

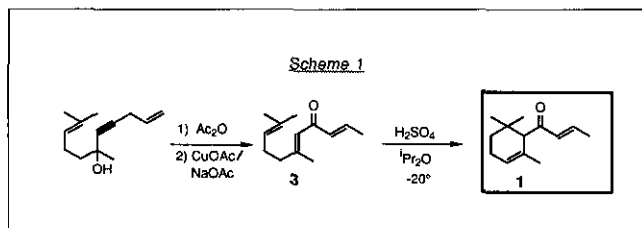
Dynascone: The Ultimate Captive¹

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In 1972, one of the early technical syntheses of α -damascone [1]¹ (Scheme 1) gave a final product that, even after fraction distillation, was often refused by quality control. This problem initiated an in-depth analytical investigation in order to locate and to identify the chemical structures of the responsible trace impurities, and thus to provide the synthetic chemist with a clue on how the process could be improved.

An integral part of this analysis involved careful olfactive monitoring by gas chromatography-sniffing techniques and eventually revealed the presence of a trace constituent whose extremely powerful odor was reminiscent of galbanum (Figure 1).

In 1973, isolation and structure elucidation by NMR and MS showed this substance to be the hitherto unknown unsaturated ketone **2**, having the same molecular formula as α -damascone but possessing a different molecular structure; this ketone has been named α -Dynascone.



Allo-cyclization: The Way to α -Dynascone

At the time, it was quickly realized that the formation of this new compound could be explained by analogy with a

well-known process, discovered in 1950 by Schinz and Vodoz² during the acid-catalyzed treatment of "synthetic" (impure!) geranic acid, in which γ -geranic acid underwent allo-cyclization to allo-cyclogeranic acid (Scheme 2).

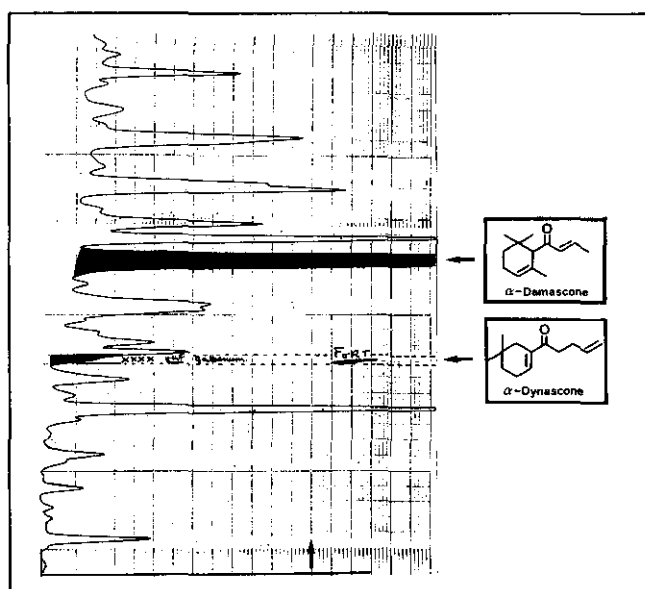
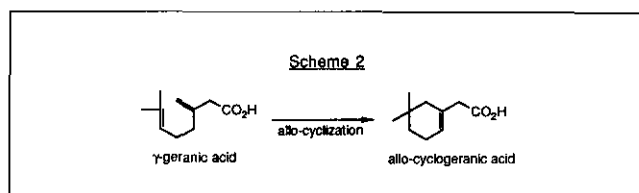


Figure 1. Gas chromatogram of a fraction of α -damascone (April 1973)

¹Dynascone, a registered tradename of Firmenich SA, contains ca. 70% α -Dynascone and is covered by various Firmenich patents: cf. US Patents 4147672/4264467.

