Synthesis and Nematocidal Activity of Aralkyl- and Aralkenylamides Related to Piperamide on Second-Stage Larvae of *Toxocara canis*[1)]

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Seventy-nine aralkyl- and aralkenylamides related to piperamides were synthesized and their nematocidal activity against second-stage larvae of dog roundworm, *Toxocara canis*, was examined. The activity was greatly dependent on the alkyl chain length and the nature of the amine moiety, but was scarcely affected by the presence or absence of double bond(s) in the chain. The alkyl chain lengths which showed the strongest activity in a series of homologues were m = 11 for the pyrrolidine amides and m = 13 for the *N*-methylpiperazine amides. Although piperamides (3,4-methylenedioxyphenyl homologues) showed the strongest activity among the homologues tested, methoxy substituent(s) on the aromatic ring did not have much effect on the activity. However, conversion of the methoxy group to a hydroxy group greatly decreased the activity and shortened the chain length giving the strongest activity. Calculated log P values of non-phenolic aryl-piperamides fell in the range from 3.5 to 4.5, whereas those of hydroxyphenyl-piperamides were smaller, suggesting that different mechanisms are involved in the nematocidal activity of phenolic and non-phenolic compounds.

Key words piperamide; synthesis; nematocidal activity; structure–activity relationship; *Toxocara canis*; hydrophobicity

In a previous paper,[3)] we revealed that piperamides (PA's, Chart 1) are the nematocidal principles of pepper (*Piper nigrum* L.) against second-stage larvae of dog roundworm, *Toxocara canis*, and suggested that the nematocidal activity of these compounds was dependent on the length of the alkyl chain and the nature of the amine moiety. In this paper, we report systematic synthesis of various aralkyl- and aralkenylamides related to piperamides and we discuss their nematocidal activity.

In addition to piperamides of the natural type, all of which have a 3,4-methylenedioxyphenyl group, aralkyl- and aralkenylamides which have phenyl, 4-methoxyphenyl, and 3,4-dimethoxyphenyl as the aromatic moiety are synthesized and designated, for convenience, as phenylpiperamide, 4-methoxyphenylpiperamide, and 3,4-dimethoxyphenylpiperamide, respectively. They are abbreviated as aryl-PA-Xm:n, in which X corresponds to an amine moiety, m represents the number of cabon atoms in the chain, and n the number of double bonds therein. Thus, the compounds of natural type are 3,4-methylenedioxyphenylpiperamides, which are simply called piperamides and abbreviated as PA-Xm:n as proposed

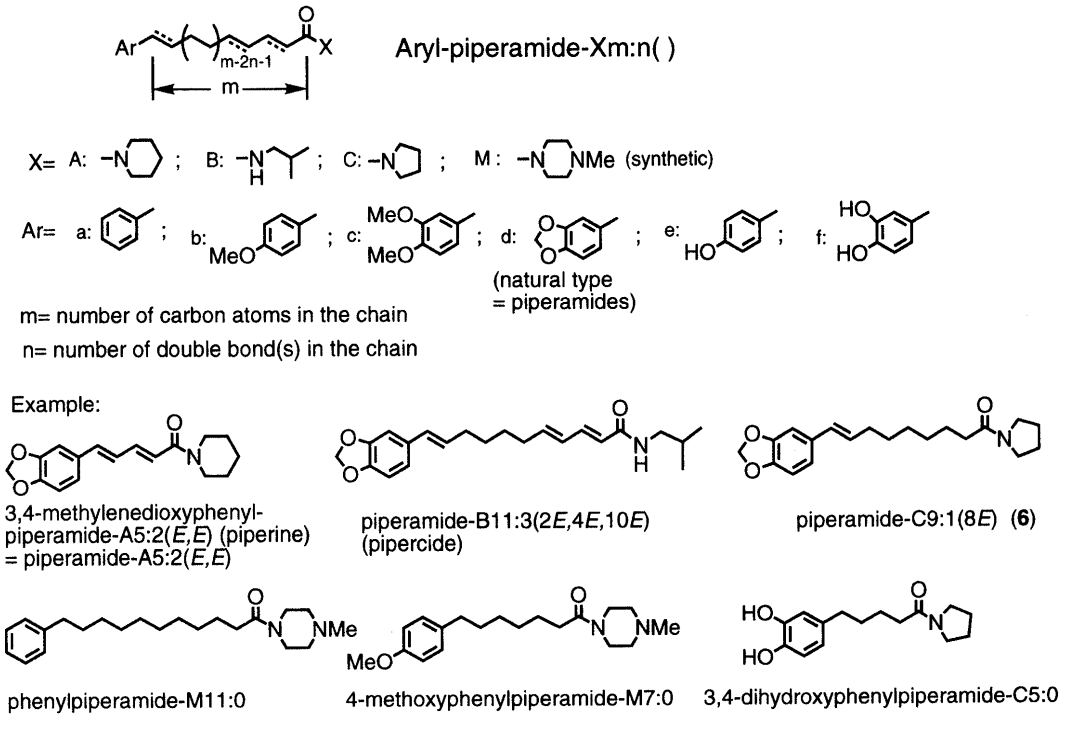

Chart 1

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previously.[3,4]

Synthesis

Aralkyl- and aralkenylamides related to piperamides have been synthesized by several researchers.[5-8] For the systematic synthesis of piperamides and their analogs carrying various side chains with and without a double bond at C-2 and/or at the position adjacent to the aryl group (designated as an arylic position, hereafter), we adopted the synthetic strategy shown in Charts 2 and 3. The target molecules were constructed by connection of three parts, *i.e.* an aromatic moiety carrying a C1 unit (①), a middle chain moiety carrying different functionalites at the two termini (②), and an amine (③).

As the aromatic moiety of part ①, 3,4-methylenedioxyphenyl (piperamide type, **d**), phenyl (**a**), 4-methoxyphenyl (**b**) and 3,4-dimethoxyphenyl (**c**) groups were selected. Arylmethyltriphenylphosphonium bromides, which are readily preparable from arylmethylcarbinols by heating with triphenylphosphine hydrobromide,[9] or arylaldehydes were the best precursors.

The alkyl chain building blocks (②) were prepared from commercially available lactones or olefins (Chart 2). Triphenylphosphonium bromides of C4 (**1**) and C6 (**2**) carboxylic acids were prepared from triphenylphosphine hydrobromide[10] and γ-butylolactone or ε-caprolactone, respectively, by the method of Hamanaka *et al.*[9] The C8 aldehyde-ester unit (**3**) was prepared from cyclooctene by unsymmetrical ozonolysis.[11] The C10 aldehyde-ester unit (**4**) was synthesized by the Lemieux oxidation of methyl 10-undecenoate. The Wittig reaction of an appropriate combination of parts ① and ② (Ia + IIb or Ib + IIa, Chart 3) gave an aralkenylcarboxylic acid or its ester (III) of m = 5 to 11 with a double bond (*E*/*Z* mixture) at the arylic position. The stereochemically pure *E*-isomers (IV) were obtained by isomerization of this mixture with a catalytic amount of iodine in benzene.[12] Hydrogenation of the above mixture (III) over Pd–C gave saturated aralkylcarboxylates (V) of m = 5 to 11. For the higher saturated alkyl homologues (m = 13 and 15), the aralkylcarboxylates (III) of m = 7 and 9 were converted to the alcohols and then to the aldehydes (VI) (m = 7 and 9), which were condensed with the C6 unit (**2**) by means of the Wittig reaction, and the product was hydrogenated to afford the saturated compounds (VII) of m = 13 or 15.

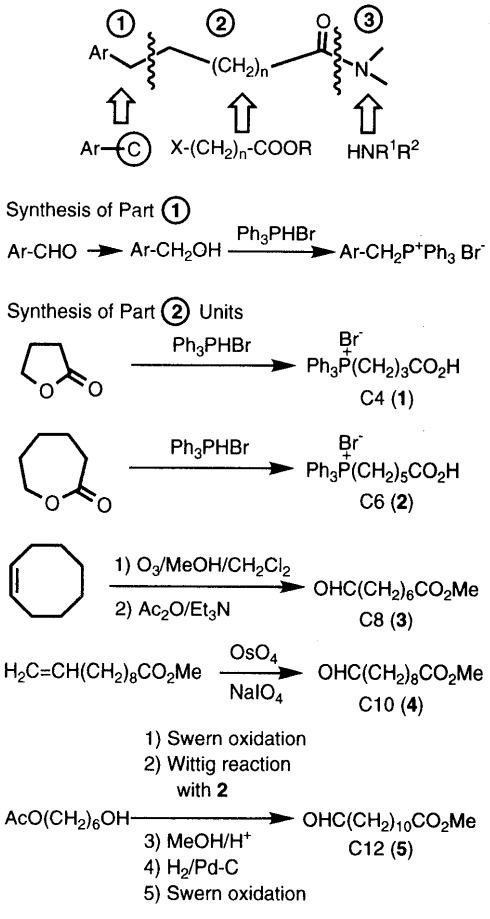


Chart 2

For preparation of the molecule with a double bond at the C-2 position, the carboxylate (V) was converted to the corresponding aldehyde (VIII) and then reacted with triethyl phosphonoacetate to afford a two-carbon-elongated homologue (IX) with an (*E*)-double bond at the C-2 position. A (2*E*,ω*E*)-aralkyldienoate (X) was prepared from the (ω*E*)-carboxylate (IV) by this method. A (2*E*,4*E*)-aralkyldienoate was obtained by the reaction of saturated aldehydes with triethyl phosphonocrotonate.

The carboxylates thus obtained were converted to amides by either of the following methods: the carboxylic acids were converted to corresponding mixed anhydrides with ethyl chloroformate and reacted with appropriate amines[13]; the methyl esters were directly converted to the amides by the trimethylaluminum method[14] (see Experimental). As an amine moiety, pyrrolidine (natural type) and *N*-methylpiperazine (unnatural type) were employed in most cases, since other types of amides were found to be inactive or less active than those two (see below). 4-Hydroxyphenyl (**e**) and 3,4-dihydroxyphenyl (**f**) analogs in the aromatic moiety were prepared from the corresponding methoxy derivatives by BBr_3 demethylation at the amide stage. Thus we prepared 79 aryl-piperamides.

Nematocidal Activity of Piperamides and Their Analogs Nematocidal Activity of Piperamides: *In vitro* nematocidal activity against second-stage larvae of *Toxocara canis* was determined as described previously.[15] Firstly, we compared the activity of piperamides having various amine moieties. As PA-C9 : 1(8*E*) (**6**) showed the strongest nematocidal activity among the piperamides isolated from pepper,[3] the activities of the compounds with an alkyl chain length of 9 (PA-X9 : n) were firstly compared (Table 1). In a previous paper,[16] we examined the nematocidal activity of long-chain fatty acid amides with various amine moieties and various chain lengths. In that work, *N*-monosubstituted amides did not show any activity, whereas *N*,*N*-disubstituted amides with small *N*-substituents, especially *N*-acyl cyclic amines, showed strong activity: the smaller the ring size was, the stronger was the activity. We also found that amides of polar cyclic

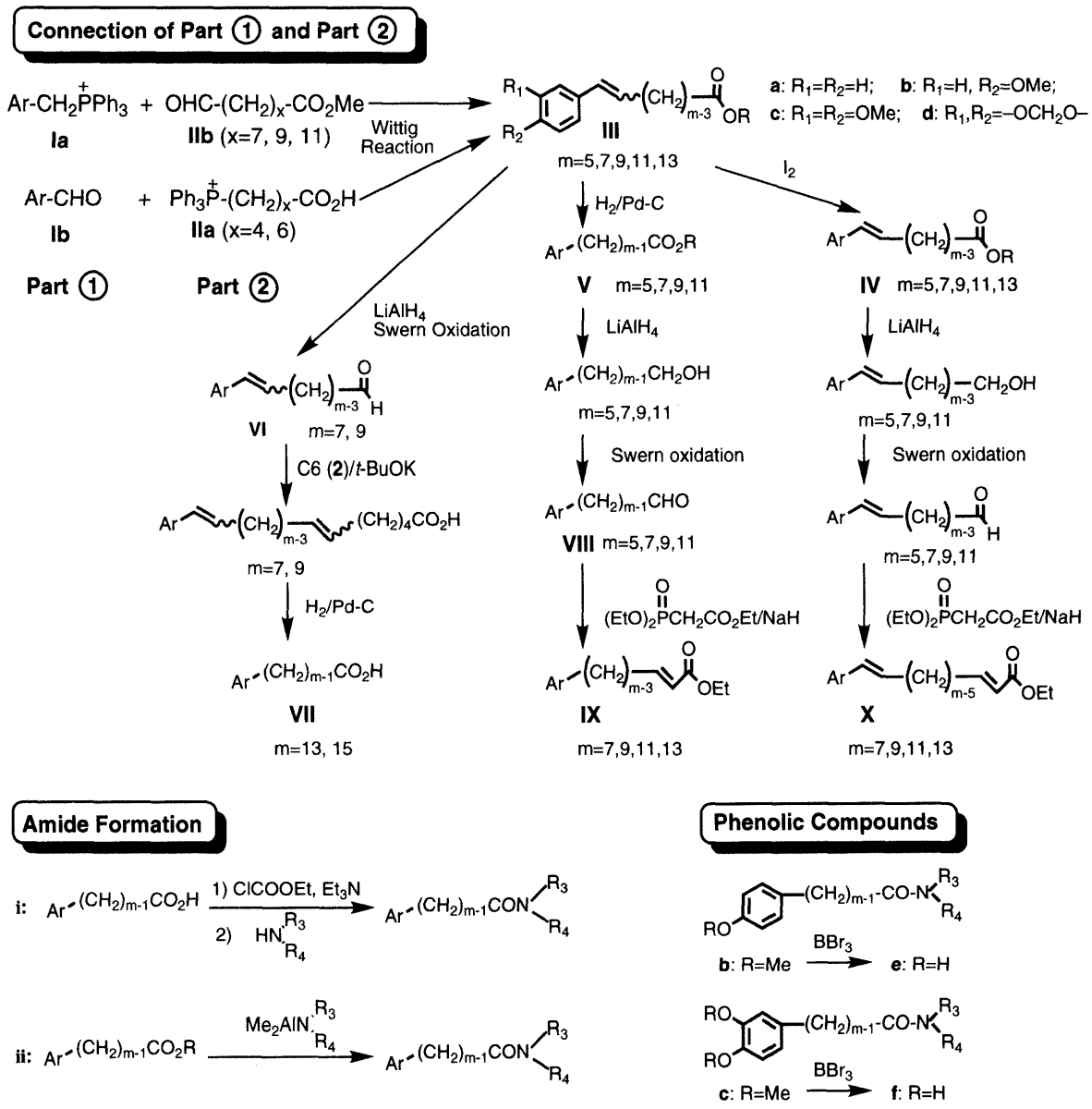


Chart 3

amines such as morpholine and *N*-methylpiperazine, showed strong activity. Therefore, three natural-type amides, piperidine amides (PA-A), isobutylamide (PA-B), pyrrolidine amides (PA-C), and unnatural-type *N*-methylpiperazine amides (PA-M) were tested. Among the compounds with a saturated chain (PA-X9 : 0), isobutylamide (PA-B9 : 0) and piperidine amide (PA-A9 : 0) were inactive, but pyrrolidine amide (PA-C9 : 0) and *N*-methylpiperazine amide (PA-M9 : 0) showed strong activity [minimal lethal concentration (MLC) = 40—100 μM and 100 μM, respectively]. A similar tendency was observed for PA-X11 : 0, where the activity of PA-C11 : 0 was the strongest (MLC = 20 μM). This result is in good agreement with that obtained for long-chain fatty acid amides: *i.e.* isobutylamides did not show any activity, while pyrrolidine and *N*-methylpiperazine amides showed stronger activity than piperidine amides.[16]

Introduction of a double bond at the arylic position or the C-2 position had almost no effect on the nematocidal activity [PA-C9 : 1(2*E*), MLC = 40 μM; PA-C9 : 1(8*E*), MLC = 40—50 μM]. However, the activity was lowered by introduction of double bonds at both positions [PA-C9 : 2(2*E*,8*E*), MLC = 100—150 μM].

