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RESEARCH ARTICLE — OPEN ACCESS

Substitution of synthetic waxes by plant-based waxes in lipsticks☆

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Abstract – The ultimate symbol of femininity, lipstick is often a brand's most attractive makeup product. First created several thousand years ago, its composition has evolved a great deal since then, particularly in the 20th century, when petroleum and its derivatives were discovered. But today, with the emergence of Clean Beauty, customers are looking to go back to more natural compositions that respect the environment and their health. However, the total substitution of synthetic waxes has inevitably brought with its problems of product stability, lipstick solidity, sweating, incompatibilities and oxidation, which today's ever more demanding consumers are not ready to accept. Beyond stability, the sensoriality and the performance of lipsticks can be altered by such substitution. The objective of this study is therefore to find plant-based substitutes for synthetic waxes, which do not reduce the stability and the overall quality of lipsticks. To this end, the physicochemical properties of plant-based waxes will first be measured, and the best candidates will then be introduced into an all-natural lipstick formula. Some waxes tested have a value equivalent to synthetic wax on one physico-chemical parameter but are less efficient on another. The mixtures of waxes with oils of different polarities show that no wax is as ubiquitous as petroleum wax. To conclude, none of the waxes evaluated can substitute the synthetic wax weight for weight in a formula.

Keywords: synthetic wax / lipstick / petroleum-based / cosmetic formulation / substitution

Résumé – Substitution des cires synthétiques par des cires d'origine végétale dans les rouges à lèvres. Symbole absolu de féminité, le rouge à lèvres est souvent le produit de maquillage le plus attractif d'une marque. Né il y a plusieurs milliers d'années, sa composition a depuis beaucoup évolué, en particulier au XX^e^ siècle lors de la découverte du pétrole et de ses dérivés. Mais aujourd'hui, avec l'émergence de la Clean Beauty, les clients cherchent à revenir vers des compositions plus naturelles, respectueuses de l'environnement et de leur santé. Cependant, la substitution totale des cires synthétiques a fait inévitablement resurgir des problèmes de stabilité du produit, de solidité du rouge à lèvres, d'exsudation, d'incompatibilités et d'oxydation, avec lesquels les consommateurs toujours plus exigeants ne sont pas prêts à composer. Au-delà de la stabilité, la sensorialité et les performances du rouges à lèvres peuvent se trouver altérées par cette substitution. L'objectif de cette étude est donc de trouver des substituts d'origine végétale aux cires synthétiques ne diminuant pas la stabilité et la qualité globale des rouges à lèvres. Dans cet objectif, les propriétés physico-chimiques des cires végétales seront d'abord mesurées et les meilleurs candidats ensuite introduits dans une formule de rouge à lèvres entièrement naturelle. Certaines cires testées présentent certaines valeurs physico-chimiques équivalentes à la cire synthétique d'origine pétrosourcée mais sont moins performantes sur d'autres paramètres. Les mélanges de cires avec des huiles de différentes polarités montrent qu'aucune cire n'est aussi ubiquitaire en termes de compatibilité que la cire synthétique. Pour conclure, aucune des cires évaluées ne peut substituer poids pour poids la cire synthétique dans une formule.

Mots clés : cire synthétique / rouge à lèvres / pétrosourcé / formulation cosmétique / substitution

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1 Introduction

An essential part of any makeup kit, lipstick is one of the most widely used cosmetics. It is also the most accessible product of a brand (de Clermont-Gallerande, 2006). First used around 5000 years ago in Mesopotamia, it has seen its composition change greatly over time, notably over the past 25 years (L'Oréal, 2021). Indeed, without customers necessarily realizing it, toxicological and regulatory constraints, as well as cosmetic trends, have largely imposed on formulators the need to adapt the compositions of lipsticks, so that today's lipsticks are very different from those of the past. For the last ten years, the phenomenon of Clean Beauty has taken an increasingly significant role in the cosmetics market. Consumers, helped by apps and labels, are now ever more attentive to the products they buy, and are clearly looking for more natural compositions (de Clermont-Gallerande, 2020). Environmental assessments after the health crisis highlighted a 50% to 70% reduction in nitrogen dioxide emissions during lockdown, proof of the indisputable link between human health and the health of the planet (Pin, 2020). The pandemic has generated a collective awareness, and increased demand for natural products (Utroske, 2017). To meet this demand for the withdrawal of controversial ingredients, either for publicity reasons, or for more effective naturalness, formulators have no choice but to gradually modify their portfolios of raw materials. Over the last five years, an increasing number of lip products, claiming to be natural, and therefore, by definition, free of synthetic or petroleum-based materials, have emerged (Mintel, 2021).

In this article, we will focus on finding high-performance plant-based waxes to replace synthetic waxes, which are still present in most lipsticks on the market.

2 The current state of the art

2.1 Composition of lipsticks

A classic lipstick is an anhydrous product, mainly made up of waxes (10–20%), oils (40–60%), and fat-pastes (5–10%), forming what is known as the white body. The white body orients the general structure of the lipstick, influencing properties such as hardness, smoothness, softness, and shine (de Clermont-Gallerande *et al.*, 2018). Thus, formulators must adapt the proportions of oils, waxes and pastes, according to the desired finish. Oils bring shine, softness, and smoothness, and waxes bring hardness and hold (Abidh *et al.*, 2019). Added to the white body, are 5 to 15% of pigments and pearl scent agents, and possibly active ingredients (anti-aging, anti-UV, etc.), (0–5%), and a fragrance (0–1%).

In fact, the wax originally used was exclusively beeswax. Then, much later, in the twentieth century, plant-based waxes were included, such as Carnauba wax or Candelilla wax, other animal waxes, such as spermaceti (sperm whale wax) or lanolin, and, with the discovery of petroleum waxes, from mineral and synthetic origins such as polymers and silicones (de Clermont-Gallerande, 2006).

2.2 Mineral waxes

Mineral waxes have several significant advantages that explain their presence in most modern lipsticks. First, they considerably improve the firmness of sticks, and limit the phenomena of exudation. They are also considered to have excellent oxidative stability, as they only become rancid very slowly in air and light. Mineral waxes are also able to form a waterproof film that adheres to the epidermis, and this helps to preserve the hydration of the skin. On another level, they are also cheap raw materials (Brochette, 2017).

The reason we are now seeking to replace them is because they are, among other things, a source of environmental pollution. There are also real risks to human health (Cosmetics Europe, 2018). As they come from petroleum refining, they may still contain small amounts of polycyclic aromatic hydrocarbons (PAHs), compounds that are classed as highly carcinogenic (Cosmeticobs, 2010). In the case of lipsticks, this is even more worrying as users inevitably ingest part of the product. PAHs, being lipophilic, tend to accumulate in fatty tissues such as the liver or spleen, and present a real long-term danger. For all these reasons, mineral waxes do attract good publicity, and claiming to be "free of any petrochemical origin ingredient" is a real selling point for customers, hence brands' desire to find natural substitutes for these waxes.

Among the mineral waxes used for the formulation of lipsticks, we exclusively find highly nonpolar waxes, composed of a mixture of hydrocarbons (Tab. 1). There is, for example, Ceresin, obtained by the purification of ozokerite, a natural wax extracted from petroleum deposits. There is also microcrystalline wax (*Cera Microcristallina*), formed by a dense and plastic network of small crystals, and bringing a lot of suppleness to lipsticks. Finally, there is paraffin wax, obtained by treating the heavy fraction resulting from the distillation of petroleum (Brochette, 2017).

2.3 Synthetic-based waxes

The synthetic-based waxes present in lipsticks can be polymers or silicone waxes. The major advantage of synthetic waxes is that they are waxes with a high melting point, and without exhibiting polymorphism. However, most of them are petroleum-based, and industrials therefore seek to substitute them as much as mineral waxes (Brochette, 2017; Mintel, 2021).

2.4 Plant-based waxes

There are several plant-based waxes used in the formulation of lipsticks. However, since the arrival of mineral and synthetic waxes, the waxy composition of a lipstick rarely comes down to the simple use of plant-based waxes, but rather a mixture of plant-based and petroleum-based waxes. Indeed, plant-based waxes bring hardness and shine to lipsticks, but are particularly subject to oxidation, rancidity, and polymorphic crystallization, potentiating the risk of exudation. From a sensory point of view, they often have poorer smoothness and softness qualities than petroleum-based waxes (de Clermont-Gallerande *et al.* 2018). This explains why the latter have been so successful. To promise customers the same quality, the same comfort, the same stability, and the same hold, it now appears difficult to do without them, and this is the entire objective of this study.

