Malodor Formation in Alcoholic Perfumes Containing Vetiveryl Acetate and Vetiver Oil

By Edouard P. Demole, Günther W. Holzner and M. Joseph Youssefi,
Firmenich SA, Geneva, Switzerland

Vetiver oil by itself is already a perfume. It has a unique long-lasting sweet woody note with a fresh herbal top-note. The oil and its derivatives (mainly vetiveryl acetate and vetiverol) are among the most valuable and important raw materials used for compounding alcoholic perfumes such as extrait, eau de parfum, cologne and aftershave. In some creations, vetiver is the main ingredient and has even given its name to a famous men's cologne (Vetiver, by Carven, 1957).

Vetiver imparts pleasant, strong and long-lasting notes to the perfume compositions, and also acts as a natural fixative due to its heavy constituents. Vetiver blends particularly well with vanilla, sandalwood, patchouli and rose. Because of its odor strength, vetiver oil has to be used with some caution, as an overdose may result in a pronounced woody note.

Today, vetiver oil is mainly produced in Haiti and Java, but China also contributes to this market. The oil originating from Reunion Island, which was for a long time the most preferred quality, has now become less important. Prominent Haiti and Java vetiver qualities have different olfactive properties and, therefore, are used by professional perfumers as two distinct raw materials.

Chemistry of the Oil and its Acetate

It is a well-known phenomenon among perfumers that alcoholic perfumes containing a high concentration of vetiveryl acetate can develop a very unpleasant "acidic" and "oxidized" top-note upon aging. We wanted to investigate the cause of this malodor formation in commercial vetiveryl acetate. Laboratory experiments demonstrated that the same off-odor can be produced when alcoholic solutions of pure commercial vetiveryl acetate (from four manufacturers: Charabot, NIFI, Sanofi and Firmenich), without any other perfume ingredients added, were stored for some time or subjected to accelerated aging tests. Therefore, it was assumed that some of the components in vetiveryl acetate were responsible for this "acidic" off-odor formation.

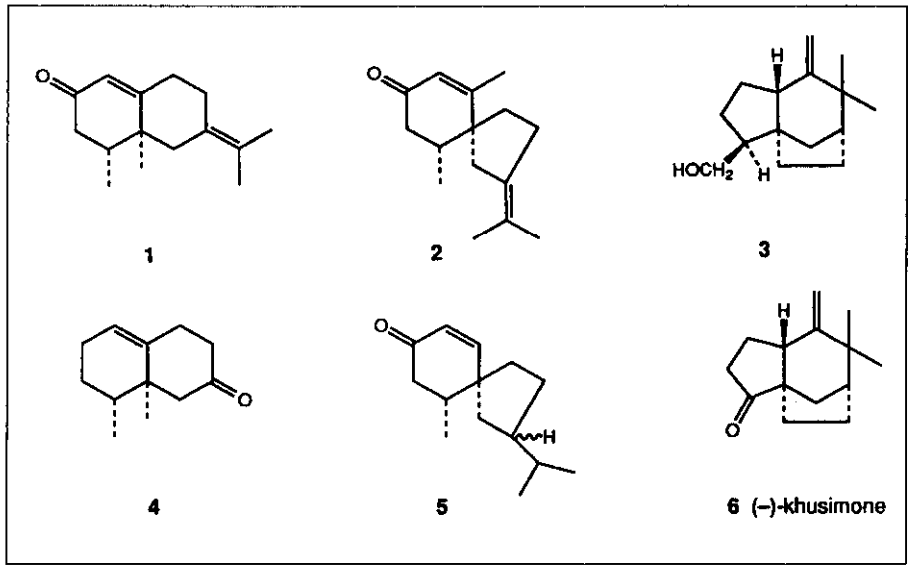
Vetiveryl acetate results from direct acetylation of crude vetiver oil with acetic anhydride. Excess acid is subsequently neutralized, and the product is subjected to a washing procedure to remove any acidic and hydrosoluble impurities. The process ends with a fractional distillation, a very important and decisive step for the production of good quality vetiveryl acetate.

