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New Methods for the Identification of Prehistoric Resins in the Southwest and Great Basin, U.S.A.: Proof of Concept

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The use of various organic resins as mastics and sealants in prehistoric North America is well documented in the archaeological and ethnographic literature. While the utilization of the creosote lac resin by people in western North America is known, resinous materials discovered in archaeological contexts are most often attributed to genus Pinus *without formal analysis, partly due to the difficulty and cost of standard methods of identification. Here, three new techniques for the identification of resinous materials are described that are simpler and more cost effective than previous methods, and which will hopefully lead to the further study and better understanding of this aspect of ancient technology.*

Although it is known that prehistoric peoples of the Great Basin and Southwest utilized several types of resins for a variety of purposes, such materials, when found on ethnographic or prehistoric artifacts, are rarely specifically identified, and are commonly assumed to be some form of "pine pitch" (*Pinus* spp.). However, when formal analyses of these resins are conducted, it has been discovered that some of them are actually derived from a variety of other plant or insect sources.

Previous work on the formal identification of resins (Euler and Jones 1956) utilized a number of chemical methods, such as gas chromatography (GC; Sutton et al. 1987), gas chromatography-mass spectrometry (GC-MS; Fox et al. 1995), the o-toluidine test for complex carbohydrates (Bisulca et al. 2016), and Fourier transform infrared spectroscopy (Bisulca et al. 2017). That work demonstrated that the resin of the creosote lac insect (*Tachardiella larreae*) was more commonly utilized in the prehistoric southwestern North America than was previously recognized (Bisulca et al. 2017; Euler and Jones 1956; Fox et al. 1995; Sutton 1990; Sutton et al. 1987; van Balgooy 1983). However, the high cost and limited availability of the necessary specialized equipment has constrained the use of these methods in identifying resinous materials.

Three new methods of identifying unknown resinous materials have been developed and are reported here. These methods involve (1) measuring the solubility of samples in dichloromethane (DCM) solvent; (2) characterizing their fluorescence under UV light; and (3) extracting and identifying residual pollen in samples to determine their original environmental context. These new methods require little specialized equipment and are inexpensive, thus making the identification of unknown resins both simpler and more cost effective.

KNOWN RESINS AND USES

Creosote lac insect (Tachardiella larreae) *resin*

The creosote lac insect (*Tachardiella larreae*) exudes a resin that was used ethnographically for a variety of purposes, including as chewing gum, medicine, and as an adhesive (Castetter and Underhill 1935; Essig 1931:19–21; also see Dittemore et al. 2010). Creosote lac resin has been identified on a number of both ethnographic and prehistoric artifacts, primarily from the Great Basin (Fox et al. 1995; Stacey et al. 1998; Sutton 1990, 2019; van Balgooy 1983) and the Southwest (Bisulca et al. 2017). Although resin from several species of *Tachardiella* was utilized in the southwestern United States and northwestern Mexico, resin from *T. larreae* is the most commonly referenced in the literature and was used in this study.

The distribution of the creosote lac scale follows that of the creosote bush (*Larrea tridentata*), with a range that includes the Mojave and Colorado deserts of California and the Sonoran and Chihuahuan deserts of Arizona, New Mexico, Baja California, and northern Mexico (Euler and Jones 1956; Hunziker et al. 1977:14; Sutton 1990:Fig. 1). The annual life cycle of the *Tachardiella larreae* insect begins when the larvae hatch in February–March. For a short time, the hatchlings are mobile until a suitable location is found near the parent cell; they

then permanently affix their mouthparts to the plant to feed and begin to excrete a protective shell of lac (Sutton 1990). After pupating, the males leave this shell to find a female with which to breed, thus ending their annual life cycle (Kondo and Gullan 2011). The secretion of the lac resin begins around the time that the creosote bush blooms (Porter 2016); the resin would thus be expected to accumulate ambient environmental pollen and debris while it was plastic.

