Pteridaceae Fragrant Resource and Bioactive Potential: A Mini-review of Aroma Compounds
Françoise Fons, Didier Froissard, Sylvie Morel, Jean-Marie Bessiere, Bruno Buatois, Vincent Sol, Alain Fruchier, Sylvie Rapior

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Seven ferns of Pteridaceae, grown in a botanical garden or wild, harvested in France were investigated for their Volatile Organic Compounds (VOC) profile using GC-MS: Adiantum pedatum L., Adiantum peruvianum Klotzsch, Anogramma leptophylla (L.) Link, Cheilanthes maderensis Lowe, Cryptogramma crispa (L.) R. Br., Pteris cretica L. and Pteris vittata L. Fifty-three VOC biosynthesized from lipidic, shikimic, terpenic and carotenoid pathways were identified. The two Adiantum species show different VOC composition. The main linalool (10.8%) in A. pedatum has several biological activities of great interest. This Maidenhair fern contains the highest proportion (57.9%) of isoprenoid flavor precursors, i.e., ionone derivatives with various scent notes. The two major odorant unsaturated hexenoic acids derivatives of A. peruvianum are used as flavouring agents. Anogramma leptophylla concentrates 6-methoxymellein (71.5%), a bitter phytoallexin which contributes to stress or pathogen resistance. Cheilanthes maderensis produces mainly coumarin (89%) and vanillin (5.3%) with a low odor detection threshold, both used in perfumery and cosmetic industry or as flavouring agent and drug additives. Cryptogramma crispa accumulates a broad-spectrum of carotenoid derivatives (52.1%) and three major shikimic derivatives: the spicy 4-vinylguaiacol (flavouring agent), the floral phenylethanal and benzyl alcohol with floral, balsamic scent. Pteris cretica accumulates mostly furan derivatives, i.e., 5-hydroxyethylfurfural (33.2%) and 3-hydroxy-2,3-dihydroxymethyl (18.3%) used as food and beverage additives with caramel or roasty flavour and also found in fortified wines, toasty or heat-treated foods. Pteris vittata produces predominantly shikimic derivatives applied in perfumery and food industries as benzaldehyde (26%, with almond scent), benzyl alcohol (22%, floral fruity balsamic scent), nonanal (19.8% cucumber note) and phenylethanal (11%; floral note). Pteridaceae resources are of great interest as a reservoir of odorous and bioactive compounds.

**Keywords:** Benzaldehyde, Coumarin derivatives, Furan derivatives, Linalool, 6-Methoxymellein, Nonanal, 4-Vinylguaiacol.
With a view to continue our study of Volatile Organic Compounds (VOC) with bioactive potential, fresh aerial parts of seven ferns of Pteridaceae harvested in France were investigated for their VOC profile using GC-MS: Adiantum pedatum L., Adiantum peruvianum Klotzsch, Anogramma leptophylla (L.) Link, Cheilanthes maderensis Lowe, Cryptogramma crispa (L.) R. Br., Pteris cretica L. and Pteris vittata L.

In the concentrated diethyl ether extracts of the seven species, fifty-three components biosynthesized from lipidic, shikimic, terpenic and carotenoid pathways were identified (Table 1). The volatile fraction of the ferns represents about 0.01% of the fresh aerial materials.

Twenty volatile compounds were identified in *Adiantum pedatum*. Lipidic derivatives are mainly represented by 1-octen-3-ol (5%) responsible for the mushroom-like odor and flavor [3b-d] but also found in many plants [3e-g]. This fatty alcohol is valuable to perfume and food industries [3h, 4a,b] and more recently proposed for mosquito control as an insect attractant [4c,d]. Benzyl alcohol (5.6%), the major compound of the shikimic pathway with floral odor also described as phenolic or balsamic [4a] and the main terpenic derivative linalool (10.8%) with floral scent [4c] or woody note (depending on the enantiomer) were also reported in table 1. Linalool is a well-known terpenic alcohol of essential oil from various plant families (*Lauraceae, Rutaceae, Lamiaceae*...); it gives insect repellent property as well as anxiolytic, anti-
inflammatory, antioxidant, antifungal, antibacterial, antiparasitic, antimural activities [4e-i]. This fern contained the highest proportion of isoprenoid flavor precursors (57.9%), i.e., mainly (E,E)-pseudoneione (11%) with odor descriptors as sweet, waxy, citrus, floral balsamic, spicy [4a], 4-hydroxy-5,6-epoxy-ionol (13.4%), 3-hydroxy-5,6-epoxy-β-ionone (6.5%) and 9-methyl-α-ionol (5%).

