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EXTRACTION OF COLORED SUBSTANCES FROM MATÉ (ILEX PARAGUARIENSIS)

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ABSTRACT

Liquid-liquid extraction of pigments present in maté (Ilex Paraguariensis) was studied using various organic solvents and different connterions. The best results were obtained using diethyl ether and sodium lauryl sulfate. The effect of the addition of ethanol on the extraction process was also analyzed.

KEY WORDS: Maté (Ilex Paraguariensis), liquid-liquid extraction, saponins, sodium lauryl sulfate, pigments.

RESUMO

Foram estudados sistemas de extração liquido-liquido para os corantes da erva mate, testando-se vários solventes orgânicos e diferentes contra-íons. O melhor sistema extrator foi éter dietilico-lauril sulfato de sódio. O efeito da adição de etanol sobre o sistema também foi estudado.

INTRODUCTION

The maté beverage ("mate" or "chimarrão") is widely used in Southern Brazil, Argentina, Paraguay and Uruguay and it is an integral part of the "Gaúcho" culture. It is also widely used as a medicinal plant, having stimulant, diuretic, antirheumatic and antinflammatory properties. The genuine maté comes from Ilex Paraguariensis Saint Hilaire, a South American native perennial tree coming from the holly family.[11] According to Gaucho tradition, the ceremony of drinking maté (tea), passing the "cuia" (a receptacle made from a native pumpkin) among the participants leads to an atmosphere of respect, friendship and solidarity and at the same time the tea is efficient against food intoxications and acts as a general tonic.[1-3]

The main active components of maté (erva mate) are saponins, more specifically they are glycosides of ursolic and oleanolic acids.[3-5] Their general structure is given in Figure 1. The isolation procedure usually involves the extraction of dried and ground leaves by maceration in CH_3CH_2OH-H_2O followed by successive extraction with CH_2Cl_2 and n-butanol and repeated column chromatography. The structure determination is usually done using ^1H and ^{13}C nuclear magnetic resonance, mass spectra and visible and ultraviolet spectroscopy, known secondary

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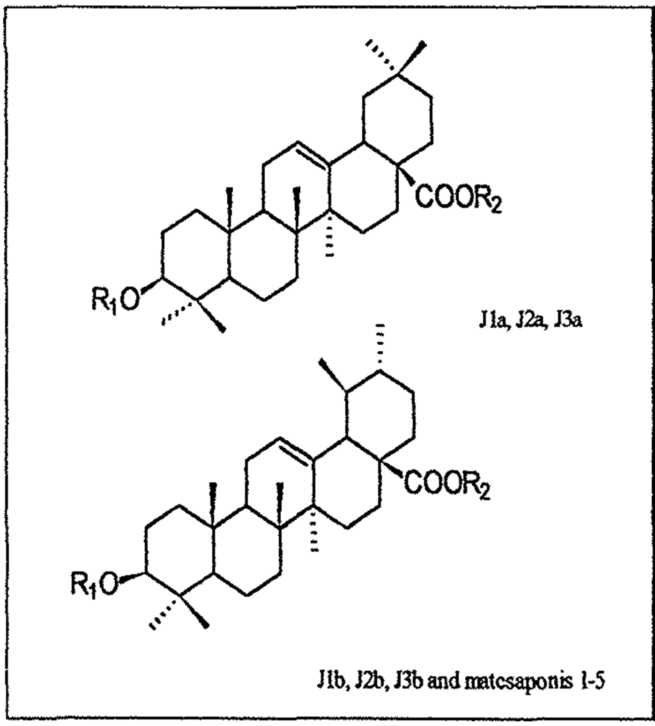
metabolites are xanthines (mainly caffeine), flavonoid glycosides (rutin) and caffeoylquinic acid derivatives or chlorogenic acids.[3]

The purpose of the present work was to study some rapid methods for the extraction of pigmented or colored substances present in maté beverage (tea). It is well Known that compounds with formal positive or negative charge can be readily extracted with organic solvents through ion-pair formation using connterions. This method has been widely used for the extraction of artificial dyes in industrialized foods and in phase transfer catalysis.[7,8] Surfactants have often been used as phase transfer agents.[6-9]



