DOI:10.1021/jf903264n

JOURNAL OF AGRICULTURAL AND FOOD CHEMISTRY
ARTICLE

Chemical Composition of French Mimosa Absolute Oil

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Since decades mimosa (*Acacia dealbata*) absolute oil has been used in the flavor and perfume industry. Today, it finds an application in over 80 perfumes, and its worldwide industrial production is estimated five tons per year. Here we report on the chemical composition of French mimosa absolute oil. Straight-chain analogues from C6 to C26 with different functional groups (hydrocarbons, esters, aldehydes, diethyl acetals, alcohols, and ketones) were identified in the volatile fraction. Most of them are long-chain molecules: (*Z*)-heptadec-8-ene, heptadecane, nonadecane, and palmitic acid are the most abundant, and constituents such as 2-phenethyl alcohol, methyl anisate, and ethyl palmitate are present in smaller amounts. The heavier constituents were mainly triterpenoids such as lupenone and lupeol, which were identified as two of the main components. (*Z*)-Heptadec-8-ene, lupenone, and lupeol were quantified by GC−MS in SIM mode using external standards and represents 6%, 20%, and 7.8% (*w*/*w*) of the absolute oil. Moreover, odorant compounds were extracted by SPME and analyzed by GC-sniffing leading to the perception of 57 odorant zones, of which 37 compounds were identified by their odorant description, mass spectrum, retention index, and injection of the reference compound.

KEYWORDS: Mimosa (*Acacia dealbata*); absolute oil; GC-sniffing; triterpenoids

INTRODUCTION

Acacia dealbata is commonly known as mimosa. The plant was improperly named because of the similarity of its leaves with the ones of the real *Mimosa* genus. As most of the species of the *Acacia* genus, this tree originates from Australia, where it is known as "Silver Wattle". It was acclimated in warm regions all over the world and was introduced on the French Riviera in the nineteenth century, where cultivated and also wild forests of mimosa have existed since then (*1*, *2*). Mimosa absolute oil is produced for its use in the flavor and perfumery industry. Its odor is described as sweet, honey-like, and floral. It is typically used to round off the harsh notes of synthetic compounds, and thus confers a natural note to a composition (*3*). Since steam-distillation of the flowers of *Acacia dealbata* provides low yields or no essential oil at all, the flowers can be extracted by a volatile nonpolar solvent, such as petroleum ether or *n*-hexane. The latter, despite its known toxicity, is used because it gives higher yields of concrete. The *n*-hexane extraction of mimosa in the south of France yields about 1% of concrete, leading to 20 to 25% of absolute oil after treatment with ethanol (*3*). Extraction with petroleum ether yields only about 0.7% of concrete and no better yield of absolute oil from the concrete.

According to the REACH regulation (registration, evaluation, authorization, and restriction of chemical substances), natural extracts used in the perfumery industry have to be tested for their impact on both human health and the environment (*4*). Previous studies of mimosa absolute oil showed that the absolute oil is neither irritant, nor toxic by ingestion, and it does not show toxicity or phototoxicity for microorganisms (*5*, *6*). However, its chemical composition has to be known comprehensively.

Joulain studied mimosa flowers by headspace analysis and described ten constituents, heptadecene being the main component (*7*). Besides heptadecene, other main constituents of mimosa absolute oil (present at > 1%) were found by Petrzilka and Ehret to be hydrocarbons and fatty acid esters with presumably no olfactive impact. Components present between 0.1 and 1% such as octanal, (*E*)-non-2-enal, (*E*,*Z*)-nona-2,6-dienal, esters, and alcohols allowed the first attempt of the odor's reconstitution showing that trace compounds have an important impact on the odor of mimosa absolute oil (*8*). At the Sepawa congress in 1986, Ehret reported 130 compounds identified in the distillate of mimosa absolute oil, and a brief summary was published (*9*). Waxes formed during the absolute oil production process were described by Peyron as containing 36% of *n*-tritriacontane-16,18-dione and 7% of C23−C29 *n*-alkanes (*10*). Pereira extracted and identified lupenone, lupeol, and two esters of the latter in *Acacia dealbata* (*11*). David et al. used mimosa absolute oil as a matrix to test the recovery of spiked allergens by GC−MS using a PTV injector with automated linear exchange, and hence proved the interest of this technique for the analysis of "dirty" samples (*12*). Mimosa extract was chosen to be suitable for this purpose because of the high molecular weight major compounds such as hydrocarbons, sterols, and esters.

