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FUNCTIONALISATION OF TEXTILE MATERIALS WITH VOLATILE COMPOUNDS

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Abstract: *The aim of this research work was the determination of volatile oils components of textile materials treated with essential oils extracted from Eucalyptus globulus and Pine. Two types of textile materials (Variant 1 - 80% cotton / 20% Elastane and Variant 2 - 45% cotton / 55% Polyester) were prepared and treated with the solutions of essential oils in the concentration of 0,002%. Initially, a 1% gum Arabic solution was made to which the corresponding amount of essential oil dissolved in ethyl alcohol was added by dripping. Textile materials were treated by exhaustion with the two solutions obtained for 30 min at 40°C. The Ugolini apparatus with a 1:10 hydromodulus (500 mL float) was used. After completion of the treatment, the samples were dried freely at room temperature for 24 hours. The Gas Chromatography-Mass Spectrometry (GC-MS) method was applied to obtain the chromatograms of the essential oils and the constituent chemical compounds. The following compounds were identified in eucalyptus essential oil: Caryophyllene oxide, m-cymene, Eucalyptol, Spathulenol, and in pine essential oil: 1R-alpha-Pinene, Aromadendrene oxide-(2), Caryophyllene. In the textile samples treated with eucalyptus/pine essential oil, the compound 17-Pentatriacontene, belonging to the terpenoid class, recognized for its antibacterial properties, was identified.*

Key words*: essential oil, textile, chemical compounds, chromatograph, functionalization*

1. INTRODUCTION

According to *European Pharmacopoeia,* essential oils are defined as an "odorous product, usually of complex composition, obtained from a botanically defined plant raw material by steam distillation, dry distillation, or a suitable mechanical process without heating. Essential oils are usually separated from the aqueous phase by a physical process that does not significantly affect their composition" [1].

Essential oil is a secondary metabolite synthesized by medicinal and aromatic plants. They represent less the 5% of the total composition of the plants and consist of mixtures of hydrocarbons (terpenes, aldehydes, alcohols, esters, and phenols) and are extracted from plants by conventional methods (hydro distillation, organic solvent extraction, and cold pressing) and innovative methods (supercritical fluid extraction, ultrasound-assisted extraction, solvent-free microwave extraction [2,3], etc.). They can be derived from one or more plant parts, such as flowers (rose, jasmine, clove, lavender), leaves (mint, lemongrass, jamrosa), stems (geranium, verbena, cinnamon), or seeds (fennel, coriander, nutmeg). Essential oils are widely used in various domains due to their beneficial properties such as fragrance, flavors, and medical properties [4]. Essential oils such as eucalyptus, rosemary, tea tree, lemongrass, etc. possess natural antibacterial properties, being a natural alternative to the use of antibiotics and chemical additives [5]. Textile functionalization with essential oils can help inhibit the growth of bacteria and fungi, enhancing the hygiene of fabric-based products. Microencapsulation of essential oils and embedding into clothing fibers assure the resilience and durability of treatment and allow the fragrance and beneficial effect to be released gradually over time [6,7].

2. MATERIALS AND METHOD

2.1 Sample preparation

Textile materials: Sample 1 – 80 % Cotton / 20% Elastane, Sample 2 – 45 % Cotton / 55 % Polyester, were treated with 2 types of essential oils: pine essential oil and eucalyptus essential oil of 0.002% concentration. The textiles were washed for 30 minutes at 30°C with Kemapon PC/LF solution. Subsequently, they were rinsed twice with warm water (30°C) and once with cold water (20°C) and dried freely at room temperature.

Two treatment solutions with essential oils (pine essential oil and eucalyptus essential oil) of 0.002% concentration were obtained. Initially, a 1% gum Arabic solution was made to which the corresponding quantity of essential oil dissolved in ethyl alcohol was added by dripping. The three textile samples were treated by exhaustion with the two solutions obtained for 30 min at 40°C. The Ugolini apparatus was used with a 1:10 hydromodulus (500 mL float). After the treatment, the samples were dried freely at room temperature for 24 hours.

