

Solid State ^{13}C NMR Analysis of Brazilian Cretaceous Ambers

Ricardo Pereira,^{*,a} Rosane A. S. San Gil,^b Ismar S. Carvalho,^c
Antonio Carlos S. Fernandes^d and Débora A. Azevedo^{*,a}

^aLaboratório de Geoquímica Orgânica Molecular e Ambiental, Instituto de Química,
Universidade Federal do Rio de Janeiro 21941-909 Rio de Janeiro-RJ, Brazil

^bLaboratório de RMN de Sólidos, Instituto de Química, Universidade Federal do Rio de Janeiro,
21941-909 Rio de Janeiro-RJ, Brazil

^cDepartamento de Geologia, Instituto de Geociências, Universidade Federal do Rio de Janeiro,
21910-200 Rio de Janeiro-RJ, Brazil

^dDepartamento de Geologia e Paleontologia, Museu Nacional, Universidade Federal do
Rio de Janeiro, 20940-040 Rio de Janeiro-RJ, Brazil

Espectros de ressonância magnética nuclear de ^{13}C com polarização cruzada e rotação no ângulo mágico (RMN-CPMAS de ^{13}C) foram obtidos pela primeira vez para três amostras de âmbar provenientes do Mesozóico da América do Sul. As amostras foram datadas como pertencentes ao Cretáceo Inferior e coletadas em sedimentos das bacias do Amazonas, Araripe e Recôncavo, Brasil. Todas as amostras apresentaram espectros muito similares, o que é consistente com uma fonte paleobotânica em comum. Algumas características dos espectros, tais como sinais mais intensos entre 38-39 ppm, sugerem relação entre os âmbares brasileiros e a família Araucariaceae. Todas as amostras são formadas de estruturas polilabdânicas que permitem associação com resinas de Classe Ib, estruturalmente constituídas por polímeros de diterpenos labdânicos. Informações quanto às mudanças estruturais ocorridas durante a maturação, tais como isomerização de insaturações $\Delta^{8(17)}$ e $\Delta^{12(13)}$, também foram obtidas pelas análises por RMN-CPMAS de ^{13}C . Os resultados quanto à origem botânica das amostras são concordantes com aqueles alcançados por análises mediante cromatografia gasosa acoplada à espectrometria de massas (GC-MS).

^{13}C cross polarization with magic angle spinning nuclear magnetic resonance (^{13}C CPMAS NMR) spectra have been obtained for the first time to three Cretaceous amber samples from South America. The samples were dated to Lower Cretaceous and collected in sediments from the Amazonas, Araripe and Recôncavo basins, Brazil. All samples have very similar spectra, consistent with a common palaeobotanical source. Some aspects of the spectra suggest a relationship between Brazilian ambers and Araucariaceae family, such as intense resonances at 38-39 ppm. All samples are constituted by polylabdane structure associated to Class Ib resins, constituted by polymers of labdanoid diterpenes. Finally, information concerning some structural changes during maturation, such as isomerization of $\Delta^{8(17)}$ and $\Delta^{12(13)}$ unsaturations, were obtained by ^{13}C NMR analyses. The results concerning botanical affinities are in accordance with previous results obtained by gas chromatography-mass spectrometry (GC-MS).

Keywords: amber, ^{13}C CPMAS, solid state NMR, botanical affinities, Lower cretaceous, Brazilian basins

Introduction

Terpenoid resins from gymnosperms and angiosperms are chemically stable and when they become fossilized

are named amber.^{1,2} So, ambers are fossilized plant resins constituted mainly by organic compounds and its chemical composition remains almost constant over geological time.³ Distinction of the different types of amber is very important in order to evaluate its possible botanical origins, classification and maturation. In this way, several

*e-mail: ricardopereira@iq.ufrj.br, debora@iq.ufrj.br

characterization techniques have been proposed such as pyrolysis-gas chromatography-mass spectrometry (Py-GC-MS),^{4,5} gas chromatography-mass spectrometry (GC-MS)^{6,7,8}, solid state Fourier transform infrared (FT-IR)⁹ and carbon 13 nuclear magnetic resonance spectroscopy (¹³C NMR).^{1,2}

An important classification system based on the structural characteristics of the resins was proposed by Anderson and co-workers,¹⁰⁻¹² establishing five classes: Class I – polymers of labdanoid diterpenes, subclassified into Classes Ia, Ib and Ic; Class II – polymers of bicyclic sesquiterpenoid hydrocarbons; Class III – natural fossil polystyrene; Class IV – sesquiterpenoids based on the cedrane carbon skeleton; and Class V – non-polymeric diterpenoid carboxylic acid. The Class I resins are the most widespread and abundant form of resins in the geosphere, based primarily on polymers of labdatriene diterpenoids carboxylic acids, especially isomers of communic acid, ozic acid and/or zanzibaric acid.¹⁰ Modern resins based on these diterpenoids are produced by numerous plant taxa, such as Araucariaceae (*Agathis*), Leguminosae (*Hymenaea*), Cupressaceae, Taxodiaceae and others.¹⁰