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 Published on Web 01/13/2010

Here we report on the chemical composition of French mimosa absolute oil. To the best of our knowledge, neither the analysis of the odorant compounds of mimosa absolute oil by GC-sniffing nor the analysis by direct injection in GC−MS has previously been reported.

MATERIALS AND METHODS

Extracts, Isolation, and Chemicals. *French Mimosa Absolute Oil.* French mimosa absolute oil was supplied by Albert Vieille SAS (Vallauris, France). The flowers were harvested in the mimosa forests in the vicinity of Grasse, France, in winter 2005.

Production of Mimosa Absolute Oil. The flowers, together with leaves and small branches, were extracted twice by *n*-hexane, and the solution was filtrated and evaporated to yield 0.98% of concrete. The concrete was solubilized in ethanol, frozen to 0 °C, and filtrated to eliminate the nonsoluble parts. The same procedure was repeated two times. The three fractions were gathered and ethanol was partially evaporated under reduced pressure. After 24 h, two immiscible layers were obtained and the lower phase was eliminated (2.5%). The complete evaporation of ethanol yielded 25% of absolute oil from the concrete.

Molecular Distillation. 110 g of mimosa absolute oil heated at 50 °C was slowly introduced into the apparatus (Modverre, France) in 30 min. The wipers produced a thin film of the absolute oil on the inner surface heated at 110 °C. Distillation occurred at 2×10^{-6} bar during 100 min. The distillate cooled down on the internal condenser (50 °C), and both parts were collected separately at the bottom in round flasks. A cold trap with liquid nitrogen was installed in order to trap the most volatile compounds.

Isolation and Identification of (*Z*)*-Heptadec-8-ene (13, 14).* The volatile hydrocarbon fraction of mimosa absolute oil was isolated from the distillate by elution with pentane on a silica gel column. The separation of the alkanes from the alkenes was achieved on a silica gel column impregnated with 5% of silver nitrate. Alkanes eluted with pentane, and heptadecene was the only alkene eluting with diethyl ether (purity 94%, GC/FID). Heptadecene (119 mg, 0.5 mmol) was placed in acetone (10 mL) and oxidized by potassium permanganate (800 mg, 5 mmol) assisted by iron(III) chloride (500 mg, 3 mmol) (*15*). Octanoic and nonanoic acids were observed in GC−MS after oxidative cleavage. IR spectroscopy allowed determination of the geometry of the double bond: the presence of an out-of-plane C−H vibration at 722 cm^{-1} indicated the *Z* conformation of the double bond.

