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Identification of VOCs Responsible of Odour during Field Retting of Hemp Stems

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Incorporation of natural fibres into polymers to manufacture biocomposites is a way of limiting the environmental impact of these materials. However, the fibres quality is essential to fulfil their assigned role as reinforcement in biocomposites. The extraction of fibres from hemp stems requires a retting step. Retting is a bioprocess applied to plant stems to easily separate fibres from the central woody part. Nowadays, this process is carried out directly on the field in an empirically way due to its dependence on environmental conditions which could cause problems of the inconsistency of the hemp fibres quality.

During few weeks of retting, odours are generated by the degradation of plant material by microorganisms. The modification of these odours can be correlated with the progress of the retting degree of hemp stems. This change in odour is obviously combined with a change in the type and quantity of VOCs emitted. Identifying odours and VOCs emitted when the retting is optimal can lead to make sensors able to survey the progress of this biological process. Then, if this process is well controlled, much higher quality with more uniform fibres could be produced.

This article will focus on the identification of the odour emitted when the optimal retting of the stems is reached as well as the identification of the VOCs analysed at this stage.

1. Introduction

The increasing depletion of fossil energy resources is forcing people to define alternative strategies to limit the use of these non-renewable resources by promoting the development of renewable resources while ensuring the protection of the environment. The use of hemp fibres is among of responses of this issues. Indeed, hemp fibres have specific mechanical properties (ratio between the mechanical properties and the density (Aziz & Ansell, 2004)) identical to those of glass fibres commonly used for the reinforcement of composite materials (Joshi et al., 2004). Hemp fibres are obtained after various steps transformations. The retting process is one of these steps which allow separating lignocellulosic fibres from plant stems. This process consists in the degradation of natural cements (pectins and waxes) which constitute the gummy resinous material in which the fibre bundles of stems plants are contained (Pakarinen et al., 2012). The fibres quality obtained depends on this stage, and therefore, controlling retting treatment is a crucial step for high performances hemp fibre (Mazian et al., 2018).

Many VOCs compounds are naturally emitted by the hemp plant (*Cannabis sativa L*) as terpenes, alcohols, aldehydes (Turner et al. 1980; El Sohly and Slade 2005). Depending on the plant hemp situation during growth and retting, emitted VOCs would differ. Some of them are odorous; therefore the resulting odour must be different as well. Thus, following these gaseous emissions and odours would give some data about the retting-degrees progress.

Historically, to identify molecules at the odours origin, only a physico-chemical analysis was carried out coupled with an expertise on the potentiality of molecules to generate an odour. Then, the approach by calculation of odour activities has been developed (Anet et al., 2013; Kamarulzaman et al., 2019; Parker et al.,

2013; Sivret et al., 2016). However, due to certain biases (precision of physico-chemical quantification, unavailability of perception thresholds, and uncertainty of existing data) (Cariou et al., 2016), the identification of the molecules causing odours was still incomplete. To remedy this shortcoming, this paper proposes to complete the odour activity value approach by a search for a relationship between the different odour notes perceived by the evaluators and the individual odour qualities of the molecules identified previously.

2. Materials and methods

2.1 Hemp cultivation and sampling

Hemp plants (*cannabis sativa* L., Cultivar 'Santhica 27') were cultivated in south of France near to Alès and harvested at the seed maturity (26th September, 2017). Retting was conducted on the field during nine weeks. Regularly, hemp stems were collected (each week until week 7 and then two weeks later at the end of the retting period). At each sampling time, 100g of stems was introduced in a Nalophan© bags. This bag was then filled with 40L of dry compressed air and let in a room with stable thermal conditions until stabilization, reached after three days of waiting.

2.2 Physico-chemical and olfactometric analyses

Physico-chemical analyses by thermal desorption-gas chromatography-mass spectrometry and odour concentration analyses were conducted according the protocol described in Mazian et al. (2019). The best possible quantification is realized for each compound: if the compound was used as standard the real concentration is calculated if not, the mean of standard for each family is used to quantify the compound.

