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A xanthone and a polyketide derivative from the leaves of *Cassia obtusifolia* (Leguminosae)

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ABSTRACT

A new xanthone, 1,8-dihydroxy-3-methoxy-6-methylxantone and a new polyketide derivative, (4*R**,5*S**,6*E*,8*Z*)-ethyl-4-((*E*)-but-1-enyl)-5-hydroxypentdeca-6,8-dienoate, together with 20 known secondary metabolites, including 2 steroids, 4 xanthones, 10 anthraquinones, 2 triterpenoids, 1 fatty ester, and (*E*)-eicos-14-enoic acid, were isolated from the leaves of *Cassia obtusifolia*. To the best of our knowledge, the last compound was isolated from a natural source for the first time. The structures of all the compounds were elucidated on the basis of 1D and 2D NMR experiments. Some of the compounds were tested against *Salmonella typhi*, *Staphylococcus aureus*, *Candida albicans* ATCC 9002, and *Candida tropicalis*, they did not show any activity.

1. Introduction

Cassia obtusifolia Lam (Syn. *Senna obtusifolia*=*Chamaecrista obtusifolia*) belongs to the medically and economically important family Leguminosae (Syn. Cesalpiniaceae), subfamily Ceasalpinioideae.[1,2] It is an annual herb of West Tropical regions. *Cassia* leaves and pods have been widely used as purgatives and laxatives. *Cassia* species are known to be a rich in anthraquinones, anthrones, flavonoids, and triterpenoids. The anthraquinone derivatives, anthronic, dianthronic, and anthraquinone glycosides of *Cassia* are responsible for their purgative action.[3] Previous phytochemical investigation on the seeds of *C. obtusifolia* led to the identification of naphto-α-pyrone tetraglucosides and lactones.[4–6] As part of our continuing search for bioactive compounds,[7] we have studied the ethyl acetate and methanol extracts of the leaves of this plant and report herein the isolation and structural elucidation of two new compounds, 1,8-dihydroxy-3-methoxy-6-methylxantone (**1**) and (4*R**,5*S**,6*E*,8*Z*)-ethyl-4-((*E*)-but-1-enyl)-5-hydroxypentdeca-6,8-dienoate (**2**).

2. Results and discussion

The dried powdered leaves of *C. obtusifolia* were macerated with ethyl acetate (3×72 h) and the solvent removed under reduced pressure to afford an ethyl acetate extract. The residue was further extracted with methanol (3×72 h). The ethyl acetate and methanol extracts were subjected to flash column chromatography. Purification of the fractions from the methanol extract yielded one new xanthone, 1,8-dihydroxy-3-methoxy-6-methylxantone (**1**) and the known euxanthone,[8] chrysophanol,[9] physcion,[9] aloe-emodin,[9] emodin,[9] 1,2,8-trihydroxy-6,7-dimethoxyanthraquinone,[10] obtusifolin,[11] 1,5-dihydroxy-3-methoxy-7-methylanthraquinone,[12] 1,7-dihydroxy-3-methoxyxanthone,[13] 1-hydroxy-7-methoxy-3-methylanthraquinone,[10] 3,7-dihydroxy-1-methoxyxanthone,[14] 1-*O*-methylchrysophanol,[10] 8-*O*-methylchrysophanol,[10] and 1,3,6-trihydroxy-8-methylxanthone.[15] The ethyl acetate extract afforded one new polyketide derivative, (4*R**,5*S**,6*E*,8*Z*)-ethyl-4-((*E*)-but-1-enyl)-5-hydroxypentdeca-6,8-dienoate (**2**), along with the known stigmasterol,[16] (24*S*)-24-ethylcholesta-5,22(*E*),25-trien-3β-ol,[17] (−)-acetoxy-9,10-dimethyl-1,5-octacosanolide,[1] friedelin,[18] lupeol,[19] and (*E*)-eicos-14-enoic acid,[20] which was isolated for the first time from a natural source.

