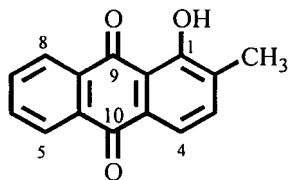


3 RESULTS AND DISCUSSION

3.1 Structural Determination

The stems of *Morida elliptica* collected from Pattani province in the southern part of Thailand, was dried, chopped and extracted with acetone and methanol, successively. The acetone extract was dissolved in hexane, methylene chloride and acetone. The methylene chloride soluble was purified by column chromatography using silica gel as the stationary phase and eluted with hexane, hexane-methylene chloride, methylene chloride and methylene chloride-methanol to give fifteen fractions. The selected fractions were further purified to afford eleven pure compounds: three new anthraquinones (**LK5**, **LK6** and **LK7**), seven previously reported anthraquinones (**LK1**, **LK3**, **LK4**, **LK8**, **LK9**, **LK10** and **LK11**) and an artifact anthraquinone (**LK2**). The acetone soluble was subjected to column chromatography on silica gel, eluted with methylene chloride and methylene chloride-methanol to give six fractions. The selected fractions were further purified by column chromatography to give three previously reported anthraquinones (**LK3**, **LK12** and **LK13**).

LK1 : 1-Hydroxy-2-methylantraquinone

LK1 is a yellow solid, m.p. 185-186 °C. The UV spectrum showed maximum absorption bands at 225, 245, 252, 280, 329 and 406 nm. The IR spectrum showed the absorption bands of O-H stretching at 3448 cm^{-1} , C=O stretching at 1672 and 1636 cm^{-1} . The ^1H NMR spectral data (Table 4) exhibited the resonances of a chelated phenolic hydroxy proton at δ 12.99 (s, 1-OH), a methyl proton at δ 2.40 (s, 2- CH_3). Six protons were detected in aromatic region. A doublet signal at δ 7.77 ($J = 8.0$ Hz) was assigned for the resonance of H-4. A quartet of doublet signal at δ 7.55 ($J = 0.5, 8.0$ Hz) was assigned for H-3. Three multiplet signals at δ 8.32, 8.30 and 7.80 with integration of 1:1:2 were assigned for H-8, H-5 and H-6, H-7, respectively. These assignments were confirmed by the ^1H - ^1H COSY experiments (Table 5). The HMBC correlation of methyl protons (2- CH_3) to C-1, C-2 and C-3 confirmed that it was connected at C-2. The ^{13}C NMR spectra showed two carbonyl carbons at δ 189.01 and 182.46 and were assigned for C-9 and C-10, respectively. Hence, **LK1** was identified to be 1-hydroxy-2-methylantraquinone (Chang and Lee, 1985).

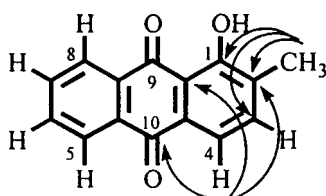
Major HMBC correlation of **LK1**

Table 4 ^{13}C , ^1H and HMBC spectral data of LK1

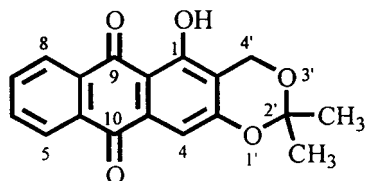
Position	δ_{C} (C-Type)	δ_{H} (mult, J_{Hz})	HMBC
1	161.09 (C)	-	-
2	135.00 (C)	-	-
3	137.27 (CH)	7.55 (1H, <i>qd</i> , 0.5, 8.0)	C-1, C-4a, 2-CH ₃
4	119.26 (CH)	7.77 (1H, <i>d</i> , 8.0)	C-2, C-9a, C-10
4a	131.34 (C)	-	-
5 ^a	127.32 (CH)	8.30 (1H, <i>m</i>)	C-7, C-8a
6 ^b	134.00 (CH)	7.80 (1H, <i>m</i>)	C-10a
7 ^b	134.56 (CH)	7.80 (1H, <i>m</i>)	C-8a
8 ^a	126.88 (CH)	8.32 (1H, <i>m</i>)	C-6, C-10a
8a	133.81 (C)	-	-
9	189.01 (C=O)	-	-
9a	115.25 (C)	-	-
10	182.46 (C=O)	-	-
10a	133.29 (C)	-	-
2-CH ₃	16.19 (CH ₃)	2.40 (3H, <i>s</i>)	C-1, C-2, C-3
1-OH	-	12.99 (1H, <i>s</i>)	C-1, C-2, C-9a

^{a, b} assignment with the same superscript may be interchanged

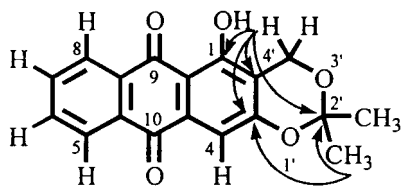
Table 5 ^1H - ^1H COSY spectral data of LK1

Proton (δ_{ppm})	Correlated proton (δ_{ppm})
H-3 (7.55)	↔ H-4 (7.77)
H-4 (7.77)	↔ H-3 (7.55)
H-5 (8.30)	↔ H-6, 7 (7.80)
H-6, 7 (7.80)	↔ H-5 (8.30), H-8 (8.32)
H-8 (8.32)	↔ H-6, H-7 (7.80)

LK2 : 1-Hydroxy-2',2'-dimethyl-1',3'-dioxane(2,3:5',6')anthraquinone



LK2 is a yellow solid, m.p. 186-187 °C. The molecular formula was determined as $C_{18}H_{14}O_5$ by HR-MS ($[M]^+310.0827$). The UV spectrum showed maximum absorption at 239, 244, 274 and 406 nm. The IR spectrum showed the stretching of O-H (3441 cm^{-1}), non-chelated C=O (1673 cm^{-1}) and a chelated C=O (1630 cm^{-1}). The ^1H NMR spectral data (Table 6) showed signals of a chelated hydroxy proton (*s*, 1-OH) at δ 13.08, gem-dimethyl protons (*s*, 2'-(CH_3)₂) at δ 1.60, a methylene protons (*s*, 4'- CH_2) at δ 4.91 and an aromatic proton (*s*, H-4) at δ 7.28. Two doublet of doublet signals at δ 8.26 and 8.28, with coupling constants of 2.0 and 6.0 Hz, were assigned for H-5 and H-8. Two doublet of triplet signals at δ 7.77 and 7.79, with coupling constants of 2.0 and 6.0 Hz, were assigned for H-6 and H-7. The assignments of aromatic protons H-5, H-6, H-7 and H-8 were confirmed by ^1H - ^1H COSY experiment (Table 7). The location of 4'-H was deduced from the correlation of 4'-H to C-1, C-2, C-3 and C-2'. In addition, 2'- CH_3 was found to have correlation to C-3 and C-2'. Consequently, the presence of 2',2'-dimethyl-1',3'-dioxane ring was suggested and was proposed to be at C-2 and C-3. The ^{13}C NMR spectrum and DEPT experiments (Table 6) indicated the presence of two carbonyl carbons (δ 181.99 and 186.90), five methine carbons (δ 109.12, 126.61, 127.30, 134.05 and 135.10), one methylene carbon (δ 57.53), two methyl carbons (δ 24.63) and eight quaternary carbons (δ 101.21, 109.56, 109.56, 113.10, 133.22, 133.35, 133.45 and 160.24). **LK2** was identified to be 1-hydroxy-2',2'-dimethyl-1',3'-dioxane(2,3:5',6')anthraquinone. This compound was assumed to be artifact from the reaction of **LK11** with acetone.

