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Rotenoid derivatives and other constituents of the twigs of *Millettia duchesnei*

François Ngandeu [a], Merhatibeb Bezabih [b,*], Dieudonne Ngamga [a], Alembert T. Tchinda [c], Bonaventure T. Ngadjui [d], Berhanu M. Abegaz [b,*], Hanh Dufat [e], François Tillequin [e]

[a] *Department of Chemistry, Faculty of Science, University of Dschang, P.O. Box 67, Dschang, Cameroon*
[b] *Department of Chemistry, Faculty of Science, University of Botswana, Private Bag 00704, Gaborone, Botswana*
[c] *Institute of Medical Research and Medicinal Plants Studies (I.M.P.M), P.O. Box 6163, Yaoundé, Cameroon*
[d] *Department of Organic Chemistry, Faculty of Science, University of Yaoundé I, P.O. Box 812, Yaoundé, Cameroon*
[e] *Laboratoire de Pharmacognosie U.M.R au C.N.R.S. No. 8638, Faculté des Sciences Pharmaceutiques et Biologiques, Université René Descartes, Paris 5, 4 Avenue de l'Observatoire-75270, Paris, Cedex 06, France*

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Abstract

Three prenylated rotenoids, elliptol, 12-deoxo-12α-methoxyelliptone and 6-methoxy-6a,12a-dehydrodeguelin were isolated from the twigs of *Millettia duchesnei*, together with the known compounds, 6a,12a-dehydrodeguelin, 6-hydroxy-6a,12a-dehydrodeguelin, 6-oxo-6a,12a-dehydrodeguelin, elliptone, 12a-hydroxyelliptone and eriodictyol. Their structures were elucidated on the basis of spectral data and comparison with information reported in the literature and with authentic specimens for some known compounds. The full NMR data of 6-oxo-6a,12a-dehydrodeguelin and 6-hydroxy-6a,12a-dehydrodeguelin are reported here for the first time.

Keywords: *Millettia duchesnei*; Leguminosae; Rotenoids; Rotenoloids; 12-Deoxo-12α-methoxyelliptone; 6-Methoxy-6a,12a-dehydrodeguelin; Elliptol

1. Introduction

Many plants of the Leguminosae family, especially, in the genera *Derris*, *Lonchocarpus*, *Millettia*, *Mundulea* and *Tephrosia* are used as fish poison and insecticides (Thasana et al., 2001; Kumar et al., 1989). The genus *Millettia*, represented by more than 200 species of climbers and trees, is distributed in tropical Africa, Asia and Australia (Thulin, 1983). Plants of this genus are used by some communities in Cameroon for the treatment of intestinal parasites, colic in children (Fuendjiep et al., 1998) and oral treatment for boils (Yankep et al., 2003). *Millettia duchesnei* is a liana growing in the rain tropical forest of Cameroon and Democratic Republic of Congo. A saponin has been reported from the roots of this plant (Kapundu et al., 1984). Previous phytochemical studies on some *Millettia* species revealed the presence of chalcones, isoflavones, rotenoids (Dagne et al., 1989; Yenesew et al., 1998), isoflavans (Khalid and Waterman, 1983), flavanones, isocoumarins (Baruah et al., 1984), and pterocarpans (Sritularak et al., 2002). The present paper describes the isolation of three new rotenoids, elliptol (**1**), 12-deoxo-12α-methoxyelliptone (**2**) and 6-methoxy-6a,12a-dehydrodeguelin (**3**) together with the known compounds, 6-oxo-6a,12a-dehydrodeguelin (**5**) (Pereira et al., 1998) 6-hydroxy-6a,12a-dehydrodeguelin (**6**) (Fang and Casida, 1998, 1999), 12a-hydroxyelliptone (**8**) (Ito et al., 2004), elliptone (**9**) (Crombie et al., 1975), and 6a,12a-dehydrodeguelin (**10**) (Lin and Kuo, 1995).

