Characterization and Sensory Properties of Volatile Nitrogen Compounds from Natural Isolates

By Mans H. Boelens, Boelens Aroma Chemical Information Service, and
Leo J. van Gemert, TNO Nutrition and Food Research, The Netherlands

Volatile nitrogen compounds play an important role in the sensory properties of food flavors. Character-impact nitrogen compounds have, for instance, been found in the flavors of processed foods and drinks, such as bread, meat, coffee and cocoa. During the last decade attention has been paid to the characterization and sensory properties of nitrogen compounds from natural isolates such as headspaces and absolutes of flowers and essential oils.

A study was made of the occurrence, identities and sensory properties of volatile nitrogen compounds emitted by flowers and isolated from flower absolutes and essential oils. More than 130 aliphatic- and aromatic-nitrogen compounds, substituted pyridines, quinolines, pyrazines, (iso)oxazoles and thiazoles have been detected in these natural isolates.The sensory properties (i.e., the odor qualities) of various representatives of the nitrogen compounds were studied. Some of the nitrogen compounds contribute significantly to the sensory properties of the naturals.

Introduction

It is general knowledge that volatile nitrogen compounds are organoleptically important constituents of flavors. Thorough reviews have been published about this subject.[1-4] In the early 1970s much work was done to determine the sensory properties of these flavor compounds.During the last decade the characterization and determination of the sensory properties of volatile nitrogen compounds from natural isolates came more and more into focus. This interest arose from the improvements in the isolation and concentration of volatile trace constituents from natural products and was initiated by modern chromatographic techniques, such as gas chromatography on high resolution, high precision fused silica capillary columns.

An excellent review on headspace analysis by modern gas chromatographic methods was written by Bicchi et al.[5] Formerly, say about 25 years ago, little attention was paid to trace constituents present in concentrations below 0.01% (100 ppm) in an essential oil. Today it is possible to characterize compounds in concentrations less than 1 part per billion (0.001 ppm). In this paper, we'll discuss the chemical characterization and sensory properties of volatile nitrogen compounds emitted or extracted from flowers and essential oils.

Volatile Nitrogen Compounds in Isolates from Flowers

Several scientists have reported on the emission of volatile nitrogen compounds from picked and/or living flowers. Kaiser and Lamparsky[6] in 1980 published their results on trace nitrogen constituents of some absolutes from flowers and the corresponding headspace. They studied the trace nitrogen compounds in the absolutes of hyacinth, tuberose, ylang-ylang and bitter orange flower. Furthermore they investigated the occurrence of these constituents in the headspace emitted by picked flowers of bitter orange, honeysuckle and longoza.The identified nitrogen compounds are shown in Table I. In 1986 Joulain[7] reported on his studies of the fragrance given off by certain springtime flowers. He determined the nitrogen compounds in the concentrated headspace of the picked flowers of broom, narcissus, honeysuckle, lilac, *Pittosporum tobira* Ait., false acacia, *Wistaria sinensis* D.C., lily, olive tree flowers, seringat and *Coronilla emerus* L. The identified compounds are also shown in Table I.

Mookherjee et al.[8,9] in 1988 and 1989 published their results of a comparative analysis of the headspace volatiles of some important fragrance and flavor raw materials. They studied the main constituents, including nitrogen compounds, emitted by living and picked flowers of jasmine, freesia, purple lilac, Easter lilies and narcissus. They showed

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Table I. Nitrogen compounds in absolutes and headspaces of flowers

