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Benzoquinone derivatives of *Myrsine africana* and *Maesa lanceolata*

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Abstract

The fruits of *Myrsine africana* afforded two new benzoquinone derivatives, methylvilangin and methylanhydrovilangin. On the other hand, from the fruits of *Maesa lanceolata* two more novel compounds; 2,5-dihydroxy-3-(nonadec-14-enyl)-benzoquinone and lanciaquinone were isolated. Their structural elucidation was achieved by spectroscopic measurements including 2D NMR experiments.

Keywords: *Myrsine africana*; *Maesa lanceolata*; Myrsinaceae; Alkylhydroxy-1,4-benzoquinones

1. Introduction

The family Myrsinaceae consists of nearly 1000 species of trees and shrubs spread in 33 genera and is characterized by the presence of 2,5-dihydroxy-3-alkyl-benzoquinones and a number of triterpenoids based on oleanane and/or ursane skeleton (Januaro et al., 1992). In Kenya, the family is represented by five species spread in four genera, namely: *Myrsine, Maesa, Rapanea* and *Embelia* and are widely used in herbal medicine (Kokwaro, 1976). In previous communications (Midiwo et al., 1988, 1990, 1992; Midiwo and Manguro, 1996), we reported the isolation of hydroxylated 1,4-benzoquinone derivatives from both *Myrsine africana* and *Maesa lanceolata* parts. In a search for further related chemical constituents of the plants, we now report the isolation and structure determination of methylvilangin (1), methylanhydrovilangin (2), from *M. africana* in addition to 2,5-dihydroxy-3-(nonadec-14-enyl)-1,4-benzoquinone (3) and a bisbenzoquinone, lanciaquinone (4) from *M lanceolata*. All the compounds have been reported for the first time as natural products. Their structures were determined by physical, chemical and spectroscopic methods.

2. Results and discussion

Fractionation of the ethyl acetate extract of *M. africana* powdered fruits has led to the isolation and characterization of two benzoquinone derivatives **1** and **2**.

Compound **1** was isolated as an orange amorphous powder, mp 129–130 °C. Its mass spectrum obtained at 70 eV failed to show the molecular ion peak, but instead afforded characteristic fragments at m/z 320 ($C_{19}H_{28}0_4$) and 294 ($C_{17}H_{26}0_4$) (Fig. 1), suggesting the presence of a bisbenzoquinone (Venkateswarlu and Rao, 1962). Also evident from the spectrum was the base peak at m/z 154 and low abundant ions at m/z 180, 155 and 153.

Such fragmentation peaks have been reported in vilangin (**11**) and other related hydroxylated 1,4-benzoquinones with an alkyl side chain (Ogawa and Natori, 1968; Venkateswarlu and Rao, 1962).

The absorption bands at 3320 and 1625 cm^{-1} in the IR spectrum coupled with the UV peaks at 430 and 290 nm further supported the presence of an enolic 1,4-diketo system in which the OH groups are either 2,5- or 2,3-positioned on the ring (Midiwo et al., 1992; Muhammad et al., 1993; Kiuchi et al., 1998a,b).

In the ^1H NMR spectrum, the doublet peak of a methyl on a tertiary carbon at δ 1.58 and a quartet methine proton at δ 4.40 were similar to those previously reported for a corresponding synthetic derivative (Venkateswarlu and Rao, 1962). Furthermore, the

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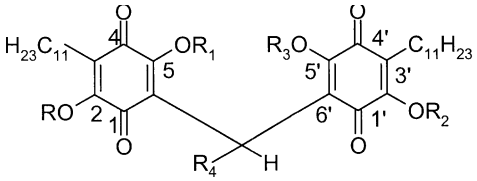
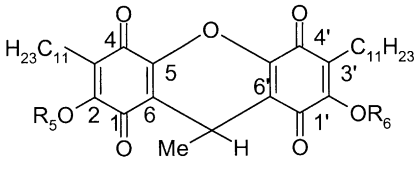
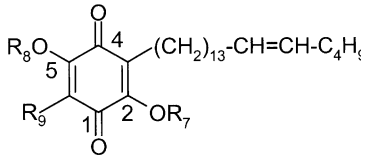


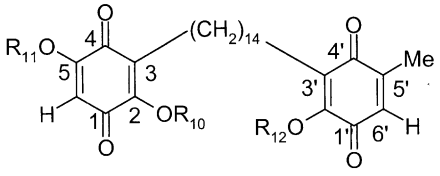
1 R = R_1 = R_2 = R_3 = H, R_4 = Me
5 R = R_1 = R_2 = R_3 = Me, R_4 = Me
11 R = R_1 = R_2 = R_3 = R_4 = H



