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Alkylated benzoquinone derivatives from *Maesa lanceolata*

Jaber S. Mossa[a], Ilias Muhammad[a], Ahmed F. Ramadan[a], Humayun H. Mirza[a], Farouk S. El-Feraly[a,*], Charles D. Hufford[b]

[a]*Department of Pharmacognosy and Medicinal, Aromatic and Poisonous Plants Research Center (MAPPRC), College of Pharmacy, P.O. Box 2457, King Saud University, Riyadh 11451, Saudi Arabia*

[b]*Department of Pharmacognosy and the National Center for the Development of Natural Products, Research Institute of Pharmaceutical Sciences, School of Pharmacy, University of Mississippi, University, MS 38677, USA*

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Abstract

Five new alkylated benzoquinones were isolated as methyl ether derivatives from a complex mixture containing alkylated hydroxy benzoquinones, obtained from the fruits of *Maesa lanceolata*. The structures of the benzoquinones, named, 2-acetoxy-5-methoxy-6-methyl-3-tridecyl-1, 4-benzoquinone, 2-methoxy-5-acetoxy-6-methyl-3-tridecyl-1, 4-benzoquinone, 2-acetoxy-5-methoxy-6-methyl-3-[(*z*)-10′-pentadecenyl]-1,4-benzoquinone, 2-methoxy-5-acetoxy-6-methyl-3-[(*z*)-10′-pentadecenyl-1, 4-benzoquinone and 2,5-dimethoxy-6-methyl-3-tridecyl-1,4-benzoquinone, were based on ^{1}H and ^{13}C NMR data, mainly 2D NMR experiments, including ^{1}H–^{13}C HMBC correlations, as well as chemical derivatization.

Keywords: *Maesa lanceolata*; Myrsinaceae; Benzoquinones; 2-Acetoxy-5-methoxy-6-methyl-3-tridecyl-1, 4-benzoquinone; 2-Methoxy-5-acetoxy-6-methyl-3-tridecyl-1, 4-benzoquinone; 2-Acetoxy-5-methoxy-6-methyl-3-[(*z*)-10′-pentadecenyl]-1,4-benzoquinone; 2-Methoxy-5-acetoxy-6-methyl-3-[(*z*)-10′-pentadecenyl]-1,4-benzoquinone; 2,5-Dimethoxy-6-methyl-3-tridecyl-1,4-benzoquinone; 2D NMR

1. Introduction

In our previous report (Muhammad, Mossa, & El-Feraly, 1993), we described the structures of two new alkylated benzoquinones, namely, 2-hydroxy-5-methoxy-3-pentadecyl-1, 4-benzoquinone (dihydromaesanin) and 3-[(*z*)-10′-pentadecenyl]-2,5-dihydroxy-6-methyl-1, 4-benzoquinone (maesanol), isolated from the leaves of *Maesa lanceolata* Forssk. Locally, the fresh leaves of this plant are used as a poultice for the treatment of rheumatic arthritis, while in East Africa the fruit is used as an anticholera medication (Kubo, 1981). Earlier investigations reported on the antimicrobial activity of this plant (Taniquichi, Chapya, Kubo, & Nakanishi, 1978) and the isolation of 2,5-dihydroxy alkylbenzoquinones (Midiwo, Odingo, & Arot, 1990) and maesanin (Kubo, Kim, Ganjan, Komikawa, & Yamagia, 1987) from the fruits of the East African plant. Maesanin possesses nonspecific host defense stimulatory and anti-5-lipoxygenase activities (Kubo et al., 1987; Fukuyama et al., 1993). It also inhibits the mitochondrial oxidative phosphorylation (Makawiti, Kanji, & Olowookere, 1990). However, other species of *Maesa* yielded different alkylated hydroxybenzoquinones (i.e. *M. formosana* (Chen & Koo, 1973) and *M. macrophylla* (Chandrasekhar, Prabhu, & Venkateswarlu, 1970), a dimeric phenol (i.e. *M. montana* and *M. indica* (Wall et al., 1988)), sterols and triterpenes (i.e. *M. chisia* (Ali, Giri, & Pakrashi, 1975)) and a triterpene glycosidal fraction from *M. chisia*, which possesses anti-inflamatory and tranquilosedative activities (Gomes, Sharma, & Ghatak, 1987).