Pine (Pinus *spp.*) *resin*

Pine resin is known from ethnographic and archeological records to have been used as a mastic and sealant all across North America (Arno 1973; Eerkens 2002; Smith 1940). Pine nuts (especially from *P. monophylla* and *P. edulis*) were a staple food for the people of the Great Basin and surrounding areas (e.g., Dutcher 1893; Palmer 1878; Steward 1938), so pine resin would have been readily available. In southwestern North America, pines are generally found on arid slopes between 1,300 and 2,700 meters above mean sea level, often intermixed with *Juniperus* species to form what is known as a pinyon-juniper woodland (Haller and Vivrette 2016).

Juniper (Juniperus *spp.*) *resin*

Juniper was used ethnographically and prehistorically for a variety of purposes, including medicine, food, and wood for bow staves (Palmer 1878; Steward 1938). Junipers are found throughout North America in arid flats and mountainous environments between about 50 and 1,500 meters above mean sea level (Martin and Drew 1969). However, there is little evidence for the use of juniper resin as a mastic (Fox et al. 1995). Nevertheless, its possible use is considered here.

Other Mastics

Other sources of mastics are mentioned in the literature from the Great Basin and southwestern United States, including mesquite (*Prosopis* spp.), brittlebush (*Encelia farinosa*; Castetter and Underhill 1935), the hides of rabbit and deer, and even collagen from the horns of bighorn sheep (*Ovis canadensis*). Although the use of these sources is described ethnographically, they have not been identified in the archaeological record; for the sake of simplicity, those sources are not considered in this study. Nevertheless, the identification of pollen within a sample (discussed below) would be applicable in the case of those sources as well.

PREVIOUS APPROACHES TO IDENTIFICATION

Microscopic and Chemical Analyses

Euler and Jones (1956) identified lac resin as the material used to hermetically seal an olla found near Kingman in Arizona. The microscopic and chemical analytical methods that were used are not described.

Various chromatographic methods (GC and GC-MS) have been utilized in the identification of unknown resins. The general process includes the distillation of a sample to analyze the vapor pressure, or boiling point, of its components (using GC) to obtain a chemical "fingerprint." For example, van Balgooy (1983:178) used a chromatographic method (likely GC) to analyze the residue in a stone bowl from the Oro Grande site on the Mojave River. The results indicated a wax-based material was present, and Westgate (1943) thought it had an insect origin. Based on the environmental provenance and the assumption of an insect source, the composition of the material was most likely lac (Sutton 1990). Sutton et al. (1987) used GC to analyze a sample from a ceramic vessel excavated at the Southcott Cave site in California, and determined that the material was lac.

The addition of mass spectrometry (GC-MS) to specifically identify the molecular mass of each component in a sample makes identification more accurate. GC-MS assays of samples from various artifacts from across the Great Basin and the Southwest have demonstrated the presence of a variety of materials, including pine and lac resins (Fox et al. 1995). A GC-MS analysis of resin on a chuckwalla hunting barb found at the Breakfast Canyon rock shelter in California indicated a mixture of pine and lac resins (Stacy et al. 1996). Tests on the possible chemical modifications occurring during the prehistoric processing of lac, utilizing comparative GC-MS testing between experimental and archaeological samples from Newberry Cave in the Mojave Desert, California, raised questions about the processing methods employed prehistorically (Stacey et al. 1998). Using GC-MS, Eerkens (2002) identified *Pinus* resin on pottery sherds found in southern Nevada.

Bisulca et al., (2016, 2018) employed the o-toluidine test for complex carbohydrates on a number of samples

from the collections at the Arizona State Museum. Bisulca et al. (2017) went on to use Fourier transform infrared spectroscopy (FTIR) in the identification of resins from numerous samples from the museum. The FTIR method identifies the composition of a sample by analyzing the wavelengths that are absorbed and reflected when an unknown material is exposed to infrared light.

