New Flavones from *Millettia erythrocalyx*

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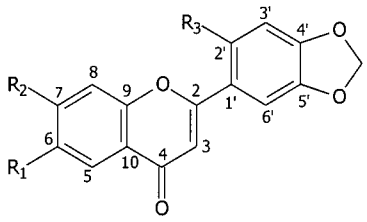
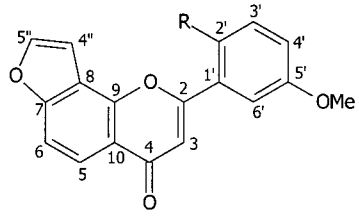
Received October 19, 2001

From the stem bark of *Millettia erythrocalyx*, three new compounds, namely, millettocalyxins A−C (**1**−**3**), and the new natural product pongol methyl ether (**4**) were isolated, along with 10 other known compounds. The structures of the new isolates were elucidated on the basis of spectroscopic data interpretation.

Plants of the genus *Millettia* (Leguminosae) are well known for elaborating prenylated flavones and isoflavones with annellated furan and pyran rings.[1] As part of our continuing studies on bioactive compounds from medicinal plants,[2] we have investigated the constituents of *M. erythrocalyx* Gagnep., a plant growing in the central part of Thailand with no previous record of chemical examination. The bark of this plant has been used by the local people for treating stomach pain. The ethyl acetate extract prepared from the powdered stem bark upon repetitive chromatography afforded three new flavones, millettocalyxins A (**1**), B (**2**), and C (**3**), and a new natural compound (**4**).[3] In addition, 10 known compounds were identified by means of spectroscopic analysis and comparison with published data: 7-γ,γ-dimethylallyloxyflavanone,[4] 2′-hydroxy-3,4-methylenedioxy-4′-γ,γ-dimethylallyloxychalcone,[5] derricidin,[6] 5-hydroxyprunetin,[7,8] pongaglabrone,[9,10] 3′,4′-methylenedioxy-7-methoxyflavone,[11] 3′,4′-methylenedioxy-6,7-dimethoxyflavone,[12] ponganone I,[13] milletenone,[11,14] and ovalifolin.[10]



	R_1	R_2	R_3
1	H	OMe	OMe
2		OMe	H



	R
3	OMe
4	H

Compound **1** was obtained as a pale yellow powder. The molecular formula was determined as $C_{18}H_{14}O_6$ by HREIMS of its [M$^+$] ion at *m*/*z* 326.08335 (calcd 326.07904). The UV absorptions at 300 and 354 nm and the ^{1}H NMR signal at δ 6.94 (1H, s, H-3) were indicative of a flavone skeleton.[11,15] The ^{13}C and ^{13}C-DEPT NMR and HMQC spectra showed 18 carbon signals, corresponding to two methoxyls, one methylene, six methines, and nine quaternary carbons. Three substituents were attached to the flavone nucleus, as indicated by signals for two methoxyls at δ 4.02 (6H, s) and for a methylenedioxy group at δ 6.15 (2H, s) in the ^{1}H NMR spectrum (Table 1). The first methoxyl could be placed on ring A, while the second methoxyl and the methylenedioxy were assigned to ring B, as supported by the fragment ions at *m*/*z* 151 and 176 due to retro-Diels−Alder cleavage of ring C in the mass spectrum.[15] For ring A, the ABM splitting system consisting of two doublets at δ 7.26 (J = 2.4 Hz, H-8) and δ 8.03 (J = 8.8 Hz, H-5) and a double doublet at δ 7.06 (J = 8.8, 2.4 Hz, H-6), together with the HMBC correlation of H-5 with C-4 (δ 177.6), suggested the location of the first methoxyl at C-7. For ring B, the appearance of two aromatic proton singlets at δ 6.95 and 7.52 indicated their *para*-correlation, placing the second methoxyl at C-2′ and the methylenedioxy moiety at C-4′ and 5′. This was confirmed by the three-bond correlation between H-6′ (δ 7.52) and C-2 (160.8) in the HMBC spectrum. A NOESY experiment revealed interactions of H-8 with MeO-7 and of H-3′ with MeO-2′. A NOESY cross-peak between H-6 and MeO-7 was also observed. Based on the above spectral evidence, compound **1** was identified as 4′,5′-methylenedioxy-7,2′-dimethoxyflavone and has been named millettocalyxin A.

