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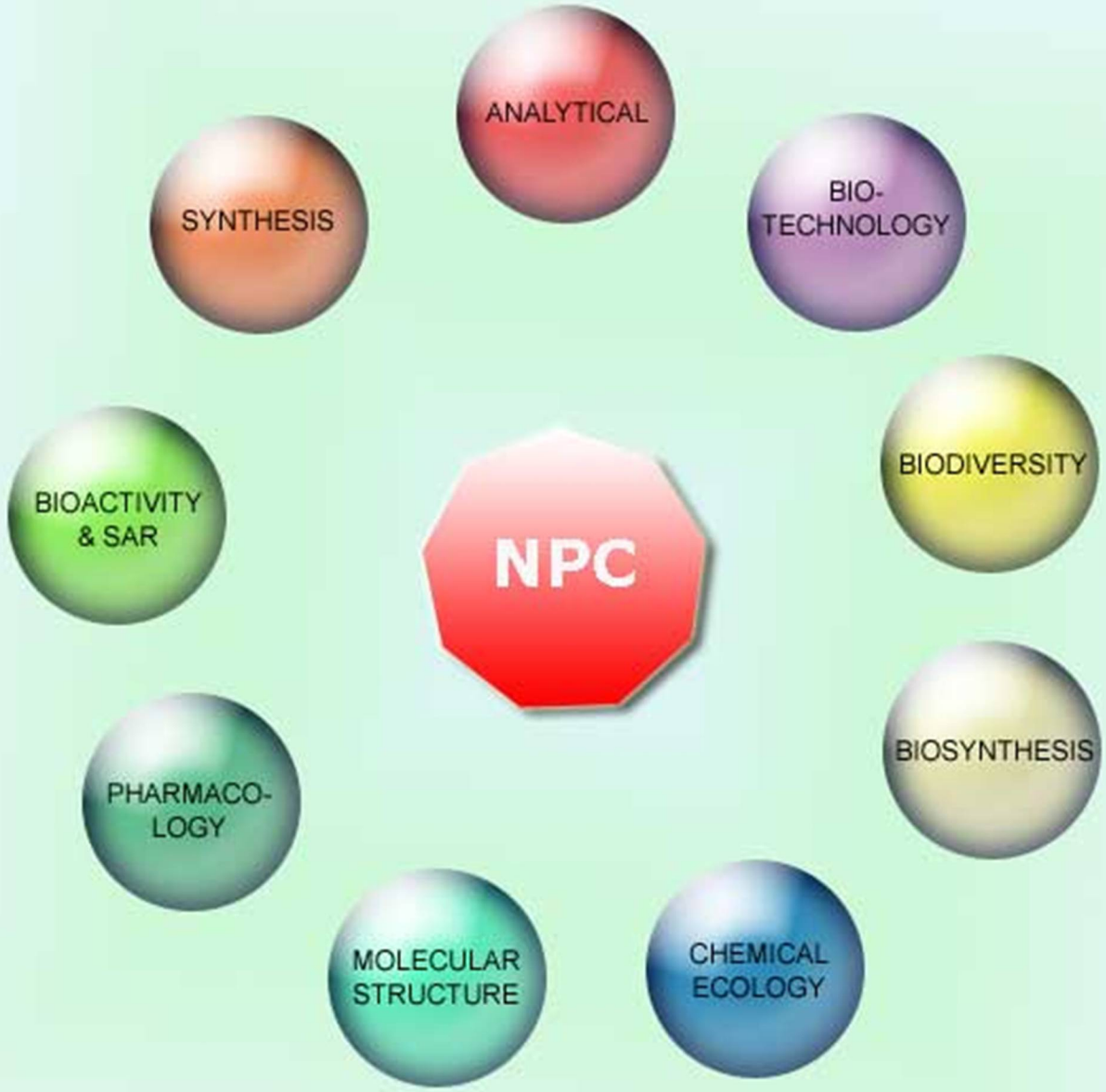

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Volatiles of French Ferns and "fougère" Scent in Perfumery

Didier Froissard[a], Françoise Fons[b]*, Jean-Marie Bessière[c], Bruno Buatois[c] and Sylvie Rapior[b]

[a]*Laboratoire de Botanique*, *Faculté de Pharmacie de Limoges*, *2 rue du Dr Marcland*, *F-87025 Limoges cedex*, *France*

[b]*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*

[c]*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* (Forskal) 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 volatizable 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_7 to C_{10} 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_6-compounds, mainly heavy polyketides with plastic or fatty odor (decadienal isomers, (*E*)-2-decenal).