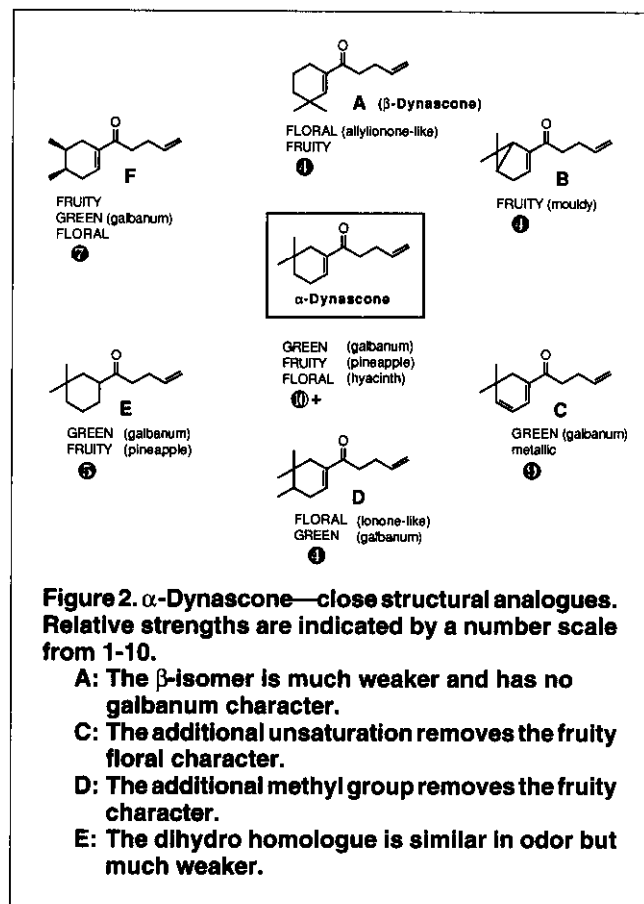
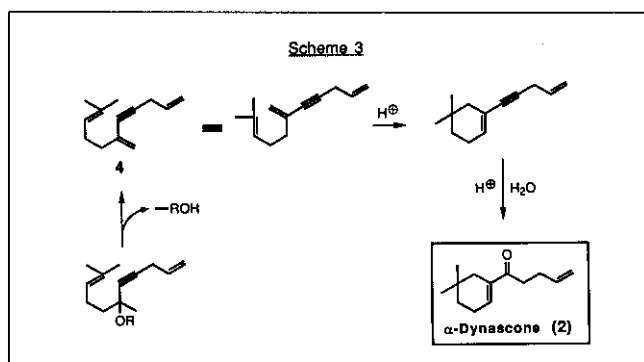


Figure 2. α -Dynascone—close structural analogues. Relative strengths are indicated by a number scale from 1-10.

- A:** The β -isomer is much weaker and has no galbanum character.
- C:** The additional unsaturation removes the fruity floral character.
- D:** The additional methyl group removes the fruity character.
- E:** The dihydro homologue is similar in odor but much weaker.

Accordingly, during acetylation and/or the subsequent *Saicy-Marbet* rearrangement³ to pseudo-damascone [3], the unsaturated hydrocarbon **4** must have been formed as an elimination by-product; allo-cyclization followed by acid-catalyzed hydration then afforded α -Dynascone (Scheme 3).



Confirmation of this explanation was soon provided by the first preparative access to α -Dynascone involving a directed synthesis of **4** and its subsequent acid-catalyzed rearrangement.⁴ A more specific, unambiguous route was developed later on by Snowden⁵ and Büchi,⁶ whose key step involved a double addition of a vinyl Grignard reagent to methyl ester **5** (Scheme 4).

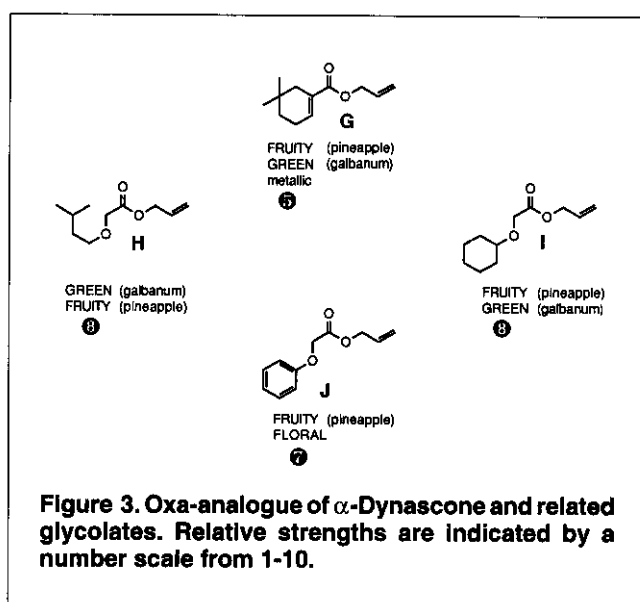
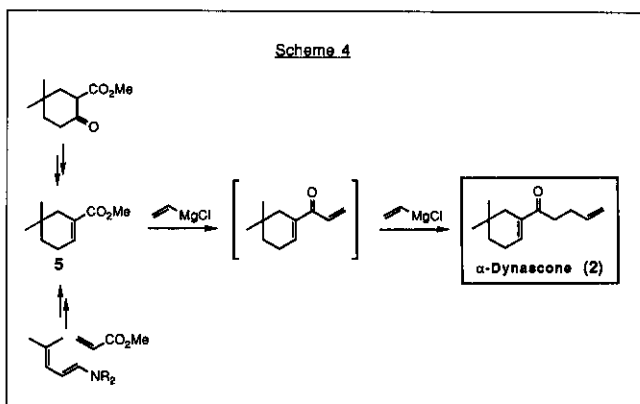


