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Development of a novel Green conditioning agent produced by a sustainable route from the Amazon Pracaxi Oil

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1. Introduction

Amazon Pracaxi Oil, extracted from the seeds of the tree Pentaclethra macroloba (Willd.) Kuntze, is known for its numerous and remarkable properties for therapeutic and care use. It exhibits significant properties relevant to the cosmetics industry, including benefits for the treatment of skin conditions like hyperpigmentation and stretch marks, due to its antioxidant activity, as well as hair health, such as enhanced shine, prevention of hair loss, strengthening of hair roots and its anti-frizz action, in addition to promoting shine and softness to hair, improving combability. Most of these properties are attributed to the high content of behenic acid on its composition [1,2].

Vegetable oils are composed of triglycerides, which are triesters of glycerol with fatty acids of different lengths and degrees of unsaturation. Most Brazilian vegetable oils are composed of fatty acids up to 18 carbons length. Some of these oils, however, can have on its composition ultra long-chain fatty acids (over to 18 carbons tail) [3]. Rapeseed oil, for example, contains fatty acids of 22 carbons, although they are unsaturated, as erucic acid (C22.1).

Behenic acid (C22.0) has gained prominence in cosmetic formulations due to its properties, such as emollience. Unlike erucic acid (C22.1), which contains a double bond in its structure, behenic acid features an entirely saturated chain, providing greater oxidative stability and the ability to form cohesive lipid barriers. This characteristic allows behenic acid to act as an occlusive agent, similar to silicone, promoting the formation of a protective layer over hair fibers. This layer contributes to moisture retention, improved combability, and protection against environmental stressors. In this context, Pracaxi oil stands out as being the vegetable oil with the highest content of behenic acid (C22.0) known in the world (15 to 20%). In addition, this oil also contains about 10% of lignoceric acid (C24.0) [3;4].

The outstanding performance conditioning agents, such as behentrimonium chloride (BTAC) and cetrimonium chloride (CTAC), have long and saturated chains combined with cationic groups, which adsorb on the negative charges present in the hair strands, while the hydrocarbon segments promote the desired smoothing effect. However, these cationic products are considered eco-toxic, especially for aquatic environments, in addition to not being obtained through sustainable routes [5]. On the other hand, the alkylamidopropyl dimethylamine (AAPDMA) behenamidopropyl dimethylamine (BAPDMA) has a terminal tertiary amine group. Therefore, it only becomes cationic in the product formulation when it is protonated by an acid, such as lactic acid, for example. So, it is classified as pseudo-cationic, exhibiting a positive charge only in the formulation and during use, while upon rinsing and disposal, it is deprotonated, reverting to its non-ionic, biodegradable form and thus not harmful to the environment. All of this is coupled with the fact that it also has a long, saturated hydrocarbon chain with 22 carbon atoms. However, the process to obtain BAPDMA typically includes hydrogenation, hydrolysis and distillation steps, which is expensive and not sustainable [6].

In this work it is presented a new quat-free green conditioning agent obtained from Amazon Pracaxi Oil, produced from a sustainable route. The developed product (AAPDMA C22-C24) was characterized by FTIR and 1H NMR, and compared with commercial BAPDMA. Typical hair conditioner formulations were prepared, using commercial BTAC, BAPDMA and AAPDMA C22-C24 as active ingredients. The conditioners were initially evaluated by rheometry and then by sensory tests and hair luster (shine) measurements, in order to confirm the potential of the developed product.

2. Materials and Methods

2.1 Materials

N,N-dimethyl-1 3-propanediamine (DMAPA) used for amidation reaction was purchased from Sigma-Aldrich (Germany); Pentaclethra macroloba Seed Oil (Pracaxi Oil) was provided by Bielus ingredients (Brazil); Behentrimonium Chloride (BTAC) was purchased from Engenharia das Essências (Brazil); Behenamidopropyl Dimethylamine (BAPDMA) was purchased from Kao Chemicals; Cetearyl alcohol was purchased from Cosmética Casa (Brazil); Lactic Acid (85%) was purchased from Dinâmica Química contemporânea Ltda (Brazil).

