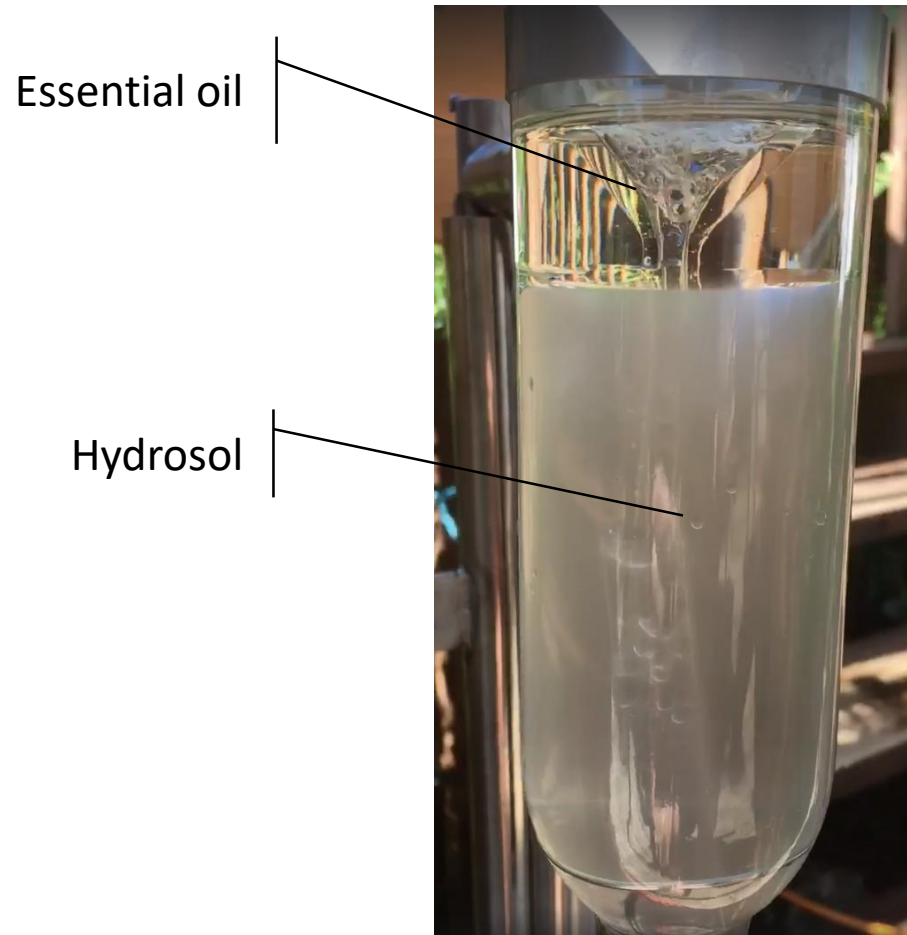




Testing the water: the rewards and challenges of hydrosol analysis

Hubert Marceau B. Sc. ; Benoit Roger Ph. D. ; Ann Harman
Botanica 2018, Brighton, University of Sussex

What are hydrosols



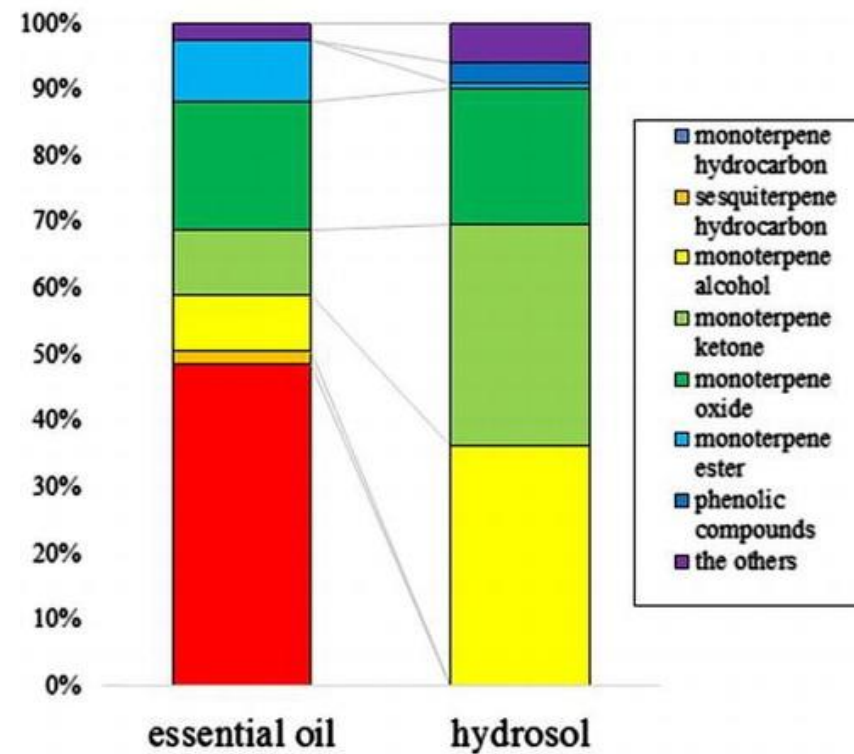
Also known as:

- Hydrolates
- Floral waters
- Aromatic waters
- Herbal waters
- Essential waters
- Herbal distillates