Compound **1** was obtained as a yellow powder from hexane–EtOAc, mp 152–153 °C. The molecular formula was determined as

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$C_{15}H_{12}O_5$ by HREIMS $[M]^+$ m/z 272.0679, in conjunction with the NMR spectra. This formula accounted for 10 degrees of unsaturation. Absorptions of hydroxyl groups (ν_{max} 3394 cm^{-1}), hydrogen-bonded carbonyl (ν_{max} 1626 cm^{-1}), and aromatic double bonds (ν_{max} 1479 cm^{-1}) were observed in the IR spectrum. The UV spectrum showed absorption bands of xanthone chromophore at λ_{max} 243–246 nm (strong), 258–268 nm (strong), 311–318 (medium), and 352–387 nm (weak).[21] The ^1H NMR spectrum (Table 1) showed the presence of two chelated phenolic hydroxyl groups at δ 12.33 (1-OH) and δ 12.12 (8-OH), one methoxy group at δ 3.92 (3-OCH_3), and one aromatic methyl at δ 2.42 (6-CH_3). Two typical AB spin systems with *meta*-coupling were observed at δ 7.63 (d, J=1.1 Hz, H-5), 7.08 (d, J=0.8 Hz, H-7) and δ 7.37 (d, J=2.5 Hz, H-4), 6.66 (d, J=2.5 Hz, H-2). The ^{13}C NMR spectrum (Table 1) revealed 15 carbon signals that were sorted by DEPT experiments into two CH_3, four CH, and nine C including that of a conjugated carbonyl group (δ 190.8, C-9). In the HMBC spectrum (Table 1), the chelated phenolic protons at δ 12.33 and 12.12 showed correlations with carbons at δ 106.8 (C-2), 110.3 (C-9a), 165.2 (C-1) and δ 124.5 (C-7), 113.5 (C-8a), 162.5 (C-8), respectively, confirming their location at C-1 and C-8 of the xanthone nucleus. Further correlations were observed between the proton at δ 3.92 and the carbon at δ 166.6 (C-3) and between the proton at δ 2.42 and the carbons at δ 124.5 (C-7), 121.3 (C-5), and 148.4 (C-6) indicating the position of the methoxyl group and the aromatic methyl at C-3 and C-6, respectively. Compound **1** was thus characterized as 1,8-dihydroxy-3-methoxy-6-methylxantone.

Compound **2** was obtained as yellow oil. The molecular formula $C_{21}H_{36}O_3$ was deduced from the ESIMS $[M+H]^+$ m/z 337.2. This molecular formula was confirmed by the HREIMS $[M]^+$ m/z 336.2667 and the 1D NMR spectral data. The IR spectrum indicated absorption bands due to hydroxyl (ν_{max} 3400 cm^{-1}) and ester carbonyl (ν_{max} 1737 cm^{-1}) groups, and also of a conjugated diene (ν_{max} 1465 cm^{-1}). The mass spectrum exhibited fragmentation confirming the presence of double bonds (gaps of 26 amu or 40 amu).[22] The ^1H NMR spectrum (Table 2) showed signals of six olefinic protons at δ 6.52 (dd, J=10.0, 15.2 Hz, H-7), 5.98 (t, J=10.9 Hz, H-8), 5.68 (dd, J=6.4, 15.2 Hz, H-6), 5.56 (dt, J=5.7, 16.1 Hz, H-2″), 5.45 (dt, J=7.6, 15.3 Hz, H-9), and 5.35 (dd, J=8.9, 16.5 Hz, H-1″), one ethoxyl group at δ 4.12 (q, J=7.1 Hz, H-1′) and 1.25 (t, J=7.3 Hz, H-2′). This spectrum also exhibited signals of two ethyl groups at δ 2.05 (m, H-3″) and 1.09 (t, J=7.5 Hz, H-4″) and δ 1.29 (m, H-14) and 0.85 (t, J=7.0 Hz, H-15), and one oxymethyne at δ 4.20 (dd, J=6.4, 8.5 Hz, H-5). The ^{13}C NMR (Table 2) and DEPT spectra indicated three CH_3, nine CH_2, eight CH, and one C signals, including that of an ester carbonyl at δ 173.9 (C-1). Spin systems of CH_3–CH_2–CH=CH–CH–CH–, –CH=CH–CH=CH–CH_2–, –CH_2–CH_2–, and two CH_3–CH_2– were deduced from ^1H–^1H COSY (Fig. 1) and HMQC spectral analyses. HMBC correlations (Table 2) enabled us to complete the structural elucidation of **2**. Correlations were observed between H-6 and C-4, C-5 and C-8; H-2″ and C-4; H-8 and C-6, C-7 and C-10; H-5 and C-1″, C-4, C-6 and C-7. Further more, other correlations were observed between H-4 and C-1″, C-2″; H-2 and C-1; H-10 and C-9, C-11; H-1′ and C-1, C-2′ as well as between H-4″ and C-2″, C-3″; H-15 and C-13, C-14. The relative stereochemistry of **2** was deduced from its NOESY spectrum (Fig. 2). Pertinent correlations were observed between H-4 and H-5, H-1′ and H-2 as well as between H-5 and H-7. Further correlations were also observed between H-7 and H-10. The configuration of the double bonds was determined on the basis of the ^3J values between the vinylic

