116. Phenols and Quinones from Seeds of Different *Iris* Species

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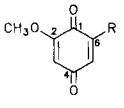
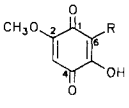
(18.III.92)

The seed oils of *I. pseudacorus* LINN., *I. sibirica* LINN., and *I. missouriensis* NUTTAL. contain appreciable amounts of phenols, quinones, and resorcinols, substituted with homologous alkyl or alkenyl side chains. The structure elucidation of these compounds is described, and their possible biosynthesis is discussed.

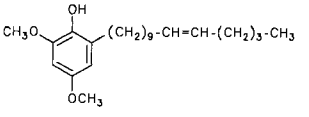
Introduction. – Our interest in structure, biosynthesis, and biological significance of the iridals, unusual triterpenoids, which can be isolated from different *Iris* species [1], led us to look for these compounds in various parts of the plants. Whereas they are abundant in roots, rhizomes, and leaves [2], no iridals are found in seeds, and they are not formed until several days after germination. Instead, besides triglycerides, several substances, showing mass spectra with a fragmentation pattern characteristic for aromatic compounds, are the main lipid components of the seed oil. In earlier investigations, several phenols and quinones have been found in lipid extracts of seeds from different Iridaceae. Thus, irisquinone **1a** was isolated from the seed of *I. pseudacorus* LINN. [3], and *I. pallasii* FISCH. *var. chinensis* FISCH. seed contains the hydroxy derivative **2a** [4]. The corresponding homologue, irisoquin (**2b**), bearing a saturated C_{18} side chain, is a constituent of *I. missouriensis* NUTTAL. roots [5]. Recently, the methylated hydroquinone **3** and the resorcinol derivative **4a** were found in the seed oil of *Belamcanda chinensis* L. [6]. By GC/MS, we



1a R = CH_3–$(CH_2)_5$–CH=CH–$(CH_2)_9$
b R = CH_3–$(CH_2)_5$–CH=CH–$(CH_2)_7$
c R = CH_3–$(CH_2)_{14}$
d R = CH_3–$(CH_2)_{18}$



2a R = CH_3–$(CH_2)_7$–CH=CH–$(CH_2)_9$
b R = CH_3–$(CH_2)_{17}$
c R = CH_3–$(CH_2)_5$–CH=CH–$(CH_2)_9$
d R = $C_{15}H_{29}$
e R = CH_3–$(CH_2)_{14}$



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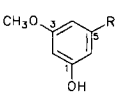
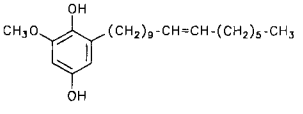


4a R = CH_3–$(CH_2)_3$–CH=CH–$(CH_2)_9$
b R = CH_3–$(CH_2)_5$–CH=CH–$(CH_2)_9$
c R = $C_{15}H_{29}$
d R = CH_3–$(CH_2)_{14}$



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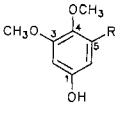


6a R = CH_3–$(CH_2)_5$–CH=CH–$(CH_2)_9$
b R = CH_3–$(CH_2)_{16}$
c R = $C_{15}H_{29}$
d R = CH_3–$(CH_2)_{14}$
e R = $C_{19}H_{37}$

found in seed extracts from *I. pseudacorus* LINN., *I. sibirica* LINN., and *I. missouriensis* NUTTAL. more than 15 homologous and related compounds. Therefore, it seemed appropriate, to undertake a thorough analysis of these extracts.

Results. – Initial separation of the crude lipid extract of *I. pseudacorus* seeds was carried out by chromatography on silica gel. Four groups of homologous substances, which were easily distinguished by their base peaks in the mass spectra, were separated by rechromatography on silica gel or preparative reversed-phase (RP) HPLC.