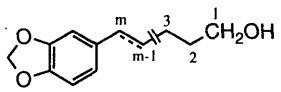
Next, we examined the effect of side chain length (Table 1). In the previous work,[16] we revealed that the nematocidal activity of long-chain alkyl amides was greatly dependent on the alkyl chain length: an optimum length was observed in a series of homologues and the length became greater with a more polar amine moiety and shorter with a less polar amine moiety. This phenomenon was analyzed in relation to the log *P* values of the compounds and attributed to the hydrophobic/hydrophilic balance. In the series of PA-Cm : 0, the nematocidal activity increased with increase of the chain length up to m = 11 (PA-C11 : 0, MLC = 20 μM), and then decreased sharply. The piperamide-C family with one or two double bonds (PA-Cm : 1 and PA-Cm : 2) showed the same tendency and gave a maximum activity at m = 11. Unnatural *N*-methylpiperazine amides (PA-Mm : 0), which have a more polar amine moiety than piperamides-C,

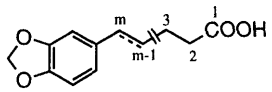
Table 1. Minimal Lethal Concentrations (MLC's) of Piperamides against *T. canis* after 24 h Incubation (μM)

m	PA-Am:0	PA-Bm:0	PA-Cm:0	PA-Cm:1 (m−1*E*)	PA-Cm:1 (2*E*)	PA-Cm:2 (2*E*, m−1*E*)	PA-Mm:0
5	800	>1000	400—800	1000	>1000[a]	>1000[a]	>1000
7	200—300	>1000	150	150—250[a]	200	300[a]	400
9	>1000	>1000	40—100	40—50[a]	40	100—150[a]	100
11	>1000	>1000	20	20	20	20[b]	60
13	—	—	400	50—80	500	>1000	25
15	—	—	>1000	—	—	—	400

a) Naturally occurring compound. *b*) PA-C11:2 (2*E*,4*E*): MLC = 200 μM.

Table 2. Minimal Lethal Concentrations (MLC's) of Alcohols and Acids against *T. canis* after 24 h Incubation (μM)





m	Saturated	Unsaturated	Saturated	Unsaturated
3	>1000	>1000	1000	>1000
4	>1000	—	600	—
5	800	1000	600	400
7	150	250	400	>1000
9	50	80	>1000	>1000
11	40	>1000	>1000	>1000
13	>1000	—	—	>1000
15	>1000	—	—	—

showed a similar activity profile, but maximum activity was observed at a longer chain length (m = 13, PA-M13 : 0) with an MLC of 25 μM. This is also in good agreement with the case of long-chain fatty acid amides.[16]

Among the fatty acid amide homologues, piperidine amides showed a shorter optimum chain length and less activity than pyrrolidine amides.[16] In agreement with this, PA-Am : 0 showed a shorter optimum length (m = 7) and less activity (MLC = 200—300 μM) than those of PA-Cm : 0 (m = 11, MLC = 20 μM): the lower polarity of the amine moiety shortens the optimum chain length needed to maintain the hydrophobic/hydrophilic balance of the molecule, and a larger *N*-substituent decreases the maximum activity.

Nematocidal Activity of Carboxylic Acids and Alcohols Nematocidal activity of the carboxylic acids and alcohols was also tested (Table 2). As was the case for fatty acids and fatty alcohols,[15] the activity of the alcohols markedly increased with increase of the side chain length, reached a maximum at m = 11 (MLC = 40 μM), and then decreased sharply, whereas the activity change in the carboxylic acids was moderate and the maximum activity was observed at a shorter chain length (m = 7) with an MLC of 400 μM. Introduction of a double bond at the arylic position decreased the activity and shortened the side chain length of the maximum activity by two methylenes in both carboxylic acids and alcohols.

Nematocidal Activity of Aryl-piperamides Next, we examined the nematocidal activity of synthetic aryl-piperamides, using phenyl (**a**), 4-methoxyphenyl (**b**), and 3,4-dimethoxyphenyl (**c**) derivatives (Fig. 1). As in the case of piperamides (**d**), nematocidal activity was dependent on the alkyl chain length and the maximum activity was observed at m = 11 in pyrrolidine amides (Fig. 1a) and m = 13 in *N*-methylpiperazine amides (Fig. 1b). The order of the activity at the chain length giving the strongest activity (m = 11 for the pyrrolidine amides and m = 13 for the *N*-methylpiperazine amides) was 3,4-methylenedioxyphenyl (**d**) ≫3,4-dimethoxyphenyl (**c**) ≈phenyl (**a**) >4-methoxyphenyl (**b**). However, the nematocidal activity profiles of these compounds were very similar, indicating that the methoxy substituents on the phenyl ring only modify the activity and do not have any fundamental importance. This suggests that, in aryl-piperamides, the chain length and the amide group are the most important functionalities for nematocidal activity.

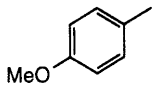
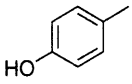
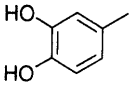
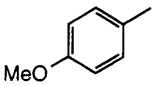
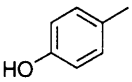
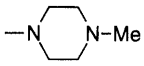
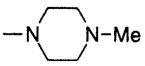
Conversion of the methoxy group to a hydroxy group did have a significant effect on the activity (Table 3). When the 4-methoxy group (**b**) was converted to a hydroxy group (**e**), the activity decreased, and the length of the side chain giving the strongest activity became two carbons shorter than in the corresponding methoxy homologues (m = 9 for pyrrolidine amide and m = 11 for *N*-methylpiperazine amide). Introduction of another hydroxy group on the aromatic ring (3,4-dihydroxyphenyl homologues, **f**) further decreased the activity with shortening of the chain length of the maximum activity.

Relationship between the Nematocidal Activity and Hydrophobicity of Aryl-piperamides In the previous paper,[16] we revealed that the nematocidal activity of long-chain fatty amides was greatly dependent on the length of the alkyl chain and the nature of the amine moiety, and that the hydrophobic/hydrophilic balance of the compound is important for the activity. Therefore, we examined the relationship between the nematocidal activity (MLC) and hydrophobicity (log *P*) of aryl-piperamides. The log *P* values were calculated by the method proposed by Moriguchi *et al.*[17] For the non-phenolic compounds, the calculated log *P* values which corresponded to the strongest activity fell in the range of 3.5 to 4.5 (Fig. 2). On the other hand, the values for hydroxyphenyl analogs were smaller (2.10 for 4-hydroxyphenyl-piperamide-M series, see Table 3).

As described above, the amide group has a very important effect on the nematocidal activity in aryl-piperamides. On the other hand, a phenolic OH group has an important effect on the nematocidal activity in malabaricone analogs.[18] Hydroxyphenyl-piperamides have both functionalities; one at each end of the molecule. It seems that plural mechanisms are involved in the nematocidal activity of these compounds and it is difficult to explain the activity profiles of these homologues only

Table 3. Nematocidal Activity and Calculated log *P* Values of Hydroxyphenylpiperamides

$Ar\text{–}(CH_2)_{m-1}\text{–}CO\text{–}X$

Type	b	e	f	b	e
Ar					
X					
m	RM[a] (MLC)	RM[a] (MLC)	log *P*[b]	RM[a]	log *P*[b]	RM[a] (MLC)	RM[a] (MLC)	log *P*[b]
7	0 (400 μM)	8	2.88	56	2.85	0 (1000 μM)	96	1.20
9	0 (100 μM)	0 (100 μM)	3.35	89	3.32	0 (100 μM)	10	1.66
11	0 (90 μM)	18	3.80	97	3.77	0 (80 μM)	0 (500 μM)	2.10
13	0 (200 μM)	94	4.23	95	4.20	0 (90 μM)	94	2.53
15	—	100	4.65	96	4.62	—	100	2.94

a) The relative mobility (RM) value calculated according to ref. 15 at 1000 μM after 24 h incubation. A smaller value indicates a stronger activity. *b*) Calculated by the equation proposed by Moriguchi *et al.* (ref. 17).

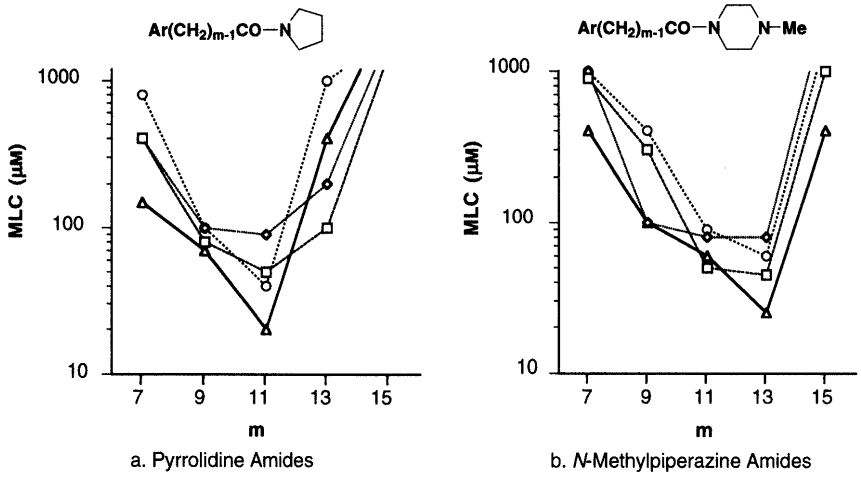


Fig. 1. Nematocidal Activity of Piperamides and Analogs

---□---, Ar = phenyl (**a**); ---◇---, Ar = 4-methoxyphenyl (**b**); ···○···, Ar = 3,4-dimethoxyphenyl (**c**); —△—, Ar = 3,4-methylenedioxyphenyl (**d**).

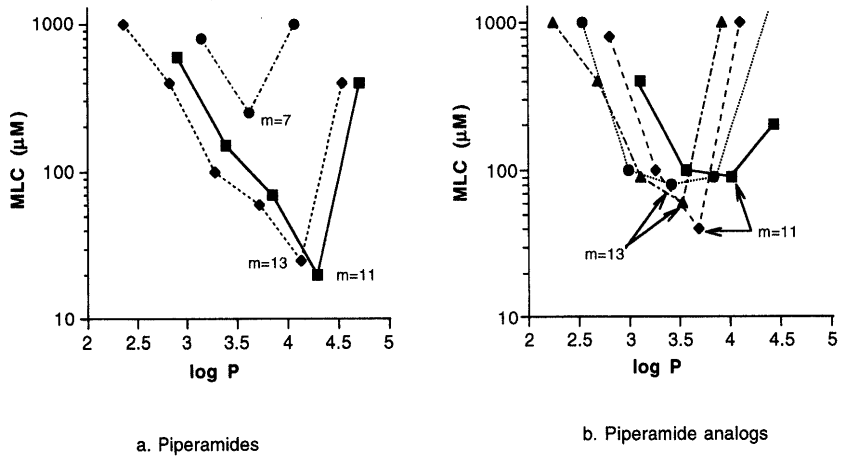


Fig. 2. Relationship between Nematocidal Activity and Calculated log *P* Value

a: –·–●–·–, piperamide-A; —■—, piperamide-C; – – –◆– – –, piperamide-M. b: —■—, 4-methoxyphenylpiperamide-C; – – –◆– – –, 3,4-dimethoxyphenylpiperamide-C; ---●---, 4-methoxyphenylpiperamide-M; – – –▲– – –, 3,4-dimethoxyphenylpiperamide-M.

in terms of the hydrophobic/hydrophilic balance. The effect of the phenolic OH group will be discussed in a forthcoming paper.[18]

Discussion

Amide constituents of plant origin have long been recognized to have various biological activities[19] such as antimicrobial, anti-inflammatory, insecticidal, and molluscicidal activities. Among these activities, the insecticidal activity of olefinic isobutylamides[20] has been drawing much attention. Elliot *et al.*[6] surveyed the insecticidal activity of 172 naturally occurring amide compounds, selected isobutylamides containing 2-ene or 2,4-diene systems as key structures for the activity, and investigated the structure–activity relationship of analogous compounds. On the other hand, starting from aralkenylisobutylamides such as pipercide [PA-B11 : 3(2*E*,4*E*,10*E*)] from black pepper (*Piper nigrum*), Miyakado *et al.*[7] studied the structure–activity relationship of olefinic isobutylamides and related compounds. Both groups concluded that monosubstituted amides such as isobutylamide showed stronger activity than disubstituted amides such as piperidine amide. Recently, Gbewonyo *et al.*[21] also investigated insecticidal activity of Piperaceous amides and reached the same conclusion. This is in sharp contrast to our results. In our bioassay, olefinic (and also saturated) isobutylamides did not show any activity; instead, pyrrolidine amides showed strong nematocidal activity. At first, this discrepancy was thought to be ascribed to the difference of application method of the samples. Both Elliot's and Miyakado's groups applied their samples topically to the organisms as an organic solution. We carried out our assay in a saline solution in which the solubility of the sample might have a marked influence on the results. In fact, isobutylamides readily crystallized out from the solution. However, some compounds which readily crystallized out from the solution still showed strong nematocidal activity. Therefore, we concluded that isobutylamides inherently lack nematocidal activity against *T. canis*.

