Available online at www.sciencedirect.com
SCIENCE DIRECT®
Phytochemistry 66 (2005) 1088–1093
PHYTOCHEMISTRY
www.elsevier.com/locate/phytochem

Four tetranortriterpenoids from the stem bark of *Khaya anthotheca*

Michel K. Tchimene [a], Pierre Tane [a], Dieudonne Ngamga [a], Joseph D. Connolly [b,*], Louis J. Farrugia [b]

[a] *Department of Chemistry, University of Dschang, Box 67, Dschang, Cameroon*
[b] *Chemistry Department, The University of Glasgow, University Avenue, Glasgow G12 8QQ, Scotland, UK*

Received 20 January 2005; received in revised form 24 March 2005
Available online 12 May 2005

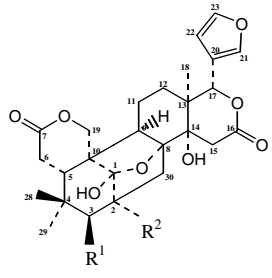
Abstract

Eight limonoids, anthothecanolide (**1**), 3-*O*-acetylanthothecanolide (**2**), 2,3-di-*O*-acetylanthothecanolide (**3**), 6*R*,8α-dihydroxycarapin (**4**), 3β-acetoxy-3-deoxo-6*R*-hydroxycarapin (**5**), methyl angolensate, methyl 6-hydroxyangolensate and khayalactone together with sitosterol glucoside, have been isolated from the extracts of the stem bark of *Khaya anthotheca*. Compounds **1**–**4** are described for the first time. Their structures were established by analysis of the high-field NMR and MS data. The structure of compound **4** was confirmed by a single crystal X-ray structure analysis.

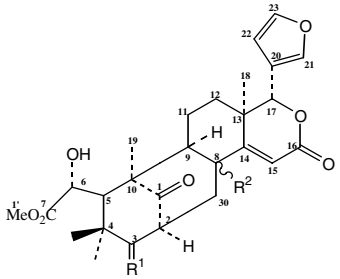
Keywords: Tetranortriterpenoids; *Khaya anthotheca*; Meliaceae; Anthothecanolide; 6,8-Dihydroxycarapin

1. Introduction

The genus *Khaya* is the main source of African mahogany and is closely related to the South American genus *Swietenia*, the original source of mahogany. *Khaya anthotheca* extends as far South as Angola in Western Africa but only occurs in Nigeria close to the Cameroon frontier (Adesogan and Taylor, 1968). The genus was surveyed by Taylor and collaborators (Adesida et al., 1971) who outlined chemical means of distinguishing the heartwoods of the various species and also pointed out that the Western and Eastern forms of *K. anthotheca* are chemically different. The Western variety is unique in the genus because it contains no ring D expanded limonoids (Halsall and Troke, 1975), in contrast to the other species. Previous investigations of the timber of the Western form of *K. anthotheca* have shown the presence of only anthothecol and its 11-deacetyl derivative (Bevan et al., 1963a,b) while the root bark and seeds contained anthothecol, cedrelone and derivatives of havanensin and deoxyhavanensin (Adesogan et al., 1970). In connection with our investigations of Cameroonian medicinal plants, the CH_2Cl_2–MeOH (1:1) extract of the stem bark *K. anthotheca* was studied.



1 R^1 = OH, R^2 = OH
2 R^1 = OAc, R^2 = OH
3 R^1 = OAc , R^2 = OAc



4 R^1 = O; R^2 = αOH
5 R^1 = H, βOAc, R^2 = βH

Chromatographic separation afforded four new tetranortriterpenoids, anthothecanolide (**1**), 3-*O*-acetylantho-

* Corresponding author. Tel.: +44 141 330 5499; fax: +44 141 330 4888.
E-mail address: joec@chem.gla.ac.uk (J.D. Connolly).

0031-9422/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.phytochem.2005.03.028

thecanolide (**2**), 2,3-di-*O*-acetylanthothecanolide (**3**), 6*R*,8α-dihydroxycarapin (**4**) and five known compounds, 3β-acetoxy-3-deoxo-6*R*-hydroxycarapin (**5**) (Khalid et al., 1998), methyl 6-hydroxyangolensate (Connolly et al., 1967), methyl angolensate (Bevan et al., 1967), khayalactone (Tchuendem et al., 1998) and sitosterol glycoside.

