

**Comparison of Volatile Constituents of *Persicaria odorata* (Lour.) Soják (*Polygonum odoratum* Lour.) and *Persicaria hydropiper* L. Spach (*Polygonum hydropiper* L.)**

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*Polygonum odoratum* Lour. has been reclassified as *Persicaria odorata* (Lour.) Soják [Wilson, K. L. *Polygonum sensu lato* (Polygonaceae) in Australia. *Telopea* **1988**, *3*, 177–182]; other synonyms currently used are Vietnamese mint or Vietnamese coriander and, in Malaysia, Daun Laksa or Laksa plant. The aerial parts of Laksa plant are highly aromatic, and they contain many organic compounds such as (*Z*)-3-hexenal, (*Z*)-3-hexenol, decanal, undecanal, and dodecanal that are typical for green, citrus, orange peel, and coriander odors. In addition to these aldehydes, 3-sulfanyl-hexanal and 3-sulfanyl-hexan-1-ol were discovered for the first time in this herb. The fresh leaves are pungent when they are chewed, although the active compound has never been identified. The pungency of *Persicaria hydropiper* (L.) Spach (formerly *Polygonum hydropiper* L., synonym water pepper) is produced by polygodial, a 1,4-dialdehyde derived from drimane terpenoids. We also identified polygodial as the active pungent compound in *P. odorata* (Lour.) Soják.

**KEYWORDS:** *Persicaria odorata* (Lour.) Soják; *Persicaria hydropiper* (L.) Spach; *Polygonum odoratum* Lour.; *Polygonum hydropiper* L.; 3-sulfanyl-hexanal; 3-sulfanyl-hexan-1-ol; Laksa plant; water pepper; polygodial

**INTRODUCTION**

*Polygonum odoratum* Lour. has been reclassified as *Persicaria odorata* (Lour.) Soják (1); other synonyms currently used are Vietnamese mint or Vietnamese coriander and, in Malaysia, Daun Laksa or Laksa plant (2). The Laksa plant is a perennial herb 30–35 cm height with pointed leaves 6–15 cm with a distinctive dark purple marking in the center of the leaves. The plant has a strong coriander leaf, lemony, green type of smell and is an intrinsic part of the famous Singaporean seafood soup, Laksa. It is also one of those numerous herbs that give Vietnamese cuisine its unique touch. The strong green, orange peel, coriander leaf odor of Laksa plant is due to (*Z*)-3-hexenal, (*Z*)-3-hexen-1-ol, decanal, undecanal, and dodecanal (3–6).

The use of *Persicaria hydropiper* (L.) Spach. (formerly *Polygonum hydropiper* L.), water pepper, smartweed, or marsh pepper in cooking is not documented, although its pungent active component, polygodial (4), is well-described (7). The volatile

composition of water pepper is partially described on the Katzer internet web site (2), where monoterpenoids and sesquiterpenoids are listed as the main components of the essential oil. Water pepper grows wild in Switzerland, and unlike Laksa plant, the leaves do not have a purple dark spot. Moreover, the clear difference is in the odor; water pepper is almost odorless as compared to the Laksa plant. The only way to determine exactly the species of *Persicaria* taxonomically is to have the plant in flower. In a recent paper, the author confused the two plants and ended up analyzing Laksa plant instead of water pepper (8).

The Laksa plant produces a pungent and hot effect in the mouth, but to our knowledge, the active compound has never been formally identified; therefore, we postulated that the active principle is polygodial, identified in water pepper (7). The occurrence of polygodial in terrestrial and marine organisms has been reviewed (9). It is an unusual drimane type sesquiterpenoid due to the presence of two aldehyde functions. Recently, (–)-oleocanthal, which also has a similar type of dialdehyde function, was shown to be the principal irritating compound of olive oil (10). The pungent sensation caused by these molecules is due to interactions with the vanilloid receptors in the human mouth (11–13).

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The objective of this paper is to determine the volatile composition of the Laksa plant and water pepper via gas chromatography–olfaction (GC-O) and to determine if our hypothesis concerning the identity of the pungent compound in the Laksa plant is in fact polygodial (**4**).

