Synthesis of New Phytogrowth-Inhibitory Substituted Aryl-*p*-Benzoquinones

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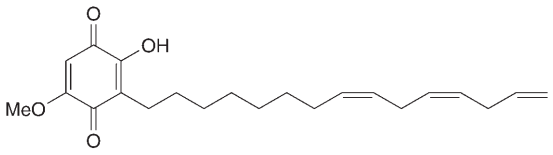
Reaction of [(2-alkyloxy)methyl]-1,4-dimethoxybenzene **10** (alkyl = butyl, hexyl, decyl, tridecyl, tetradecyl, hexadecyl, and octadecyl) with ceric ammonium nitrate in order to produce *p*-benzoquinones (= cyclohexa-2,5-diene-1,4-diones) afforded 5-[(alkyloxy)methyl]-2-(4-formyl-2,5-dimethoxyphenyl)-benzo-1,4-quinones **12a**–**12g** in yields that varied from 46 to 97%, accompanied by 2-[(alkyloxy)methyl]benzo-1,4-quinones **11a**–**11g** in only small quantities ($\leq$5%). These quinones resemble the natural phytotoxic compound sorgoleone, found in *Sorghum bicolor*. This reaction exemplifies a general procedure for the synthesis of novel aryl-substituted *p*-benzoquinones. The selective effects of compounds **12a**–**12g**, at the concentration of 5.5 ppm, on the growth of *Cucumis sativus*, *Sorghum bicolor, Euphorbia heterophylla*, and *Ipomoea grandifolia* were evaluated. All compounds caused some inhibition upon the aerial parts and root growth of the tested plants. The most active compound, 2-(4-formyl-2,5-dimethoxyphenyl)-5-[(tridecyloxy)methyl]-benzo-1,4-quinone (**12d**), caused between 3 and 18%, and 12 and 29% inhibition on the roots and aerial parts development of *Cucumis sativus* and *Sorghum bicolor*, respectively, and between 77 and 85%, and 34 and 52% inhibition on the roots and aerial parts growth of *Euphorbia heterophylla* and *Ipomoea grandifolia*, respectively.

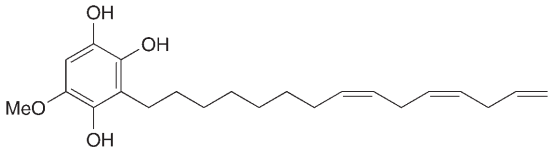
Introduction. – The development and use of synthetic organic herbicides during the last six decades have greatly facilitated weed management in crops, but their extensive use leads to potential environmental and toxicological problems [1]. As a consequence, natural products and their derivatives have been viewed as a source of new potential environment-friendly herbicides [2–4].

The study of allelophatic interactions involving microorganism and plant species has led to the discovery of several phytotoxic substances that have potential use as herbicides, or could be used as lead structures for the development of more active compounds [5][6]. Among such substances is a compound called sorgoleone, characterized as 2-hydroxy-5-methoxy-3-[(8*Z*,11*Z*)-pentadeca-8,11,14-trienyl]cyclohexa-2,5-dienyl-1,4-dione (*Fig. 1*) which was isolated from the root exsudates from *Sorghum bicolor* [7].

Since its discovery, it has been demonstrated that sorgoleone (**1**) is a potent inhibitor of chlorophyll formation in *Lemma minor* L., and it also inhibits the growth of several grass and broadleaf weeds at concentration as low as 10 μM [8]. Further studies revealed that sorgoleone is a very effective inhibitor of electron transfer between Q_A^- to Q_B at reducing side of the photosystem II [9] and also of the mitochondrial electron transport [10][11]. During *in vitro* assay, sorgoleone (**1**) has been shown to be more



1 Sorgoleone



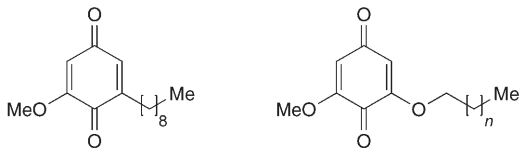
2 Dihydrosorgoleone

Fig. 1. *Structures of sorgoleone* (**1**) *and dihydrosorgoleone* (**2**), *the major lipophilic compounds isolated*

potent than the commercial herbicide atrazine in inhibiting the PSII [12]. This quinone also causes disturbance of plasma H^+-ATPase activity in root cells [13].

Although the total synthesis of sorgoleone (**1**) has been known for over a decade [14], only a few papers describing evaluation of the herbicidal activity of synthetic analogues and natural sorgoleone have been published [15–17]. Considering the potential use of sorgoleone (**1**) as herbicide and our interest in using natural products as models to prepare new agrochemicals [18–24], we report in this paper the unexpected formation of several new arylbenzoquinones that are more active than sorgoleone (**1**) against selected weeds.

Results and Discussion. – *Chemistry.* In our previous work [17], we have used the 3,5-dimethoxybenzyl alcohol as a starting material for the preparation of sorgoleone analogue **3** (*Fig. 2*) that proved more active than sorgoleone (**1**) on the root inhibition of the weeds *Euphorbia heterophylla* and *Brachiaria decumbens.*



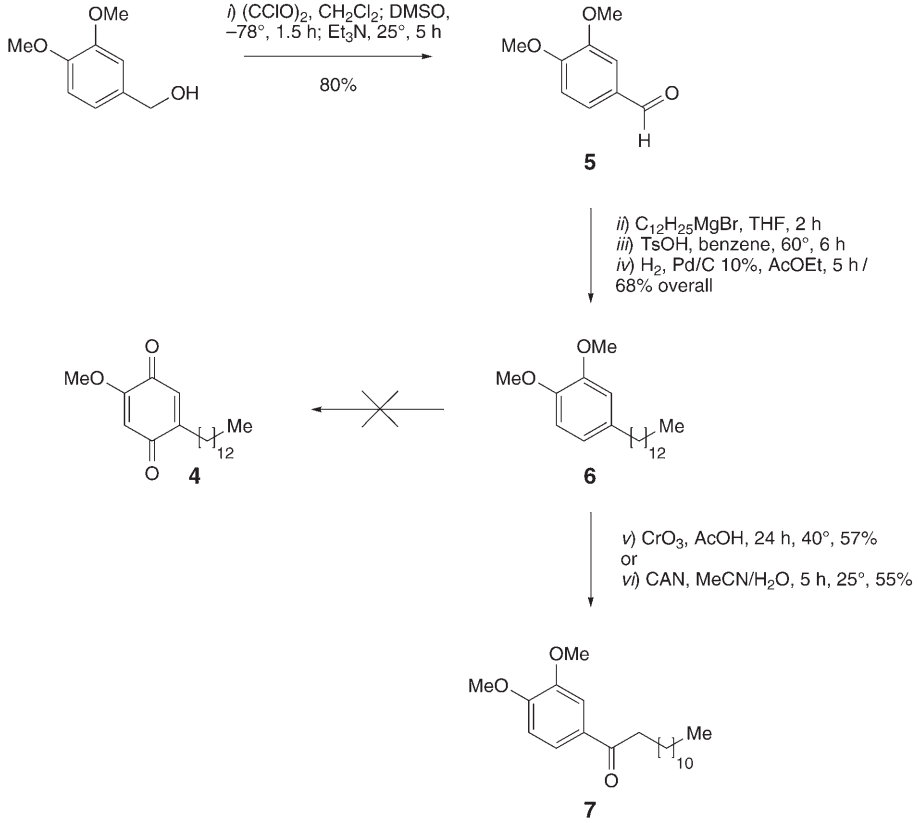
3 **8** $n = 2, 4, 6$

Fig. 2. *Structures of synthetic sorgoleone analogues*

We then envisaged that, employing the same synthetic methodology with 3,4-dimethoxybenzyl alcohol as the starting material, the preparation of a regioisomer of compound **3**, with the MeO group in the *para*-position with respect to the alkyl chain, could be easily carried out. This would allow the evaluation of the influence of the relative position of the MeO group upon biological activity. Following this idea, we initially attempted at the preparation of compound **4**, according to *Scheme 1.* The benzaldehyde **5** was then obtained in 80% yield from the corresponding benzyl alcohol.

Addition of *Grignard* reagent to **5**, followed by dehydration and catalytic hydrogenation, led to the required 1,2-dimethoxy-4-tridecylbenzene (**6**) in 55% overall yield (*Scheme 1*).

