Biology-Based Hydrocarbons as Extraction and Carrier Solvents for a New Generation of Fragrance Products

Reimar C. Bruening, Ph.D., California Cosmetic Creations SPC

2018 WORLD PERFUMERY CONGRESS

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Palais des Congrès Nice Acropolis, Nice, France

Vegetable Oil, Alcohol, and Biology-Based Hydrocarbons (BBHCs) in Multifunctional Beauty Applications

	Scented Oils	BBHC-based Scents	Alcohol-based Scents
Perfume	Oldest application; limited stability; limited intensity; weak sillage.	New application; unlimited stability; good intensity; moderate sillage.	Traditional application; good stability; good intensity; good sillage.
Skin Care	Emollient with oily skin feel; long stay; shiny; (stains fabric).	Proven application; velvety skin feel; short stay; compatible with most ingredients	Non-Paraben Preservative
Hair Care	Good scenting ability; heavy; greasy.	Good scenting ability; light; dry; shiny.	Non-Paraben Preservative

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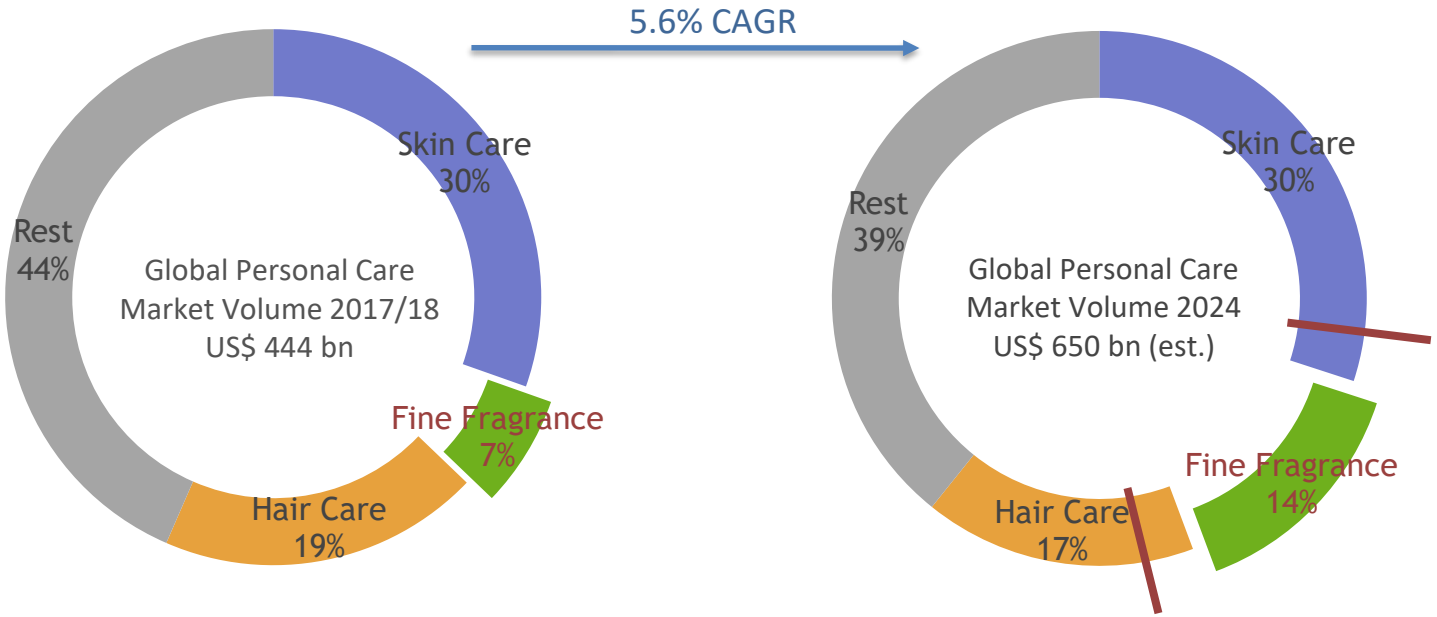
Global Beauty Care Market Predictions: an Opportunity for Multi-Functional Fragrance Products



17.4% CAGR !

Sources: euromonitor.com
cossma.com
statista.com
kpmg.com

Growth spaces for multifunctional and "green" fragrance products

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The MEA Beauty Market: An Example of Key Indicators for Global Growth

- The Middle East and Africa still keeps solid growth rate globally, overall category growth is promising compared to historic period.
- Growth is driven by young and aspirational population who want to invest in grooming, looking beautiful and maintaining their health in the process
- Demand on ethical, natural, cultural demand product development for international and local players
- Multi category integration offers opportunities
- The rise of beauty influences is boosted by social media exposure that acts as a positive word of mouth and effective marketing tool

Influencing factors for buying decision: Consumer awareness on issues of health ("natural" is "healthier"), sustainability, cultural preferences, multi-functionality, encouragement by opinion leaders.

Regional CAGR: 7 - 21% (Global: 4%)

Table source: Euromonitor 2017: https://www.beautyworldme.com/uploads/editor_images/file/beautyworld17/amna.pdf

Evolving Global Consumer Preferences Indicate Future Market Success for BBHCs in Hybrid Beauty Care / Fragrance Products

Trending:

• Light, close-up "individuality" scents	• BBHC- based fragrances are "immediate"
• Safe to use	• BBHCs are "Approved" by leading skincare blogs and "influencers"
• "Clean" ingredients	• BBHCs are non-petrochemical "nature-derived" silicone-replacers
• Preference for "natural"	• BBHCs are Ecocert-COSMOS approved,
• Simple, multifunctional formulae	• BBHC-based fragrances are also emollients, moisturizers, and produce shine and glide on hair
• Anti-pollution activity	• BBHCs can be protective film-formers
• Sustainably produced	• Increasing consumer pressure for RSPO certification; promising alternatives from bio-fuel processes
• Microbiome compatibility	 • Yes

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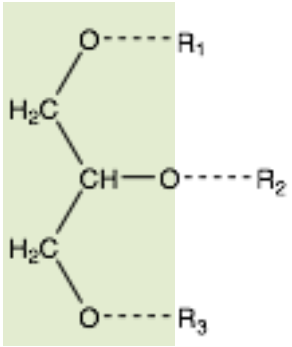
… but not so for Alcohol (if used outside of Fragrance Applications)

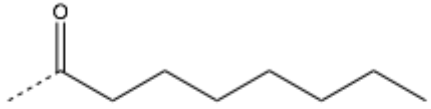
Consumer preferences for future beauty care:		**Alcohol as fragrance carrier meeting future product criteria?**
• Safe to use	→	• Considered "drying out" and "irritating" the skin; might damage **skin microbiome**
• "Clean" ingredients	→	• In fragrances alcohol is usually derived from petrochemical processes,
• Preference for "natural"	→	• and therefore not Ecocert-COSMOS
• Simple, multifunctional formulae	→	• in personal care products alcohol acts as a potent preservative (@15%); compatible with most ingredients
• Anti-pollution activity	→	• might actually damage barrier function
• Sustainably produced	→	• only if produced by fermentation
• Microbiome compatibility	→	• No

Vegetable Oil Chemistry 1: The Players

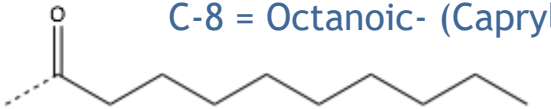
Triglyceride



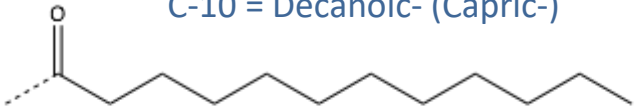
R1 = R2 = R3 or
R1 = R2 ≠ R3 or
R1 ≠ R2 ≠ R3