Odour concentration is measured according the EN 13725 (2003).

Odour quality is evaluated according a non-oriented method developed by LSR and Olentica and presented in Medjkoune (2018).

2.3 Determination of VOCs responsible of odours

VOCs responsible of odour during the retting process are identified by calculating odour activity values (OAV) for all the identified compounds (Cariou et al., 2016).

$$OAV_i = \frac{C_i}{ODT_i}$$

OAV_i : Odor Activity Value of compound i (dimensionless)

C_i : Chemical concentration of compound i ($\text{mg}\cdot\text{m}^{-3}$)

ODT_i : Odor Detection Threshold of compound i ($\text{mg}\cdot\text{m}^{-3}$)

Odour detection thresholds (ODT) are not available for all compounds. So, if the ODT was measured in the laboratory, the value is used to calculate OAV. If an individual ODT is referenced in the literature ((Van Gemert, 2011), the geometric mean of all values for the compound is used and if no ODT is available, the geometric mean of all ODT of the compound chemical family is used to estimate an individual ODT.

Then, the sum of all the odour activity values is compared with odour concentration. If the two values are in the same order of magnitude, all the molecules responsible of odours are considered in our opinion. To confirm this hypothesis, the odour quality obtained with our method is compared with individual quality of identified molecules. If all the olfactory notes are recovered by the individual odour qualities of the different molecules identified then the method is considered valid. If not, odour quality of molecules with an $OAV < 1$ is checked.

3. Results

3.1 Odour concentration versus sum of odour activity value

Table 1 displays the comparison between the sum of OAV and odour concentration measured by olfactometry according the EN13725 standard.

Table 1: evolution of calculated OAV sum and measured odour concentration

	W0	W1	W2	W3	W4	W6	W9
OAV Sum	2201	1724	726	426	120	170	124
Odour concentration (UO_E/m^3)	1467	770	358	564	253	396	86

As a first approach, the OAV sum is in the same order of magnitude that the odour concentration measured. Moreover, a correlation factor of 0.91 is obtained between the two data sets. Therefore, it can be concluded that all major molecules responsible of odour are identified by our approach.

Considering the evolution of odour concentration over the nine-weeks of retting period, a clear decrease can be observed. Indeed, the odour concentration is around 1500 UO_E/m³ at the beginning of the retting process and then falls by a factor 5 and stabilizes from week 4.

3.2 Evolution of individual odour activity value

Table 2 shows the evolution of odour activity values for all the molecules with an OAV upper than 1 on the nine weeks of retting.

Table 2: Evolution of individual OAV during retting process

CAS	Nom	W0	W1	W2	W3	W4	W6	W9
431-03-8	2,3-butanedione	998	1054	480	272	86	140	99
470-82-6	eucalyptol	468	84	74	33	10	8	4
80-56-8	alpha-pinene	273	40	32	16	6	11	14
590-86-3	3-methylbutanal	152	325	78	77	8	1	2
66-25-1	hexanal	81	43	17	9	5	6	1
96-17-3	2-methylbutanal	80	122	23	8	1	0	0
75-18-3	dimethylsulfide	49	12	0	0	0	0	0
75-07-0	acetaldehyde	43	5	4	1	1	1	0
79-31-2	2-methylpropanoïc acid	18	13	10	4	4	3	2
64-17-5	ethanol	13	4	1	1	0	0	1
78-84-2	2-methylpropanal	12	12	3	2	0	0	0
110-62-3	pentanal	3	1	0	0	0	0	0
123-38-6	propanal	2	2	2	0	0	0	0
26882-03-1	α-Campholenal	2	0	0	0	0	0	0
123-51-3	3-methyl-1-butanol	1	0	0	0	0	0	0

At the seed maturity of hemp and at the beginning of the retting process (W0), TD-GC-MS analysis leads to identify 69 VOCs belonging to eleven different chemical families more or less odorous as presented in (Mazian et al., 2019).

