Anthraquinones and other constituents from the roots of Hemerocallis fulva L. var. sempervirona M. Hotta

Anthraquinones and other constituents from the roots of *Hemerocallis fulva* L. *var. sempervirona* M. Hotta

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Abstract

Four anthraquinone derivatives were isolated from *n*-hexane- and chloroform-soluble fractions in a methanol extract from the roots of *Hemerocallis fulva* L. *var. sempervirona* M. Hotta, in addition to aliphatic hydrocarbons, fatty acid methyl esters, and phytosterols. The anthraquinone derivatives were identified as chrysophanol (**1**), kwanzoquinone B (**2**), obtusifolin (**3**), and aloe-emodin(**4**), respectively, by spectroscopic methods. It is found that the aliphatic hydrocarbons, the fatty acid methyl esters, and the phytosterols, were mainly composed of pentacosane, methyl parmitate, and stigmasterol, respectively, on the basis of these GC/MS analyses.

Introduction

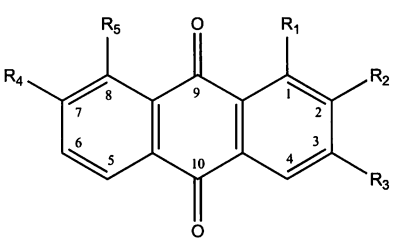
Hemerocallis fulva L. *var. sempervirona M. Hotta* (Okinawan name: Kwanso, Japanese name: Akinowasuregusa) is Okinawa childbirth Liliaceae plant and is distributed from Yakushima Island in Nansei Islands in Japan to Taiwan.[1)] In Okinawa, this plant has been introduced as the folk medicine of the insomnia cancellation.[2-3)] In connection with studies on the available constituents from Okinawan medicinal plants, we examined the constituents from the roots of *H. fulva var. sempervirona* and isolated four anthraquinone derivatives and other constituents from *n*-hexane- and chloroform- soluble fractions of the methanol extract.

Herein, We wish to describe the isolation and structural elucidation of these constituents.

Results and Discussion

Each of *n*-hexane- and chloroform ($CHCl_3$) -soluble fractions from a methanol (MeOH) extract of the roots of *H. fulva var. sempervirona* was subjected to column chromatography on silica gel to give anthraquinone derivatives **1-3**, in addition to aliphatic hydrocarbons, fatty acid methyl esters, and phytosterols from the *n*-hexane-soluble fraction and one anthraquinone derivative (**4**) from the $CHCl_3$ -soluble fraction, respectively. ^{1}H- and ^{13}C-NMR signals (Tables 1 and 2) for these anthraquinone derivatives (**1-3**) were assigned by means of those DEPT, HMQC, and HMBC spectroscopic techniques.

Structures



	R_1	R_2	R_3	R_4	R_5
1	OH	H	CH_3	H	OH
2	OH	$COCH_3$	CH_3	CH_3	H
3	OCH_3	OH	CH3	H	OH
4	OH	H	CH_2OH	H	OH

Anthraquinone **1**, brown plates, mp 197-199 °C (hexane-$CHCl_3$-EtOAc), has the molecular formula $C_{15}H_{10}O_4$ based on the observation of molecular ion peak at *m/z* 254 in its EI-MS and the observations of 10 proton signals and 15 carbon signals in its ^{1}H- and ^{13}C-NMR spectra, respectively. The IR [υ_{max} (KBr)

