CHEMICAL CHARACTERIZATION OF AMBER FROM ARKANSAS

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INTRODUCTION

Ambers are the result of millions of years of fossilization of terpenoid compounds in tree resins. The analysis of the organic extract of ambers has been used to identify the different types of terpenes from monoterpenes, sesquiterpenes, diterpenes, and triterpenes. The terpene composition of ambers can reveal information on the possible botanical source of the ambers, as well as the environment conditions and geographical distribution of extinct tree species. Triterpenes (C30) are most frequently present in dammar resins from trees of the Dipterocarpaceae family, a family of trees common to Southeast Asia and India that thrive in tropical environments *(1-3)*. Amber samples that are abundant in triterpenes usually lack diterpenes (C20). Therefore, ambers that have diterpenes are unlikely to come from dammar resins and have been attributed to several other possible botanical sources.

Two analytical techniques, gas chromatography-mass spectrometry (GC-MS) and infrared spectroscopy (FTIR), were used to study four geological amber samples from Arkansas. FTIR spectroscopy was used to characterize the ambers by comparing spectra to an in-house database of IR spectra of ambers with known geological origin.

Figure 1. Representative example of the Arkansas ambers.

EXPERIMENTAL METHODOLOGY

GCMS ANALYSIS

Amber samples were extracted with diethyl ether/CH_2Cl_2 (1:1 v/v) and methylated with diazomethane to convert the terpene acids to methyl esters. Methylation improves the GC detection of terpenoid compounds. The methylated samples were analyzed by GC-MS using Agilent Technologies 6890GC/5973 MS model fitted with a Hewlett Packard poly (methyl siloxane) capillary column set to the following parameters: injection port at 250°C, electron impact at eV, and column from 50-250° at 5°C/minute. Terpenes were identified by comparison to previous studies, the NIST library, and information from primary literature.

FTIR SPECTROMETRY

The four Arkansas ambers were analyzed using Thermo Nicolet FTIR spectrometer model Nexus 670. The samples were prepared as KBr pellets.

Scan me!

RESULTS AND DATA ANALYSIS

FTIR SPECTROSCOPY ANALYSIS

The FTIR spectra of the Arkansas ambers (a representative example in Figure 2) shows peaks consistent with an organic composition typically seen for ambers: saturated CH stretches and bends, and ester linkages (C=O and C-O). Another Arkansas amber from the Acme Brick Co. Perla pit in Hot Spring County, Arkansas, was previously studied in the Amber Research Laboratory. An overlap of the FTIR spectra of the Acme Brick Co. pit and Arkansas-4 ambers in Figure 2 show that both correspond very well.

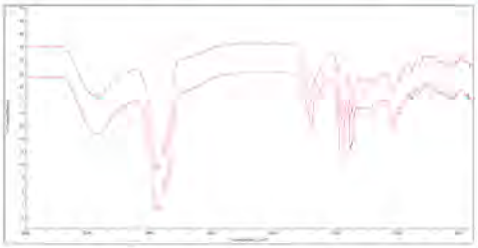

Figure 2. FTIR spectra overlay of Arkansas-4 (bottom) and Acme Brick Co. (top).

A review of the literature provides further confirmation that the Arkansas ambers studied here are likely from the Acme Brick Co. Pit *(2)*. The Acme Brick Co. ambers were classified as Claiborne ambers, fossilized resin that very likely came from tropical hardwood trees *(2)*. The IR for the Claiborne amber in Figure 3 compares very well with the FTIR spectra in Figure 2.

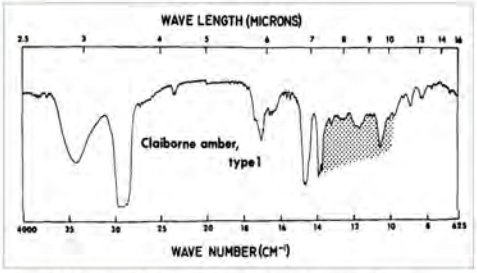

Figure 3. IR spectra of a Claiborne amber from Saunders et al.

GC-MS ANALYSIS

The GC-MS scan in Figure 4 shows the presence of monoterpenes (2-10 minutes), sesquiterpenes (10-20 minutes), and triterpenes (20-35 minutes). There were no diterpenes (20-35 minutes) observed. All samples showed the same sesquiterpenes and triterpenes present (Table 1). A representative example of the mass spectral data for a terpene is shown in Figure 5, where the identification of amyrin was made based on 426 and 218 m/z peaks, and the use of a NIST database. The presence of triterpenes in North American ambers is unusual as most samples from this region are diterpenes.

TABLE 1. 13 MOST ABUNDANT TERPENES OF ARKANSAS AMBERS

Tentative Identification	1	2	3	4
C2 tetrahydronaphthalene	X	X	X	X
Dimethyl naphthalene	X	X	X	X
1, 6, 7-cadina-4, 9-diene	X	X	X	X
Trimethyldimethylene(HTO)naphthalene			X	X
Dihydrocurcumene	X	X	X	X
Cadina-1, 3, 5-triene	X	X	X	X
Cadina-1(10), 6, 8-triene	X	X	X	X
dimethyl-4-(1-methylethyl)naphthalene	X	X	X	X
Olean-18-ene	X	X	X	X
Beta amyrin	X	X	X	X
28-norolean-17-en-3-ol	X	X		X
Olean-12-en-3-ol		X		X
Triterpene		X		X

DISCUSSION AND CONCLUSION

Based on GC-MS and FTIR analysis all four Arkansas ambers in this project are very similar. They are clearly triterpene-based ambers, a peculiar chemical composition for this region as most ambers are diterpene ambers. Finally, based on FTIR analysis, there is strong evidence that the Arkansas ambers studied in this project are most likely Claiborne ambers from the same site as the Acme Brick Co. pit.

ACKNOWLEDGEMENTS + REFERENCES

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2. Saunders, W.B.; Mapes, R. H.; Carpenter, F. M.; Elsik, W. C. "Fossiliferous Amber from the Eocene (Claiborne) of the Gulf Coastal Plain", Geological Society of America Bulletin, 1974.
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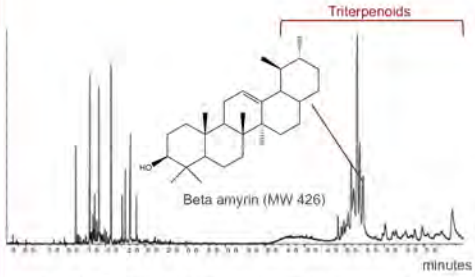

Figure 4. GC-MS scan of Arkansas-4 sample as a representative of the four samples since the scans were similar between samples.

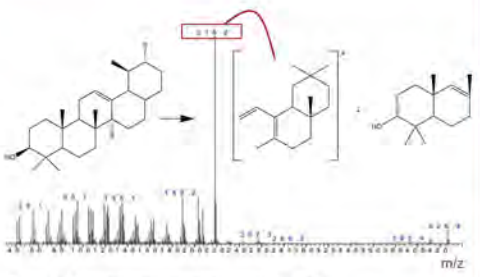

Figure 5. Mass spectrometry of triterpene β-amyrin.