New Aroma Chemicals: The Rosy Future

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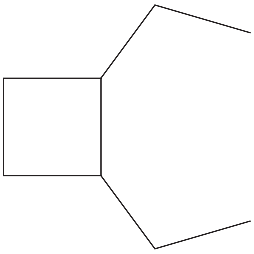
The odor of roses is deeply ingrained in the consciousness of modern man. From its origins in ancient Persia, this species has spread to all corners of the world, cultivated for one purpose alone: to satisfy man's desire for beauty, both visual and fragrant. Even though roses have been extensively studied, chemists and perfumers continue to search, both in nature and in the laboratory, for new rose notes that may contribute greater substantivity, better performance or an original odor impression. This paper will review recent developments in the study of roses and rose perfumery.

Back to Nature

Of all odor descriptors, "rose" is perhaps the most readily recognizable to the layperson. However, it is generally recognized that this descriptor is very general, considering the wide variations in the odor of rose hybrids. Any gardener can readily learn to distinguish between the fragrances of different hybrids, a remarkable fact considering the narrow genetic base from which modern garden roses are derived. Of the approximately 150 known wild species, only seven contributed to the genetic makeup of the modern garden rose, and six of those belong to the same closely related genetic clade.[1,2]

Although the various species of roses and their fragrance constituents are well documented, chemists continue to find new chemicals in this diverse family. An example of this is the curious discovery of 1,2-diethylcyclobutane (Figure 1) as the main component in the oil of *Rosa webbiana*, a wild rose from Karakoram.[3]

Figure 1. 1, 2-Diethylcyclobutane



It remains to be seen whether this unusual material will become a commercial fragrance item, but its unexpected appearance does reflect the fact that much remains to be discovered in the field of natural products.

For biochemists, the past few years have seen exciting developments in the understanding of the mechanisms by which fragrances are generated in the living plant. It was known from the 1960s that the terpenic alcohols are attached to sugar molecules within the plant, forming water-soluble glycosides that can conveniently be transported by the plant's vascular system. These glycosides, which are themselves odorless and tasteless, are the fragrance precursors released from the flower by the action of a glucosidase enzyme. A team at POLA Corp. have isolated the geraniol and citronellyl glycosides from *Rosa damascena*.[4,5] The glycoside precursors to β-damascenone and rose oxide have been isolated at the Universities of Erlangen-Nurnberg and Shizuoka, respectively.[6,7] A review of this topic has shown that the discoveries in this field have important implications for both flavor and fragrance systems.[8]

A recent study showed that the emission of fragrance from a hybrid rose followed a circadian pattern; that is, the output of fragrance rose and fell rhythmically throughout a 24-27 h period, independent of the day/night cycle.[9] This is believed to be the first demonstration of such a pattern in terpenoid emissions from a flower whose petals do not open and close. The subject of the study was the rose variety, Honesty, a large white hybrid tea rose that has an intense rosy-lemon fragrance, probably due to an unusually high level of geranial and neral in the headspace.[10]

Perhaps the most remarkable experiment in this area was a study of the effect of microgravity on aroma emission from miniature roses conducted aboard the NASA Space Shuttle Discovery.[37] The results of this study were used by IFF in the formulation of Shiseido's Zen fragrance.

Working with Nature: Synthetic Rose Oxides

As a general rule, the fragrance consumer is likely to characterize almost any floral fragrance as "rosy", and, indeed, this is not unreasonable, since the principal components of rose odor—usually phenyl ethyl alcohol, citronellol, geraniol and their acetates—are also found in many other

