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The chemistry of flowers, fruits and spices: live vs. dead a new dimension in fragrance research

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Abstract - The aromas of fruits, flowers, herbs, and spices perceptably change following picking of the plant part because the plant part is then, in effect, biologically dead. By collection and analysis of the headspace volatiles over various living and picked flowers, fruits, herbs, and spices the differences in the aroma profiles are traceable to quantitative differences in key volatile components. In addition, the same analytical technique permits the comparison of day vs. night volatile profiles for selected flowers and of various flower colors among the same family. The commercial application of this noble technology is also discussed.

INTRODUCTION

In the days before the advent of modern synthetic organic chemistry the art of perfumery depended, for the most part,on natural oils and extracts of flowers, fruits, roots, or exudates of plants. Before the extraction process, the fruits, flowers, and other plant parts must, of course, be picked. Very few people are aware of the fact that most fruits and flowers when picked soon exhibit a modified aroma from that of the living entity. This aroma continues to change with the process of decay. Hence, the oil obtained from the picked plant part does not replicate the aroma of the living material. The reason is that, when the umbilical cord connecting the fruit or flower to the plant is severed, the excised plant part may then be thought of as being, in effect, biologically dead, and the aroma changes perceptably.

We have now characterized the chemical differences in the aroma between living and picked fruits, flowers, herbs, and spices (1,2). In addition, compositional differences observed between the day and night blooming of fragrant blossoms and among different colors of the same family will be discussed.

At the beginning of our work we chose a flower which is not only essential to the perfumery industry but also has been highly appreciated by Orientals since time immemorial. That flower is the jasmin. The pretty jasmin flower originated in the lower valleys of the Himalayas of northern India. The Moors brought this flower to Spain, and from there, in the sixteenth century, it started to spread along the Mediterranean coast. All commercial jasmin extracts are obtained from the flowers of Spanish jasmin (Jasminum grandiflorum, L.). The yield of absolute from the flower is very low; one kilogram (about 8,000 flowers) yields only 1.5 gms of absolute. The price of jasmin absolute ranges up to more than $2000 per pound, depending on its source.

EXPERIMENTAL

We have performed two side-by-side experiments on jasmin, first on the picked blossoms and then on the blossoms still attached to the plant. The latter technique we call "Living Flower Analysis". In the case of the picked flower the freshly picked blossoms are placed in a flask equipped with a Tenax trap on one sidearm. The flask is then purged with purified air for a period of 6-12 hours depending on the type of flower. The volatiles emanating from the blossoms are collected on the Tenax for later desorption into the gas-liquid chromatograph for analysis by GC/MS.

