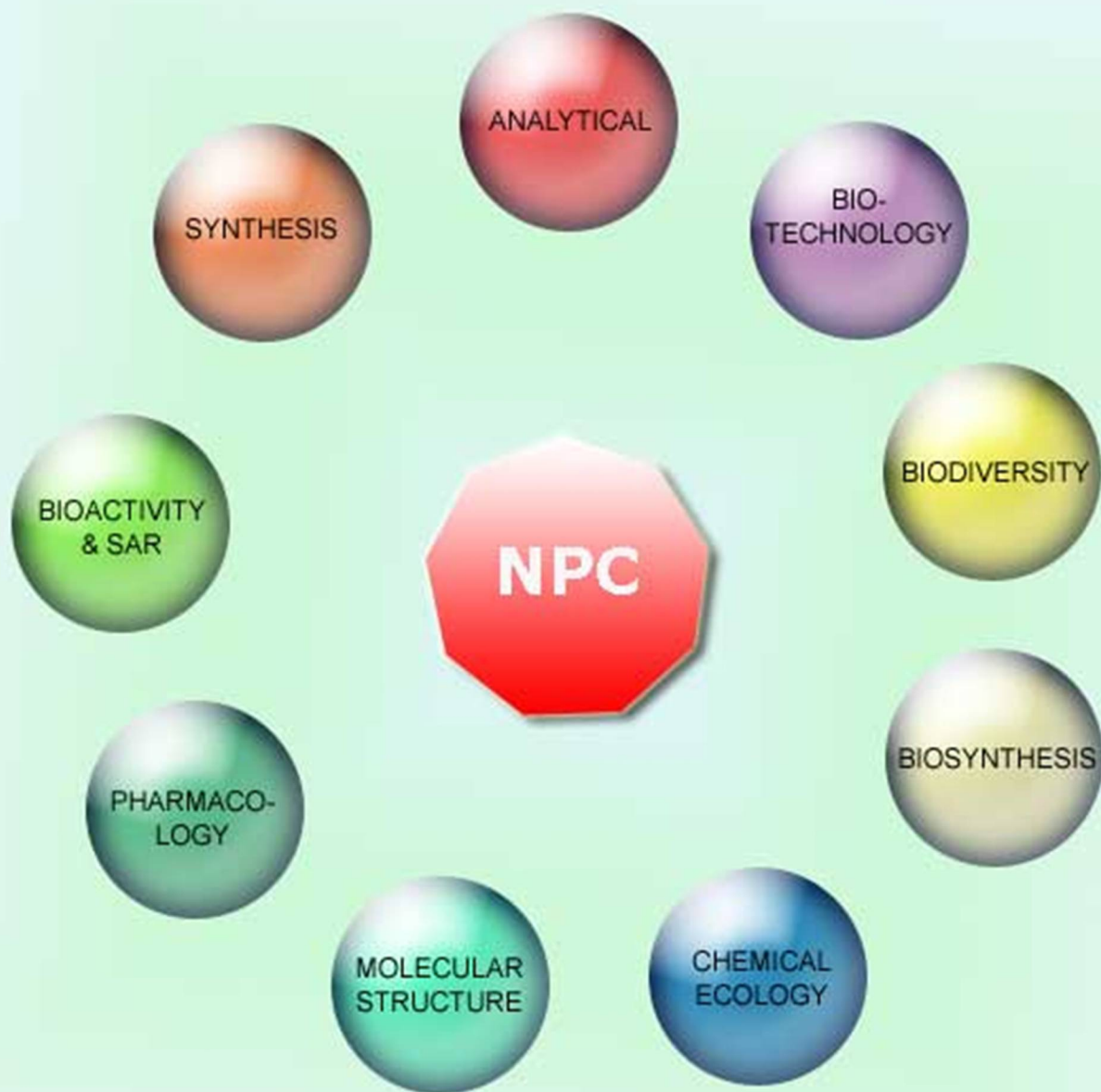


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## Volatiles of French Ferns and “fougère” Scent in Perfumery