2.2 Synthesis and Chemical Characterization

The conditioning agent AAPDMA C22-C24 was obtained by a new sustainable route which avoids hydrogenation, hydrolysis and distillation steps. It involves the isolation of the fatty constituents and amidation reactions with dimethylaminopropylamine (DMAPA), using pracaxi oil as raw material. The amidation reactions were conducted under DMAPA reflux and inert atmosphere using nitrogen. DMAPA was used in a molar excess of 25%. The product obtained was characterized by Fourier Transform Infrared spectroscopy (FTIR) and proton Nuclear Magnetic Resonance (1H NMR). FTIR analyses were carried out using a Bruker (Tensor 27) spectrometer equipped with an attenuated total reflectance (ATR) accessory with diamond crystal, in transmittance mode with range from 4000 to 400 cm^{-1}, using 32 scans and resolution of 4 cm^{-1}. 1H NMR spectroscopy was performed using a Bruker Avance spectrometer (DPX-200), with deuterated chloroform as solvent. The 1H NMR spectra were obtained at 400 and 500 MHz Chemical shift values were reported in parts per million (ppm) relative to Tetramethylsilane.

2.3 Hair Masks and Hair Conditioners Formulation

A series of hair masks and conditioners were formulated using as active ingredient the developed product AAPDMA C22-C24 or conventional used conditioning agents such as behentrimonium chloride (BTAC) and behenamidopropyl dimethylamine (BAPDMA), for comparison. For hair masks, the formulations were prepared containing 8wt.% of cetearyl alcohol, 3.2wt.% of active surfactant (AAPDMA C22-C24 or BAPDMA),0.8wt% of lactic acid (85%) and water q.s.p. For hair conditioners, the formulations were prepared containing 5wt% of cetearyl alcohol, 2wt.% of active surfactant (AAPDMA C22-C24 or BTAC or BAPDMA), 0.5wt.% of lactic acid (85%) and water q.s.p. In the formulation process, lactic acid was employed as an acidifying agent to adjust the pH of the product to a target range between 4.0 and 4.5. The pH was monitored, and additional lactic acid was added as needed to achieve the desired range. The formulations were prepared with vigorous mechanical stirring in water bath at approximately 70°C. After complete dissolution of the components, the conditioners were cooled in ice bath in order to improve consistency. The formulations were stocked under refrigeration until the analysis.

2.4 Rheological Properties

The rheological properties of the hair masks and hair conditioners were evaluated by rheometry using a Haake Mars 60 (Thermo Fisher Scientific) rheometer. A parallel plates geometry was used, employing a plate of 35 mm diameter (P35/Ti). The measurements were performed in steady-state rotational mode with shear rate ranging from 0.1 s^{-1} to 1,200s^{-1} and in oscillation amplitude sweeps with oscillatory stress from 100 to 1000000 mPa and frequency of 1Hz.

2.5 Performance evaluation

For sensory tests, four samples of naturally straight hair, measuring 25 cm in length and weighing 3 grams were subjected to a cleaning process using a shampoo base solution of 10 wt.% Sodium Lauryl Ether Sulfate (SLES). 0.5 mL/g of shampoo was applied in hair and massaged for one minute before rinsing under running water at flow rate of 0.5 mL/min. Then, 0.5 mL/g of the tested product was applied and massaged for one minute before rinsing under running water at flow rate of 0.5 mL/min. The previously formulated hair conditioning samples were the products tested in these experiments. The hair samples were completely blow-dried in a standardized manner with a hairdryer applying hot air at a distance of 15 cm. After that, the hair samples treated with the products were submitted to sensory evaluation by trained technicians assessors specialized in hair care product. The following parameters were applied by the trained panels: application; wet detangling; wet combing and dry fell. The specialists attributed scores from 0 to 5 for each sample, were 0 is the lowest quality response and 5 is the highest.

The evaluation of hair shine (hair luster) was performed using the polarization Image device Samba Hair, which utilizes the polarization properties of light with a polarimetric camera, allowing separate analysis of diffuse light—which scatters in the hair and provides color information—and specular light, which reflects the hair's shine. Five samples of natural Caucasian hair measuring 25 cm in length and weighing 3 grams were washed with 0.5 mL/g of SLES 10 wt.% solution. The shampoo was applied and massaged for one minute before rinse thoroughly. The hair samples were blow-dried using a hairdryer at distance of 15 cm. After that, 0.5 mL/g of the conditioners were applied, massaged for one minute, left on for 5 minutes, and then rinsed thoroughly. Finally, the hair samples were completely blow-dried with a hairdryer applying hot air at a distance of 15 cm. Hair samples treated just with the SLES solution were used as control. The treated samples and the control were conducted to the equipment. The Minitab Statistical Software 19 was used for the statistical analysis. Ten brightness measurements were taken for each sample using the Samba Hair® device. The samples were kept in a standardized environment at 55 ± 5% relative humidity and 22 ± 2°C during the measurements. The statistical analysis was performed using analysis of variance (ANOVA) followed by the Tukey test for independent samples, comparing the mean brightness values (BNT) of the hair samples subjected to the control and treated conditions. The significance level was considered to be $p<0.05$.

