Biobased platform chemicals in flavours & fragrances

Marcel van Berkel of **GFBiochemicals** and **Henry Gill** of **De Monchy Aromatics**
look at levulinic acid in flavour and fragrance applications

Materials derived from renewable feedstocks find increasing uses in flavourings, fragrances and consumer products as alternatives to fossil-fuel based materials. Biobased platform chemicals, such as levulinic acid, lactic acid, n-butanol and succinic acid, offer the obvious solution for producers. Whilst biobased ingredients may already be consumed in many food and aroma products, platform chemicals offer true versatility.

The increasing occurrence of weather fluctuations and seasonality shifts means that buyers of flavouring substances are also seeking alternatives to vulnerable natural-grown materials. This helps to explain why, in recent years, there has been a surge in the development of speciality chemicals from robust renewable feedstock. These offer platforms for a range of markets and the opportunities for flavours and fragrances (F&F) are no exception.

Levulinic acid

Levulinic acid has been shown to be an incredibly versatile building block for chemicals and materials, more so than the majority of biobased platform chemicals available today. It has been repeatedly recognised as one of the top biobased building block chemicals of the future by the US Department of Energy.[1]

Also known as 4-oxopentanoic acid, levulinic acid is an organic compound which occurs in nature. It is classified as a keto acid and its physical form is a white crystalline solid which is soluble in a range of liquids.

GFBiochemicals recently completed a stakeholder survey with a partner. Of the responses, 22.8% of stakeholders in the bioeconomy agreed that they foresaw biobased levulinic acid being consumed in F&F, while 17.1% foresaw its use in personal care and beauty products.

Levulinic acid is colourless and exhibits rum, sugar cane and maple aromas, providing a range of options in sweet and savoury compositions. Although levulinic acid is commonly used to create caramel and maple flavours, further sweet and syrupy tastes are possible when using it as an ingredient. Levulinic acid normally has a tart acid-like taste which is accompanied with caramel-like flavours. This helps give the impression of sweetness alongside acidity. Sweet flavour types which are made possible include cola, chocolate, hazelnut and vanilla.

Levulinic acid can also be used for savoury flavour types, such as soy sauce, lamb or tobacco. As a speciality chemical, it can be used directly in flavour formulations or as a feedstock to derive further flavour-enhancing ingredients.

Levulinic acid esters ethyl levulinate and butyl levulinate can be produced via the esterification of levulinic acid. They are known for their distinct features and are used in a wide-range of compositions.

Ethyl levulinate brings sweet, fruity, floral, berry, green pineapple, rhubarb flavours, which are extensively used in beverages. This ester also blends well with cashmeran, for melon and pear notes. Butyl levulinate, meanwile, can be used as an ingredient for both flavours and fragrances. It is useful for a number of savoury applications, for example, to create flavours with smoky notes and fruit applications, such as melon, banana and cherry.

Levulinic acid is used in both sweet and savoury flavours

Pure levulinic acid has a number of beneficial properties as a food-grade preservative. Moreover in certain conditions it also acts as a pH regulator. This could allow producers to use the flavour profile of levulinic acid and also benefit from its value-added properties.

Case studies

The sweet, rounded character of levulinic acid fits very well with South-East Asian cuisine. In particular, soy sauce flavours benefit from its use. This flavour can be used in finished products such as instant noodles with very good effect. Figure 1a shows an example.

Levulinic acid has also been identified in some fish sauces. This is the main ingredient in many Asian dishes. In particular, the distinctive flavour of Vietnamese cuisine depends on the use of fish sauce. Thus flavours like *nuoc cham* (a dipping sauce) can be enhanced by the use of the biobased flavouring ingredient that includes levulinic acid.

As with sweet flavours the use of levulinic acid can enhance the sugar profile that is widely appreciated in Asian cuisine. That sweet profile is commonly associated with dishes such as sweet and sour, *nasi goreng* and barbecue spare ribs, to name just a few examples.

Because levulinic acid has a sweet sugar aroma and a flavour reminiscent of golden syrup or unrefined cane sugar and it is very useful in cola flavours. Figure 1b shows a cola oils blend. This is then emulsified with gum Arabic, kola nut extract and caramel colour to give the final cola flavour.

Levulinic acid plays a part here in rounding out the whole cola flavour profile. This is also brought about by the combination with caramel colour. The oil can also be used in confectionery if diluted in triacetin, for example 'Kola Kubes'.