Table 1
^1H[a] and ^{13}C[b] NMR data for compound **1** (J in Hz)

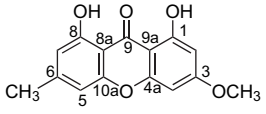
Position	δ_C	δ_H	HMBC (H→C)
1	165.2	—	
2	106.8	6.66 (d, 2.5)	C-4, C-9a, C-3, C-1
3	166.6	—	
4	108.2	7.37 (d, 2.5)	C-9a
4a	155.0	—	
5	121.3	7.63 (d, 1.1)	C-7, C-8a
6	148.4	—	
7	124.5	7.08 (d, 0.8)	C-5, C-8a
8	162.5	—	
8a	113.5	—	
9	190.8	—	
9a	110.3	—	
10a	152.3	—	
3-OMe	56.0	3.92 (s)	C-3
6-Me	22.1	2.42 (s)	C-7, C-5, C-6
1-OH	—	12.33 (s)	C-1, C-2, C-9a
8-OH	—	12.12 (s)	C-7, C-8, C-8a

[a] Spectra recorded in $CDCl_3$, 400 MHz.
[b] Spectra recorded in $CDCl_3$, 100 MHz.

Table 2
^1H[a] and ^{13}C[b] NMR data for compound **2** (J in Hz)

Position	δ_C	δ_H	HMBC (H→C)
1	173.9	—	
2	35.3	2.30 (t, 7.6)	C-1
3	24.9	1.69 (m)	
		1.29 (ov. m)	
4	37.3	2.34 (m)	C-2″, C-1″
5	72.1	4.20 (m)	C-1″, C-4, C-6, C-7
6	135.2	5.68 (dd, 6.4, 15.2)	C-4, C-5, C-8
7	125.8	6.52 (dd, 10.0, 15.2)	C-5, C-8
8	127.8	5.98 (t, 10.9)	C-6, C-7, C-10
9	132.9	5.45 (dt, 7.6, 10.7)	C-7
10	27.7	2.16 (m)	C-9, C-11
11	29.7	1.30–1.40 (ov. m)	
12	29.5	1.30–1.40 (ov. m)	
13	31.9	1.30–1.40 (ov. m)	
14	22.7	1.30–1.40 (ov. m)	
15	14.1	0.85 (t, 7.0)	C-13, C-14
1′	60.2	4.12 (q, 7.1)	C-1, C-2′
2′	14.2	1.25 (t, 7.3)	C-1′
1″	123.8	5.35 (dd, 8.9, 16.5)	C-3″
2″	135.1	5.56 (dt, 5.7, 16.1)	C-4
3″	20.7	2.05 (m)	C-2″, C-4″
4″	14.2	1.09 (t, 7.5)	C-3″, C-2″

ov. m: Overlapping multiplet.
[a] Spectra recorded in $CDCl_3$, 400 MHz.
[b] Spectra recorded in $CDCl_3$, 100 MHz.



