Antioxidant *C*-Glucosylxanthones from the Leaves of *Arrabidaea patellifera*

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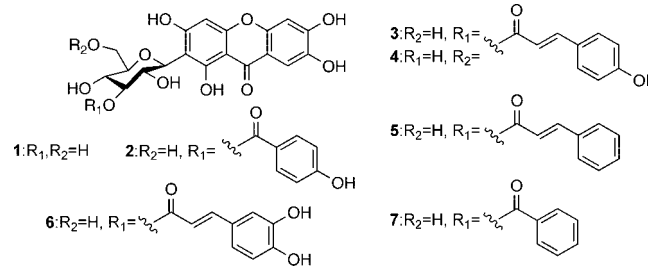
Chemical investigation of the methanol extract from the leaves of *Arrabidaea patellifera*, a Bignoniaceae from Panama, afforded mangiferin, isomangiferin, and six new derivatives (3′-*O*-*p*-hydroxybenzoylmangiferin, 3′-*O*-*trans*-coumaroylmangiferin, 6′-*O*-*trans*-coumaroylmangiferin, 3′-*O*-*trans*-cinnamoylmangiferin, 3′-*O*-*trans*-caffeoylmangiferin, and 3′-*O*-benzoylmangiferin). All these compounds had antioxidant and radical-scavenging activities, and four of them were relatively active *in vitro* against *Plasmodium falciparum*. The structures were determined by spectrometric and chemical methods, including 1D and 2D NMR experiments and MS analysis.

As part of our ongoing investigations on Panamanian Bignoniaceae,[1] 16 extracts (DCM and MeOH) from six Panamanian plants of the family Bignoniaceae were submitted to a rapid TLC 1,1-diphenyl-2-picrylhydrazine (DPPH) test,[2] which revealed radical-scavenging activity, and to an *in vitro* test against *Plasmodium falciparum*. The Bignoniaceae family comprises about 120 genera and 800 species, growing mainly in Africa and Central and South America. Species of the Bignoniaceae are used for many purposes, such as horticulture, timber, dyes, and medicine. The best-known medicinal use of the Bignoniaceae is the application of bark preparations of various species of *Tabebuia* as cancer cures.[3] Members of the family have not been extensively chemically investigated.[4] The genus *Arrabidaea* belongs to the tribe Bignonieae, a large and morphologically diverse clade of neotropical lianas.[5] The genus contains about 70 species, spread from Mexico to Argentina. Previous phytochemical studies indicate that this genus is a source of *C*-glucosylxanthones, phenylpropanoids, flavonoids, anthocyanidins, allantoins, and triterpenes.[6−9] *Arrabidaea patellifera* (Schltdl.) Sandwith is a liana with a distribution from Mexico to Brazil in tropical dry forest and less frequently in moist or wet forest. This species seems to be botanically close to *A. samydoides* (Cham.) Sandwith.[10] The MeOH extract from the leaves of *A. patellifera* was selected due to its good activities and moreover was not investigated before. This paper describes the isolation and characterization of mangiferin (**1**), isomangiferin, and six new mangiferin derivates (**2**−**7**) and their associated activities. For pure compounds, antioxidant and radical-scavenging activities were tested in solution.

Results and Discussion

An initial phytochemical analysis using UPLC/UV-HRMS-TOF was done to investigate the constituents of the MeOH extract from the leaves of *A. patellifera*. The UV spectrum (λ_{max} around 240, 260, 320, and 365 nm, see Experimental Section) suggested the presence of mangiferin derivatives. Moreover, HRMS of the constituents were close to those isolated from the EtOH extract of the stems from *A. samydoides* by Pauletti et al.[5] However, pairs of constituents with the same molecular formula were detected, thus implying the presence of different metabolites from those found in *A. samydoides*. In order to isolate some potentially new active compounds, separation, isolation, and structure elucidation were carried out.



