New Xanthones from *Calophyllum caledonicum*

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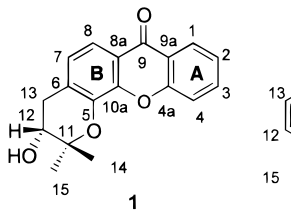
Four new xanthones, caledonixanthones A−D (**1**−**4**), were isolated from the trunk bark of *Calophyllum caledonicum*, in addition to 17 known compounds. The structures of **1**−**4** were determined by means of spectroscopic analysis and chemical derivatization.

Plants from the genus *Calophyllum* (Clusiaceae) are known as a rich source of secondary metabolites such as xanthones,[1−13] coumarins,[14] chromenes,[15] flavonoids,[16] and triterpenes.[17] Some of these compounds exhibit significant biological effects such as anti-HIV,[18,19] antifungal,[11] antimicrobial,[20] and immunomodulatory[12] activities. As part of an ongoing study on species from the Clusiaceae,[21−23] we report herein the first phytochemical investigation on *Calophyllum caledonicum* Vieill.,[24] collected in New Caledonia, where it is called "Tamanou de Montagne" and used by local populations as a diuretic. Four new xanthones (**1**−**4**) along with 17 known xanthones were isolated and characterized from a CH_2Cl_2 extract of the trunk bark of this plant.



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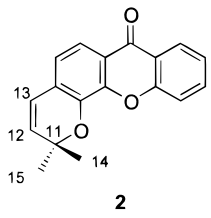

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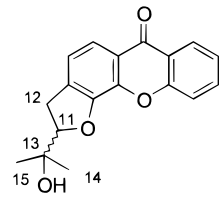

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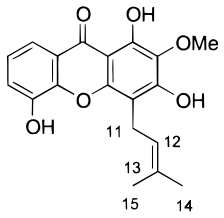

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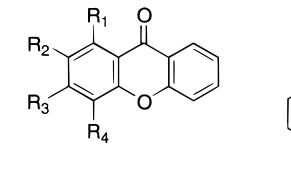
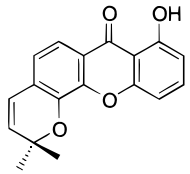


5 R_1=OMe, R_2=OH, R_3=R_4=H
6 R_1=R_2=OMe, R_3=R_4=H
7 R_1=R_2=H, R_3=OH, R_6=OMe
8 R_1=H, R_2=OH,R_3=R_4=OMe



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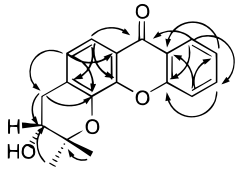
Results and Discussion

The CH_2Cl_2 extract from the trunk bark of *C. caledonicum* was fractionated by repeated column chromatography on Si gel using *n*-hexane−EtOAc and $CHCl_3$−MeOH as the eluents.

Caledonixanthone A (**1**) crystallized as white prisms (mp 246 °C) from acetone. The HRLSIMS of **1** showed a pseudomolecular ion at *m/z* 297.1142 $[M + H]^+$ corresponding to $C_{18}H_{17}O_4$ (Δ +1.5 mmu). The UV spectrum exhibited four absorption bands characteristic of a xanthone (λ_{max} 237, 253, 285, and 346 nm).[25] These bands remained unaffected by addition of NaOMe, $AlCl_3$, or NaOAc, suggesting the lack of a free hydroxyl group on the xanthone nucleus. The ^{1}H NMR spectrum of **1** showed the presence of a 1,2-disubstitued benzene ring with typical signals at δ_H 7.39 (1H, dd, J = 8.0, 8.0 Hz), 7.63 (1H, d, J = 8.0 Hz), 7.73 (1H, ddd, J = 8.0, 8.0, 1.5 Hz), and 8.34 (1H, dd, J = 8.0, 1.5 Hz), while two *ortho*-coupled protons appeared as two doublets (J = 8.0 Hz) at δ_H 7.08 and 7.83, respectively. In the HMBC spectrum (Figure 1), one of these *ortho*-coupled protons (δ_H 7.83) was correlated to the keto group of the xanthone at δ_C 177.1 and to two quaternary carbons at δ_C 125.1 and 146.3. The proton signal at δ_H 7.83 was then assigned to H-8, and **1** could be deduced to be a 5,6-disubstitued xanthone.

