Stability of Monoterpenes Encapsulated in Gum Arabic by Spray-Drying

A. C. Bertolini,[†] A. C. Siani,[‡] and C. R. F. Grosso*,[†]

Department of Food Planning and Nutrition, State University of Campinas, Campinas, São Paulo, Brazil 13083-970, and Laboratory of Chemistry of Natural Products, Far-Manguinhos, Oswaldo Cruz Foundation, Rio de Janeiro, RJ, Brazil 21041-250

Microencapsulation using spray-drying was tested with gum arabic and monoterpenes as wall and core materials, respectively. Citral, linalool, β-myrcene, limonene, and β-pinene were used at concentrations of 10, 20, and 30% with respect to the wall material. The greatest percentages of retention occurred at a concentration of 10%. Linalool and citral presented the greatest losses with increase in concentration. The hydrocarbons used were the most retained. Of the hydrocarbons, β-pinene was better retained in the capsules than limonene, and β-myrcene was the least retained of all. The capsules presented similar external morphologies, with no apparent cracks or porosity and an average size varying between 15.7 and 23.2 μm. The stability of the capsules to temperature was monitored for 33 days. The degradation products of the monoterpenes were evaluated. The results indicated a greater stability of the capsules containing β-pinene and citral than of those containing linalool and β-myrcene presenting the lowest retentions.

Keywords: *Monoterpenes; essential oils; gum arabic; microencapsulation*

INTRODUCTION

Microencapsulation is a technique in which a membrane encloses small particles of solid, liquid, or gas, with the objective of offering protection to the core material from adverse environmental conditions such as undesirable effects of light, moisture, and oxygen, thus contributing to an increase in the shelf life of the product and promoting a controlled liberation of the encapsulate (*1*). Liberation can occur as a result of the effect of a solvent, dissolution, breakage of the capsule, or controlled diffusion (*2*). The latter effect is controlled by a concentration gradient and intermolecular forces of attraction (*1*), permeation being controlled by the solubility of the encapsulated substance in the matrix and by its mobility through the wall material (*3*).

The wall materials most used as encapsulants include carbohydrates, cellulose and derivatives, lipids, some proteins, and gums (*1*). Of the latter, gum arabic stands out due to its excellent emulsification properties and is widely used. However, its capsules present a limited capacity against oxidation because they act as semipermeable membranes, and there are sufficient indications that its porosity to oxygen is a preponderant factor in the shelf life of the core material (*4*, *5*).

In addition to factors inherent to the encapsulation process, the retention of flavor is governed by factors related to the chemical nature of the core, including its molecular weight, chemical functionality, polarity, and relative volatility (*6*, *7*). With respect to the wall material, the retention capacity is associated mainly with the physical state of the encapsulant and its physicochemical characteristics such as molecular weight, molecular conformation, and chemical functionality (*2*, *8*).

Included in the main substances of natural and synthetic origin used as flavor ingredients are the essential oils, especially those rich in monoterpenes. According to their molecular structures, the monoterpenes can be classified as acyclic, monocyclic, or bicyclic, and their properties as flavorings are intimately related to the different chemical functions they present, including hydrocarbons, alcohols, aldehydes, ethers, ketones, and esters (*9*).

In this study, some monoterpenes showing different chemical functions and commonly present in essential oils and used as aromas in foods, cosmetics, and perfumes were encapsulated in gum arabic using the technique of spray-drying.

The effects of the chemical and steric characteristics of the compounds on the process yield were verified by measuring the degrees of retention of the monoterpenes in the capsules. The morphological distribution and characterization of the particles was also determined. The degree of protection of the encapsulated monoterpenes against oxidation was inferred from studies of their stability by observing the formation of secondary products during storage.

MATERIALS AND METHODS

Gum arabic (Synth, batch 28162, Campinas, Brazil), limonene (orange essential oil, 95% pure, Citrosuco S/A, Bebedouro, Brazil), β-pinene, β-myrcene, linalool (Sigma, St. Louis, MO), and citral (98%, Dierberger Essential oils S/A, Barra Bonita, Brazil) were used.

Core percentages of 10, 20, and 30% of monoterpenes were used in relation to the wall material to evaluate the post-drying yields. The percentage of 20% was used in the stability studies and in the evaluation of the formation of secondary products.