2 R_5 = R_6 = H
6 R_5 = R_6 = Ac



3 R_7 = R_8 = R_9 = H
7 R_7 = R_8 = H, R_9 = Me
8 R_7 = R_8 = Me, R_9 = H
10 R_7 = R_8 = R_9 = Me



4 R_{10} = R_{11} = H
9 R_{10} = R_{11} = Ac

multiplet resonance at δ 1.50–1.20 on integration relative to the peak at δ 4.40 corresponded to 36 protons calculated for 18 methylenes. The remaining ^{1}H NMR peaks at δ 7.80, 2.43 and 0.88 were unequivocally assigned to four hydroxyls, two benzylic methylenes and two side chain terminal methyl groups, respectively. From the foregoing evidences, compound **1** was considered to be a bisbenzoquinone in which the two benzoquinone moieties are bridged by a tertiary carbon holding a methyl function. The ^{13}C NMR spectrum of the compound did not exhibit all the ring carbon signals but showed only two peaks at δ 117.45 (C-3 and C-3′) and 114.50 (C-6 and C-6′). Normally, the ^{13}C NMR spectra of 2,5- and/or 2,3-dihydroxy-3-alkyl-1,4-benzoquinones do not show the ring carbon peaks particularly those attached to oxygen atoms due to fluxional effect caused by intramolecular hydrogen bonding. The result of this is long spin relaxation time which leads to saturation of oxygen-carbon signals (Midiwo and Manguro, 1996). For instance, maesaquinone (**7**) showed only two quinonoid carbon peaks above δ 100 at 119.60 and 116.20 for C-3 and C-6, respectively (Fig. 2). The fluxional effect can be precluded if at least one of the hydroxyl group is removed through structural modification such as methylation or acetylation. Such modifications lead to observation of all the ring carbons as shown in the ^{13}C NMR spectra of 2,5-dimethoxymaesaquinone (**10**) (see Table 1). Further confirmation of the structure 1 was achieved by chemical reaction. Treatment of 1 with excess diazomethane at room temperature gave **5** with a molecular ion peak at m/z 670 ($C_{40}H_{62}O_5$), thus confirming free hydroxyl groups in the benzoquinone derivative. Its ^{1}H NMR spectrum was similar to that of the parent compound except the hydroxyl signals were replaced by four methoxy groups at δ 4.00 (6H) and δ 3.85 (6H) while the ^{13}C NMR data (Table 1) clearly exhibited the characteristics of a methoxylated 1,4-benzoquinone (Midiwo and Manguro, 1996). The relative positions of the methoxy groups in **5** was provided by NOESY experiments and further confirmed by HMBC correlations (Fig. 3). Saturation of the methoxy signal at δ 4.00 gave an NOE cross peak with