NEW METHODS OF RESIN IDENTIFICATION

Three new analytic methods were developed to allow for the simpler and faster identification of unknown resinous materials. These methods involve (1) variations in sample solubility in dichloromethane (DCM); (2) variations in sample fluorescence in an acetone solution under a UV source; and (3) the isolation and identification of fossil pollen and other organic matter trapped and preserved within a sample. Each of these methods (Table 1) could be expected to identify, or at least exclude, certain resins. Reference samples of resins from pinyon pine (*Pinus monophylla*), juniper (*Juniperus californica*), and insect lac (*Tachardiella larreae*) were employed in testing each of these methods.

Solubility in Dichloromethane

Dichloromethane (DCM) was used to test the solubility of three reference samples of pine, juniper, and lac. Each of the samples was placed in a vial of DCM and left to soak for about ten minutes while its dissolvability was visually observed, estimated, and recorded. This process was repeated three times.

Pine resins are primarily abietane/pimarane type diterpenoids, compounds that do not polymerize and so should remain soluble indefinitely. It was found that pine resin fully dissolved in the DCM. Juniper resins are usually labdane diterpenoids and will polymerize over time, so it would be expected that they would not remain fully soluble (the polymerized portion would be the insoluble fraction). As predicted, the juniper resin only partly (ca. fifty percent) dissolved. The lac resin showed little to no solubility in the DCM. Thus, this method holds the potential to be able to distinguish between these three resins. It seems unlikely that combinations of resins (e.g., a mixture of pine and juniper) could be identified in this manner. It should also be noted that these results might not be the same if other solvents were used. (It is worth noting that pine resin appears to be soluble in 99 percent methanol, while lac is not.)

Table 1

DATA EXPECTATIONS FOR PROPOSED IDENTIFICATION METHODS

Resin/ID Method	Solubility in Dichloromethane (DCM)	Color of Fluorescence under UV	Pollen Record
pinyon pine (*Pinus monophylla*)	fully dissolved	bright yellow-green	pine
juniper (*Juniperus californica*)	partly (ca. 50%) dissolved	bright yellow-green	juniper
insect lac (*Tachardiella larreae*)	insoluble	bright orange-red	creosote

Fluorescence under Ultraviolet Light

Inspired by the study conducted by Bisulca et al., (2017), a fluorescence test using simple equipment was developed. Samples of each of the three resins (pine, juniper, and lac) were first dissolved in acetone. Each of the solutions was then exposed to ultraviolet light from an inexpensive (ca. $20) UV blacklight purchased from a novelty store. The resins were exposed to the UV light prior to being placed in acetone and all fluoresced to some degree, but each fluoresced much more brightly in solution. The color expressed by each resin type is an indicator of its makeup, and it was observed that the plant resins (pine and juniper) both fluoresced a bright yellow-green color (cf. Pantone 809 C), while the lac resin fluoresced a bright orange-red color (cf. Pantone 151 C). This latter result was also reported by Bisulca et al. (2017).

In measuring the florescence of lac resin, the possibility that the resin was subjected to high heat during its processing and application should be considered (M. Pool, personal communication 2017). It is possible that in ethnographic or archaeological samples, the polyester polymer expected to fluoresce might be degraded from the heat and would give a weaker response than expected.

Pollen Analysis

Based upon the premise that resins should contain pollen from their plant or environment of origin, it was hypothesized that the pollen content of each sample could indicate its origin and provide an identification. The preservation of pollen was expected to be rela-

tively good in the matrix of the resin since the resin should seal the pollen and prevent its degradation by oxidation or hydration, much like an insect preserved in amber. Furthermore, the identification of any pollen extracted from the resin matrix should also indicate the environmental conditions present during its excretion by plants or insects, or during its later processing.

A PILOT STUDY

A pilot study was undertaken involving three resin samples. One sample each was collected from two Navajo baskets coated in an unknown resin (A1996.1.1434 and A1996.1.1383) in the David W. May collection, University of San Diego. The third sample consisted of a small amount of natural lac collected from a creosote bush. These samples were analyzed as described below.