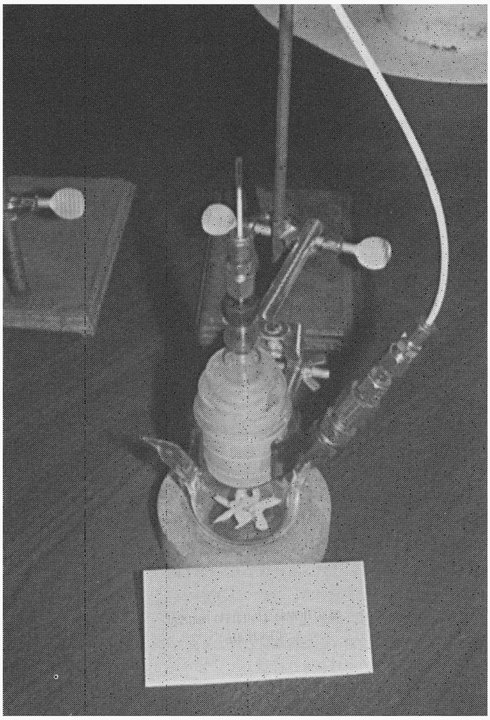

Figure 1.
Analysis of picked jasmin blossoms

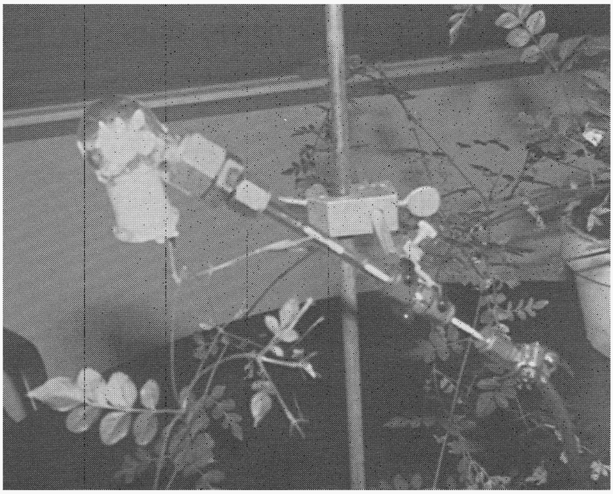

Figure 2. Analysis of living Jasmin flower.

Figure 1 shows the apparatus used for the picked flower analysis.

Our method of analysis of the living flower is as follows: one single blossom still attached to the plant is placed into a suitable glass chamber in such a way that the petals are not injured. This chamber, again, contains a Tenax trap on one sidearm. Air is drawn over the blossom and through the Tenax trap by a pump under the same conditions employed for the picked flower. In this way we have been able to compare the aroma profiles of many different flowers. Figure 2 shows a picture of living jasmin flower analysis.

The comparative headspace analysis of living vs. picked Jasminum grandiflorum is shown in Table I.

As you can see, benzyl acetate which is 40% in the picked flower now represents almost two-thirds of the volatiles emitted by the living flower. At the same time, the linalool content has increased from 3% in the living blossom to 30% in the picked flower. On the other hand, the important constituent, indole, which is in high concentration (11%) in the living flower, has decreased to 2% in the picked blossom.

The next flower chosen not only has the highest priority in the fragrance industry but also is heavily used for flavoring foods by oriental people. This flower is none other than the rose which was called the "Queen of Flowers" by the Greek poetess, Sapho, in 600 B.C. The rose most likely originated in China and was introduced into Spain from China by invading Arabs in the 10th century. The rose is prized chiefly for its blossoms, and, though it has been known since ancient times for the making of fragrance, it was Empress Nurjuhan, the wife of Indian Emperor Jahangir, in the 13th century who first made attar of rose by spreading rose petals on her morning bath water.

Of the 200 varieties of rose the most coveted for the making of otto of rose for fragrance use is Rosa damascena which comes from Bulgaria. It takes about 4000 pounds of rose to produce one pound of rose otto, hence the cost of $2500 per pound. Although most roses grown for commercial oil production come from Bulgaria or the south of France, in the 1930's American horticulturists started to breed hybrid tea roses for both their form and fragrance. Many of these have unique aromas in their own right, although none is the equal of Rosa damascena. The yellow hybrid tea rose was chosen for analysis because it possesses one of the best aromas.

TABLE I. Major Differences in the Headspace Constituents of Living and Picked Jasmin (Jasminum grandiflorum)

COMPOUND	LIVING FLOWER %	PICKED FLOWER %
6-Methyl 5-hepten-2-one	0.2	-
cis 3-Hexenyl acetate	0.2	-
Benzyl alcohol	-	4.0
cis/trans Ocimene	0.2	1.1
Benzyl acetate	60.0	40.0
Linalool	3.0	30.0
Indole	11.0	2.0
cis Jasmone	3.0	-
3, 5-Dimethyl 2-ethyl pyrazine	-	0.5
Methyl jasmonate	0.3	-

TABLE II. Major Differences in the Headspace Constituents of Living and Picked Yellow Tea Rose

COMPOUND	LIVING FLOWER %	PICKED FLOWER %
cis 3-Hexenyl acetate	20.7	5.4
Hexyl acetate	8.4	4.3
Phenyl ethyl alcohol	5.7	3.3
Phenyl ethyl acetate	5.5	1.5
3,5-Dimethoxy toluene	10.0	18.6
alpha Elemene	-	4.1
Geranyl acetone	2.2	-
Dihydro beta ionol	-	2.6
alpha Caryophyllene	0.3	2.1
alpha Farnesene	5.8	3.0

Employing the same analytical technique described for jasmin, the results obtained in Table II were obtained.

