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SESQUITERPENOID SPIRO COMPOUNDS FROM POTATO TUBERS INFECTED WITH *PHOMA FOVEATA* AND *FUSARIUM* SPP.

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Key Word Index—*Solanum tuberosum*; Solanaceae; potato; *Phoma foveata*; *Fusarium*; sesquiterpenoid; phytoalexin; post-infectional metabolite.

Abstract—The main sesquiterpenoids found in potato tubers infected by the fungi *Phoma foveata* and *Fusarium* spp. were identified as the C-1′ epimers of (2*R*,5*S*,10*R*)-2-(1′,2′-dihydroxy-1′-methylethyl)-6,10-dimethylspiro[4,5]dec-6-en-8-one and their 2′-*O*-β-D-glucopyranosides, by using NMR techniques, conformational analysis, CD measurements and chemical methods. The 1′*S* epimers predominated. The pattern of post-infectional metabolites in the stress zone and mycelia as well as in healthy tuber tissue was monitored by HPLC.

INTRODUCTION

In 1977, four sesquiterpene glucosides were isolated from tobacco [1]. One of them was identified as (1′*S*,2*R*,5*S*,10*R*)-2-(1′,2′-dihydroxy-1′-methylethyl)-6,10-dimethylspiro[4,5]dec-6-en-8-one 2′-*O*-β-D-glucopyranoside (**1a**) or its 1′*R* epimer (**2a**). Both epimers **1a** and **2a** were synthesized from (−)-solavetivone (**3**) via their aglycones (**1b** and **2b**). Unfortunately, no polarimetric data were given, and other physical data were reported only for the aglycones of the glucosides found in tobacco.

In this department, a similar glucoside and its aglycone were later isolated from potato tubers (*Solanum tuberosum* L.) infected by the fungus *Phoma foveata* [2]. The glucoside turned out to be a 4:1 mixture of diastereomers (G1 and G2), each identical to, or a steric isomer of **1a**. The physical data given for the aglycone refer to a similar mixture of diastereomers (A1 and A2). A comparison between the glucosides found in tobacco [1] and potato [2] was further complicated by the use of different solvents in obtaining the ^{13}C NMR spectra of the aglycones.

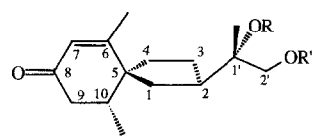
In order to establish their stereochemistry, the compounds G1, A1 and A2 found in potato have now been reinvestigated, using modern chromatographic and spectroscopic techniques. The experimental procedures were also used to isolate other metabolites in the stress zone. These results will be published elsewhere.

RESULTS AND DISCUSSION

In order to simplify the stereochemical discussion and the presentation of the ^1H NMR spectral data (Tables 1–3), the geminal ring hydrogens are labeled β and α according to whether they are *cis* or *trans* relative to a substituent in the same ring.

Both aglycones A1 and A2 and the predominating glucoside G1 were extracted from the stress zone of potato tubers, infected by the fungi *P. foveata* and *Fusarium* spp., and purified by chromatography on silica gel and C_{18} reversed phase columns, and by reversed phase HPLC. The NMR spectral data are listed in Table 1. A complete assignment of all signals was achieved by the use of various H,H- and C,H-COSY techniques, and of NOE difference and HMQC experiments. Cross peaks in the NOESY spectra distinguished H-1β, H-3β and H-4β on the C-1′ side of the cyclopentane ring from H-1α, H-2, H-3α and H-4α on the opposite side. The coupling constants and similar chemical shifts for these protons were checked by iterative computer simulations. H-9α and H-9β were distinguished by the presence of cross peaks between H-1α and H-9α, and between H-9β and Me-10.