The various qualities of vetiveryl acetate used in our industry are complex mixtures still containing 5-15% of sesquiterpene hydrocarbons, depending on how the final distillation is conducted. While this hydrocarbon fraction imparts a pleasant fresh top-note to vetiveryl acetate and enhances the genuine vetiver odor, it can also undergo prejudicial autoxidation reactions when exposed to unfavorable conditions in alcoholic solutions, as described below. The presence of polar solvents such as ethanol and water exacerbates chemical reactions in the perfume material, causing off-odor formation and color changes if the perfume is not correctly stabilized and packaged. Usual stabilization procedures involve addition of one or more of the following:

- UV-absorber, such as 0.05-0.10% of Uninul D-50^{R}.
- Antioxidants such as 0.05% BHT, or a synergistic mixture of BHT and γ-tocopherol (Tenox GT II).
- Chelating agents such as 0.1-0.2% lipophilic EDTA derivatives (see U.S. patent 4217250).
- Triethanolamine to neutralize the alcoholic perfume solution to pH 6.5-7.0.

Vetiver oil: Even today, one does not know exactly which constituents of this oil are responsible for the true vetiver fragrance.[1] This fact is far from surprising, however, if we consider that many vetiver components have low volatility, similar physical properties and complex molecular structures that make them difficult to investigate. Vetiver oil is commonly said to contain some 150 sesquiterpene-type compounds and derivatives thereof, belonging to 11

 0272-2666/95/0001-0035$04.00/0—© 1995 Allured Publishing Corp.



structural classes: bisabolane, elemane, cadinane, eudesmane, valencane, vetispirane, zizaane, prezizaane, cyclocopacamphane, cedrane and acorane.[2-5] Among the numerous compounds hitherto identified, the major representatives (+)-α-vetivone [**1**], (–)-β-vetivone [**2**] and khusimol [**3**] can be considered as the "fingerprint" of vetiver oil.[4]

Taken together, these three components can represent up to 35% in vetiver oil, but only the key compound [**2**] appears to bring a major contribution to the true vetiver fragrance.[6] Besides this, ten or so quantitatively minor, ketonic sesquiterpene metabolites such as those exemplified in [**4**],[2] [**5**][6] and [**6**][7] contribute to other parts of the whole odor picture of vetiver oil.[6]

Vetiveryl acetate: Obviously, the statement that our knowledge of the composition of vetiver oil is still incomplete also applies to its acetylation product. Vetiveryl acetate is a complex essential oil and produces more than 100 GC/MS peaks.[10] Typical total ion chromatograms of the oil and its corresponding acetate are shown in Figure 1 with the major peaks identified.

Analysis of Malodor Formation

In order to understand the cause of off-odor formation in alcoholic solutions of vetiveryl acetate, we needed to identify the culprit compounds. Samples of perfumes which were formulated with a relatively high concentration of vetiveryl acetate and had developed a very unpleasant acidic and oxidized off-odor upon aging were analyzed by GC/MS. For comparison purposes, we also analyzed some reference materials having the correct odor quality. The whole investigation involved the following samples:

- Aged perfume with strong off-odor (sample not stabilized, rejected by the perfumers).
- Relatively recent, acceptable sample having no objectionable off-odor.
- A freshly prepared perfume.

GC/MS (direct injection of the perfume samples): GC/MS analyses performed by direct, conventional injection of the above three samples resulted in similar chromatograms that did not allow identification of the organic compound(s) responsible for the off-odor. Obviously, the malodorous component(s) occurred at trace level (below 1 ppm) in the perfumes, and thus a preconcentration step was required to make them detectable.

GC/MS (headspace techniques): The sampling and GC/MS analysis of the vapor phase above a liquid provides a mild but powerful approach to the investigation of trace odorous compounds. Among the various headspace sampling procedures now available, the most commonly used is a "dynamic" one in which the purged volatiles are first trapped on a porous, lipophilic polymer such as Tenax. The volatiles are then thermally desorbed and directly transferred into a cooled trap connected to a GC/MS system.

The analysis of the above three perfume samples using this technique led (again) to similar chromatograms from which it was hardly possible to deduce the presence of any contaminating peaks. Serious problems associated with this technique appeared, due mostly to the high alcohol content (72%) of the perfume that seemed to prevent efficient adsorption of trace volatile compounds on the Tenax (washing-out effect). Moreover, there was also the possibility that the large ethanol peak eluting first on the chromatograms obscured the presence of minor volatile components.