Hatakoshi *et al.*[22] demonstrated, using the central nerve cord of the American cockroach, that the isobutylamides such as pipercide are neurotoxic. Using the locust *retractor unguis* nerve-muscle preparation, Gbewonyo *et al.*[21] also showed that pipercide caused a reduction in both the frequency and the amplitude of miniature excitatory postsynaptic potentials. Although second-stage larvae of *T. canis* have a primitive nervous system, no evidence has been obtained that piperamides exert their activity through the nervous system. Thus, the action mechanism of piperamides and their analogs on nematodes remains to be elucidated.

Experimental

General Melting points were taken on a Yanagimoto micro hot-stage melting point apparatus without correction. Infrared (IR) spectra were taken in chloroform solution on a JASCO A-202 or Shimadzu IR-460 spectrometer and data (ν_{max}) are given in cm^{-1}. Unless otherwise stated, ^{1}H-NMR spectra were measured in $CDCl_3$ solution with tetramethylsilane as an internal standard on a JEOL GSX-500 spectrometer (500 MHz) and the chemical shifts are given in δ values. The 100 MHz spectra were recorded on a JEOL FX-100 spectrometer. Mass spectra (MS) were taken on a Hitachi M-80 or JEOL JMS-SX102 spectrometer, and M^+ and base peaks are given as m/z (%). All organic extracts were washed with brine and dried over anhydrous sodium sulfate before concentration. Column chromatography was performed on Wako-gel C-200 (silica gel). All new compounds gave satisfactory elementary analyses or high-resolution MS data. Nematocidal activity against second-stage larvae of *T. canis* was determined as described previously.[15] MLC was defined as the lowest concentration which gave a relative mobility (RM) value of zero after 24 h of incubation.

Piperamides which are not described below were reported previously.[3,4]

3-Carboxypropyltriphenylphosphonium Bromide (1) A mixture of γ-butyrolactone (5.16 g) and triphenylphosphine hydrobromide[10] (20.6 g) was heated at 160 °C for 1 h, during which time the solid dissolved and then crystallized again. It was cooled, and liberated water was removed by evaporation under reduced pressure. The resultant crystalline mass was treated with a small amount of chloroform, crushed finely, collected by filtration, then washed with ether to give **1** as colorless prisms (24.1 g, 94%), mp 252—254 °C.

5-Carboxypentyltriphenylphosphonium Bromide (2) A mixture of ε-caprolactone (5.7 g) and triphenylphosphine hydrobromide (17.2 g) was heated at 160 °C for 1 h as described above. It was cooled, and the solid was recrystallized from chloroform–ether to give **2** as colorless prisms (20.9 g, 92%), mp 205—206 °C.

Methyl 7-Formylheptanoate (3) Ozone was bubbled through a stirred mixture of cyclooctene (8.25 g) and $NaHCO_3$ (2.0 g) in CH_2Cl_2 (250 ml) and MeOH (50 ml) at −78 °C until the solution turned blue. Nitrogen was passed through the solution until the blue color was discharged and then the cooling bath was removed. The solution was filtered to remove insoluble material. The filtrate was concentrated, after addition of benzene (80 ml), to *ca.* 50 ml under reduced pressure. This solution was diluted with CH_2Cl_2 (150 ml) and cooled with ice, then Et_3N (15 ml) and Ac_2O (20 ml) were added, and the mixture was stirred at 0 °C for 15 min and at room temperature for 4 h. It was then washed with 0.1 N HCl and 10% NaOH, and concentrated. The residue was distilled under reduced pressure to give **3** as a colorless oil (10.3 g, 80%), bp 112 °C/5 mmHg. ^{1}H-NMR: 1.35 (4H, m), 1.64 (4H, m), 2.32 (2H, t, J=7.3 Hz), 2.43 (2H, dt, J=7.3, 1.8 Hz), 3.67 (3H, s), 9.76 (1H, t, J=1.8 Hz).

Methyl 9-Formylnonanoate (4) A mixture of $NaIO_4$ (32.0 g), OsO_4 (50 mg), and Bu_4NHSO_4 (211 mg) in water (100 ml) was added to methyl 10-undecenoate (5.0 g) in ether (100 ml), and the mixture was vigorously stirred at room temperature for 22 h. The ether layer was separated and the aqueous layer was extracted with ether. The combined organic layer was concentrated to dryness and the residue was chromatographed (benzene : acetone = 3 : 1) to give **4** (4.89 g, 97%) as a colorless oil. ^{1}H-NMR (60 MHz): 1.00—1.83 (12H), 1.96—2.46 (4H), 3.53 (3H, s), 9.56 (1H, br s).

Methyl 11-Formylundecanoate (5) A mixture of oxalyl chloride (2.1 ml) and dimethyl sulfoxide (DMSO) (3.5 ml) in dry CH_2Cl_2 (60 ml) was stirred for 15 min at −78 °C, then 1,6-hexanediol monoacetate (3.2 g) in dry CH_2Cl_2 (12 ml) was added, and the mixture was stirred for 25 min. Triethylamine (10 ml) was added. The whole was stirred at room temperature for 1.5 h, then the reaction was quenched with water and the mixture was extracted with $CHCl_3$. The organic layer was washed with saturated $NaHCO_3$ solution and dilute H_2SO_4, and concentrated to dryness. Chromatography (hexane : AcOEt = 4 : 1) of the residue gave the corresponding aldehyde as a colorless oil (73%).

A stirred suspension of **2** (6.85 g) in dry tetrahydrofuran (THF) (80 ml) was treated with *tert*-BuOK (3.36 g) in dry THF (30 ml) at 0 °C and the mixture was stirred for 20 min. The above aldehyde (1.58 g) in dry THF (15 ml) was added dropwise and the mixture was stirred at 0 °C for 2.5 h, then poured into ice-cold 1 N HCl (30 ml) and extracted with ether. The organic layer was concentrated to dryness and the residue was heated with 5% H_2SO_4–MeOH (100 ml) under reflux for 2 h. The cooled mixture was poured into ice-cold saturated $NaHCO_3$ solution and extracted with AcOEt. The organic extract was concentrated to dryness and the residue was chromatographed (hexane : AcOEt = 2 : 1) to give methyl 12-hydroxy-6-dodecenoate (2.12 g) as an *E*/*Z* mixture. This was hydrogenated over 5% Pd–C (200 mg) in EtOH (60 ml) at room temperature for 2 h to give methyl 12-hydroxydodecanoate (yield 86% from the aldehyde) as colorless scales (hexane), mp 31—32 °C. IR: 1730. MS: 231 (M^+ + 1, 49), 74 (100). ^{1}H-NMR: 1.22—1.38 (14H), 1.54—1.65 (4H, m), 2.30 (2H, t, J=7.6 Hz), 3.64 (2H, t, J=6.6 Hz), 3.67 (3H, s).

The above hydroxy ester was oxidized with oxalyl chloride–DMSO as described above to give the formyl ester (**5**) in 92% yield as a colorless

oil. ^{1}H-NMR: 1.25—1.38 (12H), 1.62 (4H, m), 2.30 (2H, t, J=7.6 Hz), 2.42 (2H, dt, J=2.0, 7.3 Hz), 3.67 (3H, s), 9.76 (1H, t, J=2.0 Hz).

5-Arylpentenoic and 5-Arylpentanoic Acids (4*E*)-5-(3′,4′-Methylenedioxyphenyl)-4-pentenoic Acid A stirred suspension of **1** (4.29 g, 10 mmol) in dry THF (60 ml) was treated with *tert*-BuOK (2.24 g, 20 mmol) in dry THF (20 ml) at 0 °C and the mixture was stirred for 30 min. Piperonal (1.0 g, 6.7 mmol) in dry THF (10 ml) was added and the whole was stirred at room temperature for 1 h, cooled with ice, acidified with 1 N HCl, diluted with water, and extracted with ether. After removal of the solvent, the residue was chromatographed on oxalic acid-impregnated silica gel (hexane–AcOEt=4 : 1) to give the 4-pentenoic acid (E/Z=94 : 6) which was recrystallized from benzene to give the pure (E)-isomer (1.12 g, 76%) as colorless plates, mp 132—133 °C. IR: 1711. MS: 220 (M^+, 85), 131 (100). ^{1}H-NMR: 2.52 (4H, s), 5.93 (2H, s), 6.03 (1H, m), 6.36 (1H, br d, J=15.6 Hz), 6.73 (1H, d, J=7.8 Hz), 6.76 (1H, dd, J=7.8, 1.5 Hz), 6.88 (1H, d, J=1.5 Hz).

5-(3′,4′-Methylenedioxyphenyl)pentanoic Acid The above unsaturated acid in EtOH was hydrogenated over 10% Pd–C to give the corresponding saturated acid (yield 97%) as colorless plates (benzene–hexane), mp 96.5—97.5 °C. IR: 1710. MS: 222 (M^+, 100). ^{1}H-NMR: 1.64 (4H, m), 2.37 (2H, t, J=7.1 Hz), 2.55 (2H, t, J=7.1 Hz), 5.91 (2H, s), 6.61 (1H, dd, J=7.8, 1.5 Hz), 6.66 (1H, d, J=1.5 Hz), 6.72 (1H, d, J=7.8 Hz).

7-Arylheptanoic Acids (General Procedure) A stirred suspension of **2** (11 mmol) in dry THF (60 ml) was treated with *tert*-BuOK (25 mmol) in dry THF (20 ml) at 0 °C and the mixture was stirred for 20 min. Arylaldehyde (10 mmol) in dry THF (7 ml) was added and the mixture was stirred at room temperature for 1—4 h, then poured into ice-water, acidified with 1 N HCl, and extracted with ether. After removal of the solvent, the residue was chromatographed on oxalic acid-impregnated silica gel (hexane–AcOEt=4 : 1) to give 7-aryl-6-heptenoic acid (E/Z mixture) as a pale yellow oil (yield 80—95%).

This was dissolved in EtOH and hydrogenated over 10% Pd–C (20—100% of the weight of the substrate) at an H_2 pressure of 4 kg/cm^2. Removal of the solvent and catalyst left a residue, which was purified by chromatography and/or recrystallization to give the corresponding saturated carboxylic acid (yield 79—100%). The following compounds were prepared by this method.

7-Phenylheptanoic Acid Colorless oil. IR: 1708. MS: 260 (M^+, 11), 91 (100). ^{1}H-NMR: 1.36 (4H, m), 1.63 (4H, m), 2.34 (2H, t, J=7.3 Hz), 2.60 (2H, br t, J=7.8 Hz), 7.17 (3H, m), 7.26 (2H, m).

7-(4′-Methoxyphenyl)heptanoic Acid Colorless prisms (ether–hexane), mp 75—77 °C. IR: 1705. MS: 236 (M^+, 37), 121 (100). ^{1}H-NMR: 1.35 (4H, m), 1.55—1.65 (4H, m), 2.34 (2H, t, J=7.3 Hz), 2.54 (2H, br t, J=7.6 Hz), 3.78 (3H, s), 6.82 (2H, d, J=8.8 Hz), 7.08 (2H, d, J=8.8 Hz).

7-(3′,4′-Dimethoxyphenyl)hepanoic Acid Colorless crystalline solid, mp 60—62 °C. IR: 1708. MS: 266 (M^+, 27), 151 (100). ^{1}H-NMR (100 MHz): 1.20—1.84 (8H), 2.2—2.6 (4H, m), 3.84, 3.86 (each 3H, s), 6.64—6.78 (3H, m).

7-(3′,4′-Methylenedioxyphenyl)hepanoic Acid Colorless crystalline solid, mp <30 °C. IR: 1710. MS: 250 (M^+, 53), 135 (100). ^{1}H-NMR (100 MHz): 1.19—1.81 (8H), 2.35 (2H, t, J=7.0 Hz), 2.53 (2H, t, J=7.5 Hz), 5.90 (2H, s), 6.49—6.80 (3H, m).

9-Arylnonanoic Acids and Methyl Esters (General Procedure) A solution of *tert*-BuOK (13.1 mmol) in THF (10 ml) was added to a stirred mixture of arylmethyltriphenylphosphonium bromide (12.1 mmol) in THF (60 ml) and DMSO (10 ml) at −10 °C, and the mixture was stirred for 30 min. Methyl 7-formylheptanoate (**3**) (7.7 mmol) in THF (10 ml) was added, and stirring was continued for 1—1.5 h at the same temperature. Acidification of the mixture with cold 1 N HCl and extraction with AcOEt gave a semi-solid, which was re-extracted with ether. The ether-soluble fraction was chromatographed (benzene) to give methyl 9-aryl-8-nonenoate (E/Z mixture) as a pale yellow oil (yield 59—76%), which was hydrogenated in acetone to afford the corresponding 9-arylnonanoates as described above (yield 86—94%). If necessary, the methyl ester was hydrolyzed with 5% NaOH–MeOH to give the corresponding acid, for the purpose of purification. The following compounds were prepared by this method.

Methyl 9-Phenylnonanoate Colorless oil. IR: 1731. MS: 248 (M^+, 44), 91 (100). ^{1}H-NMR (100 MHz): 1.08—1.78 (12H), 2.29 (2H, t, J=7.5 Hz), 2.59 (2H, t, J=7.5 Hz), 3.64 (3H, s), 7.03 (5H).

Methyl 9-(4′-Methoxyphenyl)nonanoate Colorless oil. IR: 1731. MS: 278 (M^+, 64), 121 (100). ^{1}H-NMR (100 MHz): 1.16—1.80 (12H), 2.29 (2H, t, J=7.5 Hz), 2.53 (2H, t, J=7.5 Hz), 3.65, 3.77 (each 3H, s), 6.78, 7.06 (each 2H, d, J=10 Hz).