Compound **2**, a pale yellow powder, exhibited a molecular ion [M$^+$] peak at *m*/*z* 380.11738 in the HREIMS, indicating a molecular formula of $C_{22}H_{20}O_6$ (calcd 380.12598). The IR band at 1632 cm^{-1} and the UV absorptions at 240 and 329 nm were characteristic of a flavone skeleton.[15,16] The ^{1}H NMR spectrum confirmed the existence of the flavone nucleus (H-3, δ 6.69 Hz) and also displayed two sharp proton singlets at δ 7.59 and δ 6.99, assignable to the two *para*-coupled aromatic protons H-5 and H-8 of ring A. The assignment of H-5 was based on its long-range (^3J) coupling to the carbonyl carbon (C-4, δ 177.6) observed in the HMBC

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10.1021/np010513z CCC: $22.00
Published on Web 03/07/2002

Table 1. ^{1}H and ^{13}C NMR Spectral Data of Compounds **1** (Acetone-d_6) and **2** ($CDCl_3$)

	^{1}H[a]		^{13}C	
position	**1**	**2**	**1**	**2**
2			160.8 (s)	162.4 (s)
3	6.94 (s)	6.69 (s)	111.7 (d)	106.1 (d)
4			177.6 (s)	177.6 (s)
5	8.03 (d, 8.8)	7.59 (s)	127.1 (d)	105.6 (d)
6	7.06 (dd, 8.8, 2.4)		114.9 (d)	146.9 (s)
7			165.0 (s)	154.8 (s)
8	7.26 (d, 2.4)	6.99 (s)	101.4 (d)	99.7 (d)
9			158.9 (s)	152.1 (s)
10			118.4 (s)	117.1 (s)
1′			113.5 (s)	126.0 (s)
2′		7.49 (br d, 8.4)	156.1 (s)	121.1 (d)
3′	6.95 (s)	6.95 (d, 8.4)	96.1 (d)	108.7 (d)
4′			151.9 (s)	150.3 (s)
5′			142.7 (s)	148.4 (s)
6′	7.52 (s)	7.37 (br s)	108.2 (d)	106.2 (d)
1″		4.71 (d, 6.6)		66.1 (t)
2″		5.60 (t, 6.3)		119.0 (d)
3″				138.7 (s)
4″		1.84 (s)		25.9 (q)
5″		1.81 (s)		18.3 (q)
$-OCH_2O-$	6.15 (s)	6.10 (s)	103.1 (t)	101.9 (t)
MeO-7	4.02 (s)	4.03 (s)	56.4 (q)	56.4 (q)
MeO-2′	4.02 (s)		57.1 (q)	

[a] Coupling constants (J in Hz) are in parentheses.