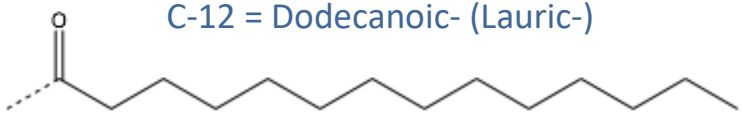
C-8 = Octanoic- (Caprylic-)



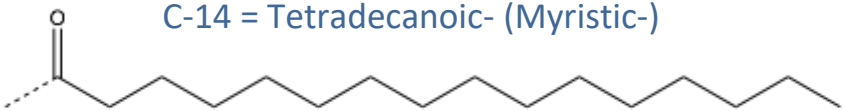
C-10 = Decanoic- (Capric-)



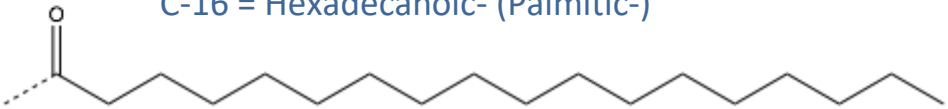
C-12 = Dodecanoic- (Lauric-)



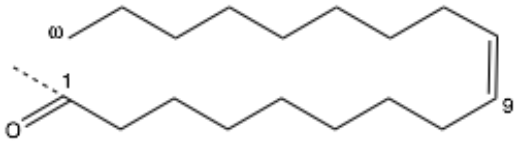
C-14 = Tetradecanoic- (Myristic-)



C-16 = Hexadecanoic- (Palmitic-)



C-18 = Octadecanoic- (Stearic-)



(9Z)-C-18:1 = (9Z)-Octadec-9-enoic- (Oleic-)

	8:0	10:0	12:0	14:0	16:0	18:0	18:1	18:2
Palmkernel	3	4	45	18	9	3	15	2
Coconut	8	7	48	16	9	2	7	2

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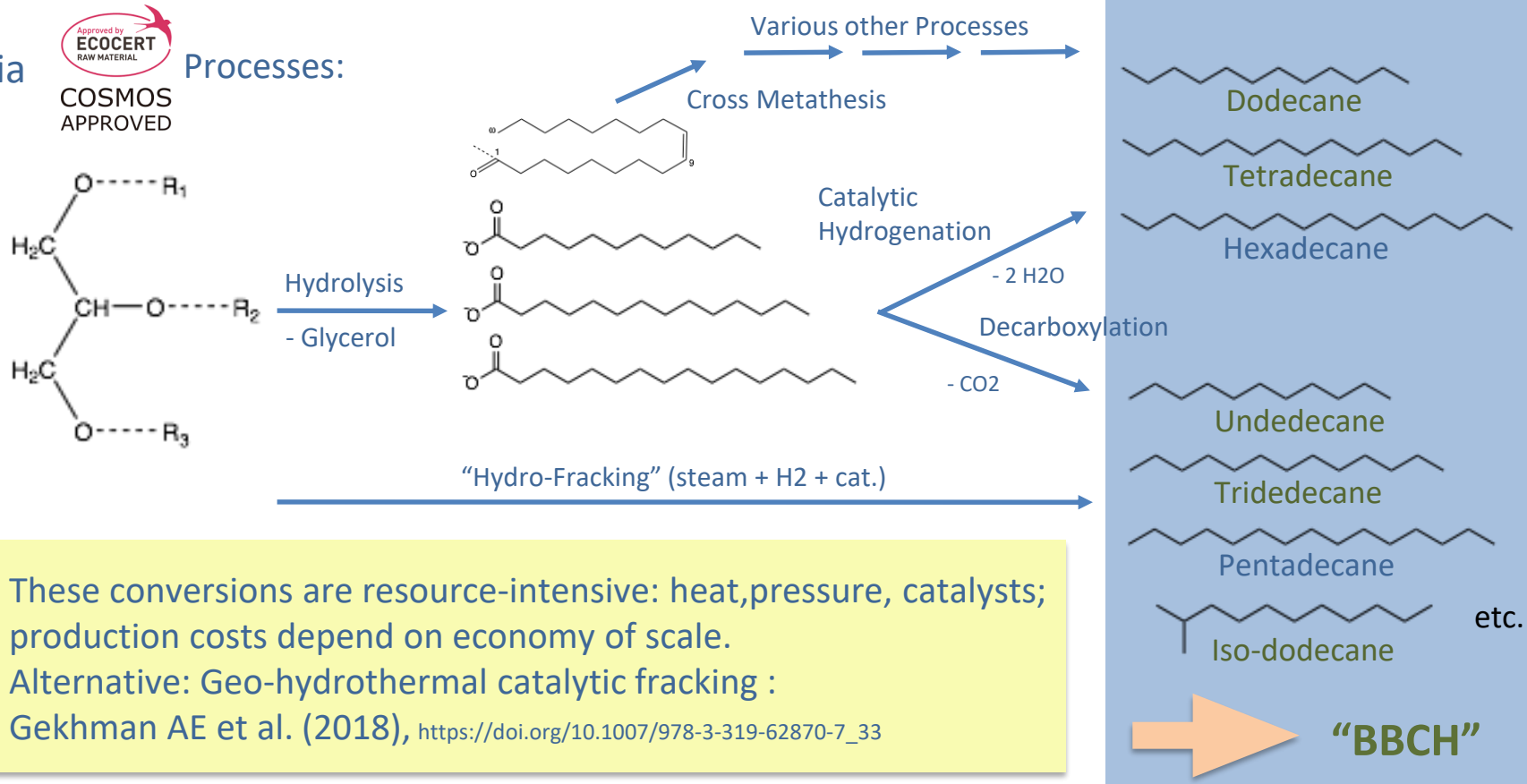
Vegetable Oil Chemistry 2: Conversions into Hydrocarbons (High-Value Cosmetic Ingredients from Sustainable Processes 1)

via Approved by ECOCERT RAW MATERIAL COSMOS APPROVED Processes:

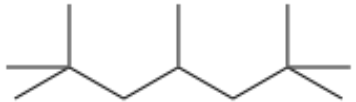


These conversions are resource-intensive: heat,pressure, catalysts; production costs depend on economy of scale.
Alternative: Geo-hydrothermal catalytic fracking :
Gekhman AE et al. (2018), https://doi.org/10.1007/978-3-319-62870-7_33

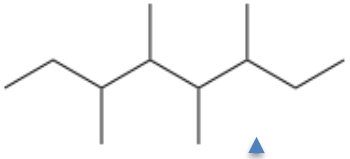
High-Value Cosmetic Ingredients from Sustainable Processes 2

Biomass

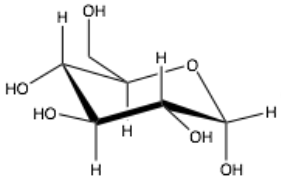
Chemical or Biological Degradation



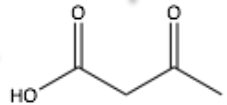
Iso-Dodecane



BBHCs (iso-)



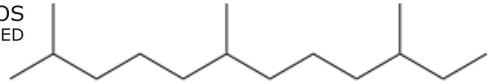
Sugars
(e.g. Glucose)