2. Results and discussion

Compound **1** was obtained as colorless crystals. The EIMS exhibited a molecular ion peak at *m/z* 504, corresponding to the molecular formula $C_{26}H_{32}O_{10}$. The IR spectrum of **1** showed hydroxyl absorption at 3443 cm^{-1} and a very strong broad lactonic carbonyl band at 1728 cm^{-1}. In the ^1H NMR spectrum, signals of three tertiary methyl groups were observed at δ 0.91, 0.97 and 1.26. The DEPT and HMQC experiments revealed a total number of 26 carbon atoms including three methyl groups, six methylenes, seven methines (including two oxygenated and three sp^2 carbons) and 10 quaternary carbons (including two carbonyls, one sp^2 and four oxygenated carbons). Further examination of the NMR spectra revealed the presence of a β-substituted furan and suggested a mexicanolide skeleton (Daniewski et al., 1993). The NMR data of **1** were very similar to those reported for utilin C (Daniewski et al., 1994). The mass fragment observed at *m/z* 121 in the EIMS could be rationalised as the loss of furfuraldehyde, characteristic for limonoids with a furan ring attached to a D-ring lactone (Daniewski et al., 1994). The furan protons appeared at δ 6.42 (*dd*, $J = 0.7$, 0.9 Hz), 7.45 (*t*, $J = 1.8$ Hz), 7.52 (*d*, $J = 1.8$ Hz) in the ^1H NMR spectrum while H-17 resonated at δ 5.52 (*s*). The corresponding carbon chemical shifts are shown in Table 1. A strongly coupled system observed in the ^1H NMR and COSY spectra comprised H-9 (2.54, *m*), 2H-11 (δ 2.53/2.59, *m*) and 2H-12 (1.45/1.76, *m*), excluding any substitution at these positions. HMBC correlations were observed between H-9 and C-11, C-12 and an oxygen-bearing carbon atom at δ 83.4, attributed to C-8 and the 2H-15 methylene signals at δ 2.75 (*d*, $J = 18.9$ Hz) and 3.29 (*d*, $J = 18.9$ Hz) with the lactonic carbonyl C-16 and the oxygen-bearing C-14. Another characteristic pattern in the ^1H NMR and COSY spectra of **1** was the ABX system consisting of 2H-6 [7 2.49 (*dd*, $J = 9.8$, 15.5 Hz) and 2.59 (*dd*, $J = 7.6$, 15.5 Hz)] and H-5 [δ 2.25, *dd*, $J = 9.8$, 7.6 Hz]. HMQC correlations enabled the unequivocal assignments of C-5 and C-6. The ^1H NMR spectrum indicated the presence of a secondary hydroxyl group attached to C-3 [δ 3.61 (*s*, H-3)] which showed correlations in the HMBC spectrum to C-5, C-30 and Me-29. NOE interactions were observed between H-9, Me-29 and H-3. This enabled us to assign a β-orientation to the 3-OH, in agreement with related compounds (Daniewski et al., 1993). The presence of the geminal methyl groups Me-28 and Me-29 was apparent from their HMBC correlations with C-3, C-4 and C-5 as well as with each other. 2H-30 [δ 1.54 (*d*, $J = 14.5$ Hz) and 2.42 (*d*, $J = 14.5$ Hz)] appeared as an isolated AB system, consistent with the presence of a hydroxyl group on C-2. A signal at δ 110.0 in the ^{13}C NMR spectrum, characteristic of a hemiacetal carbon, was assigned to C-1 as found in utilin C and related compounds (Daniewski et al., 1994). Examination of a model indicated that the hydroxyl group located at C-8 could form a hemiacetal group with C-1. The signal corresponding to Me-19 was not observed in the ^1H NMR spectrum of **1** but was replaced by two oxymethylene proton signals [δ 4.20 (*d*, $J = 11.4$ Hz) and 4.40 (*d*, $J = 11.4$ Hz)]. They showed HMBC correlations with C-5, C-9 and C-10. The same spectrum showed an important correlation between these protons and the lactone carbonyl at δ 177.7. These results allowed us to deduce the presence of a six-membered ring lactone as in structure (**1**), a new mexicanolide derivative, to which the trivial name anthothecanolide

