Natural Synthetics

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Many of you must have wondered what this title implies as it is in itself a contradiction. Certainly there can be many interpretations.

Perfumes were made from purely natural ingredients until the introduction of synthetic perfumery materials such as benzyl acetate, coumarin, phenyl ethyl alcohol, terpineol, ionone, etc., in the later 1800s and early 1900s. For the last 80 years, the perfumer has had at his or her disposal a range of materials of both natural and synthetic origin, that can be classified as follows:

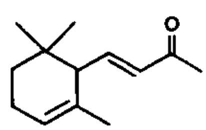
A. Natural perfumery oils, absolutes, etc.
B. Materials obtained by separation from the natural oils, etc. Examples: Eugenol, terpeneless oils, Rhodinol, etc.
C. Materials derived from natural oils, etc. but which are produced by a simple chemical change. Examples: Eugenol to Iso Eugenol and Cedrene to Acetyl Cedrene.
D. Materials, naturally existing or not, and produced from natural source by a complex process. Example: Geraniol ex Pinene.
E. Materials not existing naturally and made from a synthetic source. Examples: Musk Ketone, Mayol.
F. Materials occurring naturally and made from a synthetic source. Examples: Linalol ex Acetylene, Damascones.

The use of materials in groups A and B has progressively diminished over the years and this tendency also applies to group C.

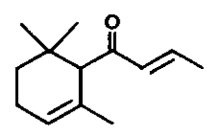
To meet the growing demands for perfumed products by the consumer, we have seen already for many years the increase in use of perfume raw materials from groups E and F; that is, from synthetic sources.

Research and development in the companies in our industry continuously not only seek new fragrance materials, but also new and better processes for making materials as classified by groups E and F.

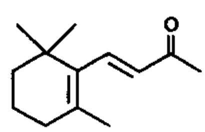
Let us look at some old and recent history (see fig. 1). We see here the similarity of the structures of the ionones and the rose ketones. The discovery of the rose ketones by Demole et al.[1] came seventy years after the publication of the ionone



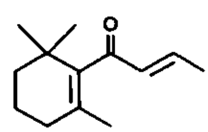
α-Ionone
1898



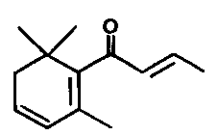
α-Damascone
1968



β-Ionone
1898



β-Damascone
1968



β-Damascenone
1968

Figure 1

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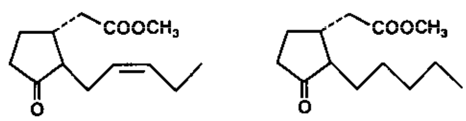
structures. Interestingly the rose ketones were discovered in nature and not, as one might believe, from "transplant surgery."

Methyl jasmonate was first found in jasmin absolute by Demole et al.[2] in 1957, but because of the presence of a double bond in the side chain, no commercial method of production could be found at that time. So Hedione was born (see fig. 2). The dihydro material was easier to produce and so became commerically available in the early 1970s. As perfumers, we were therefore able to use Hedione for ten years before the equally beautiful, although different, methyl jasmonate became commercially available.



Methyl Jasmonate	Hedione
First discovered 1957	Patent 1960
First commercial syntheses 1978	
Commercially available 1980	1970

Figure 2

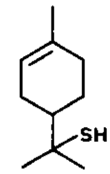
All these materials we have examined are coming from group F, although Hedione for many years was classified in the E group. And as we all know, Hedione was the most important new fragrance material in the 1970s. Will the damascones be the equivalents for the 1980s?

The sources of inspiration for the research chemist for new fragrance materials (NFM) have not greatly changed over the years and still remain:

- Natural perfumery materials
- Creative synthetic chemistry

However, the understanding that certain elements of a structure are key has led to chemists carrying out transplant surgery.

The reconstitution of natural products has reached a level of complexity, where to go beyond brings uneconomical results. However, natural materials have not yet yielded their all. It is true that the interesting materials now being found are often extremely potent. The menth-1-en-8-thiol (see fig. 3) found in grapefruit has a threshold value of 1 in 10 trillion, i.e., 1 in 10^{13}.[3]



Menth-1-en-8-thiol

1 in 10^{13}

1982

Figure 3

This is, to our knowledge, the lowest threshold reported to date for an aroma chemical.

What is it that interesting new fragrance materials have in common? In January 1977, I defined the word SHAPE.* In 1960s, the 1970s, and even more so in the 1980s, research chemists together with perfumers have sought beautiful shapes. In a chemist's terms, this may imply the molecular shape, but to a perfumer

Shape is	Ability to diffuse	
	Tenacity	
	Substantivity	= Performance in use
	Stability	with a useful odour

If perfumery materials are classified into Building Block ingredients and Modifiers, we can also divide materials into those of (a) short tenacity, up to 6 hours, (b) medium tenacity, 6-48 hours, and (c) long tenacity, 48 hours and over. We seek NFM that are either Building Blocks or Modifiers, that have good ability to diffuse, have good stability, and wherever possible possess secondary effects such as substantivity or performance in a wide range of product applications.