Didier Froissard<sup>a</sup>, Françoise Fons<sup>b\*</sup>, Jean-Marie Bessière<sup>c</sup>, Bruno Buatois<sup>c</sup> and Sylvie Rapior<sup>b</sup><sup>a</sup>Laboratoire de Botanique, Faculté de Pharmacie de Limoges, 2 rue du Dr Marcland, F-87025 Limoges cedex, France<sup>b</sup>Laboratoire de Botanique, Phytochimie et Mycologie, Faculté de Pharmacie (Université Montpellier 1), UMR 5175 CEFE, B.P. 14 491, 15 avenue Charles Flahault, F-34093 Montpellier cedex 5, France<sup>c</sup>Centre d'Ecologie Fonctionnelle et Evolutive – Plateforme d'analyses chimiques en écologie, UMR 5175 CEFE, 1919 Route de Mende, F-34293 Montpellier cedex 5, France

francoise.fons@univ-montp1.fr

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Six French ferns were investigated for volatile organic compounds (VOC) by GC-MS using organic solvent extraction. Seventy-seven VOC biosynthesized from the shikimic, lipidic and terpenic pathways, including isoprenoid derivatives, were identified from these putative natural resources. *Asplenium trichomanes* subsp. *trichomanes* contained mainly polyketides with an oily or waxy odor. (*E*)-2-Hexenal and (*Z*)-3-hexenol, responsible for the “green odor”, were found in high contents in *Polystichum setiferum*, *Dryopteris dilatata* and *Phegopteris connectilis*. In the last, 7.4% of coumarin with a cut hay scent was highlighted from the volatile fraction. (*E*)-3-Hexenoic acid and (*E*)-2-hexenoic acid, both with herbal and fruity notes, were identified in *Gymnocarpium dryopteris* and *Pteridium aquilinum*. 1-Octen-3-ol, well-known for its mushroom-like odor, was abundant in all analyzed French ferns. While the “fougère” fragrance is claimed by the perfumers to be a fantasy scent, coumarin, (*E*)-2-hexenal, (*Z*)-3-hexenol and 1-octen-3-ol are the main odorous components of the perfumes belonging to the fougère accord family. This suggests that the fougère scent from the perfumers’ imagination is a natural fragrance.

**Keywords:** Ferns, fougere, volatile organic compounds, (*E*)-2-hexenal, (*E*)-3-hexenoic acid, coumarin, 1-octen-3-ol, Pteridophyta.

Ferns and fern allies (Monilophytes and Lycophytes [1a,1b]) are widely distributed in France due to the geological variety of soils, different climatic interactions, contrasted altitudes and various ecosystems. Indeed, there are over one hundred species of native ferns and fern allies in mainland France [1c]. In this way the French fern flora shows a great biodiversity of volatile organic compounds (VOC) [1d]. These plants have given perfumers great inspiration for a long time. In 1882, the French perfumer Jean-François Houbigant created a modern perfume called “Fougère Royale” with aromatic, spicy, oakmossy notes adding synthetic coumarin for the first time in perfumery [2a-2c]. Nowadays, the French word “fougère” is commonly used in perfume composition. The fougère note refers to a basic scent of great interest for fine fragrances, cosmetics and soaps. In the perfume classification described by the French society of perfumers, fougère is one of the seven scent families contributing to the olfactory description of a fragrance [2d,2e]. However, few reports [1d,3a-3f] have been published on VOC from wild ferns. As a part of our ongoing work on the VOC of Monilophytes [1d], six French ferns were investigated for their volatile profiles using GC-MS: *Asplenium trichomanes* subsp. *trichomanes* L. (Aspleniaceae), *Dryopteris dilatata* (Hoffm.) A. Gray, *Polystichum setiferum* (Forsk.) Woynar (Dryopteridaceae), *Gymnocarpium dryopteris* (L.)

Newman (Woodsiaceae), *Pteridium aquilinum* (L.) Kuhn (Dennstaedtiaceae), and *Phegopteris connectilis* (Michx) Watt (Thelypteridaceae). The main volatile components were compared, in particular, with those reported in the literature, including the five French ferns previously studied [1d].

Aerial parts of fresh ferns were analyzed for volatilizable and volatile organic compounds. Seventy-seven components biosynthesized from the shikimic, lipidic and terpenic pathways were identified from the concentrated organic extracts of the six ferns (Table 1).

Twenty-eight volatiles were identified for *A. trichomanes* subsp. *trichomanes*, with mostly polyketide compounds (87.5%) and minor aromatic compounds (8.2%), i.e., benzofuran with an aromatic note [4a]. High amounts of fatty acid derivatives (alcohols, aldehydes, acids) from C<sub>7</sub> to C<sub>10</sub> series, i.e., (*E*)-2-heptenal (green fatty note), nonanal, octanoic acid (fatty, soapy odor), (*E*)-2-decenal, (*E*)-2-decenol (waxy note), nonanoic acid (waxy dairy note), and decadienal isomers were found [4b-4d]. This fern volatile composition showed a likeness to the *Adiantum capillus-veneris* volatiles [1d]: lack of green odor C<sub>6</sub>-compounds, mainly heavy polyketides with plastic or fatty odor (decadienal isomers, (*E*)-2-decenal).

