 136.8 (C-1″), 107.9 (C-2″), 147.4 (C-3″), 145.3 (C-4″), 108.8 (C-5″), 120.9 (C-6″), 100.6 (O—CH_2—O).

(2S,3R,4S)-3-*Hydroxy*-4-*methyl*-2-(15′-*piperonyl*-n-*pentadecyl*)-*butanolide* (**1d**)

$[\alpha]_D = +27^\circ$ (MeOH, $c = 0.40$). ^{13}C NMR (50 MHz, $CDCl_3$): δ 177.6 (C-1), 43.7 (C-2), 73.7 (C-3), 82.5 (C-4), 18.0 (C-5), 23.2 (C-1′), 27.6 (C-2′), 29.1 (C-3′), 29.4, 29.5 (C-4′—C-13′), 31.7 (C-14′), 35.6 (C-15′), 136.7 (C-1″), 107.9 (C-2″), 147.3 (C-3″), 145.2 (C-4″), 108.8 (C-5″), 120.9 (C-6″), 100.6 (O—CH_2—O). For other data, see Ref. [7].

(2S,3S,4S)-3-*Hydroxy*-4-*methyl*-2-(9′-*piperonyl*-n-*nonyl*)-*butanolide* (**2a**)

$[\alpha]_D = -6.5^\circ$ (MeOH, $c = 0.10$). EIMS 70 eV, m/z (rel. int.): 362 $[M]^+$ (27), 344 (3), 135 (100).^{1}H NMR (200 MHz, $CDCl_3$): δ 2.66 (1H, *m*, H-2), 4.2 (1H, *t*, $J = 4.5$ Hz, H-3), 4.63 (1H, *br q*, $J = 6.5$ Hz, H-4), 1.39 (3H, *d*, $J = 6.5$ Hz, Me-4), 1.72 (2H, *m*, H-1′), 1.25 (14 H, *br*, H-2′—H-8′), 2.51 (2H, *t*, $J = 7.9$ Hz, H-9′), 6.66 (1H, *d*, $J = 1.3$ Hz, H-2″), 6.72 (1H, *d*, $J = 7.8$ Hz, H-5″), 6.62 (1H, *dd*, $J = 1.3$ and 7.8 Hz, H-6″), 5.91 (2H, *s*, O—CH_2—O). ^{13}C NMR (50 MHz, $CDCl_3$): δ 49.2 (C-2), 74.1 (C-3), 78.0 (C-4), 13.9 (C-5), 27.2 (C-1′), 27.9 (C-2′), 29.2, 29.4, 29.6 (C-3′—C-7′), 31.7 (C-8′), 35.7 (C-9′), 136.8 (C-1″), 108.0 (C-2″), 147.4 (C-3″), 145.3 (C-4″), 108.8 (C-5″), 121.0 (C-6″), 100.7 (O—CH_2—O).

(2S,3S,4S)-3-*Hydroxy*-4-*methyl*-2-(13′-*piperonyl*-n-*tridecyl*)-*butanolide* (**2b**)

$[\alpha]_D = -20^\circ$ (MeOH, $c = 0.10$). EIMS 70 eV, m/z (rel. int.): 418 $[M]^+$ (25), 400 (3), 135 (100).^{1}H NMR (200 MHz, $CDCl_3$): δ 2.50 (1H, *m* covered by H-13′, H-2), 4.13 (1H, *t*, $J = 4.5$ Hz, H-3), 4.55 (1H, *br q*, $J = 6.5$ Hz, H-4), 1.33 (3H, *d*, $J = 6.5$ Hz, Me-4), 1.68 (2H, *m*, H-1′), 1.38 (22 H, *br*, H-2′—H-12′), 2.44 (2H, *t*, $J = 7.8$ Hz, H-13′), 6.59 (1H, *d*, $J = 1.3$ Hz, H-2″), 6.65 (1H, *d*, $J = 7.8$ Hz, H-5″), 6.54 (1H, *dd*, $J = 1.3$ and 7.8 Hz, H-6″), 5.84 (2H, *s*, O—CH_2—O). ^{13}C NMR (50 MHz, $CDCl_3$): δ 177.3 (C-1), 49.2 (C-2), 74.1 (C-3), 78.0 (C-4), 13.8 (C-5), 27.2 (C-1′), 28.4 (C-2′), 29.1 (C-3′), 29.3, 29.5 (C-4′—C-11′), 31.7 (C-12′), 35.7 (C-13′), 136.8 (C-1″), 108.0 (C-2″), 147.6 (C-3″), 145.5 (C-4″), 108.8 (C-5″), 121.0 (C-6″), 100.6 (O—CH_2—O).

