33. Isolation, Structure, and Biological Activities of Long-Chain Catechols of *Plectranthus sylvestris* (*Labiatae*)

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Antioxidant activity guided fractionation of extracts of the aerial parts of the title plant and HPLC separation yielded a series of oxygenated long-chain alkylcatechols. Their structures were inferred by spectroscopic methods and chemical transformations to be the novel 4-[(2*S*,4*R*,6*S*)-4-acetyloxy)tetrahydro-6-pentyl-2*H*-pyran-2-yl]benzene-1,2-diol (**1a**), 4-[(2*S*,4*R*,6*S*)-tetrahydro-4-hydroxy-6-pentyl-2*H*-pyran-2-yl]benzene-1,2-diol (**1b**), 4-[(3*S*,5*S*)-5-(acetyloxy)-3-hydroxydecyl]benzene-1,2-diol (**2a**), 4-[(3*S*,5*S*)-3-(acetyloxy)-5-hydroxydecyl]benzene-1,2-diol (**2b**), (3*S*,13*Z*)-1-(3,4-dihydroxyphenyl)-3-hydroxydocos-13-en-5-one (**3a**), (*Z*)-1-(3,4-dihydroxyphenyl)docos-13-en-5-one (**4**), besides the known 1-(3,4-dihydroxyphenyl)icosan-5-one (**5**). The absolute configurations of the optically active compounds which are structurally related to the [*n*]-gingerols (**6**) and -diols (**7**) were established by the high-field ^{1}H-NMR application of *Mosher*'s method. All compounds are *in vitro* potent antioxidants, inhibiting the Fe^{2+}-catalysed autooxidation of linoleic acid in the same order of magnitude as the commercial antioxidant 2,6-di(*tert*-butyl)-4-methylphenol (BHT). The dose-dependent inhibitory effects on soybean-lipoxygenase are in the μmol range, that of the most effective compound (**3a**) in the nmol range, hence being significantly more potent than the known anti-inflammatory and analgesic drugs indomethacin and nordihydroguaiaretic acid.

Introduction. – In continuation of our current program concerning the isolation and synthesis of genuine constitutents of African and Asian *Labiatae* species of the genera *Coleus*, *Plectranthus* and *Solenostemon* with respect to antioxidants, inhibitors of the arachidonate metabolism and allergens [1–3], we have investigated *Plectranthus sylvestris* GÜRKE[2]). Extraction of the aerial parts of the plant followed by partition (hexane/MeOH 1:9) and antioxidant activity guided chromatography (*Sephadex LH-20*, silica gel, modified β-carotene assay [5]) and crystallization afforded the main constituent **1a** (0.052%)[3]). Subsequent prep. HPLC (*C-18*) yielded the catechols **1b** (0.004%), **2a**/**2b** (0.01%) as an unseparable mixture (*ca.* 1:1), and **3a** (0.004%), besides the already known long-chain alk(en)ylcatechols **4** (0.083%) and **5** (0.047%) [1] [2][4]). The structures of the isolated crystalline constituents were established by spectroscopic methods and chemical transformations.

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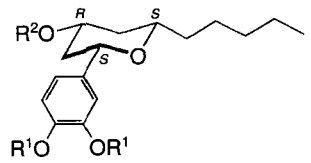
[1]) Part of the Ph. D. Thesis of *M.J.*, in preparation.

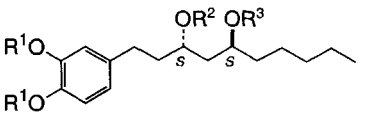
[2]) *Plectranthus sylvestris* is native of East Africa; it was found originally in the Woody Hills and gorges around the Kilimandscharo [4]. The plant material was collected in the surroundings of Nairobi by *J. Kahurananga*, East-African Herbarium, Nairobi, and the air-dried aerial parts were sent to us on May 10, 1977.

[3]) Yields are given for crystalline, pure compounds from air-dried plant material. As the catechols decompose rather quickly on silica gel and in solution, the real content in the plant is definitely higher.

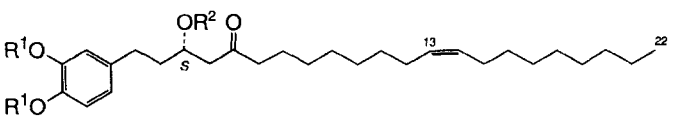
[4]) Compounds **4** and **5** are also constituents of *P. albidus*. However, the structure of the C_{22}-olefin **4** has only been tentatively assigned [2].



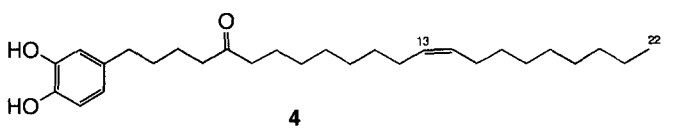
1a $R^1 = H$, $R^2 = COMe$
b $R^1 = R^2 = H$
c $R^1 = Me$, $R^2 = H$
d $R^1 = Me$, $R^2 = (S)$-MTPA
e $R^1 = Me$, $R^2 = (R)$-MTPA



2a $R^1 = R^2 = H$, $R^3 = COMe$
b $R^1 = R^3 = H$, $R^2 = COMe$
c $R^1 = Me$, $R^2 = H$, $R^3 = COMe$
d $R^1 = Me$, $R^2 = (S)$-MTPA, $R^3 = COMe$
e $R^1 = Me$, $R^2 = (R)$-MTPA, $R^3 = COMe$
f $R^1 = Me$, $R^2 = COMe$, $R^3 = H$
g $R^1 = Me$, $R^2 = COMe$, $R^3 = (S)$-MTPA
h $R^1 = Me$, $R^2 = COMe$, $R^3 = (R)$-MTPA
i $R^1 = Me$, $R^2 = R^3 = H$
j $R^1 = Me$, $R^2 = R^3 = Me_2C$



3a $R^1 = R^2 = H$
b $R^1 = Me$, $R^2 = H$
c $R^1 = Me$, $R^2 = (S)$-MTPA
d $R^1 = Me$, $R^2 = (R)$-MTPA



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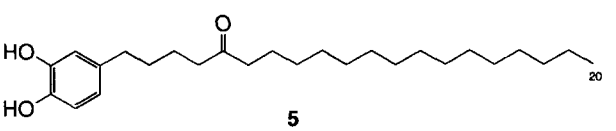

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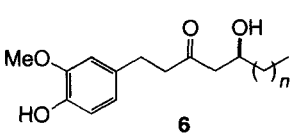

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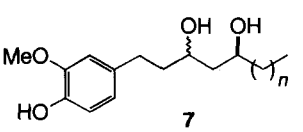

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$n = 0\text{-}16$, even

MTPA = α-methoxy-α-(trifluoromethyl)phenylacetyl

Structures of the Isolated Compounds. – *(+)-4-[(2S,4R,6S)-4-(Acetyloxy)tetrahydro-6-pentyl-2H-pyran-2-yl]benzene-1,2-diol* (**1a**). The compound (white plates) is optically active, and its UV spectrum (EtOH; 282 nm, log ε 3.49), together with the bathochromic when recorded in EtOH/1N NaOH (420 nm, decomposition) is indicative of a catechol. On the basis of its ^{1}H- and ^{13}C-NMR and EI-mass spectra, the molecular formula $C_{18}H_{26}O_5$ (*m/z* 322) could be established. As the signals of the ^{1}H-NMR strongly overlapped in the high-field region even at 600 MHz and were too simple in the aromatic region, unequivocal assignments were only possible with ^{1}H,^{1}H-COSY, ^{13}C,^{1}H-COSY (HSQC) and ^{13}C,^{1}H long-range (HMBC) spectra.

From the 6 double-bond equivalents calculated from the molecular formula of **1a**, 5 were assigned to a 4-substituted catechol moiety (6.74 (br. '*s*', 2H) and 6.76 ppm (br. '*s*', 1H); 113.5, 115.1 and 118.6 (each CH), and 134.2, 143.3 and 143.5 ppm (quaternary C)) and to an acetate (2.07 ppm (*s*, 3H); 171.0 ppm), whereas the lack of an additional sp^2 C suggested the presence of a cyclic structure. Of decisive diagnostic value proved to be three oxymethine protons at 3.54 (*quint.*-like, ^3J = 11.5, *ca.* 5.5), 4.28 (*d*, ^3J = 11.7) and 5.03 ppm (*tt*, ^3J = 11.5, 4.7 Hz) which are not coupled to each other, and the magnitude of the ^3J established the axial location of the latter two. Their chemical shifts and the respective multiplicities suggested a 2,4,6-trisubstituted tetrahydro-2*H*-pyran moiety with an acetoxy group at C(4). The equatorial arrangement of all the substituents was shown by the strong mutual NOE of all three oxymethine protons.

The absolute configuration of **1a** was determined by the high-field ^{1}H-NMR application of the *Mosher* method [6]: Saponification of **1a** ($LiAlH_4$, THF) gave the secondary alcohol **1b** which was methylated (MeI, Na_2CO_3, acetone) to yield the dimethoxy derivative **1c**. Esterification of **1c** with (−)-(*R*)-MTPA-Cl (= (−)-(*R*)-α-methoxy-α-(trifluoromethyl)phenylacetyl chloride = (−)-(*R*)-3,3,3-trifluoro-2-methoxy-2-phenylpropanoyl chloride) afforded the (*S*)-ester **1d**, and the corresponding (*R*)-ester **1e** (each 5.31 ppm, (*tt*, ^3J = 11.5, 4.8 Hz, H–C(4)) was isolated after reaction of **1c** with (+)-(*S*)-MPTA-Cl. From the $\delta(S) - \delta(R)$ values in the ^{1}H-NMR spectra of the **1d**/**1e** couple the (4*R*)-configuration could be unambiguously determined (see *Exper. Part*)[5]). Hence, the structure of **1a** is established as 4-[(2*S*,4*R*,6*S*)-4-(acetyloxy)-tetrahydro-6-pentyl-2*H*-pyran-2-yl]benzene-1,2-diol.

(−)-4-[(2S,4R,6S)-Tetrahydro-4-hydroxy-6-pentyl-2H-pyran-2-yl]benzene-1,2-diol (**1b**). The natural product **1b** proved to be identical in every respect with the compound **1b** obtained after saponification of **1a**.