2.2 Method and equipment

Main constituents of essential oil of pine, eucalypt from textile materials were determined by Gas Chromatography-Mass Spectrometry (GC-MS) on an Agilent 6890N Gas Chromatograph System, 5973N MS detector (70 eV), Agilent ChemStation software, ZB-5MSi (5%, 95% dimethylpolysiloxane), 0.25 µm x 30 m x 0.25 mm column. The GC operating conditions were as follows: 100 to 310ºC at a heating rate of 5 ºC/min and then isothermally held for 2 min, injector temperature of 260ºC, injected volume was of 1µL of the volatile oil, split less, with flow rate of 1.0 mL/min, He gas used as carrier gas. MS detector parameters were as follows: ionization voltage: 70 eV; ion source temperature 280 ºC, mass range: 35-500, and scan time 0.32s. The identification of each oil constituent was made by matching unknown peaks with an MS data bank (Wiley 6, NIST02, Mass Finder 2.3 Software).

3. RESULTS AND DISCUSSIONS

3.1. Chromatographic analysis

Chemical compounds were identified for eucalyptus essential oil and pine essential oil. **Fig. 1** presents the GS-MS chromatogram for eucalyptus essential oil. The following compounds were identified in eucalyptus essential oil: a) Caryophyllene oxide, b) m-cymene, c) Eucalyptol, and d) Spathulenol (**Fig. 2**).

Fig. 3 presents the GS-MS chromatogram for pine essential oil. In pine essential oil the following compounds were identified: a) 1R-alpha-Pinene, b) Aromadendrene oxide-(2), c) Caryophyllene (**Fig. 4**).

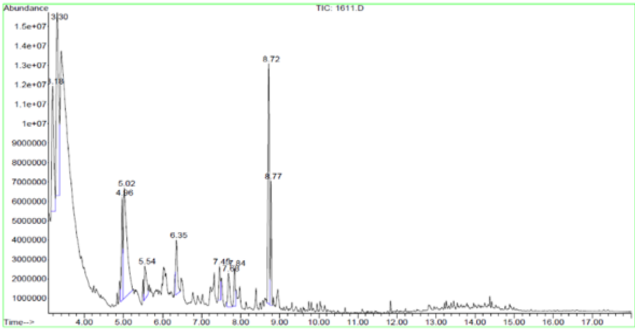
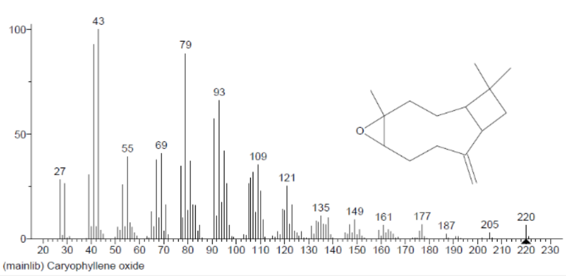
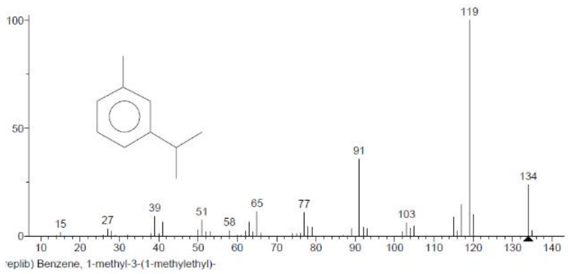


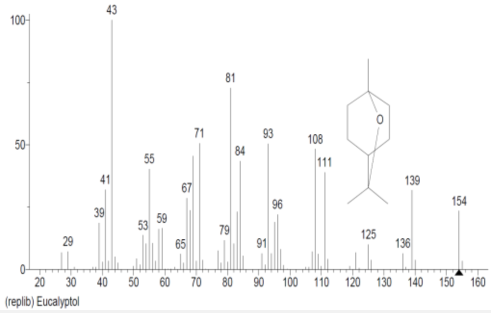
***Fig. 1**. Chromatogram of eucalyptus essential oil*