Major HMBC correlation of **LK2****Table 6** ^{13}C , ^1H and HMBC spectral data of **LK2**

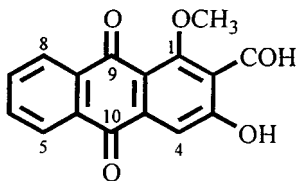
Position	δ_{C} (C-Type)	δ_{H} (mult, J_{Hz})	HMBC
1	160.24 (C)	-	-
2	109.56 (C)	-	-
3	158.21 (C)	-	-
4	109.12 (CH)	7.28 (1H, <i>s</i>)	C-2, C-2', C-9a, C-10
4a	133.22 (C)	-	-
5 ^a	127.30 (CH)	8.26 (1H, <i>dd</i> , 2.0, 6.0)	C-7, C-8a, C-10
6 ^b	134.10 (CH)	7.77 (1H, <i>dt</i> , 2.0, 6.0)	C-8, C-10a
7 ^b	134.05 (CH)	7.79 (1H, <i>dt</i> , 2.0, 6.0)	C-5, C-8a
8 ^a	126.61 (CH)	8.28 (1H, <i>dd</i> , 2.0 6.0)	C-6, C-9, C-10a
8a	133.43 (C)	-	-
9	186.90 (C=O)	-	-
9a	133.10 (C)	-	-
10	181.99 (C=O)	-	-
10a	133.35 (C)	-	-
2'	101.21 (C)	-	-
4'	57.53 (CH ₂)	4.91 (2H, <i>s</i>)	C-1, C-2, C-3, C-2'
1-OH	-	13.08 (1H, <i>s</i>)	C-1, C-2, C-9a
2'-(CH ₃) ₂	24.63 (CH ₃)	1.60 (3H, <i>s</i>)	C-3, C-2', 2'-(CH ₃) ₂

^{a, b} assignment with the same superscript may be interchanged

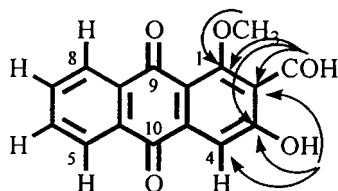
Table 7 ^1H - ^1H COSY spectral data of **LK2**

Proton (δppm)		Correlated proton (δppm)
H-5 (8.26)	\longleftrightarrow	H-6 (7.77), H-7 (7.79)
H-6 (7.77), H-7 (7.79)	\longleftrightarrow	H-5 (8.26), H-8 (8.28)
H-8 (8.28)	\longleftrightarrow	H-6 (7.77), H-7 (7.79)

LK3 : 2-Formyl-3-hydroxy-1-methoxyanthraquinone (damnacanthal)



LK3 was obtained as a yellow solid, m.p. 212-213 °C. The UV spectrum showed maximum absorption bands at 247, 278, 314 and 375 nm. The IR spectrum showed the absorption bands of a hydroxy group at 3446 cm^{-1} and carbonyl groups at 1675 and 1642 cm^{-1} . The $^1\text{H-NMR}$ spectral data (Table 8) showed signals of a hydroxy proton at δ 12.29 (*s*, 3-OH), a formyl proton at δ 10.47 (*s*, 2-COH), a methoxy proton at δ 4.13 (*s*, 1-OCH₃), an aromatic proton at δ 7.68 (*s*, H-4) and four aromatic protons at δ 8.26 (*ddd*, $J = 0.5, 1.5, 7.5$ Hz, H-5), δ 7.78, (*dt*, $J = 1.5, 7.5$ Hz, H-6), δ 7.84 (*dt*, $J = 1.5, 7.5$ Hz, H-7) and δ 8.31 (*ddd*, $J = 0.5, 1.5, 7.5$ Hz, H-8). The substituent group, 2-COH, was assigned to be at C-2 by the HMBC correlation of 2-COH to C-1, C-2 and C-3. The correlation of 3-OH to C-2, C-3 and C-4 indicated that the hydroxy group was at C-3. The correlation of 1-OCH₃ to C-1 confirmed the location of methoxy group at C-1. The presence of three carbonyl carbons (2-COH, C-9, C-10) were suggested from the ^{13}C NMR signal at δ 195.48, 180.17 and 181.92. Therefore **LK3** was identified to be 2-formyl-3-hydroxy-1-methoxyanthraquinone which was corresponded to damnacanthal (Koumaglo, *et al.*, 1992).



Major HMBC correlation of **LK3**

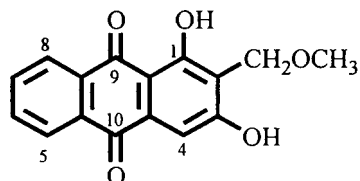
Table 8 ^{13}C , ^1H and HMBC spectral data of LK3

Position	δ_{C} (C-Type)	δ_{H} (mult, J_{Hz})	HMBC
1	166.62 (C)	-	-
2	118.05 (C)	-	-
3	166.62 (C)	-	-
4	113.11 (CH)	7.68 (1H, <i>s</i>)	C-2, C-9a, C-10
4a	141.63 (C)	-	-
5	127.11 (CH)	8.26 (1H, <i>ddd</i> , 0.5, 1.5, 7.5)	C-7, C-8a, C-10
6	133.69 (CH)	7.78 (1H, <i>dt</i> , 1.5, 7.5)	C-8, C-10a
7	134.75 (CH)	7.84 (1H, <i>dt</i> , 1.5, 7.5)	C-5, C-8a
8	127.39 (CH)	8.31 (1H, <i>ddd</i> , 0.5, 1.5, 7.5)	C-6, C-9, C-10a
8a	133.67 (C)	-	-
9	180.17 (C=O)	-	-
9a	117.66 (C)	-	-
10	181.92 (C=O)	-	-
10a	132.46 (C)	-	-
3-OH	-	12.29 (1H, <i>s</i>)	C-2, C-3, C-4
1-OCH ₃	64.74 (OCH ₃)	4.13 (3H, <i>s</i>)	C-1
2-COH	195.48 (C=O)	10.47 (1H, <i>s</i>)	C-1, C-2, C-3

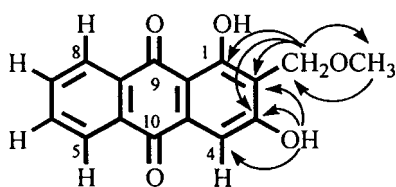
Table 9 ^1H - ^1H COSY spectral data of LK3

Proton (δ_{ppm})		Correlated proton (δ_{ppm})
H-5 (8.26)	\longleftrightarrow	H-6 (7.78), H-7 (7.84)
H-6 (7.78)	\longleftrightarrow	H-5 (8.26), H-7 (7.84), H-8 (8.31)
H-7 (7.84)	\longleftrightarrow	H-8 (8.31), H-6 (7.84), H-5 (8.26)
H-8 (8.31)	\longleftrightarrow	H-7 (7.84), H-6 (7.78)

LK4 : 1,3-Dihydroxy-2-methoxymethylanthraquinone (lucidin- ω -methyl ether)