Finally, we tried a modified, "static" headspace sampling procedure. A 10 g sample of the perfume to be analyzed was placed into a 50 ml septum-capped bottle. After keeping the bottle two hours at room temperature to ensure phase equilibration, the sampling was effected by means of a 10 ml gas-tight syringe fitted with a locking mechanism. A 2 ml sample of the gas phase was sucked into the syringe, then the lock was closed and the gas was compressed to the volume of 0.2 ml with the aid of the plunger. The compressed headspace sample was then injected into a cooled loop (–78°C) connected to a capillary column (60 m, Carbowax) and the GC analysis was performed as usual.

This technique worked quite well, enabling us to detect the presence of extremely volatile compounds appearing before the ethanol peak on the chromatograms of the aged and tainted perfume samples (Figure 2, a, b). Interestingly enough, the freshly prepared perfume samples contained practically no such volatile materials (Figure 2, c), whose major representatives were found by mass spectrometry to be butene (undetermined isomer) and 1,1-diethoxyethane.

Both these compounds have bad odors quite similar to the unpleasant top-note observed in the aged perfume

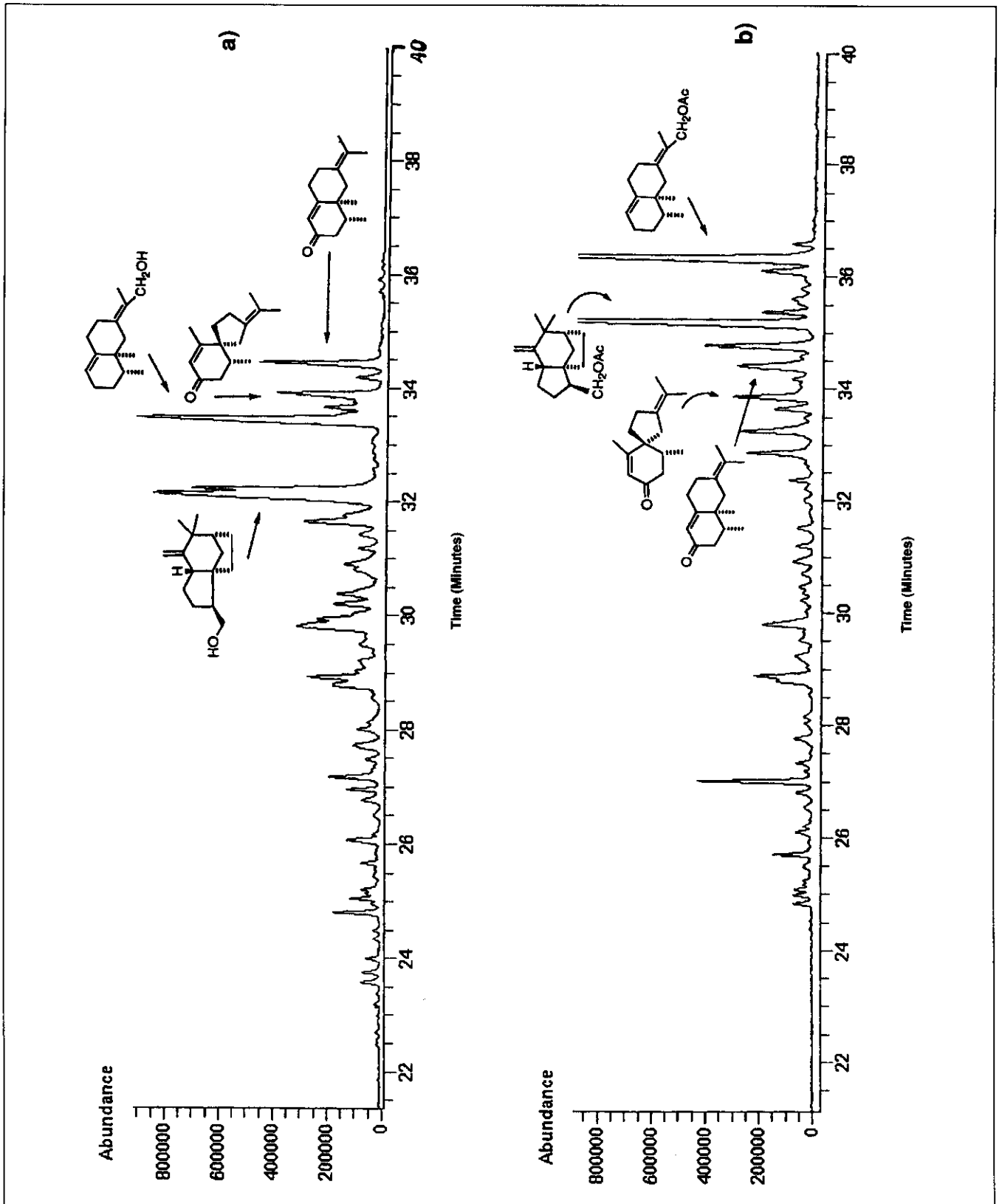


Figure 1. GC/MS total ion chromatograms of:
a) Haiti vetiver oil SPB 30 m, T_1 = 80°C for 10 min
b) Corresponding vetiveryl acetate T_2 = 230°C, rate = 4°C/min

