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Phytochemistry 64 (2003) 845–849

PHYTOCHEMISTRY

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Pentacyclic triterpenoid and saponins from *Gambeya boukokoensis*

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Received 7 January 2003; received in revised form 15 July 2003

Abstract

Chemical studies of the EtOAc extract of *Gambeya boukokoensis* Aubr. et Pellegr. stem bark led to the isolation of eight compounds. Three of them were elucidated as new compounds and designated as: gamboukokoensein A, 1α,2α,3β,19α,23-pentahydroxyurs-12-en-28-oic acid; gamboukokoenside A, 2β,3β,6β,28-tetrahydroxyolean-12-en-23-oic acid 23-*O*-α-L-arabinopyranosyl ester and gamboukokoenside B, 6β,28-dihydroxy-3-oxoolean-12-en-23-oic acid 23-*O*-α-L-arabinopyranosyl ester. The other five compounds were known and identified as myrianthic acid, protobassic acid, oleanolic acid, erythrodiol and chondrillasterol. Their structures were elucidated on the basis of one and two dimensional NMR spectroscopic techniques, FABMS, ESMS and chemical evidence.

Keywords: Gambeya boukokoensis; Sapotaceae; Stem bark; Triterpenoids; Saponins; Gamboukokoensein A; Gamboukokoensides A and B

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1. Introduction

The genus *Gambeya* belongs to the Sapotaceae family. It is related to *Chrysophyllum* Linn, a pantropical genus of about 80 species widely distributed in West and Central Africa (Keay, 1989). They are used in folk medicine to treat various diseases including vaginal infections and sterility. Some of them are reported to exhibit anti-tumor and anti-inflammatory properties (Bouquet, 1969; Bouquet and Debray, 1974; Dalziel, 1937). Our recent chemical research on *Gambeya africana*, *synonym* of *Chrysophyllum delevoyi* De Wild, led to the isolation and characterization of fatty acid esters of triterpenoids and steroid glycosides with high concentrations (Wandji et al., 2002). As a continuation of our investigation on the genus *Gambeya*, we report in this paper on the chemical study of *G. boukokoensis* from Cameroon. A new pentacyclic triterpenoid (**1**) and two new saponins (**3**, **4**) have been isolated for the first time from this species along with five known compounds (**2**, **5**–**8**).

2. Results and discussion

The stem bark of *G. boukokoensis* was chopped, air-dried and ground. The powder was successively extracted with EtOAc and MeOH. Part of the EtOAc extract was repeatedly subjected to column chromatography on silica gel to afford eight compounds (**1**–**8**). Compound **1** was characterized as a novel pentacyclic triterpenoid, while **3** and **4** were characterized as two novel saponins and compounds **2**, **5**–**8** were identified by comparison as known constituents.

Compound **1** was obtained as white powder. Its IR spectrum indicated absorption bands assigned to the carboxylic acid (1705 cm^{-1}), hydroxyl (3300–3500 cm^{-1}) and a double bond (1635 cm^{-1}) in the molecule.

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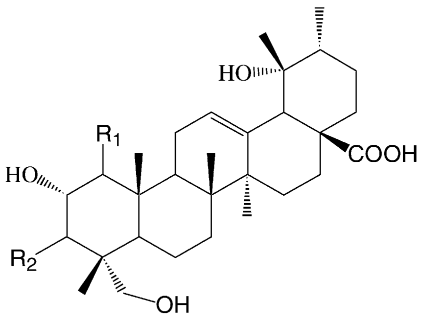
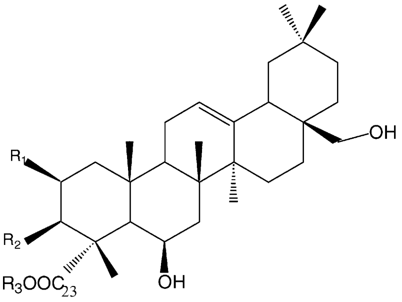
doi:10.1016/S0031-9422(03)00495-3



1 R_1 = α-OH R_2 = β-OH

2 R_1 = H R_2 = α-OH



3 R_1 = OH R_2 = OH R_3 = Ara

3a R_1 =OH R_2 = OH R_3 = H

4 R_1 = H R_2 = O R_3 = Ara

4a R_1 = H R_2 = O R_3 = H

Fig. 1. Structures of compounds **1**–**4**.