Levulinic Acid

Microbial Conversion

Approved by ECOCERT RAW MATERIAL
COSMOS APPROVED



Hemisqualane, Neossance®

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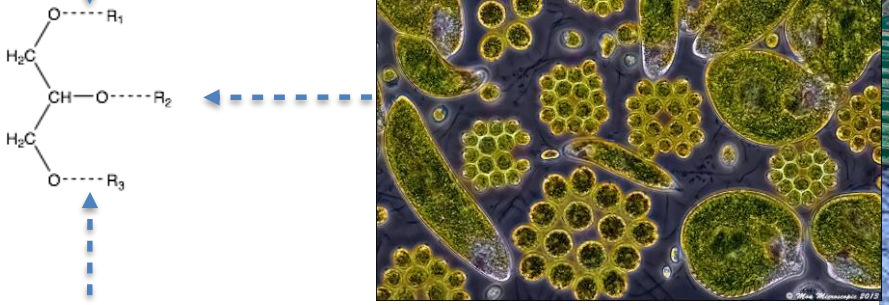
Sustainability: Vegetable Oil Sources, Present and Future

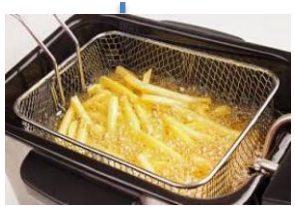
Palm & Coconut Oil:
Oil palm plantations cover >27 mio ha globally, mostly former rainforest.
Source: rainforest-rescue.org

Source: Cyanotech



Source: nextnature.net

Source: united withisrael.com



Waste Cooking Oil:
11,000,000,000 liters/year in US alone.
Source: US EPA

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High-Value Cosmetic Ingredients from Sustainable Processes 3

The direct production of hydrocarbons from solar-powered algae farms will make BBHCs competitive as universal beauty care ingredients:

Plant Physiology®, August 2016, Vol. 171, pp. 2393–2405, www.plantphysiol.org © 2016 American Society of Plant Biologists. All Rights Reserved.

Microalgae Synthesize Hydrocarbons from Long-Chain Fatty Acids via a Light-Dependent Pathway[1][OPEN]

Damien Sorigué, Bertrand Légeret, Stéphan Cuiné, Pablo Morales, Boris Mirabella, Geneviève Guédeney, Yonghua Li-Beisson, Reinhard Jetter, Gilles Peltier, and Fred Beisson*

CEA and CNRS and Aix-Marseille Université, Biosciences and Biotechnologies Institute (UMR 7265), Cadarache 13108, France (D.S., B.L., S.C., P.M., B.M., G.G., Y.L.-B., G.P., F.B.); and Department of Botany and Department of Chemistry, University of British Columbia, Vancouver V6T 1Z4, Canada (R.J.)

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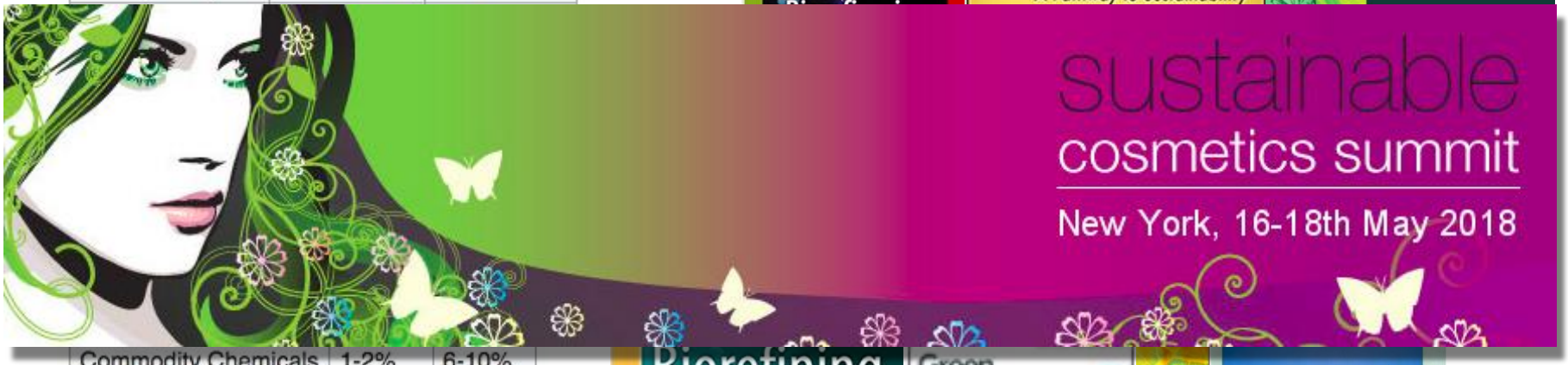
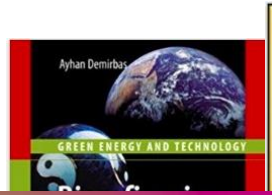
Sustainability Guaranteed: Green Chemistry and Biotechnology

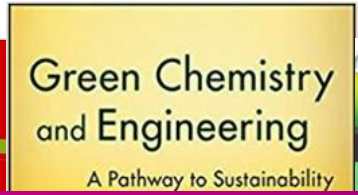
Biotechnology Penetration in the Chemical Industry

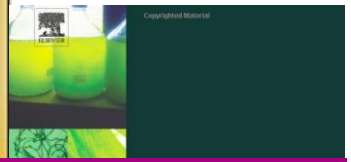
Year	Value	Penetration
2000 (actual)	$67 billion	5.3%
Commodity Chemicals	1-2%	6-10%
Specialty Chemicals	20-25%	45-50%
Fine Chemicals	20-25%	45-50%
Polymers	5-10%	10-20%

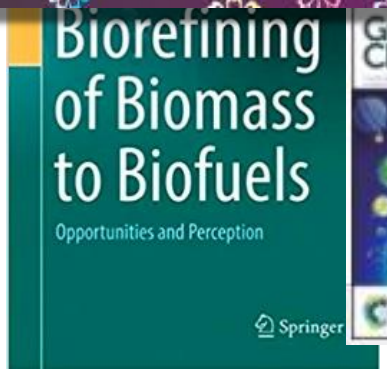
McKinsey & Co, 2015

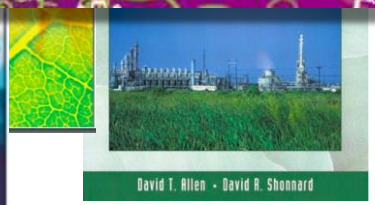












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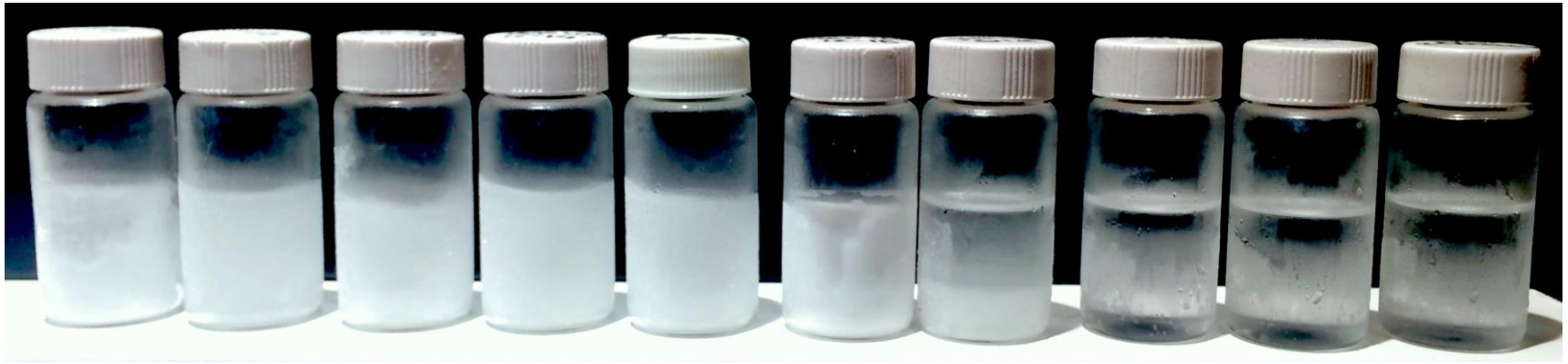
Comparison of Physical, Sensorial, and Olfactory Properties of BBCHs