spectrum. In the ^{1}H NMR spectrum, in addition to the signals for a γ,γ-dimethylallyloxy group [δ 1.81, 1.84 (6H, 2 × Me), 4.71 (2H, d, J = 6.6 Hz, H_2-1″), and 5.60 (1H, t, J = 6.6 Hz, H-3″)], two singlets at δ 6.10 (2H) and 4.03 (3H) were observed for a methylenedioxy and a methoxyl substituent, respectively. The methylenedioxy was placed on *m*- and *p*-positions in relation to C-1′ of ring B, as a result of the fragment ion at *m*/*z* 146 in the EIMS and the ^{1}H NMR ABM spin system at δ 7.37 (1H, br s, H-6′), 7.49 (1H, br d, J = 8.4 Hz, H-2′), and 6.95 (1H, d, J = 8.4 Hz, H-3′). This led to the placement of the methoxyl and the γ,γ-dimethylallyloxy units on ring A. In the EIMS, the [M^+] through the loss of the prenyl group with H transfer gave a fragment ion at *m*/*z* 312, and this ion subsequently underwent retro-Diels−Alder cleavage of ring C to yield an ion at *m*/*z* 166, thereby confirming the presence of the prenoxyl unit on ring A. The methoxyl was placed at C-7 according to its NOESY correlation peak with H-8, leaving the γ,γ-dimethylallyloxy unit to be located at C-6. This was substantiated by the NOESY interaction of H_2-1″ with H-5. The HMBC spectrum confirmed the proposed structure of **2**, demonstrating a ^3J correlation peak for each pair of these H-C atoms: H-5 and C-4; H-8 and C-6; H_2-1″ and C-6; H-2′ and C-2; H-6′ and C-2. Structure **2** was assigned as 3′,4′-methylenedioxy-6-γ,γ-dimethylallyloxy-7-methoxyflavone and has been given the trivial name millettocalyxin B.

Compound **3**, a yellow powder, showed a molecular ion [M^+] at *m*/*z* 322.08367 in the HREIMS, corrresponding to the molecular formula $C_{19}H_{14}O_5$ (calcd 322.08414). The IR band at 1637 cm^{-1} and the UV absorptions at 249 and 295 nm were indicative of a furanoflavone.[17] This was supported by the ^{1}H and ^{13}C NMR signals (Table 2) for H-3/C-3 at δ 7.23 (1H, s)/δ 113.2 and for a furan ring at δ 7.16 (1H, d, J = 2.0 Hz, H-4″)/δ 104.3 (C-4″) and δ 7.75 (1H, d, J = 2.0 Hz, H-5″)/δ 145.7 (C-5″). Furthermore, the presence of two methoxyls was revealed by the proton resonances at δ 3.91 (3H, s) and 3.95 (3H, s) and the carbon signals at δ 56.0 (q) and 56.2 (q). In the EIMS, the fragment ions at *m*/*z* 160 and 162 resulting from retro-Diels−Alder cleavage of the [M^+] suggested the placement of the furan ring on

Table 2. ^{1}H and ^{13}C NMR Spectral Data of Compounds **3** and **4** ($CDCl_3$)

	^{1}H[a]		^{13}C	
position	**3**	**4**	**3**	**4**
2			159.8 (s)	162.5 (s)
3	7.23 (s)	6.92 (s)	113.2 (d)	108.3 (d)
4			178.7 (s)	178.2 (s)
5	8.16 (d, 9.0)	8.22 d (9.0)	121.8 (d)	121.8 (d)
6	7.54 (d, 9.0)	7.61 d (9.0)	110.0 (d)	110.2 (d)
7 (2″)			158.3 (s)	158.4 (s)
8 (3″)			117.2 (s)	117.2 (s)
9			151.0 (s)	150.8 (s)
10			119.3 (s)	119.4 (s)
1′			121.4 (s)	133.2 (s)
2′		7.60 (br d, 7.8)	152.5 (s)	118.6 (d)
3′	6.99 (d, 9.0)	7.52 (dd, 7.8, 7.8)	113.2 (d)	130.2 (d)
4′	7.04 (dd, 9.0, 3.0)	7.15 (dd, 7.8, 2.1)	117.3 (d)	116.9 (d)
5′			153.6 (s)	160.1 (s)
6′	7.50 (d, 3.0)	7.53 (br d, 3.6)	114.7 (d)	111.9 (d)
4″	7.16 (d, 2.0)	7.26 (d, 2.1)	104.3 (d)	104.2 (d)
5″	7.75 (d, 2.0)	7.82 (d, 2.1)	145.7 (d)	145.8 (d)
MeO-2′	3.95 (s)		56.2 (q)	
MeO-5′	3.91 (s)	3.98 (s)	56.0 (q)	55.5 (q)