When calculating OAV, only fifteen VOCs seem to have an impact on odour (Table 2). First, 2,3-butanedione, eucalyptol and alpha-pinene represent almost 80% of OAV sum at the beginning of the retting process (W0). Then, 2,3-butanedione is the biggest contributor to the OAV sum during the nine weeks of the process but an increase of the percentage of 3-methyl butanal and 2-methyl butanal instead of eucalyptol and alpha-pinene modify the odour quality from week one to week three.

At week four, six and nine, the molecules responsible of odour are at very low level and stable and should generate a stable odour quality.

3.3 Evolution of odour quality

Figure 1 shows the evolution of odour quality description from during retting treatment.

On the day of the harvest (W0), the odour is described with a predominantly green vegetal note and a secondary note of dry plant. It is to be noted the presence of a sweet note for all samples but at a very low level.

As the retting process progresses, the green plant notes disappear and the smell of dried plant becomes predominant. A note of fermentation also appears during the following weeks.

At week 9, it is important to note that the sweet note becomes the second most intense note.

All the other minor notes (pungent, fresh, woody, musty, humus and mushroom) appear only once or twice in the descriptor of the evaluators.

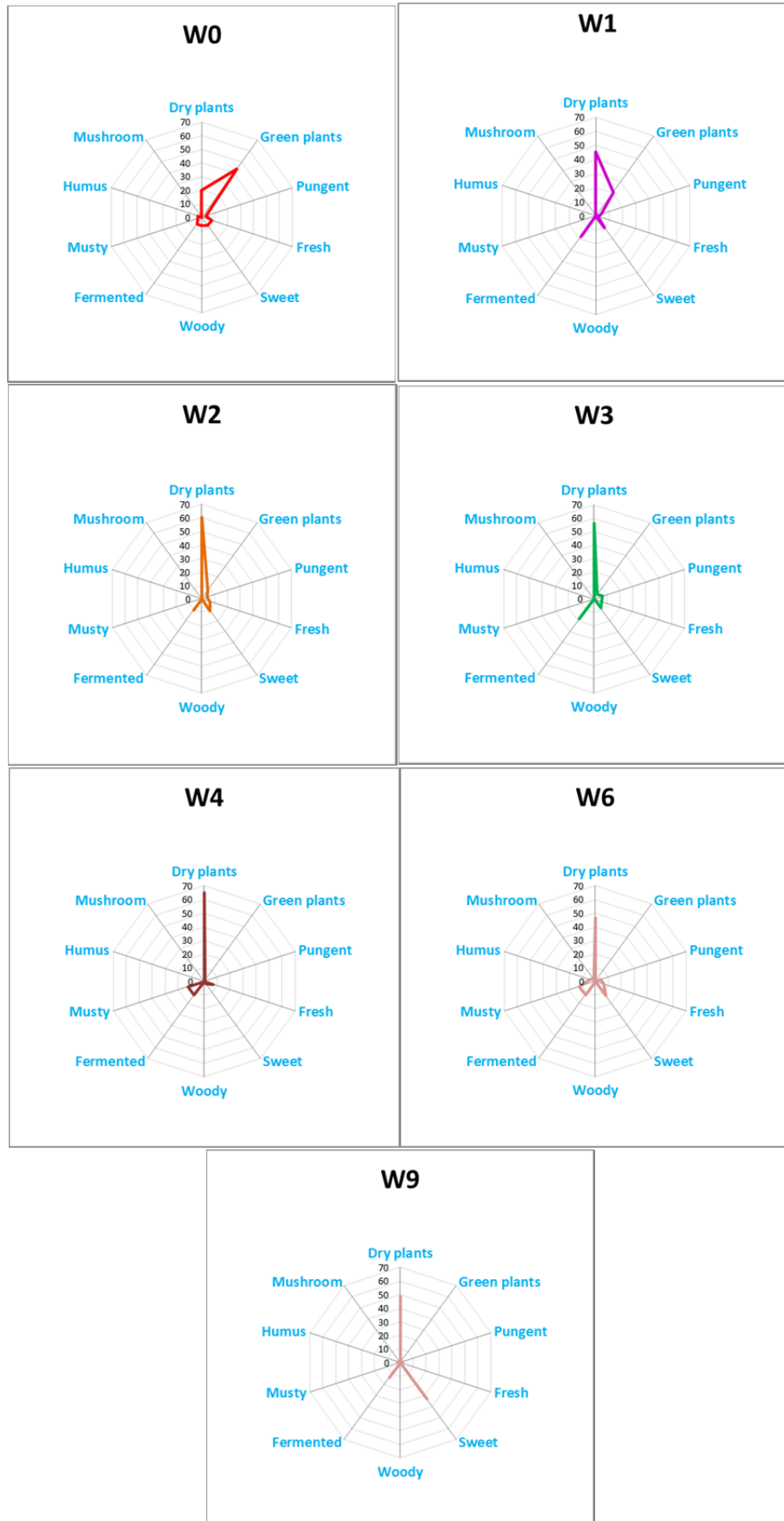


Figure 1 The evolution of odour quality description from during retting treatment.

4. Discussion

The most important olfactory notes to explain are therefore those of green plant, dried plants, fermentation and sweetness. A database (The good scents company) is used to identify the odour quality associated with each molecule.

When looking at the molecules identified with the OAV calculation (table 2), many of them are described in the literature by a green note. In our case, eucalyptol, alpha-pinene and hexanal can explain the odour perceived by the evaluators. This note, well perceived at week 0 is correlated with the importance of OAV for these molecules. Until week 2, their OAV decreased and the evaluators described this note less and less.

The presence of 3-methyl butanal, 2-methyl butanal, hexanal and pentanal is responsible for the fermentation note. These compounds have a real impact on odours perceived at week 1, 2 and 3.