J1a R_1=α-L-rhamnopyranosyl-(1→2)-α-L-arabinopyranosyl; R_2=H
J1b R_1=α-L-rhamnopyranosyl-(1→2)-α-L-arabinopyranosyl; R_2=H
J2a R1=β-D-glucopyranosyl-(1→3)- α-L-arabinopyranosyl; R_2=H
J2b R1=β-D-glucopyranosyl-(1→3)- α-L-arabinopyranosyl; R_2=H
J3a R_1=α-L-rhamnopyranosyl-(1→2)-α-L-arabinopyranosyl; R_2=β-D-glucopyranosyl
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Matesaponin 5 R1=β-D-glucopyranosyl-(1→3)-[α-rhamnopyranosyl-(1→2)]-α-L-arabinopyranosyl;
R_2=β-D-glucopyranosyl-(1→4)-β-D-glucopyranosyl-(1→6)-β-D-glucopyranosyl

Structures of the saponins isolated from **Ilex paraguariensis**.(3)

FIGURE. 1. General Strutura of the Saponiuns Isolated from Ilex paraguariensis.

Liquid-liquid extraction is on experimental technique where a solution (usually aqueous) is placed in contact with a second solvent (usually an organic solvent), essentially immiscible in the first one, with the purpose to transfer one or move solutes from the first solvent to the second one. The separations are usually simple, clean, rapid and practical. In many cases the separation may be done by simple agitation during a few minutes using a separatory funnel.

One would not expect that it would be possible to extract organic compounds from aqueous solutions with organic solvents, because there would be a large loss of energy of electrostatic solvation. The most obvious way to make an aqueous ionic species extractable is to neutralize its charge. This can be attained by the formation of a neutral metal chelate complex or by ionic association, i.e., ion-pairing. The more hydrophobic the resulting molecule, the better its extraction.[10,12] An alternative is the solubilization of the pigments with micelles.

In spite of the fact the consumption of maté is significant in the southern part of Latin America, systematic research in this subject is still in an incipient stage and our effort represents a step is this direction.

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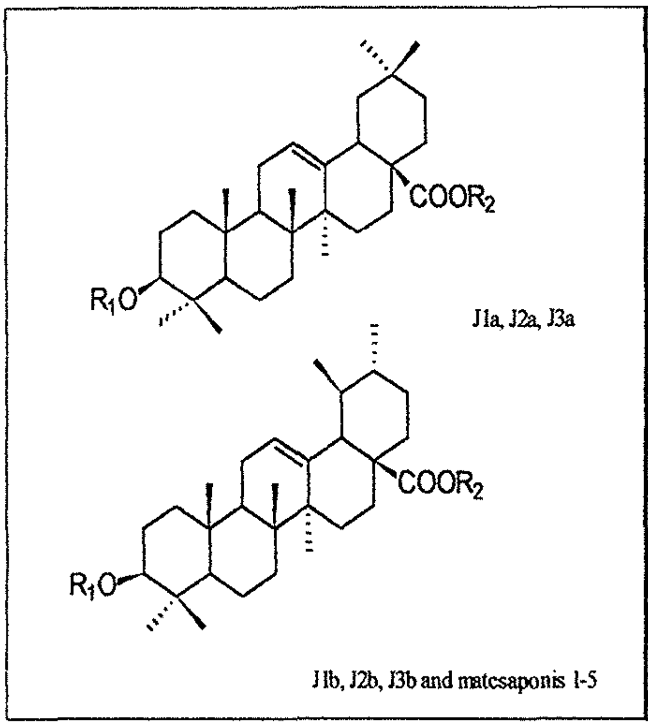

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EXPERIMENTAL PROCEDURE

Liquid-liquid extraction was performed an "cold tea of erva mate"(aqueous solutions at room temperatura) in the presence or absence of ethanol using various organic solvents such as diethyl ether, methanol, n-propanol, n-butanol, chloroform, etc and counter-ions of NaLS (sodium lauryl sulfate), CPCl (cetylpyridinium chloride) and CTAB (cetyltrimethylammonium bromide) at concentrations ranging from 0,4 x 10^{-3} M to 6,0 x 10^{-3} M.

All the reagents used were of analytical reagent grade and the water was deionized and distilled. The erva mate employed was always of the same commercial brand (Raizes). ----

The absorption spectrum of the extracts was determined in the visible region (500-700 nm) using a Carl Zeiss spectrophotometer.

RESULTS AND DISCUSSION

Typical absorption spectra obtained for the extract using the three different surfactants or phase transfer agents are shown in Figure 2. As can be seen, NaLS, na anionic species, is by far the most efficient as far as extraction is concerned. The maximum absorption band is present at 680 nm and was subsequently used as a criterion for the best extraction.