The ^{1}H NMR spectrum of **1** also exhibited signals for two methyls [δ_H 1.46 and 1.53 (3H each, s)], one oxygenated methine [δ_H 3.95 (1H, t, J = 5.0 Hz)], one methylene [δ_H 2.93 (1H, dd, J = 18.0, 5.0 Hz) and 3.21 (1H, dd, J = 18.0, 5.0 Hz)], and one hydroxyl group [δ_H 1.94, s, exchangeable



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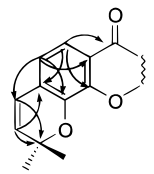

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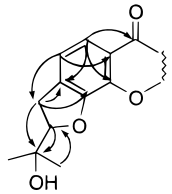

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Figure 1. HMBC correlations (J = 6 Hz) of **1**−**3**.

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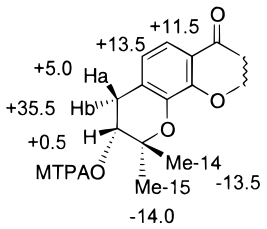

Figure 2. Δδ (in Hz) values obtained for the MTPA esters of **1**.

Table 1. ^{1}H NMR Data of the MTPA Esters of **1**[a]

position	δ (ppm) (*S*)-MTPA ester	δ (ppm) (*R*)-MTPAester	Δδ (Hz) = $\delta_S - \delta_R$
H-1	8.35	8.34	+2.0
H-3	7.74	7.73	+2.0
H-4	7.62	7.62	+1.0
H-7	7.06	7.01	+13.5
H-8	7.86	7.82	+11.5
H-13a	3.08	2.95	+35.5
H-13b	3.39	3.37	+5.0
H-12	5.26	5.25	+0.5
Me-14	1.45	1.50	−14.0
Me-15	1.38	1.43	−13.5

[a] Spectra run in $CDCl_3$.

with D_2O]. In the HMBC spectrum (Figure 1), the methyl protons were correlated with one oxygenated quaternary carbon (δ_C 78.1) and with the oxygenated methine carbon (δ_C 69.1), which correlated with both methylene protons. In turn, H-7 correlated with the methylene carbon at δ_C 31.3, and the other relevant correlations observed are presented in Figure 1. In this way, a 3-hydroxy-2,2-dimethyl-3,4-dihydropyrane ring was identified as the 5,6-substituent in this xanthone.

The relative stereochemistry of **1** (Figure 2) was deduced from its NOESY spectrum showing that Me-14 (δ_H 1.53), H-13a (δ_H 2.93), and H-12 (δ_H 3.95), on one hand, and OH-12 (δ_H 1.94), Me-15 (δ_H 1.46), and H-13b (δ_H 3.21), on the other hand, were oriented on the same sides of the molecule. To establish the absolute configuration of the OH-12 group, the (*S*)- and (*R*)-MTPA esters of **1** were prepared and the $\Delta\delta$ ($=\delta_{S-\text{MTPA ester}} - \delta_{R-\text{MTPA ester}}$) values were calculated for the respective protons.[26] The results are presented in Table 1 and Figure 2, which show that the $\Delta\delta$ values for the protons oriented on the left side of the MTPA plane are all negative, while those for the protons located on the right side of the MTPA plane are positive. Thus, this modified Mosher's method allowed us to assign the absolute configuration of **1** as 12*R*. Therefore, the structure of caledonixanthone A was assigned as **1**, and complete assignments of its ^{1}H and ^{13}C NMR resonances are listed in Tables 2 and 3, respectively.