Several studies have been published concerning fossil resin ¹³C NMR from different deposits, ages and botanical origins. The greater part of amber samples analyzed date to the Tertiary period.^{1-2,4,10-11,13-17} However, studies reporting ¹³C NMR spectra of Cretaceous ambers are limited. Bulk (elemental composition, FT-IR, ¹³C CP/MAS NMR) and molecular (GC-MS) analyses were performed by Grimalt and co-workers¹⁸ on a series of ambers and resins, including samples of Cretaceous age from Canada (Late Cretaceous) and Israel (Early Cretaceous). Lambert and co-workers¹⁹⁻²¹ reported ¹³C NMR data to samples of Early and Late Cretaceous period collected in United States of America (Alaska, New Jersey, Mississippi and Kansas), Greenland, France, Switzerland, Canada, Lebanon, Jordan, Israel, Australia and New Zealand. In addition, there are reports about ¹³C NMR spectra of Lower Cretaceous amber samples from coal deposits in the Zubair Formation (Saudi Arabia, Kuwait) and Myanmar.^{22,23}

Important NMR studies regarding the classification of modern resins, its taxonomic and chemical relationships have been reported.^{24,25} According to these works, there are nine groups with distinctive spectral signatures associated to gymnosperms and angiosperms: Group CA, for Cupressaceae-Araucariaceae; Group S, constituting a small and separate group for *Sequoia sempervirens* of the Cupressaceae family (formerly Taxodiaceae); Group P, for Pinaceae; Group E, for Euphorbiaceae; Group C, for

Clusiaceae; Group FL, for Fabaceae/Leguminosae; Group D, for Dipterocarpaceae; Group B, for Burseraceae; and Group R, for Rutaceae.

There are no reports about fossil resin ¹³C NMR spectroscopic data from Cretaceous period in the South America. The main occurrences of amber in this region are found in Tertiary deposits from Brazil, Colombia, Ecuador, French Guyana and Peru.^{3,26-28} Moreover, the literature have no more than three works reporting Cretaceous Brazilian ambers of the Amazonas, Araripe and Recôncavo basins analyzed by IR and GC-MS.^{7,8,29} In this way, the present paper presents for the first time a solid state ¹³C NMR study of Cretaceous amber in South America, providing complementary information about the nature of Brazilian ambers samples from Amazonas, Araripe and Recôncavo basins.

Experimental

Geological setting and sample characteristics

The samples were collected in fluvial sediments of the Alter do Chão Formation (Amazonas Basin, Albian) and in lacustrine sediments of the Maracangalha Formation (Recôncavo Basin, Berriasian-Barremian), states of Amazonas and Bahia (Brazil) respectively. The other Lower Cretaceous amber sample analyzed in this study (Figure 1) was collected in the Araripe Basin, Santana Formation (Crato Member, Aptian), locality of Porteiras, state of Ceará (Brazil). This Araripe sample was reported previously in 1970 by Castro and co-workers.³⁰ The amber samples from Amazonas and Recôncavo basins analyzed in this work are the same described in our previous study concerning GC-MS data.⁷



Figure 1. Photo from Araripe Basin amber sample (Santana Formation, Crato Member). Scale bar represents 1.0 cm.

NMR analysis

Solid state ^{13}C NMR data were obtained before chemical extraction on powdered samples on a 7.05 T Bruker DRX300 spectrometer (^{13}C Larmor frequency 75.4 MHz) equipped with a double resonance Bruker 4 mm MAS probe, by using 4 mm ZrO_2 rotors with Kel-F caps, spinning at a MAS rate of 7 KHz. A double resonance Bruker 2.5 mm and 2.5 mm ZrO_2 rotors with Macor caps were used for cases where sample quantities were limited (around 10 mg). The number of scans varied from 15 k to 80 k. Acquisition conditions: 90° pulse was 5.0 μs , using the cross-polarization with magic angle spinning (CPMAS) pulse sequence, contact time (optimized) 2 ms, recycle delay 4 s. Hexamethylbenzene (CH_3 at 17.3 ppm) was employed as reference for chemical shifts.

