# The Chemical and Sensory Evaluation of Edible Oleoresins

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By Mans Boelens, Boelens Aroma Chemical Information Service, Huizen, The Netherlands, and Harrie Boelens, Leiden University, Leiden, The Netherlands

E dible oleoresins are natural isolates obtained by extracting plant material with suitable solvents and recovering of the solvent, mostly by evaporation. The residue is called the oleoresin. Various types of solvents are used to extract oleoresins (e.g. hydrocarbons, chlorinated hydrocarbons, alcohols, ethers, ketones and carbon dioxide). The oleoresins contain all the chemical compounds, volatile and non-volatile, that are soluble in the chosen solvent.

The extracted volatile constituents, also called the essential oil, may concern several hundred compounds, most of which are unknown. The volatile part of the oleoresin is responsible for the flavoring and scent properties of the product.

The isolated non-volatile components consist of several groups of chemical compounds, such as carotenoids, steroids, alkaloids, anthocyanins, glycosides etc. The nonvolatile constituent of the oleoresin can be important for the taste, color, mouthfeel, texture and antioxidative properties of the material. Oleoresins are economically useful because of their facile application, their higher concentration of organoleptically interesting substances (e.g. smelling and tasting compounds), and their content of coloring and antioxidative constituents. A series of edible oleoresins will be discussed, including anis, caraway, carrot seed, citrus peels, coriander, cumin, fennel, fenougreek, hops, laurel leaf, marjoram Spanish, origanum, paprika, pepper, peppermint, rosemary and thyme. Their most interesting chemical components will be mentioned. The characterimpact volatile constituents will be shown. Some important non-volatile tasting, coloring and antioxidative compounds will be treated. The organoleptic quality of the edible oleoresins will be discussed in more detail.

# **Production and Yields**

The production of oleoresins seems a simple process. The plant material is extracted with a suitable solvent. The

solvent is then recovered by distillation and the residue produced is the oleoresin. This simple manufacture, however, may have several complications. Often the plant material has to be prepared before use. This can include drying and grinding. Various questions have to be answered during processing. For instance: What is the most suitable solvent? To what extend can the solvent be recovered? Can the loss of essential components be circumvented during the process?

Various solvents are used for the extraction of oleoresins (Tables 1 and 2). The solvent can be apolar and lipophile (like hexane), or polar and hydrophile (like ethanol). It is common knowledge that likes dissolves likes; that is to say that apolar chemical compounds will easily dissolve in hexane and polar compounds in ethanol. Plant material mainly consists of woody (lichen) and cell-wall material (primary metabolites and secondary metabolites). The cell-wall material, the woody material and lichen in general is not soluble in any solvent. This is the ballast material that has to be separated and discarded. The primary metabolites, such as carbohydrates, fats, proteins and vitamins, are only partly soluble in most solvents. Most of the carbohydrates and part of the proteins are often insoluble. The secondary metabolites concern a wide series of compounds like isoprenoids, benzenoids, carotenoids, steroids, waxes, alkaloids and anthocyanins.<sup>1</sup>

In isoprenoids and benzenoids. Most of the essential oils are found in the isoprenoids (mono- and sesquiterpenoids). The phenylpropanoids occur in the group of benzenoids and are found in many spices. A lot of hot and bitter tasting compounds are encountered in the group of alkaloids. Carotenoid and anthocyanin groups include a large number of pigments of flowers and fruits. Natural antioxidants have been found in the groups of isoprenoids combined with benzenoids.

