PERFUMER & FLAVORIST

Aroma Chemicals and Citrus Oils

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We created a computer database based on information from 1400 volatile food compounds. The database can be searched by "chemical compounds" or "food products." For example, under "phenylacetaldehyde" we find the following information:

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One Compound has been selected:

Name: Phenylacetalaldehyde
CAS number: 122-78-1
FEMA-GRAS: 2874
Other names: Benzeneacetaldehyde; Phenylethanal
Supplier(s): Givaudan, BASF/FDO, Toyotama, H&R

Phenylacetaldehyde is found in these foods at the
following concentrations:
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	ppm
Grapefruit juice	0.02
Tomato	0.1
Cider	0.2
Black tea	1.9-2.0
Bilberry	0.002-0.003
White bread	0.8-1.5
White wine	0.12
Mushroom fr	0.1-0.3
Asparagus	0.001
Beer	0.01
Potato chips	1.8-5.4
Beans	0.01

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If we search for "food products" and choose "citrus fruits," we find:

Aroma Chemical Information
Search by product: Citrus Fruits

Product	Profile	Function Group
Orange	Aliphatic	Aldehydes
Lemon	Monoterpenoid	Alcohols
Grapefruit	Sesquiterpenoid	Ketones
Grapefruit juice	Cyclic	S-compounds
Mandarin	Aromatic	N-compounds
		Hydrocarbons
		Acids
		Esters
		Lactones
		Acetals
		Phenols
		(EP)oxides
		Ethers
		Inorganic
		Miscellaneous

Three sets of data for citrus fruits are shown. The first, product, lists orange, lemon, grapefruit (juice), and Mandarin. The other two sets line up as columns: one with profiles, and the other with functional groups. By choosing one item from each column, for example, the screen shows:

Enter: 'Orange' - 'Aliphatic' - 'Alcohols'
Output:

		ppm
64-17-5	Ethanol	380.00
71-36-3	1-Butanol	1.50
556-82-1	2-Butenol-1,3-methyl	0.01
513-86-0	Butanone-2,3-hydroxy	0.01
6032-29-7	2-Pentanol	0.01
2305-21-7	Hexenol-1,trans-2	0.01

If only one of the citrus fruits had been chosen, then the following numbers of constituents would have appeared for each fruit, each with its quantitative occurrence.

Numbers of Citrus Oils Constitutents with Quantitative Data

Oil	Number
Orange	84
Lemon	47
Grapefruit	188
Mandarin	77

Because of overlap, there are about 275 different chemical compounds, from which about 180 are commercially available. These are only the compounds which have been quantified. Many more constituents (465) exist which have been qualified in citrus oils. For instance, in orange oils only 245 compounds have been identified.

A citrus oil can not be compounded on the basis of the known quantitative data, because many of the chemicals are not available.

Analysis of Citrus Oils

On a gaschromatogram of bitter orange bigerade oil, there are about one hundred peaks. The gaschromatograph separates the compounds and quantifies, but can not be used for identification.

Now couple the gaschromatograph with a mass-spectrometer. The mass-spectrometer makes a picture of each chemical but at the same time cuts or shoots the picture into pieces, so-called ions (of the chemical). If the pieces are put together, a complete, or almost complete, picture of the chemical appears and now we know its identity. In this way, with a GC coupled MS we could identify about 50 of the 100 chemicals which were present in the oil.

Next we concentrated bitter orange oil 30 times, which now shows 260 peaks from which about 100 could be identified by mass-spectrometric analysis, leaving 160 chemicals unidentified (at an average concentration of 25 ppm each). We believe that the same is true for other citrus oils. Citrus oils contain hundreds of chemical compounds, from which a great deal is unknown. For this reason it is impossible to exactly reconstitute a citrus oil.

Constituents occurring in citrus oils can be termed characteristic or essential or balance compounds or artifacts.

Characteristic—Compounds which are recognized by experts as representing a great deal of the organoleptic quality of the fruit or oil. So-called: character-impact-compounds.

Essential—Constituents are compounds necessary for the organoleptic quality but not characteristic.