The extract was first rapidly separated by VLC (vacuum liquid chromatography) on reversed-phase to afford four fractions. The 80% MeOH−H_2O fraction contained the major UV-active metabolites present in the MeOH extract. This fraction was then purified by MPLC to yield mangiferin (**1**). Its identity was confirmed by HRMS and comparison of the ^1H and ^{13}C NMR spectra with literature data.[11] Compounds **2**, **3**, **4**, and **5** were obtained in the same manner. Compound **6** was isolated using Lobar chromatography and compound **7** by Sephadex LH-20 gel filtration. Isomangiferin was purified by semipreparative LC and identified in the same way.[12]

Compound **2** was shown to have the molecular formula $C_{26}H_{22}O_{13}$ ([M − H]$^-$, *m*/*z* 541.0985 by HRMS). The ^1H and ^{13}C NMR spectra (Tables 1 and 2) showed proton and carbon signals equivalent to those of mangiferin: three aromatic singlets (at δ 6.31, 6.75, and 7.37) and several hydroxymethine protons, indicating the presence of a sugar moiety. The MS and MS^2 data in the APCI positive mode showed a fragment at *m*/*z* 423 corresponding to a mangiferin moiety and another fragment at *m*/*z* 405 characteristic for *C*-glucosylxanthones.[6] All these elements indicated that compound **2** was mangiferin with an additional $C_7H_4O_2$ residue. Additional aromatic proton signals could be observed in the ^1H NMR spectrum at δ 7.97 (2H, d, J = 8.9 Hz) and 6.83 (2H, d, J = 8.9 Hz) together with ^{13}C NMR signals showing the presence of an ester carbonyl carbon at δ 168.4, a phenolic carbon at δ 163.5, and two aromatic carbons at δ 116.2 and 133.2. These elements indicated that compound **2** was esterified by a *p*-hydroxybenzoyl group. A similar compound has been isolated from *Senecio*

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Table 1. ^{1}H NMR Spectroscopic Data of Compounds **1**−**7** (500 MHz, in CD_3OD)

^{1}H	mangiferin (**1**)[a]	**2**	**3**	**4**	**5**	**6**	**7**
4	6.37 s	6.31 s	6.32 s	6.32 s	6.34 s	6.35 s	6.37 s
5	6.86 s	6.75 s	6.77 s	6.76 s	6.79 s	6.77 s	6.81 s
8	7.38 s	7.37 s	7.40 s	7.40 s	7.42 s	7.42 s	7.45 s
1′	4.61 d (J = 9.9 Hz)	5.05 d (J = 10.1 Hz)	5.03 d (J = 9.8 Hz)	4.95 d (J = 10.2 Hz)	5.03 d (J = 10.2 Hz	5.02 (J = 9.8 Hz)	5.06 (J = 10.2 Hz)
2′	4.05 t (J = 9.1 Hz)	4.53 t (J = 9.6 Hz)	4.47 t (J = 9.8 Hz)	4.26 t (J = 9.3, 8.8 Hz)	4.48 t (J = 9.5 Hz)	4.46 t (J = 9.8, 8.8 Hz)	4.55 m
3′	3.20 m	5.27 t (J = 9.2 Hz)	5.17 t (J = 9.3 Hz)	3.53 m	5.18 t (J = 9.3 Hz	5.15 t (J = 9.3 Hz)	5.31 t (J = 9.3 Hz)
4′	3.14 m	3.78 m	3.72 m	3.53 m	3.73 m	3.70 m	3.79 m
5′	3.16 m	3.58 m	3.55 m	3.69 m	3.54 m	3.54 m	3.56 m
6′	3.69 d (J = 10.7 Hz)	3.93 dd (J = 12.2, 2.1 Hz)	3.92 dd (J = 12.2, 2.0 Hz)	4.55 dd (J = 12.2, 2.0 Hz)	3.91 dd (J = 12.2, 2.0 Hz)	3.90 brd (J = 12.7 Hz)	3.90 d (J = 12.0, 2.0 Hz)
	3.42 dd (J = 11.7, 5.8 Hz)	3.79 m	3.79 m	4.37 dd (J = 12.0, 5.6 Hz)	3.77 dd (J = 12.2, 5.4 Hz)	3.77 dd (J = 12.0, 5.6 Hz)	3.77 m
2″		7.97 d (J = 8.9 Hz)	7.46 d (J = 8.8 Hz)	7.42 d (J = 8.3 Hz)	7.61 m	7.06 d (J = 1.0 Hz)	8.11 d (J = 7.3 Hz)
3″		6.83 d (J = 8.9 Hz)	6.80 d (J = 8.8 Hz)	6.78 d (J = 8.3 Hz)	7.40 m		7.60 t (J = 7.3 Hz)
4″					7.40 m		7.49 t (J = 7.8 Hz)
5″		6.83 d (J = 8.9 Hz)	6.80 d (J = 8.8 Hz)	6.78 d (J = 8.3 Hz)	7.40 m	6.78 d (J = 8.3 Hz)	7.60 t (J = 7.3 Hz)
6″		7.97 d (J = 8.9 Hz)	7.46 d (J = 8.8 Hz)	7.42 d (J = 8.3 Hz)	7.61 m	6.96 dd (J = 8.3, 1.5 Hz)	8.11 d (J = 7.3 Hz)
7″			7.68 d (J = 16.0 Hz)	7.62 d (J = 15.9 Hz)	7.75 d (J = 16.1 Hz)	7.61 d (J = 15.6 Hz)	
8″			6.43 d (J = 16.0 Hz)	6.35 d (J = 15.9 Hz)	6.62 d (J = 16.1 Hz)	7.36 d (J = 15.6 Hz)	