Table 1. List of the main mineral and plant-based waxes used in the formulation of lipsticks.

Mineral waxes			
Commercial Name	INCI name	Composition	Melting point (°C)
Ceresin	*Ceresin*	Linear and cyclic hydrocarbons C29-C35	55–80
Microcristalline wax	*Cera Microcristallina*	Branched alkanes C31-C70	60–95
Paraffin wax	*Paraffin*	Linear and cyclic hydrocarbons C16-C40	50–70
Plant-based waxes			
Commercial Name	INCI name	Composition	Melting point (°C)
Candelilla wax	*Candelilla Cera (Euphorbia Cerifera (Candelilla) Wax)*	Hydrocarbons, esters, fatty alcohols and resins	68–73
Carnauba wax	*Cera Carnauba (Copernicia Cerifera (Carnauba) Wax)*	Long chains fatty esters	80–86
Rice wax/ Rice Bran wax	*Oryza Sativa Cera Cera (Oryza Sativa (Rice) Bran Wax)*	Esters, fatty acids and alcohol	75–82
Sunflower wax	*Helianthus Annus Cera Seed (Helianthus Annus (Sunflower) Seed Wax*	Very long chains fatty esters (C40-C60)	74–77

Among the most widely used plant-based waxes (Tab. 1), there is Candelilla wax (*Candelilla Cera* (*Euphorbia Cerifera* (*Candelilla*) *Wax*)), obtained by collecting the waxy deposit naturally appearing on the leaves and stems of a small shrub growing in Mexico and Texas (de Clermont-Gallerande, 2006; Brochette, 2017). Candelilla wax does not have a good reputation, due to the questionable working conditions of Central American harvesters. Indeed, its extraction process uses sulphuric acid, and protective equipment is not always provided to workers by producers (Richardson, 2020). Carnauba wax (*Cera Carnauba* (*Copernicia Cerifera* (*Carnauba*) *Wax*)) is also extracted from the leaves of a tree, a palm tree that grows in South America (de Clermont-Gallerande, 2006). It is probably the hardest plant-based wax with the highest melting point, but it is very brittle, nonetheless. This is particularly useful when removing sticks from molds as it shrinks slightly on cooling (Brochette, 2017). Rice wax and Rice Bran wax (*Oryza Sativa Cera* (*Oryza Sativa* (*Rice*) *Bran Wax*)) are obtained from the husk of rice grains. They are shiny, brittle, and soft waxes. Rice Bran wax is highly valued for its strong binding properties with oils. Sunflower wax (*Helianthus Annus Cera Seed* (*Helianthus Annus* (*Sunflower*) *Seed Wax*)), is obtained by hydrogenating sunflower oil. There are obviously many other plant-based waxes used in the formulation of lipsticks, which are often waxes obtained by simple hydrogenation of plant-based oils such as Jojoba oil, Castor oil, etc. (Rossow, 2008).

The objective of this study is to determine which plant-based wax has the physico-chemical and sensory behaviors closest to those of the petroleum-based waxes traditionally used in lipsticks. The synthetic wax selected as a reference for the purposes of this study is *Ethylene/Propylene Copolymer and Synthetic Wax*, particularly appreciated for its structure, its smoothness, and its compatibility with oils with different polarities. A list of plant-based waxes authorized in cosmetics in products applied to lips, and therefore potential substitutes for our reference wax, has been established. To avoid biasing the results, several qualities of the same wax were identified where possible (Tab. 2). Two natural fatty phase gelling agents (*Tribehenin* and *Glyceryl Behenate/Eicosadioate*) were also added to the list of potential substitutes, which thus includes 13 candidates.

3 Materials and methods

3.1 Selection of waxes

First, physicochemical tests were carried out, with the aim of quickly reducing the number of plant-based candidates listed in Table 2.

The reference, *Ethylene/Propylene Copolymer and Synthetic Wax*, is a lipophilic polymer, with a high melting point and wide melting range (high enthalpy). Its physicochemical characteristics are the reason for the thermal stability of the sticks (thanks to its high melting point of around 85 °C), of their glossiness, and allows for better hold on the lips (de Clermont-Gallerande *et al.*, 2018). Its nonpolar character demonstrates its ability to establish numerous Van der Waals interactions, which is probably partly the reason for its versatile character. This apolarity is also linked to its moisturizing properties, with low-polar fatty substances forming occlusive films on the surface of the epidermis, which prevents water loss through the skin (Vayssière, 2018). Three physicochemical tests make it possible to compare the characteristics of plant-based waxes and the reference wax. These are DSC (Differential Scanning Calorimetry), infrared, and texturometry of wax/oil binaries in the 30/70 ratio. The hypothesis is that the closer the physicochemical characteristics of the waxes are, the greater the organoleptic properties of lipsticks will be. Only the waxes closest to the reference wax will be formulated into lipsticks following the study.

3.1.1 DSC

DSC is a thermal analysis technique that measures the differences in heat exchange between a reference and a sample to be analyzed. It provides information on melting point, start of melting or enthalpy. Solid fats, and crystals more generally,

Table 2. List of candidates for the replacement of *Ethylene/Propylene Copolymer and Synthetic Wax*.

INCI Name	Number of qualities tested
Copernicia Cerifera (Carnauba) wax	2
Oryza Sativa (Rice) Bran wax	2
Candelilla Cera (Euphorbia Cerifera (Candelilla) Wax)	4
Hydrogenated Castor Oil	1
Jojoba Esters	1
Helianthus Annuus Cera Seed (Helianthus Annuus (Sunflower) Seed Wax)	1
Tribehenin	1
Glyceryl Behenate/Eicosadioate	1

can sometimes exhibit what is called polymorphism. Polymorphism is the possibility of forming different types of crystals, depending on external conditions (cooling rate, or storage time, for example). Thus, these different types of crystals, which can coexist, are characterized by different melting points, densities, plasticity, and so forth. different. For some waxes, the cooling rate has an impact on the crystals formed. It is essential to avoid waxes that exhibit this type of polymorphism, in the interests of the stability and repeatability of industrial batches (Kermarec, 2011). Polymorphism can be anticipated from the DSC profile, by successively cooling the sample at different rates.

All these parameters are evaluated for each of the 13 candidates for plant-based waxes, using a differential scanning calorimeter (DSC 25, Discovery DSC Series, TA Instruments, France), connected with a computer to the Trios software (TA Instruments, France), allowing measurements to be performed and the spectra obtained to be analyzed. For each candidate, 11 ± 0.5 mg of wax are taken, and placed in a standard crucible, sealed using a crimper (Tzero Sample Press, TA Instruments, France). The program responds to the following protocol: three heating, one to erase the thermal past of the product, and two after two kinds of cooling. The comparison of the profiles of the second and third heating processes, allows us to draw a conclusion as to the polymorphism or not of each raw material. For all the candidates, two samples are prepared, to ensure the repeatability of measurements.

3.1.2 Infrared

Infrared spectroscopy is used to obtain the infrared absorption spectrum of a sample, and to deduce the chemical groups that make up that sample. In this study, this analytical technique is used to determine the presence or absence of polar groups in the candidate plant-based waxes, for replacement of non-polar synthetic wax. Particular attention is paid to the presence or absence of an absorption band of around 1730 cm^{-1}, characteristic of ketone and ester functions.

These data are retrieved using a Fourier transform infrared spectrometer (Nicolet iS5 FT-IR spectrometer, Thermo Fisher Scientific, United States), connected *via* a computer with the Omnic software (Thermo Fisher Scientific, United States), allowing measurements to be performed and the spectra obtained to be analyzed. For each plant-based wax candidate, a few grams of the raw material are deposited at the infrared light emitting source and crushed using a diamond crystal. The optical range of the device is between 650 and 4000 cm^{-1}.

3.2 Binaries tests

3.2.1 Firmness of binaries

As explained previously, the polarity of a wax is directly related to the interactions it can establish with the other materials in the mixture. The more polar a type is, in the case of waxes, the more it contains bonds with oxygen (OH or CO), and therefore the more it can establish hydrogen bonds. The more apolar it is, the more it establishes Van der Waals type interactions. Theoretically, two types have good compatibility if they have similar polarities, as they can more easily create interactions between themselves. In practice, and in the case of anhydrous products, it turns out that wax/oil interactions do not depend only on the polarity, but also on other parameters, such as the volatility of the oil, or the purity of the wax. So, even though their polarity gives some indication of the compatibility between a wax and an oil, it is best to go through the formulation process, to make sure.