Balance compounds—Neither characteristic nor essential, but make up the remainder of the naturally occurring materials in the oil.

Artifacts—Compounds which do not really occur in nature. They are, for instance, derived from herbicides, fungicides, pesticides or solvents or products formed during processing.

Let us not underestimate the artifacts. Up to now, 5,000 volatile compounds have been found in foods of which, in my opinion, at least 10% are artifacts.

Some constituents which are more or less characteristic of a particular citrus oil are in Table I. Each fruit also contains (so-called) character-impact compounds, as will be evident later on.

The concentration of characteristic or essential constituents in citrus oils sometimes may vary a

Table I. Characteristic Constituents

Fruit	Constitutents
Orange	decanal
Lemon	citral
Mandarin	anthranilates
Grapefruit	(D)-nootkatone
Lime	germacrene B

lot due to different circumstances. 1.55% citral was found in a lemon oil from lemons cultivated in a rural area of a Mediterranean country with a hot climate where summers are over 35° C and winters are below 10° C. 2.9% citral was found in a lemon oil from lemons cultivated at the coast with a moderate climate with summers over 25° C and winters below 15° C. The first low-citral-content oil shows a lack of character-impact in its organoleptic qualities. Another example is the total aldehyde content of bitter orange oils: From a hot climate, the range is 1-1.5%, and from a moderate climate, 2-3%.

Even more dramatic are the differences in concentrations of the main constituents due to different processing methods. A normal steam-distilled petitgrain bigerade oil (leaves of bitter orange) contains 25% linalool and 46.5% linalyl acetate. A hydrodiffusion oil contains 4.8% linalool and 72.8% linalyl acetate.

The principle of hydrodiffusion is the osmotic action of low pressure steam on vegetable cells. The steam flow goes through the vegetal load from the top directly down through the condenser. Another example is neroli oil. Steam-distilled oil from orange flowers contains 40-50% terpenes, while an absolute obtained by extraction contains 5-10% monoterepenes. One hundred constituents were identified and quantified from the peel, leaf and flower oils of the Seville bitter orange (see Table II).

Table III.

Chemical Composition (no.)	Unripe on Tree	Ripe on Tree	Dead 1-2 Weeks
Aliphatics (6)	0.00	0.5-1.0	Trace
Aliphatics aldehydes (20)	0.48	0.67	0.38
Monoterpenes (16)	98.00	96.50	96.00
Monoterpenoid deriv. (19)	0.74	1.00	1.67
Sesquiterpenes (5)	0.21	0.21	0.30
Sesquiterpenes deriv. (4)	0.04	0.17	0.40
Coumarin deriv. (2)	0.23	0.25	0.55
TOTAL	99.70	99.60	99.30

Last year and also this year we analysed the peel oils of living bitter oranges while ripening directly on the tree (see Table III). Something is happening during ripening and after picking the fruits (see Table IV).

Constituents of Citrus Oils

The most dominant (mono)terpene in all citrus oils is d-limonene. There also exists L-limonene. Look at the different names for one and the same limonene: cajeputene, carvene, cinene, citrene, dipentene, kautschin, p-1 8(9)-menthaldiene, and 1-methyl-4-isopropenyl-1-cyclohexene.

Quite a difference exists between the olfactive and organoleptic qualities of d- and L-limonene. Once d-limonene was purified from orange terpenes and L-limonene from turpentine to a purity over 99.9%. Experts immediately recognized d-limonene as orange-like and found L-limonene as harsh, turpentine-like.

The differences in organoleptic qualities of d- and L- forms is even more striking between (+)-nootkatone and (−)-nootkatone. (+)-nootkatone has a grapefruity odor, a bitter taste, and its threshold is 0.8 ppm in water and 30 ppm in air.

Table II.