Results and Discussion

Some indirect inferences points to the possibility that the Brazilian Cretaceous ambers could be associated to Class I resins of Anderson and co-workers.¹⁰⁻¹² The structural characteristics of the resins Class II, III, IV and V cannot be associated to our samples. Recently, some possible paleobotanical origins were proposed for the Amazonas and Recôncavo samples by considering the absence or presence of specific terpenoid compounds, probed by GC-MS.⁷ The biomarker composition of the soluble fraction of Brazilian ambers from Amazonas and Recôncavo basins points to Cupressaceae, Araucariaceae or Podocarpaceae families. The soluble portion of these ambers is composed of diterpene acids having labdane skeletal structures (Figure 2; mass spectra from labdanic compounds are given in the Supplementary Information), as well as some norabietanes, abietanes, kauranes, phyllocladanes and low concentration of pimaranes and isopimaranes.⁷ In addition, small quantities of sesquiterpenes and monoterpenes have been identified.⁷ The most probable botanical affinities of the mentioned classes are Dipterocarpaceae, to the Class II; Hammelidaceae, to the Class III; Cupressaceae, to the Class IV; and Pinaceae, to the Class V.^{10,11} Taken this into account, NMR data from the Brazilian ambers will be discussed considering that there is an association among our samples with Class I resins, probably Class Ib, related to araucarian resins.

It is relevant to emphasize that ^{13}C NMR spectral data of the ambers reflect the whole sample, showing the properties of soluble and insoluble fractions. The spectra of the Cretaceous Brazilian ambers show the typical pattern of fossil resins, in particular to that of Cretaceous age,²¹ but with peculiarity of peak abundance. Solid state ^{13}C CPMAS NMR spectra for the samples are very similar

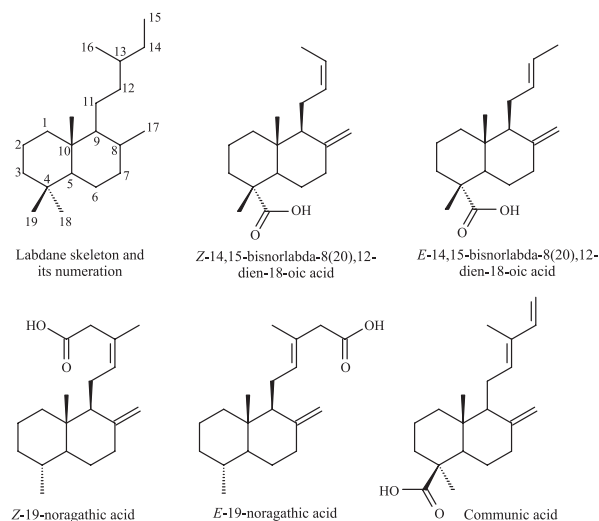


Figure 2. General structure of labdane and some labdenoic acids detected in the soluble fractions of the Brazilian ambers from Amazonas and Recôncavo basins, according to Pereira and coworkers.⁷

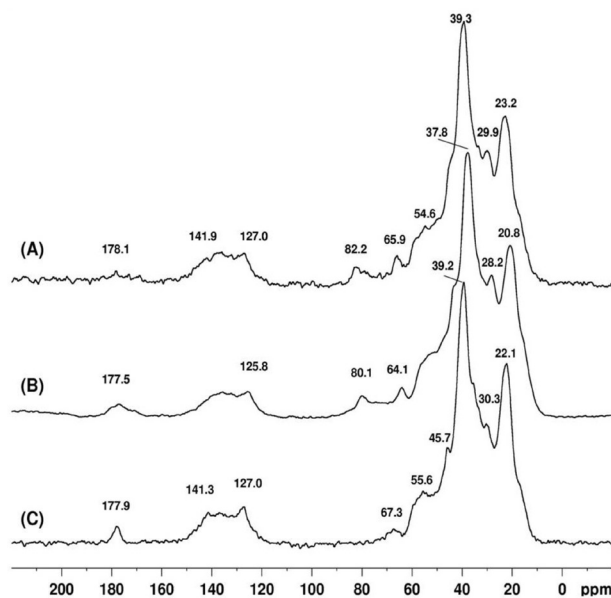


Figure 3. Solid state ^{13}C CPMAS NMR spectra of ambers from Amazonas (A), Araripe (B) and Recôncavo (C) with normal decoupling.

(Figure 3), indicating that these ambers are all derived from the same, or similar, botanical source. The general features include signals in the aliphatic region with intense absorption centered around 39 ppm (Amazonas and Recôncavo samples) and 37 ppm (Araripe sample), accompanied by secondary groups of olefinic signals and one carboxylic carbon peak present in the sample from Recôncavo. Considering these general features, samples A and B are most similar to each other if compared to the sample C.

In the amber sample from Amazonas basin (Figure 3A), four peaks can be clearly distinguished in the aliphatic

region between 0 and 60 ppm. The spectrum exhibits two main peaks at 23 and 39 ppm, which are the dominant peaks in the spectrum. There it can be also visualized broad signals centered at 29 and 54 ppm. To the Araripe sample (Figure 3B), peaks were observed at 37 (most intense), 20 and 28 ppm. In the Recôncavo sample (Figure 3C), a similar pattern was observed: peaks at 22, 30, 39 (most intense), 45 and 55 ppm. The region between 60-100 ppm has signals at 65 and 82 ppm for the Amazonas sample, 64 and 80 ppm to the Araripe sample, and 67 ppm for the Recôncavo sample.