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cm^{-1}: 1676, 1627 (C=O)] and ^1H- and ^{13}C-NMR spectra (Tables 1 and 2) showed the characteristics of an anthraquinone derivative as follows. The ^{13}C-NMR spectrum (Table 2) revealed the presence of two carbonyl groups [δ_C 192.5 and 181.9] and twelve aromatic carbons [δ_C 162.7, 162.4, 149.3, 136.9, 133.6, 133.2, 124.5, 124.3 121.3, 119.9, 115.8, and 113.7]. The ^1H-NMR spectrum (Table 1) revealed the presence of two pairs of *ortho*-coupled protons [δ_H 7.82 (1H, *dd*, *J*=1.5 and 8.0 Hz), 7.67 (1H, *t*, *J*=8.0 Hz), and 7.28 (1H, *dd*, *J*=1.5 and 8.0 Hz)] and one pair of *meta*-coupled protons [δ_H 7.64 (1H, *d*, *J*=1.0 Hz) and 7.09 (1H, *d*, *J*=1.0 Hz)]. These spectral data suggested that **1** was an anthraquinone derivative and had 1,2,3,5-tetrasubstituted and 1,2,3-trisubstituted aromatic rings as partial structures. Moreover, the ^1H- and ^{13}C-NMR spectra (Tables 1 and 2) revealed the presence of two chelated hydroxyl groups [δ_H 12.12 (1H, *s*) and 12.03 (1H, *s*)] and one aromatic methyl group [δ_H 2.47 (3H, *s*) and δ_C 22.3].

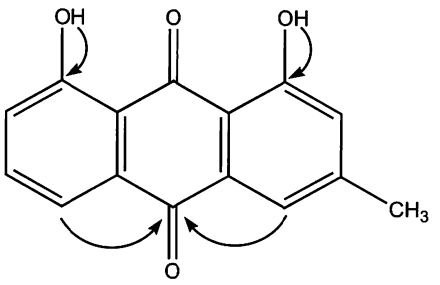

Fig. 1. Selected HMBC correrations of 1.

The heteronuclear multiple-bond connectivity (HMBC) spectrum (Fig. 1) showed long-range correlations between the doublet of doublets due to H-5 at δ_H 7.82 and the signal due to C-10 at δ_C 181.9 and between the doublet due to H-4 at δ_H 7.64 and the signal due to C-10 at δ_C 181.9. This HMBC spectrum indicated that one of the rings of the anthraquinone was mono-substituted (no substitution at C-5, 6, and 7) and another one was di-substituted (no substitution at C-2 and 4). Thus, two chelated hydroxyl groups were located at *peri*-positions (C-1 and C-8) of the carbonyl group at C-9. In the HMBC spectrum, correlation between one pair of *meta*-coupled protons (H-2 and H-4) and the methyl carbon (δ_C 22.3) suggested that the methyl group was located at C-3. Thus, **1** was identified as 1, 8-dihydroxy-3-methyl- anthraquinone (**1**, chrysophanol, chrysophanic acid). The physical and spectral data of **1** coincided with those in references.[4-6)]

Anthraquinone **2**, yellow-brown plates, mp 192-195 °C (hexane-$CHCl_3$), has the molecular formula $C_{18}H_{14}O_4$ based on the observation of molecular ion peak at *m/z* 294 in its EI-MS and the observations of 14 proton signals and 18 carbon signals in its ^1H- and ^{13}C-NMR spectra, respectively. The IR [υ_{max} (KBr) cm^{-1}: 1700, 1670, 1630, and 1595 (C=O)] and ^1H- and ^{13}C-NMR spectra (Tables 1 and 2) showed the characteristics of an anthraquinone derivative as follows. The ^{13}C-NMR spectrum (Table 2) revealed the presence of two carbonyl groups [δ_C 188.5 and 181.9] and twelve aromatic carbons [δ_C 159.5, 145.6, 144.8, 135.7, 135.6, 121.5, 133.0, 133.0, 131.2, 127.7, 127.1, and 114.4]. The ^1H-NMR spectrum (Table 1) revealed the presence of one pair of *ortho*-coupled protons [δ_H 8.17 (1H, *d*, *J*=8.0 Hz), 7.60 (1H, *dd*, *J*=1.0 and 8.0 Hz)], one pair of *meta*-coupled protons [δ_H 8.08 (1H, *d*, *J*=1.0 Hz) and 7.60 (1H, *dd*, *J*=1.0 and 8.0 Hz)], and one aromatic proton [δ_H 7.65 (1H, *s*)]. These spectral data suggested that **2** was an anthraquinone derivative and had 1,2,3,4,5-pentasubstituted and 1,3,4-trisubstituted aromatic rings as partial structures. Moreover, the ^1H- and ^{13}C-NMR spectra (Tables 1 and 2) revealed the presence of one chelated hydroxyl group [δ_H 12.94 (1H, *s*)], two aromatic methyl groups [δ_H 2.54 (3H, *s*) and 2.39 (3H, *s*) and δ_C 21.9 and 20.2], and one acetyl group [δ_H 2.62 (3H, *s*) and δ_C 203.0 and 31.8]. The chelated hydroxyl group was located at *peri*-position (C-1) of the carbonyl group of which the chemical shift was observed at the more downfield than that of another one in the ^{13}C-NMR spectrum due to the hydrogen bonding.