Compound A1 ($[\alpha]_D$ −120°) showed the same physical data (λ_{max}, EIMS, ^1H- and ^{13}C NMR) as those reported [2] for the mixture of A1 and A2, except for the specific rotation. The less negative value ($[\alpha]_D$ −55°) in the previous investigation might be due to impurities and to a low sample concentration (*c* 0.1). The coupling constants (*J* 4.8 and 4.4 Hz) between H-10 and the protons at C-9 showed that the cyclohexenone ring is adopting a half-chair conformation with Me-10 predominantly in a pseudoaxial position. Significant NOESY connectivities were observed between H-1β, H-4β and Me-6, and between H-4α and Me-10,



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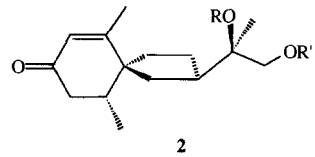

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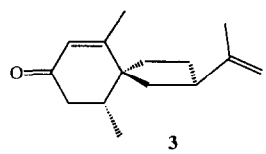
a: R = H, R' = β-D-Glc*p*
b: R = R' = H
c: R = R' = Bz



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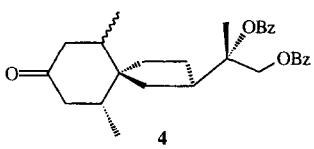

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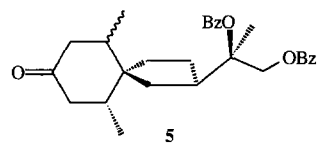

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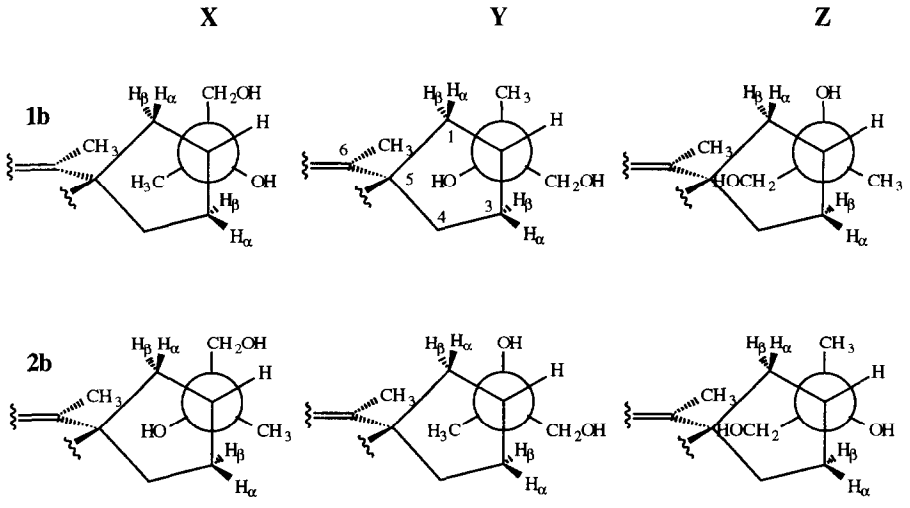
Table 1. NMR spectral data for **1a** (G1)[a] in CD_3OD, and for **1b** (A1) and **2b** (A2) in $CDCl_3$

	δH				J (Hz)				δC		
H	**1a**	**1b**	**2b**	H,H	**1a**	**1b**	**2b**	C	**1a**	**1b**	**2b**
1α	2.04	1.94	1.94	1α,1β	13.3	13.3	13.4	1	37.8	37.0	36.4
1β	1.67	1.59	1.70	1α,2	7.6	7.6	7.8	1′	74.0	73.6	73.7
1′[b]	1.21	1.15	1.19	1β,2	11.5	11.6	11.5	1′[b]	22.5	21.8	22.2
2	2.24	2.12	2.12	2,3α	6.7	3.0	6.0	2	47.4	46.1	46.1
2′a	3.83	3.51	3.50	2,3β	10.0	9.8	9.6	2′	78.0	69.5	69.6
2′b	3.42	3.39	3.41	2′a,2′b	9.8	10.9	10.8	3	28.3	27.5	28.4
3α	1.82	1.78	1.80	3α,3β	12.2	12.2	11.6	4	35.1	34.1	34.0
3β	1.76	1.69	1.61	3α,4α	6.0	6.0	6.0	5	51.4	50.0	50.2
4α	1.69	1.62	1.64	3α,4β	3.8	3.8	3.3	6	170.6	167.1	166.8
4β	1.92	1.85	1.86	3β,4α	9.6	9.6	9.6	6[b]	21.3	21.1	21.3
6[b]	2.00	1.92	1.92	3β,4β	7.0	7.0	7.5	7	125.8	125.6	125.6
7	5.75	5.74	5.74	4α,4β	13.2	13.0	13.2	8	200.2	199.4	199.2
9α	2.74	2.63	2.63	6[b],7	1.2	1.2	1.2	9	43.7	42.9	43.0
9β	2.16	2.17	2.17	9α,9β	17.7	16.8	16.8	10	39.7	38.6	38.8
10	2.16	2.07	2.07	9α,10	5.6	4.8	4.8	10[b]	16.1	16.0	16.1
10[b]	0.98	0.94	0.94	9β,10	4.3	4.4	4.4				
				10,10[b]	6.6	7.0	6.8				

