

## Formulating with citrus

# New Developments in Citrus Fragrance Ingredients

The aroma chemical aspects and new discoveries in both natural and synthetic citrus ingredients

Michael Britten-Kelly

Of all the ingredients on the perfumer's palette, surely none are more instantly recognizable to the public than those in the citrus category. Fresh juicy oranges, sulfurous tangy grapefruit, tart puckery lemons and heady sweet limes all bring to mind a host of pleasant associations in which taste and smell play an equal part. Perfumers have made good use of these ingredients to add freshness and lift in many classic colognes, such as *Eau de Rochas*, *Ô de Lancôme* and *Acqua di Parma*, and modern fragrances, such as *ck One* and *Paco*.

The term *citrus* applies to a range of olfactory experiences. A citrus odor may refer to a natural type such as orange, lemon, grapefruit, lime, bergamot, mandarin, tangerine, or even citronella, which is not a citrus fruit but fits into this odor category. The dominant note may be juicy, bitter, sulfurous, herbal, green, peely, or even *hesperidic* or *hesperidian*—a term that implies freshness and sparkle, as opposed to mere fruitiness.

Nature has generously shared the citrus note with unrelated botanicals, such as in lemon thyme and lemon basil. These genotypes produce oils dominated by citral and geraniol, giving a totally different impression from the standard oil. Sometimes grapefruit appears in other places, such as in the fruity notes of certain sauvignon blanc wines, which are enhanced by the presence of 3-mercaptohexan-1-ol. The *R*-isomer contributes the zesty grapefruit, and the *S*-isomer the tropical passion fruit note (**F-1**).<sup>1</sup>

The use of citrus ingredients is an essential part of every perfumer's education, and the topic is greater than can be covered in a single paper. This report will focus on the aroma chemical aspects and discuss some new discoveries in both natural and synthetic citrus ingredients.

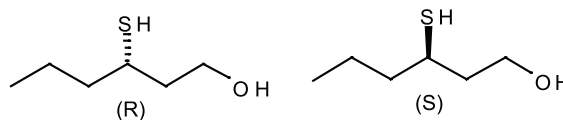
### Lemon

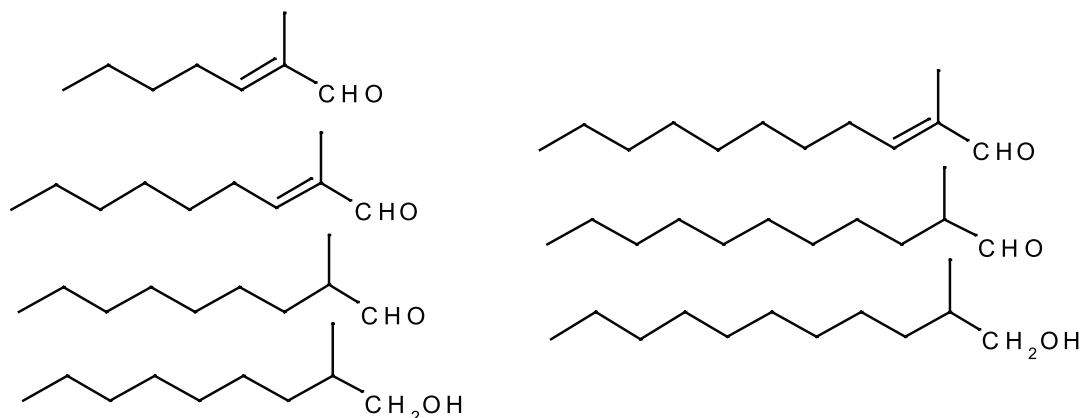
In flavors, orange is king among citrus notes. However, in fragrances, lemon notes are favored, especially in the United States where popular perception associates the odor of lemon with cleanliness. Due to this perception, household and personal care fragrance creators have found many ways to add this note. The ingredient at the heart of lemon is citral, especially the somewhat rougher version known as Lemsyn (IFF); citral dimethyl acetal has a similar effect. The saturated aldehydes from C<sub>8</sub> through C<sub>17</sub> are all orange-citrus types to some degree.