* Author to whom correspondence should be addressed (telephone 55-19-37884079; fax 55-19-37884060; e-mail grosso@fea.unicamp.br).

[†] State University of Campinas.

[‡] Oswaldo Cruz Foundation.

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After dissolution of the gum arabic and addition of the monoterpene, the material was vigorously homogenized (10000 rpm/3 min) at 22 °C and maintained under slow agitation during spray-drying. The spray dryer (Lab-Plant model SD 04, Huddersfield, U.K.) was operated under the following conditions: entrance and exit air temperatures of 150 and 93 °C, respectively, air pressure of 5 kgf/cm^2, entrance flow rate of liquid of 15 mL/min, aspersion nozzle diameter of 1 mm. Each spray-drying was processed in triplicate, and the resulting products were homogenized to minimize the sources of variation of the process. When necessary, the products were maintained at −13 °C and protected against the actions of light and oxygen.

Quantification of the total monoterpenes encapsulated was carried out in triplicate, using steam stripping with the aid of a Clevenger apparatus for 2 h (*10*). The yields were calculated from the volumes obtained in the water distillation and the specific density of each compound (β-pinene, 0.86 g/mL; β-myrcene, 0.79 g/mL; limonene, 0.84 g/mL; linalool, 0.86 g/mL; and citral, 0.89 g/mL).

The morphology of the microcapsules was evaluated by scanning electronic microscopy (JEOL, JMS-T330, Tokyo, Japan), using an acceleration voltage of 15 kV. The encapsulated samples were fixed in stubs containing a double-faced adhesive metallic tape and coated with gold in a Balzers evaporator (SCD 050, Baltec, 40 mA/75 s, Lichtenstein, Austria) (*11*). The particle size distribution and measurement of the average particle size was carried out in triplicate for each percentage of encapsulation, using 2-propanol as the solvent in the Lumosed Photo-Sedimentometer (Retsch, Haan, Germany).

The samples containing 20% core material were maintained in an incubator at 50 °C for 33 days, with weekly sampling to check on the composition of the encapsulates. Extraction of the encapsulated material was made using acetone (*4*), including a final centrifugation (4000 rpm/10 min). Quantification of the extracted material was carried out by gas chromatography, using a Varian 3600 chromatograph (Walnut Creek, CA) equipped with a DB-Wax 30 m × 0.25 mm capillary column coated with a polyethylene glycol film (0.25 μm thickness). The chromatographic conditions were as follows: flame ionization detector (FID) at 250 °C, H_2 carrier gas, flow rate of 1.0 mL/min, split ratio of 1:30, injector at 200 °C, column head pressure of 7.0 psi, 70 °C/4 min, 70−130 °C, 6 °C/min, 130−190 °C, 10 °C/min, and 190 °C/4 min.

Identification of the monoterpene degradation products was carried out by GC-MS in a 5988 Hewlett-Packard chromatograph (Wilmington, DE) using an Ultra-2 column 25 m × 0.20 mm coated with a phenylmethylsiloxane film (0.33 μm thickness), detector at 250 °C, injector at 200 °C, and split ratio of 1:100. The programming conditions were the same as previously cited (FID), and the identification of the components was from an analysis of their mass spectra, with the aid of the HP-G1035A spectrum library of the Wiley Library, their retention times being compared with those of a homologous series of linear alkanes from C5 to C40 (*12*).

RESULTS AND DISCUSSION

Retention of the Monoterpenes in the Microcapsules. The greatest retention during the drying process was observed when 10% core material was used, as compared to 20 and 30%. Thus, the recuperation varied from 91 to 75% for limonene, from 64 to 44% for linalool, from 86 to 47% for citral, from 88 to 74% for β-myrcene, and from 97 to 81% for β-pinene, for the core percentages varying from 10 to 30%, respectively, with standard deviations between the repetitions from 0.3 to 3.3%.

In the case of limonene, the recuperation of 91%, obtained with 10% core material, was similar to previously published values, which were between 81.8 and 86.0% (*10*, *13*, *14*). The reduction in the rate of recuperation of citral was also related to the increase in concentration of the monoterpene in the gum arabic (*15*).