Benzene is prohibited for use in food products. Haloge-

Table 1. Yields (%) and physicochemical properties of some Spanish herbal and citrus oleoresins*						
Oleoresin	Plant parts	Yield oleoresin	Oil-content %	Density	Optical rotation	Refractive index
Anis	dried seeds	12-16	10 - 14	0.98-0.99	0 to + 2	1.552-1.557
Caraway	dried seeds	5-7	13- 15	0.91-0.92	+70 to +81	1.484-1.488
Carrot seed	seeds	8-12	3-5	0.870-0.944	–8 to -37	1.482-1.491
Coriander	fruits	7-10	7-8	0.86-0.88	+5 to +13	1.463-1.471
Cumin	seeds	5-7	30-35	0.917-0.924	+4 to + 6	1.501-1.504
Fennel (sweet)	seeds	7-10	16-21	0.960-0.980	+4 to +25	1.498-1.551
Fenougreek	fruits	3-4	ca 25	not determined (dark yellow color)		
Laurel	dried leaves	7-10	5-7	0.905-0.930	-4 to -22	1.460-1.470
Majoram (spanish)	dried leaves	8-12	9-14	0.900-0.922	–5 to –11	1.463-1.466
Origanum	dried leaves	10-16	7-9	0.930-0.960	-2 to +3	1.500-1.508
Peppermint	dried leaves	5-8	18-22	0.900-0-908	-20 to -30	1.460-1.463
Sage (spanish)	dried leaves	10-16	9-12	0.910-0.940	+15 to +25	1.465-1.475
Thyme (grey)	dried leaves	8-11	8-9	0.890-0.930	−1 to −5	1.480-1.500
Citrus peel oleoresins						
Lemon peel	dried peel	2.5-3	75-85	0.850-0-860	+55 to +65	1.474-1.476
Orange peel (bitter)	dried peel	2-2.5	70-80	0.845-0.855	+85 to +100	1.472-1.476
Orange peel (sweet)	dried peel	3-5	70-80	0.844-0.849	+87 to +99	1.473-1.476

\* data courtesy from Destilaciones Bordas Chinchurreta S.A., Seville Spain.

Table 2. Yields (%) and oil-contents of some tropical spice oleoresins <sup>2</sup>					
Spice	Plant parts	Solvent	Oleoresin yield	Oil content	Essential oil yield
Cassia	bark/leaves	benzene	3.3 - 4	unknown	1.0 - 3.8
Cinnamon	bark	unknown	10 - 12	unknown	1.6 - 3.5
Clove	buds	diethyl ether	10 - 15	70 - 80	15 - 20
Ginger	rhizome	diethyl ether	3.5 - 7.8	21 - 42	0.3 - 3.5
		ethanol	3.1 - 6.9		
		acetone	3.9 - 10.3		
		trichloroethane	2.7 - 7.2		
Mace	aril	petr.ether	27 - 32	8.5 - 22	10 - 13
		ethanol (hot)	22 - 27		
Nutmeg	seed	benzene	31 - 37	10 - 90	2.6 - 8.8
		ethanol	18 - 26		
		diethyl ether	28 - 37		
Pepper	fruit	ethanol	10 - 13	15 - 20	1.0 - 2.6
(black)		dichloroethane	5 - 15	15 - 27	
		diethyl ether	10 - 11		
Turmeric	rhizome	ethanol, acetone	8 - 10	3 - 7	2.0 - 7.2
Vanilla	seed	ethanol	30 - 60		

nated hydrocarbons are tolerated. However, the final concentration in the oleoresin generally should be below 25 parts per million. Dichloromethane is used for the extraction of Mediterranean dried herbs and seeds. It is a good solvent: low boiling and easy to remove.Hexane is used, even under pressure, to extract the natural pigments from prepared paprika plant material. Acetone is applied to extract rosemary leaves for production of the natural antioxidants.Diethyl ether was once used in France for the extraction of vanilla beans. The use of this ether is dangerous, because of the formation of peroxide and the risk of explosion.

The yields of the oleoresins after removal of the solvents are always several times higher than those of essential oils, and depend on the solvent use. Part of the essential oil is lost during the recovery of the solvent. Therefore, sometimes