* Corresponding authors. Tel.: +267 3552830; fax: +267 3552836 (M. Bezabih); Tel.: + 267 3552497; fax: +267 3552836 (B.M. Abegaz).
E-mail addresses: bezabihm@mopipi.ub.bw (M. Bezabih), abegazb@mopipi.ub.bw (B.M. Abegaz).

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2. Results and discussion

Compound **1** was obtained as light brown gummy substance. It was assigned the molecular formula $C_{20}H_{18}O_6$ from HR-FABMS measurement that showed a molecular ion peak at *m/z* 354.1101 (Calc. 354.1103). The IR spectrum exhibited bands at $\nu_{max} = 3414$ and 1635 cm^{-1} due to hydroxyl and conjugated carbonyl groups, respectively. It showed UV absorptions at $\lambda_{max} = 224$ and 279 nm. NMR spectral analysis indicated that compound **1** is a derivative of the rotenoid elliptone (**9**) (Anzeveno, 1979; Crombie et al., 1975) (Tables 1 and 2). Thus the ^{1}H NMR spectrum of **1** displayed two singlets at δ 6.40 and 6.50 assignable to H-1 and H-4, respectively, and two methoxyl groups at δ 3.72 and 3.86 placed on C-2 and C-3 as derived from HMBC correlations (Table 3). A group of AX pattern signals resonates at δ 7.04 (*d*, $J = 1.9$ Hz, H-3′) and 7.70 (*d*, $J = 1.9$ Hz, H-2′) that are assigned for the 2,3-disubstituted furan ring. Two *ortho*-coupled protons resonating at δ 7.13 (*d*, $J = 9.0$ Hz) and 7.84 (*d*, $J = 9.0$ Hz) assignable to H-10 and H-11, respectively, also support the similarity of ring D of **1** to that of elliptone (**9**). The attachment of the furan ring to ring D was established to be through C-8 and C-9 from the HMBC cross-peaks that both H-2′ and H-3′ showed to C-8 and C-9. Biosynthetic considerations also support the oxygenation pattern in ring D.

The major difference between the ^{1}H NMR spectra of **1** and **9** is in the resonance position and the splitting patterns of signals from the aliphatic protons at C-6a and C-12a (Table 1). Hence, protons at C-6a in **1** showed two sets of multiplets each integrating for one proton at δ 2.43 and 2.20. In compound **9**, the signal for the proton on the corresponding carbon is integrated for one proton and appeared as a multiplet at δ 5.10. The chemical shift positions for H-6a in the two compounds indicated that an oxymethine group in **9** is replaced by a methylene group in **1**. The signal due to H-12a in compound **9** resonated at δ 3.97 as a doublet while in **1** it appeared as a triplet at δ 4.82

Table 2
^{13}C NMR data (δ) for compounds **1**, **2**, **5** and **6** (150 MHz, $CDCl_3$) and **3** (75 MHz, $CDCl_3$)

Position	1	2	3	5	6
1	112.2	111.7	109.2	109.1	108.2
2	143.5	143.5	144.8	144.3	151.2
3	149.5	149.2	149.4	149.3	146.9
4	101.1	100.2	100.9	101.2	99.6
4a	149.5	149.17	142.8	142.4	145.3
6	63.2	65.6	95.5	89.4	156.1
6a	27.1	70.2	152.6	153.8	142.1
7a	160.1	146.6	151.3	151.1	151.5
8	111.8	117.2	109.7	109.1	109.6
9	159.9	156.7	157.5	157.8	158.9
10	104.2	103.8	111.5	115.4	116.3
11	126.2	125.7	126.5	126.3	126.5
11a	111.8	113.7	118.3	117.9	117.9
12	207.0	76.8	175.4	175.9	176.6
12a	41.9	37.3	111.3	110.5	121.4
12b	109.7	109.9	108.9	107.9	107.9
2′	144.7	144.0	77.9	78.1	78.6
3′	105.1	104.0	130.3	130.5	130.5
4′			114.9	114.6	114.8
5′			29.2	28.1	28.3
6′			29.7	28.3	28.3
2-OMe	56.4	55.8	56.3	55.8	56.3
3-OMe	55.8	56.6	55.9	56.0	56.2
6-OMe			55.8		
12-OMe		57.3			