Compound **2**, caledonixanthone B, was assigned the molecular formula $C_{18}H_{14}O_3$ from the HRLSIMS (*m/z* 279.1028 $[M + H]^+$, Δ +0.7 mmu). The UV and ^{1}H and ^{13}C NMR spectra of **2** were very similar to those of **1** (see Tables 2 and 3), suggesting that **2** was also a 5,6-disubstitued xanthone oxygenated at C-5. Direct comparison of the ^{1}H NMR spectra of **1** and **2** showed that the signals for the H-12 and H-13 protons of **1** were replaced in **2** by two deshielded doublets (δ_H 5.83 and 6.44) associated with two *cis*-olefinic protons (J = 10.0 Hz). The 5,6-substituent of the xanthone was then readily identified as a 2,2-dimethylpyran unit from the HMBC spectrum (Figure 1), thus confirming the structure of caledonixanthone B as **2**.

The HREIMS spectrum of **3**, caledonixanthone C, showed a molecular ion at *m/z* 296.1052 associated with the molecular formula $C_{18}H_{16}O_4$ (Δ +0.4 mmu). The UV and

Table 2. ^{1}H NMR Spectral Data for **1**−**4** in $CDCl_3$[a]

position	1	2	3	4[b]
1	8.34 dd (8.0, 1.5)	8.33 dd (8.0, 2.0)	8.35 dd (8.0, 1.5)	
2	7.39 dd (8.0, 8.0)	7.37 dd (8.0, 8.0)	7.39 dd (8.5, 8.0)	
3	7.73 ddd (8.0, 8.0, 1.5)	7.73 ddd (8.5, 8.0, 2.0)	7.73 ddd (8.5, 8.0, 1.5)	
4	7.63 d (8.0)	7.63 d (8.5)	7.57 d (8.0)	
6				7.34 d (8.0)
7	7.08 d (8.0)	7.02 d (8.0)	7.19 d (8.0)	7.23 dd (8.0, 8.0)
8	7.83 d (8.0)	7.82 d (8.0)	7.86 d (8.0)	7.65 d (8.0)
11			4.89 t (9.0)	3.58 d (7.0)
12	3.95 t (5.0)	5.83 d (10.0)	3.38 d (9.0)	5.33 t (7.0)
13	2.93 3.21 dd each (18.0, 5.0)	6.44 d (10.0)		
14	1.53 s	1.58 s	1.30 s	1.60 s
15	1.46 s		1.48 s	1.81 s
OH-1				13.14 s
OH-12	1.94			
OMe-2				3.87 s

[a] Values in parentheses are J (Hz). [b] Spectrum recorded in acetone-d_6.

Table 3. ^{13}C NMR Spectral Data for **1**−**4** ($CDCl_3$)

carbon	1	2	3	4[a]
1	126.5	126.6	126.8	152.6
2	123.9	123.8	124.0	130.8
3	134.5	134.5	134.7	156.5[b]
4	118.4	118.4	118.1	107.2
4a	155.9	156.1	155.8	150.9[b]
5	141.7	141.3	147.1	146.8
6	125.1	126.0	134.2	120.9
7	124.7	121.3	120.0	124.4
8	116.9	117.6	118.9	116.0
8a	121.2	122.4	122.2	121.6
9	177.1	176.9	176.8	182.2
9a	121.6	121.7	121.7	103.5
10a	146.3	145.7	141.5	146.2
11	78.1	77.2	91.2	22.2
12	69.1	133.5	31.5	122.9
13	31.3	122.0	71.8	131.8
14	22.1	27.8	24.2	25.7
15	24.7		26.3	17.8
OMe				60.6

[a] Spectrum recorded in acetone-d_6. [b] Signals with the same superscript are interchangeable.

