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Photoinduced functionalization of diterpenes: photochemical behaviour of grandiflorolic acid in methanol and acetonitrile

Silvestre Buscemi [a,*], Sergio Rosselli [a], Maurizio Bruno [a], Leonardo Scaglioni [b], Nicolò Vivona [a], Franco Piozzi [a]

[a] *Dipartimento di Chimica Organica E. Paternò, Università degli Studi di Palermo, Viale delle Scienze-Parco d'Orleans II, I-90128 Palermo, Italy*
[b] *Dipartimento di Scienze Molecolari Agroalimentari, Università di Milano, Via Celoria 2, 20133 Milano, Italy*

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Abstract

Irradiation of grandiflorolic acid (**11**) at $\lambda = 254$ nm in acetonitrile gave the two epimers **13** and **14** through a photodecarboxylation reaction of the carboxylic group on C-4. Irradiation of compound **11** in methanol at $\lambda = 254$ nm provided the transformation of the C-20 angular methyl into a carbomethoxymethyl group. In this case, unlike compounds **13** and **14**, only one of the two possible isomers (**15**) was obtained (equatorial methyl at C-4). A mechanistic approach of this reaction in discussed, and the role of mutual stereochemistry between C-20 methyl and C-19 carboxylic group in determining the course of the reaction is pointed out.

Keywords: Natural compounds; Diterpenes; Photochemistry; Grandiflorolic acid

1. Intoduction

We recently investigated on the photochemical behaviour of the nor-kaurane atractyligenin (**1a**) as part of our ongoing program on the photochemistry of diterpenoids. In literature only a previous paper [1] described the irradiation of atractyligenin (**1a**) in acetonitrile solution, yielding the decarboxylated derivative **2**. Besides this reaction, we observed [2,3] the unespected photofunctionalization of the C-20 methyl group of atractyligenin (**1a**), which was transformed in a carbomethoxymethyl group or carbamoylmethyl group. In fact, irradiation of compound **1a** in methanol, gave the expected decarboxylation product **2** (30%) and the methyl ester **3a** (20%). The irradiation in the presence of ammonia or methylamine gave the amides **3b, c** (Scheme 1). Such reaction can be explained by assuming that the excited C-19 carboxylic group abstracts a hydrogen atom from the C-20 methyl group, in a key-step determined by the proximity of the two groups (due to their mutual stereochemistry) as well as by steric compression due to ring C. The resulting intermediate (**5**; $R = H$) will evolve through a C19–C20 bond formation and then, in a thermal or photochemical reaction pattern, into the ketene **9** that, in its turn, will capture the nucleofilic methanol or amines. This unprecedented transformation, which assumes great significance in diterpenes photochemistry, differs from well-documented oxidative photo-functionalizations of the C-20 methyl group of diterpenes involving the C-19 carboxylic moiety and producing lactones and lactams [4]. In order to confirm the stereochemical requirements on the photofunctionalization reaction, 4-epi-atractyligenin (**10**) [5], the C-4 epimer of atractyligenin with an equatorial carboxylic group at C-4, and grandiflorolic acid (**11**), with an axial carboxylic group at C-4 and carrying an additional methyl group on the same carbon, were considered for photochemical investigations (Schemes 2 and 3).

2. Results and discussion

Concerning the nomenclature of compound **11**, it is worth to point out some remarks. 15α-Hydroxy-*ent*-kaur-16-en-19-oic acid was isolated for the first time by Piozzi [6] in 1968 from *Espeletia grandiflora* and indicated as grandiflorolic acid. Brieskorn and Poehlmann [7] in 1969 described the same product from *Espeletia schultzii* and maintained the name grandiflorolic. In the following years, the acid and several derivatives were isolated from many plants. In 1971, Pakrashi et al. [8] used only the systematic nomenclature, but in 1974, Yahara et al. [9] introduced

* Corresponding author. Tel.: +39-091596903; fax: +39-091596825.
E-mail address: sbuscemi@unipa.it (S. Buscemi).