Table 1
^{13}C NMR data of compounds **1**–**5**

Carbon	**1**[a]	**2**[a]	**3**[b]	**4**[a]	**5**[a]
1	110.0	109.2	108.0	216.1	219.2
2	82.5	82.7	93.8	4 8.4	47.0
3	82.1	83.6	76.1	212.0	80.3
4	43.1	42.2	40.7	42.2	38.2
5	38.3	39.3	37.7	43.0	44.6
6	31.6	31.2	30.1	74.3	73.1
7	177.6	177.5	173.5	177.4	176.2
8	83.4	81.2	81.5	73.2	34.7
9	55.0	54.9	52.9	51.5	49.5
10	46.6	46.8	47.8	53.3	51.4
11	23.6	21.9	20.9	20.1	18.3
12	32.6	32.2	30.8	28.1	26.4
13	32.8	39.1	39.2	39.9	38.1
14	73.6	73.4	72.2	169.9	165.3
15	38.6	31.2	38.0	116.6	112.5
16	173.1	172.8	175.5	167.6	171.2
17	79.4	79.3	77.4	81.4	81.3
18	17.1	16.8	25.0	23.5	18.3
19	75.5	73.5	73.6	20.6	16.7
20	122.3	122.6	120.8	121.6	119.7
21	144.7	144.6	141.2	144.8	141.1
22	117.7	111.6	110.3	112.0	109.7
23	143.0	143.1	143.6	143.5	143.1
28	22.4	22.3	22.4	23.0	22.8
29	26.2	24.8	25.7	21.5	23.4
30	42.1	43.2	40.3	58.4	35.2
$OCOCH_3$		172.9	170.4		170.5
		21.5	21.2		20.5
			169.4		
			21.2		
CH_3O				58.4	52.8

Carbon multiplicities were determined by DEPT 135 experiments.
[a] ^{13}C NMR data of **1**, **2**, **4** and **5** recorded in $CDCl_3$–CD_3OD.
[b] ^{13}C NMR data of compound **3** recorded in $CDCl_3$.

was given. Two other 7,19-lactone derivatives, seneganolide and 2-hydroxyseneganolide, have been published recently (Nakatani et al., 2000, 2001).

Compound (**2**) was obtained as colourless crystals. The EIMS revealed a molecular ion peak at *m/z* 546 consistent with the molecular formula $C_{28}H_{34}O_{11}$. The NMR data of **2** (Table 1) were similar to those of **1** except for the presence of an acetate methyl group at δ 2.10 and a downfield shift of H-3 from δ 3.61 to 5.08. An HMBC correlation between H-3 and the ester carbonyl at δ 172.9 confirmed the attachment of the acetate group to C-3. Accordingly, compound (**2**) is 3-*O*-acetylanthothecanolide.

Compound (**3**) exhibited a molecular ion peak at *m/z* 588 in its EIMS. Analysis of its ^{1}H and ^{13}C NMR data allowed us to establish the molecular formula as $C_{30}H_{36}O_{12}$. The ^{1}H and ^{13}C NMR spectra of **3** (Tables 1 and 2) showed similarities with those of **1** except for the presence of two acetate groups revealed in the ^{1}H NMR spectrum by two methyl signals at δ 2.14 (6H). The ^{13}C NMR spectrum confirmed the presence of these acetate groups with characteristic signals at δ 169.4 and 170.4. The HMBC correlation of H-3 with one of these carbonyls and the downfield carbon shift of C-2 indicated that the acetates were attached to C-2 and C-3. Thus **3** is 2,3-di-*O*-acetylanthothecanolide.