^{1}H and ^{13}C NMR spectra (Tables 2 and 3) of **3** permitted the characterization of a 5,6-disubstitued xanthone without any phenolic group, whereas a hydroxyl group (ν_{max} 3567 cm^{-1}) was in evidence from the IR spectrum of **3**. In the ^{1}H NMR spectrum, a doublet of two magnetically equivalent benzylic protons (δ_H 3.38) appeared coupled with a low-field methine proton (δ_H 4.89, J = 9.5 Hz). The HMBC spectrum of **3** (Figure 1) showed that these features could be associated with a 2-substituted dihydrofuran ring at the 5,6 position of the xanthone. The nature of this dihydrofuran ring was finally determined from the HMBC spectrum, in which a quaternary carbon at δ_C 71.8 (C−OH) was correlated with two angular methyls (δ_H 1.30 and 1.48) as well as with the aforementioned dihydrofuran protons. The structure of caledonixanthone C was thus deduced as **3**,

Table 4. UV Data for **4**

solvent	λ_{max} nm (log ϵ)			
MeOH	389 (3.23)	320 (3.97)	258 (4.23)	243 (4.29)
MeOH + NaOMe		363 (4.14)	292 (4.09)	255 (4.27)
MeOH + $AlCl_3$	427 (3.27)	327 (4.03)	270 (4.17)	243 (4.31)
MeOH + $AlCl_3$ + HCl	429 (3.19)	330 (3.82)	367 (4.22)	246 (4.24)
MeOH + NaOAc		362 (3.89)	277 (4.08)	242 (4.32)
MeOH + H_3BO_3/NaOAc	368 (3.60)	321 (3.90)	257 (4.26)	244 (4.34)

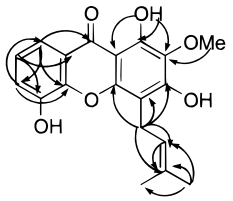

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Figure 3. HMBC correlations (J = 6 Hz) of **4**.

i.e., a new 5-oxygenated xanthone substituted at C-5 and C-6 by a 2-(1-hydroxy-1-methylethyl)dihydrofuran moiety.

The HREIMS of caledonixanthone D (**4**) showed a molecular ion peak at *m*/*z* 342.1091, which corresponded to the molecular formula $C_{19}H_{18}O_6$ (Δ −1.2 mmu). Upon addition of NaOMe, a strong bathochromic shift effect (43 nm) was observed in its UV spectrum (Table 4), pointing to the phenolic nature of the molecule. In this respect, the presence of hydroxyl groups located *peri* to the carbonyl function was supported by the acid-stable complexation of **4** with $AlCl_3$. In addition, the presence of a free hydroxyl group at C-3 or C-6 of the xanthone was deduced from the observed bathochromic shift of the 320 nm band in the presence of NaOAc. It could be thus established that **4** was substituted by two hydroxyl groups at C-1 and either C-3 or C-6 on the xanthone nucleus.

The low-field portion of the ^{1}H NMR spectrum exhibited the typical signal of the chelated OH-1 at δ_H 13.14 (s). In the aromatic resonance area, the spin system of three *ortho*-coupled protons was in evidence at δ_H 7.23 (1H, dd, J = 8.0, 8.0 Hz), 7.34 (1H, d, J = 8.0 Hz), and 7.65 (1H, d, J = 8.0 Hz). These chemical shifts were then readily assigned to H-7, H-6, and H-8, respectively, from the HMBC spectrum of **4** (Figure 3). Indeed, in this experiment, one of these protons (δ_H 7.65, H-8) gave cross-peaks with the heterocyclic carbonyl at δ_C 182.2 together with one aromatic CH (δ_C 120.9, C-6) and one oxygen-bearing sp^2 carbon at δ_C 146.2. These results thus allowed us to locate this proton (H-8) at a *peri*-position (C-8) to the keto function. Since H-7 (δ_H 7.23) correlated with another oxygenated aromatic carbon (δ_C 146.8), an OH group was assigned as the C-5 substituent of this xanthone.