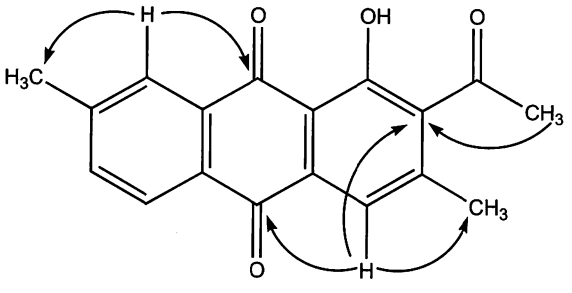

Fig. 2. Selected HMBC correlations of **2**.

The HMBC spectrum (Fig. 2) showed long-range correlations between the doublet of doublets due to the *meta*-coupled proton (H-8) at δ_H 8.08 and the signal due to C-9 at δ_C 188.5 and between the singlet due to the aromatic proton (H-4) at δ_H 7.65 and the signal due to C-10 at δ_C181.9. This HMBC spectrum indicated that one of the rings of the anthraquinone was mono-substituted (no substitution at C-5, 6 and 8) and another one was tri-substituted (no substitution at C-4). The HMBC spectrum also showed correlations between the *meta*-coupled proton (H-8) and one of the methyl carbons (δ_C 21.9) and between the aromatic proton (H-4) and another methyl carbon (δ_C 20.2). This HMBC spectrum indicated that one of the methyl group (δ_C 21.9) was located at C-7 and another one at C-3. As one of the rings of anthraquinone **2** was tri-substituted, the acetyl group was located at C-2. Thus, **2** was identified as 2-acetyl-1-hydroxy-3, 7-dimethylanthraquinone (**2**, kwanzoquinone B). The physical and spectral data of **2** coincided with those in references. [4, 7]

Anthraquinone **3**, yellow needles, mp 227-229°C (hexane-EtOAc), has the molecular formula $C_{16}H_{12}O_5$ based on the observation of molecular ion peak at *m/z* 284 in its EI-MS and the observations of 12 proton signals and 16 carbon signals in its ^{1}H and ^{13}C-NMR spectra, respectively. The IR [υ_{max} (KBr) cm^{-1}: 1635 (C=O)] and ^{1}H and ^{13}C-NMR spectra showed the characteristics of an anthraquinone derivative as follows. The ^{13}C-NMR spectrum (Table 2) revealed the presence of two carbonyl groups [δ_C 188.6 and 181.7] and twelve aromatic carbons [δ_C 162.5, 153.9, 146.2, 136.3, 133.0, 132.2, 126.9, 126.4, 124.2, 123.0, 119.0, and 116.8]. The ^{1}H-NMR spectrum (Table 1) revealed the presence of two pairs of *ortho*-coupled protons [δ_H 7.78 (1H, *dd*, *J*=1.0 and 8.0 Hz), 7.63 (1H, *t*, *J*=8.0 Hz), and 7.27 (1H, *dd*, *J*=1.0 and 8.0 Hz)] and one aromatic proton [δ_H 7.98 (1H, *d*, *J*=0.5 Hz, long-range coupling)]. These spectral data suggested that **3** was an anthraquinone derivative and had 1,2,3,4,5-tetrasubstituted and 1,2,3-trisubstituted aromatic rings as partial structures. Moreover, the ^{1}H- and ^{13}C-NMR spectra (Tables 1 and 2) revealed the presence of one chelated hydroxyl group [δ_H 12.84 (1H, *s*)], one free hydroxyl group [δ_H 6.80 (1H, *s*)], one aromatic methyl group [δ_H 2.41 (3H, *d*, *J*=0.5 Hz, long-range coupling) and δ_C 16.4], and one methoxyl group [δ_H 4.02 (3H, *s*) and δ_C 62.2].