Experiments with the microencapsulation of linalool in cyclodextrin resulted in a recuperation of the core material of up to 44%. Linalool still presented a greater recuperation than the aldehyde, acid, and ketone functions, the retentions of which were below 33% (*16*). On the other hand, the results obtained in this study gave retentions of linalool and citral equal to those observed with maltodextrin as wall material, with which the aldehyde function was better retained than the alcohol function (*17*).

Experiments described with citral (neral and geranial) and linalyl acetate showed little degradation of these compounds during spray-drying when a mixture of gum arabic and maltodextrin was used as wall material, giving recuperation percentages of up to 98% with respect to the initial amount of core material used (*15*).

Of the monoterpenes studied, the hydrocarbons presented the greatest retentions, greater than the aldehyde, which for its part presented a greater retention than linalool. Compounds containing electronegative electron-donating groups, such as alcohols and aldehydes, can form hydrogen bonds with surfaces containing hydroxyl groups (*18*), as is the case of gum arabic. Thus, these compounds should be more strongly associated with the wall material and therefore present greater retentions than the hydrocarbons, which was not shown experimentally.

The loss of volatiles during the spray-drying process can be explained by hypotheses, which include a mechanism of selective permeability. This assumes that the retention of the compound in the atomized drop is a function principally of parameters related to the relative volatility of the compounds. After the skin that constitutes the wall of the covering has been formed, other factors emerge and become preponderant in the parameters which control the phenomenon of diffusion through the wall (*19*).

On the other hand, the greater polarity, and consequently the greater solubility of the encapsulated compound in an aqueous medium, results in a greater capacity for diffusion through the matrix during the spray-drying process, leading to greater losses during the formation of the capsules (*20*, *21*). In this way, the greater polarity of the chemical functions aldehyde and alcohol as compared to the hydrocarbons may have determined a smaller retention during the spray-drying encapsulation process.

The molar masses of the different hydrocarbons were identical, and β-pinene showed a greater percentage of retention. This occurred despite β-pinene's having the lowest boiling point of the hydrocarbons studied (164−166, 167.7, and 175−176 °C for β-pinene, β-myrcene, and limonene, respectively; *Merck Index*, 1996), which could indicate greater volatility. β-Pinene also presented the lowest retention time on the polar column used in the chromatographic analysis. The elution order on this column would provide a parallel to the forces of interaction between the monoterpenes studied and the polar matrix of the gum arabic, principally between the geometric hydrocarbon isomers, which should aid diffusion. However, this was not observed experimentally.

The diffusivities in the binary system [water/monoterpenes = 70:3 g/g, 90 °C, estimated according to the Wilk and Chang equation (*22*)] were 0.16332×10^{-3}, 0.15598×10^{-3}, and 0.15905×10^{-3} cm^2/s for β-pinene,

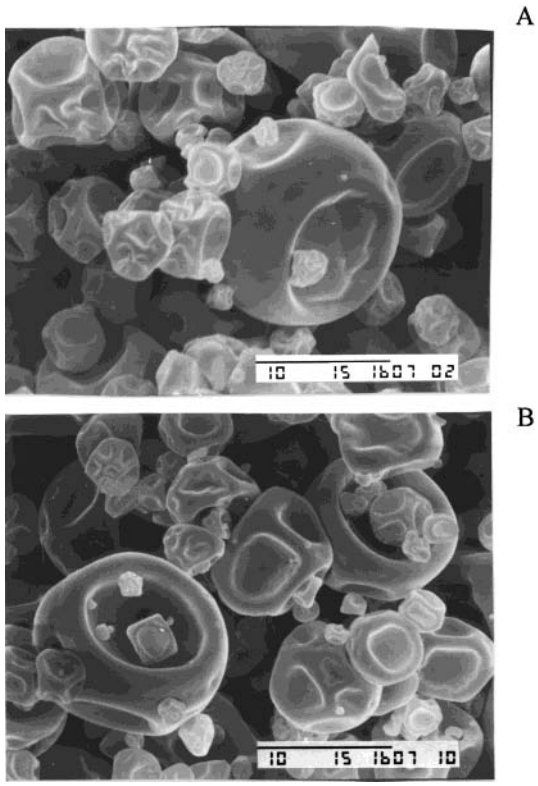

Figure 1. Micrographs of microcapsules (SEM) of limonene (A) and linalool (B) containing 10% core material with respect to the wall material.

