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“Sustainable Beauty from the Garden: Bio-resins Derived from Tomato Skin”

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1. Introduction

This study [1] investigates the utilization of waste materials from industrial tomato processing for the development of cosmetic ingredients. Specifically, it examines the use of tomato peels (cutin) to synthesize polyesters with a high natural content (biopolyesters), which can be incorporated into various cosmetic products.

The primary chemical compound obtained through cutin depolymerization is 10,16-dihydroxyhexadecanoic acid (10,16-diHDA). In recent years, the principles of upcycling and the circular economy have become increasingly important as industries seek effective solutions to mitigate and recycle their environmental impact in the fight against climate change.

Research across all industrial sectors is focused on discovering innovative technological solutions that utilize waste products, fostering synergies and relationships based on industrial symbiosis. The cosmetic industry, in particular, is well-positioned to adopt upcycling practices by using waste materials. Concurrently, the industry is moving towards the use of more natural materials.

The adoption of renewable raw materials of natural origin offers several benefits, including enhanced profitability and competitiveness of products, innovation potential, improved environmental performance, and product diversification. However, these advantages may be accompanied by challenges such as higher production costs, price fluctuations of renewable sources, and the difficulty of achieving the same quality or functional properties as fossil fuel-based raw materials, which is crucial in decorative cosmetics. Additionally, regulatory studies are necessary to ensure the safety of these products for consumers and the environment.

By utilizing by-products from industrial processing, new sustainable raw materials can be developed to replace fossil-based ones, thereby reducing environmental impact in both raw material production and waste disposal. Recently, two parameters have been introduced to assess the natural origin of cosmetic raw materials and products: the Natural Origin Index (NOI), also known as the "naturalness index," and the Natural Origin Content (NOC), as defined by the ISO 16128-2:2017 standard "Guidelines on technical definitions and criteria for natural and organic cosmetic ingredients — Part 2: Criteria for ingredients and products."

The NOI indicates the extent to which a cosmetic ingredient meets the definition of a natural ingredient, derived natural ingredient, or mineral-derived ingredient, as specified in the ISO 16128-1:2016 standard "Guidelines on technical definitions and criteria for natural and organic cosmetic ingredients and products — Part 1: Definitions for ingredients." The NOI ranges from >0.5 to ≤1, with 1 representing the highest degree of natural origin. Ingredients with a calculated value of ≤0.5 have an NOI of 0.

The NOC of a product is the mass percentage, ranging from 0% to 100%, of all natural ingredients, natural portions of ingredients, and ingredients of natural origin in the product. It is calculated as the sum of the relative concentrations of the ingredients in a product, multiplied by their corresponding NOI.

These parameters are widely used today to position cosmetic ingredients and products in terms of naturalness, primarily considering the origin of the raw material and the production process. The demand for cosmetics with a high natural index is now commonplace, reflecting increasing consumer awareness and perception of sustainability.

Polyesters are polymers formed through the condensation of polycarboxylic acids and polyols, incorporating ester functional groups along the main carbon chain. Depending on the monomers used for their synthesis and the orientation of the polymeric chains, polyesters can exhibit various characteristics that determine their applications. Polyesters are utilized in numerous fields, including textiles, paper, cleaning products, and cosmetics. Many ingredients commonly used in the cosmetic industry belong to this chemical class and can be combined to create stable final products.

The synthesis of polyesters involves a polycondensation reaction, where an ester group is formed between the carboxylic group of the acid and the hydroxyl group of the alcohol, with the release of a water molecule. The mechanism can be summarized by the following general formula:

$$\text{HOOC-R'-COOH} + \text{HO-R-OH} \rightleftarrows [\text{-R'COOR-}]n + n\text{H2O}$$

The reaction is at equilibrium; by working with equimolar quantities of acid and alcohol, a complete transformation can be reached through the elimination of the water produced and shifting the equilibrium toward the products, according to Le Chatelier’s principle. To enhance the reaction speed, acid or metallic or enzymatic catalyzers are used, lowering the activation energy, so stabilizing the transition state.