Table 1
^{1}H NMR data (δ) for compounds **1**, **2**, **5** and **6** (600 MHz, $CDCl_3$) and **3** and **7**[a] (300 MHz, $CDCl_3$) and **9**[b] (60 MHz, $CDCl_3$)

Position	1	2	3	5	6	7	9
1	6.40 *s*	6.86 *s*	8.64 *s*	8.47 *s*	9.02 *s*	6.72 *s*	6.81, *s*
4	6.50 *s*	6.47 *s*	6.71 *s*	6.61 *s*	6.92 *s*	6.48 *s*	6.50, *s*
6α	4.28 *m*	4.65 *t* (10.2)	5.85 *s*	6.23 *d* (9.0)		4.66 *t* (11.4)	4.76, *dd* (3.5, 12.0)
6β	4.22 *m*	4.32 *dd* (10.2, 4.5)				4.28 *dd* (11.4, 5.3)	4.23, *dd* (1.0, 12.0)
6a	2.43 *m*, 2.20 *m*	4.92 *dd* (10.2, 4.8)				4.94 *m*	5.10, *m*
10	7.13 *d* (9.0)	7.11 *d* (7.8)	6.90 *d* (9.0)	6.84 *d* (8.4)	6.95 *d* (8.4)	7.12 *d* (8.4)	7.18, *dd* (0.5, 9.0)
11	7.84 *d* (9.0)	7.17 *d* (7.8)	8.08 *d* (9.0)	7.93 *d* (8.4)	8.08 *d* (8.4)	7.18 *d* (8.4)	7.93, d (9.0)
12		4.62 *d* (3.4)				5.04 *d* (4.8)	
12a	4.82 *t* (6.0)	3.53 *t* (4.8)				3.48 *t* (4.8)	3.97, *d* (3.5)
2′	7.70 *d* (1.9)	7.55 *d* (1.8)				7.54 *d* (2.0)	7.60, *d* (2.0)
3′	7.04 *d* (1.9)	6.87 *d* (1.8)	5.75 *d* (10.0)	5.74 *d* (10.2)	5.79 *d* (10.2)	6.84 *d* (2.0)	6.95, *dd* (0.5, 2.0)
4′			6.85 *d* (10.0)	6.84 *d* (10.2)	7.05 *d* (10.2)		
5′			1.55 *s*	1.52 *s*	1.52 *s*		
6′			1.55 *s*	1.52 *s*	1.52 *s*		
2-OMe	3.72 *s*	3.86 *s*	3.99 *s*	3.90 *s*	4.05 *s*	3.84 *s*	3.84, *s*
3-OMe	3.86 *s*	3.85 *s*	3.94 *s*	3.84 *s*	3.98 *s*	3.86 *s*	3.84, *s*
6-OMe			3.64 *s*				
12-OMe		3.42 *s*					
6-OH				4.51 *d* (9.0)			
7a-OH	13.40 *s*						

Coupling constant in Hz are given in parentheses.
[a] Taken from Lin et al. (1993).
[b] Taken from Anzeveno (1979).