Methyl 9-(3′,4′-Dimethoxyphenyl)nonanoate Pale yellow oil. IR: 1731. MS: 308 (M^+, 84), 151 (100). ^{1}H-NMR (100 MHz): 1.07—1.70 (12H), 2.30 (2H, t, J=7.5 Hz), 2.55 (2H, t, J=7.5 Hz), 3.66, 3.85, 3.87 (each 3H, s), 6.61—6.87 (3H).

9-(3′,4′-Methylenedioxyphenyl)nonanoic Acid This was purified after alkaline hydrolysis in the yield of 59%. Colorless needles (hexane–$CHCl_3$), mp 69—70 °C. IR: 1715. MS: 278 (M^+, 92), 135 (100). ^{1}H-NMR (100 MHz): 1.17—1.80 (12H), 2.35 (2H, t, J=8.0 Hz), 2.52 (2H, t, J=8.0 Hz), 5.90 (2H, s), 6.48—6.77 (3H).

11-Arylundecanoic Acids and Esters (General Procedure) A solution of *tert*-BuOK (12.3 mmol) in THF (16 ml) was added with stirring to arylmethyltriphenylphosphonium bromide (11.8 mmol) in THF (60 ml) at −10 °C, and the mixture was stirred for 5 min. Methyl 9-formylnonanoate (**4**) (7.25 mmol) in THF (10 ml) was added, and stirring was continued for 1—2.5 h at the same temperature. The mixture was poured into cold 1 N HCl and extracted with AcOEt. The extract was concentrated to dryness and the residue was extracted with ether. The ether-soluble fraction was chromatographed (benzene) to give methyl 11-aryl-10-undecenoate (E/Z mixture) as a pale yellow oil (yield 68—78%), which was hydrogenated to afford the saturated compound as described above (yield 73—97%). Purification of the product was done by chromatography, or, by alkaline hydrolysis to give the corresponding acid, if necessary. The following compounds were obtained by this method.

Methyl 11-Phenylundecanoate Colorless oil. IR: 1731. MS: 276 (M^+, 43), 91 (100). ^{1}H-NMR (100 MHz): 1.08—1.72 (16H), 2.29 (2H, t, J=7.5 Hz), 2.59 (2H, t, J=7.5 Hz), 3.64 (3H, s), 7.03—7.31 (5H).

Methyl 11-(4′-Methoxyphenyl)undecanoate Colorless prisms, mp <30 °C. IR: 1731. MS: 306 (M^+, 46), 121 (100). ^{1}H-NMR (100 MHz): 1.08—1.77 (16H), 2.29 (2H, t, J=7 Hz), 2.53 (2H, t, J=7 Hz), 3.64, 3.76 (each 3H, s), 6.78, 7.06 (each d, J=9 Hz).

Methyl 11-(3′,4′-Dimethoxyphenyl)undecanoate Colorless oil. IR: 1727. MS: 336 (M^+, 100). ^{1}H-NMR (100 MHz): 1.08—1.80 (16H), 2.16—2.64 (4H), 3.65 (3H, s), 3.85, 3.87 (each 3H, s), 6.60—6.70 (3H, m).

11-(3′,4′-Methylenedioxyphenyl)undecanoic Acid Colorless needles (benzene–hexane), mp 72—73 °C. IR: 1710. MS: 306 (M^+, 76), 135 (100). ^{1}H-NMR (100 MHz): 1.18—1.72 (16H), 2.33 (2H, t, J=7.0 Hz), 2.50 (2H, t, J=7.0 Hz), 5.88 (2H, s), 6.48—6.75 (3H).

13-Aryltridecanoic Acids (General Procedure) 7-Aryl-6-heptenol: A solution of 7-aryl-6-heptenoic acid (an E/Z-mixture, 3.7 mmol) in dry THF (100 ml) was added dropwise to a stirred suspension of $LiAlH_4$ (5.5 mmol) in dry THF (200 ml) at 0 °C and the mixture was stirred for 1.5 h at 0 °C. The excess reagent was decomposed with water. The precipitates were collected by filtration and washed thoroughly with ether. The filtrate and washings were combined and concentrated to dryness. The residue was chromatographed over silica gel to give 7-aryl-6-heptenol as a pale yellow oil in 60—93% yield.

7-Arylhept-6-enal: A mixture of oxalyl chloride (11 mmol) and DMSO (22 mmol) in dry CH_2Cl_2 (40 ml) was stirred at −70 °C for 15 min. The above prepared 7-aryl-6-heptenol (5.5 mmol) in dry CH_2Cl_2 (5 ml) was added and stirring was continued for 20 min. After addition of Et_3N (22 mmol), the cooling bath was removed and the mixture was stirred at room temperature for 30 min. The reaction mixture was diluted with water (30 ml) and extracted with AcOEt (20 ml × 3). The combined extract was washed with dilute H_2SO_4, saturated $NaHCO_3$ solution, and brine, dried and concentrated. The residue was chromatographed (hexane : AcOEt=4 : 1) to give 7-arylhept-6-enal (E/Z mixture) as a colorless oil (yield 78—99%).

13-Aryltrideca-6,12-dienoic acid: A solution of *tert*-BuOK (20 mmol) in dry THF (20 ml) was added to a stirred suspension of **2** (10 mmol) in dry THF (100 ml) at 0 °C and the mixture was stirred for 20 min. The above prepared 7-arylhept-6-enal (6.7 mmol) in dry THF (10 ml) was added and stirring was continued for 50 min at room temperature. The cooled reaction mixture was acidified with 1 N HCl and extracted with AcOEt. The product obtained from the extract was chromatographed over oxalic acid-impregnated silica gel (hexane : AcOEt=9 : 1) to give 13-aryltrideca-6,12-dienoic acid (a mixture of four stereoisomers) as a colorless oil (yield 84—94%).

13-Aryltridecanoic acid: The dienoic acid obtained above was hydrogenated in EtOH to afford the saturated acid (yield 65—96%). The following compounds were prepared by this method.

13-Phenyltridecanoic Acid Colorless fine needles (hexane), mp 52—

53 °C. IR: 1705. MS: 290 (M^+, 16), 91 (100). ^{1}H-NMR: 1.21—1.35 (16H), 1.57—1.67 (4H), 2.34 (2H, t, J=7.6 Hz), 2.60 (2H, t, J=7.8 Hz), 7.17—7.82 (5H, m).

13-(4′-Methoxyphenyl)tridecanoic Acid Colorless fine needles (hexane), mp 73.5—74.5 °C. IR: 1700. MS: 320 (M^+, 100). ^{1}H-NMR: 1.21—1.34 (16H), 1.55—1.65 (4H), 2.34 (2H, t, J=7.5 Hz), 2.53 (2H, t, J=8.8 Hz), 3.78 (3H, s), 6.81 (2H, d, J=8.5 Hz), 7.08 (2H, d, J=8.5 Hz).

13-(3′,4′-Dimethoxyphenyl)tridecanoic Acid Colorless prisms (hexane), mp 89—90 °C. IR: 1704. MS: 350 (M^+, 67), 151 (100). ^{1}H-NMR: 1.23—1.37 (16H), 1.56—1.67 (4H), 2.35 (2H, t, J=7.5 Hz), 2.54 (2H, t, J=7.8 Hz), 3.78, 3.85 (each 3H, s), 6.70 (2H, m), 6.78 (1H, d, J=8.8 Hz).

13-(3′,4′-Methylenedioxyphenyl)tridecanoic Acid Colorless fine needles (hexane), mp 68—69 °C. IR: 1710. MS: 334 (M^+, 100). ^{1}H-NMR (100 MHz): 1.09—1.79 (20H), 2.33 (2H, t, J=7.0 Hz), 2.51 (2H, t, J=6.5 Hz), 3.78, 5.89 (2H, s), 6.48—6.76 (3H).

15-Arylpentadecanoic Acids (General Procedure) An E/Z-mixture of methyl 9-aryl-8-nonenoate (see above) was reduced with $LiAlH_4$ (1 mol eq) in THF at 0 °C for 2 h as described above to give 9-aryl-8-noenol (yield 86—100%). The alcohol was oxidized with oxalyl chloride–DMSO and the resulting aldehyde (yield 90—92%) was reacted with **2** as described for 13-aryltridecanoic acid to give 15-arylpenadeca-6,14-dienoic acid (a mixture of four stereoisomers) in 70—98% yield. This was hydrogenated over 10% Pd–C in EtOH to afford the corresponding 15-arylpentadecanoic acids (yield 70—100%). The following compounds were obtained by this method.

15-Phenylpentadecanoic Acid Colorless needles (hexane–AcOEt), mp 62—63 °C. IR: 1710. MS: 318 (M^+, 51), 92 (100). ^{1}H-NMR: 1.24—1.33 (20H, m), 1.57—1.67 (4H, m), 2.35 (2H, t, J=7.3 Hz), 2.60 (2H, t, J=7.8 Hz), 7.15—7.19 (3H, m), 7.25—7.28 (2H, m).

15-(4′-Methoxyphenyl)pentadecanoic Acid Colorless needles (hexane–AcOEt), mp 78—79 °C. IR: 1710. MS: 348 (M^+, 100), 92 (100). ^{1}H-NMR: 1.20—1.38 (20H), 1.51—1.68 (4H), 2.34 (2H, t, J=7.8 Hz), 2.54 (2H, t, J=7.8 Hz), 3.78 (3H, s), 6.81 (2H, d, J=8.3 Hz), 7.08 (2H, d, J=8.3 Hz).

15-(3′,4′-Dimethoxyphenyl)pentadecanoic Acid Colorless needles (hexane–AcOEt), mp 94—95 °C. IR: 1710. MS: 378 (M^+, 100). ^{1}H-NMR: 1.24—1.34 (20H), 1.56—1.66 (4H), 2.35 (2H, t, J=7.8 Hz), 2.54 (2H, t, J=7.8 Hz), 3.86, 3.88 (each 3H, s), 6.71 (1H, br s), 6.72 (1H, br d, J=8.8, 2.0 Hz), 6.79 (1H, d, J=8.8 Hz).

15-(3′,4′-Methylenedioxyphenyl)pentadecanoic Acid Colorless solid. IR: 1710. MS: 362 (M^+, 100). ^{1}H-NMR (100 MHz): 1.11—1.79 (24H), 2.33 (2H, t, J=7.0 Hz), 2.51 (2H, t, J=6.5 Hz), 5.89 (2H, s), 6.47—6.77 (3H).

Isomerization of an (E/Z)-Mixture to an E-Isomer An (E/Z)-mixture at the arylic double bond of the acid was dissolved in benzene and stirred with iodine (one-fourth of the weight of the acid) at room temperature for 1.5—3 h. The solution was washed with 5% sodium hydrogen sulfite solution and concentrated. The residue was purified by chromatography and/or crystallizations to give the pure (E)-isomer almost quantitatively. The following compounds were prepared by this method.

(6*E*)-7-(3′,4′-Methylenedioxyphenyl)-6-heptenoic Acid Colorless scales (benzene), mp 101—102 °C. IR: 1710. MS: 248 (M^+, 84), 131 (100). ^{1}H-NMR (100 MHz): 1.38—1.86 (4H), 2.06—2.46 (4H), 5.90 (2H, s), 5.95 (1H, dt, J=15.5, 6.0 Hz), 6.28 (1H, d, J=15.5 Hz), 6.68—6.88 (3H).

(8*E*)-9-(3′,4′-Methylenedioxyphenyl)-8-nonenoic Acid Colorless scales (benzene–hexane), mp 75—77 °C. IR: 1710. MS: 276 (M^+, 100). ^{1}H-NMR (100 MHz): 1.19—1.79 (8H), 2.01—2.45 (4H), 5.91 (2H, s), 5.97 (1H, dt, J=15.5, 6.0 Hz), 6.27 (1H, d, J=15.5 Hz), 6.67—6.93 (3H).

(10*E*)-11-(3′,4′-Methylenedioxyphenyl)-10-undecenoic Acid Colorless prisms (benzene–hexane), mp 80—81 °C. IR: 1710. MS: 304 (M^+, 100). ^{1}H-NMR (100 MHz): 1.20—1.72 (12H), 2.04—2.43 (4H), 5.89 (2H, s), 5.97 (1H, dt, J=16.0, 6.0 Hz), 6.27 (1H, d, J=16.0 Hz), 6.69—6.90 (3H).

(12*E*)-13-(3′,4′-Methylenedioxyphenyl)-12-tridecenoic Acid This compound was prepared as follows. A solution of *tert*-BuOK (504 mg, 1.5 eq) in THF (10 ml) was added to 3,4-methylenedioxyphenylmethyltriphenylphosphonium bromide (2.15 g, 1.5 eq) in THF (40 ml) with stirring at 0 °C, and the mixture was stirred for 5 min. Methyl formylundecanoate (**5**) (684 mg) in THF (10 ml) was added and the whole was stirred for 1 h at the same temperature. The reaction was quenched with cold 1 N HCl and the mixture was extracted with ether to give, after concentration and chromatography of the residue, methyl 13-(3′,4′-methylenedioxyphenyl)-12-tridecenoate as an (E/Z)-mixture. This was isomerized with iodine as described above and hydrolyzed with 1 N NaOH in MeOH (1 : 2) under reflux for 1 h to give the (12*E*)-acid in 90% yield from **5**. Colorless needles (benzene–hexane), mp 67—69 °C. IR: 1709. MS: 332 (M^+, 3), 304 (100). ^{1}H-NMR: 1.25—1.38 (12H), 1.44 (2H, m), 1.64 (2H, m), 2.17 (2H, br q, J=7.6 Hz), 2.34 (2H, t, J=7.6 Hz), 5.93 (2H, s), 6.05 (1H, dt, J=15.6, 6.9 Hz), 6.28 (1H, br d, J=15.6 Hz), 6.72 (1H, d, J=8.3 Hz), 6.75 (1H, dd, J=8.3, 1.4 Hz), 6.89 (1H, d, J=1.4 Hz).

Unsaturated and Saturated Alcohols These alcohols were prepared from the corresponding acids or methyl esters by $LiAlH_4$ reduction. The following compounds were obtained.