The third selection test thus consists of formulating binaries composed of 30% wax, and 70% oil. This wax/oil ratio corresponds to that which can be found in classic lipsticks. Each candidate plant-based wax is tested with 11 natural oils of different polarities (Tab. 3). The formulation of the binaries is carried out as follows: the two raw materials are mixed at 90–95 °C (depending on the 100% melt of the wax studied), under agitation at 400 rpm with a deflocculator (Turbotest, VMI Linxis Group, France), for 30 minutes. The mixture is poured at 90 °C to 90 °C into four round sealed pots, around 1 cm deep. Several parameters are measured for these binaries: maximum firmness one day after formulation (minimum maturation time for a stable and homogeneous texture), visual appearance and stability two months after formulation at room temperature, 40 and 45 °C.

The measurement of their maximum firmness is useful for understanding the compatibilities between a wax and a given oil. It allows us, for example, to anticipate the gelation of the wax within a stick. This measurement is carried out using a texturometer (TAXTPlus, Micro Stable Systems, United Kingdom), equipped with a 5 kg force cell and its P/2 probe

Table 3. List of oils tested in binaries with their parameters.

	INCI Name	Hansen Solubility parameters			Octanol/water partition coefficient Log Kow
		London dispersion force δd	Keesom Polarity forces δp	Hydrogen bonds δh	
Alcanes	Squalane	15.9	0.1	0.1	14.78
	C15-19 Alkane (Renewable)	15.9	0.1	0.1	8.07
	Isododecane	15.6	0.1	0.1	6.16
Esters	Coco-Caprylate/Caprate	16	2.2	2.7	8.95
	Ethyl Oleate and Ethyl Linoleate and Ethyl Palmitate and Ethyl Stearate and Tocopherol	16.1	2.3	2.9	1.67
Triglycerides	Caprylic/Capric Triglyceride	16.97	7.37	15.5	1.67
	C8-12 Acid Triglyceride	16.4	2.5	3	11.64
Fatty alcohols	Octyldodecanol	16.1	2.2	7.4	8.87
Vegetable oils	Meadowfoam Seed Oil (Limannthes Alba)	16.4	2.8	5	–

Table 4. All-natural lipstick formula in which the candidates were tested.

Raw materials	INCI Name	%
Wax to evaluate		12
Oils	DIISOSTEARYL MALATE – SQUALANE – OCTYLDODECANOL	57.9
Butters and Gelling agents	OCTYLDODECANOL & DISTEARDIMONIUM HECTORITE & PROPYLENE CARBONATE – HYDROGENATED COCONUT OIL	19
Pigments and pearls	MICA & TITANIUM DIOXIDE – CI 77891 (TITANIUM DIOXIDE) & ALUMINUM HYDROXIDE – CI 15850 (RED 7 LAKE)& ALUMINUM HYDROXIDE – FD&C YELLOW N°6 ALUMINIUM LAKE	11
Antioxidant	TOCOPHEROL	0.1

(fine cylindrical tip). The five firmness measurements were taken in one same pot as it never happened that the probe cracked the sample.

This analysis makes it possible to measure the maximum resistance force of the wax/oil mixture during the penetration of the probe, to a depth of 2 mm in the binary, and with a speed of 1 mm/s. To ensure the reproducibility of the analysis, five firmness measurements are taken in the one same pot. The relative difference between measurements should be no more than 10%, and ideally less than 5%.

The firmness measurements provide an initial assessment of wax/oil compatibility. Visual observations on a second pot, and its stability over time (one pot at 40 °C and another at 45 °C), are essential for identifying other defects (heterogeneities, curling, crusts, or white marks), which sometimes indicate incompatibilities within a formula. An evaluation of the surface appearance of each binary is carried out, looking for binaries that are hard, homogeneous, glossy, smooth, and soft, or sometimes completely non-homogeneous.

3.3 Lipstick formulation

The first three selection tests allow the plant-based wax candidates closest to the reference's wax to be picked out. The number of potential substitutes to be used in the complete natural lipstick formula is therefore reduced (Tab. 4).

The lipstick manufacturing process is as follows: the ingredients (wax, oils, pastes, film-forming and gelling agents), are mixed at 450 rpm with a deflocculator (Turbotest, VMI Linxis Group, France) in a beaker at 98 °C, for 30 minutes. The pigments and pearls are then added to the mixture, and left agitating at 400 rpm for 15 minutes. Finally, the active ingredients, the fragrance and the antioxidant are introduced and homogenized for 5 minutes at 400 rpm. The mixture is then poured at 90 °C into molds previously treated with mold release agent. After 10 minutes at ambient temperature, the surplus is leveled. The molds are placed in the freezer for 10 minutes (−17 °C). After 2–3 minutes placed out of the freezer, the sticks are packaged in lipsticks' case.

The sticks obtained are characterized by DSC, cutting wire, hot melt rheology, sensoriality and stability, as compared to a reference stick formulated with the petroleum-based wax.

3.3.1 DSC

The protocol is identical to the one described for waxes. The onset of melting, the melting point, the 100% melting point, the enthalpy, and the polymorphic character, or otherwise of the formula, is determined.

3.3.2 Butter cutting wire

The butter cutting wire allows for a quick assessment of the firmness of a lipstick, notably by measuring the cut resistance of the product in stick form. This measurement is carried out 24 h after formulation, using a texturometer (TAXTPlus, Micro Stable Systems, United Kingdom), equipped with a 5 kg force cell and its Wire Cutter A/BC probe (Swantech, Micro Stable Systems, United Kingdom). It measures the maximum resistance force of the stick during the penetration of the cutting wire, to a depth of 9 mm at a speed of 1.6 mm/s. To ensure the reproducibility of measurements, the analysis is repeated on six sticks, and the relative difference between the measurements should not be greater than 10%, and ideally 5%.

3.3.3 Hot melt rheology

The hot melt rheology method is a method that allows us to anticipate potential problems with the molding of sticks. It is carried out using a rheometer (DHR2 rheometer, TA Instruments, France), connected to a PC with the Trios software (TA Instruments, France).

After heating the product, this method consists of looking at the elastic modulus G' and the viscous modulus G" of the product during a cooling, a stabilization at 20 °C and a stabilization at 35 °C.

We look at the elastic modulus at different temperatures; hot, thus close to 100% melted, to study the risk of imperfections in the final product; at 20 °C at the end of cooling, and at the end of stabilization, to get an idea of the final structure of the product; at 35 °C, to find out how the structure of the product changes when going from 20 to 35 °C, and from this information we derive the percentage of solidity loss between 20 and 35°.

This G’ at different temperatures is a decisive factor, the aim being to have the highest values to obtain the hardest stick. We also need the lowest possible loss of strength between 20 and 35 °C, to avoid excessive changes in texture between these two temperatures, which could affect use.

3.3.4 Sensoriality

The sensoriality (texture and makeup result) of the different lipstick tests is evaluated 24 h after formulation by trained panelists. Each test is applied to the lips according to the following protocol: three passes on the upper lip and three passes on the lower lip. The attributes evaluated are smoothness, softness, comfort, stickiness, and ease of spreading.

3.3.5 Stability

Two lipsticks (1 vertically and 1 horizontally) are placed in 4 ovens at different temperatures: 5, 20, 40 and 45 °C. The sticks are visually assessed on taking them out of the ovens. Their texture is evaluated once the sticks have returned to room temperature. The evaluation times are as follows: 15 days, one month, two months, and three months after formulation.

4 Results and discussion

4.1 Selection of waxes

This first step makes it possible to characterize the potential substitute waxes of the reference mineral wax. The objective is to identify the waxes closest to mineral wax in terms of physico-chemical specifications. The underlying assumption is that similar physico-chemical specifications lead to similar behavior in formulation, sensory properties, and stability.

4.1.1 DSC

From a general point of view, when several qualities of the same wax were tested, the results obtained by DSC and infrared were essentially the same (Tab. 5).

The DSC performed on the reference wax shows a very specific profile (Fig. 1).

The petroleum-based wax has a single, very sharp melting peak. The melting profile is the same whether after slow cooling or rapid cooling. It is therefore a wax that does not exhibit polymorphism, and which can undergo an industrial process with several successive heating, without altering the stability or the texture of the stick. If we compare it with the DSC of Candelilla wax quality B (Fig. 2), we see a very different melting profile.