	Appearance	m.p. (°C)	b.P. (°C)	f.P (°C)	Volatility (VP mm/Hg)	Flammability	Solvation Power	Smell	Skin Feel
n-Hexane	clear& colorless	-68	68.7	-23.3	151	++++	+++	++	dry, cooling, ultra light
n-/iso-Undecane/ Tridecane Blend	clear& colorless	< -17	195 235	60 79	0.56 0.08	++	++	++	fast spreading, ultra light, dry
n-Dodecane	clear& colorless	-12	215	71	0.13	++	++	++	fast spreading, light
iso-Dodecane	clear& colorless	-81	208	60	0.3	++	+	+	fast spreading, silky
n- and iso-Dodecane/ Tertadecane Blend	clear& colorless	> -17	208 - 250	66	~0.1	++	++	+	fast spreading, silky
n-Dodecane/ n-Tetradecane D	clear& colorless	> -17	215 - 250	83	~0.05	++	++	-	fast spreding, silky, long play
n-Tetradecane	clear& colorless	5-6	251	99.4	0.03	+	++	-	fast spreading, light
n-Tridecane/ n-Tetradecane/ n-Pentadecane	clear& colorless	> -17	235 - 270	~100	~0.02	+	++	-	fast spreading, dry, short play, silicon-feel
iso-Penta-, -Hepta-, -Nona-decanes Blend	clear& colorless	< -17	240 - 270	108	~0.02	+	++	-	fast spreading, silky, long play, cushion
Ethanol	clear& colorless	-115	78	49	44.6	+++	++++	++++	irritating, drying, cooling

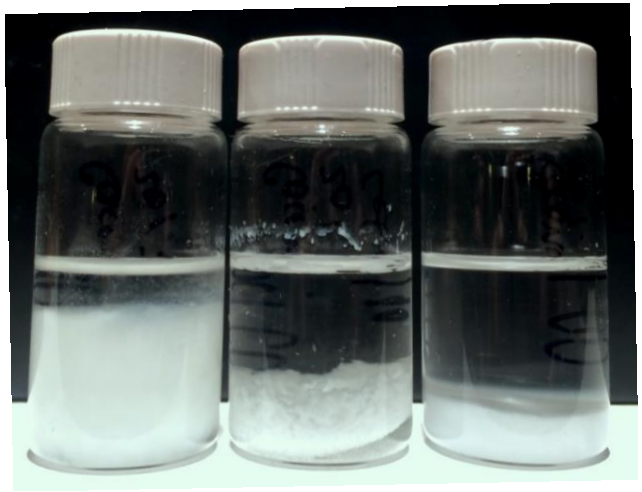
Processes involving n-Hexane/Petrol-ether or Ethanol need special precautions because of volatility/flammability.
BBHCs are safer to handle on a production scale.
BBHCs have selective solvation characteristics towards non-polar solutes.
BBHCs are sufficiently volatile to leave skin or hair non-oily after application.

Working with BBHCs and Related Bio-based Solvents: Freezing Behavior and Volatility Determine Application



All solvents kept at -18ºC for 12 hours

Working with BBHCs and Related Bio-based Solvents: Interaction with Extractables Determines Selection



iso-C13-19

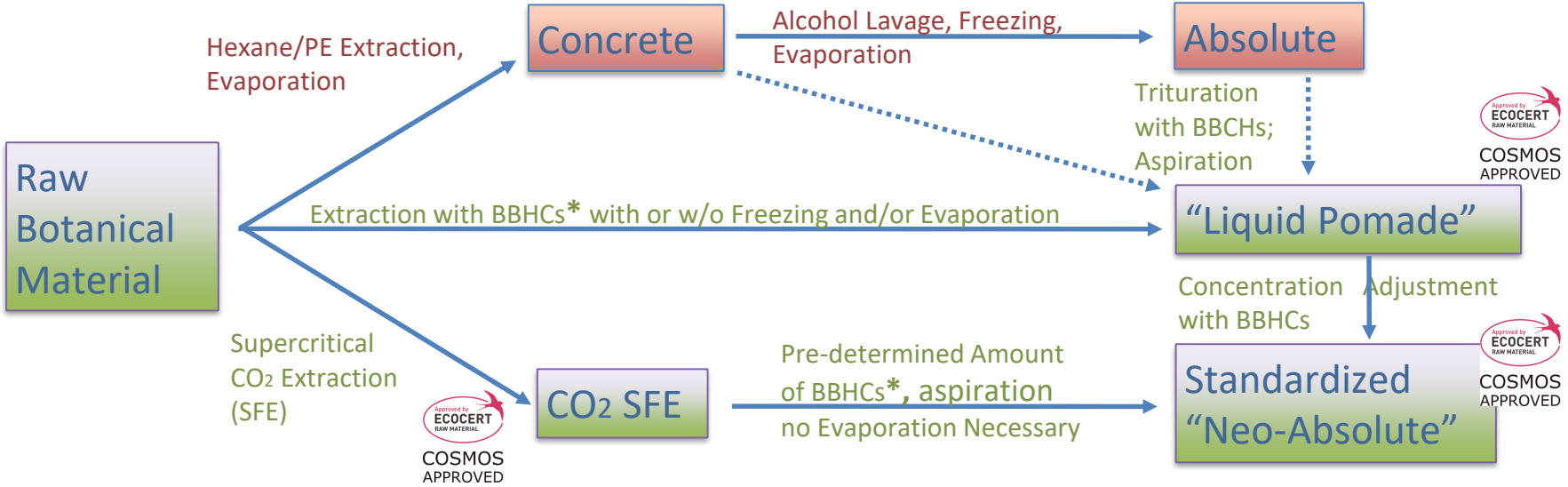
n + iso-C12-14

iso-C11-13

At low temperature (-18ºC) iso-BBHCs show different solvent affinities to particular solutes, that warrant exploring to obtain optimal yields of fragrant molecules.

Example: Coconut SFE contains high amounts of fat, which iso-C13-19 does not dissolve at low temperature, leaving a more concentrated fragrance solution.

Working with BBHCs and Related Bio-based Solvents: Extraction of Fragrance Raw Materials



* Auxilliary, "green" solvents may be added to achieve selectively - enriched extracts: Di-Caprylyl Ether, Di-Caprylyl Carbonate, etc.

Extraction of Fragrance Raw Materials with BBHCs - Example: Liquid Pomades from Raw/Fresh Botanicals

From left to right (all 1:1 extracts with 10% CC in C-12), Frankincense Oman, Mastix Chios, Labdanum Spain, Labdanum resinoid France, *Schinus molle* berries Cal., Jasmine flowers Cal., Red Pomelo pulp Cal..

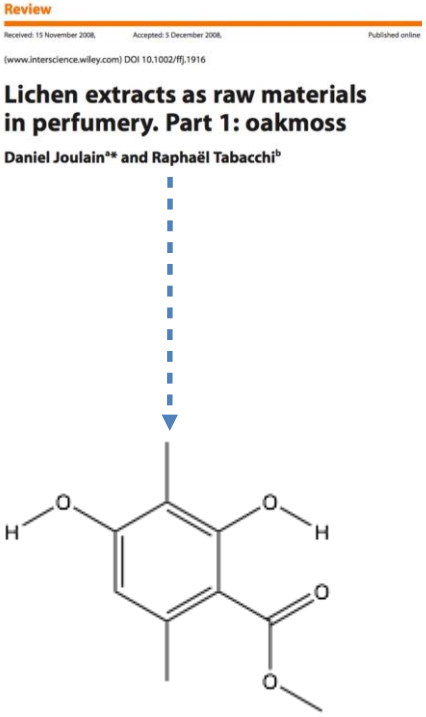
Extraction of Fragrance Raw Materials with BBHCs - Example: Concretes, Absolutes and Essential Oils

Concretes (from left to right, all 20%) -
row 1: Tonka butter, Clary Sage,
Carnation, Champaca, Osmanthus, Michelia.