[a] Coupling constants (J in Hz) are in parentheses.

ring A and the two methoxyls on ring B. The appearance of H-5 and H-6 as doublets at δ 8.16 (d, J = 9.0 Hz) and 7.54 (J = 9.0 Hz) and the HMBC correlations of H-5 with C-4 and C-7 indicated that the furan ring should be fused in an angular position at C-7 (oxygenated) and C-8. Interactions through ^3J coupling of C-7 with H-4″ and H-5″, and of C-8 with H-5″, were also observed. To determine the locations of the two methoxyls on ring B, a NOESY experiment was carried out. The NOE interactions of the methoxyl at δ 3.95 with H-3 and with the proton at δ 6.99 (d, J = 9.0 Hz, H-3′) placed this methoxyl at C-2′. The other methoxyl at δ 3.91 could be located at C-5′ according to its NOE effects with the protons at δ 7.04 (dd, J = 9.0, 3.0 Hz, H-4′) and 7.50 (d, J = 3.0 Hz, H-6′). A three-bond correlation was also found between H-6′ and C-2 in the HMBC spectrum. On the basis of the above spectroscopic studies, compound **3** was thus identified as 2′,5′-dimethoxy-[2″,3″:7,8]-furanoflavone and has been given the trivial name millettocalyxin C.

Compound **4**, a pale yellow powder, was analyzed for $C_{18}H_{12}O_4$ from its [M^+] at *m*/*z* 292.07252 (calcd 292.07355) in the HREIMS. Its UV and IR properties were similar to those of **3**, suggesting a furanoflavone skeleton. It could be inferred from the molecular weight and the ^{1}H and ^{13}C NMR data [δ 3.98 (3H, s); δ 55.5 (q)] that **4** differed from **3** by one methoxyl group. The fragment ions at *m*/*z* 160 and 132 in the EIMS suggested that the furan ring could be located on ring A and the methoxyl group on ring B. The HMBC correlations of H-5 with C-4 and C-7 indicated the location of the furan ring on C-7 and C-8. For ring B, the methoxyl was situated at the *m*-position in relation to C-1′, as shown by its NOESY interactions with the protons at δ 7.53 (1H, br d, J = 3.6 Hz, H-2′) and 7.15 (1H, dd, J = 7.8, 2.1 Hz, H-4′). Although **4** has been obtained synthetically by methylation of pongol,[3] this is the first time that it has been found as a naturally occurring compound. Regarding the NMR properties of **4**, it should be noted that prior to this investigation only partial ^{1}H NMR data have been available,[3] and no ^{13}C NMR study has been reported.

Experimental Section

General Experimental Procedures. UV spectra were obtained on a Shimadzu UV-160 spectrophotometer, and IR spectra were recorded with a Perkin-Elmer FT-IR 1760X

spectrophotometer. ^{1}H (500 MHz) and ^{13}C (125 MHz), DEPT, HMQC, HSQC, and HMBC spectra were obtained with a Varian Inova NMR spectrometer. EIMS and HREIMS were obtained with a Finnigan MAT TSQ 700 spectrometer.

Plant Material. The stem bark of *M. erythrocalyx* Gagnep. was collected from Tayang district, Petchaburi Province, Thailand, in April 1999. Authentication was performed at the Royal Forest Department, Ministry of Agriculture and Cooperatives, and a voucher specimen (KL-032542) is on deposit at the Department of Pharmacognosy, Faculty of Pharmaceutical Sciences, Chulalongkorn University, Thailand.