Table 1
^{13}C NMR data of compounds **1**, **2**, **3**, **3a**, **4**, **4a** and **5** in DMSO[a]

Attribution	**1**	**2**	**3**	**3a**	**4**	**4a**	**5**
1	77.5	42.4	47.7	47.1	39.7	39.6	47.1
2	71.0	65.8	71.8	71.8	36.8	36.9	71.3
3	80.1	77.0	73.3	72.5	211.8	211.5	71.8
4	43.5	44.4	55.9	54.0	56.5	55.0	43.1
5	44.1	47.9	48.6	49.0	53.9	51.5	48.8
6	18.6	18.6	67.0	67.0	65.0	66.0	67.0
7	33.6	33.4	40.5	40.6	40.9	40.8	40.7
8	40.0	40.8	39.1	39.2	39.1	39.2	39.1
9	48.6	47.7	47.9	48.0	50.7	50.6	48.0
10	39.8	38.7	36.8	36.7	36.8	36.7	36.8
11	27.0	24.3	23.6	23.5	23.2	23.3	23.7
12	129.3	127.8	123.1	123.0	122.4	122.5	123.0
13	138.4	139.7	144.2	144.2	144.2	144.2	144.2
14	42.1	42.3	42.9	48.2	42.8	48.2	42.9
15	29.2	29.1	28.1	28.2	28.1	28.2	28.1
16	26.3	26.2	24.2	24.1	24.2	24.1	24.1
17	48.0	48.0	47.3	47.2	47.1	47.1	46.5
18	54.2	54.2	41.7	41.6	41.7	41.6	41.9
19	72.7	72.7	46.2	46.1	46.3	46.2	46.7
20	42.4	42.2	31.4	31.3	31.4	31.3	31.4
21	27.9	27.0	34.2	34.2	34.2	34.2	34.4
22	38.3	38.2	33.7	33.6	32.7	32.9	33.2
23	70.1	70.2	176.2	180.1	176.2	180.2	65.6
24	13.8	17.5	15.0	14.6	14.5	14.5	16.1
25	18.0	17.7	17.3	17.2	18.0	18.1	18.7
26	18.0	17.8	18.7	18.8	19.1	19.0	19.1
27	25.2	25.1	26.8	26.9	27.0	27.1	26.8
28	180.0	180.0	72.3	72.1	72.3	72.1	179.6
29	27.4	27.4	33.8	33.7	33.8	33.7	33.9
30	17.3	17.3	24.4	24.5	24.4	24.5	24.4
23-COO-Ara							
1′			95.0		95.0		
2′			76.5		76.6		
3′			70.6		70.6		
4′			66.5		66.9		
5′			64.4		64.3		

[a] Assignments were based on HETCOR, HSQC, HMBC and NOESY experiments.