While the major components in orange, lemon, mandarin, tangerine and other edible citrus oils are very similar, their odors are quite different. The importance of  $\alpha$ -terpineol in lime and octanal, decanal and linalool in orange are well-known, but the complexity of the oils continues to yield new information. A recent study<sup>2</sup> identified five aldehydes and two alcohols not previously identified in lemon oil (**F-2**). Curiously, none of the newly identified lemon compo-

Isomers of 3-mercaptohexan-1-ol

**F-1**

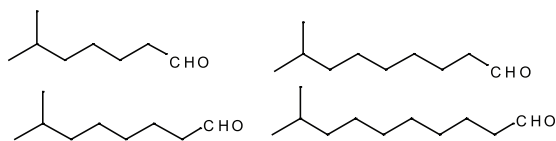




nents gave a characteristic citrus note when evaluated separately, thus showing that the magic is in the mixture. The absence from lemon of certain orange oil aldehydes, such as 6- and 8-methyl aldehyde (**F-3**), provides a further clue to the differences.

#### Aldehydes found in orange and yuzu, but not in lemon

F-3



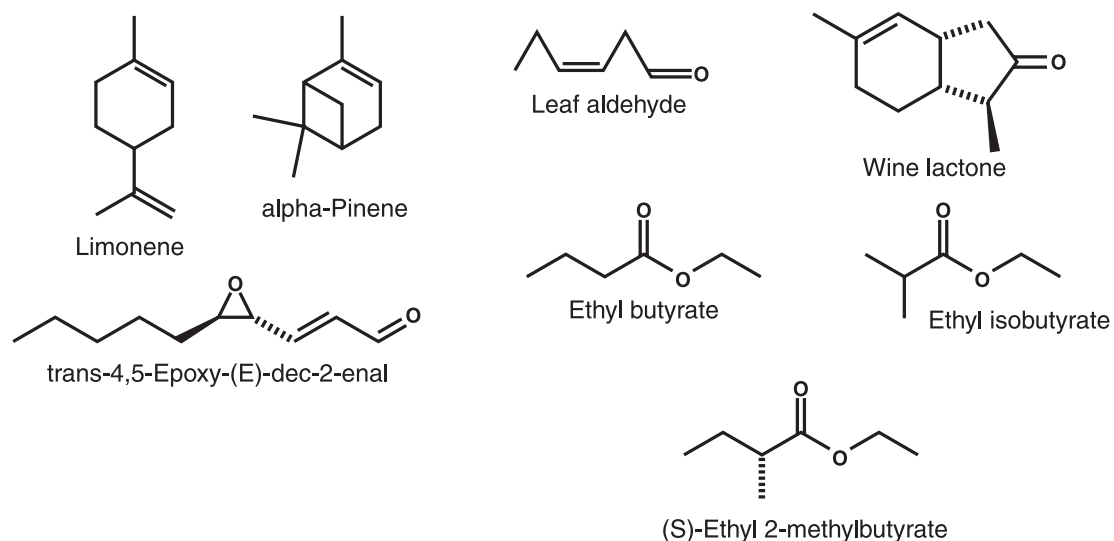
The aromas of citrus juices, which are distinctively fresher than the oils, have been studied intensively by flavorists. The selection of key aroma impact materials in fresh orange juice (**F-4**) may be of interest to perfumers looking for a juicy orange note.<sup>3</sup>

#### Aldehydes

Probably the most intense of all the citrus aldehydes is (*Z*)-8-tetradecenal (**F-5**), which has an odor threshold of 0.009 parts per billion.<sup>4</sup> This is highly unusual for a molecule that contains neither sulfur nor nitrogen. This material is cleared for use in

#### Key aroma impact materials in fresh orange juice

F-4



flavors in the United States. It is of interest to note that this aldehyde was discovered in nature in the exocrine secretions of the Oribi antelope of South Africa (*Ourebia ourebi*).<sup>5</sup> The scent gland, located close to the eyes, is used for territorial marking.

Since aldehydes are susceptible to oxidation and other reactions, they are often replaced by similar molecules that have been modified for greater stability. The cyclopropanated derivatives of citral were recently reported to have a lemonlike fresh fragrance and stability under acidic conditions.<sup>6</sup> A large number of synthetic nitriles (**F-6**) are now available as alternatives to aldehydes and provide similar odors but are much more stable.