Accordingly, compound **4** was identified as a 1,3,5-trihydroxyxanthone. A methoxyl group could then be located at C-2 since the chelated OH-1 was correlated in the HMBC spectrum to C-2 (δ_H 130.8), which in turn exhibited long-range coupling with the methoxyl protons. Finally, an isoprenyl moiety was characterized by typical proton chemical shifts at δ_H 5.33 (1H, t, J = 7.5 Hz), 3.58 (2H, d, J = 7.0 Hz), and 1.81 and 1.60 (3H each, s). The HMBC spectrum then confirmed that the 3-methylbut-2-enyl substituent was located at C-4 (Figure 3), and caledonixanthone D was thus identified as structure **4**.

In addition to the four new compounds, 17 mono-, di-, tri-, and tetraoxygenated xanthones of known structure were identified by NMR (HMQC, HMBC) and by comparison of their spectral data (^{1}H, ^{13}C) with literature values. The ^{13}C NMR spectra of 7-hydroxy-8-methoxyxanthone (**5**),[27] 7,8-dimethoxyxanthone (**6**),[28] 6-hydroxy-5-methoxyxanthone (**7**),[29] 7-hydroxy-5,6-dimethoxyxanthone (**8**),[30] and dehydrocycloguanandin (**9**)[31] were assigned in the Experimental Section since these data have not been reported previously.

Experimental Section

General Experimental Procedures. Melting points were determined with a Electrothermal 8100 melting point apparatus and are uncorrected. Optical rotations were recorded on a Schmidt-Haensch polarimeter, and UV spectra were recorded on a Schimadzu UV-1601 spectrophotometer. CD spectra were recorded on a CD5 spectrometer from Jobin Yvon Instruments S.A. (France). IR spectra were obtained on a Perkin-Elmer 580 spectrometer. ^{1}H and ^{13}C spectra were recorded on a JEOL GSX 270 MHz instrument. 2D NMR experiments (DQF−COSY, HMQC, HMBC) were recorded on a Bruker Avance DRX 500 MHz. HREIMS (70 eV) were determined on a Varian Mat 311 mass spectrometer, and HRLSIMS were determined on a Micromass Autospec instrument. Solvents were distilled before use, and spectral grade solvents were used for spectroscopic measurements. Si gel 60 (Macherey-Nagel, 230−400 mesh) was used for column chromatography, precoated Si gel plates (Macherey-Nagel, SIL G25 UV254, 0.25 mm) were used for analytical TLC, and precoated Si gel plates (Macherey-Nagel, SIL G/UV254, 0.25 mm) were used for preparative TLC. The compounds were detected by UV at 254 and 366 nm.

Plant Material. The trunk bark of *C. caledonicum* was collected in the "Rivière Bleue" forest, New Caledonia, in September 1997. A herbarium specimen (LIT 0315) is deposited at the Laboratoire des Plantes Medicinales, CNRS, Noumea, New Caledonia.

