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 madereensis* 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 phytolaelixin which contributes to stress or pathogen resistance. *Cheilanthes madereensis* produces mainly coumarin (89%) and vanillin (3.5%) 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-vinylguaiaicol (flavouring agent), the floral phenylethanal and benzyl alcohol with floral, balsamic scent. *Pteris cretica* accumulates mostly furan derivatives, i.e., 5-hydroxy methylfurfural (33.2%) and 3-hydroxy-2,3-dihydromaltol (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-Vinylguaiaicol.

**Pteridaceae** E. D. M. Kirchner is a heterogeneous family of ferns including approximately nine hundred species worldwide distributed. Only twelve species belonging to seven genera (*Adiantum*, *Cheilanthes*, *Cryptogramma*, *E. D. M. Kirchner* is a heterogeneous family of ferns including approximately nine hundred species worldwide distributed. Only twelve species belonging to seven genera (*Adiantum*, *Cheilanthes*, *Cryptogramma*, *Paragymnopteris*, *Pteris*, *Tod.* and *Triphotonium*) are reported in France. *Pteridaceae* includes several species well-known in traditional medicines and non-pharmacological interventions, i.e., Native American people medicine (Navajo Indian Tribe), Ayurvedic medicine, homeopathy linked with various diseases or disorders as follows. Leaves of *Adiantum pedatum* L. are employed for pectoral affections, *Adiantum piletii* Wickstr. against fever and diabetes, *Notholaena eckloniana* Kunze (L.) as ointment on the scalp and *Pteris wallachiana* J. Agardh applied to stop bleeding. Fronds of *Pellaea colomelanos* (Sw.) Link are used against asthma; those of *Pteris multifida* Poir. and *Pteris cretica* L. are applied against dysentery and wounds, respectively [1c-f]. Leaves of *Adiantum capillus-veneris* L. (also known as Venus-hair fern) are used against throat affections and, as purgative and demulcent. This fern is also the main ingredient of the renowned "Sirop de Capillaire" supposed to cure a large number of diseases [1f]. On the other hand, Venus-hair fern produces a pleasant tonic flavor and syrups which are used as a flavor modifier [1f]. Rhizomes of *Cheilanthes ternifolia* (Burn. f.) Sw., are administered as general tonic while those of *Pteris ensiformis* Burn. f. and *Pteris quaduaucita* Retz. are applied on swollen glands in the neck or healing of boils, respectively. It should be mentioned *Adiantum lunatum* Burn. to be used against fever due to elephantiasis. Finally root of *Cheilanthes farinosa* (Forsk.) Kaulf. treats eczema and stomachache [1c-f].

During the last decades several studies have been carried out regarding the biological properties of *Pteridaceae*: an antioxidant activity was detected in *Adiantum trapeziformis* L. and *C. ternifolia* [2a,b] and antimicrobial compounds were characterized in *Pteris vittata* L. and *Pteris biuaria* L. [2c,d]. Biological activities involved in metabolic syndrome and anti-tumor activity were investigated for *P. vittata* [2e,f]. The impact of heavy metals on antioxidant polyphenols of this hyperaccumulator fern was also analysed [2g]. In addition, an anti-tumor activity was detected in *Pteris seminapina* L. and *Pteris multifida* [2h,i] while an aqueous extract of *Pteris ensiformis* demonstrates an immunomodulatory activity [2j].

Very few *Pteridaceae* are known having an odor [3a]: only *Adiantum pantadactylon* Langsd. & Fisch. and *Pteris tremula* R. Br. are reported to smell tom cat urine. *Pteris multifida* has an acrid and biting flavor whereas *Adiantum pedatum* has a slightly aromatic odor.

**Keywords:** Benzaldehyde, Coumarin derivatives, Furan derivatives, Linalool, 6-Methoxymellein, Nonanal, 4-Vinylguaiaicol.
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 compounds were 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%), 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 [4e] or odor also described as woody note (depending on the enantiomer) were also reported in table 1. Linalool is a well-known terpenic alcohol of essential oil which gives insect repellent property as well as anxiolytic, anti-inflammatory and anti-allergic activity [4a, e].

### Table 1: Percentage of volatile organic compounds

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<thead>
<tr>
<th>Compounds</th>
<th>RI</th>
<th>Adiantum pedatum</th>
<th>Adiantum peruvianum</th>
<th>Anogramma leptophylla</th>
<th>Cheilanthes maderensis</th>
<th>Cryptogramma crispa</th>
<th>Pteris cretica</th>
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* Relative percentage of the VOC based on the GC-MS chromatographic area; RI = Retention Indices on SLB5MS column (Supelco); NP = Non Identified.
inflammatory, antioxidant, antifungal, antibacterial, antiparasitic, antitumoral activities [4e-i]. This fern contained the highest proportion of isoprenoid flavor precursors (57.9%), i.e., mainly (E,E)-pseudionone (11%) with odor descriptors as sweet, waxy, citrus, floral balsamic, spicy [4a,j], 4-hydroxy-5,6-epoxy-ionol (13.4%), 3-hydroxy-5,6-epoxy-β-ionone (6.5%) and 9-methyl-α-ionol (5%).