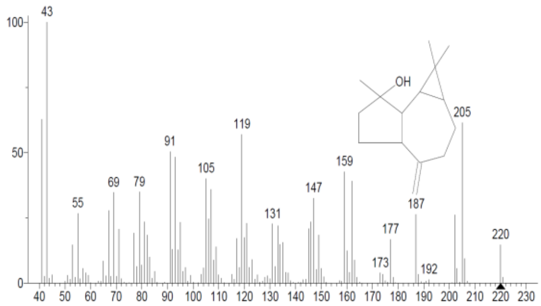
a) caryophyllene oxide



b) m-cymene



c) eucalyptol



d) spathulenol

***Fig. 2**. Compounds identified in eucalyptus essential oil*

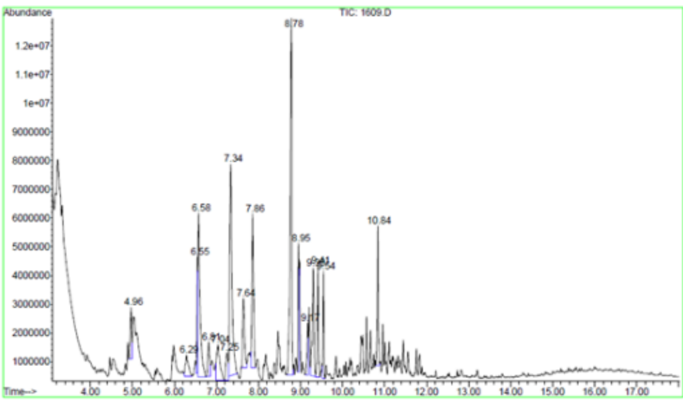
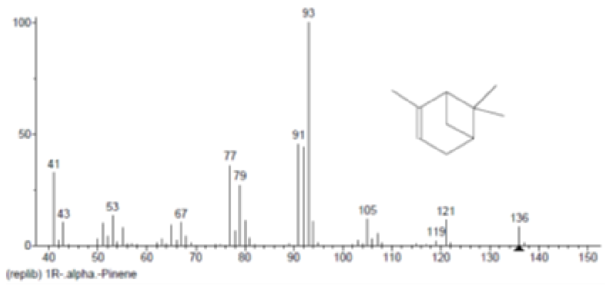
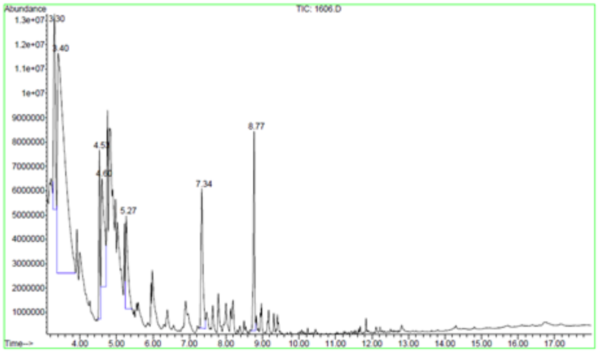
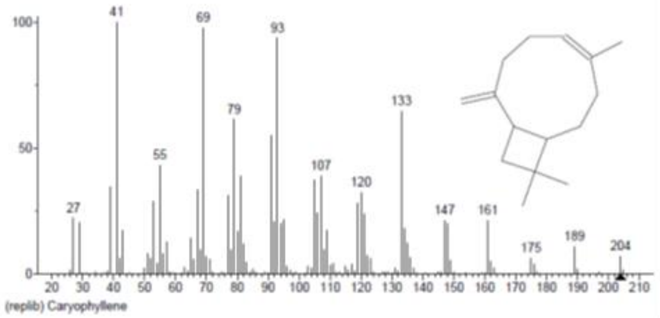


***Fig. 3**. Chromatogram of pine essential oil*





1R-.alpha.-Pinene *Aromadendrene oxide-(2)*



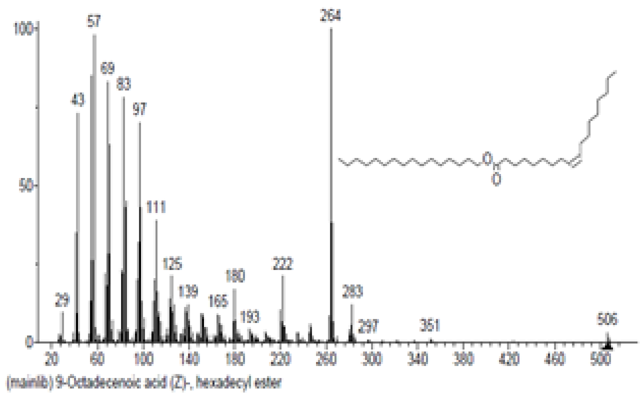
Caryophyllene

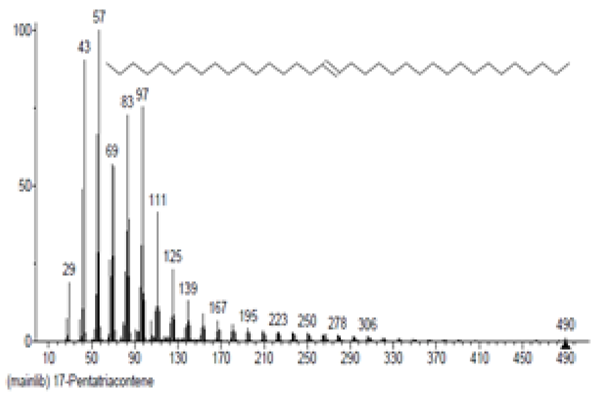
***Fig. 4**. Compounds identified in pine essential oil*