[a] In DMSO-d_6.

Table 2. ^{13}C NMR Data of Compounds **1**−**7** (125 MHz, in CD_3OD)

^{13}C	mangiferin (**1**)[a]	**2**	**3**	**4**	**5**	6	7
1	161.6	163.5	163.5	163.5	163.6	163.4	163.7
2	107.4	107.5	107.5	107.4	107.5	107.4	107.6
3	163.7	165.3	165.3	165.3	165.3	165.3	165.5
4	93.2	94.9	94.9	95.0	94.9	94.8	94.9
4a	156.1	158.9	158.9	158.9	158.9	158.8	158.8
5	102.5	103.6	103.6	103.6	103.6	103.4	103.6
6	156.7	155.4	155.4	155.3	155.4	156.5	156.3
7	143.7	144.9	145.0	144.9	145.0	145.2	145.7
8	107.9	109.3	109.3	109.3	109.3	108.8	109.0
8a	111.5	113.9	113.9	114.0	114.0	113.3	113.7
9	178.9	181.3	181.4	181.4	181.4	181.2	181.4
9a	101.1	103.3	103.3	103.4	103.3	103.2	103.3
10a	154.1	153.1	153.2	153.2	153.2	153.4	153.1
1′	73.0	75.4	75.4	75.6	75.4	75.5	75.5
2′	70.2	70.9	70.9	72.7	70.8	70.8	70.8
3′	78.8	81.6	81.4	80.0	81.7	81.5	82.0
4′	70.5	70.4	70.4	72.0	70.3	70.3	70.3
5′	81.4	82.7	82.7	80.1	82.7	82.7	82.8
6′	61.4	62.9	62.9	65.2	62.8	62.8	62.9
1″		122.9	127.5	127.3	136.1	127.9	132.1
2″		133.2	131.2	131.3	129.3	115.1	130.9
3″		116.2	116.9	116.9	130.1	149.5	129.6
4″		163.5	161.2	161.3	131.5	146.8	134.2
5″		116.2	116.9	116.9	130.1	116.6	129.6
6″		133.2	131.2	131.3	129.3	123.0	130.9
7″		168.4	146.6	146.9	146.3	146.9	168.3
8″			115.9	115.1	119.5	115.7	
9″			169.5	169.4	168.8	169.4	

[a] In DMSO-d_6.

mikanioides,[13] where the *p*-hydroxybenzoyl group was linked to C-2′. However, in **2**, the esterification pattern seemed to be different. The 2D COSY ^{1}H−^{1}H short-range correlation spectrum permitted assignment of the hydroxymethine protons. Starting from the anomeric H-1′ at δ 5.05 (1H, d, J = 10.1 Hz), the 2D correlation spectrum showed that H-2′ had a chemical shift at δ 4.53 (1H, t, J = 9.6 Hz) and H-3′ at δ 5.27 (1H, t, J = 9.2 Hz). The long-range ^{1}H−^{13}C HMBC spectrum showed correlation between C-7″ (δ 168.4) and H-3′. These elements indicated that in **2** the *p*-hydroxybenzoyl group was linked via an ester bond at C-3′. It explained the deshielded chemical shifts corresponding to position C-3′ (δ 81.6) and H-3′ (δ 5.27) compared to those for mangiferin. Compound **2** is thus a new natural product, 3′-*O*-*p*-hydroxybenzoylmangiferin.