Sample Collection

Using a small lab spatula, small amounts (ca. one gram) of resin were carefully scraped from the inside of the baskets from larger masses of resin. The samples were taken from the interior (concave) walls of the baskets to avoid the possibility that other pollen may have settled in the matrix at the bottom of the baskets. Immediately after sampling, the specimens were placed into small glass vials and sealed to prevent further contamination from modern pollen, spores, or other organic materials. During sampling, a strong odor of pine was detected—a scent similar to that of the control pine samples.

Laboratory Methods

The samples for both the DMC solubility and fluorescence analyses were processed using the same methods. First, the samples were crushed using a 600 ml. porcelain mortar and pestle. The resulting powder was then placed into two sets of labeled, clean, two-dram glass vials, with care taken to prevent contamination from modern pollen rain. Next, a few milliliters of solvent (enough to cover the sample) was added—DCM to one set of vials and acetone to the other (note that glass vials must be used with these chemicals). All of the samples were then agitated and left for about ten minutes, or until fully dissolved. Once dissolved, the solubility of each sample in the DCM was recorded, while the samples in the acetone were analyzed under UV light in a darkened room (following Bisulca et al. 2017).

The samples in the acetone were then used for the pollen analysis. After the fluorescence test was completed, an exotic indicator pollen (in this case spores from *Cyathea cooperi*, a species of tree fern from Australia) was added to the solution to show the efficacy of the extraction process in the later microscopic analysis. The samples were then centrifuged at 3,000 rpm for five minutes to settle any pollen and other particulate matter to the bottom of the tube, and the solvent then decanted off, preserving the particulate matter. A second wash of acetone was performed to clean any leftover resin, and the tube then centrifuged and decanted as before.

As much of the solvent as possible was decanted each time without losing the settled particulate matter, and a dense solution of deionized water and zinc chloride ($ZnCl_2$) was added in order to separate the organic from the mineral particulates. The zinc chloride solution was made to a specific gravity of 2.0 and checked with a hydrometer in a graduated cylinder at room temperature (the zinc chloride solution was allowed to cool before use since dissolving zinc chloride in water causes an exothermic reaction). After the addition of the solution, the sample was run through a five-minute cycle in the centrifuge to float the pollen. The zinc chloride solution, with its high specific gravity, causes the pollen to float to the surface, and other mineral particulate matter to sink, allowing the pollen and other organic material to be pipetted off of the top, transferred to a fresh two-dram vial, and mixed with a few drops of 91% isopropyl alcohol. This mixture was then run through another five-minute cycle in the centrifuge to sink the pollen to the bottom of the vial (in the low specific gravity of isopropyl, the pollen sinks). This was then carefully decanted, and the remaining pollen-rich solution stabilized with a few drops of vegetable glycerin (glycerol); the alcohol eventually evaporates off or emulsifies into the glycerin. This mixture is stable and can be mounted for microscopic analysis.

A drop of the pollen sample was added to the surface of a sterile microscope slide using the pointed end of a lab spatula. A small amount of fuchsin or safranin stain was added by dipping the tip of a sterilized needle into the stain and mixing it in with the drop of solution on the slide. The stain bonds to the organic material, allowing it to be more readily recognized under microscopic analysis and leaving any leftover mineral debris undyed. A cover

slip was placed on top of the drop of solution, with care taken to prevent the trapping of air bubbles within the matrix. The slide was quickly scanned through the microscope to ensure that it was clear and then immediately labeled and sealed around the edges using a layer of fresh, clear nail polish. This method was repeated for each sample.

A goal of 50 grains for the preliminary pollen count was set to allow for a statistical study of the pollen and debris identified. Using the key from the *Textbook of Pollen Analysis* (Faegri et al. 1989), the University of Arizona catalog of internet pollen and spore images, and reference pollen collected in the field by the senior author, the species of plants from which the pollen was derived was determined with a Swift Instruments Collegiate 400 stereo light microscope.

