Studies of some balsamics in perfumery

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The most important natural balsams used in perfumery are benzoin, cistus, copáiba, galbanum, myrrh, labdanum, olibanum, opoponax, peru, styrax and tolu. Of these, we studied the chemical composition of the following balsamic products:

- Benzoin Sumatra (styrax benzoin)
- Peru Balsam (myroxylon pereirae)
- Tolu Balsam (myroxylon toluiferum)
- Styrax (liquidambar orientalis)

Furthermore we investigated the strengths of the main odor aspects of the natural balsams and of a series of aroma chemicals having a balsamic odor character.

It is difficult to describe the odor character of the balsams. According to Müller all materials "with a certain richness and warmth, and also possessing a fruity/aromatic sweetness" can be regarded as having a balsamic note.[1] Tolu Balsam, for instance, has been described as having a rich, sweet, slightly cinnamon-like and very tenacious odor.[2]

In perfumery the balsamic note is mostly used as a modifier, especially in compounds of the heavy-sweet-floral type, such as hyacinth and gardenia,[3,4] but its use is certainly not restricted only to these. In perfumes of the oriental type, such as the classics Maya, Youth Dew, and Tabu, and also in the more recently launched Opium, the balsamic note is equally important. Moreover, balsams exhibit excellent fixative properties. The importance of this class of fragrance raw materials is already well established.

Some historical remarks

A natural material with a balsamic odor, myrrh, is one of the oldest fragrance raw materials known. It is mentioned several times in the Bible: the Ishmaelites who bought Joseph from his brothers were on their way from Gilead to Egypt, with their camels carrying spices, balm and myrrh (Genesis 37:25). In ancient Egypt myrrh was one of the ingredients of Kyphi, a mixture of scented herbs and resins that was used in their temples; the recipes of Kyphi are described by the Greeks Plutarch and Democritus.[5] Styrax was also known to the Egyptians and to the Romans.[6] This is not surprising, since these materials were and still are obtained from areas in the then known world (myrrh from Arabia and styrax from Asia Minor).

Later, during the Byzantian Empire, benzoin (Benjamin) became known and, after the discovery of the Americas, materials like peru balsam and tolu balsam were introduced in Western Europe. During the 16th to 19th centuries these

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materials were already widely used as a kind of air freshener. The Italian Alexis de Predmont described "a perfume for the chamber" in which styrax and benzoin, together with other ingredients, are made to a pulp and compressed to small cakes; these cakes were heated on hot coal to get a nice smell all over the chamber.[6] The oiselets in 18th-century France were used in the same way. They were usually made from benzoin gum and a flammable material.

In more modern perfumery we see the use of the balsams and resinoids mainly for their fixative properties, although nowadays, of course, synthetic materials are also used. However, with some of the natural materials dermatological problems are encountered.[44-52]

Analysis of some natural balsamic products

Many natural materials show a balsamic odor,[1] but only a few are actually used in perfumery. The greater part of the materials used are plant exudates from which balsams and resinoids are manufactured.[2,7] We selected the four that are used rather frequently and which, at least in our opinion, have the most pronounced balsamic note.

Table I. Chemical composition of some resinoids

Hydrocarbons	Benzoin	Tolu	Styrax	Peru
benzenoid				
styrene	t (2)	t (16)	t (40)	t
p-cymene		(16)	(24)	
stilbene				(40)
1,2-diphenylmethane		(16)		
monoterpenoids				
limonene			(24)	
cis- and trans-ocimene		(16)		
alpha- and beta-pinene		(16)	(24)	
terpinolene			(24)	
sesquiterpenoids				
alpha- and beta-bourbonene		(16)		
cadalene		(16)		
delta-cadinene		(16)	x	(24)
calacorene		(16)		
calamenene		(16)		
beta-caryophyllene		(16)	x	
alpha-copaene		(16)		
alpha-cubebene			x	
beta- and gamma-elemene		(16)		
humulene			x	
alpha- and gamma-muurolene		(16)		
beta-selinene		(16)		
Alcohols				
benzyl alcohol	x	x (16)	x	x (34)
alpha-phenylethanol			x	
cinnamic alcohol	x	(16)	x (24)	(29)
3-phenylpropanol	x	x	x (40)	
geraniol			(24)	
alpha-terpineol			(24)	
delta-cadinol			x	
elemol			x	
farnesol		(40)		(40)
nerolidol			x (29,36, 34,40)	

Table I continues on page 10

Benzoin Sumatra resin[8-13]

This balsamic resin is secreted by a small tree, Styrax Benzoin, that grows in Indonesia. Another variety, Benzoin Siam, has a more or less similar odor character and is obtained from Styrax Tonkinsis, also a small tree, native to South East Asia (Cambodia, Thailand). These two resins differ greatly in chemical composition, the latter consisting mainly of coniferyl benzoate (75-80%).