... are not essential
oils in water

Hydrosols vs essential oils

Classification of volatile components in rosemary

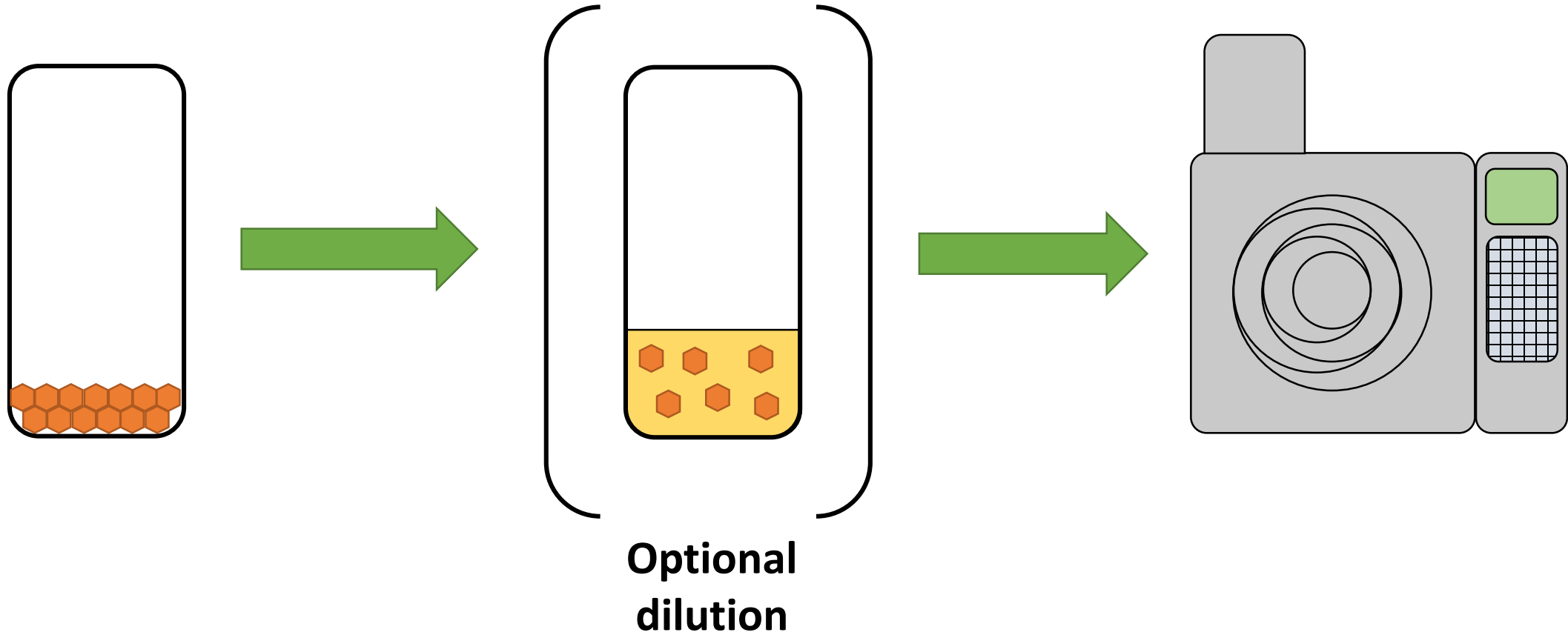


K. Tomi, M. Kitao, N. Konishi, H. Murakami, Y. Matsumura, T. Hayashi.
Enantioselective GC-MS analysis of volatile components from
rosemary (*Rosmarinus officinalis* L.) essential oils and hydrosols.
Biosci. Biotech. Bioch., 2016, 80 (15), 840-847.

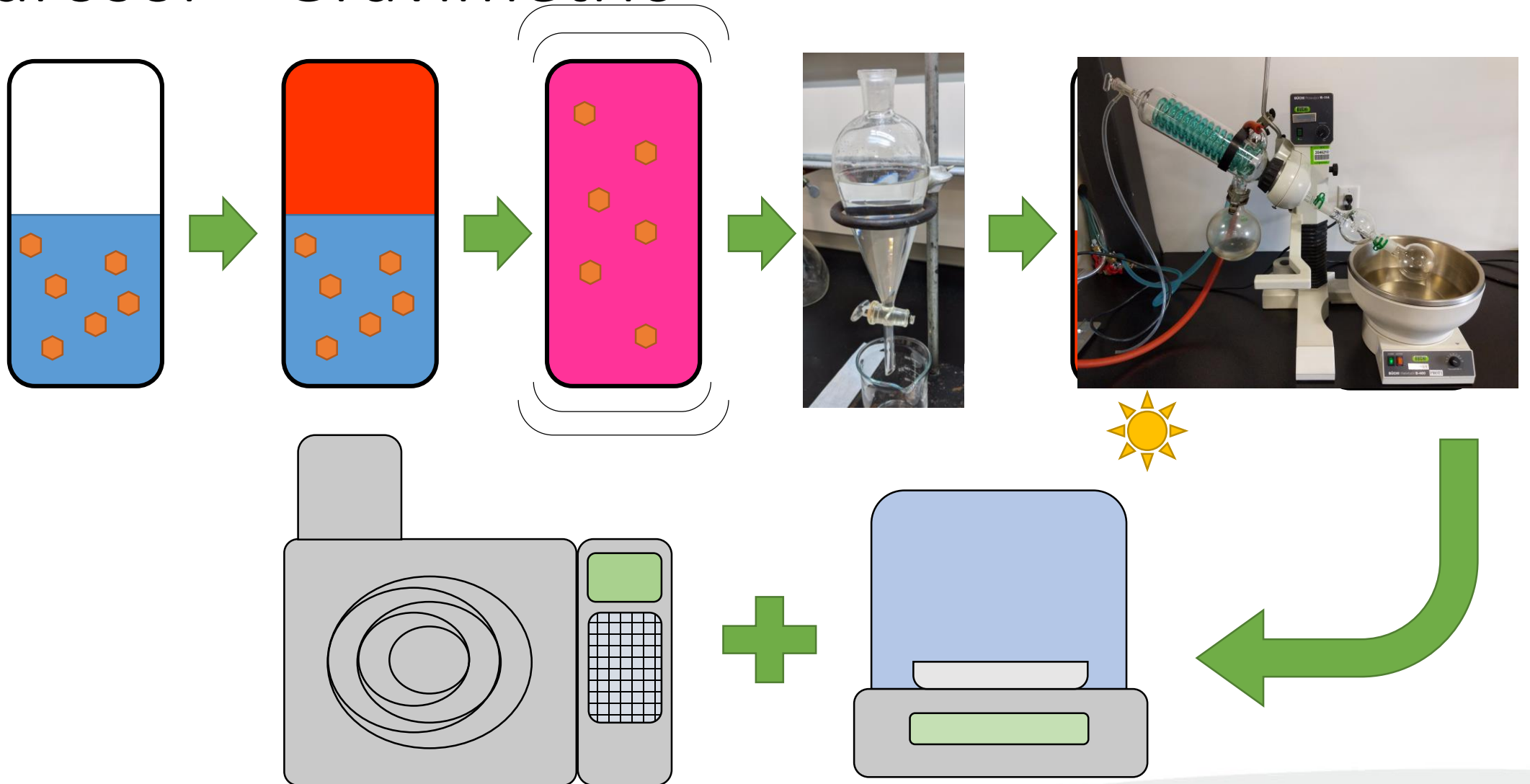
Main components (over 1 %)	% in EO	% in HY
α -Pinene	1.15	0.37
2-Phenylethyl alcohol	4.32	55.16
Linalool	0.81	7.93
α -Terpineol	0.86	2.79
Citronellol + nerol	35.14	13.02
Geraniol	21.33	12.23
Eugenol	2.04	3.47
Geranyl acetate	3.22	0.15
β -Bourbonene	1.05	-
α -Humulene	1.00	-
Heptadecane	3.31	0.51
E,E-Farnesol	2.72	-
9-Eicosene	2.10	-
Nonadecane	15.42	-
Oxides	0.29	tr
Stearoptenes	21.23	0.55
Alcohol	68.13	96.62
hydrocarbon + esters	2.59	2.05