The ES mass spectrum displayed a pseudo-molecular ion peak at m/z 543 $[M+Na]^+$ which suggested the molecular formula of $C_{30}H_{48}O_7$, containing seven insaturation equivalents. This result was consistent with the CI/NH_3 mass spectrum which displayed pseudo-molecular ion at m/z 538 $[M+NH_4]^+$ and confirmed by the ^{13}C NMR spectrum (Table 1). The characteristic retro-Diels–Alder fragment peaks at m/z 256 (A/B rings) and 264 (D/E rings) indicated a C-12 / C-13 double bond which suggested a ursane or oleanane skeleton for compound **1** (Bao-Zhi Li et al., 1998), and four oxygenated substitutions on rings A/B, one oxygenated and one carboxylic acid substitutions on rings D/E. The ^1H NMR spectrum of **1** showed a singlet at δ_H 2.38 which is a characteristic signal for the H-18 of an ursane-type with 19-*O*- substitution, together with five tertiary methyl singlets at δ_H 0.75, 0.78, 0.95, 1.12 and 1.32, a methyl doublet at δ_H 0.88 (J=6.0 Hz, CH_3-30) and the olefinic proton at δ_H 5.20 (J=2.5 Hz, H-12). In addition, the ^{13}C NMR spectrum of **1** showed six methyl signals, and two olefinic carbons signals at δ_C 129.3 (C-12) and 138.4 (C-13), confirming a 19α-hydroxyurs-12-en skeleton for compound **1**. Furthermore, from the ^1H NMR, HSQC and NOESY spectra, three hydroxyl-bearing methine protons exhibiting two doublets at δ_H 3.50 (J=3.0 Hz) and 3.17 (J=10.0 Hz) and a double doublet at δ_H 3.42 (J=3.0, 10.0 Hz) were assignable to H-1β, H-3α and H-2β respectively. The coupling constants $J^3_{H\text{-}1/H\text{-}2}$ (*cis*)=3.0 Hz and $J^3_{H\text{-}2/H\text{-}3}$ (*trans*)=10.0 Hz was consistent with the 1α, 2α, 3β-trihydroxyl substitution on ring A, in agreement with the literature (Bao-Zhi Li et al., 1998). From the ES MS data, the fourth hydroxyl group resulted attached to ring A, and the position was at either C-23 or C-24. Usually, the chemical shift of the C-24 methyl group is about δ_C 12.8–13.8 if the hydroxyl group is linked at C-23 (δ_C 68–71) and the chemical shift of the C-23 methyl group is about δ_C 23.5 if the hydroxyl group is linked at C-24 (δ_C 63–66) (Zhang and Yang, 1994). The chemical shift of C-24 in **1** was δ_C 13.8, thus, the fourth hydroxyl was linked at C-23 (δ_C 70.1). In the NOESY and HMBC spectra, the correlation data were consistent with the 1α, 2α, 3β, 23-tetrahydroxyl substitution on ring A. Therefore, the structure of **1** is 1α, 2α, 3β, 19α, 23-pentahydroxyurs-12-en-28-oic acid designated as gamboukokoensein A. However, the xylopyranosyl ester of compound **1** has previously been isolated (Gupta and Singh, 1989).

Compound **3** showed a $[M+Li]^+$ ion peak at *m/z* 659 in the positive ion FABMS and its high resolution FABMS analysis established the molecular formula as $C_{35}H_{56}O_{11}$. On acid hydrolysis, **3** gave the L-arabinose (Ara) as component sugar and the aglycone **3a**. The ^{1}H NMR spectrum of **3** showed the signal of one sugar anomeric proton at δ_H 6.43 (*d*, $J=3.0$ Hz). In the ^{13}C NMR spectrum (Table 1), one anomeric carbon signal appeared at δ_C 95.0, suggesting the presence of an ester-linked sugar moiety. The olefinic carbon signals at δ_C 123.1 and 144.2 were consistent with an olean-12-en type triterpenoid. The characteristic RDA fragment peaks at *m/z* 234 and 203 suggested the presence of one hydroxymethylene substitution on rings D/E, more probably at the C-28 position, in agreement with its ^{13}C NMR data (δ_C 72.3) compared to the reported values. Other fragment ion peaks were observed at *m/z* 494 $[M+Li–Ara]^+$, 425 $[M+Li–234]^+$, 270 $[A/B–Ara]^+$ and 252 $[A/B–Ara–H_2O]^+$, which revealed the elimination of the arabinosyl moiety from the intermediate A/B rings. The ion peaks at *m/z* 270 and 252 suggested the presence of three hydroxyl-bearing and one COOAra substitution on A/B rings. Furthermore, the ^{1}H NMR spectrum of **3** displayed signals for H-2α and H-3α at δ_H 4.36 (*br* s) and 4.10 (*d*, $J=4.0$ Hz), which gave correlations, in the HSQC spectrum, with carbon signals at δ_C 71.8 and 73.3 respectively, suggesting the β-configuration for the two OH groups on ring A, in agreement with the literature (Sakai et al., 1999; Mitaine-Offer et al., 2002). The signal at δ_H 5.00 (*br* s) correlated with the carbon signal at δ_C 67.0 which was assigned to C-6, in comparison with the reported ^{13}C NMR data of the 6β-OH-bearing olean-12-en or urs-12-en type compounds (Dijoux et al., 1993). Thus, the third OH in **3** was attached to the C-6 position. The chemical shift at δ_C 15.0 assigned to C-24, implied that the COOAra group was linked at C-23 (δ_C 176.2). The C-23 α-oriented COOAra was responsible for the downfield shift of H-3α (δ_H 4.10). The HMBC and NOESY spectra were in accordance with the 2β,3β,6β-trihydroxy-23-COO-Ara substitutions on rings A/B. Accordingly, the structure of compound **3** was established as 2β,3β,6β,28-tetrahydroxyolean-12-en-23-oic acid 23-*O*-α-L-arabinopyranosyl ester, and also named as gamboukokoenside A.