The compounds of the first group, amounting to 10% of the oil, showed a base peak at m/z 154. The two main components were isolated by TLC and crystallization from MeOH. By comparison of its properties with the data in [3], the major product, showing a molecular ion at m/z 374, was easily identified as irisquinone **1a**. A benzoquinone moiety with identical substitution pattern is present in the second component as seen by the ^{1}H-NMR spectrum. A molecular ion at m/z 346 indicated that a pentadecenyl instead of a heptadecenyl side chain is located at C(6). The lack of an IR absorption in the region 980–960 cm^{-1} proved a (*Z*)-configuration of the C=C bond. Heptanal was found after ozonolysis with reductive workup (Ph_3P). Thus, 2-methoxy-6-(pentadec-8-enyl)-1,4-benzoquinone (**1b**) is at hand. Two further quinones of this type are present in very small amounts and, therefore, could not be isolated. From their mass spectra and their GC retention behaviour, they were identified as the pentadecyl derivative **1c** and the nonadecyl homologue **1d**. The nature of **1c** was confirmed by catalytic hydrogenation of **1b** (Pd/C) and subsequent regeneration of the quinone moiety (O_2).

In the crude oil, irisquinone **1a** and the corresponding hydroquinone **5** were found in a ratio of 6:1. The structure of **5** was established by $Na_2S_2O_4$ reduction of **1a** and comparison of retention time and mass spectrum of the product. Presumably, compound **5** is oxidized during the initial separation on silica gel, as only the quinone **1a** but no hydroquinone was eluted from the column. In the crude extract, no other hydroquinone corresponding to the quinones **1b–d** could be detected by GC/MS.

The second homologous series constituted 4% of the lipid extract and consisted of three compounds, which are characterized by a base peak at m/z 168 in their MS. Due to the rather high polarity of the substances, and since the mixture is dominated by one component, this product was readily isolated during the initial column chromatography on silica gel. As seen by the UV spectrum, again a 1,4-benzoquinone is present. The ^{1}H-NMR spectrum shows a MeO group and an alkenyl side chain as substituents. Besides the two olefinic H-atoms of the side chain, however, a *singlet* of only one additional olefinic H-atom is found at 5.80 ppm. A broad signal at 7.20 ppm, which disappears upon addition of D_2O and the ready reaction of the compound with trifluoro-*N*-methyl-*N*-(trimethylsilyl)acetamide (TFMSA), to form a mono-Me_3Si derivative, prove that the fifth substituent of the ring system is an OH group. A NOE between the MeO group and the olefinic ring proton and comparison of the spectral properties with the data published for **2b** [5] showed that the same substitution pattern is present. A molecular ion at m/z 390, however, indicates that C(6) of the ring is substituted by a heptadecenyl instead of a C_{18} side chain. As shown for **2b**, the base peak at m/z 168 may be explained by loss of the side chain between C(1′) and C(2′), coupled with the transfer of an H-atom to the benzylic C-atom [5] [7]. (*Z*)-Configuration of the C=C bond and its position at C(10′) again was established by IR spectroscopy and ozonolysis. Thus, the compound is 6-(heptadec-10-enyl)-5-hydroxy-2-methoxy-1,4-benzoquinone (**2c**). The homologous structures with

pentadecenyl (**2d**) or pentadecyl side chains (**2e**) are tentatively assigned to the two minor constituents on the basis of their molecular ions at *m/z* 360 and 362, respectively. Due to the small amount of oil at hand, their isolation was not possible, and, therefore, the position and configuration of the C=C bond in the side chain of **2d** was not determined, but the compound may be identical with maesanin, which has a (*Z*)-C=C bond in C(10′) position, and recently was isolated from *Maesa lanceolata* [7].

In contrast to the compounds described above, the five constituents of the third group, making up 7% of the oil, possess an aromatic ring system, which cannot be oxidized to a quinone. They are characterized by a strong peak at *m/z* 168 and a base peak at *m/z* 153 in the MS, and the main component, showing a molecular ion at *m/z* 390, was isolated by preparative RP-HPLC. As shown by the addition of one Me_3Si group upon reaction with TFMSA and by two Me signals at 3.71 and 3.77 ppm, respectively, in the ^{1}H-NMR spectrum, the aromatic ring holds one OH and two MeO groups. An *AB* system at 6.18 and 6.27 ppm, showing a coupling constant $J(AB) = 2.9$ Hz, is brought about by two ring protons in *m*-position. Thus, the same ring substituents as in **3** are present, except for a heptadecenyl side chain with a (*Z*)-C=C bond at C(10′) instead of the pentadecenyl group. Distinct differences in the ^{13}C resonances of the ring C-atoms show, however, that the substitution pattern is different. Upon irradiation of the aromatic H at 6.27 ppm an NOE is observed with the MeO group at 3.77 ppm, whereas the MeO group at 3.71 ppm only gives a NOE with the benzylic H-atoms (2.52 ppm), which in turn are affected upon irradiation of the second aromatic H (6.18 ppm). Thus, unambiguous choice was made for structure **6a**. The peak at *m/z* 168 in the MS may be formed by the same rearrangement, as outlined for compound **2c**, and additional loss of Me leads to the base peak *m/z* 153. Hydrogenation of **6a** proved that one of the side components in this series (**6b**) holds a saturated C_{17} chain. The other minor constituents, present in too small quantities to be isolated, contain pentadecenyl (**6c**), pentadecyl (**6d**), and nonadecenyl (**6e**) substituents, as seen by their GC and MS behaviour.