LK4 was isolated as a yellow solid, m.p.166-168 °C. The UV spectrum showed maximum absorption bands at 217, 257, 278, 307 and 429 nm. The IR spectrum showed the stretching of O-H (3423 cm^{-1}), C=O (1618 cm^{-1}). The ^1H NMR spectral data (Table 10) showed five singlet signals of a chelated hydroxy proton (1-OH, δ 13.30), a free hydroxy proton (3-OH, δ 9.39), a methylene protons (2- CH_2OCH_3 , δ 4.94), a methoxy proton (2- CH_2OCH_3 , δ 3.57) and an aromatic proton (H-4, δ 7.35). The remaining signals at δ 8.27 (*dd*, $J = 2.0, 6.0$ Hz), δ 7.77 (*dt*, $J = 2.0, 6.0$ Hz), δ 7.79 (*dd*, $J = 2.0, 6.0$ Hz) and δ 8.29 (*dd*, $J = 2.0, 6.0$ Hz) were the signals of H-5, H-6, H-7 and H-8, respectively. The assignment of the aromatic protons was confirmed from the COSY spectrum (Table 11). The substituent group, $-\text{CH}_2\text{OCH}_3$ was assigned at C-2 by the HMBC correlation of 2- CH_2 to C-1, C-2, C-3 and 2- CH_2OCH_3 . The correlation of 3-OH to C-2, C-3 and C-4 confirmed the location of a hydroxy group at C-3. The presence of two carbonyl groups was suggested from the resonance carbon signals at δ 182.24 and 186.92. The resonances of five methine carbons, one methylene carbon, one methyl carbon and eight quaternary carbons confirmed the assignment. **LK4** was then identified to be 1,3-dihydroxy-2-methoxymethylanthraquinone which was corresponded to lucidin- ω -methyl ether (Chang and Lee, 1984).



Major HMBC correlation of **LK4**

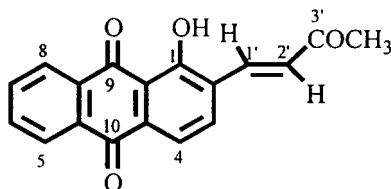
Table 10 ^{13}C , ^1H and HMBC spectral data of LK4

Position	δ_{C} (C-Type)	δ_{H} (<i>mult</i> , J_{Hz})	HMBC
1	161.86 (C)	-	-
2	114.33 (C)	-	-
3	164.07 (C)	-	-
4	109.74 (CH)	7.35 (1H, <i>s</i>)	C-2, C-9a, C-10
4a	114.33 (C)	-	-
5 ^a	127.34 (CH)	8.27 (1H, <i>dd</i> , 2.0, 6.0)	C-7, C-8a
6 ^b	134.13 (CH)	7.77 (1H, <i>dt</i> , 2.0, 6.0)	C-8, C-10a
7 ^b	134.11 (CH)	7.79 (1H, <i>dt</i> , 2.0, 6.0)	C-5, C-8a
8 ^a	126.71 (CH)	8.29 (1H, <i>dd</i> , 2.0, 6.0)	C-6, C-10a
8a	133.54 (C)	-	-
9	186.92 (C=O)	-	-
9a	109.63 (C)	-	-
10	182.24 (C=O)	-	-
10a	133.49 (C)	-	-
2- CH_2OCH_3	68.98 (CH_2)	4.94 (2H, <i>s</i>)	C-1, C-2, C-3, 2- CH_2OCH_3
2- CH_2OCH_3	59.35 (OCH_3)	3.57 (3H, <i>s</i>)	2- CH_2OCH_3
1-OH	-	13.30 (1H, <i>s</i>)	C-1, C-2, C-9a
3-OH	-	9.39 (1H, <i>s</i>)	C-2, C-3, C-4

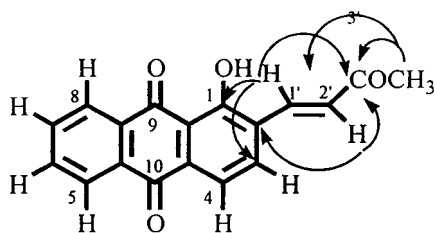
^{a, b} assignment with the same superscript may be interchanged

Table 11 ^1H - ^1H COSY spectral data of LK4

Proton (δ_{ppm})	Correlated proton (δ_{ppm})
H-5 (8.27), H-8 (8.29)	\longleftrightarrow H-6 (7.77), H-7 (7.79)
H-6 (7.77), H-7 (7.79)	\longleftrightarrow H-5 (8.27), H-8 (8.29)

LK5 : 1-Hydroxy-2-[(E)-1'-buten-3'-one]anthraquinone


LK5 was obtained as a yellow solid, m.p.198-199 °C. The molecular formula was determined as $C_{18}H_{12}O_4$ by HR-MS ($[M]^+$ m/z 292.0785). The UV spectrum showed maximum absorption at 242, 278 and 407 nm. The IR spectrum showed the stretching of hydroxy group (3447 cm^{-1}) and carbonyl group ($1671, 1630\text{ cm}^{-1}$). The ^1H NMR spectral data (Table 12) exhibited the signals of a chelated phenolic hydrogen proton at δ 13.45 (*s*, 1-OH), acyl methyl protons at δ 2.45 (*s*, 3'-COCH₃) and two trans-olefinic protons at δ 7.91 (*d*, $J = 16.5$ Hz, H-1') and δ 6.97 (*d*, $J = 16.5$ Hz, H-2'). The HMBC correlation of olefinic protons H-1' and H-2' to C=O (C-3') of acyl group suggested the presence of -CH=CHCOCH₃. This group was placed at C-2 according to the HMBC correlation of H-1' to C-1, C-3 and H-2' to C-2. The remaining signals in the ^1H NMR spectrum were those signals of six aromatic protons. Two doublet signals at δ 7.94 and 7.89 with *ortho* coupling constant ($J = 8.0$ Hz) were assigned for *ortho* protons H-3 and H-4. The multiplet signals at δ 8.33, 8.36 and 7.85 with integration ratio of 1:1:2 were assigned for the signals of H-5, H-8 and H-6, H-7, respectively. ^1H - ^1H COSY correlation of H-3 to H-4, H-5 to H-6, H-7 and H-8 to H-6, H-7 confirmed the assignment of the aromatic protons. The ^{13}C NMR spectra showed three signals of three carbonyl carbons of which the signal at δ 198.83 belonged to acyl carbon and the signals at δ 181.90 and 189.03 were the signals of 9-C=O and 10-C=O, respectively. The structure of **LK5** was finally confirmed by HMBC (Table 15). **LK5** was then proposed to be 1-hydroxy-2-[(*E*)-1'-buten-3'-one]anthraquinone, a new compound.



