Cassie (Acacia) in Perfumery

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Cassie flower oil is used in fine fragrances of various types, including floral, aldehydic, as well as semi-oriental and oriental types. In less expensive perfumes, synthetic cassie compounds are used.

Botanical Origin

Acacia farnesiana Willd. and *Acacia Cavenia* Hook et Arn., both belonging to the family Leguminosae, are two species originally cultivated in the Mediterranean countries. The latter is being considered by some botanists as a variety of the former. *Acacia farnesiana* Willd. is small trec up to ten feet in height, bearing small yellow flowers in a shape of a ball.[1]

Among many other species, *Acacia farnesiana* Willd. grows wild in many warm and tropical countries, such as Australia, western India, south China and Africa.

Type of Oil, Yield, Mode of Production

In the beginning of this century, cultivated *Acacia farnesiana* Willd. (known in France as *Cassie ancienne*) was used for the extraction of the flower oil in preference to the *Acacia Cavenia.*

Cassie pomades were obtained by maceration of the flowers in heated fat (50° to 70°C) which on treatment with alcohol yielded lavages or flower extraits No. 36, 24, or 12, according to the concentration of the flower oil they contained. On evaporation in vaccum of the alcohol, concentrates of the flower pomades, also called absolute, were obtained.[2]

Later, volatile solvent extraction was used, yielding cassie concrete and, on treatment with alcohol, the absolute was obtained. Further treatment results in partially decolorized absolute.

The yield of the concrete oil obtained by volatile solvents varies within 0.5 and 0.7 per cent, but may be as high as 0.82 per cent.[3]

Cassie concrete has a tendency to become lighter in color on exposure to air and light. On treatment with alcohol, the concrete yields from 30 to 35 per cent of the absolute. On steam distillation, the concrete yields 6.5 to 9 per cent of the volatile oil, which is used only for analysis and research.[4]

Cassie oil production has declined in southern France, and presently *Acacia farnesiana* Willd. is cultivated in several north African countries, Egypt, Algeria and Morocco for the production of cassie flower oil, as well as in South Africa.

Chemical Composition

In the beginning of this century, research on cassie absolute, obtained from an Indian pomade, revealed the following components:[5]

- Benzaldehyde
- Anisic aldehyde
- Decyl aldehyde
- Cuminic aldehyde
- Benzyl alcohol
- Geraniol (?) (not definitely established)
- Linalool (?) (not definitely established)
- p-Cresol (small quantities)
- Methyl salicylate
- A ketone with a menthone-like odor
- A ketone with a violet-like odor (important for the odor of cassie flower)

Another source reported farnesol in the high boiling constituents.[6]

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Table I. Constituents of Acacia farnesiana Willd. Absolute

	1969	1970	1974
Anisic aldehyde	+	+	–
Benzaldehyde	–	+	+
Cuminic aldehyde	–	+	+
Hexanal	+	–	–
Heptanal	+	–	–
Octanal	+	–	–
Nonanal	+	–	–
Decanal	+	–	–
Veratraldehyde	+	–	–
Anisyl alcohol	+	–	–
Benzyl alcohol	+	+	–
Cuminic alcohol	–	+	–
Farnesol	–	+	+
Geraniol	+	+	+
Linalool	–	+	+
Nerolidol	–	+	+
α-terpineol	–	+	+
o-Cresol	–	–	+
Eugenol	–	–	+
Anisyl acetate	+	–	–
Benzyl acetate	+	–	–
Benzyl benzoate	+	–	–
Ethyl hexanoate	+	–	–
Ethyl lineolate	+	–	–
Ethyl linolenate	+	–	–
Ethyl palmitate	+	–	–
Ethyl salicylate	+	–	–
Geranyl acetate	+	+	–
Linalyl acetate	–	+	–
Methyl benzoate	+	–	+
Methyl 2,6-dihydroxy benzoate	+	–	–
Methyl 2,6-hydroxy-3-methoxy benzoate	+	–	–
Methyl-2-hydroxy-6-methyl oxy benzoate	+	–	–
Methyl 2-methoxy benzoate	+	–	–
Methyl salicylate	+	+	+
Methyl veratrate	+	–	–
α-ionone	+	+	–
β-ionone	+	–	+
Dihydryo-β-ionone	+	+	+
Methyl heptenone	–	–	+
6,10,14-trimethyl pentadecan-2-one	+	–	–
Heptadecane	+	–	–
Nonadecane	+	–	–
Myrcene	+	–	+
β-pinene	–	–	+
Dihydroactin-diolide	+	–	–
Anisic acid	+	–	–
Linoleic acid	+	–	–
Linolenic acid	+	–	–
Myristic acid	+	–	–
cis-3-methyl-decen-4-oic acid	+	–	–
cis-3-methyl-decen-3-ol	+	–	–
trans-3-methyl-decen-4-oic acid	+	–	–