Finally, three resorcinol derivatives of the general structure **4** are found, amounting to 2% of the oil. They are easily recognized by a base peak at *m/z* 138 in their MS, again derived from the loss of the side chain, leaving one H-atom at the benzylic C-atom [6]. The main component **4b** has identical NMR resonances for the ring system, as found for belamcandol B (**4a**) [6]. It is substituted, however, by a heptadecenyl chain with (*Z*)-C=C bond in position C(10′). The two other substances in this series, only present in analytical amounts, are the pentadecenyl and pentadecyl homologues **4c** and **4d**, respectively. Compound **4c** may be identical with **4a**, but again the C=C bond in the alkenyl chain of this minor component was not characterized any further.

As shown in the *Table*, the relative composition of these compounds, adding up to 24.5% of the extract, is not significantly different in the three *Iris* species studied. In contrast to the oil of *Belamcanda chinensis* [6], each series of the phenols or quinones is dominated by the heptadecenyl derivatives, whereas the C_{15} or C_{19} homologues are present in much smaller quantity.

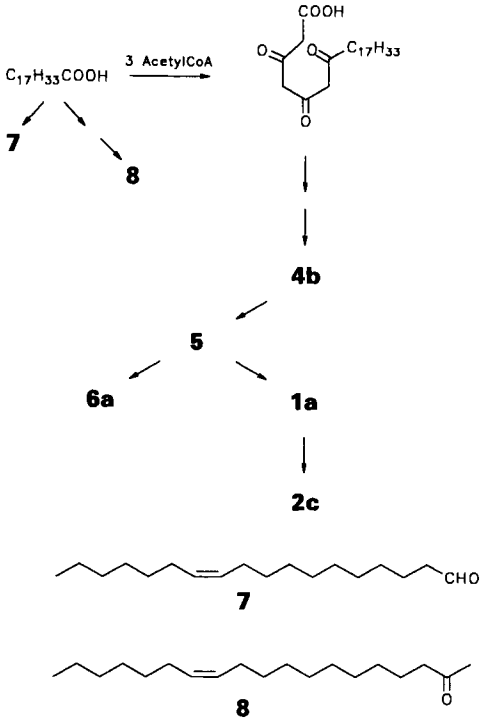
Discussion. – The rather high amount of these substances in the seed oil of various Iridaceae raises the question as to their biological function. At least two of the known compounds, mentioned above, have been shown to possess interesting biological activities. Thus, cytotoxic properties are reported for irisoquin (**2b**) [5]. Its homologue with a $C_{11}H_{23}$ substituent, isolated from the mangrove *Aegiceras corniculatum*, shows piscicidal

Table. *Relative Composition* [%] *of the Phenols and Quinones in Seed Oils from Different* Iris *Species* (tr. = trace component < 0.1%)

Compound	*I. pseudacorus*	*I. missouriensis*	*I. sibirica*	Compound	*I. pseudacorus*	*I. missouriensis*	*I. sibirica*
1a	32.0	49.5	40.8	**4c**	tr.	tr.	tr.
1b	6.5	1.3	9.3	**4d**	0.9	0.1	tr.
1c	0.9	1.3	3.4	**5**	6.2	6.7	21.0
1d	tr.	tr.	tr.	**6a**	34.0	21.6	14.0
2c	11.5	13.0	8.2	**6b**	tr.	tr.	tr.
2d	0.2	0.1	tr.	**6c**	1.7	0.9	2.2
2e	0.2	1.0	tr.	**6d**	1.8	0.1	0.5
4b	3.9	3.8	0.6	**6e**	0.2	0.6	tr.

activity [8], and belamcandol A (**3**), the corresponding quinone [6], and maesanin [7] are potent inhibitors of 5-lipoxygenase. It is worth mentioning that the contact allergen primin, found in *Primula obconica* and responsible for the primrose dermatitis, has the same overall structure **1** with a pentyl substitution at C(6) [9]. It is very probable, therefore, that the compounds, reported here, are produced by the plant and stored in the seed to protect it or the young seedling. This assumption is supported by the observation that the compounds disappear a short time after germination. It is interesting to note that, at least in *I. pseudacorus* seeds, another protective mechanism exists. Thus, we found that the shells, but not the kernel, contained considerable amounts of resveratrol. It is

Scheme



well known that the production of this phytoalexin is usually caused by infestation with pests.