4-[(3S,5S)-5-(Acetyloxy)-3-hydroxydecyl]benzene-1,2-diol (**2a**) *and 4-[(3S,5S)-3-(Acetyloxy)-5-hydroxydecyl]benzene-1,2-diol* (**2b**). According to the ^{1}H- and ^{13}C-NMR and EI-mass spectra, the molecular formula $C_{18}H_{28}O_5$ (*m/z* 324) was assigned to the chromatographically pure fraction. Interpretation of the spectral data suggested a catechol (UV 284 nm) with an acetoxy-hydroxy-disubstituted C_{10} side chain. However, the occurrence of several double signals in the NMR spectra showed it to be a mixture of two isomers (*ca.* 1:1). All attempts to separate the genuine mixture failed, and the individual components could only be separated by prep. HPLC after methylation of the catechol

[5]) For the determination of $\Delta\delta$ of overlapped *ms* in the *Mosher*-ester couples **1d**/**1e**, **2d**/**2e**, **2g**/**2h** and **3c**/**3d**, the shape of the individual signals and their respective line frequencies have been thoroughly compared. The data of both diastereoisomers were consistent in every respect and showed the relative displacements as expected [6]. Moreover, the *Mosher* esters proved the natural products to be enantiomerically pure as no trace of the corresponding diastereoisomeric MTPA ester could be detected.

moiety (MeI, Na_2CO_3, acetone). As a consequence, the structure elucidation of the natural products was performed on the corresponding dimethoxyphenyl derivatives **2c** and **2f**.

The ^{1}H-NMR spectra (*ABC* pattern for a 1,2,4-trisubstituted benzene and two oxymethine protons) showed **2c** to be a 5-acetoxy-1-(3,4-dimethoxyphenyl)decan-3-ol (2.05, (*s*, MeCO), 3.46, (*t*-like *m*, $w_{1/2} \approx 25$, H–C(3)); 5.07 ppm, (*quint.*-like *m*, $w_{1/2} \approx 25$, H–C(5)) and **2f** as a 3-acetoxy-1-(3,4-dimethoxyphenyl)decan-5-ol (2.10 (*s*, MeCO), 3.47 (*quint.*-like *m*, $w_{1/2} \approx 25$, H–C(5)) and 5.14 ppm (*t*-like *m*, $w_{1/2} \approx 25$ Hz, H–C(3))). Remarkably, no 3,5-acyl shift was observed during the separation and storage of the compounds.

Saponification (2N KOH/EtOH) of **2c** and **2f** afforded from both compounds the identical (–)-1-(3,4-dimethoxyphenyl)decane-3,5-diol (**2i**). The acetonides **2j** prepared from the two individual diols **2i** (acetone, $CuSO_4$) were also identical. Their ^{13}C-NMR data (24.8 and 25.0 ppm, 2 $MeC(O)_2$) unequivocally established the 3,5-*anti* relationship for **2j** [7][6]), hence the same relative configuration for **2c** and **2f**. The absolute configuration was determined on the *Mosher* esters **2d**/**2e** (from **2c**) and **2g**/**2h** (from **2f**) as mentioned above. From the $\delta(S) - \delta(R)$ values of the **2d**/**2e** couple, the (3*S*)-configuration for **2c**, and from those of **2g**/**2h** the (5*S*)-configuration for **2f** was deduced (see *Exper. Part*)[5]). Hence, the structures of **2c** and **2f** are (3*S*,5*S*)-5-(acetyloxy)-1-(3,4-dimethoxyphenyl)decan-3-ol (**2c**) and (3*S*,5*S*)-3-(acetyloxy)-1-(3,4-dimethoxyphenyl)-decan-5-ol (**2f**). As a consequence, the structures of the genuine compounds are established as 4-[(3*S*,5*S*)-5-(acetyloxy)-3-hydroxydecyl]benzene-1,2-diol (**2a**) and 4-[(3*S*,5*S*)-3-(acetyloxy)-5-hydroxydecyl]benzene-1,2-diol (**2b**), respectively[7]).

(–)-(3S,13Z)-1-(3,4-Dihydroxyphenyl)-3-hydroxydocos-13-en-5-one (**3a**). Based on the EI-MS (*m*/*z* 446), the optically active compound has the molecular formula $C_{28}H_{46}O_4$ and is a 4-substituted catechol (UV, ^{1}H-NMR). The hydroxydocosenone substituent was evident from the ^{13}C-NMR spectrum (22 signals for 1 Me (14.4), 18 CH_2, 1 CH_2O (67.2), an olefin (130.0, 130.3) and a CO (211.7 ppm)). The relative positions of the O-substituents were determined by the ^{1}H,^{1}H-COSY spectra[8]) and the location of the double bond at C(13) established after ozonolysis, reductive workup (Me_2S) and identification of nonanal (pelargonaldehyde) as the main fragment. According to the shape of the olefinic ^{1}H-NMR signal of **3a** which was identical to those of known long-chain (*Z*)-olefins [1] [2], the (13*Z*)-configuration was assigned to **3a**[9]). The absolute (3*S*)-configuration was determined by means of the *Mosher* esters **3c**/**3d** which were prepared from the dimethoxy derivative **3b** (see *Exper. Part*)[5]).

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[6]) Acetonides derived from *syn*-1,3-diols exist in a well defined chair conformation with the two alkyl substituents in equatorial positions. Due to the shielding effect, the geminal Me groups resonate at *ca.* 20 and 30 ppm, respectively. Acetonides of *anti*-1,3-diols exist in a twist boat conformation to avoid the 1,3-diaxial interaction. As a consequence, both Me groups are almost equivalent and resonate at *ca.* 25 ppm [8]. These two conformations can also be distinguished by analysis of the appropriate ^{1}H,^{1}H coupling constants [9].

[7]) As it was not possible to prepare the natural products from the dimethyl derivatives **2c** and **2f**, the chiroptic data of **2a** and **2b** are not known.

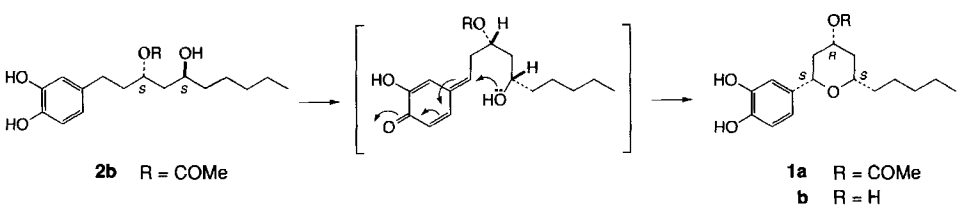
[8]) The partially well resolved individual vicinal couplings show that the C(1) to C(6) moiety of the side chain is conformationally restricted due to the H-bond C(3)–OH···O=C(5) (see *Exper. Part*).

[9]) This assignment is tentative as the synthesis of (*Z*)- and (*E*)-1-(4-hydroxyphenyl)oct-13-en-5-one and (*Z*)- and (*E*)-1-(3,4-dihydroxyphenyl)oct-13-en-5-one has shown [1] [2] that an unambiguous assignment is only possible if both isomers are available.

(Z)-1-(3,4-Dihydroxyphenyl)docos-13-en-5-one (**4**) *and 1-(3,4-Dihydroxyphenyl)-icosan-5-one* (**5**). Compounds **4** and **5** proved to be identical to the natural products which have been isolated earlier from *Plectranthus albidus* [1] [2][4]). The double bond in **4** was definitely located at C(13) as the main degradation product after ozonolysis also was found to be nonanal, and the shape of the ^{1}H-NMR signal of the olefinic protons suggested the (*Z*)-configuration as discussed above[9]).

Biogenetic Considerations. – Being structurally related to the [*n*]-gingerols (**6**) [10] [12][10]) and -diols (**7**) [12] [14][11]) which are constituents of *Zingiber officinale* ROSCOE (ginger), the alkylcatechols isolated from *P. sylvestris* are supposed to follow the same biogenetic route [15]. The respective absolute configurations might be interpreted in terms of an NAD(P)H-dependent reduction of the corresponding oxo precursors from the *Re*-face by an E_3-type enzyme [16], hence leading to **2a**, **2b** and **3a**. Phenol oxidation of **2b**[12]) followed by intramolecular attack of OH–C(5) at the intermediate quinone methide would explain the formation of the cyclic compounds **1a** and **1b** (*Scheme*).

Scheme



2b R = COMe

1a R = COMe
b R = H

Biological Activity. – Long-chain alkylphenols and -catechols, exhibit an array of physiological activities. They are potent inhibitors of enzymes of the arachidonic-acid metabolism (prostaglandin synthetase, cyclooxygenase, lipoxygenase) [13] [17], contact allergens [18], and DNA-cleavage reagents [19]. The rhizome of ginger containing [*n*]-gingerols and related compounds is not only used as a seasoning spice, it is also an important drug in the traditional Chinese and Japanese medicine [20]. Current research interests concern the application of the ginger substances as anti-inflammatory [13], cardiotonic [21], stomachic [22] and anti-platelet aggreggation agents [23]. A preliminary report on the biological activities of the novel catechols of *P. sylvestris* is presented in the following[13]).

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[10]) The (*S*)-configuration of [6]-gingerol (**6**, $n = 4$) was established by chemical degradation [10] and later confirmed by enantioselective syntheses [11]. For a review of the history of the structure elucidation and the systematics of the [*n*]-gingerols and related compounds, see [10]. It is quite characteristic of most of the following papers in this series, that there is no reference to stereochemical implications (see *e.g.* [13]).

[11]) The absolute configurations of compounds related to [6]-gingerdiol (**7**, $n = 4$) were established by chemical transformations and comparison of the chiroptic data [14].

[12]) Although the corresponding catechol has not been isolated as a natural product, it might be a precursor of **1b**. An alternative route to **1b** is the hydrolysis of **1a**.

[13]) Detailed results of our current studies on biological activities of the novel constituents isolated from *P. albidus* [1] and *P. sylvestris* as well as for synthetic compounds will be published in due time elsewhere.

The activity-guided fractionation showed the substances to be antioxidants. The 50% inhibitory concentrations (IC_{50}) of selected compounds[14]) were measured by the Fe^{2+}-catalysed autooxidation of linoleic acid according to [24]. The natural products are almost as efficient as the commercial antioxidant 2,6-di(*tert*-butyl)-4-methylphenol (BHT) (*Table 1*). Chain length and functional groups in the alkyl chain do not seem to be of significant influence; presumably the dominant structural element is the catechol moiety.