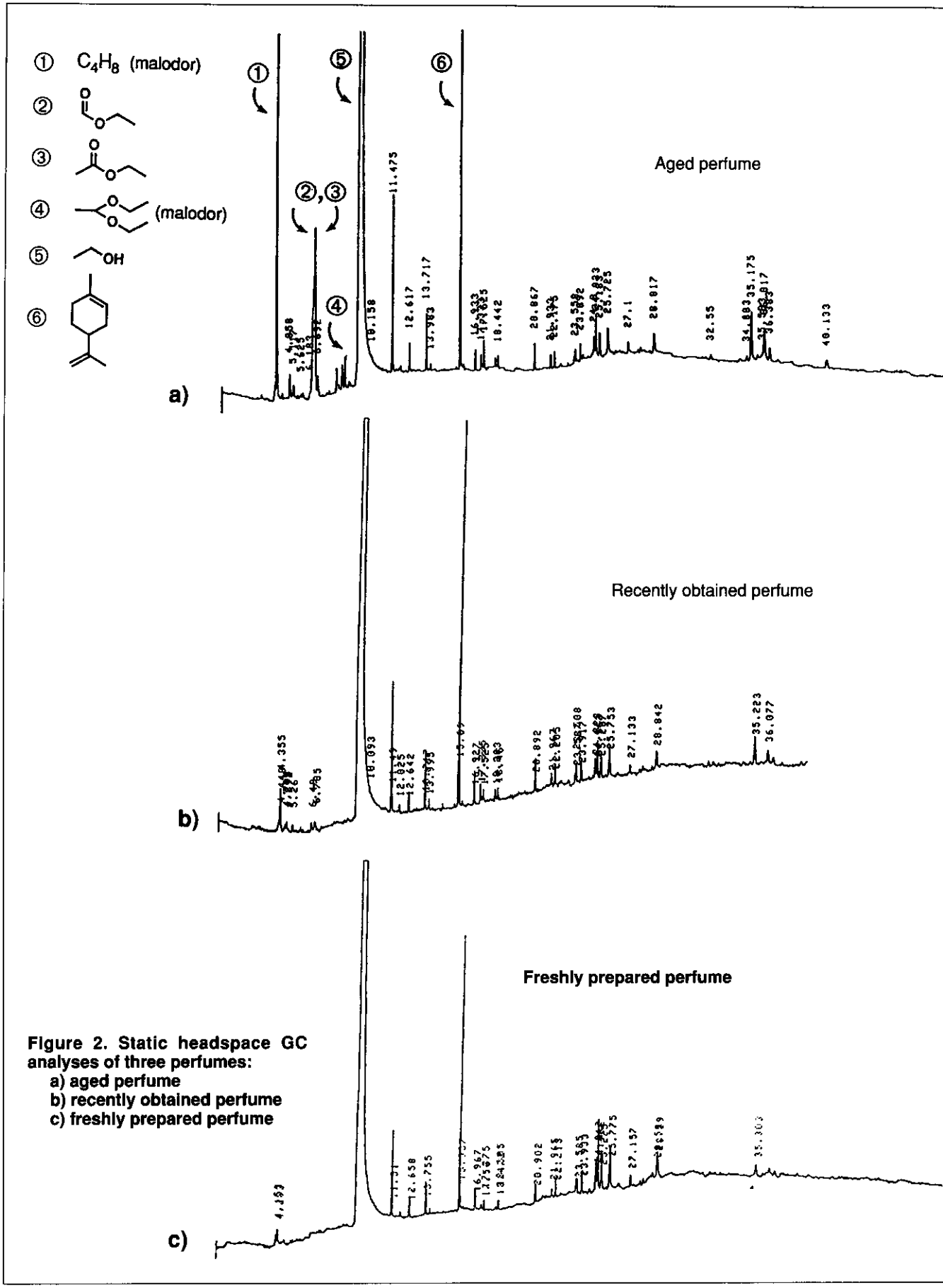


Figure 2. Static headspace GC analyses of three perfumes:
a) aged perfume
b) recently obtained perfume
c) freshly prepared perfume

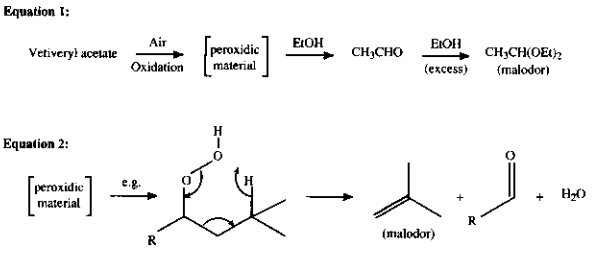


Figure 3. Mechanism of malodor formation in perfumes containing vetiveryl acetate

samples. In fact, subsequent olfactive evaluations and GC-"sniffing" experiments demonstrated that butene and 1,1-diethoxyethane were undoubtedly the principal culprits responsible for the off-odor sometimes exhibited by alcoholic perfumes rich in vetiveryl acetate. As discussed below, such prejudicial by-products result from autoxidation processes. Stabilized alcoholic perfume solutions show no or only a considerably reduced formation of butene and 1,1-diethoxyethane under the same test conditions.

Isolation of a Highly Autoxidizable Hydrocarbon Fraction

By chromatography of either vetiveryl acetate or vetiver oil samples on silica gel, we could isolate a first fraction eluting with toluene that represented 11-12% by weight of the respective starting materials, and had the appearance of a free-flowing liquid with a relatively weak, unspecific "hydrocarbon" odor. As GC and IR data indicated this product to be essentially a mixture of at least 20 hydrocarbon constituents, we called it "HC."