Table 3
HMBC correlations (H → C) observed for compounds **1**, **2**, **3**, **5** and **6**

Proton	1	2	3	5	6
1	C-2, C-3/C-4a, C-12a	C-2, C-3, C-4, C-4a, C-12a, C-12b	C-2, C-12b	C-2, C-3, C-4a, C-12a, C-12b	C-2, C-3, C-4a, C-12a, C-12b
4	C-2, C-3, C-4a, C-12b	C-12a, C-12b	C-3, C-4a	C-2, C-3, C-4a, C-12a, C-12b	C-2, C-3, C-4a, C-12b
6	C-4a, C-12a	C-4a, C-6a, C-12b	C-4a	C-6a, C-12a	
6a	C-12a	C-6, C-12, C-12a			
10	C-9, C-11a	C-7a, C-8, C-9	C-2′, C-7a, C-8, C-9	C-2′, C-7a, C-8, C-9, C-11a	C-7a, C-8, C-11a
11	C-8, C-11a, C-12	C-7a, C-8, C-9, C-11a, C-12	C-9, C-12	C-7a, C-9	C-7a, C-9, C-12
12		C-6a, C-11, C-11a, C-12a, C-12b, 12-OMe			
12a	C-1, C-4a, C-6, C-6a, C-12, C-12b	C-1, C-4a, C-6, C-6a, C-11a			
2′	C-8, C-9	C-3′, C-8, C-9			
3′	C-2′, C-8, C-9	C-2′, C-8, C-10	C-2′, C-5′, C-6′, C-8	C-2′, C-5′, C-6′, C-8	C-5′, C-6′
4′			C-7a, C-8, C-9	C-2′,C-8, C-9, C-11a	C-2′, C-7a, C-9
5′			C-2′, C-3′, C-6′	C-2′, C-3′, C-6′	C-2′, C-3′, C-6′
6′			C-2′, C-3′, C-5′	C-2′, C-3′, C-5′	C-2′, C-3′, C-5′
2-OMe		C-2	C-2	C-2	C-2
3-OMe		C-3	C-3	C-3	C-3
6-OMe			C-6		
12-OMe		C-12			
7a-OH	C-7a, C-8, C-11a				

further supporting that C-6a is secondary and tertiary in **1** and **9**, respectively. Analysis of the ^{13}C NMR and DEPT spectra also revealed that the signal for the sp^3 oxygenated C-6a in **9** at δ 71.8 is not appearing in the spectra of **1**, instead a signal for a methylene carbon at δ 27.1 is observed. Additional proof for the structure of compound **1** was available from the ^1H–^1H COSY spectrum that showed connectivities among H-12a, 2H-6a and 2H-6.

On the basis of the foregoing discussion compound **1** can only have a rotenoloid skeleton (Yenesew et al., 2006). The biosynthesis of rotenoids is well established and the formation of ring C is taking place prior to ring B (Crombie and Whiting, 1998). Hence, it is unlikely that **1** may be a precursor to **9**. Rather, compound **1** could have been derived from elliptone through the opening of ring C between C-6a and 7-*O* and rotation along the C-12/C-11a bond to allow the placement of the hydroxyl group on C-7a *peri* to the carbonyl group on C-12. Evidence for the presence of a hydroxyl group on C-7a was available from the signal in the ^1H NMR spectrum at δ 13.40. In the HMBC spectrum this signal correlated to C-7a, C-8 and C-11a. In the literature, two rotenoloids, rotenol and deguelol are named after the names of the parent rotenoids rotenone and deguelin, respectively (Yenesew et al., 2006). Accordingly, the name elliptol is suggested for compound **1**, which is a new modified prenylated rotenoid derived from elliptone. Elliptol is the fourth rotenoid belonging to the recently identified sub-class of compounds known as rotenoloid (Yenesew et al., 2005, 2006). The absolute stereochemistry of **1** is not determined. Its levorotatory ($[\alpha]D = -32.2°$) optical rotation however, is suggesting that **1** may have the same stereochemistry as 7a-*O*-methyldeguelol at C-12a (Yenesew et al., 2005).

