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Dr. Pawan K. Agrawal
On the Occasion of his 60th Birthday

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Asplenioidae Species as a Reservoir of Volatile Organic Compounds with Potential Therapeutic Properties

Didier Froissard*a, Sylvie Rapiorb, Jean-Marie Bessièrec, Bruno Buatoisc, Alain Fruchierd, Vincent Solae and Françoise Fonsb*

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Twelve French Asplenium ferns (genera Asplenium and subgenus Ceterach and Phyllitis) were investigated for the first time for volatile organic compounds (VOC) using GC-MS. Sixty-two VOC biosynthesized from the lipidic, shikimic, terpenic and carotenoid pathways were identified. Several VOC profiles can be highlighted from Asplenium jahandiezii and A. ×alternifolium with exclusively lipidic derivatives to A. onopteris with an equal ratio of lipidic/shikimic compounds. Very few terpenes as caryophyllene derivatives were identified, but only in A. obovatum subsp. bilotii. The main odorous lipidic derivatives were (E)-2-decyl alcohol (waxy and fatty odor), nonanal (aldehydic and waxy odor with a fresh green nuance), (E)-2-heptenal (green odor with a fatty note) and 1-octen-3-ol (mushroom-like odor), reported for all species. A few VOC are identified in several species in high content, i.e., 9-oxononanoic acid used as a precursor for biopolymers (19% in A. jahandiezii), 4-hydroxyacetophenone with a sweet and heavy floral odor (17.1% in A. onopteris), and 4-hydroxybenzoic acid used as a precursor in the synthesis of parabens (11.3% in A. foreiense). Most of the identified compounds have pharmacological activities, i.e., octanoic acid as antimicrobial, in particular against Salmonellas, with fatty and waxy odor (41.1% in A. petrarchae), tetradecanoic acid with trypanocidal activity (13.3% in A. obovatum subsp. bilotii), 4-hydroxybenzoic acid (8.7% in A. onopteris) with antimicrobial and anti-aging effects, 3,4-dihydroxybenzaldehyde as an inhibitor of growth of human cancer cells (6.7%) in Ceterach officinarum, and phenylacetic acid with antifungal and antibacterial activities (5.8% in A. onopteris). Propionylfilicinic acid was identified in the twelve species. The broad spectrum of odorous and bioactive VOC identified from the Asplenium, Ceterach and Phyllitis species are indeed of great interest to the cosmetic and food industries.

Keywords: Asplenium, Ceterach, Phyllitis, Volatile Organic Compounds, 9-Oxononanoic acid, 3,4-Dihydroxybenzaldehyde, Antimicrobial, Anti-aging.

Asplenioidae Link is a great and homogeneous subfamily of Aspleniacae Newman. Asplenium L. is the major genus with approximately seven hundred subcosmopolitan ferns distributed worldwide, and seventeen species in France. Several subgenera have been separated, such as Ceterach (Willd) Vida ex Bir, Fraser-Jenkins & Lovis and Phyllitis (Hill) Jermy & Viane [1a-1e].

The scientific name Asplenium was given by Pedanius Dioscorides (Roman physician, pharmacologist and botanist of Greek origin) to these plants that are well-known for their medicinal properties to cure the spleen; their common name “spleenwort” derives from the doctrine of signatures. Aspleniacae includes many species reported for various traditional medicinal uses. Leaves and/or rhizomes of Asplenium adiantum-nigrum, L., Ceterach officinarum Willd. (= A. ceterach L.), A. cuneatum Lam., A. falcatum Lam., A. marinum L., A. monanthes L., A. nidus L., A. ruta-muraria L., Phyllitis scolopendrium (L.) Newman (= A. scolopendrium L.) and A. trichomanes L. are used against worms, lung affictions, cough inflammation, hypertension, jaundice, enlarged spleen, intestinal disorder, kidney stones, burns, elephantiasis and ulcers, and as an emetic, deparutive, diaphoretic and sedative in traditional medicine [2a-2g]. Recently, antioxidant, antimicrobial and antibacterial properties of A. ceterach and A. nidus were demonstrated [2h-2i].

Regarding the chemical composition of Aspleniaceae, A. adiantum nigrum, A. fontanum, A. foreiense, A. incisum, A. normale, A. obovatum, A. ruta-muraria, A. trichomanes and Ceterach officinarum were investigated for their phenolic derivatives [3a-3e].