Compound **4** showed a $[M+Li]^+$ ion peak at *m/z* 641 in the positive ion FABMS and its high resolution FABMS analysis established the molecular formula as $C_{35}H_{54}O_{10}$. On acid hydrolysis, **4** gave the L-arabinose (Ara) as component sugar and the aglycone **4a**. The ^{1}H NMR spectrum of **4** showed the signal of one sugar anomeric proton at δ_H 6.40 (d, $J=3.0$ Hz). In the ^{13}C NMR spectrum (Table 1), one anomeric carbon signal appeared at δ_C 95.0, suggesting the presence of an ester-linked sugar moiety like in **3**. The ^{1}H and ^{13}C NMR spectra of **4** were similar to those of **3** except for the ring A where the 2β-OH was absent and the 3β-OH was transformed to a ketone function which appeared in the carbon spectrum at δ_C 211.8. Thus, the structure of compound **4** was elucidated as 6β,28-dihydroxy-3-oxoolean-12-en-23-oic acid 23-*O*-α-L-arabinopyranosyl ester, also designated as gamboukokoenside B.

Compound **2** was identified as myrianthic acid (Hirai et al., 2000). Compound **5** was identified as protobassic acid (Sahu, 1996). Compounds **6** and **7** were identical to oleanolic acid and erythrodiol, respectively (Mahato and Kundu, 1994). Compound **8** was identified as chondrillasterol (Itoh et al., 1981).

3. Experimental

3.1. General

MPs were determined using a Kofler microhot stage apparatus. IR spectroscopy was performed on a Perkin-Elmer 257 spectrometer. $[\alpha]_D$ were read on a Perkin-Elmer 241 polarimeter. MS were registered on a Micromass Q–T of instrument, on a Nermag R10-10C spectrometer and the HP-5973 Mass Selective Detector. NMR experiments were performed on a Varian Gemini 400 MHz instrument and a Bruker AC 300 spectrometer. The solvents used for NMR were $CDCl_3$, CD_3OD and DMSO-d_6, also considered in each case as internal reference. Si gel 60 (240–400 mesh) was used for CC under normal pressure while 60H (5–40 μm) and 60C (20–40 μm) were used for CC under compressed air (300 mbar); precoated Si gel 60 F_{254} aluminium plates were used for TLC.

3.2. Plant material

The stem bark of *Gambeya boukokoensis* (Sapotaceae) was harvested in August 1997 at Mintima, situated in Meyo Messala Sub-division of the South Province of Cameroon, and then identified. The herbarium specimen documenting the collection has been deposited in the National Herbarium of Yaoundé, Cameroon (ref. 61210 hnc).

3.3. Extraction and isolation

The stem bark was chopped, air-dried and ground to yield 5.78 kg of the plant material. Part of the powder (5.50 kg) was extracted successively with EtOAc (7 l) for four days and MeOH (6 l) for four days at room temperature. The solvents were evaporated under reduced pressure to afford EtOAc extract (165 g) and MeOH extract (60 g). Part of the EtOAc–soluble residue (150 g) was subjected to column chromatography over silica gel 60 (240–400 mesh) (500 g). A total of 85 fractions were eluted with mixtures of hexane–EtOAc (300 ml each, from 100:0 to 0:100) and EtOAc–MeOH (300 ml each, from 100:0 to 0:100). The fractions were combined on the basis of similar TLC profiles to give many series denoted **A–I**. Further chromatography of the series B [fr. 12–20] (10 g) over Si gel 60H (5–40μm) eluted with hexane-EtOAc (50:50) yielded oleanolic acid **6** (50 mg), erythrodiol **7** (40 mg) and chondrillasterol **8** (150 mg). Further chromatography of the series D [fr. 41–51] (18 g) over Si gel 60C (20–40 μm) eluted with CH_2Cl_2–MeOH (95:5) afforded protobassic acid **5** (200 mg) and myrianthic acid **2** (20 mg). The combined series F [fr. 53–56] (21 g) was repeatedly subjected CC over Si gel 60C (20-40 μm) eluted with CH_2Cl_2–MeOH (90:10) to provide gamboukokoensein A **1** (30 mg). Further CC of the series G [fr. 57–59] (9 g) over Si gel 60C (20–40 μm) eluted with CH_2Cl_2–MeOH (90:10) afforded gamboukokoenside A **3** (15 mg) and gamboukokoenside B **4** (18 mg).