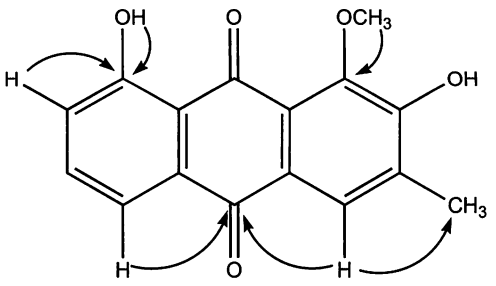

Fig. 3. Selected HMBC correlations of **3**.

The HMBC spectrum of **3** (Fig. 3) showed long-range correlations between the doublet of doublets due to the *ortho*-coupled proton (H-5) at δ_H 7.78 and the signal due to C-10 at δ_C 181.7, between the singlet due to the aromatic proton (H-4) at δ_H 7.98 and the signal due to C-10 at δ_C 181.7, between the singlet due to the chelated hydroxyl group at δ_H 12.84 and the signal due to C-8 at δ_C 162.5, and between the doublet of doublets due to the *para*-coupled proton (H-7) at δ_H 7.27 and the signal due to C-8 at δ_C 162.5. This HMBC spectrum indicated that one of the rings of the anthraquinone was mono-substituted (no substitution at C-5, 6 and 7) and another one was tri-substituted (no substitution at C-4). Thus, the chelated hydroxyl group was located at *peri*-positions (C-8) of the carbonyl group at C-9. In the HMBC spectrum, the correlations also observed between the aromatic proton (H-4) and the methyl carbon (δ_C 16.4) and between the singlet due to the methoxyl group at δ_H 4.02 and the signal due to C-1 at δ_C 146.3. These observations suggested that the methyl group was located at C-3 and the methoxyl group at C-1. As one of the rings of anthraquinone **3** was tri-substituted (no substitution at C-4), the free hydroxyl group was located at C-2. Thus, **3** was identified as 2, 8-dihydroxy-1-methoxyl-3-methylanthraquinone (**3**, obtusifolin). The physical and spectral data of **3** were coincided with those described in references.[4,8]

Anthraquinone **4**, was obtained as brown needles, mp 225-228 °C (hexane-$CHCl_3$-EtOAc). The ^{1}H-NMR spectrum (Table 1) was in agreement with that of **1**, except for the signal due to the methyl group for **1**. In the ^{1}H-NMR spectrum of **4**, the singlet due to the

methyl group at δ_H 2.50 for **1** disappeared and the doublets newly appeared at δ_H 4.84 (2H, *d*, *J*=6.0 Hz) and 1.95 (1H, *d*, *J*=6.0 Hz). This observation indicated that the methyl group for **1** was substituted to a hydroxymethyl group for **4**. Thus, **4** was identified as 1,8-dihydroxy-3-hydroxymethylanthraquinone (**4**, aloe-emodin). The physical and spectral data of **4** coincided with those in references.[4, 9)]

Table 1. ^{1}H (500 MHz) NMR spectral data for chrysophanol (**1**), kwanzoquinone (**2**), obtusifolin (**3**), and aloe-emodin (**4**)