Undoubtedly, the biosynthesis of all compounds, found in the course of this study, follows a common polyketide pathway. Thus, by the addition of three acetate units to the appropriate fatty acid a triketide may be formed, which after cyclization, decarboxylation, aromatization, and methylation yields the resorcinols with structure **4**. Subsequent oxidation gives the hydroquinones or quinones (*Scheme*). The position of the C=C bond in the alkenyl side chains proves that predominantly vaccenic and palmitoleic acid are the educts of this biogenetic sequence. This assumption is supported by the occurrence of (*Z*)-octadec-11-enal (**7**) and (*Z*)-nonadec-12-en-2-one (**8**) in one silica-gel fraction of the crude extract. The nature of these compounds was elucidated by MS and confirmed by comparison with synthetic reference samples. The most plausible explanation of their formation is reduction of vaccenic acid or its elongation with one acetate moiety and subsequent decarboxylation. The seeds contain, however, no free vaccenic acid or its derivatives and only trace amounts of palmitoleic acid. Therefore, the use of vaccenic acid, which is formed in higher plants by chain elongation of palmitoleic acid or isomerization of oleic acid [10], during the synthesis and storage of the phenols and quinones in the seeds may be restricted to the polyketide synthase, responsible for the production of the aromatic compounds.

Financial support of the *Deutsche Forschungsgemeinschaft*, Bad Godesberg (Ma 1172/2-1), and the *Fonds der chemischen Industrie*, Frankfurt, is gratefully acknowledged.

Experimental Part

General. Plant Material: Seeds of *I. pseudacorus* and *I. sibirica* were harvested in the garden of our institute or purchased from *Bornträger & Schlemmer*, D–6521 Offstein. The seed of *I. missouriensis* was collected in September 1988 north of Lake Superior, close to White River, Ontario, Canada. GLC: *Shimadzu GC 8A*, cap. column *OV 1* (15 m, 0.25 mm i.d.) Temp. progr.: 80° (1 min) –300° (10°/min). The compounds described were eluted between 220° and 300°. Anal. HPLC: *Kontron* model *200*, column: *LiChroCart RP 18* (125 mm, *Merck*), solvent: MeOH/H_2O 7:3 (5 min), lin. gradient to 100% MeOH (15 min), 100% MeOH (20 min); *Hewlett-Packard-1040A* diode-array detector. UV spectra were recorded during the HPLC analysis. Prep. HPLC: *Altex* model *420*, column: *Spherisorb 5 ODS* (240 mm, 5-mm i.d., *Chromatographie-Service*). IR spectra: *Pye-Unicam SP3-200*. NMR spectra: *Bruker WH-300* (^{1}H: 300 MHz, ^{13}C: 75.4 MHz), *Bruker AC 80E* (^{1}H: 80 MHz) in $CDCl_3$, chemical shifts in ppm δ relative to TMS (= 0 ppm), coupling constants *J* in Hz. MS: *Finnigan-MAT 4510*; GC/MS (EI: 70 eV), *m/z* (rel. intensity in %).