Data from K. G. D. Babu, B. Singh, V. P. Joshi, V. Singh.
Essential oil composition of Damask rose (*Rosa damascena*
Mill.) distilled under different pressures and temperatures.
Flavour and frag. J., 2002, 17, 136-140

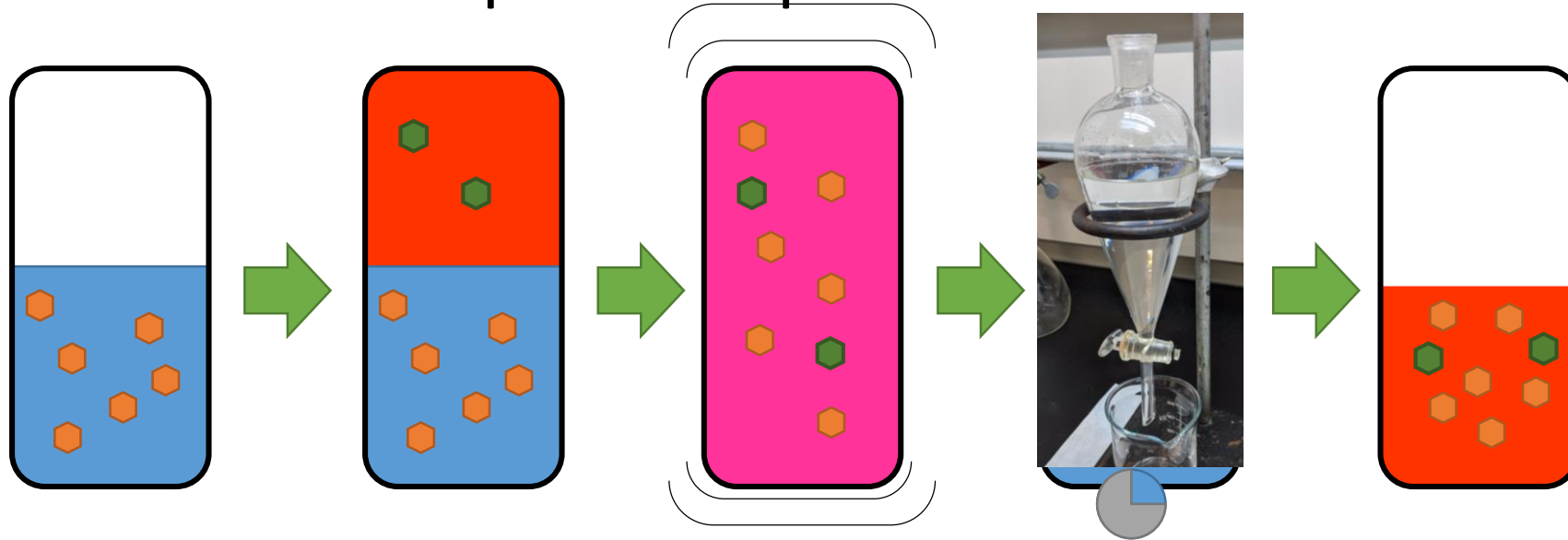
Essential oil analysis



Hydrosol – Gravimetric

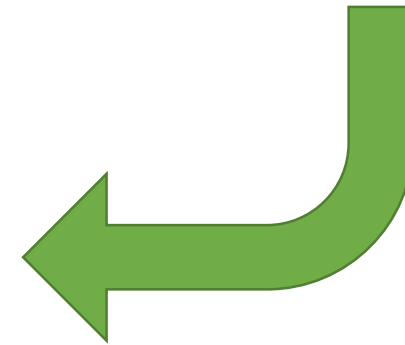
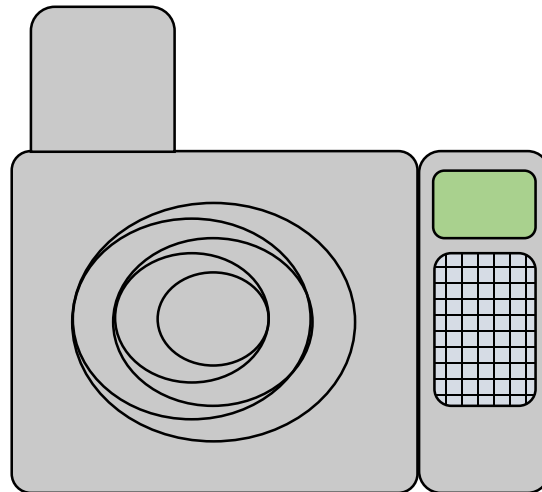