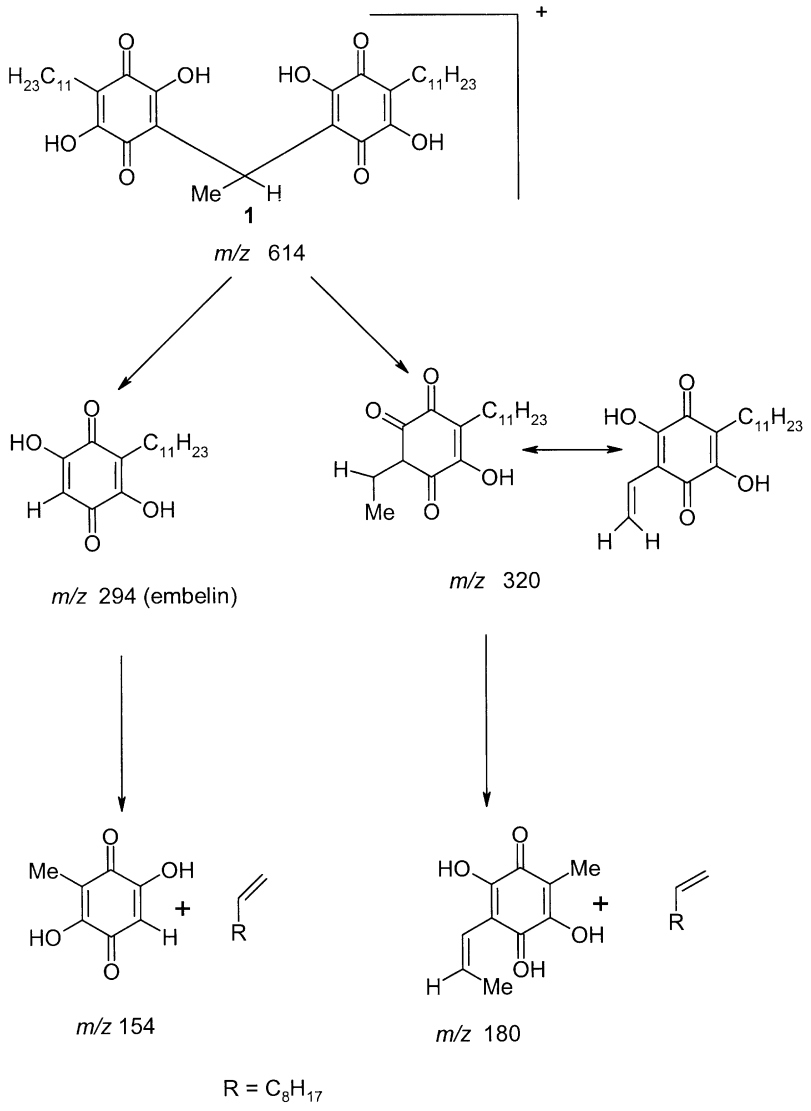


Fig. 1. Fragmentation pattern of **1** in EIMS (70 eV).

the benzylic methylene (δ 2.37), thus confirming the 2,5-orientation of OH groups in compound **1**. On the basis of the above data, compound 1 was confirmed as a bisbenzoquinone, methylvilangin.

Compound **2**, isolated as an orange amorphous solid showed ^{1}H NMR data which were strongly reminiscent of those reported for compound **1** except for the shift of peaks arising from two hydroxyls (δ 7.04), a methine proton (δ 4.00) and a secondary methyl (δ 1.30) upfleld. The proposal of the hydroxyl groups being at 2,2′- and not at 3,3′-position on the ring was supported by analysis of relevant fragments in the mass spectrum. The peaks at m/z 320 and 294, respectively were consistently interpreted as outlined in Fig. 1. On the basis of the above data, **2** was presumed to be a bisbenzoquinone similar to compound **1** in which both an oxygen atom and a tertiary carbon holding a methyl group bridged the two benzoquinone moieties. This suggestion was strongly supported by the molecular ion peak at m/z 596, calculated for a formula of $C_{36}H_{52}O_7$.

Acetylation of **2** with acetic anhydride-pyridine produced **6**, with a $[M]^+$, 84 units more than that of the parent compound, corresponding to addition of two acetate units. The relative positions of the acetoxy units in **6** was similarly provided by NOESY experiments. Irradiation of the acetoxy peak at δ 1.90 (6H) showed an NOE effect on a benzylic methylene at δ 2.44 (4H), suggesting that the methylene and the acetoxy groups

are vicinally oriented. Accordingly, from the above results the structure of compound **2** was elucidated as methylanhydrovilangin.

From the ethyl acetate extract of *M. lanceolata* fruits were by repeated flash chromatography and recrystallization two more new compounds **3** and **4** isolated. Compound 3, an orange amorphous powder showed IR characteristic absorption bands at 3300 (hydrogen bonded OH) and 1610 (chelated C=O) cm^{-1} which together with the UV spectrum peaks at 426 and 290 nm signified

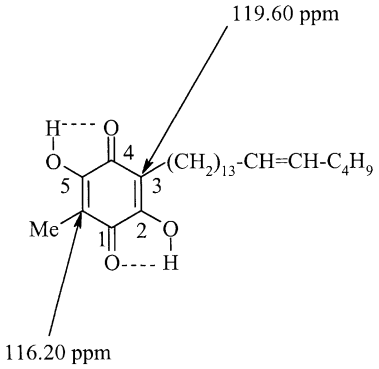


Fig. 2. The effect of intramolecular bonding on ^{13}C NMR of **7**.

the presence of an hydroxylated-1,4-benzoquinone derivative (Chandrasekhar et al., 1970; Kiuchi et al., 1998a,b).

The structural similarity between **3** and maesaquinone (**7**) previously reported from the plant (Midiwo et al., 1992; Midiwo and Manguro, 1996) was indicated by the resemblance of their ^1H NMR spectra with a major structural difference being the arrangement of the substituents around the quinonoid ring. Comparison of their ^1H NMR spectra suggested the location of a proton at C-6 in **3**, as evidenced by a singlet peak at δ 6.0. Furthermore, its molecular ion and base peaks at m/z 404 and 154, respectively compared to those at m/z [M]* 418 and 168 in **7** is explained by the presence of a quinonoid methyl function in the latter (Ogawa and Natori, 1968). As was the case in **7**, the position of the double bond in the side chain was identified to be between C-14 and C-15 by alkaline hydrogen peroxide oxidation reaction (Ogawa and Natori, 1968).