Table 3. Yields (%) of various extraction methods collected by Moyler <sup>4</sup>					
Botanical	Part	Steam distillation	Liquid carbondioxide extraction	Fluidized carbondoxide extraction	Ethanol extraction (or specified)
Anisseed	seed	2.1 - 2.8	4.3	7	15
Anise star	seed	8 - 9	10	-	28
Caraway	seed	3 - 6	3.7	-	20
Celery	seed	2.5 - 3.0	3	_	13
Clove bud	flower	15 - 17	16	20	20
Нор	fruit cone	0.3 - 0.5	12	16	20
Lovage	dried root	0.5 - 1	0.9	_	20
Mace	aril	4 - 15	13	-	40
Parsley	seed	2.0 - 3.5	3.6	-	20
Pepper	fruit	1.0 - 2.6	3.5 - 6.7	10	10-20 (acetone)
Rosemary	leaf	0.5 - 1.1	1.9	7.5	5
Sage	leaf	0.5 - 1.1	_	4.3	8

essential oil of a fraction is added to the oleoresin to obtain a balanced flavor of the product. This is called "standardizing" of the oleoresin. The content of essential oil in the oleoresin is an important parameter for the organoleptic quality of the material. In 1983 Pagington<sup>3</sup> wrote a review of oleoresin black pepper and its extraction solvents. He remarked that at that time, 50% of the world's oleoresin production was black pepper oleoresin. The major producers are India, Indonesia, and Malaysia. He also discussed the solvents used to extract oleoresins from pepper and mentioned the problem arising from their toxicity.

Richard<sup>2</sup> in 1991 discussed some aspects of oleoresins in a chapter about spices and condiments. He stated that freshly prepared pepper oleoresin is a dark green, viscous liquid with a strong flavor, but as it ages, peperine crystals appear, and it must be homogenized before use. He also mentioned that there has been renewed interest in carbon dioxide as a solvent. It is inexpensive, nonflammable, nonreactive and above all nontoxic. It seems ideal for use in the food industry, especially because it can be used at temperatures generally below 50°C, which considerably limits the risk of being denatured by heat.

The physical properties of supercritical carbon dioxide, its density and diffusion coefficient, are midway between those of its gaseous phase and its liquid phase. Its viscosity is comparable to that of its gaseous phase. It therefore has excellent penetration power, which is necessary for rendering flavors soluble. Carbon dioxide has a low polarity providing it with an excellent capability for extracting low polar or apolar compounds. However, this polarity varies between that of hexane and that of methylene chloride, depending on the pressure and temperature of use. All authors agree on the attraction of supercirtical carbon dioxide extraction to produce oleoresins lies mainly in the high quality of the extracts. Operating costs are lower than for conventional techniques, but the instruments required are expensive. As a result, the products obtained are more expensive than essential oils and oleoresins obtained with conventional methods. The flavor of extracts obtained with carbon dioxide are close to the oraganoleptic quality of the spice or natural product. There are no offnotes, and abundant top an back notes. Moyler<sup>4</sup> has demonstrated that extraction of various spices with carbon dioxide gives results comparable to essential oils at the same yields.

### **Chemical Evaluation**

Oleoresins consist of a volatile and a non-volatile part. As shown in Tables 1 and 2, the volatile part of the oleoresins can sometimes be up to 80%, as with the extraction of citrus peels. In general, however, the concentration of the volatile part is between 10 and 20%. The volatile part consists mainly of the essential oil, which can be obtained by steam-distillation of the plant material. Often some higher fatty acid esters are present in the oleoresin, like oleates and linoleates. Excellent reviews have been published about the chemical composition of edible essential oils.<sup>1,5,8,9</sup> Essential oils are complex mixtures of hundreds of chemical compounds, most of which still are unknown. With respect to the relation between number of compounds and their concentration, the so-called "10 to 90" rule can be applied. That is to say that 10% of the total number of the compounds present in the essential oil concern more than 90% of the concentration.

Most of the chemical constituents of essential oils can be grouped into a few major classes, but there are also components of essential oils that bear little resemblance to these classes. In the overview of important and characteristic constituents given below, the compounds are classified into four major groups: aliphatic compounds, isoprenoids, benzenoids and miscellaneous compounds.