[a] Glucose moiety: δ (H-1) 4.28, J(H-1,H-2) 7.7 Hz, δ(C-1) 105.0, J(C-1,H-1) 160 Hz, and other data typical of β-D-glucopyranosides.
[b] Me.

proving that the *relative* configuration at C-2, C-5 and C-10, was the same as in formulas **1**–**3**.

The enantiomer of **3**, (+)-solavetivone, has apparently never been observed. By contrast, **3** is a well-known stress metabolite in potato and tobacco [1, 3], and closely related glucosides have been found in tobacco [1]. Moreover, the sign of the specific rotation for **1b**, **3** and their stereoisomers, i.e., including A1 and A2, should be governed by the structure and stereochemistry near the enone chromophore rather than by the nature of the remote side-chain at C-2. Accordingly, the sign of $[\alpha]_D$ does not change on selective inversion of the configuration at C-1′ in A1, as will be shown below. For these reasons, and since



Scheme 1. Staggered conformers of **1b** and **2b**, viewed from C-2 towards C-1′.

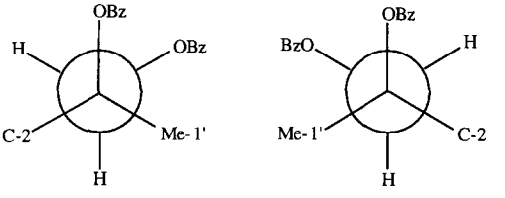
both A1 and **3** are laevorotatory, these compounds have obviously also the same *absolute* configuration at C-2, C-5 and C-10. Hence, A1 is identical with **1b** or **2b**.

The staggered conformers around the C2—C1′ bond in **1b** *or* **2b** are illustrated by Newman projections in Scheme 1. Information about the conformation around this bond in A1 was obtained from its NOESY spectrum. The relative intensities of the cross peaks between Me-1′ and neighboring protons are listed in Table 2. These data show that, on the average, Me-1′ is closer to C-1 and H-2 than to C-3. In Scheme 1, this is the case only for the Y conformer of **1b** and for the Z conformer of **2b**. However, the latter species should be unfavourable due to the crowded position of the bulky hydroxymethyl group. The Y conformer of **1b** should therefore be the most abundant form of A1, indicating that A1 was identical with **1b**.

This conclusion was supported by the use of a method [4] for determining the absolute configuration of chiral glycols from the circular dichroism (CD)

Table 2. NOE connectivities (relative areas of the cross peaks in the NOESY spectrum) between the CH_3-1′ and neighbouring protons for **1b** (A1) and **2b** (A2) in $CDCl_3$

	1b (A1)		**2b** (A2)	
H	δ	Area	δ	Area
1α	1.94	32	1.94	9
1β	1.59	99	1.70	75
2	2.12	73	2.12	76
2′a	3.51	100	3.50	100
2′b	3.39		3.41	
3α	1.78	14	1.80	59
3β	1.69	60	1.61	95



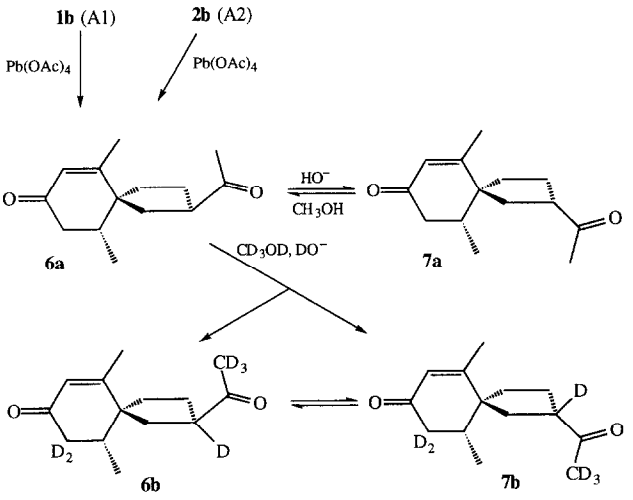
4 **5**

Scheme 2. Most abundant conformers of **4** and **5**, viewed from C-1′ towards C-2′.