The major absorption centered near 38-40 ppm corresponds to a C-7 labdane carbon.¹ Diterpenoids of labdane structure (Figure 2), such as *Z*(and *E*)-14,15-bisnorlabda-8(20),12-dien-18-oic acid, *Z*(and *E*)-19-noragathic acid and communic acid, were found in the soluble fraction of the amber from Amazonas and traces of the 14,15-bisnorlabda-8(20),12-dien-18-oic acid were detected in the soluble fraction of the amber from Recôncavo.⁷ Similarly, unpublished GC-MS data revealed the presence of similar labdanic structures in the soluble fraction from Araripe amber sample, such as labdanoic acids. The 15-30 ppm region corresponds to methyl and methylene groups, represented in the spectra by signals at 22 and 29 ppm in the sample from Amazonas, 22 and 30 ppm in the sample from Recôncavo, and 20 and 28 ppm in the sample from Araripe. Signals in the 50-80 ppm region are found corresponding to carbons singly bonded to hydroxyl groups (*e.g.*, CHOH, CH₂OH). The samples are similar in this region, showing signals at 55 ppm (Amazonas and Recôncavo samples), 64 ppm (Araripe sample), 65 and 82 ppm (Amazonas amber), 67 ppm (Recôncavo amber) and 80 ppm (Araripe sample). These absorptions may derive from ester and alcohol groups, including small amounts of tertiary alcohol^{2,14} at 80 and 82 ppm to the Amazonas and Araripe ambers. According to Lambert and co-workers,¹⁴ the relatively low intensity of these peaks indicates that there is no large carbohydrate component in amber and nearly all of the intensity in this region may derive from ester and alcohol groups.

However, it is possible that these signals can be associated to alcohols instead of esters or acids due to the low concentration of such compounds in the soluble fraction and the absence of significant signals in the carbonyl region to the Amazonas and Araripe samples. On the other hand, it is interesting to note that signals around 80 ppm were not observed in the Recôncavo sample. This may be due to the loss of functional groups by polylabdanic structures during the fossilization/polymerization of the resins. In fact, it might even justify the low intensity observed for the signals between 50-80 ppm in carbonyl

region. This can be demonstrated by the fact that modern resins have intense signals in the mentioned regions.^{24,25}

In another work, Lambert and coworkers²¹ found two major peaks at 25 and 40 ppm, and four smaller peaks or shoulders at about 30, 45, 55 and 65 ppm to Cretaceous ambers produced by the Araucariaceae family (*Agathis*) from Canada and United States of America (Alaska, Mississippi, Kansas and New Jersey). For samples from Greenland, Jordan, Lebanon and Israel these authors described the saturated region dominated by the peak at 40 ppm, besides signals at 25 and 45 ppm. In this way, the signals observed in the saturated carbon region of Brazilian ambers are similar to other reported Cretaceous samples, mainly regarding to the signals between 20-40 ppm in the ambers from Canada, Alaska and Kansas.

In the unsaturated region, Amazonas and Recôncavo samples show a broad peak at 127 and 141 ppm, more intense in the fossil resin from Recôncavo basin. Other small peaks in this region are centered at 125 ppm (Araripe sample) and 141 ppm (Amazonas and Recôncavo samples). Typical absorptions at 108-110 ppm and 148-150 ppm due to exocyclic methylene and non-protonated unsaturated carbons were not observed.

The unsaturated region is the most important for distinguishing amber types and provides specific information on the predominant diterpenoids skeleton involved. The presence of signals near 110 ppm can arise from a terminal methylene group and that near 150 ppm from a fully substituted carbon. Important differences between several amber samples may be recognized from the degree of resolution of the olefinic/aromatic region and have been reported.^{1,2,18} Signals at 108-110 ppm and 148-150 ppm has been assigned to exocyclic methylene groups in diterpenoids of the labdane series, particularly the $\Delta^{8(17)}$ unsaturation in the C-8 and C-17 carbons, while signals centered at 125 ppm and 140 ppm are related to $\Delta^{12(13)}$ double bond in the terminal chain of labdanes structures in the C-12 and C-13 carbons.^{1,2} These characteristics are commonly observed to samples younger or less mature, as reported for Tertiary samples from several sites of Europe.¹⁴

However, this trend is reduced for Cretaceous samples where the olefinic/aromatic bands are depleted or less resolved,^{18,21,23} as observed in the Brazilian ambers. The formation of amber from plant resins is associated to extensive polymerization of labdanes to Class I resins. The mechanism of this process was very well explained in the literature.^{15,31} The general aspects in the maturation of resins to amber is associated to cyclization, isomerization and defunctionalization reactions. The isomerization is very important to explain the ¹³C NMR data and the intensity for

the exomethylene peaks can be interpreted as an indicator of resin maturity. The most readily apparent effect of maturation on the structure of Class I resins is the loss by isomerization of exomethylene functionality forming more thermodynamically favorable isomers.¹⁰ The absence of these structures is clearly apparent in the spectra of the Brazilian samples, showing the great maturity of these amber samples.