Scheme 1. *Tentative Synthesis of* p-*Quinones from 3,4-Dimethoxybenzyl Alcohol*

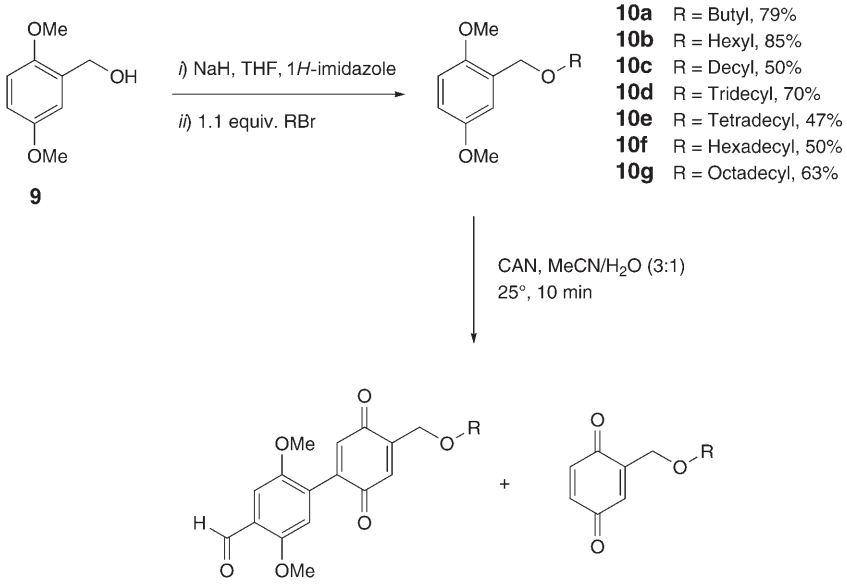


Compound **6** was then subjected to the same oxidation procedure (CrO_3 in AcOH) used for the preparation of **3** [17]. Unexpectedly, the required quinone **4** was not obtained, but ketone **7** was formed in 57% yield. When the same procedure was carried out with an analogue of **6**, having a C_5 alkyl chain (experimental data not shown), the oxidation at the benzylic position also occurred, resulting in the corresponding ketone, an analogue of **7**, in 40% yield. Another attempt to convert **6** into **4** was carried out using cerium ammonium nitrate (CAN), a strong one-electron oxidant [25] which has been used to convert polymethoxylated aromatic rings into quinones [26]. Even with this reagent, we observed that the only product isolated from the reaction was ketone **7** in 55% yield. This change in reactivity of 4-alkyl-1,2-dimethoxybenzene in relation to the 5-alkyl-1,3-dimethoxybenzene described earlier [17] was attributed to the presence of a MeO group in the *para*-position with respect to the alkyl chain, which was activating the benzylic CH_2 group.

Unable to prepare quinone **4**, we turned our attention to obtaining new sorgoleone analogues with an ether function in the side chain, as compounds of type **8** previously prepared [17] (especially with $n=4$) were more active than sorgoleone (**1**) in inhibiting the aerial parts and roots of *B. decumbens*, an aggressive weed commonly found in several crop plantations in Brazil.

The reaction of 2,5-dimethoxybenzyl alcohol (**9**) with various alkyl bromides in THF in the presence of NaH and 1*H*-imidazole afforded a series of ethers **10a**–**10g**, in reasonable yields (*Scheme 2*) [27].

Scheme 2. *Synthesis of* p-*Quinones from 2,5-Dimethoxybenzyl Alcohol*



12a	97%	**11a**	3%
12b	58%	**11b**	3%
12c	58%	**11c**	<1% (not purified)
12d	60%	**11d**	2%
12e	52%	**11e**	<1% (not purified)
12f	58%	**11f**	2%
12g	46%	**11g**	5%

These ethers **10a**–**10g** were then submitted to oxidation with CAN, anticipating the formation of the corresponding quinones **11a**–**11g**, once the oxidative demethoxylation of substituted 1,4-dimethoxybenzenes has already been reported [28]. Upon addition of ethers **10a**–**10g** to a solution of CAN in MeCN, the reaction mixture that was initially pale orange progressively became red and culminated in a brown color. After 10-min stirring at room temperature, the starting material was consumed in all cases, and exposure to the reaction conditions for longer periods resulted in the formation of complex mixtures. The expected monosubstituted *p*-benzoquinones **11a**–**11g**, formed

by oxidative demethoxylation of the ethers **10a**–**10g**, were isolated as yellow oils or solids in very low yields (*Scheme 2*). In all reactions, the major products were obtained as red or pink solids that were characterized as arylbenzoquinones **12a**–**12g**. The structures of quinones **12a**–**12g** were elucidated by spectroscopic means, and, for all of them, the major spectral differences were considered related to the absorptions of the side chain. For instance, the IR spectrum of compound **12f**, with the hexadecyl side chain, showed very strong absorptions at 1692 (ν(C=O)), 1656 ($\tilde{\nu}$(C=O)), and 1600 cm^{-1} ($\tilde{\nu}$(C=C)). The absorption due to the aldehyde C–H stretching was not clearly observed. Special features in the ^{13}C-NMR spectrum were the absorptions at 185.29 and 186.99 ppm due to C-atoms C(1)[1]) and C(4) of the quinone ring. The absorption at 188.94 ppm, corresponding to a CH group according to the DEPT spectrum, was assigned to the C-atom of the aldehyde group. The ^{1}H-NMR spectrum (300 MHz) showed a *doublet* at δ 4.38 (J = 2.1 Hz) due to H–C(7), which is coupled to H–C(2) of the quinone ring, as confirmed by the COSY spectrum. A *singlet* at δ 10.45 ppm due to the aldehyde group was correlated with the ^{13}C-NMR signal at δ 188.94 ppm in the HMQC contour plot. All ^{1}H- and ^{13}C-NMR shifts were unambiguously and directly assigned by DEPT, COSY, HMQC, and HMBC experiments. Some of the major ^{2}J(H,C) and ^{3}J(H,C) couplings by HMBC are shown in *Fig. 3*.

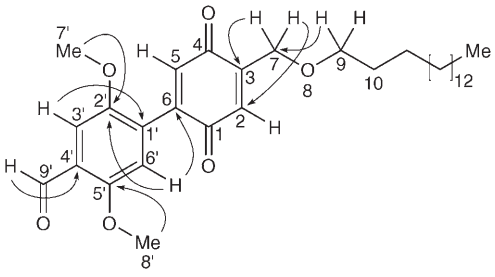
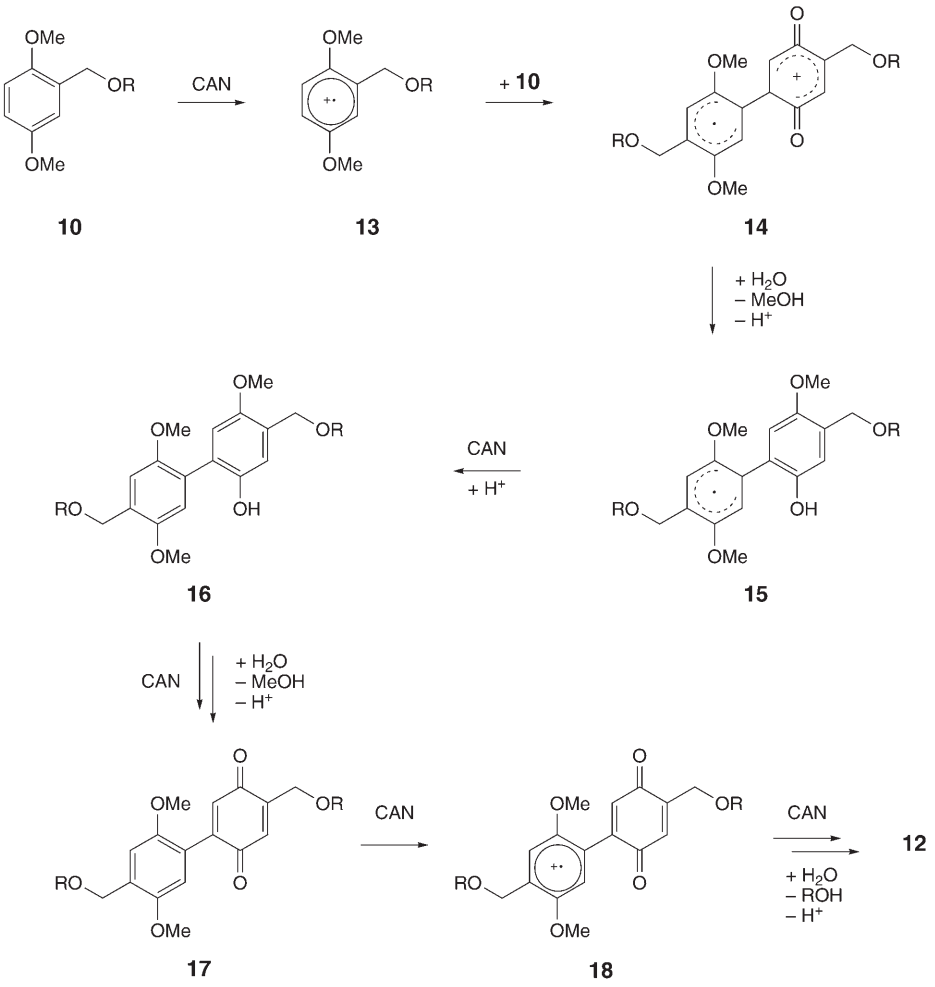


Fig. 3. *Important HMBC couplings for compound* **12f**[1])

To account for the formation of quinones **12a**–**12g**, we proposed the mechanism shown in *Scheme 3*, whereby the initial dimethoxy compound **10** undergoes a one-electron oxidation process by Ce^{4+}, resulting in the formation of a cation radical **13**. This electrophilic radical attacks the π-donor-substituted starting material **10**. The thus formed dimeric cation radicals **14** are structurally symmetric (*Scheme 3*), since the electrons can jump intramolecularly from one ring to the other. Uptake of H_2O, and loss of MeOH and H^+ may generate the cyclohexadienyl radical **15**, which, on further oxidation with CAN, may give **16** [29]. The next oxidation step with CAN results in the formation of benzoquinones **17**. The last two oxidation steps with CAN finally result in side-chain deprotonation of the primarily formed radical cation, and oxidation of the intermediate radical in an O-stabilized benzylic cation, which, after uptake of H_2O, and loss of ROH and H^+, yields the main products **12**. To account for the unexpected formation of **12**, the torsion angles between the two rings for all intermediates **17** were calculated (AM1), and the value of *ca.* 42° was found. With this conformation, the

[1]) Arbitrary numbering; for systematic names, see the *Exper. Part.*

Scheme 3. *Mechanism of the Ceric Ammonium Nitrate (CAN) Oxidation of 2-[(Alkyloxy)methyl]-1,4-dimethoxybenzene*



uptake of H_2O at the *o*-MeO of **18** is sterically hindreded on both sides of the π system, thus favoring the deprotonation at the benzylic position in these molecules (**18**).