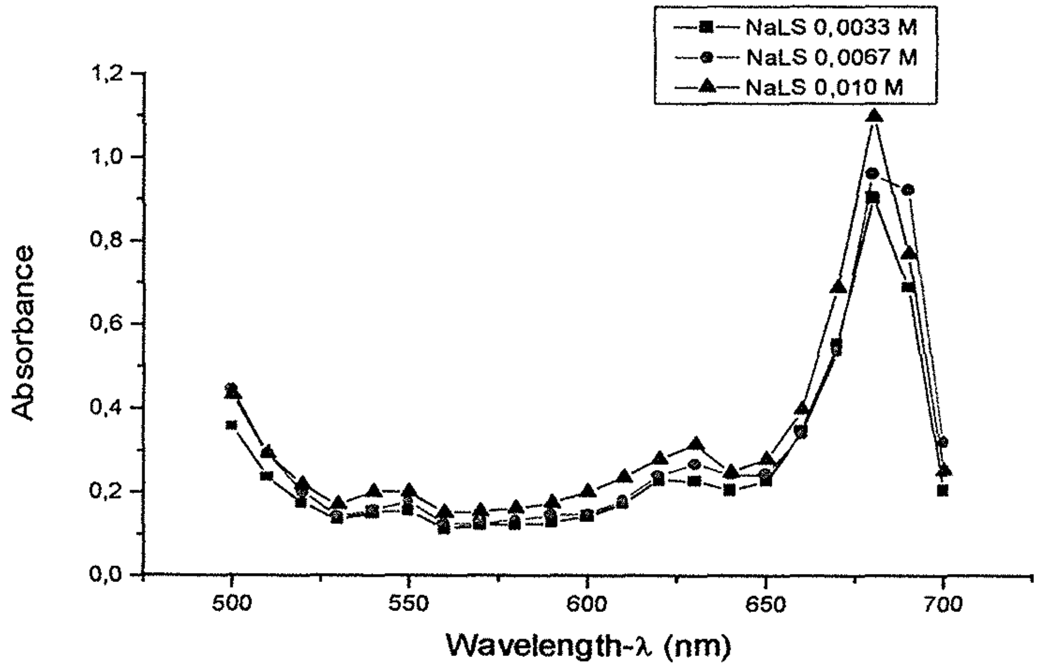

FIGURE 2. Absorption Spectrum of the Pigments of Erva Mate Using Diethyl Ether and Various Phase Transfer Agents.

Figure 3 illustrates the absorption spectra obtained for the extracts using NaLS (0,003 M) and diethyl ether and butanol as organic solvents.

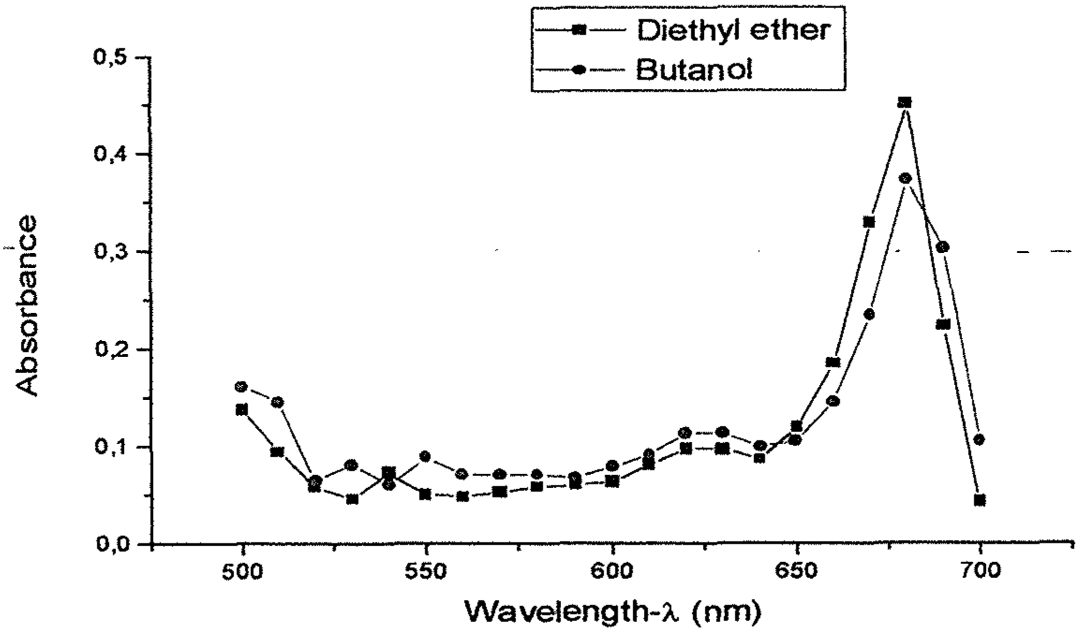

FIGURE 3. Absorption Spectrum of the Pigments of Erva Mate Using NaLS (0,003 M) and Diethyl Ether or Butanol as Organic Solvents.

