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On the origin of "Goût de Lumiere" in champagne

Maurizio D'Auria*, Lucia Emanuele, Giacomo Mauriello, Rocco Racioppi

Dipartimento di Chimica, Università della Basilicata, Via N. Sauro 85, Potenza 85100, Italy

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Abstract

The flavour of champagne before and after UV irradiation was analysed by using SPME (solid phase microextraction). Fourteen components in the flavour were detected; some significant modifications in the composition of the flavour were observed: 1-propanol and 1-hexanol contents did not change during the irradiation, the amount of 2-methylpropanol increased, while 2,6-di-*t*-butylphenol disappeared after the irradiation. Furthermore, the presence of esters in the wine after the irradiation was completely modified. Ethyl acetate, ethyl butanoate, ethyl 2-hydroxypropanoate, 3-methyl-1-butanol acetate, ethyl hexanoate, and ethyl octanoate reduced their presence in the wine; ethyl decanoate disappeared in the flavour after the irradiation. In order to verify if riboflavin is responsible for the observed modifications in flavour composition, the irradiation of ethyl hexanoate in the presence of riboflavin in ethanol water with a 125 W mercury arc through Pyrex was carried out showing 9% decomposition of the ester.

Keywords: Champagne; Goût de Lumiere; Solid phase microextraction

1. Introduction

Photodegradation can be responsible of off-flavours in some edible materials. Some components of the flavour can be modified in the presence of light. For example, the photoisomerisation of humulone into *trans*- and *cis*-isohumulone in the beer has been studied [1]. The problem of a particular off-flavour in beer exposed to light was recognised as early as in 1875, and simple tests on the protective power of glass indicated that brown bottles were most effective [1]. Gray et al. [2] were the first to show that thiols were involved in the development of an offending off-flavour. In the early sixties, Kuroiwa et al. [3] used model systems to establish that a photochemical reaction in the wavelength range of 350–500 nm, involving a flavin such as riboflavin, beer bitter agents (isohumulones), and sulphur-containing compounds, led to the so-called "light-struck flavour". Other drinks including champagne, wine, and milk are also sensitive to light; however, none produces the unique "skunky" odour and taste of light struck beer. Then, the need to avoid light irradiation is not restricted to beer.

Champagne is one of the most famous sparkling wines in the world. It is obtained from three types of grapes, pinot noir, pinot meunier, and chardonnay, in a particular and well defined region in the North of France. With its northern geographical position at the limits of the vine's cultural zone, the climate is harsh, softened only by an oceanic influence. The chalky sub-soil provides the vine with naturally constant irrigation. The vines' position on the slopes provides the best sunlight and the run-off of any excess water.

French experts observed that the quality of champagne was distinctly inferior when the bottles were sold in supermarkets as opposed to traditional liquor stores. Eventually, it was discovered that the intense fluorescent lighting traditionally present in large retail stores produced that the struck favour (Goût de Lumière), triggered by photochemical transformations involving sulphur components, such as methionine and cisteine, which produce H_2S, CH_3SH, and $(CH_3)_2S$ [4].

The "sunlight flavour" is reported to be produced easily in clear bottles of chardonnay and pinot gris wine with a riboflavin content of over 200 $\mu g\,l^{-1}$, when exposed to reflected light for 2–3 weeks, while a concentration below 100 $mg\,l^{-1}$ is considered safe for such wines [5].

In this paper we want to report our results obtained through UV irradiation of champagne and subsequent analysis of the flavour. We found that irradiation modifies the flavour of champagne though degradation of some esters present in the wine. Furthermore, we did not find formation of sulphur compounds as reported previously.

* Corresponding author. Tel.: +39-0971-202240; fax: +39-0971-202223.
E-mail address: dauria@unibas.it (M. D'Auria).

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2. Materials and methods

We used samples of commercially available Piper-Heidsieck Champagne. Wine (20 ml) was irradiated in Pyrex flask with a 15 W UV lamp for 2, 6, and 24 h.

Solid phase microextraction (SPME) is a sample preparation technique based on sorption, which is useful for extraction and concentration analyses either by submersion in a liquid phase or exposure to a gaseous phase. Following exposure of the fibre to the sample, sorbed analytes can be thermally desorbed in a conventional gas chromatography injection port. SPME has been used in a range of fields including studies of flavours and taints, especially for quick screening of the volatile composition of a wide range of products.