**Table 1:** Percentage of volatile organic compounds<sup>a</sup> in fresh aerial part of ferns.

Compounds	RI <sup>b</sup>	<i>Asplenium trichomanes</i>	<i>Dryopteris dilatata</i>	<i>Polystichum setiferum</i>	<i>Gymnocarpium dryopteris</i>	<i>Pteridium aquilinum</i>	<i>Phegopteris connectilis</i>
<b>Aromatic compounds</b>		<b>8.2</b>	<b>13.9</b>	<b>10.6</b>	<b>14.7</b>	<b>16.8</b>	<b>25.3</b>
Benzaldehyde	962		2.2	1.9	0.8	2.3	
Phenylethanal	1046				1.7		5.3
Acetophenone	1068		4.0	0.9			0.8
2-Phenylethanol	1117	0.1	2.2				
Benzoic acid	1187		1.4	1.6	3.4	5.2	
Benzothiazole	1228		0.6		0.6		
Benzofuran	1235	7.4					
4-Amino-2-methoxyphenol	1243			1.5			
Phenylacetic acid	1266		1.6		0.8	0.9	
Hydroquinone	1283						1.5
4-Vinylguaiacol	1318					2.6	1.9
4-Hydroxybenzaldehyde	1388	0.7					
Isovanillin	1404		0.8	0.9		1.4	
Coumarin	1431						7.4
Methyl 4-hydroxybenzoate	1477				3.4		
Methyl vanillate	1518			0.6	3.4		
4-Hydroxybenzoic acid	1551			3.2	0.6		0.6
Vanillic acid	1592		1.0			4.3	5.9
Homovanillic acid	1639						0.6
Coniferol	1732						1.3
<b>Polyketide compounds</b>		<b>87.5</b>	<b>55.4</b>	<b>61.9</b>	<b>26.7</b>	<b>63.0</b>	<b>50.6</b>
Isovaleric acid	850	0.4			1.4	1.7	
( <i>E</i> )-2-Hexenal	851		10.1	6.6	2.0		9.1
( <i>Z</i> )-3-Hexenal	855		3.0	3.2	1.7	2.3	3.2
Furfurol	863					1.4	
( <i>E</i> )-2-Hexenal	866		2.8				
Hexanol	870					1.4	
Heptanal	902	0.6	1.6			1.7	2.1
Sorbaldehyde	914			1.6			
Cyclopentan-1,2-dione	933					2.0	
( <i>E</i> )-2-Heptenal	956	8.0		0.9			4.2
1-Octen-3-one	977	0.4	0.8	1.5	0.6		1.1
1-Octen-3-ol	983	3.4	13.1	21.3	4.5	9.8	6.8
Octan-2,3-dione	985		0.6	1.3	0.8		1.3
2-Pentylfuran	990	0.4					
(2 <i>E</i> ,4 <i>Z</i> )-Heptadienal	999	0.4			1.1		
3-Octanol	1000		2.0	1.5			
Hexanoic acid	1009	1.2	2.0	1.1	1.4	2.3	
(2 <i>E</i> ,4 <i>E</i> )-Heptadienal	1013	1.2					
( <i>E</i> )-3-Hexenoic acid	1017		3.4	6.4	7.1	4.3	2.7
( <i>E</i> )-2-Hexenoic acid	1035		5.0		2.8	7.2	
( <i>E</i> )-2-Octenal	1059	1.0		1.9			
( <i>E</i> )-2-Octenol	1072	0.7	1.4	2.2			0.6
1-Octanol	1089	0.9					1.3
Nonanal	1106	4.3	4.8	3.4			4.6