The molecular formula $C_{28}H_{24}O_{13}$ could be assigned by HRMS to compound **3** ([M − H]$^-$, *m*/*z* 567.1122). The ^{1}H and ^{13}C NMR spectra (Tables 1 and 2) indicated that this compound had a mangiferin skeleton with an additional $C_9H_6O_2$ residue. In contrast to **2**, deshielding of the aromatic proton signals at δ 6.80 (2H, d, J = 8.8 Hz) and 7.46 (2H, d, J = 8.8 Hz) together with the presence of two *trans* olefinic protons at δ 7.68 (1H, d, J = 16.0 Hz) and 6.43 (1H, d, J = 16.0 Hz) could be observed. In the same way, the presence of two olefinic carbons at δ 146.6 and 115.9 (C7″ and C8″) was suggested by comparison with the ^{13}C NMR spectrum of **2**. These elements indicated the presence of a *p*-coumaroyl moiety. Similarities between the chemical shifts of the sugar moieties in **2** and **3**, together with a long-range HMBC correlation observed between C-9″ and H-3′, led to the identification of **3** as 3′-*O*-*trans*-coumaroylmangiferin, a new compound.

Compound **4** had the same molecular formula ($C_{28}H_{24}O_{13}$) as **3** ([M − H]$^-$, *m*/*z* 567.1118 by HRMS). This suggested that **4** was a regioisomer of **3**. Furthermore, the ^{1}H and ^{13}C NMR spectra (Tables 1 and 2) were similar to those of **3**, especially for the xanthone and coumaroyl signals. The only noticeable differences were the downfield chemical shifts of H-6′ (1H, δ 4.37 and 4.55, dd each) and C-6′ (δ 65.2) and the upfield chemical shifts of H-3′ (1H, δ 3.53, m) and C-3′ (δ 80.0). These indicated that the coumaroyl moiety was not linked via an ester bond at C-3′, but at C-6′. This

Table 3. Activities of Pure Compounds on *P. falciparum* 3D7 (^{3}H-Hypoxanthine Assay)

compound	IC_{50} (μM)
mangiferin (**1**)	23.8
2	26.5
3	18.1
4	>38.2
chloroquine	4.70×10^{-3}

linkage was corroborated by a long-range HMBC correlation between C-9″ and H-6′. Compound **4** is thus a new natural product, 6′-*O*-*trans*-coumaroylmangiferin. It is the only compound isolated from *A. patellifera* esterified at C-6′, which may explain the sign difference in the optical rotation. It should be noted that 6′-*O*-benzoylmangiferin has already been isolated from *Senecio mikaniodes* (Asteraceae)[14] and showed the same downfield shifts for C-6′ and H-6′.

Direct comparison of ^{1}H NMR data for compounds **5** and **3** showed that the two aromatic doublets at δ 6.80 and 7.46 for the coumaroyl moiety were replaced by two multiplets at δ 7.61 and 7.40. In contrast, the two olefinic protons in the *trans* arrangement at δ 7.75 (H-7″, d, J = 16.1 Hz) and 6.62 (H-8″, d, J = 16.1 Hz) had similar chemical shifts to those observed for **3** and **4** (Tables 1 and 2), suggesting that the coumaroyl moiety in **3** and **4** was replaced in **5** by a cinnamoyl moiety. This was confirmed by HRMS data: compound **5** was assigned the molecular formula $C_{28}H_{24}O_{12}$ ([M − H]$^-$, *m*/*z* 551.1185), which differed from **3** and **4** by the lack of an oxygen atom. Because the chemical shifts in the ^{1}H NMR spectrum of the sugar moiety were close to those observed in **3**, the cinnamoyl group was linked at the C-3′ position. Thus, the new compound **5** is 3′-*O*-*trans*-cinnamoylmangiferin.