These data reveal that the composition of the picked tea rose is remarkably different from that of the living rose. As one can see, cis-3-hexenyl acetate, which constitutes 20% of the living rose headspace volatiles, is drastically reduced to 5% in the picked rose. At the same time, 3,5-dimethoxytoluene, one of the character-donating components of tea rose, is dramatically doubled in the picked flower, whereas important constituents like phenyl ethyl alcohol and its acetate are reduced in the picked flower.

Following the rose I would like to talk about a pretty flower with a delicate fragrance which is not common in the United States but is highly appreciated in Europe, especially in Holland, and which originated in South Africa. This flower is freesia. Table III shows differences in the aroma constituents of the headpace of living vs. picked freesia.

One can easily see the drastic difference between the living and picked flowers. Many components which are present in the living freesia are not found at all in the picked flower. Even though linalool represents 80-90% in both, odorous constituents such as ionone and its derivatives are almost absent in the picked freesia.

After this European flower we analyzed an exotic oriental flower from Japan. This flower is osmanthus which possesses a very delicate, fruity-floral aroma which is in high demand by the perfumery industry. Table IV shows the analysis of the headspace of living vs. picked osmanthus.

As one can see, character-donating components like beta damascenone, jasmin lactone, and 4-keto beta ionone are totally absent in the picked flower. Moreover, beta ionone which constitutes 13% of the living flower volatiles is drastically reduced to 6% in the picked flower.

TABLE III. Major Differences in the Headspace Constituents of Living and Picked White Freesia (Freesia Sp.)

COMPOUND	LIVING FLOWER %	PICKED FLOWER %
Linalool oxides (4)	1.0	-
Linalool	78.0	91.0
cis 3-Hexenyl butyrate	0.2	trace
alpha Terpineol	4.0	10.0
beta Cyclocitral	0.1	-
Nerol/geraniol	0.2	-
Dihydro beta ionone	3.7	trace
beta Ionone	3.0	trace
4-Oxo beta ionone	5.4	-
4-Oxo beta ionol	2.2	-
Ethyl dimethyl pyrazine	-	0.1
Ethyl trimethyl pyrazine	-	0.2

TABLE IV. Major Differences in the Headspace Constituents of Living and Picked Osmanthus (Osmanthus fragrans)

COMPOUND	LIVING FLOWER %	PICKED FLOWER %
Geraniol	15.00	11.40
Geranial	2.10	1.0
beta-Damascenone	0.10	-
Dihydro beta ionol	0.45	-
Jasmin lactone	0.20	-
beta Ionone	13.20	5.74
4-Keto beta ionone	1.90	-

TABLE V. Major Differences in the Head-space Constituents of Living and Picked Lotus (Nelumbium nucifera 'Chawan Basu')

COMPOUND	LIVING FLOWER %	PICKED FLOWER %
Sabinene	6.0	12.0
para Dimethoxy benzene	18.0	8.0
4-Terpineol	3.0	1.5
alpha Terpineol	9.0	1.0
cis Jasmone	0.1	-
C_{15} Hydrocarbons	20.0	30.0

TABLE VI. Major Differences in the Head-space Constituents of Living Honeysuckle (Lonicera americana)- Day vs. Night

COMPOUND	Day %	Night %
cis 3-Hexenyl acetate	4.0	1.0
Hexyl acetate	2.0	0.1
Benzyl alcohol	5.0	1.0
Linalool	17.0	34.0
Indole	3.0	1.0
cis Jasmone	1.0	0.4

After osmanthus we analyzed the most coveted oriental flower, lotus, which is not only the national flower of India but all Hindu gods and goddesses sit on this flower because of its beauty and purity. Table V shows the difference between the headspace components of living vs. picked lotus.

This table shows that alpha terpineol which possesses a very floral odor decreases drastically from 9% in the living to 1% in the picked lotus blossom. Similarly, the character-donating component, para dimethoxy benzene, decreases markedly from 18% in the living lotus to 8% after picking.

By this way we have analyzed many other American, European, and oriental flowers such as lily-of-the-valley, mimosa, and magnolia to name only a few. For each of these flowers considerable differences are observed in the aroma profiles of the living and picked blossoms.

Since it is well known to naturalists that some flowers smell different from day to night, we have also analyzed living blossoms from several flowers which are noted for this phenomenon. The very first flower we analyzed is the honeysuckle which is very common in America. This flower has a definite indolic note during the daytime but exhibits extreme diffusivity after nightfall. Table VI shows the day vs. night data for this flower.