Identification of the chemical compounds of the treated textile structures revealed:

Variant 1- treated with eucalyptus essential oil

For this variant the following chemical compounds were identified: Palmityl oleate, 17-Pentatriacontene, and 1-Tridecene (**Fig. 5 a, b, c**).



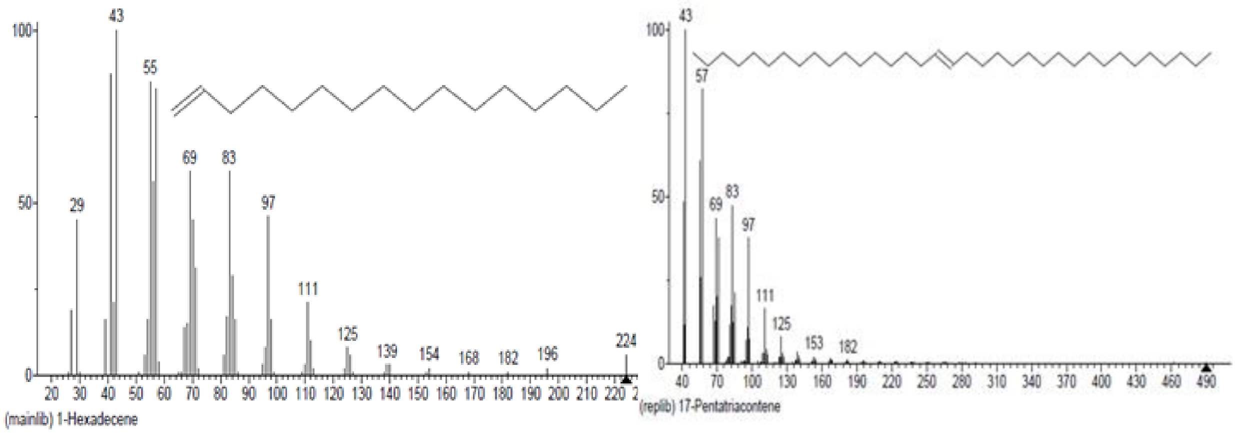


a) Palmityl oleate *b) 17-Pentatriacontene*

***Fig. 5.** Chromatograms of chemical compounds variant 1-treated with eucalyptus oil*

Variant 2- treated with eucalyptus essential oil

For this variant the following chemical compounds were identified: 1-Hexadecene, 17-Pentatriacontene (**Fig. 6 a, b**).