The sweet note can only be explained by the presence of 2,3-butanedione in the gaseous emissions of the retting process. This molecule is present all along the process with an impact that increases with the disappearance of other important molecules.

Other minor notes can also be explained by the presence of identified molecules

- Pungent: acetaldehyde, 2-methylpropanoic acid, 2-methyl propanal
- Musty: 2-methyl butanal, propanal
- Woody: propanal

But a major note, the dry vegetal one, is not correlated with any molecule with an OAV upper than 1 (table 2). If we considered the other molecules identified but without an OAV upper than 1, Beta-pinene is described in literature with an odour of hay in some case, so it might explain the dry vegetal note identified by jury members. In our analyses, beta-pinene never appears with an OAV upper than one; a bad quantification due to a calibration not made with this molecule or the use of a wrong odour detection threshold may lead to a misidentification of VOCs responsible for odour. The approach conducted in this paper adds a new validation of VOCs identification with a first step with the OAV calculation and a confirmation with the search for correlation between the olfactory notes and the identified molecules.

5. Conclusions

Odours generated by retting treatment evolve regularly during nine weeks studied both in terms of concentration and quality. From green vegetal, the dominant note at the beginning, the odour evolves towards a note of dried vegetal with minor notes of fermentation and sweetness. This evolution is correlated with the modification of gaseous emissions. From a majority of terpenes, the VOCs emitted evolve to aldehydes and alcohols. This modification is the result of biodegradation of hemp stems.

The approach developed in this paper brings an additional brick in the methods of identification of VOCs at the origin of odours. Some points still need to be improved; for example, quantification in physico-chemical analyses and odour detection threshold accuracy are important to obtain the more accurate OAV and finally the most detailed identification.

In addition, the database of molecule odour qualities found in the literature is very incomplete. Indeed, besides the missing data, the quality of an odour is dependent on its concentration, which the available data do not provide, leading to difficult interpretations.

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