## MATERIALS AND METHODS

**GC/Electron Impact–Mass Spectrometry.** An Agilent-GC-6890 system connected to an Agilent-MSD-5973 quadrupole mass spectrometer was operated at an electron energy of 70 eV. Helium was the carrier gas at a constant flow of 0.7 mL/min used with either an apolar fused silica capillary column (30 m × 0.25 mm; film thickness, 1 μm; SPB-1 from Supelco) or polar column Supelcowax10 (SPWax, Supelco; 0.25 mm i.d. × 30 m; film thickness, 0.25 μm); a standard oven program was used as follows: 50 °C for 5 min, then 50–240 °C at 5 °C/min, and hold at 240 °C. Retention indices (*I*) were calculated by linear extrapolation from the retention times (*t<sub>R</sub>*; in min) of the analytes and the two closest alkanes eluting just before and just after the analyte. Retention indices (*I*) are given for polar and apolar columns; in brackets are the reference values measured from authentic samples (a variation of 5% is accepted).

**Analytical GC-Atomic Emission Detector (AED).** An Agilent-GC-6890 instrument was coupled to an AED (Jass, Germany). Injections were performed on an apolar fused silica capillary column (30 m × 0.25 mm; film thickness, 1 μm; SPB-1 from Supelco) with the standard oven program as described above.

**GC-MS-O.** An Agilent-GC-6890 system connected to an Agilent-MSD-5973 quadrupole mass spectrometer was operated at an electron energy of 70 eV. Helium was used as the carrier gas at a constant flow of 0.7 mL/min with a fused silica apolar capillary (SPB-1; 30 m × 0.53 mm; film thickness, 1.5 μm). A glass Y-connection split the effluent to the sniffing port. A standard oven program was used as follows: 50 °C for 5 min, then 3 °C/min to 120 °C, then at 5 °C/min to 250 °C, and hold at 250 °C.

**Affi-Gel 501 (Bio-Rad).** The organomercurial agarose gel was prepared according to a procedure obtained from Bio-Rad. Affi-Gel 10 (Bio-Rad #153-6099, 25 mL, 0.25 mequiv) was placed on a Büchner funnel, washed with 2-propanol (75 mL), and then transferred to an Erlenmeyer flask. A solution of (4-aminophenyl)mercury(II) acetate (375 mg, ca. 1.0 mmol) in dimethylformamide (DMF) (7.5 mL) was added, and the suspension was stirred for 4 h. Upon addition of 2-aminoethanol (0.25 mL) and further stirring for 1 h, the gel was recovered by filtration and washed with DMF (65 mL) followed by 2-propanol (175 mL). The gel was then suspended in 2-propanol (75 mL) and kept at 3 °C until used.

**Analytical High-Performance Liquid Chromatography (HPLC).** Separations were carried out with an Agilent 1100 Series HPLC system consisting of a G1312A binary pump, G1329A autosampler, G1316A column compartment (18 °C), and G1315B diode array detector. Separations were carried out using a Zorbax (Agilent catalog no. 822700-902) SB-C18 column (2.1 mm inside diameter, 50 mm length, 1.8 μm particle size). Solvent A was water, and solvent B was acetonitrile. The gradient profile was as follows: 0–3.1 min, 45% B; 3.10–3.30 min, 45–95% B; 3.30–4.30 min, 95% B; 4.30–4.50 min, 95–45% B; and 4.50–8 min, 45% B; the flow rate was 0.5 mL/min. The total analysis time was 8 min. The wavelength was set at 233 nm for UV detection.

**Chemicals.** 3-Sulfanylhexanal (**2**) (*15*) and 3-sulfanylhexan-1-ol (**3**) (*13*, protocol b) were prepared according to procedures obtained from the literature (*14*, *15*). (*E*)-Caryophyllene was obtained from Fluka (catalog 22075) *I*<sub>SPWAX</sub> 1580, *I*<sub>SPB1</sub> 1420. (*E/E*)-Farnesene *I*<sub>SPWAX</sub> 1650, *I*<sub>SPB1</sub> 1457, and (*E/Z*)-farnesene *I*<sub>SPWAX</sub> 1619, *I*<sub>SPB1</sub> 1428, were prepared from (*E/E*)-farnesol (Fluka), and the stereochemistry was determined by <sup>1</sup>H NMR according to the literature (*16*). Polygodial was obtained from Alpin Chemicals Ltd. (United Kingdom).

