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IRIDOID GLUCOSIDES FROM *VIBURNUM AYAVACENSE*

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Key Word Index—*Viburnum ayavacense*; Caprifoliaceae; iridoid glucosides; valerosidates; suspensolides; viburtinosides.

Abstract—Nine new iridoid glucosides, all characterized by a β-D-glucopyranosyl moiety linked to the C-11 oxymethylene and either a 3-methylbutyroyl (isovaleroyl) or a 2-methylbutyroyl group at position 1, have been isolated from leaves and branches of *Viburnum ayavacense*, together with three related known compounds. The nine new structures (namely 7,10,2′,3′ tetra-acetylsuspensolide F, 7,10,2′,3′ tetra-acetylisosuspensolide F, 7,10,2′,6′ tetra-acetylisosuspensolide F, 2′,3′ diacetylvalerosidate, 2′,3′ diacetylisovalerosidate, isoviburtinoside II, isoviburtinoside III, isosuspensolide E and isosuspensolide F) have been elucidated by spectroscopic means.

INTRODUCTION

Viburnum spp. are known to possess sedative, spasmolytic and uterus relaxant properties [1–3]. The present study reports on the isolation of 12 iridoid glucosides, nine of which are new, from *Viburnum ayavacense* H. B. et K., an evergreen shrub that grows on the mountains of Ecuador, Peru and Bolivia at an altitude of 2000 to 3000 m [4]. No previous phytochemical works on *V. ayavacense* have been carried out so far, though the isolation of iridoids from many other species of *Viburnum* is reported in the literature [5–11].

RESULTS AND DISCUSSION

The extraction of leaves and young branches of *V. ayavacense* with methanol and preliminary purification of the extract afforded a medium polarity fraction, mainly consisting of a complex mixture of iridoid glucosides, which was concentrated *in vacuo*. After the subsequent addition of water, the resulting solution was extracted with ethyl acetate and *n*-butanol.

The ethyl acetate extract, submitted to column chromatography separation, afforded pure compound **1** and four chromatographic fractions (A–D). Compound **1** proved to be suspensolide A aglucone, a non-glucosidic iridoid already isolated from *Viburnum suspensum* Lindley [7].

The NMR monitoring of fractions A–D showed that each of them was constituted by a pair of isomeric iridoids. Only fraction A showed in addition a third compound in lower amount. All the iridoids were characterized by a β-glucopyranose moiety attached to C-11, and with an oxidation pattern corresponding either to that of suspensolide F [12] or to valerosidate [10, 13]. Each of the above mentioned pairs differed only in the ester group at C-1. Of these, one had a isovaleroyl group, while the other had a 2-methylbutyroyl group. Each pair differed from the other by the nature, number and position of further acylating groups.

Since the isomers of each couple showed almost identical R_fs by TLC analysis, it was impossible to obtain their separation by ordinary chromatographic means. An analogue problem was considered insoluble for the isomeric pairs of iridoid allosides (opulus iridoids I–IV) found in *Viburnum opulus* L. [14].

Each fraction was therefore submitted to countercurrent distribution (CCD) on a Craig–Post apparatus. This approach proved fruitful, allowing separation of the isomers of all the pairs on the basis of the very small polarity difference due to the two methylbutyric units.

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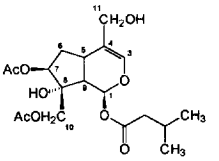

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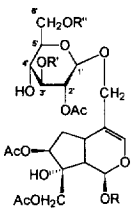
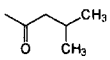
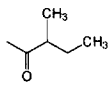
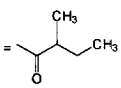
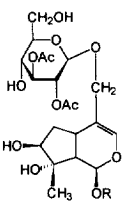
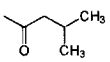