β-myrcene, and limonene, respectively. In general, an increase in the size of the molecule reduces diffusion and, as a consequence, retards migration of the compound to the surface of the matrix, increasing its retention (*5*, *20*). The molar volumes (*23*, *24*) were 170.2, 153.1, and 141.5 cm ^{3} mol^{-1} for limone, β-myrcene, and β-pinene, respectively. Both the diffusivity in water and the molar volume indicate that β-pinene would be the least retained if these factors determined the retention levels.

In fact, it could be the "molecular diameter" and not the molar volume that determines the diffusion of the compounds through the matrix during the drying process. The lower the molecular diameter, the greater the coefficient of diffusion (*25*). An additional factor results from the different tendencies of the three hydrocarbons to undergo induced polarization. The calculated average polarizabilities (*23*, *24*) were 67.0, 73.4, and 71.3 atomic units for β-pinene, β-myrcene, and limonene, respectively. β-Pinene, with the smallest potential for induction, presented the greatest retention, whereas the contrary was observed for β-myrcene. Apparently, the tendency to polarize was the determining factor on the different retention levels observed by the hydrocarbons encapsulated in arabic gum.

Morphology of the Microcapsules and Particle Size Distribution. The capsules obtained in gum arabic, with different percentages of monoterpenes, presented very similar external morphologies, with a rounded external surface containing characteristic concavities and teeth (*26*, *27*) (Figure 1). The external surfaces presented no apparent cracks or porosity, aspects indicative of good protection of the core material. The results obtained for the particle size distribution indicated similar behaviors for the various core materials studied. With slight variations, the mean sizes of the particles varied from 15.7 to 23.2 μm for the different core materials, with slightly higher average particle sizes for the lower core concentrations. This is in agreement with previously published data (*7*, *28*).

Table 1. Shelf Life of Encapsulated Essential Oils Expressed as the Percent Remaining of the Initial Amount Present at Zero Time

time (days)	limonene	β-myrcene	β-pinene	linalool	citral
0	100.0	100.0	100.0	100.0	100.0
6	95.6	95.1	94.2	98.5	96.7
12	97.9	88.2	88.8	94.3	97.8
19	86.8	74.7	87.4	91.4	98.4
26	75.4	58.7	85.7	37.9	74.2
33	52.6	34.2	84.9	25.0	70.9

Stability of the Encapsulated Monoterpenes. In addition to the volatility and diffusion of the core material through the wall of the dry capsule, the action of temperature and oxygen on the samples can catalyze reactions that lead to the formation of derivatives, resulting in a decrease in the content of the compound originally encapsulated (*29*). On the other hand, this decrease is also a function of the susceptibility of the core material to degradation processes, including principally oxidative and dehydration reactions.

The results in Table 1 show a decrease in the amounts of encapsulated monoterpenes in all of the experiments. In the time interval studied, the greatest loss was registered for linalool, which reached 75.0% when compared to the amount initially present at the start of the stability assay. β-Myrcene also showed low retention under the same conditions, with a 65.8% loss. The lowest loss was observed for β-pinene, followed by citral, with 15.1 and 29.1% losses, respectively. The limonene capsules showed a reduction of 47.4% with respect to the amount present at zero time. In all cases, the GC analyses showed that there were no significant chemical variations between the pure monoterpene at zero time and the samples immediately after encapsulation.

With the exception of β-myrcene, the decrease in the amount of core material remained only slightly altered up to day 20 for the monoterpenes studied. After this point there was a visible acceleration in the rate of loss of the monoterpenes. This decrease was especially drastic for linalool and β-myrcene. This was probably due to the high susceptibility of the former to oxidation and that of the latter to undergo dimerization.

Linalool is a tertiary alcohol highly susceptible to dehydration in media containing traces of acid (*30*). The chemical structure of gum arabic, rich in hydroxyl groups, could favor the degradation of linalool by processes of dehydration and subsequent oxidation with the formation of rearranged products. Chromatographic analysis of the pure compound with those of the encapsulate reveals the appearance of signals corresponding to oxidized derivatives of linalool, mainly linalool oxide.