Compound **4** was found to possess a molecular formula of $C_{27}H_{32}O_9$ (*m/z* 500) as determined by EIMS and confirmed by the ^{13}C NMR data. The IR spectrum revealed absorption bands for hydroxyl (3437 cm^{-1}), ketone (1702 cm^{-1}) and ester/lactone (1730 cm^{-1}) groups. The ^{1}H and ^{13}C data (Tables 1 and 2), including the presence of two ketonic carbonyls, were consistent with a mexicanolide skeleton for **4**. The ^{1}H NMR spectra spectrum revealed signals for four tertiary methyl groups (δ 1.06, 1.16, 1.29 and 1.57) and an olefinic proton singlet (δ 5.79, H-15) while the ^{13}C NMR spectrum showed signals for three quaternary carbons [39.9 (C-13), 42.2 (C-4), 53.3 (C-10)], three oxygenated carbons, two secondary [δ 74.3 (C-6), 81.4 (C-17)] and one tertiary [73.2 (C-8)], two ketonic carbonyl groups [δ 212.0 (C-3) and 216.1 (C-1)], an unsaturated lactone carbonyl [δ 167.6 (C-16)] and an ester group [δ 177.4 (C-7)]. These data showed close similarity to those described for utilin B (Daniewski et al., 1993) and 6-hydroxycarapin (Connolly and Handa, 1969). A broadened singlet at δ 4.65 (H-6) was similar to those reported for H-6 in methyl 6-hydroxyangolensate (Connolly et al., 1967) and 6-hydroxycarapin (δ 4.60) (Connolly and Handa, 1969). In addition, HMBC correlations between H-6 and C-5, C-7 and C-10 confirmed the positioning of a hydroxyl group at C-6. Correlations were also observed between

Table 2
^{1}H NMR data of compounds **1**–**5**

Position	**1**[a]	**2**[a]	**3**[b]	**4**[a]	**5**[a]
2				3.36 *dd* (8.6, 3.6)	3.05 *m*
3	3.61 *s*	5.08 *s*	5.58 *s*		4.81 *d* (9.9)
5	2.25 *dd* (9.8, 7.6)	2.42 *m*	2.50 *dd* (2.3, 9.0)	2.96 *bs*	3.30 *bs*
6	2.49 *dd* (9.8,15.5)	2.46 *m*	2.55 *m*	4.65 *s*	4.55 *s*
	2.59 *dd* (7.6;15.5)	2.50 *m*			
9	2.54 *m*	2.53 *m*	2.55 *m*	2.25 *dd* (9.1, 6.2)	1.79 *m*
11	2.53 *m*	1.72 *m*	1.65 *m*	1.61 *m*	1.82 *m*
	2.59 *m*	1.46 *m*	1.40 *m*	2.05 *m*	
12	1.76 *m*	1.72 *m*	1.55 *m*	1.8 *m*	1.61 *m*
	1.45 *m*	1.46 *m*	1.87 *m*	1.6 *m*	1.44 *m*
15	2.75 *d* (18.9)	3.30 *d* (19.1)	2.87 *d* (19.1)	5.79 *d*	5.76 *d* (2.0)
	3.29 *d* (18.9)	2.72 *d* (19.1)	3.04 *d* (19.1)		
17	5.52 *s*	5.50 *s*	5.28 *s*	5.50 *s*	5.13 *s*
18	0.97 *s*	0.96 *s*	1.00 *s*	1.29 *s*	1.04 *s*
19	4.40 *d* (11.4)	4.45 *d* (11.3)	4.21 *d* (11.6)	1.57 *s*	1.33 *s*
	4.20 *d* (11.4)	4.19 *d* (11.3)	4.41 *d* (11.6)		
21	7.52 *d* (1.8)	7.51 *s*	7.46 *bs*	7.49 *s*	7.45 *s*
22	6.42 *dd* (0.7, 0.9)	6.48 *d* (0.7)	6.40 *bs*	6.48 *dd* (0.7,0.9)	6.43 *d* (0.7)
23	7.45 *t* (1.8)	7.66 *t* (1.7)	7.45 *t* (1.4)	7.52 *bs*	7.51 *s*
28	1.26 *s*	1.39 *s*	1.48 *s*	1.06 *s*	1.09 *s*
29	0.94 *s*	0.88 *s*	0.92 *s*	1.16 *s*	0.92 *s*
30	1.54 *d* (14.5)	1.52 *dd* (14.2. 1.6)	1.90 *dd* (14.7, 1.9)	1.90 *d* (14.6)	2.25 *ddd* (13.7, 4.9, 2.8), 1.61 *m*
	2.42 *d* (14,5)	2.89 *d* (14.2)	2.71 *d* (14.7)	2.70 *d* (14.6)	
OAc		2.10 *s*	2.14 (6H) *s*	2.15 *s*	2.18 *s*
MeO				3.85 *s*	3.84 *s*

[a] ^{1}H NMR data of **1**, **2**, **4** and **5** recorded in $CDCl_3$–CD_3OD.
[b] ^{1}H NMR data of compound **3** recorded in $CDCl_3$.