Compound **6** has a molecular formula of $C_{28}H_{24}O_{14}$ ([M − H]$^-$, *m*/*z* 583.1083), which differed from **4** by an additional oxygen atom. Furthermore, the ^{1}H and ^{13}C NMR spectra showed virtually no difference in the signals corresponding to the xanthone and sugar moieties. Even the olefinic protons and carbons in the *trans* arrangement had similar chemical shifts. The only notable difference was observed for signals assigned to the aromatic protons and carbons: in **6**, a phenolic carbon and three aromatic protons in an ABX system could be observed (1H, δ 7.06, d, J = 1.0 Hz; 1H δ 6.78, d, J = 8.3 Hz and 1H, δ 6.96, dd, J = 8.3, 1.5 Hz). These differences indicated the presence of a caffeoyl moiety, linked at C-3′ via an ester bond. Compound **6** is thus a new compound, 3′-*O*-*trans*-caffeoylmangiferin.

The molecular formula of compound **7** ($C_{26}H_{22}O_{12}$: [M − H]$^-$, *m*/*z* 525.1024) showed that **7** had an oxygen atom less than **2**. Comparing the ^{1}H and ^{13}C NMR spectra, an aromatic proton (H-4″, δ 7.49, t, J = 7.8 Hz) could be observed in the spectrum of **7**. The pattern of the aromatic protons and carbons was typical of a benzoyl instead of a *p*-hydroxybenzoyl moiety. The chemical shifts of the sugar protons and carbons were similar to those in **2**. Furthermore, the long-range HMBC correlation between C-7″ and H-3′ corroborated the substitution pattern. Compound **7** is thus 3′-*O*-benzoylmangiferin, a new natural product.

Because of the good activities observed for the crude extract of *A. patellifera* against *P. falciparum* and the DPPH radical, the isolated compounds were all evaluated for their antioxidant and antiplasmodial activities (Tables 3 and 4).

As shown in Table 3, mangiferin (**1**) and compounds **2**, **3**, and **4** were all active *in vitro* against the *P. falciparum* 3D7 clone, which is chloroquine-sensitive. Compounds **5**, **6**, and **7** were not tested, due to lack of material. However they were less active than the positive control, chloroquine. Reports of xanthones as antiplasmodial agents are numerous, and even the mode of action has been proposed.[15] However this is the first description of the antiplasmodial activity of *C*-glucosylxanthones.

Table 4. Activities of Compounds in DPPH and ALP Assays

compound	ER_{50} (DPPH)[a]	EC_{50} (ALP) (μM)[b]
mangiferin (**1**)	0.12 ± 0.06	1.26 ± 0.10
2	0.11 ± 0.05	0.98 ± 0.07
3	0.16 ± 0.01	0.83 ± 0.04
4	0.23 ± 0.01	1.48 ± 0.10
5	0.16 ± 0.01	0.98 ± 0.05
6	0.10 ± 0.01	1.18 ± 0.08
7	0.35 ± 0.06	1.87 ± 0.72
quercetin (positive control)	0.092 ± 0.01	1.00 ± 0.07

[a] ER_{50} is the ratio of antioxidant concentration to DPPH$^\bullet$ concentration producing a 50% decrease in DPPH at steady state. [b] EC_{50} is the antioxidant concentration that protects ALP to 50% from peroxyl radical-induced activity loss.

The radical-scavenging effect of compounds **1**−**6** with DPPH is shown in Table 4. All of the xanthones showed activity, with the same order of magnitude as the positive control, quercetin.[16]

The alkaline phosphatase test (ALP) is a simple fluorimetric test[17] to assess the antioxidant capacity of chemical entities to protect proteins from loss of activity caused by reactive oxygen species (ROS). All of the tested compounds show activity in this assay (Table 4). Compounds **2**, **3**, and **5** had similar activities to the positive control, quercetin.