Very few Asplenium are known to have an odor: A. auritum Sw. has pleasantly fragrant fronds and A. lamprophylum Carse smells of wintergreen [4a]. Consequently, little is known about the volatile organic compounds (VOC) of these ferns. The terpenoid constituents of A. scolopendrium were studied [4b]. In addition, A. trichomanes subsp. trichomanes was investigated for its volatile profile [4c], which showed mainly polyketides, for example octanoic acid (= caprylic acid; fatty and waxy odor), nonanoic acid (waxy, dairy note), (E)-2-decenol (waxy note), (E)-2-heptenal (green odor with a fatty note) with globally an oily or waxy odor.

In this new work, fresh aerial parts of twelve French species of Aspleniaceae were investigated for their volatile profiles using GC-MS, as reported in the literature for the twenty-three monilophytes previously studied [4c-4f]. Sixty-two components biosynthesized from the shikimic, lipidic, terpenic and carotenoid pathways were identified from the concentrated diethyl ether extracts of the twelve Aspleniaceae (Table 1).

The VOC profile of Ceterach officinarum is widely dominated by lipidic derivatives (77.4%), in particular (E)-2-decyl alcohol (10.5%), a natural plant and mushroom VOC with waxy and fatty odor type...
Table 1: Percentage of volatile organic compounds in fresh aerial part of Asplenium, Ceterach and Phyllitis species.

<table>
<thead>
<tr>
<th>Compounds</th>
<th>RF</th>
<th>Ceterach officinarum scopulinum</th>
<th>Asplenium aeruginosum</th>
<th>A. jahadorii</th>
<th>A. lobatum</th>
<th>A. septentrionale foreczense</th>
<th>A. balteatum</th>
<th>A. ruta-muraria</th>
<th>A. fontanum *alterfolium</th>
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<td>Lipidic derivatives</td>
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</table>

*Relative percentage of the VOC based on the GC–MS chromatographic area; **RI = Retention Indices on SLB**–**MS column (Supelco); ***N.I = Not identified.*
Volatile organic compounds from twelve French Asplenioideae ferns

[5a-5c], nonanal (10%), with an aldehydic and waxy odor type and a fresh green nuance [5d] and recently reported to attract Culex mosquitoes [5e], (E)-2-heptenal (8.6%), with a green vegetable-odor with fatty undertone, 1-octen-3-ol (5.7%), previously reported for mushrooms [5f, 5g], ferns [4c, 4d, 4f], horsetails [4e] and Angiosperms [5h], (E)-2-tridecanolic acid (5.6%) and hexahydrofarnesyl acetone (4.8%), which are used as flavor and fragrance agents. C. officinarum also contains several aromatic compounds (24.9%), i.e., 3,4-dihydroxybenzaldehyde (= protocatechic aldehyde; 6.7%), a precursor of vanillin using biologically recently reported to inhibit the growth of human cancer cells [5i], and 4-hydroxybenzoic acid (5.8%).

Phyllitis scolopendrium demonstrated a broad spectrum of VOC from the lipidic pathway (79.3%) including nonanal (9.3%), 1-octen-3-ol (8.8%), a C₆-derivative responsible for the mushroom-like aroma [6a], nonanoic acid (7.3%), a C₆-derivative with waxy dairy note, (E)-2-decanal (6.5%), 9-oxononanoic acid (6.2%), (E)-2-heptenal (3.9%), (E,Z)-dodecadienal (2.9%), tetradecanoic acid (myristic acid; 2.8%), octanoic acid (2.2%) and octanol (2.1%). It should be noted that propionylflicic acid (5.4%), a filicinic derivative of biological interest to the pharmaceutical, cosmetic and hygiene industries [4f], was identified in P. scolopendrum, as well as in the other ferns (Table 1). Benzoic acid, 4-hydroxybenzonic acid, methyl 3-methoxy-4-hydroxybenzoate (= methyl vanillate), with a warm spicy vanilla odor, and benzaldehyde, with a bitter almond odor [6b-6e], complete the aromatic profile (14.1%). Dihydroactinidiolide (3.8%), with a fruity odor [5d], and α-ionone (2.1%), with a floral smell, represent the major VOC of the carotenoid profile.