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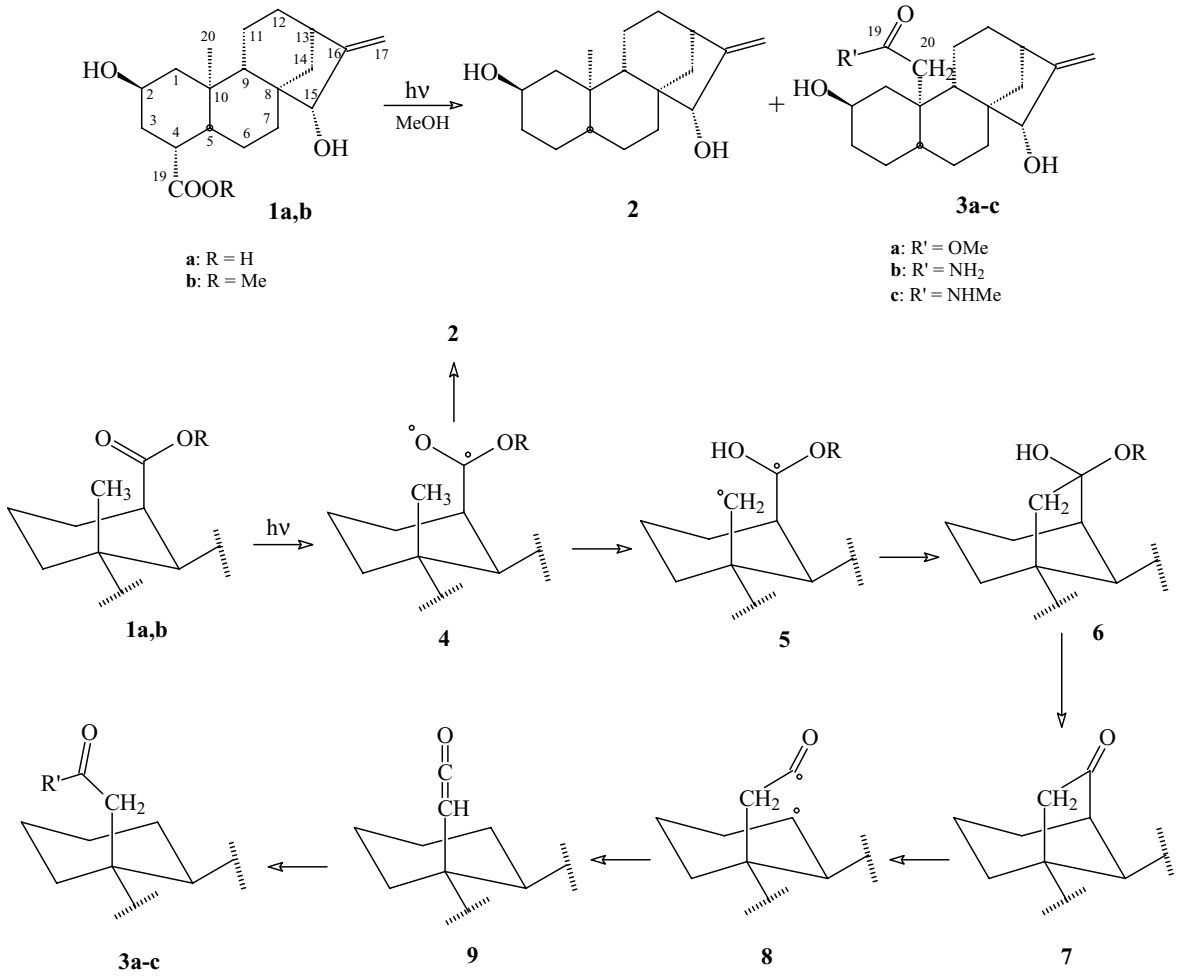