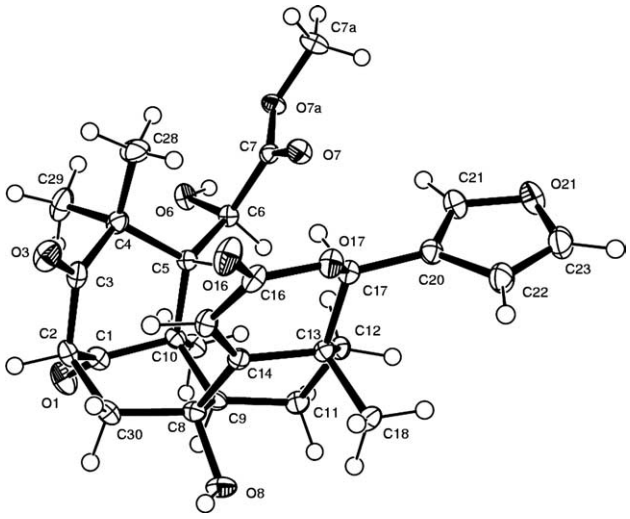


Fig. 1. ORTEP diagram of **4**.

H-9 and C-11, C-12 and C-14 and between H-2, H-9, H-15 and the oxygenated carbon at δ 73.2, attributable to C-8. Thus, the second hydroxyl group was attached to C-8 and **4** was assigned the structure 6,8-dihydroxycarapin. The failure of the C-8 hydroxyl to form a hemiacetal with the C-1 carbonyl group could have indicated that it was β. However, a single crystal X-ray analysis (Fig. 1) revealed the relative stereochemistry, as in **4**, for this new carapin derivative, 6*R*,8α-dihydroxycarapin. The bicyclononane ring system adopts a boat-chair conformation that prevents the formation of the 8,1-hemiacetal present in compounds (**1**–**3**). The corresponding 14,15-dihydro derivative, khayanone (Nakatani et al., 2001) from *Khaya senegalensis*, exists in equilibrium with its hemiacetal form. The absolute configuration of C-6 in khayanone has been assigned as *S* on the basis of CD evidence.

Compound (**5**) was assigned the molecular formula $C_{29}H_{36}O_{10}$, as deduced from its EIMS and ^{13}C NMR spectra. The NMR data of **5** were very similar to those of **4**. The ^{13}C NMR spectrum of **5** indicated only one ketonic carbonyl group [δ 219.2 (C-1)] and revealed a lactone carbonyl [δ 171.2 (C-16)] and an acetate group [δ_H 2.18, δ_C 170.5], in addition to four quaternary carbons [[δ 38.1 (C-13), 38.2 (C-4), 34.7 (C-8), 51.4 (C-10)]. The ^1H NMR spectrum showed signals for four tertiary methyl groups (δ 0.92, 1.04, 1.09, 1.33) and an unsaturated lactone (δ 5.76, H-15). These data suggested that **5** was an 8-deoxy-dihydro derivative of **4** with an acetate attached to C-2 or C-3. The lowfield shift of H-3 and its HMBC correlation to the acetate carbonyl indicated that the acetate was attached to C-3. Thus compound (**5**) was 3β-acetoxy-3-deoxo-6*R*-hydroxycarapin. This compound has been described in the literature (Khalid et al., 1998) but its physical and spectroscopic properties are incomplete and are recorded here. A NOE from H-8 to H-5 confirmed its 8-βH configuration.