Solvents and Chemicals. Chloroform, dichloromethane, tetrahydrofuran (THF), methanol, benzyl alcohol (Aldrich W213705), phenethyl alcohol (Aldrich W285811), $MgSO_4$, $NaHCO_3$, thionyl chloride, acetyl chloride and $LiAlH_4$ were purchased from Sigma-Aldrich/Fluka (Saint-Quentin Fallavier, France). All fatty acids were purchased from Sigma-Aldrich/Fluka (St. Quentin Fallavier, France) [hexanoic acid (Aldrich W255912), heptanoic acid (Aldrich W334812), octanoic acid (Aldrich W279927), nonanoic acid (Aldrich W278408), decanoic acid (Aldrich W236403), undecanoic acid (Aldrich W324507), dodecanoic acid (Aldrich W261416), tridecanoic acid (Fluka T0502), tetradecanoic acid (Fluka 70082), pentadecanoic acid (Sigma P6125), palmitoleic acid (Sigma P6212), hexadecanoic acid (Sigma P0500), heptadecanoic acid (Sigma H3500), linoleic acid (Aldrich 233927), linolenic acid (Sigma L2376), oleic acid (Sigma-Aldrich O1008), elaidic acid (Fluka 45089), octadecanoic acid (Sigma-Aldrich 175366), nonadecanoic acid (Fluka 72332), eicosanoic acid (Aldrich 10930). Lupenone was supplied by Laboratoire Monique Rémy SAS (Grasse, France). Lupeol was obtained by reduction of lupenone with $LiAlH_4$ in THF. All chemical reference compounds for GC-sniffing were purchased from Sigma-Aldrich/Fluka (St. Quentin Fallavier, France) [butanone (Aldrich W217018), pent-1-en-3-ol (Aldrich W515906), pentanal (Aldrich W309818), ethyl propanoate (Aldrich W245615), (*E*)-pent-2-enal (Aldrich W3218188), ethyl isobutanoate (Aldrich W242810), (*Z*)-pent-2-en-1-ol (Aldrich W515906), hexanal (Aldrich W255726), ethyl butanoate (Aldrich W242705), butyl acetate (Aldrich W217417), (*E*)-hex-2-enal (Aldrich W256110), (*Z*)-hex-3-en-1-ol (Aldrich W256323), (E)-hex-2-en-1-ol (Aldrich W256218), hexan-1-ol (Aldrich W256714), heptanal (Aldrich W254010), ethyl pentanoate (Aldrich W246204), isobutyl butanoate (Aldrich W218715), oct-1-en-3-ol (Aldrich W280518), 6-methylhept-5-en-2-one (Aldrich W270733), ethyl hexanoate (Aldrich W243914), phenylacetaldehyde (Aldrich W287407), 1,8-cineole (Aldrich W246506), nonanal (Aldrich W278203), (E,Z)-nona-2,6-dienal (Aldrich 294675), benzyl acetate (Aldrich W213519), (*E*)-non-2-enal (Aldrich W321303), guaiacol (Aldrich W253200), methyl benzoate (Aldrich W268313), (*E*)-oct-2-enal (Aldrich W321508), *p*-cresol (Aldrich W233706), benzyl formate (Aldrich W214507), ethyl benzoate (Aldrich W242217), decanal (Aldrich W236209), (*E*)-dec-2-enal (Aldrich W236-608), methyl *p*-anisate (Aldrich W267902), vanillin (Aldrich W310727), (*Z*)-jasmone (Aldrich W319600), ethyl *p*-anisate (Aldrich W242004)]. Phytyl, eicosanyl, docosanyl acetates were synthesized from phytol (Aldrich W502200), docosan-1-ol (Fluka 43960), eicosan-1-ol (Aldrich 234494), and acetyl chloride (Aldrich 320129). Commercial sources of other compounds can be found in the Supporting Information.

Analytical Studies. *Headspace Solid Phase Microextraction.* A SPME 75 μm Carboxen/polydimethylsiloxane (CAR/PDMS) fiber purchased from Supelco (Bellefonte, PA) was used for the extraction of volatile compounds from the mimosa absolute oil headspace. The fiber was conditioned according to manufacturer recommendations prior to analysis. Mimosa absolute oil (200 mg) was placed in a sealed 20 mL SPME vial. After headspace equilibrium procedure (30 min) at 30 °C, the SPME needle was inserted in the vial (2 cm), and the fiber was exposed to the headspace for 15 min at 30 °C without stirring. After sampling, the fiber was thermally desorbed (manual injection) in the glass SPME linear of the GC injection port (either on an Agilent 6890N chromatograph (Agilent, Massy, France) for GC−MS analyses or on a Shimadzu GC-2010 (Shimadzu, Champs-sur-Marne, France) for GC-sniffing analyses) during 2 min at 250 °C (splitless mode).

Gas Chromatography-Sniffing. Various GC-O methodologies such as detection frequency methods, time-intensity methods, and dilution to threshold methods have been developed in order to obtain information on the odor impact of the constituents and are extensively discussed in the literature (*16*−*19*). When no specific method is applied and the sniffers only describe the odor perceived, this is generally referred to as GC-sniffing. GC-sniffing analyses were performed on a Shimadzu GC-2010 GC (Shimadzu, Champs-sur-Marne, France) equipped with a FID and an ATAS olfactory port OP275 with a glass nasal cone (ATAS, Veldhoven, Netherlands). Samples were analyzed on a fused-silica capillary column: DB-1 (50 m × 0.32 mm i.d. × film thickness 0.52 μm; J&W, Folsom, USA). Carrier gas, nitrogen; constant pressure, 80 kPa; injector temperature, 250 °C; detector temperature, 250 °C; splitless mode, sampling time 1 min; purge flow, 100 mL/min. Since the nose is very sensitive to odors and in order to increase the chances of finding peaks in the chromatogram corresponding to the odors detected, 60% of the flow was directed to the FID while 40% was directed into the heated sniffing port. Transfer line for nearly simultaneous detection: length inside oven, 0.89 m; length outside oven, 1.49 m; internal diameter, 0.25 mm; temperature, 250 °C. Capillary transfer line leading to the FID: length, 1.50 m; internal diameter, 0.25 mm. Temperature program of the GC oven: 40 °C held for 2 min, then ramped to 200 at 4 °C/min. Analysis was conducted by two nonsmoker panelists with no known anosmia, trained according to J. N. Jaubert's "Field of Odors" and used to the organoleptic evaluation of natural extracts (*20*). Training was carried out by sniffing standard compounds classified in odor poles according to the "Field of Odors" and then by performing GC-O/dilution to threshold analyses on a standard mixture of 12 odorants in order to evaluate panelist performance and to exclude specific anosmia. Sniffing sessions lasted 25 min in order to avoid fatigue.