Various studies have been conducted on the synthesis of biopolymers derived from tomato cutin or 10,16-dihydroxyhexadecanoic acid (10,16-diHDA), including some by the start-up Tomapaint. However, none of these studies have explored applications in the cosmetic field. Instead, the research focuses on the use of bioresin in the food industry, particularly as an internal coating for tin cans used for preserving food [2,3].

TomaPaint is an innovative Italian green Start-up. Meets the demand for sustainable production and for the safeguarding of consumer health by aligning with the principles of the circular economy, valorizing agro-industrial by-products and using renewable resources.

This is thanks to a patented process for extracting cutin from tomatoes industrial by-products [4,5], a component that is the basis to produce the innovative Bio-polyester.

2. Materials and Methods

The depolymerization product of cutin extracted from tomato peels represents the key component of the synthesized cosmetic ingredients. The other components are monomers and oligomers of natural origin or derived from natural sources, particularly from vegetal sources.

The work objective is achieved by preparing cosmetic ingredients (biopolyesters) using the following reagents:

a. Product of cutin depolymerization extracted from peels that are waste products of tomato industrial processing;

b. A short diol or polyol (C2-C8);

c. A long diol or polyol with a high molecular weight, i.e., greater than 500 Daltons, comprising at least 20 carbon atoms;

d. A dicarboxylic acid (C4-C50).

<u>REAGENT a</u>:

The main component of tomato (Solanum lycopersicum L.) is cutin, a non-toxic and biodegradable biopolyester, made of esterified hydroxy acids having 16 and 18 carbon atoms. Cutin can undergo extraction processes which allow to obtain such monomers, the main one being 10,16-dihydroxyhexadecanoic acid. By exploiting the functional groups of such acid, polymers of high molecular weight can be synthetized through polycondensation reactions, that can be used in cosmetic compositions in order to replace raw materials of fossil origin.

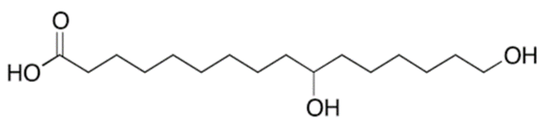

Fig.1 - 10,16-dihydroxyhexadecanoic acid

The depolymerization products of cutin can be obtained through various extraction techniques starting from tomato peels, which are the primary by-product of tomato processing for the production of tomato preserves.

Preferably, a product of tomato cutin depolymerization with a high content of 10,16-dihydroxyhexadecanoic acid, not less than 60%, is used. This product can be obtained through the techniques described in the aforementioned Tomapaint patent applications.

The product of cutin depolymerization appears as a sticky mass that does not dry at room temperature and conforms to the shape of its container.

Fig.2 - Product of cutin depolymerization

Its brownish color is due to the presence of lycopene, the carotenoid responsible for the red color of tomatoes. Gas chromatographic analysis reveals that the product primarily consists of 10,16-dihydroxyhexadecanoic acid. Other components include 4-hydroxycinnamic acid and its isomers, sebacic acid, and 9,12-octadecadienoic acid, as shown in Table 1.

Table 1: Principal component of cutin depolimerization

Componente	**%w/w**
10,16-dihydroxyhexadecanoic acid	62%
4-hydroxycinnamic acid	9%
sebacic acid	9%
9,12-octadecadienoic acid	7%

<u>REAGENT b</u>:

The second reagent in the synthesis of biopolyesters is a short diol or polyol, defined as a diol or polyol with a carbon chain comprising 2 to 8 carbon atoms (C2-C8). These short diols of natural origin are derived from glucose fermentation, a by-product of cane sugar processing.

Examples include pentylene glycol, commercially known as Hydrolite 5 – Green (Symrise), caprylyl glycol, commercially known as Hydrolite 8 – Green (Symrise), propanediol, commercially known as Zemea Propanediol (DuPont Tate), and hexanediol.

REAGENT c:
The third reagent in the synthesis of biopolyesters is a high molecular weight diol or polyol (long diol) with a molecular weight exceeding 500 Daltons and a carbon chain containing more than 20 carbon atoms. Preferred diols include hydrogenated dilinoleyl alcohol, castor oil, hydro-genated castor oil, esters of polyglycerols with more than 20 carbon atoms, and diol esters composed of natural or naturally derived components.