**Miscellaneous.** The hydrodistillation was performed with a Büchi rotavapor (catalog R-200/205 E). Optical rotations were obtained with a Perkin-Elmer-241 polarimeter; the cell was maintained at 20 °C if not stated otherwise; [ $\alpha$ ]<sub>D</sub> (c in CHCl<sub>3</sub>). The differential thermal analysis was performed using a Mettler DSC, model 27 HP.

**Botanical Determination.** Cuttings were brought from a market in Singapore to the curator at the Conservatory and Botanical Gardens in Geneva, CJBG (<http://www.ville-ge.ch/cjb/>), in May 2005. They were cultivated in a greenhouse by a horticulturist, under the curator's scientific supervision. Blooming happened around the end of October 2005. Two samples with flowers and leaves were collected from the flowering plant on November 11, 2005. The determination was made by the curator in charge. He certified that the plant was a *P. odorata* (Lour.) Soják (synonym *P. odoratum* Lour.); determination was based on ref *17*. The two samples were deposited in the Herbarium of the CJBG (G) under collection number Roguet D. 19001 (G). Specimina visa: Botanical Gardens of Geneva, 11. XI. 2005; Roguet D. 19001 (G) (origine: Singapore Central Market).

**Preparation of the Essential Oil of Laksa Plant.** Fresh leaves of Laksa plant (166 g) (Jussa S. A. Magasin Lyzambar, 3 rue des Corps Saints, CH-1201 Genève, lyzambar@swissonline.ch) were pureed with a blender and suspended in water (700 mL). The hydrodistillation was performed under vacuum (50 mbar) at 45 °C. The distillate was saturated with NaCl and extracted with diethyl ether. The organic phase was dried over MgSO<sub>4</sub>, filtered, and concentrated at atmospheric pressure using a Vigreux column (yield, 20 mg).

**Preparation of Water Pepper Extract for GC Profile.** Fresh leaves of water pepper (provided by François Couplan, Ethnobotanist, CH-1692 Massonnens, fc@couplan.com) (100 g) were minced to a coarse paste and covered with dichloromethane. This mixture stood overnight at 4 °C and was dried with Na<sub>2</sub>SO<sub>4</sub>, filtered, and distilled at atmospheric pressure using a Vigreux column (yield, 660 mg) and then injected into a GC-MS on a polar and an apolar column (**Figure 3**).

**Preparation of Extracts of Laksa Plant for Comparative GC Profile and for Affinity Chromatography.** Laksa plant (900 g) was extracted as described for water pepper. The crude extract was analyzed by GC-MS using the apolar SPB-1 column (**Figure 3**). The remaining green liquid was loaded on an Affi-Gel column (2.5 cm high of the gel in a 0.5 cm diameter column) and washed three times with dichloromethane. The desorption was performed with dithioethiol (10 mmol of dichloromethane) (*18*). The thiol-enriched organic phase was concentrated and analyzed by GC-AED and GC-MS on a polar and an apolar column.

**Determination of Polygodial (**4**) Concentration.** The procedure was to accurately weigh about 10 g of green leaves, mince them to a coarse paste, and then cover them with ethyl acetate (50 mL) and stir for 30 min. The solution was filtered and dried over MgSO<sub>4</sub>, and the solvent was evaporated under vacuum. The green mixture was then diluted with acetonitrile in a volumetric flask to 20 mL. Appropriate dilutions were further performed in order to have a concentration of polygodial (**4**) between 0.1 and 0.2 mg/mL. Analysis was done by HPLC and UV detection at 233 nm. The linear calibration curve was established using pure crystalline **4** with solutions containing 0.25–0.0125 mg/mL, which were analyzed in triplicate ( $R^2 = 0.9998$ ).