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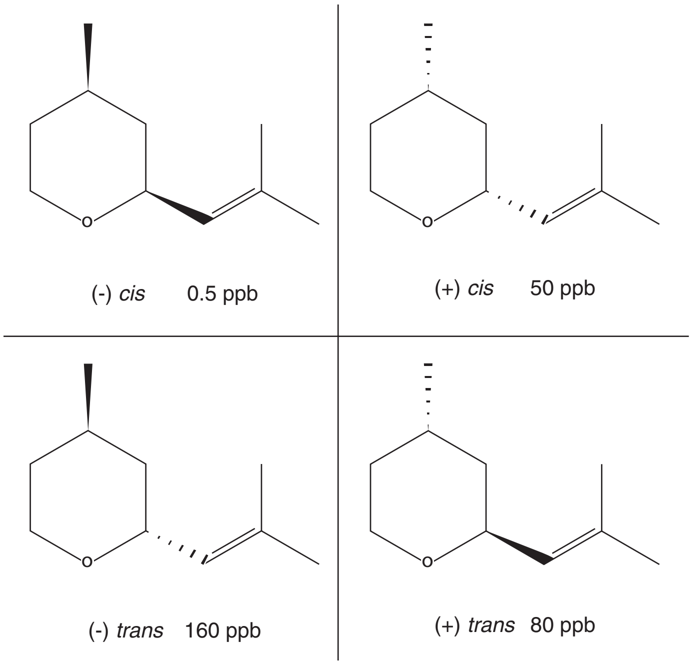
Figure 2. Rose oxide isomers and their odor threshold values[15]



(-) *cis* 0.5 ppb

(+) *cis* 50 ppb

(-) *trans* 160 ppb

(+) *trans* 80 ppb

floral species. As the sophistication of analytical instruments improved over time, chemists began to look more deeply into the minor components of rose oils to find new materials which, although present in low concentration, contribute mightily to the overall impression. Rose oxide was discovered by Firmenich in Bulgarian rose oil in 1959, and has subsequently become a key fragrance tool.[11] The (-) *cis* isomer shown in Figure 2 is the predominant form in nature.

Several synthetic routes are known, generally using citronellol as starting material. Recent developments in this area include a photochemical process for the initial oxidation step, and an improved cyclization step that enhances the level of the desirable *cis* isomers.[12,13] A new process takes the cyclization in the other direction, using proprietary phosphine-palladium catalysts to enhance the level of *trans* isomers.[14] The *trans* isomers are generally recognized as having a green-herbal character in the direction of geranium, as opposed to the more powerful green-rosy *cis* isomers, which have the sweet fruitiness typical of rose oil.[15]

Rose oxide is one of many oxidized terpenoids found in rose oil. A related compound is rose furan, pictured in Figure 3, which contributes a

Figure 3. Rose furan

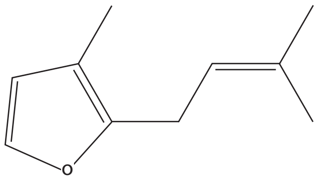


Figure 4. β-Damascenone

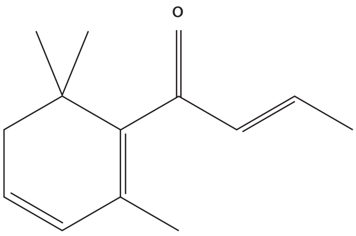


Figure 5. β-Damascone

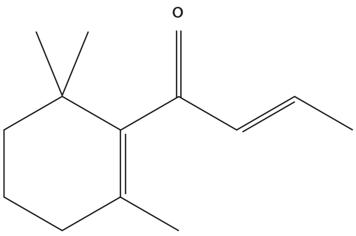
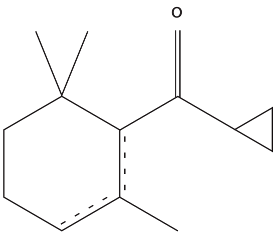


Figure 6. Damascone Analogue



green citrusy note to the rose impression. A new synthesis uses Grignard chemistry to obrain the pure product in high yield.