Adiantum pervianum showed a VOC profile based on twenty-nine compounds, radially 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. pervianum (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. pervianum and A. trapeziforme [5d]. Three minor terpenic compounds including limonol were also identified in A. pervianum (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-methoxymellein (71.5%) and the minor 6-hydroxymellein (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%; haylike, 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 lepidozioides [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]. It was previously found in a horsetail, Equisetum telmateia [5c]. Phenylethanol (8.8%) with floral odor ( lilac, hyacinth, geranium; [3b, 4b]) was also identified in other ferns and plant allies (Athyrium filix-femina, Blechum spicant, 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).

Table 1 lists a broad spectrum of VOCs for Pteris cretica based on twenty-seven identified components mainly lipidic derivatives (49.9%), shikimic derivatives (26.1%) and carotenoid derivatives (22.8%) in low amounts. Only two VOCs were abundant as 5-hydroxymethylfurfural (33.2%) and 3,5-dihydroxy-6-methyl-2,3-dihydro-4H-pyran-4-one (18.3%). The major 5-hydroxymethylfurfural is described with odor of chamomile flowers (or butter, caramel, musty) while the four others furan derivatives (10%) have various descriptors [8a-d] as furfural (almond, woody, sweet, toasty), furfuryl alcohol (faint burning odor), furanole (sweet, caramel, pineapple, strawberry) and 5-methylfurfural (caramel, almond, spicy, sweet, roasty). These compounds usually found in fortified wines, in roasted, toasted or heat-treated foods and drinks, are produced, in particular, by sugar alteration (Maillard reaction). Suspected but not proved to be carcinogenic, they contribute to caramel aroma and colour in food additives [8e-h]. 3,5-Dihydroxy-6-methyl-2,3-dihydro-4H-pyran-4-one (or 3-hydroxy-2,3-dihydromaltol 18.3%, Table 1), the second major VOC exhalates an odor with toasty character and fruity-caramel overtones [7a].

Pteris cretica was the single species of the seven analysed ferns with a high level of furanole and furfural derivatives (43.2%, Table 1) whereas the others (in particular P. viitata) contain none at all. Furan derivatives were not found in A. capillus-veneris, another species from Pteridaceae previously studied [5a]. However, ferns species from other families may also produce furan derivatives in small amounts, i.e., Pteridium aquilinum, Asplenium trichomanes, and the twelve species of the Asplenioideae family [5b,9a]. Other authors found furan derivatives in coalified Trigonocarpus grandis [9b] or in aerial parts and rhizomes of current species of ferns: Angiopteris esculenta, Cibotium barometz, Coniogramme japonica, P. aquilinum, and five species of Polypodiaceae [9e-g].

Pteris viitata revealed a VOC fraction very different from that of P. cretica with a low diversity (ten volatile compounds), barely any carotenoid derivatives and a majority of shikimic derivatives (69.4%) with the three major odorant benzaldehyde (26%; bitter almond scent), benzyl alcohol (22%; floral notes) and phenylethanol (11%; sweet odor of hyacinth-type). These three VOCs were also detected in five others ferns of the same family analysed in this work but in lower amounts. Lipidic derivatives were represented by nonanal (19.8%; floral-waxy note, [7a]) and 1-octen-3-ol (9.5%; fungal aroma, [3b-d]) recently reported as antifungal agent [10a] and attractant for Anopheles and Aedes mosquitoes, repellent to Culex quinquefasciatus [10b], respectively.
This paper demonstrates that Peridaceae 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-protective products. Peridaceae 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); *Chelanihes 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 *Peridaceae* 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).

**Acknowledgments** – The authors greatly thank the Botanical Garden of Col de Saverne for providing *Adiantum pedatum*, the Botanical Garden of Strasbourg for providing *Adiantum peruvianum*, *Pteris cretica and Pteris vittata*, and the Botanical Garden of Nancy for providing *Cryptogramma crispa*.

**References**


Element Content is a Highly Reliable Marker for Niche Vegetable Oils
Faez Mohammed, Dom Guillaume, Nada Abdulwali, Rahma Bchetou, 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 Chaong, Van The 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. SanthoshKumar 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 linearts Leaf Essential Oil
Jesús García Díaz, Julio César Escalona Arranz, Denise da Gama Jaen 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 Helcio 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
Francoise Fons, Didier Froissard, Sylvie Morel, Jean-Marie Bessiere, Bruno Buatois, Vincent Sol, Alain Frucher and Sylvie Rapior 651
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  

513

**Original Paper**

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

521

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

527

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

531

**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  

535

**Hairy Root Cultures of Eucalyptus 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, Tadamitsu Kishimoto, Minh Van Chau and Hoa Hong Chu  

539

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

543

**Chemical Constituents of 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  

547

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

551

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

555

**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  

561

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

565

**Bioactive Metabolites from a Hydrothermal Vent Fungus Aspergillus sp. YQ-13**  
Qianan Tao, Chihong Ding, Bibi Nazia Auckkoo and Bin Wu  

571

**Osmanthus fragrans Flower Aqueous Extract and its Enriched Acetoside inhibit Melanogenesis and Ultraviolet-induced Pigmentation**  
Shuo Liu, Zhen Zhao, Zhijun Huo, Zhiru Ye, Yan Zhong, Xiaoling Wang, Yiting Yang and Zhiyong Wang  

575

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

581

**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  

585

**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, Jyothi Kashanna, Boggu Jagan Mohan Reddy, Basireddy Venkata Subba Reddy and Jhillu Singh Yadav  

589

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

593

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

599

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

603

Continued inside backcover