Compound **2** was isolated as colourless oil. The HR-FABMS of **2** showed a molecular ion peak at *m/z* 368.1296 (Calc. 368.1260), corresponding to the molecular formula $C_{21}H_{20}O_6$. The IR spectrum exhibited bands at $\nu_{max} = 1633\ cm^{-1}$ due to aromatic double bonds (C=C). It showed UV absorptions at $\lambda_{max} = 217$, 248, 256 and 291 nm. General similarities were observed between the NMR data of compound **2** and those reported for 12-deoxo-12α-acetoxyelliptone (**4**) and 12-deoxo-12α-hydroxyelliptone (**7**) (Lin et al., 1993) (Table 1). The ^1H–^1H COSY spectrum showed connectivities among H-12, H-12a, H-6a and 2H-6. The characteristic carbonyl signal of rotenoids (*ca.* δ 176) (Lin and Kuo, 1995; Crombie et al., 1975) was not observed in the ^{13}C NMR spectrum of compound **2**. A pair of coupled methyne protons at δ 6.87 (*d*, $J = 1.8$ Hz) and 7.55 (*d*, $J = 1.8$ Hz) and their associated carbons at δ 104.0 (C-3′) and 144.0 (C-2′), respectively were assigned for the furan moiety. The ^1H NMR spectrum along with the ^1H–^1H COSY displayed two *ortho*-coupled protons at δ 7.11 (*d*, $J = 7.8$ Hz) and 7.77 (*d*, $J = 7.8$ Hz) which were readily assigned to H-10 and H-11, respectively. Like in elliptone (**9**), the points of attachment of the furan ring to ring D were established to be at C-8 and C-9 from the HMBC cross-peaks that both H-2′ (δ 7.55) and H-3′ (δ 6.87) showed with C-8 (δ 117.2) and C-9 (δ 156.7). The HMBC correlation between the methoxyl protons at δ 3.42 and C-12 (δ 76.8) is used to place one of the methoxy groups on C-12. HMBC cross-peaks (Table 3) were also used to assign the remaining two methoxy groups to ring A which are very similar to those of compounds **4** and **7**. NOE irradiation of H-6a (δ 4.92) resulted in the enhancement of the signals at δ 3.53 (H-12a) and 4.32 (H_1-6). Moreover, irradiation of H-12a produced a positive NOE

enhancement on H-12 (δ 4.64). Thus, the *cis*-B/C fusion and the 12 α-OMe relative configuration were assigned to compound **2**. Hence compound **2** was determined to be 12-deoxo-12α-methoxyelliptone which is reported here for the first time. Further confirmation of the structure of compound **2** was obtained from reduction of elliptone (**9**) using $NaBH_4$ that provided compound **7**, followed by methylation with Me_2SO_4 to give a compound with levorotatory optical rotation and which was identical (TLC and NMR spectral data) with compound **2**.

Compound **3** was obtained as yellow oil. The molecular formula of **3** was determined to be $C_{24}H_{22}O_7$ from HR-ESMS measurements which gave a sodiated molecular ion peak at *m*/*z* 445.1250. The IR spectrum exhibited bands at $\nu_{max} = 1667\ cm^{-1}$ due to a conjugated carbonyl group. It showed UV absorptions at $\lambda_{max} = 229$, 262 and 302 nm. The NMR data generated for compound **3** were similar to those of 6-hydroxy-6a,12a-dehydrodeguelin (**5**). Thus, its ^1H NMR displayed one ketal proton signal at δ 5.85 and six vinyl/aromatic proton signals consisting of two singlet signals of one proton each at δ 8.64 and 6.71 assignable to H-1 and H-4; two of them form an AX spin system at δ 6.90 (*d*, $J = 9.0$ Hz) and 8.08 (*d*, $J = 9.0$ Hz) which can be assigned to H-10 and H-11 of ring D; the remaining two proton signals form also an AX system at δ 5.75 (*d*, $J = 10.0$ Hz) and 6.85 (*d*, $J = 10.0$ Hz); the later AX spin system together with an intense singlet at δ 1.55 integrating for six protons are characteristic of 2,2-dimethylpyrano moiety which is connected to ring D through C-8 and C-9. The molecular mass of compound **3** is 14 amu higher than that of compound **5**, suggesting that **3** is a monomethyl ether of **5**. The major difference in the NMR spectra of **3** and **5** is the presence of one additional methoxyl group (δ_H 3.64 and δ_C 55.8), in **3** which showed a cross-peak in the HMBC spectrum (Table 3) with the ketal carbon (δ_C 95.5) assigned to C-6. It is also observed that H-6 in **3** (δ 5.58) is experiencing an up field shift due to the shielding effect of the methoxyl group on C-6 when compared to that in **5** (δ 6.23). On the basis of the above evidences, the new rotenoid **3** is deduced to be 6-methoxy-6a,12a-dehydrodeguelin.