Tolu Balsam[14-22]

This product is obtained from injuries to the trunk of Myroxylum Balsamum, a tall tree native to the jungles of northern South America (Venezuela and Colombia). It is also grown in Cuba.

Table I. Chemical composition of some resinoids (Continued)

Carbonyl compounds	Benzoin	Tolu	Styrax	Peru
benzaldehyde	x	t (16)	t	t
cinnamic aldehyde	x	x (16)	x (24)	
acetophenone	t		x	
1-phenyl-2-methyl-1,3-butanedione	x			
vanillin	x (2)	x (16)	(24,40)	x (29,34)
acetovanillone	t			
(3-methoxy-4-hydroxyphenyl)-2-propanone	x			
camphor			(24)	
carvone			(24)	
fenchone			(24)	
menthone	t			
Carboxylic acids				
myristic acid	x			
benzoic acid	x (2)	x (16,20)	x	x (34)
cinnamic acid	x (2)	x (16,20)	x (2,24)	x (34)
3-phenylpropionic acid			x	
Esters				
methyl benzoate	t	t (20)		(34)
ethyl benzoate	x	x (16)	t	t
allyl benzoate	t			
benzyl benzoate	x	x (16,20)	t	(29,34)
cinnamyl benzoate	x	(16)		(7)
methyl cinnamate	t	x (16,20)	(24)	(34)
ethyl cinnamate	x	x (16)	x (24,40)	t
propyl cinnamate	t			
benzyl cinnamate	x	(16,20)	(24,40)	x (29,34)
cinnamyl cinnamate			(24,40)	(40)
3-phenylpropyl cinnamate		t	x	
benzyl ferulate		(16)		
bornyl acetate			(24)	
Phenolic compounds				
4-ethyl phenol	x		x	
4-vinyl phenol			x	
p-ethyl guaiacol	x			
eugenol	t	x (16)		

x,t: this study; t = trace component (less than 0.1% in the volatile part of the resinoid)

The odor can be described as sweet-balsamic, cinnamon-like, and faintly floral.

Styrax resin[23-28]

This resin is formed in the sapwood and bark tissues of Liquidambar Orientalis, a medium-sized tree native to Asia Minor (Turkey). Another and quite similar product is obtained from Liquidambar Styraciflua, a wild-growing tree from Honduras.

Peru Balsam[29-37]

In contrast with its name the main growing area for this product is not Peru but San Salvador. The product is obtained when the bark is removed from the trunk of a large tree, Myroxylon Pereira.

From commercial samples of these natural products, obtained from regular sources, the volatile part was isolated by distillation and then analyzed with GC-MS technique. The identity of the components was checked on GC-retention time with reference substances.

GC conditions were as follows: 50 m glass column (support coated open tubular, with UCON phase and aerosil as support), inside diameter 0.75 mm; column temperature 70-170°C, 1°C/minute; injector temperature 240°C; flow 5.5 ml He/min.

Table I summarizes the components identified in the different natural products, together with literature references. Characteristic components are the benzenoid esters (benzoates and cinnamates), but undoubtedly vanillin plays an important role in augmenting the sweetness. Phenolic components are also likely to contribute to the overall odor impression.

Odor evaluation

The olfactive properties of the natural resinoids were evaluated by consulting six of our perfumers, who rated the odor character on a scale from 1-9 against given references. In this way we studied the similarity of the products with reference materials having the following particular odor aspects:

- floral (reference: jasmin oil absolute)
- vegetable (clary sage oil)
- sweet (heliotropin)
- aromatic (vanillin)
- powdery (musk ketone)
- balsamic (olibanum resinoid)

Table II shows the results. From the data of Table II it can be concluded that Benzoin Sumatra and Benzoin Siam are very similar. Apart from the balsamic aspect, also sweet, aromatic and powdery notes, and to a lesser extent floral and vegetable connotations, contribute to the overall odor complex of these natural materials.