Gas Chromatography−*Mass Spectrometry.* GC−MS analyses were carried out on an apolar capillary HP-1 column (polydimethylsiloxane, 50 m × 0.20 mm i.d. × film thickness 0.33 μm; Interchim, Montluçon, France) on a 6890/5973N system (Agilent, Massy, France) and a polar HP-20 M phase (polyethyleneglycol, 50 m × 0.20 mm i.d. × film thickness 0.10 μm; Interchim, Montluçon, France) on a 5890/5971A system (Agilent, Massy, France). Carrier gas, helium; constant flow 1 mL/min on HP-1 column and constant pressure 220 kPa (polar column); injector temperature, 270 °C (220 °C for polar column); split ratio, 1:100; temperature program, 60 to 270 °C (220 °C), at 2 °C/min then held isothermal 60 min at 270 °C (120 min at 220 °C); ion source temperature, 155 °C; transfer line temperature, 280 °C (230 °C); ionization energy, 70 eV; electron ionization mass spectra were acquired over the mass range 40−450 u.

GC−MS analyses with HS-SPME sampling were carried out on an apolar HP-1 phase (polydimethylsiloxane, 50 m × 0.20 mm i.d. × film thickness 0.33 μm; Interchim, Montluçon, France); constant flow 1 mL/min; injector and detector temperature, 250 °C; splitless mode; temperature program, 40 °C held during 2 min, then ramped to 200 at 4 °C/min. Ion source temperature, 155 °C; transfer line temperature, 250 °C; ionization energy, 70 eV; electron ionization mass spectra were acquired over the mass range 35−350 u.

Quantification by GC−MS in single ion mode (SIM) was carried out with a fused-silica capillary column DB-XLB (patent-registered stationary phase with a polarity equivalent to a phase composed of 12% diphenylsiloxane, 88% dimethylpolysiloxane, 15 m × 0.25 mm i.d. × film thickness 0.25 μm; Interchim, Montluçon, France). This capillary column allows higher temperatures up to 360 °C with a more contained column bleeding for the analysis of semivolatile compounds. Carrier gas, helium; constant flow 1.6 mL/min; injector temperature, 270 °C; split ratio, 1:50; temperature program, 60 to 250 °C, at 10 °C/min then held isothermal 30 min at 250 °C; ion source temperature, 230 °C; transfer line temperature, 270 °C; ionization energy, 70 eV.

The overall chemical composition of French mimosa absolute oil was studied by GC−MS with (direct) liquid injection on the HP-1 column. Some of the existing coelutions were resolved by injection of the fractions obtained by silica gel chromatography with a gradient from 100% petroleum ether to 100% diethyl ether, or by injection of the distillate on the HP-20 M column. The raw absolute oil was not studied by direct injection on the polar column because of abundant late eluting compounds whose elution temperatures exceed the working temperature of the HP-20 M stationary phase.

Component Identification. Identification of the constituents was based on computer matching against commercial libraries (Wiley6N, MassFinder 2.1 Library, NIST98), laboratory mass spectra libraries built up from pure substances, and MS literature data combined with comparison of GC linear retention indices (LRI), calculated with the help of a series of linear alkanes C6−C40, on apolar and polar columns (*21*, *22*). Odorant compounds were identified by attributing them to a signal in the FID chromatogram (if possible), LRI, and odor descriptors according to a laboratory-made GC-O database. Identification was confirmed by injection of the reference compound in GC-O (odor comparison) and GC−MS. Compounds with no referenced mass spectra were tentatively identified by analysis of the mass spectrometric fragmentation pattern.