Nitrogen Compound	Flower/Ref.
alkanaloximes (C-9,10,11)	orange[6]
alkanenitriles (C-9,10,11)	orange[6]
2-methylpropanal oxime	longoza[6]
2-methypropanenitrile	honeysuckle, longoza[6]
2-methyl-1-nitropropane	longoza[6]
2-methylbutanal oxime	honeysuckle, longoza[6]
2-methylbutanenitrile	bitter orange blossom, honeysuckle, longoza[6]
2-methyl-2-butenenitrile	honeysuckle[6]
3-methylbutanenitrile	honeysuckle, longoza[6]
3-methyl-1-nitrobutane	honeysuckle, longoza[6]
6-methyl-5-hepten-2-one oxime	orange[6]
citral oxime	orange[6]
citral-isooxazole derivative	orange[6]
farnesylacetone oxime	orange[6]
farnesylacetone isooxazole derivative	orange[6]
2-aminobenzaldehyde	broom, *Pittosporum tobira* Ait., false acacia, lily, seringat, *Coronilla emerus* L.[7]
phenylacetonitrile	ylang-ylang, bitter orange blossom[6] broom, narcissus, honeysuckle, false acacia, seringat, *Wistaria sinensis* D.C.[7]
phenylacetaldehyde oxime	bitter orange blossom[6] broom, honeysuckle, false acacia[7]
1-nitro-2-phenylethane	ylang-ylang, bitter orange blossom[6] honeysuckle, false acacia[7]
methyl anthranilate	hyacinth, ylang-ylang, bitter orange blossom[6] lilac, false acacia, lily, *Coronilla emerus* L.[7]
N-methyl methyl anthranilate	bitter orange blossom, hyacinth, ylang-ylang[6]
N-formyl methyl anthranilate	hyacinth, bitter orange blossom[6]
N-acetyl methyl anthranilate	bitter orange blossom[6]
ethyl anthranilate	hyacinth[6]
methyl nicotinate	tuberose[6] false acacia, *Coronilla emerus* L.[7]
ethyl nicotinate	tuberose[6]
indole	bitter orange blossom, hyacinth, tuberose[6] broom, narcissus, honeysuckle, lilac, *Pittosporum tobira* Ait., *Wistaria sinensis* D.C, false acacia, lily, seringat, *Coronilla emerus* L., olive tree flower[7] jasmin, purple lilac, Easter lily, narcissus[8,9]
skatole	tuberose[6]
quinoline	hyacinth[6]
6-methylquinoline	hyacinth[6]
6-methyltetrahydroquinoline	hyacinth[6]
2,5-dimethylpyrazine	tuberose[6]
2-ethyl-3,5-dimethylpyrazine	jasmin[8]
an ethyldimethylpyrazine	freesia[8]
ethyltrimethylpyrazine	freesia[8]
2-isobutyl-3-methoxypyrazine	hyacinth[6]
benzothiazole	narcissus, olive tree flower, seringat, *Coronilla emerus* L.[7]
benzothiazolone	narcissus[7]

that there were definite differences in the chemical composition of the living and picked flowers. For instance, indole, which occurred in high concentration in the living flowers, decreased significantly in the picked flowers.

Having discussed some general publications about nitrogen compounds in various flower isolates, we will now treat some particular flowers in more detail with respect to the occurrence of nitrogen derivatives.

Jasmine Flower: The fragrance of jasmine was described in detail by Demole[10] in 1982. He also discussed the chemical composition of jasmine flower oil, and mentioned that up to 1980, 22 nitrogen compounds have been detected in the oil. These compounds comprise, apart from indole and methyl anthranilate, mainly pyridine derivatives, which are important for the sensory qualities of jasmine flowers. Toyoda et al.[11] reported that jasmine absolute contains nicotinic acid derivatives and 3/4-alkyl-substituted pyridines. They determined 3- and 3,4-alk(en)yl substituted pyridines in the absolute and mentioned that those compounds modulated the floral notes of other constituents.

Nofal et al.[12] found four 2-substituted pyridines in jasmine absolute of Egyptian origin. These compounds contribute to a specific, slightly burnt roasted aroma touch of the absolute.

Flower of Narcissus: Various studies have been devoted to different species of narcissus during the last decade.

Joulain[7] studied the fragrance given off by the picked flower of narcissus. Apart from the main oxygen derivatives, he detected a new nitrogen compound, benzothiazolone.

Mookherjee et al.[9] made a comparative analysis of the headspace volatiles of living and picked flowers of narcissus. They determined 5.0% (percentage of GC peak-area surface) indole and 0.2% phenylacetonitrile in the headspace of living narcissus flowers, whereas the headspace of the picked flowers contained only 1.0% indole and no phenylacetonitrile at all.