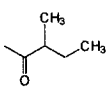
2 R =  ; R' = Ac ; R'' = H

3 R =  ; R' = Ac ; R'' = H

4 R =  ; R' = H ; R'' = Ac



5 R = 

6 R = 

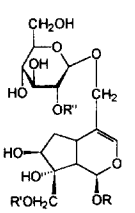
Fraction A yielded the isomeric compounds **2** and **3**, together with the third iridoid glucoside, **4**, a positional isomer of the latter. On the basis of their NMR data, the base structure of suspensolide F [7, 12] was shown for all three products, with small differences directly related to the acylation effects. In particular, the ^{1}H NMR spectrum of compound **2** showed the presence of four acetyl groups (singlets at δ 2.00, 2.02, 2.03 and 2.06) and in addition four low field signals assigned to H-3′, H-7, H-2′ and H-10 (δ 5.07, 5.02, 4.79 and 4.22, respectively). All the data, confirmed by the ^{13}C NMR spectrum (Table 1), allowed **2** to be assigned the structure 7,10,2′,3′ tetra-acetylsuspensolide F. The ^{1}H and ^{13}C NMR spectra of compound **3**, identical to those of **2** except for the signals of a 2-methylbutyroyl moiety, confirmed the structure of **3** to be that shown. We have named it 7,10,2′,3′ tetra-acetylisosuspensolide F by analogy with **2**. Compound **4** differed from **3** only by the lack of the acylating group at C-3′ and the presence of an acetyl group linked to the hydroxyl at 6′ (^{1}H NMR δ 4.26 and 4.41; ^{13}C NMR δ 64.3). Therefore, compound **4** corresponded to 7,10,2′,6′ tetra-acetylisosuspensolide F.

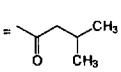
Fraction B yielded the isomeric compounds **5** and **6**, which both presented the characteristics of a diacetylvalerosidate. Comparison of their NMR data with those of valerosidate [5, 13], showed that **5** was 2′,3′-diacetylvalerosidate and by analogy **6** was named 2′,3′-diacetylisovalerosidate.

The isolation of the isomeric compounds **7** and **8** of fraction C, and **9** and **10** of fraction D, proved to be very difficult, due to their very similar chromatographic behaviour. In fact, it was necessary to submit all compounds obtained by CCD separation, to further purification by preparative HPLC (see experimental).

Compound **7** was identified as viburtinoside II, an iridoid glucoside already isolated from *Viburnum tinus* L. [10]. In **7** the iridoid moiety of suspensolide F is esterified at positions 1, 10 and 2′ by a 3-methylbutyroyl, an acetyl and a *trans-p*-coumaroyl, respectively. Compound **8** presented NMR spectra superimposable to those of **7**, except for the presence of the 2-methylbutyroyl group at C-1, and we have therefore named the new iridoid glucoside isoviburtinoside II. Compounds **9** and **10** were very similar to **7** and **8** but both showed signals typical for a *cis-p*-coumaroyl group. Therefore, **9** was viburtinoside III (also reported from *V. tinus* [10]), while **10** was new and by analogy with the above was named isoviburtinoside III.

Unlike the ethyl acetate fraction, the more polar *n*-butanol fraction was characterized by the predominance of less acylated compounds in the 2-methylbutyroyl form. In fact, the simple CC separation of the *n*-BuOH extract allowed the isolation of pure **11** and **12**. Compounds **11** and **12**, corresponding to the isomers of the known suspensolide



7 R =  ; R' = Ac ;
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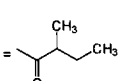
8 R =  ; R' = Ac ;
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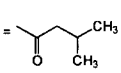
9 R =  ; R' = Ac ;
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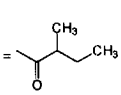
10 R =  ; R' = Ac ;
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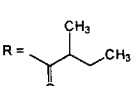
11 R =  ; R' = Ac ; R'' = H