Quantification. The two main constituents of mimosa absolute oil, the triterpenoids lupenone and lupeol, were quantified in single ion monitoring (SIM) mode on a short capillary column (DB-XLB; 15 m) authorizing high temperatures for the analysis of semivolatile compounds. Mimosa absolute oil was injected five times in chloroform at a concentration of 10 g L^{-1}, and external standards of lupenone and lupeol were injected at respectively 1, 1.5, 2, 3, 4.5 g L^{-1} and 0.5, 0.75, 1, 1.5, 2 g L^{-1} (*23*). As several isomers of ketones and alcohols with the same molecular weights (respectively 424 and 426 u) coeluted, specific fragment ions of 313 u for lupenone and 315 u for lupeol were chosen to be detected in SIM (*24*). (*Z*)-Heptadec-8-ene was quantified following the same procedure with 0.1, 0.3, 0.5, 0.7, 1 g L^{-1} solutions and 238 u as the chosen (molecular) ion.

Infrared Spectroscopy. The infrared spectrum of (*Z*)-heptadec-8-ene was recorded on a FT-IR PerkinElmer Spectrum BX series spectrometer (PerkinElmer, Courtaboeuf, France) on potassium bromide windows (GS01831, Eurolab, Paris, France) with a resolution of 2 cm^{-1}.

Synthesis. *Reductions with $LiAlH_4$*. Lupeol was quantitatively obtained by reduction of lupenone with $LiAlH_4$ (3 equiv) in THF (*25*). Chemical reduction of the distillation residue (5 g, <12 mmol) was performed with $LiAlH_4$ (1.14 g, 30 mmol) in THF (20 mL).

Synthesis of Fatty Acid Esters. Mixtures of fatty acid (FA) esters were synthesized to be used as external standards for GC−MS analyses. A dichloromethane solution of the corresponding acids (5 g L^{-1} each) was prepared from saturated FA C6−C20 and unsaturated FA: palmitoleic, oleic, elaidic, linoleic, and linolenic acids. The mixture containing 20 FA was used to synthesize separately four series of esters with methanol, ethanol, benzyl alcohol, and 2-phenethyl alcohol. Acyl chlorides were prepared from the solution of FA (200 μL; 1 mg of each FA) in dichloromethane (5 mL) with $SOCl_2$ in a large excess (75 μL; ∼10 equiv). A large excess of the alcohol was then added (100 μL), and the mixture was heated to reflux during eight hours. The solution was neutralized with 5 mL of saturated $NaHCO_3$. The organic layer was dried with $MgSO_4$, filtrated and evaporated. 10 and 12 mg of methyl and ethyl esters mixtures were respectively obtained. Remaining benzyl alcohol and 2-phenethyl alcohol were not separated from the mixture of their corresponding esters.

Synthesis of Acetates. A mixture of phytyl (30 mg), eicosan-1-ol (30 mg), docosan-1-ol (33 mg) (0.1 mmol each) was placed in chloroform (10 mL). Acetyl chloride (29 μL; 0.4 mmol) was slowly added and stirred for 5 min. The solution was neutralized with 5 mL of saturated $NaHCO_3$. The organic layer was dried with $MgSO_4$, filtrated and evaporated, yielding 88 mg of the mixture of acetates.

RESULTS AND DISCUSSION

Absolute oils are solvent extracts and contain volatile and nonvolatile molecules. In order to gain information on the proportion of volatile and nonvolatile matter in the absolute oil, a molecular distillation of mimosa absolute oil was realized and yielded ∼20% of yellow semisolid volatile distillate composed of compounds with $LRI_{HP\text{-}1}$ inferior to 3000, corresponding to molecular weights inferior to 400 g mol^{-1}. The nonvolatile residue (∼80%) was a dark olive-green solid. The odor of the volatile fraction was very strong, but lacked the floral and hay-like notes of the absolute oil. On the contrary, the nonvolatile residue was nearly odorless and GC−MS confirmed the elimination of almost all the volatile constituents.

As the distillate lacks the typical mimosa note, it was not suitable for GC-sniffing analyses. However, the absolute could not be directly used because of the presence of nonvolatile (and odorless) compounds. Thus, HS-SPME with a CAR/PDMS 75 μm fiber (extraction of highly volatile compounds) was chosen as sampling method. Fifty-seven odorant zones were detected by the two sniffers during HS-SPME-GC-sniffing. Thirty-seven compounds could be identified with certainty (LRI, MS, odor comparison, and injection of the reference compound). Three compounds were tentatively identified, and 17 zones were not identified (**Table 1**). Eighteen odorant zones were described as fruity and could be attributed to esters such as ethyl propanoate, butanoate, pentanoate, and hexanoate. Phenylacetaldehyde, 2-phenethyl alcohol, benzyl acetate, and (*Z*)-jasmone were the main "floral" compounds responsible for four of the thirteen floral zones. Fresh and green notes were perceived, often due to aldehydes (hexanal, heptanal, nonanal, and (*E*,*Z*)-nona-2, 6-dienal). Three out of five mushroom notes were identified as (*Z*)-pent-2-en-1-ol, (*E*)-oct-2-en-1-ol, and oct-1-en-3-ol. Vanillin, methyl and ethyl anisates were identified, contributing to sugar and anise-like odors. Four zones with similar notes could not be identified.