Extraction and Isolation. The powdered trunk bark (1.8 kg) of *C. caledonicum* was extracted successively with *n*-hexane (6 L) for 24 h and then with dichloromethane (6 L) for 24 h in a Soxhlet apparatus. Concentration under reduced pressure gave 131 g (7.3%) of a *n*-hexane extract and 30 g (1.7%) of a dichloromethane extract. Part of the CH_2Cl_2 extract (16.6 g) was subjected to column chromatography over Si gel using 100% *n*-hexane to 40% hexane/60% EtOAc in 5% stepwise elutions and then 99% $CHCl_3$/1% MeOH to 90% $CHCl_3$/10% MeOH in 1% stepwise elutions and afforded 24 fractions. The first seven fractions were combined and further chromatographed over Si gel (elution with 90% *n*-hexane/10% EtOAc) to yield **2** (47 mg, 0.28%), dehydrocycloguanandin (**9**)[31] (4 mg, 0.02%), and 8-hydroxy-7-methoxyxanthone[3] (20 mg, 0.12%). Fractions 8 and 9 were mixed and chromatographed over Si gel (elution with 85% *n*-hexane/15% EtOAc) and yielded 7-hydroxyxanthone[28,32] (6 mg, 0.04%), 7-hydroxy-8-methoxyxanthone (**5**)[27] (25 mg, 0.15%), **4** (9 mg, 0.05%), and 5-hydroxyxanthone[32,33] (6 mg, 0.04%). Fraction 10 was chromatographed over Si gel (elution with 80% *n*-hexane/20% EtOAc) and afforded 7,8-dimethoxyxanthone (**6**)[28] (12 mg, 0.07%), 1,5-dihydroxyxanthone[4] (4 mg, 0.02%), and 6,8-dihydroxy-7-methoxyxanthone[27] (2 mg, 0.01%). Fractions 11−13 were combined, then chromatographed over Si gel (elution with 97% $CHCl_3$/3% MeOH) to yield 1,6-dihydroxy-7,8-dimethoxyxanthone[34] (5 mg, 0.03%), caloxanthone F[7] (8 mg, 0.05%), 6-hydroxy-7-methoxyxanthone[27,35] (7 mg, 0.04%), 6-hydroxy-5-methoxyxanthone (**7**)[29] (8 mg, 0.05%), 1,5-dihydroxy-3-methoxyxanthone[27] (4 mg, 0.02%), caloxanthone G[7] (6 mg, 0.04%), **3** (8 mg, 0.05%), and 7-hydroxy-5,6-dimethoxyxanthone[30] (10 mg, 0.06%). Fraction 14 was crystallized from acetone to give **1** (53 mg, 0.32%). Fractions 15−24 were combined and chromatographed over Si gel, eluted with 70% cyclohexane/30% EtOAc, and yielded 1,3,5-trihydroxy-2-methoxyxanthone[36] (18 mg, 0.11%) and 2-deprenylrheediaxanthone[37] (15 mg, 0.09%).

Caledonixanthone A (1): white prisms (acetone); mp 246 °C; R_f 0.14 (cyclohexanes−EtOAc, 7:3); $[\alpha]^{25}_D$ −48° (*c* 0.17,

MeOH); UV (MeOH) λ_{max} (log ϵ) 346 (3.73), 285 (3.95), 253 (4.60), 237 (4.48) nm; IR (CH_2Cl_2) ν_{max} 3408, 1659, 1611, 1464, 1265, 738, 706 cm^{-1}; ^1H and ^{13}C NMR, see Tables 2 and 3; HRLSIMS *m/z* 297.1142 ([M + H]$^+$ calcd for $C_{18}H_{17}O_4$, 297.1127).

Preparation of (*R*)- and (*S*)-MTPA Esters of 1. In a screw-top pressure tube, a solution of **1** (8 mg, 0.027 mmol), dry CH_2Cl_2 (5 mL), (*R*)-(−)-MTPA chloride (5.5 μL, 0.029 mmol), and a few crystals of DMAP were combined, and the solution was heated in an oil bath (110 °C) for 24 h. After this time, the solution was cooled to room temperature and concentrated. The resulting residue was subjected to preparative TLC (70:30, hexanes−EtOAc) affording the (*S*)-MTPA ester (3.8 mg, 47% yield). The corresponding ^1H NMR data are listed in Table 1.

The preparation of the (*R*)-MTPA ester of **1** followed the same procedure as described above. Starting from 12 mg of **1** and 8.3 μg of (*S*)-(+)-MTPACl, 6.2 mg of the (*R*)-MTPA ester of **1** was obtained in 52% yield (NMR data in Table 1).

Caledonixanthone B (2): pink prisms (pentane−EtOAc); mp 162 °C; R_f 0.54 (cyclohexanes−EtOAc, 7:3); UV (MeOH) λ_{max} (log ϵ) 360 (3.62), 321 (4.13), 268 (4.31), 241 (4.38) nm; IR (CH_2Cl_2) ν_{max} 1724, 1651, 1489, 1446, 1329, 1269, 1122, 738 cm^{-1}; ^1H and ^{13}C NMR, see Tables 2 and 3; HRLSIMS *m/z* 279.1028 ([M + H]$^+$ calcd for $C_{18}H_{15}O_3$, 279.1021).