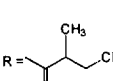
12 R =  ; R' = R'' = H

Table 1. ^{13}C NMR spectral data of compounds **2–6**, **8** and **10–12***

C	**2**	**3**	**4**	**5**	**6**	**8**	**10**	**11**	**12**
1	91.1		91.1	91.6		91.6	91.5	91.7	91.9
3	140.8		140.7	139.6		140.0	140.0	140.0	140.1
4	115.0		114.9	116.2		116.0	115.8	116.4	116.6
5	33.8		33.8	31.8		32.5	32.5	32.9	33.1
6	36.3		36.2	38.0		38.4	38.4	36.1	38.2
7	80.5		80.6	80.8		78.9	78.9	78.5	79.5
8	82.0		81.9	80.9		82.7	82.7	82.8	83.9
9	45.5		45.5	47.9		45.5	45.5	45.4	44.9
10	67.6		67.7	22.8		68.9	68.9	68.7	66.4
11	69.3		69.3	69.9		69.7	69.7	69.5	69.8
1′	99.7		100.1	100.4		101.1	101.2	103.2	103.4
2′	73.1		74.8	73.2		75.2	75.2	74.9	75.1
3′	76.8		75.6	76.8		76.2	76.2	77.6	77.9
4′	69.3		71.2	69.3		71.7	71.7	71.4	71.7
5′	77.3		75.0	77.3		78.0	78.0	77.8	78.1
6′	62.1		64.3	62.1		62.7	62.7	62.6	62.8
$\underline{CH_3}COO$-	20.6		20.7	20.8		20.8	20.8	20.8	
	20.7		20.8	20.8					
	20.7		21.0						
	20.9		21.1						
$CH_3\underline{COO}$-	171.0		171.4	171.4		173.0	173.0	173.1	
	171.4		171.4	172.1					
	171.9		172.3						
	172.3		172.4						
3-methyl-butyroyl									
$(CH_3)_2$	22.5			22.6					
CH	27.5			26.6					
CH_2	44.0			44.1					
COO-	172.6			173.0					
2-methyl-butyroyl									
$\underline{CH_3}$-CH_2		11.6	11.7		11.7	11.7	11.7	11.7	11.7
$\underline{CH_3}$-CH		16.6	16.6		16.5	16.6	16.6	16.6	16.6
CH_2		27.4	27.4		27.5	27.7	27.7	27.6	27.7
CH		41.9	41.9		41.9	42.1	42.1	42.0	42.2
COO-		176.1	176.3		176.6	176.6	176.6	176.5	176.6
p-coumaroyl									
1″						127.2	127.4		
2″, 6″						131.0	133.9		
3″, 5″						116.8	115.5		
4″						160.9	160.9		
α						115.3	115.9		
β						146.7	145.6		
COO-						168.2	168.2		

* The ^{13}C NMR values, from C-1 to $CH_3\underline{COO}$-, in columns **2** and **5** must be considered as common to the two isomers, **3** and **6**, respectively.

E and suspensolide F [12], were named isosuspensolide E and isosuspensolide F, respectively.

The stereochemical assignment for chiral centres (C-7 and C-8 of all the new isolated compounds were confirmed by NOE-difference NMR experiments, whereas the unambiguous confirmation of the acylation sites assignments was obtained by ^1H-^{13}C COLOC experiments.

EXPERIMENTAL

^1H NMR: 500 MHz (the CHD_2OD peak is assigned to δ 3.30); ^{13}C NMR: 125 MHz (the CD_3OD peak is assigned to 49.0 ppm).

Extraction and isolation. The plant material was collected in the district of Aguas Calientes, near Machu Picchu (Peru), at 2200 m of altitude, and ident-

ified by Mrs R. Urrunaga Soria, at the Universidad de S. Antonio Abad (Cuzco), where a voucher specimen is deposited. Specimens of *V. ayavacense* are also deposited in Lima, at the herbarium of the Museo de Historia Natural de la Universidad de S. Marcos (no. 8516). Dry leaves and young branches (250 g) were exhaustively extracted with MeOH at room temp. The extract was concd *in vacuo* to dryness and the residue partitioned between H_2O and cyclohexane to remove chlorophylls. The H_2O phase was furtherly extracted with EtOAc and with *n*-BuOH. The EtOAc extract, up on CC on silica gel with MeOH–$CHCl_3$ (1:9), afforded pure **1** (15 mg) and frs A–D. Fr. A, submitted to counter-current distribution (CCD) on recycling between H_2O–EtOH–EtOAc–cyclohexane (5:2:4:3) in a Craig-Post apparatus (200 stages, 10:10 ml upper and lower phase), yielded pure **2** (130 mg), **3** (260 mg) and **4** (32 mg). Fr. B, submitted to CCD between H_2O–EtOH–EtOAc–cyclohexane (10:4:9:5), gave pure **5** (110 mg) and **6** (250 mg). The CCD sepn, between H_2O–EtOH–EtOAc–cyclohexane (5:2:5:2), afforded compounds **7** and **8** from fr. C, and **9** and **10** from fr. D, in a partially purified form. Compounds **7**–**10** were individually subjected to semi-preparative HPLC purification (on a Bondapak RP-18 column; H_2O–MeCN 7:3 as eluent), allowing isolation of **7** (80 mg), **8** (115 mg), **9** (30 mg) and **10** (63 mg) in pure form. The *n*-BuOH extract, subjected to CC on silica gel with MeOH–$CHCl_3$ (1:4), gave pure **11** (28 mg) and **12** (14 mg).