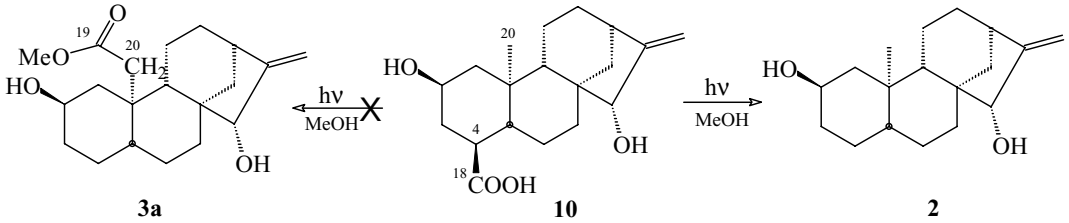
Scheme 1.

the name grandifloric acid, that was then adopted by other authors. In specialistic books the acid is indicated as grandiflorolic [10], or grandifloric [11,12], or with both names in two different entries [13]. Just for priority reason we prefer to retain the name grandiflorolic.

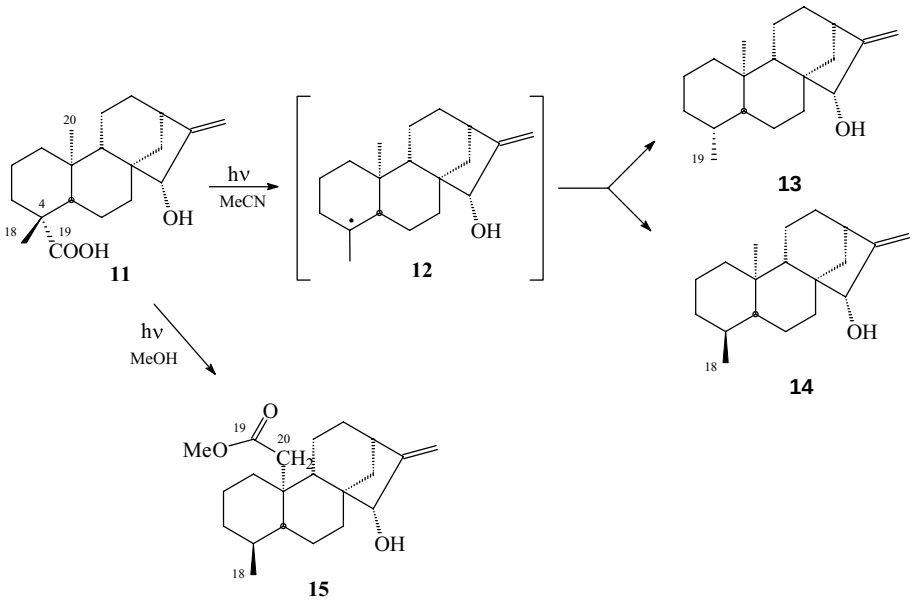
A full attribution of ^{1}H and ^{13}C signals, not previously described, was obtained by HMQC and HMBC experiments as reported in Tables 1 and 2.

Irradiation of compound **10** in methanol at 254 nm gave only the decarboxylation product **2**, without detecting any amount of compond **3a**. This result gives a conclusive proof on the importance of the chemical environment in the photofunctionalization of methyl C-20, that in this case did not take place due to the unfavorable mutual sterechemistry of C-20 and C-19 groups in compound **10** with respect to that present in atractyligenin (**1a**) (Scheme 2).

We then explored the photoreactivity of grandiflorolic acid (**11**). Irradiation of compound **11** in acetonitrile at 254 nm yielded an unseparable mixture (2:3) of two compounds. They were isomers with a molecular formula of $C_{19}H_{30}O$ as indicated by the MS of the mixture (M^{+} 274). ^{1}H and ^{13}C spectra showed the presence of an exocyclic double bond ($\delta_{H\text{-}17a}$ 5.21 brs, $\delta_{H\text{-}17b}$ 5.08 brs, $\delta_{C\text{-}17}$ 108.12 t and 108.17 t, $\delta_{C\text{-}16}$ 160.40 s), of a secondary hydroxy group



Scheme 2.



Scheme 3.