NI <sup>c</sup>	1146					1.7	
3,5-Dihydroxy-2,3-dihydro-4-pyranone	1153					10.1	
( <i>E</i> )-2-Nonenal	1162		0.8	1.7			1.9
( <i>E</i> )-2-Nonenol	1172			1.3			
Octanoic acid	1193	18.4					
5-Hydroxymethylfurfural	1226					5.5	
( <i>E</i> )-2-Decenal	1250	2.1					
( <i>E</i> )-2-Decenol	1263	9.2					4.6
4-Methyl-3-vinylmaleimide	1273			1.6		0.9	
Nonanoic acid	1283	12.3	1.2		1.1		1.1
(2 <i>E</i> ,4 <i>Z</i> )-Decadienal	1296	3.5					1.7
(2 <i>E</i> ,4 <i>E</i> )-Decadienal	1321	4.7		1.3			1.5
( <i>E</i> )-2-Undecenal	1366	0.6		3.2			
9-Oxononanoic acid	1498	2.8					
Tridec-9-enoic acid	1660	9.8				5.8	
Tetradecanoic acid	1773	1.2	2.6		2.0	4.6	3.0
<b>Monoterpenic compounds</b>		<b>0</b>	<b>0</b>	<b>1.3</b>	<b>4.0</b>	<b>0</b>	<b>1.5</b>
$\alpha$ -Pinene	933			1.3			
<i>trans</i> -Linalool oxide (pyran)	1393				3.4		1.5
<i>cis</i> -Linalool oxide (pyran)	1396				0.6		
<b>Isoprenoid derivatives</b>		<b>4.3</b>	<b>30.6</b>	<b>26.2</b>	<b>50.7</b>	<b>20.2</b>	<b>22.6</b>
NI <sup>c</sup>	1582		2.6		2.8		
NI <sup>c</sup>	1590				3.1		
NI <sup>c</sup>	1597	0.6	2.8		7.4	1.4	3.2
5-Hydroxy-5,6-dihydro- $\beta$ -ionol	1606		1.6				
NI <sup>c</sup>	1617		1.6		1.1		0.6
4-Hydroxy-7,8-dihydro- $\beta$ -ionone	1631		2.0				2.5
6-Hydroxy- $\alpha$ -ionone	1635		2.2	3.4	2.0	1.7	
3-Oxo- $\alpha$ -ionol	1644	0.4	6.0		1.1		
4-Oxo-7,8-dihydro- $\beta$ -ionone	1649				3.7		
NI <sup>c</sup>	1649			2.1			
3-Oxo- $\alpha$ -ionone	1650			2.3	6.5	1.7	0.6
5-Hydroxy-5,6,7,8-tetrahydroionone	1652				6.5	1.7	
4-Hydroxy-5,6-epoxy- $\beta$ -ionol	1661	3.4	5.8			2.3	12.7
4-Oxo-5,6-epoxy- $\beta$ -ionol	1673				13.6		
4-Oxo-7,8-dihydro- $\beta$ -ionone	1678			1.5			2.1
2-Hydroxy-5,6-epoxy- $\beta$ -ionone	1689				2.8		
3-Hydroxy-5,6-epoxy- $\beta$ -ionone	1691		5.8	13.9		2.3	0.8
3-Oxo-7,8-dihydro- $\alpha$ -ionol	1705					5.2	
3-Oxo-7,8-dihydro- $\beta$ -ionol	1721			3.0		2.9	
3-Oxo-6-hydroxy- $\alpha$ -ionone	1800					0.9	
<b>Extraction process<sup>d</sup></b>		<b>2.85 / 30</b>	<b>17.56 / 150</b>	<b>7.05 / 100</b>	<b>2.58 / 50</b>	<b>14.08 / 120</b>	<b>18.8 / 200</b>