Improving on Nature 1: a Damascone Homologue

A major breakthrough for rose perfumery was Firmenich's discovery in 1970 of the so-called rose ketones, β-damascenone (Figure 4) and β-damascone (Figure 5).[17]

Synthetic versions of these ketones were developed in order to add greater complexity and naturalness to rose compositions, but they are now widely used in fragrance compositions of all types. The analogues ketone mixture (Figure 6), recently patented by IFF, represents a new variation on this structural theme.[18]

The odor is described as "rose, sweet, woody, tobacco, dried fig, with floral undertones." The replacement of an olefin in the side chain by a cyclopropylgroup is expected to confer greater stability, and less potential for photosensitization, often associated with conjugated systems.

Improving on Nature 2: Phenylalkanols

It has been observed that the replacement of an isobutenyl group in a terpenoid alcohol with a phenyl group appears to maintain the original odor character, while adding greater depth and substantivity.[19] Thus, the alcohol, known variously as phenyl hexanol, Phenoxanol or Mefrosol and depicted in Figure 7 as "b", can be viewed as a synthetic counterpart to citronellol ("a").

Improvements to the synthesis of "b" continue to appear in the patent literature.[20] The structure of "b" may be altered further to obtain novel and interesting effects, while maintaining the fundamental rosy character, as demonstrated in Rosaphen and a variety of more recently discovered chemicals with related structures (Figure 8).

Improving on Synthetics: New Rose Chemicals

Although the natural components of rose oils are well known and widely used, perfumers continue to find it necessary to use synthetics in many situations. The synthetic rose chemical, known variously as Rosone, Rose Crystals and Rosacetol (among others) and depicted in Figure 9, has long been a perfumery standard, prized for its mild green-rosy note and fixative properties.

Although this material has been known and used since the 1800s, there is a general trend away from the use of chlori-

Figure 7. Citronellol (a) and phenyl hexanol (b)

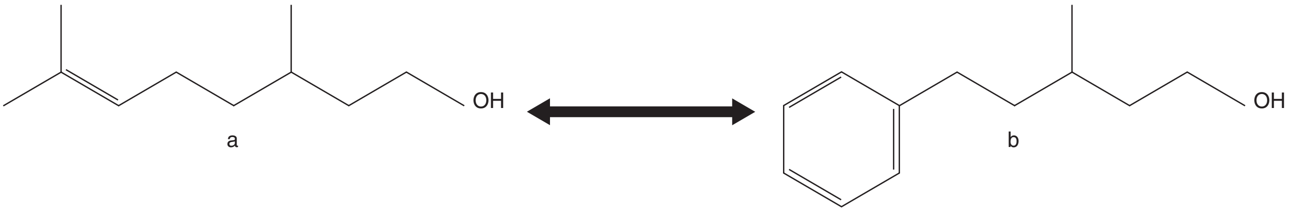


Figure 8. Structural variants of phenyl hexanol (all rosy floral with descriptors shown)