Loo and Richard[13] reported on an intensive study of narcissus absolute. They mentioned that, although 192 compounds were identified, it was found that the major compounds were not directly responsible for the characteristic odor of narcissus. Although they isolated a basic fraction, they did not determine any nitrogen compound. The authors mentioned that in the past it was found that indole and methyl anthranilate were major components in the basic fraction; they could not confirm these findings.

Ehret et al.[14] more recently published an investigation on new organoleptically important constituents of narcissus absolute.They studied its volatile and olfactive important fractions and found 80 new minor constituents in addition to almost 200 components already known in the literature. Among these, more than 20 contribute significantly to the complex floral odor of this absolute, whose aspects are reminiscent of jasmine, rose, violet, tuberose and orange flower. They mentioned that, for instance, phenylacetonitrile contributed significantly to the odor aspect of jasmine or orange flower absolute. Maurer and Hauser[15] in 1991 detected four new pyridine derivatives in jonquil absolute (*Narcissus jonquilla* L.)

These compounds were (Z)- and (E)-isomers of 3-(1-butenyl)-pyridine and 3-(1-butenyl)-4-propylpyridine. Researchers found that the compounds have very strong pungent pyridine-like odors in concentrated form. When diluted, however, these compounds exhibit different nuances of green and flowery odors. Very recently van Dort et al.[16] reported on an extensive study of the essential oils of two narcissus varieties, *N. trevithian* and *N. geranium*. The researchers described the analysis and synthesis of a number of new compounds found for the first time in narcissus oil. On the basis of their findings no characterimpact compounds were found in narcissus. They detected the following nitrogen compounds in the oils:indole, oxindole, diphenylamine, phenylacetonitrile, benzothiazole and 2-isobutyl-3-methoxypyrazine. Regarding the nitrogen-containing heterocyclic compounds, such as methoxypyrazines, they mentioned that such minor components can be of great influence on the quality of the fragrance.

Table II. Frequency of occurrence of nitrogen compounds in the headspace of living orchid flowers (total of 156 headspace analyses)

Nitrogen compound	Frequency of occurrence number	percentage
indole	46	29
methyl anthranilate	14	9
2-aminobenzaldehyde	14	9
phenylacetonitrile	9	6
phenylacetaldehyde oxime	5	3
2-methylbutanenitrile	5	3
N-methyl 2-aminobenzaldehyde	3	2
1-nitro-2-phenylethane	3	2
2-methylbutanal oxime	3	2
3-methylbutanal oxime	3	2
3-methylbutanenitrile	2	1
2-isobutyl-3-methoxypyrazine	2	1

Bitter Orange Flower: In 1979 Sakurai et al.[17] studied the odorous constituents of the absolute from the flowers of *Citrus unshiu* Marcovitich, which resembles *Citrus aurantium* L., ssp. *amara* Engl., the normal bitter orange. They mentioned that the *Citrus unshiu* flower has a very delicate, floral, fruity, green and somewhat sweet-pungent odor. They determined in the oil, apart form the main constituents, the following nitrogen compounds: phenylacetonitrile (4.7%), methylanthranilate (2.0%), indole (0.3%) and trace constituents phenyl acetaldoxime, 1-nitro-2-phenylethane and 3-ethyl-4-methylpyridine. As mentioned before, Kaiser and Lamparsky[6] also investigated the absolute and headspace of bitter orange flowers. The identified nitrogen compounds are shown in Table I.

Orchid Flowers: In his excellent book entitled *The Scent of Orchids* Kaiser[18] describes 156 quantitative analyses of the headspace composition of living orchid flowers. Apart from indole and methyl anthranilate all nitrogen compounds were present as minor (< 0.1%) constituents. The most frequently occurring nitrogen compounds were indole (in 29% of the analyses), methyl anthranilate (9%) and 2-aminobenzaldehyde (9%). The frequency of the occurrence of the nitrogen derivatives is shown in Table II.

Champaca Flower: In 1989 Kaiser[19] reported the results of an investigation on the new volatile constituents of the flower concrete of *Michelia champaca* L. More than 20 nitrogen compounds occurred in the flower extract. The main nitrogen constituents were phenylacetonitrile, methyl anthranilate and indole. As minor constituents oximes and isooxazoles were found.