H	1	2	3	4
2	7.09 (1H, d, 1.0)*			7.36 (1H, *d*, 1.0)
4	7.64 (1H, d, 1.0)	7.65 (1H, *s*),	7.98 (1H, *d*, 0.5)	7.81 (1H, *d*, 1.0)
5	7.82 (1H, dd, 1.5, 8.0)	8.17 (1H, *d*, 8.0)	7.78 (1H, *dd*, 1.0, 8.0)	7.85 (1H, *dd*, 1.0, 8.0
6	7.67 (1H, t, 8.0)	7.6 (1H, *dd*, 1.0, 8.0)	7.63 (1H, *t*, 8.0 Hz,)	7.69 (1H, *t*, 8.0)
7	7.28 (1H, dd, 1.5, 8.0)		7.27 (1H, *dd*, 1.0, 8.0)	7.31 (1H, *dd*, 1.0, 8.0
8		8.08 (1H, *d*, 1.0)		
3-CH_3	2.47 (3H, s)	2.39 (3H, *s*)	2.41 (3H, *d*, 0.5)	
7-CH_3		2.54 (3H, *s*)		
O=CH_3		2.62 (3H, *s*)		
1-OH	12.03 (1H, s)			12.1 (1H, *s*)
2-OH			6.8 (1H, *s*)	
8-OH	12.12 (1H, s)	12.94 (1H, *s*)	12.8 (1H, *s*)	12.1 (1H, *s*)
1-OMe			4.02 (3H, *s*)	
3-CH2OH				4.84 (2H, *d*, 6.0)
				1.95 (1H, *t*. 6.0)

* Coupling constants (J) are expressed in Hz.

Table 2. ^{13}C (125 MHz) NMR spectral data for chrysophanol (**1**), kwanzoquinone (**2**), obtusifolin (**3**), and aloe-emodin (**4**)

C	1	2	3	4
1	163	160	146	163.0
2	124	136	154	125
3	149	145	132	149
4	121	122	127	121
4a	133	133.0	123.0	133
5	120	127	119.0	121
6	137	136	136	137
7	125	146	124	125
8	162	128	163	163.0
8a	116	133.0	117	118
9	193	189	189	190
9a	114	114	126	114
10	182	182	182	181
10a	134	131	133.0	134
3-CH_3	22.3	20.2	16.4	
7-CH_3		21.9		
O=CCH_3		203.0		
		31.8		
1-OMe			62.2	
3-CH_2OH				64.1

The aliphatic hydrocarbons were composed of pentacosane (57.2%), tricosane (27.8%), heptacosane (5.4%), tetracosane (3.3%), and heneicosane (1.6%) (Table 3), the fatty acid methyl esters of methyl parmitate (40.6%), methyl linoate (26.1%), methyl stearate (7.1%), methyl oleate (5.5%), and methyl linoleate (5.4%) (Table 4), and the phytosterols of β-sitosterol (33.1%), stigmasterol (55.7%), and campesterol (11.2%) by these GC/MS analyses (Table 5).

Experimental

General Procedures. Melting points were measured on a Yanaco micro melting point apparatus MP-S3. Spectral data were obtained using the following instruments: IR on a Shimadzu FTIR-8200A; EI-MS on a Hitachi M-2500 (ion source temp.: 150 °C , ionization energy: 70 eV, direct inlet system); ^{1}H- and ^{13}C-NMR on a JEOL α 500 (^{1}H: 500 MHz, ^{13}C: 125 MHz). Chemical shifts are given on a δ (ppm) scale with tetramethylsilane (TMS) as an internal standard. The symbols *s*, *d*, *t*, *q*, and *dd* denote singlet, doublet, triplet, quartet, and doublet of doublets, respectively. Column chromatography (C.C.) and flash-column chromatography (F.C.C.) were carried out with Kieselgel 60 H (Merck). GC/MS analyses were performed with a Agilent 5975C GC/MSD instrument (column: DB-1 0.25 mm, 0.25 mm I.D × 30 m, carrier gas: He, injection temp.: 250 °C, column temp.: 50-250 °C, temp. program rate: 4 °C /min., ion source temp.: 150 °C, ionization energy: 70 eV).