An SPME fibre coated with 100 μm of nongrafted poly(dimethysiloxane) (PDMS) phase (Supelco 57300-U, mounted on a Supelco 57330 support) was conditioned for 1 h at 250 °C in a stream of helium. A single fibre was used for the complete study. A blank run was performed after the analysis in order to confirm that no residual compound was polluting the fibre or the column. The samples were brought to ambient temperature overnight before the bags were opened. The headspace was generated from 10 ml samples placed in a 20 ml flask. The flasks were sealed and heated for 20 min in an aluminium block maintained at 45 °C (40° in the flask). During this time, the fibre was maintained over the sample. The fibre was then introduced into the injection port of a HP6890 plus gas-chromatograph equipped with a Phenomenex Zebron ZB-5 MS capillary column (30 m × 0.25 mm ID × 0.25 μm film thickness). As detector we used a HP 5973 mass selective detector (mass range: 15–800 amu; scan rate: 1.9 scans/s; EM voltage: 1435), helium at 0.8 ml/min was used as carrier gas. The injection port, equipped with glass insert (internal diameter 0.75 mm) was splitless at 250 °C. The desorption time of 0.4 min was used. Detector was maintained at 230 °C. Oven was maintained at 40 °C for 2 min, then the temperature increased until 250 °C (8 °C/min); finally, this temperature was maintained for 10 min. All the analyses were performed in triplicate. The chromatograms obtained from the total ion current (TIC) were integrated without any correction for coelutions and the results were expressed in arbitrary surface units (asu). All the peaks were identified from their mass spectra by comparison with spectra in Wiley6N and NIST98 libraries (Table 1).

Photochemical reaction of ethyl hexanoate in the presence of riboflavin. Ethyl hexanoate (14 mg) was dissolved