Bird Cherry Flowers: Surburg et al.[20] in 1990 reported their studies on the volatile constituents of European bird cherry flowers. More than 70 compounds were identified, from which a number of nitrogen-containing constituents, like phenylacetonitrile, indole, methylanthranilate, anthranilic aldehyde, 2'-aminoacetophenone and nicotinic aldehyde. Some nitrogen compounds have previously not been found in nature, such as methyl esters of N-formyl-leucine and N-formylisoleucine, N-(2-acetylphenyl)formamide and 1,4-dihydro-2-methyl-2H-3,1-benzoxazine.

Volatile Nitrogen Compounds in Essential Oils

Volatile nitrogen compounds, often called the basic fraction, can easily be isolated from essential oils by an acidic extraction, as recently described by Maurer and Hauser.[15] Almost every essential oil contains some nitrogen compounds as trace constituents. More than 20 years ago[21,22] researchers at Naarden detected a series of olfactively interesting nitrogen compounds in the basic fraction of the following oils: *Artemisia absinthium*, angelica, carrot seed, coriander seed, clary sage, celery, lavandin, parsley, rosemary, spike lavender and vetiver. The qualitative sensory properties of the whole basic fraction are shown in Table III.

Tables IV, V, VI and VII list the essential oils known to contain derivatives of pyridine, quinoline, pyrazine, and thiazole, respectively. The occurrence of published nitrogen derivatives in selected essential oils will be discussed below.

Coriander Oil: In 1988 Lamparsky and Klimes[23] published their results of an investigation of heterocyclic trace components in the essential oil of coriander. They determined 15 N-containing compounds: 9 substituted pyrazines, 3 substituted pyridines and 3 substituted thiazoles.

Galbanum Oil: As early as 1969 Bramwell et al.[24] detected 2-sec.butyl-3-methoxy-pyrazine in galbanum oil. In 1970 Murray et al.[25] found additional substituted methoxy-pyrazines in galbanum oil.

Lavandula Oils: The lavandula oils concern lavender, lavandin and spike lavender. Substituted pyridines and pyrazines play an important role for the modification of the floral odor of lavandin.[21,22] Spike lavender oil has been studied in detail by ter Heide et al.[26] They confirmed the presence of heterocyclic nitrogen derivatives.

Orange Oil: Recently Thomas and Bassols[27] published their results on the occurrence of pyridines and other bases in orange oil. They found that cold-pressed Florida (Valencia) orange oil contained 16 substituted pyridines, the main one of which is 3-hexylpyridine at approximately 20 ppb. Alkyl-substituted pyridines were also detected in Brazilian (Pera)

Table III. Odor descriptions of basic fractions of essential oils

Oil	Odor descriptions of basic fraction
Artemisia absinthium	strong green note, pyridine-like; somewhat pea-like
angelica	intensive green, pyrazine-like
carrot seed	green, pyridine characteristic
coriander seed	intensive unripe green, peas-like, more pyrazine than pyridine connotation
clary sage	green, tobacco-like
celery	green bean, vegetable-note, rye bread connotation
lavandin	intensive note, fresh, green, somewhat spicy
parsley	characteristic rye bread-note
rosemary	interesting, musty leaf-like
spike lavender	intensive green note, modifier for main constituents
vetiver	intensive vetiver-like, pyrazine note

Table IV. Pyridine derivatives identified in essential oils[21-31]