(4*E*)-5-(3′,4′-Methylenedioxyphenyl)-4-pentenol Colorless scales, mp 67—69 °C. MS: 206 (M^+, 100). ^{1}H-NMR (100 MHz): 1.70 (2H, quint, J=7.0 Hz), 2.24 (2H, q, J=7.0 Hz), 3.66 (2H, t, J=7.0 Hz), 5.91 (2H, s), 5.98 (1H, dt, J=15.5, 6.5 Hz), 6.30 (1H, d, J=15.5 Hz), 6.66—6.90 (3H).

(6*E*)-7-(3′,4′-Methylenedioxyphenyl)-6-heptenol Colorless needles (benzene–hexane), mp 45—49 °C. MS: 234 (M^+, 88), 131 (100). ^{1}H-NMR (100 MHz): 1.20—1.78 (6H), 2.08—2.32 (2H), 3.63 (2H, t, J=6.5 Hz), 5.90 (2H, s), 5.97 (1H, dt, J=15.5, 6.0 Hz), 6.26 (1H, d, J=15.5 Hz), 6.66—6.88 (3H).

(8*E*)-9-(3′,4′-Methylenedioxyphenyl)-8-nonenol Colorless needles (ether–hexane), mp 59—60 °C. MS: 262 (M^+, 100). ^{1}H-NMR (100 MHz): 1.12—1.72 (10H), 2.04—2.29 (2H), 3.63 (2H, t, J=7.0 Hz), 5.91 (2H, s), 5.99 (1H, dt, J=16.0, 6.5 Hz), 6.28 (1H, d, J=16.0 Hz), 6.68—6.90 (3H).

(10*E*)-11-(3′,4′-Methylenedioxyphenyl)-10-undecenol Colorless prisms (hexane–benzene), mp 62—63 °C. MS: 290 (M^+, 100). ^{1}H-NMR (100 MHz): 1.17—1.59 (14H), 2.01—2.36 (2H), 3.58 (2H, t, J=6.0 Hz), 5.89 (2H, s), 5.97 (1H, dt, J=15.5, 6.0 Hz), 6.27 (1H, d, J=15.5 Hz), 6.67—6.87 (3H).

7-(3′,4′-Methylenedioxyphenyl)heptanol Colorless oil. MS: 236 (M^+, 37), 135 (100). ^{1}H-NMR (100 MHz): 1.15—1.76 (10H), 2.52 (2H, t, J=7.0 Hz), 3.62 (2H, t, J=6.5 Hz), 5.89 (2H, s), 6.50—6.77 (3H).

9-(3′,4′-Methylenedioxyphenyl)nonanol Colorless oil. MS: 264 (M^+, 59), 135 (100). ^{1}H-NMR (100 MHz): 1.16—1.76 (14H), 2.51 (2H, t, J=7.0 Hz), 3.61 (2H, t, J=7.0 Hz), 5.89 (2H, s), 6.48—6.76 (3H).

11-(3′,4′-Methylenedioxyphenyl)undecanol Colorless solid, mp <40 °C. MS: 292 (M^+, 84), 135 (100). ^{1}H-NMR (100 MHz): 1.08—1.72 (18H), 2.50 (2H, t, J=7.0 Hz), 3.49—3.71 (2H), 5.88 (2H, s), 6.49—6.74 (3H).

13-(3′,4′-Methylenedioxyphenyl)tridecanol Colorless crystalline solid, mp 47—49 °C. MS: 320 (M^+, 100). ^{1}H-NMR (100 MHz): 1.11—1.68 (22H), 2.51 (2H, t, J=7.0 Hz), 3.61 (2H, t, J=6.5 Hz), 5.88 (2H, s), 6.49—6.74 (3H).

15-(3′,4′-Methylenedioxyphenyl)pentadecanol Colorless crystalline solid, mp 61—64 °C. MS: 348 (M^+, 57), 135 (100). ^{1}H-NMR (100 MHz): 1.09—1.69 (26H), 2.50 (2H, t, J=7.0 Hz), 3.62 (2H, t, J=6.0 Hz), 5.88 (2H, s), 6.50—6.75 (3H).

(2*E*)-2-Enoic Acids and Esters (General Procedure) A saturated aralkylalcohol was converted to the corresponding aldehyde by Swern oxidation as described for 7-arylhept-2-enal. This aldehyde (2.1 mmol) in dry benzene (10 ml) was added dropwise to a stirred mixture of an ylide [prepared from ethyl diethylphosphonoacetate (2.2 mmol) and NaH (60% oil suspension, 2.2 mmol) in benzene (20 ml) with stirring for 5 min] and the mixture was stirred for 5 min. The reaction was quenched by the addition of water, and the mixture was acidified with HCl and extracted with AcOEt. The product thus obtained was purified by chromatography to give the corresponding ethyl ester, which was hydrolyzed in refluxing 4% KOH–water (1 : 1) for 30 min to give the 2-enoic acid (yield 47—99% from the corresponding alcohol). The following compounds were obtained by this method.

(2*E*)-7-(3′,4′-Methylenedioxyphenyl)-2-heptenoic Acid Colorless prisms (benzene), mp 118—119 °C. IR: 1695. MS: 248 (M^+, 15), 135 (100). ^{1}H-NMR (100 MHz): 1.36—1.79 (4H), 2.11—2.37 (2H), 2.53 (2H, t, J=7.0 Hz), 5.77 (1H, d, J=15.5 Hz), 5.89 (2H, s), 6.49—6.78 (3H), 7.04 (1H, dt, J=15.5, 7.0 Hz).

(2*E*)-9-(3′,4′-Methylenedioxyphenyl)-2-nonenoic Acid Colorless prisms (benzene), mp 89—90 °C. IR: 1690. MS: 276 (M^+, 35), 135 (100). ^{1}H-NMR (100 MHz): 1.20—1.73 (8H), 2.07—2.34 (2H), 2.51 (2H, t, J=6.0 Hz), 5.77 (1H, d, J=15.5 Hz), 5.89 (2H, s), 6.49—6.76 (3H), 7.04 (1H, dt, J=15.5, 6.5 Hz).

(2*E*)-11-(3′,4′-Methylenedioxyphenyl)-2-undecenoic Acid Colorless needles (hexane–acetone), mp 92—94 °C. IR: 1700. MS: 304 (M^+, 82), 135 (100). ^{1}H-NMR (100 MHz): 1.07—1.73 (12H), 2.09—2.28 (2H), 2.51 (2H, t, J=7.0 Hz), 5.75 (1H, d, J=16.0 Hz), 5.89 (2H, s), 6.48—6.76

(3H), 7.05 (1H, dt, $J=16.0$, 7.0 Hz).

(2*E*)-13-(3′,4′-Methylenedioxyphenyl)-2-tridecenoic Acid Colorless prisms (hexane), mp 96—98 °C. IR: 1700. MS: 332 (M^+, 79), 135 (100). ^{1}H-NMR (100 MHz): 1.09—1.73 (16H), 2.05—2.36 (2H), 2.51 (2H, t, $J=7.0$ Hz), 5.76 (1H, d, $J=15.5$ Hz), 5.88 (2H, s), 6.48—6.73 (3H), 7.04 (1H, dt, $J=15.5$, 7.0 Hz).

(2*E*,ω*E*)-2, ω-Dienoic Acids (General Procedure) A stereochemically pure (*E*)-ω-aralkenol was converted to the corresponding aldehyde by Swern oxidation, and then reacted with ethyl diethylphosphonoacetate as described above. Alkaline hydrolysis of the product gave the corresponding (2*E*,ω*E*)-dienoic acid (yield 53—91% from the corresponding alcohol). The following compounds were obtained by this method.

(2*E*,6*E*)-7-(3′,4′-Methylenedioxyphenyl)-2,6-heptadienoic Acid Pale yellow needles (benzene), mp 146—147 °C. IR: 1695. MS: 246 (M^+, 32), 131 (100). ^{1}H-NMR (100 MHz): 2.26—2.45 (4H), 5.82 (1H, d, $J=15.5$ Hz), 5.90 (2H, s), 5.94 (1H, dt, $J=15.5$, 6.5 Hz), 6.29 (1H, d, $J=15.5$ Hz), 6.66—6.87 (3H), 7.06 (1H, dt, $J=15.5$, 6.5 Hz).

(2*E*,8*E*)-9-(3′,4′-Methylenedioxyphenyl)-2,8-nonadienoic Acid Colorless needles (hexane–acetone), mp 125—133 °C. IR: 1695. MS: 274 (M^+, 54), 131 (100). ^{1}H-NMR (100 MHz): 1.28—1.58 (4H), 1.93—2.36 (4H), 5.78 (1H, d, $J=15.5$ Hz), 5.88 (2H, s), 5.94 (1H, dt, $J=15.5$, 6.2 Hz), 6.25 (1H, d, $J=15.5$ Hz), 6.68—6.82 (3H), 7.28 (1H, dt, $J=15.5$, 6.9 Hz).

(2*E*,10*E*)-11-(3′,4′-Methylenedioxyphenyl)-2,10-undecadienoic Acid Pale yellow prisms (hexane–acetone), mp 105—107 °C. IR: 1695. MS: 302 (M^+, 100). ^{1}H-NMR (100 MHz): 1.15—1.64 (8H), 2.00—2.35 (4H), 5.78 (1H, d, $J=15.5$ Hz), 5.90 (2H, s), 5.97 (1H, dt, $J=15.5$, 6.0 Hz), 6.27 (1H, d, $J=15.5$ Hz), 6.66—6.87 (3H), 7.03 (1H, dt, $J=15.5$, 6.5 Hz).

(2*E*,12*E*)-13-(3′,4′-Methylenedioxyphenyl)-2,12-tridecadienoic Acid Colorless prisms (hexane–acetone), mp 88—89 °C. IR: 1695. MS: 330 (M^+, 100). ^{1}H-NMR (100 MHz): 1.12—1.56 (12H), 1.98—2.28 (4H), 5.76 (1H, d, $J=15.5$ Hz), 5.89 (2H, s), 5.96 (1H, dt, $J=15.5$, 6.0 Hz), 6.25 (1H, d, $J=15.5$ Hz), 6.62—6.88 (3H), 7.03 (1H, dt, $J=15.5$, 7.0 Hz).

(2*E*,4*E*)-11-(3′,4′-Methylenedioxyphenyl)-2,4-undecadienoic Acid A solution of *tert*-BuOK (302 mg) in dry THF (10 ml) was added to a stirred solution of triethyl 4-phosphonocrotonate (678 mg) in dry THF (15 ml) at 0 °C and the mixture was stirred for 2 h. To this mixture, 7-(3′,4′-methylenedioxyphenyl)heptanal (316 mg) in dry THF (15 ml) was added and the whole was stirred at room temperature for 3 h. It was acidified with 1 N HCl and extracted with ether. The organic layer was washed with brine and concentrated to dryness. The residue was purified by silica gel column chromatography (hexane–AcOEt = 19 : 1) to give the ethyl 2,4-dienoate (223 mg). The ester was hydrolyzed by heating with 1 N NaOH–MeOH (1 : 1, 10 ml) at 80 °C for 1.5 h to give the dienoic acid (207 mg, 51% from the aldehyde). Colorless plates (benzene–hexane), mp 105—106.5 °C. IR: 1687, 1639, 1615. MS: 302 (M^+, 76), 135 (100). ^{1}H-NMR: 1.29—1.37 (4H), 1.43 (2H, m), 1.56 (2H, m), 2.17 (2H, m), 2.52 (2H, t, $J=7.6$ Hz), 5.78 (1H, d, $J=15.6$ Hz), 5.91 (2H, s), 6.18 (2H, m), 6.61 (1H, dd, $J=8.3$, 2.0 Hz), 6.66 (1H, d, $J=2.0$ Hz), 6.72 (1H, d, $J=8.3$ Hz), 7.33 (1H, dd, $J=15.6$, 10.0 Hz).

Amide Formation (General Procedure) from Carboxylic Acids A mixture of a carboxylic acid (1.8 mmol), Et_3N (3.6 mmol) in dry CH_2Cl_2 (10—30 ml) was stirred at 0 °C for 15 min, then ethyl chloroformate (2.0 mmol) was added. After 30 min of stirring, an amine (2.7—3.6 mmol) was added and stirring was continued for 1 h. The reaction mixture was washed with 2% H_2SO_4 (in the case of *N*-methylpiperazine amide, this washing was omitted), and saturated $NaHCO_3$ solution, and concentrated. The residue was chromatographed ($CHCl_3$–MeOH = 9 : 1 for *N*-methylpiperazine amides and $CHCl_3$–AcOEt = 19 : 1 for the other amides) to give the corresponding amide. The following compounds were prepared by this method.

PA-A5 : 0 Yield quant. Colorless oil. IR: 1621. MS: 289 (M^+, 64), 127 (100). ^{1}H-NMR: 1.52 (4H, m), 1.63 (6H, m), 2.32 (2H, t, $J=7.1$ Hz), 2.56 (2H, t, $J=7.1$ Hz), 3.36 (2H, t, $J=5.6$ Hz), 3.54 (2H, t, $J=5.6$ Hz), 5.91 (2H, s), 6.62 (1H, dd, $J=7.8$, 1.5 Hz), 6.67 (1H, d, $J=1.5$ Hz), 6.71 (1H, d, $J=7.8$ Hz).

PA-B5 : 0 Yield 97%. Colorless needles (benzene–hexane), mp 62—63 °C. IR: 1662, 1518. MS: 277 (M^+, 100). ^{1}H-NMR: 0.90 (6H, d, $J=6.8$ Hz), 1.58—1.70 (4H), 1.75 (1H, hept, $J=6.8$ Hz), 2.18 (2H, t, $J=7.3$ Hz), 2.55 (2H, t, $J=7.3$ Hz), 3.07 (2H, t, $J=6.3$ Hz), 5.78 (1H, br s), 5.91 (2H, s), 6.61 (1H, dd, $J=7.8$, 1.5 Hz), 6.66 (1H, d, $J=1.5$ Hz), 6.71 (1H, d, $J=7.8$ Hz).

PA-C5 : 0 Yield 89%. Colorless oil. IR: 1625. MS: 275 (M^+, 82), 113 (100). ^{1}H-NMR (100 MHz): 1.53—1.77 (4H), 1.77—2.00 (4H), 2.13—2.34 (2H), 2.44—2.63 (2H), 3.26—3.52 (4H), 5.88 (2H, s), 6.49—6.74 (3H).