Extraction and Isolation. Dried powdered stem bark (2 kg) was extracted with ethyl acetate and methanol. The ethyl acetate extract was filtered and evaporated under reduced pressure to give a viscous mass (37 g) of dried extract. This material was subjected to vacuum-liquid chromatography on silica gel (ethyl acetate−hexane gradient) to give fractions A−I. Fraction E (536 mg) was separated by column chromatography (silica gel; ethyl acetate−hexane, 3:97) and then by gel filtration (Sephadex LH-20, acetone) to give derricidin as yellow crystals (25 mg; R_f 0.40, silica gel, ethyl acetate−hexane, 1:20). Fraction F (785 mg) was separated by column chromatography (silica gel; ethyl acetate−hexane, 1:9) and then by RP-18 HPLC (Bischoff HPLC 250 × 25 mm column, LiCrospher 100 RP-18, 10 μm; acetonitrile−water, 7:3; 4 mL/min) to give 7-γ,γ-dimethylallyloxyflavanone (1.5 mg; R_f 0.13, silica, ethyl acetate−hexane, 1:9) and 2′-hydroxy-3,4-methylenedioxy-4′-γ,γ-dimethyl-allyloxychalcone (1 mg; R_f 0.14, silica gel, ethyl acetate−hexane, 1:9). Separation of fraction I (8.8 g) was performed on a polyamide column eluted with the mixture of ethanol−water (1:4) and then by medium-pressure liquid chromatography (MPLC) gel filtration (Sephadex LH-20, methanol) to give 13 fractions (I-XIII). Fraction XII (1.8 g) was purified by MPLC (silica gel; ethyl acetate−petroleum ether, 1:4) to give fractions C1−C22. Ponganone I (2 mg, R_f 0.27, silica gel, $CHCl_3$−toluene, 1:4) and 3′,4′-methylenedioxy-6,7-dimethoxyflavone (31 mg, R_f 0.22, silica gel, ethyl acetate−petroleum ether, 3:2) were obtained from fractions C1 and C17−19, respectively. Fractions C4−7 (25 mg) were combined and further subjected to repeated column chromatograhy over silica gel, eluted with ethyl acetate−petroleum ether (1:4), to afford ovalifolin (6 mg, R_f 0.46, silica gel, ethyl acetate−petroleum ether, 1:1) and **4** (6 mg, R_f 0.38, silica gel, ethyl acetate−petroleum ether, 2:3). Fraction C11 (235 mg) was separated by column chromatography (silica gel, ethyl acetate−petroleum ether, 3:7) and then further purified by repeated column chromatography (silica gel) using ethyl acetate−$CHCl_3$ (1:9) to furnish **2** (19 mg, R_f 0.43, silica gel, ethyl acetate−petroleum ether, 1:1) and **3** (34 mg, R_f 0.20, silica gel, ethyl acetate−petroleum ether, 1:1). Fraction IX (615 mg) was subjected to MPLC (silica gel, ethyl acetate−petroleum ether, 1:4) to give 13 fractions: fractions 3 and 4 gave **4** (9 mg, R_f 0.38, silica gel, ethyl acetate−petroleum ether, 2:3); fraction 9 yielded **1** (8 mg, R_f 0.25, silica gel, ethyl acetate−petroleum ether, 3:2); fraction 6 was further separated by RP-18 HPLC (Bischoff HPLC, 250 × 25 mm column, LiCrospher 100 RP-18, 10 μm; acetonitrile−water, 1:1; 4 mL/min) to give 3′,4′-methylenedioxy-7-methoxyflavone (3.8 mg, R_f 0.40, silica gel, ethyl acetate−petroleum ether, 2:3). Fraction XI (71 mg) was purified by column chromatography (silica gel, ethyl acetate−petroleum ether, 2.5:6.5) to furnish milletenone (4 mg, R_f 0.38, silica gel, ethyl acetate−petroleum ether, 2:3) and pongaglabone (9 mg, R_f 0.27, silica gel, ethyl acetate−petroleum ether, 2:3). Separation of fraction XII (41 mg) was performed by RP-18 HPLC (Bischoff HPLC, 250 × 25 mm column, LiCrospher 100 RP-18, 10 μm; acetonitrile−water, 4.5:5.5; 4 mL/min) to yield 5-hydroxyprunetin (11 mg, R_f 0.67, silica gel, ethyl acetate−petroleum ether, 3:2). Known compounds were identified by comparison of their physical properties with literature values: 7-γ,γ-dimethylallyloxyflavanone (UV and ^{1}H NMR),[4] 2′-hydroxy-3,4-methylenedioxy-4′-γ,γ-dimethylallyloxychalcone, (UV, IR, and ^{1}H NMR),[5] derricidin (UV, IR, ^{1}H NMR, and MS),[6] 5-hydroxyprunetin (UV, IR, ^{1}H NMR and MS),[7,8] pongaglabrone (UV, ^{1}H NMR, and MS),[9,10] 3′,4′-methylenedioxy-7-methoxyflavone (UV, ^{1}H NMR, and MS);[11] 3′,4′-methylenedioxy-6,7-dimethoxyflavone (UV, IR, ^{1}H NMR, and MS),[12] ponganone I (UV, ^{1}H and ^{13}C NMR, and MS),[13] milletenone (UV, IR, ^{1}H NMR, and MS),[11,14] and ovalifolin (^{1}H NMR and MS).[10]