Substituted pyridine	Essential oil in which the substituted pyridine was identified	Substituted pyridine	Essential oil in which the substituted pyridine was identified
unsubstituted	peppermint, spearmint	(E)-3-(1-butenyl)-	jonquil, orange, spearmint, peppermint
2-methyl-	lavandin, palmarosa, petitgrain, peppermint, spearmint	2-pentyl-	coriander, orange, spearmint, vetiver
		4-pentyl-	vetiver
3-methyl-	palmarosa, petitgrain, spearmint	2-ethyl-4-isopropenyl-	spearmint, peppermint
4-methyl-	palmarosa, petitgrain	2-isobutenyl-4-methyl-	fig leaf, palmarosa
2,3-dimethyl-	palmarosa	3-(4-methylpentyl)-	orange
2,4-dimethyl-	palmarosa, petitgrain	3-hexyl-	orange
3,5-dimethyl-	palmarosa	2,4-diisopropenyl-	spearmint, peppermint
2,6-dimethyl-	palmarosa, petitgrain, clary sage, spearmint	3-heptyl-	orange
		5-hexyl-2-methyl-	orange
2-ethyl-	palmarosa, spearmint	3-(4-methylhexyl)-	orange
3-ethyl-	palmarosa, orange, spearmint	3-octyl-	orange
4-ethyl-	palmarosa	5-(Z)-(1-butenyl)-2-propyl-	spearmint, peppermint
3-ethyl-5-methyl-	petitgrain	5-(E)-(1-butenyl)-2-propyl-	spearmint, peppermint
5-ethyl-2-methyl-	spearmint	3-(Z)-(1-butenyl)-4-propyl-	jonquil, spearmint, peppermint
2-propyl-	spearmint	3-(E)-(1-butenyl)-4-propyl-	jonquil, spearmint, peppermint
3-propyl-	orange, spearmint	2-phenyl-	orange
4-propyl-	spearmint	3-phenyl-	orange, palmarosa, peppermint, spearmint
4-isopropenyl-	spearmint		
3-isopropyl-	carrot seed, lavandin, rosemary	4-phenyl-	orange
2-isopropyl-4-methyl-	peppermint, spearmint	2-methyl-5-phenyl-	orange
2-isopropyl-5-methyl-	carrot seed, lavandin, parsley	3-phenyl-4-propyl-	peppermint, spearmint
3-isopropyl-6-methyl-	carrot seed, clary sage, lavandin	5-phenyl-2-propyl-	peppermint, spearmint
4-isopropyl-2-methyl-	peppermint, spearmint	3-benzyl-	peppermint, spearmint
2-isopropenyl-4-methyl-	peppermint, spearmint	3-phenyl-4-propyl-	peppermint, spearmint
2-isopropenyl-5-methyl-	palmarosa, spike lavender	5-phenyl-2-propyl-	peppermint, spearmint
4-isopropenyl-2-methyl-	lavandin, peppermint, spearmint	2-acetyl-	coriander, celery seed, petitgrain, peppermint, spearmint
5-isopropenyl-2-methyl-	orange, palmarosa		
2-butyl-	coriander, spearmint	2-acetyl-4-isopropyl-	spearmint
3-butyl-	orange, palmarosa, spearmint	2-acetyl-4-isopropenyl-	spearmint
4-butyl-	spearmint	4-acetyl-2-isopropenyl-	spearmint
(Z)-3-(1-butenyl)-	jonquil, spearmint, peppermint	2-pentanoyl-	celery seed

orange oil. The flavor threshold concentration of 3-hexylpyridine in water was found to be 0.28 ppb. The authors mentioned that trained flavorists described 3-hexylpyridine as having a fatty, citrus, orange note.

Recently Maurer[82] for the late A. F. Thomas wrote an interesting article on alkaloids, bases and essential oils. They mentioned the identities and organoleptic qualities of a series of alkaloids, such as substituted pyridines in tobacco flavor, juniper oil, sweet orange peel oil and jonquil absolute.

Palmarosa Oil: Surburg[28] made a thorough study of the minor components of palmarosa oil. Special attention was paid to the basic nitrogen-containing heterocyclics, comprising more than 40 pyrazines, pyridines, oxazoles and thiazoles. He mentioned that the substances contributed to the typical rye bread odor of palmarosa oil.

Patchouli Oil: As early as 1970 van der Gen et al.[29] demonstrated the occurrence of heterocyclic nitrogen compounds in patchouli oil. More recently Maurer and Hauser[14] reported on 3- and 3,4-substituted pyridines in patchouli oil.

Petitgrain Oil: It has been known since 1973[21,22] that 2-alkyl-3-methoxypyrazines are characteristic for the leafy green odor of petitgrain oil.