Although *Rao et al.* [30] have obtained (in one occasion) one aryl-substituted benzoquinone in a very small yield, by silver oxide mediated oxidation of 1,4-dimethoxy-2-methylbenzene, we envisaged that the simple procedure we have described could be used for the economical preparation of several new quinones for biological evaluation.

Bioassays. The effect of quinones **12a**–**12g**, at the concentration of 5.5 ppm, on the development of the cultivars *Cucumis sativus* and *Sorghum bicolor* L., and the weeds *Euphorbia heterophylla* and *Ipomoea grandifolia* were evaluated, and the results of the

biological tests are shown in the *Table*. For comparison, the results obtained with the natural quinone sorgoleone (SGL), used as a positive control, are also included.

For *C. sativus*, compound **12d** was the most active, causing 29.5% inhibition on the aerial parts of the plant. It had practically no effect on the root development of this plant as observed for sorgoleone [17]. The other compounds, including sorgoleone, showed virtually no effect on this plant, under the test conditions.

As sorgoleone (**1**) itself had no effect on the development of *S. bicolor* (*Table*), we expected that the quinones **12a**–**12g** would also display little effect on this species. This, in fact, was observed, with a major exception of compound **12d**, which caused a significant 12.1 and 17.5% inhibition on the aerial parts and roots, respectively. Compounds **12e** and **12g** also caused a small but significant inhibition on the roots development of this species.

In a previous study, and also in the present one, we have observed that sorgoleone (**1**) had no effect on the development of *E. heterophylla* [17]. Considering that this species is a very aggressive weed associated with beans, cotton, and soybean crop plantations, and that its control is difficult, particularly due the development of biotypes resistant to imidazolinone herbicides in Brazil [31–33], we evaluated the effect of the new quinones **12a**–**12g** on the development of this plant. Among all the compounds tested, it was observed that quinone **12d** caused 34.2 and 76.5% inhibition on the aerial parts and roots, respectively.

When tested on *I. grandifolia*, an important weed in cotton, sugar-cane, coffee, soybean, and corn plantations [34], sorgoleone (**1**), and compounds **12a** and **12f** caused a small effect on the development of its aerial parts (5.3, 19.8, and 17.7%, resp.). The most significant effect was observed for compound **12d** that caused 51.7 and 85.2% inhibition of aerial parts and roots, respectively.

Although no structure–activity relationship could be established from the results presented, we have demonstrated that the chemistry described could be explored for the economical preparation of new quinones with potential use as herbicides.

Experimental Part

General. The required 3,4-dimethoxybenzaldehyde (**5**) was prepared, in 80% yield, by *Swern* oxidation [35] from the commercially available 3,4-dimethoxybenzyl alcohol. A pure sample of sorgoleone, used as a control in the bioassays, was obtained as described in [37]. Reagents and solvents were purified, when necessary, according to the usual procedures [36]. Flash column chromatography (CC): *Crosfield Sorbil C60* (32–63 μm). M.p.: an electrothermal digital apparatus (with correction). IR: *Perkin-Elmer Spectrum 1000* grating spectrometer, KBr disk or NaCl plates, scanning between 4000 cm^{-1} to 500 cm^{-1}. ^1H- and ^{13}C-NMR spectra: *Varian Mercury 300* instrument at 300 and 75 MHz, resp., $CDCl_3$ as solvent and TMS as internal reference standard ($\delta = 0$); the coupling constants (J) in Hz. MS: electron impact (EI; 70 eV) with a *VG Analytical ZAB-IF* high-resolution spectrometer. The geometry optimizations for compounds **18** were according to the semi-empirical method AM1 [38] with the program Spartan04 [39].

1-(3,4-Dimethoxyphenyl)tridecan-1-ol. To a two-neck round-bottomed flask (100 ml) were added Mg turnings (1.82 g, 75 mmol) and one small crystal of I_2 in dry THF (10 ml). The system was stirred under N_2 for 20 min, then 1-bromododecane (17.15 ml, 71.44 mmol) dissolved in dry THF (10 ml) was added. When 50% of this soln. remained, a further 5 ml of dry THF was charged into the flask concluding the addition. The formation of the *Grignard* reagent was confirmed when the color of the reaction mixture changed from yellow to gray. The *3,4-dimethoxybenzaldehyde* (**5**, 3.0 g, 17.86 mmol) dissolved in

Table. *Effect of the Quinones* **12a**–**12g**, *at the Concentration of 5.5 ppm, on the Development of Roots and Aerial Parts of Four Plant Species, after 12 to 16 Days at 25°*

Treatment (Products)	Aerial parts[a]) [g]	Aerial parts [% inhibition]	Roots [g]	Roots [% inhibition]
Cucumis sativus				
Control	0.375 a[b])	–	0.105 a	–
SGL[c])	0.355 a	5.3	0.098 a	6.5
12a	0.389 a	−3.8	0.111 a	−5.9
12b	0.468 a	−24.8	0.107 a	−2.4
12c	0.386 a	−2.9	0.113 a	−8.0
12d	0.264 b	*29.5*	0.101 a	3.5
12e	0.361 a	3.8	0.105 a	0.0
12f	0.439 a	−17.1	0.116 a	−10.1
12g	0.371 a	1.0	0.120 a	−14.7
CV [%]	16.8		23.8	
Sorghum bicolor L.				
Control	0.248 a	–	0.189 a	–
SGL	0.247 a	0.4	0.189 a	0
12a	0.234 a	6.5	0.190 a	−0.5
12b	0.261 a	−5.2	0.182 a	3.7
12c	0.278 a	−12.1	0.182 a	3.7
12d	0.218 a	12.1	0.156 b	17.5
12e	0.241 a	2.8	0.169 ab	10.6
12f	0.213 a	14.1	0.192 a	−1.6
12g	0.276 a	−11.3	0.167 ab	11.6
CV [%]	29.6		14.2	
Euphorbia heterophylla				
Control	0.114 a	–	0.017 a	–
SGL	0.112 a	1.5	0.017 a	0
12a	0.096 a	15.8	0.016 a	5.9
12b	0.120 a	−5.3	0.020 a	−17.6
12c	0.097 a	14.9	0.015 a	11.8
12d	0.075 b	*34.2*	0.004 b	*76.5*
12e	0.094 a	17.5	0.017 a	0.0
12f	0.117 a	−2.6	0.019 a	−11.8
12g	0.108 a	5.3	0.014 a	17.8
CV [%]	15.4		23.7	
Ipomea grandifolia				
Control	0.232 a	–	0.027 b	–
SGL	0.219 a	5.3	0.210 bc	22.3
12a	0.186 ab	19.8	0.020 bc	25.9
12b	0.248 a	−6.9	0.033 a	−22.2
12c	0.220 a	5.2	0.026 b	3.7
12d	0.112 c	*51.7*	0.004 c	*85.2*
12e	0.258 a	−11.2	0.029 ab	−7.4
12f	0.191 a	17.7	0.029 ab	−7.4
12g	0.230 a	0.9	0.026 b	3.7
CV [%]	16.4		26.7	

[a]) Values as means of six observations. [b]) Means within a column sharing the same letter are not significantly different at the 0.05 probability level according to *Tukey*'s test. [c]) SGL: Natural sorgoleone used as a positive control.

dry THF (10 ml) was then added to the *Grignard* reagent *via* a syringe (over a period of 30 min), and the resultant mixture stirred at r.t. for 4 h. The reaction was quenched by addition of an aq. sat. NH_4Cl soln. (20 ml). The mixture was then filtered at the pump, and the org. solvent was evaporated under reduced pressure (rotary evaporator). The residue was extracted with CH_2Cl_2 (3×15 ml), and the combined org. layers were washed with brine (20 ml). The CH_2Cl_2 soln. was dried ($MgSO_4$) and concentrated in a rotary evaporator producing a yellow oil. This oil was purified by CC (silica gel; hexane/Et_2O 1:1 (*v*/*v*)) to afford the title (5.34 g, 15.9 mmol; 89%). M.p. 62.2–63.2°. IR: 3335, 2952, 2916, 2849, 1594, 1520, 1466, 1418, 1253, 1147, 1028, 906, 847, 810, 765, 721. ^{1}H-NMR ($CDCl_3$): 0.86 (*t*, *J* = 7.2, Me(13)); 1.30 (*s*, CH_2(3)–CH_2(12)); 1.59–1.92 (*m*, CH_2(2), OH); 3.87 (*s*, MeO); 3.89 (*s*, MeO); 4.59 (*t*, *J* = 6.9, CH(1)); 6.81 (*d*, *J* = 8.4, H–C(1′)); 6.84 (*d*, *J* = 1.8, H–C(2′)); 6.88 (*dd*, *J* = 8.4, 1.8, H–C(6′)). ^{13}C-NMR ($CDCl_3$): 14.4 (C(13)); 22.9 (C(12)); 26.2 (C(3)); 29.6 (C(4)); 29.8 (C(5)); 29.8 (C(10)); 29.8 (C(6)); 29.9 (C(8)); 29.9 (C(9)); 32.2 (C(11)); 39.3 (C(2)); 56.0 (MeO); 56.1 (MeO); 74.8 (C(1)); 109.1 (C(5′)); 111.1 (C(6′)); 118.4 (C(2′)); 137.9 (C(1′)); 148.6 (C(4′)); 149.2 (C(3′)). MS: 336.2657 (1, M^+, $C_{21}H_{36}O_3^+$; calc. 336.2664), 319 (12), 318 (51), 178 (13), 177 (100), 167 (18), 164 (17), 151 (42), 146 (27), 131 (11), 121 (10), 91 (12), 77 (7), 65 (4), 55 (8), 41 (24).