Table 1
Mass spectral data of compound found in the flavour of champagne

Compound	Mass spectrum (*m/z* (relative abundance, %))
1-Propanol	61 (1), 60 (15), 59 (28), 57 (2), 55 (1), 53 (1), 46 (1), 45 (6), 44 (6), 43 (8), 42 (19), 41 (12), 40 (2), 39 (10), 38 (3), 37 (2).
Ethyl acetate	88 (7), 73 (7), 71 (1), 70 (18), 62 (1), 61 (19), 60 (1), 46 (1), 45 (15), 44 (4), 43 (100), 42 (8), 41 (1).
2-Methyl-1-propanol	75 (1), 74 (18), 73 (4), 67 (1), 59 (5), 58 (1), 57 (8), 56 (9), 55 (11), 53 (3), 51 (2), 50 (2), 49 (1), 46 (1), 45 (6), 44 (11), 43 (100), 42 (62), 41 (78), 40 (7), 39 (33), 38 (6), 37 (2), 34 (1), 33 (33), 32 (2), 31 (44), 29 (17).
3-Methyl-1-butanol	88 (1), 73 (1), 71 (6), 70 (75), 69 (7), 67 (1), 60 (1), 59 (1), 58 (1), 57 (24), 56 (12), 55 (100), 54 (2), 53 (4), 51 (2), 50 (1), 47 (1), 46 (6), 45 (14), 44 (4), 43 (50), 42 (60), 41 (52), 40 (4), 39 (21), 38 (2), 37 (1), 31 (20), 30 (1), 29 (18), 28 (6), 27 (14).
Ethyl butanoate	116 (5), 101 (10), 90 (1), 89 (18), 88 (61), 87 (1), 75 (1), 74 (1), 73 (23), 72 (5), 71 (100), 70 (12), 69 (1), 61 (9), 60 (20), 57 (1), 55 (4), 46 (2), 45 (18), 44 (20), 43 (69), 42 (15), 41 (22), 40 (4), 39 (9), 38 (1).
Ethyl 2-hydroxypropanoate	118 (1), 103 (1), 75 (10), 56 (1), 55 (1), 47 (2), 46 (3), 45 (100), 44 (2), 43 (8), 42 (1).
3-Methyl-1-butanol acetate	88 (2), 87 (15), 85 (2), 73 (11), 71 (5), 70 (68), 69 (10), 61 (16), 60 (2), 58 (4), 57 (3), 56 (5), 55 (49), 53 (2), 46 (2), 45 (12), 44 (28), 43 (100), 42 (16), 41 (15), 40 (5), 39 (8).
Ethyl hexanoate	144 (1), 117 (6), 116 (1), 115 (10), 102 (4), 101 (29), 100 (4), 99 (56), 98 (1), 97 (2), 90 (1), 89 (6), 88 (100), 87 (7), 83 (1), 81 (1), 80 (1), 75 (1), 74 (1), 73 (26), 72 (1), 71 (24), 70 (27), 69 (6), 68 (1), 67 (1), 62 (1), 61 (19), 60 (31), 59 (1), 57 (3), 56 (3), 55 (14), 54 (1), 53 (2), 45 (12), 44 (3), 43 (41), 42 (14), 41 (18), 40 (2), 39 (8).
2-Phenylethanol	122 (29), 93 (7), 92 (57), 91 (100), 78 (6), 77 (10), 75 (7), 65 (14), 60 (6), 51 (7), 45 (32), 44 (81), 43 (14), 40 (17), 39 (6).
Diethyl butanedioate	147 (3), 130 (6), 129 (64), 128 (18), 103 (2), 102 (14), 101 (100), 100 (5), 75 (3), 74 (8), 73 (15), 60 (1), 57 (4), 56 (7), 55 (15), 45 (11), 44 (11), 43 (5), 42 (2), 40 (3).
Ethyl octanoate	172 (2), 157 (1), 145 (2), 144 (1), 143 (5), 130 (1), 129 (12), 128 (3), 127 (32), 125 (1), 116 (1), 115 (10), 109 (2), 102 (4), 101 (39), 98 (3), 97 (3), 90 (1), 89 (8), 88 (100), 87 (4), 85 (1), 84 (5), 83 (6), 82 (1), 81 (1), 80 (1), 79 (1), 75 (1), 74 (3), 73 (23), 71 (2), 70 (21), 69 (7), 68 (1), 67 (2), 61 (16), 60 (21), 59 (1), 58 (1), 57 (26), 56 (4), 55 (19), 54 (1), 53 (2), 45 (7), 44 (1), 43 (15), 42 (7), 41 (17), 40 (1), 39 (5).
Ethyl decanoate	200 (3), 173 (1), 171 (3), 158 (2), 157 (18), 156 (2), 155 (18), 153 (1), 144 (1), 143 (5), 130 (1), 129 (3), 116 (1), 115 (7), 112 (1), 111 (1), 110 (1), 103 (1), 102 (4), 101 (42), 98 (3), 97 (4), 95 (2), 89 (9), 88 (100), 87 (3), 85 (4), 84 (4), 83 (5), 82 (1), 81 (3), 79 (1), 75 (1), 74 (3), 73 (20), 72 (1), 71 (8), 70 (18), 69 (10), 68 (2), 67 (2), 61 (14), 60 (15), 59 (1), 58 (1), 57 (9), 56 (4), 55 (16), 54 (1), 53 (1), 45 (6), 44 (2), 43 (18), 42 (6), 41 (17), 40 (1), 39 (4).
2,6-Di-*t*-butylphenol	207 (3), 206 (16), 205 (100), 189 (3), 177 (7), 161 (4), 145 (10), 141 (3), 133 (3), 131 (4), 129 (4), 128 (4), 121 (3), 119 (4), 117 (2), 115 (5), 105 (7), 91 (6), 81 (5), 80 (3), 79 (3), 77 (4), 75 (2), 73 (3), 67 (4), 60 (2), 57 (14), 55 (4), 46 (3), 45 (8), 44 (30), 43 (7), 41 (7), 40 (7).

in 1:1 ethanol/water mixture (10 ml) in the presence of riboflavin (2 mg) and an internal standard (tetracosane). The mixture was irradiated with a 125 W high pressure mercury arc (Helios-Italquartz), surrounded with a Pyrex water jacket. After 1 h irradiation the mixture was analysed by using the GC–MS apparatus described above.

3. Results and discussion

We analysed the photochemical behaviour of two samples of Piper-Heidsieck Champagne. In order to obtain valuable data on the modification of the flavour, we carried out the analysis of head space of champagne sample by using solid phase microextraction technique.

SPME provides many advantages over conventional sample preparation techniques. The SPME technique is simple to use, takes less than 1 h to complete, is less expensive, does not require solvent extraction and allows characterisation of the headspace in contact with the sample. This method obviates the classical steam distillation, which is liable to modify unstable constituents.

In the last 10 years this new non-invasive methodology was adopted to perform the analysis of volatile organic compounds [6,7]. This technique was applied to the analysis of flavours [8–15].

