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Phytochemistry 68 (2007) 1255–1260
PHYTOCHEMISTRY
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Diterpenoids and triterpenoids from *Euphorbia guyoniana*

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Received 11 December 2006; received in revised form 18 January 2007
Available online 6 March 2007

Abstract

Two new compounds with tigliane and cycloartane skeletons: 4,12-dideoxy(4α)phorbol-13-hexadecanoate (**1**) and 24-methylenecycloartane-3,28-diol (**2**), respectively, in addition of four known diterpenoids and 13 triterpenoids: 3-benzoyloxy-5,15-diacetoxy-9,14-dioxojatropha-6(17),11-diene (**4**), *ent*-abieta-8(14),13(15)-dien-16,12-olide (**5**), *ent*-8α,14α-epoxyabieta-11,13(15)-dien-16,12-olide (**6**), *ent*-3-hydroxyatis-16(17)-ene-2,14-dione (**7**), 3β-hydroxytaraxer-14-en-28-oic acid (**8**), β-sitosteryl-3β-glucopyranoside-6′-*O*-palmitate (**9**), multiflorenyl acetate (**10**), multiflorenyl palmitate (**11**), peplusol (**12**), 24-methylenecycloartanol (**3**), lanosterol (**13**), euferol (**14**), butyrospermol (**15**), cycloartenol (**16**), obtusifoliol (**17**), cycloeucalenol (**18**) and β-sitosterol (**19**), were isolated from the roots of *Euphorbia guyoniana*. Their structures were established on the basis of physical and spectroscopic analysis, including 1D and 2D homo- and heteronuclear NMR experiments (COSY, HSQC, HMBC and NOESY) and by comparison with the literature data.

Keywords: *Euphorbia guyoniana*; Euphorbiaceae; Diterpenoids; Triterpenoids

1. Introduction

Euphorbia guyoniana (Boiss. and Reut.) is an endemic Saharan plant growing in sandy and desert habitat (Quezel and Santa, 1963), and belongs to the large family of Euphorbiaceae. With more of 1600 species, *Euphorbia* genus is the most representative of the family (Ozenda, 1991). Plants of this genus are known for their rich content in secondary metabolites. Indeed, numerous studies undertaken on this genus have revealed presence of triterpenes (Lima et al., 2003), diterpenes (Shi et al., 2005), macrocyclic diterpenes (Rédei et al., 2003), steroids (Tanaka et al., 1999) and aromatic compounds (Öksüz et al., 2002). Chemically, *E. guyoniana* has received little attention apart from the work done recently on the aerial parts from which two new diterpene polyesters with jatrophane skeleton have been isolated (Ahmed et al., 2006). This species contains an irritant white latex for the eyes and skin (Bellakhdar, 1997), alike the other species of the genus *Euphorbia*. Present work describes the isolation and structural determination of one new diterpenoid (**1**) and one new cycloartane-type triterpene (**2**), together with 17 known compounds isolated from the roots of *E. guyoniana*. Structures were established mainly by 1D and 2D homo- and heteronuclear NMR and mass spectrometry experiments.

2. Results and discussion

The chloroform extract of the roots of *Euphorbia guyoniana* was subjected to silica gel chromatography and

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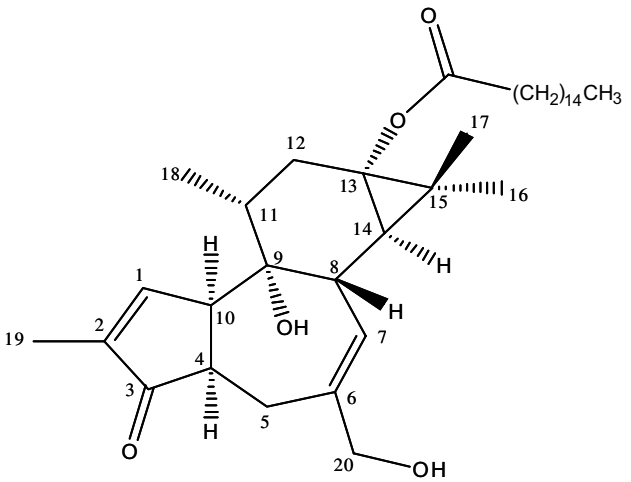
doi:10.1016/j.phytochem.2007.01.017

semi-preparative HPLC to afford two new compounds **1** and **2**, in addition to 17 known products (**3**–**19**).