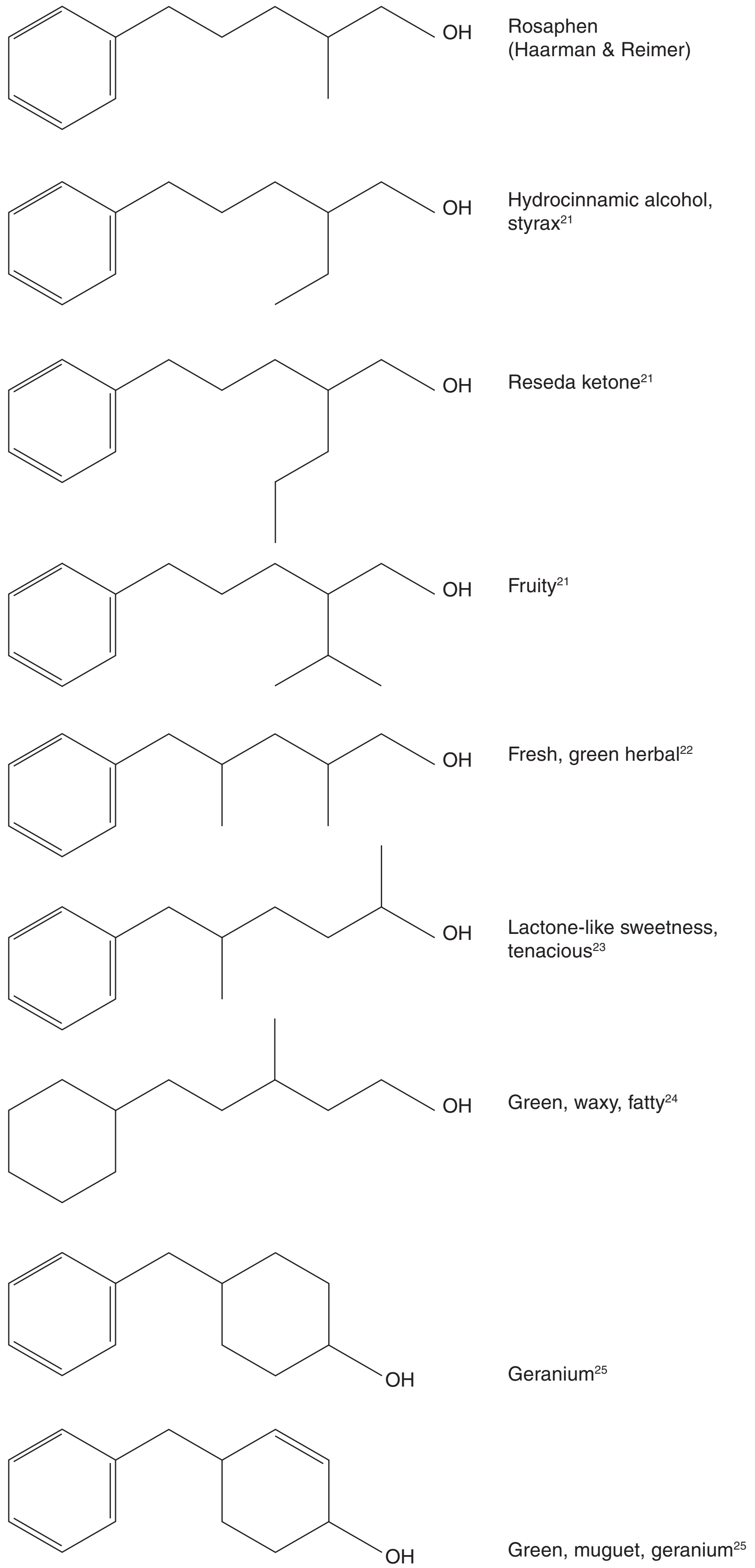


Figure 9.
Synthetic rose chemical

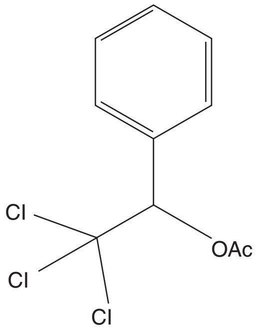
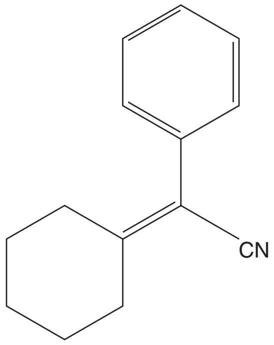


Figure 10.
Peonile



nated materials in perfumery. An alternative is now offered in the form of a new nitrile (Figure 10) described as having a "geranium-rosy" character. It is available to perfumers under the trade name Peonile. However, manufacturers of the synthetic rose chemical depicted in Figure 9 need not despair: this material has found a new use as a key component of thermally responsive imaging materials.[27]

A series of substituted cyclohexanones provides an instructive demonstration of the variation of odor type with molecular structure.[28] The series shown in Figure 11 gives the assigned odor descriptors.

As the side chain is lengthened, the fresh impression changes from rosy to aldehydic to fatty, whereas the dryout changes from green to marine-ozone.