## RESULTS AND DISCUSSION

**Odor Profile of Laksa Plant.** A hydrodistillation was performed on fresh leaves. The hydrodistillate, after extraction with diethyl ether and concentration, had the same type of odor as compared to the fresh leaves. The odor was dominated by strong citrus, coriander leaf olfactive notes attributed to aldehydes such as dodecanal and decanal; green notes were a consequence of (*Z*)-3-hexenal, (*E*)-2-hexenal, and (*Z*)-3-hexen-1-ol, and in the background, some spicy odors were attributed to eugenol and terpenes. These assumptions were determined by GC-MS-O. Analysis of the volatiles present in Laksa plant is well-documented (*3–6*), but the occurrence of sulfur compounds has not yet been reported. The presence of sulfur compounds in Laksa plant was confirmed by GC-MS-O. The typical potato odor of 3-methylthiopropional (**1**) was observed on both polar and apolar columns [retention indices *I*<sub>SPWAX</sub> 1493 (1454) and *I*<sub>SPB1</sub> 879 (871)], and MS fragmentation patterns were

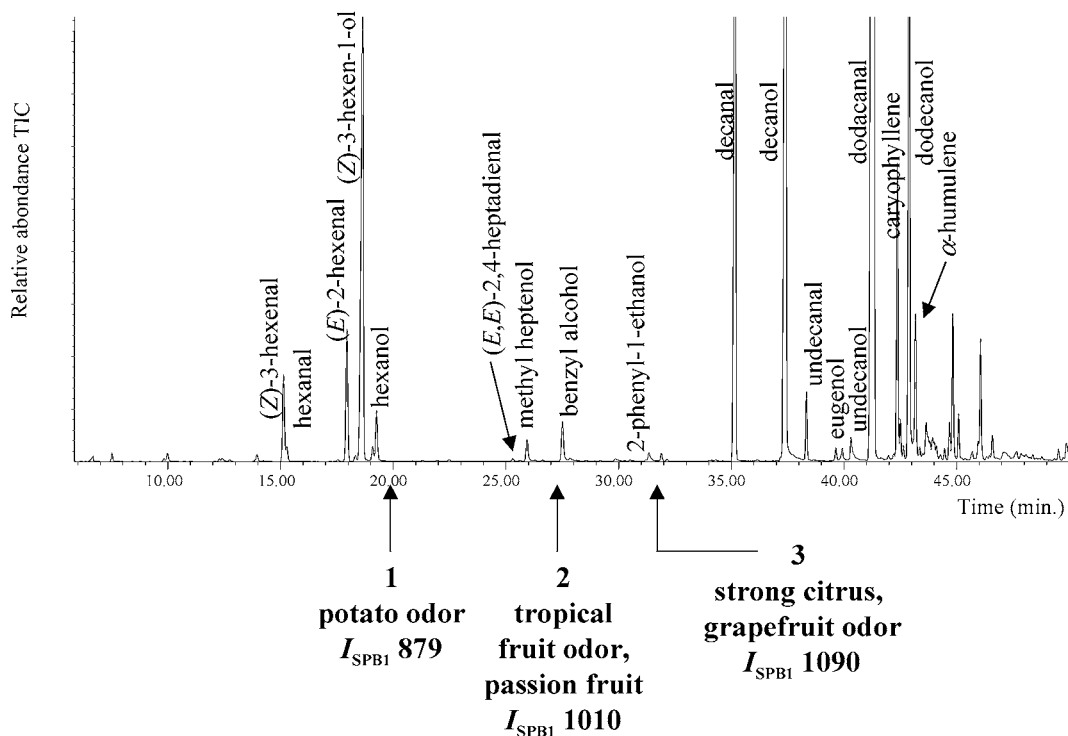


Figure 1. GC-MS-olfaction of the essential oil of fresh leaves of Laksa plant. Only odors associated to unknown compounds are listed.