In continuation of our previous investigation (Muhammad et al., 1993), we herein report on the isolation and characterization of four new alkylated benzoquiones as methyl ethers from complex mixtures containing isomeric monohydroxy alkylbenzoquinones (**1**+**2**) and (**3**+**4**), together with a new dimethyl ether derivative from a mixture of dihydroxy alkylbenzoquinones, isolated from the fruits of *M. lanceolata*. The new compounds are 2-acetoxy-5-methoxy-6-methyl-3-tridecyl-1, 4-benzoquinone (**5**), 2-methoxy-5-acetoxy-6-methyl-3-tridecyl-1, 4-benzoquinone (**6**), 2-acetoxy-5-methoxy - 6 - methyl - 3 - [(*z*) - 10′ - pentadecenyl] - 1,4 - benzoquinone (**7**), 2-methoxy-5-acetoxy-6-methyl-3-[(*z*)-10′-pentadecenyl]-1,4-benzoquinone (**8**) and 2,5-dimethoxy-6-methyl-3-tridecyl-1,4-benzoquinone (**9**).

* Corresponding author.

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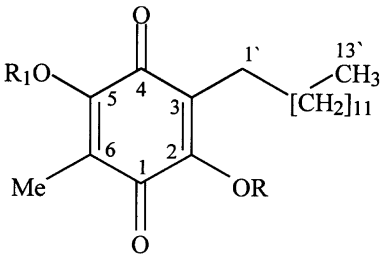
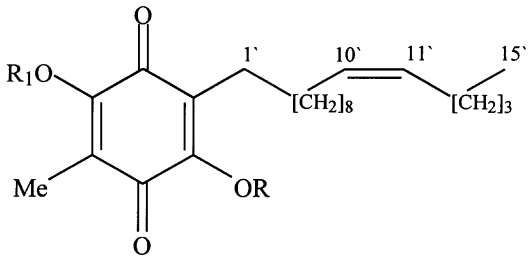


	R	R_1
1	Ac	H
2	H	Ac
5	Ac	Me
6	Me	Ac
9	Me	Me
11	Ac	Ac
14	H	H



	R	R_1
3	Ac	H
4	H	Ac
7	Ac	Me
8	Me	Ac
13	H	H
15	Me	Me

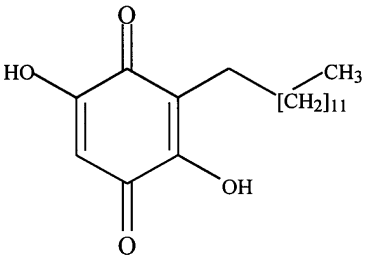
2. Results and discussion

Column chromatography of the *n*-hexane extract of *M. lanceolata* fruits, using *n*-hexane–EtOAc–AcOH mixture as eluent (see Section 3), resulted in the isolation of two constituents, namely, dihydromaesanin (**16**) (Muhammad et al., 1993) and maesanin (**12**) (Kubo et al., 1987) together with a fraction consisting of a complex mixture of hydroxy-alkylbenzoquinones, as suggested by its ^{1}H and ^{13}C NMR data Table 2. Subsequent separation of the mixture by chromatography over 7% $AgNO_3$-impregnated silica gel (using CH_2Cl_2 as solvent), followed by C-18 reversed phase chromatography (using Lichroprep silica gel RP-18 and MeCN as solvent) yielded two fractions, each consisting of a mixture of isomeric monohydroxy-alkybenzoquinones, **1**+**2** and **3**+**4**, in yields of 0.03% and 0.013%, respectively. These two fractions were not amenable to further separation and their benzoquinone components, **1**–**4**, were only separable as their methyl ethers. The methyl ethers were prepared by treatment with ethereal solution of CH_2N_2 to give **5**–**8**, respectively, which were separated by flash chromatography, followed by centrifugal preparative chromatography (Chromatotron®).