Finally, broad peaks due to the carbonyl carbons of acids and esters are observed in the range of 170 and 190 ppm in Recôncavo sample. The more distinctive characteristic in the samples is an intense signal at 177 ppm in the spectrum of the Recôncavo amber attributed to carboxylic acid groups and the absence of such signal in the other ambers. Actually, noises around 178 and 177 ppm were observed to Amazonas and Araripe samples, respectively, but very weak to be considered as signal in the carbonyl region. No detectable ketone or aldehyde carbons (> 190 ppm) were present in the Brazilian fossil resins.

We tried to relate the Brazilian ambers to the groups proposed by Lambert and co-workers.²⁵ The samples obviously can not be associated to the groups E, C, L, FL, D, B and R because they were produced by gymnosperms and the groups cited were described to angiosperms. Additionally, the patterns in the ^{13}C solid state NMR spectra are very different when compared to the angiosperm resins. However, there are some diagnostic characteristics. The defining pattern in the spectra with normal decoupling of many members of Cupressaceae and Araucariaceae (group CA) is a dominant peak at 38-39 ppm with two significant peaks to the left and three significant peaks to the right in the saturated region.²⁵ In addition, another diagnostic for this group is the presence of pronounced unsaturated peaks between 108 and 148 ppm, usually a single carbonyl peak at 185 ppm, and the unsaturated peak at 150 ppm can be weak or entirely lost.²⁵ This characteristic is an important variant of the pattern.

So, the dominant peak at 39 ppm and the absence of resonances at 150 ppm is possibly indicative that the samples under study are linked to group CA (Cupressaceae-Araucariaceae). We do not observe the same trend in the saturated region certainly due to the maturation and age of the ambers. Finally, the similarities between the ^{13}C NMR data of the three Brazilian Cretaceous amber analyzed in this work and other samples of the same age originated by Araucariaceae family (*Agathis*)²¹ are indicative of a similar botanical origin, probably Araucariaceae but not *Agathis* genera. In this way, the solid state ^{13}C NMR spectra for the whole samples of Amazonas and Recôncavo ambers allowed the same conclusion that we get using GC-MS data⁷ concerning to Araucariaceae family as a possible

botanical origin for these samples. On the other hand, the work of Castro and co-workers³⁰ suggested Pinaceae family as the botanical source for the Araripe amber studied here. Nevertheless, the ^{13}C NMR data obtained point to Araucariaceae family.

Finally, it is important to note that palaeobotanical data related to micro and macrofossil plants suggest *Araucaria* genera as an important source for Brazilian fossil resins founded in Lower Cretaceous sediments.³² So, this fact supports the conclusion reached by GC-MS and ^{13}C NMR data regarding to the paleobotanical origin of Brazilian ambers. These amber occurrences are important evidences about the widespread distribution of Araucariaceae family in Brazil during the Lower Cretaceous.

Conclusions

Cretaceous amber from Amazonas, Araripe and Recôncavo basins, Brazil, have essentially identical ^{13}C NMR spectra, characterized by small or depleted exomethylene resonances and intense absorption centered around 37 or 39 ppm in the aliphatic region. Also, the carbonyl region is weak for all samples except to the Recôncavo amber, where an intense signal at 177 ppm was observed. The solid state ^{13}C NMR data indicate that a single palaeobotanical origin, composed possibly of Araucariaceae family, may have been a general source of amber samples from Amazonas, Araripe and Recôncavo basins analyzed here. The Brazilian ambers have a polilabdane structure associated to Class Ib resins and an apparent effect of maturation observed in the samples is related to isomerization of exomethylene functionalities forming more thermodynamically favorable isomers.

Supplementary Information

Supplementary data are available free of charge at <http://jbcs.sbq.org.br>, as PDF file.

Acknowledgments

R. Pereira acknowledges the doctoral fellowship from CNPq. The authors thank professors Dr. Leonardo Borghi (UFRJ) and Dr. Rodolfo Dino (UERJ) for the samples from Recôncavo and Amazonas basins, respectively; MSc Claudio de Castro (UFPE) for Araripe samples and Dr. Raphael Salles Ferreira Silva (LADETEC/IQ-UFRJ) for contributions and suggestions. Financial support from CAPES, CNPq, FAPERJ and FUJB is thankfully acknowledged. I. S. Carvalho, A. C. S. Fernandes and D. A. Azevedo are CNPq Senior research scholars.