Fragments of insect exoskeletons (chitin) linger during the flocculation and deflocculation procedures used to isolate pollen (Faegri et al. 1989:76). Thus, it is possible that such remains could also be recovered and identified (e.g., Sutton 1995).

Results

The samples of unknown resin taken from the two Navajo baskets were analyzed using the three methods described above (Table 2). The resin was fully soluble in the DCM. In the fluorescence test, both samples fluoresced a bright greenish-yellow (cf. Pantone 809 C), indicating a plant origin consistent with either pine or juniper but not with lac.

Both basketry samples contained both pine and juniper pollen, suggesting that either both pine and juniper resins were combined or that the resin was obtained or processed in or near a pinyon-juniper woodland. An additional identifying trait was the strong pine odor noted during the sampling of the baskets. However, since it is known that pine resin was sometimes mixed with other resins (Stacy et al. 1996), odor alone is not sufficient for a proper identification. One should also note that pine resin can remain soft for many months and so can trap considerable pollen.

Table 2

RESULTS FROM SAMPLE IDENTIFICATION BY METHOD

Resin/ID Method	Solubility in Dichloromethane (DCM)	Color of Fluorescence under UV	Pantone Value	Pollen Record
basket (A1996.1.1434)	fully dissolved	bright yellow-green	809 C	pine and juniper
basket (A1996.1.1383)	partly (ca. 50%) dissolved	bright yellow-green	809 C	pine and juniper
modern insect lac (*Tachardiella larreae*)	insoluble	bright orange-red	151 C	creosote

The sample of lac resin was found to be partially soluble in the DCM, and it fluoresced a strong orange-red color (cf. Pantone 151 C) when tested in solution. A small amount of degraded pollen was found and identified as coming from creosote bush (*Larrea tridentata*); in addition, some fragments of exoskeleton were found that are most likely from the lac insects themselves. A relatively small amount of pollen would be expected to be trapped in lac since it would harden relatively quickly.

CONCLUSIONS

The use of various resins by the prehistoric peoples of the Great Basin and Southwest is not fully understood, partly due to a dearth of formal analyses. Available analytic methods have been expensive or cumbersome, making analysis difficult. The three new methods described here were found to successfully distinguish between the three sources of resin tested. These tests, which are simple and relatively inexpensive to employ, could be an important addition to the analytical methods used to identify unknown resins. It is recognized that pollen analysis is more complex than the other two methods, but pollen data obtained from such samples can be used in additional ways, such as in environmental reconstruction.

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REFERENCES

Arno, S. F.
1973 *Discovering Sierra Trees*. Yosemite National Park, California: Yosemite Natural History Association.

Bisulca, C., N. Odegaard, and W. Zimmt
2016 Testing for Gums, Starches, and Mucilages in Artifacts with O-toluidine. *Journal of the American Institute for Conservation* 55(4):217–227.

Bisulca, C., M. Pool, and N. Odegaard
2017 A Survey of Plant and Insect Exudates in the Archaeology of Arizona. *Journal of Archaeological Science: Reports* 15:272–281.
2018 Resin and Lac Adhesives in Southwest Archaeology and Microchemical Tests for Their Identification. *Objects Specialty Group Postprints* 23:221–232.

Castetter, E. F., and R. Underhill
1935 *The Ethnobiology of the Papago Indians. Ethnobiological Studies in the American Southwest II, Ethnobiological Studies of the Papago Indians.* [*University of New Mexico Bulletins (Biological Series)* 4].

Dutcher, B. H.
1893 Pinon gathering among the Panamint Indians. *American Anthropologist* 6(4):351–361.

Eerkens, J.
2002 The Preservation and Identification of Piñon Resins by GC-MS in Pottery from the Western Great Basin. *Archaeometry* 44(1):95–105.

Essig, E. O.
1931 *A History of Entomology*. New York: Macmillan.

Euler, R. C., and V. H. Jones
1956 Hermetic Sealing as a Technique of Food Preservation among the Indians of the American Southwest. *Proceedings of the American Philosophical Society* 100(1): 87–99.