Experimental Section

General Experimental Procedures. Optical rotations were measured on a Perkin-Elmer 241 polarimeter (MeOH, *c* in g/100 mL). UV were recorded on a Perkin-Elmer Lamdba-20 UV−vis spectrophotometer. UV spectra were recorded in MeOH. ^{1}H and ^{13}C NMR spectra were recorded on a Varian Unity Inova NMR instrument. ^{1}H and ^{13}C NMR spectra were recorded in CD_3OD or DMSO-d_6 at 500 and 125 MHz, respectively: chemical shifts are given in ppm as δ relative to TMS. HRMS spectra were obtained on a Micromass LCT Premier (Waters) using electrospray as the ion source, negative mode, capillary voltage 2.8 kV, cone voltage 40 V, MCP detector voltage 2650 V, source temperature 120 °C, desolvation temperature 250 °C, cone gas flow 10 L/h, desolvation gas flow 550 L/h. TLC was performed on silica gel 60 F_{254} Al sheets (Merck) using EtOAc−HCO_2H−HOAc−H_2O (100:11:11:26). VLC separation was carried out on RP-18 Lichroprep (40−63 μm, 120 g of phase). MPLC was performed with a Büchi 681 pump equipped with a Knauer UV detector using a RP-18 Lichroprep (40−63 μm; 460 × 50 mm i.d.; Merck). LPLC was carried out on a Lobar RP-18 column (LiChroprep 40−63 μm, 310 × 25 mm i.d.; Merck using a CFG ProMinent Duramatt pump equipped with a Bromma 2238 Uvicord SII detector). Semipreparative HPLC was performed with a LC-8 pump equipped with a SPD-10A VP (Shimadzu) detector using a X-Terra Prep-MS C18 ODB column (5 μm, 19 × 150 mm; Waters), with detection at 254 nm. HPLC-UV-DAD analysis was carried out on an HP 1100 system equipped with a photodiode array detector (Agilent Technologies) with a Nova-Pak RP-18 column (4 μm; 150 × 3.9 mm i.d.; Waters) using a CH_3CN + 0.05% TFA/H_2O + 0.05% TFA gradient (2:98−40:60) in 40 min. The detection was performed at 210, 254, 280, and 360 nm. UPLC was performed on an Acquity UPLC system (Waters) with a AcquityBEH C_{18} UPLC column (1.7 μm; 150 × 2.1 mm i.d.; Waters).

Plant Material. The leaves of *A. patellifera* were collected in April 2003 in Valle de Antón, los Llanitos, Panama, and identified by Prof. Mireya Correa, director of the Herbarium of the University of Panama. Vouchers are deposited at the University of Panama (FLORPAN 6659) and at the Laboratory of Phamarmacognosy and Phytochemistry, Geneva, Switzerland (No. 2005005).

Extraction and Isolation. The air-dried, powdered leaves of *A. patellifera* (500 g) were first extracted at room temperature with CH_2Cl_2, then with MeOH to afford, respectively, 22.2 and 61.5 g of extracts. The MeOH extract (30.0 g) was separated by VLC using a MeOH−H_2O step gradient. This afforded four fractions: 2.4 g from 25% MeOH, 2.8 g from 50% MeOH, 16 g from 80% MeOH, and 5 g from 100% MeOH. A portion of the 80% fraction (10.0 g) was separated by MPLC with a MeOH−H_2O step gradient (5:95 to 60:40 in 5% steps) to afford 52 fractions. This separation yielded 477 mg of mangiferin (**1**, fraction 15), 800 mg of **2** (fraction 28), 90 mg of **3** (fraction 34), 88 mg of **5** (fraction 44), and 98 mg of **4** (fraction 45).

Fraction 29 was purified by low-pressure liquid chromatography (LPLC) with a MeOH−H_2O step gradient, yielding 10 mg of **6**. Fraction 37 was purified on Sephadex LH-20 eluted with MeOH to give compound **7** (4 mg). Semipreparative LC with the eluent H_2O−MeCN 7% in the isocratic mode on fraction 13 afforded isomangiferin.

Radical-Scavenging Activity (DPPH•) TLC Assay.[10] A TLC autographic assay of radical-scavenging activity using the stable DPPH radical was applied for extract screening. After application of 100 μg of the samples on silica gel 60 F_{254} Al plates (Merck), development was with *n*-hexane−EtOAc (1:1) for the CH_2Cl_2 extracts or CH_2Cl_2−MeOH−H_2O (13:7:1) for the MeOH extracts. Plates were thoroughly dried for complete removal of solvents. A solution of 2,2-diphenyl-1-picrylhydrazyl radical (DPPH, 2 mg/mL in MeOH) was then sprayed. Inhibitors appeared as yellow spots against a purple background.