Hydrosol – Liquid-Liquid extraction

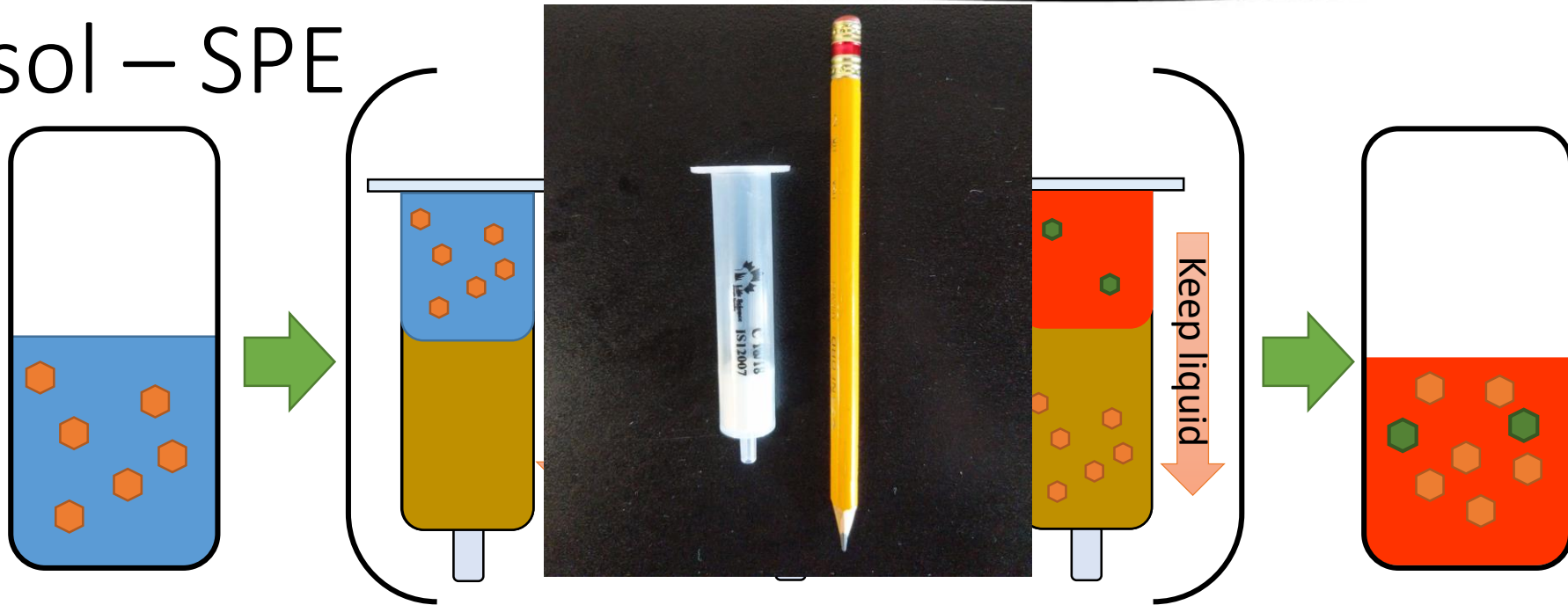


$$\sum_{k=0}^n \binom{n}{k} x^k$$

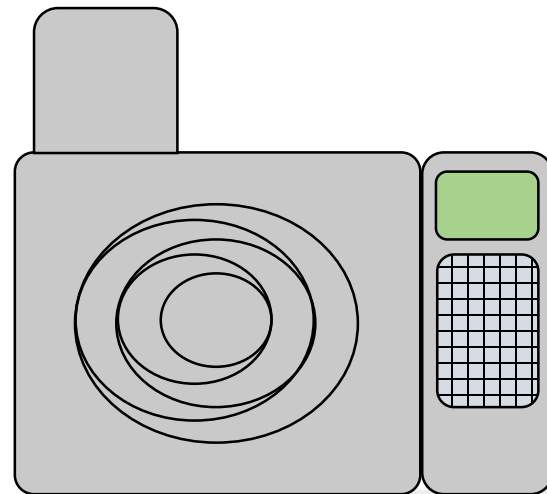