Peppermint and Spearmint Oil: Sakata et al.[30] reported the presence of 3-phenylpyridine, 3-phenyl-4-propylpyridine and 2-phenyl-5-propylpyridine in cornmint

Table V. Quinoline derivatives in essentials oils

Substituted quinoline	Essential oil in which the substituted quinoline was identified
unsubstituted	absinth, clary sage, parsley, peppermint, spearmint
2-methyl-	clary sage
2-acetyl-	parsley

Table VI. Pyrazine derivatives in essential oils[21-31]

Substituted pyrazine	Essential oil in which the substituted pyrazine was identified
methyl-	palmarosa
2,3-dimethyl-	carrot seed, coriander, lavandin, palmarosa
2,5-dimethyl-	coriander, palmarosa, spearmint, vetiver
2,6-dimethyl-	carrot seed, coriander, lavandin, palmarosa, rosemary
vinyl-	palmarosa
ethyl-	palmarosa
2-ethyl-5-methyl-	carrot seed, coriander, lavandin, petitgrain, palmarosa, vetiver
2-ethyl-6-methyl-	carrot seed, coriander, lavandin, palmarosa, spearmint, vetiver
trimethyl-	coriander, palmarosa
tetramethyl-	coriander, palmarosa
2,5-diethyl-	lavandin, vetiver
2,6-diethyl-	palmarosa
2-ethyl-3,5-dimethyl-	coriander, palmarosa
2-ethyl-3,6-dimethyl-	carrot seed, coriander, palmarosa
2,3-diethyl-5-methyl-	palmarosa
2,5-diethyl-3-methyl-	palmarosa
2,6-diethyl-3-methyl-	palmarosa
2-isobutyl-3-methyl-	carrot seed
2-isopentyl-3,6-dimethyl-	palmarosa
2-methoxy-3-methyl-	absinth
2-isopropyl-3-methoxy-	absinth, angelica root
2-isobutyl-3-methoxy-	absinth
2-sec.butyl-3-methoxy-	absinth
2-isopropyl-3-methoxy-6-methyl-	absinth, angelica root, carrot seed, clary sage, coriander, galbanum, parsley seed, petitgrain, rosemary
2,6-dimethoxy-3-isopropyl-5-methyl-	angelica, galbanum, geranium
2-acetyl-	sesame
2-acetyl-3-methoxy-6-methyl-	galbanum
2-(alpha-hydroxyisopropyl)-3-methoxy-5-methyl-	galbanum

Table VII. Thiazole derivatives in essential oils[21-31]

Thiazole derivative	Essential oil in which the thiazole derivative was identified
2,4,5-trimethyl-	coriander
2-isopropyl-4-methyl-	coriander
2-isobutyl-	rosemary
2-isobutyl-4,5-dimethyl-	coriander
benzothiazole	celery seed

oil. Ishihara et al.[31] recently found new pyridine and other basic components in spearmint and peppermint oil. A total of 38 nitrogen-containing components, including 11 new pyridine derivatives, were identified. A major component was 2-acetyl-4-isopropenylpyridine, which possesses a powerful grassy-sweet and minty odor.

Sensory Properties of Nitrogen Compounds

The determination of the sensory properties of nitrogen compounds (i.e. the odor quality and threshold value in various media) is a complicated matter.

First, this determination is a rather subjective task due to intra- and inter-individual differences. Secondly, the qualitative sensory properties of the compounds often are strongly dependent on their concentration. This olfactive dependence on stimulant concentration may be caused by the so-called multiplicity of the compound. Multiplicity of a compound is its ability to trigger different receptor sites at various concentrations. Another aspect of the sensory evaluation of nitrogen compounds is that the determination of the odor quality often is influenced by the type of pleasantness or unpleasantness. Buttery et al.[32] for instance reported that the odors of the alkylpyrazines are generally associated with pleasant roasted food (such as chocolate, coffee, roasted nuts), whereas the odors of alkyl-pyridines are less pleasant, more amine-like. Moreover the sensory properties of strong-smelling (intensity) trace constituents are dependent on the media in which the properties are determined.

Summarizing, it is advisable to determine the sensory properties of natural nitrogen trace constituents in their original media and at genuine concentration. The odor characters of series of compounds will be discussed in more detail below.

Aliphatic Nitrogen Compounds: Relatively little is known about the sensory properties of natural aliphatic nitrogen compounds. A series of these compounds has been found in flower scents.[6,20] These compounds concern amino acid derivatives and degradation products, for instance from leucine, as there are oxime, nitrile and nitro derivatives. The odor qualities of these compounds show resemblance with the corresponding aldehydes, alcohols and ethers.