PA-C5 : 1(4*E*) Yield 60%. Pale yellow oil. IR: 1625. MS: 273 (M^+, 100). ^{1}H-NMR (100 MHz): 1.70—1.96 (4H), 2.26—2.67 (4H), 3.27—3.55 (4H), 5.91 (2H, s), 6.04 (1H, dt, $J=15.5$, 6.0 Hz), 6.33 (1H, d, $J=15.5$ Hz), 6.67—6.91 (3H).

PA-M5 : 0 Yield 76%. Pale yellow oil. IR: 1625. MS: 304 (M^+, 74), 70 (100). ^{1}H-NMR (100 MHz): 1.48—1.71 (4H), 2.11—2.65 (8H), 2.29 (3H, s), 3.31—3.68 (4H), 5.87 (2H, s), 6.48—6.73 (3H).

PA-A7 : 0 Yield 98%. Colorless oil. IR: 1622. MS: 317 (M^+, 79), 127 (100). ^{1}H-NMR: 1.30—1.38 (4H), 1.50—1.65 (10H), 2.30 (2H, t, $J=7.8$ Hz), 2.51 (2H, t, $J=7.8$ Hz), 3.39 (2H, br s), 3.53 (2H, br s), 5.89 (2H, s), 6.60 (1H, dd, $J=7.8$, 1.5 Hz), 6.65 (1H, d, $J=1.5$ Hz), 6.70 (1H, d, $J=7.8$ Hz).

PA-B7 : 0 Yield 53%. Colorless waxy solid, mp 51—52 °C. IR: 1664, 1518. MS: 305 (M^+, 67), 135 (100). ^{1}H-NMR: 0.91 (6H, d, $J=6.8$ Hz), 1.31—1.38 (4H), 1.53—1.66 (4H), 1.76 (1H, hept, $J=6.8$ Hz), 2.16 (2H, t, $J=7.6$ Hz), 2.51 (2H, t, $J=7.8$ Hz), 3.08 (2H, t, $J=6.4$ Hz), 5.40 (1H, br s), 5.91 (2H, s), 6.60 (1H, dd, $J=7.8$, 1.5 Hz), 6.65 (1H, d, $J=1.5$ Hz), 6.71 (1H, d, $J=7.8$ Hz).

PA-C7 : 0 Yield 76%. Pale yellow oil. IR: 1625. MS: 303 (M^+, 55), 113 (100). ^{1}H-NMR (100 MHz): 1.15—2.02 (12H), 2.24 (2H, t, $J=6.5$ Hz), 2.51 (2H, t, $J=6.5$ Hz), 3.21—3.55 (4H), 5.88 (2H, s), 6.45—6.78 (3H).

PA-C7 : 1(2*E*) Yield 83%. Pale yellow oil. IR: 1660, 1600. MS: 301 (M^+, 83), 152 (100). ^{1}H-NMR (100 MHz): 1.37—1.70 (4H), 1.79—2.00 (4H), 2.09—2.34 (2H), 2.52 (2H, t, $J=7.0$ Hz), 3.36—3.59 (4H), 5.88 (2H, s), 6.04 (1H, d, $J=15.0$ Hz), 6.59—6.75 (3H), 6.87 (1H, dt, $J=15.0$, 7.0 Hz).

PA-C7 : 1(6*E*) Yield 98%. Pale yellow oil. The spectral data were identical with those of the natural product.[3]

PA-C7 : 2(2*E*,6*E*) Yield 62%. Colorless crystalline solid, mp 91—92 °C. The spectral data were identical with those of the natural product.[3]

PA-M7 : 0 Yield 77%. Pale yellow oil. IR: 1625. MS: 332 (M^+, 57), 70 (100). ^{1}H-NMR (100 MHz): 1.17—1.77 (8H), 2.13—2.61 (8H), 2.31 (3H, s), 3.33—3.70 (4H), 5.88 (2H, s), 6.48—6.77 (3H).

Phenyl-PA-C7 : 0 Yield 41%. Colorless oil. IR: 1622. MS: 259 (M^+, 49), 113 (100). ^{1}H-NMR: 1.33—1.40 (4H), 1.59—1.68 (4H), 1.84 (2H, m), 1.93 (2H, m), 2.24 (2H, t, $J=7.8$ Hz), 2.60 (2H, t, $J=7.8$ Hz), 3.38 (2H, m), 3.45 (2H, m), 7.15—7.28 (5H).

Phenyl-PA-M7 : 0 Yield 47%. Pale yellow oil. IR: 1629. MS: 288 (M^+, 43), 70 (100). ^{1}H-NMR (100 MHz): 1.2—1.8 (8H), 2.28 (3H, s), 2.22—2.66 (8H), 3.4—3.7 (4H), 7.0—7.2 (5H).

4-Methoxyphenyl-PA-C7 : 0 Yield 56%. Pale yellow oil. IR: 1621. MS: 289 (M^+, 42), 113 (100). ^{1}H-NMR (100 MHz): 1.11—1.99 (12H), 2.18 (2H, t, $J=7.5$ Hz), 2.48 (2H, t, $J=7.5$ Hz), 3.2—3.4 (4H), 3.71 (3H, s), 6.70 (2H, d, $J=8$ Hz), 6.98 (2H, d, $J=8$ Hz).

4-Methoxyphenyl-PA-M7 : 0 Yield 71%. Pale yellow oil. IR: 1628. MS: 318 (M^+, 61), 70 (100). ^{1}H-NMR (100 MHz): 1.18—1.80 (8H), 2.0—2.7 (8H), 2.30 (3H, s), 3.4—3.7 (4H), 3.77 (3H, s), 6.66 (2H, d, $J=8.6$ Hz), 7.84 (2H, d, $J=8.6$ Hz).

3,4-Dimethoxyphenyl-PA-C7 : 0 Yield 57%. Pale yellow oil. IR: 1613. MS: 319 (M^+, 46), 113 (100). ^{1}H-NMR: 1.35—1.39 (4H), 1.57—1.69 (4H), 1.96 (4H, br s), 2.27 (2H, t, $J=8$ Hz), 2.55 (2H, t, $J=8$ Hz), 3.44 (4H, br s), 3.87, 3.90 (each 3H, s), 6.68—6.72 (2H), 6.78 (1H, d, $J=8$ Hz).

3,4-Dimethoxyphenyl-PA-M7 : 0 Yield 63%. Pale yellow oil. IR: 1628. MS: 348 (M^+, 36), 70 (100). ^{1}H-NMR: 1.36—1.37 (4H), 1.57—1.66 (4H), 2.30 (2H, t, $J=7.8$ Hz), 2.34 (3H, s), 2.41—2.45 (4H), 2.55 (2H, t, $J=7.8$ Hz), 3.51 (2H, t-like, $J=5$ Hz), 3.66 (2H, t-like, $J=5$ Hz), 3.85, 3.87 (each 3H, s), 6.69—6.71 (2H), 6.78 (1H, d, $J=8$ Hz).

PA-A9 : 0 Yield 76%. Colorless oil. IR: 1620. MS: 345 (M^+, 53), 127 (100). ^{1}H-NMR: 1.30—1.38 (8H), 1.53 (6H, m), 1.62 (4H, m), 2.30 (2H, t, $J=7.8$ Hz), 2.50 (2H, t, $J=7.8$ Hz), 3.40 (2H, br s), 3.55 (2H, br s), 5.90 (2H, s), 6.60 (1H, dd, $J=7.8$, 1.9 Hz), 6.65 (1H, d, $J=1.9$ Hz), 6.70 (1H, d, $J=7.8$ Hz).

PA-B9 : 0 Yield 94%. Colorless needles (hexane–benzene), mp 69 °C. IR: 1661, 1518. MS: 333 (M^+, 100). ^{1}H-NMR: 0.91 (6H, d, $J=6.4$ Hz), 1.28—1.32 (8H), 1.52—1.68 (6H), 1.76 (1H, hept, $J=6.4$ Hz), 2.16 (2H, t, $J=7.8$ Hz), 2.51 (2H, t, $J=7.6$ Hz), 3.08 (2H, t, $J=6.4$ Hz), 5.43 (1H, br s), 5.91 (2H, s), 6.61 (1H, dd, $J=7.8$, 1.5 Hz), 6.66 (1H, d, $J=1.5$ Hz), 6.71 (1H, d, $J=7.8$ Hz).

PA-B9 : 2(2*E*,8*E*) Yield 71%. Colorless needles (AcOEt–hexane), mp 122—123 °C (lit. 120 °C).[23] ^{1}H-NMR (100 MHz): 0.92 (6H, d, $J=7.0$ Hz), 1.38—1.60 (4H), 1.78 (1H, m), 2.05—2.30 (4H), 3.12 (2H, t,

J=6.0 Hz), 5.42 (1H, br s), 5.71 (1H, dt, J=15.0, 1.5 Hz), 5.89 (2H, s), 5.93 (1H, dt, J=15.5, 6.0 Hz), 6.26 (1H, d, J=15. 5 Hz), 6.65—6.88 (3H), 6.78 (1H, dt, J=15.0, 7.0 Hz).

PA-C9:0 Yield 84%. Pale yellow oil. IR: 1620. MS: 331 (M^+, 30), 113 (100). ^{1}H-NMR (100 MHz): 1.20—1.75 (12H), 1.75—2.00 (4H), 2.25 (2H, t, J=7.0 Hz), 2.51 (2H, t, J=7.0 Hz), 3.30—3.56 (4H), 5.88 (2H, s), 6.50—6.76 (3H).

PA-C9:1(2*E*) Yield 64%. Pale yellow oil. IR: 1655, 1600. MS: 329 (M^+, 69), 152 (100). ^{1}H-NMR (100 MHz): 1.12—1.66 (8H), 1.72—2.03 (4H), 2.03—2.32 (2H), 2.51 (2H, t, J=7.0 Hz), 3.35—3.62 (4H), 5.89 (2H, s), 6.04 (1H, d, J=15.0 Hz), 6.51—6.73 (3H), 6.88 (1H, dt, J=15.0, 6.5 Hz).

PA-C9:1(8*E*) Yield 74%. Pale yellow oil. The spectral data were identical with those of the natural product.[3)]

PA-C9:2(2*E*,8*E*) Yield 87%. Colorless solid, mp <30 °C. The spectral data were identical with those of the natural product.[3)]

PA-M9:0 Yield 77%. Pale yellow oil. IR: 1625. MS: 360 (M^+, 52), 70 (100). ^{1}H-NMR (100 MHz): 1.15—1.77 (12H), 2.17—2.60 (8H), 2.31 (3H, s), 3.37—3.70 (4H), 5.89 (2H, s), 6.48—6.76 (3H).

PA-A11:0 Yield 98%. Colorless oil. IR: 1620. MS: 373 (M^+, 32), 127 (100). ^{1}H-NMR (100 MHz): 1.12—1.70 (22H), 2.27 (2H, t, J= 7.0 Hz), 2.47 (2H, t, J=7.0 Hz), 3.23—3.56 (4H), 5.89 (2H, s), 6.46—6.71 (3H).

PA-B11:0 Yield 95%. Colorless crystalline solid, mp 80—82 °C. IR: 1660. MS: 361 (M^+, 100). ^{1}H-NMR (100 MHz): 0.90 (6H, d, J=6.5 Hz), 1.14—1.90 (17H), 2.16 (2H, t, J=7.0 Hz), 2.50 (2H, t, J=7.5 Hz), 3.06 (2H, t, J=6.5 Hz), 5.52 (1H, br s), 5.90 (2H, s), 6.49—6.74 (3H).

PA-C11:0 Yield 52%. Pale yellow oil. IR: 1620. MS: 359 (M^+, 62), 113 (100). ^{1}H-NMR (100 MHz): 1.12—1.79 (16H), 1.79—2.03 (4H), 2.25 (2H, t, J=7.0 Hz), 2.51 (2H, t, J=7.5 Hz), 3.29—3.55 (4H), 5.89 (2H, s), 6.51—6.75 (3H).

PA-C11:1(2*E*) Yield 70%. Pale yellow oil. IR: 1660, 1600. MS: 357 (M^+, 81), 113 (100). ^{1}H-NMR (100 MHz): 1.12—1.66 (12H), 1.74—2.02 (4H), 2.02—2.30 (2H), 2.51 (2H, t, J=7.0 Hz), 3.38—3.60 (4H), 5.89 (2H, s), 6.05 (1H, d, J=15.0 Hz), 6.48—6.71 (3H), 6.88 (1H, dt, J=15.0, 7.0 Hz).

PA-C11:1(10*E*) Yield 84%. Pale yellow oil. IR: 1625. MS: 357 (M^+, 100). ^{1}H-NMR (100 MHz): 1.10—1.73 (12H), 1.73—2.02 (4H), 2.02—2.34 (4H), 3.20—3.56 (4H), 5.90 (2H, s), 5.98 (1H, dt, J=15.5, 6.5 Hz), 6.27 (1H, d, J=15.5 Hz), 6.59—6.90 (3H).

PA-C11:2(2*E*,4*E*) Yield 74%. Colorless crystalline solid, mp 57—59 °C. IR: 1650, 1622, 1590. MS: 355 (M^+, 61), 135 (100). ^{1}H-NMR (100 MHz): 1.28—1.35 (4H), 1.42 (2H, m), 1.56 (2H, m), 1.88—1.96 (4H), 2.14 (2H, br q, J=6.8 Hz), 2.52 (2H, t, J=7.8 Hz), 3.54 (2H, t-like, J=6.6 Hz), 5.91 (2H, s), 6.08 (2H, m), 6.17 (1H, br dd, J=14.7, 3.9 Hz), 6.61 (1H, dd, J=7.8, 1.5 Hz), 6.66 (1H, d, J=1.5 Hz), 6.72 (1H, d, J=7.8 Hz), 7.30 (1H, dd, J=15.1, 10.7 Hz).

PA-C11:2(2*E*,10*E*) Yield 75%. Colorless crystalline solid, mp 46—48 °C. IR: 1655, 1600. MS: 355 (M^+, 33), 152 (100). ^{1}H-NMR (100 MHz): 1.19—1.67 (8H), 1.75—2.02 (4H), 3.39—3.61 (4H), 5.91 (2H, s), 5.98 (1H, dt, J=15.5, 6.5 Hz), 6.06 (1H, d, J=14.5 Hz), 6.27 (1H, d, J=15.5 Hz), 6.67—6.90 (3H), 6.89 (1H, dt, J=14.5, 7.0 Hz).

