Counter Current Deterpenation of Cold Pressed Sweet Orange Peel Oil

By David A. Moyler and Martin A. Stephens
Universal Flavors Ltd., Bletchley, United Kingdom

There are five main commercial methods currently used for removing some or all of the water insoluble monoterpene hydrocarbons from orange oils to make flavors: Washing, folding and washing, folding, chromatographic and counter current.

Washing Process

The traditional method of incorporating expressed citrus oils into flavors is to dissolve the soluble portion into an alcohol-water mixture, then rejecting the insoluble portion (the washed oil).

This process is about 50% efficient and the remaining 50% of flavor stays unpartitioned in the washed oil.

A study of different concentrations of aqueous alcohol and cold pressed orange oil to solvent ratios, for deterpenation by washing techniques, has been published.[1] It was shown that by varying the proportions of alcohol and water solvent mix for extraction and the ratio of oil to solvent, a spectrum of monoterpene, sesquiterpene, aldehyde and alcohol contents from the orange oil could be derived.

Distillation and Washing

The essential oil is concentrated by heating and volatilization of some of the monoterpenes during vacuum distillation. This concentrate is then used for the washing process.

A sophisticated variation of this method using a simultaneous distillation-extraction of orange peel has been researched and a detailed GC/MS analysis of the important oxygenated flavor constituents published. Details of four papers on this method by Sugisawa et al. were reviewed by Lawrence.[2]

Distillation or Folding

A multiple folded concentrate, prepared by distilling off monoterpene hydrocarbons, can be used directly to make a soluble essence by dissolving in alcohol and water.

The distillation of cold pressed orange oil using a thin film evaporator (molecular still) to produce a partly deterpenated oil has been reported by Tateo.[3] This method has the advantage of short distillation residence time of orange oil in the heated zone, thus minimizing the thermal degradation.[4]

Preparative Adsorption Chromatography

Column chromatography with silica gel as an absorbant has been used to deterpenate orange and lemon oils.[5] These authors used slurry packed columns instead of the dry packed column used earlier,[6] to reduce the "risk of decomposition, isomerization or polymerization of the sensitive components of the oil." Ethyl acetate and hexane in varying proportions were used for deterpenation by elution.

An absorption chromatographic technique using "poroplast" (Teflon, P.T.F.E., polytetrafluorethylene) packed columns to deterpenate orange and lemon oils has been reported.[7,8]

Counter Current Extraction

It is possible for non-polar carbon dioxide to be used to dissolve the non-polar terpene by-product from orange oil.[9] However, this method involves a capital expenditure more than ten times that of ambient temperature and pressure equipment.

The principle of using mixtures of alcohol and water to extract the soluble flavoring from orange oil are well established.[1] The differences of the two phases (orange oil and diluted alcohol) has to be sufficient to enable quick and easy phase separation. In practice this is achieved with a density differential of 0.04 g/ml or more. As the density of singlefold

0272-2666/92/0002-0037$4.00/00—

orange oil is 0.845, the practical working alcohols are:

Alcohol	B.pt°C @ 760mm	Density @ 20°C	Advantages	Status
Methanol	65°	0.791	easiest to remove at low temp.	N.I.*
Ethanol	78°	0.790	most acceptable food grade	N.I.
Propan-2-ol	82°	0.784	minimal acetal formation	N.I. (but not in orange)

*N.I. = nature identical

The amount of water included in the aqueous alcohol determines the density differential for extraction, so if a specific optimum mixture does not reach the target of 0.04 g/ml differential, two options remain:

(i) Reduce the density of the orange oil by diluting with a lower density non-polar solvent, which has to be subsequently recovered for re-use from the terpenes after deterpenation. Suitable solvents for the terpenes are liquid carbon dioxide, pentane and hexane.

(ii) Preferably, increase the density of the aqueous alcohol by dissolving a processing adjunct to raise the density to 0.885, that is 0.04 above that of singlefold orange. High density organic solvents can be used but in practice food grade ionic salts such as sodium chloride, sulphate and citrate work as efficiently.