ALP and DPPH Microplate Assay. The microplate alkaline phosphatase (ALP) oxidation protection assay was used to determine the pEC_{50} of the pure compounds as described before.[16] In the same approach the determination of the ER_{50} of pure compounds for the radical-scavenging activity of the stable DPPH radical was done in a microplate assay, based on the technique described by Ancerewicz et al.[17]

Antiplasmodial Assay. Antiplasmodial activity was determined using the 3D7 and K1 strains of *P. falciparum* as previously described.[18]

Mangiferin (1): yellow, amorphous solid; $[\alpha]_D^{25}$ see Ajdanga;[19] UV see Shahat et al.;[20] ^{1}H and ^{13}C NMR see Tables 1 and 2; HRESIMS *m/z* 421.0747 ($C_{19}H_{17}O_{11}$: [M − H]$^-$, requires 421.0771).

3′-*O*-*p*-Hydroxybenzoylmangiferin (2): yellow, amorphous solid; $[\alpha]_D^{25}$ 65 (MeOH, *c* 1.0); UV (MeOH) λ_{max} (log ϵ) 203 (4.64), 243 (4.48), 258 (4.58), 316 (4.14), 365 (4.06) nm; ^{1}H and ^{13}C NMR see Tables 1 and 2; HRESIMS *m/z* 541.0985 ($C_{26}H_{21}O_{13}$: [M − H]$^-$, requires 541.0982).

3′-*O*-*trans*-Coumaroylmangiferin (3): yellow-orange, amorphous solid; $[\alpha]_D^{25}$ 61 (MeOH, *c* 1.0); UV (MeOH) λ_{max} (log ϵ) 203 (4.52), 231 (4.41), 258 (4.43), 237 (4.23), 316 (4.41), 361 (4.01) nm; ^{1}H and ^{13}C NMR see Tables 1 and 2; HRESIMS *m/z* 567.1122 ($C_{28}H_{23}O_{13}$: [M − H]$^-$, requires 567.1139).

6′-*O*-*trans*-Coumaroylmangiferin (4): orange, amorphous solid; $[\alpha]_D^{25}$ −12 (MeOH, *c* 1.0); UV (MeOH) λ_{max} (log ϵ) 203 (4.58), 239 (4.50), 258 (4.51), 315 (4.46), 363 (4.06) nm; ^{1}H and ^{13}C NMR see Tables 1 and 2; HRESIMS *m/z* 567.1118 ($C_{28}H_{23}O_{13}$: [M − H]$^-$, requires 567.1139).

3′-*O*-*trans*-Cinnamoylmangiferin (5): orange, amorphous solid; $[\alpha]_D^{25}$ 21 (MeOH, *c* 1.0); UV (MeOH) λ_{max} (log ϵ) 203 sh (4.56), 222 (4.39), 241 (4.38), 258 (4.46), 314 (4.18), 361 (3.97) nm; ^{1}H and ^{13}C NMR see Tables 1 and 2; HRESIMS 551.1185 *m/z* ($C_{28}H_{23}O_{12}$: [M − H]$^-$, requires 551.1190).

3′-*O*-*trans*-Caffeoylmangiferin (6): yellow, amorphous solid; $[\alpha]_D^{25}$ 20 (MeOH, *c* 1.0); UV (MeOH) λ_{max} (log ϵ) 204 sh (4.52), 219 (4.42), 241 (4.46), 258 (4.48), 316 (4.33), 363 (4.08) nm; ^{1}H and ^{13}C NMR see Tables 1 and 2; HRESIMS *m/z* 583.1083 ($C_{28}H_{23}O_{14}$: [M − H]$^-$, requires 583.1088).

3′-*O*-*p*-Benzoylmangiferin (7): yellow, amorphous solid; $[\alpha]_D^{25}$ 18 (MeOH, *c* 1.0); UV (MeOH) λ_{max} (log ϵ) 204 sh (4.48), 239 (4.37), 258 (4.37) 316 (4.10) 364 (3.99) nm; ^{1}H and ^{13}C NMR see Tables 1 and 2; HRESIMS *m/z* 525.1024 ($C_{26}H_{21}O_{12}$: [M − H]$^-$, requires 525.1033).

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