Chemical Composition	Number of Compounds	Peel Oil %	Leaf Oil %	Flower Oil %
Aliphatic compounds	30	0.7	trace	trace
Monoterpenes	17	95.4	13.0	43.0
Monoterpenoid derivatives	25	1.8	84.0	50.7
Sesquiterpenoids	15	0.8	2.2	5.0
Benzenoids and miscellaneous	13	0.8	0.4	0.5
TOTAL	100	99.5	99.6	99.2

Table IV. Maximum Linalyl Derivatives

	Unripe 24-48 Hrs.		Ripe 24-48 Hrs.		Unripe	Ripe
	Blank	NR_3	Blank	NR_3	NR_3	NR_3
Aliphatics aldehydes	0.45	0.50	0.70	0.70	0.50	0.65
Monoterpenes	97.90	97.00	96.80	95.00	95.65	94.80
Monoterpenoid deriv.	1.05	2.00	0.50	2.70	3.56	4.00
Sesquiterpenes	0.17	0.17	0.17	0.17	0.16	0.19
Sesquiterpenes deriv.	0.04	0.05	0.10	0.15	0.03	0.16

On the other hand, (−)-nootkatone has a soft woody odor, is virtually tasteless, and its threshold is 700 ppm in water.

Most constituents of citrus oils, which contain an asymetric carbon atom are optically active. Generally, if the possibility of right- and left-handed citrus compounds exists, these compounds will be either left- or right-handed. In other words, citrus oils contain either the right-handed or the left-handed compounds, and the organoleptic qualities of these constituents in general are different. Synthetic aromatic chemicals with asymmetric C-atoms are almost always inactive (half right-handed and half left-handed). As a consequence, they have different olfactive and organoleptic qualities. So, a reconstituted oil with synthetic chemicals must have different properties from a natural oil.

During the 1986 Essential Oil Congress in Washington, there were two lectures of great interest about the adulteration of citrus oils. Drs. David McHale and John Sheridan used high pressure/performance liquid chromatography for the detection of adulteration of cold-pressed lemon oil. They demonstrated that this oil often was adulterated with lower quality steam-stripped oil. Besides they confirmed that non-natural components for lemon oil such as ethyl p-dimethylamino benzoate, auraptene and herniarin were used for adulteration.

Their technique, high pressure/performance liquid chromatography is very useful for the separation of high-boiling and nonvolatile constituents. It works at room temperature (or below) and has no problems with thermolabile (heat sensitive) compounds. With the right columns, one can also separate d- and L-forms of one product. However, the separation capacity of HPLC is not as good as GC. This HPLC technique is used every day for the separation and quantification of natural carotenoids.

Dr. Frey discussed detection of synthetic flavorant addition to some essential oils by selected ion monitoring GC/MS. With this method, he detected small amounts of dihydrolinalool in bergamot and neroli oil which means that they were adulterated with synthetic linalool.

Let me try to explain this technique. As already mentioned: GC = gaschromatograph *separates* mixtures of chemicals, citrus oils, and *quantifies* each compound. GC cannot *identify* then. We find A% of X, B% of Y, and so on. A and B are known; X and Y are unknown. The mass spectrometer (MS) makes a picture of each individual chemical, and at the same time cuts/shoots the picture into pieces, so-called ions. If all or most of the pieces are known, we put them together to get the complete picture; that is the identity of the chemical—X = limonene, and Y = linalool.

We can also work the other way around. With a known chemical, like a completely synthetic compound, put it into the mass spectrometer, which makes its picture and cuts it into pieces (ions). Thereafter, program the machine (MS) with one of the pieces and then feed the MS through the GC with a citrus oil. Now ask the MS to select only that chemical, which gives the same piece. Then the gaschromatograph shows, if present, a peak at exactly the same place and time (retention time) as the known chemical.

For the insiders, the MS was set as a detector for the GC for one important selected ion of a single compound, with a known fragmentation pattern and GC-retention time. Repeat the whole procedure five to ten times with different pieces, and if there is always a peak at the same place, more than likely the chemical is present in the oil. Because the MS is extremely sensitive, the whole method is very sensitive. One can detect down to 1 ppb and even lower.

The method can be used for the detection and identification of trace impurities in essential oils, other naturals, drugs, and so on. It can also be used to identify synthetic aroma chemicals as nature-identical compounds. In order to fully understand how this method works on synthetic aroma chemicals, a little biochemistry background is necessary.