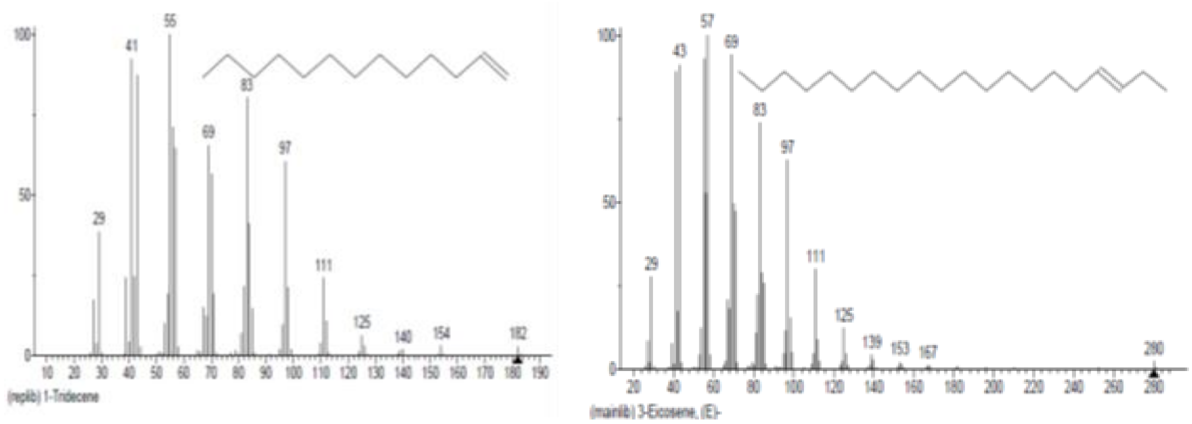


a) 1-Hexadecene *b) 17-Pentatriacontene*

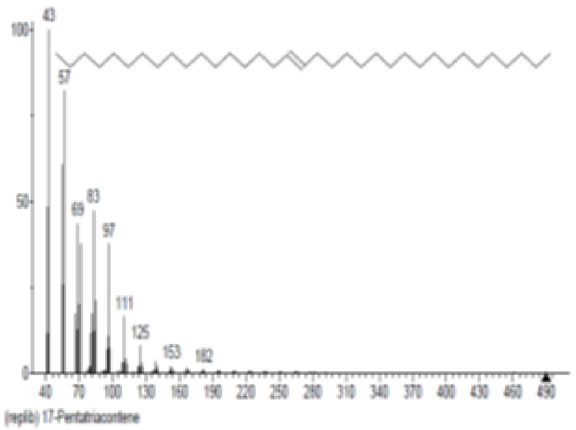
Fig. 6*. Chromatograms of chemical compounds variant 1-treated with eucalyptus oil*

Variant 1- treated with pine essential oil

For this variant the following chemical compounds were identified: 3-Eicosenes, 1-Tridecenes, and 17-Pentatriacontenes (**Fig. 7 a, b, c**).



a) 3-Eicosenes *b) 1-Tridecenes*

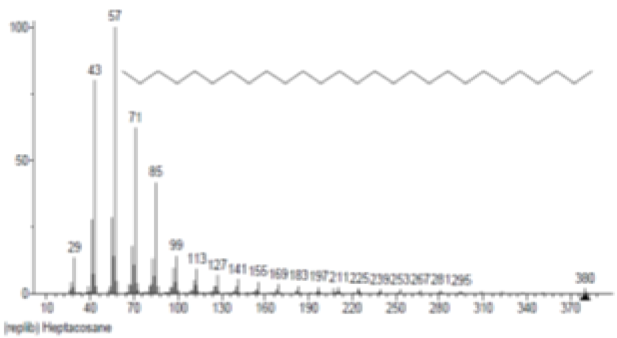


c) 17-Pentatriacontenes

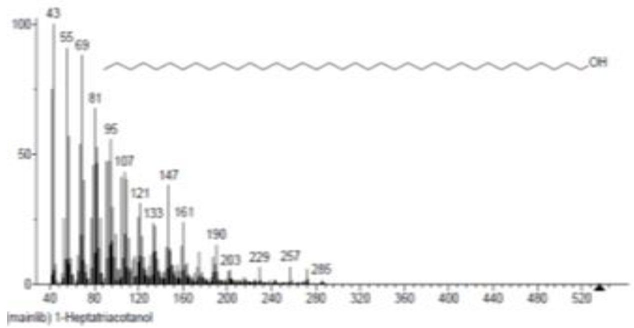
Fig. 7*. Chromatograms of chemical compounds variant 1, treated with pine oil*

Variant 2- treated with pine essential oil

For this variant the following chemical compounds were identified: 1-Heptatriacotanol, 17-Pentatriacontene (**Fig. 8 a, b**).



a) 1-Heptatriacotanol



b) 17-Pentatriacontene

Fig. 8*- Chromatograms chemical compounds variant 2 - treated with pine oil*

Antibacterial activity

The antibacterial activity was evaluated based on SR EN ISO 20645/2005 Textile fabrics - Agar diffusion plate test. The principle of the method is that the specimens are placed on agar plates with two layers. The lower layer consists of a bacteria-free culture medium while the upper layer is seeded with selected bacteria. The level of antibacterial activity is assessed by examining the bacterial growth surface in the contact zone between the agar and the test specimen, and if appropriate the surface of the inhibition zone around the test specimen. The evaluation is based on the absence or presence of bacterial growth in the contact zone between the agar and the specimen and on the appearance of an inhibition zone around the specimen, if any. The tests were performed using the bacteria Staphylococcus aureus ATCC 6538 (gram-positive) and Escherichia coli ATCC10536 (gram-negative) for untreated textiles treated with essential oils of pine, and eucalyptus.The textile structures treated by exhaustion with pine and eucalyptus oil in a concentration of 0.002% and gum Arabic (1%) showed an antibacterial effect on Escherichia coli and Staphylococcus aureus of *satisfactory* level compared to untreated samples *(unsatisfactory*) (**Fig. 9**).