($\delta_{H\text{-}15}$ = 3.83 m, $\delta_{C\text{-}15}$ = 82.96 d), of an allilyc proton ($\delta_{H\text{-}13}$ 2.75 brs, $\delta_{C\text{-}13}$ 42.37 d and 42.27 d), of a tertiary methyl group ($\delta_{H\text{-}20}$ 0.96 s and 1.02 s, $\delta_{C\text{-}20}$ 15.23 q and 15.59 q) and of a secondary methyl group on C-4 ($\delta_{H\text{-}19}$, axial, 0.83 d J = 6.5 Hz, $\delta_{C\text{-}19}$ 18.05 q and $\delta_{H\text{-}18}$, equatorial, 0.91 d J = 7.5 Hz, $\delta_{C\text{-}18}$ = 20.52 q). Consequently, we assign to them the epimeric structures **13** and **14**.

The formation of compounds **13** and **14** can be easily explained by considering the α-clevage of the C(19)–C(4) bond induced by the excited carboxylic group and the subsequent stabilization of radical **12** by the ad-

Table 1
^{1}H NMR (in $CDCl_3$, 600 MHz) of compound **11**

H	ppm	J (Hz)			
1α	1.83 ddd (13.8, 3.8, 3.8)	1α, 1β	13.8	13, 14a	1.8
1β	0.79 ddd (13.8, 13.8, 4.3)	1α, 2α	3.8	13, 14b	n.d.
2a[a]	1.87 o.s.	1α, 2β	3.8	14a, 14b	11.8
2b[a]	1.40 o.s.	1β, 2α	13.8		
3α	2.15 ddd (13.4, 3.6, 3.6)	1β, 2β	4.3		
3β	1.00 ddd (13.4, 13.4, 4.4)	2α, 2β	n.d.		
5 β	1.06 dd (12.1, 2.2)	2α,3α	3.6		
6α	1.76 dddd (13.5, 13.5, 12.1, 3.1)	2α, 3β	13.4		
6β	1.92 o.s.	2β, 3α	3.6		
7α	1.74 ddd (13.5, 3.1, 3.1)	2β, 3β	4.4		
7β	1.35 ddd (13.5, 13.5, 3.2)	3α, 3β	13.4		
9	1.01 brd (8.4)	5,6α	12.1		
11a	1.60 o.s.	5,6β	2.2		
11b	1.53 o.s.	6α, 6β	13.5		
12a	1.60 o.s.	6α, 7α	3.1		
12b	1.43 o.s.	6α, 7β	13.5		
13	2.72 m ($W_{1/2}$ = 9.2)	6β, 7α	3.1		
14a	1.90 dd (11.8, 1.8)	6β, 7β	3.2		
14b	1.37 o.s.	7α, 7β	13.5		
15β	3.80 brs ($W_{1/2}$ = 2.9)	9, 11a	n.d.		
17a	5.20 brs ($W_{1/2}$ = 2.0)	9, 11b	n.d.		
17b	5.05 brs ($W_{1/2}$ = 2.2)	11a, 11b	n.d.		
$CH_3$18	1.24 s	11a, 12a	n.d.		
$CH_3$20	0.94 s	11a, 12b	n.d.		
		12a, 12b	n.d.		
		12a, 13	n.d.		
		12b, 13	n.d.		

[a] The stereochemistry of protons 2a and 2b has not been assigned.