The predominance of fruity, floral, fresh, green, mushroom, sugar and anise-like odorant notes is in agreement with the descriptors used for mimosa absolute oil. Although observed by liquid injection GC−MS, no diethyl acetals were detected by SPME-GC-sniffing or SPME-GC−MS in the used conditions. None of the odorant zones were perceived as "mimosa" in the applied conditions, confirming that the characteristic smell of the absolute oil is not due to a single compound.

GC−MS allowed identification of 232 constituents of mimosa absolute oil. 145 compounds were identified by MS and LRI and confirmed by external standard injection. The main component of the volatile part was isolated and identified as (*Z*)-heptadec-8-ene and quantified by external standard calibration as being present at 6% (w/w) in the absolute oil (*23*). Esters were prepared as standard mixtures from 20 fatty acids (FA): 15 saturated and five unsaturated. Methyl, ethyl, benzyl, and 2-phenethyl esters were synthesized separately and afforded 80 fatty esters as standards for GC−MS analysis. In mimosa absolute oil, 32 of

Table 1. Odorant Compounds in Mimosa Absolute Oil Determined by HS-SPME-GC-Sniffing

compound	LRI[a] HP-1	LRI[a] HP-20M	odor descriptor	identification method[b]
butanone	619		butter	LRI, MS, odor, std
pent-1-en-3-ol	677		glue	LRI, MS, odor, std
pentanal	686		fatty, green apple, glue, plastic	LRI, MS, odor, std
ethyl propanoate	700		fruity, red fruit, peach	LRI, MS, odor, std
(*E*)-pent-2-enal	720		fruity, pineapple, red fruit	LRI, MS, odor, std
ethyl isobutanoate	743		fruity, red fruit	LRI, MS, odor, std
(*Z*)-pent-2-en-1-ol	753		glue, mushroom	LRI, MS, odor, std
hexanal	777	1128	cut grass	LRI, MS, odor, std
ethyl butanoate	785		fruity	LRI, MS, odor, std
butyl acetate[c]	794		fruity	LRI, odor, std
unknown	810		mushroom metallic	
(*E*)-hex-2-enal	828	1195	fatty	LRI, MS, odor, std
(*Z*)-hex-3-enol	836	1348	fruity, green apple	LRI, MS, odor, std
(*E*)-hex-2-enol	846	1370	nutty-green sesame, empyreumatic	LRI, MS, odor, std
hexan-1-ol	849	1320	green, bitter	LRI, MS, odor, std
unknown	874		cheesy, rancid	
heptanal	876	1177	aldehyde, fresh, marine, dusty	LRI, MS, odor, std
ethyl pentanoate	881		fruity, pineapple	LRI, MS, odor, std
unknown	887		floral	
unknown	899		mushroom	
unknown	933		fruity	
unknown	940		fruity, glue	
isobutyl butanoate[c]	946		fruity, red fruit	LRI, odor, std
oct-1-en-3-ol	955	1418	mushroom	LRI, MS, odor, std
6-methylhept-5-en-2-one	958		green-bitter	LRI, MS, odor, std
ethyl hexanoate	981	1213	floral, fruity, sugar, powdery	LRI, MS, odor, std
unknown	1002		floral-rotten	
phenylacetaldehyde	1010	1587	honey, floral, rose	LRI, MS, odor, std
1,8-cineole	1024	1192	eucalyptus	LRI, MS, odor, std
(*E*)-oct-2-enal	1031	1391	nutty, grilled	LRI, MS, odor, std
p-cresol	1048		phenolic, ink, bitter	LRI, MS, odor, std
benzyl formate	1049	1633	green	LRI, MS, odor, std
(*E*)-oct-2-en-1-ol[c]	1057	1576	mushroom	LRI, MS, odor
guaiacol	1064		smoked, leather	LRI, MS, odor, std
methyl benzoate	1070	1569	spicy	LRI, MS, odor, std
unknown	1081	1311	fresh, cucumber, fatty	
nonanal	1083	1365	aldehyde, dusty, fresh	LRI, MS, odor, std
2-phenethyl alcohol	1084	1850	floral-spicy, rose	LRI, MS, odor, std
unknown	1107		floral	
unknown	1109		earthy, stones	
unknown	1113		sugar, fruity-floral	
unknown	1120		green	
(*E*,Z)-nona-2,6-dienal	1124	1541	fresh, aldehyde, cucumber, marine, green	LRI, MS, odor, std
unknown	1129		floral-fresh	
benzyl acetate	1134	1678	floral-fruity	LRI, MS, odor, std
(*E*)-non-2-enal	1136	1495	peach, fruity, old lipstick	LRI, MS, odor, std
ethyl benzoate	1147	1614	green, waxy	LRI, MS, odor, std
decanal	1188	1448	waxy, aldehyde, floral	LRI, MS, odor, std
(*E*)-dec-2-enal	1232		green-bitter, geranium	LRI, MS, odor, std
unknown	1297		herbaceous, anise-like	
unknown	1324		floral, candy, sugary, powdery	
methyl *p*-anisate	1348	2021	anise-like, liquorice, herbaceous	LRI, MS, odor, std
vanillin	1363	2464	vanilla, candyfloss, hot sugar, powdery	LRI, MS, odor, std
unknown	1372		candy, sugary, fruity	
(*Z*)-jasmone	1377	1878	fruity, floral	LRI, MS, odor, std
unknown	1403		candy, sugary, fruity	
ethyl *p*-anisate	1427	2065	anise-like, floral, earthy, fruity, lemon	LRI, MS, odor, std

