Thoughts On Essential Oils and Aroma Chemicals for Flavors and Fragrances

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The ultimate goal of the flavor and fragrance industry is to improve the quality of life through production and focused application of flavors and fragrances. In order to do this, one must first understand the basic role of smell and taste in life. This means investing in research into the science of smell and taste.

As a next step, our industry must absolutely control the production and application of flavors and fragrances so that they do not pollute the environment. They should not harm forests and animals. They should not adversely affect the workers involved in their production. They should not degrade the neighborhood around their production centers. Perfumes and flavors, after having fulfilled their tasks, should discretely disappear. They should biodegrade and not, through accumulation, annoy people and disturb the ecological equilibrium.

This consolidated approach to improving the quality of life through taste and smell not only targets our clients and the end-users, but addresses everyone involved in the research, creation, supply and production chain, urging all possible respect for an *ecological, economical and social equilibrium on a world-wide basis*.

Trends Toward a Global Government

The industrialized world must develop a solid partnership with the developing countries, which more and more become the source for natural and chemical raw materials. The future of our industry will be governed by a *global long-term strategy* rather than by the short-term interests of isolated national, regional and industrial entities.

It is interesting to see how, over the last decades, countries of lesser economic wealth have profitted from their favorable climate and biological resources, managing to become producers of high value-added essential oils of strategic importance to our industry. These countries include Argentina (lemon oil), Brazil (orange oil), Guatemala (lemongrass and cardamom oils), Egypt (jasmin concrete and several other oils), Turkey (rose oil and concrete), India (jasmin concrete and mint oils), Indonesia (patchouli and clove oils), China (litsea cubeba, eucalyptus, geranium and many other oils) and, soon, Vietnam.

A similar trend could be observed for some of our basic chemicals, such as l-menthol (China and Brazil), coumarin (China), camphor (China), isobornyl acetate (Eastern Europe and China), phenylethyl alcohol (China) and vanillin (China).

Another reason why these countries rapidly become important producers of raw materials is their positive attitude toward a rigorous application of modern science and technology by way of investments in their chemical industry. In India, Indonesia, Taiwan, Korea and China, to name a few of these countries, emphasis on schooling and higher education provides the necessary skilled and motivated human resources.

Revolution in Science and Technology

Science and technology have progressed rapidly toward new disciplines over the last 100 years and helped foster today's industry.

* This article is adapted from a speech presented at the 13th International Congress of Flavours, Fragrances and Essential Oils in Istanbul, Turkey, in October 1995.

0272-2666/96/0002-0013$04.00/0

If, 100 years ago, the perfumery and flavor business was still dominated by an empirical approach utilizing artisanal methods to extract natural materials, then mixing them together and selling them in small bottles on the local retail market, chemistry was the first science to bring a dramatic change. The molecules responsible for certain scents and aromas were identified and then produced by synthesis (Table I). Hand in hand with chemistry, we find that isolation and separation technologies were also improved (solvent extractions, crystallization, fractional distillation). After chemistry came biology, biochemistry, biotechnology, information technology and, slowly, the study of the physiological and psychological aspects of odors and flavors. Understanding the impact of flavors and fragrances in their final applications requires an understanding of physical phenomena such as adsorption, desorption and mass transport in the liquid and gaseous state. If art will always be a key element of the perfume and flavor business, the importance of scientific-technical aspects will increase dramatically and determine competitiveness and survival of the players.

More complex science and technology in a broadening field of activities needs critical mass and capital investments; it automatically leads to partnership, collaborative agreements with suppliers and clients and, ultimately, to fusions among smaller companies or to the takeover of smaller industries by larger ones. "Giant dinosaurs," however, lose their dynamics and innovative power to adjust to a rapidly changing world; they do not present the ultimate situation and leave real opportunities for medium-sized industries.

But what is the optimum size for a company in our field? We do not know yet. The future will tell us!