1,2-Dimethoxy-4-(tridec-1-en-1-yl)benzene (**5b**). To a two-neck round-bottomed flask was added *1-(3,4-dimethoxyphenyl)tridecan-1-ol* (1 g, 2.98 mmol) dissolved in benzene (30 ml), followed by TsOH (50 mg). The mixture was stirred at 60° for 3 h, diluted with H_2O, and submitted to extraction with CH_2Cl_2 (5×20 ml). The org. phase was washed with brine (20 ml), dried ($MgSO_4$), and filtered. The filtrate was concentrated under reduced pressure in a rotary evaporator to give a brown oil. This oily residue was purified by CC (silica gel; hexane/Et_2O 1:1 (*v*/*v*)) to afford the title benzene derivative (780 mg, 2.44 mmol, 82%) white solid. M.p. 64.9–65.2°. IR: 3080, 2951, 2915, 2849, 1600, 1580, 1514, 1467, 1420, 1320, 1265, 1238, 1158, 1041, 961, 854, 795, 766, 719, 624. ^{1}H-NMR ($CDCl_3$): 0.88 (*t*, *J* = 7.2, Me(13′)); 1.20–1.40 (*m*, CH_2(5′)–CH_2(12′)); 1.40–1.52 (*m*, CH_2(4′)); 2.16 (*q*, *J* = 6.6, CH_2(3′)); 3.86 (*s*, MeO); 3.86 (*s*, MeO); 6.08 (*dt*, *J* = 15.9, 6.6, H–C(2′)); 6.30 (*d*, *J* = 15.9, H–C(1′)); 6.80 (*d*, *J* = 8.4, H–C(5)); 6.85 (*d*, *J* = 1.8, H–C(2)); 6.88 (*dd*, *J* = 8.4, 1.8, H–C(6)). ^{13}C-NMR ($CDCl_3$): 14.37 (C(13′)); 22.9 (C(12′)); 29.5 (C(4′)); 29.6 (C(5′)); 29.7 (C(10′)); 29.8–29.9 (C(6′)–C(9′)); 32.2 ((C11′)); 33.2 (C(3′)); 55.9 (MeO); 56.2 (MeO); 108.7 (C(6)); 111.3 (C(2)); 118.9 (C(1)); 129.5 (C(2′)); 129.6 (C(1′)); 131.3 (C(5)); 148.4 (C(4)); 149.2 (C(3)). MS: 318.2542 (45, M^+, $C_{21}H_{34}O_2^+$; calc. 318.2559), 191 (3), 177 (100), 164 (19), 151 (43), 146 (27), 131 (13), 115 (9), 91 (14), 77 (6), 65 (5), 55 (7), 43 (24), 41 (27).

1,2-Dimethoxy-4-(tridec-1-yl)benzene (**6**). *1,2-Dimethoxy-4-(tridec-1-en-1-yl)benzene* (700 mg, 2.2 mmol) was dissolved in AcOEt (10 ml) in a round-bottomed flask, followed by addition of 10% Pd/C (88 mg). The mixture was stirred magnetically under an atmosphere of dry H_2 (1 atm) for 5 h. The catalyst was filtered off, and the soln. was concentrated in a rotary evaporator to give **6** (655 mg, 2.05 mmol; 93%) White solid. M.p. 40.6–41.3°. IR: 2994, 2954, 2915, 2848, 1590, 1517, 1466, 1452, 1418, 1340, 1260, 1237, 1155, 1136, 1025, 935, 850, 802, 766, 719, 635. ^{1}H-NMR ($CDCl_3$): 0.87 (*t*, *J* = 7.2, Me(13′)); 1.20–1.36 (*m*, CH_2(3′)–CH_2(12′)); 1.52–1.64 (*m*, CH_2(2′)); 2.54 (*t*, *J* = 7.2, CH_2(1′)); 3.85 (*s*, MeO); 3.86 (*s*, MeO); 6.69 (*d*, *J* = 1.8, H–C(2)); 6.70 (*dd*, *J* = 8.1, 1.8, H–C(6)); 6.77 (*d*, *J* = 8.1, H–C(5)). ^{13}C-NMR ($CDCl_3$): 14.1 (C(13′)); 22.6 (C(12′)); 29.2 (C(3′)); 29.3 (C(4′)); 29.5 (C(5′)); 29.6 (C(6′); 29.7 C(10′)); 31.7 (C(11′)); 31.9 (C(2′)); 35.5 (C(1′)); 55.7 (MeO); 55.8 (MeO); 111.0 (C(6)); 111.6 (C(2)); 120.0 (C(1)); 135.5 (C(5)); 147.2 (C(4)); 148.9 (C(3)). MS: 320.2709 (43, M^+, $C_{21}H_{36}O_2^+$; calc. 320.2715), 164 (3), 152 (20), 151 (100), 137 (4), 121 (4), 107 (5), 91 (3), 77 (3), 55 (4), 41 (10).

Oxidation of **6** *Leading to 1-(3,4-Dimethoxyphenyl)tridecan-1-one* (**7**). To a round-bottomed flask were added CrO_3 (31.25 mg, 0.3 mmol), AcOH (10 ml), and a few drops of dist. H_2O up to complete dissolution. The oxidizing mixture was stirred at 0° for 30 min before addition of **6** (100 mg, 0.31 mmol) dissolved in AcOH (6 ml). The mixture was stirred at r.t. for 24 h and at 40° for 16 h. The mixture was then diluted with dist. H_2O (15 ml) and extracted with CH_2Cl_2 (5×20 ml). The combined org. layers were washed with brine (15 ml), dried ($MgSO_4$), filtered, and concentrated under reduced pressure in a rotary evaporator. The yellow oil obtained was purified by CC (silica gel; hexane/Et_2O 1:1) to give **7**, which was recrystallized from a mixture of CH_2Cl_2/hexane: 60 mg (0.18 mmol, 58% of **7**). Yellow crystals. M.p. 42.2–43.8°. IR: 3080, 3000, 2950, 2916, 2850, 1675, 1596, 1515, 1470, 1417, 1341, 1267, 1161, 1023, 877, 813, 755, 719. ^{1}H-NMR: 0.87 (*t*, *J* = 7.2, Me(13)); 1.30 (*s*, CH_2(4)–CH_2(12)); 1.60–1.80 (*m*, CH_2(3)); 2.91 (*t*, *J* = 7.2, CH_2(2)); 3.93 (*s*, MeO); 3.94 (*s*, MeO)); 6.87 (*d*, *J* = 8.4, H–C(5′)); 7.53 (*d*, *J* = 2,1, H–C(2′)); 7.57

(*dd*, *J* = 8.4, 2.1, H–C(6′)). ^{13}C-NMR ($CDCl_3$): 14.4 (C(13)); 22.9 (C(12)); 25.0 (C(3)); 29.4 (C(4)); 29.5 (C(5)); 29.6 (C(10)); 29.7 (C(6)); 29.8 (C(7)); 29.9 (C(8)); 30.0 (C(9)); 32.2 (C(11)); 38.4 (C(2)); 56.2 (MeO); 56.3 (MeO); 110.1 (C(5′)); 110.3 (C(6′)); 122.9 (C(2′)); 131.8 (C(1′)); 149.0 (C(3′)); 153.0 (C(4′)); 199.2 (C(1)). MS: 334.2501 (5, M^+, $C_{21}H_{34}O_3^+$; calc. 334.2508), 193 (8), 180 (100), 165 (71), 151 (3), 137 (6), 122 (3), 107 (3), 92 (2), 77 (7), 55 (11), 41 (12).