The VOC fraction of Asplenium onopteris is based on equal contents of shikimic and lipidic derivatives (48% and 46.9%, respectively). Twenty-one lipidic derivatives were identified, i.e., (E)-2-decanal (6.2%), (E)-2-heptenal (5.8%), 1-octen-3-ol (5.8%), (E,E)-2,4-dodecanal (3.1%) with aldehyde, oily and fatty odor, and which is a potent plant nematicidal agent [7e]. The major aromatic compounds are 4-hydroxyacetophenone (17.1%), an aromatic ketone with a sweet, and heavy floral odor used for the synthesis of pharmaceuticals, agrochemicals, flavor and fragrances, and 4-hydroxybenzoic acid (8.7%), used in cosmetic and ophthalmologic industries as a precursor in the synthesis of parabens, and which also shows antimicrobial activity and an anti-aging effect [7a, 7b], as well as a hypoglycemic property in rats [7c]. Phenylactic acid (5.8%), used in the flavor industry for its honey-like odor, is a powerful antifungal and antibacterial agent, which is also produced by ants [7d]. Benzoic acid (2.1%), methyl 3-methoxy-4-hydroxybenzoate (2.1%), 2,3-dihydrobenzofuran (2%), and 3-phenylpropionic acid (= dihydrocinnamic acid) with a sweet, floral scent (1.8%), complete the shikimic derivatives. 7,8-Epoxy-β-ionone (1.4%) and 3-oxo-α-ionone (1.2%), with spicy odor, represent the main carotenoid derivatives (4.3%).

Asplenium petrarchae is a small and thermophile fern growing only on the sunny calcareous rocks of the Mediterranean coast. Its VOC profile is dominated by twenty-seven identified lipidic compounds (71.3%), with a very high level of octanoic acid (41.1%) with a fatty, soapy odor. This fatty acid is an antimicrobial ingredient used in particular against Salmonella species in cosmetics and foods; it presents the advantage of being less toxic than most other antimicrobial agents and does not affect beneficial organisms [8a-8c]. (E)-2-Decanal, (E)-2-heptenal, nonanal, 9-oxononanoic acid and 1-octen-3-ol were also identified as lipidic derivatives from A. petrarchae. The volatile fraction contains 13.5% of aromatic compounds, i.e., benzoic acid (4.6%), used as a food additive for its preservative property, as well as 9% of carotenoid derivatives, i.e., 4-hydroxy-β-ionone (4.6%) and 4-hydroxy-5,6-epoxyionol (2.3%).

Asplenium jahandiezii is a small and protected fern only located in the canyon of Verdon (France) [1a]. Its VOC spectrum is almost exclusively dominated by twenty-nine identified lipidic compounds (98%). The major volatile is 9-oxononanoic acid (19%), an interesting VOC as a renewable resource of a precursor for biopolymers [9a]. It was recently discovered that 9-oxononanoic acid stimulates the activity of phospholipase A₂, the key enzyme of the arachidonate cascade [9b]. The other lipidic derivatives with various odorous or pharmacological properties were (E)-2-decanal (13.1%), (E)-2-heptenal (10.5%), nonanal (7.2%), octanoic acid (5.4%), 1-octen-3-ol (3.7%) and tetradecanoic acid (3%). The minor odorous and bioactive lipidic derivatives were 2,3-octanedione (2.9%), with a dill cooked broccoli buttery odor [9c], and octanol (2.4%), with a sweetish odor and toxic to Colletotrichum gloeosporioides, an endophytic plant pathogen [9d], as well as (E,Z)-2,4-decadienal (2.3%), with a fatty, green and waxy odor, (E,E)-2,4-decadienal (2.2%), octanol (2.2%), with an aldehyde, fatty, orange peel, pungent and soapy flavor, (E)-2-decenol (2.1%), with a waxy, citrus and fresh note, and hexanoic acid (2%).

Asplenium obovatum subsp. bilottii has a broad spectrum of VOC with a high content of lipidic derivatives (59.4%) including 13.3% of tetradecanoic acid. This saturated fatty acid is one of the lipidic constituents of the cellular membrane of Eucaryotes. It is used as a lubricant and in the manufacture of flavors, pharmaceuticals, soaps and cosmetics, and has a trypanocidal activity, which was highlighted against Trypanosoma evansi two decades ago [10a]. This acid was identified in eleven of the studied ferns (Table 1). Nonanal (7.2%), (E)-2-decanal (6.1%), 1-octen-3-ol (4.5%), (E)-2-heptenal (3.9%), nonanoic acid (2.7%), hexahydrofarnesylacetone (2.7%), 9-oxononanoic acid (2.2%), and octanoic acid (1.8%) were also identified from the organic extract. Aromatic compounds represent 25.5% of the VOC content of A. obovatum subsp. bilottii with 4-hydroxybenzonic acid (7.8%), 3-methoxy-4-hydroxybenzoic acid (4.4%), 2-amino-4-methoxyphenol (2.7%) as well as 3,4-dihydroxystyrrene (1.8%), an inhibitor of phenylalanine hydroxylase used for the production of experimental phenylketonuria [10b]. Finally, the carotenoids (13.1%) are dominated by 4-hydroxy-β-ionone (1.9%), 4-hydroxy-5,6-epoxyionol (1.7%) and 4-hydroxy-7,8-dihydro-β-ionone (1.6%), which is well-known as a key odorant in yellow wines [10c]. Two sesquiterpenes, i.e., caryophyllene alcohol and caryophyllene oxide, complete the VOC composition of A. obovatum subsp. bilottii. This oxygenated terpenoid, which is a flavoring agent used in cosmetics and food, also displays biological activities (anti-inflammatory, antifungal, skin enhancing and anticarcinogenic) [10d].