Isolation. The ground seeds were extracted with $CHCl_3$/MeOH 1:2 (*v/v*). After evaporation, the residue was partitioned between Et_2O and H_2O. The org. phase was dried ($MgSO_4$) and evaporated to give the crude oil. In this way, from 20 g of *I. pseudacorus* seeds 1.66 g (8.3%) of extract were obtained. The seeds of *I. sibirica* and *I. missouriensis* (1 g each) yielded 117 mg (11.7%) and 111 mg (11.1%) crude oil, respectively. Initial separation of the extracts was carried out on silica gel using petroleum ether/Et_2O/$CHCl_3$/acetone/MeOH. Only the fractions obtained from the extract of *I. pseudacorus* subsequently were used for the isolation of individual compounds, whereas the fractions from the *I. sibirica* and *I. missouriensis* oils were merely analyzed by GC/MS. The fraction eluted with petroleum ether/Et_2O 7:3 (*v/v*) contained the homologous series (**1**, **4**, and **6**), the aldehyde **7**, and the ketone **8**. From this mixture, the following compounds were isolated: the quinones **1a** (120 mg) and **1b** (15 mg) by TLC on silica gel (toluene/MeOH 9:1, *v/v*) and subsequent recrystallization from MeOH, the phenol **6a** (45 mg) by prep. HPLC (MeOH/H_2O 95:5, *v/v*) followed by an additional purification on a silica-gel column (petroleum ether/Et_2O 97:3, *v/v*), and the resorcinol **4b** (17 mg) by a second chromatography on silica gel (petroleum ether/Et_2O 97:3, *v/v*). The hydroxy-quinone **2c** (40 mg) was obtained from the initial silica-gel column with Et_2O/acetone 9:1 (*v/v*). The minor constituents were identified by GC/MS in the appropriate fractions of the first separation. Synthetic samples of **7** and **8** were prepared from vaccenic acid (*Sigma*).

Reduction of **1a** to the corresponding hydroquinone **5** was achieved by shaking a soln. of the quinone (10 mg) in 10 ml of Et_2O with an equal volume of a 10% aq. $Na_2S_2O_4$ soln. for 15 min. The org. phase was washed (sat. brine) and dried ($MgSO_4$) before use for GC and GC/MS analysis.

Hydrogenation of **1b** was carried out by passing a slow stream of H_2 for 4 h through a 5% soln. of the compound in heptane. Pd/C (10%) served as the catalyst. The H_2 subsequently was substituted by O_2 (4 h) to regenerate the quinone system.

Silylation of the phenols was achieved by adding 5 µl of trifluoro-*N*-methyl-*N*-(trimethylsilyl)acetamide to a 0.1% soln. of the compound in Et_2O. After 15 min at r.t. the soln. was used for GC or GC/MS without further workup.

2-Methoxy-6-[(Z)-pentadec-8′-enyl]-1,4-benzoquinone (**1b**). UV: 268. IR (KBr): 2920, 2840, 1680, 1640, 1580, 1450, 1310, 1220. ^{1}H-NMR: 6.44 (*dt*, *J*(5,3) = 2.4, *J*(5,1′) = 1.3, H–C(5)); 5.83 (*d*, *J*(3,5) = 2.4, H–C(3)); 5.30 (*t*, *J* = 4.8, H–C(8′), H–C(9′)); 3.77 (*s*, MeO); 2.38 (*t*, 2 H–C(1′)); 1.95 (*m*, H–C(7′), H–C(10′)); 1.46 (*m*, 2 H–C(2′)); 1.24 (br., 16 H); 0.84 (*t*, 3 H–C(15′)). ^{13}C-NMR: 187.5 (*s*, C(4)); 182.0 (*s*, C(1)); 158.8 (*s*, C(6)); 147.5 (*s*, C(2)); 138.8 (*s*, C(5)); 130.3 (*d*, C(8′), C(9′)); 107.0 (*d*, C(3)); 56.2 (*q*, MeO); 31.7 (*t*, C(1′)); 29.7 (*t*, C(2′)); 27.2–29.6 (9 C); 22.6 (*t*, C(14′)); 14.0 (*q*, C(15′)). EI-MS: 346 (13, M^+), 166 (16), 154 (100), 153 (90), 152 (8).

2-Methoxy-6-pentadecyl-1,4-benzoquinone (**1c**). EI-MS: 348 (37, M^+), 166 (10), 154 (100), 153 (90), 152 (10).

2-Methoxy-6-nonadecyl-1,4-benzoquinone (**1d**). EI-MS: 404 (11, M^+), 154 (100), 153 (92).

6-[(Z)-Heptadec-10′-enyl]-5-hydroxy-2-methoxy-1,4-benzoquinone (**2c**). UV: 290. IR (KBr): 3340, 2920, 1680, 1630, 1590, 1380, 1310, 1200. ^{1}H-NMR: 7.20 (br. *s*, OH); 5.80 (*s*, H–C(3)); 5.32 (*t*, H–C(10′), H–C(11′)); 3.85 (*s*, MeO); 2.43 (*m*, 2 H–C(1′)); 1.98 (*m*, 2 H–C(9′), 2 H–C(12′)); 1.25 (br., 22 H); 0.86 (*t*, 3 H–C(17′)). EI-MS: 390 (32, M^+), 169 (67), 168 (100), 167 (29), 153 (42).

