Ultra-Tech Citrus Concentrates—a New Series of Deterpenified Citrus Oils

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A series of citrus oils—orange, distilled lime, lemon, grapefruit and tangerine—were deterpenified by a cold process utilizing a proprietary production scale poroplast extraction technique. The oils obtained are practically free of mono- and sesquiterpene hydrocarbons while the composition of the oxygenated components remains nearly intact. This includes the low and high boiling oxygenated constituents of citrus oils which are usually lost during conventional deterpenification by fractional distillation. Being substantially more soluble in alcohol-water solutions, the new deterpenified oils also possess a noticeably higher stability under accelerated aging conditions in finished beverages. The detailed chemical composition of these oils is compared to a number of commercial terpeneless citrus oils prepared by conventional methods.

It is commonly agreed that the hydrocarbons naturally found in all essential oils contribute very little to the overall odor and flavor profile of the essential oil. Moreover, years of worldwide flavor and fragrance experience and research leaves no doubt that the presence of substantial quantities of hydrocarbons in the essential oil create very serious problems for the users of these products. The flavor intensity of hydrocarbon rich oils is generally low and these oils are poorly soluble in alcohol-water systems. Their

Table I. The Chemical Composition of Orange Concentrate in Comparison with Commercial Terpeneless Orange Oils

Compound	"Ultra-Tech"	A*	B*
Octanal	4.8%	-	-
Limonene	0.8	3.8%	0.3%
Octanol	2.9	0.4	0.4
Nonanal	1.4	1.7	0.5
Linalool	27.9	22.7	9.9
Citronellal	2.6	3.0	2.1
α-Terpineol	3.4	3.0	4.0
Decanal	11.5	16.0	20.0
Citronellol	1.4	0.9	1.3
Geraniol	1.6	2.0	2.7
Neral	4.5	4.4	5.8
Geranial	5.6	5.9	8.0
Perilla aldehyde	0.8	0.5	1.0
Undecanal	0.9	1.0	1.6
Dodecanal	2.0	2.9	4.2
Total major sesquiterpenes	-	11.1	22.0
Elemol	0.6	0.8	0.6
β-Sinensal	1.3	1.1	0.5
α-Sinensal	0.8	1.0	0.3
Nootkatone	1.4	0.3	0.2

*Commercial terpeneless orange oils

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major disadvantage, however, is the very high susceptibility of the hydrocarbons to be oxidized by air. The combined effect of chemical reaction following the hydrocarbon oxidation results in the complete deterioration of the oils' odiferous profiles. Obviously, these problems are most serious in the case of citrus oils in which the hydrocarbons are found in quantities ranging from 95-99%.

In 1937, van Dijck and Ruys proposing a method of deterpenation wrote that "The preparation of citrus and essential oils absolutely free from terpenes and sesquiterpenes presents many difficulties to the manufacturer. In many cases the terpeneless oils are still obtained by a fractional distillation process only. Nearly all the oxygenated constituents are very sensitive to heat and are readily polymerised or resinified first during the distillation of the terpenes and secondly during the distillation of the higher boiling parts of the oil, even if the distillation is carried out in a high vacuum. Of course, the resinification accompanied by decomposition, does very serious harm to taste and odour of the oil thus obtained, and by the same cause the yield of terpeneless oil is lowered".[1]

Twenty years later, in 1957, Ruys justifying the liquid-liquid extraction process which he developed wrote that the "distillation of essential oils to render them hydrocarbon-free is based on the assumption that the hydrocarbons have a lower boiling point than the oxygen compounds, an assumption which, because of its sweeping generality, must be regarded as completely erroneous.

"First of all there are a number of oxygenated components, which play a vital role in the odour and have a lower or similar boiling point to the terpenes; secondly there is the sesquiterpene group, hydrocarbons with fifteen carbon atoms, the boiling point of which is actually in the same range as that of the oxygenated compounds with ten carbon atoms.

"It is for these very reasons that a hydrocarbon-free lavender oil, obtained by distillation, can be scarcely said to possess a fresh scent—one might almost term it "dead" due to the fact that the vital ketones and secondary alcohols are eliminated with the terpenes during the distillation process.

"The same also applies to a so-called 'terpeneless' lemon oil produced in this way, which loses a great deal of its solubility, as the sesquiterpene hydrocarbons are still present in the oil in their entirety.