Compounds **2** and **3** are both levorotatory with optical rotation values of $[\alpha]D = -36.66°$ and $-7.50°$, respectively. However the absolute configurations at all stereo centers remain to be determined. Crombie and Whiting (1998) observed that although 6a,12a-dehydrorotenoids are reported from nature, they may sometimes be artefacts of aerial oxidation of the corresponding rotenoids and rotenolones (12a-hydroxyrotoenoids) particularly during work-up or storage. The isolation condition for the 6a,12a-dehydro derivative compound **3**, is not quite different from that followed in the isolation of compounds **2**, **8** and **9**. Hence, there seems no doubt that **3** is genuine natural product.

Compounds **5** and **6** were isolated and characterized as 6-oxo-6a,12a-dehydrodeguelin and 6-hydroxy-6a,12a-dehydrodeguelin, respectively. Oxidation of **5** using excess manganese oxide gave compound **6** which was previously reported from Cubé Resin (roots of *Lonchocarpus utilis* and *L. urucu*) (Fang and Casida, 1998, 1999). Compound **5** was previously only characterized by high resolution GC-MS in *Tephrosia candida* roots (Pereira et al., 1998). The full spectroscopic data for both compounds is reported here for the first time.

3. Experimental

3.1. General experimental procedures

Melting points were obtained on Griffin melting point apparatus and are uncorrected. UV spectra were taken in methanol solution on Shimadzu UV-2101PC spectrometer. IR spectra were measured as KBr disk on Perkin-Elmer system 2000 FT-IR spectrometer. Optical rotation was measured on Autopol IV automatic polarimeter model Rudolph Research Analytical. FABMS were recorded on JOEL MS route instrument. EIMS were recorded on GIT premier, Waters spectrometer. ESMS were recorded on ZQ 2000 Waters spectrometer. ^1H NMR (300 and 600 MHz) and ^{13}C NMR (75 and 150 MHz) spectra were recorded on Bruker Avance spectrometers in $CDCl_3$ with residual solvent peaks as internal references. TLC were performed on Merck precoated plates (Kieselgel 60 $F_{254-360}$). Silica gel (0.040–0.006 mm) was used for column chromatography (CC). $20 \times 20\ cm^2$ self-made glass plates (0.50 mm layer of silica gel 60 $F_{254-360}$ Merck) were used for preparative TLC. Spots were visualised by UV illumination (254 and 366 nm).

3.2. Plant material

Twigs of *M. duchesnei* were collected in April 2003 from Kumba (South West Province, Cameroon) and identified by Mr Victor Nana of the National Herbarium, Yaoundé, Cameroon, where a voucher specimen (No. 23360/SRF/CAM) is deposited.