Such HC fractions proved to be extremely sensitive to autoxidation. For instance, a sample of HC isolated from vetiveryl acetate became highly viscous when left in contact with air for three to four days at room temperature and in diffuse light. Moreover, a very thick, six-day-old sample of a similar material was found to have a peroxide index of 7,350. (However, the true value was estimated to be as high as 15,000 or more, because a violent decomposition reaction had occurred just when the peroxide titration was started!)

Besides HC, the above chromatographic separations afforded further fractions eluted with toluene/ethyl acetate mixtures, representing the oxygenated components of vetiveryl acetate and vetiver oil. In sharp contrast to HC, these more polar fractions did not readily undergo aerial autoxidation.

Formation of Acetaldehyde by HC Autoxidation

It was of great interest to demonstrate whether the autoxidation of HC fractions or vetiveryl acetate itself could produce acetaldehyde as a by-product. We first performed "blank" experiments by bubbling pure nitrogen into various samples of HC or vetiveryl acetate (neat, or in the presence of water, ethanol and tartaric acid) and did not observe any acetaldehyde production under these conditions. (The detection of acetaldehyde and other carbonyl compounds was effected by leading the effluent gas into wash bottles filled with an aqueous, acidic solution of 2,4-dinitrophenylhydrazine.) However, and most significantly, a consistent production of acetaldehyde took place when air was substituted for nitrogen in these experiments, and *when ethanol was used as a solvent.*