3. Results

3.1. Chemical characterization of the new conditioning agent AAPDMA C22-C24

The developed product AAPDMA C22-C24 was characterized by FTIR and 1H NMR. The FTIR spectra of the starting material, Pracaxi Oil, and of the final product are presented in Figure 1.

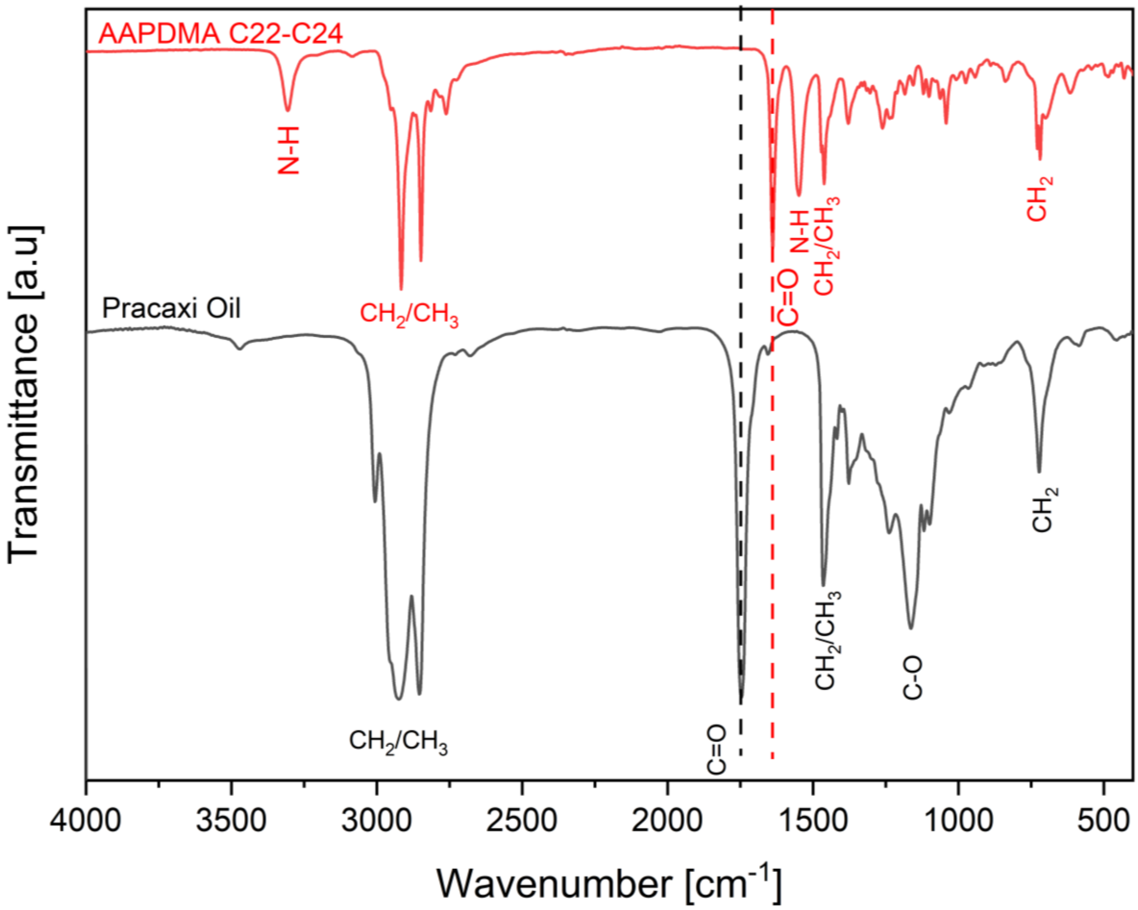

Figure 1. Comparative FTIR spectra of AAPDMA C22-C24 and Pracaxi Oil

The developed product, AAPDMA C22-C24 consists in an alkylamidopropyl dimethylamine, while the Pracaxi oil is a triglyceride. Thus, the main observable difference between the starting material and product is the change from ester to amide functional group. The presence of amide in the product was confirmed by the appearance of the band in 1640 cm^{-1}, attributed to stretching of secondary amide carbonyls, and by the absence of bands at 1743 cm^{-1} or 1705 cm^{-1}, which would be corresponding to the