Preparation of **10a**. A mixture of *2,5-dimethoxybenzyl alcohol* (**9**; 1500 mg, 8.93 mmol), 1*H*-imidazole (20.0 mg), and NaH (80% dispersion in mineral oil; 803.7 mg, 26.79 mmol) in dry THF (15 ml) was stirred for 3 h under N_2 at r.t. BuBr (4922.0 mg, 3.86 ml, 35.72 mmol) was added to the mixture, and it was stirred for 6 h. The reaction was quenched by addition of dist. H_2O (20 ml), and the product was extracted with CH_2Cl_2 (3 × 20 ml). The combined org. phases were washed with brine (20 ml), dried ($MgSO_4$), filtered under vacuum, and concentrated in a rotary evaporator. The crude residue was purified by CC (silica gel; hexane/Et_2O 7:1) to yield a colorless oil (1580 mg, 7.05 mmol; 79%). The same procedure was applied for preparation of compounds **10b**–**10g**, and yields are indicated in *Scheme 2*.

1-(Butoxymethyl)-2,5-dimethoxybenzene (**10a**). Colorless oil. IR: 3050, 2956, 2868, 2834, 1593, 1503, 1463, 1362, 1275, 1217, 1179, 1158, 1094, 1050, 1029, 940, 879, 802, 712. ^{1}H-NMR ($CDCl_3$): 0.90 (*t*, *J* = 7.2, Me(4′)); 1.32–1.40 (*m*, CH_2(3′)); 1.54–1.64 (*m*, CH_2(2′)); 3.49 (*t*, *J* = 6.6, CH_2(1′)); 3.74 (*s*, 2 MeO); 4.49 (*s*, CH_2O); 6.75 (*dd*, *J* = 8.7, 2.4, H–C(4)); 6.78 (*d*, *J* = 8.7, H–C(3)); 6.99 (*d*, *J* = 2.4, H–C(6)). ^{13}C-NMR ($CDCl_3$; * the assignments can be interchanged): 14.2 (C(4′)); 19.7 (C(3′)); 32.1 (C(2′)); 56.0 (MeO)*; 56.2 (MeO)*; 67.6 (CH_2O); 70.7 (C(1′)); 111.5 (C(6)); 112.9 (C(3)); 114.6 (C(4)); 128.6 (C(1)); 151.4 (C(2)); 153.9 (C(5)). Anal. calc. for $C_{13}H_{20}O_3$: C 69.61, H 8.99, O 21.40; found: C 69.25, H 8.86, O 21.89.

1-[(Hexyloxy)methyl]-2,5-dimethoxybenzene (**10b**). Colorless oil. IR: 3050, 2931, 2857, 1593, 1500, 1464, 1361, 1275, 1217, 1179, 1158, 1095, 1050, 802, 712. ^{1}H-NMR ($CDCl_3$): 0.89 (*t*, *J* = 7.2, Me(6′)); 1.26–1.46 (*m*, CH_2(3′)–CH_2(5′)); 1.58–1.69 (*m*, CH_2(2′)); 3.51 (*t*, *J* = 6.6, CH_2(1′)); 3.78 (*s*, 2 MeO); 4.52 (*s*, CH_2O); 6.75 (*dd*, *J* = 8.7, 2.4, H–C(4)); 6.78 (*d*, *J* = 8.7, H–C(3)); 7.00 (*d*, *J* = 2.4, H–C(6)). ^{13}C-NMR ($CDCl_3$; * the assignments can be interchanged): 14.6 (C(6′)); 23.2 (C(5′)); 26.4 (C(3′)); 30.3 (C(4′)); 32.2 (C(2′)); 56.1 (MeO)*; 56.6 (MeO)*; 67.7 (CH_2O); 71.2 (C(1′)); 111.5 (C(6′)); 112.9 (C(3′)); 114.6 (C(4′)); 128.5 (C(1′)); 151.2 (C(2′)); 153.7 (C(5′)). Anal. calc. for $C_{15}H_{24}O_3$: C 71.39, H 9.59, O 19.02; found: C 71.42, H 9.47, O 19.11.

1-[(Decyloxy)methyl]-2,5-dimethoxybenzene (**10c**). Pale yellow oil. IR: 3020, 2924, 2853, 1594, 1499, 1460, 1361, 1275, 1217, 1179, 1158, 1097, 1050, 802, 712. ^{1}H-NMR ($CDCl_3$): 0.85 (*t*, *J* = 7.2, Me(10′)); 1.23 (*s*, CH_2(3′)–CH_2(9′)); 1.50–1.70 (*m*, CH_2(2′)); 3.47 (*t*, CH_2(1′)); 3.74 (*s*, 2 MeO); 4.49 (*s*, CH_2O); 6.37 (*dd*, *J* = 8.7, 2.4, H–C(4)); 6.39 (*d*, *J* = 8.7, H–C(3)); 6.97 (*d*, *J* = 2.4, H–C(6)). ^{13}C-NMR ($CDCl_3$; * the assignments can be interchanged): 14.4 (C(10′)); 22.9 (C(9′)); 26.5 (C(3′)); 29.6 (C(4′)); 29.7 (C(5′)); 29.8 (C(7′)); 29.9 (C(6′)); 30.1 (C(8′)); 32.2 (C(2′)); 55.9 (MeO)*; 56.2 (MeO)*; 67.6 (CH_2O); 71.1 (C(1′)); 111.5 (C(6)); 112.9 (C(3)); 114.6 (C(4)); 128.6 (C(1)); 151.4 (C(2)); 153.9 (C(5)). Anal. calc. for $C_{19}H_{32}O_3$: C 73.98, H 10.46, O 15.56; found: C 73.68, H 10.68, O 15.64.

1-[(Tridecyloxy)methyl]-2,5-dimethoxybenzene (**10d**). White crystals. M.p. 32.0–33.1°. IR: 3020, 2924, 2853, 1593, 1499, 1464, 1362, 1275, 1218, 1179, 1158, 1097, 1051, 880, 802, 712. ^{1}H-NMR ($CDCl_3$): 0.88 (*t*, *J* = 7.2, Me(13′)); 1.26 (*s*, CH_2(3′)–CH_2(12′)); 1.60–1.70 (*m*, CH_2(2′)); 3.50 (*t*, *J* = 6.6, CH_2(1′)); 3.78 (*s*, 2 MeO); 4.52 (*s*, CH_2O); 6.75 (*dd*, *J* = 8.7, 2.4, H–C(4)); 6.78 (*d*, *J* = 8.7, H–C(3)); 6.99 (*d*, *J* = 2.4, H–C(6)). ^{13}C-NMR ($CDCl_3$; *: the assignments can be interchanged): 14.7 (C(13′); 23.2 (C(12′)); 26.7 (C(3′)); 29.8 (C(4′)); 30.0–30.2 (C(5′)–C(10′)); 30.3 (C(11′)); 32.4 (C(2′)); 56.1 (MeO)*; 56.4 (MeO)*; 67.7 (CH_2O); 71.2 (C(1′)); 111.5 (C(6)); 112.9 (C(3)); 114.5 (C(4)); 128.5 (C(1)); 151.2 (C(2)); 153.7 (C(5)). MS: 350 (55, M^+, $C_{22}H_{38}O_3^+$), 167 (10), 152 (100), 137 (36), 135 (10), 121 (40), 108 (7), 91 (17), 77 (11), 57 (14), 55 (17), 43 (36), 41 (32). Anal. calc. for $C_{22}H_{38}O_3$: C 75.38, H 10.93, O 13.69; found: C 75.41, H 10.88, O 13.71.

1-[(Tetradecyloxy)methyl]-2,5-dimethoxybenzene (**10e**). White crystals. M.p. 37.5–39.0°. IR: 3010, 2922, 2849, 1498, 1481, 1468, 1441, 1412, 1362, 1262, 1293, 1219, 1193, 1184, 1161, 1135, 1094, 1044, 942, 866, 818, 723, 699. ^{1}H-NMR ($CDCl_3$): 0.88 (*t*, *J* = 7.2, Me(14′)); 1.25–1.35 (*m*, CH_2(3′)–CH_2(13′)); 1.56–1.68 (*m*, CH_2(2′)); 3.50 (*t*, *J* = 6.6, CH_2(1′)); 3.78 (*s*, 2 MeO); 4.52 (*s*, CH_2O); 6.75 (*dd*, *J* = 8.7, 2.4, H–C(4)); 6.79 (*d*, *J* = 8.7, H–C(3)); 7.00 (*d*, *J* = 2.4, H–C(6)). ^{13}C-NMR ($CDCl_3$; * the assignments can be interchanged): 14.4 (C(14′)); 22.9 (C(13′)); 26.5 (C(3′)); 29.6 (C(4′)); 29.8 (C(5′)); 29.8–29.9 (C(6′)–C(11′)); 30.0 (C(12′)); 32.2 (C(2′)); 55.9 (MeO)*; 56.2 (MeO)*; 67.6 (CH_2O); 71.1 (C(1′)); 111.5

(C(6)); 112.9 (C(3)); 114.6 (C(4)); 128.6 (C(1)); 151.3 (C(2)); 153.8 (C(5)). MS: 364 (58, M^+, $C_{23}H_{40}O_3^+$), 167 (10), 152 (100), 151 (98), 137 (35), 121 (37), 108 (6), 91 (17), 77 (11), 57 (15), 55 (16), 43 (37), 41 (29). Anal. calc. for $C_{23}H_{40}O_3$: C 75.78, H 11.06, O 13.17; found: C 75.80, H 11.10, O 13.10.