The Need for New Raw Materials

So far, we have tried to define the very large frame of situations and trends likely to influence the future of our industry. What are the consequences for our long-term planning as regards technical and raw-material-related issues?

The consequences can be taken as threats or opportunities, depending on our optimism and determination to find solutions more rapidly than the competition. As already stated, our capability to cope with rapidly evolving science and technology will be the decisive element, although it is evident that the political and economic frame is equally important and has to be favorable. Since we cannot influence this latter point, we can only direct our future activities toward countries where the local environment promises to be supportive of our activities. In these settings, we need to recognize the following changes induced by our clients:

- *Globalization of our clients' business.* This obliges the successful flavor and fragrance company to act as the clients' global partner by servicing and supplying all the world's markets and geographical zones equally well.
- Request for complete solutions. Supplying flavors and fragrances will be insufficent. We'll need to supply delivery systems specifically engineered to the client's end-product. These complete solutions will become more difficult to achieve technically and will require a better knowledge of our clients' products and the consumers' behavior.
- Increasingly complex environmental, safety and health issues. These will become more important and necessitate expensive testing and screening.
- Demand that flavors and fragrances provide additional benefits, such as mood and health improvement, insect repellency and bactericidal action.
- Pressure on price. Even if we, as suppliers, provide the demanded additional benefits, we will face pressure on price with the threat of decreasing margins.

Table I. Industrial syntheses of natural odorants in the 19th century[1]

Year	Substance	Discoverer
1855	benzyl alcohol	S. Cannizzaro
1855	phenylacetic acid	S. Cannizzaro
1866	coumarin	W. H. Perkin
1870	benzaldehyde	F. W. Wilhelmi
1876	salicylaldehyde	K. Reimer
1876	vanillin	K. Reimer, F. Tiemann
1878	cinnamic acid	W. H. Perkin
1883	phenylacetaldehyde	E. Erlenmeyer, A. Lipp
1884	cinnamaldehyde	G. Peine
1885	α-terpineol	O. Wallach
1886	methyl salicylate	Schimmel & Co.
1890	piperonal	G. Ciamician, P. Silber
1891	nitromusk	A. Baur
1893	ionone	F. Tiemann, P. Krueger

Table II. New scents as driving force for creation

Perfume (chemical)	Year	Key raw material
Mitsouko (Guerlain)	1919	α-iso-methyl ionone
Chanel No. 5 (Chanel)	1921	aliphatic aldehydes
Eau Sauvage (Dior)	1966	Hedione*
Nocturne (Caron)	1981	rose ketones
Tuscany (Estée Lauder)	1984	Ambrox*
Coolwater (Davidoff)	1988	Dynascone*
Samsara (Guerlain)	1989	Polysantol*
J.P. Gaultier (Gaultier)	1993	Muscenone**
CK ONE (Calvin Klein)	1994	Hedione High Cis**

*Hedione, Ambrox, Dynascone and Polysantol are registered trade names of Firmenich SA, Geneva, Switzerland

**Currently not commercially available

If our clients ask much more from us with respect to the *perceived performance* of products and service at lower cost, there will be direct consequences for our raw materials. In addition, we will have to know exactly the properties of our raw materials, how they interact with the matrices of the end-products, and how these whole assembled systems influence consumers' perception.

Let's look at what is meant by performance of a raw material. There must be an odor or a taste. The working library for the creative perfumer or flavorist in most companies contains over 1,000 different raw materials, all more or less different in odor and/or taste. Do we really need so many raw materials, and do we have to do research to find new ones?

The performance of a raw material is primarily made up of odor and/or taste. Secondary properties include substantivity, tenacity, diffusiveness (related to the physics of application), chemical stability in the product, toxicity to humans and animals of the food chain, and biodegradability.

Among future changes in our industry, raw materials will certainly play a role. *Is there a need for new raw materials*? Yes, there certainly is! The reasons are (1) to design new creations based on new odor tonalities, (2) to replace disappearing classical raw materials and (3) to improve on secondary properties of raw materials. Let's discuss each point separately and give examples.