Millettocalyxin A (1): yellow powder; UV (MeOH) λ_{max} (log ϵ) 300 (2.97), 354 (2.98) nm; IR (KBr) ν_{max} 1616, 1382, 1259 cm^{-1}; ^{1}H NMR (300 MHz, acetone-d_6) and ^{13}C NMR (75 MHz, acetone-d_6), see Table 1; EIMS *m*/*z* 326 [M]$^+$ (100), 295 (40), 283 (26), 176 (78), 150 (30), 28 (28); HREIMS *m*/*z* 326.08335 (calcd for $C_{18}H_{14}O_6$, 326.07904).

Millettocalyxin B (2): yellow powder; UV (MeOH) λ_{max} (log ϵ) 240 (3.33), 329 (3.12) nm; IR (KBr) ν_{max} 3438, 1632, 1452, 1336, 1265 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) and ^{13}C NMR (75 MHz, $CDCl_3$), see Table 1; EIMS *m*/*z* 380 [M]$^+$ (2), 312 (100), 166 (18), 146 (16); HREIMS *m*/*z* 380.11738 (calcd for $C_{22}H_{20}O_6$, 380.12598).

Millettocalyxin C (3): yellow powder; UV (MeOH) λ_{max} (log ϵ) 249 (3.59), 295 (3.28) nm; IR (KBr) ν_{max} 3438, 1632 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) and ^{13}C NMR (75 MHz, $CDCl_3$), see Table 2; EIMS *m*/*z* 322 [M]$^+$ (84), 162 (46), 160 (18), 147 (36), 119 (12), 76 (16); HREIMS *m*/*z* 322.08367 (calcd for $C_{19}H_{14}O_5$, 322.08414).

Pongol methyl ether (4): yellow powder; UV (MeOH) λ_{max} (log ϵ) 263 (3.11), 295 (2.97) nm; IR (KBr) ν_{max} 3437, 1641 cm^{-1}; ^{1}H NMR (300 MHz, $CDCl_3$) and ^{13}C NMR (75 MHz, $CDCl_3$), see Table 2; EIMS *m*/*z* 292 [M]$^+$ (99), 264 (44), 160 (100), 132 (79), 76 (59), 28 (74); HREIMS *m*/*z* 292.07252 (calcd for $C_{18}H_{12}O_4$, 292.07355).

Acknowledgment. B.S. is grateful to the Thailand Research Fund for a 1999 Royal Golden Jubilee Scholarship and the German Academic Exchange Service (DAAD) for a research grant.

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NP010513Z