Absolutes-row 2:
Cocoa, Mimosa, Carnation,
Beeswax, Fir Balsam,
Tuberose, Jasmine, Cistus,
Bitter Orange, Michelia,
Osmanthus, Boronia.

Essential Oils - row 3:
Ylang, Peru Balsam, Benzoe “Heart”,
Ruby Grapefruit, Bergamot, Lemon.

Extraction of Fragrance Raw Materials with BBHCs: Example Oak Moss Absolute, IFRA-compliant


Review

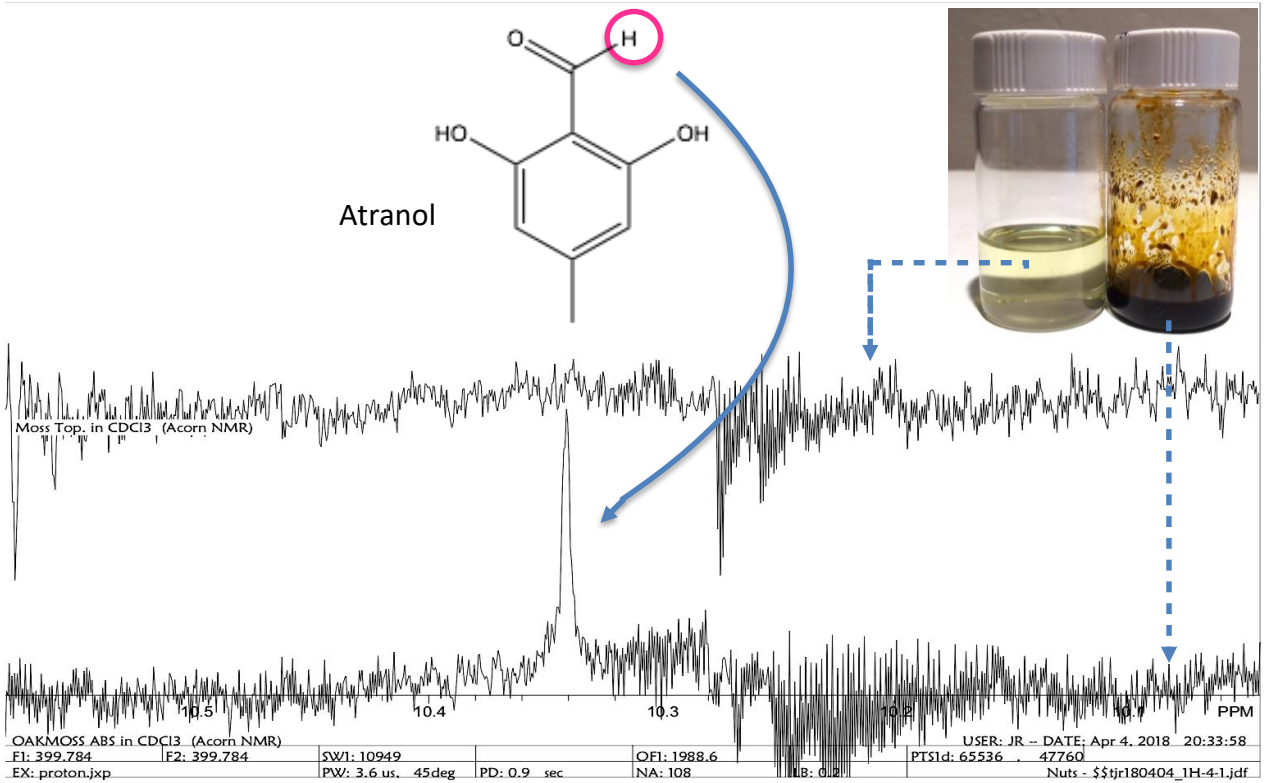
Received: 15 November 2008, Accepted: 5 December 2008, Published online

(www.interscience.wiley.com) DOI 10.1002/ffj.1916

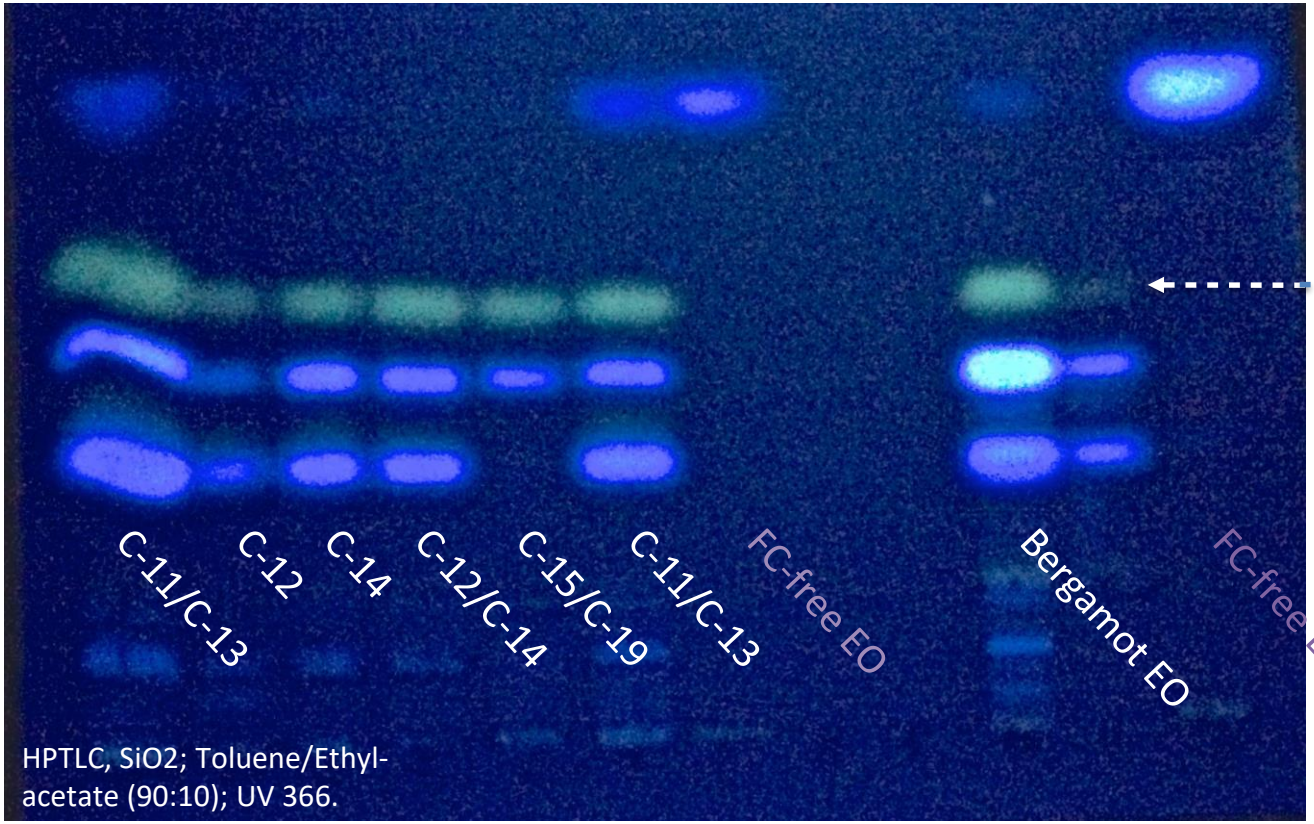
Lichen extracts as raw materials in perfumery. Part 1: oakmoss

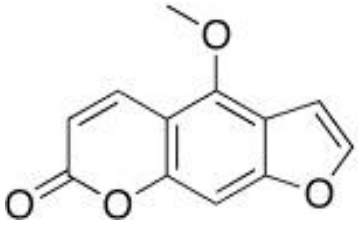
Daniel Joulain[a]* and Raphaël Tabacchi[b]

Methyl-beta-Orcinol Carboxylate
(Evernyl, Veramoss, etc.)