SPME is an extraction method involving adsorption of analytes on a solid phase deposited on a silica fibre [16]. The extraction of the volatile components is achieved either by immersing the fibre into the liquid to be analysed (L-SPME), or by simple contact with its headspace under static conditions (SHS-SPME). SPME has been widely used in the determination of wine flavour [17–25].

The sample we used showed the UV spectrum reported in Fig. 1. It showed absorptions at 290 and 301 nm and a shoulder at 330 nm. We irradiated the first sample for 24 h with 15 W ultraviolet lamp through Pyrex. To estimate modifications in the flavour composition we performed a calibration curve of one of the most abundant component after ethanol, 3-methyl-1-butanol. On the basis of this calibration curve we observed that in our sample 3-methyl-1-butanol was contained in concentration of 155 mg l^{-1}. This concentration did not change after the irradiation. On the basis of this result we report the concentration of the other components of champagne flavour as percent referred to 3-methyl-1-butanol (100%). The result of this test is reported in Fig. 2. We showed the presence of 14 components in the flavour; some of these compounds were observed in very low concentration. We did not observe the formation of compounds containing sulphur. However, we observed some significant modifications in the composition of the flavour; 1-propanol and 1-hexanol contents did not change during the irradiation, the amount of 2-methylpropanol increased, while 2,6-di-*t*-butylphenol disappeared after the irradiation. Furthermore, the presence of esters in the wine after the irradiation was completely modified. Ethyl acetate, ethyl butanoate, ethyl 2-hydroxypropanoate, 3-methyl-1-butanol acetate, ethyl hexanoate, and ethyl octanoate reduced their presence in the wine; ethyl decanoate disappeared in the flavour after the irradiation. Furthermore, we did not find the corresponding acids.

The second sample of champagne was irradiated for 2 and 6 h. This way we could follow the evolution of the wine during the time: we follow this behaviour in order to understand whether some other intermediates were formed. The results are collected in Figs. 3 and 4. The

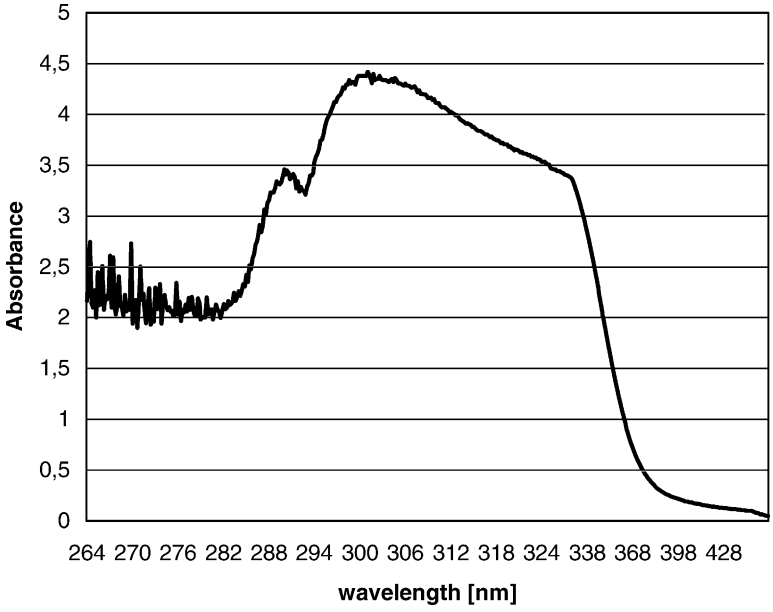


Fig. 1. UV spectrum of champagne. Path length of the cell: 1 cm.