3.3.1. Gamboukokoensein A 1, 1α,2α,3β,19α,23-pentahydroxyurs-12-en-28-oic acid

White powder; mp > 300 °C; IR νmax cm^{-1} 3300–3500, 1705, 1635, 1075; CI/NH_3 MS $m/z = 521$ $[M+H]^+$, 538 $[M+NH_4\ ]^+$; ES MS $m/z = 543$ $[M+Na]^+$, 521 $[M+H]^+$, 264, 256, 255, 247, 235, 224, 220, 219, 202, 189, 188; M.F. $C_{30}H_{48}O_7$; ^1H NMR (400 MHz, DMSO): δ 0.75 (*s*, CH_3), 0.78 (*s*, CH_3), 0.88 (*d*, *J* = 6.0 Hz, CH_3-30), 0.95, 1.12 and 1.32 (each *s*, $3\times CH_3$), 2.38 (*s*, H-18), 3.17 (*d*, *J* = 10.0 Hz, H-3), 3.42 (*dd*, *J* = 3.0, 10.0 Hz, H-2), 3.50 (*d*, *J* = 3.0 Hz, H-1), 5.20 (*t*, *J* = 2.5 Hz, H-12); ^{13}C NMR (100 MHz, DMSO), see Table 1.

3.3.2. Myrianthic acid 2, 2α,3α,19α,23-tetrahydroxyurs-12-en-28-oic acid

White crystals; mp > 300 °C; IR νmax cm^{-1} 3300–3500, 1707, 1640, 1070; CI/NH_3 MS $m/z = 505$ $[M+H]^+$, 522 $[M+NH_4\ ]^+$; ES MS $m/z = 527$ $[M+Na]^+$, 505 $[M+H]^+$, 264, 247, 240, 222, 219, 202, 193; M.F. $C_{30}H_{48}O_6$; ^1H NMR (400 MHz, DMSO): δ 0.68 (3H, *s*), 0.70 (3H, *s*), 0.84 (3H, *d*, *J* = 6.0 Hz, CH_3-30), 0.90 (3H, *s*), 1.08 (3H, *s*), 1.28 (3H, *s*), 2.35 (1H, *s*, H-18), 3.40 (1H, *m*, H-3), 3.70 (1H, *m*, H-2), 5.19 (1H, *t*, *J* = 2.5 Hz, H-12); ^{13}C NMR (100 MHz, DMSO), see Table 1.

3.3.3. Gamboukokoenside A 3, 2β,3β,6β,28-tetrahydroxyolean-12-en-23-oic acid 23-O-α-L-arabinopyranosyl ester

White crystals; mp > 300 °C; IR νmax cm^{-1} 3300–3500, 1730, 1650, 1075; FAB MS $m/z = 659$ $[M+Li]^+$, 653 $[M+H]^+$, 494 $[M+Li - Ara\ ]^+$, 425 $[M\ +Li - 234]^+$, 270 $[A/B - ara]^+$, 252 $[A/B - ara - H_2O]^+$, 234, 203; M.F. $C_{35}H_{56}O_{11}$; ^1H NMR (400 MHz, DMSO): δ 0.86 (3H, *s*, CH_3-29), 0.87 (3H, *s*, CH_3-30), 0.98 (3H, *s*, CH_3-26), 1.04 (3H, *s*, CH_3-27), 1.10 (3H, *s*, CH_3-25), 1.50 (3H, *s*, CH_3-24), 5.12 (1H, *t*, *J* = 2.48 Hz, H-12), 6.43 (1H, *d*, *J* = 3.0 Hz, H-1′), 5.00 (*br s*, H-6), 4.52 (1H, *dd*, *J* = 3.0, 4.0 Hz, H-2′), 4.48 (1H, *m*, H-3′), 4.41 (1H, *m*, H-4′), 4.36 (*br s*, H-2α), 4.10 (*d*, *J* = 4.0 Hz, H-3α), 3.92 (1H, *m*, H-5′); ^{13}C NMR (100 MHz, DMSO), see Table 1.