References

1. Cunningham, A.; Gay, A. D.; Oehlschlager, A. C.; Langenheim, J. H.; *Phytochemistry* **1983**, *22*, 965.
2. Martinez-Richa, A.; Vera-Graziano, R.; Rivera, A.; Joseph-Nathan, P.; *Polymer* **2000** *41*, 743.
3. Langenheim, J. H.; *Plant Resins: Chemistry, Evolution, Ecology and Ethnobotany*, 1st ed., Timber Press: Portland, 2005.
4. Anderson, K. B.; Muntean, J. V.; *Geochem. Trans.* 2000, <http://www.geochemicaltransactions.com/content/1/1/1>, accessed in July 2010.
5. Anderson, K. B.; *Geochem. Trans.* 2001, <http://www.geochemicaltransactions.com/content/2/1/21>, accessed in July 2010.
6. Otto, A.; Simoneit, B. R. T.; Wilde, V.; Kunzmann, L.; Püttmann, W.; *Rev. Palaeobot. Palynol.* **2002**, *120*, 203.
7. Pereira, R.; Carvalho, I. S.; Simoneit, B. R. T.; Azevedo, D. A.; *Org. Geochem.* **2009**, *40*, 863.
8. Pereira, R.; Carvalho, I. S.; Fernandes, A. C. S.; Azevedo, D. A.; *Quim. Nova* **2009**, *32*, 1528.
9. Peñalver, E.; Delclòs, X.; Soriano, C.; *Cret. Res.* **2007**, *28*, 791.
10. Anderson, K. B.; Winans, R. E.; Botto, R. E.; *Org. Geochem.* **1992**, *18*, 829.
11. Anderson, K. B.; Botto, R. E.; *Org. Geochem.* **1993**, *20*, 1027.
12. Anderson, K. B.; *Org. Geochem.* **1994**, *21*, 209.
13. Lambert, J. B.; Frye, J. S.; Poinar Jr., G. O.; *Archaeometry* **1985**, *27*, 43.
14. Lambert J. B.; Beck, C. W.; Frye, J. S.; *Archaeometry* **1988**, *30*, 248.
15. Clifford, D. J.; Hatcher, P. G.; *Org. Geochem.* **1995**, *23*, 407.
16. Czechowski, F.; Simoneit, B. R. T.; Sachanbinski, M.; Chojcan, J.; Wotowiec, S.; *Appl. Geochem.* **1996**, *11*, 811.
17. Clifford, D. J.; Hatcher, P. A.; Botto, R. E.; Muntean, J. V.; Anderson, K. B.; *Org. Geochem.* **1999**, *30*, 635.
18. Grimalt, J. O.; Simoneit, B. R. T.; Hatcher, P. G.; Nissenbaum, A.; *Org. Geochem.* **1988**, *13*, 677.
19. Lambert, J. B.; Frye, J. S.; Poinar, G. O.; *Geoarchaeol.* **1990**, *5*, 43.
20. Lambert, J. B.; Johnson, S. C.; Poinar Jr., G. O.; Frye, J. S.; *Geoarchaeol.* **1993**, *8*, 141.
21. Lambert, J. B.; Johnson, S. C.; Poinar Jr., G. O.; *Archaeometry* **1996**, *38*, 325.
22. Poinar Jr., G. O.; Lambert, J. B.; Wu, Y.; *J. Pet. Geol.* **2004**, *27*, 207.
23. Poinar Jr., G. O.; Lambert, J. B.; Wu, Y.; *J. Bot. Res. Inst. Texas* **2007**, *1*, 449.
24. Lambert, J. B.; Shawl, C. E.; Poinar Jr., G. O.; Santiago-Blay, J. A.; *Bioorg. Chem.* **1999**, *27*, 409.
25. Lambert, J. B.; Wu, Y.; Santiago-Blay, J. A.; *J. Nat. Prod.* **2005**, *68*, 635.
26. Langenheim, J.; Beck, C. W.; *Bot. Mus. Leaflet* **1968**, *22*, 65.
27. Martinez-Delclòs, X.; Briggs, D. E. G.; Peñalver, E.; *Palaeogeogr. Palaeoclimat. Palaeoecol.* **2004**, *203*, 19.
28. Antoine, P. O.; Franceschi, D.; Flynn, J. J.; Nel, A.; Baby, P.; Benammi, M.; Calderón, Y.; Espurt, N.; Goswami, A.; Gismondi, R. S.; *Proc. Natl. Acad. Sci.* **2006**, *103*, 13595.
29. Martill, D. M.; Robert, F. L.; Andrade, J. A. F. G.; Cardoso, A. H.; *Palaeontology* **2005**, *48*, 1399.
30. Castro, C.; Menor, E. A.; Campanha, V. A.; Descoberta de resinas fósseis na Chapada do Araripe, município de Porteira, Ceará. *Notas Prévias*. Série C, 1, p. 1-12, Universidade Federal do Pernambuco, Instituto de Geociências: Recife, Brasil, 1970.
31. Clifford, D. J., Hatcher, P. G. In *Amber, Resinite and Fossil Resins*; Anderson, K. G.; Crelling, J. C., eds.; American Chemical Society Symposium Series 617, Washington, 1995, p. 92-104.
32. Pereira, R.; *PhD Thesis*, Universidade Federal do Rio de Janeiro, Brazil, 2009.