[a] LRI of the compounds determined on a HP-1 and a HP-20M column. [b] LRI = linear retention index, MS = mass spectrum, odor = odor determined by GC-sniffing, compared to our GC-O database, std = external injection of the reference compound in GC−MS and GC-sniffing for odor comparison. [c] Tentatively identified (no detection by MS or reference compound not available for injection).

these esters were consequently confirmed. Nineteen constituents were tentatively identified by comparison of their mass spectra and LRI with those given in the literature. The other detected compounds, mostly the heaviest, were tentatively identified by mass spectra comparison or interpretation, as no retention indices or mass spectra were found in the literature and reference compounds are hitherto unavailable. Compounds identified in mimosa absolute oil were mainly straight-chain molecules: hydrocarbons, alcohols, aldehydes and corresponding diethyl acetals, ketones, fatty acids and various related esters. An overview

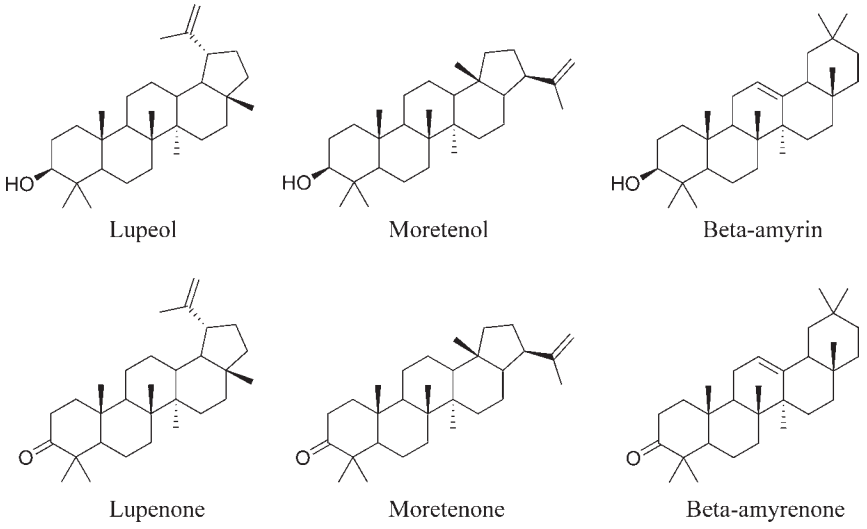

Figure 1. Chemical structure of triterpenoids.