The high content of indole (3%) in the daytime obviously accounts for the indolic character observed at that time while the 34% linalool content found during the night totally justifies the strong diffusivity associated with the flower after dark.

The next flower which we analyzed for the purpose of differentiating between day and night blooming is of Indian origin and is in high demand by the perfumery industry. This flower is tuberose. This flower is noted for its much fuller floral-lactonic aroma after sunset, hence it is called in India Raajanigandha (night-scent). Table VII shows the differences between the day and night constituents of tuberose.

This table shows that methyl anthranilate which is noted for its fruity floral odor increases from 1-3% from day to night. At the same time, character-donating components of the flower, namely jasmin lactone and delta dodecalactone, dramatically increase during the nighttime. This fully justifies the observed true floral character of tuberose in the nighttime.

A third flower which was chosen for day/night studies was the white flower, Stephanotis floribunda, which is used in America for bridal bouquets for its delicate appearance and odor. The difference in aroma constituents between day and night blooms is shown in Table VIII.

TABLE VII. Major Differences in the Head-space Constituents of Living Tuberose (Polyanthes tuberosa) - Day vs. Night

COMPOUND	DAY %	NIGHT %
Limonene	8.0	14.0
Methyl salicylate	12.0	6.0
alpha Terpineol	11.0	3.5
Methyl anthranilate	1.0	3.0
Jasmin lactone	0.2	1.0
delta Dodecalactone	0.1	0.6

TABLE VIII. Major Differences in the Head-space Constituents of Living Stephanotis (Stephanotis floribunda) - Day vs. Night

COMPOUND	DAY %	NIGHT %
n-Hexanol	7.0	2.0
Benzaldehyde	3.0	0.5
Methyl benzoate	21.0	33.0
2-Phenyl nitroethane	10.0	16.0
Eugenol	0.1	1.0
alpha Farnesene	0.1	1.0

TABLE IX. Major Differences in the Headspace Constituents of Living American Hybrid Tea Tea Roses

COMPOUND	RED CHRYSLER IMPERIAL %	WHITE J.F.K. %	RED/ YELLOW DOUBLE DELIGHT %	PURPLE INTRIGUE %	OTTO OF ROSE BULGARIAN %
Phenyl ethyl alcohol	9.5	5.8	25.0	-	1.3
Rose oxide	1.5	-	1.8	-	0.6
Citronellol	22.8	-	3.0	-	33.0
Nerol-geraniol	-	-	-	2.6	30.2
3,5-Dimethoxy toluene	24.0	10.0	7.0	6.0	-
Dihydro beta ionone	-	7.0	-	-	-

One can easily see that floral constituents such as methyl benzoate, 2-phenyl nitroethane, eugenol, and farnesene all increase appreciably at night giving more floralcy to the stephanotis blossoms after nightfall.

Following these experiments we decided to investigate whether the color of flowers within the same family has any influence on the aroma profile. To do this, we chose again the American hybrid tea rose which varies in color including white, red, yellow, purple, etc. Table IX shows the major differences in the headspace constituents of living blossoms of American hybrid tea rose of different colors.

This table clearly shows that the headspace constituents are completely different for each color of rose. Nerol/geraniol, which is one of the most characteristic and major constituents of otto of rose Bulgarian, is not present at all in 3 of the 4 tea roses studied. At the same time, 3,5-dimethoxy toluene, the characteristic odor component of American hybrid tea rose, not only varies in amount from color to color but is completely absent in otto of rose Bulgarian. From my knowledge of perfumery from 25 years in the business, no one ever thought of making rose aroma without using citronellol/nerol/geranion which, together, constitute 60% of highly coveted otto of rose Bulgarian. These data clearly demonstrate that what man could not do Nature has already done.

Another flower of highly desired odor which exists in a wide range of colors from white to dark purple is lilac. Table X shows the headspace aroma profiles of lilacs of various colors.

It is obvious that each flower is remarkably different in aroma profile. The three components which are most characteristic of lilac: lilac alcohol, lilac aldehyde, and 1,4-dimethoxy benzene, vary considerably from color to color.