The deterpenation takes place at ambient temperature by mixing orange oil and aqueous alcohol at a ratio of 1 to 3 and a high level of contacting efficiency is achieved by a motor driven rotor within the emulsification chamber. This rotor disperses the orange oil by centrifugal force into microscopic droplets in aqueous alcohol. The more polar flavor containing oxygenated orange components dissolve in the alcohol and this aqueous alcohol phase is separated quickly and efficiently, in situ, by the spinning rotor, utilizing the difference in density.

The alcohol is removed from the concentrate by evaporation at 40°C and 120 mm vacuum as an azeotrope with the water. This leaves the orange oil as a dispersion in a water-ionic salt solution from which it readily separates. The concentrated oil is then filtered and dried. If necessary, the last traces of solvent are removed with a high vacuum falling film evaporator. The composition of cold pressed sweet orange peel oil which has been counter current deterpenated, is shown in Table I.

The concentrate is virtually terpene free (1% or less monoterpene hydrocarbon content is typical) and the terpene by-product has a low aldehyde content. In the case of orange oil, less than 0.1% of aldehyde is lost to the terpenes which means a better than 95% utilization of the expressed oil, without using heat during the extraction. This oil can be dissolved directly into an alcohol-water mixture to make a flavoring essence.

Counter current oils can contain the furocoumarins and some sesquiterpene hydrocarbons which make an important contribution to the flavor of the citrus concentrate. The furocoumarins are known to have natural antioxidant properties. Their presence does cause haziness if propylene glycol and water only are used as solvent. These oils are, however, soluble and full flavored when dissolved in the conventional alcohol-water mixtures normally used for beverage manufacture.

Table I. Chemical composition of monoterpene-free orange peel oil

Compound	Percentage	Compound	Percentage
trans-2-hexenol	t	geraniol	0.2
heptanal	t	geranial	6.5
methyl heptenone	t	perillaldehyde	1.1
octanal	11.6	decanol	0.3
heptyl formate	t	undecanal	0.8
D limonene	0.2	2,4-decadienal	0.1
octanol	2.5	neryl acetate	0.2
nonanal	2.3	geranyl acetate	0.1
linalool	28.0	α-copaene	<0.1
trans-limonene oxide	0.2	dodecanal	3.3
citronellal	3.2	β-caryophyllene	<0.1
terpinen-4-ol	0.4	valencene	0.1
α-terpineol	3.0	trans-trans-α-farnesene	<0.1
decanal	17.0	elemol	0.4
octyl acetate	0.4	trans-nerolidiol	0.2
nerol	1.2	β-sinensal	0.9
neral	4.0	α-sinensal	0.6
carvone	<0.01	nootkatone	0.5
piperitenone	0.2	aldehyde acetals total	8.0
2-decan-1-al	0.1	others	2.4
			100.0

t = trace

As with all citrus concentrates made by contacting oil with alcohol, the counter current deterpenated orange oil contains acetal compounds formed from the chemical condensation of aldehydes and alcohol. In flavor applications, they tend to have a "smoothing and fixing effect" in product, which is normally considered as advantageous.

References

Address correspondence to David Moyler, Universal Flavors Ltd., Bilton Road, Bletchley MK1 1HP, United Kingdom

1. J Owusu-Yaw, RF Matthews and PF West, *J Food Sci* **51**(5) 1180-1182 (1986)
2. BM Lawrence, *Perf & Flav* **15**(6) 45-55 (1990)
3. F Tateo, Production of Concentrated Orange Oils Using a Thin Film Evaporator, *J Essent Oil Res* **2**(1) 7-13 (1990)
4. Universal Flavors Ltd, *Templar Molecular Distilled Oils, Part III, Application to Flavors and Fragrances.* Publ Universal Flavors, Bilton Road, Bletchley MK1 1HP, UK (1990)
5. NE Tzamtzis and SE Wodakis and GK Parissakis, *Flav & Frag J* **5** 57-67 (1990)
6. JBS Braverman, *Perfumery Essent Oil Record* **6** 284 (1957)
7. A Fleisher, *Perf & Flav* **15**(5) 27-36 (1990)
8. A Fleisher, G Biza, N Secord and J Dono, *Perf & Flav* **12** 57-61 (1987)
9. F Temelli, CS Chen and RJ Braddock, Supercritical Fluid Extraction in Citrus Oil Processing, *Food Technology* **42** 145-150 (1988)