stretching of carbonyl from fatty esters or fatty acids, respectively. The band present in 1549 cm^{-1} and the signal in 3300 cm^{-1} refer to N-H bending and N-H stretching from amide group, respectively. Note that in Pracaxi Oil spectra it is possible to see an intense band in 1743cm^{-1}, of ester carbonyl stretching. The band that appears in 719 cm^{-1} in both spectra corresponds to the rocking vibration of methylenes (CH_2). The intense bands in both spectra near to 3000cm^{-1} are related to CH_2 and CH_3 stretching along the carbon chains.

Figures 2 shows the 1H NMR spectra of Pracaxi oil and the developed conditioning agent AAPDMA C22-C24, while Figure 3 shows the 1H NMR spectra of the commercial conditioning agent BAPDMA, for comparison.

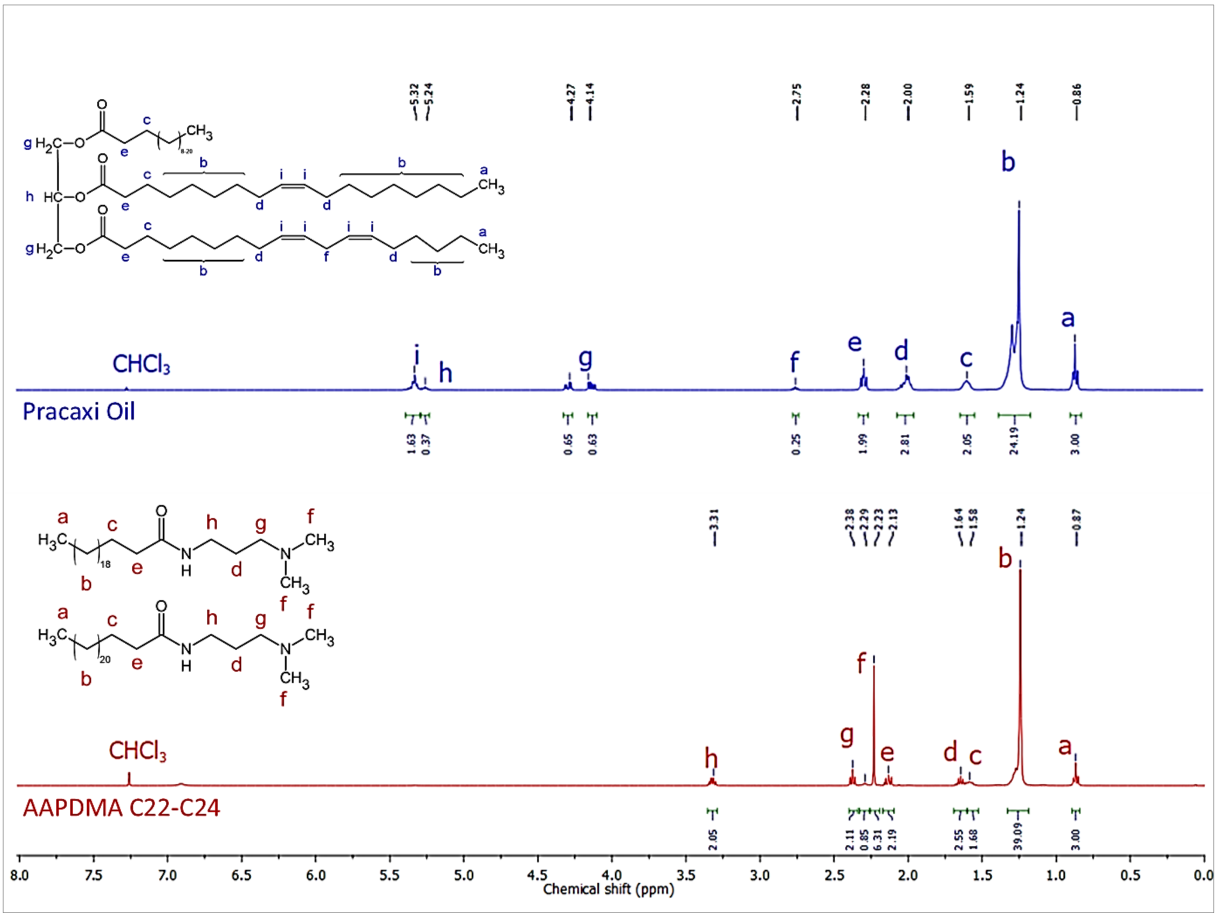

Figure 2. 1H NMR spectra and molecular structures of AAPDMA C22-C24 and Pracaxi Oil.