7,10,2′,3′ *tetra-acetylsuspensolide F* (**2**). Amorphous powder, $[\alpha]_D^{20} = -47.3°$ (MeOH; *c* 5.0); ^{1}H NMR (CD_3OD); δ 0.96 (6H, *d*, *J* = 6.6 Hz, $\underline{Me}_2CHCH_2$-), 1.96-2.12 (2H, *m*, H_2-6), 2.00 (3H, *s*, Ac), 2.02 (3H, *s*, Ac), 2.03 (3H, *s*, Ac), 2.06 (3H, *s*, Ac), 2.15 (1H, *m*, $Me_2\underline{CH}CH_2$-), 2.25 (2H, *d*, *J* = 7.8 Hz, $Me_2CH\underline{CH}_2$-), 2.38 (1H, *dd*, *J* = 5.2 and 6.0 Hz, H-9), 2.92 (1H, *q-shaped m*, H-5), 3.43 (1H, *ddd*, *J* = 2.2, 5.6 and 9.0 Hz, H-5′), 3.57 (1H, *t*, *J* = 9.0 Hz, H-4′), 3.71 (1H, *dd*, *J* = 5.6 and 12.0 Hz, H-6′a), 3.88 (1H, *dd*, *J* = 2.2 and 12.0 Hz, H-6′b), 4.14 (1H, *d*, *J* = 11.6 Hz, H-11a), 4.22 (2H, *bs*, H_2-10), 4.28 (1H, *d*, *J* = 11.6 Hz, H-11b), 4.64 (1H, *d*, *J* = 7.8 Hz, H-1′), 4.79 (1H, *dd*, *J* = 7.8 and 9.0 Hz, H-2′), 5.02 (1H, *m*, H-7), 5.07 (1H, *t*, *J* = 9.0, Hz H-3′), 6.13 (1H, *d*, *J* = 5.2 Hz, H-1), 6.40 (1H, *bs*, H-3). (Found: C, 53.78; H, 6.60. $C_{29}H_{42}O_{16}$ requires C, 53.87; H, 6.55%).

7,10,2′,3′ *tetra-acetylisosuspensolide F* (**3**). Amorphous powder, $[\alpha]_D^{20} = -38.9°$ (MeOH; *c* 5.0); ^{1}H NMR (CD_3OD) (for all values, except those of the methylbutyroyl moiety, see compound **2**): δ 0.92 (3H, *t*, *J* = 7.2 Hz, $\underline{Me}CH_2CH(Me)$-), 1.14 (3H, *d*, *J* = 6.6 Hz, $MeCH_2CH(\underline{Me})$-), 1.50 and 1.67 (1H + 1H, 2*m*, $Me\underline{CH}_2CH(Me)$-), 2.40 (1H, *m*, $MeCH_2\underline{CH}(Me)$-). (Found: C, 53.80; H, 6.62. $C_{29}H_{42}O_{16}$ requires C, 53.87; H, 6.55%).