Table 1. *Antioxidant Activity* (2 incubation periods)

	1a	**1b**	**3a**	**4**	**5**	BHT
IC_{50} [μM] 2 h	0.64	0.60	0.58	1.03	0.95	0.40
IC_{50} [μM] 5 h	0.89	0.82	1.11	1.30	1.10	0.71

Antioxidant activity is supposed to be directly associated with the inhibition of the prostaglandin biosynthesis, and preliminary biological testing of related compounds isolated from *P. albidus* [1] showed them to be significant inhibitors of 5-lipoxygenase [3]. Therefore, the novel constituents of *P. sylvestris* were tested in that respect, too. The lipoxygenase activity was determined in a direct spectrophotometric assay by a modified method related to [25] [26] (see *Exper. Part*). Most of the tested compounds[14]) are significantly stronger inhibitors than the known anti-inflammatory and analgesic drugs nordihydroguaiaretic acid (NDGA) and indomethacin (INDO)[15]), the best ones being *ca.* 3 orders of magnitude more efficient (*Table 2*). They show a tendency of increasing inhibitory power with increasing chain length. An influence of the functional groups cannot be inferred yet, although a hydroxy-ketone moiety is suggested to be optimal.

Table 2. *Inhibition of Soybean Lipoxygenase*

	1a	**1b**	**3a**	**4**	**5**	NDGA	INDO
IC_{50} [μM]	9	74	0.09	0.21	0.46	54	181

Remarks. – Non-isoprenoid long-chain alkylphenols and -catechols are constitutents of several plant families, especially the *Anacardiaceae* [28]. It is characteristic that these compounds occur as mixtures of homologues which differ only in the length of the usually odd-numbered alkyl chain (to C_{31}) and the number and position of the (*Z*)-double bonds. From the chemotaxonomic point of view, it is remarkable that such compounds are found now also in the *Labiatae* family[16]). The reported catechols are congeners of the even-numbered [*n*]-gingerols (**6**) and -diols (**7**) which are essential

[14]) As the mixture **2a**/**2b** could not be separated into the individual components, its biological activity was not assayed.

[15]) It proved rather difficult to reproduce and compare absolute numeric values of reference compounds determined by various research groups. NDGA (*e.g.* IC_{50} = 6.1 [26] and 44 μM [27], resp.) and INDO (IC_{50} = 87.5 μM [26]) were markedly weaker in our hands. As our assay proved to be reproducible in every respect, the relative values are significant, and they demonstrate the real efficacy of the natural products.

[16]) This report is the second account on the occurrence of long-chain alkylphenols and -catechols in *Labiatae* species. Previously, such compounds have been isolated from *P. albidus* [1] [2].

constitutents of *Zingiber officinale* [10] [12–14]. Relevant constituents of the *Zingiberaceae* are also the curcuminoids (diarylheptanoids) which have a similar substitution pattern in the alkyl part and which exhibit similar biological activities [12] [13] [29]. Very recently, several diarylheptanoids with a 2,4,6-trisubstituted tetrahydro-2*H*-pyranyl moiety similar to **1a** and **1b** have been isolated from the rhizomes of *Zingiber officinale* and their constitutions determined [30][17]).

The authors are indebted to the *Swiss National Science Foundation* for the financial support.

Experimental Part

1. *General.* See [1]. Prep. HPLC: *Applied Biosystems* solvent delivery system *400*; *Applied Biosystems* programmable absorbance detector *783A*; columns: *Spherisorb* CN 5 μm, 250 × 20 mm; *Spherisorb* ODS 10 μm, 250 × 20 mm. To avoid decomposition of the labile catechols, *ca.* 0.1–1% of acetic acid was generally added to the LC solvents. $[\alpha]_D^{20}$: *Perkin-Elmer-241-MC* polarimeter with thermostat *B. Braun Thermomix 1441*; 10-cm cell. CD (nm, $\Delta\varepsilon$): *JASCO-J-500A* spectropolarimeter. ^{1}H- and ^{13}C-NMR: *Bruker ARX-300* (300, 75.4 MHz, resp.) and *AMX-600* (600, 150.9 MHz, resp.), chemical shifts in ppm rel. to the assigned solvent (Me_4Si = 0 ppm), coupling constants J in Hz; assignments based on ^{1}H,^{1}H-COSY, DEPT135, ^{13}C,^{1}H-COSY (HSQC), and ^{13}C,^{1}H long-range (HMBC) spectra; spin systems are interpreted according to 1st-order approximation, although in several complex cases, significant *AB* character shows higher order-spectra. GC/MS: *Hewlett-Packard HP-5890* Series *II* (GC), *HP-5971 MSD* (mass-selective detector), column *HP-5*, 25 m × 0.2 mm.

2. *Antioxidant Activity.* Antioxidants were detected on TLC according to [5] (purified linoleic acid (2 drops) in EtOH (60 ml) is mixed with 12 mg β′,β-carotene in $CHCl_3$ (30 ml)). After exposing the developed plate to light, remaining orange spots are indicative of antioxidants. The antioxidant activity of isolated compounds was measured by the Fe^{2+}-catalysed autooxidation of linoleic acid according to [24] on an *HP-8452A* diode-array spectrophotometer. The IC_{50} values were determined from the individual inhibitory ratios at various concentrations according to [31].

3. *Inhibition of Lipoxygenase.* The lipoxygenase activity was determined in a direct spectrophotometric assay at 30° by a modified method related to [25] [26]: To the reaction mixture containing 500 units of enzyme (soybean lipoxydase (linoleate: oxygen oxidoreductase), EC 1.13.11.12, *Sigma*, type I-B, *L 7395*) and ethanolic inhibitor soln. (total concentration of EtOH > 1%) in 0.1M borate buffer (pH 9, 2.9 ml), linoleic acid (100 μl of a 0.2 mM in borate buffer) was added to initiate the reaction. The initial rate of increase in absorbance (236 nm) was measured on an *HP-8452A* diode-array spectrophotometer (30–80 s), and the kinetic parameters were determined with the *HP-89532A* kinetic software. The known anti-inflammatory and analgesic drugs nordihydroguaiaretic acid (NDGA) and indomethacin (INDO) were used as internal controls.

4. *General Procedure for the Preparation of the (S)- and (R)-MTPA Esters for the Determination of the Absolute Configuration.* The corresponding 3,4-dimethoxyphenyl derivatives (each 4 mg) were dissolved in dry pyridine (200 μl) and treated with (+)-(*R*)-MTPA-Cl (10 μl, *ca.* 3 equiv.) at 50° for 4 h under Ar. Evaporation of the solvent, extraction (2N HCl/Et_2O), and column chromatography (SiO_2) of the crude products afforded the (*S*)-MTPA esters. The same procedure was adopted for the reaction with (−)-(*S*)-MTPA-Cl to yield the (*R*)-MTPA esters. All MTPA derivatives were isolated in pure form as colourless viscous oils.

5. *Extraction and Isolation.* Air-dried leaves of *Plectranthus sylvestris* GÜRKE (300 g) were extracted twice with Et_2O (3.5 l, 5 h and overnight at r.t.) and the extracts concentrated, combined, and partitioned (hexane/90% MeOH). The hexane layer yielded after evaporation, 5.98 g (2%) of a green waxy solid which were devoid of antioxidant activity (discarded). The MeOH extract was concentrated and dried azeotropically with abs. EtOH to yield 5.62 g (1.9%) of a reddish brown residue. It was chromatographed on *Sephadex LH-20* (100 g, 3.5 × 50 cm) with hexane/CH_2Cl_2 6:1 (*ca.* 600 ml), CH_2Cl_2 (*ca.* 300 ml), CH_2Cl_2/acetone 2:1 (*ca.* 300 ml) and acetone (*ca.* 500 ml) to afford 6 fractions. Only fractions which showed antioxidant activity were investigated: *Fr. 1*, 2.10 g (0.7%) of brown-green viscous oil (not examined); *Fr. 2*, 1.15 g (0.38%) of brown-yellow solid (flavonoids); *Fr. 3*, 0.37 g (0.12%) of brown-yellow solid (not examined); *Fr. 4*, 0.90 g (0.3%) of brown solid; *Fr. 5*, 1.17 g (0.39%) of brown solid; *Fr. 6*, 0.02 g (0.007%) of dark brown oil (not examined). *Fr. 4* was further chromatographed (SiO_2, hexane/acetone 10:1) followed by prep. HPLC (*C-18*, H_2O/MeOH 1:5) and crystalliza-

[17]) There are no arguments concerning the absolute configuration in [30].

tion to yield the long-chain alk(en)ylcatechols **4** (25 mg, 0.083%) and **5** (14 mg, 0.047%). Chromatography of *Fr. 5* (SiO_2, (hexane/AcOEt 10:1 → 1:1 and hexane/acetone 2:1) and crystallization afforded the main antioxidant constituent **1a** (155 mg, 0.052%). Prep. HPLC (*C-18*, H_2O/MeOH 3:7) of the mother liquor yielded **1b** (12 mg, 0.004%), the unseparable mixture of **2a**/**2b** (*ca.* 1:1; 30 mg, 0.01%), and **3a** which was further purified by prep. HPLC (*C-18*, H_2O/MeOH 1:9) to yield pure **3a** (12 mg, 0.004%). All the isolated natural compounds decomposed slowly in soln.