<sup>a</sup> Relative percentage of the VOC based on the GC-MS chromatographic area<sup>b</sup> RI = Retention Indices on SLB<sup>100</sup>-5MS column (Supelco)<sup>c</sup> NI = non identified<sup>d</sup> Fresh Weight of fern and volume of diethyl ether used for the extraction (g/mL).

Thirty compounds participated in the general aroma of *D. dilatata* with aromatic compounds (13.9%) such as 2-phenylethanol, with a rose odor [4e,4f] and benzaldehyde with an almond note [4g,4h] already found in *Blechnum spicant* [1d]. Polyketides formed the major group of compounds (55.4%) with (*E*)-2-hexenal (10.1%), 1-octen-3-ol (13.1%), and (*E*)-2-hexenoic acid (5%), with a powerful fruity, herbal, and fatty odor, and nonanal (4.8%) with an orange and green scent [4i].

The broad spectrum of volatile components (thirty-one) identified in *P. setiferum* contributed to its complex smell, including, among others, polyketide derivatives (61.9% of the volatile fraction), isoprenoid derivatives (26.2%), various aromatics (10.6%) and an odorous monoterpene,  $\alpha$ -pinene. The main volatiles were 1-octen-3-ol (21.3%), (*E*)-2-hexenal (6.6%) and (*E*)-3-hexenoic acid (6.4%), with a honey odor that is somewhat waxy, fruity and herbal [4b]. The first, the C<sub>8</sub>-alcohol well-known for its mushroom odor [4e,4g,4i,4j], was abundant in the eleven ferns analyzed in our studies [1d]. High contents of (*E*)-2-hexenal, (*Z*)-3-hexenol and C<sub>6</sub>-acid derivatives were also measured in *D. dilatata* (13.1%), *P. connectilis* (12.3%) and the previously reported *Athyrium filix-femina* (15.1%) [1d]. It should be noted that C<sub>6</sub>-aldehydes and -alcohols are commonly released after either plant stress or herbivory-induced damage [5a-5b]. The C<sub>6</sub>-derivatives are notably responsible for the green odor of the plants [4j]. This pleasant odor would be beneficial for mammals, with an antidepressant-like effect [5c].

The volatile pattern (twenty-nine volatiles) of *G. dryopteris* was dominated by a large number of isoprenoid derivatives (50.7%), i.e., ionone derivatives. The investigation indicated lower amounts of polyketides and aromatics (26.7% and 14.7%, respectively), as well as 1-octen-3-ol (4.5%) and (*E*)-3-hexenoic acid (7.1%). The terpenic pathway produces either fragrant monoterpenes ( $\alpha$ -terpineol, pinenes) or sesquiterpenes ( $\beta$ -caryophyllene, (*E*)-nerolidol), which give a pleasant scent [4f,4h] to the concerned fern, for example, *Oreopteris limbosperma* [1d] and *Dryopteris filix-mas*, while sesquiterpene glucosides, such as the illudane-type ptaquiloside may induce a carcinogenic effect, as in the case of *P. aquilinum* [6a-6b]. Glycosides of hemiterpenes, diterpenes, sesterpenes or triterpenes have been isolated from different ferns, as well as carotenoids [6c-6f], but are not accessible by GC-MS. Only ionone derivatives, produced after carotenoid degradation and widely found in six of the eleven studied ferns, were detectable by GC-MS.

The complex volatile profile of *P. aquilinum* is based on twenty-nine volatiles, mainly polyketides (63%), as well as isoprenoids (20.2%) and aromatics (16.8%). Among the former group, 3,5-dihydroxy-2,3-dihydro-4-pyranone (10.1%), 1-octen-3-ol (9.8%), (*E*)-2-hexenoic acid (7.2%) and 5-hydroxymethylfurfural (5.5%) were the major components. Table 1 lists also benzoic acid and oxo-7,8-

dihydro- $\alpha$ -ionol (5.2% each), as well as vanillic acid and 4-vinylguaiacol, with a spicy, clove, smoky odor [4b,4k,4l].

Thirty-two volatiles were identified in *P. connectilis*, mainly polyketides (50.6%), aromatics (25.3%) and isoprenoids (22.6%). Coumarin (hay and dried herb odor; 7.4%), 1-octen-3-ol (6.8%), vanillic acid (sweet cream with vanilla aroma; 5.9%), phenylethanal (5.3% hyacinth, lilac note), nonanal (4.6%) and (*E*)-2-decenol (4.6%) were the main volatile odorous components [4h-4j,4m].

While the fougère fragrance is claimed by the perfumers to be a fantasy scent [2a,2b], coumarin (hay and dried herb odor), (*E*)-2-hexenal and (*Z*)-3-hexenol (green odors), 1-octen-3-ol (mushroom-like odor), terpenic compounds with citrus, floral and spicy notes ( $\alpha$ -terpineol, (*E*)-nerolidol,  $\beta$ -caryophyllene, linalool, pinenes, limonene,  $\gamma$ -terpinen-7-al, ionone derivatives...) are the main fragrant components of the perfumes belonging to the fougère accord family. Most of these sweet-smelling compounds have been found in the wild French ferns [1d]. Because of the increasing requirements of the perfumery, cosmetic and hygienic product industries for natural odor materials, fern resources are of great interest as natural sources of odorous ingredients.

## Experimental

**Plant material:** Fresh aerial parts of ferns were collected from metropolitan France as follows: *Asplenium trichomanes* subsp. *trichomanes* L., *Dryopteris dilatata* (Hoffm.) A. Gray, *Gymnocarpium dryopteris* (L.) Newman and *Pteridium aquilinum* (L.) Kuhn: 20/9/2009, Meymac, Corrèze. *Polystichum setiferum* (Forskål) Woynar: 14/09/2009, Botanical Garden of Limoges. *Phegopteris connectilis* (Michx) Watt: 14/7/2009, Gimelles-Cascades, Corrèze. Voucher specimens are deposited at the Laboratory of Botany (Faculty of Pharmacy, Limoges, France).