Treatment of **3** with excess diazomethane at room temperature and after usual work up afforded **8**. Its ^1HNMR spectrum revealed the presence of two methoxy groups at δ 4.10 and 3.95 with corresponding ^{13}C NMR peaks at δ 60.60 and 60.30, respectively. The MS

Table 1
^{13}C NMR assignment for the hydroxybenzoquinones

Carbon no.	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
1	–	178.90	–	–	184.60	184.43	–	184.30	182.50	181.70
2	–	151.07	–	–	155.80	151.91	–	157.70	155.90	157.70
3	117.45	120.15	117.60	119.50	132.30	122.80	119.60	126.70	130.80	127.20
4	–	182.05	–	–	183.40	183.90	–	184.70	183.60	182.55
5	–	154.40	–	–	158.80	160.10	–	156.00	158.90	151.85
6	114.50	127.00	102.40	101.20	130.00	122.80	116.20	108.60	105.40	119.50
1′	–	178.90	–	179.80	184.60	184.43	–	–	181.40	–
2′	–	151.07	–	155.30	155.80	151.91	–	–	155.60	–
3′	117.45	120.15	–	117.30	132.30	120.80	–	–	130.80	–
4′	–	182.05	–	175.50	183.40	183.90	–	–	181.00	–
5′	–	154.40	–	118.30	158.80	160.10	–	–	126.30	–
6′	114.50	127.00	–	104.10	130.00	120.80	–	–	108.50	–
H–C–Me	28.50	22.14	–	–	28.40	29.40	–	–	–	–
H–C–Me	17.60	21.67	–	–	17.80	18.90	–	–	–	–
Benzylic-CH_2	29.70	29.52	29.50	29.80	29.50	29.56	29.65	29.60	29.30	29.30
Chain-CH_2	31.8, 29.5, 29.4, 29.3, 29.2, 22.9	31.6, 29.3, 29.3, 27.9, 22.6, 22.5	31.4, 29.4, 27.6, 25.7, 23.1, 22.1	31.7, 29.7, 28.3, 28.2, 22.6, 22.4	31.8, 29.4, 29.3, 29.2, 28.7, 22.9	31.8, 29.4, 29.0, 28.6, 28.2, 23.0	31.8, 29.9, 29.4, 29.5, 23.4, 22.5	31.0, 29.4, 29.2, 28.6, 25.5, 23.0	31.9, 29.6, 28.7, 27.8, 22.8, 22.7	31.6, 29.3, 28.1, 27.7, 23.9, 22.6
6-Me	–	–	–	–	–	–	8.70	–	–	9.70
5′-Me	–	–	–	8.90	–	–	–	–	8.80	–
end-Me	14.00	–	–	–	14.00	14.00	14.00	14.00	–	13.70
2-OMe	–	–	–	–	61.10	–	–	60.60	–	56.50
2′-OMe	–	–	–	–	61.10	–	–	60.60	–	–
5-OMe					60.90	–	–	60.30	–	56.70
5′-OMe	–	–	–	–	60.90	–	–	60.30	–	–
–CH=CH–	–	–	128.10	–	–	–	127.90	129.90	–	129.70
2-OAc	–	–	–	–	–	170.20	–	–	169.50	–
2′-OAc	–	–	–	–	–	170.20	–	–	169.50	–
5-OAc	–	–	–	–	–	–	–	–	–	–
5′-OAc	–	–	–	–	–	–	–	–	170.10	–
O=C–Me	–	–	–	–	–	25.00	–	–	–	–

data corroborated these findings by displaying a molecular ion peak at m/z 432, calculated for $C_{27}H_{44}O_4$. Placement of the OH groups at C-2 and C-5, respectively and the proton at C-6 in **3** were established by NOESY spectral data of the methylated derivative **8**, which showed connectivities between CH_2-3 and MeO-2 and between H-6 and MeO-5. This was further corroborated by data generated from HMBC spectra as illustrated in Fig. 3. On this basis compound **3** was identified as 2,5-dihydroxy-3-(nonadec-14-enyl)-1,4-benzoquinone.