The known compounds were identified by using spectroscopic methods including $[\alpha]_D^{25}$, ESIMS, 1D and 2D NMR analysis and also by comparing experimental data with those described in the literature as 3-benzoyloxy-5,15-diacetoxy-9,14-dioxojatropha-6(17),11-diene (**4**) (Ahmed et al., 2006), *ent*-abieta-8(14),13(15)-dien-16,12-olide (**5**), *ent*-8α,14α-epoxyabieta-11,13(15)-dien-16,12-olide (**6**) (Crespi-Perellino et al., 1996; Che et al., 1999) and *ent*-3-hydroxyatis-16(17)-ene-2,14-dione (**7**) (Appendino et al., 2000; Gustafson et al., 1991), 3*β*-hydroxytaraxer-14-en-28-oic acid (**8**) (McPhail et al., 1989), *β*-sitosteryl-3*β*-glucopyranoside-6′-*O*-palmitate (**9**) (Yili and Yuting, 1992), multiflorenyl acetate (**10**), multiflorenyl palmitate (**11**) (Ciccio and Hoet, 1981; Ageta and Arai, 1983), peplusol (**12**) (Giner et al., 2000), 24-methylenecycloartanol (**3**), lanosterol (**13**), euferol (**14**), butyrospermol (**15**), cycloartenol (**16**), obtusifoliol (**17**), cycloeucalenol (**18**) and *β*-sitosterol (**19**) (Teresa et al., 1987; Satyanarayana et al., 1992; Öksüz et al., 1993).



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Compound **1** was obtained as colourless oil. The ESI^+ mass spectrum of compound **1** showed a quasi-molecular ion signal at *m*/*z* 593 $[M+Na]^+$, indicating a molecular mass of 570 uma. The molecular formula was confirmed as $C_{36}H_{58}O_5$ by HRESIMS (*m*/*z* 593.4174; calc. for $C_{36}H_{58}O_5Na$, 593.4176). In the UV spectrum, maximum absorptions were observed at 236 and 335 nm suggesting the presence of an enone system. The IR spectrum indicated the presence of an OH group (3405 cm^{-1}), a conjugated carbonyl (1715 cm^{-1}) and a double bond (1630 cm^{-1}). The ^1H and ^{13}C NMR spectra (Table 1) showed typical signals of phorbol esters with tigliane-type diterpene skeleton (Marco et al., 1999). The ^1H NMR displayed signals for four methyl groups (δ_H 1.12, *d*, $J = 6.4$ Hz, H-18; 1.09, *s*, H-17; 1.19, *s*, H-16; 1.83, brs, H-19) and two olefinic protons (δ_H 7.11, brs, H-1 and 5.15, brs, H-7). The doublet at δ_H 0.58 with a coupling constant $J = 5.0$ Hz was attributed to H-14, and an AB system corresponding to an oxymethylene group was detected at δ_H 4.06 (1H, *d*, $J = 12.1$ Hz, H-20a) and 3.93 (1H, *d*, $J = 12.1$ Hz, H-20b). A large deshielded singlet at δ_H 5.32 that showed no correlation in the HSQC spectrum, was assigned to the hydroxyl group 9-OH (Miana et al., 1985). The lack of a downfield doublet signal at 5.40 ppm ascribable to H-12 in the case of an ester derivative of phorbol and the appearance of two doublets of doublets centered at δ_H 2.16 (1H, *dd*, $J = 14.5$, 6.4 Hz, H-12*β*) and 1.75 (1H, *dd*, $J = 14.5$, 12.0 Hz, H-12α) indicated that compound **1** is an ester derivative of 12-deoxyphorbol (Miana et al., 1985). The *J*-modulated ^{13}C NMR (Table 1) showed signals characteristic of a 12-deoxyphorbol except for the signal due to C-4 which appeared at 50.1 ppm for **1** instead of 74 ppm reported for the 12-deoxy (Ma et al., 1997). This shielding of Δ23.9 ppm indicated that it did not bear a hydroxyl group. The presence of an hexadecanoyl (palmitoyl) ester was deduced from the characteristic fragment ion peak in the mass spectrum at *m*/*z* 337 $[(M+Na)- 256]^+$, due to the loss of a C_{16} saturated fatty acid; the triplet of a methyl group at δ_H 0.92 ($J = 6.9$ Hz) and δ_C 14.1, signals for methylene groups at δ_H 2.32 (2H, *t*, $J = 7.6$ Hz), 1.62 (2H, *m*), 1.30–1.35 (24H, *m*) and δ_C 34.6, 24.7, 22.7, 29.1–29.7, 31.9, and the carbonyle carbon at δ_C 176.0 attested the nature of palmitoyl ester. The values of chemical shifts for allylic protons H-20 indicated that the C-20 hydroxyl was free (Miana et al., 1985). Therefore, the ester hexadecanoyl moiety was connected to the C-13. These observations were further confirmed by analysis of the HSQC, HMBC and COSY experiments. This latter experiment showed the expected correlations between the protons H-4 at δ_H 2.85 with H-5 (δ_H 2.54 and 3.54) and H-10 (δ_H 3.57). The HMBC spectrum revealed significant correlations between H-4 and carbons at δ_C 25.1 (C-5), 47.1 (C-10) and 213.8 (C-3) (Table 1). The relative stereochemistry of (**1**) was studied by analysis of the NOESY spectrum (Fig. 1). All tigliane diterpenoids discovered in nature up to now show a configuration H-8*β*, C-9-OHα and H-10α (Ma et al., 1997). The coupling constants of H-12 with H-11 (12.0 and 6.4 Hz) and the NOE effects of H-18 with H-12α indicated that H-11 was *β*-axial. The observed NOE correlations from H-17 to H-8 and H-11*β* indicated that these protons were on the same side of the molecule and involved in a *β* configuration. The absence of NOE effects between H-8*β* and H-14 proved that H-14 was α oriented. The NOE effect between H-18 and H-10 confirmed the α orientation of H-10. Further NOE correlations were observed between H-17*β* and H-12*β*, H-16α and H-14α, H-7 and H-14α. Since, H-4 exhibited NOE interaction with H-10, the two protons were α oriented.