The 1H NMR spectrum from Pracaxi oil (Figure 2) show signals in 4.14, 4.27 and 5.24 ppm referring to the methylene (H_g) and methine (H_h) hydrogens, related to the glycerol portion of the triglycerides segments of the oil. It is also observed a signal in 5.31 ppm referred to the hydrogens directly attached to the carbons of the double bond from unsaturated fatty acids. On BAPDMA (Figure 3) and AAPDMA C22-C24 (Figure 2, bottom) spectra, however, this signal is not present. The same spectra (BAPDMA and AAPDMA C22-C24) also show a singlet signal at 2.25 ppm from methyl groups attached to the nitrogen atom from the tertiary amine. These results corroborate with the FTIR spectra previously (Figure 1) for the AAPDMA formation. The absence of the unsaturation signal at 5.31 ppm also confirms that although the developed ingredient AAPDMA C22-C24 was obtained from Pracaxi Oil, which has high contents of the unsaturated fatty acids oleic acid (C18.1) and linolenic acid (C18.2), around 54% and 13%, respectively[4], the route developed in this work showed to be efficient in the production of a mixture of alkylamidopropyl dimethylamines (AAPDMA) only from the saturated fatty acids of the oil. Furthermore, analyzing the areas of the 1H NMR signals at 0,87 and 1,24 ppm, it is also possible to state that the AAPDMA mixture obtained by the developed route contains essentially ultra-long and saturated chains, more specifically from behenic (C22.0) and lignoceric acids (C24.0). As 1H NMR is a quantitative technique, the area of the signals is proportional to the amount of the respective hydrogen. Thus, taking the signal at 0,87 ppm as reference (H_a, terminal methyl group, 3H), the signal at 1,24 ppm refers to H_b (Figure 2, bottom). If the AAPDMA product was completely made from C22.0, H_b would have area 36, while if it was made from C24.0 it would have area 40. Thereby, as the Hb area on the product is 39,09, it is possible to state that the product consists in a mixture of alkylamidopropyl dimethylamines from behenic and lignoceric acid, AAPDM C22-C24. The similarity on the spectra from AAPDMA C22-C24 and BAPDMA also corroborates this affirmation.