For Candelilla Wax Quality B, there are several domed peaks from the first temperature rise. These peaks are more defined during the second and third melting, which may indicate slight maturation during storage. Unlike petroleum-based wax, there are two melting peaks, not just one. This means that this wax has two different populations of crystals, but we find them identically, regardless of the cooling rate. Both melting peaks are lower than that of petroleum-based wax, although they are relatively high. Furthermore, none of the plant-based candidates exhibited polymorphism. However, this analysis showed that a good number of candidates did not have the necessary melting point to be able to substitute petroleum-based waxes. Indeed, the reference has a melting point of around 82 °C and using a wax with too low a melting point would inevitably harm the structure of the lipstick. This is the case with waxes from *Candelilla*, *Jojoba Esters*, from *Tribehenin* and *Glyceryl Behenate/Eicosadioate*. *Hydrogenated Castor Oil* has two melting peaks, including one situated in the lipstick stability zone (around 40 °C), which indicates a risk of thermal instability.

4.1.2 Infrared

The infrared analysis revealed the presence of ketone or ester groups in all the plant-based waxes in the study, unlike the petroleum-based wax, and thus, by definition, only hydro-

Table 5. DSC and infrared analysis results.

Waxes		DSC				Infrared	
INCI Name	Quality	Start of melting (°C)	Melting point (°C)	100% melted (°C)	Enthalpy (J/g)	Polymorphism	1730 cm^{-1} signal
Ethylene/Propylene Copolymer & Synthetic Wax	–	25	82	94	240	No	No
Copernicia Cerifera (Carnauba) wax	Quality A	44	83	87	192	No	Yes, low intensity
	Quality B	52	83	87	206	No	Yes, low intensity
Oryza Sativa (Rice) Bran Wax	Quality A	52	84	81	195	No	Yes, medium intensity
	Quality B	46	85	80	190	No	Yes, medium intensity
Candelilla Cera (Euphorbia Cerifera (Candelilla) Wax)	Quality A	53	66	76	112	No	Yes, low intensity
	Quality B	50	68	76	174	No	Yes, low intensity
	Quality C	41	65	80	126	No	Yes, low intensity
	Quality D	38	66	76	134	No	Yes, low intensity
Hydrogenated Castor Oil	–	7	80	83	93	No	Yes, very intense
Jojoba Esters	–	58	70	75	238	No	Yes, medium intensity
Helianthus Annuus Cera Seed (Helianthus Annuus (Sunflower) Seed Wax)	–	58	76	81	231	No	Yes, medium intensity
Tribehenin	–	51	59	63	127	No	Yes, low intensity
Glyceryl Behenate/Eicosadioate	–	48	64	68	125	No	Yes, medium intensity

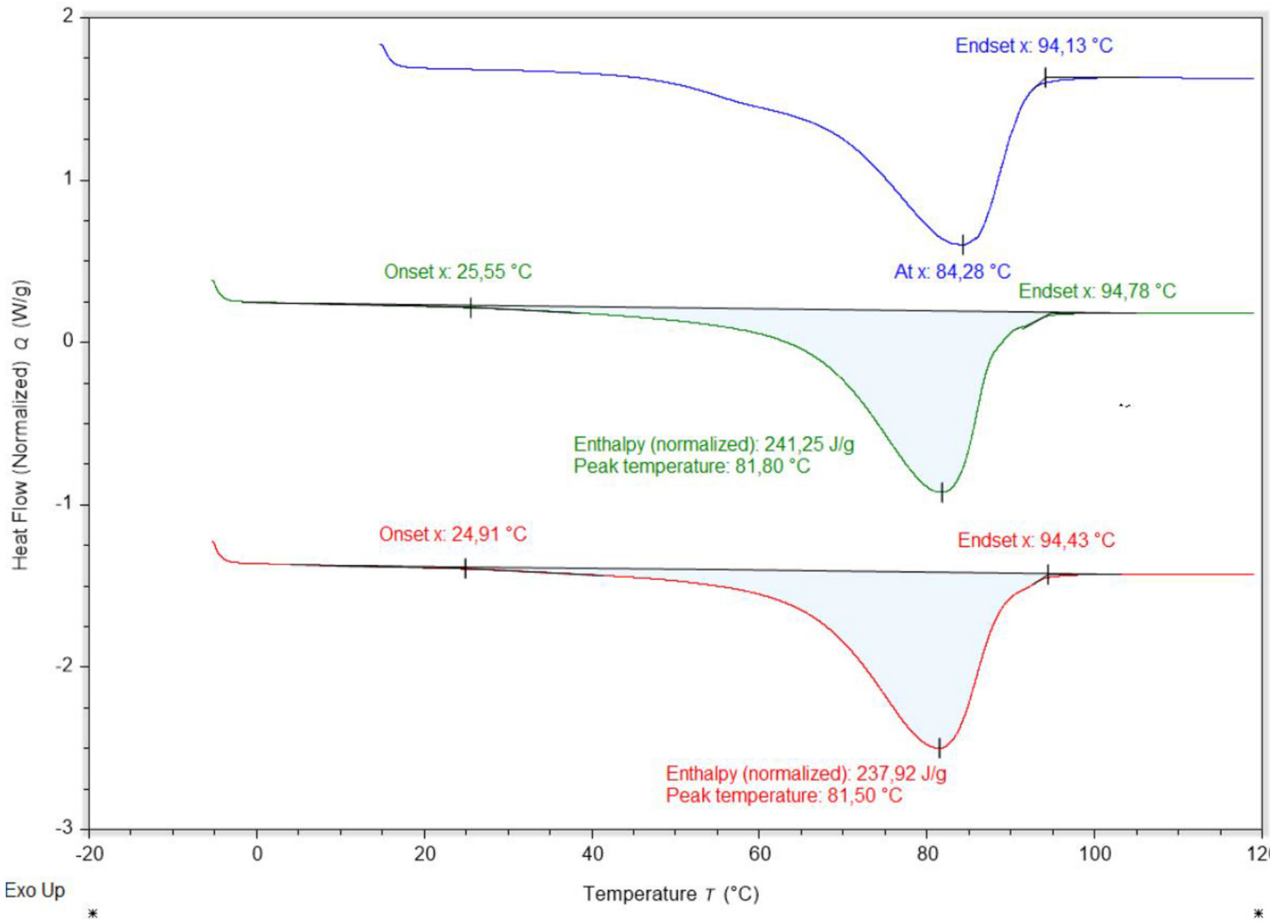

Fig. 1. The DSC of the Ethylene/Propylene Copolymer & Synthetic Wax reference petroleum-based wax.

carbon (Fig. 3). All the candidates therefore contain carbon-oxygen bonds, making them polar. The more carbon-oxygen bonds the wax contains, the more intense the characteristic peak of these bonds are, and the more the wax is polar. Two infrared spectra of vegetable waxes are given as examples (Figs. 4 and 5).

Therefore, in the light of these two analyses, the best plant-based candidates for substituting synthetic petroleum-based waxes are Carnauba wax, Rice wax and Sunflower wax (Fig. 6).

4.2 Binaries tests

These preliminary tests put the wax in the presence of one oil. This makes it possible to know whether the wax is compatible with a wide range of chemical natures of oils or on the contrary a very small chemical group. There are therefore several oils to evaluate for each wax, each with different polarities, variable chain lengths... The goal is to challenge the most ubiquitous waxes, which seem more appropriate for lipstick formulation.

4.2.1 Firmness of the binaries

The behavior of each wax with a given oil is compared to the petroleum-based reference wax. In this instance, we observe a great variability in textures and appearances, depending on the quality of wax used for an identical INCI name; however, some general observations can be made. Sunflower wax gels well in all-natural oils tested, but the alkanes, not well. The Candelilla and Carnauba waxes, on the other hand, gel alkanes very well, probably because they are partially composed of hydrocarbons, which aid in the formation of Van der Waals bonds between the wax and the oil. They also gel triglycerides very well. Rice wax, itself largely composed of esters, is particularly compatible with oils from the fatty ester family. Carnauba wax gives the highest firmness with tested plant-based oil (*Meadowfoam Seed Oil* (*Limnanthes Alba*)).