Table 1
^{1}H and ^{13}C NMR data of compound **1** in $CDCl_3$

Atom	**1**		
	δ_H (*m*, *J* Hz)	δ_C	HMBC (H to C)
1	7.11 *brs*	156.9	–
2	–	143.0	–
3	–	213.8	–
4	2.85 *ddd* 6.7, 5.0, 3.0, H-4α	50.1	C-3, C-5, C-10
5	2.54 *dd* 15.4, 5.0, H-5α	25.1	C-4, C-6, C-7, C-10, C-20
	3.54 *dm* 15.4, H-5*β*		
6	–	136.3	–
7	5.15 *brs*	127.7	C-20
8	1.82 *m* H-8*β*	41.0	C-9, C-10
9	OH 5.32 *brs*	75.5	–
10	3.57 *brs* H-10α	47.1	–
11	1.58 *m* H-11*β*	37.1	C-8, C-18
12	1.75 *dd* 14.5, 12.0, H-12α	30.5	C-11, C-13, C-15, C-18
	2.16 *dd* 14.5,6.4, H-12*β*		C-9, C-11, C-13, C-14, C-15
13	–	62.7	–
14	0.58 *d* 5.0, H-14α	33.1	C-7, C-12, C-13, C-15, C-16, C-17
15	–	22.5	–
16	1.19 *s*	23.7	C-13, C-14, C-15, C-17
17	1.09 *s*	15.2	C-13, C-14, C-15, C-16
18	1.12 *d* 6.4	15.9	C-9, C-11, C-12
19	1.83 *brs*	10.4	C-1, C-2, C-3
20	4.06 *d* 12.1, H-20a	69.5	C-6, C-7
	3.93 *d* 12.1, H-20b		C-5, C-6, C-7
$COCH_2CH_2(CH_2)_{12}CH_3$	–	176.0	–
$COCH_2CH_2(CH_2)_{12}CH_3$	2.32 *t* 7.6	34.6	$COCH_2CH_2(CH_2)_{12}CH_3$
			$COCH_2CH_2(CH_2)_{12}CH_3$
			$COCH_2CH_2(CH_2)_{12}CH_3$
$COCH_2CH_2(CH_2)_{12}CH_3$	1.62 *m*	24.7	$COCH_2CH_2(CH_2)_{12}CH_3$
$COCH_2CH_2(CH_2)_{12}CH_3$	1.30–1.35 *m*	22.7, 29.1–29.7,	$COCH_2CH_2(CH_2)_{12}CH_3$
		31.9	$COCH_2CH_2(CH_2)_{12}CH_3$
$COCH_2CH_2(CH_2)_{12}CH_3$	0.92 *t* 6.9	14.1	$COCH_2CH_2(CH_2)_{12}CH_3$