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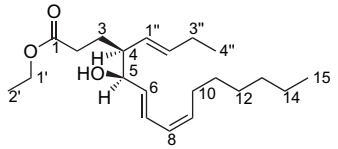

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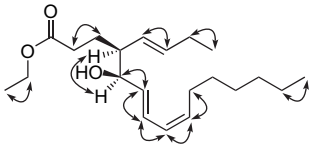

Figure 1. Selected COSY correlations for compound **2**.

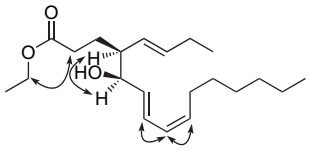

Figure 2. Selected NOESY correlations for compound **2**.

protons as well as the IR spectrum, which exhibited characteristic peaks for the trans isomers in the range of ν_{max} 960–980 cm^{-1}.[22] Compound **2** was thus established to be (4*R**,5*S**,6*E*,8*Z*)-ethyl-4-((*E*)-but-1-enyl)-5-hydroxypentdeca-6,8-dienoate.

Euxanthone,[8] chrysophanol,[9] physcion,[9] aloe-emodin,[9] emodin,[9] 1,2,8-trihydroxy-6,7-dimethoxyanthraquinone,[10] obtusifolin,[11] 1,5-dihydroxy-3-methoxy-7-methylanthraquinone,[12] 1,7-dihydroxy-3-methoxyxanthone,[13] 1-hydroxy-7-methoxy-3-methylanthraquinone, 3,7-dihydroxy-1-methoxyxanthone,[14] 1-*O*-methylchrysophanol,[10] 8-*O*-methylchrysophanol,[10] and 1,3,6-trihydroxy-8-methylxanthone,[15] stigmasterol,[16] (24*S*)-24-ethylcholesta-5,22(*E*),25-trien-3β-ol,[17] (−)-acetoxy-9,10-dimethyl-1,5-octacosanolide,[1] friedelin,[18] lupeol,[19] and (*E*)-eicos-14-enoic acid,[20] spectral data were in agreement with those reported in the literature.

Compounds **1** and **2** as well as chrysophanol, 1,3,6-trihydroxy-8-methylxanthone, 1,7-dihydroxy-3-methoxyxanthone, 1,5-dihydroxy-3-methoxy-7-methylanthraquinone, 1,2,8-trihydroxy-6,7-dimethoxyanthraquinone, 1,7-dihydroxy-3-methoxyxanthone, and (*E*)-eicos-14-enoic acid were tested against *Salmonella typhi*, *Staphylococcus aureus*, *Candida albicans* ATCC 9002, and *Candida tropicalis*. These compounds were found not to be active (MICs>200 μg/mL).

3. Experimental

3.1. General experimental procedures

Melting points were determined on a Reitcher Nr-229 micro-melting point apparatus and were uncorrected. Mass spectra (70 eV) were recorded in the EI and ESI modes on a Jeol JMS 700 apparatus and no fragments below *m*/*z* 40 were registered. The UV spectra were obtained with a Shimadzu 3101 PC instrument and the IR spectra determined with a JASCO FT-IR 410 apparatus. ^1H NMR (400.6 MHz) and ^{13}C NMR (100.13 MHz) spectra with DEPT program were recorded in $CDCl_3$ (with its signal at δ 7.25 and 77.0 ppm as standard reference) on Brüker DPX 400 apparatus. The coupling constants (*J*) are given in hertz. NMR data acquisition and processing were performed with the aid of the XWIN and NUTS NMR software packages. ^1H–^1H COSY, HMBC, and HMQC experiments were recorded with gradient enhancements using sine shaped gradient pulses. NOESY experiments were carried out using a Brüker AM 360 instruments. High Performance Liquid Chromatography (HPLC) was run using a Shimadzu LC-10AS Micro pump with a Shimadzu RID-2A RI-Detector and preparative recycling HPLC was carried out on an LC-09 instrument (Nihon Bunseki Kogyo). For HPLC, Nova-Pak Cartridge C_{18} (100 mm×5 mm i.d., Millipore Co. Ltd.) and GS-310 (20 mm×500 mm, Nihon Bunseki Kogyo) were used. Column chromatographies were run with Merck silica gel 60 and Sephadex LH-20, while TLC was carried out on silica gel 60 GF_{254} pre-coated plates with detection accomplished by spraying with 50% H_2SO_4 followed by heating at 100 °C, or by visualizing with a UV lamp at 254 and 366 nm.