Although the retention of citral reached the significant value of 71%, there is a lack of literature on the identification of the oxidation products of this monoterpene. In the stability assay, the subproducts of oxidation and consequent reduction of the signals corresponding to neral and geranial are evident from a comparison of the chromatograms for pure citral and the encapsulate after the period of the assay (Figure 2). The structure of the majority of these oxidation products was only suggested by an analysis of the fragmentation of the mass spectra (Table 2).

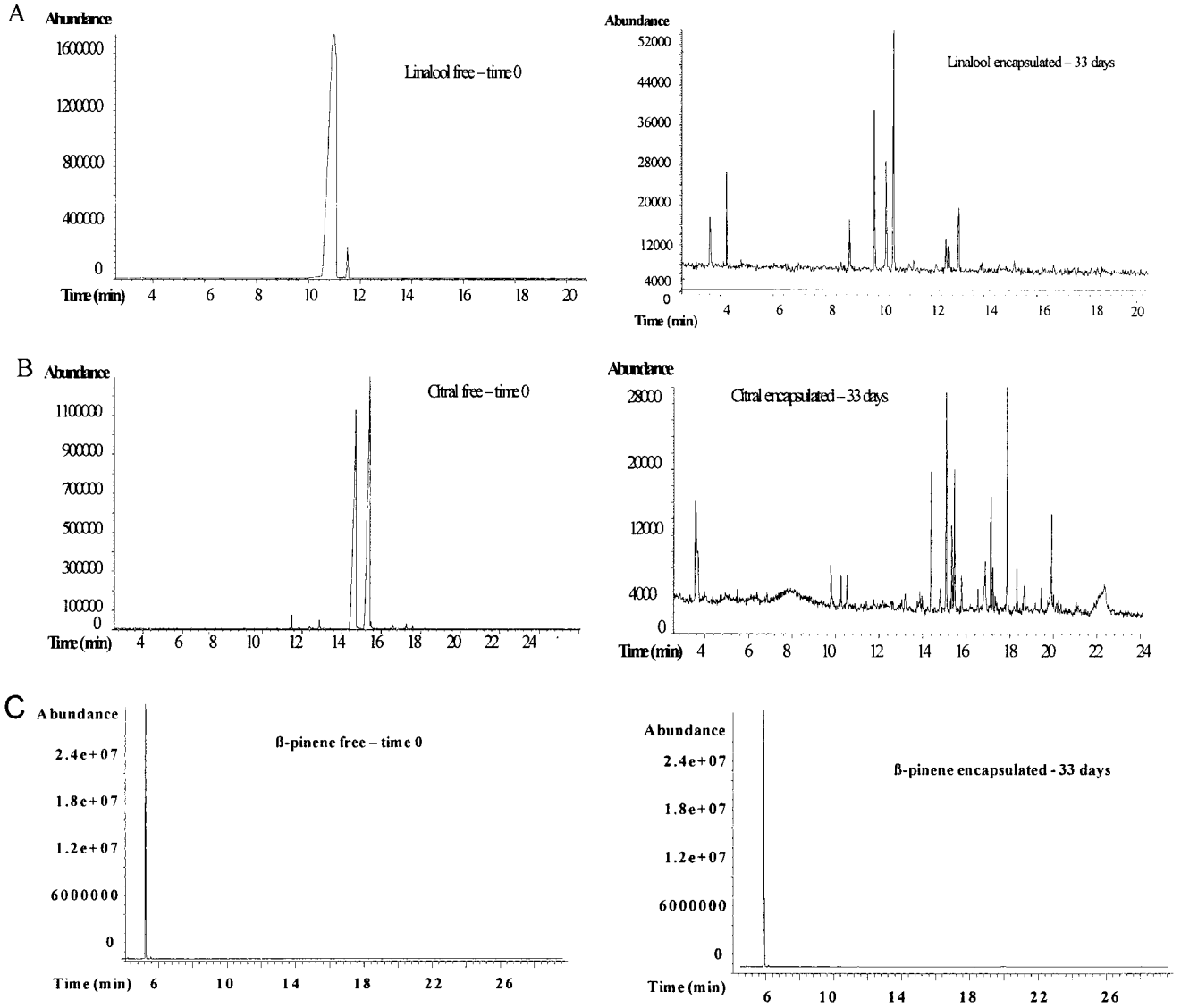

Figure 2. Chromatograms of pure and encapsulated monoterpenes submitted to a stability study (50 °C, 33 days): (A) linalool; (B) citral; (C) β-pinene.