In a typical experiment, air (100 ml per min) was bubbled at 20°C into a partially heterogeneous solution of 1.2 g of HC (from vetiveryl acetate) in 15 ml of ethanol. After about four days of operation, with regular addition of ethanol to compensate for losses due to evaporation, 21 mg of a precipitate had formed in the 2,4-dinitrophenylhydrazine-containing detection flasks. ^{1}H-NMR analysis demonstrated that this material was a 7:3 mixture of acetaldehyde and acetone 2,4-dinitrophenylhydrazones. On the other hand, the autoxidized HC sample could be recovered from this experiment as a highly polymeric material with a peroxide index of 69,000.

When vetiveryl acetate samples were themselves subjected to the above autoxidation procedure, they yielded amounts of acetaldehyde roughly proportional to their HC contents. Thus, the oxygenated components of vetiveryl acetate contribute very little (if at all) to the formation of acetaldehyde.

Possible Mechanisms Governing Malodor Formation

Our preceding experiments provided strong evidence that the formation of 1,1-diethoxyethane and a butene isomer in alcoholic perfumes rich in vetiveryl acetate or vetiver oil was primarily due to the autoxidation of both these raw materials. Chemically, two reaction sequences need to be considered to fully rationalize the phenomenon.

In the first sequence (Equation 1 in Figure 3), the ill-defined peroxidic material resulting from HC autoxidation acts as an "oxygen carrier" able to oxidize a small portion of the ethanol solvent, giving off some acetaldehyde, as described above. The aldehyde is then rapidly converted to 1,1-diethoxyethane by acetalization with excess ethanol present.

The second, hypothetical reaction sequence (Equation 2 in Figure 3) involves the decomposition via β-scission[8] of some suitable hydroperoxides expected to be formed during HC autoxidation. This radical reaction could in principle lead to all butene isomers; not solely to isobutene as exemplified in our scheme. Supporting this mechanism is the fact that the production of saturated or unsaturated gaseous C_2-C_5 hydrocarbons by decomposition of hydroperoxides is well documented in the literature. The hydrocarbon gases thus released have even been used as an index of lipid peroxidation in vivo and in vitro.[9]

Although hypothetical, the proposed schemes explain reasonably well how butene isomers and 1,1-diethoxyethane can arise from vetiveryl acetate or vetiver oil autoxidation in alcoholic perfumes. Unsaturated perfume ingredients other than vetiveryl acetate or vetiver oil could possibly exhibit a similar behavior.

References

Address correspondence to M Joseph Youssefi, Firmenich SA, Research Laboratories, PO Box 239, CH-1211 Genéva 8, Switzerland.

1. H van den Dool, in *Fragrance Chemistry*, ET Theimer, ed, New York: Academic Press (1982) pp 317-348
2. B Maurer, *Seifen-Öle-Fette-Wachse* **106** 347 (1980); B Maurer, M Fracheboud, A Grieder and G Ohloff, *Helv Chim Acta* **55** 2371 (1972)
3. A Nikiforov, G Buchbauer, L Jirovetz, B Remberg and G Remberg, *Z Naturforsch* **47b** 439 (1992)
4. G Ohloff, in *Riechstoffe und Geruchssinn: Die molekulare Welt der Düfte*, Berlin, Heidelberg: Springer-Verlag (1990) pp 169-170
5. A Akhila, MC Nigam and OP Virmani, *CROMAP* **3** 195 (1981)
6. BD Mookherjee, RW Trenkle and RA Wilson, *Proc of 12th Intern Congress of Flavours, Fragrances and Essential Oils*, Vienna, Austria (Oct 4-8, 1992) pp 248-253
7. DC Umarani, R Seshadri, KG Gore and KK Chakravarti, *Flavour Ind* **1** 623 (1970)
8. A Fish, in *Organic Peroxides*, Vol I, D Swern, ed, New York: J Wiley and Sons (1970) pp 162-164
9. EE Dumelin and AL Tappel, *Lipids* **12** 894 (1977) and references cited therein
10. A Cazaussus, PY Rosé and N Sellier, *Chromatographia* **28** 579 (1989)