5-Hydroxy-2-methoxy-6-(pentadecenyl)-1,4-benzoquinone (**2d**). EI-MS: 362 (11, M^+), 169 (40), 168 (100), 167 (11), 153 (24).

5-Hydroxy-2-methoxy-6-pentadecyl-1,4-benzoquinone (**2e**). EI-MS: 364 (10, M^+), 169 (18), 168 (100), 167 (10), 153 (22).

3-Methoxy-5-[(Z)-heptadec-10′-enyl]phenol (**4b**). EI-MS: 360 (2, M^+), 151 (7), 139 (6), 138 (100), 137 (17). UV: 203. IR: 3590, 3320, 1590, 1460, 1140. ^{1}H-NMR: 6.31 (br. *t*, *J* = 2.2, H–C(6)); 6.24 (br. *t*, *J* = 2.2, H–C(6)); 6.21 (*t*, *J* = 2.2, H–C(2)); 5.33 (*t*, *J* = 4.6, H–C(10′), H–C(11′)); 4.87 (*s*, OH); 3.74 (*s*, OCH_3); 2.49 (*t*, 2 H–C(1′)); 1.57 (*m*, 2 H–C(2′)); 1.25 (br., 20 H); 0.87 (*t*, 3 H–C(17′)). ^{13}C-NMR: 160.8 (*s*, C(3)); 156.5 (*s*, C(1)); 145.7 (*s*, C(5)); 129.9 (*d*, C(10′), C(11′)); 107.9 (*d*, C(6)); 106.8 (*d*, C(4)); 98.7 (*d*, C(2)); 55.2 (*q*, OCH_3); 31.8 (*t*, C(1′)); 31.1 (*t*, C(2′)); 29.7–27.2 (9 C); 22.6 (*t*, C(16′)); 14.1 (*q*, C(17′)).

3-Methoxy-5-(pentadecenyl)phenol (**4c**). EI-MS: 332 (2, M^+), 151 (8), 139 (6), 138 (100), 137 (14).

3-Methoxy-5-pentadecylphenol (**4d**). EI-MS: 334 (2, M^+), 151 (8), 139 (7), 138 (100), 137 (15).

5-[(Z)-Heptadec-10′-enyl]-3,4-dimethoxyphenol (**6a**). UV: 203. IR (KBr): 3550, 1600, 1470, 1150. ^{1}H-NMR: 6.27, 6.18 (*AB*, J_{AB}(2,6) = 2.9, H–C(2), H–C(6)); 5.32 (*t*, *J* = 4.6, H–C(10′), H–C(11′)); 3.77 (*s*, MeO); 3.71 (*s*, MeO); 2.52 (*t*, 2 H–C(1′)); 1.99 (*m*, 2 H–C(10′), 2 H–C(11′)); 1.52 (*m*, 2 H–C(2′)); 1.25 (br., 20 H); 0.85 (*t*, 3 H–C(17′)). ^{13}C-NMR: 153.3 (*s*, C(1)); 151.7 (*s*, C(3)); 140.8 (*s*, C(4)); 137.2 (*s*, C(5)); 129.9 (*d*, C(10′), C(11′)); 107.3 (*d*, C(6)); 98.1 (*d*, C(2)); 60.8 (*q*, MeO); 55.6 (*q*, MeO); 31.8 (*t*, C(1′)); 30.6 (*t*, C(2′)); 29.7–27.2 (11 C); 22.6 (*t*, C(16′)); 14.1 (*q*, C(17′)). EI-MS: 390 (63, M^+), 168 (46), 167 (26), 154 (20), 153 (100).

3,4-Dimethoxy-5-(pentadecenyl)phenol (**6c**). EI-MS: 362 (40, M^+), 168 (33), 167 (17), 154 (14), 153 (100).

3,4-Dimethoxy-5-pentadecylphenol (**6d**). EI-MS: 364 (30, M^+), 168 (29), 167 (18), 153 (100), 152 (44).

3,4-Dimethoxy-5-(nonadecenyl)phenol (**6e**). EI-MS: 418 (23, M^+), 168 (31), 154 (15), 153 (100), 152 (33).

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