3.3.4. Gamboukokoenside B 4, 6β,28-dihydroxy-3-oxoolean-12-en-23-oic acid 23-O-α-L-arabinopyranosyl ester

White crystals; mp > 300 °C; IR νmax cm^{-1} 3300–3500, 1732, 1710, 1645, 1075; FAB MS $m/z = 641$ $[M+Li]^+$, 635 $[M+H]^+$, 476 $[M+Li - Ara]^+$, 407 $[M+Li - 234]^+$, 252, 234, 203; M.F. $C_{35}H_{54}O_{10}$; ^1H NMR (400 MHz, DMSO): δ 0.67 (3H, *s*, CH_3-26), 0.68 (3H, *s*, CH_3-27), 0.88 (3H, *s*, CH_3-29), 0.89 (3H, *s*, CH_3-30), 1.22 (3H, *s*, CH_3-25), 1.26 (3H, *s*, CH_3-24), 5.24 (1H, *t*, *J* = 2.48 Hz, H-12), 6.40 (1H, *d*, *J* = 3.0 Hz, H-1′), 4.50 (1H, *dd*, *J* = 3.0, 4.0 Hz, H-2′), 4.46 (1H, *m*, H-3′), 4.40 (1H, *m*, H-4′), 3.90 (1H, *m*, H-5′); ^{13}C NMR (100 MHz, DMSO), see Table 1.

3.3.5. Acid hydrolysis of 3 and 4

A solution of each compound **3** and **4** (5 mg) in 2N aqueous CF_3COOH (3 ml) was heated for 2 h at 80 °C. After extraction with $CHCl_3$, the aqueous layer was repeatedly evaporated to dryness with MeOH and then analyzed in each case by TLC on silica gel on comparison with standard sugar, [solvent system: $CHCl_3$–MeOH–H_2O (8:5:1)]. The purification of the $CHCl_3$ extract of **3** by CC on silica gel using CH_2Cl_2–MeOH (9:1) yielded the aglycone **3a**. The purification of the $CHCl_3$ extract of **4** by CC on silica gel using CH_2Cl_2–MeOH (9:1) yielded the aglycone **4a**.

3.3.6. Compound 3a, 2β,3β,6β,28-tetrahydroxyolean-12-en-23-oic acid

White crystals; ^1H NMR (400 MHz, DMSO): δ 0.85 (3H, *s*), 0.86 (3H, *s*), 0.97 (3H, *s*), 1.05 (3H, *s*), 1.10 (3H, *s*), 1.48 (3H, *s*), 5.15 (1H, *t*, *J* = 2.48 Hz, H-12); ^{13}C NMR (100 MHz, DMSO), see Table 1.

3.3.7. Compound ***4a****, 6β,28-dihydroxy-3-oxoolean-12-en-23-oic acid*

^1H NMR (400 MHz, DMSO): δ 0.69 (*s*, CH_3), 0.70 (*s*, CH_3), 0.87 (*s*, CH_3), 0.89 (*s*, CH_3), 1.23 (*s*, CH_3), 1.26 (*s*, CH_3), 5.22 (1H, *t*, $J=2.48$ Hz, H-12); ^{13}C NMR (100 MHz, DMSO), see Table 1.

3.3.8. Protobassic acid ***5***

White powder from MeOH; mp 354–356 °C; CI/NH_3 MS $m/z=505$ $[M+H]^+$, 522 $[M+NH_4]^+$; ^{13}C NMR (DMSO), in agreement with literature data (Sahu, 1996).