Major HMBC correlation of LK5

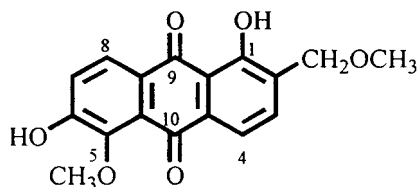
Table 12 ^{13}C , ^1H and HMBC spectral data of LK5

Position	δ_{C} (C-Type)	δ_{H} (mult, J_{Hz})	HMBC
1	161.40 (C)	-	-
2	129.66 (C)	-	-
3	134.39 (CH)	7.94 (1H, <i>d</i> , 8.0)	C-1, C-1', C-4a
4	119.17 (CH)	7.86 (1H, <i>d</i> , 8.0)	C-2, C-9a, C-10
4a	132.90 (C)	-	-
5 ^a	127.52 (CH)	8.32 (1H, <i>m</i>)	C-7, C-8a
6 ^b	135.01 (CH)	7.85 (1H, <i>m</i>)	C-10a
7 ^b	135.04 (CH)	7.85 (1H, <i>m</i>)	C-8a
8 ^a	127.09 (CH)	8.35 (1H, <i>m</i>)	C-6, C-10a
8a	133.52 (C)	-	-
9	189.03 (C=O)	-	-
9a	116.38 (C)	-	-
10	181.90 (C=O)	-	-
10a	134.02 (C)	-	-
1'	135.69 (CH)	7.91 (1H, <i>d</i> , 16.5)	C-1, C-3, C-3'
2'	130.53 (CH)	6.97 (1H, <i>d</i> , 16.5)	C-2, C-3'
3'	198.59 (C=O)	-	-
3'-CH ₃	27.58 (CH ₃)	2.45 (3H, <i>s</i>)	C-2', C-3'
1-OH	-	13.45 (1H, <i>s</i>)	C-1, C-2, C-9a

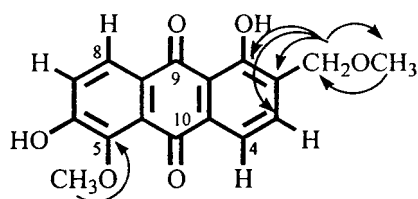
^{a, b} assignment with the same superscript may be interchanged

Table13 ^1H - ^1H COSY spectral data of **LK5**

Proton (δ ppm)		Correlated proton (δ ppm)
H-3 (7.94)	\longleftrightarrow	H-4 (7.86)
H-4 (7.86)	\longleftrightarrow	H-3 (7.94)
H-5 (8.33)	\longleftrightarrow	H-6, H-7 (7.85)
H-6, H-7 (7.85)	\longleftrightarrow	H-5, 8.36 H-8 (8.33)
H-8 (8.36)	\longleftrightarrow	H-6, H-7 (7.85)
H-1' (7.91)	\longleftrightarrow	H-2' (6.97)
H-2' (6.97)	\longleftrightarrow	H-1' (7.91)

LK6 : 1,6-Dihydroxy-5-methoxy-2-methoxymethylantraquinone

LK6 was isolated as a yellow solid, m.p. 218-219 °C. The molecular formula was determined as $C_{17}H_{14}O_6$ by HR-MS ($[M]^+$ m/z 314.0819). The UV spectrum showed maximum absorptions at 224, 250, 266, 291, 318 and 413 nm. The IR spectrum showed the stretching of a hydroxy group (3387 cm^{-1}), a chelated carbonyl group (1632 cm^{-1}) and unchelated carbonyl group (1668 cm^{-1}). The ^1H NMR spectral data of **LK6** in CDCl_3 (Table 14) showed signals of a chelated hydroxy proton at δ 13.04 (*s*, 1-OH), a free hydroxy proton at δ 6.78 (*s*, 6-OH), a methylene proton at δ 4.64 (*s*, 2- CH_2OCH_3) and two methoxy protons at δ 4.03 (*s*, 5- OCH_3) and 3.51 (*s*, 2- CH_2OCH_3). Two sets of resonances characteristic of *ortho* protons were shown as two doublets at δ 7.37 and 8.15 (H-7, H-8, $J = 8.5$ Hz, each) and a singlet at 7.80 (2H, H-3, H-4). To confirm the assignment of H-3 and H-4, the spectrum of **LK6** was then recorded in $\text{CDCl}_3 + \text{C}_6\text{D}_6$. The resonances of H-3 and H-4 were shown as two doublets at δ 7.76 (H-3) and 7.78 (H-4) with an *ortho* coupling constant ($J = 8.0$ Hz). The substituent group, $-\text{CH}_2\text{OCH}_3$ was assigned to be at C-2 by the HMBC correlation of 2- CH_2OCH_3 to C-1, C-2, C-3 and 2- CH_2OCH_3 . The correlation of 5- OCH_3 to C-5 suggested a position of OCH_3 at C-5. The ^{13}C signals of four methine carbons (δ 118.98, 120.07, 125.57 and 134.44), one methylene carbon (δ 68.57), two methyl carbons (δ 58.90 and 62.36), eight quaternary carbons (δ 114.87, 125.95, 126.95, 133.24, 133.94, 146.86, 156.04 and 159.46) and two carbonyl carbons (δ 181.91 and 187.78) confirmed the assignment of **LK6**. Therefore **LK6** was assigned to be 1,6-dihydroxy-5-methoxy-2-methoxymethylantraquinone, a new naturally occurring compound.



Major HMBC correlation of LK6

Table 14 ^{13}C , ^1H and HMBC spectral data of LK6

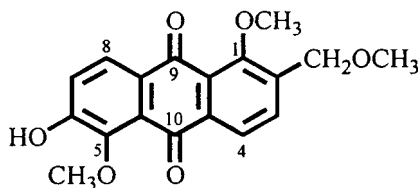
Position	δ_{C} (C-Type)	δ_{H} (mult, J_{Hz}) ^a	δ_{H} (mult, J_{Hz}) ^b	HMBC
1	159.46 (C)	-	-	-
2	133.94 (C)	-	-	-
3	134.44 (CH)	7.80 (1H, s)	7.76 (1H, d, 8.0)	C-1, 2- <u>CH</u> ₂ OCH ₃ , C-4a
4	118.98 (CH)	7.80 (1H, s)	7.78 (1H, d, 8.0)	C-2, C-9a, C-10
4a	133.24 (C)	-	-	-
5	146.86 (C)	-	-	-
6	156.40 (C)	-	-	-
7	120.07 (CH)	7.37 (1H, d, 8.5)	7.31 (1H, d, 8.5)	C-5, C-6, C-8a
8	125.57 (CH)	8.15 (1H, d, 8.5)	8.11 (1H, d, 8.5)	C-6, C-9, C-10a
8a	126.95 (C)	-	-	-
9	187.78 (C=O)	-	-	-
9a	114.87 (C)	-	-	-
10	181.81 (C=O)	-	-	-
10a	125.95 (C)	-	-	-
2- <u>CH</u> ₂ OCH ₃	68.57 (CH ₂)	4.64 (2H, s)	4.61 (2H, s)	C-1, C-2, 2- CH ₂ O <u>CH</u> ₃ , C-3
2-CH ₂ O <u>CH</u> ₃	58.90 (OCH ₃)	3.51 (3H, s)	3.48 (3H, s)	2- <u>CH</u> ₂ OCH ₃
5-OCH ₃	62.36 (OCH ₃)	4.03 (3H, s)	3.97 (3H, s)	C-5
1-OH	-	13.04 (1H, s)	13.03 (1H, s)	C-1, C-2, C-9a
6-OH	-	6.78 (1H, s)	6.70 (1H, s)	-

^a in CDCl₃ ^b in CDCl₃+C₆D₆

Table 15 ^1H - ^1H COSY spectral data of LK6

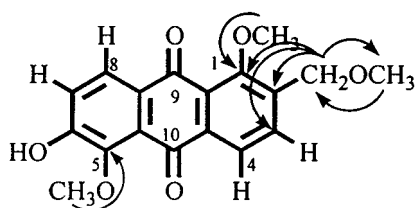
Proton δ_{H} (ppm)		Correlated proton (δ_{ppm})
H-7 (7.37)	\longleftrightarrow	H-8 (8.15)
H-8 (8.15)	\longleftrightarrow	H-7 (7.37)