A study published in the 1950s on cassia absolute, prepared from a Calabrian concrete obtained by volatile solvent extraction, confirmed the presence of benzyl alcohol and linalool, but no methyl salicylate was found.[7]

Additional components identified were:

Alpha terpineol
Nerolidol or farnesol (or both, partly esterified)
A mixture of cresols
A mixture of ethyl phenols
Hydroxyacetophenone
A ketone with an ionone configuration (probably optically active alpha ionone)
Coumarin
Butyric acid
Palmitic acid
Benzoic acid
Salicylic acid
n-Eicosane

In the next two decades additional research work was done on *Acacia farnesiana* absolute using a combination of techniques, including thin layer chromatography.[8-10] In all three studies *Acacia farnesiana* Willd. absolute Egyptian was used. The results are shown in Table I.

The last three compounds listed in Table I play an important role in the odor of cassie oil, and they have been synthesized.[11]

Ethyl salicylate was considered as a possible artefact.[8]

In a study done in Japan on *Acacia farnesiana*, published in 1976, the acetone soluble part of the flower oil was divided into acidic and neutral positions by saponificaiton.[12]

The major components of the fatty acids were saturated C-16 and unsaturated C-18.

The major compound of the neutral portion appeared to be alpha-spinasterol.

In a more recent research work on *Acacia farnesiana* blossoms extracted with heptane, a combination of GC-MS and Kovats Index were used, and 59 components were revealed.[13] Among previously identified compounds are shown in Table II.

The other components identified for the first time are listed in Table III. The researchers assume that the three phthalates may be artefacts.[13]

Synthetic Compounds

According to the Cerbelaud odor classification, cassie belongs to the mimosa group of

Table II. Previously Identified Compounds of Acacia farnesiana

p-Anisaldehyde	34.36
Benzaldehyde	5.98
Benzyl alcohol	0.01
Geraniol	19.45
Linalool	0.86
3-Methyl-dec-3-en-1-ol	3.83
3-Methyl-dec-4-en-1-ol	0.92
p-Anisyl acetate	0.13
Benzyl acetate	0.75
Benzyl benzoate	0.09
Dimethyl phthalate	0.68
Ethyl salicylate	0.18
Geranyl acetate	6.56
Methyl benzoate	0.09
Methyl 2,6-dihydroxy benzoate	2.02
Methyl salicylate	94.40
Methyl 6-methoxy salicylate	0.59
α-ionone	0.68
β-ionone	1.34
Methyl heptone	0.18
6,10,14-trimethylpenta-decan-2-one	0.26
2,6,6-trimethyl-2-hydroxy-cyclohexyl-idene-acetic acid lactone	0.11
n-eicosane	0.40
n-Heptadecane	0.51
n-Nonadecane	6.25
Myrcene	1.06

Table III. New Constituents of Acacia farnesiana (1983)