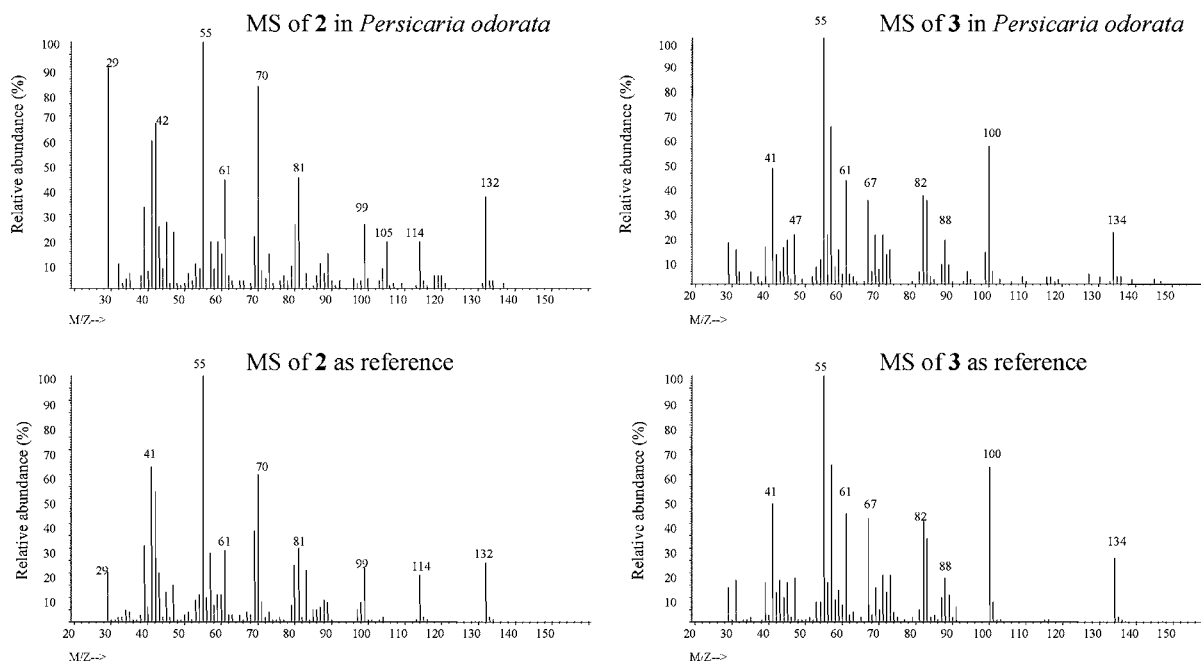
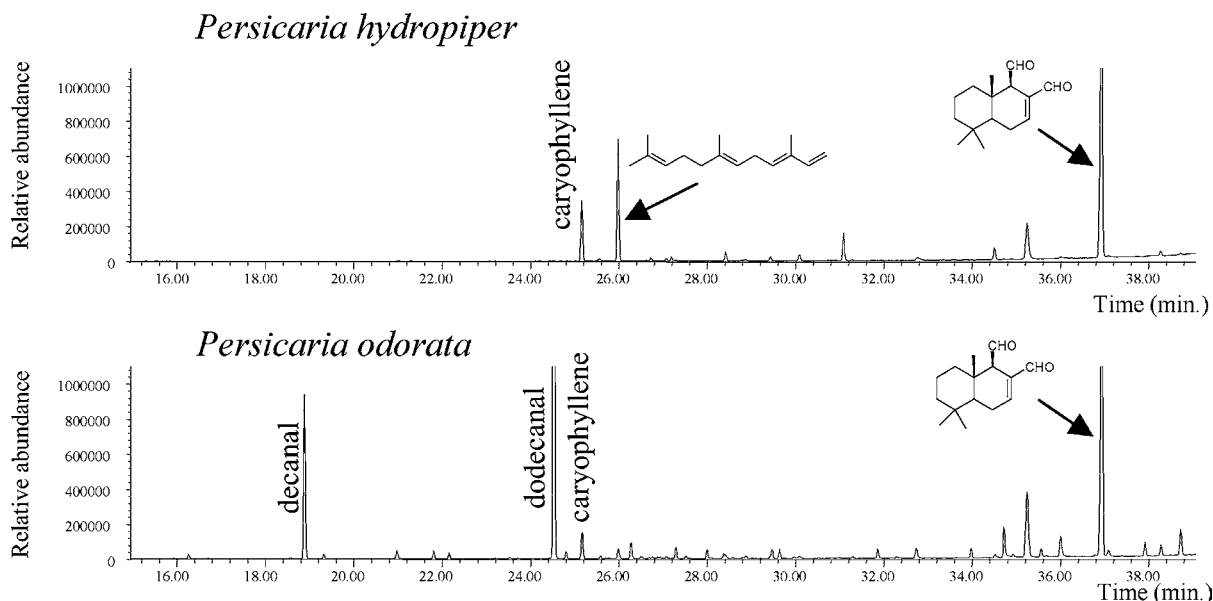