LK7 : 1,5-Dimethoxy-6-hydroxy-2-methoxymethylantraquinone



LK7 was obtained as a yellow solid, m.p. 197-198 °C. Its molecular formula of C₁₈H₁₆O₆ was established on the basis of mass spectrum ([M]⁺ *m/z* 328.0948). The UV spectrum showed maximum absorptions at 248, 268 and 355 nm. The IR spectrum showed the stretching of hydroxy group (3483 cm⁻¹) and carbonyl group (1668 cm⁻¹). The ¹H NMR spectral data (Table 16) showed the resonances of four aromatic protons, a hydroxy proton, a methylene proton and three methoxy protons. Two *ortho* coupled aromatic protons resonated at δ 8.09 and 7.36 (*J* = 8.5 Hz) were assigned for H-8 and H-7. A doublet signal at δ 8.11 (*J* = 8.0 Hz) and a triplet of doublet signal at δ 7.86 (*J* = 0.5 and 8.0 Hz) were found to couple to each other, therefore they were assigned for the signals of H-4 and H-3, respectively. Proton H-3 resonated as a triplet of doublet due to long-range coupling by adjacent methylene protons 2-CH₂OCH₃. These assignments were confirmed by ¹H-¹H COSY experiments (Table 17). Correlation of methylene protons 2-CH₂OCH₃ to C-1, C-2, C-3 and 2-CH₂OCH₃ confirmed that -CH₂OCH₃ was at C-2. Two methoxy groups resonated at δ 3.94 and 4.02 were assigned according to HMBC (Table 16) to be substituent groups at C-1 and C-5 whereas the methoxy group at δ 3.50 was connected to methylene proton. A broad singlet at δ 6.66 was a resonance of hydroxy proton located at C-6. The ¹³C NMR and DEPT confirmed the numbers of four methine carbons (δ 120.40, 123.40, 125.53 and 133.53), one methylene carbon (δ 68.99), three methyl carbons (δ 58.83, 62.16 and 62.27), eight quaternary carbons (δ 124.84, 124.99, 128.73, 135.75, 140.31, 145.94, 154.83 and 157.92) and two carbonyl carbons (δ 181.51 and 182.52).

Therefore **LK7** was assigned to be 1,5-dimethoxy-6-hydroxy-2-methoxymethyl-anthraquinone. This compound is a novel one.



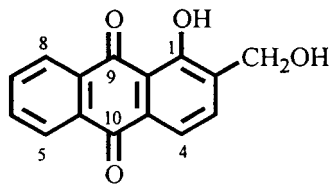
Major HMBC correlation of **LK7**

Table 16 ^{13}C , ^1H and HMBC spectral data of LK7

Position	δ_{C} (C-Type)	δ_{H} (mult, J_{Hz})	HMBC
1	157.92 (C)	-	-
2	140.31 (C)	-	-
3	133.53 (CH)	7.86 (1H, <i>td</i> , 0.5, 8.0)	C-1, C-4a, 2- <u>CH</u> ₂ OCH ₃
4	123.41 (CH)	8.11 (1H, <i>d</i> , 8.0)	C-2, C-9a, C-10
4a	135.75 (C)	-	-
5	145.94 (C)	-	-
6	154.83 (C)	-	-
7	120.40 (CH)	7.35 (1H, <i>d</i> , 8.5)	C-5, C-6, C-8a
8	125.53 (CH)	8.09 (1H, <i>d</i> , 8.5)	C-6, C-9, C-10a
8a	128.73 (C)	-	-
9	182.52 (C=O)	-	-
9a	124.84 (C)	-	-
10	181.51 (C=O)	-	-
10a	124.99 (C)	-	-
2- <u>CH</u> ₂ OCH ₃	68.99 (CH ₂)	4.65 (2H, <i>s</i>)	C-1, C-2, C-3, 2- CH ₂ <u>O</u> CH ₃
2-CH ₂ <u>O</u> CH ₃	58.83 (OCH ₃)	3.50 (3H, <i>s</i>)	2- <u>CH</u> ₂ OCH ₃
1-OCH ₃	62.15 (OCH ₃)	3.94 (3H, <i>s</i>)	C-1
5-OCH ₃	62.27 (OCH ₃)	4.02 (3H, <i>s</i>)	C-5
6-OH	-	6.66 (1H, <i>br s</i>)	-

Table 17 ^1H - ^1H COSY spectral data of **LK7**

Proton (δppm)	Correlated proton (δppm)
H-3 (7.86)	H-4 (8.11)
H-4 (8.11)	H-3 (7.86)
H-7 (7.35)	H-8 (8.09)
H-8 (8.09)	H-7 (7.35)

LK8 : 1-Hydroxy-2-hydroxymethylantraquinone (digiferruginol)


LK8 was obtained as a yellow solid, m.p. 208-210 °C. The UV spectrum showed maximum absorptions at 223, 252, 280, 326 and 406 nm. The IR spectrum showed the stretching of O-H (3446 cm^{-1}) and C=O ($1671, 1635\text{ cm}^{-1}$). The ^1H NMR spectral data of **LK8** in CDCl_3 (Table 18) showed the signals of a chelated hydroxy proton 1-OH (δ 13.06, *s*), methylene proton 2- CH_2OH (δ 4.87, *d*, $J = 4.5\text{ Hz}$) and free hydroxy proton 2- CH_2OH , (δ 2.36, *t*, $J = 4.5\text{ Hz}$). The resonances of six protons were detected in the aromatic region. A signal at δ 7.88 (*d*, $J = 8.0\text{ Hz}$) was assigned for H-4. A signal at δ 7.79 (*dd*, $J = 1.0, 8.0\text{ Hz}$) assigned for H-3, was long range coupled with methylene proton 2- CH_2OH . The signal at δ 8.33 (*dd*, $J = 1.5, 8.5\text{ Hz}$), δ 7.84 (*m*) and δ 8.34 (*dd*, $J = 1.5, 8.5\text{ Hz}$) were assigned for H-5, H-6, H-7 and H-8, respectively. These assignments were confirmed by COSY experiment (Table 19). The substituent group, $-\text{CH}_2\text{OH}$ were assigned to be at C-2 according to the correlations of 2- CH_2OH to C-1, C-2 and C-3. The ^{13}C NMR and DEPT experiment indicated the presence of two carbonyl carbons (δ 182.25 and 189.08), six methine carbons (δ 119.50, 126.94, 127.48, 134.17, 134.46 and 134.5), one methylene carbon (δ 60.86) and six quaternary carbons (δ 115.00, 132.46, 133.15, 133.72, 136.36 and 160.32). **LK8** then was identified to be 1-hydroxy-2-hydroxymethylantraquinone which was corresponded to digiferruginol (Chang and Lee, 1984).