Aliphatic compounds: Aliphatic compounds are acyclic organic compounds with a straight or branched carbon chain. These compounds can be saturated or unsaturated, which means they possess one or more double or triple bounds between two carbon atoms. These compounds can for instance be derived from fats or amino acids. The leaves of plants can produce a series of volatile aliphatic compounds; For example, (Z)-3-hexenol (leaf alcohol) and E-2-hexenal (leaf aldehyde) by enzymatic lipoxidation of linoleic acid. The alcohol has the characteristic odor of freshly cut grass, while the aldehyde has a sharp herbalgreen odor somewhat reminiscent of bitter almond. Aliphatic aldehydes, such as octanal and decanal are organolepticly important constituents of sweet orange oil.

The oil isolated from coriander leaves, so-called cilantro oil, contains a series of higher saturated and unsaturated aliphatic aldehydes, which are characteristic for the odor of the oil. In many essential oils, 3-methylbutyl derivatives occur, such as the alcohol, aldehyde and acetate that are derived from the amino acid leucine by rection with a sugar. Aliphatic esters are important flavor and fragrance compounds occurring widely in nature.

Terpenoids (Terpene hydrocarbons and terpene *derivatives*): Isoprene is one of the basic compounds in animal and plant biochemistry from which terpenoid, carotenoids, steroids and rubber are also formed. Isoprene is formed from acetyl-CoA viamevalonic acid and dimethylallyl pyrophosphate. The terpenoids are built from two isoprene units (monoterpenoid) or three isoprene units (sesquiterpenoids). The terpene hydrocarbons contribute to a limited extent only to the organoleptic quality of the oils. Monoterpene hydrocarbons conform to the molecular formula C10H16 and can be acyclic as in myrcene and ocimenes, monocyclic as in limonene and p-menthatriene, bicyclic as in  $\alpha$ - and  $\beta$ -pinene and even tricyclic as in cyclofenchene and tricyclene. The quantitatively most important monoterpene hydrocarbons are limonene and the pinenes. The dominant monoterpene hydrocarbon in all citrus oils is d- or (+)-(R)-limonene, which occurs in coldpressed sweet orange oil for over 95%. Limonene most probably is formed during growing and ripening of the fruit via mevalonate, geranyl- and (-)-(R)-linally pyrophosphate.

Limonene is also in important constituent of caraway oil. The biochemical and molecular genetic aspects of monoterpene formation have been studied.<sup>6</sup> The stucture of limonene synthase isolated from Perilla frutescens has been elucidated .<sup>7</sup> 1,3,8-p-Menthatriene occurs up to 65% in the oil of parsley leaves. The p-menthane skeleton in monoterpene hydrocarbons can be converted to p-cymene by oxidation. p-Cymene is an important benzenoid in essential oils and can be converted into thymol and carvacrol. Monoterpene hydrocarbons in general have harsh, turpentine-like odors.

The most important sesquiterpene hydrocarbon (C15H24) quantitatively occurring in spice oils is caryophyllene, which is present in clove leaf oil up to 20%. Caryophyllene can easily be oxidized to caryophyllene oxide.

Oxygen-containing monoterpene derivatives are important for the organoleptic quality of spice oils.

The aliphatic monterpene alcohol d- or (S)-(+)-linalool (coriandrol) occurs in coriander fruit oil and lends this oil its fresh floral odor, whereas its enantiomer (optical antipod) l- or (R)-(–)-linalool (licareol) is characteristic for the odor of lavender oil. The monocyclic terpene alcohols  $\alpha$ -terpineol and terpinen-4-ol are essential for the odor properties in several herb oils. The monocyclic terpene ketone d- or (S)-(+)-carvone is characteristic for the organoleptic quality of caraway oil, which finds for its freshness application in liquors. l- or (R)-(–)-Carvone has a different odor and is a character impact compound of spearmint oil, which is applied in toothpaste for its minty note. The bicyclic ketone fenchone affords a camphoraceous odor aspect to bitter fennel oil. Additionally, the bicyclic ketone verbenone, although present in rather low concentration is in rosemary oil, gives it this oil a characteristic odor aspect.  $\alpha$ - and  $\beta$ -Thujone are important for the organoleptic quality of oil of Salvia officinalis. Dill ether (3,6-dimethyl-2,3,3a,4,5,7ahexahydrobenzofuran) is characteristic for dill oil.

