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Volatiles of French Ferns and “fougère” Scent in Perfumery

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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.) Woyнар (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 C₇ to C₁₀ 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 C₆-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 | <i>Asplenium trichomanes</i> | <i>Dryopteris dilatata</i> | <i>Polystichum setiferum</i> | <i>Gymnocarpium dryopteris</i> | <i>Pteridium aquilinum</i> | <i>Phegopteris connectilis</i> |
|--|-----------------|------------------------------|----------------------------|------------------------------|--------------------------------|----------------------------|--------------------------------|
| 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 | | | | | |
| (2E,4Z)-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 | |
| (2E,4E)-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 |
| (2E,4Z)-Decadienal | 1296 | 3.5 | | | | | 1.7 |
| (2E,4E)-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 | | | |
| <i>trans</i> -Linalool oxide (pyran) | 1393 | | | | 3.4 | | 1.5 |
| <i>cis</i> -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 SLBTM-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 C₈-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 C₆-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 C₆-aldehydes and -alcohols are commonly released after either plant stress or herbivory-induced damage [5a-5b]. The C₆-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, 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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