Figure 2. MS spectrum of **2** and **3**, after the Affi-Gel thiol concentration of Laksa plant extract, and MS spectrum of authentic samples.

in agreement with structure **1**. Two strong tropical fruit odors were detected at  $I_{SPBI}$  1010 and at  $I_{SPBI}$  1090 (Figure 1). On the polar column, only one zone smelled like grapefruit, tropical fruit, at  $I_{SPWAX}$  1850.

**Identification of 3-Sulfanylhexanal (2) and 3-Sulfanylhexan-1-ol (3).** To elucidate the structure of these highly potent sulfur compounds, suspected to be responsible for the strong tropical fruit odors, a fresh dichloromethane extract was prepared and fractionated by affinity gel chromatography (18). The thiol fraction was analyzed by GC-MS and GC-AED on polar and apolar columns. It was therefore possible to attribute the first tropical fruit, citrus fruit peel, blackcurrant odor, to 3-sulfanylhexanal (**2**), based on published Kovats indices [ $KI_{FFAP}$  1560

and  $KI_{CP-Si15}$  1004 (14)], confirmed by injection of an authentic sample on GC-AED and GC-MS. The MS fragmentation corresponded to published data for **2** (15) (Figure 2). The second zone corresponded to 3-sulfanylhexanol (**3**),  $I_{SPWAX}$  1850 (1845, authentic sample) and  $I_{SPBI}$  1090 (1090, authentic sample), and the MS fragmentation corresponded to published data (15). Compound **2** was found for the first time in 1976 in yellow passion fruit (15) and later in tomato and beef liver (19). Compound **3** was found in wine and passion fruit; all associated references can be found in an exhaustive review (19). Compounds **2** and **3**, which are highly potent odorants, have now been identified for the first time in an herbaceous plant, *P. odorata* (Lour.) Soják, or Laksa plant.



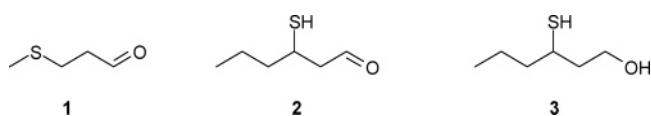
**Figure 3.** Comparative GC-MS profile of Laksa plant and water pepper (dichloromethane extract injected on SPB-1 column).

**Comparative Analysis of Volatiles in Laksa Plant and Water Pepper.** It was not possible to find any documented information concerning the volatile composition of water pepper. A web site discusses the composition of the essential oil (2), which is mainly made up of monoterpenoids and sesquiterpenoids, but it was not possible to link this information to a scientific publication. The water pepper leaves were freshly collected in Switzerland by a botanist. They smelled weakly green and herbal; therefore, the odor was very different as compared to the highly odoriferous Laksa plant. The long leaves looked the same, the dark spot was not visible, and the veins were more pronounced, but the challenge was to have flowers of Laksa plant, because the taxonomic determination key, between both species, is in the flowers. From the cuttings, around 5 months later, nice small pink flowers were observed. The curator certified that the plant was *P. odorata* (Lour.) Soják (synonym Laksa plant). In old botanical classifications, the water pepper or *P. hydropiper* (L.) Spach was classified in *Polygonaceae* family, the genus was *Polygonum*, and the species was *hydropiper* (20). The new nomenclature is not yet validated by the Missouri Botanical Garden's (VAScular Tropicos), but the reclassification work of K. L. Wilson is solid and is the most-cited reference (1).