3.2. Plant material

The leaves of *C. obtusifolia* were collected in October 2004 at Mount Eloumden (Yaounde) in the Centre Province of Cameroon. The plant was identified by Mr. Nana Victor, botanist at the National Herbarium of Cameroon where a voucher specimen (No. 39847/HNC) has been deposited.

3.3. Extraction and isolation

Air-dried and powdered leaves of *C. obtusifolia* (500 g) were extracted by percolation at room temperature with ethyl acetate (3×8 L). After evaporation in vacuo, a crude extract was obtained (67.25 g). The residue was further extracted with methanol (3×8 L) to afford a methanol extract (48.24 g). The ethyl acetate extract was subjected to open dry flash column chromatography over silica gel and eluted with step gradients of *n*-hexane–EtOAc and EtOAc–MeOH to yield seven major fractions (A_1–A_7): A_1 (22.6 g) was eluted with *n*-hexane–EtOAc (9:1), A_2 (11.3 g) was eluted with *n*-hexane–EtOAc (9:1, 8:2), A_3 (1.6 g) was eluted with *n*-hexane–EtOAc (8:2), A_4 (6.6 g) was eluted with *n*-hexane–EtOAc (7:3), A_5 (1.26 g) was eluted with *n*-hexane–EtOAc (1:1) and EtOAc, A_6 (2.4 g) was eluted with *n*-EtOAc–MeOH (95:5), and A_7 (4 g) was eluted with EtOAc–MeOH (9:1) and MeOH. Further purification of fraction A_1 through repeated silica gel column chromatography with gradient of *n*-hexane–EtOAc and Sephadex LH-20 using $CHCl_3$–MeOH (1:1) as eluent yielded stigmasterol (86 mg), lupeol (16 mg), friedeline (71 mg), (−)-acetoxy-9,10-dimethyl-1,5-octacosanolide (5 mg), and compound **2** (24 mg). Fraction A_2 was purified with the same procedure as A_1 to afford (24*S*)-24-ethylcholesta-5,22(*E*),25-trien-3β-ol (12 mg) and (*E*)-eicos-14-enoic acid (56 mg). The methanol extract was subjected to dry flash column chromatography with a step gradient of CH_2Cl_2–MeOH to give nine major fractions (B_1–B_9): B_1 (743 mg) was eluted with CH_2Cl_2, B_2 (1.11 g) was eluted with CH_2Cl_2–MeOH (95:5), B_3 (280 mg) was eluted with CH_2Cl_2–MeOH (9:1), B_4 (3.4 g) was eluted with CH_2Cl_2–MeOH (9:1), B_5 (260 mg) and B_6 (600 mg) were eluted with CH_2Cl_2–MeOH (85:15), B_7 (1.4 g) was eluted with CH_2Cl_2–MeOH (8:2), B_8 (3.5 g) was eluted with CH_2Cl_2–MeOH (7:3), and B_9 (1.8 g) was eluted with MeOH. Repeated column chromatography of fraction B_1 eluting with a gradient of CH_2Cl_2–acetone followed by purification through Sephadex LH-20 eluting with CH_2Cl_2–MeOH (1:1) and HPLC (with a CH_3CN–H_2O gradient) gave chrysophanol (2 mg) and compound **1** (1.5 mg). Fraction B_2 was re-chromatographed on a silica gel column with a step gradient of PE–EtOAc and further purified by HPLC (with a CH_3CN–H_2O gradient) to give 1-hydroxy-7-methoxy-3-methylanthraquinone (5 mg) and 1,8-dihydroxy-3-methoxy-6-methylanthraquinone (physcion) (3.6 mg). Fraction B_4 was purified by preparative TLC plates using CH_2Cl_2–acetone (95:5) as eluent followed by gel permeation over Sephadex LH-20 (CH_2Cl_2–MeOH, 1:1) to yield obtusifolin (3.4 mg), aloe-emodin (2.8 mg), emodin (8 mg), 1,5-dihydroxy-3-methoxy-7-methylanthraquinone (2 mg), and 1,2,8-trihydroxy-6,7-dimethoxyanthraquinone (1.5 mg). Fractions B_5 and B_6 treated in the same manner, gave 1,3,6-trihydroxy-8-methylxanthone (11 mg) and euxanthone (5 mg), 3,7-dihydroxy-1-methoxyxanthone (10 mg), 1-*O*-methylchrysophanol (18 mg), and 8-*O*-methylchrysophanol (2.5 mg), respectively, while fraction B_7 underwent the same purification procedure to give 1,7-dihydroxy-3-methoxyxanthone (2 mg).