6. *(+)-4-[(2S,4R,6S)-4-(Acetyloxy)-tetrahydro-6-pentyl-2H-pyran-2-yl]benzene-1,2-diol* (**1a**). White plates from Et_2O/hexane. M.p. 112.5–113.5°. R_f (hexane/acetone 2:1) 0.33, R_f (toluene/AcOEt 5:2) 0.38. $[\alpha]_D^{20} = +2.6$ ($c = 1.7$, $CHCl_3$). UV/VIS (EtOH): 224(3.75), 282(3.49). CD (EtOH, $c = 2.5 \times 10^{-4}$, $d = 1$ cm, r.t.): 280, (+0.17). IR ($CHCl_3$): 3600,3560,3007, 2957, 2932, 2860, 1720, 1522, 1448, 1363, 1315, 1160, 1103, 1069, 1032, 980, 912, 869, 815. ^{1}H-NMR (600 MHz, $CDCl_3$): 0.88 (*t*, $^3J = 7.0$, Me(5″)); 1.29 (*m*, $w_{1/2} \approx 20$, CH_2(3″), CH_2(4″)); 1.36, 1.44 (2*m*, $w_{1/2} \approx 28$, each 1H, CH_2(2″)); 1.37 (*q*, $^2J = {}^3J$(5′ax,4′) $= {}^3J$(5′ax,6′) = 11.9, H_{ax}–C(5′)); 1.50, 1.67 (2*m*, $w_{1/2} \approx 28$, each 1H, CH_2(1″)); 1.56 (*q*, $^2J = {}^3J$(3′ax,2′) $= {}^3J$(3′ax,4′) = 11.8, H_{ax}–C(3′)); 2.04 (*dm*, $^2J = 11.9$, $w_{1/2} \approx 22$, H_{eq}–C(5′))[18]; 2.07 (*s*, MeCO); 2.17 (*dm*, $^2J = 11.8$, $w_{1/2} \approx 22$, H_{eq}–C(3′))[19]; 3.54 (*quint.*-like *m*, ^3J(6′,5′ax) = 11.5, ^3J(6′,5′eq) ≈ ^3J(6′,1″) ≈ 5.5, H–C(6′)); 4.28 (*d*, ^3J(2′,3′ax) = 11.7, H–C(2′))[20]; 5.03 (*tt*, ^3J(4′,3′ax) $= {}^3J$(4′,5′ax) = 11.5, ^3J(4′,3′eq) $= {}^3J$(4′,5′eq) = 4.7, H–C(4′)); 5.78, (*s*, OH–C(1)); 5.93 (*s*, OH–C(2)); 6.74, (br. '*s*', H–C(5), H–C(6)); 6.76 (br. '*s*', H–C(3)). ^{13}C-NMR (150.9 MHz, $CDCl_3$): 14.0 (C(5″)); 21.3 (*Me*CO); 22.6 (C(4″)); 25.1 (C(2″)); 31.8 (C(3″)); 35.9 (C(1″)); 36.9 (C(5′)); 38.7 (C(3′)); 71.0 (C(4′)); 76.1 (C(6′)); 77.0 (C(2′)); 113.5 (C(3)); 115.1 (C(6)); 118.6 (C(5)); 134.2 (C(4)); 143.3 (C(1)); 143.5 (C(2)); 171.0 (MeCO). EI-MS: 322 (71, M^+, $[C_{18}H_{26}O_5]^+$), 262 (46, $[M - AcOH]^+$), 233 (25), 219 (8), 205 (5), 191 (13), 162 (52), 152 (63), 138 (100, $[(HO)_2C_6H_3CH_2O]^+$), 123 (28, $[(HO)_2C_6H_3CH_2]^+$), 110 (16), 83 (13), 69 (16), 55 (13), 43 (70).

Saponification of **1a**. $LiAlH_4$ (39 mg) in dry THF (5 ml) and **1a** (57 mg) were refluxed under Ar for 4 h. Usual workup and chromatography (SiO_2, hexane/acetone 3:1) afforded **1b** (46.5 mg, 94%) as white needles. Physical data: identical to those of the natural product **1b**, see *Sect.* 7.

7. *(−)-4-[(2S,4R,6S)-Tetrahydro-4-hydroxy-6-pentyl-2H-pyran-2-yl]benzene-1,2-diol* (**1b**). White needles. M.p. 117° (dec.). R_f (hexane/acetone 2:1) 0.18, R_f (CH_2Cl_2/EtOH 20:1) 0.2. $[\alpha]_D^{20} = -37.5$ ($c = 1.2$, MeOH). UV/VIS (EtOH): 222(3.75), 282(3.44). IR (KBr): 3439 (br.), 3200 (br.), 2928, 2855, 1705, 1603, 1537, 1456, 1360, 1239, 1103, 1056, 889, 852, 813. ^{1}H-NMR (300 MHz, CD_3OD): 0.90 (*t*, $^3J = 6.8$, Me(5″)); 1.17 (*q*, $^2J = {}^3J$(5′ax,4′) $= {}^3J$(5′ax,6′) = 11.5, H_{ax}–C(5′)); 1.32 (*m*, $w_{1/2} \approx 15$, CH_2(3″), CH_2(4″)); 1.37–1.64 (*m*, CH_2(1″), CH_2(2″)); 1.39 (*q*, $^2J = {}^3J$(3′ax,2′ax) $= {}^3J$(3′ax,4′) = 11.5, H_{ax}–C(3′)); 1.96 (*quint.*-like *dm*, $^2J = 12.4$, ^3J(5′eq,4′) = 4.7, ^3J(5′eq,6′) ≈ ^4J(5′eq,3′eq) ≈ 2, H_{eq}–C(5′)); 2.06 (*quint.*-like, *dm*, $^2J = 12.4$, ^3J(3′eq,4′) = 4.7, ^3J(3′eq,2′) ≈ ^4J(3′eq,5′eq) ≈ 2, H_{eq}–C(3′)); 3.46 (*quint.*-like *m*, $w_{1/2} \approx 30$, H–C(6′)); 3.84 (*tt*, ^3J(4′,3′ax) $= {}^3J$(4′,5′ax) = 11.5, ^3J(4′,3′eq) $= {}^3J$(4′,5′eq) = 4.7, H–C(4′)); 4.22 (*dd*, ^3J(2′,3′ax) = 11.4, ^3J(2′,3′eq) = 1.8, H–C(2′)); 6.66 (*dd*, $^3J = 8.2$, $^4J = 1.9$, H–C(5)); 6.72 (*d*, $^3J = 8.2$, H–C(6)); 6.81 (*d*, $^4J = 1.9$, H–C(3′)). ^{13}C-NMR (75.4 MHz, CD_3OD): 12.9 (C(5″)); 22.2 (C(4″)), 24.8 (C(2″)); 31.6 (C(3″)); 35.6 (C(1″)); 40.3 (C(5′)), 42.2 (C(3)); 67.6 (C(4′)); 75.8 (C(6′)); 77.3 (C(2′)); 113.1 (C(3)); 114.5 (C(6)); 117.3 (C(5)); 138.8 (C(4)); 144.1 (C(1)); 144.5 (C(2)). EI-MS 280 (73, M^+, $[C_{16}H_{24}O_4]^+$), 262 (8, $[M - H_2O]^+$), 191 (28), 181 (21), 139 (97), 138 (100), $[(HO)_2C_6H_3CH_2O]^+$), 137 (90), 136 (81), 110 (29), 81 (11), 55 (20), 41 (25).

(−)-(2S,4R,6S)-2-(3,4-Dimethoxyphenyl)tetrahydro-6-pentylpyran-4-ol (**1c**). The mixture of **1b** (46.5 mg), dry acetone (2 ml), dry Na_2CO_3 (200 mg), and MeI (0.5 ml) was stirred in a closed flask for 4 d at 70°. The crude product was chromatographed (SiO_2, hexane/acetone 7:1): **1c** (42.5 mg, 83%). Colourless wax which crystallized slowly. M.p. 56.5–58.0°. R_f (hexane/acetone 2:1) 0.33. $[\alpha]_D^{20} = -38$ ($c = 1.7$, $CHCl_3$). UV/VIS (EtOH): 232 (3.86), 278 (3.42). IR ($CHCl_3$): 3607, 2937, 2859, 1597, 1516, 1461, 1371, 1263, 1138, 1072, 1030, 886. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.88 (*t*, $^3J = 6.8$, Me(5″)); 1.20–1.65 (*m*, H_{ax}–C(3), H_{ax}–C(5), $Me(CH_2)_4$); 2.02 (*quint.*-like *dm*, $^2J = 12.3$, ^3J(5eq,4) = 4.6, ^3J(5eq,6) ≈ ^4J(5eq,3eq) ≈ 2, H_{eq}–C(5)); 2.19 (*quint.*-like *dm*, $^2J = 12.3$, ^3J(3eq,4) = 4.6, ^3J(3eq,2) ≈ ^4J(3eq,5eq) ≈ 2, H_{eq}–C(3)); 3.45–3.46 (*quint.*-like *m*, $w_{1/2} \approx 30$, H–C(6)); 3.86, 3.89 (2*s*, 2 MeO); 3.93 (*tt*, ^3J(4,3ax) $= {}^3J$(4,5ax) = 11.0, ^3J(4,3eq) $= {}^3J$(4,5eq) = 4.6, H–C(4)); 4.30 (*dd*, ^3J(2,3ax) = 11.3, ^3J(2,3eq) = 1.9, H–C(2)); 6.83 (*d*, $^3J = 8.2$, H–C(5′)); 6.89 (*dd*, $^3J = 8.2$, $^4J = 1.9$, H–C(6′)); 6.92 (*d*, $^4J = 1.9$, H–C(2′)). ^{13}C-NMR (75.4 MHz, $CDCl_3$): 13.9 (C(5″)); 22.5 (C(4″)); 25.1 (C(2″)); 31.7 (C(3″));

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[18]) According to the ^{1}H,^{1}H-COSY spectrum the *m* is due to a superposition of ^3J(5′eq,4′), ^3J(5′eq,6′), and ^4J(5′eq,3′eq).

[19]) According to the ^{1}H,^{1}H-COSY spectrum the *m* is due to a superposition of ^3J(3′eq,2′), ^3J(3′eq,4′), and ^4J(3′eq,5′eq).

[20]) The ^3J(2′,3′eq) is not visible in the 1D spectrum; it is only resolved in the ^{1}H,^{1}H-COSY spectrum (*ca.* 2 Hz).

35.9 (C(1'')); 40.8 (C(5)); 42.6 (C(3)); 55.7, 55.8 (MeO); 68.5 (C(4)); 75.9 (C(6)); 77.0 (C(2)); 109.4 (C(2')); 110.9 (C(5')); 118.0 (C(6')); 134.8 (C(1')); 148.2 (C(4')); 148.8 (C(3')). EI-MS: 308 (100, M^+, $[C_{18}H_{28}O_4]^+$), 277 (8, $[M - MeO]^+$), 259 (5, $[M - MeO - H_2O]^+$), 177(6), 167(21), 166(37, $[(MeO)_2C_6H_3CH_2O]^+$), 164(12), 152(8), 151(17, $[(MeO)_2C_6H_3CH_2]^+$), 139(8), 135(7), 55(7).