Table II. Odor evaluation of the resinoids

Odor aspect	Benzoin Sumatra	Benzoin Siam	Tolu	Styrax	Peru
floral	3	3	2	3	2
vegetable	1	2	3	3	2
sweet	5	5	6	4	5
aromatic	5	6	6	3	5
powdery	3	4	3	3	3
balsamic	9	9	8	6	7

Aroma chemicals for balsamic notes

Following the same procedure we subsequently selected a number of aroma chemicals having odor strengths not less than 2 points for the balsamic aspect. These products are shown in Table III, together with the strengths for the important secondary odor aspects: sweet, aromatic, and powdery.

The rather low intensity ratings for the balsamic aspect in these chemicals is noteworthy —none scored higher than 4. The two main groups contain benzenoid compounds (especially benzoates and cinnamates) and terpenoids (notably sesquiterpenoid alcohols); among these are also the main constituents of the natural products discussed above. To our knowledge up to now no single aroma chemical has been found that shows a balsamic odor strength comparable to that of the natural products, although it can be imitated well.

Toxicological aspects

For several years the safety in use of fragrance raw materials has been a matter of concern in the fragrance industry, as illustrated by the foundation of the International Fragrance Association (IFRA) and the Research Institute for Fragrance Materials (RIFM) in 1967. The members of IFRA have adopted a Code of Practice for the fragrance industry and the IFRA Guidelines to Restrict Ingredient Usage.[41]

From the RIFM monographs as published in *Food and Cosmetic Toxicology* and from the IFRA guidelines, based on the RIFM findings, it can be taken that some of the described products (naturals as well as synthetics) may give rise to toxicological/dermatological problems.[44 52] For example, RIFM reported that Peru Balsam has a sensitizing potential,[43] which is absent in Peru Balsam oil. It is recommended not to use Peru Balsam as such, but only the volatile part, which apparently does not contain the allergens.[41] More or less the same holds for Styrax,[41] whereas Benzoin seem to be less suspect.[42]

As to the aroma chemicals mentioned in Table III, restrictions for use have been recommended for cinnamic alcohol, cinnamic aldehyde, and dihydrocoumarin. For cinnamic alcohol it is

Table III. Aroma chemicals with a balsamic note

Benzenoids	Balsamic	Powdery	Aromatic	Sweet
amyl benzoate	4	3	2	2
cinnamyl acetate	4	3	4	5
dihydrocoumarin	4	4	5	6
benzyl eugenol	3	5	5	2
benzyl benzoate	3	0	2	3
3-phenylpropanol	3	2	2	4
benzyl-isobutyl carbinol	3	3	7	4
isobutyl cinnamate	3	3	4	5
cinnamyl alcohol	3	3	4	4
methyl cinnamate	3	3	2	4
linalyl cinnamate	3	3	5	4
vanillin	3	4	9	6
ethyl vanillin	3	5	9	7
isoeugenyl acetate	2	6	4	4
amyl phenylacetate	2	1	4	4
amyl salicylate	2	4	2	3
benzyl cyanide	2	2	1	2
benzyl cinnamate	2	3	2	4
benzyl isoeugenol	2	4	4	4
isoeugenol	2	3	4	5
cinnamic aldehyde	2	2	5	3
styrene	2	1	1	2
everniate	2	3	1	1
Isoprenoids				
3-isocamphyl-cyclohexanol (mysorol)	4	3	1	3
Fixateur 404 (Firmenich)	4	3	0	2
Vetiverol	3	5	2	3
Vetiveryl acetate	3	4	0	2
Acetyl cedrene (Naarden)	3	3	1	2
Bornyl acetate	2	5	0	0
Isolongifolanone (Naarden)	2	5	0	0
Patchoulol	2	4	0	2
Grisalva (IFF)	2	6	0	2
Acetylisolongifolene	2	4	0	2
Miscellaneous				
2-methyl-undecanal (MNA)	3	1	0	0
4-cyclohexyl-4-methyl-2-pentanone (Vetivertone-Naarden)	2	2	0	1
5-(2,4,6-trimethyl-cyclohex-3-en-1-yl)-4-penten-3-one	2	2	0	2

tentatively recommended to limit the use level to 4% in a compound; further toxicological studies are in progress. Cinnamic aldehyde and dihydrocoumarin have sensitizing properties; for cinnamic aldehyde this problem can be met by using a so-called quenching mixture (with equal weights of limonene or eugenol).

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