Adiantum perruvianum showed a VOC profile based on twenty-nine compounds, radically different from the previous Adiantum species: lipidic derivatives (54.6%) were mainly represented by (E)-3-hexenoic acid (23.3%) with honey odor and waxy, fruity or herbal notes [4a], (E)-2-hexenoic acid (19%) with fruity odor and 1-octen-3-ol (7.1%) with mushroom-like scent. The two major odorant hexenoic acids, used as flavouring agents, were previously found in other ferns such as Athyrium filix-femina, Gymnocarpium dryopteris, Polystichum setiferum, Pteridium aquilinum [5a,b] and plant allies (Equisetum palustre) [5c] but not in Adiantum capillus-veneris. In Venus-hair fern, (E)-2-decenal, lauric amide or (E)-2-heptenal were found in high quantities with a plastic or oxidized mutton fat odor [5a], also responsible for the unpleasant scent of “stink bug”. The VOC profiles of the three species of Adiantum are therefore different.

Carotenoid derivatives of A. perruvianum (28.3%) were composed by small amounts of α-ionone, β-ionone and ionone derivatives, i.e., 3-hydroxy-5,6-epoxy-β-ionone. The VOCs from the shikimic pathway (12.1%) were represented by few compounds including benzyl alcohol (4.6%) also described in A. pedatum (Table 1) as well as 2-phenylethanol, vanillin or coumarin previously found in A. pedatum, A. perruvianum and A. trapeziforme [5d]. Three minor terpenic compounds including limalool were also identified in A. perruvianum (3.4%). This second Adiantum species, as well as the previously analysed Venus-hair fern, produced small amounts of terpenic derivatives. The five other ferns analysed in this work and belonging to four other genera of Pteridaceae did not produce any terpenic derivatives.

Ten VOCs were detected from Anogramma leptophylla. The volatile pattern was mainly based on lipidic derivatives (76%), i.e., the major 6-methoxymellemine (71.5%) and the minor 6-hydroxymellemine (1.8%) which are 3,4-dihydroisocoumarins. The former is a polyketide-derived phytoalexin well-known in the carrot and would contribute to pathogen or stress resistance. It is the first compound related to the bitterness of the carrot and its content varies in the commercial products with storage and processing conditions [6a-c]. Dihydroisocoumarins have been isolated from other plants species and also from macrofungi [6d,e]. The others VOC isolated from A. leptophylla were shikimic derivatives (22.1%), i.e., benzaldehyde (7.7%) widespread in plants and mushrooms with bitter almond odor and coumarin (7.8%) with pleasant scent. These VOCs are two aroma agents commonly used in perfume, cosmetic and food industries.

The volatile content of Cheilanthes maderensis was mainly dominated by shikimic derivatives (95.9%) essentially coumarin (89%: hay and dried herb odor), 3,4-dihydrocoumarin (3.4%; baylike, herbal, coconut note) and vanillin (3.5%; vanilla, sweetish smell) usually used in perfume and food industries [3h, 4a,b]. Such high content of coumarin and coexistence of its dihydro derivative as natural products are very rare. Recently, a Japanese group reported the similar data from the bryophyte, Takakia lepidizioides [3i], as those reported in the present paper. At the same time, chemophylogenetic relationship between both phyla (Pteridophytes and Bryophytes) has been fully discussed [3j].