Table 1: Percentage of volatile organic compounds[a] in fresh aerial part of ferns.

Compounds	RI[b]	*Asplenium trichomanes*	*Dryopteris dilatata*	*Polystichum setiferum*	*Gymnocarpium dryopteris*	*Pteridium aquilinum*	*Phegopteris connectilis*
Aromatic compounds		**8.2**	**13.9**	**10.6**	**14.7**	**16.8**	**25.3**
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
Polyketide compounds		**87.5**	**55.4**	**61.9**	**26.7**	**63.0**	**50.6**
Isovaleric acid	850	0.4			1.4	1.7	
(*E*)-2-Hexenal	851		10.1	6.6	2.0		9.1
(*Z*)-3-Hexenol	855		3.0	3.2	1.7	2.3	3.2
Furfurol	863					1.4	
(*E*)-2-Hexenol	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	
(*E*)-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*E*,4*Z*)-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*E*,4*E*)-Heptadienal	1013	1.2					
(*E*)-3-Hexenoic acid	1017		3.4	6.4	7.1	4.3	2.7
(*E*)-2-Hexenoic acid	1035		5.0		2.8	7.2	
(*E*)-2-Octenal	1059	1.0		1.9			
(*E*)-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[c]	1146					1.7	
3,5-Dihydroxy-2,3-dihydro-4-pyranone	1153					10.1	
(*E*)-2-Nonenal	1162		0.8	1.7			1.9
(*E*)-2-Nonenol	1172			1.3			
Octanoic acid	1193	18.4					
5-Hydroxymethylfurfural	1226					5.5	
(*E*)-2-Decenal	1250	2.1					
(*E*)-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*E*,4*Z*)-Decadienal	1296	3.5					1.7
(2*E*,4*E*)-Decadienal	1321	4.7		1.3			1.5
(*E*)-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
Monoterpenic compounds		**0**	**0**	**1.3**	**4.0**	**0**	**1.5**
α-Pinene	933			1.3			
trans-Linalool oxide (pyran)	1393				3.4		1.5
cis-Linalool oxide (pyran)	1396				0.6		
Isoprenoid derivatives		**4.3**	**30.6**	**26.2**	**50.7**	**20.2**	**22.6**
NI[c]	1582		2.6		2.8		
NI[c]	1590				3.1		
NI[c]	1597	0.6	2.8		7.4	1.4	3.2
5-Hydroxy-5,6-dihydro-β-ionol	1606		1.6				
NI[c]	1617		1.6		1.1		0.6
4-Hydroxy-7,8-dihydro-β-ionone	1631		2.0				2.5
6-Hydroxy-α-ionone	1635		2.2	3.4	2.0	1.7	
3-Oxo-α-ionol	1644	0.4	6.0		1.1		
4-Oxo-7,8-dihydro-β-ionone	1649				3.7		
NI[c]	1649			2.1			
3-Oxo-α-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-β-ionol	1661	3.4	5.8			2.3	12.7
4-Oxo-5,6-epoxy-β-ionol	1673				13.6		
4-Oxo-7,8-dihydro-β-ionone	1678			1.5			2.1
2-Hydroxy-5,6-epoxy-β-ionone	1689				2.8		
3-Hydroxy-5,6-epoxy-β-ionone	1691		5.8	13.9		2.3	0.8
3-Oxo-7,8-dihydro-α-ionol	1705					5.2	
3-Oxo-7,8-dihydro-β-ionol	1721			3.0		2.9	
3-Oxo-6-hydroxy-α-ionone	1800					0.9	
Extraction process[d]		2.85 / 30	17.56 / 150	7.05 /100	2.58 / 50	14.08 / 120	18.8 / 200

[a] Relative percentage of the VOC based on the GC-MS chromatographic area
[b] RI = Retention Indices on SLB™-5MS column (Supelco)
[c] NI = non identified
[d] 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, α-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_8-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_6-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_6-aldehydes and -alcohols are commonly released after either plant stress or herbivory-induced damage [5a-5b]. The C_6-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 (α-terpineol, pinenes) or sesquiterpenes (β-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-α-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 (α-terpineol, (*E*)-nerolidol, β-caryophyllene, linalool, pinenes, limonene, γ-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, Gimel-les-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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Contents

(*Continued inside back cover*)