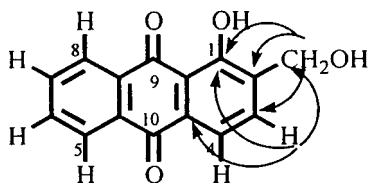

 Major HMBC correlation of **LK8**

Table 18 ^{13}C , ^1H and HMBC spectral data of LK 8

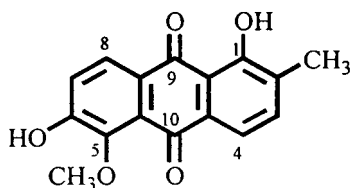
Position	δ_{C} (C-Type)	δ_{H} (mult, J_{Hz})	HMBC
1	160.22 (C)	-	-
2	136.36 (C)	-	-
3	134.17 (CH)	7.79 (1H, <i>dd</i> , 1.0, 8.0)	C-1, C-4a, 2- $\underline{\text{C}}\text{H}_2\text{OH}$
4	119.50 (CH)	7.88 (1H, <i>d</i> , 8.0)	C-2, C-9a, C-10
4a	132.46 (C)	-	-
5 ^a	127.48 (CH)	8.33 (1H, <i>dd</i> , 1.5, 8.5)	C-7, C-8a
6 ^b	134.75 (CH)	7.84 (1H, <i>m</i>)	C-10a
7 ^b	134.81 (CH)	7.84 (1H, <i>m</i>)	C-8a
8 ^a	126.94 (CH)	8.34 (1H, <i>dd</i> , 1.5, 8.5)	C-6, C-10a
8a	133.15 (C)	-	-
9	189.08 (C=O)	-	-
9a	115.00 (C)	-	-
10	182.25 (C=O)	-	-
10a	133.72 (C)	-	-
2- $\underline{\text{C}}\text{H}_2\text{OH}$	60.86 (CH ₂)	4.87 (2H, <i>d</i> , 4.5)	C-1, C-2, C-3
1-OH	-	13.06 (1H, <i>s</i>)	C-1, C-2, C-9a
2- CH_2OH	-	2.36 (1H, <i>t</i> , 4.5)	-

^{a, b} assignment with the same superscript may be interchanged

Table 19 ^1H - ^1H COSY spectral data of LK8

Proton (δ ppm)		Correlated proton (δ ppm)
2-CH ₂ O <u>H</u> (2.36)	↔	2-CH ₂ OH (4.87)
2-CH ₂ O <u>H</u> (4.87)	↔	2-CH ₂ O <u>H</u> (2.36)
H-3 (7.79)	↔	H-4 (7.88)
H-4 (7.88)	↔	H-3 (7.79)
H-5 (8.33)	↔	H-6, 7 (7.84)
H-6, 7 (7.84)	↔	H-5 (8.33), H-8 (8.34)
H-8 (8.34)	↔	H-6, 7 (7.84)

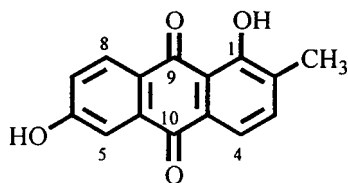
LK9 : 1,6-Dihydroxy-5-methoxy-2-methylanthraquinone (morindone-5-methyl ether)



LK9 was obtained as a yellow solid, m.p. 280-282 °C. The UV spectrum showed maximum absorptions at 223, 251, 266, 293 and 412 nm. The IR spectrum showed the stretching of a hydroxy group (3339 cm^{-1}), a non-chelated carbonyl group (1671 cm^{-1}) and a chelated carbonyl group (1631 cm^{-1}). The ^1H NMR spectral data (Table 20) showed signals of a chelated hydroxy proton at δ 13.04 (*s*, 1-OH), a free hydroxy proton at δ 6.76 (*s*, 6-OH), a methoxy proton at δ 4.03 (*s*, 5-OCH₃), and a methyl proton at δ 2.34 (*s*, 2-CH₃). The spectrum further showed the resonances of ortho protons H-7 and H-8 at δ 7.37 (*d*, $J = 8.5$ Hz), and 8.15 (*d*, $J = 8.5$ Hz). The remaining resonances were a doublet signal at δ 7.71 ($J = 8.0$ Hz.) and a triplet of doublet signal at δ 7.52 ($J = 0.5, 8.0$ Hz), which were assigned for the resonances of *ortho* H-4 and H-3, respectively. Proton H-3 resonated as a triplet of doublet as a result of long-range coupling by 2-CH₃. The aromatic protons were confirmed by ^1H - ^1H COSY spectral data (Table 21). Correlation of 5-OCH₃ to C-5 suggested the position of OCH₃ at C-5, whereas 2-CH₃ correlated to C-1, C-2 and C-3 indicated the methyl group at C-2. In addition, the correlation of 6-OH to C-6 and C-7 supported a free hydroxy group at C-6. The ^{13}C signals (Table 20) of four methine carbons, two methyl carbons, eight quaternary carbons and two carbonyl carbons corresponded to proton assignment. **LK9** then was assigned to be 1,6-dihydroxy-5-methoxy-2-methylanthraquinone which was known as morindone-5-methyl ether (Wunsma, *et al*, 1984).

Table 21 ^1H - ^1H COSY spectral data of **LK9**

Proton (δ ppm)		Correlated proton (δ ppm)
H-3 (7.52)	\longleftrightarrow	H-4 (7.71)
H-4 (7.71)	\longleftrightarrow	H-3 (7.52)
H-7 (7.36)	\longleftrightarrow	H-8 (8.15)
H-8 (8.15)	\longleftrightarrow	H-7 (7.36)

LK10 : 1,6-Dihydroxy-2-methylantraquinone (soranjidiol)

LK10 is a yellow solid, m.p. 271-273 °C. The UV spectrum showed maximum absorption at 216, 268, 293 and 411 nm. The IR spectrum showed the stretching of O-H (3405 cm^{-1}), a non-chelated C=O (1663 cm^{-1}) and a chelated C=O (1636 cm^{-1}). The ^1H NMR spectral data (Table 22) showed the signals of a chelated hydroxy proton (δ 13.20, *s*, 1-OH), a free hydroxy proton (δ 5.80, *br s*, 6-OH) and a methyl proton (δ 2.35, *s*, 2-CH₃). The spectrum further showed the *ortho* coupling of H-3 (δ 7.48, *d*, $J = 7.5\text{ Hz}$) and H-4 (δ 7.68, *d*, $J = 7.5\text{ Hz}$). The remaining resonances were shown as an ABX system which were attributable to aromatic protons H-8 (δ 8.16, *d*, $J = 8.7\text{ Hz}$), H-7 (δ 7.20, *dd*, $J = 2.4, 8.7\text{ Hz}$) and H-5 (δ 7.65, *d*, $J = 2.4\text{ Hz}$). The ^1H - ^1H COSY spectral data (Table 23) confirmed the assignment. The HMBC correlation of methyl proton (2-CH₃) to C-1, C-2 and C-3 confirmed the position of the methyl group at C-2. The ^{13}C NMR (Table 22) spectral data showed two carbonyl carbons of which the signals at δ 188.12 and 182.65 were assigned for C-9 and C-10, respectively. **LK10** then was identified to be 1,6-dihydroxy-2-methylantraquinone and was known as soranjidiol (Brisson and Brassard, 1981).