7,10,2′,6′ *tetra-acetylisosuspensolide F* (**4**). Amorphous powder, $[\alpha]_D^{20} = -24.1°$ (MeOH; *c* 2.2); ^{1}H NMR (CD_3OD): δ 0.90 (3H, *t*, *J* = 7.2 Hz, $\underline{Me}CH_2CH(Me)$-), 1.12 (3H, *d*, *J* = 6.6 Hz, $MeCH_2CH(\underline{Me})$-), 1.50 and 1.67 (1H + 1H, 2*m*, $Me\underline{CH}_2CH(Me)$-), 1.96-2.12 (2H, *m*, H_2-6), 1.98 (3H, *s*, Ac), 2.00 (3H, *s*, Ac), 2.04 (3H, *s*, Ac), 2.05 (3H, *s*, Ac), 2.38 (2H, *m*, $MeCH_2\underline{CH}(Me)$- and H-9), 2.90 (1H, *q*-shaped *m*, H-5), 3.38 (1H, *t*, *J* = 9.0 Hz, H-4′), 3.48 (1H, *m*, H-5′), 3.53 (1H, *t*, *J* = 9.0 Hz, H-3′), 4.08 (1H, *d*, *J* = 11.6 Hz, H-11a), 4.18 (2H, *bs*, H_2-10), 4.26 (2H, *m*, H-11b and H-6′a), 4.41 (1H, *dd*, *J* = 1.2 and 12.0 Hz, H-6′b), 4.49 (1H, *d*, *J* = 7.8 Hz, H-1′), 4.72 (1H, *dd*, *J* = 7.8 and 9.0 Hz, H-2′), 5.02 (1H, *m*, H-7), 6.12 (1H, *d*, *J* = 5.2 Hz, H-1), 6.43 (1H, *bs*, H-3). (Found: C, 53.73; H, 6.60. $C_{29}H_{42}O_{16}$ requires C, 53.87; H, 6.55%).

2′,3′ *diacetylvalerosidate* (**5**). Amorphous powder, $[\alpha]_D^{20} = -24.9°$ (MeOH; *c* 1.0); ^{1}H NMR (CD_3OD): δ 0.95 (6H, *d*, *J* = 6.6 Hz, $\underline{Me}_2CHCH_2$-), 1.37 (3H, *s*, H_3-10), 1.89–2.05 (2H, *m*, H_2-6), 2.02 (3H, *s*, Ac), 2.04 (3H, *s*, Ac), 2.12 (1H, *m*, $Me_2\underline{CH}CH_2$-), 2.25 (2H, *d*, *J* = 7.8 Hz, $Me_2CH\underline{CH}_2$-), 2.38 (1H, *dd*, *J* = 5.2 and 6.0 Hz, H-9), 2.88 (1H, *q*-shaped *m*, H-5), 3.42 (1H *m*, H-5′), 3.58 (1H, *t*, *J* = 9.0 Hz, H-4′), 3.70 (1H, *dd*, *J* = 5.6 and 12.0 Hz, H-6′a), 3.75 (1H, *bs*, H-7), 3.88 (1H, *dd*, *J* = 1.2 and 12.0 Hz, H-6′b), 4.09 (1H, *d*, *J* = 11.6 Hz, H-11a), 4.20 (1H, *d*, *J* = 11.6 Hz, H-11b), 4.62 (1H, *d*, *J* = 7.8 Hz, H-1′), 4.78 (1H, *dd*, *J* = 7.8 and 9.0 Hz, H-2′), 5.05 (1H, *t*, *J* = 9.0 Hz, H-3′), 6.17 (1H, *d*, *J* = 5.2 Hz, H-1), 6.39 (1H, *bs*, H-3). (Found: C, 54.78; H, 7.06. $C_{25}H_{38}O_{13}$ requires C, 54.94; H, 7.01%).

2′,3′ *diacetylisovalerosidate* (**6**). Amorphous powder, $[\alpha]_D^{20} = -19.4°$ (MeOH; *c* 0.6); ^{1}H NMR (CD_3OD) (for all values, except those of the methylbutyroyl moiety, see compound **5**): δ 0.89 (3H, *t*, *J* = 7.2 Hz, $\underline{Me}CH_2CH(Me)$-), 1.12 (3H, *d*, *J* = 6.6 Hz, $MeCH_2(\underline{Me})$-), 1.48 and 1.63 (1H + 1H, 2*m*, $Me\underline{CH}_2CH(Me)$-), 2.37 (1H, *m*, $MeCH_2\underline{CH}(Me)$-). (Found: C, 54.80; H, 7.08. $C_{25}H_{38}O_{13}$ requires C, 54.94; H, 7.01%).