Compound **5**, $C_{23}H_{36}O_5$, exhibited UV, IR, ^{1}H NMR and mass spectral data that were comparable to those of compound **6**, which also analyzed for $C_{23}H_{36}O_5$. For example, both compounds showed the same base peak at m/z 350 $[M–Ac]^+$ in their mass spectra and four similar substituents (i.e. –Me, –OMe, –OAc, and $–C_{13}H_{27}$ hydrocarbon chain) as suggested by their ^{1}H and ^{13}C NMR data (Tables 1 and 2). Thus, the long tridecyl hydrocarbon chain at C-13 in both compounds was the same as observed in rapanone (**10**) (Dallacker and Lohnert, 1972), rather than the pentadecyl chain of dihydromaesanin(**16**) (Muhammad et al., 1993).

The arrangement of the four substituents on the benzoquinone ring as shown in **5** and **6** were determined by 2D NMR experiments, including COSY, HETCOR and HMBC. The 2D NMR ^{13}C–^{1}H HMBC experiment on **5** showed a three-bond correlation between δ 1.94 (C-6-Me), δ_{c-1} 181.0 and δ_{c-5} 155.8, and δ 2.37 (H-1′), δ_{c-2} 148.7 and δ_{c-4} 183.0, as well as δ 4.01 (C-5-OMe), δ_{c-4} 183.0, and δ_{c-6} 127.2, thus confirming that the methyl and methoxy groups were *ortho* to each other in a 1,4-benzoquinone ring system. In addition, the HMBC experiment further demonstrated two-bond correlations between the C-6-methyl group and δ_{c-6} 127.2, and the H-1′ methylene group and δ_{c-3} 135.0.

A similar HMBC experiment on compound **6** showed three bond correlations between δ1.92 (C-6-Me), δ_{c-1} 183.4 and δ_{c-5} 148.6, and δ 2.41 (H-1′), δ_{c-2} 155.8 and δ_{c-4} 180.7, as well as δ 4.01 (C-2-OMe), δ_{c-1} 183.4 and δ_{c-3} 131.7, thus confirming that the methyl and methoxy groups were *meta* to each other, while the acetoxy group was placed *para* to the methoxy group. From the foregoing data compound **6** is the methyl ether of 2-hydroxy-5 acetoxy-6-methyl-3-tridecyl-1,4-benzoquinone (**2**), while **5** is the methyl ether of compound **1**. Finally, the mixture (**1**+**2**) was acetylated to give the same diacetate **11**, which analyzed for $C_{24}H_{34}O_6$ by CIMS (Tables 1–2),



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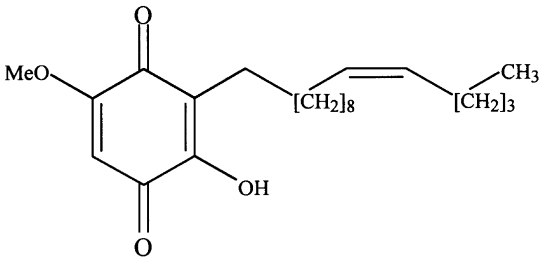

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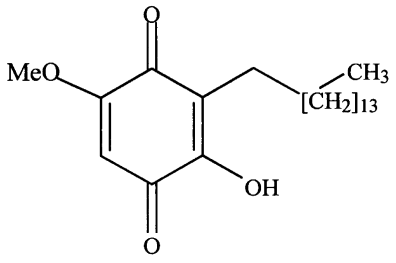

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thus confirming that compound **1** is a positional isomer of **2**.

The methyl ethers **7** and **8**, each analysed for $C_{25}H_{38}O_5$, had spectral data (UV, IR, ^1H and ^{13}C NMR) that were generally similar to those of the methyl ethers **5** and **6**. Thus, the ^1H and ^{13}C NMR data (Tables 1–2) of the 1, 4-benzoquinone nucleus of **7** and **8** were almost indistinguishable from those of **5** and **6**, respectively, while the long hydrocarbon chain at C-3 was the same in both compounds, but different from the tridecyl side chain of **5** and **6**. Instead, the long pentadecenyl chain found in **7** and **8** was clearly the same as in maesanin, (**12**) (Kubo et al., 1987) and maesanol (**13**) (Muhammad et al., 1993), including the signals due to the *cis* double bond system at C-10′-C-11′ (Tables 1–2), which were very close. The ^{13}C NMR data for the benzoquinone nucleus of **7** and **8** were assigned by comparison with those of compounds **5** and **6**, respectively, and were found to be very close, thus confirming **7** and **8** are the methyl ethers of **3** and **4**, respectively.