The evaluation of the appearance and the sensoriality of the binaries are compiled (Tab. 6). Thus, the Carnauba wax and certain qualities of the Rice and Candelilla waxes give binaries with a firmness like that of synthetic wax. However, three waxes did not solidify any of the tested oils homogeneously. *Tribehenin* and *Hydrogenated Castor Oil* consistently produced soft binaries, which can be easily explained by their low melting points. The *Jojoba Esters*, meanwhile, produced hard but very non-homogeneous binaries (Fig. 7). Some waxes have made it possible to obtain heterogeneous binaries with some oils and very homogeneous with others. This is the case of rice wax (Figs. 7 and 8). We can observe on the surface matte areas or even real crystals. Conversely, a binary is homogeneous

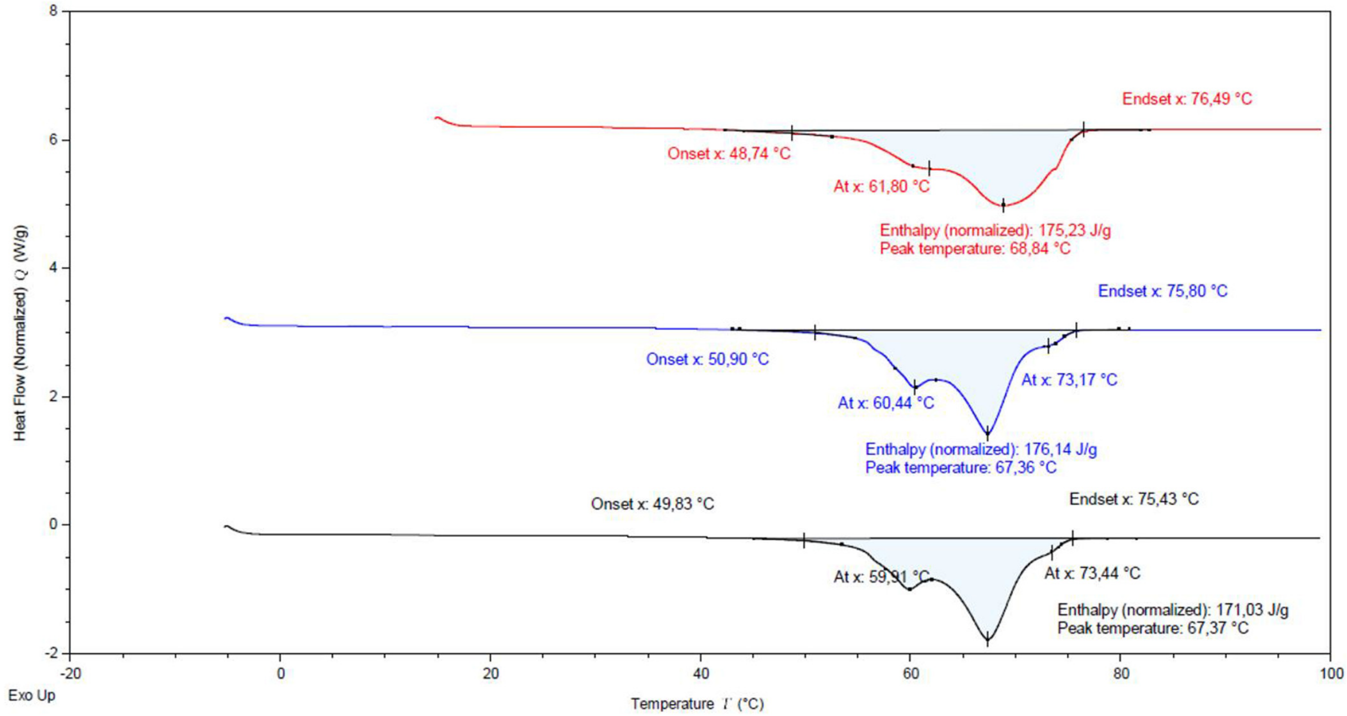

Fig. 2. The DSC of Candelilla Wax quality B *Candelilla Cera* (*Euphorbia Cerifera* (*Candelilla*) *Wax*)).

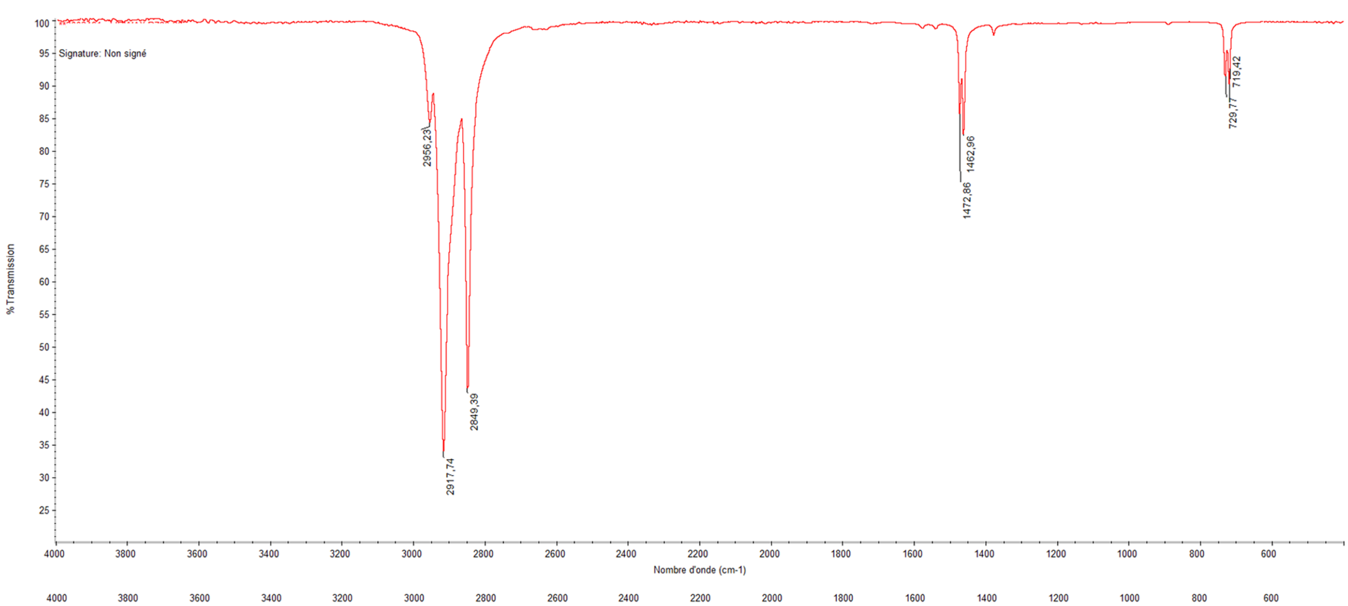

Fig. 3. IR spectrum of the reference petroleum-based wax *Ethylene/Propylene Copolymer & Synthetic Wax*

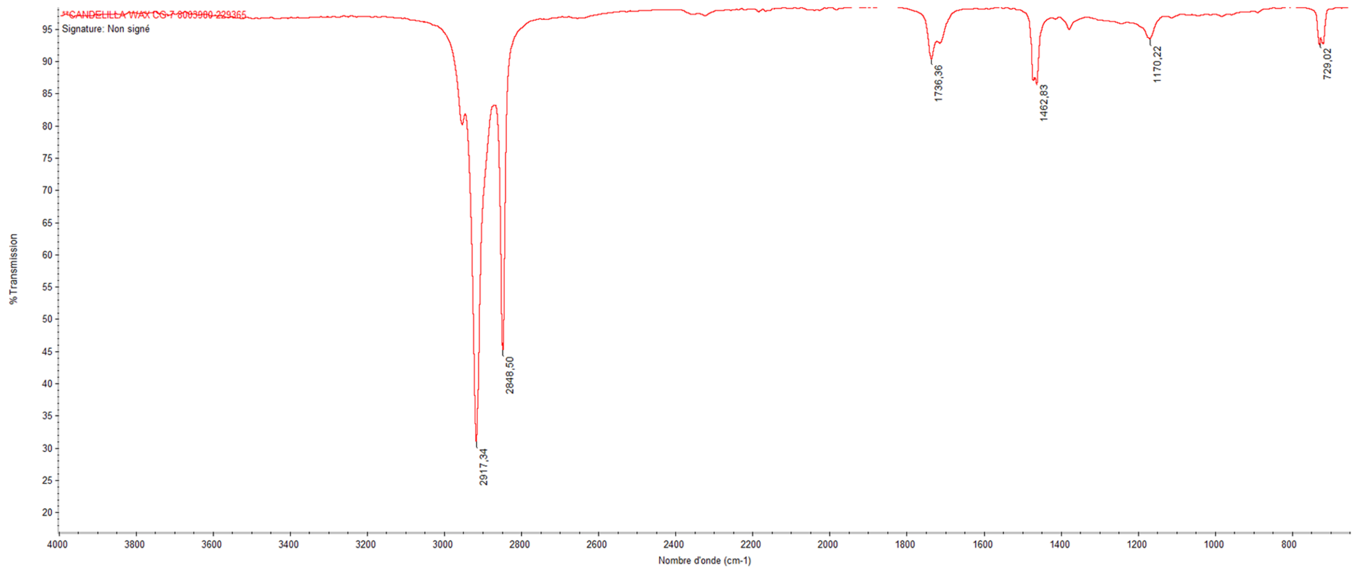

Fig. 4. IR spectrum of Candelilla wax quality B *Candelilla Cera* (*Euphorbia Cerifera* (*Candelilla*) *Wax*)).