Table II lists some classical perfumes that only became possible thanks to a new original chemical material. It is encouraging to see that, even today, with so many available chemicals, our creative perfumers eagerly wait for new captive chemicals and use them successfully in our new perfumes!

Unfortunately, various excellent classical chemical materials are under threat. Some disappear because of problems with a starting material (such as acrolein, which can no longer be transported) (Figure 1). Others disappear when the unique process by which they are produced is found to be polluting. These processes include the Wittig reaction (if Ph_3PO cannot be recycled), some CrO_3 oxidations, and

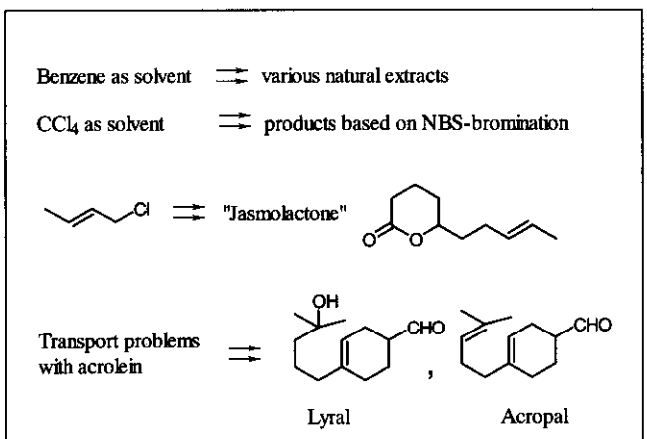


Figure 1. Pressure on classical raw materials because of problems with starting materials/solvents