spectra of their dibenzoates. Thus, A1 was converted to its dibenzoate (**1c** or **2c**). This was hydrogenated, in order to avoid interference from the enone chromophore. In the most stable conformer of the product (**4** or **5**), the bulky benzoate group at C-2′ is pointing away from the ring system, i.e., the C1′—C2 and C2′—O bonds are antiperiplanar (Scheme 2). According to [4], **4** should then give rise to a positive Cotton effect around 233 nm and **5** to a negative such effect. For the dibenzoate prepared from A1, $\Delta\varepsilon = +0.87$ ($1 \times mol^{-1} \times cm^{-1}$) was observed, confirming that A1 was identical with **1b**.

Compound G1 ($[\alpha]_D - 84°$) was identified as the 2′-*O*-β-D-glucopyranoside of A1 and, hence, as **1a**; the λ_{max} and ^1H NMR data corresponded closely to the data reported [2] for the mixture of G1 and G2. Trifluoroacetic acid hydrolysis yielded D-glucose and an aglycone with data identical with **1b** (TLC, $[\alpha]_D$, ^1H and ^{13}C NMR, EIMS). The anomeric configuration of the glucoside was determined from the NMR spectral data for the anomeric proton and carbon (δ_H 4.28, $^3J_{H,H}$ 7.7 Hz; δ_C 105.0, $^1J_{C,H}$ 160 Hz). The D configuration of the glucose was established by GLC analysis of the derivative obtained by its reaction with (+)-2-butanol, followed by trimethylsilyation [5].

Compound A2 ($[\alpha]_D - 72°$) revealed spectral data



Scheme 3. Chemical proof that A1 and A2 are C-1′ epimers.

(λ_{max}, EIMS, ^{1}H and ^{13}C NMR) very similar to those for A1 (**1b**). The only exceptions were the NMR signals from the C-1 and C-3 regions of the cyclopentane ring; the C-1 and C-3 resonance frequencies were shifted −0.6 and +0.9 ppm, and H-1β and H-3β +0.11 and −0.08 ppm, respectively, in comparison to those of the corresponding signals in the spectra of A1. This implied A1 and A2 to be a diastereomeric pair with different configuration only at C-2 and/or C-1′. Lead tetraacetate oxidation of A1 and A2 (Scheme 3) yielded the same (^{1}H NMR, GLC) methyl ketone **6a**, showing A1 and A2 to have the same configuration at C-2, but opposite configurations at C-1′. Compound **6a** was further treated with ordinary or deuterated methanolic sodium hydroxide, to yield an epimeric mixture of **6a** and **7a**, and **6b** and **7b**. This was done to verify that C-2 epimers, such as **6a** and **7a**, can be distinguished by ^{1}H NMR spectroscopy (Table 3). The NOESY spectra of A1 and A2 revealed similar cross peaks involving Me-6 and Me-10, further confirming that the two compounds had identical ring systems.

Hence A2 was the C-1′ epimer of A1 (**1b**), i.e., **2b**. Accordingly, the data for A2 in Table 2 show that, on average, Me-1′ is closer to H-2 and C-3 than to C-1. In Scheme 1, this is the case only for the X conformer of **2b** and for the unfavourable Z conformer of **1b**, indicating that A2 was identical with **2b**. Moreover, the hydrogenated dibenzoate of A2 showed $\Delta\varepsilon = -0.70$ ($1 \times mol^{-1} \times cm^{-1}$), consistent with formula **5**, and again confirming that A2 is identical with **2b**.