The six others Asplenium species also investigated for their VOC content for the first time were A. septentrionale, A. foreziense, A. balearicum, A. ruta-muraria, A. fontanum and Asplenium xalternifolium.

Most of their volatile constituents were mentioned above for the six first detailed VOC fern profiles. The main VOCs identified for A. septentrionale were two aldehydes, i.e., (E)-2-decanal (10.9%) and nonanal (5%). In addition A. septentrionale contained the highest concentration of hexahydrofarnesylacetone (5.6%), hexanoic acid (3.7%), a fatty acid found in animal oils with a fatty, waxy or cheesy flavor, N-acetylpyrrolidone (3.1%) and 3-hydroxy-5,6-epoxy-β-ionone (3.1%). A. foreziense also produced a high level of aldehydes (nonanal, (E)-2-decanal...) and the highest proportions of 4-hydroxybenzonic acid (11.3%), (E,Z)-2,4-decadienal (5.3%), with a
fatty, green and waxy odor, and 7,8-epoxy-β-ionone (3.8%) when compared with the other Asplenioidae (Table 1).

The highest percentages of (E)-2-decanal (20.2%), with a waxy fatty odor, and (E)-2-heptanal (13%), with a green fatty note, were found in Asplenium ruta-muraria, which also produced a high level of nonanal (13.5%), with an aldehydic and green scent. The volatile fraction of A. ruta-muraria contained 13.5% of shikimic compounds, i.e., phenylacetic acid (5.6%), as well as 11.4% of carotenoid derivatives, i.e., 4-hydroxy-5,6-epoxyionol (7.8%). Its major lipid derivatives (74.5%) were nonanal (14%), (E)-2-decanal (13.1%), nonanoic acid (7.8%) and (E)-2-heptanal (5.6%), already found in the other Asplenium species. The global VOC profile of this species (lipidic derivatives / shikimic derivatives ratio) can be compared with those of P. scolopendrum and P. petrarchae.

The major VOC of A. fontanum were three aldehydes, i.e., (E)-2-decanal, nonanal and (E)-2-heptanal, as well as tetradecanoic acid, already found in most of the Asplenium species. The Asplenium \*alternifolium VOC profile was close to that of A. jahandiezii, with uniquely lipidic derivatives (99.3%) and no shikimic compounds. The major lipid compounds of A. \*alternifolium were (E)-2-decanal (12.8%), (E)-2-heptanal (8.8%), 9-oxononanoic acid (7%), (E)-2-tridecanonic acid (6.4%) and 1-octen-3-ol (6.1%), also produced by C. officinarum and A. septentrionale. Compared with the eleven other species investigated (Table 1), A. \*alternifolium contained the highest amount of 2-pentylfuran (4.3%), 3-octen-2-one (4.2%); earthy spicy herbal with mushroom nuances), octanol (4.1%), (E,E)-2,4-decadienal (4.1%), heptanal (3.3%), and 2,3-octanedione (3.2%).

Conclusion: The twelve French ferns from the family Aspleniaceae investigated for VOC mainly contain derivatives of lipid origin. Several VOC profiles can be highlighted from A. \*alternifolium, with exclusively lipidic derivatives, to A. onopteris, with an equal ratio of lipid / shikimic compounds. Minor volatile components were identified from the shikimic pathway and very few terpenes, as caryophyllene derivatives, were found. Aldehydes, i.e., (E)-2-heptanal, nonanal and (E)-2-decanal, were often identified from the species, as well as acids (octanoic, nonanoic, 9-oxononanoic and tetradecanoic acids). 1-Octen-3-ol was found in all samples, as in most of the previously reported ferns [4c-4f]. It should be mentioned that propionylflicinic acid (from 0.3% to 5.4% of the volatile fraction) was identified in the twelve studied Aspleniaceae. This chemical trait must be noticed because many other ferns previously studied do not produce these volatile phloroglucinol derivatives; flicinic acids were mainly found in large amounts in Dryopteris [4f]. The broad spectrum of odorous and bioactive VOC identified from the twelve Asplenium, Ceterach and Phyllitis species from France are indeed of great interest for their various odorous and pharmacological properties that could be of interest to the cosmetics and food industries. Further investigations should be carried out through plant tissue cultures.