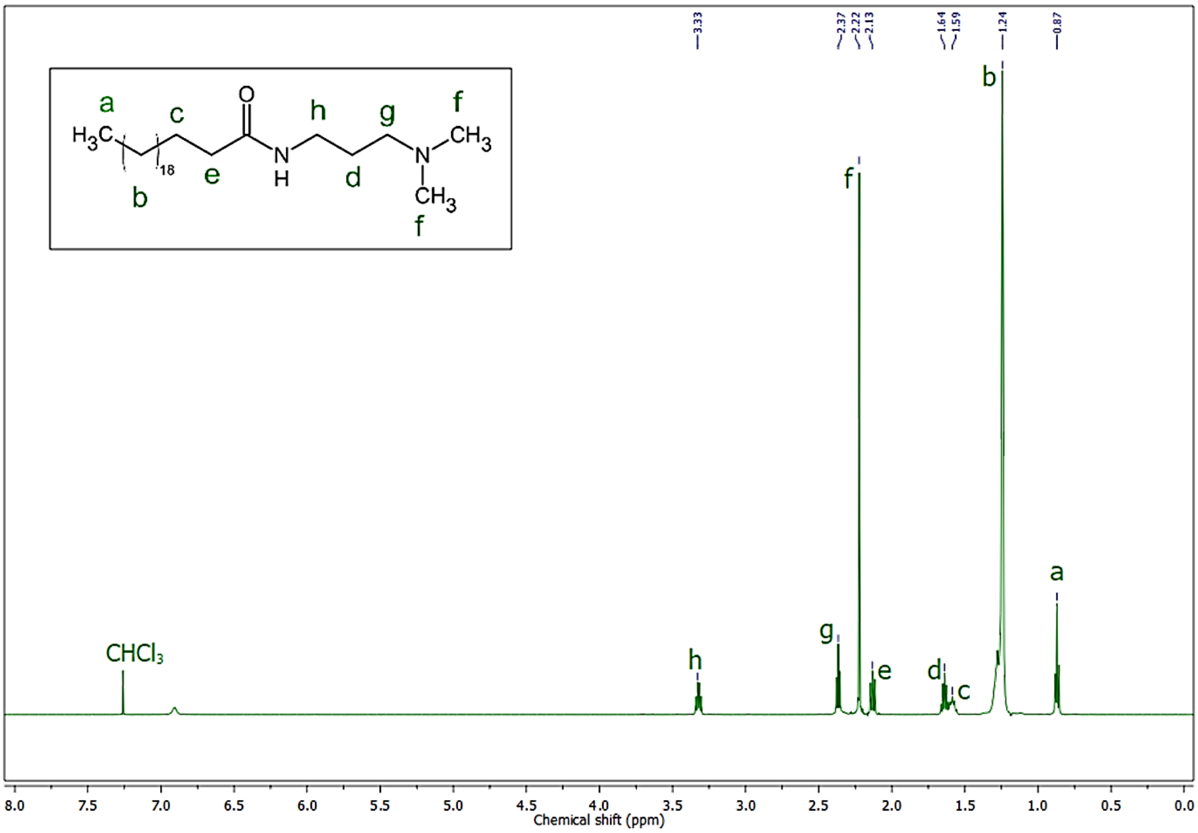

Figure 3. 1H NMR spectrum and molecular structure of BAPDMA.

3.2. Rheological characterization

The Rheological curves of the hair masks and conditioners are presented in Figure 4. The oscillatory curves with the signed yield points (τ_y) are presented in Figures 4.a and 4.c, while Figures 4.b and 4.d present the viscosity curves. The storage modulus (G´) corresponds to the elastic response to stress, which means the ability of the sample to recovery after shearing. The yield point (τ_y) corresponds to the value of the shear stress at the limit of the linear visco-elastic region, which means the amount of shear stress at which the sample undergoes irreversible deformation—that is, permanent deformation of the sample's microstructure. The shear viscosity is the resistance of the fluid under an applied shear stress. In cosmetic formulations, rheology it is a crucial parameter, because it defines how a product will behave when applied or pumped. Thus, it is an important factor both for ease of use and for formulation. The obtained results show that rheological profile of all samples is quite similar. The hair masks showed basically the same viscosity curves (Figure 4.b), while the yield point (τ_y), Figure 4.a, obtained with the mask formulated with BAPDMA instead of AAPDMA C22-C24 was slightly higher. Both hair conditioner and mask formulations exhibited a pseudoplastic behavior, characterized by a decrease in viscosity with increasing shear rate. The hair conditioner formulations exhibited a shear thinning behavior (Figure 4.d), as well as the hair masks. However, as the concentration of active surfactants and cetearyl alcohol are lower than in hair masks, it was possible to notice significant differences in the obtained viscosities, especially at low shear rates. Samples with BAPDMA and AAPDMA C22-C24 showed similar viscosity curves, while the one with BTAC resulted in lower viscosity. On respect to oscillatory experiments, the differences between the systems were even more evident (Figure 4.c). The hair conditioning containing the developed product resulted both in higher elastic modulus (G') and yield point (τ_y), followed by BAPDMA and BTAC.