A third flower chosen to demonstrate color differences reflected in aroma is well known in India. This flower is the water lily. Even though most Indian people are well aware that the eye-soothing water lily exists in many varieties of color, they are not aware that the lilies also exhibit very interesting odors. Table XI shows the headspace constituents of living water liles of different color.

TABLE X. Major Differences in the Headspace Constituents of Living Purple, and White Lilacs (Syringa Sp.)

COMPOUND	DARK PURPLE LILAC %	PURPLE LILAC %	WHITE LILAC %	FRENCH PURPLE LILAC %
Benzyl methyl ether	7.0	6.5	2.6	1.5
trans beta Ocimene	26.0	38.0	31.5	52.0
Lilac aldehydes	9.3	11.0	-	1.5
1,4-Dimethoxy benzene	3.0	7.0	21.4	5.0
Lilac alcohols	8.0	4.3	1.0	1.0
Indole	-	0.2	0.8	0.2

TABLE XI. Major Differences in the Headspace Constituents of Living Water Lily (Nymphaea Sp.)

COMPOUND	Light Blue Bagdad %	Clear White Alice Tricker %	White Mrs. G. Pring %	Strong Blue Colorata %	Pale Blue Dauben %
Benzyl alcohol	13.0	1.0	4.0	-	17.0
Benzyl acetate	9.0	2.0	3.0	-	4.0
Anisic aldehyde	2.0	-	0.1	3.0	-
Anisyl acetate	3.0	0.4	2.3	-	0.1
n-Pentadecane	25.0	40.0	32.0	18.0	41.0
Heptadecadiene	16.0	21.0	26.0	35.0	4.5

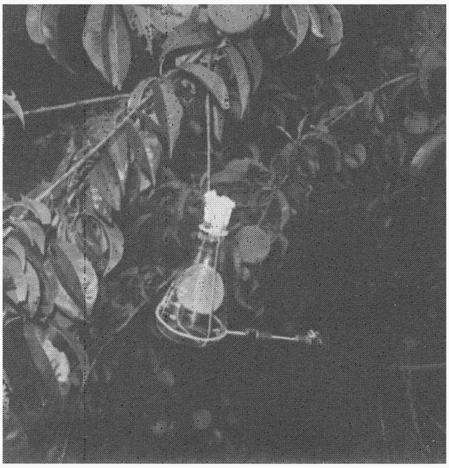

Figure 3. Analysis of Living Peach

TABLE XII. Major Differences in the Headspace Constituents of Living and Picked Peach (Prunus persica)

COMPOUND	LIVING PEACH %	PICKED PEACH %
Ethyl acetate	6.2	-
Dimethyl disulfide	0.6	-
cis 3-Hexenyl acetate	9.7	-
Methyl octanoate	34.2	7.1
Ethyl octanoate	7.4	11.0
6-Pentyl alpha pyrone	trace	10.6
gamma Decalactone	2.5	39.2

It is apparent that both anisic aldehyde and anisyl acetate, the two aroma-donating components of water lily, vary in quantity from color to color. The same is true for benzyl alcohol and its acetate.

We have also analyzed other flowers which come in different colors such as hyacinth, lily-of-the-valley, etc. In each case we found that the aroma varies with the color.

In connection with our living flower program, we have also extended this concept into the area of fruits and spices (2). It does not take a great deal of imagination to conceive that what is true for living and picked flowers also could be true for fruits. Our first subject for testing this theory was peach. Figure 3 shows live peach analysis.

A peach still attached to the tree was selected for analysis on the basis of its possessing a full, rich, at-the-peak-of-ripeness aroma. Taking extra care not to bruise the fruit, the peach was placed into a suitable flask with a Tenax trap and a pump attached, and the volatiles were collected for 24 hours. At the same time, a peach from the same tree and at the same degree of ripeness was harvested, and, without delay, the procedure was repeated for the same time interval for the collection of volatiles. The comparative headspace analytical data for living vs. picked peach are shown in Table XII.

The volatiles of living peach are, for the most part, lower boiling with methyl octanoate predominating. Very little gamma decalactone, the so-called peach lactone, and pentyl pyrone are seen in the living peach whereas these are major constituents of the picked fruit. Methyl octanoate decreases considerably on picking while ethyl octanoate increases.

We have also compared living and picked samples of other fruits such as strawberry, raspberry, etc. In each case, differences were observed.