Extraction and Isolation. The fresh roots (4.7

kg) of *H. fulva*. L. *var. sempervirona* M. Hotta collected at Naha, Okinawa, in April 2006, were soaked in MeOH (20 L) for 7 days. The extract was evaporated to dryness, and the residue was partitioned between *n*-hexane, $CHCl_3$, *n*-BuOH and H_2O. The *n*-hexane layer was concentrated. After 10 ml of *n*-hexane was added, the *n*-hexane soluble fraction was filtered to give a filtrate and a deposit (122 mg). After removal of the solvent, the filtrate (5.67 g) was subjected to F.C.C. on silica gel with a gradient of hexane–EtOAc to give seven fractions A-G. Fractions A was subjected to F.C.C. on silica gel with a gradient of hexane–EtOAc to give aliphatic hydrocarbons: colorless scales (acetone), mp 29-31 °C and fatty acid methyl esters: yellow oils. The compositions of the aliphatic hydrocarbons and the fatty acid methyl esters by GC/MS analyses are shown in Tables 3 and 4, respectively. Fraction C (51 mg) was subjected to F.C.C. on silica gel with a gradient of hexane–EtOAc to give chrysophanol (**1**: 13 mg) and kwanzoquinone B (**2**: 23 mg), respectively. Fraction E (12 mg) was recrystallized to yield obtusifolin (**3**: 6mg). Fraction G was subjected to C.C. on silica gel with a gradient of *n*-hexane–EtOAc to give phytosterols: white needles (*n*-hexane–EtOAc), mp 140-141 °C. The compositions of phytosterols by GC/MS analysis are shown in Table 5. The $CHCl_3$ layer was subjected to F.C.C. on silica gel with a gradient of $CHCl_3$-EtOAc to give aloe-emodin (**4**, 2 mg).

Table 3. Composition (%) of the aliphatic hydrocatbons from the hexane-soluble fraction in the extract of the roots of *Hemerocallis fulva* L. *var. sempervirona* M. Hotta by the GC/MS analysis.

Hydrocarbons	M. F.[1)]	M.W.[2)]	%
Heneicosane	$C_{21}H_{44}$	296	1.6
Docosane	$C_{22}H_{46}$	310	0.4
Tricosane	$C_{23}H_{48}$	324	27.8
Tetracosane	$C_{24}H_{50}$	338	3.3
Pentacosane	$C_{25}H_{52}$	352	57.2
Hexacosane	$C_{26}H_{54}$	366	1.9
Heptacosane	$C_{27}H_{56}$	380	5.4
Octacosane	$C_{28}H_{58}$	394	0.4
Noonocasane	$C_{29}H_{60}$	408	0.9
Triacontane	$C_{30}H_{62}$	422	0.3
Hentriacontane	$C_{31}H_{64}$	436	0.8

1) Molecular Formula.
2) Molecular Weight.

Table 4. Composition (%) of the fatty acid methyl esters from the hexane-soluble fraction in the extract of the roots of *Hemerocallis fulva* L. *var. sempervirona* M. Hotta by the GC/MS analysis