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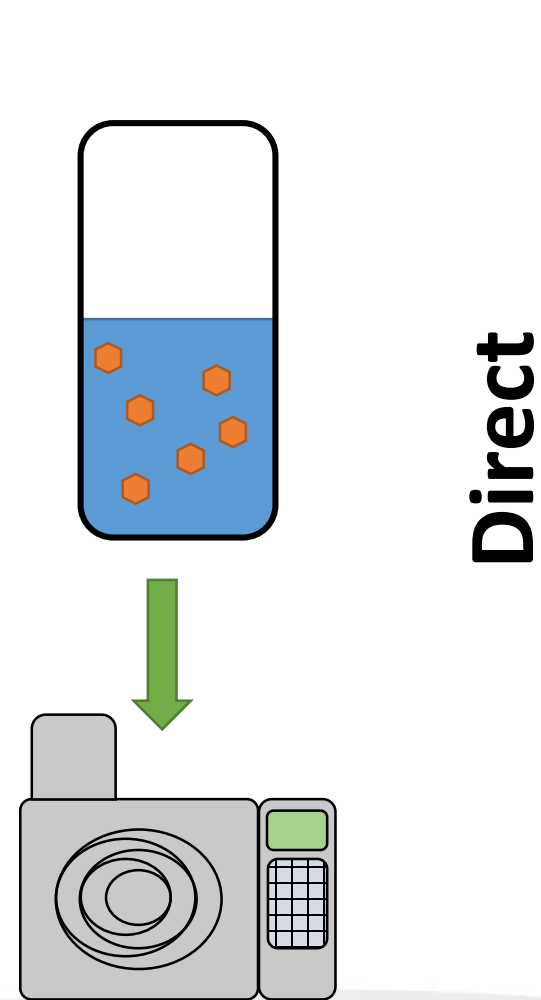
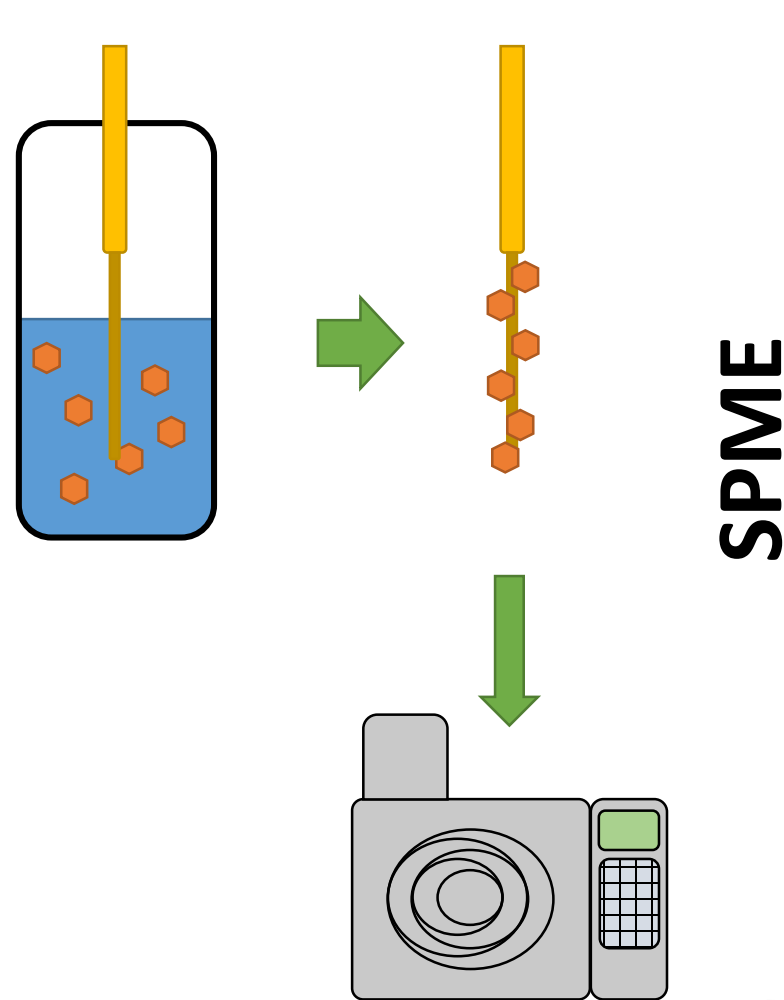
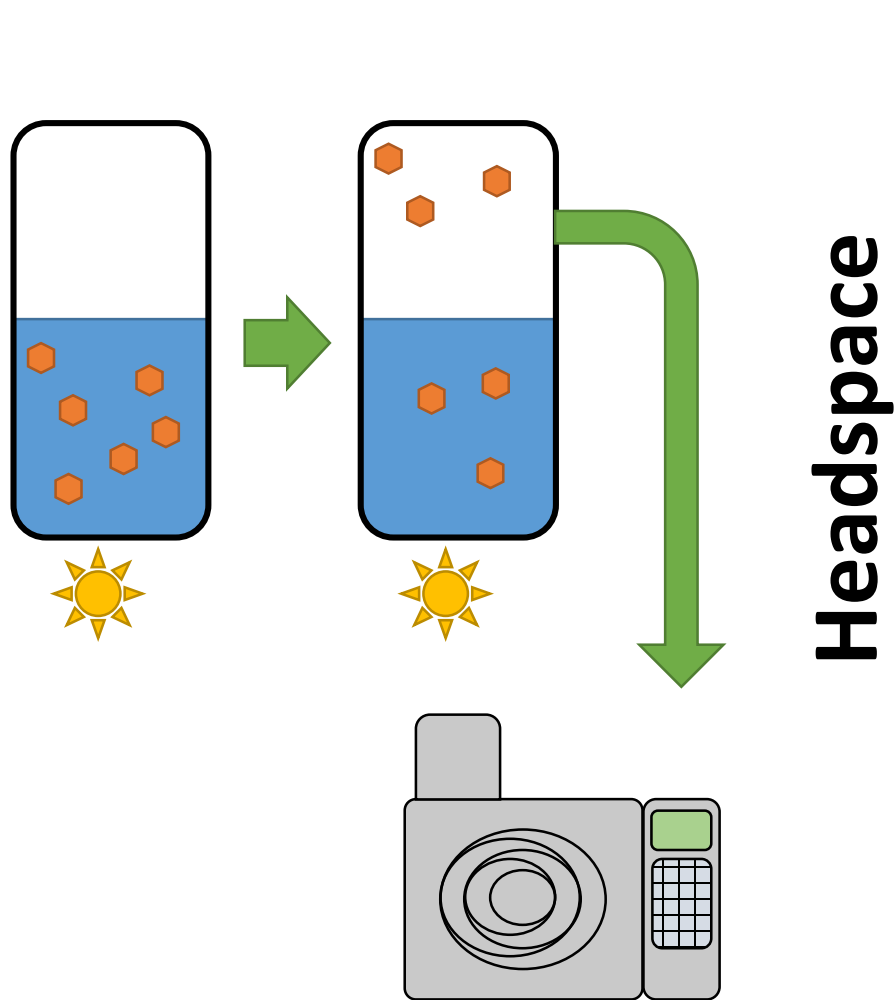
Hydrosol – SPE