Table 3. ^{1}H NMR chemical shifts (δ) for **6** and **7** in $CDCl_3$

H	6a	6a+7a	6b+7b
1$\alpha\beta$,3$\alpha\beta$,4$\alpha\beta$,10	1.93–2.15 *m*	1.75–2.20 *m*	1.75–2.20 *m*
2	3.04 *m*	3.01–3.11 *m*	—
7	5.79 *d*	5.79 *d*, 5.77 *d*	5.79 *d*, 5.77 *d*
9α	2.64 *dd*	2.64 *dd*, 2.53 *dd*	—
9β	2.22 *dd*	2.20–2.25 *m*	—
1′[a]	2.20 *s*	2.20 *s*	—
6[a]	1.93 *d*	1.93 *d*, 1.96 *d*	1.93 *d*, 1.96 *d*
10[a]	0.99 *d*	0.99 *d*	0.99 *d*

[a] Me.

P. foveata and *Fusarium* spp. are the most prominent fungi responsible for causing dry storage rots of potato tubers. They are difficult to distinguish by visual inspection, and this was therefore done by a chemical method [6]. The ratio between the two fungi in the naturally infected tubers in this study was estimated to 45/55.

According to the results from HPLC analyses, the content of UV absorbing extractives is distinctly different in the stress zone compared to the non-infected tissue located 2 mm beneath this area. The former has a rich content of UV absorbing extractives while the latter is almost free of them. The two major peaks in the stress zone represent **1a** and **1b**, while **2b** is present in much lower amount. In the extractive of the dry mycelia sampled far away (>5 mm) from the stress zone, the most obvious differences compared to the stress zone is the total lack of the glucoside **1a** and the smaller number of peaks in the chromatogram.

EXPERIMENTAL

FAB-MS: positive mode using glycerol as matrix; EIMS: 70 eV; NMR: 600 and 400 (^{1}H) or 101 (^{13}C) MHz using $CDCl_3$ or CD_3OD as solvent and with TMS as internal standard. DEPT, NOE difference spectroscopy, 2D experiments (different H,H-COSY, H,C-COSY, NOESY and HMQC) and spin simulations were carried out with programs available in the Varian (VNMR) software. A mixing time of 0.5 s was used in the NOESY experiments. CD: MeCN at

a conc. of 80 mg/l, and the cuvette length was 1 mm. A 1.0 nm band width and 0.2 nm step resolution were used. Optical rotations were recorded at 20–23°. UV: MeOH.

TLC: silica gel plates, inspected under UV light and sprayed with 50% H_2SO_4. HPLC: Nova-Pak C_{18} Radial-Pak Cartridge (8 × 100 mm) column was used. The mobile phase (mixture by vol of 10 mM phosphate buffer, pH 2.8, and MeCN) consisted of a linear gradient from 5 to 25% MeCN for 30 min followed by a linear gradient to 70% MeCN for 10 min. Conditions were kept constant for another 5 min after which the column was prepared for the next sample by running a 3 min reverse gradient back to initial conditions followed by a 10 min equilibration. For analytical HPLC the flow rate was maintained at 1.5 ml/min and the components were monitored with a diode array detector at 250 nm (50 nm bandwidth), and for semi-prep. HPLC, a 1.0 ml/min flow rate was used and the components were detected with a UV detector at 245 nm. For reversed phase CC of the crude extract, a 40–64 μm C_{18} material made according to the literature [7] was used.

Potato material

Healthy potato tubers from *Solanum tuberosum* L. cv. Bintje, and tubers naturally infected with *Phoma foveata* (Foister) (gangrene) and *Fusarium* spp. (dry rot) were used. The tubers had been stored at 4° for about eight months after harvest. From the infected potato material, 22 rotted tubers were selected at random to test the proportion of *P. foveata* and *Fusarium* spp. in the material.

HPLC analysis of potato tuber tissue

Tissue samples (5 g) were taken from healthy tubers, from the stress zones reaching about 5 mm below the rot surface of infected potato tubers, and from healthy tissue 2–5 mm below the stress zone. The procedure was repeated for at least 3 tubers. The samples were immediately homogenized in 95% EtOH (10 ml), followed by 80% EtOH (10 ml). The combined extracts were filtered and evaporated. Residues were dissolved in 90% MeOH (1.5 ml) prior to HPLC analysis.