3. Experimental section

3.1. General experimental procedures

Optical rotations were measured on a Polar 2000 polarimeter. Melting points were determined on a Reichert apparatus and are uncorrected. The UV spectra were obtained with a Shimadzu 3101 PC instrument and the IR spectra determined with a Jasco FT-IR 410 apparatus. ^1H (400.6 MHz) and ^{13}C (100.13 MHz) Nmr spectra were recorded in $CDCl_3$ (with its signals at δ 7.25 and 77.0 ppm as reference) or in a mixture of $CDCl_3$–CD_3OD (with the signals of CD_3OD at δ 3.30 and 49.0 as reference) with a Brüker DPX 400 apparatus using the XWIN NMR software (version 2.6) package for data acquisition and processing. NOE experiments were carried out using a Brüker AM 360 instrument. The mass spectra (70 eV) were recorded with a JOEL JMS 700 apparatus. Column chromatography was run on Merck silica gel 60 and Sephadex LH-20. TLC was carried out on silica gel 60 GF_{254} pre-coated plates with detection by UV light or by spraying with 50% H_2SO_4 followed by heating at 100 °C. MPLC was carried out using a chromatotron connected to a FMI lab pump (flow rate 10 ml/mn), Model QD, the plates being prepared with silica gel 60 PF_{254} containing $CaSO_4$.

3.2. Plant material

The stem bark of *Khaya anthotheca* Welw. C.D.C. was collected in Mbokam North Western province of Cameroon, in July 1999. The plant material was identified by Dr. Wirmun. A voucher specimen HNC 23435 has been deposited at the National Herbarium, Yaoundé, Cameroon.

3.3. Extraction and isolation

The air-dried and powdered plant material (5 kg) was macerated in a mixture of CH_2Cl_2–MeOH (1:1) for 24 h. Removal of the solvent in vacuo in a rotary evaporator provided an organic extract (400 g). This extract was then partitioned between a mixture of $CHCl_3$–MeOH–H_2O (2:2:1). The resulting organic phase was then concentrated in vacuo and subjected to vacuum flash column chromatography using hexane–EtOAc mixtures as eluent. Fractions of 500 ml were collected and regrouped on the basis of their TLC profiles. The fractions eluted with hexane–EtOAc (8:2) (200 mg) were further purified by repeated column chromatography on silica gel (70–230 mesh) to yield methyl angolensate (90 mg) and methyl 6-hydroxyangolensate (90 mg). The combined fractions (500 mg) eluted with hexane–EtOAc (1:1) revealed the presence of at least six limonoids (Ehrlich's reagent). Further purification of this fraction by column chromatography on silica gel with $CHCl_3$–acetone

afforded anthothecanolide (**1**) (100 mg), 3-*O*-acetylanthothecanolide (**2**) (40 mg), 2,3-di-*O*-acetylanthothecanolide (**3**) (80 mg), 6*R*,8α-dihydroxycarapin (**4**) (50 mg), 3β-acetoxy-3-deoxo-6*R*-hydroxycarapin (**5**) (60 mg) and khayalactone (8 mg). The polar fraction obtained with hexane–EtOAc (1:4) yielded sitosterol glycoside (100 mg).

3.4. Anthothecanolide (*1*)

Colorless crystals (EtOAc/petrol); m.p. 184–185 °C; $[\alpha]_D^{22}$ − 59 (*c* 1.16, MeOH); IR (KBr) ν_{max} 3443, 1728, 1634 cm^{-1}; UV (CH_2Cl_2) λ_{max} no maximum above 210 nm; ^1H and ^{13}C NMR data see Tables 1 and 2; EIMS *m/z* 504 (1) [M^+], 486 (28), 426 (25), 372 (60), 348 (73), 330 (67), 254 (20), 229 (17), 177 (25), 121 (100), 95 (78), 43 (74).

3.5. 3-O-Acetylanthothecanolide (*2*)

Colorless crystals (EtOAc/petrol); m.p. 240–241 °C; $[\alpha]_D^{22}$ − 51 (*c* 1.8, MeOH); IR (KBr) ν_{max} 3378, 1718, 1666, 800 cm^{-1}; UV (MeOH) λ_{max} no maximum above 210 nm; ^1H and NMR ^{13}C data see Tables 1 and 2; EIMS *m/z* 546 (25) [M^+], 528 (10), 486 (22), 459 (21), 417 (5), 390 (15), 227 (10), 195 (13), 169 (25), 135 (30), 121 (57), 83 (43), 83 (43), 69 (5), 43 (100), 28 (45).

3.6. 2,3-Di-O-acetylanthothecanolide (*3*)

Colorless crystals (EtOAc/petrol); m.p. 190–191; $[\alpha]_D^{22}$ − 101.7 (*c* 1.19, $CHCl_3$); IR (KBr) λ_{max} 3440, 1744, 1632 cm^{-1}; UV (EtOH) λ_{max} no maximum above 210 nm. ^1H and ^{13}C NMR data see Tables 1 and 2; EIMS *m/z* 588 (1) [M^+], 528 (4), 468 (6), 432 (5), 390 (50), 328 (20), 313 (20), 284 (9), 216 (10), 168 (8), 95 (28), 69 (35), 43 (100).