Table 2
^{13}C NMR (in $CDCl_3$), HMQC and HMBC of compound **11**

C	ppm	HMQC	HMBC
1	40.67 t	1.83; 0.79	
2	19.05 t	1.87; 1.40	0.79 (H1β)
3	37.74 t	2.15; 1.00	
4	43.70 s		1.24 (Me18), 1.06 (H5)
5	56.97 d	1.06	2.15 (H3α), 1.92 (H6β), 1.76 (H6α), 1.24 (Me18)
6	20.91 t	1.92; 1.76	1.35 (H7β), 1.06 (H-5)
7	35.20 t	1.74; 1.35	
8	47.70 s		1.90 (H14a), 1.74 (H7α), 1.60 (H11a), 1.35 (H7β), 1.01 (H9)
9	53.33 d	1.01	3.80 (H15), 1.74 (H7α), 1.35 (H7β)
10	39.80 s		0.79 (H1β)
11	18.26 t	1.60; 1.53	2.72 (H13)
12	32.55 t	1.60; 1.43	5.20 (H17a), 5.05 (H17b), 1.01 (H9), 1.90 (H14a), 1.37 (H14b)
13	42.29 d	2.72	5.20 (H17a), 5.05 (H17b), 3.80 (H15)
14	36.20 t	1.90; 1.37	
15	82.68 d	3.80	5.20 (H17a), 5.05 (H17b), 1.90 (H14a), 1.01 (H9)
16	160.25 s		5.20 (H17a), 5.05 (H17b), 1.90 (H14a), 1.60 (H12a)
17	108.28 t	5.20; 5.05	3.80 (H15)
18	28.91 q	1.24	
19	183.80 s		1.24 (Me18), 1.06 (H5)
20	15.80 q	0.94	

Table 3
^{1}H NMR (in $CDCl_3$ 600 MHz) of compound **15**

H	ppm	J (Hz)			
1α	2.80 ddd (13.0,3.4,3.4)	1α, 1β	13.0	11a, 12b	n.o.
1β	0.69 ddd (13.0,13.0,3.9,1.2)	1α, 2α	3.4	12a, 12b	n.o.
2α	1.36 ddddd (13.8,13.0,12.0,3.8,3.4)	1α, 2β	3.4	12a, 13	n.o.
2β	1.52 ddddd (13.8,7.0,5.0,3.9,3.4,)	1β, 2α	13.0	12b, 13	n.o.
3α	1.67 overlap sig.	1β, 2β	3.9	13, 14a	1.1
3β	0.93 dddd (12.0,12.0,12.0,5.0)	2α, 2β	13.8	13, 14b	5.5
4α	1.38 overlap sig.	2α, 3α	3.8	14a, 14b	12.0
5	0.71 ddd (11.5,11.5,2.4)	2α, 3β	12.0	20a, 20b	16.3
6α	1.05 dddd (13.6,13.0,11.5,3.5)	2β, 3α	7.0	20a, 1β	1.2
6β	1.70 dddd (13.0,3.5,3.5,2.4)	2β, 3β	5.0		
7α	1.67 ddd (13.6,3.5,3.5)	3α, 3β	12.0		
7β	1.47 ddd (13.6,13.6,3.5)	3α, 4α	n.o.		
9	1.10 dd (7.6,1.1)	3β, 4α	12.0		
11a	1.87 overlap. sig	4α, 5	11.5		
11b	1.38 overlap. sig	4α, 18	6.3		
12a	1.38 overlap. sig	5, 6α	11.5		
12b	1.38 overlap. sig	5, 6β	2.4		
13	2.72 m ($W_{1/2} = 7.6$)	6α, 6β	13.0		
14a	1.85 dd (12.0,1.1)	6α, 7α	3.5		
14b	1.42 dd (12.0,5.5)	6α, 7β	13.6		
15β	3.80 brs ($W_{1/2} = 4.0$)	6β, 7α	3.5		
17a	5.20 brs ($W_{1/2} = 2.4$)	6β, 7β	3.5		
17b	5.06 brs ($W_{1/2} = 2.8$)	7α, 7β	13.6		
$CH_3$18	0.85 d (6.3)	9, 11a	1.1		
20a	2.79 dd (16.3,1.2)	9, 11b	7.6		
20b	2.58 d (16.3)	11a, 11b	n.o.		
OCH_3	3.64 s	11a, 12a	n.o.		