In nature, for example with citrus plants, acetic acid is formed from (CO_2 and H_2O) carbon dioxide and water. Acetic acid is bound to an enzymatic system as acetyl-co-enzyme-A. A good analogy would compare this complex with a car and the enzymatic part with its motor. Nature can make a trail of such cars just by putting a new one in front of the others and finally parking a number of cars in line as fatty acids or derivatives. In this case, five cars give decanal.

Nature can also park one car vertically between two others. This develops beta-hydroxy methyl glutaryl, which goes via mevalonyl pyrophosphate (another enzymatic system) pathway to isoprenoids. For instance, citral. In fact, it is a bit more complicated, but starting materials and end products are correct.

Let us assume that nature starts to make a fatty acid and after parking four cars in line, nature changes its mind and parks one vertically between the first and the second. What happens then? Beta-methyl alkenyl-derivatives are produced. Where in nature are decanal and citral found together? In most citrus fruits. Citrus fruits contain the enzymatic systems to form decanal and citral.

In citrus fruits, expect beta-(3)-methyl alkenals. We synthesized a series of beta-3-methyl alkenals and could, indeed, detect beta-(3)-methyl-oct-2-enal in lemon oil (some hundreds ppm). Beta-(3)-methyl-oct-2-enal has a distinct citrusy odor and reinforces the organoleptic quality of lemon oil.

Citrusy Aroma Chemicals

Functional perfumery asks for fresh, floral, clean, and citrusy odors; chemically stable end products; certain tenacity, long-lastingness, fiber-, hair-, skin-substantivity; and olfactive value for the money. Chemical stability is the first requirement. Therefore, a lot of synthetic aroma chemicals with citrusy odors have been produced for functional perfumery.

Let us see what happens with linalool in a so-called heavy duty detergent during the wash procedure. Detergents contain sodiumperborate and tetra-acetal-ethylene diamine, which react with water at that temperature under formation of peracetic acid. Peracetic acid oxidizes the dirt, but also part of the perfume. It reacts with poly-substituted double bonds as present in linalool and its acetate. For this reason, certain synthetic aroma chemicals with citrusy odors are preferred in functional perfumery over the natural products.

We entered over 1,000 aroma chemicals with their commercial names and their chemical identities into the computer. We called the commercial names synonyms. Now we can study the structures and olfactive qualities of commercial chemicals with names referring to any kind of citrus fruit. When we search for all chemicals whose names start with "AGR" of Agrumen, the output is as shown in computer listing below. Some of the products referring to "Agrumen," indeed, have citrusy properties, others completely not, such as hexyl benzoate and 2-t.butyl-cyclohexyl acetate. With the argumen group, we cannot do much.

Next we search for chemicals starting with "AURA." Only three products appear and all are the same. These are condensation products of methyl anthranilate with hydroxy-citronellal, so-called Schiffs' bases, known for more than 50 years. Condensation products of anthranilates with aldehydes, so-called Schiffs' bases, often are in equilibrium with their starting materials. If this reaction is forced to the right (toward the end product) by distilling off all the water, nice yellow-brown tars are formed, which are practically odorless. Schiffs' bases can be crystallized from aromatic aldehydes, for instance, and make odorless crystals. Only when lower aldehydes are used (up to C_6), do odorifous Schiffs' bases develop, which can even be distilled.

These products have strong, long-lasting Mandarin-like odors. But where are the lower aldehydes in petitgrain-, neroli- and Mandarin oils? Could they be condensed with methyl anthranilate? These products may (could) be nature-identical.

The "bergamot" group is important in an economic way for compounding the fresh, floral bergamot-like perfumes. The products show good performance in extrait-perfumes, toilet waters and air fresheners, but are rather poor in functional perfumery (maybe except in soap) because of their chemical instability.

Linalyl acetate is well-known. Synthetic products are inactive and often contain impurities from starting materials (dihydrolinalyl-, pinanyl-, plinyl).