$$\sum_{k=0}^n \binom{n}{k} x^k$$



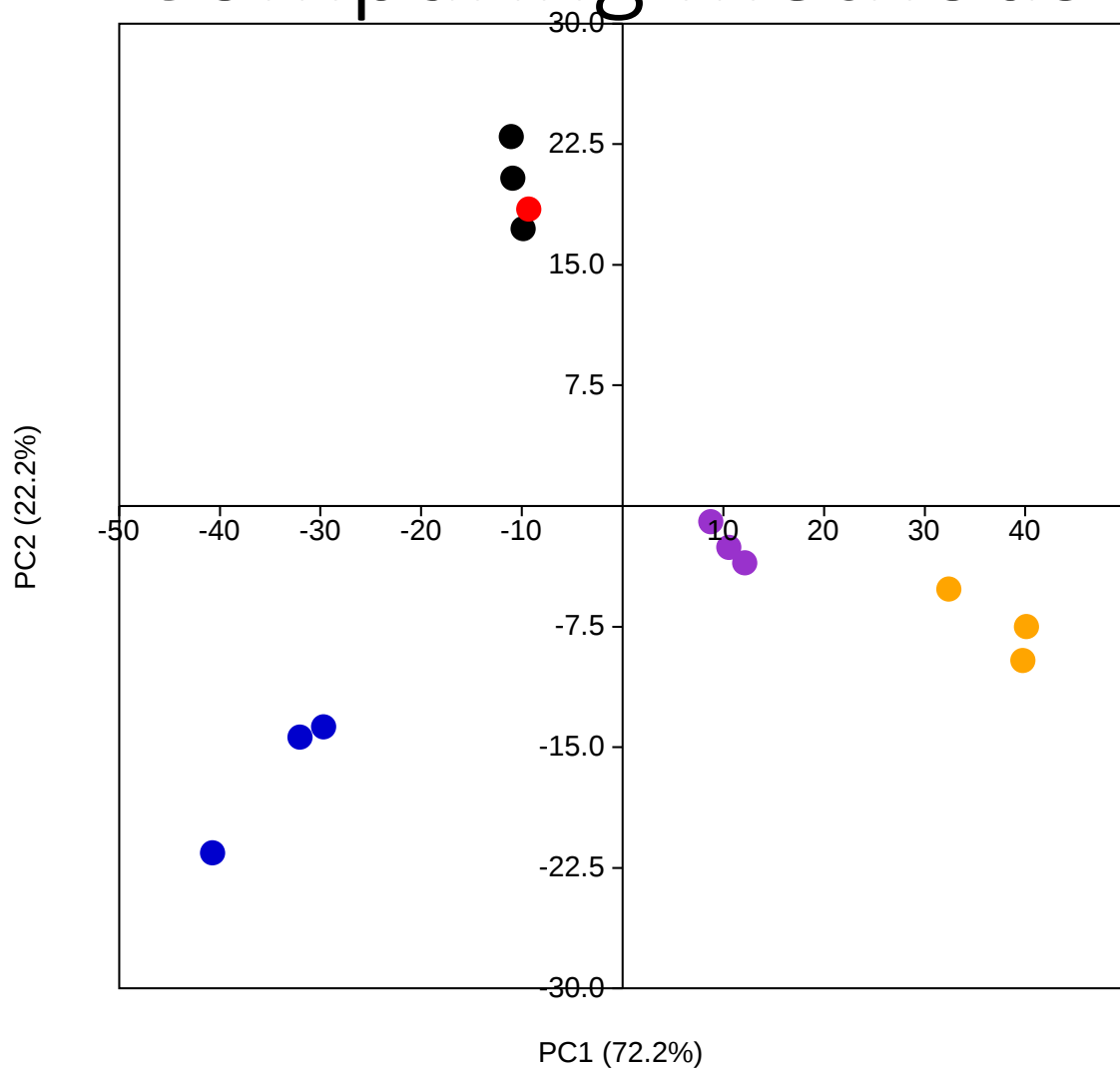
Hydrosol – Other method



Comparing methods

Parameters	Gravimetric	LLE	SPE	Headspace	SPME	Direct
Solvent use	High	High	Low	None	None	None
Selectivity	Low	Low	Medium	High	Medium	None
Time required	High	Medium	Low	Low	Low	Very low
Material cost	Low	Low	High	Very low	Average	Very Low
Require special module	No	No	No	Yes	Yes	No
Waste produced	Medium	Medium	High	Low	Low	Low
Sensitivity	High	High	Medium	Medium	Medium	Very Low

Comparing methods



- Reference value
- Liquid-Liquid Extraction/Internal Standard/Dichloromethane
- Liquid-Liquid Extraction/Internal Standard/Hexane
- Liquid-Liquid Extraction/Gravimetry/Diethyl Ether
- SPE/Internal Standard/C18

Comparing methods

	[C] in water (mg/L)	LLE IS DCM		LLE IS HEX		SPE IS C18		LLE G ETH	
		(mg/l)	Δ%	(mg/l)	Δ%	(mg/l)	Δ%	(mg/l)	Δ%
Hexanol	31,5	29,3	-7,00	17,0	-46,10	32,7	3,57	18,2	-42,36
1,8-Cineole	60,2	61,3	1,81	58,3	-3,17	64,3	6,80	29,7	-50,62
→ Linalool	40,9	47,0	15,06	47,3	15,87	52,0	27,29	41,0	0,41
Phenylethyl alcohol	93,5	98,7	5,54	68,3	-26,91	44,3	-52,58	95,5	2,14
Camphor	39,6	43,7	10,16	42,7	7,64	46,0	16,04	32,1	-19,00
Menthol	43,4	47,0	8,27	47,0	8,27	49,3	13,65	43,8	0,81
Methyl salicylate	30,3	30,7	1,34	30,0	-0,86	30,3	0,24	17,5	-42,30
Decanal	10,4	10,0	-4,21	9,7	-7,41	5,7	-45,72	8,1	-22,41
Carvone	30,9	35,0	13,31	35,7	15,46	37,0	19,78	30,0	-2,83
Geraniol	40,5	45,0	11,11	44,7	10,29	48,3	19,34	44,0	8,72
→ Linalyl acetate	20,8	11,3	-45,54	9,7	-53,55	5,7	-72,77	5,1	-75,35
Indole	14,5	15,3	7,53	15,0	5,19	13,3	-6,50	15,4	7,77
Eugenol	61,9	63,7	2,87	64,0	3,41	66,0	6,64	55,4	-10,46
α-Bisabolol	10,2	10,7	4,88	10,7	4,88	8,0	-21,34	10,8	6,42
Total (mg/l)	528,4	548,7	3,84	500,0	-5,37	503,0	-4,81	450	-14,84
Average absolute deviation from real value		9,90		14,93		22,30		20,83	