1-[(Hexadecyloxy)methyl]-2,5-dimethoxybenzene (**10f**). White Crystals. M.p. 43.1–43.5°. IR: 3050, 2980, 2921, 2849, 1610, 1498, 1481, 1468, 1411, 1364, 1293, 1264, 1192, 1219, 1183, 1161, 1136, 1095, 1044, 941, 866, 818, 722, 699. ^{1}H-NMR ($CDCl_3$): 0.88 (*t*, *J* = 7.2, Me(16′)); 1.20–1.42 (*m*, CH_2(3′)–CH_2(15′)); 1.56–1.68 (*m*, CH_2(2′)); 3.50 (*t*, *J* = 6.6, CH_2(1′)); 3.78 (*s*, 2 MeO); 4.52 (*s*, CH_2O); 6.76 (*dd*, *J* = 8.7, 2.4, H–C(4)); 6.79 (*d*, *J* = 8.7, H–C(3)); 6.99 (*d*, *J* = 2.4, H–C(6)). ^{13}C-NMR ($CDCl_3$; * the assignments can be interchanged): 14.4 (C(16′)); 22.9 (C(15′)); 26.5 (C(3′)); 29.6 (C(4′)); 29.8 (C(5′)); 29.8–29.9 (C(6′)–C(13′)); 30.0 (C(14′)); 32.2 (C(2′)); 55.9 (MeO)*; 56.2 (MeO)*; 67.6 (CH_2O); 71.1 (C(1′)); 111.5 (C(6)); 112.9 (C(3)); 114.6 (C(4)); 128.6 (C(1)); 151.3 (C(2)); 153.8 (C(5)). Anal. calc. for $C_{25}H_{44}O_3$: C 76.48, H 11.30, O 12.23; found: C 76.31, H 11.29, O 12.40.

1-[(Octadecyloxy)methyl]-2,5-dimethoxybenzene (**10g**). White crystals. M.p. 50.0–50.5°. IR: 3050, 3000, 2921, 2849, 1593, 1498, 1469, 1412, 1384, 1292, 1262, 1219, 1161, 1135, 1096, 1045, 942, 866, 818, 720, 699. ^{1}H-NMR ($CDCl_3$): 0.89 (*t*, *J* = 6.6, Me(18′)); 1.20–1.50 (*m*, CH_2(3′)–CH_2(17′)); 1.60–1.72 (*m*, CH_2(2′)); 3.51 (*t*, *J* = 6.6, CH_2(1′)); 3.78 (*s*, 2 MeO); 4.53 (*s*, CH_2O); 6.76 (*dd*, *J* = 8.7, 2.4, H–C(4)); 6.78 (*d*, *J* = 8.7, H–C(3)); 7.00 (*d*, *J* = 2.4, H–C(6)). ^{13}C-NMR ($CDCl_3$; *: the assignments can be interchanged): 14.7 (C(18′)); 23.2 (C(17′)); 26.8 (C(3′)); 29.9 (C(4′)); 30.0 (C(5′)); 30.1–30.2 (C(6′)–C(15′)); 30.3 (C(16′)); 32.4 (C(2′)); 56.1 (MeO)*; 56.3 (MeO)*; 67.7 (CH_2O); 71.2 (C(1′)); 111.4 (C(6)); 112.9 (C(3)); 114.6 (C(4)); 128.5 (C(1)); 151.6 (C(2)); 153.9 (C(5)). Anal. calc. for $C_{27}H_{48}O_3$: C 77.09, H 11.50, O 11.41; found: C 76.93, H 11.41, O 11.66.

Oxidation of **10a**. Compound **10a** (224 mg, 1.0 mmol) dissolved in MeCN (5 ml) was added to a soln. of CAN (197.3 g, 3.0 mmol) in MeCN/H_2O 3:1 (24 ml). After the addition of Et_2O, the color of the mixture changed from light orange to either dark red or brown. The mixture was stirred for 10 min at r.t. and extracted with CH_2Cl_2 (3 × 20 ml). The combined org. layers were washed with brine (20 ml), dried ($MgSO_4$), filtered, and finally concentrated under reduced pressured in a rotary evaporator. The crude residue was purified by CC (silica gel; hexane/Et_2O 2:1 (*v*/*v*)) to produce a pink solid identified as *4-[4-(butoxymethyl)-2,5-dioxocyclohexa-3,6-dienyl]-2,5-dimethoxybenzaldehyde* (**12a**; 174.0 mg, 97%) and a brown oil corresponding to *2-(butoxymethyl)cyclohexa-2,5-diene-1,4-dione* (**11a**; 4.9 mg, 3%).

Data of **12a**. M.p. 89.5–90.8°. IR: 3100, 3010, 2980, 2931, 2860, 1691, 1654, 1496. ^{1}H-NMR ($CDCl_3$): 0.96 (*t*, *J* = 7.2, Me(4″)); 1.36–1.50 (*m*, CH_2(3″)); 1.58–1.70 (*m*, CH_2(2″)); 3.59 (*t*, *J* = 6.6, CH_2(1″)); 3.78 (*s*, MeO–C(5)); 3.91 (*s*, MeO–C(2)); 4.40 (*d*, *J* = 2.1, CH_2O); 6.81 (*s*, H–C(6′)); 6.84 (*s*, H–C(3)); 6.94 (*t*, *J* = 2.1, H–C(3′)); 7.39 (*s*, H–C(6)); 10.46 (*s*, CHO). ^{13}C-NMR ($CDCl_3$): 14.7 (C(4″)); 19.8 (C(3″)); 32.2 (C(2″)); 56.7 (MeO–C(5)); 56.7 (MeO–C(2)); 66.1 (CH_2O); 71.8 (C(1″)); 109.8 (C(6)); 114.8 (C(3)); 125.8 (C(1)); 129.9 (C(4)); 131.8 (C(3′)); 134.8 (C(6′)); 144.7 (C(1′)); 145.9 (C(4′)); 151.3 (C(5)); 156.0 (C(2)); 185.3 (C(2′)); 187.0 (C(5′)); 188.9 (C(2″)). MS: 358 (35, M^+, $C_{20}H_{22}O_6^+$, 286 (8), 271 (43), 255 (61), 243 (11), 227 (17), 215 (15), 200 (10), 175 (5), 144 (7), 128 (7), 115 (13), 91 (6), 67 (30), 57 (39), 41 (100). Anal. calc. for $C_{20}H(22)O_6$: C 67.03, H 6.19, O 26.79; found: C 66.94, H 6.14, O 26.92.

Data of **11a**. Brown oil. IR: 3083, 2965, 2933, 2854, 1649, 1469, 1299, 1153, 1077, 722. ^{1}H-NMR ($CDCl_3$): 0.92 (*t*, *J* = 7.2, Me(4′)); 1.34–1.45 (*sext.*, *J* = 7.2, CH_2(3′)); 1.55–1.65 (*quint.*, *J* = 7.2, CH_2(2′)); 3.53 (*t*, *J* = 7.2, CH_2(1′)); 4.32 (*d*, *J* = 1.8, CH_2O); 6.75 (*s*, H–C(5), H–C(6)); 6.78–6.83 (*m*, H–C(3)). ^{13}C-NMR ($CDCl_3$): 14.1 (C(4′)); 19.5 (C(3′)); 31.9 (C(2′)); 66.0 (CH_2O); 71.6 (C(1′)); 131.4 (C(3)); 136.7 (C(6)); 136.8 (C(5)); 146.2 (C(2)); 187.3 (C(1)); 187.8 (C(4)).

The same procedure was applied for oxidation of compounds **10b**–**10g**, and yields are indicated in *Scheme 2*.

4-[4-[(Hexyloxy)methyl]-2,5-dioxocyclohexa-3,6-dienyl]-2,5-dimethoxybenzaldehyde (**12b**). Red solid. M.p. 89.4–91.0°. IR: 3050, 2990, 2938, 2858, 1686, 1652, 1601, 1497, 1468, 1403, 1344, 1285, 1224, 1211, 1146, 1087, 1040, 912, 871, 732, 646. ^{1}H-NMR ($CDCl_3$): 0.90 (*t*, *J* = 6.9, Me(6″)); 1.20–1.50 (*m*, CH_2(3″)–CH_2(5″)); 1.60–1.70 (*m*, CH_2(2″)); 3.57 (*t*, *J* = 6.6, CH_2(1″)); 3.77 (*s*, MeO–C(5)); 3.90 (*s*, MeO–C(2)); 4.39 (*d*, *J* = 2.1, CH_2O); 6.80 (*s*, H–C(6′)); 6.83 (*s*, H–C(3)); 6.92 (*t*, *J* = 2.1, H–C(3′)); 7.39 (*s*, H–C(6)); 10.45 (*s*, CHO). ^{13}C-NMR ($CDCl_3$): 14.6 (C(6″)); 23.1 (C(5″)); 26.3 (C(3″)); 30.1 (C(4″)); 32.1 (C(2″)); 56.7 (*Me*O–C(5)); 56.8 (*Me*O–C(2)); 66.1 (CH_2O); 72.1 (C(1″)); 109.8 (C(6)); 114.8 (C(3)); 125.8 (C(1)); 129.8 (C(4)); 131.8 (C(3′)); 134.8 (C(6′)); 144.7 (C(1′)); 145.9 (C(4′)); 151.3 (C(5));

156.0 (C(2)); 185.3 (C(2′)); 187.0 (C(5′)); 188.9 (CHO). MS: 386 (18, M^+, $C_{22}H_{26}O_6^+$), 271 (14), 255 (17), 67 (24), 56 (56), 43 (100), 41 (71). Anal. calc. for $C_{22}H_{26}O_6$: C 68.38, H 6.78, O 24.84; found: C 68.16, H 6.68, O 25.16.