*3.3.1. 1,8-Dihydroxy-3-methoxy-6-methylxantone (**1**)*

Yellow powder from hexane–EtOAc, mp 152–153 °C; UV (MeOH) λ_{max} nm (log ε): 246 (4.41), 262 (4.38), 318 (4.16), 365 (3.61); IR (KBr) ν_{max} cm^{-1}: 3394 (OH), 2926, 1626 (C=O), 1479, 1326, 1228, 1164, 1099, 1028, 982, 874, 757; for ^1H NMR ($CDCl_3$, 400 MHz) and ^{13}C NMR ($CDCl_3$, 100 MHz) data see Table 1; HREIMS *m*/*z* 272.0679 $[M]^+$ (calcd. for $C_{15}H_{12}O_5$, 272.0685); EIMS (70 eV) *m*/*z* (rel int.): 272 $[M]^+$ (1), 43 (100), 57 (82), 41 (49), 69 (44), 71 (34), 85 (27).

3.3.2. (4R,5S*,6E,8Z)-Ethyl-4-((E)-but-1-enyl)-5-hydroxypentdeca-6,8-dienoate (**2**)*

Yellow oil; UV (MeOH) λ_{max} nm: 244; IR (CH_2Cl_2) ν_{max} cm^{-1}: 3400 (OH), 2926, 2854, 1737 (C=O), 1465, 1375, 1184, 1034, 971, 960; for ^1H NMR ($CDCl_3$, 400 MHz) and ^{13}C NMR ($CDCl_3$, 100 MHz) data see Table 2; HREIMS *m*/*z* 336.2667 $[M]^+$ (calcd. for $C_{21}H_{36}O_3$, 336.2664); ESIMS *m*/*z* (rel int.): 337 $[M+H]^+$ (15), 319 (18), 313 (12), 307 (16), 305 (100), 279 (9), 251 (15), 241 (11), 191 (19).

3.4. Antimicrobial assay

The microorganisms used in this study consisted of two strains of bacteria (*S. typhi* and *S. aureus*) and two strains of yeasts (*C. albicans* ATCC 9002 and *C. tropicalis*) kindly provided by the '*Centre Pasteur du Cameroun*' health institute and monitored in the Laboratory of Microbiology and Antimicrobial Substances of the University of Dschang. The bacteria strains were grown at 37 °C and maintained on nutrient agar slants while the yeasts were grown at 30 °C and maintained in Sabouraud dextrose agar slants. The antimicrobial assay was determined by broth dilution method in 24 wells micro plates. Twofold serial dilutions (0–400 μg/mL) with appropriate antibiotic control were prepared in Mueller Hinton broth for bacteria and Sabouraud dextrose broth for yeasts.[23,24] Standardized suspension (10 μL) of bacteria (10^6 CFU/mL) or yeasts (2×10^5 cells/mL) was added to each well (containing pure products at a final concentration of 0–400 μg/mL), and incubated either at 37 °C for bacteria or at 30 °C for yeasts for 24 h or 48 h. Gentamicin (bacteria) and nystatin (yeasts), diluted in water, were used as reference antibiotics.

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