But it does not always work like that : Example Bergamot EO, Cold-Pressed





Bergaptene (Furo-coumarin/ Psoralene: Photo-sensitizer)

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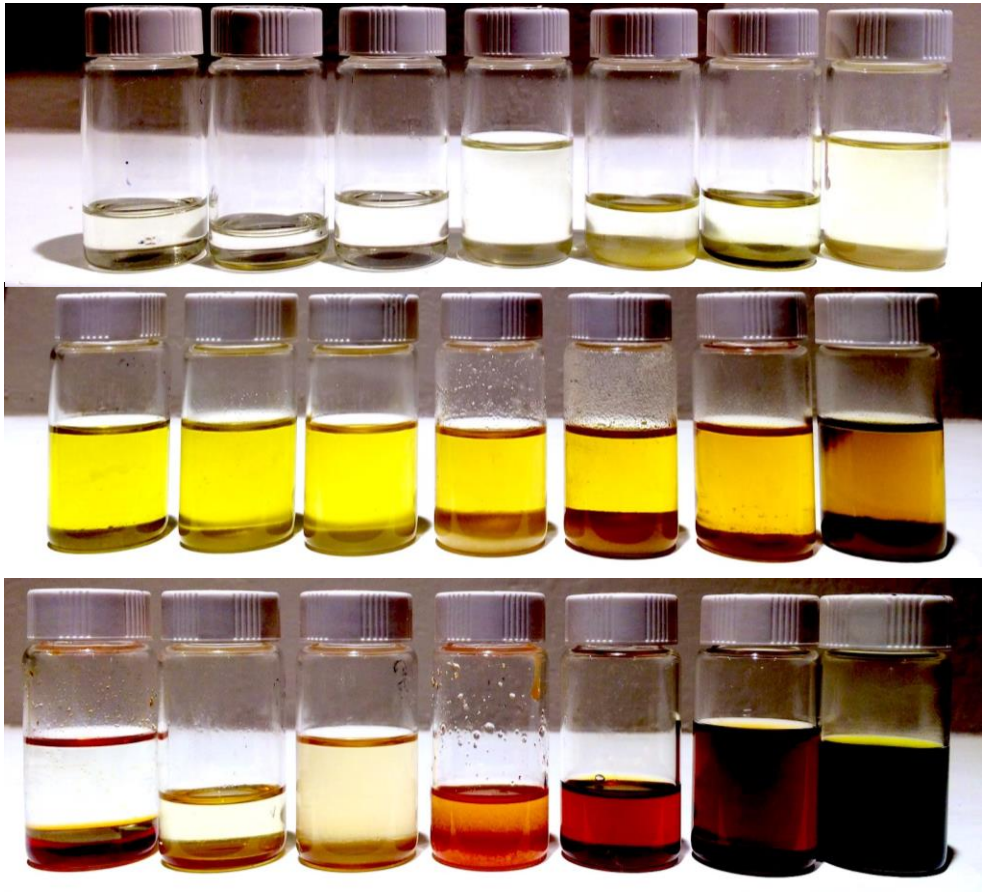
Extraction of Fragrance Raw Materials with BBHCs - Example: Supercritical-Fluid Carbon Dioxide Extracts (SFEs)



From left to right (all 20%),
row 1: Galbanum, Saffron, Ambrette seed, Frankincense, White Rose, Damasc Rose, Ylang.

row 2: Patchouli (C-15/19), Patchouli (C-11/13), Sandalwood, Vanilla, Champaca (C-15/19), Champaca (C-11/13), Vetiver.

row 3: Oakwood, Angelica root, Galangal, Jasmine gr., Agarwood, Vanilla Extr.,
Chamomile.

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Extraction of Fragrant Raw Materials with BBHCs - Example: Kitchen-Inspired Extracts

Selected SFEs @20% ea. in BBHC blend

Butter
Coriander
Cinnamon
Ginger
Cardamom
Roasted Coffee

Gourmand note:
"Salty", "Umami"

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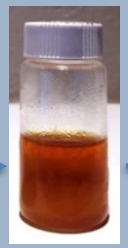
Optical and Olfactory Differences between BBHC- based and Ethanol-based Extracts and Compositions 1

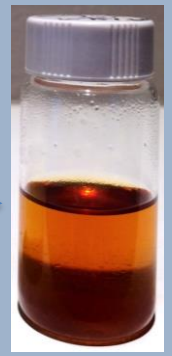
Natural Jasmine - Citrus - Chocolate Accord

	weight (g)	weight (g)
Jasminum auriculatum Hydrodistillate ("Ruh Juhi") (White Lotus)	1.70	1.70
Coconut CO2 Extract (Flavex)	0.80	0.80
Benzoin "Heart" (Robertet)	0.70	0.70
Grapefruit "Ruby" FCF EO(The Perfumery)	0.50	0.50
Vanilla CO2 Extract 12% (Flavex)	0.50	0.50
Cacao Absolute "France" (The Perfumery)	0.50	0.50
Cistus Absolute (Albert Vieille)	0.40	0.40
Musk Ambrette Seed CO2 Extract (Flavex)	0.35	0.35
Carrot Seed EO (Robertet)	0.03	0.03
Ambrettolide Natural (Penta)	0.02	0.02
Total	**5.50**	**5.50**
Ethanol 75% USDA Organic (Alchemical Solutions)	22.0 -> 20%	
BBHC Blend (California Cosmetic Creations)		22.0 -> 20%

Raw EtOH Dilution



cold-filter



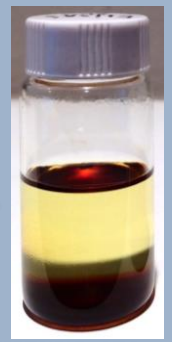
add 75% EtOH to give 20% conc.;
stir until uniform; store @ -18ºC/12 hrs