The broad spectrum of volatile components identified in Cryptogramma crispa showed a VOC profile including nineteen identified compounds. Table 1 lists major carotenoid derivatives (52.1%), i.e., 3-hydroxy-5,6-epoxy-ionone, 9-methyl-α-ionol, 8-methyl-α-ionone, 4-hydroxy-7,8-dihydro-β-ionone and 3-oxo-α-ionol. Shikimic derivatives (40.2%) are mainly represented by three VOCs. 4-Ethenyl-2-methoxyphenol also called 2-methoxy-4-vinylphenol or 4-vinylguaiacol (10%) with powerful, clove-like, spicy, smoky odor is also a flavouring agent and a pheromone for insects [4b; 7a,b]. It was previously found in a horsetail, Equisetum telmateia [5c]. Phenylethanal (8.8%) with floral odor (lilac, hyacinth, geranium: [3b, 4b]) was also identified in other ferns and plant allies (Athyrhum filix-femina, Blechium spican, Phegopteris connectilis, Equisetum scirpioides) [5a-c]. The third shikimic derivative was benzyl alcohol (6.1%) with floral or balsamic odor. Only 1-octen-3-ol from lipidic pathway was identified in a significant amount (Table 1).
This paper demonstrates that *Peridiceae* can generate a broad spectrum of VOCs for both odorous and bioactive ingredients. Within the former, lipidic derivatives, terpenic compounds and ionone derivatives with fruity odor, herbal scent or floral notes, are the main fragrant components required for cosmetic and hygiene products industries as well as aroma applications: it should be noted that suprising high amount of furan derivatives with caramel or roasty flavor was detected to be used as food additives. Within the last, coumarin derivatives are of various biological interests for pharmaceutical industry and plant protection products. *Peridiceae* species resources are potential candidates for bioactive aroma ingredients and for the discovery of new drugs with various therapeutic applications due to their potential anti-inflammatory [10c] and antitumor [10d] promoting properties.

**Experimental**

**Plant material:** Fresh aerial parts of ferns were collected in France, as follows: *Pteris cretica, P. vittata and Adiantum peruvianum:* 31/08/2010, Botanical Garden of Strasbourg; *Cryptogramma crispa:* 01/09/2010, Botanical Garden of Nancy; *Adiantum pedatum:* 01/09/2010, Botanical Garden of Col de Saverne; *Anogramma leptophylla:* 14/04/2010, Le Lavandou (Var); *Cheilanthes maderensis:* 13/04/2010, Rayol-Canadel-sur-Mer (Var); Voucher specimens are deposited at the Laboratory of Botany (Faculty of Pharmacy, Limoges, France).

**Plant part and GC-MS analyses:** Fresh aerial parts of ferns were cubed and extracted with diethyl ether (Carlo Erba, 6 ppm BHT). After one week of maceration at room temperature, the concentrated organic extracts were used for Gas Chromatography Mass Spectrometry (GC-MS) analyses as reported in the literature [5a-c]. The main volatile components of *Peridiceae* were identified by comparison with National Institute of Standards and Technology Mass Spectral Library [11a-b]. Internal standards (α-alkanes) were used as reference points in the calculation of relative retention indices. GC-MS analyses were performed at the « Plateforme d’Analyses Chimiques en Ecologie », technical facilities of the LabEx CeMEB (Centre Méditerranéen pour l’Environnement et la Biodiversité).

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**References**


Bioactive aroma compounds of Pteridaceae

Natural Product Communications Vol. 13 (5) 2018 655


Element Content is a Highly Reliable Marker for Niche Vegetable Oils
Faez Mohammed, Dom Guillaume, Nada Abdulwali, Rahma Bchitou, Souad El Hajjaji and Ahmed Bouhaouss 609

Bentonite as a Refining Agent in Waste Cooking Oils Recycling: Flash Point, Density and Color Evaluation
Alberto Mannu, Gina Vlahopoulou, Veronica Sireus, Giacomo Luigi Petretto, Gabriele Mulas and Sebastiano Garroni 613

Chemical Composition of the Essential Oils of Pogostemon auricularius, a Vietnamese Medicinal Plant
Prabodh Satyal, Nguyen Thi Hong Chuong, Van Th Pham, Nguyen Huy Hung, Vu Thi Hien and William N. Setzer 617

Comparative Chemical Profiles of Essential Oil Constituents of Eight Wild Cinnamomum Species from the Western Ghats of India
Ramamoorthy Ananthakrishnan, Ettickal. S. Santhosh Kumar and Koranappullil B. Rameshkumar 621

Constituents of Essential Oils from Dasymaschalon bachmaensis and Phaeanthus vietnamensis
Le T. Huong, Dao T.M. Chau, Ly N. Sam, Tran D. Thang, Do N. Dai and Isiaka A. Ogunwande 627