Experimental

Plant material: Fresh aerial parts of the ferns were collected as follows: C. officinarum: 13/07/2010, Limoges; P. scolopendrum: 13/07/2010, Limoges; A. onopteris: 05/04/2010, Le Pradet (Var); A. petrarchae: 15/04/2013, Toulon; A. jahandiezii: 26/07/2013, Aiguine (Var); A. obovatum subsp. bulotii: 14/04/2010, Le Lavandou (Var); A. septentrionale: 30/05/2011: Saint-Étienne-Vallée Française (Lozère); A. foreziense: 20/09/2009, Meymac (Corrèze); A. balearicum: 16/07/2013, Porquerolles Island (Var); A. ruta-muraria: 13/07/2010, Limoges; A. fontanum: 20/07/2010 Plan d’Aups Sainte Baume (Var); Asplenium \*alternifolium: 30/05/2011: Saint-Étienne-Vallée Française (Lozère). Authorization of harvest of the protected Aspleniae: 80-2013/06. Voucher specimens are deposited at the Laboratory of Botany (Faculty of Pharmacy, Limoges, France).

Plant part and GC-MS analyses: Fresh aerial parts of Asplenium, Ceterach and Phyllitis species were cubed and extracted with diethyl ether (Carlo Erba, 6 ppm BHT). After 1 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 [4c-4f]. The main volatile components were identified by comparison with the National Institute of Standards and Technology Mass Spectral Library [10a-10b]. Internal standards (n-alkanes) were used as reference points in the calculation of relative retention indices. The analyses were performed at the Platform for Chemical Analyses in Ecology of the “SFR 119 Montpellier Environnement Biodiversité”.

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References


Volatile organic compounds from twelve French Asplenioideae ferns

Natural Product Communications Vol. 10 (6) 2015 1083


A New Aromatic Compound from the Stem Bark of *Terminalia catappa*
David Pertuit, Anne-Claire Mitaine-Offer, Tomofumi Miyamoto, Chiaki Tanaka, Stéphanie Delemasure, Patrick Dutartre and Marie-Aleth Lacaille-Dubois  
1005

Effect of Non-psychoactive Plant-derived Cannabinoids on Bladder Contractility: Focus on Cannabigerol
Ester Pagano, Vittorino Montanaro, Antonio di Girolamo, Antonio Pistone, Vincenzo Altieri, Jordan K. Zjawiony, Angelo A. Izzo and Raffaele Capasso  
1009

In Cell Interactome of Oleocanthal, an Extra Virgin Olive Oil Bioactive Component
Chiara Cassiano, Agostino Casapullo, Alessandra Tosco, Maria Chiara Monti and Raffaele Riccio  
1013

Synthesis of γ-Viniferin Glycosides by Glucosyltransferase from *Phylolacca americana* and their Inhibitory Activity on Histamine Release from Rat Peritoneal Mast Cells
Hiroki Hamada, Hatsuyuki Hamada and Kei Shimoda  
1017

Stability of the Ellagitannin Fraction and Antioxidant Capacity of Varietal Pomegranate Juices
Pedro Mena and Cristina Garcia-Viguera  
1019

Phthalide Anions in Synthetic Organic Synthesis. A Direct Total Synthesis of Furomollugin
George A. Kraus and Pengfei Dong  
1025

Absolute Configuration Assignment of 3',4'-di-O-acycOllhexaCtanes Using Vibrational Circular Dichroism Exciton Chirality
Abigail I. Buendia-Trujillo, J. Martin Torres-Valencia, Pedro Joseph-Nathan and Eleuterio Burgueño-Tapia  
1027

Antifouling Compounds from the Marine-Derived Fungus *Aspergillus terreus* SCSGAF0162
Xu-Hua Nong, Xiao-Yong Zhang, Xin-Ya Xu and Shu-Hua Qi  
1033