**Benzenoids (Benzene derivatives):** Compounds with tasteful and spicy odors are found amongst the benzenoids. This is why the chemistry of the benzene derivatives is called aromatic chemistry. All compounds contain the characteristic benzene nuclues to which one or more functional groups are connected, such as allyl, propenyl-, hydroxy-, methoxy-, methylenedioxy- and aldehyde. The benzenoid constituents can be divided into two groups: the para-menthanoids, including cumic aldehyde, carvacrol

and thymol; and the phenylpropanoids including cinnamaldehyde, methylchavicol, anethole, eugenol, myristicin and apiol. Cumic aldehyde is the character impact odor compound in cumin. Carvacrol and thymol are characteristic for the organoleptic quality of thyme oils and oil of organo.

Cinnamaldehyde is olfactively characteristic for cinnamon and where its 2-methoxy derivative lends its aromatic odor character to cassia oil. Methyl chavicol is organolep-

tically in chervil, anethole affords the sweet anisic note to anis oil and other umbelliferous oils (dill and sweet fennel). Eugenol is indispensable for the flavoring properties of clove oils and of some other spice oils. Myristicin is a character impact compound in oil of nutmeg. Apiol is organolepticly an important constituent of parsley. Benzenoid aldehydes are importent constituents of spice oils, as in benzaldehyde in bitter almond oil, vanillin in vanilla spice, and heliotropin in some exotic flowers. These aromatic aldehydes have tasteful, sweet aromatic flavors.

*Miscellaneous compounds:* Nitrogen and sulphur compounds can play an important role for the organoleptic quality of oleoresins. Several nitrogen compounds import characteristic sensory properties to the oils, even when they are present in concentration of less than 0.1%(alkylmethoxypyrazines, which occur in green bell pepper and other green leaves). Sulphur compounds are rare in spice oils, but they can be characteristic like for instance di-alkyl disulphides and alkenyl isothiocyanates, which are character impact constituents of garlic, onion, horseradish and mustard.<sup>2</sup>

Non-volatile part: As mentioned before, oleoresins consist partly of the primary plant-metabolites such as carbohydrates, fats, proteins and vitamins, isoprenoids, benzenoids, carotenoids, steroids, waxes, alkaloids and anthocyanins.<sup>1</sup> Apart from the volatile isoprenoids and benzenoids, there are the non-volatiles (carotenoids, alkaloids and anthocyanins important groups of constituents of oleoresins). Moreover, the plant extracts and oleoresins contain pigments that are mostly carotenoids, often derived from  $\beta$ -carotene. These carotenoids occur in paprika -, crocus - and citrus-peel oleoresins. Examples of these pigments are:  $\alpha$ -carotene, capsanthin, capsorubin, zeax-

Table 4. Character-impact and essential compounds in some oleoresins				
Oleoresin	Character-impact compounds	Essential constituents		
Anis Caraway	(E)-Anethole d-Carvone	Anisyl derivatives Carvone derivatives		
Carrot seed Coriander	Carotol d-Linalool	Geranyl esters Linalyl esters		
Cumin	Cuminaldehyde Menthadienals	Cumin derivatives		
Fennel Fenougreek	(E)-Anethole 4,5-Dimethyl-3-hydroxy-	Fenchone (sweet) Dihydrobenzofuran		
Laurel	2,5-dihydro-3(2H)-furan-2-one Eugenyl derivatives	Dihydroactininodiolide Linalool, 1,8-Cineole		
Majoram Origanum	c/t Sabinene hydrates Carvacrol	Terpinen-4-ol Thymol		
Peppermint Sage (spanish)	Menthol c/t Sabinyl acetate	Menthone, Menthofuran 1,8-Cineole, Camphor Bornyl acetate		
Thyme (grey)	Thymol	Carvacrol		
<i>Citrus leaf oleoresins</i> Lemon peel Orange peel (bitter) Orange peel (sweet)	Geranial/Neral Octanal, Decanal, Alka(e)nals	Geranyl derivatives Monoterpenyl derivatives Linalyl derivatives		

anthin, criptoxanthin in paprika oleoresin;  $\alpha$ -crocin,  $\alpha$ crotecin,  $\beta$ -crocetin,  $\gamma$ -crocetin in crocus oleoresin. In turmeric (curcuma) oleoresin a series of benzenoid pigments have been found (e.g. curcumin, demethoxycurcumin, bis-demethoxycurcumin).