(S)- and (R)-MTPA Esters of **1c**. Chromatography of the crude products (SiO_2, toluene/AcOEt 30:1) afforded the (*S*)-MTPA ester **1d** (5.5 mg, 81%). and the (*R*)-MTPA ester **1e** (2.2 mg, 32%). R_f (hexane/acetone 3:1) 0.4.

Data of the (S)-MTPA Ester **1d**. IR ($CHCl_3$): 3007, 2934, 2857, 1746, 1595, 1518, 1465, 1264, 1170, 1122, 1080, 1025. ^{1}H-NMR (600 MHz, $CDCl_3$): 0.88 (*t*, ^3J = 6.8, Me(5'')); 1.26–1.33 (*m*, CH_2(2''), CH_2(4'')); 1.39, 1.45 (2 *quint.*-like *m*, $w_{1/2} \approx 25$, each 1H, CH_2(2'')); 1.51 (*q*, $^2J = {}^3J$(5ax,4) = ^3J(5ax,6) = 11.5, H_{ax}–C(5)); 1.51–1.57 (*m*, H_a–C(1'')); 1.60 ($^2J = {}^3J$(3ax,2ax) = ^3J(3ax,4) = 11.5, H_{ax}–C(3)); 1.68 (*sept.*-like *m*, $w_{1/2} \approx 30$, H_b–C(1'')); 2.14 (*dm*, $w_{1/2} \approx 22$, H_{eq}–C(5)); 2.22 (*dm*, $w_{1/2} \approx 22$, H_{eq}–C(3)); 3.55 (*s*, MeO (MTPA)); 3.56 (*m*, $w_{1/2} \approx 30$, H–C(6)); 3.86, 3.88 (2*s*, 2 MeO); 4.39 (br. *d*, ^3J = 10.5, H–C(2)); 5.31 (*tt*, ^3J(4,3ax) = ^3J(4,5ax) = 11.5, ^3J(4,3eq) = ^3J(4,5eq) = 4.8, H–C(4)); 6.82 (*d*, ^3J = 8.3, H–C(6')); 6.87 (br. *d*, ^3J = 8.3, H–C(5')); 6.88 (br. *s*, H–C(2')); 7.39–7.40 (*m*, 3 arom. H (MTPA)); 7.51–7.52 (*m*, 2 arom. H (MTPA)). CI-MS (NH_3): 542 (100, $[M + NH_4]^+$), 524 (10, M^+, $[C_{28}H_{35}F_3O_6]^+$), 308 (18, $[M - MTPA]^+$), 291 (20, $[M + H\text{-}MTPA - H_2O]^+$).

Data of the (R)-MTPA Ester **1e**. ^{1}H-NMR (600 MHz, $CDCl_3$): 0.88 (*t*, ^3J = 6.8, Me(5'')); 1.27–1.32 (*m*, CH_2(3''), CH_2(4'')); 1.38 (*m*, $w_{1/2} \approx 20$, H_a–C(2'')); 1.42 (*m*, $w_{1/2} \approx 20$, H_b–C(2'')); 1.42 (*q*, $^2J = {}^3J$(5ax,4) = ^3J(5ax,6) = 11.5, H_{ax}–C(5)); 1.52 (*sept.*-like *m*, $w_{1/2} \approx 25$, H_a–C(1'')); 1.67 (*m*, $w_{1/2} \approx 30$, H_b–C(1'')); 1.68 (*q*, $^2J = {}^3J$(3ax,2ax) = ^3J(3ax,4) = 11.5, H_{ax}–C(3)); 2.06 (*dm*, $w_{1/2} \approx 22$, H_{eq}–C(5)); 2.29 (*dm*, $w_{1/2} \approx 22$, H_{eq}–C(3)); 3.54 (*s*, MeO (MTPA)); 3.56 (*m*, $w_{1/2} \approx 30$, H–C(6)); 3.86, 3.89 (2*s*, 2 MeO); 4.40 (br. *d*, ^3J = 11.0, H–C(2)); 5.31 (*tt*, ^3J(4,3ax) = ^3J(4,5ax) = 11.5, ^3J(4,3eq) = ^3J(4,5eq) = 4.8, H–C(4)); 6.83 (*d*, ^3J = 8.3, H–C(6')); 6.89 (br. *d*, ^3J = 8.3, H–C(5')); 6.90 (br. *s*, H–C(2')); 7.39–7.40 (*m*, 3 arom. H (MTPA)); 7.51-7.52 (*m*, 2 arom. H (MTPA)).

$\Delta\delta = \delta(S) - \delta(R)$ (in Hz)[5]): H–C(2) –7; H_{ax}–C(3) –47; H_{eq}–C(3) –42; H–C(5') –6; H–C(2'), H–C(6') –10; MeO–C(3'), MeO–C(4') –4, –5; H–C(4) –1; H_{eq}–C(5) + 45; H_{ax}–C(5) + 52; H–C(6) + 6; CH_2(1'') + 11, + 12; CH_2(3''), CH_2(4'') + 5; Me(5'') + 3.

8. *4-[(3S,5S)-5-(Acetyloxy)-3-hydroxydecyl]benzene-1,2-diol* (**2a**)/*4-[(3S,5S)-3-(Acetyloxy)-5-hydroxydecyl]benzene-1,2-diol* (**2b**). Colourless viscous oil. R_f (hexane/acetone 2:1) 0.21. UV/VIS (EtOH, qual.): 220(1), 284(0.47). ^{1}H-NMR (600 MHz, $CDCl_3$): 2.07, 2.08 (2*s*, each 3H, MeCO), 3.49, 5.06 (2 br. *m*, $w_{1/2} \approx 30$, each 2H, H–C(3'), H–C(5')). ^{13}C-NMR (75.4 MHz, (D_6)aceton): 14.3, 14.35 (C(10')), 23.2, 23.4 (C(9')); 43.2, 43.3 (C(4')); 67.3, 67.8 (C(3) (**2a**), C(5') (**2b**)); 72.1, 72.3 (C(3') (**2b**), C(5') (**2a**)). EI-MS: 324 (53, M^+, $[C_{18}H_{28}O_5]^+$), 307 (9, $[M - H_2O]^+$), 264 (25, $[M - AcOH]^+$), 246 (16, $[M - H_2O - AcOH]^+$), 175(6), 165(14), 135(17), 123(100, $[(HO)_2C_6H_3CH_2]^+$), 109(7), 76(6), 55(10). The two compounds could only be separated after methylation of the catechol moiety and are characterized as the corresponding dimethoxy derivatives **2c** and **2f**.

Methylation of **2a**/**2b**. The mixture of **2a**/**2b** (10.5 mg), dry acetone (1 ml), dry Na_2CO_3 (42 mg), and MeI (0.1 ml) was stirred in a closed flask for 3 d at 70°. The crude product was chromatographed (SiO_2, hexane/acetone 8:1) to yield **2c**/**2f** (8 mg, 71%) which after prep. HPLC (CN, hexane/CH_2Cl_2/EtOH 18:1:0.1) gave **2c** (4 mg) and **2f** (3.5 mg).

(–)-(3S,5S)-5-(Acetyloxy)-1-(3,4-dimethoxyphenyl)decan-3-ol (**2c**). Colourless viscous oil. R_f (hexane/acetone 3:1) 0.36. $[\alpha]_D^{20} = -3.4$ (*c* = 1.5, $CHCl_3$). UV/VIS (EtOH): 230(3.89), 280(3.50). IR ($CHCl_3$): 3511 (br.), 3006, 2936, 2863, 1712, 1593, 1514, 1458, 1374, 1257, 1147, 1029, 948, 857. ^{1}H-NMR (600 MHz, $CDCl_3$): 0.88 (*t*, ^3J = 6.7, Me(10)); 1.24–1.35 (*m*, CH_2(7), CH_2(8), CH_2(9)); 1.51 (*ddd*, ^2J = 14, $^3J \approx 9$, 5, H_a–C(6)); 1.56–1.62 (*m*, CH_2(4), H_b–C(6)); 1.65 (*dddd*, ^2J = 14, $^3J \approx 9$, 7, 5, H_a–C(2)); 1.76 (*ddt*, ^2J = 14, $^3J \approx 9$, 7 H_b–C(2)); 2.05 (*s*, MeCO); 2.62 (*ddd*, ^2J = 14, $^3J \approx 9$, 7, H_a–C(1)); 2.75 (*ddd*, ^2J = 14, $^3J \approx 9$, 5, H_b–C(1)); 3.10 (br. *s*, $w_{1/2} \approx 10$, OH–C(3)); 3.46 (*t*-like *m*, $w_{1/2} \approx 25$, H–C(3)); 3.85, 3.86 (2*s*, 2 MeO); 5.07 (*quint.*-like *m*, $w_{1/2} \approx 25$, H–C(5)); 6.71 (*m*, H–C(2'), H–C(6')); 6.78 (*d*, ^3J = 8.2, H–C(5')). ^{13}C-NMR (75.4 MHz, $CDCl_3$): 14.9 (C(10)); 21.1, (*Me*CO); 22.5 (C(9)); 25.2 (C(7)); 31.5 (C(1)); 31.8 (C(8)); 34.9 (C(6)); 38.9 (C(2)); 43.1 (C(4)); 55.8, 55.9 (MeO); 66.3 (C(3)); 71.9 (C(5)); 111.3 (C(2')); 111.9 (C(5')); 120.2 (C(6')); 134.9 (C(1')); 147.2 (C(4')); 148.8 (C(3')); 172.6 (Me*C*O). CI-MS (NH_3): 370 (100, $[M + NH_4]^+$), 352 (8, M^+, $[C_{20}H_{32}O_5]^+$), 335 (26, $[M + H - H_2O]^+$), 310 (10, $[M + NH_4 - AcOH]^+$), 292 ($[M - AcOH]^+$), 275 (41, $[M + H - H_2O - AcOH]^+$), 177(9), 151 (8, $[(MeO)_2C_6H_3CH_2]^+$).