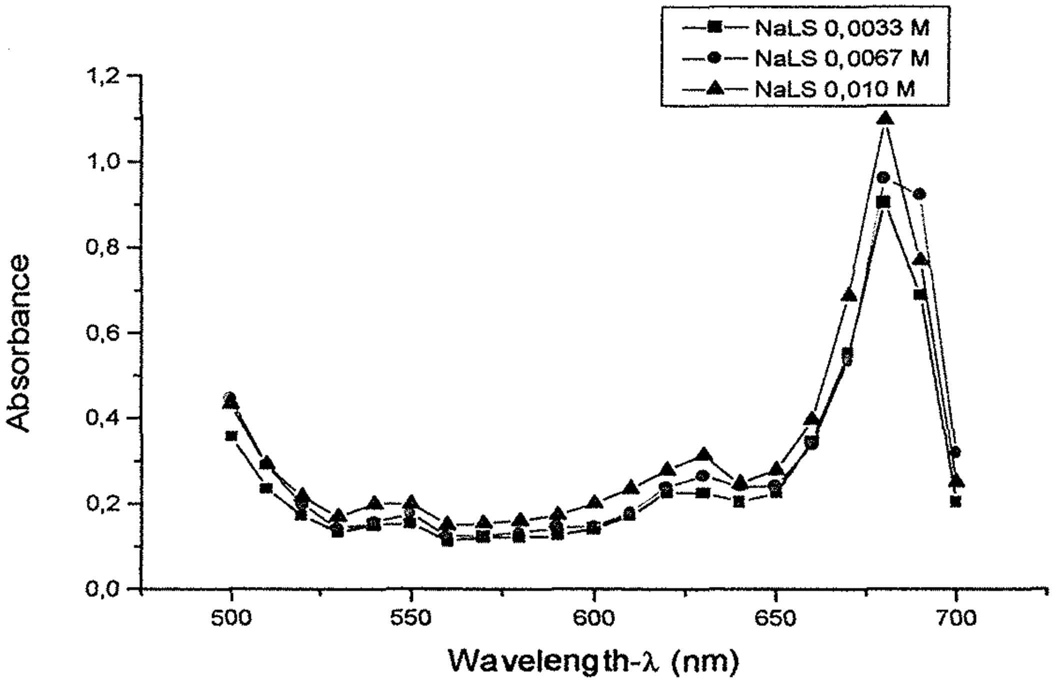

FIGURE 4. Absorption Spectrum of the Pigments of Erva Mate Extracted with Diethyl Ether and Different Concentrations of Sodium Lauryl Sulfate (NaLS).

The effect of the concentration of sodium lauryl sulfate (NaLS) on the extraction process is shown in Figure 4. In all cases shown in the figure, the surfactant is present in concentrations above the CMC (critical micellar concentrations). However we also observed extraction when the surfactant was below the CMC, indication the ion-pair formation and subsequent phase transfer is also important.

The effect of the addition of ethanol on the extraction of pigments with diethyl ether and sodium lauryl sulfate (NaLS) is illustrated in Figures 5 and 6.