Faegri, Knut, P. Kaland, and K. Krzywinski
1989 *Textbook of Pollen Analysis* (4th ed.) Chichester, United Kingdom: John Wiley & Sons.

Fox, A., C. Heron, and M. Q. Sutton
1995 Characterization of Natural Products on Native American Archaeological and Ethnographic Materials from the Great Basin Region, U.S.A.: A Preliminary Study. *Archaeometry* 37(2):363–375.

Haller, J. R., and N. J. Vivrette
2016 *Pinus edulis*. In Jepson Flora Project, *Jepson eFlora*. Online document, http://ucjeps.berkeley.edu/eflora/eflora_display.php?tid=38269, accessed Dec. 2019.

Hunziker, J. H., R. A. Palacios, L. Poggio, C. A. Naranjo, and T. W. Wang
1977 Geographic Distribution, Morphology, Hybridization, Cytogenetics, and Evolution. In *Creosote Bush: Biology and Chemistry of Larrea in New World Deserts*, T. J. Mabry, J. H. Hunziker, and D. R. Difeo, Jr., eds., pp. 10–47. Stroudsburg, Pa.: Dowden, Hutchinson and Ross.

Kondo, T., and P. Gullan
2011 Taxonomic Review of the Genus *Tachardiella Cockerell* (Hemiptera: Kerriidae), with a Key to Species of Lac Insects Recorded from the New World. *Neotropical Entomology* 40(3):345–367.

Martin, P. S., and C. M. Drew
1969 Scanning Electron Photomicrographs of Southwestern Pollen Grains. *Journal of the Arizona Academy of Sciences* 5(3):147–176.

Palmer, E.
1878 Plants Used by the Indians of the United States. *The American Naturalist* 12(9):593–606.

Porter, D. M.
2016 *Larrea tridentata*. In Jepson Flora Project, *Jepson eFlora*. Online document, http://ucjeps.berkeley.edu/eflora/eflora_display.php?tid=30255, accessed Dec. 2019.

Smith, A. S.
1940 *An Analysis of Basin Mythology*. 2 Vols. Ph.D. dissertation, Yale University.

Stacey, R. J., C. Heron, M. Q. Sutton, and A. Fox
1996 Recent Results in Identification of Residues and Adhesives from the Southwestern Great Basin. Paper presented at the Society of Ethnobiology Conference, Santa Barbara.

Stacey, R. J., C. Heron, M. Q. Sutton
1998 The Chemistry, Archaeology, and Ethnography of a Native American Insect Resin. *Journal of California and Great Basin Anthropology* 20(1):53–71.

Steward, J. H.
1938 Basin-Plateau Aboriginal Sociopolitical Groups. *Bureau of American Ethnology Bulletins* 120. Washington, D. C.: Government Printing Office.

Sutton, M. Q.
1990 Notes on Creosote Lac Scale Insect Resin as a Mastic and Sealant in the Southwestern Great Basin. J*ournal of California and Great Basin Anthropology* 12(2):262–268.
1995 Archaeological Aspects of Insect Use. *Journal of Archaeological Method and Theory* 2(3):253–298.
2019 Notes on a Bar of Lac Insect Resin from the Saline Valley, California. *Journal of California and Great Basin Anthropology* (this issue).

Sutton, M. Q., C. Donnan, and D. Jenkins
1987 The Archaeology of Southcott Cave, Providence Mountains, California. *Journal of California and Great Basin Anthropology* 9(2):232–250.

van Balgooy, J. N. A.
1983 Chemical Analysis of Residue from a Stone Bowl. In *Archaeological Studies at Oro Grande, Mojave Desert, California*, C. H. Rector, J. D. Swenson, and P. J. Wilke, eds., pp. 177–181. Redlands: San Bernardino County Museum Association.

Westgate, M. W.
1943 Brief Notes on Pinyon Resin and Stick Lac from Arizona. *National Paint, Varnish, and Lacquer Association Circulars* 665:190–198. Washington, D.C.