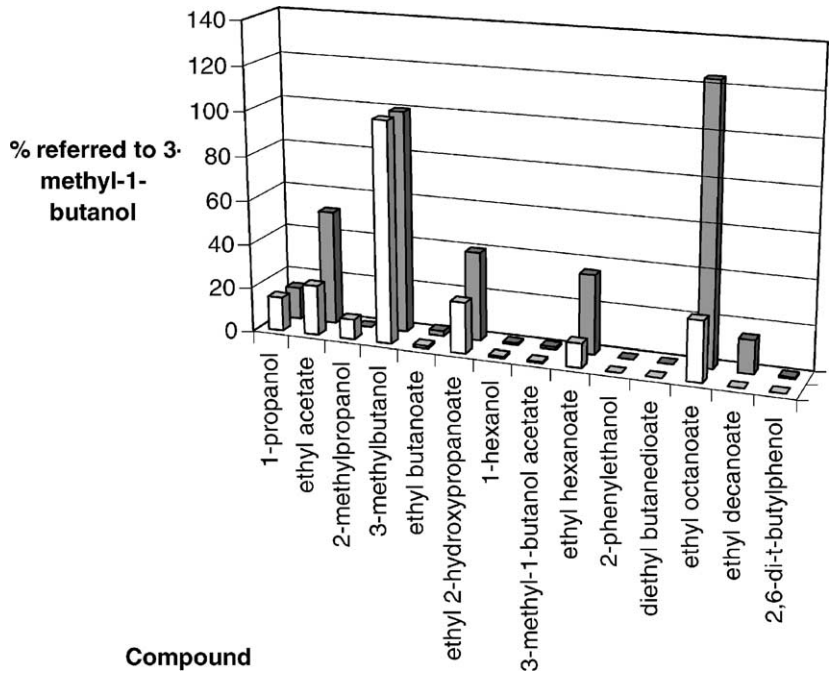


Fig. 2. Change in the composition of champagne flavour after 24 h irradiation. The concentration is reported as percent referred to 3-methyl-1-butanol. Back: before irradiation; front: after irradiation.

concentrations during irradiation of the minor components are collected in Fig. 3: we can see that, while the contents of 2-methyl-1-propanol, 1-hexanol, and 2-phenylethanol did not undergo severe modifications, the concentrations of 1-propanol, ethyl butanoate, diethyl butanedioate, 3-methyl-1-butanol acetate, and 2,6-di-*t*-butylphenol decreased during irradiation. The same behaviour was observed considering the main components (Fig. 4); the concentrations of ethyl octanoate, ethyl 2-hydroxypropanoate, ethyl hexanoate, and ethyl decanoate decreased during the irradiation.

On the basis of the above reported results we can conclude that the irradiation of champagne does not affect proteins in the wine with the formation of compounds containing

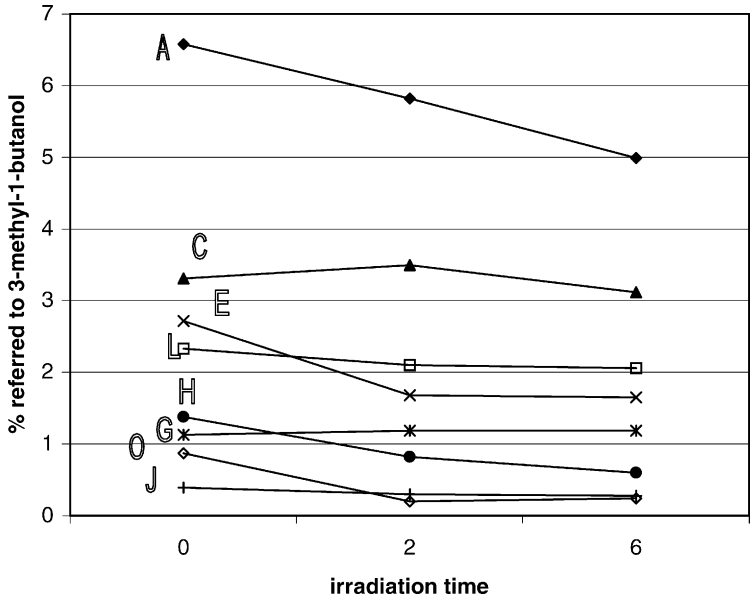


Fig. 3. Evolution of the concentration of suitable components of champagne during irradiation. A: 1-propanol; C: 2-methyl-1-propanol; E: ethyl butanoate; G: 1-hexanol; H: 3-methyl-1-butanol acetate; J: 2-phenylethanol; L: diethyl butanedioate; O: 2,6-di-*t*-butylphenol.