Myrcenyl acetate is produced in pure form, but mostly in mixtures with other acyclic and monocyclic terpenyl acetates. The product has a fine fresh floral odor resembling that of bergamot oil.

Still a more delicate odor comes from ocimenyl acetate, which to the best of our knowledge, is not commercially available. Surprisingly enough, this product has not yet been found in citrus oils. It could be present in bergamot oil.

Chemicals beginning with "CITR" also form an important group. Here again is a series of nitriles.

Most of these products are substitutes for citral. A few, like citrotone B and citroviol, hardly possess citrusy odors. All these products have been manufactured for stability reasons for functional perfumery. A mixed group with different structures is found in the "LEM/LIM" group.

Chemicals beginning with "NERO" also form an important group, with all synthetic aroma chemicals. None of these has been found in nature.

The beta-naphthyl derivatives are well known, which on dilution have some resemblance to orange blossom. These are pure synthetics. They

Sample Computer Listing

Synonyms Aroma Chemicals-Citrus

```
Enter:  *AGR*
Output:
AGREA (IFF)             : Ethyl anthranilate/dimethylcyclohexenecarboxaldehyde
AGRESTOL (Synarom)      : Hydratopaldehyde propylene glycol acetal
AGRUMEA (IFF)           : Methyl anthranilate/dimethylcyclohexenecarboxaldehyde
AGRUMAT (Dragoco)       : Hexyl benzoate
AGRUMEX (H&R)           : 2-t.Butylcyclohexyl acetate
AGRUNITRILE (Drag.)     : 3,7-Dimethyl-oct-6-ene nitrile
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Synonyms Aroma Chemicals-Citrus

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ENTER:  *AURA*
OUTPUT:
AURALVA (IFF)           : Methyl anthranilate/hydroxycitonellal
AURANTIOL (UC-BBA)      : Methyl anthranilate/hydroxycitonellal
AURANTESIN (H&R)        : Methyl anthranilate/hydroxycitonellal
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Synonyms Aroma Chemicals-Citrus

ENTER: *BERGA*
OUTPUT:

BERGAMAL (IFF)	: 2-Methylene-3,6-dimethyl-oct-6-enal
BERGAMOL (IFF)	: Linalyl acetate
BERGAMYL ACETATE (Giv.)	: Myrcenyl acetate
BERGAMATE (neo) (Quest)	: Myrcenyl acetate
BERGAMATE pseudo (DBCH)	: Myrcenyl acetate
BERGAMIATE iso (Drag.)	: Homomenthadienyl formates

Synonyms Aroma Chemicals-Citrus

ENTER: *CITR*
OUTPUT:

CITRALVA (IFF)	: 3,7-Dimethyl-2,6-octadiene nitrile
CITRANILE (Quest)	: 3,7-Dimethyl-2,6-octadiene nitrile
CITRONAMA (IFF)	: Methyl anthranilate/citronellal
CITRONELLYL NITRILE (DBCH)	: 3,7-Dimethyl-oct-6-ene nitrile
CITRONITRILE (PFW)	: 2,3,7-Trimethyl-2,6-octadiene nitrile
CITRONITRIL (H&R)	: 5-phenyl-3-methyl-pentenonitrile
CITRONWANIL (Wacker)	: 2-Benzyl-2-methyl-3-butenenitrile
CITROTONE B (IFF)	: 2-Hexyl-1,3-dioxolane
CITROVIOL (Dow)	: Nopyl acetate
CITRYL ACETATE (Dragoco)	: 10-Methyl-p-mentha-1,8-dienyl acetate
CITRYL NITRILE (Ni-Mo)	: 3,7-Dimethyl-2,6-octadiene nitrile

Synonyms Aroma Chemicals-Citrus

ENTER: *LEM* / *LIM*
OUTPUT:

LEMONILE (Givaudan)	: 3,7-Dimethyl-2(3),6-nonadiene nitrile
LEMORALE (IFF)	: Mix. limonene, citral, hydroxycitronellal
LIME OXIDE (Givaudan)	: Cyclic monoterpenoid ether
LIMETTAL (Quest)	: Mix. with 2-tridecenal
LIMONENE ALD (Takasago)	: p-Menthadiene aldehyde

Synonyms Aroma Chemicals-Citrus