Levulinic acid gives a sweet, sugar-like body and aroma that could help with a reduction in sugar in the finished drink. This is especially useful and effective in low calorie colas. The additional use of other sweetness-enhancing flavour compounds, such as maltol and 2,5-dimethyl-4-hydroxy-3(2H) furanone, can also provide a synergistic effect.

Alternative applications

Produced directly from biomass, GFBiochemicals' levulinic acid provides a renewable biobased alternative to petro-based biocides and preservatives. These properties offer opportunities not only in food and fragrance applications, but also in cosmetics where preventing degradation is a key consideration. Levulinic acid is typically used at 0.5-1.5% in such a formulation.

Like levulinic acid, the salts derived are water-soluble and are also commonly used within beauty and personal care products. These salts give an inherent fresh odour to emulsions and, in skin care products, help to prevent wrinkles too.

Figure 1 – Flavours incorporating levulinic acid

Maple Lactone	0.30
Maple Furanone	0.08
Propylene Glycol	86.32
Phenyl Ethyl Alcohol	1.00
Guaiacol	0.11
Benzaldehyde	0.80
Phenyl Ethyl Acetate	0.08
Isovaleric Acid	0.20
Methional	0.02
2-Methyl Pyrazine	0.15
Isobutanol	0.80
Dimethyl Sulphide	0.10
Isovaleraldehyde	0.01
Dimethyl Disulphide	0.03
Levulinic Acid	**10.00**
	100.0

Borneol	1.9
Lime Oil Distilled	14.5
Lime Oil Distilled 5X	30.0
Lemon Oil 5X	25.6
Cassia Oil Rectified	2.0
Nutmeg Oil Rectified	0.4
Ginger Oil	1.5
Peru Balsam Oil	0.6
Pimento Berry Oil	1.0
Levulinic Acid	**20.0**
Vanillin*	2.5
	100.0

Other biobased ingredients

Traditionally produced from grapefruit peel oil or the chemical oxidation of valencene, nootkatone, is a key component in grapefruit and other citrus flavours. Considerable work has been done on developing biobased production routes for nootkatone. This is in part due to its stereochemistry but also because of high market value, which makes developing profitable bio-transformation pathways easier when the technology is still relatively new.

Most manufacturers rely upon fermentation technology to produce natural valencene from sugar. This is followed by conventional oxidation into nootkatone, giving a synthetic product.

One source however takes a different approach, starting with natural valencene which can be sustainably extracted from orange peel oil, before carrying out an enzymatic transformation to nootkatone. This gives what the F&F industry considers a natural product under both EU and US legislation.

Vanilla flavours are amongst the most popular in the world and global demand for the natural flavour far exceeds what can be supplied from vanilla beans alone. Vanillin is the principle component that gives vanilla beans their characteristic taste. Structurally similar to ferulic acid, which is found in rice bran oil and until recently was considered a waste product, the biotransformation to vanillin is one of the earliest commercial success stories for the industry.

A green future

The demand for sustainability is driving the chemical sector towards new renewable solutions by developing products from biobased resources. It is only now that levulinic acid is becoming a viable feedstock for wider consumption. The material has historically found use in F&F applications but there is more to it than meets the eye.

The raw feedstock for levulinic acid can include biomass, bagasse and waste streams. Downstream companies based in Europe and America have historically sourced levulinic acid from Chinese manufacturers. Most producers currently use a three-step process for production of the chemical.

In contrast, GFBiochemicals produces levulinic acid without intermediary process steps. It currently uses industrial starch as feedstock, though the company is targeting a switch to cellulosic biomass in 2016.

The company also brought a 10,000 tonnes/year commercial-scale production plant online in July 2015 in Caserta, southern Italy. This is itself a very strong region in the development and production of biobased speciality products, such as food ingredients.[2]

References:

1. J. Bozell & G.R. Petersen, Technology Development for the Production of Biobased Products from Biorefinery Carbohydrates – The US Department of Energy's 'Top 10' Revisited, **2010**
2. ERRMA, Accelerating the Development of the Market for Bio-based Products in Europe

Contact

Marcel van Berkel
Chief Commercial Officer
GFBiochemicals
Tel: +31 622 203 144
E-mail: m.vanberkel@gfbiochemicals.com
Website: www.gfbiochemicals.com