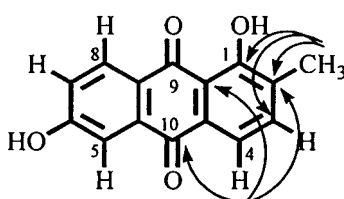
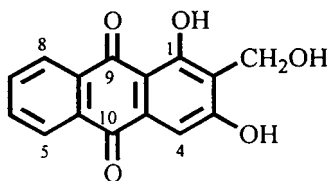
Major HMBC correlation of **LK10**

Table 22 ^{13}C , ^1H and HMBC spectral data of **LK 10**

Position	δ_{C} (C-Type)	δ_{H} (mult, J_{Hz})	HMBC
1	160.79 (C)	-	-
2	134.74 (C)	-	-
3	136.37 (CH)	7.48 (1H, <i>d</i> , 7.5)	C-1, C-4a, 2-CH ₃
4	118.79 (CH)	7.68 (1H, <i>d</i> , 7.5)	C-2, C-9, C-9a, C-10
4a	131.53	-	-
5	113.28 (CH)	7.65 (1H, <i>d</i> , 2.4)	C-6, C-7, C-8a, C-10
6	163.78 (C)	-	-
7	121.36 (CH)	7.20 (1H, <i>dd</i> , 2.4, 8.7)	C-5, C-6, C-8a
8	129.67 (CH)	8.16 (1H, <i>d</i> , 8.7)	C-6, C-9, C-10, C-10a
8a	135.94 (C)	-	-
9	188.12 (C=O)	-	-
9a	115.09	-	-
10	182.65 (C=O)	-	-
10a	135.94	-	-
2-CH ₃	16.06 (CH ₃)	2.35 (3H, <i>s</i>)	C-1, C-2, C-3
1-OH	-	13.20 (1H, <i>s</i>)	C-1, C-2, C-9a
6-OH	-	5.80 (1H, <i>br s</i>)	-

Table 23 ^1H - ^1H COSY spectral data of **LK10**

Proton (δ_{ppm})		Correlated proton (δ_{ppm})
H-3 (7.84)	\longleftrightarrow	H-4 (7.68),
H-4 (7.68)	\longleftrightarrow	H-3 (7.84)
H-5 (7.65)	\longleftrightarrow	H-7 (7.20)
H-7 (7.20)	\longleftrightarrow	7.65 (H-5), 8.16 (H-8)
H-8 (8.16)	\longleftrightarrow	H-7 (7.20)

LK11 : 1, 3-Dihydroxy-2-hydroxymethylantraquinone (lucidin)

LK11 is a yellow solid, m.p. 178-180 °C. The UV spectrum showed maximum absorption bands at 240, 244, 279 and 416 nm. The IR spectrum showed the absorption band of O-H at 3445 cm^{-1} , non-chelated C=O at 1660 cm^{-1} and chelated C=O at 1623 cm^{-1} . The $^1\text{H-NMR}$ spectral data in d_6 -DMSO (Table 24) suggested the presence of a chelated hydroxy proton 1-OH (δ 13.20, *s*), a methylene proton 2-CH₂ (δ 4.54, *s*) and an isolated aromatic proton H-4 (δ 7.25, *s*). The spectrum further showed the resonances of H-5 at δ 8.15 (*dd*, $J = 2.0, 7.5$ Hz), H-8 at δ 8.22 (*dd*, $J = 2.0, 7.5$ Hz), H-6 at δ 7.89 (*dt*, $J = 2.0, 7.5$ Hz) and H-7 at δ 7.93 (*dt*, $J = 2.0, 7.5$ Hz). The ^{13}C signals of five methine carbons (δ 108.24, 126.76, 127.14, 134.88 and 135.05), one methylene carbon (δ 51.71), six quaternary carbons (δ 109.38, 133.13, 133.32, 133.65, 163.71 and 164.06) and two carbonyl carbons (δ 182.17 and 186.49) were detected. These signals were corresponded to the assignment. In the HMBC spectrum, protons 2-CH₂ was correlated to C-1, C-2 and C-3, therefore, the position of hydroxymethyl group was located at C-2. **LK11** then was proposed to be 1,3-dihydroxy-2-hydroxymethylantraquinone which corresponded to lucidin (Inoue, *et al.*, 1981).

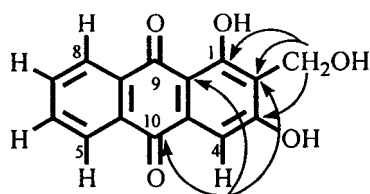
Major HMBC correlation of **LK11**

Table 24 ^{13}C , ^1H and HMBC spectral data of LK 11

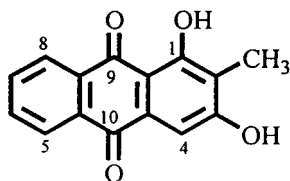
Position	δ_{C} (C-Type)	δ_{H} (mult, J_{Hz})	HMBC
1	163.51 (C)	-	-
2	120.59 (C)	-	-
3	164.05 (C)	-	-
4	108.29 (CH)	7.25 (1H, <i>s</i>)	C-2, C-9a, C-10
4a	133.13 (C)	-	-
5 ^a	127.14 (CH)	8.15 (1H, <i>dd</i> , 2.5, 7.5)	C-7, C-8a
6 ^b	134.88 (CH)	7.89 (1H, <i>dt</i> , 2.5, 7.5)	C-8
7 ^b	135.05 (CH)	7.93 (1H, <i>dt</i> , 2.5, 7.5)	C-5
8 ^a	126.76 (CH)	8.22 (1H, <i>dd</i> , 2.5, 7.5)	C-6, C-10a
8a	133.65 (C)	-	-
9	186.49 (C=O)	-	-
9a	109.38 (C)	-	-
10	182.17 (C=O)	-	-
10a	133.32 (C)	-	-
2-CH ₂ OH	51.71 (CH ₂)	4.54 (2H, <i>s</i>)	C-1, C-2, C-3
1-OH	-	13.20 (1H, <i>s</i>)	C-1, C-2, C-9a

^{a,b} assignment with the same superscript may be interchanged

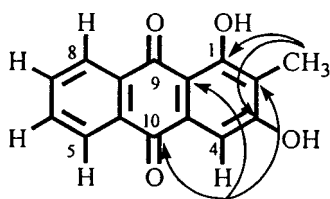
Table 25 ^1H - ^1H COSY spectral data of LK11

Proton (δ_{ppm})		Correlated proton (δ_{ppm})
H-5 (8.15)	\longleftrightarrow	H-6 (7.89), H-7 (7.93)
H-6 (7.89), H-7 (7.93)	\longleftrightarrow	H-5 (8.15)
H-8 (8.22)	\longleftrightarrow	H-6 (7.89), H-7 (7.93)
H-6 (7.89), H-7 (7.93)	\longleftrightarrow	H-8 (8.22)

LK12 : 1,3-Dihydroxy-2-methylanthraquinone (rubiadin)



LK12 is a yellow solid, m.p. 288-289 °C. The UV spectrum showed maximum absorption bands at 239, 243, 277 and 408 nm. The IR spectrum showed the absorption bands of hydroxy group at 3396 cm^{-1} , a chelated carbonyl group at 1625 cm^{-1} and a non-chelated carbonyl group at 1660 cm^{-1} . The ^1H NMR spectral data of LK12 in d_6 -DMSO (Table 26) showed signals of a chelated hydroxy proton at δ 13.10 (s, 1-OH), a methyl protons at δ 2.04 (s, 2- CH_3) and an aromatic proton at δ 7.22 (s, H-4). The resonances at δ 8.11 (dd, $J = 2.0, 7.5$ Hz), δ 8.18 (dd, $J = 2.0, 7.5$ Hz), δ 7.86 (dt, $J = 2.0, 7.5$ Hz) and δ 7.89 (dt, $J = 2.0, 7.5$ Hz) were assigned to be those of H-5, H-8, H-6 and H-7, respectively. The ^1H - ^1H COSY (Table 27) confirmed the ^1H NMR assignment. The presence of methyl protons at C-2 was assigned from the correlation between 2- CH_3 to C-1 and C-3. The structural assignment was confirmed by HMBC correlation (Table 26). The ^{13}C NMR spectrum and the DEPT experiments showed two carbonyl carbons (δ 182.28 and 186.59), seven quaternary carbons (δ 109.29, 117.81, 132.09, 133.22, 133.35, 162.81 and 163.28), five methine carbons (δ 107.76, 126.75, 127.08, 134.84 and 134.96) and one methyl carbon (δ 8.41). Therefore LK12 was assigned to be 1,3-dihydroxy-2-methylanthraquinone which was known as rubiadin (Inoue *et al.*, 1981).