Fraction A was found to contain crude **14**, a minor compound that was inseparable from maesanol (**13**). Hence it was decided to identify it as its methyl ether **9**, $C_{22}H_{36}O_4$. The ^1H and ^{13}C NMR spectral data (Tables 1–2) of **9** were remarkably similar to those of maesanol dimethyl ether (**15**) (Muhammad et al., 1993), but lacked signals associated with the C-10′-C-11′ olefinic group of hydrocarbon chain. Instead, **9**, like **5** or **6**, was concluded to have a C-3 tridecyl hydrocarbon chain, as suggested by its MS and ^{13}C-NMR spectral data. The identity of compound **9** was substantiated by comparing its ^{13}C NMR data for the benzoquinone ring carbons and attached substituents, with those established for **5**–**8** and **15** (Muhammad et al., 1993).

3. Experimental

Mp: uncorr.; IR: KBr and neat; NMR: 200, 300 or 500 MHz (^1H) and 50, 75 or 125 MHz (^{13}C) in $CDCl_3$, using TMS as int. standard; multiplicity determinations (APT and DEPT) and 2D NMR spectra (COSY, HETCOR and HMBC) were run using standard Varian or Bruker software; MS: direct probe using Shimadzu QP500 GC/mass spectrometer; CIMS: Finnigan 3300 mass spectrometer, using NH_3 as an ionizing gas; TLC: silica gel 60 F_{254} (solvent *n*-hexane–EtOAc; 7:3), $AgNO_3$-impregnated silica gel 60 F_{254} (solvent: *n*-hexane–EtOAc–AcOH; 7:3:0.1) and reversed phase RP-18 F_{254} S (solvent MeCN); CC: silica gel 60, 7% $AgNO_3$-impregnated silica gel and Lichroprep RP-18, using as solvents *n*-hexane–EtOAc–AcOH, CH_2Cl_2 and MeCN, respectively; centrifugal prep. TLC (CPTLC, using Chromatotron®, Harrison Research Inc. Model 7924): 1 or 2 mm silica gel PF_{254} disk, using a flow rate of 3 ml min^{-1}. The isolated compounds were visualized under short-wavelength (λ_{max} 254 nm) UV-light and with 1% vanillin–H_2SO_4 spray reagent.

3.1. Plant material

The fruit of *Masea lanceolata* Forrsk were collected in summer 1997, in Abha, Saudi Arabia (Blatter, 1978). A voucher specimen is deposited at the herbarium of MAPPRC, College of Pharmacy, King Saud University, Riyadh, Saudi Arabia.

3.2. Extraction and isolation of benzoquinones

The dried ground fruits (600 g) were percolated with *n*-hexane (3 × 5 L; yield 110 g). The *n*-hexane extract (25 g) was subjected to CC over silica gel (type 60, 750 g) and

Table 1
^{1}H NMR chemical shift values[a] and coupling constants (in parentheses, in Hz) for compounds **5**–**9** and **11**

H	**5**	**6**	**7**	**8**	**9**	**11**
1′	2.37, t (7.5)	2.41, t (7.5)	2.36, t (7.6)	2.41, t (7.6)	2.39, t (7.3)	2.39, t (7.8)
2′	1.40 m	1.38 m	1.40 m	1.38 m	1.36 m	1.41 m
9′	–	–	1.99 m	2.01 m	–	–
10′	–	–	5.33, t (5.4)	5.34, t (4.6)	–	–
11′	–	–	5.33, t (5.4)	5.34, t (4.6)		
12′	1.24, m[b]	1.24, m[b]	1.99 m	2.01 m	1.24, m[b]	1.24 m[b]
14′	–	–	1.26 m[b]	1.27 m[b]	–	–
15′	–	–	0.88, t (7.0)	0.89, t (7.0)	–	–
2-OMe	–	4.01 s	–	4.0 s	3.98 s[c]	–
5-OMe	4.01 s	–	3.99 s	–	3.99 s[c]	–
6-Me	194 s	1.92 s	1.92 s	1.92	1.91 s	1.95 s
OAc	2.34 s	2.35 s	2.01 s	2.02	–	2.34, 2.35, 2 × s
Other protons	1.25–1.32 m, 18H (H-3′-H-11′)	1.25-1.30 m 18H (H-3′-H-11′)	1.25–132 m 14H, (H-3′-H-8′, H-13′)	1.26–132 m 14H, (H-3′-H-11′, H-13′)	1.24–132 m, 18H, (H-3′-H-11′)	1.24–1.32 m, 18H, (H-3′-H-11′)