Compound **4**, also an orange amorphous powder showed the presence of hydroxyl (3320 cm^{-1}), α, β-conjugated carbonyl group (1650 cm^{-1}) and chelated carbonyl (1610 cm^{-1}) groups in the IR spectrum. The presence of these functionalities was supported by the UV absorptions at 430 and 285 nm. Its ^1H NMR data suggested the presence of three hydroxyl groups (δ 7.50, D_2O exchangeable), two protons (δ 6.45 and 6.00), two benzylic methylenes (δ 2.40), a methyl (δ 1.94) and side chain methylenes (δ 1.50–1.20). The molecular ion peak at m/z 472 and the base peak at m/z 154 together with another fairly strong one at m/z 152, showed that the compound consisted of two benzoquinone moieties which are not the same with regard to substitution around the rings. This led to the assumption that one ring is substituted with two hydroxyls which are either 2,5- or 2,3-positioned while the other has methyl, hydrogen and hydroxyl groups around it. Acetylation of **4** with acetic anhydride-pyridine mixture for 24 h at room temperature gave a tri-acetyl derivative **9**, which was purified by column chromatography on silica gel. A solution to clarify ambiguity concerning substitution around the rings in the parent compound **4** was obtained from HMQC, HMBC and NOESY experiments on the triacetyl product **9**. From the NOESY correlation experiments (Fig. 3), cross peaks between the proton at δ 5.94 (H-6) and the acetyl group at δ 2.20 confirmed that two OH groups are 2,5-positioned in one ring. On the other hand, irradiation of a peak at δ 6.01 (H-6′) showed an NOE correlation with a peak at δ 1.95 (Me-5′), indicating that the two functionalities are ortho positioned to each other. In the HMQC spectrum, the methyl peak at δ_H 1.95 was correlated with δ_c 8.80, the protons at δ_H 5.94 and 6.01 with δ_c 105.40 and 108.50, respectively. In addition to these, the correlation spectroscopy via long range coupling (HMBC correlation, $J=$ 12 Hz) (Fig. 3) exhibited the following correlation peaks; between the methyl at δ_H 1.95 (Me-5′) with carbons at δ_c 126.30 (C-5′), 108.50 (C-6′) and 181.40 (C-1′), between the proton at δ_H 6.01 (H-6′) with δ_c 108.50 (C-6′), 126.30 (C-5′), 181.00 (C-4′) and 181.40 (C-1′), between the proton at δ_H 5.94 (H-6) with carbons at δ_c 182.50 (C-1), 183.60 (C-4), 158.90 (C-5), 155.90 (C-2), and between the benzylic methylene at δ_H 2.40 with carbons δ_c 155.90 (C-2), 130.80 (C-3 and C-3′), 183.60 (C-4), 181.00 (C-4′), 155.90 (C-2) and 155.60 (C-2′). On this basis compound **4**, was thus designated as lanciaquinone, a new natural product.

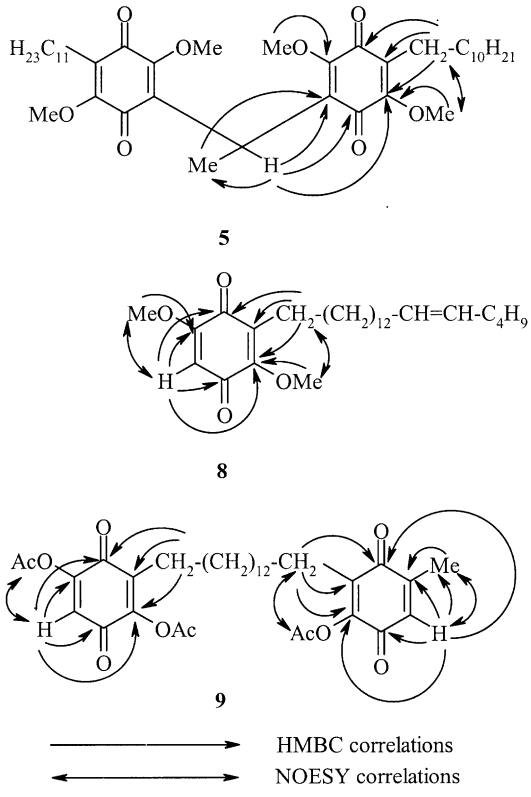


Fig. 3. Pertinent correlations in HMBC and NOESY spectra of compounds **5**, **8** and **9**.

3. Experimental

3.1. General experimental procedures

Melting points (uncorrected) were obtained on a hot plate Reichert Thermovar, Buchi SMP-20. UV data were recorded using Hewlett Packard Diode Array 8452A spectrophotometer while IR spectra were studied on an infrared IMR-125 spectrophotometer. The NMR spectra were obtained on a Brucker WM NMR spectrometer operating at 400 and 100 MHz, respectively in $CDC1_3$ with tetramethylsilane as internal standard. Mass spectrum data were obtained on MAT 8200 A Varian MAT Bremen instrument. $[\alpha]_D$ values were obtained on a Jasco dip 360 apparatus. Silica gel for column and tlc plates were impregnated with 2% oxalic acid solution.

3.2. Plant material

Plant materials for research were identified and gathered by Mr. Mathenge of Botany Department, University of Nairobi. Authentic specimens of the plants

were deposited in the Department's Herbarium. Their identification was accomplished by comparison with voucher specimens.