The α arrangement of H-4 was also supported by the absence of NOE correlations between H-4 and H-8*β*. The chemical shift of H-1 and the values of the coupling constants of H-4 agreed with an α-configuration in comparison with those reported for the H-4*β* (Appendino et al., 1999). The compound **1** exhibited a positive optical rotation alike the other phorbol derivatives isolated from *Euphorbia* species (Appendino et al., 1999; Ma et al., 1997; Marco et al. 1999). This result was indeed supported by the isolation and characterization of an ester of 4-deoxyphorbol with H-4α (Marco et al. 1999). Therefore, the relative stereochemistry of this compound was 4α-H, 8*β*-H, 9α-OH, 10α-H, 11α-Me, 13α-OCO $(CH_2)_{14}CH_3$ and 14α-H. All of the above data are compatible with the structure of **1** being 4,12-dideoxy(4α)phorbol-13-hexadecanoate (**1**).

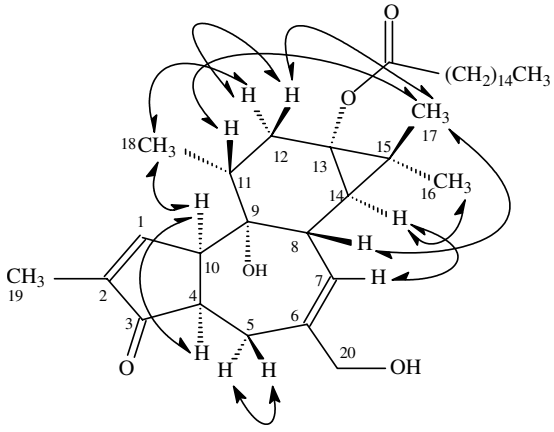


Fig. 1. Relevant NOE correlations observed for compound **1**.

Compound **2** was isolated as a white powder. Its ESI^+ mass spectrum gave quasi-molecular ion peaks at *m*/*z* 479 $[M+Na]^+$ and 935 $[2M+Na]^+$ indicating a molecular mass M = 456 corresponding to the formula $C_{31}H_{52}O_2$ which was supported by HRESIMS (*m*/*z* 479.3868; calc. for $C_{31}H_{52}O_2Na$, 479.3860). The IR spectrum showed a signal at 3430 cm^{-1}, indicating the presence of hydroxyl group. The ^{13}C NMR spectrum of **2** (Table 2) showed signals consisting of six methyl, 13 methylene, six methine and six quaternary carbon atoms which confirmed its triterpenic nature. The ^{1}H NMR spectral data of **2** are found to be closely similar to those of cycloartane-type triterpene like 24-methylenecycloartanol (**3**) which was previously isolated from numerous *Euphorbia* species (Öksüz et al., 2002; Teresa et al., 1987). The characteristic pair of high field doublets signals of the cyclopropane ring bearing two non equivalent