**Plant part and GC-MS analyses:** Aerial parts of fresh ferns were cubed and extracted with diethyl ether (Carlo Erba, 6 ppm BHT; Table 1). After maceration for one week at room temperature, the concentrated organic extracts were used for Gas Chromatography-Mass Spectrometry (GC-MS) analyses, as previously described [1d]. VOC were identified by comparison with National Institute of Standards and Technology Mass Spectral Library [7a], retention indices reported in the literature [7b] and our own data bank.

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<b>Effects of pH, Sample Size, and Solvent Partitioning on Recovery of Soluble Phenolic Acids and Isoflavonoids in Leaves and Stems of Red Clover (<i>Trifolium pratense</i> cv. Kenland)</b> Isabelle A. Kagan	1657
<b>Arbutin Derivatives from the Seeds of <i>Madhuca latifolia</i></b> Shazia Khan, M. Nadeem Kardar and Bina S. Siddiqui	1661
<b>Quinic Acids from <i>Aster caucasicus</i> and from Transgenic Callus Expressing a <math>\beta</math>-Amyrin Synthase</b> Paola Pecchia, Maria Cammareri, Nicola Malafrente, M. Federica Consiglio, Maria Josefina Gualtieri and Clara Conicella	1665
<b>Cytotoxic Activity and Cell Cycle Analysis of Hexahydro-curcumin on SW 480 Human Colorectal Cancer Cells</b> Chung-Yi Chen, Woei-Ling Yang and Soong-Yu Kuo	1671
<b>Does the Combination of Resveratrol with Al (III) and Zn (II) Improve its Antioxidant Activity?</b> Karina Dias and Sofia Nikolaou	1673
<b>Photosensitization Mechanisms of Triplet Excited State<math>\beta</math>-Lapachone. A Density Functional Theory Study</b> Liang Shen	1677
<b>AFLP Marking and Polymorphism among Progenies of <i>Gymnema sylvestre</i>: an Important Medicinal Plant of India</b> Magda Abbaker Osman, Sunita Singh Dhawan, Janak Raj Bahl, Mahendra P Darokar and Suman P S Khanuja	1679
<b>Antioxidant Activity of Protein Hydrolysates from Aqueous Extract of Velvet Antler (<i>Cervus elaphus</i>) as Influenced by Molecular Weight and Enzymes</b> Lei Zhao, Yang-Chao Luo, Cheng-Tao Wang and Bao-Ping Ji	1683
<b>Effects of <i>Sideritis euboea</i> (Lamiaceae) Aqueous Extract on IL-6, OPG and RANKL Secretion by Osteoblasts</b> Eva Kassi, Anna Paliogianni, Ismene Dontas, Nektarios Aligiannis, Maria Halabalaki, Zoi Papoutsis, Alexios-Leandros Skaltsounis and Paraskevi Moutsatsou	1689
<b><i>In vitro</i> Antiprotozoal Activity of Extracts of five Turkish Lamiaceae Species</b> Hasan Kirmizibekmez, Irem Atay, Marcel Kaiser, Erdem Yesilada and Deniz Tasdemir	1697
<b>Antimicrobial Investigation of <i>Linum usitatissimum</i> for the Treatment of Acne</b> Pratibha Nand, Sushma Drabu and Rajinder K Gupta	1701
<b>Chemical and Biological Diversity in Fourteen Selections of Four <i>Ocimum</i> Species</b> Bhaskaruni R. Rajeswara Rao, Sushil K. Kothari, Dharmendra K. Rajput, Rajendra P. Patel and Mahendra P. Darokar	1705