Goji Berry: Quality Assessment and Crop Adaptation of Plants Cultivated in Tuscany (Italy) by Combination of Carotenoid and DNA Analyses
Giada Capecczi, Emanuele Goti, Elena Nicolai, Maria Camilla Bergonzi, Roberto Monnanni and Anna Rita Bilia  
1035

Activity of *Vitis vinifera* Tendrils Extract Against Phytopathogenic Fungi
Daniele Fraternale, Donata Ricci, Giancarlo Verardo, Andrea Gorassini, Vilberto Stocchi and Piero Sestili  
1037

Long-chain Glucosinolates from *Arabis turrita*: Enzymatic and Non-enzymatic Degradations
Ivica Blažević, Sabine Montaut, Gina Rosalinda De Nicola and Patrick Rollin  
1043

Aroma of Turmeric: Dependence on the Combination of Groups of Several Odor Constituents
Toshio Hasegawa, Kenta Nakatani, Takashi Fujihara and Hideo Yamada  
1047

Terpenoids Preserved in Fossils from Miocene-aged Japanese Conifer Wood
Agnieszka Ludwiczuk and Yoshinori Asakawa  
1051

Can Ozone Alter the Terpenoid Composition and Membrane Integrity of *in vitro Melissa officinalis* Shoots?
Francesca D’Angioliolo, Mariagrazia Tonelli, Elisa Pellegrini, Cristina Nali, Giacomo Lorenzini, Luisa Pistelli and Laura Pistelli  
1055

Composition and Chemical Variability of Ivoirian *Xylopia staBdi* Leaf Oil
Thierry Acafou Yapi, Jean Brice Boti, Antoine Coffly Ahibo, Sylvain Sutour, Ange Bighelli, Joseph Casanova and Félix Tomi  
1059

Chemoinformatics Approach to Antibacterial Studies of Essential Oils
Dragoljub L. Miladinović, Budimir S. Ilić and Branislava D. Kocić  
1063

Chemical Composition of *Nardostachys grandiflora* Rhizome Oil from Nepal – A Contribution to the Chemotaxonomy and Bioactivity of *Nardostachys* 
Prabodh Satyal, Bhuvan K. Chhettri, Noura S. Dosoky, Ambika Poudel and William N. Setzer  
1067

Chemical Composition and Biological Activity of Essential Oils from Wild Growing Aromatic Plant Species of *Skimmia laureola* and *Juniperus macropora* from Western Himalaya
1071

Comparative Chemical Composition and Antioxidant Properties of the Essential Oils of three *Sideritis libanotica* Subspecies
Carmen Formisano, Filomena Oliviero, Daniela Rigano, Nelly Apostolidis Arnold and Felice Senatore  
1075

*Asplenioideae* Species as a Reservoir of Volatile Organic Compounds with Potential Therapeutic Properties
Didier Froissard, Sylvie Rapior, Jean-Marie Bessière, Bruno Buatois, Alain Fruchier, Vincent Sol and Françoise Fons  
1079

Composition and Comprehensive Antioxidant Activity of Ginger (*Zingiber officinale*) Essential Oil from Ecuador
Martina Höferl, Ivanka Stoilova, Juergen Wanner, Erich Schmidt, Leopold Jirovetz, Dora Trifonova, Veselin Stanchev and Albert Krastanov  
1085

Chemical Components of Four Essential Oils in Aromatherapy Recipe
Sarin Tadtong, Narisa Kamkraen, Rith Watthanachaiyingcharoen and Njisiri Ruangrungsi  
1091

Accounts/Reviews

Recent Advances in the Synthesis of Stemona Alkaloids
Xiao-Yu Liu and Feng-Peng Wang  
1093

Flavonoid Properties in Plant Families Synthesizing Betalain Pigments (Review)
Tsukasa Iwashina  
1103

Phytochemistry and Pharmacology of the Genus *Tovomita*
Francesco Epifano, Maria Carmela Specchiulli, Vito Alessandro Taddeo, Serena Fiorito and Salvatore Genovese  
1115

Fungal Phytotoxins with Potential Herbicidal Activity to Control *Chenopodium album*
Alessio Cimmino, Marco Masi, Marco Evidente and Antonio Evidente  
1119

Essential Oils as “A Cry for Help”. A Review
Christine Zitzelsberger and Gerhard Buchbauer  
1127
Anti-Acetylcholinesterase Alkaloids from *Annona glabra* Leaf
Shoei-Sheng Lee, Dong-Yi Wu, Sheng-Fa Tsai, and Chien-Kuang Chen 891