Submitted: March 26, 2010

Published online: August 12, 2010

Supplementary Information

Solid State ^{13}C NMR Analysis of Brazilian Cretaceous Ambers

Ricardo Pereira,^{*,a} Rosane A. S. San Gil,^b Ismar S. Carvalho,^c
Antonio Carlos S. Fernandes^d and Débora A. Azevedo^{*,a}

^aLaboratório de Geoquímica Orgânica Molecular e Ambiental, Instituto de Química,
Universidade Federal do Rio de Janeiro 21941-909 Rio de Janeiro-RJ, Brazil

^bLaboratório de RMN de Sólidos, Instituto de Química, Universidade Federal do Rio de Janeiro,
21941-909 Rio de Janeiro-RJ, Brazil

^cDepartamento de Geologia, Instituto de Geociências, Universidade Federal do Rio de Janeiro,
21910-200 Rio de Janeiro-RJ, Brazil

^dDepartamento de Geologia e Paleontologia, Museu Nacional, Universidade Federal do
Rio de Janeiro, 20940-040 Rio de Janeiro-RJ, Brazil

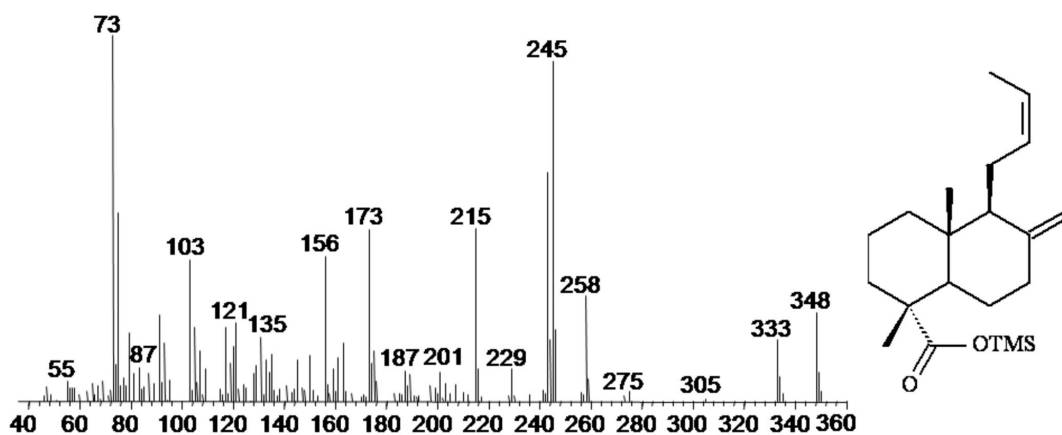


Figure S1. Mass spectrum of Z-14,15-bisnorlabda-8(20),dien-18-oic acid as TMS derivative.

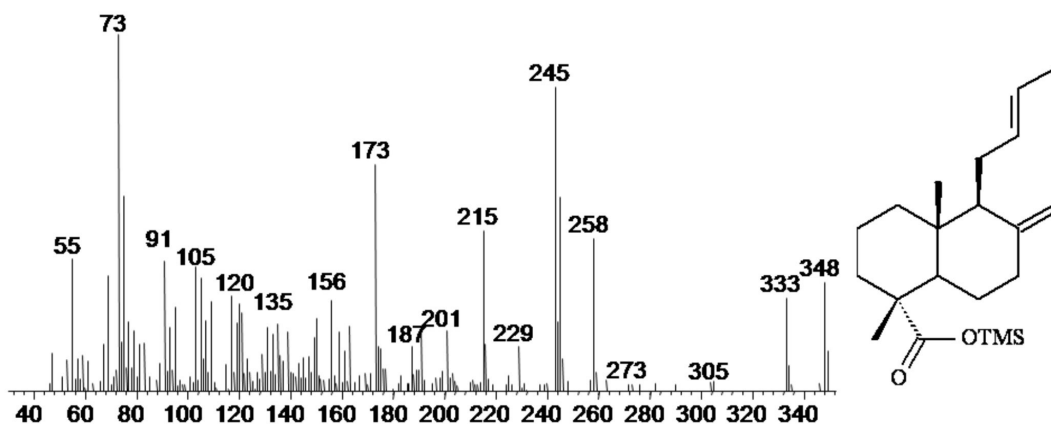


Figure S2. Mass spectrum of E-14,15-bisnorlabda-8(20),dien-18-oic acid as TMS derivative.