Examples of alkaloids in black pepper and capsicum oleoresin are piperine, chavicine, isopiperine, isochavicine, capsaicin, dihydrocapsaicin, nordihydrocapsaicin, homocapsaicin, homodihydro-capsaicin, piperyline, piperttine, piperanine, piperolein A, piperoleine B, zingerone. The main constituents of a rosemary oleoresin with antioxidative properties are: carnosic acid, carnosol, rosmanol, epirosmanol, romaridiphenol, rosmadial, rosmariquinone, rosmarinic acid acid.<sup>12</sup>

# **Sensory Evaluation**

Sensory analyses are carried out to determine the sensory properties, which may concernthe olfactive (odoriferous), organoleptic (regarding odor and taste), tasting and coloring qualities of the oleoresins. The main aspects of these evalutions are detection (yes or no), recognition or discrimination (qualitative), intensity (weak or strong), and preference (like or dislike). The essential oils are mainly responsible for the olfactive properties of most oleoresins. With respect to their olfactive qualities, essential oils may contain four groups of volatile constituents:

- Character-impact compounds, which more or less represent the characteristic odor of the product;
- Essential compounds, which are not characteristic, but are still necessary for the odor;
- Balance compounds, with are neither characteristic nor essential (these make up the balance to (100%);
- Artifacts, which do not occur in the plant material itself but, for example, are formed during processing or derived from herbicides, fungicides or insecticides.

For the organoleptic qualities of the oleoresins of the spices not only the lower molecular volatile compounds are important but also the less or involatile higher molecular compounds. The latter constituents often lends a bitter, hot or pungent taste to the spices. These compounds frequently contain one or more nitrogen atoms in their molecules. Examples of bitter, hot and pungent compounds are: gingerol, shogaol, paradol, piperine, chavicine, isopiperine, isochavicine, capsaicin,

dihydrocapsaicin, nordihydrocapsaicin, homocapsaicin, homodihydrocapsaicin, piperyline, piperttine, piperanine, piperolein A, piperoleine B, zingerone. Moreover the plantextracts and oleoresins contain pigments, which mostly are carotenoids, often derived from  $\beta$ -carotene. Example of these pigments are:  $\alpha$ -crocin,  $\alpha$ -crotecin,  $\beta$ -crocetin, gamma-crocetin, curcumin, demethoxycurcumin, bisdemethoxycurcumin.

The ability of oleoresins to impart a distinct flavor to otherwise bland and less exciting meals distinguish them from other food crops. The term flavor or sensory properties pertains to "an overall integrated perception of all contributing sense (smell, taste, sight, feeling and sound) at the time of food consumption". The perception of smell and taste cover the organoleptic quality. Perception of flavor is a combined effort of the specialized cells of the olfactory epithelium of the nasal cavity, the taste buds on the tongue and back of the oral cavity, and the non-speific or trigemal neural receptors detecting sensations such as cooling, burning, pungent or biting effects, in contrast to a true or basic taste e.g. sweet, sour, bitter, salty.

Most oleoresins are odoriferous but some stand out for their ability to induce a characteristic taste sensation, and for spices the most significant are pungency and bitterness. Taste sensation, as odor perception, is primarily dependent upon a complex of chemicals. Several natural chemical

compounds from spices providing a pungent taste sensation are nitrogen derivatives of 2-methoxyphenols. Chilipeppers for example contain a group of substances called capsaicinoids, which are vanillyl-amides of straight chain, saturated or unsaturated, monocarboxylic acids of varying chain length (C8 - C11). The group includes capsaicin and dihydrocapsaicin.