PA-M11:0 Yield 56%. Pale yellow oil. IR: 1625. MS: 388 (M^+, 54), 70 (100). ^{1}H-NMR (100 MHz): 1.10—1.78 (16H), 2.18—2.63 (8H), 2.32 (3H, s), 3.39—3.76 (4H), 5.89 (2H, s), 6.50—6.76 (3H).

PA-C13:0 Yield 92%. Pale yellow oil. IR: 1620. MS: 387 (M^+, 60), 113 (100). ^{1}H-NMR (100 MHz): 1.06—1.72 (20H), 1.72—2.01 (4H), 2.24 (2H, t, J=7.0 Hz), 2.50 (2H, t, J=7.0 Hz), 3.27—3.53 (4H), 5.88 (2H, s), 6.48—6.75 (3H).

PA-C13:1(2*E*) Yield 81%. Colorless crystalline solid, mp 58—60 °C. IR: 1655, 1600. MS: 385 (M^+, 9), 152 (100). ^{1}H-NMR (100 MHz): 1.10—1.72 (16H), 1.72—2.02 (4H), 2.02—2.33 (2H), 2.49 (2H, t, J=6.0 Hz), 3.34—3.62 (4H), 5.88 (2H, s), 6.03 (1H, d, J=15.5 Hz), 6.48—6.70 (3H), 6.86 (1H, dt, J=15.5, 7.0 Hz).

PA-C13:1(12*E*) Yield 77%. Colorless solid, mp <30 °C. IR: 1620. MS: 385 (M^+, 40), 357 (100). ^{1}H-NMR: 1.25—1.37 (12H), 1.43 (2H, m), 1.64 (2H, m), 1.84 (2H, m), 1.93 (2H, m), 2.16 (2H, br q, J=6.8 Hz), 2.24 (2H, t, J=7.6 Hz), 3.40 (2H, br t, J=6.8 Hz), 3.45 (2H, br t, J=6.8 Hz), 5.92 (2H, s), 6.04 (1H, dtd, J=15.6, 6.8, 2.0 Hz), 6.28 (1H, br d, J=15.6 Hz), 6.72 (1H, d, J=7.8 Hz), 6.75 (1H, dd, J=7.8, 1.5 Hz), 6.88 (1H, d, J=1.5 Hz).

PA-C13:2(2*E*,12*E*) Yield 79%. Colorless crystalline solid, mp 64—66 °C. IR: 1655, 1600. MS: 383 (M^+, 65), 152 (100). ^{1}H-NMR (100 MHz): 1.17—1.67 (12H), 1.73—1.97 (4H), 1.97—2.31 (4H), 3.39—3.59 (4H), 5.90 (2H, s), 5.99 (1H, dt, J=15.5, 6.5 Hz), 6.05 (1H, d, J=15.0 Hz), 6.27 (1H, d, J=15.5 Hz), 6.67—6.90 (3H), 6.88 (1H, dt, J=15.0, 6.5 Hz).

PA-M13:0 Yield 80%. Pale yellow oil. IR: 1630. MS: 416 (M^+, 48), 70 (100). ^{1}H-NMR (100 MHz): 1.11—1.72 (20H), 2.17—2.60 (8H), 2.29 (3H, s), 3.33—3.69 (4H), 5.88 (2H, s), 6.48—6.74 (3H).

Phenyl-PA-C13:0 Yield 89%. Colorless solid, mp <30 °C. IR: 1618. MS: 343 (M^+, 21), 113 (100). ^{1}H-NMR: 1.25—1.32 (16H), 1.55—1.66 (4H), 1.83, 1.93 (each 2H, quint, J=6.7 Hz), 2.24 (2H, t, J=7.6 Hz), 2.59 (2H, t, J=7.8 Hz), 3.40, 3.45 (each 2H, br t, J=6.6 Hz), 7.14—7.27 (5H).

Phenyl-PA-M13:0 Yield 96%. Pale yellow oil. IR: 1624. MS: 372 (M^+, 20), 70 (100). ^{1}H-NMR: 1.23—1.33 (16H), 1.58—1.64 (4H), 2.32 (3H, s), 2.35 (4H, m), 2.30 (2H, t, J=7.8 Hz), 2.59 (2H, t, J=7.8 Hz), 3.49, 3.65 (each 2H, br t, J=4.9 Hz), 7.12—7.29 (5H).

4-Methoxyphenyl-PA-C13:0 Yield quant. Colorless needles (ether–hexane), mp 54.5—56.5 °C. IR: 1620. MS: 373 (M^+, 30), 113 (100). ^{1}H-NMR: 1.23—1.36 (16H), 1.59 (4H), 1.84, 1.94 (each 2H, quint, J=6.7 Hz), 2.24 (2H, t, J=7.6 Hz), 2.53 (2H, t, J=7.8 Hz), 3.40, 3.46 (each 2H, t, J=6.8 Hz), 3.78 (3H, s), 6.81 (2H, d, J=8.5 Hz), 7.08 (2H, d, J=8.5 Hz).

4-Methoxyphenyl-PA-M13:0 Yield 96%. Colorless fine prisms (ether), mp 35—38 °C. IR: 1629. MS: 402 (M^+, 44), 70 (100). ^{1}H-NMR: 1.22—1.32 (16H), 1.52—1.65 (4H), 2.30 (3H, s), 2.30 (2H, t, J=7.6 Hz), 2.37 (4H, m), 2.53 (2H, t, J=7.8 Hz), 3.47, 3.63 (each 2H, br t, J=5.1 Hz), 3.78 (3H, s), 6.82 (2H, d, J=8.5 Hz), 7.08 (2H, d, J=8.5 Hz).

3,4-Dimethoxyphenyl-PA-C13:0 Yield 89%. Colorless plates (hexane–ether), mp 49—50.5 °C. IR: 1620. MS: 403 (M^+, 51), 113 (100). ^{1}H-NMR: 1.24—1.36 (16H), 1.84, 1.94 (each 2H, quint, J=6.6 Hz), 1.63 (4H), 2.24 (2H, t, J=7.6 Hz), 2.54 (2H, t, J=7.8 Hz), 3.40, 3.46 (each 2H, J=7.0 Hz), 3.85, 3.87 (each 3H, s), 6.71 (2H, m), 6.78 (1H, d, J=8.8 Hz).

3,4-Dimethoxyphenyl-PA-M13:0 Yield 94%. Colorless solid, mp <30 °C. IR: 1625. MS: 432 (M^+, 30), 70 (100). ^{1}H-NMR: 1.45—1.65 (16H), 1.51—1.75 (4H), 2.28 (3H, s), 2.28 (2H, t, J=7.6 Hz), 2.36 (4H, m), 2.53 (2H, t, J=7.8 Hz), 3.46 (2H, t-like, J=3.3 Hz), 3.62 (2H, t, J=5.4 Hz), 3.84, 3.86 (each 3H, s), 6.70 (2H, m), 6.77 (1H, d, J=8.2 Hz).

PA-C15:0 Yield 50%. Colorless crystalline solid, mp 54—55 °C. IR: 1625. MS: 415 (M^+, 32), 113 (100). ^{1}H-NMR (100 MHz): 1.10—1.72 (24H), 1.72—2.00 (4H), 2.23 (2H, t, J=7.0 Hz), 2.49 (2H, t, J=7.0 Hz), 3.27—3.51 (4H), 5.87 (2H, s), 6.48—6.74 (3H).

PA-M15:0 Yield 48%. Pale yellow oil. IR: 1630. MS: 444 (M^+, 39), 70 (100). ^{1}H-NMR (100 MHz): 1.06—1.72 (24H), 2.15—2.59 (8H), 2.29 (3H, s), 3.32—3.68 (4H), 5.87 (2H, s), 6.48—6.74 (3H).

Phenyl-PA-C15:0 Yield 94%. Colorless prisms (hexane), mp 39—41 °C. IR: 1622. MS: 371 (M^+, 73), 113 (100). ^{1}H-NMR: 1.24—1.34 (20H), 1.58—1.67 (4H), 1.84, 1.94 (each 2H, quint, J=6.6 Hz), 2.25 (2H, t, J=7.8 Hz), 2.60 (2H, t, J=7.8 Hz), 3.41, 3.46 (each 2H, t, J=6.6 Hz), 7.15—7.19 (3H), 7.25—7.29 (2H).

Phenyl-PA-M15:0 Yield 98%. Colorless solid, mp 31—32 °C. IR: 1631. MS: 400 (M^+, 22), 277 (100). ^{1}H-NMR: 1.23—1.34 (20H), 1.58—1.65 (4H), 2.30 (2H, t, J=7.3 Hz), 2.31 (3H, s), 2.39 (4H, m), 2.59 (2H, t, J=7.8 Hz), 3.48, 3.64 (each 2H, t, J=4.9 Hz), 7.15—7.19 (3H), 7.25—7.29 (2H).

4-Methoxyphenyl-PA-C15:0 Yield quant. Colorless prisms (hexane), mp 60—61 °C. IR: 1621. MS: 401 (M^+, 66), 121 (100). ^{1}H-NMR: 1.23—1.33 (20H), 1.60—1.67 (4H), 1.85, 1.94 (each 2H, quint, J=6.8 Hz), 2.24 (2H, t, J=7.8 Hz), 2.54 (2H, t, J=7.8 Hz), 3.41, 3.46 (each 2H, t, J=6.8 Hz), 3.78 (3H, s), 6.82 (2H, d, J=8.3 Hz), 7.09 (2H, d, J=8.3 Hz).

4-Methoxyphenyl-PA-M15:0 Yield quant. Colorless prisms (ether–hexane), mp 40—53 °C. IR: 1630. MS: 430 (M^+, 58), 121 (100). ^{1}H-NMR: 1.23—1.33 (20H), 1.54—1.65 (4H), 2.29 (2H, t, J=7.5 Hz), 2.30 (3H, s), 2.35—2.40 (4H), 2.54 (2H, t, J=7.8 Hz), 3.46—3.50, 3.61—3.64 (each 2H, m), 3.78 (3H, s), 6.82 (2H, d, J=8.8 Hz), 7.09 (2H, d, J=8.8 Hz).

3,4-Dimethoxyphenyl-PA-C15:0 Yield 84%. Colorless prisms (hexane), mp 52—53 °C. IR: 1622. MS: 431 (M^+, 90), 113 (100). ^{1}H-NMR: 1.24—1.34 (20H), 1.56—1.67 (4H), 1.85, 1.95 (each 2H, quint, J=6.6 Hz), 2.25 (2H, t, J=7.8 Hz), 2.55 (2H, t, J=7.8 Hz), 3.41, 3.46 (each 2H, t, J=6.8 Hz), 3.86, 3.87 (each 3H, s), 6.71 (1H, d, J=2.0 Hz), 6.72 (1H, dd, J=8.3, 2.0 Hz), 6.79 (1H, d, J=8.3 Hz).

3,4-Dimethoxyphenyl-PA-M15:0 Yield quant. Pale yellow oil. IR: 1630. MS: 460 (M^+, 72), 151 (100). ^{1}H-NMR: 1.24—1.34 (20H), 1.56—1.65 (4H), 2.31 (2H, t, J=7.8 Hz), 2.32 (3H, s), 2.39—2.43 (4H), 2.54 (2H, t, J=7.8 Hz), 3.49 (2H, t, J=5.1 Hz), 3.65 (2H, m), 3.86, 3.87

(each 3H, s), 6.72 (2H, m), 6.79 (1H, d, J=8.8 Hz).

From Esters (General Procedure) Trimethylaluminum (15% hexane solution, 2.7—3 ml) was added to a solution of an amine (6.2—6.4 mmol) in dry CH_2Cl_2 (3 ml), and the mixture was stirred for 30 min at room temperature. A methyl ester (2.1 mmol) in dry CH_2Cl_2 (7 ml) was added and the mixture was stirred at room temperature for 3.5 h, then acidified with 1 N HCl and extracted with CH_2Cl_2. For *N*-methylpiperazine, benzene was used as the solvent and the reaction was carried out at 85 °C for 3.5 h. The reaction mixture was neutralized and extracted with $CHCl_3$. The solvent was removed under reduced pressure and the residue was purified by chromatography ($CHCl_3$–MeOH=9:1 for *N*-methylpiperazine amides or benzene–AcOEt=3:1 for the others) to give the corresponding amide. The following compounds were prepared by this method.

Phenyl-PA-C9:0 Yield 92%. Pale yellow oil. IR: 1622. MS: 287 (M^+, 30), 113 (100). ^{1}H-NMR (100 MHz): 1.12—1.74 (12H), 1.74—2.06 (4H), 2.24 (2H, t, J=7.5 Hz), 2.59 (2H, t, J=7.5 Hz), 3.38, 3.44 (each 2H, t, J=6 Hz), 7.02—7.32 (5H).

Phenyl-PA-M9:0 Yield 92%. Colorless oil. IR: 1629. MS: 316 (M^+, 29), 70 (100). ^{1}H-NMR (100 MHz): 1.16—1.78 (12H), 2.12—2.46 (6H), 2.28 (3H, s), 2.58 (2H, t, J=7.5 Hz), 3.44, 3.60 (each 2H, t, J=5 Hz), 7.02—7.30 (5H).

4-Methoxyphenyl-PA-C9:0 Yield 87%. Colorless prisms (hexane–ether), mp 40.5—42 °C. IR: 1621. MS: 317 (M^+, 35), 113 (100). ^{1}H-NMR (100 MHz): 1.10—1.76 (12H), 1.80—2.04 (4H), 2.25 (2H, t, J=7.5 Hz), 2.54 (2H, t, J=7.5 Hz), 3.39, 3.44 (each 2H, t, J=5.5 Hz), 3.78 (3H, s), 6.79, 7.08 (each 2H, d, J=10 Hz).

4-Methoxyphenyl-PA-M9:0 Yield 95%. Colorless oil. IR: 1623. MS: 346 (M^+, 58), 70 (100). ^{1}H-NMR (100 MHz): 1.08—1.80 (12H), 1.88—2.66 (8H), 2.31 (3H, s), 3.47, 3.63 (each 2H, t, J=5 Hz), 3.78 (3H, s), 6.80, 7.08 (each 2H, d, J=8 Hz).