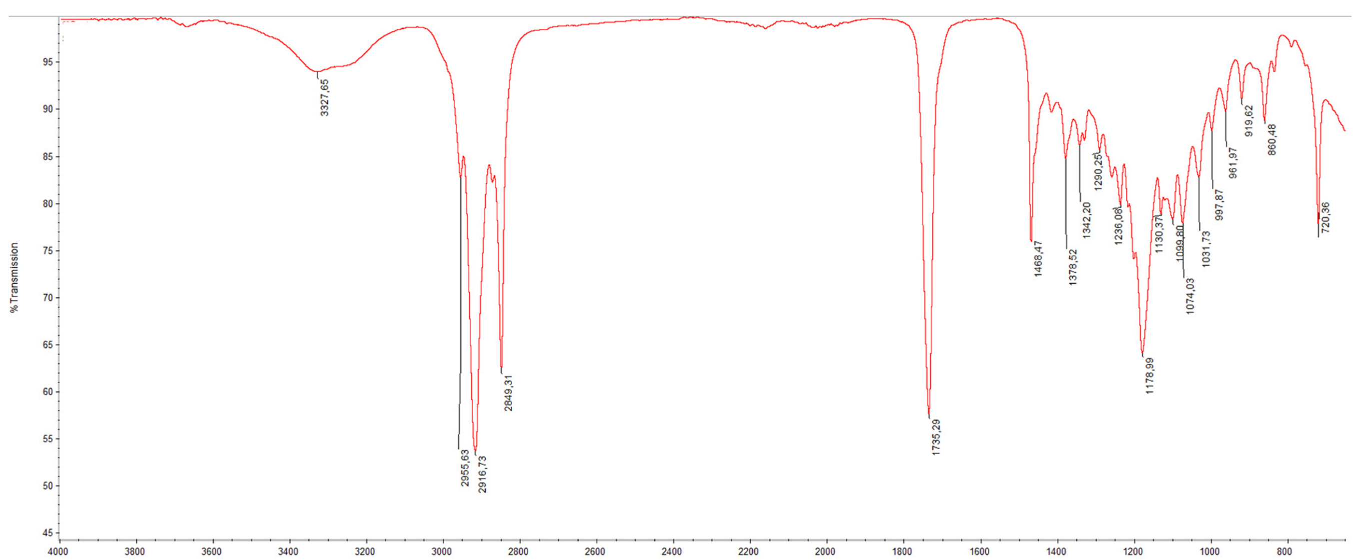

Fig. 5. IR spectrum of *Hydrogenated Castor Wax.*

when the surface is smooth, with no apparent matt or crystallized area. Several were obtained such as C*18-36 Acid Glycol Ester* with 70% *Meadowfoam Seed Oil (Limnanthes Alba)*, *Glyceryl Behenate/Eicosadioate* with 70% *Ethyl Oleate and Ethyl Linoleate and Ethyl Palmitate and Ethyl Stearate and Tocopherol* and 30% *Oryza Sativa (Rice) Bran Wax* with 70% *Coco Caprylate Caprate* (Fig. 8).

The analyses *via* DSC, infrared and firmness of 30/70 binaries, show that Carnauba wax and Rice wax are probably the best candidates for replacing the synthetic reference.

The plant-based waxes selected to be used in lipstick formulation are Carnauba wax (quality B), which is less likely to re-crystallize, Rice wax (quality B), the most stable, Sunflower wax for its compatibility with practically all the plant-based oils tested (versatility is one of the main properties of the reference wax), and finally three qualities of Candelilla wax. Even though the latter has a somewhat low melting point, its sensory and visual properties make it a very interesting wax. The three qualities are used in lipstick formulation, because the binaries have very variable textures depending on the oils. *Glyceryl Behenate/Eicosadioate* was not selected for formulating lipsticks, due to its overly low melting point, and despite the glossiness of its binaries.

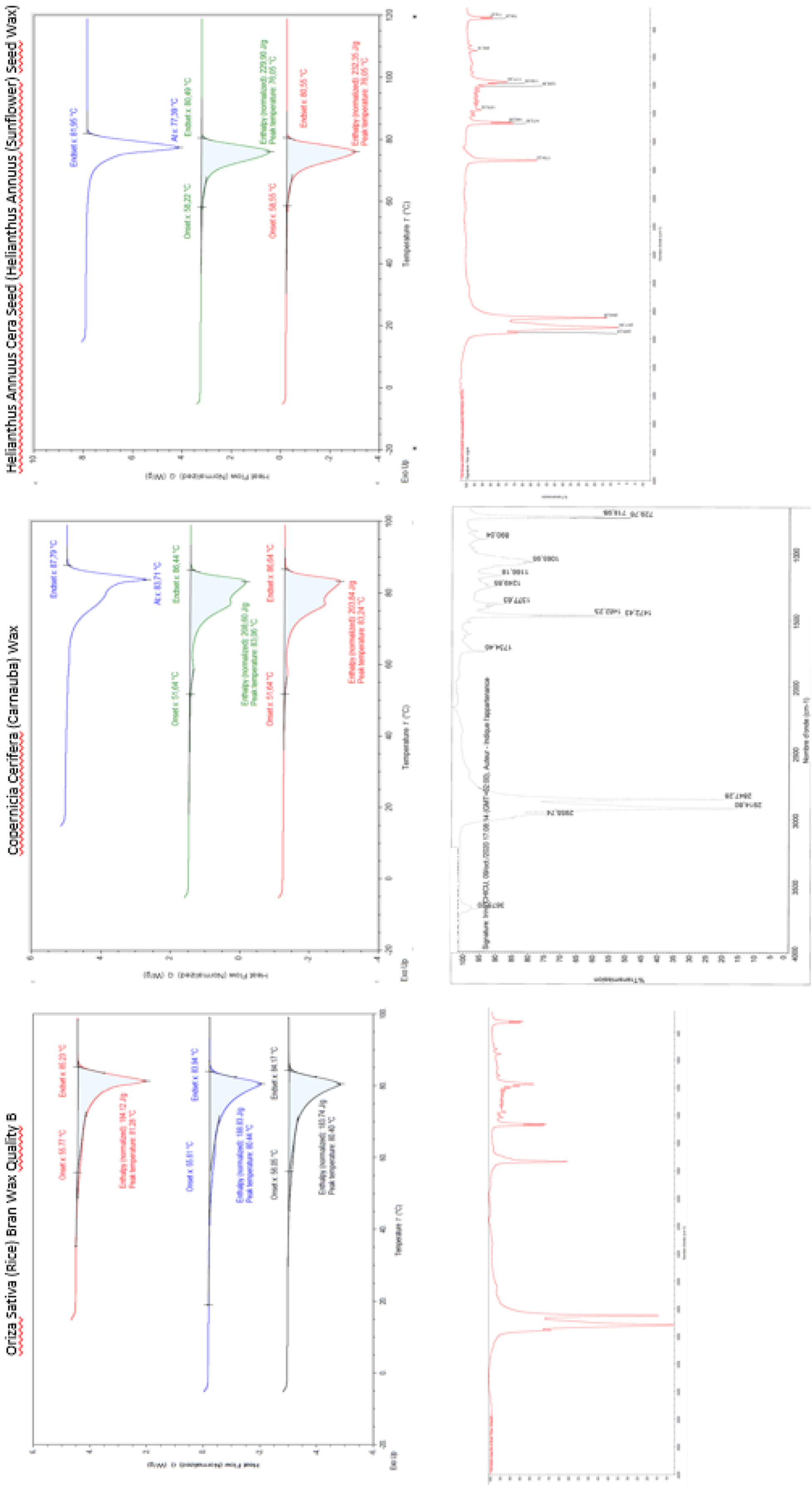

Fig. 6. DSC and IR spectra of the best candidates for the substitution of the petroleum-based reference wax.

Table 6. Two-month visual observations and stabilities for 30/70 wax/oil binaries.