Table 2
^{1}H and ^{13}C NMR data of compound **2** in $CDCl_3$

Atom	**2**		
	δ_H (*m*, *J* Hz)	δ_C	HMBC (H to C)
1	1.29–1.62 *m*	31.8	C-19
2	1.66–1.82 *m*	30.4	C-10
3	3.82 *dd* 10.6, 4.8, H-3α	77.1	C-4, C-5, C-28, C-29
4	–	43.8	–
5	1.52 *m* H-5α	42.5	C-6, C-9
6	0.88–1.49 *m*	21.0	C-7
7	1.13–1.38 *m*	25.9	C-8, C-14
8	1.55 *dd* 12.2, 5.2, H-8*β*	47.9	C-6, C-9, C-11, C-14
9	–	19.9	–
10	–	26.5	–
11	1.35–1.38 *m*	28.1	–
12	1.34 *m*	35.7	C-11, C-13
13	–	45.2	–
14	–	49.0	–
15	1.68 *m*	32.8	C-13, C-16
16	1.17–2.05 *m*	26.5	–
17	1.65 *m*	52.2	–
18	1.01 *s*	18.0	C-13, C-14, C-15, C-17
19	0.44 *d* 4.2, H-19 *exo*	30.2	C-1, C-5, C-7, C-8, C-9, C-10
	0.65 *d* 3.9, H-19 *endo*		C-5, C-7, C-8
20	1.45 *m*	36.1	–
21	0.95 *d* 5.2	18.3	C-17, C-20, C-22
22	1.19–1.62 *m*	35.1	–
23	1.93–2.18 *m*	31.3	–
24	–	156.9	–
25	2.29 *sept* 6.8	33.8	–
26	1.08 *d* 6.8	21.8	C-24, C-25, C-27
27	1.07 *d* 6.8	21.9	C-24, C-25, C-26
28	3.80 *d* 10.3, H-28a	71.3	C-3, C-4, C-5, C-29
	3.59 *d* 10.5, H-28b		C-3, C-4, C-29
29	1.00 *s*	10.1	C-3, C-4, C-5, C-28
30	0.94 *s*	19.2	C-8, C-12, C-13, C-14
31	4.77 brs H-31a	106.1	C-25
	4.71 brd 1.2, H-31b		–

protons appeared at δ_H 0.44 (1H, *d*, $J = 4.2$ Hz, H-19 *exo*) and 0.65 (1H, *d*, $J = 3.9$ Hz, H-19 *endo*). The spectrum exhibited six methyl signals at δ_H 0.94 (3H, *s*, H-30), 0.95 (3H, *d*, $J = 5.2$ Hz, H-21), 1.00 (3H, *s*, H-29), 1.01 (3H, *s*, H-18), 1.07 (3H, *d*, $J = 6.8$ Hz, H-27) and 1.08 (3H, *d*, $J = 6.8$ Hz, H-26) and an exocyclic methylene group attached to a quaternary carbon C-24 at δ_H 4.77 (1H, brs, H-31a) and 4.71 (1H, brd, $J = 1.2$ Hz, H-31b). The only difference between **3** and **2** was that compound **2** had a hydroxymethylene group at C-4 instead of a methyl group in the cycloartenol skeleton. The chemical shifts of C-4 at δ_C 43.8 and C-29 methyl group at δ_C 10.1 led to locate the $-CH_2OH$ group at the C-28 position. Two doublets of an AB system were detected at δ_H 3.80 (1H, *d*, $J = 10.3$ Hz, H-28a) and 3.59 (1H, *d*, $J = 10.5$ Hz, H-28b). This assignment was further confirmed by the detection of HMBC correlations between H-28 and C-3, C-4 and C-29 (Table 2). The COSY, HSQC and HMBC experiments allowed identification of all protons of this compound and the corresponding carbons. It was well established that cycloartenol and some related cycloartenol isomers are bent structures (9*β*, 19-cyclosterol) (Nes et al., 1998). The α-equatorial stereochemistry of the hydroxymethylene 28 was confirmed by the NOE effects between the H-28 and the protons H-3α, H-5α and H-6α observed in the NOESY spectrum (Fig. 2). Additionally, this spectrum showed correlations of H-19 *endo*, H-2*β* and H-29 as well as between H-19 *exo* and H-11*β* and H-18 confirming the *β*-axial position of both methyl 29 and 18. These spectral data allowed

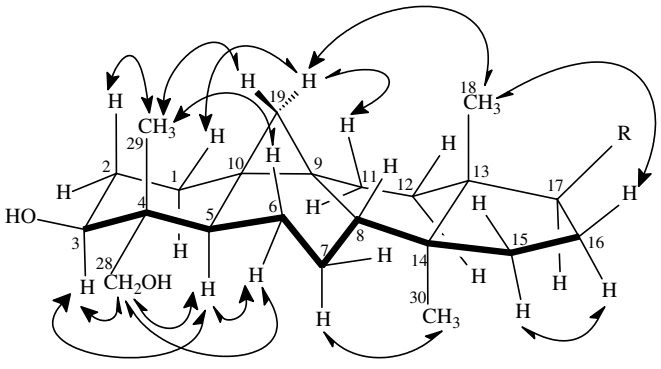
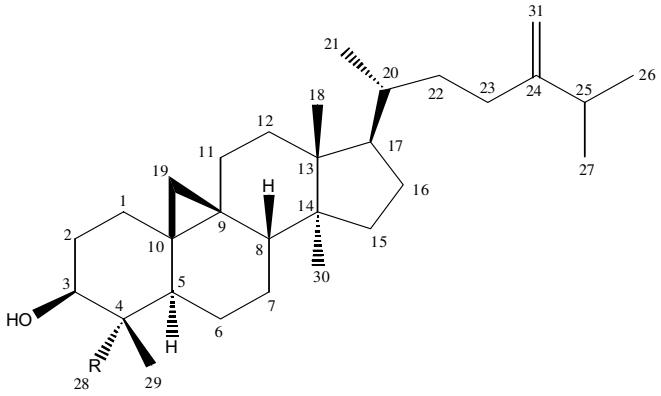