<b>Environmental Effect on Essential Oil Composition of <i>Aloysia citriodora</i> from Corrientes (Argentina)</b> Gabriela Ricciardi, Ana Maria Torres, Ana Laura Bubenik, Armando Ricciardi, Daniel Lorenzo and Eduardo Dellacassa	1711
<b>Essential Oil of Three <i>Uvaria</i> species from Ivory Coast</b> Koffi A. Muriel, Tonzibo Z. Félix, Gilles Figueredo, Pierre Chalard and Yao T. N'guessan	1715
<b>Composition of the Essential Oil of <i>Origanum tyttanthum</i> from Tajikistan</b> Farukh S. Sharopov, Muhammadsho A. Kukaniev and William N. Setzer	1719
<b>Volatiles of French Ferns and "fougère" Scent in Perfumery</b> Didier Froissard, Françoise Fons, Jean-Marie Bessière, Bruno Buatois and Sylvie Rapior	1723
<b>Volatile Constituents of Two Species of <i>Protium</i> from the Atlantic Rainforest in the State of Pernambuco, Brazil</b> José Gildo Rufino de Freitas, Claudio Augusto Gomes da Camara, Marcilio Martins de Moraes and Henrique Costa Hermenegildo da Silva	1727
<b>Volatile Constituents of Two <i>Hypericum</i> Species from Tunisia</b> Karim Hosni, Kamel Msaâda, Mouna Ben taârit, Thouraya Chahed and Brahim Marzouk	1731
<b>Chemical Composition and Possible <i>in vitro</i> Antigermination Activity of Three <i>Hypericum</i> Essential Oils</b> Aurelio Marandino, Laura De Martino, Emilia Mancini, Luigi Milella and Vincenzo De Feo	1735
<b>Antioxidant, Antimicrobial Activities and Fatty Acid Components of Flower, Leaf, Stem and Seed of <i>Hypericum scabrum</i></b> Ali Shafaghat	1739
<b>Composition of Three Essential Oils, and their Mammalian Cell Toxicity and Antimycobacterial Activity against Drug Resistant-Tuberculosis and Nontuberculous Mycobacteria Strains</b> Juan Bueno, Patricia Escobar, Jairo René Martínez, Sandra Milena Leal and Elena E. Stashenko	1743
<b>Antimicrobial and Antioxidant Activities of the Flower Essential Oil of <i>Halimodendron halodendron</i></b> Jihua Wang, Hao Liu, Haifeng Gao, Jianglin Zhao, Ligang Zhou, Jianguo Han, Zhu Yu and Fuyu Yang	1749
<b>Composition and Antimicrobial Activity of the Leaf and Twig Oils of <i>Litsea acutivena</i> from Taiwan</b> Chen-Lung Ho, Pei-Chun Liao, Eugene I-Chen Wang and Yu-Chang Su	1755
<b>Chemical Composition and Antimicrobial Activity of the Volatile Oil from <i>Fusarium tricinctum</i>, the Endophytic Fungus in <i>Paris polyphylla</i> var. <i>yunnanensis</i></b> Ying Zhang, Jianglin Zhao, Jihua Wang, Tijiang Shan, Yan Mou, Ligang Zhou and Jianguo Wang	1759
<b>Antifungal Activity of Essential Oil from <i>Asteriscus graveolens</i> against Postharvest Phytopathogenic Fungi in Apples</b> Mohamed Znini, Gregory Cristofari, Lhou Majidi, Hamid Mazouz, Pierre Tomi, Julien Paolini and Jean Costa	1763
<b>Interspecies Comparison of Chemical Composition and Anxiolytic-like Effects of Lavender Oils upon Inhalation</b> Mizuho Takahashi, Tadaaki Satou, Mai Ohashi, Shinichiro Hayashi, Kiyomi Sadamoto and Kazuo Koike	1769
<b>Essential Oils from the <i>Hyptis</i> genus- A Review (1909-2009)</b> Megil McNeil, Petrea Facey and Roy Porter	1775