Table 4
^{13}C NMR (in $CDCl_3$), HMQC and HMBC of compound **15**

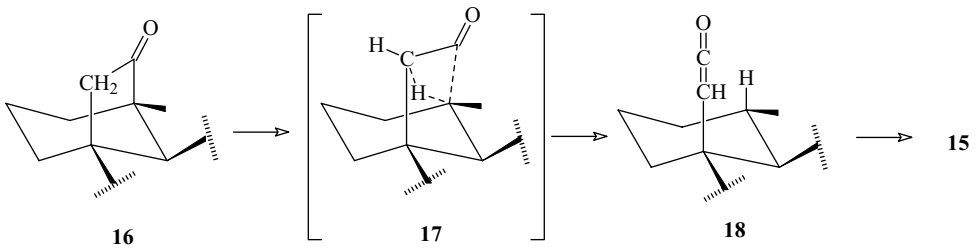
C		HMQC	HMBC
1	36.54 t	2.80; 0.69	2.79 (H20a), 2.58 (H20b), 1.67 (H3α), 1.52 (H2β)
2	21.43 t	1.52; 1.36	
3	36.16 t	1.67; 0.93	0.85 (Me18)
4	30.75 d	1.38	0.93 (H3β), 0.85 (Me18), 0.71 (H5)
5	55.83 d	0.71	2.79 (H20a), 2.58 (H20b), 1.67 (H7α), 0.85 (Me18)
6	20.84 t	1.70; 1.05	1.47 (H7β)
7	33.83 t	1.67; 1.47	
8	47.16 s		1.87 (H11a), 1.67 (H7α), 1.47 (H7β), 1.42 (H14b), 1.10 (H9)
9	52.38 d	1.10	3.80 (H15), 2.79 (H20a), 2.58 (H20b), 1.87 (H11a), 1.67 (H7α), 1.42 (H14b)
10	40.90 s		2.79 (H20a), 2.58 (H20b), 1.10 (H9), 0.71 (H5)
11	17.84 t	1.87; 1.38	1.38 (H12), 1.10 (H9)
12	31.36 t	1.38; 1.38	5.20 (H17a), 5.06 (H17b), 1.85 (H14a), 1.42 (H14b), 1.10 (H9)
13	42.08 d	2.72	5.20 (H17a), 5.06 (H17b), 3.80 (H15), 1.87 (H11a), 1.42 (H14b)
14	36.69 t	1.85; 1.42	1.47 (H7β), 1.38 (H12), 1.10 (H9)
15	83.12 d	3.80	5.20 (H17a), 5.06 (H17b), 1.85 (H14a), 1.10 (H9)
16	160.28 s		5.20 (H17a), 5.06 (H17b), 1.85 (H14a), 1.38 (H12)
17	108.36 t	5.20; 5.06	3.80 (H15)
18	20.62 q	0.85	0.93 (H3β)
19	173.55 s		3.64 (OCH_3), 2.79 (H20a), 2.58 (H20b)
20	33.17 t	2.79; 2.58	1.10 (H9), 0.71 (H5)
OCH_3	51.11 q	3.64	

dition of a hydrogen atom, that can occur from both sides.

Interestingly, the irradiation of grandiflorolic acid (**11**) in methanol at 254 nm, besides the same epimeric mixture of **13** and **14**, gave major quantity of the new C-20 functionalized compound **15**, whose structure was assigned on the basis of analytical and spectroscopical data (Scheme 3).

Compound **15** had a molecular formula of $C_{21}H_{32}O_3$ as indicated by its MS (M^+ 332). ^{1}H and ^{13}C spectra showed the presence inter alia, of an exocyclic double bond ($\delta_{H\text{-}17}$ 5.20 brs and 5.06 brs, $\delta_{C\text{-}16}$ 160.28 s and $\delta_{C\text{-}17}$ 108.36 t), of a secondary hydroxyl group ($\delta_{H\text{-}15}$ 3.80 brs, $\delta_{C\text{-}15}$ 83.12 d), of a carbomethoxy group ($\delta_{H\text{-}Me}$ 3.64 s, $\delta_{C\text{-}Me}$ 51.11 q, $\delta_{C\text{-}19}$ 173.55 s), of a methylene ($\delta_{H\text{-}20}$ 2.79 dd $J = 16.3$, 1.2 Hz and 2.58 d $J = 16.3$ Hz, $\delta_{C\text{-}20}$ 33.17 t) linked to a carbonyl group and, finally, of a secondary methyl group on C-4 ($\delta_{H\text{-}18}$ 0.85 d $J = 6.3$ Hz, $\delta_{C\text{-}18} = 20.62$ q). A full attribution of ^{1}H and ^{13}C signals was obtained by HMQC and HMBC experiments as reported in Tables 3 and 4.