Fig. 2. Pertinent correlations observed in NOESY spectrum for compound **2**.

unambiguously the proposal of the following structure: 24-methylenecycloartane-3,28-diol (**2**). Although this compound was detected by radiochemical assay, during the C4-demethylation process of phytosterols in higher plants by maize microsomes (Pascal et al., 1993), this is the first time that it has been isolated from natural source as a pure product and its spectroscopic data is herein described.



2 R = CH_2OH
3 R = CH_3

To the best of our knowledge the present work, on the roots of *E. guyoniana,* has not performed elsewhere and led successfully to the isolation and structural elucidation of two new compounds, one cycloartane-type triterpene and another diterpenoid with tigliane skeleton. It allowed also the identification of seventeen natural products whose major constituents are triterpenoids often present in the genus *Euphorbia* and used as chemotaxonomic markers (Giner et al., 2000). This result is in good agreement with that of the previous studies made on this genus (Teresa et al., 1987; Giner et al., 2000; Öksüz et al., 1993).

3. Experimental

3.1. General experimental procedures

UV spectra were measured on a Shimadzu UV-3101 spectrophotometer and IR spectra were recorded using a Shimadzu model IR-470 spectrometer. ^1H and ^{13}C NMR spectra were obtained on a Bruker Avance spectrometer and Bruker Avance 2 spectrometer equiped with dual cryosonde in $CDCl_3$ (500 MHz and 125 MHz, respectively). 2D NMR experiments were performed using standard Bruker microprograms (XWIN-NMR version 2.6 software and TOPSPIN 1.3). Positive and negative mass spectra were performed using a Bruker Esquire Ion trap. HRMS spectra were performed on a Bruker Micromass Q-TOF. Optical rotations were measured on a P 3001 electronic polarimeter. CC was carried out on Kieselgel 60 (63–200 mesh) Merck. HPLC was performed on a Dionex apparatus equiped with an ASI-100 autosampler, a P580 pump, a diode array detector UVD 340S and a chromeleon software. Column interchim (UP5 ODB.25M, 250 × 10 mm, 5 μm) was used for semi-preparative HPLC using an isocratic elution (acetonitrile–methanol: 50–50) at 25 and 35 °C, and a flow rate of 5 ml/min, the chromatogram was monitored at 205, 210 and 220 nm. Analytical and preparative (1 mm thickness) TLCs were carried out on silica gel plates (Kieselgel 60 F_{254}, Merck).

3.2. Plant material

Roots of *Euphorbia guyoniana* were collected on May 2003 in Biskra area (Algeria). The voucher specimen was identified by Dr. Bachir Oudjehih of Agronomic Institute of Batna University where a voucher was deposited under reference LCCE/03/153.