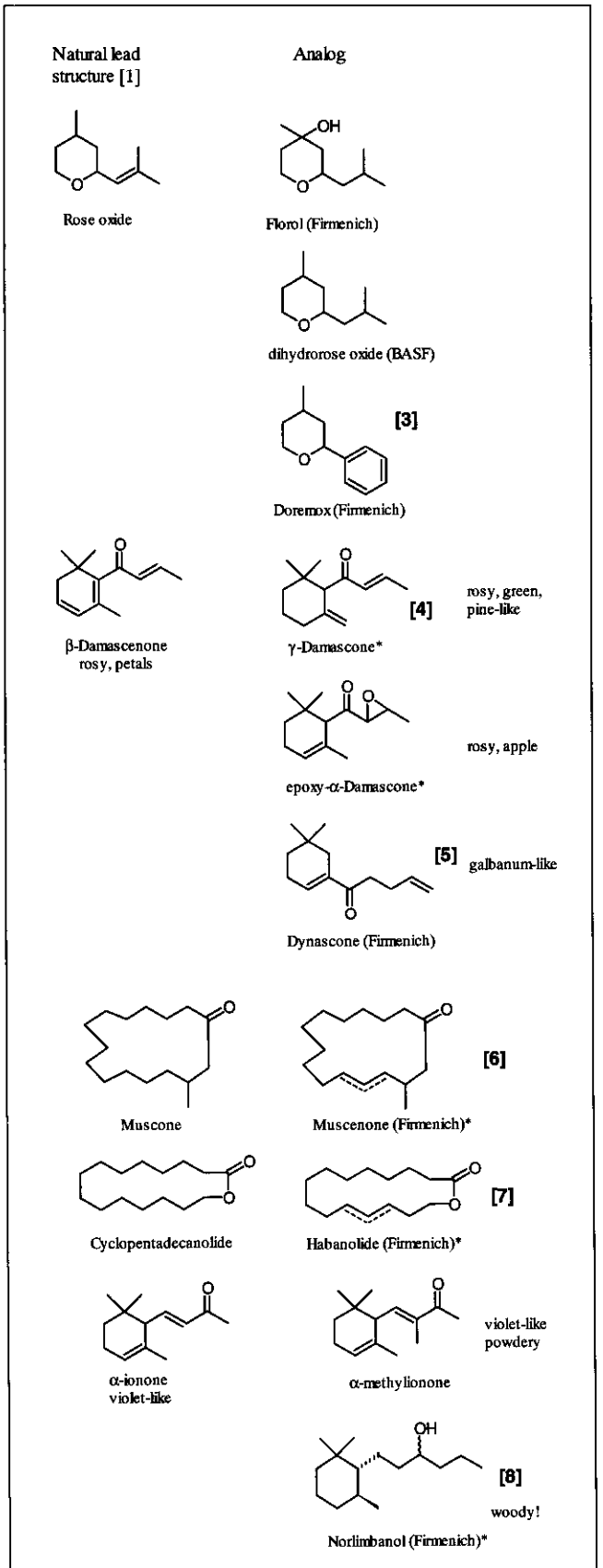


Figure 2. Aroma chemicals that are close analogs of natural materials (Note: references are identified in brackets.)

* Currently not commercially available

many Friedel-Crafts reactions with $AlCl_3$ (such as those producing polycyclic aromatic musks).

Finally, the biggest driving force for developing new raw materials is provided by their "secondary properties." There is chemical and color stability, a real nightmare in perfuming detergents and household cleaning products. There are properties that relate to toxicology and to the environment and safety. This issue has caused the disappearance of musk ambrette and severely limited musk xylol, both of which contain nitro groups. There is hard pressure on polycyclic musks. Toxicological problems also endanger natural materials, such as bergamot oil for its phototoxicity, and verbena absolute oil for its sensitizing properties.

Today's and tomorrow's product research is strongly driven by the desire for a stable citral, the demand for a cheap, biodegradable, nitro-type musk without a nitro-function, and the request for many new substantive, tenacious, diffusive chemicals.

Synthetics vs. Naturals as New Raw Materials Sources

So far, we have discussed the synthetics without referring to the specific attributes of the natural isolates, of which the essential oils make the largest contribution.

Before commenting on possible future trends of these two main classes, the synthetics and the naturals, let's look at their specific qualities or properties in use. Essential oils have the following positive attributes:

- Large array of tonalities.
- Easy to integrate into a perfume.
- Unique notes of the highest olfactive quality.
- Environmental compatibility (biodegradation and part of the eco-equilibrium for thousands of years).
- Natural status.

But they also have these problems:

- Limited and fluctuating availability.
- Fluctuating quality.
- Coloration.
- Lack of chemical stability in certain applications (functional perfumery).
- Price fluctuations.

Synthetic aroma chemicals were developed after the essential oils thanks to the progress made in industrial chemical synthesis. They were, and still are, being pushed to compensate for some of the drawbacks of essential oils and natural isolates. Synthetics often provide better stability and better control over quality (less fluctuation), toxicity, substantivity, tenacity and diffusiveness, and may also provide unlimited availability.[2]

Although the past 30 years have seen the rapid growth of the pure chemicals coming at the expense of natural oils and extracts, the present sees an increasing ideological pressure on synthetic chemicals and a consumer preference for so-called natural products. This change may be

accounted for by invoking environmental and irrational reasons. As we all know, the word "natural" has a *positive* connotation, while the words "chemical and artificial" have a *negative* connotation.

The Role of Nature in R&D of New Raw Materials

This recent trend toward "natural" and away from "chemical and artificial" is certainly not going to severely hamper the rapid progress of synthetic flavor and fragrance chemistry, if the correct strategy for the discovery and the marketing of new aroma chemicals is followed. What do we mean by this?

As an example, Firmenich was, and still is, very close to natural products when doing chemistry. Many of our aroma chemicals were found by analyzing essential oils and plant materials. Since they are produced now on an industrial scale by using organic synthesis, they are called nature-identical, as opposed to artificial.

