

# Citrus Innovations

A survey of recent patent activity unveils advances in shelf stability, solubility, citral derivatives and bitter blockers

While citrus flavor applications took novel turns in recent product introductions—mint-citrus in confectionery, and yuzu and other exotic citrus in salad dressings and condiments—they continued to dominate the beverage category in everything from blended beers to flavored waters, juices, soft drinks and liquors.<sup>a</sup> While Bell Flavors & Fragrances' "2011 Top 10 Flavor Trends" points to blood orange's rising profile, valued for its "hint of raspberry" and vitamin C and antioxidant content, lemon still reigns. In a recent *Beverage Industry* report, author Jennifer Zegler notes, "[Lemon] ranked as the top flavor used in 2010 with 46% of respondents indicating that they used the citrus fruit last year."<sup>b</sup> While the flavor is expected to continue a leading position among all varieties, orange and lime are also expected to thrive in the category. Simultaneously, technologies supporting the application of citrus in an array of flavors and fragrances have advanced.

## Stability

An Ogawa & Co. Ltd. patent application outlines a process comprised of the addition of a "deterioration inhibiting material" to foods, beverages and/or cosmetics to inhibit the production of deterioration odors—particularly those generated by citral in citruslike flavors and fragrances when exposed to heat, light and other degradation factors.<sup>1</sup> Specifically, the material can be used in applications at lower rates than "conventional deterioration inhibitors" and counters the production of p-cresol and p-methylacetophenone.

A Takasago patent application discloses the invention of a "flavor retention agent which is harmless to the human body and exhibits excellent ability to prevent deterioration of flavors" while also eschewing any browning of products.<sup>2</sup> The agent "is easily mixed and does not separate in foods," according to the authors. The application also notes that, "antioxidants formed of substances such

<sup>a</sup>A recent *Packaged Facts* ([www.packagedfacts.com](http://www.packagedfacts.com)) report, "What's Cooking for 2011," says of yuzu, "We have been spotting new foods made with the floral-flavored Japanese lime at [food shows] lately and believe this trend is ready to blossom. With lime already such a flavor standard, yuzu and other more specialty citrus varieties like *sudachi* [mandarin orange-*Citrus ichangensis* hybrid] will offer consumers an exciting exotic twist for salad dressings, beverages and condiments."

<sup>b</sup>J Zegler, Beverage R&D: 2011 New Product Development Survey. [www.bevindustry.com](http://www.bevindustry.com) (2011)



as tocopherol compounds are 'environmentally friendly' and harmless to the human body," but, "improvement is still desired in their ability to stabilize a target organic substance." The agent described in the current patent application is derived from the leaves and/or tubers of the potato plant and can be used to protect citrus flavors from oxidation and heat during the production, processing and storage of foods—thus defending the flavor quality of products.

An IFF patent application has outlined a method for storage-stable citrus flavor compositions.<sup>3</sup> The method describes a spray-dried flavor composition being placed into a vacuum sealed bag in which humidity is low. This bag allows for the storage of the composition for "an extended period of time."

## Solubility and Freshness

A patent application from Comstock et al. focuses on the solubilization of flavor oils, including citrus.<sup>4</sup> The process focuses on the solubilization of flavor oil in water to

## New US Patent Office to Expedite Innovation

By some estimates, it currently takes about two years for patent applications to be processed by the US Patent and Trademark Office (USPTO; [www.uspto.gov](http://www.uspto.gov)). In effort to reduce a backlog of more than 700,000 patent applications, the USPTO will open an office in Detroit later this year. The expansion, part of a larger national technical and personnel resource boost, will initially add 100 positions to the organization's ranks.

produce clear beverages with an oil to emulsifier ration of 2:1. According to the application, “A crude emulsion is first generated by high shear mixing of the emulsifier solution and flavor oil. The crude emulsion is then fed into a homogenizer to produce a finer emulsion. The resulting flavor concentrate can then be diluted to produce clear beverages.” This, the authors argue, better preserves aroma and flavor of, for example, citrus oil, leading to enhanced fresh qualities compared to wash/extract techniques. Furthermore, the present application claims to avoid the off taste issues associated with microemulsion techniques and the flavor load limitations of solid flavor delivery systems. “Because the composition of a given flavor oil depends on its origin and processing, microemulsions have to be tailored to cater to oil differences,” the application adds.

A Firmenich patent discloses an alternative to conventional flavor and fragrance microemulsions, allowing for low-VOC (volatile organic compound) content with no sacrifice in sensory aspects.<sup>5</sup> According to the authors: “Even very hydrophobic oils such as fragrances, flavors, or ingredients thereof, that contain only small amounts of polar solvents, or are completely free of polar solvents, can be solubilized in the form of stable compositions and clear microemulsion products. Any perfuming composition that contains for example from 5% w/w to 99% w/w of terpenes ... relative to the total amount of the oil, can thus be solubilized. Said terpenes may be of ... citrus origin, such as terpineol, or d-limonene.”