Caledonixanthone C (3): pale yellow amorphous solid; R_f 0.16 (cyclohexanes−EtOAc, 7:3); $[\alpha]^{25}_D$ 0° (*c* 0.02, MeOH); UV (MeOH) λ_{max} (log ϵ) 347 (3.19), 300 (3.41), 253 (4.07), 237 (3.97) nm; CD (*c* 0.1, MeOH) λ_{max} 250 nm ($\Delta\epsilon = -3.8 \times 10^{-3}$); IR ($CH_2Cl_2$) ν_{max} 3567, 1726, 1661, 1487, 1456, 1289, 1123, 744 cm^{-1}; ^1H and ^{13}C NMR, see Tables 2 and 3; HREIMS *m/z* 296.1052 ([M]$^+$ calcd for $C_{18}H_{16}O_4$, 296.1048).

Caledonixanthone D (4): pale yellow amorphous solid; R_f 0.34 (cyclohexanes−EtOAc, 7:3); UV see Table 4; IR (CH_2Cl_2) ν_{max} 3567, 1725, 1611, 1653, 1456, 1291, 1125, 739 cm^{-1}; ^1H and ^{13}C NMR, see Tables 2 and 3; HREIMS *m/z* 342.1091 ([M]$^+$ calcd for $C_{19}H_{18}O_6$, 342.1103).

7-Hydroxy-8-methoxyxanthone (5): ^{13}C NMR ($CDCl_3$, 67.5 MHz) δ_C 62.6 (OMe), 114.2 (C-5), 115.9 (C-8a), 117.6 (C-4), 121.9 (C-9a), 122.3 (C-6), 123.7 (C-2), 126.5 (C-1), 134.6 (C-3), 144.3 (C-8), 145.2 (C-7), 150.9 (C-10a), 155.4 (C-4a), 176.3 (C-9).

7,8-Dimethoxyxanthone (6): ^{13}C NMR ($CDCl_3$, 67.5 MHz) δ_C 57.1 (OMe-7), 61.7 (OMe-8), 113.1 (C-5), 117.1 (C-8a), 117.3 (C-4), 120.2 (C-6), 122.1 (C-9a), 123.6 (C-2), 126.7 (C-1), 134.4 (C-3), 148.8 (C-8), 149.1 (C-7), 151.2 (C-10a), 155.3 (C-4a), 176.6 (C-9).

6-Hydroxy-5-methoxyxanthone (7): ^{13}C NMR ($CDCl_3$, 67.5 MHz) δ_C 61.9 (OMe), 112.4 (C-7), 117.1 (C-8a), 117.7 (C-4), 121.6 (C-9a), 122.8 (C-8), 124.2 (C-2), 126.8 (C-1), 133.7 (C-5), 134.5 (C-3), 149.8 (C-10a), 154.2 (C-6), 155.7 (C-4a), 176.3 (C-9).

7-Hydroxy-5,6-dimethoxyxanthone (8): ^{13}C NMR ($CDCl_3$, 67.5 MHz) δ_C 61.7 (OMe-6), 61.9 (OMe-5), 99.0 (C-8), 111.0 (C-8a), 117.2 (C-4), 122.2 (C-9a), 123.7 (C-2), 126.5 (C-1), 134.0 (C-3), 137.2 (C-6), 152.3 (C-5), 154.5 (C-7), 154.8 (C-10a), 155.2 (C-4a), 175.5 (C-9).

Dehydrocycloguanandin (9): ^{13}C NMR ($CDCl_3$, 67.5 MHz) δ_C 27.9 (C-14 and C-15), 77.5 (C-11), 107.4 (C-4), 108.0 (C-9a), 110.3 (C-2), 116.8 (C-8), 121.0 (C-8a), 121.5 (C-7), 121.9 (C-13), 126.7 (C-6), 134.0 (C-12), 136.5 (C-3), 141.0 (C-5), 145.5 (C-10a), 156.5 (C-4a), 161.8 (C-1), 182.1 (C-9).

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