In black pepper the pungent principle is mainly piperidine, an amide derived from piperic acid and piperidine (hexahydropyridin). For a strong, biting effect the trans- or entgegen (E) geometry of the unsaturated part is needed and isomerization of these double bonds upon exposure to light and storage leads to loss of pungency. The pungency in fresh ginger has been atributed to the phenylketones called gingerols, with 6-gingerol as the most active compounds. Gingerols vary in benzenoid substituted chain length (C5 -C9) external to the hydroxyl substituted C-atom. Other examples of 2-methoxyphenol derivatives are eugenol found in clove and isoeugenol found in nutmeg and various other essential oils. These two are not only contributors to the taste sensation but also impart characteristic aroma because of their volatile nature. Sweet aromatic odoriferous substances like for instances vanillin can have bitter taste.

Volatile sulfur-containing compounds also contribute to the pungency of certain spices.

In black mustard and horseradish the organoleptic character impact compound is allyl isothiocyanate and in white mustard this compound is 4-hydroxybenzyl isothiocyanate. Bitterness as a basic taste in flavor is sometimes disagreeable but in subtle blend with sweet or sweet and sour condiments it can enhance the basic appeal of a given food. In drinks such as coffee, beer, campari alcoholic or bitter lemon soft drink a bitter tonality is appreciated.

Alkaloids and glycosides are chemical families associated with bitterness and so are other compounds, e.g. coumarins. Coumarins provide substantial contribution to the organoleptic properties of some spices and herb oils. The objective evaluation of flavor in spices has long been a matter of keen interest among food chemist. Correlation of the more or less subjective sensory data with objective flavor chemical profile is more the current. The subjective sensory analysis by human beings is more and more replaced by less subjective instrumental methods (the socalled "iron nose").<sup>10,11</sup>

Recent developments in more objective sensory analysis are the socalled gas chromatography -olfactometry techniques by sniffing at gas chromatography columns.<sup>10</sup> Appearance of foods or beverages provides an important psychological factor in the perception of flavor. Some species, e.g. turmeric, paprika are appreciated not only for their characteristic organoleptic quality but also for theit ability to provide color to food preparations. The color of turmeric is attributed to the major pigment curcumin, which is used to color a variety of savory products, particularly curry powders and mustard pickles. It exhibits an unusually intense yellow color in acidic products.

Table 5. Overview of some sensory aspects by tasting of edible oleoresins					
Sweet (sugars)	Acidic (acids)	Salty (sodium cloride)	Piquant-savory (Umami) (Monosodium glutamate)	Cool (menthol)	
TASTING OPPOSITES					
Bitter (quinines)	Alkaline (soaps)	Bland (distilled water)	Sickly (magnesium salts)	Hot (capsaicine)	

Paprika, on the other hand is a red-orange coloring material extracted from sweet red pepper. *Capsicum annuum* contains e.g. capsanthin and capsorubin (red pigments) and  $\beta$ -carotene (yellow-orange pigment) as the major pigment. Paprika oleo-resin is an economically important natural colorant in foods and drinks, especially for prepared meat products. The green pigment (chlorophyll) from fragrant pandan is traditionally extractred in the Philippines to color sweet, native cakes and other food preparations while perilla leaves which contains high concentrations of anthocyanins are extensively used to affod an natural appreciated red color to various Japanese and Korean cuisine products.

For spices in general visual sensory quality is assessed by the degree of retention of the original color in the final product such that care is invested in the processing of the spice, particularly during the drying stage. In recent years attention has been devoted to the use of natural pigments as food colorants. The interest has been attributed to the increasing demand for natural and organic foods coupled with the growing restrictions on the use of artificial coloring compounds. A number of spices could fill the need for such with extra benefit of providing aroma, puncency and bitterness to the foods and drinks.

## Adulterants and Substitutes

Oleoresins are applied in the food and flavor industry. Therefore these products are in many countries protected against adulteration by law. Industrialized countries are the most important producers of substitutes for natural aromatic materials. These substitutes can be isolated from other natural sources, e.g. isolation of eugenol from clove leaf oil. They may be produced by chemical modifica-

tion of natural material, e.g. methyl chavicol and anethole from turpentine (residue). They can be manufactured by chemical reactions with a natural chemical compound, e.g. condensations with citral. Other substitutes may also be produced completely synthetic, as for instance cinnamic aldehyde from toluene by oxidation via benzaldehyde and condensation with acetaldehyde. Thus the building blocks, chemical compounds, for reconstituted oleoresins can be natural, natural-identical and synthetic, not occurring in nature, as for instance ethylvanillin as replacer for natural vanillin. Natural-identical isolated or synthetic chemical compounds can be mixed with oleoresins, resulting in artificial materials.