*e-mail: ricardopereira@iq.ufrj.br, debora@iq.ufrj.br

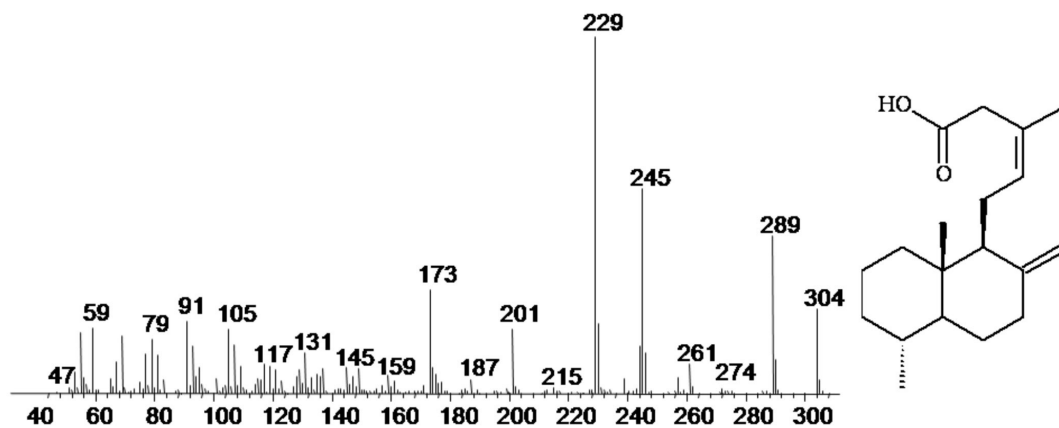
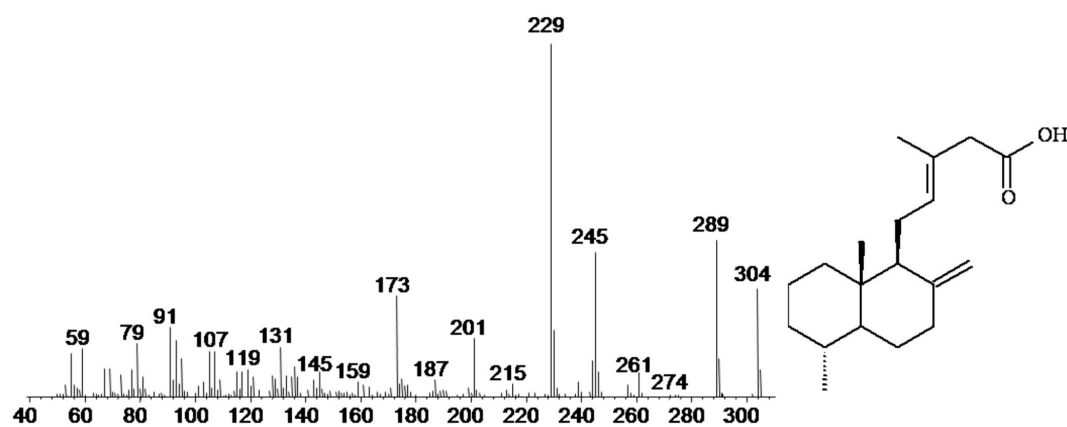
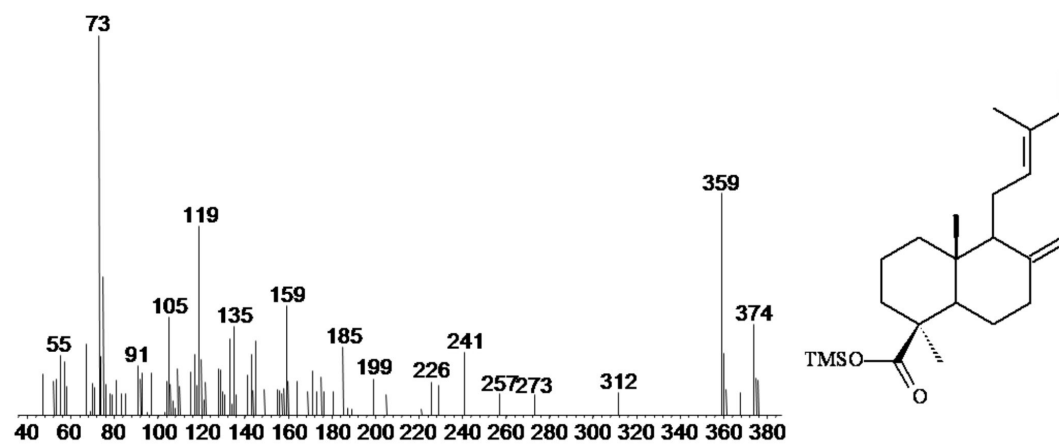
Figure S3. Mass spectrum of *Z*-nor-agathic acid.Figure S4. Mass spectrum of *E*-nor-agathic acid.

Figure S5. Mass spectrum of communic acid as TMS derivative.