Isolation

The blue-fluorescing stress zone, reaching about 5 mm below the rot surface of the infected potato tubers (30 kg) was collected and homogenized with an Ultra Turrax in 95% EtOH (3 × 6 l) for 3 × 5 min. The extracts were combine and concd *in vacuo* at 30° and the evaporation residue was diluted with H_2O (750 ml). The sample was filtered through a reversed phase C_{18} column (190 × 30 mm) and eluted with H_2O (15 l) and 95% EtOH (9 l). The EtOH eluent was concd *in vacuo* at 30°, diluted with H_2O (600 ml) and extracted with $CHCl_3$ (4 × 500 ml). The organic phase was evapd to dryness. CC of the residue (114 g) on silica gel with $CHCl_3$–MeOH–H_2O (300:35:2 and 30:10:1) as eluents yielded 8 fractions (A–H). Fraction C (8.9 g) was rechromatographed on silica gel using $CHCl_3$–MeOH (95:5) and $CHCl_3$–Me_2CO–HOAc (10:40:1), followed by fractionation with HPLC using MeCN–H_2O–HOAc (10:40:1) as eluent, yielding **1b** (49 mg) and **2b** (10 mg). Fraction H (0.5 g) was rechromatographed on silica gel using $CHCl_3$–MeOH–H_2O (30:10:1) followed by HPLC separation using MeCN–H_2O–HOAc (5:95:1) as eluents to give **1a** (15 mg).

Compound **1a**

$[\alpha]_D$ −84° (MeOH; *c* 0.5); UV λ_{max} nm: 242; FAB-MS: 415.2 $[M+H]^+$. Acid hydrolysis of compound **1a** was performed with 2 M trifluoroacetic acid at 120° for 2 hr. Evaporation of a part of the reaction mixture and extraction with $CHCl_3$ produced the aglycone **1b**. From a second part of the reaction mixture, the sugar moiety was identified as glucose by the GLC-retention of the TMSi derivative. The D-configuration of glucose was identified by reaction of a third part with (+)-2-butanol in 1 M HCl at 80° for 8 hr in a sealed glass tube. The reaction mixture was evaporated to dryness, dissolved in hexane, trimethylsilylated with TriSil for 30 min at room temp., concd to dryness, redissolved in hexane, filtered and analysed by GLC [5]. D-glucose treated in the same way with (+)-2-butanol and (±)-2-butanol, respectively, was used as a reference.

Compound **1b**

$[\alpha]_D$ −120° (MeOH; *c* 0.9); UV λ_{max} nm: 242; EIMS (probe) 70 eV, *m/z* (rel. int.): 252 $[M]^+$ (1), 237 (2), 234 (5), 221 (17), 203 (14), 192 (8), 161 (24), 137 (55).

Compound **2b**

$[\alpha]_D$ −72° (MeOH; *c* 0.4); UV λ_{max} nm: 242; EIMS *m/z* (rel. int.): 252 $[M]^+$ (6), 237 (3), 234 (3), 221 (16), 203 (14), 192 (8), 161 (26), 137 (62).

Compound **6a**

Lead tetraacetate (50 mg) was added to a soln of **1b** (10 mg) in $CHCl_3$ (1 ml) and the mixture was left at 4°C overnight. Excess $Pb(OAc)_4$ was destroyed with ethylene glycol (5 mg). Compound **2b** (2.5 mg) was treated in the same way. Compound **6a** was produced in both reactions.

Compound **7a**

MeOH (250 μl), H_2O (50 μl) and 50% aq. NaOH (2.5 μl) was added to a soln of **6a** (1 mg) in $CHCl_3$ (1 ml). After reaction for 1.5 hr at room temp. the mixture was neutralized with H_2SO_4 and extracted with

H_2O. The organic phase was evaporated. The residue consisted of a 1:1 mixture of **6a** and **7a** according to the ^1H NMR spectrum (Table 3).

Compounds **6b** *and* **7b**

Methanol-d_4 (0.25 ml), D_2O (50 μl) and 50% NaOD in D_2O (2.5 μl) was added to a soln of **6a** (1 mg) in $CHCl_3$ (1 ml). After reaction at room temp. for 1.5 hr, the sample was extracted with D_2O (3 × 2 ml). Evaporation of the organic phase yielded a 1:1 mixture of **6b** and **7b** according to the ^1H NMR spectrum (Table 3).