Oleoresins and their essential oils are complicated mixtures of hundreds of chemical compounds, most of them occurring in part per million of even less quantities and up to now unknown. Natural chemical compounds, which possess an asymmetric carbon atom are optically active. The optical antipods, co-called enantiomers, of have different organoleptic quality. Moreover a lot of the minor natural occurring chemical compounds are not commercially available. Thus the incomplete reconstituted materials often do not match the richness of their natural model.

Up to the 1930s, the scene was dominated by natural products. Developments in synthesis were relatively slow; the first step was to isolated natural compounds, e.g. cinamaldehyde from cinnamon. One of the first natural identical synthetic flavor compounds was vanillin which appeared in 1876. Identification of aromatic chemical compounds is nowadays facilitated by modern spectroscopic techniques, as there are capillary gaschromatography (GC), mass spectroscopy and infrared spectroscopy. It was by the end of the 1950s that synthetic citral, geraniol, nerol and linalool became viable alternatives for the reconstution of natural essential oils.

Substitutes for natural essential oils are reconstituted compoistion of aroma chemicals that mimic the character of the oil in question. Adulteration of natural essential oils covers a range of actions: standardization, reinforcement, liquidization, reconstitution, and commercialization. Standardization involves improving the quality of a product to meet the standard requirements. One can standardize the content of characteristic substances by adding such products that have been isolated from another natural source or

#### EDIBLE OLEORESINS

produced synthetically. Common examples are the addi-tion of eugenol from clove leaf oil to other spicy oils or of synthetic cinnamaldehyde to cinnamon oil.

Reinforcement is an extension of standardization by using a natural or synthetic organoleptically characteristic compounds as an extender for the original oil. When the odor quality of an essential oil can be improved there is always the temptation to add exaggerated amounts of the characteristic compounds to improve the quality and to make a product with "more olfactive value for money". Liquidization has the aim not to change the organoleptic quality of a product, but is appearance, to transform is in a better applicable one. Some oleoresins may be semi-solid or solid. If the liquid form is preferred, solvent or liquidizer can be added to the product. Various solvents are used for this purpose, for instance propyleneglycol, triethyl citrate and benzoates. Reconstitution is the compounding of a natural isolate using natural, nature-identical or synthetic chemical compounds to obtain a product that is similar to the original natural oil. However, it is quite impossible to reconstitute complete natural oils. Reconstituted essential oils are applied especially in functional perfumery. When a natural essential oil in a perfume composition is prohibitively expensive it can be replaced by a reconstituted oil.

Commercialization of a natural product involves expanding its volume and lowering its quality, to make it more profitable. It may involve the use of reinforced, liquidized or reconstituted products. If properly declared, commercialization is an accepted practice. Some buyers cannot afford to pay the cost of a natural product and are willing to buy a commercialized product with similar though inferior organoleptic characteristics. However, a buyer has the right to know what he or she is buying. Because of their food use the adulterations of spice oils for flavoring is more serious than that in perfumery. Some examples of adulterations of spice oils are the addition of a chemical compound from a cheaper natural source e.g. eugenol from Syzygium aromaticum leaf oil to pimento berry oil, or of 1,8-cineole for Eucalyptus globulus oil to rosemary and cardamom oil, and of camphor from *Cinnamomum camphora* to rosemary oil. Other examples of adulteration of spicer oils are the addition of (semi-) synthetic components, e.g. methychavicol and anethole from turpentine; and synthetic cuminaldehyde and cinnamaldehyde.

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Address correspondence to Ronald Boelens, Boelens Aroma Chemical Information Service, Groen van Prinstererlaan 21, 1272 GB Huizen, The Netherlands.

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