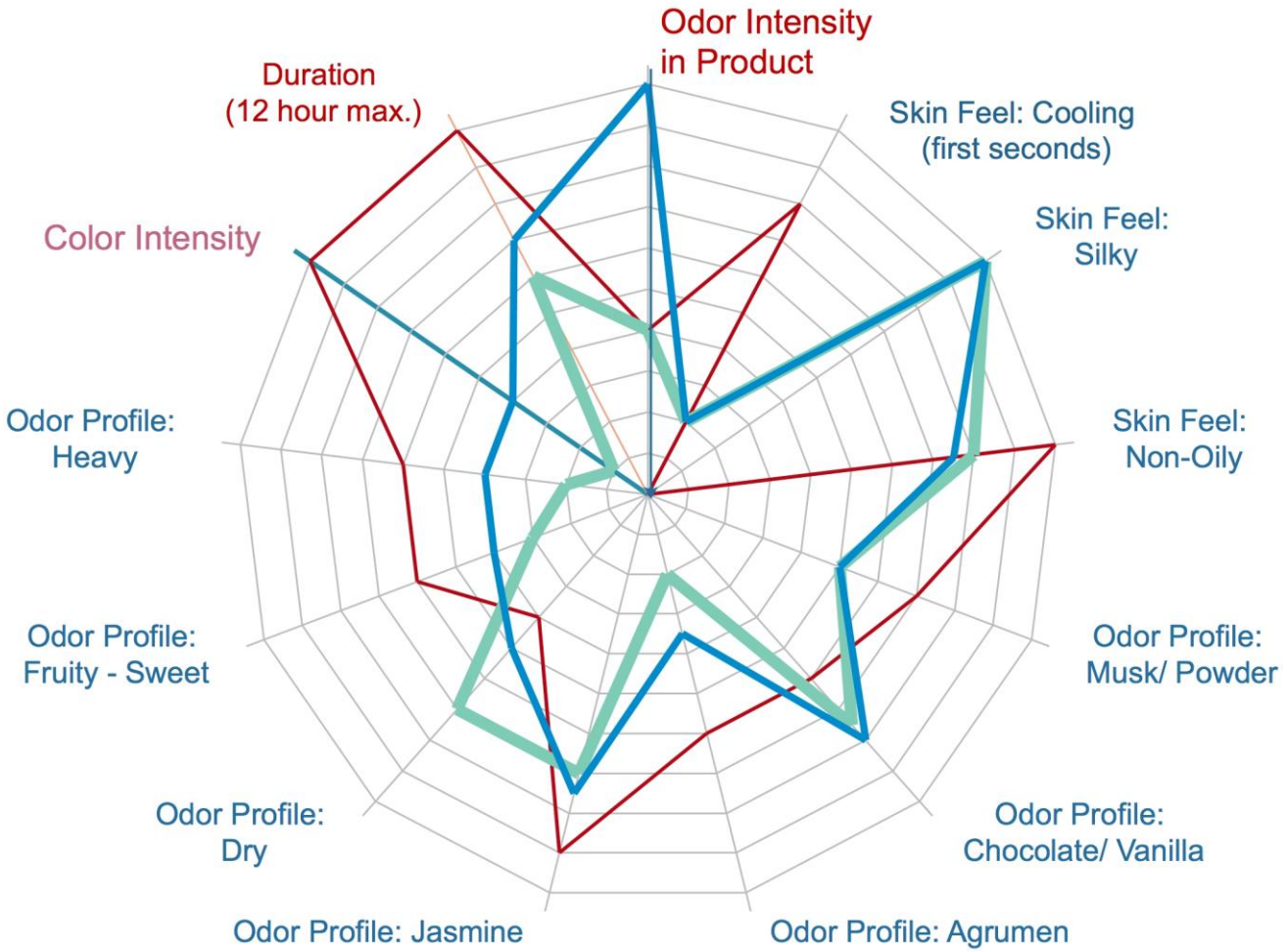
Ingredient Blend

add BBHC Blend to give 20% conc.;
sonicate 10 min; store @ -18ºC/12 hrs

Raw BBHC Dilution

warm to r.t; (aspirate)




Odor Intensity in Product
Skin Feel: Cooling (first seconds)
Skin Feel: Silky
Skin Feel: Non-Oily
Odor Profile: Musk/ Powder
Odor Profile: Chocolate/ Vanilla
Odor Profile: Agrumen
Odor Profile: Jasmine
Odor Profile: Dry
Odor Profile: Fruity - Sweet
Odor Profile: Heavy
Color Intensity
Duration (12 hour max.)

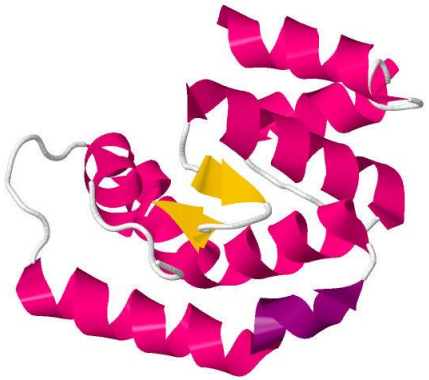
The Role of a Lipophilic Volatile Carrier: an Attempt to Explain the Enhanced Olfactory Sensation Mediated by BBHCs vs. Alcohol

Journal of Chemical Ecology
November 1992, Volume 18, Issue 11, pp 2107–2115 | Cite as

Amino acid profiles and liposomes: Their role as chemosensory information carriers in the marine environment

Authors Authors and affiliations

J. Dudley Williams, Kim N. Holland, David M. Jameson, Reimar C. Bruening



Odorant-binding Protein

Source: https://doi.org/10.1002/neu.480220108

Possibilities:

a) BBHCs concentrate more “intense” top-notes, or less non-fragrant molecules

b) Large local concentrations of BBHCs in hydrophilic *olfactory mucosa* elicit high surface concentration of OBPs by Influencing local equilibria.

c) BBCHs mediate binding kinetics via allosteric change of ObPs

d) Alcohol might attenuate olfactory sensitivity

Formulating with BBHCs and Related Bio-based Solvents: Comparison of BBHC- with Alcohol-based Extracts

Synthetics, Absolutes, EOs, Resinoids, CO2 extr., etc.

Creative Blending → Fragrance Concentrate → Dilution (EtOH) → Freezing, Filtration → Aging; Final Adjustment

Natl. Isolates, Neo-Absolutes, Standardized Building Blocks

Creative Blending → Standardized Blend → Final Adjustment*

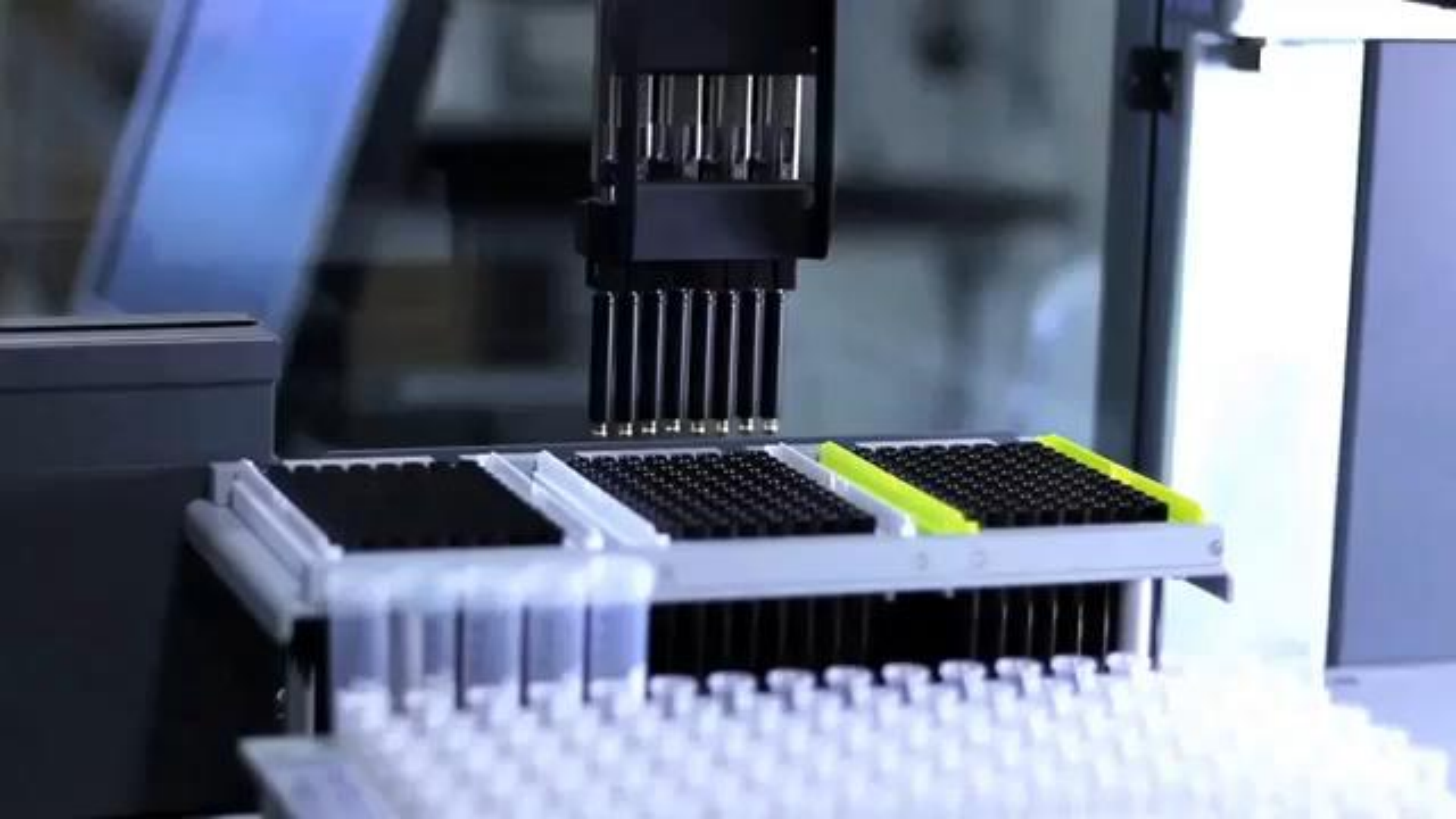
Formulating with standardized dilutions avoids guesswork about the olfactory character of the final product, as the perfumer smells the blend at its product concentration. * Final adjustments of concentration might still be necessary.
This technique lends itself to "Creativity Automation".