Compound **1c**

A mixture of **1b** (A1) (16 mg), benzoic anhydride (64 mg), triethylamine (64 mg) and 4-dimethylaminopyridine (6.4 mg) was kept at 70° overnight. Water (1 ml) was added and the mixture was extracted with $CHCl_3$ (2 × 1 ml). The organic phase was dried (Na_2SO_4) and evaporated. Fractionation of the residue by TLC on silica gel with petrol–EtOAc (4:1) as eluent yielded **1c** (19.6 mg). ^1H NMR ($CDCl_3$): δ 0.99 (3H, *d*, Me-10), 1.74 (3H, *s*, Me-1′), 1.98 (3H, *d*, Me-6), 1.72–2.18 (6H, *m*, H-1α, H-3$\alpha\beta$, H-4$\alpha\beta$, H-10), 1.82 (1H, *t*, H-1β), 2.22 (1H, *dd*, H-9β), 2.64 (1H, *dd*, H-9α), 2.83 (1H, *m*, H-2), 4.80 (1H, *d*, H-2′b), 4.86 (1H, *d*, H-2′a), 5.78 (1H, *d*, H-7), 7.40–8.00 (10H, *m*, 2Ph). *J*: 1α,1β = 12.0, 1β,2 = 12.0, 7,Me-6 = 0.6, 9α,9β = 16.7, 9α,10 = 4.4, 9β,10 = 4.8, 10,Me-10 = 6.7, 2′a,2′b = 11.6 Hz.

Compound **4**

Catalytic hydrogenation of **1c** (4.5 mg) on 10% Pd/C in EtOAc yielded **4** (2.9 mg). ^1H NMR ($CDCl_3$): δ 0.99 and 1.05 (2 × 3H, 2*d*, Me-6 and Me-10), 1.60–2.35 (12H, *m*, H-1$\alpha\beta$, H-3$\alpha\beta$, H-4$\alpha\beta$, H-6, H-7$\alpha\beta$, H-9$\alpha\beta$, H-10), 1.74 (3H, *s*, Me-1′), 2.73 (1H, *m*, H-2), 4.79 (1H, *d*, H-2′b), 4.85 (1H, *d*, H-2′a), 7.40–8.00 (10H, *m*, 2Ph). *J*: 6,Me-6 = 6.7, 10,Me-10 = 6.7, 2′a,2′b = 11.6 Hz.

Compounds **2c** *and* **5**

Were produced from **2b** (A2) in the same way as **1c** and **4**.

Compound **2c**

^1H NMR ($CDCl_3$): δ 0.99 (3H, *d*, Me-10), 1.74 (3H, *s*, Me-1′), 1.98 (3H, *d*, Me-6), 1.70–2.19 (6H, *m*, H-1α, H-3$\alpha\beta$, H-4$\alpha\beta$, H-10), 1.94 (1H, *t*, H-1β), 2.20 (1H, *dd*, H-9β), 2.60 (1H, *dd*, H-9α), 2.87 (1H, *m*, H-2), 4.78 (1H, *d*, H-2′b), 4.90 (1H, *d*, H-2′a), 5.78 (1H, *d*, H-7), 7.40–8.00 (10H, *m*, 2Ph). *J*: 1α,1β = 12.0, 1β,2 = 12.0, 7,Me-6 = 0.6, 9α,9β = 16.7, 9α,10 = 4.4, 9β,10 = 4.8, 10,Me-10 = 6.7, 2′a,2′b = 11.6 Hz.

Compound **5**

^1H NMR ($CDCl_3$): δ 0.99 and 1.05 (2 × 3H, 2*d*, Me-6 and Me-10), 1.60–2.35 (12H, *m*, H-1$\alpha\beta$, H-3$\alpha\beta$, H-4$\alpha\beta$, H-6, H-7$\alpha\beta$, H-9$\alpha\beta$, H-10), 1.74 (3H, *s*, Me-1′), 2.77 (1H, *m*, H-2), 4.74 (1H, *d*, H-2′b), 4.94 (1H, *d*, H-2′a), 7.40–7.98 (10H, *m*, 2Ph). *J*: 6, Me-6 = 6.7, 10, Me-10 = 6.7, 2′a,2′b = 11.6 Hz.

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