In order to determinate the stereochemistry of the methyl group on C-4 a ROESY experiment was carried out. Clear correlation peaks were observed between H-20a and H-1α, H-6α, H-4 and H-14a, and between H-20b and H-6α, H-4 and H-14a showing an axial stereochemistry of H-4. Consequently, we assign an equatorial sterochemistry to the methyl group (Me-18) linked at C-4 that was also confirmed by its correlation peak with H-5.



Scheme 4.

Similarly to atractyligenin (**1a**) and its derivative (**1b**), when irradiated in methanol, grandiflorolic acid (**11**) also underwent a photofunctionalization of methyl C-20 and its transformation in a carbomethoxymethyl group. In this case, differently from compounds **13** and **14**, only one of the two possible isomers was obtained (equatorial methyl at C-4). This unexpected result suggests that the formation of the ketene intermediate (**18**) occurred through a concerted step (**17**), inducing a well defined stereochemistry. In fact, it is possible to hypothesize that the cleavages of C–C and C–H bonds are simultaneous with the formation of the new C–H axial bond. These facts would prevent the formation of a planar radical, constraining the methyl group at C-4 to keep its original stereochemistry (Scheme 4).

3. Experimental section

3.1. General

Ir spectra were determined with a Perkin-Elmer 257 instrument. ^{1}H and ^{13}C NMR spectra were obtained on Bruker AMX-600 operating at 600.13 and 150.9 MHz for proton and carbon, respectively. DEPT experiments were acquired on a Bruker AMX-300 spectrometer. Measurements were made on solution in $CDCl_3$, chemical shifts were referred to TMS set at 0 ppm, and coupling constants are given in Hz. Heteronuclear two-dimensional ^{1}H–^{13}C correlations, one-bond HMQC (heteronuclear multiple quantum correlation) [14] and long-range HMBC (heteronuclear multiple bond correlation) [15], were carried out in the ^{1}H-detected mode with broad-band decoupling in the ^{13}C domain. ROESY [16] experiments were obtained using as spin-lock a continuous low power transmitter pulse and mixing time of 0.2 and 0.4 s, using standard BRUKER pulse sequence. MS were recorded on a Finnigan TSQ70 instrument (70 eV, direct inlet). Elemental analysis was carried out with a Perkin-Elmer 240 apparatus. Flash chromatography was performed by using silica gel (Merck, 0.040–0.063 mesh) and mixtures of EtOAc and light petroleum (fraction boiling in the range 40–60 °C) in varying ratios. Anhydrous methanol (from Romil Pure Chemicals) were used as received.

3.1.1. Compound *10*

Compound **10** was synthesised according to literature [5].

3.1.2. Compound *11*

Compound **11** was isolated from *Espeletia grandiflora* as previously reported [6]. For ^{1}H NMR (600.13 MHz, $CDCl_3$) and ^{13}C NMR (150.9 MHz, $CDCl_3$) see Tables 1 and 2.

3.1.3. General procedure for photochemical reactions

A solution of compounds **10** or **11** (0.6 mmol) in anhydrous methanol or acetonitrile (150 ml) was partitioned into six quartz tubes, purged by nitrogen bubbling (10 min). The solution was then irradiated by using a Rayonet RPR-100 photoreactor equipped with 16 Hg lamps at $\lambda = 254$ nm (RPR-2573 A°) and a merry-go-round apparatus. The photoreaction was followed by TLC and irradiation was stopped after 6 h (in the case of irradiation of compound **10**) or after 12 h (in the case of compound **11**) to avoid a deep degradation. The solvent was evaporated to dryness under red. pres. at low temp. (25°) yielding a residue which was subjected to column chromatography eluting with light petroleum/EtOAc at various ratios. Yields are referred to reacted product.