3.7. 6R,8α-Dihydroxycarapin (*4*)

Colorless crystals (EtOAc/petrol); m.p. 260–261 °C; $[\alpha]_D^{22}$ − 30 (*c* 0,50, MeOH); IR (KBr)ν_{max} 3437, 1730, 1701, 1437, 874 cm^{-1}; UV (MeOH) λ_{max} (log ε) 301 (1.1), 213 (4.2); ^1H and ^{13}C NMR data see Tables 1 and 2; EIMS *m/z* 500 (7) [M^+], 404 (55), 386 (33), 315 (100), 297 (23), 255 (10), 149 (22), 71 (23), 47 (21).

3.8. 3β-Acetoxy-3-deoxo-6R- hydroxycarapin (*5*)

Colorless crystals (EtOAc/petrol); m.p. 298–299 °C; $[\alpha]_D^{22}$ − 19 (*c* 1.1, $CHCl_3$); IR (KBr) ν_{max} 3453, 1709, 1626, 872 cm^{-1}; UV (CH_2Cl_2–MeOH 5:3) λ_{max} (log ε) 226 (4.09), 219 (4.29); ^1H and ^{13}C NMR data see Tables 1 and 2; EIMS *m/z* 528 (4) [M^+], 474 (3), 432 (100), 400 (7), 372 (8), 301 (20), 283 (19), 255 (20), 147 (29), 137 (31), 83 (26), 43 (29), 18 (8).

3.9. Crystal data for 6R,8α-dihydroxycarapin (*4*)

Crystals suitable for X-ray diffraction were obtained by recrystallisation from acetone. Compound **4** belongs to the orthorhombic system; molecular formula $C_{27}H_{32}O_9$. MW 500.53; space group $P2_12_12_1$; a = 11.7158 (2), b = 13.9830 (2), c = 14.4397 (3) Å, V = 2365.54 (7) $Å^3$; Z = 4; D_{calc} = 1.405 g/cm^{-3}; λ (Mo Kα) = 0.71073 Å.

A single crystal of suitable size (0.50 × 0.45 × 0.30 mm) was attached to a glass fiber using silicone grease and mounted on a goniometer head in a general position. Data were collected at 150 K on an Enraf–Nonius Kappa-CCD diffractometer, running under Nonius Collect software, and using graphite monochromated X-radiation. Precise unit cell dimensions were determined by post-refinement of the setting angles of a significant portion of the data using Scalepack (Otwinowski and Minor, 1997). The frame images were integrated using Denzo(SMN) (Otwinowski and Minor, 1997) and the resultant raw intensity files processed using a locally modified version of DENZOX (Blessing, 1997). No absorption corrections were deemed necessary. Data were sorted and merged using SORTAV (Blessing, 1997a). A total number of 22,159 data were collected, yielding 6699 unique data: *hkl* range −16 → 16, −19 → 19, −20 → 20. The structure was solved by direct methods using SIR-97 (Altomare et al., 1999). All non-H atoms were allowed anisotropic thermal motion. C–H hydrogen atoms were included at calculated positions, with C–H = 0.96 Å, and were refined with a riding model with U_{iso} set to 1.2 times that of the attached C-atom. The O–H hydrogen atoms were found from difference maps and refined with a riding model. Refinement with SHELXL97-2 (Sheldrick, 1997), using full matrix least squares on F^2 and all unique data, converged to the residuals R [$I > 2\sigma(I)$] and Rw_2 [$I > 2\sigma(I)$] of 0.0344 and 0.0847, respectively.

4. Supplementary materials

Supplementary material in the form of a CIF file has been deposited with deposition number CCDC 173032. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

Acknowledgements

The authors thank the International Programs in the Chemical Sciences (IPICS), University of Uppsala, Sweden for financial support.

References

Adesogan, E.K., Taylor, D.A.H., 1968. Extractives from *Khaya senegalensis*. J. Chem. Soc (C), 1974–1981.

