

BULK AND MOLECULAR COMPOSITION OF BRAZILIAN AMBERS (CRETACEOUS)

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Introduction

Amber is the fossilization product of plant resins. Resins are exuded by higher plants (gymnosperms and angiosperms) upon injury, apparently as a protection against further attacks by insects and micro-organisms. In contact with the atmosphere this secretion quickly hardens, forming a protective layer for the wounds (Langeheim, 1990). During the process of sedimentation the hardened resins, as well as other parts of the plants, would gradually bury, resulting, along geological periods of time, in the amber deposits found in coals and sediments.

The present study discusses the composition of two Brazilian Cretaceous ambers collected in the Recôncavo and Parnaíba Basins, with the intent of extending the knowledge of the origin and the geochemical transformations of fossilized higher plant resins. The Recôncavo Basin is a Mesozoic aulacogen located in the state of Bahia (Northeast Brazil) whose origin is related to the South America – Africa rifting. The Parnaíba Basin, situated in the states of Piauí, Maranhão and Pará (North Brazil), is a large intracratonic synclisis which comprises Paleozoic and Mesozoic sequences.

Results and Discussion

Bulk samples were analysed by means of elemental analysis, Fourier transformed infrared spectrometry (FT-IR) and solid state carbon-13 nuclear magnetic spectrometry (¹³C NMR-solid state). The H/C ratios for the Recôncavo and Parnaíba resinites are 1.60 and 1.60, respectively. These data reinforce the suggestion by Grimalt *et al.* (1988) that polymerization is the main pathway of transformation of the amber organic matter, instead of the aromatization reactions which characterize the maturation process of other higher plant materials.

In the FT-IR spectra (Figs.1 and 2) of both ambers the broad band in the region 3600-3300 cm⁻¹ can be assigned to hydroxyl groups (O-H stretching) which may also contain the signal due to

water. The contribution of alcoholic groups is reinforced by the absorptions in the 1250-1000 cm⁻¹ region which are possibly due to C-O (stretching). The C-H bonds in methyl and methylene groups are represented by the intense bands around 2900 cm⁻¹ (stretching) and also by two absorptions near 1460 and 1380 cm⁻¹ (bending). In the Recôncavo amber, the carbonyl group absorption (stretching) at 1724 cm⁻¹ could be related to ketones, aldehydes or carboxylic acids. In this region, the Parnaíba sample presents unresolved bands at 1720 and 1701 cm⁻¹, which clearly point to the occurrence of at least two different types of carbonyl compounds.

¹³C NMR (solid state) spectra (Figs. 3 and 4) evidenced the highly saturated character of both resinites since the dominant group of peaks in the

range from 10 to 60 ppm is due to saturated carbons; the shoulder at 55 ppm, however, may also correspond to carbons substituted with hydroxylic groups. The presence of olefinic and/or aromatic carbon is secondary, as indicated by the weak (unresolved signal) in the 110-150 region. Weak resonances due to carbons from carboxylic acids and/or esters appear between 150 and 185 ppm.

The ambers were separated into soluble and insoluble fractions according to the method described by van Aarssen *et al.* (1990). The solvent extractable fractions were analysed by gas chromatography coupled with mass spectrometry (GC-MS). Monoterpenoids such as fenchone, fenchyl alcohol, camphor and *endo*-borneol, characteristics of the essential oils of plants, were detected in small amounts in the Parnaíba resinite. In the elution region of sesquiterpenoids in both

samples the most prominent components are ionene, 1,1,5,6-tetramethyl-1,2,3,4-tetrahydronaphthalene and dimethylnaphthalenes, hydrocarbons that are usually considered as diagenetic products of terpenoids. Diterpenoids are by far the dominant constituents in both extracts and the most abundant compound is the aromatic hydrocarbon 13-methyl-18-nor-podocarpa-8,11,13-triene. The methyl esters of methyl 16,17-bisnordehydroabietic acid and dihydroisopimaric acid were also identified in the samples.

Pyrolysis in conjunction with GC-MS (Py-GC-MS) of the insoluble fractions revealed complex mixtures of alkyl derivatives of cyclohexene, benzene, decalin, tetrahydronaphthalene and naphthalene. Moreover, an expressive contribution of diterpenoids was evidenced, some of them also present in the soluble extracts.

Conclusions

Bulk and molecular analyses have been performed on two Cretaceous Brazilian ambers. Information deduced from the FT-IR and ¹³C NMR (solid state) spectra gives a general assessment for the presence of various kinds of bonds and functional groups. The molecular

analyses showed that, although diterpenoids are expressive constituents in both soluble and insoluble fractions, specific mixtures of components constitute each resinite. The results suggest the *Araucariaceae* family of plants as a possible source for these ambers.

References

van Aarssen, B.G.K., Cox, H.C., Hoogendoorn, P., de Leeuw, J.W., 1990. A cadinene biopolymer in fossil and extant dammar resins as a source for cadinanes and bicadinanes in crude oils from South East Asia. *Geochimica et Cosmochimica Acta* 54, 3021-3031.

Grimalt, J.O., Simoneit, B.R.T., Hatcher, P.G., Nissenbaum, A., 1988. The molecular composition of ambers. *Organic Geochemistry* 13, 677-690.

Langeheim, J.H., 1990. Plant resins. *American Scientist* 78, 16-24.