3.3. Extraction and isolation of benzoquinones from *M. africana*

Powdered ground fruit (1 kg) was extracted with ethyl acetate (3×21) at room temperature, the extracts combined and removal of the solvent under reduced pressure provided a dark brown material (50.5 g). A portion of it (45 g) was chromatographed over silica gel with petroleum ether containing increasing amounts of EtOAc and finally with MeOH. Fractions (100 ml each) were collected and their homogeneity monitored by tlc using solvent systems petroleum ether–ethyl acetate (4:1, 3:2, 1:1) and petroleum ether–ethyl acetate–acetic acid (85:15:5). This afforded myrsinone (160 mg), embelin and/or rapanone (1000 mg) and 5-O-methylembelin (70 mg) (Midiwo et al., 1992). Fractions eluted as mixtures were further subjected to medium pressure chromatography using petroleum ether–ethyl acetate (3:2) to give methylvilangin (1) 200 mg and methylanhydrovilangin (2) 90 mg.

3.4. Extraction and isolation of compounds from *M. lanceolata*

Dried and finely powdered fruits (1 kg) was similarly extracted with ethyl acetate as described for *M. africana* for 1 week to give 75 g of a semi solid brown material. The extract (50 g) was fractionated by column chromatography, first with petroleum ether followed by petroleum ether–EtOAc mixture containing varying concentrations of the latter and concluded with MeOH affording maesaquinone (9000 mg) (**7**), acetylmaesaquinone (3000 mg) and maesanin (1200 mg) (Midiwo et al., 1988). Similarly fractions eluted as mixtures were combined and further purified by medium pressure chromatography using petroleum ether–EtOAc (3:2) with aliquots of 10 ml being collected. This procedure afforded compounds **3** (70 mg) and **4** (45 mg), respectively.

3.5. Methylvilangin (*1*)

The compound crystallized from methanol as orange crystals, mp 129–130 °C, $[\alpha]_D^{25}$ +18^0 (CH_2C1_2, c 1.0). UV λ_{max} (MeOH) nm: 430 (4.26) and 290 (4.10). IR ν_{max} (KBr) cm^{-1}: 3320 (O–H), 2920, 2850 (C–H), 1625 (chelated C=O), 1570, 1120, 715. ^{1}H NMR δ ppm: 7.80 (s, OH-2, 2′, 5, 5′), 4.40 (q, J= 7.5 Hz, H–C–Me), 2.43 (t, J=15.1, 7.1 Hz, CH_2-3, 3′), 1.58 (d, J=7.5 Hz, H–C–Me), 1.50–1.20 (m, 18CH_2), 0.88 (t, J=13.3, 6.2 Hz, end-Me). ^{13}C NMR data: see Table 1. ElMS (70 eV): *m/z* (%) 320 (20), 294 (25), 182 (5), 180 (42), 155 (15), 154 (100), 153 (35), 142 (16), 139 (69), 125 (25), 69 (30).

3.6. Methylation of *1*

The compound (60 mg) in ether (30 ml) was treated with excess diazomethane at room temperature for one hour. Work up as usual afforded **5** as yellow needles (crystallized from petroleum ether–dichloromethane, 9:1), 45 mg, mp 81–82 °C; $[\alpha]_D^{25}$ −11° (MeOH, c 1.0). UV λ_{max} (MeOH) nm: 290 (4.07). IR ν_{max} (KBr) cm^{-1}: 2910, 2850 (C–H), 1645 (α, β-unsaturated C=O), 1600 (C=C), 1470, 1445, 1380, 775, 720. ^{1}H NMR δ ppm: 4.30 (q, J=7.5 Hz, H–C–Me), 4.00 (s, MeO-2, 2′), 3.85 (s, MeO-5, 5′), 2.37 (t, J=15.6, 7.7 Hz, CH_2-3, 3′), 1.60 (d, J=7.5 Hz, H–C–Me), 1.40–1.20 (m, 18CH_2), 0.90 (t, J=13.3, 6.2 Hz, terminal-Me). ^{13}C NMR data: see Table 1. MS (70 eV): *m/z* (%) M^+ 670 (100), 625 (6), 530 (10), 483 (10), 361 (25), 221 (18), 165 (15), 83 (10), 68 (24).