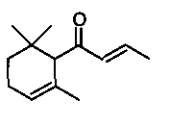
By analyzing natural materials for organoleptically new structures, we found numerous interesting so-called lead structures that serve as models for structure-activity work, helped by empirical rules and assisted by computers.

New aroma chemicals originating from such an approach possess structures close to natural products and, therefore, are likely to be as easily biodegraded as their natural prototypes. For some typical examples, see Figure 2.

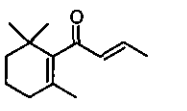
In many cases (Figure 3), such analogs were later also identified by analysis as constituents of natural materials, thanks to the prior introduction of their mass spectra into various in-house and outside MS libraries.

Among our new aroma chemicals whose structures are close to natural materials, we have some which perform well in application and are environmentally safe and aesthetically appealing. With these Firmenich can look to the future with confidence. We are strong in flowery notes and hope to become strong in new musk replacements.

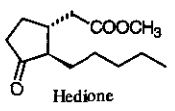
The same optimism will apply to producers of essential



α-Damascone



β-Damascone



Hedione

Natural occurrence

Black tea [9], tobacco [10], sugar cane [11]

Black tea [9], soybean [12], papaya [13], rum [14], spinach [15]

Black tea [9]

Figure 3. Aroma chemicals which were found in nature after their discovery by synthesis

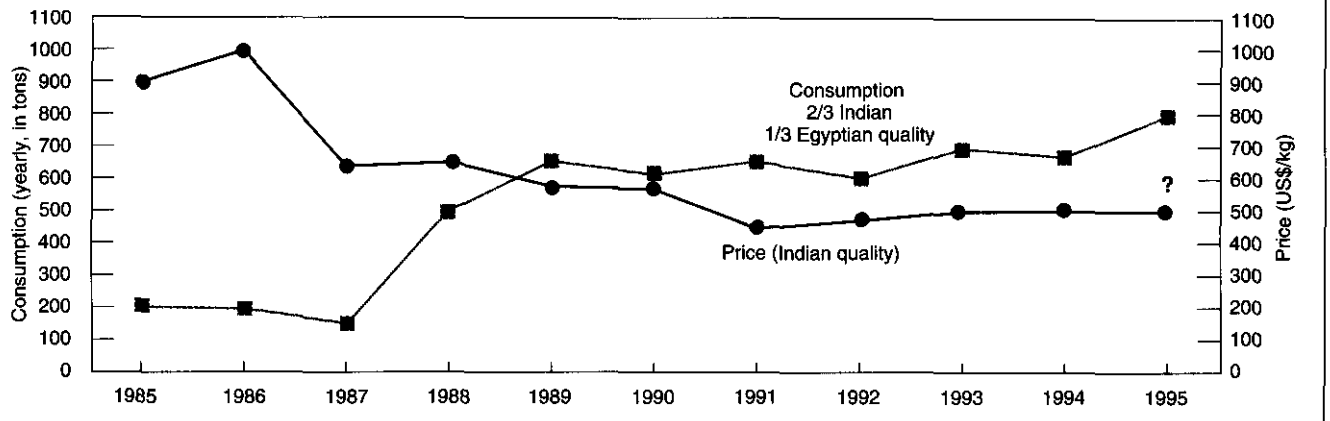


Figure 4. Jasmine concrete: Evolution of price and consumption (by Firmenich SA)