(+)-(3S,5S)-3-(Acetyloxy)-1-(3,4-dimethoxyphenyl)decan-5-ol (**2f**). Colourless viscous oil. R_f (hexane/acetone 3:1) 0.36. $[\alpha]_D^{20} = +18.3$ (*c* = 1.2, $CHCl_3$). UV/VIS (EtOH): 230(3.89), 280(3.50). IR ($CHCl_3$): 3513 (br.), 3006, 2935, 2862, 1714, 1595, 1514, 1458, 1374, 1256, 1147, 1029, 948, 856. ^{1}H-NMR (600 MHz, $CDCl_3$): 0.90 (*t*, ^3J = 7.1, Me(10)); 1.25–1.36 (*m*, H_a–C(7), CH_2(8), CH_2(9)); 1.36–1.53 (*m*, CH_2(6), H_b–C(7)); 1.57 (*ddd*,

$^2J = 14$, $^3J \approx 9, 5$, H_a–C(4)); 1.66 (*ddd*, $^2J = 14$, $^3J \approx 9, 5$, H_b–C(4)); 1.83 (*dddd*, $^2J = 14$, $^3J \approx 9, 7, 5$, H_a–C(2)); 1.96 (*ddt*, $^2J = 14$, $^3J \approx 9, 6$, H_b–C(2)); 2.10 (*s*, MeCO); 2.57 (*ddd*, $^2J = 14$, $^3J \approx 9, 6$, H_a–C(1)); 2.64 (*ddd*, $^2J = 14$, $^3J \approx 9, 6$, H_b–C(1)); 3.47 (*quint.*-like *m*, $w_{1/2} \approx 25$, H–C(5)); 3.86, 3.88 (2*s*, MeO); 5.14 (*t*-like *m*, $w_{1/2} \approx 25$, H–C(3)); 6.69 (*d*, $^4J = 1.9$, H–C(2′)); 6.70 (*dd*, $^3J = 8.0$, $^4J = 1.9$, H–C(6′)); 6.80 (*d*, $^3J = 8.0$, H–C(5′)). ^{13}C-NMR (150.9 MHz, $CDCl_3$): 14.0 (Me(10)); 21.1 (*Me*CO); 22.6 (C(9)); 25.5 (C(7)); 31.6 (C(1)); 31.9 (C(8)); 36.9 (C(2)); 37.1 (C(6)); 43.0 (C(4)); 55.8, 55.9 (MeO); 67.2 (C(5)); 71.5 (C(3)); 111.3 (C(2′)); 111.7 (C(5′)); 120.1 (C(6′)); 133.8 (C(1′)); 147.5 (C(4′)); 149.0 (C(3′)); 172.2 (Me*C*O). CI-MS (NH_3): 370 (100, $[M + NH_4]^+$), 352 (7, M^+,$[C_{20}H_{32}O_5]^+$), 335 (54, $[M + H - H_2O]^+$), 310 (13, $[M + NH_4 - AcOH]^+$), 292 ($[M - AcOH]^+$), 275 (23, $[M + H - H_2O - AcOH]^+$), 177 (9), 151 (11, $[(MeO)_2C_6H_3CH_2]^+$).

(S)- and (R)-MTPA Esters of **2c**. Chromatography of the crude products (SiO_2, hexane/acetone 13:1) afforded the (*S*)-MTPA ester **2d** (5.5 mg, 85%) and the (*R*)-MTPA ester **2e** (5.9 mg, 91%). R_f (hexane/acetone 3:1) 0.32.

Data of the (S)-MTPA Ester **2d**. IR ($CHCl_3$): 3018, 2935, 2861, 1738, 1593, 1515, 1461, 1373, 1257, 1121, 1081, 1025, 806. ^{1}H-NMR (600 MHz, $CDCl_3$): 0.86 (*t*, $^3J = 7.2$, Me(10)); 1.21–1.29 (*m*, CH_2(7), CH_2(8), CH_2(9)); 1.46, 1.55 (2*m*, $w_{1/2} \approx 25$, each 1H, CH_2(6)); 1.87 (*dddt*-like *m*, $w_{1/2} \approx 50$, CH_2(2), CH_2(4)); 2.02 (*s*, MeCO); 2.47 (*ddt*-like *m*, $w_{1/2} \approx 30$, CH_2(1)); 3.56 (*s*, MeO (MTPA)); 3.85, 3.86 (2*s*, 2 MeO); 4.85 (*quint.*-like *m*, $w_{1/2} \approx 25$, H–C(5)); 5.17 (*quint.*-like *m*, $w_{1/2} \approx 25$, H–C(3)); 6.60–6.63 (*m*, H–C(2′), H–C(6′)); 6.76 (*d*, $^3J = 8.1$, H–C(5′)); 7.41–7.42 (*m*, 3 arom. H (MTPA)); 7.58–7.59 (*m*, 2 arom. H (MTPA)). CI-MS (NH_3): 586 (100, $[M + NH_4]^+$), 568 (7, M^+, $[C_{30}H_{39}F_3O_7]^+$), 335(8), 252(8), 217(14).

Data of the (R)-MTPA Ester **2e**. ^{1}H-NMR (600 MHz, $CDCl_3$): 0.86 (*t*, $^3J = 7.0$, Me(10)); 1.18–1.21 (*m*, CH_2(8), CH_2(9)); 1.23–1.27 (*m*, CH_2(7)); 1.42, 1.52 (2*m*, $w_{1/2} \approx 25$, each 1H, CH_2(6)); 1.84 (*ddt*-like *m*, $w_{1/2} \approx 25$, CH_2(4)); 1.90, 2.01 (2*m*, $w_{1/2} \approx 30$, each 1H, CH_2(2)); 2.00 (*s*, MeCO); 2.59 (*tt*-like *m*, $w_{1/2} \approx 20$, CH_2(1)); 3.58 (*s*, MeO (MTPA)); 3.85, 3.86 (2*s*, 2 MeO); 4.76 (*quint.*-like *m*, $w_{1/2} \approx 25$, H–C(5)); 5.20 (*quint.*-like *m*, $w_{1/2} \approx 25$, H–C(3)); 6.66–6.69 (*m*, H–C(2′), H–C(6′)); 6.79 (*d*, $^3J = 8.0$, H–C(5′)); 7.26–7.42 (*m*, 3 arom. H (MTPA)); 7.57–7.59 (m, 2 arom. H (MTPA)).

$\Delta\delta = \delta(S) - \delta(R)$ (in Hz)[5]: CH_2(1) −70; CH_2(2) −70; H–C(2′), H–C(6′) −37; MeO–C(3′), MeO–C(4′) −2, −3; H–C(5′) −13; H–C(3) −16; MeCO + 10; CH_2(4) + 11; H–C(5) + 55; CH_2(6) + 17, + 24; CH_2(7) + 9; CH_2(8), CH_2(9) + 24; Me(10) + 5.

(S)- and (R)-MTPA Esters of **2f**. Chromatography of the crude products (SiO_2, toluene/AcOEt 30:1) afforded the (*S*)-MTPA ester **2g** (6 mg, 93%) and the (*R*)-MTPA ester **2h** (6.3 mg, 98%). R_f (toluene/AcOEt 5:1) 0.50.

Data of the (S)-MTPA Ester **2g**. IR ($CHCl_3$): 3007, 2958, 2933, 2861, 1737, 1592, 1516, 1465, 1420, 1357, 1260, 1171, 1141, 1122, 1080, 1027. ^{1}H-NMR (600 MHz, $CDCl_3$): 0.85 (*t*, $^3J = 6.9$, Me(10)); 1.16–1.44 (*m*, CH_2(7), CH_2(8), CH_2(9)); 1.53, 1.57 (2*m*, $w_{1/2} \approx 25$, each 1H, CH_2(6)); 1.80, 1.91 (2*m*, $w_{1/2} \approx 30$, each 1H, CH_2(2)); 1.86 (*ddt*-like *m*, $w_{1/2} \approx 25$, CH_2(4)); 2.07 (*s*, MeCO); 2.51 (*ddd*, $^2J = 14.0$, $^3J = 9.6, 6.4$, H_a–C(1)); 2.57 (*ddd*, $^2J = 14.0$, $^3J = 9.8, 5.8$, H_b–C(1)); 3.51 (*s*, MeO (MTPA)); 3.85, 3.86 (2*s*, each 3H, MeO); 4.92 (*quint.*-like *m*, $w_{1/2} \approx 25$, H–C(3)); 5.12 (*quint.*-like *m*, $w_{1/2} \approx 25$, H–C(5)); 6.67–6.68 (*m*, H–C(2′), H–C(6′)); 6.77 (*d*, $^3J = 8.5$, H–C(5′)); 7.39–7.40 (*m*, 3 arom. H (MTPA)); 7.52–7.54 (*m*, 2 arom. H (MTPA)). CI-MS (NH_3): 586 (100, $[M + NH_4]^+$), 568 (5, M^+, $[C_{30}H_{39}F_{30}O_7]^+$), 335 (5).

Data of the (R)-MTPA Ester **2h**. ^{1}H-NMR (600 MHz, $CDCl_3$): 0.88 (*t*, $^3J = 6.7$, Me(10)); 1.25–1.34 (*m*, CH_2(7), CH_2(8), CH_2(9)); 1.60, 1.67 (2*ddm*, $^2J = 14.5$, $^3J \approx 5.5$, each 1H, CH_2(6)); 1.75, 1.86 (*m*, $w_{1/2} \approx 30$, each 1H, CH_2(2)); 1.83 (*t*, $^3J \approx 6$, CH_2(4)); 2.04 (*s*, MeCO); 2.46 (*ddd*, $^2J = 14.0$, $^3J = 9.8, 6.2$, H_a–C(1)); 2.50 (*ddd*, $^2J = 14.0$, $^3J = 8.2, 4.2$, H_b–C(1)); 3.54 (*s*, MeO (MTPA)); 3.85, 3.86 (2*s*, 2 MeO); 4.82 (*quint.*, $^3J = 6.2$, H–C(3)); 5.15 (*quint.*, $^3J = 6.2$, H–C(5)); 6.65–6.66 (*m*, H–C(2′), H–C(6′)); 6.76 (*d*, $^3J = 8.4$, H–C(5′)); 7.39–7.40 (*m*, arom. H (MTPA)); 7.55–7.57 (*m*, 2 arom. H (MTPA)).