LLE IS DCM: Liquid-Liquid Extraction, Internal Standard, Dichloromethane

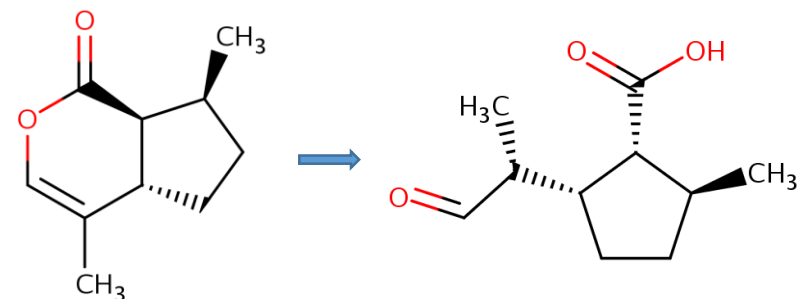
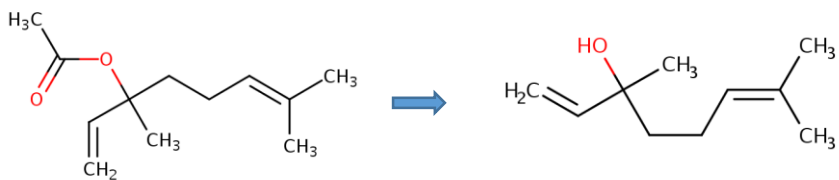
LLE IS HEX: Liquid-Liquid Extraction, Internal Standard, Hexane

SPE IS C18: Solid Phase Extraction, Internal Standard, Hexane

LLE G ETH: Liquid-Liquid Extraction, Gravimetry, Diethyl Ether

Hydrosol stability – Oxydation and hydrolysis

- Hydrolysis

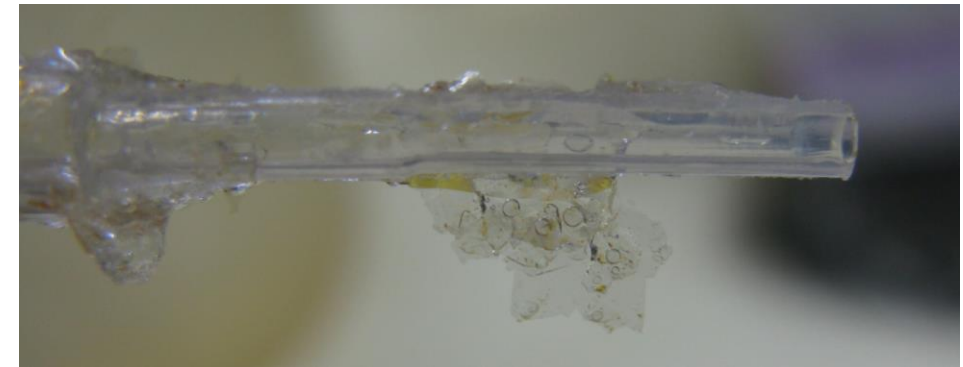
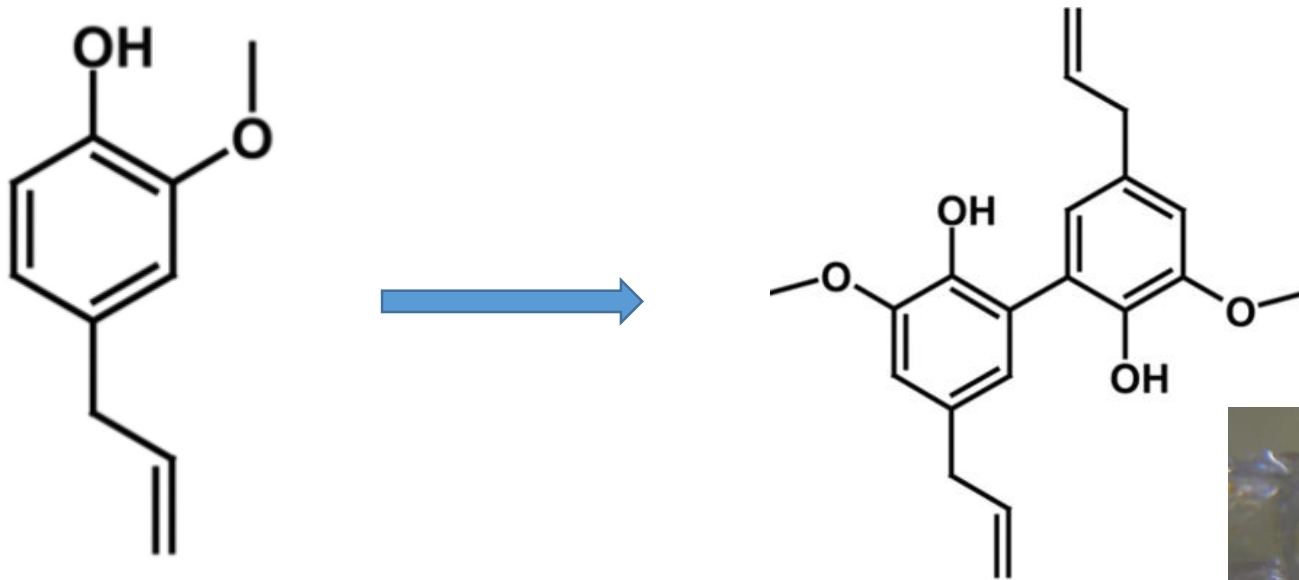