Isoviburtinoside II (**8**). Amorphous powder, $[\alpha]_D^{20} = -23.8°$ (MeOH; *c* 0.4); UV λ_{max} nm (log ε): 311 (4.1), 299 (sh 3.9), 226 (3.0); ^{1}H NMR (CD_3OD): δ 0.88 (3H, *t*, *J* = 7.2 Hz, $\underline{Me}CH_2CH(Me)$-), 1.09 (3H, *d*, *J* = 6.6 Hz, $MeCH_2CH(\underline{Me})$-), 1.46 and 1.60 (1H + 1H, 2*m*, $Me\underline{CH}_2CH(Me)$-), 1.89–2.10 (2H, *m*, H_2-6), 2.02 (3H, *s*, Ac), 2.27 (1H, *dd*, *J* = 4.5 and 9.6 Hz, H-9), 2.34 (1H, *m*, $MeCH_2\underline{CH}(Me)$-), 2.90 (1H, *q*-shaped *m*, H-5), 3.32 (1H, *m**, H-5′), 3.39 (1H, *t*, *J* = 9.0 Hz, H-4′), 3.58 (1H, *t*, *J* = 9.0 Hz, H-3′), 3.70 (1H, *dd*, *J* = 5.4 and 12.0 Hz, H-6′a), 3.88 (1H, *dd*, *J* = 1.8 and 12.0 Hz, H-6′b), 3.90 (1H, *bs*, H-7), 4.07 (1H, *d*, *J* = 11.6 Hz, H-11a), 4.18 (2H, *bs*, H_2-10), 4.22 (1H, *d*, *J* = 11.6 Hz, H-11b), 4.55 (1H, *d*, *J* = 7.8 Hz, H-1′), 4.81 (1H, *dd*, *J* = 7.8 and 9.0 Hz, H-2′), 6.18 (1H, *d*, *J* = 4.5 Hz, H-1), 6.30 (1H, *bs*, H-3), 6.40 (1H, *d*, *J* = 16.3 Hz, H-α), 6.80 (2H, *d*, *J* = 8.0 Hz, H-3″ and H-5″), 7.47 (2H, *d*, *J* = 8.0 Hz, H-2″ and H-6″), 7.64 (1H, *d*, *J* = 16.3 Hz, H-β). (Found: C, 57.59; H, 6.40. $C_{32}H_{42}O_{15}$ requires C, 57.65; H, 6.35%).

* Partially masked by the solvent signal.

Isoviburtinoside III (**10**). Amorphous powder, $[\alpha]_D^{20} = -25.4°$ (MeOH; *c* 0.4); UV λ_{max} nm (log ε): 312 (4.1), 299 (sh 3.9), 226 (3.0); ^{1}H NMR (CD_3OD): δ 0.88 (3H, *t*, $J = 7.2$ Hz, MeCH$_2$CH(Me)-), 1.09 (3H, *d*, $J = 6.6$ Hz, MeCH$_2$CH(Me)-), 1.46 and 1.60 (1H+1H, 2*m*, MeCH$_2$CH(Me)-), 1.89-2.10 (2H, *m*, H$_2$-6), 2.08 (3H, *s*, Ac), 2.33 (2H, *m*, MeCH$_2$CH(Me)- and H-9), 2.84 (1H, *q*-shaped *m*, H-5), 3.32 (1H, *m**, H-5′), 3.39 (1H, *t*, $J = 9.0$ Hz, H-4′), 3.58 (1H, *t*, $J = 9.0$ Hz, H-3′), 3.70 (1H, *dd*, $J = 5.4$ and 12.0 Hz, H-6′a), 3.88 (1H, *dd*, $J = 1.8$ and 12.0 Hz, H-6′b), 3.90 (1H, *bs*, H-7), 4.07 (1H, *d*, $J = 11.6$ Hz, H-11a), 4.18 (2H, *bs*, H$_2$-10), 4.22 (1H, *d*, $J = 11.6$ Hz, H-11b), 4.50 (1H, *d*, $J = 7.8$ Hz, H-1′), 4.81 (1H, *dd*, $J = 7.8$ and 9.0 Hz, H-2′), 5.84 (1H, *d*, $J = 12.0$ Hz, H-α), 6.13 (1H, *d*, $J = 4.5$ Hz, H-1), 6.32 (1H, *bs*, H-3), 6.74 (2H, *d*, $J = 8.0$ Hz, H-3″ and H-5″), 6.87 (1H, *d*, $J = 12.0$ Hz, H-β), 7.68 (2H, *d*, $J = 8.0$ Hz, H-2″ and H-6″). (Found: C, 57.57; H, 6.42. $C_{32}H_{42}O_{15}$ requires C, 57.65; H, 6.35%).