3.3.9. Oleanolic acid ***6***

White crystals; mp 326 °C; ^{13}C NMR data agreed with the authentic compound (Mahato and Kundu, 1994).

3.3.10. Erythrodiol ***7***

White crystals from CH_2Cl_2–hexane mixture; mp 238 °C; $[\alpha]_D^{22}$ +76° (*c* 0.70, $CHCl_3$); CI/NH_3 MS $m/z=427$ $[M+H]^+$, 442 $[M+NH_4]^+$; ^{13}C NMR ($CDCl_3$), in accordance to the literature data (Mahato and Kundu, 1994).

3.3.11. Chondrillasterol ***8***

Cream white sparkling crystals from CH_2Cl_2–hexane mixture; mp 170–172 °C; $[\alpha]_D^{22}$ +1.8° (*c* 0.50, $CHCl_3$); CI/NH_3 MS $m/z=413$ $[M+H]^+$, 430 $[M+NH_4]^+$; ^{13}C NMR ($CDCl_3$), in accordance with reference (Itoh et al., 1981).

Acknowledgements

One of the authors (J. Wandji) is grateful for IFS grant No F/2624-2 (Sweden), for the sponsorship of the "Université René- Descartes Paris V, France" during his multiple research visits in Paris, and for the financial support from the OPCW (The Netherlands), through the Internship at the University of Natal, Durban, South Africa. Thanks are due to Mr Dilip Jagjivan for the measurements of some of the NMR spectra.

References

Bao-Zhi, Li., Bin-Gui, W., Zhong, J.-J., 1998. Pentacyclic triterpenoids from *Rubus xanthocarpus*. Phytochemistry 49, 2477–2481.

Bouquet, A., 1969. Féticheurs et Médecines Traditionnelles du Congo (Brazzaville). ORSTOM 36, 223–225.

Bouquet, A., Debray, M., 1974. Plantes Médicinales de la Côte-d'Ivoire. ORSTOM, Paris, pp. 161–163.

Dalziel, J.M., 1937. The Useful Plants of West Tropical Africa. The Crown Agents for the Colonies, London.

Dijoux, M.-G., Lavaud, C., Massiot, G., Le Men-Olivier, L., Sheeley, D.M., 1993. A saponin from leaves of *Aphloia madagascariensis*. Phytochemistry 34, 497–499.

Gupta, D., Singh, J., 1989. Triterpenoid and saponins from *Centipeda minima*. Phytochemistry 28, 1197–1201.

Hirai, N., Sugie, M., Wada, M., Lahlou, E.H., Kamo, T., Yoshida, R., Tsuda, M., Ohigashi, H., 2000. Biosci. Biotechnol. Biochem. 64, 1707–1712.

Itoh, T., Kikuchi, Y., Tamura, T., Matsumoto, T., 1981. Co-occurrence of chondrillasterol and spinasterol in two Cucurbitaceae seeds as shown by ^{13}C NMR. Phytochemistry 20, 761–764.

Keay, R.W.J., 1989. Trees of Nigeria. Clarendon Press, Oxford, UK.

Mahato, S.B., Kundu, A.P., 1994. ^{13}C-NMR spectra of pentacyclic triterpenoids. A compilation and some salient features. Phytochemistry 37, 1517–1575.

Mitaine-Offer, A.C., Miyamoto, T., Khan, I.A., Delaude, C., Lacille-Dubois, M.A., 2002. Three new triterpene saponins from two species of *Carpolobia*. J. Nat. Prod. 65, 553–557.

Sahu, N.P., 1996. Triterpenoid saponins of *Mimusops elengi*. Phytochemistry 41, 883–886.

Sakai, K., Nagao, T., Okabe, H., 1999. Triterpenoid saponins from the ground part of *Aster ageratoides* var. ovatus. Phytochemistry 51, 309–318.

Wandji, J., Tillequin, F., Mulholland, D.A., Wansi, J.D., Fomum, T.Z., Fuendjiep, V., Libot, F., Tsabang, N., 2002. Fatty acid esters of triterpenoids and steroid glycosides from *Gambeya africana*. Planta Medica 68, 822–826.

Zhang, Y.-J., Yang, C.-R., 1994. Two triterpenoids from *Gentina tibetica*. Phytochemistry 36, 997–999.