# Natural Product Communications

## 2011

Volume 6, Number 11

### Contents

<u>Original Paper</u>	<u>Page</u>
<b>Antifungal Activity of Plumericin and Isoplumericin</b> Dharmendra Singh, Umakant Sharma, Parveen Kumar, Yogesh K. Gupta, M. P. Dobhal and Sarman Singh	1567
<b>A New Diacylated Labdane Diterpenoid from <i>Andrographis wightiana</i></b> Jalli Madhu Sudhana, Rachakunta Munikishore, Mopuru Vijayabhaskar Reddy, Duvvuru Gunasekar, Alain Blond and Bernard Bodo	1569
<b>Triterpenoid Acids and Lactones from the Leaves of <i>Fadogia tetraquetra</i> var. <i>tetraquetra</i> (Rubiaceae)</b> Dulcie A. Mulholland, Abdelhafeez M.A. Mohammed, Philip H. Coombes, Shafiul Haque, Leena L. Pohjala, Päivi S.M. Tammela and Neil R. Crouch	1573
<b>Isolation of Friedelin from Black Condensate of Cork</b> Ricardo A. Pires, Ivo Aroso, Susana P. Silva, João F. Mano and Rui L. Reis	1577
<b>Novel Microbial Transformation of Resibufogenin by <i>Absidia coerules</i></b> Jian Zheng, Dong-hai Su, Dong-sheng Zhang, Xiu-Lan Xin, Jun-ying Liu, Yan Tian, Qing Wei and Xun Cui	1581
<b>Antidiabetic Activity of <i>Terminalia sericea</i> Constituents</b> Nolitha Nkobile, Peter James Houghton, Ahmed Hussein and Namrita Lall	1585
<b>X-ray Crystallographic Study of Ranaconitine</b> Yang Li, Jun-hui Zhou, Gui-jun Han, Min-juan Wang, Wen-ji Sun and Ye Zhao	1589
<b>Obscure: a New Cyclostachine Acid Derivative from <i>Beilschmiedia obscura</i></b> Bruno Ndjakou Lenta, Jean Rodolphe Chouna, Pepin Alango Nkeng-Efouet, Samuel Fon Kimbu, Etienne Tsamo and Norbert Sewald	1591
<b>Alkaloids from <i>Papaver coreanum</i></b> Dong-Ung Lee, Jong Hee Park, Ludger Wessjohann and Jürgen Schmidt	1593
<b>Isolation, Structure Elucidation, and Biological Activity of a New Alkaloid from <i>Zanthoxylum rhetsa</i></b> Karsten Krohn, Stephan Cludius-Brandt, Barbara Schulz, Mambatta Sreelekha and Pottachola Mohamed Shafi	1595
<b>Amplexicine, an Antioxidant Flavan-3-ol from <i>Polygonum amplexicaule</i></b> Mudasir A. Tantry and Aziz A. Rahman	1597
<b>A New Flavonoid Glycoside from <i>Vaccaria hispanica</i></b> Haijiang Zhang, Kuiwu Wang, Jie Wu, Yao Chen and Peipei He	1599
<b>Flavonoids from Algerian Endemic <i>Centaurea microcarpa</i> and their Chemotaxonomical Significance</b> Souheila Louaar, Amel Achouri, Mostefa Lefahal, Hocine Laouer, Kamel Medjroubi, Helmut Duddeck and Salah Akkal	1603
<b>On-line (HPLC-NMR) and Off-line Phytochemical Profiling of the Australian Plant, <i>Lasiopetalum macrophyllum</i></b> Michael Timmers and Sylvia Urban	1605
<b>Chemical Fingerprint Analysis of Phenolics of <i>Albizia chinensis</i> Based on Ultra-Performance LC-Electrospray Ionization-Quadrupole Time-of-Flight Mass Spectrometry and Antioxidant Activity</b> Abha Chaudhary, Pushpinder Kaur, Neeraj Kumar, Bikram Singh, Shiv Awasthi and Brij Lal	1617
<b>Application to Classification of Mulberry Leaves using Multivariate Analysis of Proton NMR Metabolomic Data</b> Eriko Fukuda, Motoyuki Yoshida, Masaki Baba, Yoshihiro Uesawa, Ryuichiro Suzuki, Osamu Kamo, Koji Tsubono, Kazunori Arifuku, Kazuhisa Yatsunami and Yoshihito Okada	1621
<b>Phenolic Constituents of <i>Knautia arvensis</i> Aerial Parts</b> Jaroslaw Moldoch, Barbara Szajwaj, Milena Masullo, Lukasz Pecio, Wieslaw Oleszek, Sonia Piacente and Anna Stochmal	1627
<b>New Acylated Anthocyanins and Other Flavonoids from the Red Flowers of <i>Clematis</i> Cultivars</b> Masanori Hashimoto, Toshisada Suzuki and Tsukasa Iwashina	1631
<b>Prenylated Isoflavonoids from <i>Rhynchosia edulis</i></b> Ifedayo V. Ogungbe, Gabrielle M. Hill, Rebecca A. Crouch, Bernhard Vogler, Meenakshi Nagarkoti, William A. Haber and William N. Setzer	1637
<b>Antiparasitic and Antimicrobial Isoflavanquinones from <i>Abrus schimperi</i></b> Aziz A. Rahman, Volodymyr Samoylenko, Surendra K. Jain, Babu L. Tekwani, Shabana I. Khan, Melissa R. Jacob, Jacob O. Midiwo, John P. Hester, Larry A. Walker and Ilias Muhammad	1645
<b>Two New Rotenoids from <i>Boerhavia repens</i></b> Mamona Nazir, Muhammad Saleem, Naheed Riaz, Maria Hafeez, Misbah Sultan, Abdul Jabbar and Muhammad Shaiq Ali	1651
<b>A Comparison of the Diastereoisomers, Silybin A and Silybin B, on the Induction of Apoptosis in K562 cells</b> Jiyong Zhang, Qiuying Luan, Yanze Liu, David Y-W Lee and Zhao Wang	1653

(Continued inside back cover)