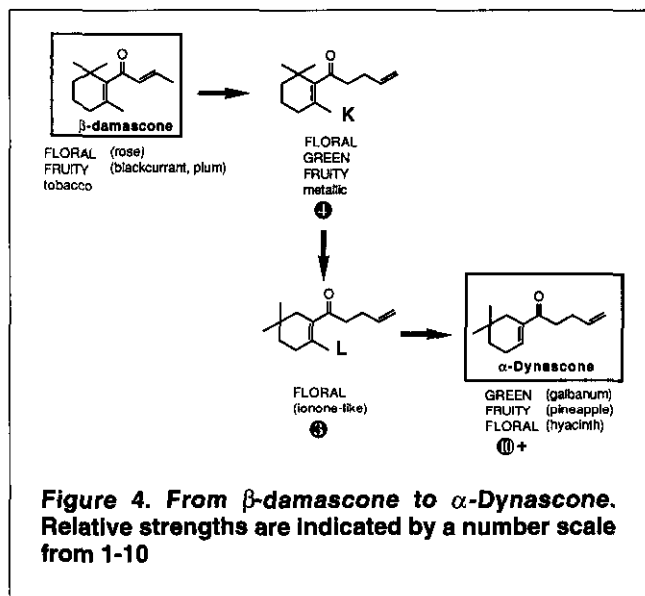
Figure 3. Oxa-analogue of α -Dynascone and related glycolates. Relative strengths are indicated by a number scale from 1-10.



Perfumery Use/Structure Activity Correlations

Dynascone has been the most important of all the captive chemicals available to Firmenich perfumers during the 1970s and 1980s. This is an exciting material that has outstanding effects and is a key element in many successful perfumes.

First found, as described above, in April 1973, its development was immediately given top priority, with the result that it was made available for internal use in July 1974. Because of its power, it was originally introduced as a 1% solution, and very quickly became one of the most frequently used chemicals in Firmenich. Its strength and unique character were rapidly exploited, not only in the form of the diluted chemical, but also by the application of two very unusual, but different, specialties. The wonderful green floral fruity harmony in a fantasy hyacinth direction was called "Jacintheme 135" created in October 1974 and released for general use in 1977. The galbanum character of Dynascone was captured in the very successful "Galbex 183" created in February 1975 and also released for general use in 1977.



A successful material needs an ideal SHAPE,^{7,8} and Dynascone possesses most of the requirements, such as:

outstanding diffusion	} performance in use
high tenacity in application	
moderate substantivity	
excellent stability	

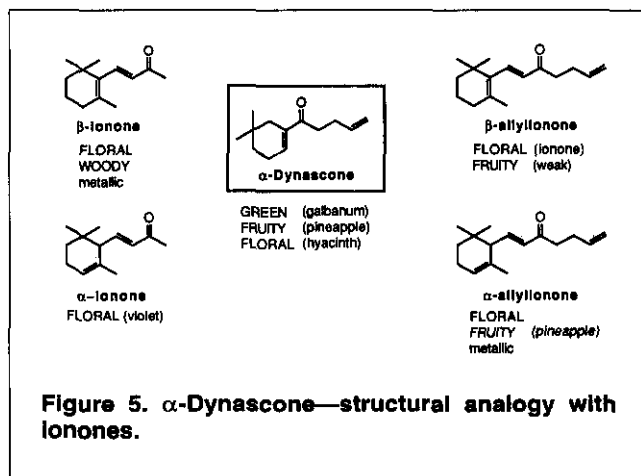
together with a unique odor useful in all product areas and a good performance/cost ratio.

Firmenich's research has synthesized many hundreds of substances that are structurally related to α -Dynascone and several of these substances are presented here to illustrate odor structure relationships (cf. Figures 2-4). The full odor description of α -Dynascone can be given as:

Odor Groups	—GREEN, FRUITY, FLORAL
Tonalities	—Galbanum, pineapple, hyacinth, ionone
Descriptors	—most important: metallic

The Firmenich presentation No. 16⁹ includes a description of Dynascone and shows a series of accords that demonstrates the different tonalities and outstanding performance of this creative material.

In Figure 4, the odor-structure relationships show that the glycolate sub-structure, with an oxygen atom replacing a methylene group, may be correlated with the Dynascone structure. In the mid 1970s glycolates **H** (allylamylglycolate) and the cyclohexyl analogue **I** (number of sources) became available. **J** is a long established material, but has no galbanum character. In general, glycolates are unstable in alkali, acid or oxidizing media, whereas Dynascone is stable.



In Figure 4, neither of these two damascone related substances (**K** and **L**) possesses the galbanum character; although the allyl sub-structure is present, neither has the pineapple fruitiness.

In Figure 5, the ionone character is only a minor part of the α -Dynascone odor, whereas it is a principal part of the β -Dynascone odor. The side-chain similarity of Dynascone and the allylionones may help to explain the pineapple note.

Conclusion

Our clients, the marketing companies, not only seek successful perfumes, but also unique ones. Although this ideal situation is not easy to achieve, these conditions can be satisfied by a perfumer using captive chemicals such as Dynascone, to create original perfumes that are difficult to copy. Dynascone, a fortuitous discovery intimately related to the history of α -damascone, thus fully justifies its tribute: "Firmenich's ultimate captive."

References

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