Aromatic Nitrogen Compounds: These compounds, as mentioned before, occur in highest concentration and most frequently in natural isolates. The most important representatives of this group are indole and methyl anthranilate, whose odors are well known. Indole has an animal, fecal odor in higher concentration (>0.1% in diethyl phthalate); in lower concentration its odor character turns to aromatic floral. Methyl anthranilate, homologues and analogues have citrusy odor notes more or less resembling mandarin. Methyl anthranilate itself is a character-impact compound in mandarin and tangerine oil. 2-Aminobenzaldehyde, 2'-aminoacetophenone, phenylacetaldoxime, phenylacetonitrile, 1-nitro-2-phenylethane all have aromatic floral and somewhat spicy odor characteristics.

Pyridines: Pyridine and its lower homologues (up to C-3) have pungent, diffusive, amine-like, disagreeable odors in higher concentration (> 0.1%) in water. Maass and Zablinsky[34] described the odor of 3-butylpyridine as sweetish, reminiscent of trimethylpyridine. Buttery et al.[32] reported that in dilute water solutions 2-pentylpyridine has a fatty and tallowy odor. According to Thomas and Bassols,[28] trained flavorists describe 3-hexylpyridine as having a fatty, citrus, orange note, while 5-hexyl-2-methylpyridine has fatty, fishy, metallic, and mandarin notes.

Table VIII. Odor descriptions of pyridine derivatives[31]

Substituted pyridine	Odor description
4-isopropenyl-	green-bitter, nutty-beany, slightly sweet
4-isopropenyl-2-methyl-	ether-like, browny-acidy, radish (ozone-like)
2-ethyl-4-isopropyl-	slightly nutty, herbal, bitter
2,4-diisopropenyl-	earthy, slightly seaweed, somewhat citrus
2-isopropyl-4-methyl-	earthy green, somewhat sour and citrus
4-isopropyl-2-methyl-	amine-like, ozonous green, violet perilla
3-[(Z) and (E)-1-buten-1-yl]-2-propyl-	herbal, white floral-like, minty
5-[(Z) and (E)-1-buten-1-yl]-2-propyl-	somewhat rose, fermented beany, wormwood
3-[(Z) and (E)-1-buten-1-yl]-4-propyl-	earthy green, green beany, powder, musk-like
3-phenyl-	nutty, roasted soybean, methyl cinnamate-like
4-methyl-3-phenyl-	minty, sweet, fermented earthy
5-phenyl-2-propyl-	green tomato leaf, slightly methyl cinnamate-like
2-acetyl-4-isopropenyl-	grassy, sweet, minty, somewhat amber-like
4-acetyl-2-isopropenyl-	weak herbal green, fermented roast
2-acetyl-4-isopropyl-	grassy-green leaf, green herbal, somewhat violet

Ishihara et al.[31] published odor profiles of synthetic pyridine compounds identified in spearmint oil. Their findings are shown in Table VIII; they concluded that the nitrogen compounds seem to greatly contribute to the characteristic odor profile of the spearmint oil because of their powerful and pungent aromas. They also mentioned that is was reported that 2-acetylpyridine has a strong roasted and coffee-like odor, while that of 2-acetyl-6-methylpyridine was chocolate-like. They reported that 2-acetyl-4-isopropenylpyridine, which is a major component (34%) in the basic fraction of spearmint oil, has a powerful grassy-sweet and minty odor.

Surburg[70] and Sonnenberg[71] reported that it may be possible that substituted pyridines are formed as a result of the isolation process.

Pyrazines: In contrast to pyridine derivatives, a great deal is known[32-78] about the sensory properties of pyrazine derivatives. With respect to their odor quality, some main groups of pyrazine derivatives can be distinguished:

- Lower alkyl-substituted (up to 5 carbon atoms).
- Higher alkyl substituted (over 5 carbon atoms).
- Alkyl- & methoxy-substituted.
- Other substituents.