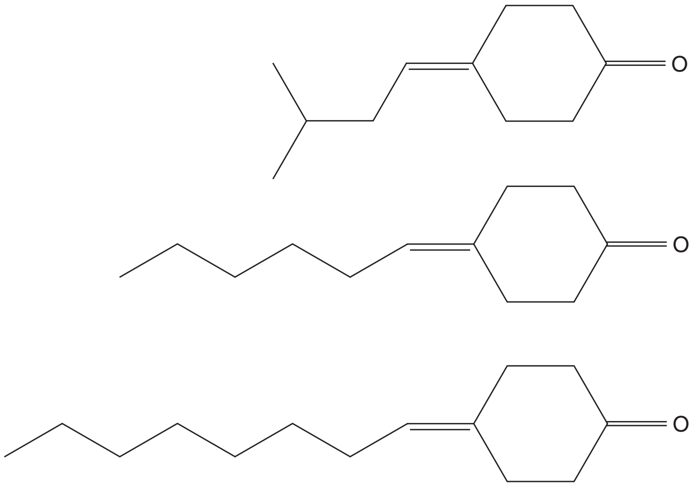
A material that has been familiar to perfumers for some time is 2-methyl-3-phenyl-1-propanol (Figure 12 "d"). It has a rosy odor, but has never been used to any great degree in perfumery. This alcohol is the starting point for two new chemicals with distinctive odors.

BBA hydrogenated the aromatic ring in "d" to give the saturated alcohol ("c"), which may be described as "green, fruity, rosy."[29] Taking a different tack, Firmenich converted "d" to the corresponding methyl ether ("e"), which has a "natural rosy note of the rose leaf type."[30]

Adding a Little Extra

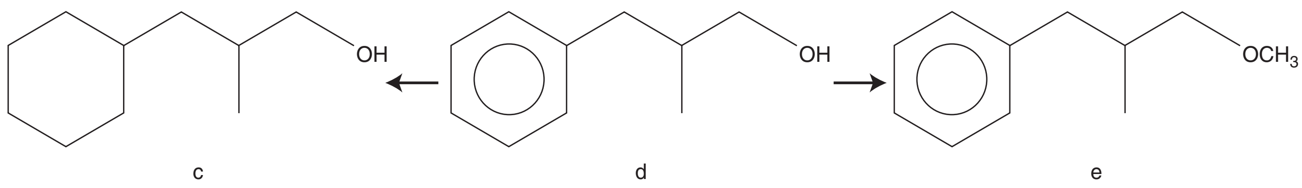
It is relatively easy to create a rose accord, given the wide range of choices now available to perfumers. The hard part is to create something which stands out from the crowd, yet remains true to the concept of rose. The desired attribute is often called "naturalness", meaning the introduction of contrasting notes, with perhaps a little roughness, carefully adjusted so as not to disturb the harmony of the whole composition. Thus, perfumers often seek to incorporate materials that do not themselves smell rosy, but which contribute a unique impression to a rose fragrance. Following this lead, chemists seeking to patent a new chemical will frequently team up with a perfumer to demonstrate the usefulness of a new item in a rose base.

Figure 11. Odor varation in a series of 4-alkylidenecyclohexanones



Fresh:	Dry:
Rose, aldehydic, green, fruity	Green, herbal, aldehydic, fruity
Aldehydic, rose, fatty, marine	Marine, aldehydic, floral, rose
Fatty, aldehydic, marine	Marine, ozone, aldehydic, nitrile

Figure 12. Saturated alcohol (c), 2-methyl-3-phenyl-1-propanal (d) and methyl ether e)



An example of this is a chemical depicted in Figure 13, which is structurally related to γ-ionone (Figure 14), but which has a completely different odor.[31]

γ-Ionone has a resinous violet odor; in contrast, the chemical depicted in Figure 13 has a tenacious green herbal, pine needle-like fragrance, which is used to add a natural impression to a rose accord.