(2S,3S,4S)-3-*Hydroxy*-4-*methyl*-2-(15′-*piperonyl*-n-*pentadecyl*)-*butanolide* (**2c**)

$[\alpha]_D = -17^\circ$ (MeOH, $c = 0.10$). EIMS 70 eV, m/z (rel. int.): 446 $[M]^+$ (27), 428 (3), 135 (100). ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.51 (1H, *m*, covered by H-15′ signal, H-2), 4.12 (1H, *t*, $J = 4.8$ Hz, H-3), 4.44 (1H, *br q*, $J = 6.5$ Hz, H-4), 1.32 (3H, *d*, $J = 6.5$ Hz, Me-4), 1.57 (2H, *m*, H-1′), 1.17 (26 H, *br*, H-2′—H-14′), 2.43 (2H, *t*, $J = 7.9$ Hz, H-15′), 6.59 (1H, *d*, $J = 1.3$ Hz, H-2″), 6.64 (1H, *d*, $J = 7.9$ Hz, H-5″), 6.54 (1H, *dd*, $J = 1.3$ and 7.9 Hz, H-6″), 5.83 (2H, *s*, O—CH_2—O). ^{13}C NMR (50 MHz, $CDCl_3$): δ 177.4 (C-1), 49.2 (C-2), 74.0 (C-3), 78.3 (C-4), 13.8 (C-5), 28.4 (C-1′), 27.2 (C-2′), 29.1 (C-3′), 29.5 (C-4′–C-12′), 29.4 (C-13′), 31.7 (C-14′), 35.6 (C-15′), 136.8 (C-1″), 107.9 (C-2″), 147.3 (C-3″), 145.2 (C-4″), 108.8 (C-5″), 120.9 (C-6″), 100.6 (O—CH_2—O).

(2S*,3R*,4S*)-2-(*Dodec*-7′-*enyl*)-3-*hydroxy*-4-*methyl*-*butanolide* (**9a**)

EIMS 70 eV, m/z (rel. int.): 282 $[M]^+$ (2), 281 (1), 264 (1), 207 (18), 129 (70), 116 (100), 111 (25), 99 (22), 85 (10), 71 (5), 57 (35). ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.86 (3H, *t*, $J = 6.7$ Hz, H-12′), 1.20 (*brs*, —$(CH_2)_n$—), 1.28 (3H, *d*, $J = 6.5$ Hz, H-5), 1.4–1.6 (2H, *m*, H-1′), 1.9–2.0 (4H, *m*, H-6′, H-9′), 2.4–2.5 (1H, *m*, H-2), 4.1–4.2 (1H, *m*, H-3), 4,45 (1H, *q*, $J = 6.6$ Hz, H-4), 5.33 (2H, *t*, $J = 5.0$ Hz, H-7′, H-8′). ^{13}C NMR (50 MHz, $CDCl_3$): δ 177.1 (C-1), 43.7 (C-2), 73.9 (C-3), 82.3 (C-4), 18.1 (C-5), 23.3 (C-1′), 29.1 (C-2′—C-5′), 27.2 (C-6′), 129.9 (C-7′, C-8′), 27.2 (C-9′), 31.8 (C-10′), 22.6 (C-11′), 14.1 (C-12′).

(2S*,3R*,4S*)-3-*Hydroxy*-4-*methyl*-2-(*octadec*-11′-*enyl*)-*butanolide* (**9b**)

EIMS 70 eV, m/z (rel. int.): 366 $[M]^+$ (2), 348 (2), 129 (57), 116 (100), 111 (23), 99 (36). ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.88 (3H, *t*, $J = 6.7$ Hz, H-18′), 1.23

(*brs*, —$(CH_2)_n$—), 1.32 (3H, *d*, $J = 6.9$ Hz, Me-4), 1.4–1.7 (2H, *m*, H-1′), 1.9–2.1 (4H, *m*, H-6′, H-9′), 2.4–2.6 (1H, *m*, H-2), 4.16 (1H, *d*, $J = 5.3$ Hz, H-3), 4,45 (1H, *q*, $J = 7.3$ Hz, H-4), 5.33 (2H, *t*, $J = 4.5$ Hz, H-7′, H-8′). ^{13}C NMR (50 MHz, $CDCl_3$): δ 177.5 (C-1), 43.7 (C-2), 73.7 (C-3), 82.5 (C-4), 18.0 (C-5), 23.2 (C-1′), 28.3 (C-2′), 28.9, 29.2, 29.3 (C-3′–C-8′, C-11′–C-15′), 129.8 (C-9′, C-10′), 31.8 (C-16′), 22.6 (C-17′), 14.0 (C-18′).

(2S*,3R*,4S*)-2-(*Eicos*-11′-*enyl*)-3-*hydroxy*-4-*methyl*-*butanolide* (**9c**)

EIMS 70 eV, *m*/*z* (rel. int.): 394 $[M]^+$ (3), 376 (2), 129 (88), 116 (100), 111 (23), 99 (30). ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.83 (3H, *t*, $J = 6.7$ Hz, H-20′), 1.21 (*brs*, —$(CH_2)_n$—), 1.28 (3H, *d*, $J = 6.9$ Hz, Me-4), 1.5–1.7 (2H, *m*, H-1′), 1.9–2.0 (4H, *m*, H-6′, H-9′), 2.5–2.6 (1H, *m*, H-2), 4.11 (1H, *d*, $J = 5.5$ Hz, H-3), 4,45 (1H, *q*, $J = 7.0$ Hz, H-4), 5.29 (2H, *t*, $J = 5.0$ Hz, H-7′, H-8′). ^{13}C NMR (50 MHz, $CDCl_3$): δ 178.3 (C-1), 43.8 (C-2), 73.2 (C-3), 83.0 (C-4), 17.8 (C-5), 23.1 (C-1′), 28.3 (C-2′), 28.9 (C-3′), 29.0 (C-4′–C-9′, C-14′–C-17′), 129.7 (C-11′, C-12′), 29.4 (C-10′, C-13′) 31.7 (C-18′), 22.1 (C-19′), 13.9 (C-20′).