Table IX. Odor descriptions of natural pyrazine derivatives

Substituted pyrazine	Odor description/Ref.
methyl-	earthy, leafy, dusty[50] roasted nutty[52] burnt, roasted[62] nutty, roasted[77]
2,3-dimethyl-	sweet dusty[50] peanut-like[52] green, nutty[77]
2,5-dimethyl-	earthy, raw potato[35] ribes, burnt, cheesy[50] burnt, wheat-like[52]
2,6-dimethyl-	estery, oxidized[50]
ethyl-	buttery, rum[62] roasted[77]
2-ethyl-3-methyl-	butterscotch, nutty[62]
trimethyl-	estery, creamy[50] sweetish, cocoa, musty, ash-tray[53] roasted, earthy[67]
tetramethyl-	creamy, sweet, cardboard[50]
2,3-diethyl-	green, grassy, musty, earthy, vegetable[53]
2,6-diethyl-	raw potato[43]
2-ethyl-3,5-dimethyl-	somewhat potato-like[41] meaty, musty, green[50]
2-ethyl-3,6-dimethyl-	baked potato[44] potato-like[46] earthy, roasty[67]
2,5-diethyl-3-methyl-	earthy, roasty[67]
2-isobutyl-3-methyl-	green (bell pepper), dry and sweet notes[21]
2-isopentyl-3,6-dimethyl-	green[56]
2-methoxy-3-methyl-	popcorn, potatoes[49] roasted peanuts[54] nutty, roasted, chocolate-like[63]
2-isopropyl-3-methoxy-	strong galbanum-like[49] earthy, musty, potato bin[57] green pepper, earthy[61] bell pepper[66] earthy, roasty[67]
2-isobutyl-3-methoxy-	strongly green (bell pepper)[21] green bell pepper[49] musty, earthy, bell pepper[57] green pepper[61] pepper[66]
2-sec.butyl-3-methoxy-	green (peas, bell pepper, galbanum)[25]
2-isopropyl-3-methoxy-6-methyl	strongly green (bean), floral and ethereal undertone; no nutty notes[21]
2,6-dimethoxy-3-isopropyl-5-methyl-	nutty, green (bell pepper), woody bynote[21]
acetyl-	breadcrust, nutty, reminiscent of acetamide, chimney soot[21]
2-acetyl-3-methoxy-6-methyl-	weak breadcrust, green, musky note, chimney soot[21]
2-(alpha-hydroxyiso-propyl)-3-methoxy-5-methyl	weak, green (bell pepper), earthy, note, chimney soot[21]

The odors of lower alkyl-substituted pyrazines are in general described as being roasted, herbaceous, nutty and chocolate-like.[32] More specific odor descriptions include burnt, roasted, brown, chocolate, butterscotch and nutty.[59,62,67]

The odors of higher alkyl-substituted pyrazines are more earthy and somewhat green, with aromatic and woody notes.[21,56] The alkyl- and methoxy-substituted pyrazines have strongly green, somewhat earthy odor characteristics with roasted, nutty and floral by-notes.[21,52,63,66,67]

Specific odor descriptions are worth mentioning: 2-isobutyl- and 2-sec.butyl-3-methoxypyrazine possess the characteristic note of green bell pepper and a clear galbanum oil connotation, respectively.

The odor descriptions of pyrazine derivatives are shown in Table IX.

Thiazole Derivatives: The odor qualities of substituted thiazoles have been described in detail by Ho and Jin.[79] Pittet and Hruza[77] stated that the low 2-alkylthiazoles have green, vegetable-like odors.

Buttery et al.[78] reported that some 4,5-dialkylthiazoles possessed potent bell pepper aroma.

Viani et al.[81] reported that 2-isobutylthiazole occurred in tomato and that it possessed a strong green odor resembling that of tomato leaf.

Conclusion

Volatile nitrogen compounds occur in many flower scents and essential oils. Although the concentration of these compounds in the natural isolates ie often lower than 0.01% (100 ppm);, they contribute significantly to the sensory properties of the naturals.

Those nitrogen compounds can modify or modulate in an olfactive way the main constituents of the isolate.

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Address correspondence to Mans H. Boelens, Boelens Aroma Chemical Information Service, Groen Van Prinstererlaan 21, 1272 GB, Huizen, The Netherlands.

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