"Another fact to which too little attention has been drawn to date is that in the distillation of pressed citrus oils the natural antioxidants remain in the residue and are consequently no longer able to protect the susceptible oil against transmutations. It is a well-known fact, for instance, that a distilled orange oil from which the hydrocarbons have been wholly or partially eliminated resinifies extremely rapidly, while similar phenomena characterize a distilled bergamot oil, rendered free of hydrocarbons, which has not a very strongly pronounced odour of its own and which turns completely sour on being allowed to stand for a few weeks, following the decomposition of the linalyl acetate. This decomposition is, in our opinion, initiated by oxidation."[2]

Table II. The Chemical Composition of Lemon Concentrate in Comparison with Commercial Terpeneless Distilled Lemon Oils

Compound	"Ultra-Tech"	A*	B*
Methyl heptenone	0.1%	-	-
Octanal	0.5	-	-
p-Cymene	-	0.1%	0.1%
Limonene	-	0.3	0.5
1,8-Cineole	0.1	-	-
γ-Terpinene	-	0.1	0.6
trans-Sabinene hydrate	1.4	0.1	trace
cis-Sabinene hydrate	1.2	0.2	0.1
Nonanal	1.0	0.2	0.2
Linalool	2.9	1.3	0.5
Citronellal	1.0	1.2	0.5
Borneol	0.3	0.2	0.1
Terpinen-4-ol	0.7	0.5	0.5
p-Cymen-8-ol	0.3	0.3	0.2
α-Terpineol	6.4	3.7	2.4
Decanal	0.5	0.6	0.5
Neral	21.0	19.2	13.0
Geranial	33.8	30.2	21.1
Geraniol	1.6	1.1	1.1
Undecanal	0.3	0.4	0.5
Methyl geranate	0.3	0.2	0.1
Citronellyl acetate	0.3	0.9	0.7
Neryl acetate	4.3	9.4	9.6
Geranyl acetate	3.2	7.9	7.1
Caryophyllene	-	2.7	5.0
α-Bergamotene	-	4.9	8.6
β-Bisabolene	-	5.4	12.8
α-Bisabolol	0.7	0.4	0.4
Nootkatone	0.2	0.1	trace
Dimethoxy coumarin	1.3	0.1	0.2

*Commercial terpeneless lemon oils

Table III. The Chemical Composition of Distilled Lime Concentrate in Comparison with Commercial Terpeneless Distilled Lime Oils

Compound	"Ultra-Tech"	A*	B*
1,4-Cineole	1.6%	-	-
1,8-Cineole	2.4	-	-
Limonene	0.3	0.4%	1.1%
p-Cymene	trace	0.2	0.1
γ-Terpinene	trace	0.6	0.8
Terpinolene	trace	1.9	1.2
p-Cymenle	trace	0.3	0.1
Linalool	1.2	0.7	0.5
Fenchol	4.3	2.8	1.9
3-Terpinen-1-ol	6.4	4.9	3.3
trans-β-Terpineol	4.8	4.1	3.4
cis-β-Terpineol	1.4	1.3	0.6
Borneol	4.5	4.1	1.2
Terpinen-4-ol	5.7	5.2	4.1
α-Terpineol	48.3	45.9	42.7
γ-Terpineol	7.4	6.9	6.8
Decanal	0.7	0.9	0.7
Geranial	0.6	0.4	0.6
Geraniol	0.4	0.1	0.3
Undecanal	0.1	0.1	0.2
Neryl acetate	0.1	0.2	0.3
Geranyl acetate	0.3	0.7	0.6
Caryophyllene	-	2.9	3.0
α-Bergamotene	-	3.8	4.1
β-Bisabolene	trace	1.3	4.3
Caryophyllenol	0.4	-	0.2

*Commercial terpeneless lime oils

Hydrocarbon-free Essential Oils

Since the original report presented by van Dijck and Ruys on counter-current liquid-liquid extraction and the application of adsorption chromatography proposed by Kirchner and Miller,[3] a great number of works published indicate that very serious efforts were devoted to finding an alternative method for the preparation of hydrocarbon-free essential oils, especially citrus oils.

Nevertheless, most of the terpeneless citrus oils marketed today are still prepared by classic methods based on fractional distillation, the reason being the complexity and high cost of efficient extraction equipment. This combined with

Table IV. The Chemical Composition of Grapefruit Concentrate in Comparison with Commercial Terpeneless Grapefruit Oils