In a further extension of this concept the same analytical technique was also applied to the herbal plants. American spearmint, Mentha spicata, although not a true native of America having been introduced from Europe during the 17th century, is now widely grown both for local, private consumption of the herb and commercially for the large-scale production of its oil. Millions of pounds of spearmint oil have been produced in America because of its extensive and popular use as a flavoring ingredient, particularly in chewing gums and oral hygiene products.

The technique for the headspace analysis of the living and picked American spearmint plant is the same as that used for live and picked flowers and fruits. The picked spearmint was taken from the same plant used for the living plant analysis. In order to simulate the commercial process of making spearmint oil, freshly picked stems and leaves were kept at room temperature

TABLE XIII. Major Differences in the Headspace Constituents of Living vs. Picked Spearmint (Mentha spicata).

COMPOUND	LIVING PLANT %	PICKED PLANT %
Hexanal	0.5	trace
Hexanol	-	2.3
Limonene	17.7	1.8
Dihydro carvone	0.7	2.6
Carvone	24.0	70.0
Menthone/isomenthone	-	-
Menthol isomers	-	-
1,3,5-Undecatriene (mixture of 4 isomers)	0.5	-

TABLE XIV. Major Differences in the Headspace Constituents of Living vs. Picked Coriander Leaves (Coriandrum sativum)

COMPOUND	LIVING LEAF %	PICKED LEAF %
n-Nonane	15.2	4.7
Decanal	11.4	4.7
trans 2-Decenal	35.5	39.2
trans 2-Decenol	2.6	-
Decanol	2.5	-
Undecanal	1.5	-

for a period of 24 hours during which time they reduced in weight by 50%. The semi-dried material was then analyzed for headspace volatiles and compared with those of the living plant. Table XIII shows the major differences between living and picked spearmint.

Carvone, the true character-donating component of spearmint, constitutes 70% of the total headspace volatiles over living spearmint. Just the opposite is true in the case of limonene; it is only a minor constituent (2%) in the picked mint but a major component (18%) of the living mint.

Another herb which we analyzed is coriander leaf, also known as Chinese parsley. This herb is used daily in cooking by many Indian people due to its intense but pleasant green flavor and aroma. Table XIV shows the major differences in the headspace constituents of living and picked coriander leaves.

The table shows that, with the exception of the major component, trans-2-decenal, all of the important aroma constituents have either decreased appreciably on picking or are totally gone.

We have now shown beyond a doubt that dramatic chemical changes occur following the picking of flowers, fruits, and herbs. In addition, these examples clearly demonstrate that flower aroma profiles vary not only from living to picked but also from day to night and from color to color. Is it not interesting to observe that we humans also show different characteristics at different times, in different places, and from color to color.

In this connection, I would also like to comment that it is apparent that not just one or two aroma components or a specific color are responsible for the attraction of bees to flowers for pollination as is popularly believed. Rather, these data lead one to the conclusion that it must be the total aroma composition in addition to color which attracts the bee. Otherwise, many flowers would never be pollinated.

I cannot resist recalling a century-old observation by the reknowned Indian biochemist, Bose (3,4). In the early 1900's Bose proved by electro-stimulation experiments that plants are not mute. In other words, as in the case of human beings, plants express their feelings in response to abuse or care. If a plant is injured, there is a definite electrical response to the injury. We have now proven that, indeed, plant chemistry also changes to reflect the changing state of the plant.

Finally, we would like to add that this new technology has revolutionized the fragrance industry. To quote from Vogue, the famous fashion magazine, "It is the first significant change in fragrance making in over 30 years, and the resulting essences ... 'are so rich and varied they will lead to fragrances never experienced before.' (So far the still developing technology has benefited Eternity, Prescriptives' Calyx, Carolina Herrera, Revlon's new Trouble, and Coty's ! Exclamation.)"(5). Moreover, according to Self Magazine (6), the technique has been used to produce such new fragrance hits as Red from Giorgio Beverly Hills, Red Door by Elizabeth Arden, and the "Living Peach" hair care collection from La Coupe all of which were introduced in 1989.

It is important to recognize that this is not just new technology but it is a fundamental breakthrough which has tremendous and unlimited application for pleasing the mind and senses of humanity for many years to come.

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