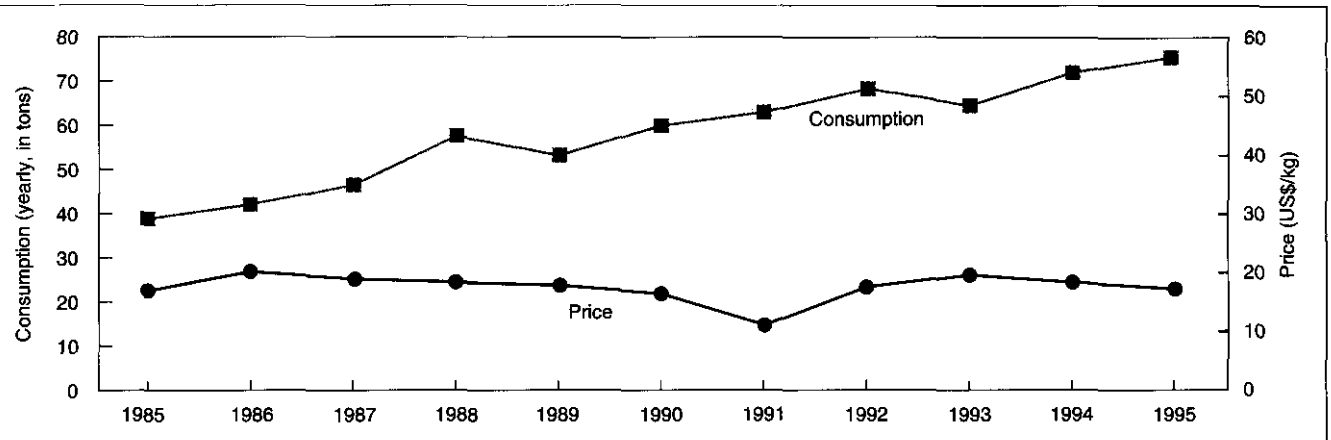


Figure 5. Indonesian patchouli oil: Evolution of price and consumption (by Firmenich SA)

oils established in countries that are politically and economically reasonably stable, as long as their quality, price, supply and service respond to the market evolution.

For instance, at Firmenich, over the last ten years, we have experienced dramatic increases in our consumption of some essential oils whose quality, price and availability have been reasonably stable or have improved, following the evolution of our customers' market:

- Lower prices followed by a remarkable stability due to the very wise commercial policy of the Indian producers have encouraged our perfumers to use four to five times more jasmin concrete (Figure 4).
- Very stable prices at a rather low level coupled with excellent availability and improved quality have led to our doubling our consumption of patchouli oil (Figure 5).
- A clearer product description (incorporating a statement about the possible addition of synthetic chemicals) for consumers and stable prices over the last ten years have tripled our consumption of lavandin *Grosso* (Figure 6).
- A dramatic reduction in the price of rose oil by the Turkish producers may not have pleased the growers of the rose flowers, but it has enabled our perfumers to again use rose oil in new fine-fragrance creations. Our consumption has more than doubled and will soon be three times what it was ten years ago (*Figure* 7).

Here we should mention that the 1995 Turkish crop, with its limited amount of flowers, was a very difficult one for the growers and distillers. The price of about US$2,500 that is shown with a question mark in Figure 7 was a kind of wishful thinking of the end-users before the harvest. Prices of rose oil finally reached the region of US$4,000 per kg, and we now just hope that our consumption curve won't follow a reverse trend.

All these important consumption increases would not have occurred without a new concept of partnership between producers and customers. This partnership has enabled an exchange of valuable information and an understanding of each partner's problems and constraints, and it has led to problem solutions in the best interest of both partners.

Conclusions

Paramount will be an open-minded R&D strategy trying to understand the flavor and fragrance industry as an inte-