(2S*,3S*,4S*)-2-(*Dodec*-7′-*enyl*)-3-*hydroxy*-4-*methyl*-*butanolide* (**10a**)

EIMS 70 eV, *m*/*z* (rel. int.): 282 $[M]^+$ (2), 281 (5), 264 (1), 207 (21), 129 (73), 116 (100), 111 (28), 99 (23), 85 (9), 71 (8), 57 (41). ^{1}H NMR: δ 0.86 (3H, *t*, $J = 6.7$ Hz, H-12′), 1.20 (*brs*, —$(CH_2)_n$—), 1.39 (3H, *d*, $J = 6.5$ Hz, Me-4), 1.4–1.6 (2H, *m*, H-1′), 1.9–2.0 (4H, *m*, H-6′, H-9′), 2.5–2.6 (1H, *m*, H-2), 4.1–4.2 (1H, *m*, H-3), 4.56 (1H, *q*, $J = 6.6$ Hz, H-4), 5.33 (2H, *t*, $J = 5.0$ Hz, H-7′, H-8′). ^{13}C NMR (50 MHz, $CDCl_3$): δ 177.5 (C-1), 49.2 (C-2), 74.1 (C-3), 78.1 (C-4), 13.8 (C-5), 28.4 (C-1′), 29.1 (C-2′—C-5′), 27.1 (C-6′), 129.9 (C-7′, C-8′), 27.1 (C-9′), 31.9 (C-10′), 22.6 (C-11′), 14.1 (C-12′).

(2S*,3S*,4S*) 3-*Hydroxy*-4-*methyl*-2-(*octadec*-11′-*enyl*)-*butanolide* (**10b**)

EIMS 70 eV, *m*/*z* (rel. int.): 366 $[M]^+$ (1), 348 (2), 129 (57), 116 (100), 111 (23), 99 (30). ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.88 (3H, *t*, $J = 6.7$ Hz, H-18′), 1.23 (*brs*, —$(CH_2)_n$—), 1.37 (3H, *d*, $J = 6.9$ Hz, Me-4), 1.4–1.7 (2H, *m*, H-1′), 1.9–2.1 (4H, *m*, H-6′, H-9′), 2.4–2.6 (1H, *m*, H-2), 4.16 (1H, *d*, $J = 5.3$ Hz, H-3), 4,61 (1H, *q*, $J = 6.9$ Hz, H-4), 5.33 (2H, *t*, $J = 4.5$ Hz, H-7′, H-8′). ^{13}C NMR (50 MHz, $CDCl_3$): δ 177.7 (C-1), 49.3 (C-2), 73.9 (C-3), 78.3 (C-4), 13.8 (C-5), 28.4 (C-1′), 28.9 (C-2′), 29.1, 29.3 (C-3′—C-7′, C-12′—C-15′), 129.8 (C-9′, C-10′), 29.2 (C-8′, C-11′), 31.8 (C-16′), 22.6 (C-17′), 14.0 (C-18′).

(2S*,3S*,4S*)-2-(*Eicos*-11′-*enyl*)-3-*hydroxy*-4-*methyl*-*butanolide* (**10c**)

EIMS 70 eV, *m*/*z* (rel. int.): 394 $[M]^+$ (2), 376 (2), 129 (80), 116 (100), 111 (23), 99 (25). ^{1}H NMR (200 MHz, $CDCl_3$): δ 0.83 (3H, *t*, $J = 6.7$ Hz, H-20′), 1.21 (*brs*, —$(CH_2)_n$—), 1.33 (3H, *d*, $J = 6.7$ Hz, Me-4), 1.5–1.7 (2H, *m*, H-1′), 1.9–2.0 (4H, *m*, H-6′, H-9′), 2.5–2.6 (1H, *m*, H-2), 4.11 (1H, *d*, $J = 5.5$, H-3), 4,57 (1H, *q*, $J = 6.7$ Hz, H-4), 5.29 (2H, *t*, $J = 5.0$ Hz, H-7′, H-8′). ^{13}C NMR (50 MHz, $CDCl_3$): δ 178.7 (C-1), 49.2 (C-2), 73.5 (C-3), 78.9 (C-4), 13.7 (C-5), 28.3 (C-1′), 28.5 (C-2′), 28.9 (C-3′), 29.0 (C-4′—C-9′, C-14′—C-17′), 129.7 (C-11′, C-12′), 29.4 (C-10′, C-13′), 31.7 (C-18′), 22.1 (C-19′), 13.9 (C-20′).

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