Working with BBHCs and Related Bio-based Solvents: “Combinatorial Perfumery” in Action

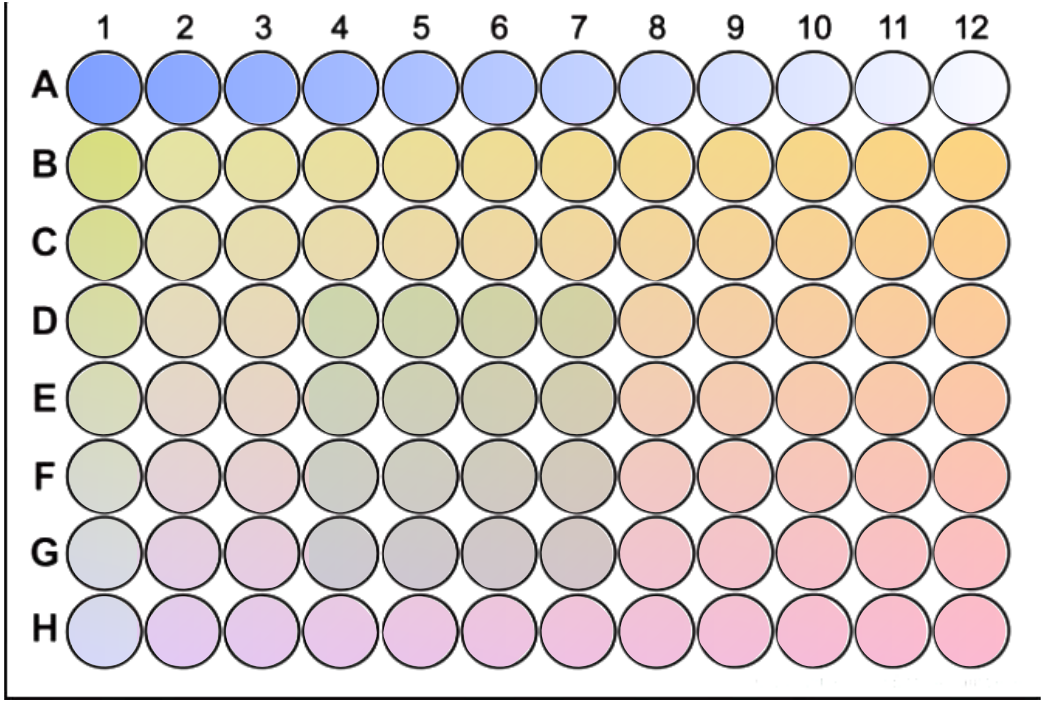
© Isabelle Doyen; Perfume Shrine/Pinterest

Advantages of working with standardized BBHC solutions instead of concentrates:

a) composition smells like the final product (20-25% extrait; 15-20% EdP; 12-15% EdT, etc.)
b) optical transparency allows easy spotting of incompatibilities (precipitation, etc.)
c) low viscosity and volatility compared to alcohol allows for automation !



Working with Standardized Solutions of Fragrance Components in BBHCs: Automated Creation of a Modern Fougere Building Block:



Chamomile CO_2, 2%; Calendula CO_2, 5%

Coriander CO_2, 20%

Schinus molle, C-12 Extr., 1%

Coffee Bean CO_2 1% in Splendione, 20%

Lav. EO, Berg. EO, Vet EO (2:1:0.5) 20%

Client Brief: Non-stinging men's aftershave mist with anti-inflammatory activity and "trendy" scent.

BBHCs at Work: Formulating Multifunctional Products at the Interface of Perfume and Skincare, Example 1

Non-stinging before-and-after shave mist:

[Formula and sample will be shown]

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BBHCs at Work: Formulating Multifunctional Products at the Interface of Perfume and Skincare, Example 2

Deep-moisturizing face and body perfume mist:

[Formula and sample will be shown]

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BBHCs at Work: Formulating Multifunctional Products at the Interface of Perfume and Skincare, Example 3

After shower leave-in hair gloss serum:

[Formula and sample will be shown]

Summary: Advantages of BBHCs as Perfume Carriers over Traditional Formulas

- *selective solubility* for fragrant components, leaving non-scented, usually strongly colored, and potentially hazardous compounds behind to be easily separated.
- *chemical stability* and inability to interact with fragrance components in any way that could negatively influence the composition.
- *sufficient volatility* to allow the fragrance to evaporate from the skin as intended and not leave any residue behind that would either create an un-desirable skin-feel or stains on clothing and fabric.
- *natural origin* allowing for certification by ECOCERT, Cosmos, NPA, or any other certifying body, thus allowing the term "*natural*" to appear on product labels and advertising.
- *chemical inertness* and consequently *excellent consumer safety* in the areas of intended application.

Loc.cit.: US **62/236,395** (Oct. 02, 2015); **15/282,510**, (Sep 30, 2016)

Fragrance Application	Green Production Chemistry	Material Cost	Intrinsic Odor	Safety Issues	Chemical Reactivity of Carrier	Production Cost of Blends	Color of Blends	Relative Odor Intensity in Products
Alcohol-based	Not Currently	Low	Yes	Fire Hazard	Reactive	Low (depending on ingredients used)	High	Standard
BBHC-based	Yes	High	No	No	Inert	Moderate	Low	High
Skin/ Hair Care Application	**Irritant**	**Skin Feel**	**Skin Action**	**Skin Care Applications**	**Interaction with Skin Microbiome**	**Hair Feel**	**Hair Care Applications**	
Alcohol-based	Yes	Cooling	Drying	Preservative, Disinfectant Wipes	Yes	Drying	Shampoo & Conditioner (Preservative) Fixatives	No (but possible)
BBHC-based	No	Warm, Gentle, Non-Oily	Emollient	Spray Lotions, Creams, etc.	No	Light, Shiny, Protecting	Leave-on Products	Yes

Summary: BBHC-based Multifunctional Beauty Products - a Future with an Ancient Past

Queen Cleopatra VII, National Museum, Berlin

Unguent Jar
1st c. BC,
Museo Archeologico,
Madrid

In Antiquity, scented body and hair oils and unguents served multiple purposes.

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Monica Shao, Honsea Sunshine
Kelly Stone, Centerchem

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