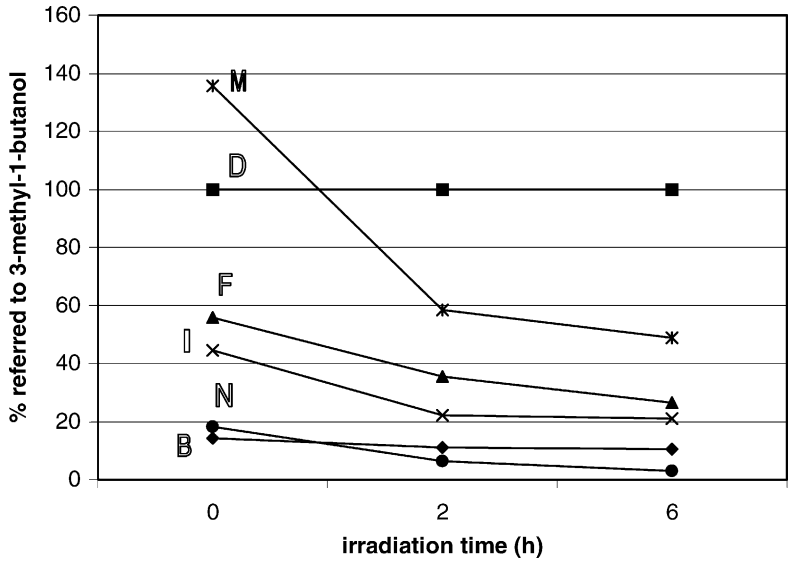


Fig. 4. Evolution of the concentration of suitable components of champagne during irradiation. B: ethyl acetate; D: 3-methyl-1-butanol; F: ethyl 2-hydroxypropanoate; I: ethyl hexanoate; M: ethyl octanoate; N: ethyl decanoate.

sulphur. Furthermore, the more relevant change in the flavour is related to the decomposition of the ester contents in the wine.

As reported above, riboflavin was considered the compounds responsible for "Goût de Lumière". The principal forms of riboflavin (Vitamin B_2) found in nature are flavin mononucleotide and flavin-adenine dinucleotide. Free riboflavin is also naturally present in raw and processed fruits [26] and fermented beverages. Flavin mononucleotide and flavin-adenine dinucleotide can be converted to riboflavin prior to quantitation, in order to obtain the total riboflavin content.

The total riboflavin content was reported to be 50–70 $\mu g\,l^{-1}$ in grape and in must, the content in wine rises to 110–250 $\mu g\,l^{-1}$ during fermentation and it can be further enriched (160–318 $\mu g\,l^{-1}$) for wines left in contact with yeast for 4–6 days after fermentation is completed [27,28].

The riboflavin absorption spectrum in aqueous medium exhibits four structure less peaks centred at 446, 375, 265 and 220 nm with high molar extinction coefficients (>$10^4\,M^{-1}\,cm^{-1}$) [29]. Riboflavin is particularly sensitive to UV and visible light and induces both type I and type II photosensitised oxidation mechanisms. The former involves the formation of free radicals through hydrogen or electron transfer between riboflavin triplet excited state and substrates. The semi-oxidised substrate can undergo further oxidation in the presence of oxygen. The type II process involves the formation of singlet oxygen by energy transfer from triplet excited riboflavin to molecular oxygen.

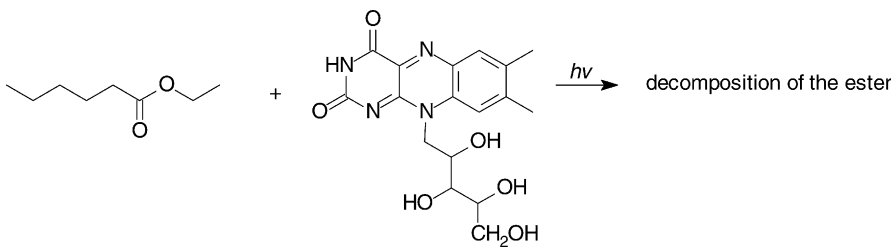
We tested the capability of riboflavin to catalyse the decomposition of aliphatic esters.

We verified whether riboflavin was able to induce decomposition of aliphatic esters. The reaction we carried out is depicted in Scheme 1.

One hour irradiation of 14 mg of ethyl hexanoate in the presence of riboflavin (2 mg) in ethanol water with a 125 W mercury arc through Pyrex induced 9% decomposition of the ester.

Riboflavin is able to induce decomposition of the esters: probably this reaction occurs through a type I photosensitised mechanism. In fact, in our knowledge, singlet oxygen is not able to attack aliphatic esters.

In conclusion, we have shown that the "Goût de Lumière", observed in champagne, can have a different origin from that described in previous reported articles in this field. We showed that irradiation induces several modifications



Scheme 1.

in flavour composition where esters are selectively decomposed. Furthermore, we showed that riboflavin is able to induce the same type of decomposition in ethyl hexanoate.

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