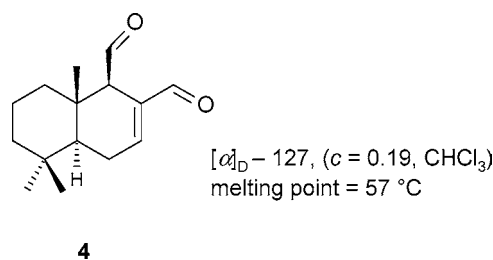
Simple extractions with dichloromethane were performed on both species. The GC-MS traces are represented in **Figure 3**. (*E,E*)-Farnesene,  $\beta$ -caryophyllene,  $\alpha$ -humulene, and polygodial are the main hydrophobic volatile constituents of water pepper and in Laksa plant; aldehydes such as decanal and dodecanal are the major volatiles in these organic extracts (**Figure 3**). As the volatile composition of Laksa plant corresponds to the description published recently for *P. hydropiper* L., the author of this publication (8) was most likely analyzing Laksa plant and not the water pepper, *P. hydropiper* (L.) Spach.

**Pungent Active Compound in Laksa Plant.** To select the best solvent for the extraction, two fresh leaves were crushed and covered with water. This operation was repeated with ethanol and ethyl acetate on separated batches of leaves. A smelling strip was dipped into the solvent, air-dried, and placed on the tongue to find the greatest pungency. This very simple experiment dictated our choice of ethyl acetate as the solvent for extraction. Then, a larger quantity (185 g) of fresh leaves was minced and stirred for 30 min in ethyl acetate. The solvent

**Scheme 1.** Chemical Structure of Sulfur Compounds Detected in Laksa Plant



**Scheme 2.** Structure of Polygodial



was removed under vacuum, and the oleoresin was chromatographed on  $\text{SiO}_2$  with a mixture of pentane and diethyl ether as the mobile phase. The chromatography was started in a gradient mode with 90% pentane and finished with 100% diethyl ether. Thirty-eight fractions of 20 mL were collected and tasted on smelling strips. The pungency was detected in fractions 28–34, which were pooled together, concentrated under vacuum, and rechromatographed on  $\text{SiO}_2$  with pentane/diethyl ether in a 3:2 ratio. A yellow oil of 60 mg was obtained that solidified when stored at 4 °C. It was recrystallized in hexane to finally give 10 mg of white, fine, crystalline needles. The GC-MS showed a  $m/z$  of 234 corresponding to polygodial ( $\text{C}_{15}\text{H}_{22}\text{O}_2$ , **4**) (**Scheme 2**), which is in agreement with our starting hypothesis.  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra, specific rotation ( $[\alpha]_D - 127, c 0.19, \text{CHCl}_3$ ), and the melting point (57 °C) were all in agreement with published data (21, 22). These results confirmed the presence of polygodial in Laksa plant, which, to our knowledge, is published for the first time.

**Quantitation of Polygodial in Laksa Plant and in Water Pepper.** The determination of the amount of polygodial in Laksa plant was performed using fresh leaves from four different lots of Laksa plant collected between April and August. The calibration curve was established with pure crystalline polygodial. The lowest concentration of polygodial  $0.28 \pm 0.03$  mg/mL was measured on the lot received in April. The highest

concentration was  $0.36 \pm 0.03$  mg/mL for the lot of plants received at the end of June. The same analysis was performed on fresh leaves of water pepper. The concentration was  $0.71 \pm 0.03$  mg/mL; this is lower than the published value of  $0.97 \pm 0.17$  mg/mL (23). The published protocol for the analysis of polygodial (23) used a refluxing ethyl acetate and hexane mixture to extract the fresh leaves. However, we have found as a result of differential thermal analysis that pure polygodial (4) has an endothermic reaction starting at  $45^\circ\text{C}$ , corresponding to its melting point, and then an exothermic reaction absorbing 7 kJ/kg starting at  $70^\circ\text{C}$ , followed by a second exothermic reaction starting at  $150^\circ\text{C}$ , indicating that polygodial is not stable when heated. Therefore, we decided not to heat our samples.

The Laksa plant, formerly *P. odoratum* Lour., has a strong coriander leaf odor due to its high content of aliphatic aldehydes. Sulfur compounds such as 1–3 also contribute to the overall odor perception. In contrast, the water pepper, formerly *P. hydropiper* L., has a weak, green odor and the major volatiles are terpenic compounds. Polygodial is responsible for the pungency of Laksa plant with a concentration around  $0.3 \pm 0.1$  mg/mL in the fresh leaves, which is about three times less than water pepper.

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