[a] Spectra for **5**, **6**, **9** and **11** were recorded at 300 MHz, and for **7** and **8** at 500 MHZ.
[b] Superimposed under other CH_2 protons.
[c] Interchangeable signals.

Table 2
^{13}C NMR chemical shift values[a] for compounds **1**+**2**, **3**+**4** and **5**–**9** and **11**

	(**1**+**2**)[b]	(**3**+**4**)	**5**[b]	**6**	**7**	**8**	**9**	**11**
1	180.5, 183.3	180.4, 183.3	181.0	183.4	181.4	183.8	184.5	179.7
2	150.3, 151.0	150.3, 151.1	148.7	155.8	149.1	156.2	155.4	149.0
3	132.7, 128.7	132.7, 128.8	135.0	131.7	135.3	132.1	130.9	135.8
4	–	–	183.0	180.7	183.3	181.1	184.0	180.0
5	151.1, 150.3	151.3, 150.4	155.8	148.6	156.2	149.0	155.4	149.0
6	115.8, 120.1	115.7, 120.2	127.2	131.1	127.5	131.5	126.4	131.8
1′	22.7, 23.3	22.8, 23.4	23.4	23.7	24.0	23.6	23.0	23.8
2′	28.1, 28.2	28.2, 29.2	28.4	28.8	28.8	29.2	28.9	28.3
9′	–	26.9, 27.2[c]	–	–	27.3[c]	27.3[c]	–	–
10′	–	129.8, 129.9	–	–	130.2	130.2	–	–
11′	–	129.8, 129.9	–	–	130.2	130.2	–	–
12′	22.6, 22.6	26.9, 28.1[c]	22.7	22.7	27.5[c]	27.6[c]	22.7	22.7
13′	14.0, 14.0	32.0, 32.0	14.1	14.1	32.3	32.4	14.1	14.1
14′	–	22.4, 22.4	–	–	22.7	22.7	–	–
15′	–	14.0, 14.0	–	–	14.4	14.4	–	–
2-OMe	–	–	–	61.2	–	61.6	61.1	–
5-OMe	–	–	61.0	–	61.4	–	61.1	–
6-Me	7.8, 8.7	7.9, 8.7	8.6	9.0	9.0	9.5	8.4	9.2
OAc	167.8, 168.0, 20.9, 20.9	168.1, 167.9, 20.3, 20.4	168.1, 20.3	167.8, 20.6	168.5, 20.7	168.3, 20.7	–	167.8, 20.2, 167.5, 20.2
Other C	29.2–31.9, 9CH × 2	29.3–29.8, 6CH_2 × 2	29.3–31.9, 9CH_2	29.3–31.9, 9CH_2	28.8–30.1, 6CH_2	29.2–30.1, 6CH_2	29.3–31.9, 9CH_2	29.2–31.9, 9CH_2

[a] Spectra for **1**–**6**, **9** and **11** were recorded at 75 MHz, and for **7** and **8** at 125 MHz.
[b] Multiplicities were determined by APT and/or DEPT, also aided by 2D NMR COSY and HETCOR experiments.
[c] Interchangeable signals.

eluted with *n*-hexane, followed by increasing amounts of EtOAc in *n*-hexane containing AcOH (0.1%). Elution with *n*-hexane gave fraction A as an orange gum containing mixtures of compounds **13** and **14** (500 mg), which was separated by rechromatography over 7% $AgNO_3$-impregnated silica gel (type 60) using CH_2Cl_2–$CHCl_3$ (1:1) as solvent to give crude **14** (250 mg; R_f 0.25, silica gel, solvent: *n*-hexane–EtOAc; 7:3), followed by maesanol (**13**, 200 mg, mp 138–140°C, Lit. Muhammad et al. (1993), mp 140–142°C) as orange needles. Further elution