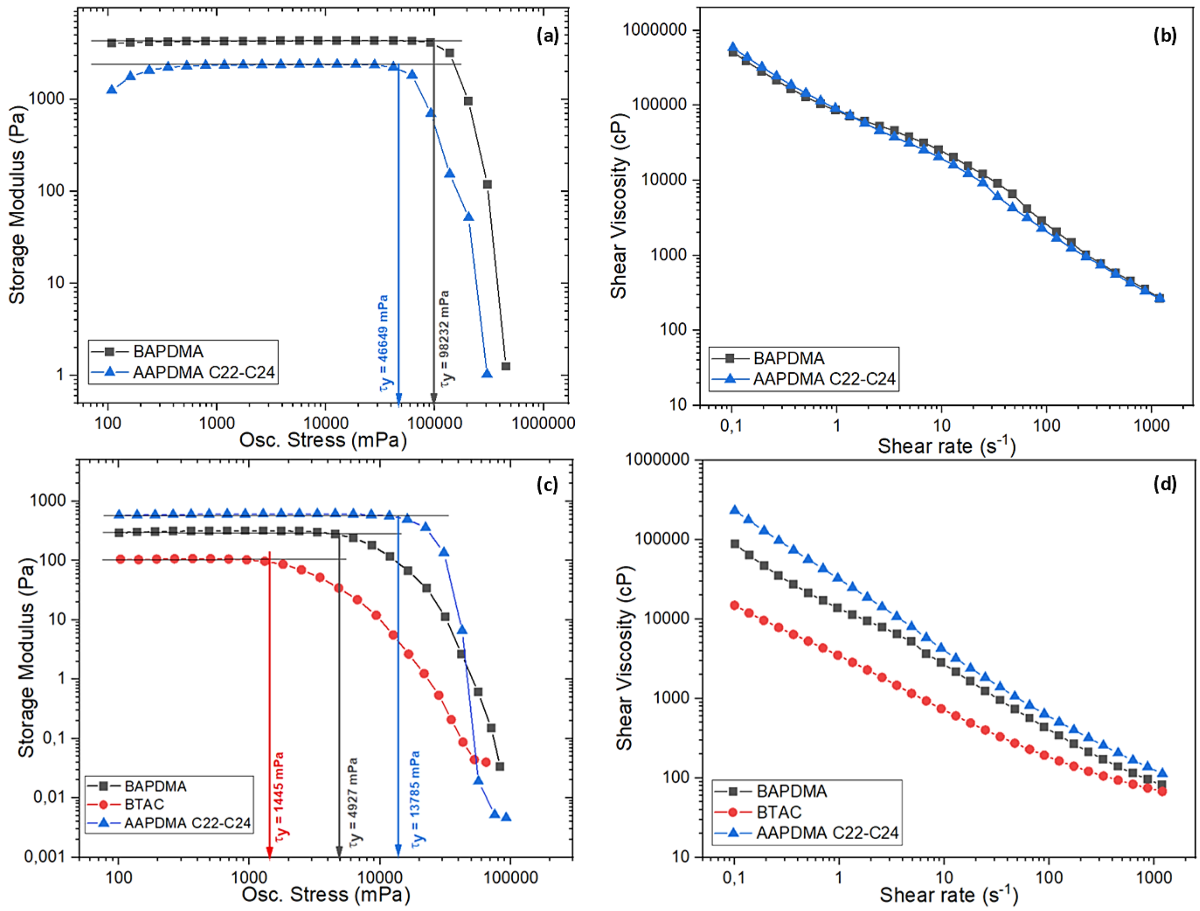

Figure 4. Rheological curves presented for Hair Masks (a and b) and Hair Conditioners (c and d) with the different surfactants applied as agent.

3.3 Performance Evaluation

The average values obtained in the sensory tests of the formulated hair conditioners are presented in Table 1. The obtained results indicate that the product AAPDMA C22-C24 developed in this work performs as a conditioning agent, with effectiveness rated between great and excellent, according to the scores given by the experts (score 4 means great and 5 means excellent on the sensory test criteria). Its performance was very similar to the other commercially used surfactants evaluated, even surpassing them in the wet combing parameter.

Table 1. Sensory results of the evaluated hair conditioners.

Parameter	AAPDMA C22-C24	BAPDMA	BTAC
Application	4.0	5.0	5.0
Wet detangling	4.3	5.0	4.3
Wet combing	5.0	4.7	4.0
Dry fell	4.0	4.3	4.3

The brightness measurements results presented in Table 2 also indicate the performance of the developed product AAPDMA C22-C24 as an efficient conditioning agent. The results show that the product not only preserves the hair's natural shine immediately after application (t0), but also enhances shine over time (t1). The product demonstrated a 9% increase in brightness compared to the control. The cationic surfactant widely used in BTAC-based products showed a 14% increase. The BAPDMA surfactant, which has a chemical composition similar to the developed product, did not show a statistically significant difference ($p > 0.05$) in hair shine compared to the control group.

Table 2. Brightness measurements of conditioners evaluated.

	Average Brightness (Gloss units) t0	**Average Brightness (Gloss units) t1**
AAPDMA C22-C24	19.7	22.7
BAPDMA	19.5	20.9
BTAC	19.4	23.6
Control	19.9	20.8

4. Discussion

The present work demonstrated the efficiency of a developed route for the production of ultra-long and saturated alkylamidopropyl dimethylamines, more specifically with chains from behenic (C22.0) and lignoceric (C24.0) acids, using the Amazonian Pracaxi oil as starting material. While the typical industrial production of behenamidopropyl dimethylamine (BAPDMA) involves the hydrogenation of oils rich in erucic acid (C22.1) such as Brassica or HEAR (High Erucic Acid Rapeseed), the use of Pracaxi oil dispenses this process, since this oil already naturally has a high content of long-chain and saturated acids.