3.3. Extraction and isolation

The air-dried and powdered twigs of *M. duchesnei* (3 kg) were macerated with CH_2Cl_2–MeOH (1:1) mixture, two times (24 h each) at room temperature. Filtration and removal of solvent under vacuum gave a dark brown residue (210 g). Part of this residue (110 g) was subjected to CC using silica gel (400 g) and eluted successively with petrol-ethyl acetate gradient of increasing polarity, pure EtOAc and then EtOAc–MeOH mixtures to give 56 fractions of 500 ml each. Fractions were combined based on their TLC profiles into five. Fractions 1–16 (10 g) revealed mainly the presence of stigmasterol and lupeol, compared with authentic samples available in our laboratory. Fractions 17–32 (6 g) obtained with petrol-EtOAc (2:8) were chromatographed with silica gel using petrol-EtOAc gradient as eluent to afford 6a,12a-dehydrodeguelin (**10**) (50 mg) and 6-hydroxy-6a,12a-dehydrodeguelin (**6**) (5 mg). Fractions 33–42 (3 g) eluted with petrol-EtOAc (4:6) were sub-

jected to a Sephadex LH-20 column and eluted with $CHCl_3$–MeOH (2:1) mixture. The post-chlorophyll fractions were combined and subjected successively to silica gel CC with $CHCl_3$–MeOH (99:1) and then to preparative TLC to give elliptol (**1**) (9 mg), 12-deoxo-12-methoxyelliptone (**2**) (4 mg) and elliptone (**9**) (30 mg) [eluent: CH_2Cl_2–Me_2CO–MeOH (8:1:1)], 6-methoxy-6a,12a-dehydrodeguelin (**3**) (4 mg), 6-oxo-6a,12a-dehydrodeguelin (**6**) (3 mg) and 12a-hydroxyelliptone (**8**) (11 mg) [eluent: CH_2Cl_2-EtOAc (96:4)]. Fractions 43–48 (1 g) obtained with petrol-EtOAc (3:7) were subjected to repeated CC over silica gel with $CHCl_3$–MeOH (9:1) to give eriodictyol (2 mg). Fractions 49–56 (1 g) on TLC did not show any thing interesting and were not worked on further.

3.4. Elliptol (*1*)

Light brown gummy substance; $[\alpha]_D^{23} = -32.20°$ (c 0.0001, $CHCl_3$); UV $\lambda_{max}^{CHCl_3}$ nm (log ε): 279(3.0), 224(4.4); IR ν_{max}^{KBr} cm^{-1}: 3414, 2923, 1635, 1618, 1512, 1464, 1088, 615, 405; ^1H NMR (see Table 1); ^{13}C NMR (see Table 2); HRFABMS (positive) *m/z* 354.1112 ($[M]^+$, Calc. for $C_{20}H_{18}O_6$: 354.1103).

3.5. 12-deoxo-12α-methoxyelliptone (*2*)

Colourless oil, $[\alpha]_D^{27} = -36.66°$ (*c* 0.0003, $CHCl_3$); UV λ_{max}^{MeOH} nm (log ε): 291 (2.9), 256 (3.2), 248 (3.2), 217 (3.5); IR ν_{max}^{KBr} cm^{-1}: 1633, 1514, 1464, 1374, 1252, 1218, 1192, 1088, 1028, 980, 820; ^1H NMR (see Table 1); ^{13}C NMR (see Table 2); HRFABMS (positive) *m/z* 368.1296 ($[M]^+$, Calc. for $C_{21}H_{20}O_6$: 368.1260).

3.5.1. Conversion of elliptone (*9*) to deoxo-12α-methoxyelliptone (*2*)

Compound **9** (22 mg) was allowed to react with $NaBH_4$ (15 mg) in MeOH (2 mL) at RT for 30 min. The reaction mixture was extracted with CH_2Cl_2 and dried over Na_2SO_4 to yield 18.4 mg (83.2%) of compound **7**. Compound **7** (15 mg) was allowed to react with NaH (3.07 g) in DMF (dimethylformamide) in a round bottom flask placed in an ice bath. After removing the flask from the ice, 10.1 mg of Me_2SO_4 were added to the reaction mixture at RT, which was cooled in an ice bath and shaken for 30 min. After drying, concentrating and purifying, 9 mg (57.7%) of a compound identical to **2** in tlc and NMR properties was obtained. The product also has an optical rotation of $[\alpha]_D^{20} = -154.04°$ (*c* 0.0018, $CHCl_3$).