REAGENT d:
The fourth reagent in the synthesis of biopolymers is a dicarboxylic acid with a chain comprising 4-50 carbon atoms (C4-C50). Have been used succinic acid (C4), azelaic acid (C9), sebacic acid (C10), dilinoleic acid (C36), and similar compounds. Examples of commercially available dicarboxylic acids with guaranteed vegetal origins include azelaic acid, marketed as Matrilox CA001M (Matrica), derived from the transformation of vegetal oils such as high oleic sunflower oil grown in Italy and Europe; succinic acid, marketed as Biosuccinum (Roquette), produced through a "carbon negative" biomass fermentation method; and dilinoleic acid, marketed as Pripol 1009 (Cargill), derived from linseed oil.

Synthesis of the cosmetic ingredient
Obtaining a material suitable for cosmetic use from the product of cutin depolymerization proved challenging. Homopolymerization tests yielded a rubbery elastomer that is difficult to use due to its complete insolubility and non-dispersibility in common cosmetic oils. The presence of multiple reaction sites on the same molecule leads to undesirable cross-linking, which is difficult to control.
Furthermore, reacting the product of cutin depolymerization with polyols (diols and triols) in a stoichiometric ratio or in excess results in the formation of solid elastomeric structures, which are unsuitable as cosmetic raw materials.
The synthesis have been designed to have a bioplyesters with fluid aspect and suitable to use in cosmetic composition. This was achieved by combining short and long diols or polyols, allowing the dissolution of the cutin depolymerization product and the dilution of its reactive groups.The optimal percentage of the cutin depolymerization product in the biopolyesters ranges from 8% to 15%
We have to choose a high molecular weight diol or polyol (long diol or polyol) was used, with a molecular weight greater than 500 Daltons, making it more viscous compared to the other

alcohols used. A naturally derived bifunctional carboxylic acid was chosen to promote the polycondensation reaction with the diols. The concentration of the cutin depolymerization product was optimized to prevent 10,16-dihydroxyhexadecanoic acid from reacting with other molecules of the same acid, which would lead to the previously described solid structures.
This approach resulted in a fluid and highly viscous product, but it contained insoluble particles that made it non-homogeneous and cloudy. The solubility of the cutin depolymerization product was then tested in various solvents, identifying the family of short diols or polyols as good solvents for this product. The short diols or polyols capable of solubilizing cutin are compounds with a maximum of 8 carbon atoms and glycerol, with which the cutin depolymerization product can be mixed in any ratio. An additional step was then added to the synthesis method, preceding the addition of other reagents, where the cutin depolymerization product is pre-dispersed, preferably in pentylene glycol or glycerol. Pentylene glycol has two OH groups (glycerol has three) and can participate in the esterification reaction. This final precaution led to a transparent and homogeneous product.

Typical Composition and Synthesis Procedure:
The reaction mixture involves homogenizing cutin with the short diol to make the system as fluid and workable as possible. Then, the other reactants are added, such as the long diol, fatty acid, and any solvent. The stoichiometric ratio typically used for the production of polyesters is equimolar, preferably with an excess of overall OH groups to ensure the polymer is terminated with hydroxyl groups and has relatively low residual acidity. To speed up the reaction, in addition to removing the water formed during synthesis by high vacuum to shift the equilibrium towards the products, a catalyst (e.g., tin oxalate or tin octanoate) is added in the range of 0.001% to 1% by weight, preferably between 0.05% and 0.5%. The reaction is conducted between 120°C and 200°C for a period ranging from 5 to 12 hours, under dynamic vacuum. The cosmetic oil functioning as a solvent, if required by the synthesis, is added at the beginning of the reaction if non-volatile or at the end of the reaction if volatile.
The reaction is monitored by measuring the residual acidic functionalities, generally below 20 mgKOH/g in the final product (preferably between 5 – 10 mgKOH/g), using infrared spectroscopy to verify the appearance of the characteristic ester peak (shifting from 1700 cm^{-1}, typical peak of COOH of the dicarboxylic acid, to 1740 cm^{-1}, typical peak of the formation of the ester COOR). Then, a molecular weight check is performed on the final product, which must be above 5000 Daltons (preferably around 20000 Daltons), and the presence of residues between 1000 Daltons and 5000 Daltons must be limited for cosmetic safety.