Table 2. Degradation Products of the Microencapsulated Monoterpenes Evaluated in the Stability Assay

encapsulated monoterpene	degradation products after 33 days (calculated retention index[a])
β-myrcene	cyclization product[b] (1006), limonene (1031), dimeric products[b] (1965, 2024)
limonene	limonene *cis*-oxide (1138), limonene *trans*-oxide (1143), carvone (1254), *trans*-carveol (1225), perillic alcohol (1284), carveol acetate (1347), perillyl acetate (1373)
β-pinene	no degradation products detected
linalool	lavender lactone (1043), linalool *cis*-oxide (1078), linalool *trans*-oxide (1094), terpendiol I[b] (1195), menthene alcohols[b] (1177, 1191)
citral	linalool *cis*-oxide (1075), linalool *trans*-oxide (1090), linalool (1101), linalool oxide analogues[c] (1285, 1288), "citral oxide" analogues[c] (1375, 1381, 1417, 1541)

[a] Reference *12*. [b] Type of chemical structure suggested by mass spectral analysis. [c] Mass spectra presented peaks corresponding typically to the linalool oxide-like dihydrofuran fragment.

In the case of limonene, analysis of the results from GC-MS indicates the formation of perillyl alcohol, perillyl acetate, and carveol acetate as subproducts in the stability assay (Table 2). Analogous products, in addition to limonene oxide and carvone, were found in similar encapsulation experiments (*4*, *31*). The results also indicated an increase in the abundance of signals that represent states of direct oxidation of limonene, such as limonene oxide, carvone, and carveol.

From the chromatographic analysis, a decrease (15.1%) in the amount of β-myrcene after the microcapsulation process, when compared to the initial terpene composition, was evident. After 33 days, the amount of β-myrcene remaining in the capsules had decreased to 34.2% of the value for the capsules extracted immediately after spray-drying (zero time).

As secondary products, encapsulated β-myrcene presented the same compounds that appear in the commercial product. The concentration of these compounds, after 33 days, increased by up to one-third in the capsules as compared to the ammount present at zero time. The GC-MS analyses indicated that these com-

pounds were dimerization isomers of β-myrcene (Table 2), which appear to be more stable in the capsules than the original β-myrcene and so are better retained. Their greater molecular weight and lower volatility are probably the factors responsible for this result. GC-MS results from β-myrcene in the stability assay also presented a series of unidentified secondary signals, which represented 2.8% of the other degradation products.

Despite the variation observed in the amounts of β-pinene extracted from the capsules at zero time and at the end of the stability assay (Table 1), the chromatographic profiles were identical to those of the commercial compound used in the experiment, there being no appearance of peaks indicating oxidation or degradation.

Conclusions. The chemical functionality, associated with the solubility and diffusion through the forming matrix, determines the degree of retention in the production of capsules by spray-drying, in the case of monoterpenes encapsulated in gum arabic. The order obtained was hydrocarbon > aldehyde > alcohol for monoterpenes with similar molecular weights.

Hydrocarbons with the same molecular weight ($C_{10}H_{16}$) and similar solubilities presented different yields in the drying process. These differences were associated with the molecular structures of the monoterpene isomers. The observed order was bicyclic > monocyclic > acyclic, demonstrating the contribution of steric factors to retention in addition to the ability to undergo polarization.

The products encapsulated in gum arabic showed a reduction in content during the shelf life study at controlled temperature. There was little variation in content during the first 20 days, but after this there was an accentuated and variable loss for the majority of the monoterpenes studied. The observed order of retention was β-pinene > citral > limonene > β-myrcene > linalool.

However, experiments with GC-MS showed that oxidative processes occurred with different intensities for the various core materials. This fact indicated that gum arabic was not efficient as a wall material, the oxidation potential of the molecule being the determining factor in the oxidation of the core material.

Although the chemical identification of the degradation products of the monoterpenes has not been intensively investigated, its importance is explicit because they are compounds frequently found in the essential oils used as flavoring and preservation agents.

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