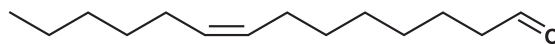
The recent banning of geranyl nitrile has spurred interest in replacements, and a patent<sup>7</sup> has been filed claiming the use of citronellyl nitrile in combination with certain other materials to cover this gap.

### Grapefruit

Perhaps the most intriguing citrus type is grapefruit, which has an unmistakable sulfurous character overlaid with woody and floral notes. It is remarkable how many

### (Z)-8-Tetradecenal (FEMA# 4066)

**F-5**

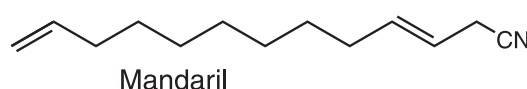
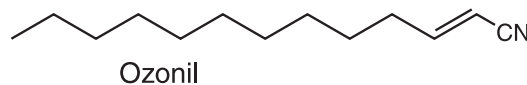
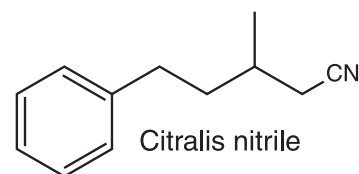
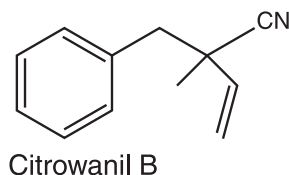
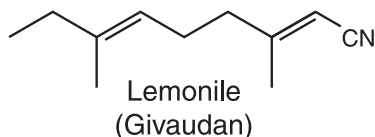
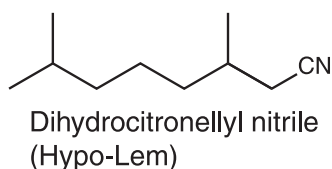
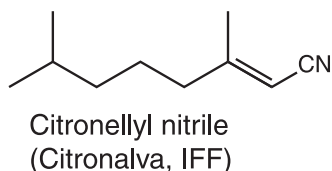
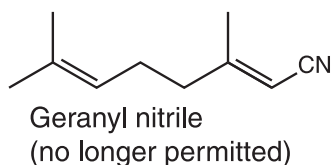


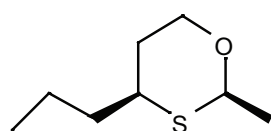
aroma chemicals with grapefruit odor also have vetiver and muguet in their descriptors. The grapefruit has many unusual components, of which perhaps the best known are nootkatone and 1-*para*-menthen-8-thiol (grapefruit mercaptan). The first of these is costly, and for use in fragrances must be greater than 98% pure. The second is extremely difficult to work with, giving burnt rubber notes unless carefully diluted and blended. Many synthetic aroma chemicals have been used to add grapefruit notes (a selection is shown in **F-7**).

From **F-7**, it can be seen that the structure of Pamplefleure (IFF) allows four optical isomers. This immediately leads to the question: which one, if any, is the best? A recent investigation that separated and evaluated all four isomers, concluded that the (2*R*,4*S*) isomer is perhaps the most typical, but that all four have distinct odors and contribute to the overall impression.<sup>8</sup>

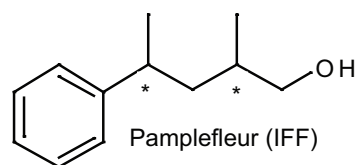
### Nitriles with lemon-citrus character

**F-6**

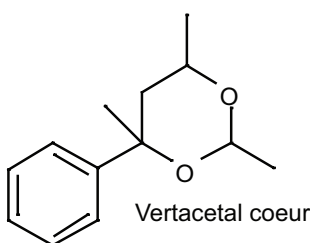




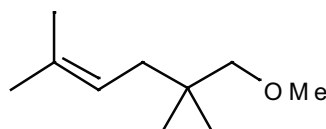
Oxane, oxathiane



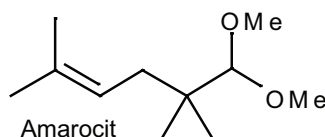
Pamplefleur (IFF)