ENTER: *NERO*
OUTPUT:

NEROLI ACETAL (Wacker)	: 1,1-Dimethoxy-2,5-dimethyl-2-vinyl-4-hexene
NEROLI ALD. (Wacker)	: 2,5-Dimethyl-2-vinyl-4-hexenal
NEROLIN BROMELIA (DBCH)	: beta-Naphthyl ethyl ether
NEROLIN (Giv./Rhone P.)	: beta-Naphthyl ethyl ether
NEROLI KETONE (Toyotama)	: 1-(p-Menthen-6-yl)propanone-1
NEROLIN YARA YARA (DBCH)	: beta-Naphthyl methyl ether
NEROLOXIDE (Dragoco)	: 4-Methyl-2-(2'-methylpropenyl)dihydropyran
NERONE (Givaudan)	: 1-(p-Menthen-6-yl)propanone-1
NEROXYL (Roure)	: Methyl-2,5-dimethyl-2-vinyl-4-hexenoate

Synonyms Aroma Chemicals-Citrus

ENTER: *ORAN*
OUTPUT:

ORANGER CRYST (Givaudan)	: Methyl beta-naphthyl ketone
ORANGINAL (H&R)	: 2-Methyldecanal
ORANIL (Roure)	: Tetradecanenitrile
ORANTHA-L-super (Takasago)	: Methyl anthranilate/L-hydroxycitronellal
ORANGE, jasm. (BASF/FDO)	: 2-Methyl-3-(p-methylphenyl)propanal
ORANGE carb. (Bedoukian)	: Aliphatic aldehydes

Synonyms Aroma Chemicals-Citrus

Miscellaneous:

MANDARIN ALD. (Firmenich)	: 2-Dodecenal
TANGENIL (Quest)	: Mix. 2-Tridecenenitrile
GRAPELIONE (Grau)	: Mix. sulphurated orange terpenes
ZESTAL (Mane F)	: Mix. sulphurated orange terpenes
ZESTORIL (Citrus & Allied)	: Mix. sulphurated orange terpenes

show a good fiber substantivity (pi-electrons) when used in detergent perfumes.

The "orange" group has mixed aroma chemicals, some of which we have mentioned before, Orantha-L-Super is again a Schiffs' base. It has been on the market for one year and is, indeed, a superb product, if compared with other Schiffs' bases of hydroxycitronellal. Notice here again, it is the optical active "left-handed" L form.

Twenty aldehydes were identified in bitter orange peel oil: C_6-C_{14}. The most important for the organoleptic quality are N-decanal, 2-trans,4-cis-decadienal. The aldehydes must be very pure and judged in dilution (lower than 1%). Higher unsaturated aldehydes C_{12} and C_{13} should have Mandarin-like odors. They show these qualities only in high dilutions of 0.1%.

Finally, we search for miscellaneous chemicals in the database. Some products of this group have been treated before. The others are so-called "sulphurated orange terpenes."

Aroma chemicals with green odors should also be mentioned because they occur in bergamot and petitgrain oil. Cis-3-hexenol and its acetate almost always occur in green leaves and green fruits. A disadvantage of these products is that they are rather volatile.

The occurrence of the methoxypyrazines is a nice demonstration of the fact that constituents at ppm level play an important role in the overall organoleptic qualities of some citrus oils. These products have very low threshold values (1 at 0.1-0.001 ppb) and are long-lasting.

Conclusion

Natural citrus oils cannot be reconstituted (substituted) by compounding aroma chemicals for three reasons: (1) Citrus oils are complex mixtures, up to 300 chemicals of which many are unknown. (2) If they are known, many are not commercially available. (3) Individual constituents with asymmetric carbon atoms, mostly are optically active. A lot of aroma chemicals are not.

On the other hand, aroma chemicals with citrusy odors deserve their own place for compounds in functional perfumery, mainly for stability reasons.

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