3. Results

The polyesters described in this work can take a linear, branched or cross-linked structure according to the composition and to the internal ratio of the monomers and oligomers constituting the polymer.

The characteristics of the final biopolyesters for cosmetic use are significantly influenced by the choice of reagents, which can result in linear, branched, or cross-linked polymers with varying cosmetic properties. The addition of a high molecular weight diol or polyol (greater than 500 Dalton) is intended to achieve a softer polymer structure, making the final product suitable for cosmetic applications. Conversely, the inclusion of a short diol or polyol is aimed at solubilizing and softening cutin, thereby ensuring a homogeneous reaction mixture and solubilizing all reagents.

In particular, we focused on obtaining a linear polymer (Fig.3 and Table 2) with a high Natural Origin Index (NOI) according to ISO 16128. Specifically, the biopolyesters have an NOI 1 and a molecular weight greater than 5000 Daltons, with residues not lower than 1000 Daltons.

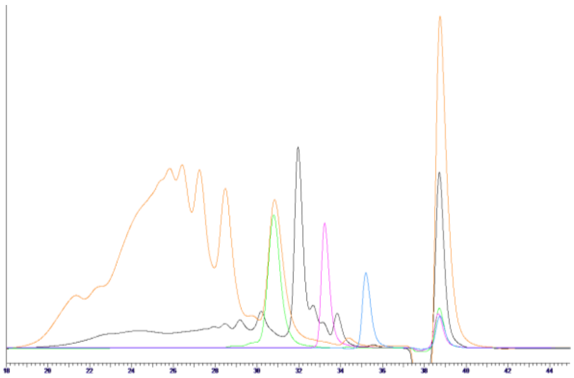

Fig.3 - Overlay GPC of Biopolyester (orange) and its Building Blocks (Black: cutin, Pink: azelaic acid, Green: Hydrogenated Dilinoleyl Alcohol, Blu: pentylene glycol)

Table 2: Principal caratheristics of new biopolyester:

INCI name	***Composition***	***Viscosity cP***	***NOI***	***Colour***
Polyester-43	100%	15000-30000	1	Dark red

4. Conclusion

In conclusion, this study demonstrates the potential to transform a by-product of the tomato industry into a valuable material with excellent cosmetic properties for use in finished products. The synthesized polyesters can effectively replace fossil-based raw materials, such as hydrogenated polyisobutenes, polyurethanes, and non-natural esters, offering similar features while significantly enhancing the natural index of the final cosmetic formulations.

Revalorizing an agri-food by-product like tomato peel to bestow it with a more prestigious second life is no trivial feat. However, with the optimal proportions of reactants and precise synthesis parameters, the resulting material exhibits ideal performance for cosmetic applications.

5. Reference

[1] PCT/IB2025/052335 Cosmetic ingredients containing a polymer derived from tomato cutin or 10,16-dihydroxyhexadecanoic acid usable in cosmetic compositions, and method for preparation thereof

[2] A. Montanari et al., Tomato bio-based lacquer for sustainable metal packaging Acta Horticulturae 1159 XIV International Symposium on Processing Tomato Article number 1159_24 pages 159-166 https://doi.org/10.17660/ActaHortic.2017.1159.24

[3] A. Cifarelli et al. Physical–Chemical Characteristics of Cutin Separated from Tomato Waste for the Preparation of Bio-lacquers. Advances in Sciences and Engineering, 2019 https://doi.org/10.32732/ase.2019.11.1.33.

[4] WO2015028299A1 Extraction method of a polyester polymer or cutin from the wasted tomato peels and polyester polymer so extracted

[5] EP4116352A1 Process for the extraction of cutin from tomato processing waste