Increased Oxidative Stress in Cultured 3T3-L1 Cells was Attenuated by Berberine Treatment
Shi-fen Dong, Naomi Yasui, Hiroko Negishi, Aya Kishimoto, Jian-ning Sun and Katsumi Ikeda 895

Synthesis and Antimicrobial Activities of 3-Methyl-β-Caroline Derivatives
Jiwen Zhang, Longbi Lo, Wenjia Dan, Jian Li, Qianliang Zhang, Hongjin Bai and Junru Wang 899

A Novel One-step Synthesis of Quinoline-2(1H)-thiones and Selones by Treating 3-Aryl-3-(2-amino phenyl)-1-propyn-3-ols with a Base and Elemental Sulfur or Selenium
Kazuaki Shimada, Hironori Izumi, Koki Otashiro, Kensuke Noro, Shigenobu Aoyagi, Yuji Takikawa and Toshinobu Korenaga 903

Normonanchocidins A, B and D, New Pentacyclic Guanidine Alkaloids from the Far-Eastern Marine Sponge *Monanchora pulchra*
Ksenya M. Tabakmakher, Tatyana N. Makarieva, Vladimir A. Denisenko, Alla G. Guzii, Pavel S. Dmitrenok, Aleksandra S. Kuzmich and Valentin A. Stonik 913

Computational and Investigative Study of Flavonoids Active Against Trypanosoma cruzi and Leishmania spp
Frederico R. Ribeiro, Francisco J.B.M. Junior, Marcelo S. da Silva, Marcus Tullius Scotti and Luciana Scotti 917

Two New Secondary Metabolites from *Tephrosia purpurea*
Yin-Ning Chen, Yan Peng, Cheng-Hai Gao, Tao Yan, Zhi-Fang Xu, Samuel X. Qiu, Wen-Hao Cao, Ligao Deng and Ri-Ming Huang 921

Regioselective Glycosylation of 3-, 5-, 6-, and 7-Hydroxyflavones by Cultured Plant Cells
Kei Shimoda, Naoki Kubota, Daisuke Uesugi, Yuuya Fujitaka, Shouta Okada, Masato Tanigawa and Hiroki Hamada 923

Unusual Flavonoid Glycosides from the Hawaiian Tree *Metrosidéros polymorpha*
Benjamin R. Clark, Swapan Pramanick, Norman Arancon and Robert P. Borris 925

Anti-inflammatory Flavonoids Isolated from *Passiflora foetida*
Thi Yen Nguyen, Dao Cuong To, Manh Hung Tran, Joo Sang Lee, Jeong Hyung Lee, Jeong Ah Kim, Mi Hee Woo and Byung Sun Min 929

Clavamide and Flavonoids from Leaves of *Trifolium pratense* and *T. pratense* subsp. *nivale* Grown in Italy
Aldo Tava, Lukasz Pecio, Anna Stochmal and Luciano Pecetti 933

Water Extract of Mentha × villosa: Phenolic Fingerprint and Effect on Ischemia-Reperfusion Injury
Silvia Fialova, Lucia Veizerova, Viera Nosalova, Katarina Drabikova, Daniela Tekelova, Daniel Grancai and Ruzena Sotnikova 937

Distribution and Taxonomic Significance of Secondary Metabolites Occurring in the Methanol Extracts of the Stonecrops (*Sedum L.*, *Crassulaceae*) from the Central Balkan Peninsula
Gordana S. Stojanović, Snejana Č. Jovanović and Bojan K. Zlatković 941

*In vitro* Xanthine Oxidase Inhibitory Studies of *Lippia nodiflora* and Isolated Phenylethanoid Glycosides as Potential Urinary Acid-lowering Agents
Lee-Chuen Cheng, Vikneswaran Murugaiyah and Kit-Lam Chan 945

Enzymatic Synthesis of Quercetin Monoglucopyranoside and Maltoligosaccharides
Ryo Yasukawa, Natsumi Mirotaki, Daisuke Uesugi, Fuya Kaneko, Hiroki Hamada and Shin-ichi Ozaki 949

Polyurethane Microstructures-a Good or Bad Partner for the Isoflavone Genistein?
Corina Danciu, Florin Borcan, Codruta Soica, Istvan Zupko, Erzsébet Csányi, Rita Ambrus, Delia Muntean, Camelia Sass, Diana Antal, Claudia Toma and Cristina Dehelean 951

Chemical Constituents of the Underground Parts of *Iris florentina* and their Cytotoxic Activity
Akihito Yokosuka, Yoshihiko Koyama and Yoshihiro Mimaki 955