a1) a2) b1) b2)

Fig. 9*. a) untreated sample; b) treated sample – Escheria coli (1); Staphylococcus aureus (2)*

The evaluation is based on the absence or presence of bacterial growth in the contact area between the agar and the sample, and on the possible appearance of an inhibition zone around the samples.

The width of the inhibition zone—that is, the area without bacteria near the edge of the test tube—is calculated using the following formula (1):

$$H = (D - d) / 2 \tag{1}$$

Where:
H = inhibition zone, in millimeters;
D=total diameter of the test tube and the inhibition zone, in millimeters;
d = diameter of the test tube, in millimeters.
A zone of inhibition greater than 1 mm, without any multiplication, means a *satisfactory effect***.** For the initial samples, the H values were between 2.5-11 and after washing, between 1-1.5.

CONCLUSION

Analysis of the volatile oils by GC-MS revealed the following phyto compounds: mono/sesqiterpenoids: 17-pentatriacontene, tridecen, hexadecen, heptacosan, eicosene, and pentatriacotanol, identified by NIST mass spectra library [8]. In all 4 samples treated with eucalyptus/pin essential oil, the compound 17-Pentatriacontene, belonging to the terpenoid class, was identified. This compound is a decomposition radical resulting from ionisation specific to the GC-MS method of analysis and is commonly found in the chromatographic analysis of essential oils, as specified in the literature [9]. The textile structures treated by exhaustion with pine and eucalyptus oil in a concentration of 0.002% and gum Arabic 1% showed an antibacterial effect on Escherichia coli and Staphylococcus aureus of a *satisfactory* level compared to untreated samples *(unsatisfactory*). For the initial samples, the H values were between 2.5-11 and after washing, between 1-1.5. The durability of the treatment is being studied further.

ACKNOWLEDGEMENTS

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REFERENCES

[1] Council of Europe, European Directorate for the Quality of Medicines & HealthCare (EDQM). In
European Pharmacopoeia, 10th ed.; EDQM, 2021, Strasbourg, France.

[2] H. A. El-Shemy, "*Active ingredients from aromatic and medicinal plants*", InTech, Croatia,
2017, http://dx.doi.org/10.5772/67161.

[3] C. Benchaar, H. Greathead, "Essential oils and opportunities to mitigate enteric methane emissions from ruminants", Anim. Feed Sci. Technol., 2011, pp. 166–167, 338–355, https://doi.org/10.1016/j.anifeedsci.2011.04.024.

[4] A. Lubbe, R. Verpoorte, "*Cultivation of medicinal and aromatic plants for specialty industrial*
materials", Ind. Crop. Prod., 34, pp. 785–801, 2011, https://doi.org/10.1016/j.indcrop.2011.01.019.

[5] A.P. DaCunha, M.T. Nogueira, O. Rodrigues Roque, " *Barroso. J.M.G. Plantas Aromáticas e Óleos Essenciais: Composição e Aplicações*", Fundação Gulbenkian: ISBN 978-972-31-1450-8, 2012.

[6] V. I. Sousa, J.F. Parente, J.F. Marques, M.A. Forte, C.J. Tavares, "*Microencapsulation of*
Essential Oils: A Review". Polymers , 14, pp. 1730, 2022,. https://doi.org/10.3390/polym14091730.

[7] C. Pinheiro, N. Belino, P. Roshan, "Application of microencapsulated natural oils in the development of functionalized sustainable clothing", Annals of the University of Oradea - Fascicle of textiles, leatherwork, vol. XX, pp. 13-18, 2019.

[8] National Institute of Standards and Technology, Mass Spectrometry Data Center – NEW https://chemdata.nist.gov/

[9] D. Salaria, R. Rolta, A. Prakash, et al., "*In silico and In vitro Antibacterial Activity of Essential oil of Eucalyptus globulus Labill*" PREPRINT (Version 1) available at Research Square, 2023, https://doi.org/10.21203/rs.3.rs-3415356/v1.