2-[(Hexyloxy)methylcyclohexa-2,5-diene-1,4-dione (**11b**). Yellow oil. IR: 3085, 2970, 2925, 2855, 1650, 1480, 1295, 1155, 1070, 721. ^{1}H-NMR ($CDCl_3$): 0.79 (*t*, *J* = 6.3, Me); 1.15–1.32 (*m*, CH_2(3′)–CH_2(5′)); 1.45–1.62 (*m*, CH_2(2′)); 3.43 (*t*, *J* = 6.3, CH_2(1′)); 4.22 (*d*, *J* = 1.5, CH_2O); 6.63 (*s*, H–C(5), H–C(6)); 6.67–6.73 (*m*, H–C(3)). ^{13}C-NMR ($CDCl_3$): 13.9 (C(6′)); 22.5 (C(5′)); 25.7 (C(3′)); 29.5 (C(4′)); 31.5 (C(2′)); 65.7 (CH_2O); 71.7 (C(1′)); 131.1 (C(3)); 136.3 (C(6)); 136.4 (C(5)); 145.8 (C(2)); 186.1 (C(1)); 187.4 (C(4)).

4-{4-[(Decyloxy)methyl]-2,5-dioxocyclohexa-3,6-dienyl}-2,5-dimethoxybenzaldehyde (**12c**). Red solid. M.p. 90.2–91.3°. IR: 3050, 2960, 2916, 2851, 1691, 1656, 1600, 1497, 1471, 1396, 1342, 1262, 1208, 1145, 1085, 1036, 916, 870, 734. ^{1}H-NMR ($CDCl_3$): 0.88 (*t*, *J* = 7.2, Me(10″)); 1.20–1.40 (*m*, CH_2(3″)–CH_2(9″)); 1.55–1.72 (*m*, CH_2(2″)); 3.60 (*t*, *J* = 6.6, CH_2(1″)); 3.78 (*s*, MeO–C(5)); 3.89 (*s*, MeO–C(2)); 4.38 (*d*, *J* = 2.1, CH_2O); 6.78 (*s*, H–C(6′)); 6.82 (*s*, H–C(3)); 6.89 (*t*, *J* = 2.1, H–C(3′)); 7.39 (*s*, H–C(6)); 10.40 (*s*, CHO). ^{13}C-NMR ($CDCl_3$): 14.16 (C(10″)); 22.7 (C(9″)); 25.9 (C(3″)); 28.3 (C(4″)); 28.7 (C(5″)); 28.9 (C(7″)); 29.2 (C(6″)); 29.5 (C(8″)); 31.7 (C(2″)); 56.4 (*Me*O–C(5)); 56.6 (*Me*O–C(2)); 66.3 (CH_2O); 72.0 (C(1″)); 109.7 (C(6)); 114.8 (C(3)); 125.8 (C(1)); 129.6 (C(2′)); 131.9 (C(3′)); 135.0 (C(6′)); 144.7 (C(1′)); 145.9 (C(4′)); 151.4 (C(5)); 155.8 (C(2)); 185.0 (C(2′)); 186.8 (C(5′)); 188.5 (CHO). Anal. calc. for $C_{26}H_{34}O_6$: C 70.56, H 7.74, O 21.69; found: C 69.99, H 7.80, O 22.21.

2,5-Dimethoxy-4-{2,5-dioxo-4-[(tridecyloxy)methyl]cyclohexa-3,6-dienyl}benzaldehyde (**12d**). Red solid. M.p. 96.0–96.7°. IR: 3050, 2970, 2915, 2850, 1692, 1657, 1600, 1497, 1472, 1396, 1342, 1262, 1232, 1208, 1145, 1086, 1037, 916, 870, 718, 622. ^{1}H-NMR ($CDCl_3$): 0.88 (*t*, *J* = 6.9, Me(13″)); 1.20–1.35 (*m*, CH_2(3″)–CH_2(12″)); 1.55–1.70 (*m*, CH_2(2″)); 3.56 (*t*, *J* = 6.6, CH_2(1″)); 3.77 (*s*, MeO–C(5)); 3.90 (*s*, MeO–C(2)); 4.39 (*d*, *J* = 2.1, CH_2O); 6.80 (*s*, H–C(6′)); 6.83 (*s*, H–C(3)); 6.92 (*t*, *J* = 2.1, H–C(3′)); 7.39 (*s*, H–C(6)); 10.45 (*s*, CHO). ^{13}C-NMR ($CDCl_3$): 14.7 (C(13″)); 23.2 (C(12″)); 26.6 (C(3″)); 29.8–29.9 (C(4″)–C(10″)); 30.2 (C(11″)); 32.4 (C(2″)); 56.6 (2 MeO); 65.7 (C(1″)); 71.8 (CH_2O); 109.4 (C(6)); 114.5 (C(3)); 125.4 (C(1)); 129.7 (C(4)); 131.5 (C(3′)); 134.5 (C(6′)); 144.3 (C(13″); 145.5 (C(4′)); 150.9 (C(5)); 155.6 (C(2)); 184.9 (C(2′)); 186.6 (C(5′)); 188.6 (CHO). MS: 182 (1), 177 (1), 154 (3), 149 (5), 125 (7), 111 (19), 97 (41), 83 (60), 69 (65), 55 (100), 43 (87), 41 (93). Anal. calc. for $C_{29}H_{40}O_6$: C 71.87, H 8.32, O 19.81; found: C 71.68, H 8.25, O 20.07.

2-[(Tridecyloxy)methylcyclohexa-2,5-diene-1,4-dione (**11d**). Yellow oil. IR: 3075, 2960, 2930, 2859, 1653, 1469, 1295, 1150, 1080, 719. ^{1}H-NMR ($CDCl_3$): 0.97 (*t*, *J* = 7.2, Me(13′)); 1.25–1.45 (*m*, CH_2(3′)–CH_2(12′)); 1.60–1.78 (*m*, CH_2(2′)); 3.59 (*t*, *J* = 6.6, CH_2(1′)); 4.36 (*d*, *J* = 2.1, CH_2O); 6.74 (*s*, H–C(3′), H–C(4′)); 6.77–6.85 (*m*, H–C(6′)). ^{13}C-NMR ($CDCl_3$; *: the assignments can be interchanged): 14.9 (C(13′)); 23.3 (C(12′)); 26.8 (C(3′)); 29.9–30.2 (C(4′)–C(10′)); 30.3 (C(11′)); 32.5 (C(2′)); 66.2 (CH_2O); 71.9 (C(1′)); 131.1 (C(3)); 136.0 (C(6))*; 136.4 (C(5))*; 145.6 (C(2)); 185.9 (C(1)); 185.9 (C(4)).

2,5-Dimethoxy-4-{2,5-dioxo-4-[(tetradecyloxy)methyl]cyclohexa-3,6-dienyl}benzaldehyde (**12e**). Pink solid. M.p. 89.0–90.4°. IR: 3070, 2980, 2915, 2850, 1692, 1656, 1633, 1600, 1497, 1472, 1395, 1395, 1343, 1262, 1232, 1220, 1208, 1145, 1086, 1037, 916, 870, 733, 716. ^{1}H-NMR ($CDCl_3$): 0.88 (*t*, *J* = 6.6, Me(14″)); 1.20–1.42 (*m*, CH_2(3″)–CH_2(13″)); 1.60–1.72 (*m*, CH_2(2″)); 3.56 (*t*, *J* = 6.6, CH_2(1″)); 3.77 (*s*, MeO–C(5)); 3.90 (*s*, MeO–C(2)); 4.39 (*d*, *J* = 2.1, CH_2O); 6.80 (*s*, H–C(6′)); 6.83 (*s*, H–C(3)); 6.92 (*t*, *J* = 2.1, H–C(3′)); 7.39 (*s*, H–C(6)); 10.45 (*s*, CHO). ^{13}C-NMR ($CDCl_3$): 14.7 (C(14″)); 23.2 (C(13″)); 26.6 (C(3″)); 29.8 (C(4″)); 29.9–30.1 (C(5″))–C(11″)); 30.2 (C(12″)); 32.4 (C(2″)); 56.6 (*Me*O–C(5)); 56.7 (*Me*O–C(2)); 66.1 (CH_2O); 72.2 (C(1″)); 109.8 (C(6)); 114.9 (C(3)); 125.8 (C(1)); 129.6 (C(4)); 131.8 (C(3′)); 134.8 (C(6′)); 144.3 (C(1′)); 145.9 (C(4′)); 151.3 (C(5)); 156.0 (C(2)); 185.3 (C(2′)); 187.0 (C(5′)); 188.9 (CHO). MS: 196 (1), 168 (3), 154 (1), 140 (2), 125 (8), 111 (21), 97 (45), 83 (70), 69 (73), 55 (100), 43 (97), 41 (91). Anal. calc. for $C_{30}H_{42}O_6$: C 72.26, H 8.49, O 19.25; found: C 72.33, H 8.41, O 19.26.