3.7. Methylanhydrovilangin (*2*)

Obtained from petroleum ether–dichioromethane (9:1) as orange crystals, mp 157–158 °C; $[\alpha]_D^{25}$ +47° (CH_2Cl_2, c 1.0). UV λ_{max} (MeOH) nm: 436 (2.43), 322 (3.3) and 262 (4.05). IR ν_{max} (KBr) cm^{-1}: 3380 (O–H), 2920, 2850 (C–H), 1640 (α,β-unsaturated C=O), 1615 (C=O, chelated), 1460, 1400, 1375, 1335, 1185, 760. ^{1}H NMR δ ppm: 7.04 (s, OH-2, 2′), 4.00 (q, J=7.6 Hz, H–C–Me), 2.44 (t, J=15.4, 7.2 Hz, CH_2-3, 3′), 1.50–1.20 (m, 18CH_2), 1.30 (d, J=7.4 Hz, H–C–Me), 0.88 (t, J= 13.2, 6.4 Hz, terminal-Me). ^{13}C NMR: see Table 1. MS (70 eV): *m/z* (%) M^++2 598 (5), M^+ 596 (100), 583 (11). 456 (10), 433 (5), 320 (21), 317 (10), 303 (12), 294 (25), 273 (3), 219 (5), 154 (20), 106 (3), 95 (15), 71(25), 69 (20), 57 (4).

3.8. Acetylation of *2*

The compound (20 mg) was treated with Ac_2O (1 ml) and pyridine (two drops) at room temperature for a period of 24 h affording **6** as yellow amorphous powder, mp 56–57 °C; $[\alpha]_D^{25}$ −23° (CH_2CI_2, c 1.0). UV λ_{max} (MeOH) nm: 465 (2.50) and 275 (4.10). IR ν_{max} (KBr) cm^{-1}: 2920, 2850 (C–H), 1770 (C=O, ester), 1675 (α, β-unsaturated C=O), 1375, 775. ^{1}H NMR δ ppm: 3.95 (q, J=6.7 Hz, H–C–Me), 2.44 (t, J=15.3, 7.0 Hz, CH_2-3, 3′), 1.90 (s, OAc-2, 2′), 1.50-1.15 (m, 18CH_2), 1.35 (d, J=6.7 Hz, H–C–Me), 0.89 (t, J=13.3, 7.6 Hz, terminal-Me). ^{13}C NMR data: see Table 1. ElMS (70 eV): *m/z* (%) M^+680 (9), 638 (5), 596 (60), 581 (100), 320 (19), 317 (15), 294 (20), 154 (40), 95 (15).

3.9. 2,5-Dihydroxy-3-(nonadec-14-enyl)-1,4-benzoquinone (*3*)

Crystallized from MeOH as yellow brown crystals, mp 138–139 °C; $[\alpha]_D^{25}$ −40° (CH_2Cl_2, c 1.0). UV λ_{max}

(MeOH) nm: 426 (2.60) and 290 (4.25). IR ν_{max} (KBr) cm^{-1}: 3300 (O–H), 2920, 2830 (C–H), 1610 (chelated C=O), 1590 (C=C), 1330, 1180. ^{1}H NMR δ ppm: 7.70 (s, OH-2, 5), 6.0 (s, H-6), 5.40 (m, –CH=CH–), 2.40 (t, J = 15.3, 7.5 Hz, CH_2-3), 2.0 (m, $–CH_2CH=CH_2–$), 1.50–1.10 (m, $14CH_2$), 0.90 (t, J = 13.5, 6.7 Hz, terminal-Me). ElMS (70 eV): m/z (%) M^+ 404 (15), 155 (40), 154 (100), 153 (10), 125 (15), 105 (12), 80 (30), 55 (80). ^{13}C NMR data are in Table 1.

3.10. Methylation of **3**

Approximately 20 mg was methylated using similar procedures described for **1** to give a yellow compound **8** (15.5 mg), crystallized in MeOH, mp 44 °C; $[\alpha]_D^{25}$ 59° (CH_2Cl_2, c 1.0). UV (max (MeOH) nm: 440 (2.70) and 272 (4.50). IR (max (KBr) cm^{-1}: 2920, 2840 (C–H), 1660 (C=O), 1600 (C=C). ^{1}H NMR δ ppm: 5.90 (s, H-6), 5.35 (m, –CH=CH–), 4.10 (s, MeO-2), 3.95 (s, MeO-5), 2.40 (t, J= 15.4, 7.1 Hz, CH_2-3), 2.0 (m, $–CH=CH_2–$), 1.50–1.20 (m, $14CH_2$), 0.90 (t, J=13.0, 7.3 Hz, terminal-Me). ElMS (70 eV): m/z (%) M^+ 432 (100), 185 (2), 183 (4), 154 (4), 153 (7), 139 (6), 123 (80), 111 (2). ^{13}C NMR data: see Table 1.