$\Delta\delta = \delta(S)$-$\delta(R)$ (in Hz)[5]: CH_2(1) + 34, + 46; CH_2(2) + 22, + 28; H–C(3) + 62; MeCO + 15; CH_2(4) + 20; H–C(2′), H–C(6′) + 10; MeO–C(3′), MeO–C(4′) + 2, −3; H–C(5′) + 3; H–C(5) −22; CH_2(6) −52, −58; CH_2(7), CH_2(8), CH_2(9): −50; Me(10) −22.

(−)-(3S,5S)-1-(3,4-Dimethoxyphenyl)decane-3,5-diol (**2i**). Hydrolysis of **2c** (10 mg) in EtOH (1 ml) and 2N KOH (0.5 ml) at r.t. for 12 h, workup and chromatography (SiO_2, hexane/acetone 6:1) afforded **2i** (8 mg, 89%). White crystals. M.p. 84.5–85.0°. R_f (hexane/acetone 2:1) 0.32. $[\alpha]_D^{20} = -2.7$ (*c* = 0.55, $CHCl_3$). UV/VIS (EtOH): 230(3.84), 280(3.40). IR ($CHCl_3$): 3617, 3502 (br.), 3004, 2935, 2859, 1591, 1515, 1464, 1418, 1260, 1154, 1141, 1074, 1029, 942, 854. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.89 (*t*, $^3J = 6.7$, Me(10)); 1.25–1.30 (*m*, CH_2(7), CH_2(8), CH_2(9)); 1.35–1.59 (*m*, CH_2(6)); 1.65 (*t*-like *m*, $w_{1/2} \approx 10$, CH_2(4)); 1.69–1.92 (*m*, CH_2(2)); 2.27 (br. *s*, 2 OH); 2.62 (*ddd*, $^2J = 14$, $^3J \approx 9, 7$, H_a–C(1)); 2.75 (*ddd*, $^2J = 14$, $^3J \approx 9, 6$, H_b–C(1)); 3.86, 3.87 (2*s*, 2 MeO); 3.98 (*m*, $w_{1/2} \approx 15$, H–C(3), H–C(5)); 6.73–6.76 (*m*, H–C(2′), H–C(6′)); 6.79 (*d*, $^3J = 8.7$, H–C(5′)). ^{13}C-NMR

(75.4 MHz, $CDCl_3$): 14.0 (C(10)); 22.6 (C(9)); 25.4 (C(7)); 31.8, 31.9 (C(1), C(8)); 37.6, 39.3 (C(2), C(6)); 42.5 (C(4)); 55.8, 55.9 (MeO); 69.0, 69.6 (C(3), C(5)); 111.3 (C(2')); 111.8 (C(5')); 120.2 (C(6')); 134.6 (C(1')); 147.3 (C(4')); 149.0 (C(3')). EI-MS: 310 (19, M^+, $[C_{18}H_{30}O_4]^+$), 292 (11, $[M - H_2O]^+$), 177(11), 164(10), 151(100, $[(MeO)_2C_6H_3CH_2]^+$), 138(10), 121(10), 107(10), 91(10), 77(9), 55(17), 43(18).

Analogous treatment of **2f** (8.5 mg) gave **2i** (7 mg, 94%) which proved to be identical with the compound obtained from **2c** (m.p., R_f, $[\alpha]_D^{20}$, UV/VIS, IR, ^{1}H- and ^{13}C-NMR, EI-MS).

4-[2-(3,4-Dimethoxyphenyl)ethyl]-2,2-dimethyl-6-pentyl-1,3-dioxane **2j**. A mixture of **2i** (obtained from **2c**, 11.5 mg), dry acetone (1.5 ml), and dry $CuSO_4$ (100 mg) was refluxed under Ar for 12 h. After workup and chromatography (SiO_2, hexane/acetone 1:12), **2j** (7.5 mg, 58%) was obtained as a colourless viscous oil. R_f (hexane/acetone 3:1) 0.53. $[\alpha]_D^{20} = +12.0$ ($c = 0.45$, $CHCl_3$). UV/VIS (EtOH): 230(4.09), 280(3.68). IR ($CHCl_3$): 3005, 2936, 2860, 1718, 1591, 1515, 1465, 1418, 1380, 1260, 1155, 1140, 1077, 1028, 855. ^{1}H-NMR (600 MHz, $CDCl_3$): 0.89 (*t*, $^3J = 6.9$, *Me*$(CH_2)_4$); 1.26–1.34 (*m*, Me$(CH_2)_3CH_2$); 1.35, 1.37 (2*s*, 2 Me–C(2)); 1.34–1.43 (*m*, Me$(CH_2)_3CH_2$); 1.58 (*dtt*-like *m*, $w_{1/2} \approx 25$, 2H–C(5); 1.71 (*dddd*, $^2J = 14.0$, $^3J \approx 9$, 7, 5, H_a–C(1')); 1.83 (*ddt*, $^2J = 14$, $^3J \approx 9$, 7, H_b–C(1')); 2.56 (*ddd*, $^2J = 14$, $^3J \approx 9$, 7, H_a–C(2')); 2.72 (*ddd*, $^2J = 14$, $^3J \approx 9$, 5, H_b–C(2')); 3.77 (*quint.*-like *m*, $w_{1/2} \approx 25$, H–C(4), H–C(6)); 3.85, 3.86 (2*s*, 2 MeO); 6.72–6.73 (*m*, H–C(2''), H–C(6'')); 6.79 (*d*, $^3J = 8.5$, H–C(5'')). ^{13}C-NMR (75.4 MHz, $CDCl_3$): 14.0 (*Me*$(CH_2)_4$); 22.6 (MeC$H_2(CH_2)_4$); 24.8, 25.0 (2*Me*–C(2)); 25.1 (Me$(CH_2)_2CH_2CH_2$); 31.4,31.8 (C(2'),MeCH$_2CH_2(CH_2)_2$); 36.0, 37.8 (C(1'), Me$(CH_2)_4CH_2$); 38.9 (C(5)); 55.8, 55.9 (MeO); 65.9, 66.7 (C(4), C(6)); 100.3 (C(2)); 111.3 (C(2'')); 111.9 (C(5'')); 120.3 (C(6'')); 134.8 (C(1'')); 147.2 (C(4'')); 148.8 (C(3'')). EI-MS: 350 (10, M^+, $[C_{21}H_{34}O_4]^+$), 292 (32, $[M - Me_2CO]^+$), 193(8), 177(16), 164(10), 151(100, $[(MeO)_2C_6H_3CH_2]^+$), 138(6), 59(13).

Analogous treatment of **2i** (obtained from **2f**; 7 mg) gave **2j** (6 mg, 76%). The physical (R_f, $[\alpha]_D^{20}$) and spectral data (UV/VIS, IR, ^{1}H-, ^{13}C-NMR, EI-MS) of both derivatives **2j** were identical.

9. *(–)-(3S,13Z)-1-(3,4-Dihydroxyphenyl)-3-hydroxydocos-13-en-5-one* (**3a**). Slightly brownish oily prisms. M.p. 31.5–32.0°. R_f (hexane/acetone 2:1) 0.33, R_f (toluene/AcOEt 5:2) 0.19. $[\alpha]_D^{20} = -30.0$ ($c = 1.1$, $CHCl_3$). UV/VIS (EtOH): 283 (3.45). IR ($CHCl_3$): 3599, 3557, 3005, 2928, 2856, 1702, 1606, 1518, 1456, 1370, 1279, 1103, 956, 896. ^{1}H-NMR (600 MHz, C_6D_6): 0.92 (*t*, $^3J = 7.3$, Me(22)); 1.14 (*quint.*, $^3J \approx 7$, CH_2(8)); 1.22 (*quint.*-like *m*, $w_{1/2} \approx 28$, CH_2(9)); 1.28–1.35 (*m*, 12H, CH_2(10), CH_2(17) to CH_2(21)); 1.37–1.42 (*m*, CH_2(11), CH_2(16)); 1,45 (*t*, $^3J = 7.5$, CH_2(7)); 1.47–1.51, 1.68–1.74 (2*m*, each 1H, CH_2(2)); 1.94 (*t*, $^3J = 7.5$, CH_2(6)); 1.98 (*dd*, $^2J = 16.5$, $^3J = 2.5$, H_a–C(4)); 2.10–2.15 (*m*, H_b–C(4), CH_2(12), CH_2(15)); 2.59, 2.68 (2 *ddd*-like *m*, $^2J = 14$, $^3J \approx 8$, 6, each 1H, CH_2(1)); 3.40 (br. *s*, OH–C(3)); 3.96 (*quint.*-like *m*, $w_{1/2} \approx 20$, H–C(3)); 5.52 (*quint.*-like *m*, $w_{1/2} \approx 12$, H–C(13), H–C(14)); 6.61 (*dd*, $^3J = 7.0$, $^4J = 1.9$, H–C(6')); 6.75 (*m*, $w_{1/2} \approx 9$, H–C(2'), H–C(5')). ^{13}C-NMR (75.4 MHz, C_6D_6): 14.4 (C(22)); 23.2 (C(21)); 23.8 (C(7)); 27.7, 27.75 (C(12), C(15)); 29.5, 29.6 (C(8), C(9)); 29.8 (3C), 30.0, 30.2 (2C), 30.3 (C(8) to C(11), C(16) to C(19)); 31.4 (C(1)); 32.3 (C(20)); 38.7 (C(2)); 43.5 (C(6)); 48.9 (C(4)); 67.2 (C(3)); 115.6 (C(2')); 116.0 (C(5')); 120.9 (C(6')); 130.0, 130.3 (C(13), C(14)); 134.8 (C(1')); 142.7 (C(4')); 144.4 (C(3')); 211.7 (C(5)). EI-MS: 446 (17, M^+, $[C_{28}H_{46}O_4]^+$), 428 (29, $[M - H_2O]^+$), 402(14), 247(6), 190(5), 162(10), 148(29), 123(100, $[(HO)_2C_6H_3CH_2]^+$), 95(8), 81(9), 67(13).