- Oxydation



Hydrosol stability – Chemical degradation

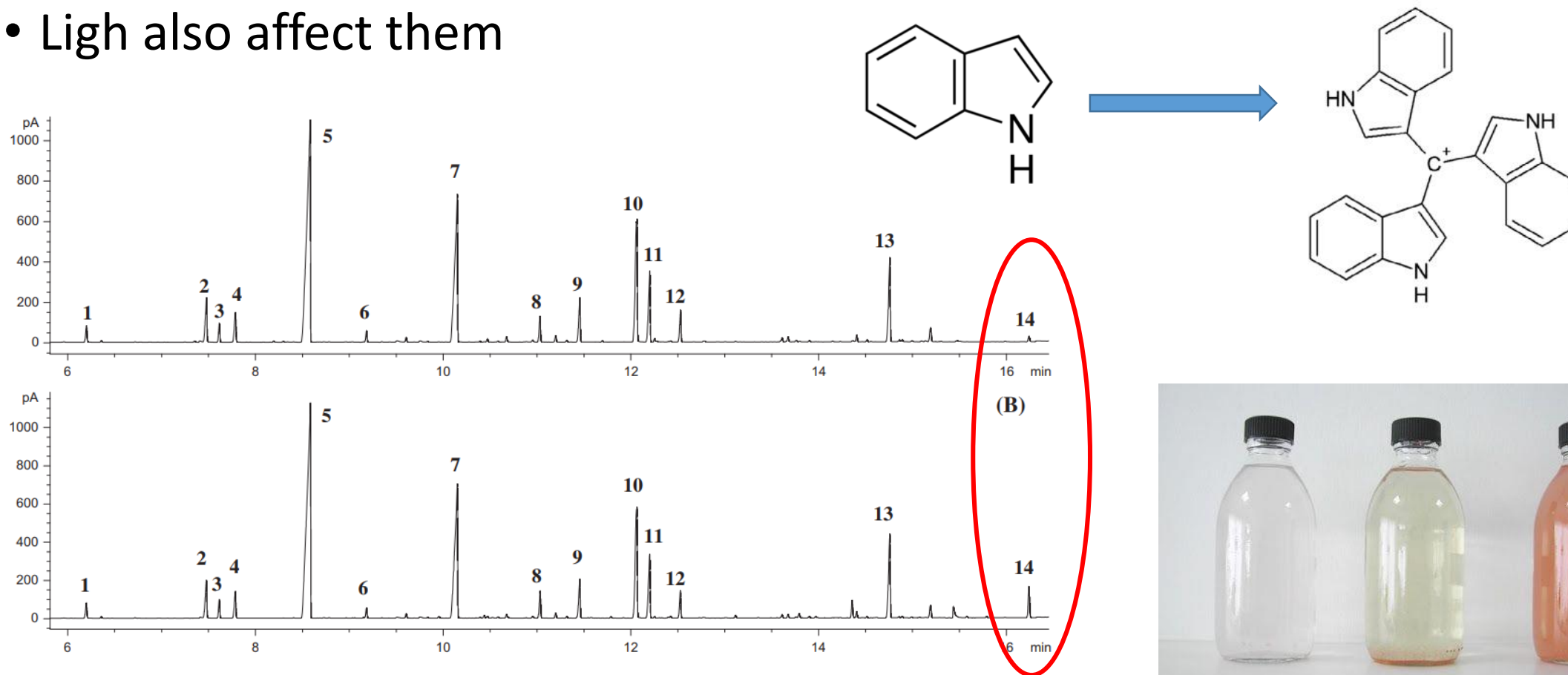
- Water is a very aggressive solvent and can produce side reaction



Isolated from *Ocimum gratissimum* hydrosol

Hydrosol stability – Chemical degradation

- Light also affect them



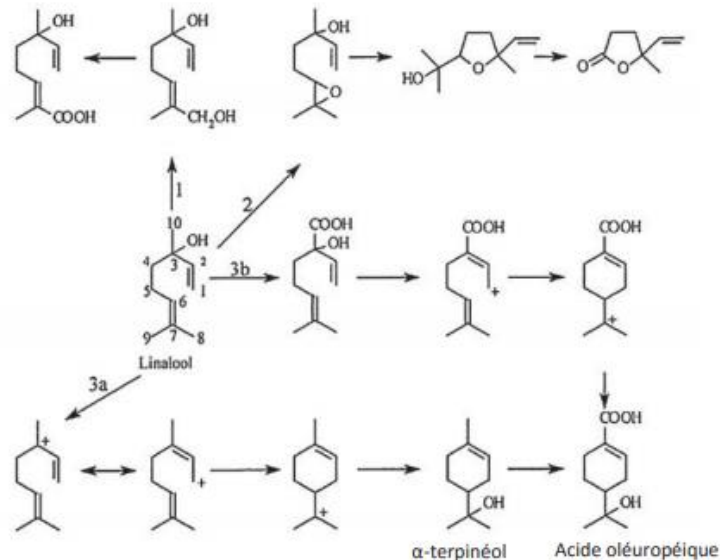
Hydrosol stability – Microbial contamination

- Hydrosol are sensitive to microbial contamination
- Opportunistic genus have been found in hydrosol:
 - Burkholderia sp.
 - Pseudomonas sp.
 - Delftia sp.
- These genus can affect immunocompromised patients

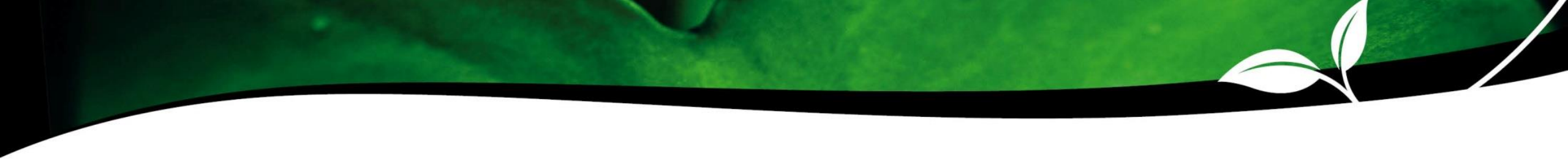


Hydrosol stability – Microbial degradation

- Bacterial metabolism change hydrosol composition



- There is a possibility that bacteria could produce toxins



Conclusion

The complexity of hydrosol analysis come from multiple sources:

- Presence of water
 - Multiple method possible, each with their benefit and drawback
 - Wider variety of compounds than those found in essential oils
 - Aggressive medium mean less stability
- 