Hydrocarbons	M. F.[1)]	M.I.P.[2)]	%
Methyl tridecanoate	$C_{12}H_{25}COOMe$	228	0.7
Methyl tetradecanoate	$C_{13}H_{27}COOMe$	242	0.3
Methyl pentadecanoate	$C_{14}H_{29}COOMe$	256	0.6
Methyl (*E*)-9-hexadecenoate	$C_{15}H_{29}COOMe$	268	0.6
Methyl (*Z*)-9-hexadecenoate	$C_{15}H_{29}COOMe$	268	0.8
Methyl hexadecanoate (Methyl parmitate)	$C_{15}H_{31}COOMe$	270	40.6
Methyl heptadecanoate	$C_{16}H_{33}COOMe$	284	1.4
Methyl (Z,Z)-9,12-octadecadienoate (Methyl linoate)	$C_{17}H_{31}COOMe$	294	26.1
Methyl (Z,Z,Z)-9,12,15-octadecatrienoate (Methyl linoleate)	$C_{17}H_{29}COOMe$	292	5.4
Methyl 14-octadecenoate	$C_{17}H_{33}COOMe$	296	4.2
Methyl (Z)-9-octadecenoate (Methyl oleate)	$C_{17}H_{33}COOMe$	296	5.5
Methyl octadecanoate (Methyl stearate)	$C_{17}H_{35}COOMe$	298	7.1
Methyl nonadecanoate	$C_{18}H_{37}COOMe$	312	0.3
Methyl (*Z*)-11-eicosenoate	$C_{19}H_{37}COOMe$	324	0.3
Methyl eicosanoate	$C_{19}H_{39}COOMe$	326	1.2
Methyl (*Z*)-11-heneicosanoate	$C_{20}H_{39}COOMe$	338	0.5
Methyl heneicosanoate	$C_{20}H_{41}COOMe$	340	0.3
Methyl docosanoate	$C_{21}H_{43}COOMe$	354	2.3
Methyl tricosanoate	$C_{22}H_{45}COOMe$	368	1.0
Metyl tetracosanoate	$C_{23}H_{47}COOMe$	382	0.8

1) Molecular Formula.
2) Molecular Ion Peak.

Table 5. Composition (%) of the phytosterols from the hexane-soluble fraction in the extract of the roots of *Hemerocallis fulva* L. *var. sempervirona* M. Hotta by the GC/MS analysis

Phytosterols	M. F.[1)]	M.W.[2)]	%
Campesterol	$C_{28}H_{48}O$	400	11.2
Stigmasterol	$C_{29}H_{48}O$	412	55.7
β-sitosterol	$C_{29}H_{50}O$	414	33.1

1) Molecular Formula.
2) Molecular Weight.

***Chrysophanol* (1)**: Brown plates (hexane-$CHCl_3$-EtOAc), mp 197-199 °C. IR υ_{max} (KBr) cm^{-1}: 1676, 1627. MS *m/z* (%): 254 $[M]^+$ (100), 237(3), 226(10), 197(6), 152(5), 127(4). ^1H ($CDCl_3$, 500 MHz)- and ^{13}C-NMR ($CDCl_3$, 125 MHz): see Tables 1 and 2. The physical and spectral data were identical with those in references. [4-6)]

***Kwanzoquinone B* (2)**: Yellow brown plates (hexane-$CHCl_3$), mp 192-195 °C. IR υ_{max} (KBr) cm^{-1}: 1700, 1670, 1630, 1595. MS *m/z* (%): 294 $[M]^+$ (42), 279(100), 195(4), 165(8), 152(9). ^1H ($CDCl_3$, 500 MHz)- and ^{13}C-NMR ($CDCl_3$, 125 MHz): see Tables 1 and 2. The physical and spectral data were identical with those in reference. [4, 7)]

***Obtusifolin* (3)**: Yellow needles (hexane-EtOAc), mp 227-229 °C. IR υ_{max} (KBr) cm^{-1}: 1635. MS *m/z* (%): 284 $[M]^+$ (100), 266(80), 238(46). ^1H ($CDCl_3$, 500 MHz)- and ^{13}C-NMR ($CDCl_3$, 125 MHz): see Tables 1 and 2. The physical and spectral data were identical with those in references. [4, 8)]

***Aloe-emodin* (4)**: Brown needles (hexane-$CHCl_3$-EtOAc), mp 225-228 °C. IR υ_{max} (KBr) cm^{-1}: 3649, 1627. MS *m/z* (%): 270 $[M]^+$ (100), 241(54), 224(3). ^1H ($CDCl_3$, 500 MHz)- and ^{13}C-NMR ($CDCl_3$, 125 MHz): see Tables 1 and 2.. The physical and spectral data were identical with those in references. [4, 9)]

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