(+)-(3S,13Z)-1-(3,4-Dimethoxyphenyl)-3-hydroxydocos-13-ene-5-one (**3b**). The mixture of **3a** (10 mg), dry acetone (1 ml), dry Na_2CO_3 (50 mg), and MeI (0.1 ml) was stirred in a closed flask for 4 d at 80°. Workup and chromatography (SiO_2, hexane/acetone 20:1 → 5:1) yielded **3b** (9 mg, 85%). Colourless viscous oil. R_f (toluene/AcOEt 10:1) 0.13. $[\alpha]_D^{20} = +3.8$ ($c = 0.6$, $CHCl_3$). UV/VIS (EtOH): 228(3.92), 280(3.51). IR ($CHCl_3$): 3500 (br.), 3007, 2929, 2855, 1728, 1591, 1515, 1465, 1418, 1375, 1259, 1155, 1140, 1028, 809. ^{1}H-NMR (400 MHz, $CDCl_3$): 0.88 (*t*, $^3J = 6.8$, Me(22)); 1.25–1.34 (*m*, 20H, CH_2(8) to CH_2(11), CH_2(16) to CH_2(21)); 1.56 (br. *t*, $^3J = 7$, CH_2(7)); 1.62–1.71, 1.77–1.85 (2*m*, each 1H, CH_2(2)); 2.01 (*q*-like *m*, $w_{1/2} \approx 15$, CH_2(12), CH_2(15)); 2.40 (*t*, $^3J = 7.4$, CH_2(6)); 2.56 (*A* of *ABM*, $^2J = 17$, $^3J = 8$, H_a–C(4)); 2.57 (*B* of *ABM*, $^2J = 17$, $^3J = 3$, H_b–C(4)); 2.62 (*ddd*, $^2J = 14$, $^3J \approx 9$, 7, H_a–C(1)); 2.77 (*ddd*, $^2J = 14$, $^3J \approx 9$, 5, H_b–C(1)); 3.14 (*d*, $^3J = 3.2$, OH–C(3)); 3.85, 3.87 (2*s*, 2 MeO); 4.05 (*dq*-like *m*, $w_{1/2} \approx 25$, H–C(3)); 5.34 (*quint.*-like *m*, $w_{1/2} \approx 12$, H–C(13), H–C(14)); 6.72–6.75 (*m*, H–C(2'), H–C(6')); 6.79 (*d*, $^3J = 8.6$, H–C(5')). CI-MS (NH_3): 492 (100, $[M + NH_4]^+$), 474 (87, M^+, $[C_{30}H_{50}O_4]^+$), 457 (16, $[M + H - H_2O]^+$), 412(16).

(S)- and (R)-MTPA Esters of **3b**. Chromatography of the crude products (SiO_2, toluene/AcOEt 20:1) afforded the (*S*)-MTPA ester **3c** (4 mg, 69%) and the (*R*)-MTPA ester **3d** (5 mg, 86%). R_f (toluene/AcOEt 10:1) 0.49.

Data of the (S)-MTPA Ester **3c**. IR ($CHCl_3$): 3007, 2928, 2855, 1747, 1716, 1516, 1465, 1379, 1261, 1141, 1123, 1079, 1027. ^{1}H-NMR (600 MHz, $CDCl_3$): 0.88 (*t*, $^3J = 7$, Me(22)); 1.24–1.35 (*m*, 20H, CH_2(8) to CH_2(11), CH_2(16) to CH_2(21)); 1.51 (*quint.*, $^3J = 7.5$, CH_2(7)); 1.93 (*dt*, $^3J = 8$, 6, CH_2(2)); 2.01 (br. *q*, $^3J \approx 7$, CH_2(12), CH_2(15)); 2.33 (*dt*, $^2J = 16.9$, $^3J = 7.4$, H_a–C(6)); 2.37 (*dt*, $^2J = 16.9$, $^3J = 7.5$, H_b–C(6)); 2.47 (*dt*, $^2J = 13.9$, $^3J = 7.6$, H_a–C(1)); 2.51 (*dt*, $^2J = 13.9$, $^3J = 6.2$, H_b–C(1)); 2.62 (*dd*, $^2J = 16.9$, $^3J = 5.2$,

H_a–C(4)); 2.87 (*dd*, ^2J = 16.9, ^3J = 7.6, H_b–C(4)); 3.53 (*s*, MeO (MTPA)); 3.85, 3.86 (2*s*, 2 MeO); 5.34 (*oct.*-like *m*, $w_{1/2} \approx 8$, H–C(13), H–C(14)); 5.55 (*dt*-like *m*, $w_{1/2} \approx 12$, H–C(3)); 6.61–6.62 (*m*, H–C(2'), H–C(6')); 6.77 (*d*, ^3J = 7.8, H–C(5')); 7.39–7.41 (*m*, 3 arom. H (MTPA)); 7.52–7.54 (*m*, 2 arom. H (MTPA)). CI-MS (NH_3): 708 (35, $[M + NH_4]^+$), 690 (22, M^+, $[C_{40}H_{57}F_3O_4]^+$), 624(24), 614(82), 606(20), 568(7), 524(11), 488(11), 474(43, $[M - MTPA]^+$), 456(100, $[M - MTPA - H_2O]^+$), 177(35), 151(18, $[(MeO)_2C_6H_3CH_2]^+$).

*Data of the (*R*)-MTPA Ester* **3d**. ^{1}H-NMR (600 MHz, $CHCl_3$): 0.88 (*t*, ^3J = 6.9, Me(22)); 1.2–1.34 (*m*, 20H, CH_2(8) to CH_2(11), CH_2(16) to CH_2(21)); 1.47 (*quint.*, ^3J = 7.5, CH_2(7)); 1.96–2.03 (*m*, CH_2(2), CH_2(12), CH_2(15)); 2.24 (*dt*, ^2J = 16.9, ^3J = 7.4, H_a–C(6)); 2.30 (*dt*, ^2J = 16.9, ^3J = 7.5, H_b–C(6)); 2.58 (*dd*, ^2J = 16.8, ^3J = 5.4, H_a–C(4)); 2.58 (*dm*, ^2J = 13.9, H_a–C(1)); 2.62 (*dt*, ^2J = 13.9, ^3J = 3.9, H_b–C(1)); 2.82 (*dd*, ^2J = 16.8, ^3J = 7.4, H_b–C(4)); 3.54 (*s*, MeO (MTPA)); 3.85, 3.86 (2*s*, 2 MeO); 5.34 (*oct.*-like *m*, $w_{1/2} \approx 8$, H–C(13), H–C(14)); 5.56 (*dt*-like *m*, $w_{1/2} \approx 12$, H–C(3)); 6.66–6.68 (*m*, H–C(2'), H–C(6')); 6.79 (*d*, ^3J = 7.8, H–C(5')); 7.37–7.40 (*m*, arom. H (MTPA)); 7.52–7.56 (*m*, arom. H (MTPA)).

$\Delta\delta = \delta(S)$-$\delta(R)$ (in Hz)[5]: CH_2(1) −72, −75; CH_2(2) −29; H–C(2'), H–C(6') −34; MeO–C(3'), MeO–C(4') −3; H–C(3) −6; CH_2(4) + 26, + 27; CH_2(6) + 42, + 50; CH_2(7) + 24; H–C(13), H–C(14) −1; CH_2(8) to CH_2(10), CH_2(17) to CH_2(21) −1; CH_2(11), CH_2(16) −2; Me(22) 0.

10. *(Z)-1-(3,4-Dihydroxyphenyl)docos-13-en-5-one* (**4**). White oily crystals. M.p. *ca.* 25°. R_f (hexane/acetone 2:1) 0.5. UV/VIS (EtOH): 222(3.72), 284(3.40). IR (KBr): 3601, 3557, 3004, 2928, 2855, 1706, 1605, 1518, 1462, 1369, 1317, 1281, 1249, 1105, 871, 805. ^{1}H-NMR (300 MHz, $CDCl_3$): 0.88 (*t*, ^3J = 6.7, Me(22)); 1.27 (*s*, $w_{1/2} \approx 9$, 20H, CH_2(8) to CH_2(11), CH_2(16) to CH_2(21)); 1.54 (*q*-like *m*, $w_{1/2} \approx 15$, CH_2(2), CH_2(3), CH_2(7)); 2.00 (*q*-like *m*, $w_{1/2} \approx 10$, CH_2(12), CH_2(15)); 2.36, 2.39, (2 *t*, ^3J = 7.5, each 2H, CH_2(4), CH_2(6)); 2.47 (*t*, $^3J \approx 7.5$, CH_2(1)); 5.33 (*t*-like *m*, $w_{1/2} \approx 10$, H–C(13), H–C(14)); 6.57 (*d*, ^3J = 7.3, H–C(6')); 6.67 ('*s*', H–C(2')); 6.75 (*d*, ^3J = 7.3, H–C(5')). ^{13}C-NMR (75.4 MHz): 14.1 (C(22)); 22.7 (C(21)); 23.7, 23.9 (C(3), C(7)); 27.1, 27.2, 29.1, 29.2, 29.3, 29.5 (2C), 29.7 (C(8) to C(11), C(16) to C(19)); 31.1, 31.9 (C(2), C(20)); 35.0 (C(1)); 42.6, 42.9 (C(4), C(6)); 115.3 (C(2')); 115.5 (C(5')); 120.6 (C(6')); 129.7, 130.0 (C(13), C(14))[21]. CI-MS (NH_3): 448 (100, $[M + NH_4]^+$), 431 (12, $[M + H]^+$, $[C_{28}H_{47}O_3]^+$).

11. *1-(3,4-Dihydroxyphenyl)icosan-5-one* (**5**). White crystals. M.p. 65.5–68.0°. R_f (hexane/acetone 2:1) 0.5. CI-MS (NH_3): 422 (100, $[M + NH_4]^+$), 405 (10, $[M + H]^+$ $[C_{26}H_{45}O_3]^+$). UV/VIS, IR, ^{1}H-, and ^{13}C-NMR: identical with those reported [1].

12. *Ozonolysis of* **3a** *and* **4**. Acetylation of **3a** (2 mg) in pyridine (0.1 ml) with Ac_2O (0.15 ml) at r.t. for 4 h yielded a crude triacetate (3 mg) which was subjected to ozonolysis without further purification. The triacetate was treated in dry EtOH (1 ml) with O_3 at −78° for 30 min. The reaction was quenched with Me_2S (2 drops) and stirred for another 30 min at r.t. After bubbling O_2 through the mixture (*ca.* 1 min), it was directly subjected to GC/MS analysis. Nonanal (pelargonaldehyde) was identified as the main product by comparison with an authentic sample (t_R, EI-MS).

Without prior acetylation, otherwise following the same protocol, nonanal was detected as the main product (t_R, EI-MS) after the ozonolysis of **4** (2 mg).

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