4-{4-[(Hexadecyloxy)methyl]-2,5-dioxocyclohexa-3,6-dienyl}-2,5-dimethoxybenzaldehyde (**12f**). Pink solid. M.p. 89.4–91.1°. IR: 3030, 2952, 2915, 2850, 1692, 1656, 1600, 1497, 1472, 1395, 1342 1262, 1208, 1145, 1086, 1036, 916, 870, 716, 622. ^{1}H-NMR ($CDCl_3$): 0.88 (*t*, *J* = 7.2, Me(16″); 1.20–1.45 (*m*, CH_2(3″)–CH_2(15″)); 1.60–1.70 (*m*, CH_2(2″)); 3.56 (*t*, *J* = 6.6, CH_2(1″)); 3.77 (*s*, MeO–C(5)); 3.90 (*s*, MeO–C(2)); 4.38 (*d*, *J* = 2.1, CH_2O); 6.80 (*s*, H–C(6′)); 6.83 (*s*, H–C(3)); 6.92 (*t*, *J* = 2.1, H–C(3′)); 7.39

(*s*, H–(6)); 10.45 (*s*, CHO). ^{13}C-NMR ($CDCl_3$): 14.7 (C(16″)); 23.2 (C(15″)); 26.6 (C(3″)); 29.8 (C(4″)); 29.9–30.1 (C(5″)–C(13″)); 30.2 (C(2′)); 32.4 (C(2″)); 56.6 (*Me*O–C(5)); 56.7 (MeO–C(2)); 66.1 (CH_2O); 72.2 (C(1″)); 109.8 (C(6)); 114.9 (C(3)); 125.8 (C(1)); 129.6 (C(4)); 131.8 (C(3′)); 134.8 (C(6′)); 144.3 (C(1′)); 145.9 (C(4′)); 151.3 (C(5)); 156.0 (C(2)); 185.3 (C(2′)); 187.0 (C(5′)); 188.9 (CHO). MS: 224 (1), 196 (2), 181 (0.5), 168 (2), 153 (1), 139 (4), 125 (11), 111 (25), 97 (57), 83 (77), 69 (72), 55 (99), 43 (100), 41 (92). Anal. calc. for $C_{32}H_{46}O_6$: C 72.97, H 8.80, O 18.23; found: C 73.03, H 8.72, O 18.25.

2-[(Hexadecyloxy)methylcyclohexa-2,5-diene-1,4-dione (**11f**). Yellow oil. IR: 3080, 2955, 2920, 2850, 1650, 1470, 1292, 1080, 933, 720. ^{1}H-NMR ($CDCl_3$): 0.93 (*t*, *J* = 7.2, Me(16′)); 1.20–1.42 (*m*, CH_2(3′)–CH_2(15′)); 1.58–1.65 (*m*, CH_2(2′)); 3.56 (*t*, *J* = 7.2, CH_2(1′)); 4.35 (*d*, *J* = 2.1, CH_2O); 6.70 (*s*, H–C(5), H–C(6)); 6.78–6.84 (*m*, H–C(3)). ^{13}C-NMR ($CDCl_3$; *: the assigments can be interchanged): 14.6 (C(16′)); 23.2 (C(15′)); 26.6 (C(3′)); 29.8 (C(4′)); 29.9 (C(5′)); 30.0–30.2 (C(6′)–C(13′)); 30.3 (C(14′)); 32.4 (C(2′)); 66.2 (C(1′)); 72.1 (C(2′)); 131.3 (C(3)); 136.5 (C(6))*; 136.6 (C(5))*; 146.0 (C(2)); 186.9 (C(1)); 187.4 (C(4)).

2,5-Dimethoxy-4-{4-[(octadecyloxy)methyl]-2,5-dioxocyclohexa-3,6-dienylbenzaldehyde (**12g**). Pink solid. M.p. 88.9–90.4°. IR: 3050, 2950, 2915, 2850, 1692, 1656, 1600, 1497, 1472, 1395, 1342, 1208, 1145, 1087, 1036, 916, 870, 716. ^{1}H-NMR ($CDCl_3$): 0.88 (*t*, *J* = 6.6, Me(18″)); 1.20–1.50 (*m*, CH_2(3″)–CH_2(17″)); 1.50–1.80 (*m*, CH_2(2″)); 3.56 (*t*, *J* = 6.3, CH_2(1″)); 3.77 (*s*, MeO–C(5)); 3.90 (*s*, MeO–C(2)); 4.38 (*d*, *J* = 2.1, CH_2O); 6.80 (*s*, H–C(6′)); 6.83 (*s*, H–C(3)); 6.92 (*t*, *J* = 2.1, H–C(3′)); 7.39 (*s*, H–C(6)); 10.45 (*s*, CHO). ^{13}C-NMR ($CDCl_3$): 14.7 (C(18″)); 23.2 (C(17″)); 26.6 (C(3″)); 29.8–29.9 (C(4″)–C(15″)); 30.2 (C(16″)); 32.4 (C(2″)); 56.6 (*Me*O–C(5)); 56.7 (*Me*O–C(2)); 66.1 (CH_2O); 72.2 (C(1″)); 109.8 (C(6)); 114.8 (C(3)); 125.8 (C(1)); 129.8 (C(4)); 131.8 (C(3′)); 134.8 (C(6′)); 144.7 (C(1′)); 145.9 (C(4′)); 151.3 (C(5)); 156.0 (C(2)); 185.3 (C(2′)); 187.0 (C(5′)); 188.9 (CHO). MS: 252 (1), 224 (2), 196 (1), 181 (1), 167 (1), 153 (2), 139 (5), 125 (14), 111 (32), 97 (63), 83 (76), 69 (72), 55 (100), 43 (93), 41 (86). Anal. calc. for $C_{34}H_{50}O_6$: C 73.61, H 9.08, O 17.30; found: C 73.81, H 9.10, O 17.09.

2-[(Octadecyloxy)methyl]cyclohexa-2,5-diene-1,4-dione (**11g**). Yellow solid. M.p. 78.5–79.3°. IR: 3070, 2950, 2918, 2849, 1651, 1471, 1292, 1147, 1076, 930, 718. ^{1}H-NMR ($CDCl_3$): 0.88 (*t*, *J* = 7.2, Me(18′)); 1.20–1.45 (*m*, CH_2(3′)–C(17′)); 1.58–1.70 (*m*, CH_2(2′)); 3.53 (*t*, *J* = 6.6, CH_2(1′)); 4.33 (*d*, *J* = 2.1, CH_2O); 6.73 (*s*, H–C(5), H–C(6)); 6.83 (*m*, H–C(3)). ^{13}C-NMR ($CDCl_3$): 14.4 (C(18′)); 22.9 (C(17′)); 26.3 (C(3′)); 29.5 (C(4′)); 29.6 (C(5′)); 29.7–29.8 (C(6′)–C(15′)); 29.9 (C(16′)); 32.1 (C(2′)); 65.9 (CH_2O); 71.8 (C(1′)); 131.0 (C(3)); 136.2 (C(5)); 136.3 (C(6)); 146.0 (C(2)); 186.7 (C(1)); 187.1 (C(4)). MS: 390 (2, M^+, $C_{25}H_{42}O_3^+$), 233 (1), 151 (2), 138 (62), 122 (62), 111 (14), 97 (32), 83 (41), 69 (46), 55 (83), 43 (100), 41 (78).

Biological Assays. The experiments were carried out in a greenhouse with *Cucumis sativus*, *Sorghum bicolor*, *Euphorbia heterophylla*, and *Ipomea grandifolia*. Seeds of these species were obtained from the collection maintained at the Plant Science Laboratory at Federal University of Viçosa. All undersized and damaged seeds were discarded, and the assay seeds were preselected for uniformity. The bioassays were carried out using plastic pots, and the total growth of the test plants was evaluated. The test solns. were prepared by dissolving 5.0 mg of each quinone (*i.e.*, **12a**–**12g**) in a mixture of xylene (60 µl), pentan-3-one (20 µl), and *Tween 40* (polyoxyethylene-sorbitan monopalmitate, 2 drops). The volumes of the resulting mixtures were completed to 100 ml with dist. H_2O. Control experiments were carried out using a soln. with the same composition described above, but without the test compound. A positive control was carried out using natural sorgoleone (SGL), isolated as described in [37] and formulated in the same way as the test compounds.

To each of plastic pots of 0.10 dm^3 containing 165 g of washed sand soaked in 20 ml of the test soln. in order to result in a concentration of 5.5 ppm of the test quinone in relation to the substrate (sand), ten seeds of each test plant were placed at 0.5-to-1.0-cm depth, and the pots were kept in a greenhouse at 25°, watered regularly to maintain the humidity at 12% (*w*/*w*), and three times a week, a solution containing the required nutrients was applied.

The test plants *C. sativus*, *S. bicolor*, *E. heterophylla*, and *I. grandifolia* were harvested 12, 12, 13, and 16 days after sowing, resp. The harvest was performed by separating the radicle from the aerial parts. These parts were kept separately in paper bags and dried at 70 ± 1°, until constant weight, and the mass of the dried matter was determined. The data were analyzed using *Tukey*'s test at 0.05 probability level. All treatments were replicated six times in a completely randomized design. The percentage growth

inhibition of aerial parts and roots was calculated in relation to the mass of the roots and aerial parts of the control, resp.

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