3.3. Extraction and isolation

Powdered roots (500 g) of *Euphorbia guyoniana* were macerated for three days with $CHCl_3$ (18 l) at room temperature. Filtration and evaporation to dryness gave 14 g of a brown gummy residue of which 10 g were chromatographed on silica gel column. Elution was performed with pure petroleum ether, petroleum ether–ethyl acetate: 99.5:0.5, 99:1, 97:3, 95:5, 93:7, 90:10, 85:15, 80:20, 70:30, 50:50, 30:70 and 0:100, then by a gradient methanol–ethyl acetate: 0.5:99.5, 1:99, 3:97, 5:95, 10:90, 20:80, 30:70, 50:50 and 80:20. 434 fractions of 50 ml were collected according to absorption at 254 and 366 nm. TLC analysis of the fractions with sulfuric vanillin and heating at 150 °C, allowed the constitution of 33 fractions. Fraction 25 (180 mg) subjected to purification by silica gel column using a gradient ethyl acetate–petroleum ether (1:99, 3:97, 5:95, 10:90, 20:80, 50:50, 70:30) and ethyl acetate gave two sub-fractions 1 and 2. Sub-fraction 1 (45 mg) showing a major component, submitted to purification by silica gel column by elution with a gradient ethyl acetate–hexane (100% hexane, then increment of 2%) provided the pure compound **1** (3.5 mg). A preparative TLC (eluent: petroleum ether–ethyl acetate 60:40) was performed on the second sub-fraction 2 (95 mg) to allow isolation of the pure separated compounds **2** (4.5 mg) and **9** (3.8 mg). Fraction 13 (65 mg) was purified on a silica gel column. Elution was performed by a gradient of ethyl acetate–hexane (1:99, 3:97, 5:95 and 10:90). The pure compound **3** (35.4 mg) was obtained. Fraction 22 (145 mg) presented three major products at close R_F, and was further purified on silica gel column eluting with a gradient ethyl acetate–hexane (3:97, 5:95, 7:93, 10:90, 20:80, 40:60, 70:30) and ethyl acetate. After repeated silica gel column chromatography using the same solvents, three pure compounds were obtained **4** (8.6 mg), **7** (5.5 mg), and **8** (6.8 mg). Fraction 11 (90 mg) showing two major components was submitted to

purification by silica gel column under the same conditions to afford two products **5** (6.5 mg) and **6** (5.3 mg). Fraction 6 (90 mg) containing a mixture of products was purified on a silica gel column. Elution performed first with hexane then by a gradient of ethyl acetate–hexane (1:99, 3:97, 5:95, 7:93 and 10:90) afforded three compounds **10** (12 mg), **11** (13.2 mg) and **12** (18.5 mg). Purification of fraction **10** (80 mg) by semi-preparative HPLC, using an isocratic elution (acetonitrile–methanol: 50:50) led to the isolation of compounds **13** (14 mg), **14** (18.3 mg), **15** (9.1 mg) and **16** (25.6 mg). Fraction 15 (130 mg) was submitted to silica gel column chromatography using petroleum ether and a gradient ethyl acetate-petroleum ether (2:98, 4:96, 6:94, 8:92, 10:90, 20:80, 50:50, and 70:30). Fractions eluted with ethyl acetate 6% were combined and purified on silica gel column. Elution was performed with petroleum ether and a gradient ethyl acetate–petroleum ether (1:99, 3:97, 5:95, 7:93 , 10:90, 15:85, 20:80 and 30:70) to provide three pure compounds **17** (6.5 mg), **18** (5.4 mg) and **19** (10.6 mg).

3.3.1. 4,12-Dideoxy(4α)phorbol-13-hexadecanoate (*1*)

Colorless oil; $[\alpha]_D^{25} + 54$ ($CHCl_3$; *c* 0.21); UV ($CHCl_3$) λ_{max} (log ε): 236 (3.50), 335 (2.25) nm; IR (CCl_4) ν_{max}: 3405, 2954, 2848, 1715, 1630, 1508, 1464, 1128, 1050 cm^{-1}; ^1H and ^{13}C NMR ($CDCl_3$), see Table 1; ESIMS positive mode: *m/z* 593 $[M+Na]^+$, 337 $[(M+Na)-256]^+$; HRESIMS: *m/z* 593.4174 (calcd for $C_{36}H_{58}O_5Na$, 593.4176).

3.3.2. 24-Methylenecycloartane-3,28-diol (*2*)

White powder; m.p. 142–144 °C; $[\alpha]_D^{25} + 64$ ($CHCl_3$; *c* 0.38); UV ($CHCl_3$) λ_{max} (log ε): 205 (3.64) nm; IR (KBr) ν_{max}: 3430, 2914, 2840, 1645, 1454, 1365, 1128, 1020 cm^{-1}; ^1H and ^{13}C NMR ($CDCl_3$) see Table 2; ESIMS positive mode: *m/z* 479 $[M+Na]^+$, 935 $[2M+Na]^+$; HRESIMS: *m/z* 479.3868 (calcd for $C_{31}H_{52}O_2Na$, 479.3860).

Acknowledgements

The authors thank Drs. G. Massiot and B. David of the Centre de Recherche sur les Substances Naturelles for fruitful discussion and to CNRS, Pierre FABRE Company and DRS (Algeria) for financial support.

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