INCI name	Visual observations and stabilities
Ethylene/Propylene Copolymer & Synthetic Wax	Binary homogeneous, satin, slippery and melting. Shrinkage observed with short chain oils
Copernicia Cerifera (Carnauba) wax – Quality A	Very hard binaries and heterogeneous crystallization / recrystallization in all vegetable oils except fatty alcohol. Cracking of the majority of binaries
Copernicia Cerifera (Carnauba) wax – Quality B	Binary hard, homogeneous and shiny but not very slippery / melting. Recrystallization in alkanes
Oryza Sativa (Rice) Bran Wax – Quality A	Homogeneous, hard, slippery and moderately melting binaries. Sweating with all oils
Oryza Sativa (Rice) Bran Wax – Quality B	Homogeneous binary except with Coco-Caprylate / Caprate (incompatibility). Stable
Candelilla Cera (Euphorbia Cerifera (Candelilla) Wax) – Quality A	Particularly shiny, slippery and melting binaries. Shrinkage observed with short chain oils
Candelilla Cera (Euphorbia Cerifera (Candelilla) Wax) – Quality B	Binary homogeneous, hard, slippery and moderately melting. Shrinkage observed with short chain oils
Candelilla Cera (Euphorbia Cerifera (Candelilla) Wax) – Quality C	Shrinkage observed in most oils, few melting sensation in alkanes and triglycerides
Candelilla Cera (Euphorbia Cerifera (Candelilla) Wax) – Quality D	Particularly shiny and homogeneous binaries but very little slippery and melting. Very slight shrinkage in all vegetable oils
Hydrogenated Castor Oil	Ungelled and inhomogeneous binaries
Jojoba Esters	Completely inhomogeneous binaries (large crystals visible)
Helianthus Annuus Cera Seed (Helianthus Annuus (Sunflower) Seed Wax)	Binary homogeneous, hard, slippery and melting. Shrinkage observed with short chain oils
Tribehenin	Pasty and inhomogeneous binaries. Formation of a whitish layer on the surface of binaries
Glyceryl Behenate/Eicosadioate	Hard binaries, particularly shiny and homogeneous, very slippery and melting. Cracking of the majority of binaries

Table 7. Sensoriality and stability of sticks formulated with the selected plant-based wax candidates.

INCI name	Sensoriality	Stability
Ethylene/Propylene Copolymer & Synthetic Wax	Pleasant	Yes
Copernicia Cerifera (Carnauba) wax – Quality B	Not slippery or melting enough	No: gel exudate
Oryza Sativa (Rice) Bran Wax – Quality B	Pleasant	Yes
Candelilla Cera (Euphorbia Cerifera (Candelilla) Wax) – Quality B	Pleasant	No: partially melted stick
Candelilla Cera (Euphorbia Cerifera (Candelilla) Wax) – Quality C	Too melting	No: partially melted stick
Candelilla Cera (Euphorbia Cerifera (Candelilla) Wax) – Quality D	Too melting	No: partially melted stick
Helianthus Annuus Cera Seed (Helianthus Annuus (Sunflower) Seed Wax)	Pleasant	Yes

4.3 Lipstick formulation

This last step is formulated with the waxes whose binary tests are the most promising. Waxes that have given heterogeneous binaries in surface appearance such as jojoba esters are eliminated. The same goes for waxes that have not gelled any oil such as hydrogenated castor oil. The goal is to determine the behavior of a wax in a realistic lipstick formula. The compatibility in a complex mixture is thus assessed as well as the ease of implementation. The melting properties in a mixture and the ability to poured into a mold as well as to unmold easily are observed. Finally, the controls carried out on the sticks make it possible to compare them with commercial formulas.

The results obtained by DSC, cutting wire, and hot melt rheology on the sticks, did not allow the best replacement candidate for the reference's wax to be determined.

In fact, only two qualities of Candelilla formed sticks with a firmness close to the synthetic reference (Fig. 9). But the DSC analysis showed that there were significant risks of thermal instabilities, as the sticks formulated with Candelilla wax had values of onset of melting, melting point, and enthalpy which were too low compared to the reference, as well as a slight polymorphism for qualities C and D (Fig. 10). This was verified experimentally with the sticks having been partially melted in an oven from 40 °C, one month after formulation (Fig. 11). Finally, from a sensory point of view,

30% Oryza Sativa (Rice) Bran Wax + 70% Caprylic/Capric Triglyceride

30% Jojoba Esters + 70% Isododecane

Fig. 7. Heterogeneous binaries: irregular surfaces with visible crystals and/or more matt areas.

30% C18-36 Acid Glycol Ester + 70% Meadowfoam Seed Oil (Limnanthes Alba)

30% Glyceryl Behenate/Eicosadioate + 70% Ethyl Oleate and Ethyl Linoleate and Ethyl Palmitate and Ethyl Stearate and Tocopherol

30% Oryza Sativa (Rice) Bran Wax + 70% Coco Caprylate Caprate

Fig. 8. Homogeneous binaries. The surface is smooth, with no apparent matt or crystallized areas.

several qualities of Candelilla wax were not retained, due to their being too soft in contact with lips (Tab. 7).

In terms of their thermal profile, the formulas with Carnauba wax and Rice wax are closest to the reference (Fig. 10). However, the formula with Carnauba wax is neither stable nor sensorially acceptable. It is too dry, not very comfortable, not very smooth, and not very soft. Thermal instability is easily noted *via* the appearance of re-crystallized exudate over the entire surface of the stick (Fig. 11) a few days after the test had been kept in the oven at 45 °C.

Hot melt rheology notably made it possible to evaluate the sensitivity of the texture to temperature. The tests with Carnauba wax and with Rice wax showed a significant loss of strength between 20 and 35 °C (Fig. 12), of 32 and 81% respectively, while it was only 9% for the petroleum-based reference wax, as well as for the other waxes.

In the light of the results of these lipstick tests, it is difficult to replace synthetic wax with a plant-based wax. None can replace the reference wax. If sensoriality or thermal stability are favored, rice or sunflower waxes seem suitable. However, if a very structured lipstick is desired, it is better to use candelilla wax.