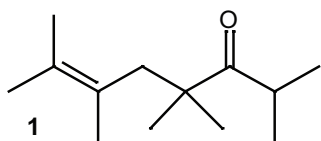
Vertacetal coeur



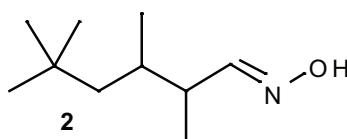
Methyl pamplemousse



Amarocit



1



2

The list of grapefruit possibilities has been extended by the recent discovery of the ketone **1** (F-7), which was used in trial citrus-fruity fragrances to add a pink grapefruit dimension.<sup>9</sup> Another new grapefruit type is the oxime **2** (F-7), which has a flowery, sweet and fruity first impression, drying down to bitter, grapefruit and cassis—an usually broad range of notes.<sup>10</sup>

## Bergamot

Bergamot oil, made from an inedible citrus fruit, is perhaps the most perfumery of the natural citrus oils. The composition of the oil is dominated by limonene, linalyl acetate and linalool; however, these ingredients alone do not create a bergamot odor. A detailed study has identified the components of bergamot oil and ranked them using aroma extraction dilution analysis.<sup>11</sup> This information enabled the authors to formulate a bergamot reconstitution (shown in **T-1**), which scored 7.1 (out of 9) by comparison with the oil. Curious perfumers may be interested to test this formulation against their own concept of what bergamot should smell like.

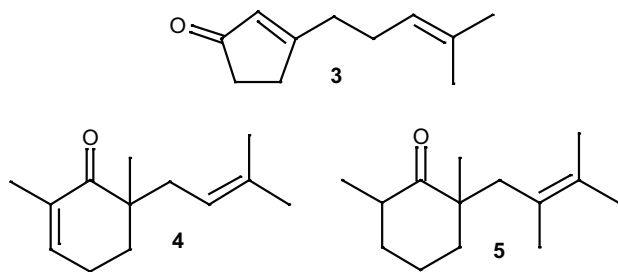
A number of synthetic materials with bergamot character are now available to perfumers, including the acetates of pseudolinalool, myrcenol, dihydro-myrcenol, ocimenol, terpineol and ethyl linalool. All of these are structurally related to linalyl acetate in one

way or another. However, some interesting new molecules have been discovered that may give perfumers wider options with additional nuances. The molecule **3** in **F-8** is reported to have “an odor of dry bergamot and nerol with a fresh citrus, fruity and floral character.”<sup>13</sup> A series of substituted cyclohexanones has been shown to have interesting citrusy odors, especially **4** and **5** (F-8), which exhibit both bergamot and grapefruit notes.<sup>14</sup>

## Bergamot reconstitution

## T-1

Component	Weight <sup>12</sup>
limonene	392
linalyl acetate	294
linalool	98
γ-terpinene	69
β-pinene	59
citral	59
geraniol	20
limonene oxide	6
(Z)-β-ocimene	2
decanal	2
Total	1000



courtesy of US Fish &amp; Wildlife Service; photographer Art Sowls

Crested Auklet

## Eau de Auklet

## T-2

Component	Weight
<i>n</i> -octanal	41
<i>n</i> -hexanal	21
2-dodecenal <sup>17</sup>	15
<i>cis</i> -4-decenal	8
hexanoic acid	8
octanoic acid	4
<i>n</i> -decanal	3
Total	100

## Antiparasitic Properties

Finally, it should be noted that the use of citrus fragrances is not unique to *Homo sapiens*. In addition to the Oribe previously mentioned, some species of birds are known to rub their plumage with citrus peel; the limonene released is harmless to the bird, but immediately lethal to avian lice.<sup>15</sup> Some birds have even developed the ability to secrete their own citrus odors. Over many years, sailors in the Bering Sea have reported a strong odor of oranges in the vicinity of certain nesting sites. Investigators recently identified the source—scent glands of the Crested Auklet (*Aethia cristatella*), a small seabird that nests in colonies of up to 2.5 million.<sup>16</sup> Large communal nesting sites are often plagued by parasites and the odor is believed to serve as a repellent against invertebrates. The scent may also play a role in mate selection, as those with a strong scent would presumably keep pests from the nesting site. (The formula for the male auklet's citrus "cologne" can be seen in T-2).

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