Isosuspensolide E (**11**). Amorphous powder, $[\alpha]_D^{20} = -26.6°$ (MeOH; *c* 1.0); ^{1}H NMR (CD_3OD): δ 0.89 (3H, *t*, $J = 7.2$ Hz, MeCH$_2$CH(Me)-), 1.11 (3H, *d*, $J = 6.6$ Hz, MeCH$_2$CH(Me)-), 1.49 and 1.64 (1H+1H, 2*m*, MeCH$_2$CH(Me)-), 2.04 (2H, *m*, H$_2$-6), 2.07 (3H, *s*, Ac), 2.34 (1H, *dd*, $J = 4.5$ and 9.6 Hz, H-9), 2.38 (1H, *m*, MeCH$_2$CH(Me)-), 3.08 (1H, *q-shaped m*, H-5), 3.21 (1H *dd*, $J = 7.8$ and 9.0 Hz, H-2′), 3.24–3.37 (3H, *m*, H-5′, H-4′ and H-3′), 3.67 (1H, *dd*, $J = 5.3$ and 11.6 Hz, H-6′a), 3.86 (1H, *dd*, $J = 2.0$ and 11.6 Hz, H-6′b), 3.98 (1H, *bs*, H-7), 4.11 (1H, *d*, $J = 11.3$ Hz, H-11a), 4.21–4.31 (4H, *m*, H$_2$-10, H-11b and H-1′), 6.18 (1H, *d*, $J = 4.5$ Hz, H-1), 6.40 (1H, *bs*, H-3). (Found: C, 52.98; H, 7.02. $C_{23}H_{36}O_{13}$ requires C, 53.07; H, 6.97%).

Isosuspensolide F (**12**). Amorphous powder, $[\alpha]_D^{20} = -19.6°$ (MeOH; *c* 1.0); ^{1}H NMR (CD_3OD): δ 0.89 (3H, *t*, $J = 7.2$ Hz, MeCH$_2$CH(Me)-), 1.12 (3H, *d*, $J = 6.6$ Hz, MeCH$_2$CH(Me)-), 1.48 and 1.62 (1H+1H, 2*m*, MeCH$_2$CH(Me)-), 2.00 (2H, *m*, H$_2$-6), 2.34 (1H, *dd*, $J = 4.5$ and 9.6 Hz, H-9), 2.38 (1H, *m*, MeCH$_2$CH(Me)-), 3.04 (1H, *q*-shaped *m*, H-5), 3.21 (1H, *dd*, $J = 7.8$ and 9.0 Hz, H-2′), 3.24–3.37 (3H, *m*, H-5′, H-4′ and H-3′), 3.66 (1H, *dd*, $J = 5.3$ and 11.6 Hz, H-6′a), 3.69 (2H, *m*, H$_2$-10), 3.86 (1H, *dd*, $J = 2.0$ and 11.6 Hz, H-6′b), 4.11 (1H, *d*, $J = 11.3$ Hz, H-11a), 4.27–4.32 (2H, *m*, H-11b and H-1′), 6.13 (1H, *d*, $J = 4.5$ Hz, H-1), 6.36 (1H, *bs*, H-3). (Found: C, 52.60; H, 7.20. $C_{21}H_{34}O_{12}$ requires C, 52.71; H, 7.16%).

* Partially masked by the solvent signal.

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