Similarly, the compound in Figure 15, which is structurally related to the violet-odored α-ionone (Figure 16), has a floral-fruity character that shows to good effect in a rose perfume.[32]

The sesquiterpene alcohol, hedycaryol (Figure 17), is widely distributed in nature, but has not yet become an article of commerce. However, some have shown its usefulness of this sweet-woody-odored material in rose compositions.[33]

The unusual cycloheptenol structure, depicted in Figure 18 as "g", has a "diffuse, cool, ozony" odor which is used to give fresh, natural character to a demonstration rose fragrance.[34]

The cycloheptenol is made from a captive raw material, *pseudo*-linalool (depicted in Figure 18 as "f"), a by-product of pyrolytic linalool processes.

Finally, nature herself provides a large number of minor components in rose fragrances, which may be used to enhance various aspects of an accord. A good example would be 3,5-dimethoxytoluene (Figure 19), which is present in many roses. The material contributes a touch of warm, sweet, oakmoss character to the flowers. Interestingly, this non-terpenoid component did not show periodic fluctuation in the study of the Honesty rose referred to above, but remained fairly constant.

Two new process patents suggest a revival of interest in this material.[35,36] So it is possible that nature, having had the first word on the subject of rose, will also have the last.

Acknowledgements

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Figure 13. γ-Ionone-related chemical

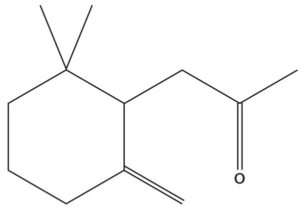


Figure 14. γ-Ionone

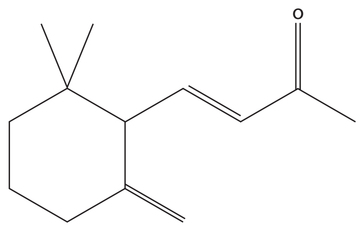


Figure 15. α-Ionone-related compound

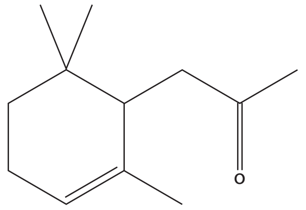


Figure 16. α-Ionone

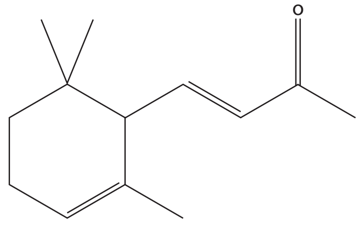
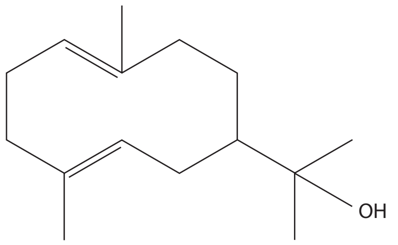


Figure 17. Hedycaryol



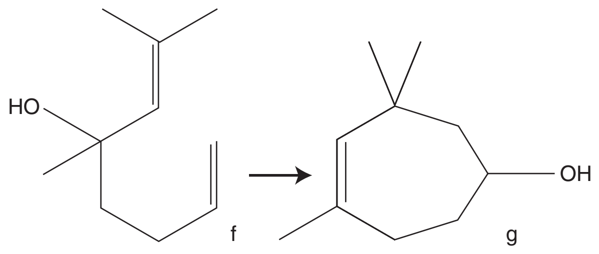


Figure 18. Pseudo-linalool (f) and cycloheptenol

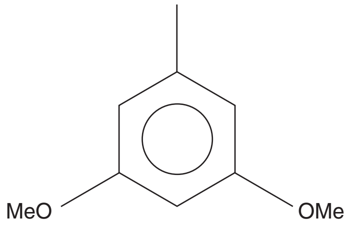


Figure 19. 3,5-Dimethoxytoluene

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