with *n*-hexane–EtOAc–AcOH (8:2:0.1) yielded fraction B as gum containing the complex mixture (**1**+**2**) and (**3**+**4**) (965 mg), which upon rechromatography over 7% $AgNO_3$-impregnated silica gel (type 60, 40 g) using CH_2Cl_2 as solvent to give yellow solid (fraction B-1, 250 mg), followed by an orange gum (fraction C, 550 mg), with R_f values of 0.40 and 0.30 ($AgNO_3$-impregnated silica gel, solvent: CH_2Cl_2). Both the fraction were further purified separately by rechromatography over Lichroprep silica gel RP-18, using MeCN as solvent, which yielded two mixtures of compounds [**1**+**2** (200 mg) and **3**+**4** (450 mg)] as pale yellow needles and an orange gum, respectively (R_f each 0.42, C-18 silica gel; solvent: MeCN). Further elution with *n*-hexane–EtOAc–AcOH (95:5:0.1) afforded fraction D (1.5 g), which was rechromatographed over 7%. $AgNO_3$-impregnated silica gel to give dihydromaesanin as yellow needles (**16**, 300 mg, mp 98–100°C, Lit. Muhammad et al. (1993), mp 101–102°C), followed by maesanin (**12**, 150 mg, mp 90–92°C, Lit. Kubo et al. (1987)), mp 91–93°C) as yellow prisms. The identity of maesanin (**12**) was confirmed by comparison of its spectral data with those reported in the literature (Kubo et al., 1987), while dihydromaesanin (**16**) and maesanol (**13**) were confirmed by direct comparison with authentic samples.

3.3. Methylation of compounds (*1*+*2*)

The mixture of compounds **1** and **2** (100 mg) was treated with an excess of an ethereal solution of CH_2N_2 at room temp for 4 h. The reaction mixture was dried in vacuo to afford a yellow residue containing two products (R_f 0.60 and 0.55, silica gel, solvent: *n*-hexane–EtOAc: 4:1) that was subjected to CC (silica gel 60, solvent: petrol–EtOAc; 19:1) to give compounds **5** (56 mg) and **6** (40 mg) as pale yellow needles.

3.4. 2-Acetoxy-5-methoxy-6-methyl-3-tridecyl-1,4-benzoquinone (*5*)

Pale-yellow needles from hot *n*-hexane, mp 56–57°C; UV λ^{EtOH}_{max} nm (log ε): 204 (4.56), 271 (3.85) and 391 (2.70); IR υ_{max} (KBr) cm^{-1}: 2900, 2860, 1780(OAc), 1660, 1610, 1510, 1370, 1270, 1180, 1125 and 1000; ^1H and ^{13}C NMR: Tabs. 1–2; MS *m*/*z* (rel. int): 392 $[M]^+$ (1), 350 $[M–Ac]^+$ (100), 182 (25), 167 (20), 153 (15), 137 (12), 83 (25), 69 (20) and 43 (60).

3.5. 2-Methoxy-5-acetoxy-6-methyl-3-tridecyl-1,4-benzoquinone (*6*)

Pale-yellow needles from hot *n*-hexane, mp 45–46°C; UV λ^{EtOH}_{max} nm (log ε): 202 (4.58), 270 (3.86) and 390 (2.72); IR υ_{max} (KBr) cm^{-1}: 2910, 2860, 1770, 1660, 1600, 1460, 1370, 1260, 1170, 1130 and 1010; ^1H and ^{13}C NMR: Tabs. 1–2; MS *m*/*z* (rel. int): 392$[M]^+$ (1), 350 $[M–Ac]^+$ (100), 182 (25), 167 (25), 153 (15), 137 (20), 83 (30), 69 (25) and 43 (70).

3.6. Methylation of compounds (*3*+*4*)

The mixture of compounds **3** and **4** (300 mg) was methylated using CH_2N_2, as previously described for **1**+**2** and the reaction mixture separated by CPTLC (2 mm silica gel PF_{254} disk, solvent: petrol–EtOAc; 49:1) to yield **7**, followed by **8** (100 and 150 mg, R_f: 0.60 and 0.55, silica gel, solvent: *n*-hexane–EtOAc, 4:1; respectively) as yellow gums.