Antileishmanial Potentialities of Croton lineartis Leaf Essential Oil
Jesús García Díaz, Julio César Escalona Arranz, Denise da Gama Jaén Batista, Lianet Monzote Fidalgo, Jorge de la Vega Acosta, Maira Bidar de Macedo and Paul Cos 629

Circadian Rhythm, and Antimicrobial and Anticholinesterase Activities of Essential Oils from Vitex gardneriana
Evaristo Jose Pires Pereira, Jean Parcelli Costa do Vale, Priscila Teixeira da Silva, Joyce dos Reis Lima, Daniela Ribeiro Alves, Patricia Silva Costa, Tigressa Helena Soares Rodrigues, Jane Eire Silva Alencar de Menezes, Selene Maia de Morais, Paulo Nogueira Bandeira, Raquel O.S. Fontenelle and Hélcio Silva Santos 635

Antiacne-causing Bacteria, Antioxidant, Anti-Tyrosinase, Anti-Elastase and Anti-Collagenase Activities of Blend Essential Oil comprising Rose, Bergamot and Patchouli Oils
Nuntapol Wongsukkasem, Orawan Soynark, Montira Suthakitmanus, Emprang Chongdiloet, Chidchanok Chairattanapituk, Peamjit Vattanakitsiri, Tapanee Hongratanaworakit and Sarin Tadtong 639

Accounts/Reviews

Tubeimoside-1, Triterpenoid Saponin, as a Potential Natural Cancer Killer
Muhammad Zafar, Iqra Sarfraz, Azhar Rasul, Faiza Jabeen, Khizar Samiullah, Ghulam Hussain, Ammara Riaz and Muhammad Ali 643

Pteridaceae Fragrant Resource and Bioactive Potential: a Mini-review of Aroma Compounds
Françoise Fons, Didier Froissard, Sylvie Morel, Jean-Marie Bessière, Bruno Buatois, Vincent Sol, Alain Fruchier and Sylvie Rapior 651
Contents

Gerald Blunden Award (2017)

Molecular Insights of Hyaluronic Acid as Potential Source of Polymer-Drug Conjugate in the Target-Mediated Treatment of Cancer
Gnanendra Shanmugam, Rajesh Salem Varadharajan, Desika Prabakar, Syed Mohammed, Sathiyapriya Renganathan, Murano Erminio and Vincent Aroulmoji

Original Paper

Sesquiterpene Lactones and Phenols from Polyfollicles of Magnolia vovidessi and their Antimicrobial Activity
Thalía Ramírez-Reyes, Juan L. Monribot-Villanueva, Oscar D. Jiménez-Martínez, Angel S. Aguilar-Colorado, Israel Bonilla-Landa, Norma Flores-Estévez, Mauricio Luna-Rodríguez and José A. Guerrero-Anacle

Chemical Composition and Antiinflammatory Potential of Plinia edulis Fruits Peels
Luciane Angela Nottar Netello, Adriana Campos, Karla Capistrano, Fátima de Campos Buzzi and Valdir Cechinel Filho

Two New Antidepressant Steroidal Aglycones from Stephanotis mucronata
Shu-juan Hao, Li-juan Gao, Shi-fang Xu, Yi-ping Ye and Xiao-ya Li

Strychnusinal, A New Alkaloid from Strychnos nux-blanda Fruits
Jirapast Sichaem, Santi Tip-pyang, Kiattisak Lugsanangarm and Lien Do Thi My

Chemical Constituents of the Different Parts of Colchicum micranthum and C. chalcedonicum and their Cytotoxic Activities
Gizem Gulsoy-Toplan, Fatih Goger, Ayca Yildiz-Pekoz, Simon Gibbons, Gunay Sariyar and Affife Mat

Hairy Root Cultures of Eurycoma longifolia and Production of Anti-inflammatory 9-Methoxycanthin-6-one
Trang Thu Tran, Nam Trung Nguyen, Ngoc Bich Pham, Huy Nhat Chu, Trong Dinh Nguyen, Tadamasaki Kishimoto, Minh Van Chau and Ha Hoang Chu

Eliciting Effect of Catharanthine on the Biosynthesis of Vallestatichromone and Isovallesiachromone in Catharanthus roseus Cambial Meristematic Cells
Jianhua Zhu, Shuijie He, Pengfei Zhou, Jiachen Zi, Jincai Liang, Liyan Song and Rongmin Yu