Compound	"Ultra-Tech"	A*	B*
Octanal	7.6%	0.2%	-
Limonene	2.1	3.0	3.6%
γ-Terpinene	0.2	-	0.2
Octanol	1.5	0.6	0.4
Nonanal	1.3	1.2	0.4
Linalool	2.5	3.1	1.3
Citronellal	1.4	2.3	0.7
Terpinen-4-ol	0.5	trace	1.5
α-Terpineol	1.9	2.1	2.9
Decanal	7.7	13.5	9.2
n-Octyl acetate	0.3	1.4	1.6
Neral	1.6	1.9	2.5
Geranial	2.4	3.0	3.9
Geraniol	0.5	0.9	0.8
Perilla aldehyde	0.2	0.4	0.7
Undecanal	0.3	0.6	0.6
Nonanal dimethyl acetal	-	0.1	-
Citronellyl acetate	0.1	0.4	0.9
α-Terpinyl acetate	0.1	0.3	0.6
Neryl acetate	0.1	0.3	1.8
Geranyl acetate	0.5	1.5	3.7
Decanal dimethyl acetal	-	0.7	-
Dodecanal	0.5	1.3	1.2
Unknown sesqui	-	0.7	4.4
α-Copaene	-	0.8	3.7
Caryophyllene	-	2.1	14.0
α-Humulene	-	0.3	1.9
δ-Cadinene	-	0.8	5.2
Elemol	0.7	1.4	1.1
Nootkatone	4.9	7.3	8.3
Bergaptene	1.5	1.2	-
7-Geranoxy coumarine	9.9	13.2	-
Unknown coumarins or psoralens total	32.4	6.9	-

*Commercial terpeneless grapefruit oils
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high operational costs is reflected in high prices of the deterpenified oils which make these products cost prohibitive.

On the other hand, a growing market demand for high soluble and stable citrus oils with emphasis on the fresh "juicy" top notes encouraged the search for new and effective methods to remove the terpene hydrocarbons.

To a large extent, the difficulties associated with the preparation of hydrocarbon-free citrus oils were resolved by utilization of a proprietary cold process which involves combined extraction and chromatographic techniques, previously developed by Fleisher.

The deterpenified oils obtained in good yield by processing single fold citrus oils were named Ultra-Tech Citrus Concentrates.* The chemical compositions of orange, lemon, distilled lime, grapefruit and tangerine concentrates determined by GC-MS are presented on Table I-V along with the chemical compositions of terpeneless oils prepared by conventional methods.

From the data presented above it can be seen that they are substantially enriched in both low and high boiling oxygenated components in comparison to the terpeneless citrus oils produced by conventional manufacturing methods. In addition, the hydrocarbons, mostly sesquiterpenes which are found in substantial concentrations in the conventional terpeneless oils, were not found in measurable quantities.

A series of tests were performed in order to determine the relative stability of these concentrates versus the conventional commercial terpeneless oils. The effect of ultra-violet irradiation was determined for lemon and distilled lime.

*Ultra-Tech Citrus Concentrates is a trade name owned by Fritzsche Dodge & Olcott.

Table V. The Chemical Composition of Tangerine Concentrate

Compound	"Ultra-Tech"
Octanal	3.2
Limonene	2.0
Octanol	0.3
trans-Sabinene hydrate	0.8
cis-Sabinene hydrate	0.4
Nonanal	1.3
Linalool	29.1
Citronellal	2.5
Terpinen-4-ol	0.6
α-Terpineol	4.6
Decanal	9.2
Carvone	1.3
Citronellol	2.7
Geraniol	0.8
Thymyl methyl ether	2.4
Perilla aldehyde	0.8
Thymol	3.8
Undecanal	0.1
2,4-Decadienal	2.4
Neryl acetate	0.3
Geranyl acetate	0.3
Dodecanal	1.5
α-Sinensal	1.4

Samples of these oils were incorporated in both still and carbonated beverages, then exposed to UV irradiation for 48 hours.

At the end of this period, the beverages were organoleptically compared to the samples of beverages incorporating the conventional terpeneless oils prepared and treated concurrently in the same manner. Control samples were refrigerated at 40°F for the same period.

After 48 hours of UV exposure the flavor of the beverages prepared incorporating the commercial terpeneless lemon oil were no longer characteristic of lemon. The beverages containing the Ultra-Tech lemon concentrate, although decreased in impact, maintained their true lemon character.

The Ultra-Tech lime concentrate evaluated in a still beverage after 48 hours showed virtually no change in flavor intensity or character while, in contrast, the beverages containing the commerical terpeneless lime oil showed marked decreases in flavor intensity and lime character. The comparative evaluation of the Ultra-Tech lime concentrate in carbonated beverages demonstrated moderate losses in flavor intensity and a slight development of an off taste. The flavor of the carbonated beverage containing the commercial terpeneless lime deteriorated completely after 48 hours.

An accelerated storage study was conducted in still and carbonated beverages, and concurrently stored at 105°F for a period of three weeks and evaluated at one week intervals. Control samples were refrigerated at 40°F for the same period. After the three week period, all the samples were organoleptically evaluated. All the Ultra-Tech citrus concentrates showed substantially higher relative stability in still and carbonated beverages under accelerated aging conditions.

References

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