β-cyclocitral	0.37
Geranial	5.57
trans,cis-2,6,nonadienal	0.13
trans-2-nonenal	0.20
Octanol	0.03
Decanol	0.09
2-ethyl hexanol	0.02
cis-3-nonenol	1.43
trans-2-nonenol	0.20
Benzothiazole	trace
Benzyl 2-methyl propionate	0.18
Citronellyl acetate	0.13
Dibutyl phthalate	0.02
Ethyl p-anisate	0.11
Methyl p-anisate	0.31
2-methylpropylbenzoate	0.04
Neryl acetate	0.66
cis-Linalool oxide	0.31
Octane	0.04
Tridecane	0.31
Pentadecane	0.26
Octadecane	0.15
Dodecane	0.15
Tetradecane	0.22
Docosane	0.09
Tricosane	0.37
Heneicosane	1.76
Methylcyclohexane	0.22
2,2,6-trimethylcyclohexanone	0.07
Limonene	0.20
1-methyl naphthalene	trace
Naphthalene	2.51
cis-ocimene	0.18
trans-ocimene	0.59

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odors.[14] Therefore, it is not surprising that both have common ingredients, and the absolutes or concretes of either are used interchangeably in their synthetic compounds.

The violet note plays an important role in cassie compounds; therefore, orris and the ionones were part of synthetic cassie compounds.

Most conventional cassie compounds are based on methyl salicylate, combined with jasmin, rose and violet components. Some contained p-methyl acetophenone.

Earlier synthetic compounds comprised large amounts of mimosa, cassie and other flower absolutes, as well as orris resinoid or concrete. Such compounds were usually fixed with ambergris and civet infusions.

Later, the amount of absolutes diminished in cassie formulas, and finally absolutes were completely eliminated or were replaced by synthetic compounds in inexpensive cassie compounds.

Anisic aldehyde or alcohol, anisyl acetate, cuminic aldehyde or cumin oil, neroli or petigrain oil, linalool, terpineol, ylang, and aldehydes C-8, C-9, C-10 or C-12(L) and alcohol C-12 are among other components used in smaller amounts.

Ciste absolute, immortelle and violet leaf absolute may be considered as trace components.

Some cassie compounds may contain cyclamen aldehyde or hydroxycitronellal or newer derivatives, guaiacwood, p-cresol, aurantiol and indol.

Bergamot or linalyl acetate, orange sweet oil and verbena may be used to impart freshness.

Benzyl salicylate or isobutylsalicylate and styrax are good fixatives.

Formula 1. Cassie Base

	Parts
Methyl salicylate	110
Methyl ionone	70
Benzyl alcohol	40
Aldehyde C-10, 10%	40
Orris concrete synthetic	30
Ylang ylang	30
Linalool	20
Cuminic aldehyde, 10%	20
Phenyl ethyl alcohol	10
Terpineol	6
Eugenol	6
	382

The illustrative conventional cassie compound Formulas #1, 2 and 3 may serve as examples.

More modern cassie compounds would include newer derivatives of methyl ionone and a choice of hydroxycitronellal substitutes, as well as new constituents of rose and jasmin. Modern specialties of the orris odor tonality or constituents of orris, i.e., irone, as well as aromatics of the violet leaf odor tonality are apt to be used.

The base of a reconstructed cassie in accordance with the major components identified in an Egyptian *Acacia farnesiana* is seen in Formula 4.[10] The amount of o-cresol in this base seems unusually high.

Formula 2. Cassie Base

	Parts
Methyl salicylate	275
Ionone AB	160
Methyl octine carbonate, 10%	150
Benzyl salicylate	100
Aldehyde C-10, 10%	100
Ylang ylang	50
Cuminic aldehyde, 10%	50
Linalool	40
Orris resinoid synthetic	30
Terpineol	30
Eugenol	20
Geraniol	10
Phenyl ethyl alcohol	10
	1025

According to the latest research done on *Acacia farnesiana*, the base of a reconstructed cassie would consist of the components shown in Formula 5.[13]

The above two cassie bases differ especially in the amount of methyl salicylate, which is much higher in the second base, not to mention the new aromatics identified in more recent research.