3.7. 2-Acetoxy-5-methoxy-6-methyl-3-[(z)-10′-pentadecenyl]-1,4-benzoquinone (*7*)

Yellow gum; UV λ_{max} EtOH nm (log ε): 204 (4.65), 271 (3.90) and 383 (2.75); IR υ_{max} (neat) cm^{-1}: 2900, 2860, 1775, 1650, 1600, 1450, 1380, 1270, 1165, 1135 and 1000; ^1H and ^{13}C NMR: Tabs. 1–2; MS *m*/*z* (rel. int): 420 $[M]^+$ (1), 376 $[M–Ac]^+$ (45), 183(20), 167(20), 153(18), 137(15), 83(28), 69(25), 55(60) and 43(100).

3.8. 2-Methoxy-5-acetoxy-6-methyl-3-[(z-10′-pentadecenyl]-1,4-benzoquinone (*8*)

Yellow gum; UV λ_{max} EtOH nm (log ε): 203 (4.64), 270 (3.91) and 382 (2.76); IR υ_{max} (neat) cm^{-1}: 2910, 2865, 1770, 1660, 1610, 1455, 1375, 1275, 1180, 1155 and 1010; ^1H and ^{13}C NMR: Tabs. 1–2; MS *m*/*z* (rel. int): 420 $[M]^+$ (1), 376 $[M–Ac]^+$ (50), 183 (25), 167 (25), 153 (20), 137 (15), 83 (28), 69 (30), 55 (60) and 43 (100).

3.9. Methylation of crude *14*

Crude **14** (100 mg) was methylated using CH_2N_2 as previously described and purified by short CC (7%. $AgNO_3$-impregnated silica gel 60, solvent: *n*-hexane–CH_2Cl_2; 1:1) to afford 2,5-dimethoxy-6-methyl-3-tridecyl-1,4-benzoquinone (**9**) (80 mg) as pale yellow solid; mp 54–55°C; UV λ^{EtOH}_{max} nm (log ε) 205 (4.65), 282 (4.08) and 395 (2.65); IR υ_{max} (KBr) cm^{-1}: 2900, 2860, 1650, 1605, 1460, 1370, 1265, 1130, 1060 and 1000; ^1H and ^{13}C NMR: Tabs. 1–2; MS *m*/*z* (rel. int): 364 $[M]^+$ ($C_{22}H_{36}O_4$) (30) 196 (25), 181 (40), 167 (35), 153 (20), 149 (35), 137 (15), 83 (20), 55 (50) and 43 (100).

3.10. Acetylation of *1*+*2*

The mixture of compounds **1**+**2** (50 mg) was dissolved in pyridine and treated with Ac_2O at room temperature for 24 h. Regular work-up of the reaction mixt. afforded a single product, that was purified by CPTLC (1 mm silica gel PF_{254} disk, solvent: petrol–EtOAc; 19:1) to give 2,5-diacetoxy-6-methyl-3-tridecyl-1,4-benzoquinone (**11**, 45 mg) as light yellow needles; mp 71–70°C; UV λ^{EtOH}_{max}

nm (log ε): 203 (4.70), 268 (3.92) and 371 (2.75); IR υ_{max} (KBr) cm^{-1}: 2900, 2860, 1765, 1670, 1630, 1460, 1370, 1180, 1120, 1010 and 940; ^{1}H and ^{13}C NMR: Tabs. 1–2; CIMS *m/z* (rel. afforded a single product, that was purified by CPTLC (1 mm silica gel PF_{254} disk, solvent: petrol–EtOAc; 19:1) to give 2,5-diacetoxy-6-methyl-3-tridecyl-1,4-benzoquinone (**11**, 45 mg) as light yellow needles; mp 71–70°C; UV $\lambda^{EtOH}{}_{max}$ nm (log ε): 203 (4.70), 268 (3.92) and 371 (2.75); IR υ_{max} (KBr) cm^{-1}: 2900, 2860, 1765, 1670, 1630, 1460, 1370, 1180, 1120, 1010 and 940; ^{1}H and ^{13}C NMR: Tabs. 1–2; CIMS *m/z* (rel. int): 438 $[M+NH_4]^+$ ($C_{24}H_{34}O_6+NH_4$) (100).

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