Synthesis of Arecaatannin A1 from Dimeric Epicatechin Electrophile
Manato Suda, Kohki Takanashi, Miyuki Katoh, Kiriko Matsumoto, Koichiro Kawaguchi, Hiroshi Fujii and Hidefumi Makabe 959

Anthocyanin Profile and Antioxidant Activity of Various Berries Cultivated in Korea
Hong-Sook Bae, Hyun Ju Kim, Jin Hee Kang, Rika Kudo, Takahiro Hosoya, Shigenori Kumazawa, Mira Jun, Oh-Yoen Kim and Mok-Ryeon Ahn 963

Metabolite Fingerprinting of *Eugenia jambolana* Fruit Pulp Extracts using NMR, HPLC-PDA-MS, GC-MS, MALDI-TOF-MS and ESI-MS/MS Spectrometry
Ram Jee Sharma, Ramesh C. Gupta, Arvind Kumar Bansal and Inder Pal Singh 969

Flavonoids and Phenolic Acids in Methanolic Extracts, Infusions and Tinctures from Commercial Samples of Lemon Balm
Mariuszka Arceusz, Marek Wesolowski and Beata Ulewicz-Magulska 973

RP-HPLC-DAD-MS*®* Analysis and Butyrylcholinesterase Inhibitory Activity of *Barbacenia blancheti* Extracts
Josómia S Barbosa, Verónica M Almeida, Rosilene M Marçal and Alexsandro Branco 983

Flavonoids and Other Phenolic Compounds in Needles of *Pinus peuce* and Other Pine Species from the Macedonian Flora
Marija Karapandzova, Gjose Stefkov, Ivana Cvetkovikj, Jasmina Petreska Stanoeva, Marina Stefova and Svetlana Kulevanova 987

Anti-inflammatory, Antioxidant and Antimicrobial Activity Characterization and Toxicity Studies of Flowers of “*Jarilla*”, a Medicinal Shrub from Argentina
Alejandra Moreno, Gabriela Nuño, Soledad Cuello, Jorge E. Sayago, María Rosa Alberto, Catiana Zampini and María Inés Isla 991

Synthesis of Resveratrol Glycosides by Plant Glucosyltransferase and Cyclodextrin Glucanotransferase and Their Neuroprotective Activity
Kei Shimoda, Naoki Kubota, Hatsuuki Hamada and Hiroki Hamada 995

Anti-austerity Constituents of the Congolese Medicinal Plant *Aframomum melegueta*
Dya Fitte Dibwe, Suresh Awale, Hiroyuki Morita and Yasuhiro Tezuka 997

The Lignan-containing Extract of *Schisandra chinensis* Berries Inhibits the Growth of *Chlamydia pneumoniae*
Elina Hakala, Leena L. Hanski, Teijo Yrjönen, Heikki J. Vuorela and Pia M. Vuorela 1001
Natural Product Communications
2015
Volume 10, Number 6

Contents

Editorial i

Preface iii

Original Paper

Chemical and Genetic Diversity of Ligularia hodgsonii in China
Chiaki Kuroda, Kou Inagaki, Xun Chao, Kiyosuke Inoue, Yasuko Okamoto, Motoo Tori, Xun Gong, and Ryo Hanai 823

Constituents of Ligularia brassicoides Collected in China: A New Diels-Alder Adduct of Eremophilan-10β-ol and Methacrylic Acid
Mizuho Taniguchi, Katsuyuki Nakashima, Yasuko Okamoto, Xun Gong, Chiaki Kuroda and Motoo Tori 827

Four New Sesquiterpenoids from Ligularia subsicata Collected in China; Isolation of a Bakkane-type Lactone, and Eremophilane-type Lactone, and Two Ortho Esters
Yoshinori Saito, Takanori Otsubo, Yuko Iwamoto, Katsuyuki Nakashima, Yasuko Okamoto, Xun Gong, Chiaki Kuroda and Motoo Tori 831

Natural Caryophyllane Sesquiterpenoids from Rumphella antipathies
Hsu-Ming Chung, Wei-Hsien Wang, Tsong-Long Hwang, Yang-Chang Wu and Ping-Jyun Sung 835

The Importance of the 5-Alkyl Substituent for the Violet Smell of Ionones: Synthesis of Racemic 5-Demethyl-α-ionone
Serena Chierici, Serena Bugoni, Alessio Porta, Giuseppe Zanoni and Giovanni Vidari 847

Antiproliferative Activity of seco-Oxacassanes from Acacia schaffneri

Continued inside backcover