3.11. Alkaline hydrogen peroxide oxidation of **3** and gas chromatography of fatty acids

To the compound (4 mg) dissolved in n-KOH was added H_2O_2 (30%, 0.2 ml) under slight warming on a water bath (Ogawa and Natori, 1968). After 3 h the reaction mixture was acidified and extracted with ether. The ethereal layer was dried, evaporated and methylated with CH_2N_2 in ether. The product was subjected to gas chromatography and the retention times compared with the methyl ester from **7** and also those from authentic fatty acids.

3.12. Lanciaquinone (**4**)

Crystallized as yellow brown crystals from MeOH, mp 141–143 °C; $[\alpha]_D^{25}$ +29° (CH_2Cl_2, c 0.5). UV λ_{max} (MeOH) nm: 430 (2.80) and 285 (4.40). IR ν_{max} (KBr) cm^{-1}: 3320 (O–H), 1650 (α, β-unsaturated C=O), 1610 (chelated C=O). ^{1}H NMR δ ppm: 7.50 (s, OH-2, 2′, 5), 6.45 (s, H-6′), 6.0 (s, H-6), 2.40 (t, J = 15.3, 7.6 Hz, CH_2-3, 3′), 1.94 (s, Me-5′), 1.50–1.20 (m, $12CH_2$). ^{13}C NMR data: see Table 1. ElMS (70 eV): m/z (%) M^+ 472 (20), 320 (12), 154 (100), 152 (80), 139 (15), 69 (45), 55 (75), 43 (65).

3.13. Acetylation of **4**

Treatment of the compound (15 mg) as described for compound **2** afforded **9** (11 mg), yellow amorphous powder (crystallized from MeOH), mp 55–57 °C; $[\alpha]_D^{25}$ −17.5° (CH_2Cl_2, c 1.0). UV λ_{max} (MeOH) nm: 276 (4.0). IR ν_{max} (KBr) cm^{-1}: 1765 (C=O, ester), 1650 (α, β-unsaturated C=O), 1570 (C=C), 1300, 1025, 760. ^{1}H NMR δ ppm: 6.01 (s, H-6′), 5.94 (s, H-6), 2.40 (t, J = 15.3, 7.7 Hz, CH_2-3, 3′), 2.20 (s, OAc-2, 5), 2.10 (s, OAc-2′), 1.95 (s, Me-5′), 1.50–1.20 (m, $12CH_2$). ^{13}C NMR: see Table 1. ElMS (70 eV): m/z (%) M^+ 598 (8), 556 (5), 322 (3), 154 (65), 152 (15), 138 (20), 69 (55), 55 (100), 43 (90).

3.14. Maesaquinone (**7**)

An orange amorphous powder from MeOH, mp 129–131 °C; $[\alpha]_D^{25}$ −22° (CH_2CI_2, c 1.0). UV λ_{max} (MeOH) nm: 424 (2.8) and 286 (4.50). IR ν max (KBr) cm^{-1}: 3320 (O–H), 1610 (C=O, chelated), 1370, 1180, 1120, 1055, 765. ^{1}H NMR δ ppm: 7.60 (s, OH-2, 5), 5.30 (m, –CH=CH–), 2.40 (t, J = 15.0, 7.5 Hz, CH_2-3), 2.0 (m, $–CH_2CH=CHCH_2–$), 1.95 (s, Me-6), 1.50–1.20 (m, $14CH_2$), 0.85 (t, J = 13.2, 74 Hz, terminal-Me). ^{13}C NMR data: see Table 1. ElMS (70 eV): m/z (%) M^+ 418 (12), 169 (55), 168 (100), 139 (30), 55 (35).

3.15. Methylation of maesaquinone

Approximately 500 mg in dry acetone (150 ml) was treated with excess diazomethane for one hour at room temperature. Work up as described for **1** afforded **10** (450 mg), yellow needles, mp 46–48 °C; $[\alpha]_D^{25}$ −37° (CH_2C1_2, c 1.0). UV λ_{max} (MeOH) nm: 284 (4.25). IR ν_{max} (KBr) cm^{-1} : 2920, 2850 (C–H), 1660 (α, β-unsaturated C=O), 1600 (C=C), 1460. ^{1}H NMR δ ppm: 5.31 (m, –CH=CH–), 3.80 (MeO-2), 3.60 (MeO-5), 2.40 (t, J = 14.7, 7.5 Hz, CH_2-3), 2.0 (m, $–CH_2CH=CHCH_2–$), 1.88 (s, Me-6), 1.60–1.25 (m,$14CH_2$), 0.90 (t, J = 13.6, 7.4 Hz, terminal-Me). ElMS (70eV): m/z (%) 446 (100), 418 (5), 197 (30), 181 (35), 167 (32), 154 (25), 137 (15). ^{13}C NMR spectral data are in Table 1.

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