## Bitter Taste

A Senomyx patent application describes the identification of human T2R receptors associated with bitter taste and their use in assays for the identification of bitter blocker taste compounds.<sup>6</sup> The company, as noted in a recent profile, has pursued the development of bitter blockers primarily for palatability in products containing hydrolyzed soy proteins, menthol, caffeine, cocoa and rebaudioside A.<sup>7</sup> While the receptors covered in the patent application respond to specific bitter compounds in coffee, their use in the identification of bitter blockers can be applied to food and beverage compositions containing citrus oils such as orange, lemon and lime.

## Citral Derivatives and 6,8,10-Undecatrien-3-ol/6,8,10-Undecatrien-4-ol

A patent issued to the former Flexitral Inc. discloses the discovery of “improved” citral derivatives and flavor and fragrance applications of same, which boast extended shelf life.<sup>8</sup> The derivatives in question impart characteristic citral impact in “lemony” flavor and fragrance applications—including candles, perfumes, cleansers, beverages and confectionery—while decreasing allergic properties. The preparation of the derivatives are detailed by the author as follows:

In one embodiment, the derivatives are prepared by replacing one or more double bonds

in citral with a cyclopropyl group, which can be unsubstituted, or substituted with one or two lower alkyl, preferably methyl groups. The alkyl groups can optionally be substituted, for example, with electron donating groups, electron withdrawing groups, groups which increase the hydrophilicity or hydrophobicity, and the like. In another embodiment, the derivatives are prepared by replacing the aldehyde group in citral with a nitrile, methyl ether or acetal group. The acetal groups can provide the compounds with a long lasting flavor or fragrance, where the acetals slowly hydrolyze to provide the aldehyde group in citral. In some

embodiments, both the aldehyde and at least one of the double bond functional groups are both derivatized as described herein.

A patent issued to T Hasegawa outlines the citrus-boosting qualities of galbanum oil-derived 6,8,10-undecatrien-3-ol and 6,8,10-undecatrien-4-ol.<sup>9</sup> The compounds feature woody green notes and impart freshness and naturalness to flavor and fragrance compositions. Specifically, the materials combine well with and boost the fresh natural fruitiness of flavor profiles such as conventional citrus—lemon, orange, grapefruit, lime, mandarin, etc.—and Japanese citrus—*mikan* (*Citrus unshiu*), *kabosu* (*Citrus sphaerocarpa*), *sudachi* (*Citrus sudachi*), *hassaku* (*Citrus hassaku*), *iyokan* (*Citrus iyo*), *yuzu* (*Citrus junos*), *shekwasha*, (*Citrus depressa*), kumquat, etc. In fragrances, the materials are appropriate for bergamot notes reminiscent of the natural essential oil.

#### References

1. T Arima and H Masuda, *Degradation Inhibitor for Flavor or Aroma*. US Patent Application 20100189822 (2010).
2. T Hiramoto, K Saiki, K Kakamoto, S Masumura, T Shimizu, T Yamashita, F Yanaka and T Saima, *Flavor-Retention Agent*. US Patent Application 20100166910 (2010).
3. LM Popplewell, L Henson and AJ Toth, *Method of Producing a Shelf-Stable Citrus Spray-Dry Product*. US Patent Application 20100055267 (2010).
4. B Comstock, MY Wang and N Lim, *Process for Solubilization of Flavor Oils*. US Patent Application 20100098821 (2010).
5. FJ Vlad, R Mounier, K Wong, A Dageron Jouault and T Herd, *Solubilizing systems for flavors and fragrances*. US Patent 7846889 (2010).
6. DS Karanewsky, J Fotsing, C Tachdjian and M Arellano, *Identification of human T2R receptors that respond to bitter compounds that elicit the bitter taste in compositions, and the use thereof in assays to identify compounds that inhibit (block) bitter taste in compositions and use thereof*. US Patent Application 20100254916 (2010).
7. J Gleason-Allured, Taste and Flavor Innovations for Healthier Products. *Perfum Flavor*; **36**(1), 28–30 (2011).
8. L Turin, *Citral derivatives*. US Patent 7704941 (2010).
9. A Nakanishi, Y Ohkubo, N Tomita, T Maeda and N Miyazawa, *6,8,10-Undecatrien-3-ol or 6,8,10-Undecatrien-4-ol, and Aroma Compositions*. US Patent Application 20100130794 (2010).

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