Major HMBC correlation of LK12

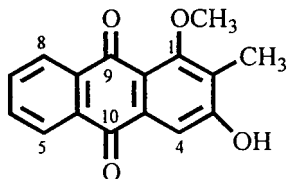
Table 26 ^{13}C , ^1H and HMBC spectral data of **LK12**

Position	δ_{C} (C-Type)	δ_{H} (<i>mult</i> , J_{Hz})	HMBC
1	162.81 (C)	-	-
2	109.29 (C)	-	-
3	163.28 (C)	-	-
4	107.76 (CH)	7.22 (1H, <i>s</i>)	C-2, C-9a, C-10
4a	132.09 (C)	-	-
5	127.08 (CH)	8.11 (1H, <i>dd</i> , 2.0, 7.5)	C-7, C-8a, C-10
6	134.84 (CH)	7.86 (1H, <i>dt</i> , 2.0, 7.5)	C-8, C-10a
7	134.96 (CH)	7.89 (1H, <i>dt</i> , 2.0, 7.5)	C-5, C-8a
8	126.75 (CH)	8.18 (1H, <i>dd</i> , 2.0, 7.5)	C-6, C-9, C-10a
8a	133.35 (C)	-	-
9	186.59 (C=O)	-	-
9a	117.81 (C)	-	-
10	182.28 (C=O)	-	-
10a	133.22 (C)	-	-
2-CH ₃	8.41 (CH ₃)	2.40 (3H, <i>s</i>)	C-1, C-3
1-OH	-	13.10 (1H, <i>s</i>)	C-1, C-2, C-9a

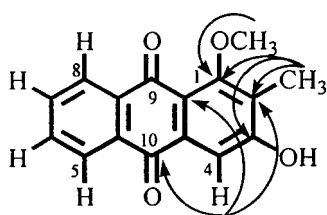
Table 27 ^1H - ^1H COSY spectral data of **LK12**

Proton (δ_{ppm})	Correlated proton (δ_{ppm})
H-5 (8.11)	\longleftrightarrow H-6 (7.86)
H-6 (7.86)	\longleftrightarrow H-5 (8.11)
H-7 (7.89)	\longleftrightarrow H-8 (8.18)
H-8 (8.18)	\longleftrightarrow H-7 (7.89)

LK 13 : 3-Hydroxy-1-methoxy-2-methylanthraquinone (rubiadin-1-methyl-ether)



LK13 was obtained as a yellow solid, m.p. 290-292 °C. The UV spectrum showed maximum absorption bands at 236, 243, 277 and 365 nm. The IR spectrum showed the absorption band of O-H stretching at 3431 cm^{-1} and C=O stretching at 1672 and 1650 cm^{-1} . The ^1H NMR spectral data of **LK13** in d_6 -DMSO (Table 24) exhibited signals of a methoxy protons at δ 3.56 (*s*, 1-OCH₃), a methyl proton at δ 2.15 (*s*, 2-CH₃) and an isolated aromatic proton at δ 7.50 (*s*, H-4). The resonances at δ 8.10 (*dd*, $J = 1.5, 7.5$ Hz), δ 8.15 (*dd*, $J = 1.5, 7.5$ Hz), δ 7.83 (*dt*, $J = 1.5, 7.5$ Hz) and δ 7.89 (*dt*, $J = 1.5, 7.5$ Hz) were the signals of H-5, H-8, H-6 and H-7, respectively. The correlation of the protons was confirmed by ^1H - ^1H COSY experiment (Table 29). The ^{13}C NMR spectrum and DEPT experiments showed the resonances of seven quaternary carbons, five methine carbons, two methyl carbons and two carbonyl carbons. Supporting information for the structure of **LK13** was provided by HMBC (Table 28). Correlation of the methyl proton (2-CH₃) to C-1, C-2 and C-3 confirmed the methyl group at C-2. The correlation of C-1 to 1-OCH₃ supported the methoxy group at C-1. **LK13** was confirmed to be 3-hydroxy-1-methoxy-2-methylanthraquinone, methyl ether derivative of **LK12**, rubiadin-1-methyl ether (Koumaglo, *et al.*, 1992).



Major HMBC correlation of **LK13**

Table 28 ^{13}C , ^1H and HMBC spectral data of LK13

Position	δ_{C} (C-Type)	δ_{H} (<i>mult</i> , J_{Hz})	HMBC
1	161.06 (C)	-	-
2	126.65 (C)	-	-
3	162.04 (C)	-	-
4	109.44 (CH)	7.50 (1H, <i>s</i>)	C-2, C-9a, C-10
4a	134.17 (C)	-	-
5	126.49 (CH)	8.10 (1H, <i>dd</i> , 1.5, 7.5)	C-7, C-8a, C-10
6	133.82 (CH)	7.83 (1H, <i>dt</i> , 1.5, 7.5)	C-8, C-10a
7	134.99 (CH)	7.89 (1H, <i>dt</i> , 1.5, 7.5)	C-5, C-8a
8	127.09 (CH)	8.15 (1H, <i>dd</i> , 1.5, 7.5)	C-6, C-9, C-10a
8a	132.49 (C)	-	-
9	180.65 (C=O)	-	-
9a	118.37 (C)	-	-
10	183.07 (C=O)	-	-
10a	134.17 (C)	-	-
2-CH ₃	9.47 (CH ₃)	2.15 (3H, <i>s</i>)	C-1, C-2, C-3
1-OCH ₃	61.05 (OCH ₃)	3.56 (1H, <i>s</i>)	C-1

Table 29 ^1H - ^1H COSY spectral data of LK13

Proton (δ_{ppm})		Correlated proton (δ_{ppm})
H-5 (8.10)	\longleftrightarrow	H-6 (7.83), H-7 (7.89)
H-6 (7.83), H-7 (7.89)	\longleftrightarrow	H-5 (8.10)
H-8 (8.15)	\longleftrightarrow	H-6 (7.83), H-7 (7.89)
H-6 (7.83), H-7 (7.89)	\longleftrightarrow	H-8 (8.15)

In conclusion, investigation of the chemical constituents from the stems of *M. elliptica* resulted in the isolation of thirteen compounds: 1-hydroxy-2-methylanthraquinone (**LK1**), 1-hydroxy-2',2'-dimethyl-1',3'-dioxane(2,3:5',6') anthraquinone (**LK2**), damnacanthal (**LK3**), lucidin- ω -methyl ether (**LK4**), 1-hydroxy-2-[(*E*)-1'-buten-3'-one]anthraquinone (**LK5**), 1,6-dihydroxy-5-methoxy-2-methoxymethylanthraquinone (**LK6**), 1,5-dimethoxy-6-hydroxy-2-methoxymethylanthraquinone (**LK7**), digiferruginol (**LK8**), morindone-5-methyl ether (**LK9**), soranjidiol (**LK10**), lucidin (**LK11**), rubiadin (**LK12**) and rubiadin-1-methyl ether (**LK13**). **LK5**, **LK6** and **LK7** are new substances. **LK2** is an artifact. Biological activities such as anti-HIV, cytotoxic and antimicrobial need to be further investigated in order to search for active compounds.