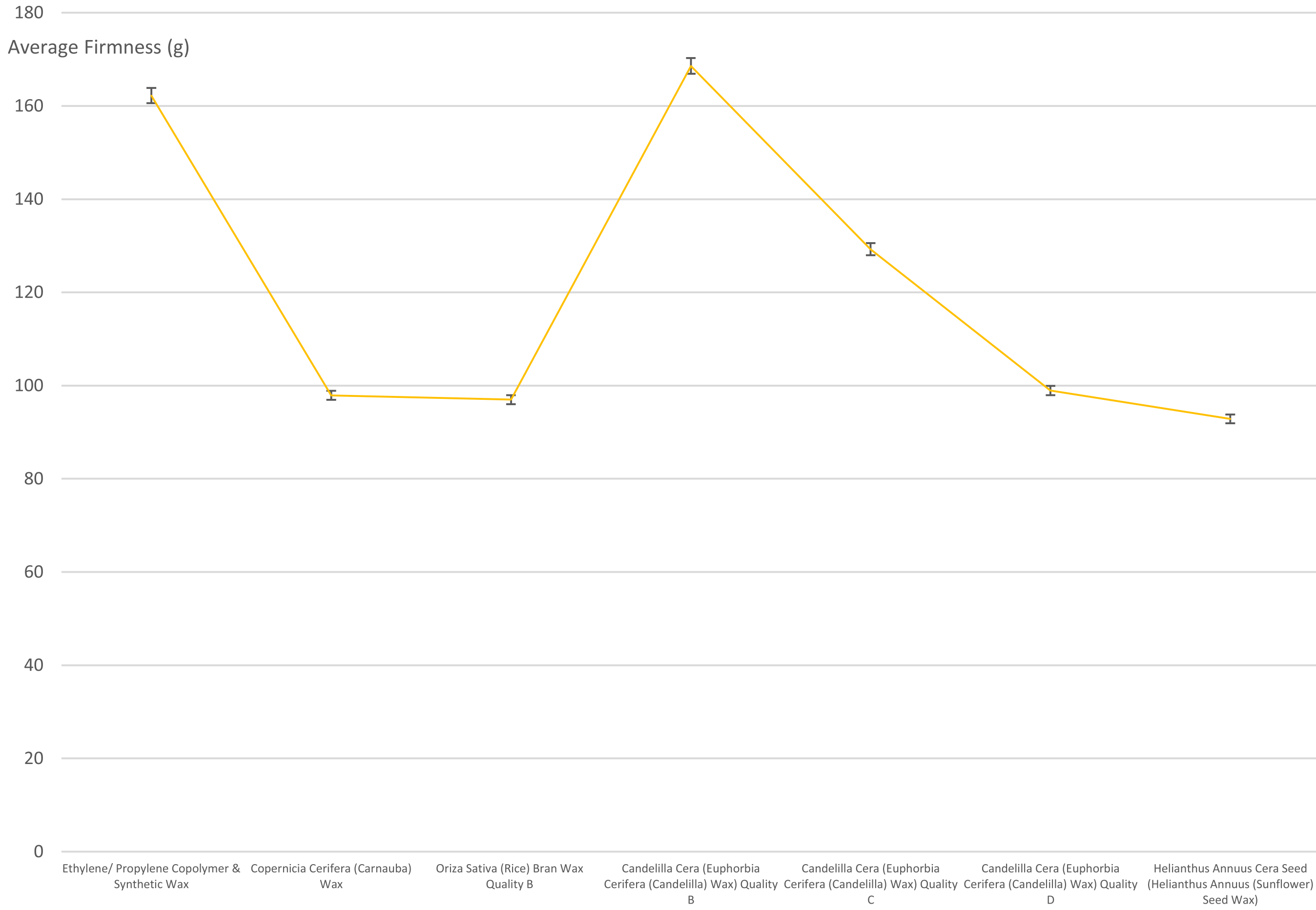

Fig. 9. The cutting wire results of lipsticks formulated with the selected plant-based wax candidates.

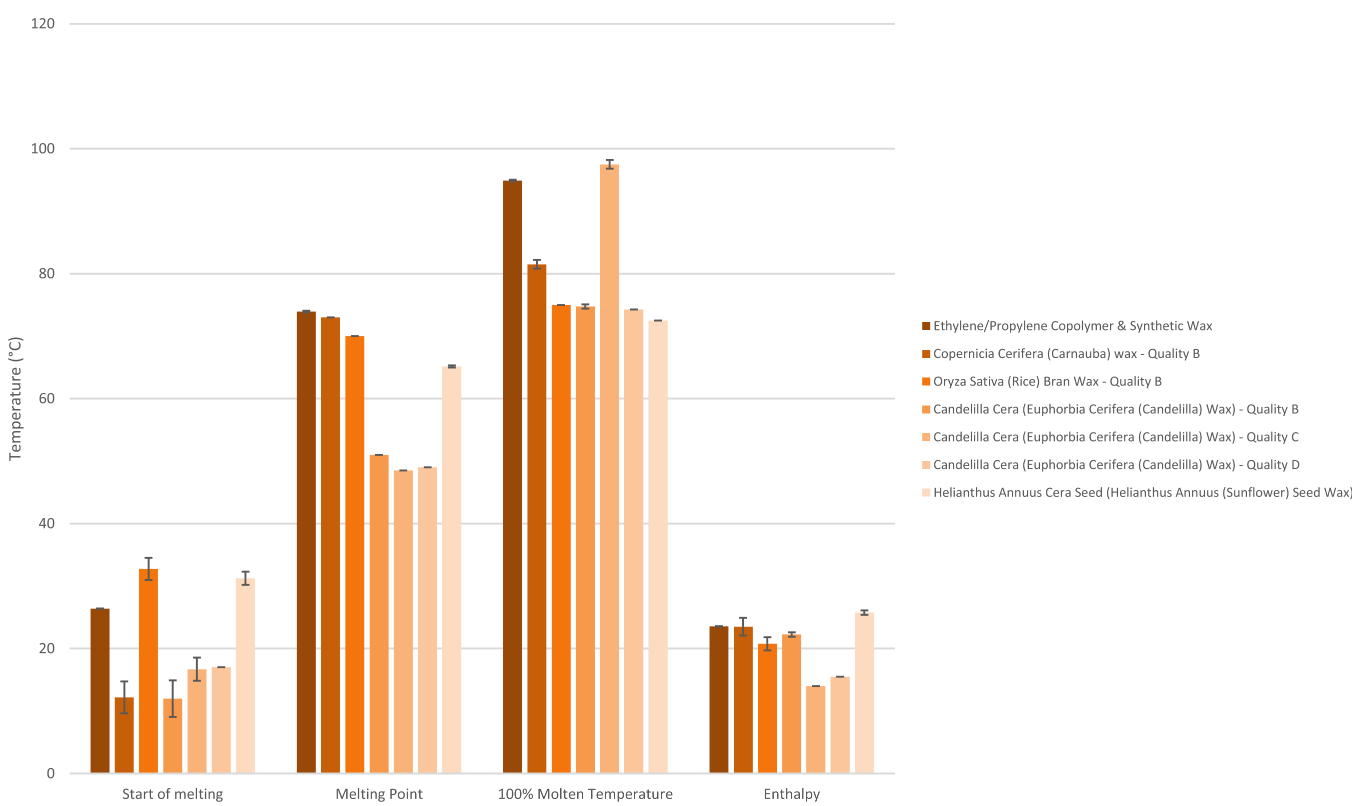

Fig. 10. Results of the DSC thermal profiles of lipsticks formulated with the selected plant-based wax candidates.

Fig. 11. Lipsticks formulated with the different plant-based waxes after one month in an oven at 45 °C.

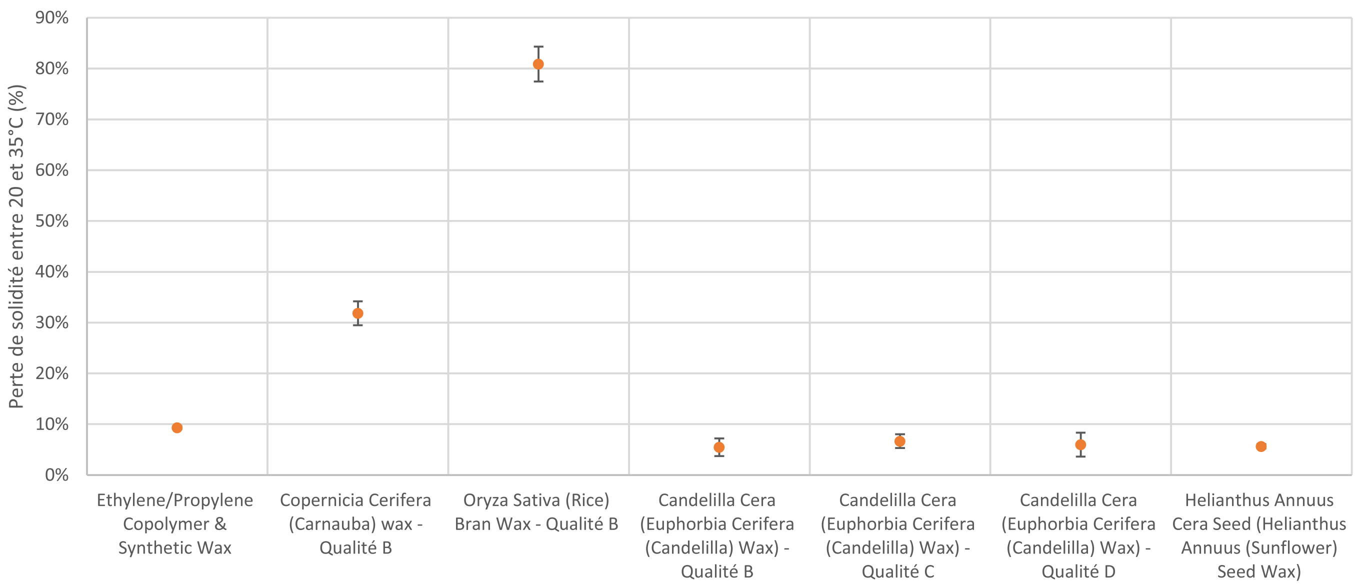

Fig. 12. Loss of solidity between 20 and 35 °C of the test lipsticks measured by hot melt rheology.

5 Conclusion

Each plant-based wax evaluated behaves in a specific way. None of them fully meets the physicochemical characteristics of the synthetic reference wax. The textures, the sensorialities, and the gelling capacities of the different oils are different. These differences are observed within the plant-based waxes themselves. Plant-based waxes gel the oils into which they are introduced in a very variable manner. There is no wax that stands out for gelling all oils, and no oil that stands out for being gelled by all the waxes. Thus, formulating lipsticks with plant-based waxes appears to require making choices about the desired priorities: softness or smoothness, or hardness, or heat resistance. We must therefore make compromises, and not be overly attached to reproducing in a similar way what has previously been offered to consumers. Consumer-education will undoubtedly have to be envisaged, to increase acceptance of these more natural formulas, even if they favor the naturalness of ingredients in cosmetic compositions.

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