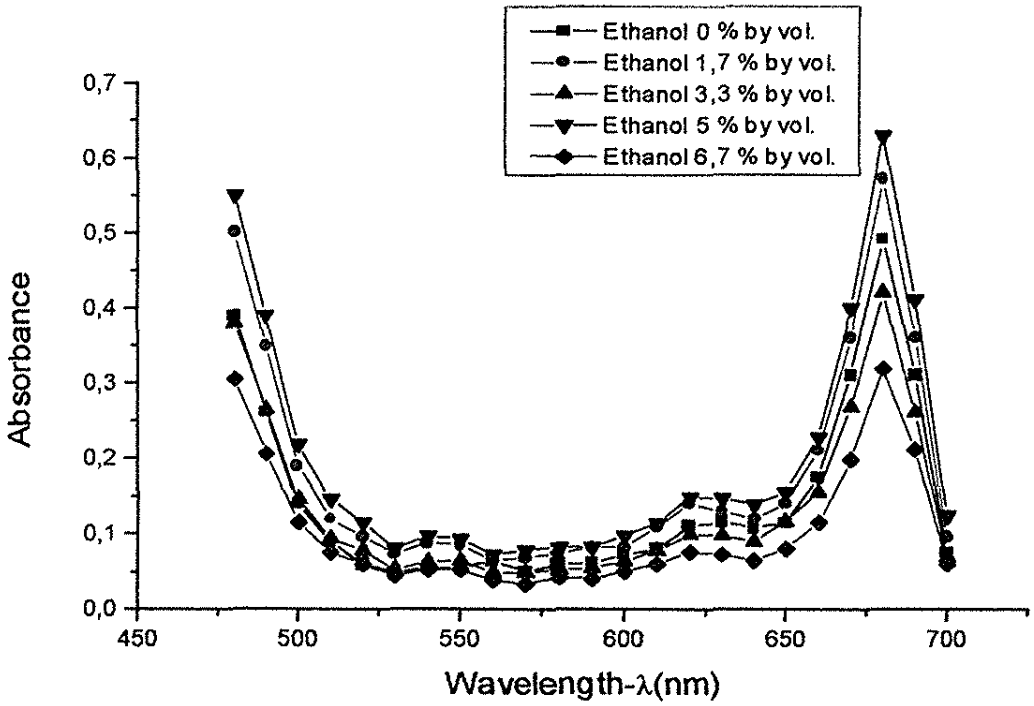

FIGURE 5. Absorption Spectrum of Pigments Extracted from Erva Mate Using Diethyl Ether, Sodium Lauryl Sulfate (NaLS) and of Low Concentrations of Ethanol.

The experimental results clearly show that the addition of ethanol at low concentrations (around 5 to 6 percenthy volume) improves the extraction process. At higher concentrations however, (more than 10%) the extraction process is hindered. The effect of ethanol may be explained by its effect on micelle formation.

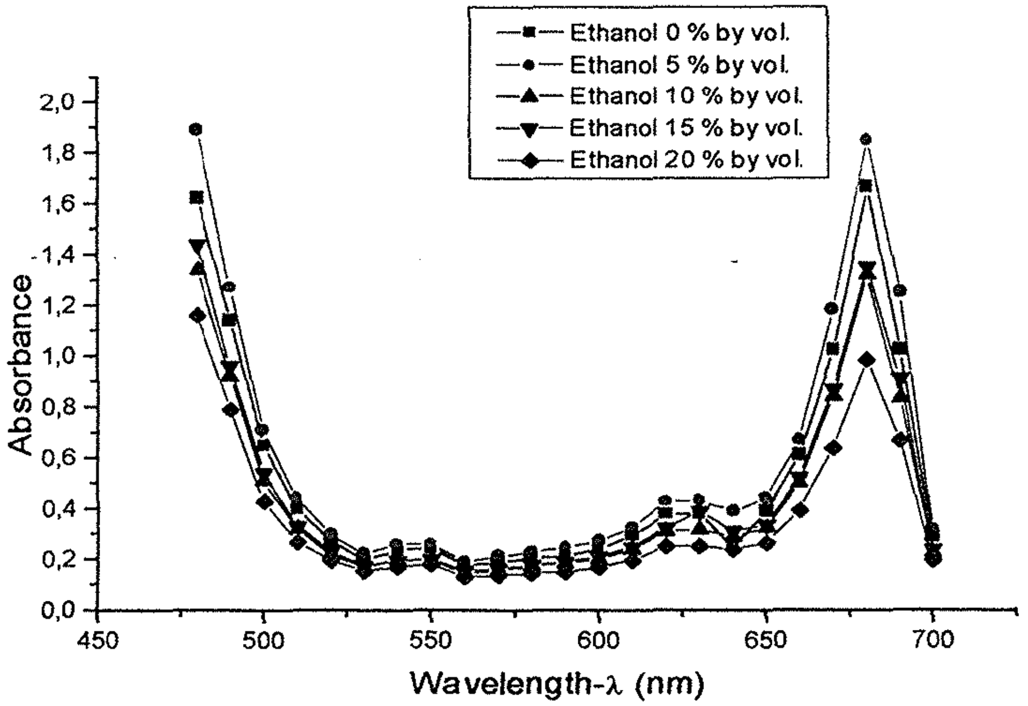

FIGURE 6. Absorption Spectrum of Pigments Extracted from Erva Mate Using Diethyl Ether, Sodium Lauryl Sulfate (NaLS) and a Wide Range of Concentrations of Ethanol.

CONCLUSION

It may be concluded that the pigments of erva mate may be extracted easily from aqueous solutions by using sodium lauryl sulfate, diethyl ether and low concentrations of ethanol. Further studies are in progress to elucidate the structure of these colored substances.

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