3.6. 6-methoxy-6a,12a-dehydrodeguelin (*3*)

Yellow oil, $[\alpha]_D^{23} = -7.50°$ (c 0.05, $CHCl_3$); UV λ_{max}^{MeOH} nm (log ε): 302 (3.1), 262 (3.1), 229 (2.8); IR ν_{max}^{KBr} cm^{-1}: 2918, 1667, 1494, 1456, 1362, 1207, 1087, 1068; ^1H NMR (see Table 1); ^{13}C NMR (see Tables 2); ESMS (positive) *m/z* (rel. int.): 445 $[M+Na]^+$ (100), 391 $[M–OCH_3]^+$ (10), 305 $[391–2\times COCH_3]^+$ (7).

3.7. 6-hydroxy-6a,12a-dehydrodeguelin (*5*)

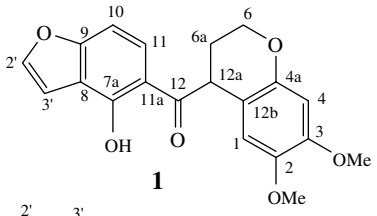
Yellow powder; m.p. 220–222 °C; $[\alpha]_D^{23} = -120.00°$ (c 0.0001, $CHCl_3$); UV $\lambda_{max}^{CHCl_3}$ nm (log ε): 306(4.4), 227(5.4); IR ν_{max}^{KBr} cm^{-1}: 3415, 2923, 2851, 2363, 2074, 1624, 1511, 1447, 1284, 1106, 618; ^1H NMR (see Table 1); ^{13}C NMR (see Table 2); HR-FABMS (positive) *m/z* 408.1220 ($[M]^+$, Calc. for $C_{23}H_{20}O_7$: 408.1209).

3.7.1. Oxidation of 6-hydroxy-6a,12a-dehydrodeguelin (*5*)

5 mg of **5** and an excess of MnO_2 (100 mg) in 40 ml of CH_2Cl_2 were refluxed for 3 days. The reaction mixture was extracted with CH_2Cl_2. The CH_2Cl_2 layer was obtained, dried with Na_2SO_4 and evaporated under reduced pressure to give 4.8 mg (96.5%) of a yellow powder identical (TLC and ^1H NMR) to 6-oxo-6a,12a-dehydrodeguelin (**6**).

3.8. 6-oxo-6a,12a-dehydrodeguelin (*6*)

Yellow powder; m.p. 222–224 °C; UV $\lambda_{max}^{CHCl_3}$ nm (log ε): 306(4.4), 227(5.76); IR ν_{max}^{KBr} cm^{-1}: 2923, 2853, 2367, 1739, 1620, 1640, 1512, 1289, 1112, 1065, 879, 754, 613; ^1H NMR (see Table 1); ^{13}C NMR (see Table 2); HR-EIMS (positive) *m/z* 406.0701 ($[M]^+$, Calc. for $C_{23}H_{18}O_7$: 406.3917).



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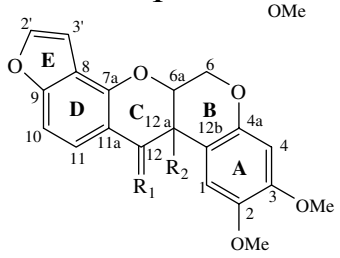
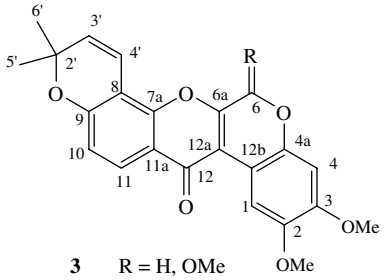


	R_1	R_2
2	H, α-OMe	H
4	H, α-OAc	H
7	H, OH	H
8	O	OH
9	O	H



3	R = H, OMe
5	R = H, OH
6	R = O
10	R = H, H

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