*3.1.3.1. Irradiation of **10** in methanol.* Compound **10** gave, in order of increasing polarity, **2** (20 mg, 26%) and starting material (90 mg, 47%).

*3.1.3.2. Irradiation of **11** in acetonitrile.* Compound **11** gave, in order of increasing polarity, mixture of **13** and **14** (30 mg, 27%) and starting material (60 mg, 32%).

Mixture of compounds **13** and **14**: Amorphous solid. IR (film) ν_{max} = 3350, 1655, 869 cm^{-1}. ^{1}H NMR (600.13 MHz, $CDCl_3$): δ 5.21 (brs, 1H, H-17a), 5.08 (brs, 1H, H-17b), 3.83 (brs, 1H, H-15), 2.75 (m, 1H, H-13), 1.02 (s, 1.8H, CH_3-20 of 14), 0.96 (s, 1.2H, CH_3-20 of 13), 0.91 (d, 1.8H, $J_{4,18} = 7.5$, CH_3-18 of 14), 0.83 (d, 1.2H, $J_{4,19} = 6.5$, CH_3-19 of 13). ^{13}C NMR (150.9 MHz, $CDCl_3$): δ 160.40 (C-16), 108.12 (C-17), 82.96 (C-15), 53.65 (C-9), 49.77 (C-5), 47.96 (C-8), 42.37 (C-13), 40.00 (C-1), 39.19 (C-10), 36.31 (C-14), 34.77 (C-7), 34.02 (C-4), 33.24 (C-3), 32.69 (C-12), 25.34 (C-6), 18.05 (C-19), 17.74 (C-11), 17.33 (C-2), 15.23 (C-20) for compound 13 and 160.40 (C-16), 108.17 (C-17), 82.96 (C-15), 54.09 (C-9), 52.02 (C-5), 47.40 (C-8), 42.27 (C-13), 39.81 (C-1), 38.81 (C-10), 36.46 (C-14), 36.46 (C-3), 34.20 (C-7), 32.58 (C-12), 30.39 (C-4), 21.41 (C-6), 21.23 (C-2), 20.52 (C-18), 18.17 (C-11), 15.59 (C-20) for compound 14. EIMS *m/z* (%): 274 $[M]^+$ (50), 257 $[M–OH]^+$ (42), 241 (38), 216 (100), 201 (37), 199 (20), 191 (15), 175 (10), 109 (20), 83 (10), 79 (7). $C_{19}H_{30}O$ (274.45): calculated C, 83.15; H, 11.02; found: C, 83.1; H, 11.1.

3.1.3.3. Irradiation of 11 in methanol. Compound **11** gave, in order of increasing polarity, mixture of **13** and **14** (23 mg, 17%), compound **15** (20 mg, 12%) and starting material (30 mg, 15%).

Compound **15**: Amorphous solid. $[\alpha]_D = -44.45$ (*c* 0.873, $CHCl_3$). IR (film) ν_{max} = 3360, 1730, 1655, 869 cm^{-1}. ^{1}H NMR (600.13 MHz, $CDCl_3$): see Table 3. ^{13}C NMR (150.9 MHz, $CDCl_3$): see Table 4. EIMS *m/z* (%): 332 $[M]^+$ (18), 315 $[M–OH]^+$ (20), 300 (24), 275 (18), 259 $[M–CH_2COOCH_3]^+$ (55), 241 $[M–CH_2COOCH_3–H_2O]^+$ (64), 201 (47), 109 (62), 107 (84), 91 (100). $C_{21}H_{32}O_3$ (332.49): calculated. C, 75.86; H, 9.70; found: C, 75.7; H, 9.6.

Acknowledgements

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