Table 2. Repartition of Straight-Chain Compounds in French Mimosa Absolute Oil (2005)

chemical type	chemical function [carbon atoms of constituents ≥0.5%]	no. of compounds	carbon atom range
hydrocarbons	alkanes [17; 19]	16	9−26
	alkenes [17]	9	14−19
fatty acids, esters	saturated fatty acids [16]	12	3−20
	unsaturated fatty acids	6	6−18
	saturated ethyl esters	9	7−22
	unsaturated ethyl esters	4	18
	other esters (methyl, benzyl, 2-phenethyl)	16	12−20
alcohols	fatty alcohols	13	6−8; 14−24
ketones	alkan-2-ones	6	6−21
aldehydes	saturated	20	6−25
	unsaturated	12	7−18
acetals	diethyl acetals	17	7−23

of these constituents is presented in **Table 2**, and the chain lengths (carbon atom range) for each chemical function are indicated. The individual 232 compounds detected by GC−MS on apolar and polar columns are given in Table S1 in the Supporting Information.

On an apolar column, several semivolatile compounds with an elution temperature of 270 °C were identified as triterpenic ketones and alcohols: lupenone and lupeol being the major compounds. Moretenone (*21*, *26*), moretenol (*21*), β-amyrenone (*27*), and β-amyrin (*21*) were, for the first time in a mimosa extract, tentatively identified according to their mass spectra. The chemical structure of the six triterpenoids is presented, **Figure 1**. Lupenone and lupeol were quantified by external standard calibration (*23*). Lupenone represents 20% and lupeol 7.8% of the total mass of mimosa absolute oil. Lupeol and lupenone having the same response factor in scan mode, extrapolation of the isomers' area in GC−MS (scan between 40 and 450 u) allowed it to be stated that the whole semivolatile fraction (triterpenic ketones and alcohols) represents about 45% of mimosa absolute oil.

However, these late-eluting triterpenoids were not the heaviest constituents of the absolute oil. Reduction of the distillation residue showed the presence of phenylpropanoid alcohols and fatty alcohols. These alcohols were probably formed from the reduction of triterpenic coumarate, ferulate, and various fatty acid esters according to literature (*11*). Fatty alcohols could also have been obtained from triglycerides by reduction of the ester functions between glycerol and fatty acids, but ^{13}C NMR studies on the absolute oil did not show any characteristic signal from the glyceryl part being and hence proved the absence of triglycerides (*28*). The results on the composition of mimosa absolute oil are summarized in **Table 3**.

Table 3. Overview of the Different Results Describing the Composition of Mimosa Absolute Oil According to Their Volatility

volatility of fractions	constituents	proportion
volatile $LRI_{HP\text{-}1} < 3000$	mainly alkanes, fatty acids (palmitic), and (*Z*)-heptadec-8-ene (6%)	20 ± 5%
semivolatile (analyzed on apolar GC columns)	triterpenic ketones (lupenone 20%) and alcohols (lupeol 7.8%)	50 ± 5%
nonvolatile	aromatic and fatty acid triterpenic esters(*11*)	30 ± 5%

Whereas the absolute possesses a very strong odor, GC−MS analyses showed very few volatile and possibly odorant compounds, but HS-SPME-GC-sniffing detected 57 odorant zones. In both SPME and liquid injection GC−MS analyses, many esters, aldehydes, ketones, and alcohols were identified in mimosa absolute. All of these compounds, some of them odorant, were only present in trace amounts. On the contrary, the main components of the absolute in the volatile part are inodorous hydrocarbons such as (*Z*)-heptadec-8-ene (6%) and fatty acids. Solvents extracts are known to contain nonvolatile matter, and, in the case of mimosa absolute, this portion represents about 80%. It seems to be exclusively composed of triterpenoids, and the semivolatile ones like lupenone can be studied by gas chromatography, even if some precautions have to be taken. The presented data provide a comprehensive tool for any risk evaluations on a molecular basis.

ACKNOWLEDGMENT

We acknowledge Albert Vieille SAS for providing the French mimosa absolute oil samples and molecular distillation apparatus. The Laboratoire Monique Rémy S.A.S., Grasse, and Robertet S.A., Grasse, France, provided lupenone standard.

Supporting Information Available: Table S1 depicting results of GC/FID and GC−MS analyses of HS-SPME, fractions, and liquid injections of mimosa absolute oil. This material is available free of charge via the Internet at http://pubs.acs.org.

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Received for review September 16, 2009. Revised manuscript received December 10, 2009. Accepted December 12, 2009. We thank Albert Vieille SAS and the Région Provence-Alpes-Côte d'Azur for a Ph.D. scholarship for R.P. The work was performed in the context of the project "Novo Arômes", supported by the French pole of competitiveness "Parfum Arômes Senteurs Saveurs" (PASS).