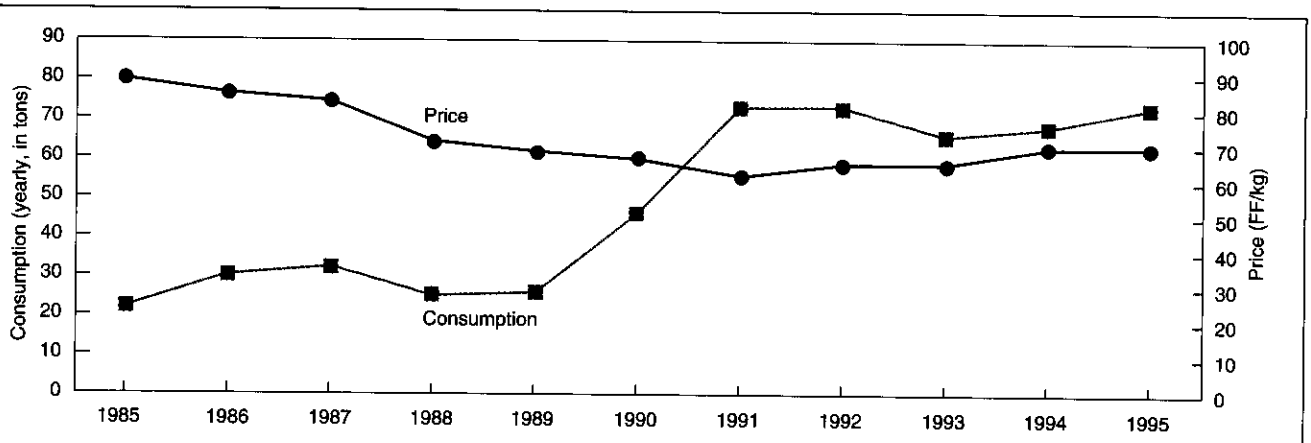


Figure 6. Lavandin *Grosso*: Evolution of price and consumption (by Firmenich SA)

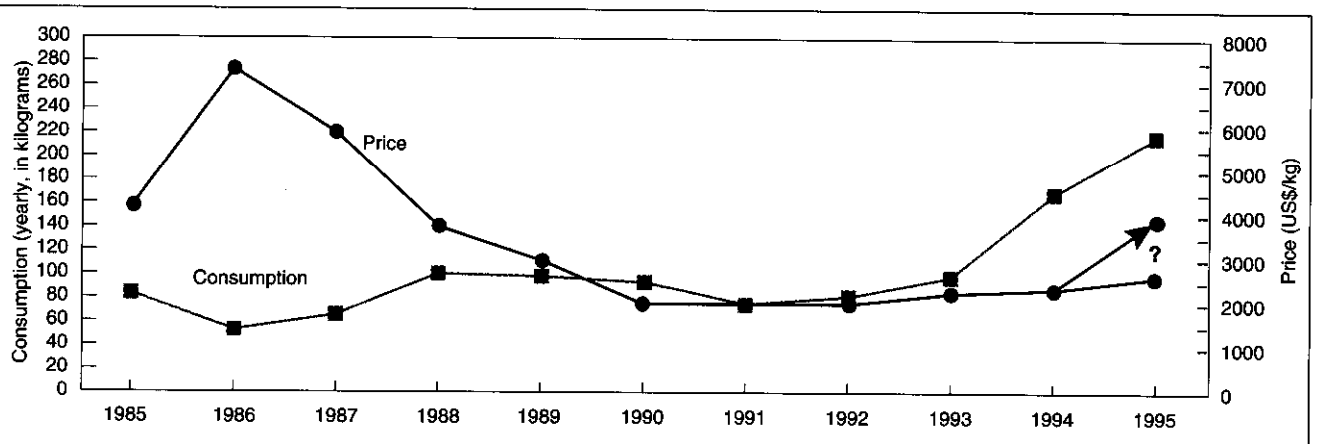


Figure 7. Turkish rose oil: Evolution of price and consumption (by Firmenich SA)

grated part of a much larger business. Social, economic, political, environmental, geographical and scientific-technical aspects will all become equally important to the long-term success of our business. The underlying science and technology of our industry is in a revolution; it becomes more complex. It will be more important to increase our focus and to perfume or flavor future products adequately and at competitive cost. Future raw materials will have to comply with the *performance standards* of modern life, but also be compatible with the *biological frame* of users and their environment. For designing new, successful raw materials, nature will have a more important role to play than in the past.

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