Every perfumer knows that the ingredients in lesser amounts play an important role, and some of the aforementioned recently identified aromatics when commercially available will have an influence on the development of synthetic cassie compounds.

Formula 3. Cassie Base

	Parts
Methyl salicylate	175
Anisyl acetate	150
Methyl ionone	150
Methyl octine carbonate, 10%	60
Beta ionone	60
Alcohol C-12, 10%	50
Linalool	40
Phenyl ethyl alcohol	40
Hexyl cinnamic aldehyde	35
Hydroxycitronellal	30
Ylang ylang	25
Benzyl salicylate	20
Cyclamen aldehyde	10
Linalyl acetate	10
p-Cresol, 10%	5
Aurantiol	5
	865

There is no question that an elaborate analysis of a natural perfume material gives the perfumer a new insight, but a perfumer still has to use imagination and sometimes use additional components to achieve a balanced odor.

Some components of synthetic cassie compounds have been completely eliminated, others are used in limited percentage, specially processed or of high purity, few are used in conjunction with quenchers, all because of dermatological reasons. Among the first group are phenyl acetic acid, orris and styrax resinoid; cumin oil, methyl heptine carbonate belong to the second group. Among the third category are farnesol, methyl ionone, bergamot and styrax. Citral and phenyl acetaldehyde belong to the last group.

Formula 4. Egyptian Acacia farnesiana Cassie Base

	Parts
Methyl salicylate	18.50
Farnesol	13.50
Geraniol	11.80
o-Cresol	8.20
Alpha ionone	4.70
Alpha terpineol	1.26
Linalool	1.04

Application

Cassie harmonizes well with ionones and irone, and it is an important component of floral compounds, especially jonquil, mimosa and violet. Among others, cyclamen, linden blossom, new mown hay, orchid, reseda, sweet pea and tuberose may be mentioned.

In cosmetics, cassie absolute has been used in perfumes for brilliantines, lipsticks and powders.

Synthetic cassie compounds have also found application in soap. The base of such compounds usually was a combination of ionone terpenes with geranium and cananga oils and methyl acetophenone. Some contained cuminic aldehyde and aurantiol. They were fixed with isobutyl salicylate and styrax resinoid.

Cassie absolute or cassie compounds are valuable components of fine fragrances. Among older types, chypre, fougère and heliotrope may be mentioned. Cassie was also used in the once popular lavender water. Of the classical and more modern fragrances, Chanel No. 5, Bob Mackie and Missoni may serve as examples.

Formula 5. 1983 Base of Reconstructed Cassie

	Parts
Methyl salicylate	94.40
p-Anisaldehyde	34.36
Geraniol	19.45
Geranyl acetate	6.56
Nonadecane	6.25
Benzaldehyde	5.98
Geranial	5.57
3-Methyl dec-3-en-1-ol	3.83
Naphthalene	2.50
Methyl 2,6-dihydroxy benzoate	2.02
Cis-3-nonenol	1.43
Heneicosane	1.76
Myrcene	1.06

Although cassie is not popular as a fragrance per se, it was used among other floral compounds in perfumes without alcohol, composed before World War II in Germany.

A given example of such cassie fragrance shows a cassie compound with a violet compound, additioned with terpineol, linalool and small amounts of aldehyde C-12 and aldehyde C-16. It is fixed with synthetic civet. The concentration of such perfume compounds varied from 5% to 20%. The solvent used was castor oil or diethyl phthalate.[15]

Conclusion

Research on *Acacia farnesiana* absolute using advanced analytical methods, especially in the last two decades, has revealed new constituents and confirmed previously identified components.

Thus a closer reproduction of cassie will be possible when the new constituents become commercially available, and cassie compound formulas will have to be revised.

Cassie contributes a special cachet to fragrances, and it will continue to find application in future fragrances.

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