Adesogan, E.K., Okorie, D.A., Taylor, D.A.H., 1970. Limonoids from *Khaya anthotheca*. J. Chem. Soc. (C), 205–211.

Adesida, G.A., Adesogan, E.K., Okorie, D.A., Taylor, D.A.H., Styles, B.T., 1971. The limonoid chemistry of the genus *Khaya* (Meliaceae). Phytochemistry 10, 1845–4853.

Altomare, A., Burla, M.C., Camalli, M., Cascarano, G.L., Giacovazzo, C., Guagliardi, A.G.G., Moliterni, G., Polidori, R., Spagna, J., 1999. SIR97: a new tool for crystal structure determination and refinement. J. Appl. Cryst. 32, 115–119.

Blessing, R.H., 1997. DENZOX – Program for processing Denzo x files. Modified for Kappa CCD data, Farrugia, L.J.; Muir, K.W. 2001.

Blessing, R.H., 1997a. Outlier treatment in data merging. J. Appl. Cryst. 30, 421–426.

Bevan, C.W.L., Powell, J.W., Taylor, D.A.H., 1963a. Extracts of the Genera *Khaya*, *Guarea*, *Carapa*, and *Cedrela*. J. Chem. Soc. (C), 980–982.

Bevan, C.W.L., Rees, A.H., Taylor, D.A.H., 1963b. Anthothecol from *Khaya anthotheca*. J. Chem. Soc. (C), 983–989.

Bevan, C.W.L., Powell, J.W., Taylor, D.A.H., Halsall, T.G., Toft, P., Welford, W., 1967. The structure of methyl angolensate. J. Chem. Soc. (C), 163–170.

Connolly, J.D., McCrindle, R., Overton, K.H., Warnock, W.D.C., 1967. 6-Hydroxy- and 6-Acetoxy-methyl angolensate from *Khaya grandifoliola*. Tetrahedron 23, 4035–4039.

Connolly, J.D., Handa, K.L., 1969. 6-Hydroxycarapin and a triterpenoid tetrol from *Cedrela glaziovii*. J. Chem. Soc. (C), 2435–2436.

Daniewski, W.M., Gumulka, M., Danikiewiez, W., Gluzinski, P.J., Pankowska, E., Bloszyk, E., Jacobsson, U., Norin, T., Szafranski, F., 1993. Utilin B, a tetranortriterpenoid of the Mexicanolide Group from *Entandrophragma utile*. Phytochemistry 33, 1534–1536.

Daniewski, W.M., Gumulka, M., Danikiewiez, W., Gluzinski, P.J., Krajewski, J., Sitkowsky, J., Bloszyk, E., Drozdz, B., Jacobsson, U., Szafranski, F., 1994. Utilin C, a tetranortriterpenoid from the heartwood of *Khaya entandrophragma*. Phytochemistry 36, 1001–1003.

Halsall, T.G., Troke, J.A., 1975. Three new meliacins from the heartwood of *Khaya anthotheca*. J. Chem. Soc., Perkin I, 1758–1764.

Khalid, S.A., Friedrichsen, G.M., Kharazmi, A., Theander, T.G., Olsen, C.E., Christensen, S.B., 1998. Limonoids from *Khaya senegalensis*. Phytochemistry 49, 1769–1772.

Nakatani, M., Abdelgaleil, S.A.M., Okamura, H., Iwagawa, T., Sato, A., Doe, M., 2000. Khayanolides A and B, new rearranged phragmalin limonoid antifeedants from *Khaya senegalensis*. Tetrahedron Lett., 6473–6477.

Nakatani, M., Abdelgaleil, S.A.M., Kurawaki, J., Okuamura, H., Iwagawa, T., Doe, M., 2001. Antifeedant rings B and D opened limonoids from *Khaya senegalensis*. J. Nat. Prod. 64, 1261–1265.

Otwinowski, Z., Minor, W., 1997. Processing of X-ray diffraction data collected in oscillation mode. Meth. Enzymol. 276, 307–326.

Sheldrick, G.M., 1997. A Program for Crystal Structure Refinement 97-2.

Tchuendem, M.H.K., Ayafor, J.F., Connolly, J.D., Sterner, O., 1998. Khayalactone, a new limonoid from *Khaya grandifoliola*. Tetrahedron Lett. 39, 719–722.