The introduction of NFM has perhaps slowed down since the 1960s. This does not mean that new structures cannot be easily found. It is the cost of commercialization that has grown and so limited the numbers. The important elements of pollution control and safety control have ensured that each new material needs to be a winner. We have seen that the evolution of methods of evaluation of potential new materials have become indispensable in order to determine which materials have the right SHAPE.

If we compare the perfumery industry of today

*"What influence do new fragrance materials have in perfumery?" presented to the British Society of Perfumers and published in August/September 1977 **Perfumer & FLavorist, 2**(4), 1, 1977.

with that of 1971, we see many important changes. Among these is that the cost of a fragrance has not increased over the years with inflation as has a motor car. Approximate calculations show that while the cost of a fragrance for many commodity products has not increased, during the same period the cost of a car has increased about three times. We can draw two possible conclusions from this:

- The quality of the perfume in a consumer product has lowered.

- The perfumer and the perfumery industry have become more efficient.

I believe that the main contribution to this is efficiency. Certainly the production of chemicals has become more efficient and the use of materials in groups A and B has decreased, but also perfumers have clearly become more creative in their work. The pressure that perfumers have been subjected to in order to create better and yet cheaper fragrances has resulted in:

- Demands that the performance of all perfumery raw materials in application is fully evaluated.

- Formulae can no longer contain ingredients that do not contribute to the character and performance of the perfume.

- New creations using new high performance materials (excellent SHAPE) have given greater cost effectiveness than ever before.

These demands have meant that the creative skills of a perfumer are being more and more exploited.

So what do the 1980s have in store for us? My message is one of optimism.

- A continued supply of new high performance fragrance materials of excellent SHAPE such as Damascones. Quality not quantity.

  Just as our clients in the consumer goods industry do market tests on their new products, so we need to make "market tests" on our new chemicals by thorough evaluation and internal use.

- The use of specialties will continue to grow with the discovery of more potent chemicals, difficult to use alone.

  Computers are able to give us safety data for any number of clients' needs, and this information is available to our customers.

- The creative talents of perfumers will be further exploited by the demands of greater performance together with acceptable originality. The use of high performance materials will continue to exert a creative challenge.

- New materials with secondary effects, e.g., substantivity, deodorancy, etc., will be available.

- A continued decline in the use of natural materials as a source of chemical production. The cedarwood derivatives are already becoming less attractive, and so woody chemicals not dependent upon natural source, but with excellent SHAPE, will change the perfumers' creative designs.

- The effectiveness of a perfumer has been greatly increased by the introduction of computers, and this is only beginning. The 1960s saw the G.L.C. developments; and the 1980s belong to the computer.

  As with the G.L.C., the computer will complement the work of the perfumer. The writing of formulae by hand or with a typewriter is fading out. Odour descriptions, prices, safety data, stability and performance data, etc., are now at the perfumer's fingertips and only as far away as the computer screen.

In conclusion, synthetics will continue to dominate the creative ideas of perfumers. These synthetics may come from the classifications:

D. Large volume natural source materials such as turpentine or limonene
E. Synthetic chemicals which may have some partial structural relationship to natural existing materials
F. The natural synthetics such as the rose ketones

Whichever the group, NFM have to possess the right SHAPE linked with "value for money."

References

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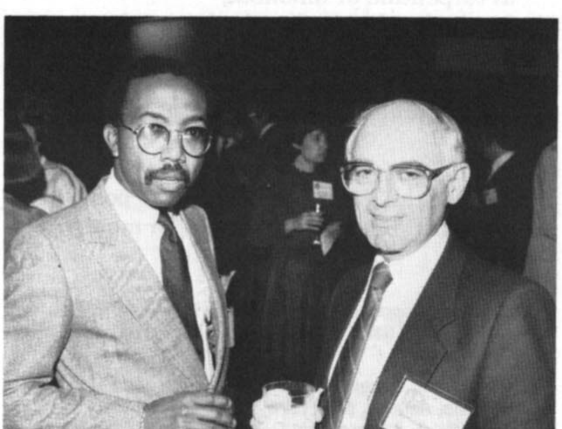
1. E. Demole, P. Enggist, U. Sauberli, M. Stoll and E. sz. Kovats, Helv. Chim. Acta **53**, 541 (1970)
2. E. Demole, E. Lederer and D. Mercier, Helv. Chim, Acta **45**, 675 (1962)
3. European Pat. Appl. No. 54847 (priority December 23, 1980) Firmenich SA

IPC "Staff" Stan Allured and Janet Ludwig (both of Perfumer & Flavorist).

Marco Jerolimic and Albert Wolkowiski (both of Dragoco).

Bruno Streschnak (Henkel KGaA) with Dr. Erich Klein (Dragoco GmbH) and Jim Rogers (Fritzsche D&O).



Hugh Spencer (Florasynth) with James Grossman (Makhteshim-Agan).

Webster Hudgins (Allied Corporation) with Lou Schmitt (Givaudan) and Henri Hoffmann.