The results showed that the developed route was efficient in producing a mixture of AAPDMA free of unsaturated fatty acids, leading to a product chemically equivalent to the commercial BAPDMA (behenamidopropyl dimethylamine), as demonstrated by the FTIR (Figure 1) and 1H NMR (Figure 2) spectra. Considering the quantitative nature of the 1H NMR technique, it was also possible to infer that the product obtained, in addition to not containing unsaturated components, is a mixture of saturated fatty chains of 22 and 24 carbon atoms, which is compatible with the typical composition of pracaxi oil in terms of saturated components, in which behenic (C22.0) and lignoceric (C24.0) acids correspond to the majority saturated fatty acids [4]. For this reason, the product developed was called AAPDMA C22-C24.

As for the rheological results, the formulated hair masks presented similar results regarding the viscosity profile and slightly different results regarding the Yield Point. It is worth noting that in this first group of results, the concentrations of both active surfactant and cetearyl alcohol were high, which reduced the differences between the products, especially since the products compared were chemically very similar (BAPDMA and AAPDMA C22-C24).

As for the rheological results of the conditioning agents, prepared in lower concentrations of both active surfactant and cetearyl alcohol, the differences between the systems were better evidenced. In general terms, it can be seen that the longer the active surfactant chain, the higher the viscosity obtained and also the yield point. The commercial BTAC has a chain of 22 carbons, while BAPDMA has 22 carbons only in its fatty fraction, in addition to its fraction related to the addition of DMAPA (diamine), making it equivalent to a molecule with 26 carbons in length. AAPDMA, in turn, being a mixture of C22.0 and C24.0, would have on average an even greater length than BAPDMA, resulting in molecules with lengths equivalent to 26 and 28 carbons.

Regarding the performance results, although they are preliminary formulations, it was possible to verify high efficiency in the conditioning agents using the developed product AAPDMA C22-C24, especially with regard to wet combing, which proved to be superior to the other products. The other parameters were considered great in the efficiency scale, according to the evaluation of expert trained panels. It is important to highlight that the methodology used to prepare the formulations was the one typically designed for usual industrial products such as BTAC and BAPDMA. Considering that the developed product AAPDMA C22-C24 contains a significantly high content of long chains of C24.0, unlike BTAC and BAPDMA, it is possible that the methodology adopted or even the formulation is not the best possible for this product. The development of new formulations and methodologies for the preparation of conditioning agents containing the developed product AAPDMA C22-C24 is underway.

5. Conclusion

We find in the Amazon biodiversity, more specifically in Pracaxi Oil, a way to develop science, innovation and technology, producing a green conditioning active ingredient with high added value, AAPDMA C22-C24, through a sustainable route with a positive impact on the environment and local communities. This is because AAPDMA C22-C24 is produced from Pracaxi Oil, which in turn is obtained in a sustainable way, promoting the conservation of nature and guaranteeing a fair income for local producers. In this way, promoting the production of Pracaxi Oil in the Amazon region directly promotes the conservation of the largest biome in the World and supports local families improve their quality of life. Thus, natural resources are used in an intelligent and respectful way, from harvest, through oil production to the production of AAPDMA C22-C24, also obtained via a clean route.

As shown in the results, the developed product is comparable to the commercial and high performance behenamidopropyl dimethylamine (BAPDMA). However, while BAPDMA production involves a considerable number of steps, including hydrogenation of a high erucic acid vegetable oils, hydrolysis and distillation, to finally reacts the behenic acid with DMAPA, the production of AAPDMA C22-C24 does not require hydrogenation, hydrolysis and distillation, been more economic and sustainable. Unlike the existing commercial products derived from pracaxi oil, which consist of mixtures of AAPDMA containing the whole fatty acids present in the oil, including approximately 50% oleic acid (C18.1), the developed product AAPDMA contains only the long and saturated chains of the behenic (C22.0) and lignoceric acids (C24.0). Thus, AAPDMA C22-C24 is a new green ingredient that has the chemical and performance characteristics comparable with BAPDMA with the advantages of being produced by a sustainable raw material, through a green and cheap route.

6.References

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