Anti-inflammatory Effect of Protal in LPS-stimulated RAW 264.7 Cells via NF-κB Signaling Pathways
You Chul Chung, Sung-Min Park, Jin Hwa Kim, Geun Soo Lee, Jung No Lee and Chang-Gu Hyun

Flavonoid Aglycones and Glycosides from the Leaves of some Japanese Artemisia Species
Ayumi Uehara, Kazuhide Shimoda, Yoshinori Murai and Tsukasa Isahita

LC-MS Identification of Proanthocyanidins in Bark and Fruit of six Terminalia species
Awantika Singh, Sunil Kumar and Brijesh Kumar

Protective Effects of Compounds in Bombax ceiba flower on Benzo[a]pyrene-Induced Cytotoxicity
Souichi Nakashima, Yoshimi Oda, Yuki Ogawa, Souichi Nakamura, Miyako Uno, Mariko Kishimoto, Masayuki Yoshikawa and Hisashi Matsuda

Antioxidant and Cosmeceutical Activities of Agarum cribrosum Phlorotannin Extracted by Ultrasound Treatment
Kasira Phasanasophon and Sang Moo Kim

Osmanthus fragrans Flower Aqueous Extract and its Enriched Acesolide inhibit Melanogenesis and Ultraviolet-induced Pigmentation
Qianan Tao, Chihong Ding, Bibi Nazia Aucklow and Bin Wu

Synthesis of Novel 2-Thioxothiazolidin-4-one and Thiazolidine-2,4-dione Derivatives as Potential Anticancer Agents
Alleni Suman Kumar, Vavilapalli Satyanarayana, Ahmad Alkhazim Alghamdi and Jhillu Singh Yadav

A Short Step Conversion of Alkynyl Propargyl Sulfoxones into Six-Membered Cyclic β-Ketosulfoxones via an Amine-Induced Novel Ring Closure
Md. Ashrafal Alam, Kazuaki Shimada, Hironobu Kamoto, Kasumi Shingo, Toshinobu Korenaga and Chizuko Kabuto

Synthesis of Sex Pheromones of the Citrus Leafminer (CLM) (Phyllocnistis citrella)
Alleni Suman Kumar, Vavilapalli Satyanarayana, Ahmad Alkhazim Alghamdi and Jhillu Singh Yadav

OSMANTHUS FRAGRANS FLOWER AQUEOUS EXTRACT AND ITS ENRICHED ACESOLIDE INHIBIT MELANOCYTES AND ULTRAVIOLET-INDUCED PIGMENTATION
Shuo Liu, Zhen Zhao, Zhijun Huo, Zhiru Xu, Yan Zhong, Xiaoling Wang, Yiting Yang and Zhiyong Wang

Synthesis of new A-conjugated Quinolone and Spiroindole Dammaranes by the Ozonolysis of 2,3-Indolodipterocarpol
Irina E. Smirnova, Elmir M. Khusnutdinova, Alexander N. Lobov and Oxana B. Kazakova

A New Cytotoxic Tetrahydroxanthene-1,3(2H)-dione Derivative from Uvaria cordata and Structure Revision of Valderramenol A
Duc Viet Ho, Hung Quoc Vo, Tho Huu Nguyen, Thao Thi Do and Hoai Thi Nguyen

Synthesis of Novel 2-Thioxothiazolidin-4-one and Thiazolidine-2,4-dione Derivatives as Potential Anticancer Agents
Alleni Suman Kumar, Rathod Aravind Kumar, Elala Pravardhan Reddy, Vavilapalli Satyanarayana, Jujula Kashanna, Boggu Jagan Mohan Reddy, Basireddy Venkata Subba Reddy and Jhillu Singh Yadav

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Alleni Suman Kumar, Vavilapalli Satyanarayana, Ahmad Alkhazim Alghamdi and Jhillu Singh Yadav

Composition, Anti-inflammatory Activity, and Bioaccessibility of Green Seaweeds from Fish Pond Aquaculture
Andrea Ripol, Carlos Cardoso, Cláudia Afonso, João Varela, Hugo Quental-Ferreira, Pedro Peirão-Ferreira and Narcisa M. Bandarra

Continued inside backcover