3,4-Dimethoxyphenyl-PA-C9:0 Yield 86%. Colorless needles (hexane–ether), mp 39—41 °C. IR: 1621. MS: 347 (M^+, 61), 113 (100). ^{1}H-NMR (100 MHz): 1.10—1.72 (12H), 1.72—2.03 (4H), 2.24 (2H, t, J=7.5 Hz), 2.53 (2H, t, J=7.5 Hz), 3.40 (4H, m), 3.83, 3.85 (each 3H, s), 6.56—6.76 (3H).

3,4-Dimethoxyphenyl-PA-M9:0 Yield 97%. Pale yellow oil. IR: 1627. MS: 376 (M^+, 83), 70 (100). ^{1}H-NMR (100 MHz): 1.16—1.80 (12H), 2.07—2.44 (6H), 2.32 (3H, s), 2.53 (2H, t, J=7 Hz), 3.45, 3.61 (each 2H, t, J=5 Hz), 3.87, 3.89 (each 3H, s), 6.53—6.83 (3H).

Phenyl-PA-C11:0 Yield 95%. Colorless oil. IR: 1621. MS: 315 (M^+, 36), 113 (100). ^{1}H-NMR (100 MHz): 1.14—1.63 (16H), 1.78—2.06 (4H), 2.44 (2H, t, J=8 Hz), 2.59 (2H, t, J=8 Hz), 3.40 (4H, m), 7.01 (5H).

Phenyl-PA-M11:0 Yield 99%. Pale yellow oil. IR: 1617. MS: 344 (M^+, 28), 70 (100). ^{1}H-NMR (100 MHz): 1.15—1.75 (16H), 2.11—2.47 (6H), 2.51 (3H, s), 2.59 (2H, t, J=7.5 Hz), 2.47, 2.62 (each 2H, t, J=5 Hz), 7.03—7.27 (5H).

4-Methoxyphenyl-PA-C11:0 Yield 65%. Colorless prisms (hexane–ether), mp 45—46 °C. IR: 1622. MS: 345 (M^+, 44), 113 (100). ^{1}H-NMR (100 MHz): 1.00—1.74 (16H), 1.74—2.04 (4H), 2.24 (2H, t, J=7 Hz), 2.52 (2H, t, J=7 Hz), 3.36 (4H, m), 3.76 (3H, s), 6.79, 7.07 (each 2H, d, J=9 Hz).

4-Methoxyphenyl-PA-M11:0 Yield 92%. Pale yellow oil. IR: 1622. MS: 374 (M^+, 34), 70 (100). ^{1}H-NMR (100 MHz): 1.16—1.76 (16H), 2.10—2.44 (6H), 2.30 (3H, s), 2.52 (2H, t, J=7.5 Hz), 3.46, 3.62 (each 2H, t, J=5 Hz), 3.76 (3H, s), 6.78, 7.07 (each 2H, d, J=9 Hz).

3,4-Dimethoxyphenyl-PA-C11:0 Yield 58%. Colorless oil. IR: 1622. MS: 375 (M^+, 80), 113 (100). ^{1}H-NMR (100 MHz): 1.08—1.80 (16H), 1.80—2.04 (4H), 2.24 (2H, t, J=8 Hz), 2.53 (2H, t, J=8 Hz), 3.38, 3.45 (each 2H, t, J=5.5 Hz), 3.84, 3.86 (each 3H, s), 6.64—6.80 (3H).

3,4-Dimethoxyphenyl-PA-M11:0 Yield 65%. Pale yellow oil. IR: 1617. MS: 404 (M^+, 54), 70 (100). ^{1}H-NMR (100 MHz): 1.16—1.76 (16H), 2.12—2.45 (6H), 2.28 (3H, s), 2.54 (2H, t, J=7.5 Hz), 3.47, 3.62 (each 2H, t, J=5 Hz), 3.81, 3.83 (each 3H, s), 6.61—6.81 (3H).

BBr_3 Demethylation (General Procedure) A methoxy-amide (100 mg) in dry CH_2Cl_2 (10 ml) was treated with BBr_3 (5 eq) at 0 °C for 10 min. The reaction mixture was poured into ice-water and extracted with $CHCl_3$. The organic layer was washed with saturated $NaHCO_3$ solution and brine, and concentrated to dryness. The residue was purified by chromatography to give the corresponding phenolic amide. The following compounds were prepared.

4-Hydroxyphenyl-PA-C7:0 Yield quant. Colorless prisms (AcOEt), mp 107—109 °C. IR: 1621. MS: 275 (M^+, 49), 113 (100). ^{1}H-NMR: 1.33—1.36 (4H), 1.54—1.60 (2H), 1.62—1.68 (2H), 1.85, 1.94 (each 2H, quint, J=6.8 Hz), 2.25 (2H, t, J=7.5 Hz), 2.52 (2H, t, J=7.5 Hz), 3.39, 3.46 (each 2H, t, J=6.8 Hz), 6.75 (2H, d, J=8.3 Hz), 7.01 (2H, d, J=8.8 Hz).

4-Hydroxyphenyl-PA-M7:0 Yield 50%. Pale yellow oil. IR: 1629. MS: 304 (M^+, 92), 70 (100). ^{1}H-NMR: 1.30—1.36 (4H), 1.53—1.65 (4H), 2.29—2.33 (2H), 2.32 (3H, s), 2.39—2.43 (4H), 2.50 (2H, t, J=7.5 Hz), 3.50—3.52, 3.64—3.66 (each 2H, m), 6.74 (2H, d, J=8.3 Hz), 6.99 (2H, d, J=8.3 Hz).

3,4-Dihydroxyphenyl-PA-C7:0 Yield quant. Colorless fine prisms (AcOEt–hexane), mp 117—118 °C. IR: 1613, 1607. MS: 291 (M^+, 69), 113 (100). ^{1}H-NMR: 1.25—1.37 (4H), 1.55 (2H, quint, J=7.1 Hz), 1.59—1.68 (2H), 1.87, 1.96 (each 2H, quint, J=6.8 Hz), 2.26 (2H, t, J=7.5 Hz), 2.47 (2H, t, J=7.5 Hz), 3.42, 3.49 (each 2H, t, J=6.8 Hz), 6.55 (1H, dd, J=7.8, 2.0 Hz), 6.73 (1H, d, J=2.0 Hz), 6.78 (1H, d, J=7.8 Hz).

4-Hydroxyphenyl-PA-C9:0 Yield quant. Colorless fine prisms (AcOEt), mp 66—68 °C. IR: 1621. MS: 303 (M^+, 73), 113 (100). ^{1}H-NMR: 1.25—1.32 (8H), 1.51—1.56 (2H), 1.60—1.66 (2H), 1.84, 1.94 (each 2H, quint, J=6.8 Hz), 2.26 (2H, t, J=7.8 Hz), 2.49 (2H, t, J=7.8 Hz), 3.41, 3.48 (each 2H, t, J=6.8 Hz), 6.79 (2H, d, J=8.3 Hz), 7.01 (2H, d, J=8.3 Hz).

4-Hydroxyphenyl-PA-M9:0 Yield 57%. Pale yellow oil. IR: 1630. MS: 332 (M^+, 80), 70 (100). ^{1}H-NMR: 1.26—1.31 (8H), 1.53—1.61 (4H), 2.29—2.33 (2H), 2.32 (3H, s), 2.42 (4H, quint, J=4.8 Hz), 2.51 (2H, t, J=7.5 Hz), 3.46—3.49, 3.64—3.67 (each 2H, m), 6.74 (2H, d, J=8.3 Hz), 7.01 (2H, d, J=8.3 Hz).

3,4-Dihydroxyphenyl-PA-C9:0 Yield 99%. Colorless crystalline solid (AcOEt–hexane), mp 100—103 °C. IR: 1618, 1604. MS: 319 (M^+, 100). ^{1}H-NMR: 1.24—1.32 (8H), 1.52—1.64 (4H), 1.87, 1.96 (each 2H, quint, J=6.5 Hz), 2.28 (2H, t, J=7.5 Hz), 2.48 (2H, t, J=7.5 Hz), 3.43, 3.50 (each 2H, t, J=6.8 Hz), 6.54 (1H, dd, J=7.8, 2.0 Hz), 6.73 (1H, d, J=2.0 Hz), 6.79 (1H, d, J=7.8 Hz).

4-Hydroxyphenyl-PA-C11:0 Yield quant. Colorless needles (ether–hexane), mp 56—57 °C. IR: 1620. MS: 331 (M^+, 74), 113 (100). ^{1}H-NMR: 1.20—1.32 (12H), 1.55 (2H, quint, J=7.8 Hz), 1.63 (2H, quint, J=6.8 Hz), 1.85, 1.94 (each 2H, dt, J=7.3, 6.8 Hz), 2.27 (2H, t, J=7.5 Hz), 2.51 (2H, t, J=7.5 Hz), 3.41, 3.49 (each 2H, t, J=6.8 Hz), 6.80 (2H, d, J=8.3 Hz), 7.00 (2H, d, J=8.8 Hz).

4-Hydroxyphenyl-PA-M11:0 Yield 71%. Pale yellow oil. IR: 1630. MS: 360 (M^+, 75), 70 (100). ^{1}H-NMR: 1.22—1.32 (12H), 1.54—1.63 (4H), 2.29—2.34 (2H), 2.32 (3H, s), 2.38—2.43 (4H), 2.52 (2H, t, J=7.5 Hz), 3.48, 3.65 (each 2H, m), 6.75 (2H, d, J=8.3 Hz), 7.01 (2H, d, J=8.3 Hz).

3,4-Dihydroxyphenyl-PA-C11:0 Yield quant. Colorless prisms (AcOEt–hexane), mp 101—102 °C. IR: 1618, 1605. MS: 347 (M^+, 100). ^{1}H-NMR: 1.16—1.32 (12H), 1.52—1.64 (4H), 1.89, 1.98 (each 2H, quint, J=6.7 Hz), 2.29 (2H, t, J=7.3 Hz), 2.49 (2H, t, J=7.3 Hz), 3.45, 3.52 (each 2H, t, J=6.8 Hz), 6.56 (1H, dd, J=8.3, 2.0 Hz), 6.78 (1H, d, J=2.0 Hz), 6.79 (1H, d, J=8.3 Hz).

4-Hydroxyphenyl-PA-C13:0 Yield quant. Colorless needles (AcOEt), mp 76—77 °C. IR: 1620. MS: 359 (M^+, 89), 113 (100). ^{1}H-NMR: 1.17—1.31 (16H), 1.53—1.59 (2H), 1.64 (2H), 1.85, 1.95 (each 2H, quint, J=6.8 Hz), 2.26 (2H, t, J=7.8 Hz), 2.53 (2H, t, J=7.3 Hz), 3.41, 3.48 (each 2H, t, J=6.8 Hz), 6.77 (2H, d, J=8.3 Hz), 7.00 (2H, d, J=8.3 Hz).

4-Hydroxyphenyl-PA-M13:0 Yield 84%. Colorless oil. IR: 1629. MS: 388 (M^+, 100). ^{1}H-NMR: 1.20—1.35 (16H), 1.52—1.65 (4H), 2.31 (2H, t, J=7.6 Hz), 2.31 (3H, s), 2.40 (4H, m), 2.52 (2H, t, J=7.6 Hz), 3.49, 3.66 (each 2H, br t, J=5.1 Hz), 6.75 (2H, d, J=8.8 Hz), 7.01 (2H, d, J=8.8 Hz).

3,4-Dihydroxyphenyl-PA-C13:0 Yield 98%. Colorless prisms (AcOEt–hexane), mp 104—105 °C. IR: 1617, 1605. MS: 375 (M^+, 100). ^{1}H-NMR: 1.19—1.33 (16H), 1.51—1.60 (2H), 1.66 (2H, quint, J=7.1 Hz), 1.89, 1.98 (each 2H, quint, J=6.3 Hz), 2.30 (2H, t, J=7.8 Hz), 2.49 (2H, t, J=7.3 Hz), 3.45, 3.52 (each 2H, t, J=6.8 Hz), 6.55 (1H, dd, J=7.8, 2.0 Hz), 6.74 (1H, d, J=2.0 Hz), 6.79 (1H, d, J=7.8 Hz).

4-Hydroxyphenyl-PA-C15:0 Yield quant. Colorless needles (AcOEt), mp 78—79 °C. IR: 1619. MS: 387 (M^+, 100). ^{1}H-NMR: 1.21—1.33 (20H), 1.54—1.59 (2H), 1.66 (2H, m), 1.85, 1.95 (each 2H, quint, J=6.8 Hz), 2.27 (2H, t, J=7.3 Hz), 2.52 (2H, t, J=7.3 Hz), 3.42, 3.48 (each 2H, t, J=6.8 Hz), 6.78 (2H, d, J=8.3 Hz), 7.02 (2H, d, J=8.8 Hz).

4-Hydroxyphenyl-PA-M15:0 Yield 53%. Colorless solid. IR: 1629. MS: 416 (M^+, 100). ^{1}H-NMR: 1.23—1.32 (20H), 1.53—1.65 (4H), 2.31—2.34 (2H), 2.32 (3H, s), 2.38—2.43 (4H), 2.52 (2H, t, J=7.5 Hz),

3.49, 3.65 (each 2H, m), 6.75 (2H, d, $J=8.8$ Hz), 7.02 (2H, d, $J=8.8$ Hz).

3,4-Dihydroxyphenyl-PA-C15 : 0 Yield 90%. Colorless needles (AcOEt), mp 107—107.5 °C. IR: 1618, 1605. MS: 403 (M^+, 100). ^{1}H-NMR: 1.23—1.30 (20H), 1.66 (4H, m), 1.88, 1.97 (each 2H, quint, $J=6.6$ Hz), 2.30 (2H, t, $J=7.5$ Hz), 2.48 (2H, t, $J=7.3$ Hz), 3.44, 3.50 (each 2H, t, $J=6.8$ Hz), 6.56 (1H, dd, $J=8.1$, 2.0 Hz), 6.73 (1H, d, $J=2.0$ Hz), 6.79 (1H, d, $J=8.1$ Hz).

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