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Desert Plants and their Exudates

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Exudates are complex mixtures of organic compounds oozed by plants often, but not always, released as a result of injury. These materials are usually collected from the outside of trees, most of the time from the shoot or above ground portion of trees, but, on occasions, we have collected exudates from roots. In a recent extraordinary moment, JASB collected exudates from the inside of *Brachychiton rupestris* Schumann (cover), a tree placed in the family Malvaceae (formerly placed in the family Sterculiaceae).

An efficient way to sample exudates is to get them from trees in botanical gardens or arboreta. To better our collections, sometimes we look for them in desert areas (regions receiving 250 mm or less of precipitation per year) as a number of plants in those areas tend to ooze exudates. Exudates include products such as gums (Nussinovitch, 2010), resins (Langenheim, 2003), gum resins, kinos (Lambert et al., 2007), and other materials that cannot be classified in any of the above categories. Fossilized plant resins are known as amber (Lambert et al., 2002, 2008; Santiago-Blay and Lambert, 2007). The gymnospermous plant families Cupressaceae and Pinaceae, as well as the angiospermous families Agavaceae, Anacardiaceae, Arecaceae, Asteraceae, Bignoniaceae, Burseraceae, Cactaceae, Euphorbiaceae, Fabaceae (Lewis et al. 2005), Malvaceae, Rosaceae, Zygophyllaceae, and many others include species that are well represented in deserts and sometimes produce exudates.

Our ultimate research goal is to generate a chemical library of plant exudates of the world, including modern exudates as well as older materials such as those used by past human civilizations as well as amber. In this paper, we describe our research emphasizing the materials produced by selected desert plant families.

Methods

We often collect 1 gram or less of the exudates and avoid harming the sampled plants. An advantage of visiting botanical gardens and arboreta is that there is a large diversity of identified plants, often representing many ecological zones of the world (Santiago-Blay, 2006). These organizations tend to assign each plant an accession code and/or house herbaria, easing access to the same sampled plants (or species) to other researchers. Identified exudates are also obtained through generous donations from colleagues worldwide.

We use the technique of nuclear magnetic resonance (NMR) spectroscopy to analyze exudates. Because plant exudates are composed of organic compounds, they have many atoms of carbon and hydrogen, which are readily examined by this technique. Recently (Santiago-Blay and Lambert, 2010), we summarized the protocol we follow. "Once the solid exudates samples are at hand, they are pulverized and analyzed. We always use solid state nuclear magnetic resonance spectroscopy (SSNMR) for detecting the pattern of abundance of the carbon-13 isotope in the samples of all harvested materials. As much as possible, we analyze more than one sample per species. If the exudates samples are soluble, we also use a complementary technique, called proton or hydrogen-1 isotope NMR. The carbon technique has the distinct advantage of analyzing samples in bulk and, while we cannot identify specific molecules in the samples, NMR does not discriminate against specific molecular components." Nuclear magnetic resonance (NMR) spectroscopy exploits the behavior of atomic nuclei in a magnetic field. When an electromagnetic pulse is applied to spinning nuclei in atoms, they absorb energy from the pulse and the nuclei radiate this energy back out. The energy radiated back out is at a specific resonance frequency that depends on the strength of the magnetic field and other factors. The results of an NMR experiment are represented in a graph for which the horizontal axis represents a frequency characteristic of the molecular environment of a given nucleus, either carbon-13 or hydrogen-1. The height of the peak represents the relative abundance of that particular type of that nucleus.

Results and Discussion

In this section, we summarize three highlights of our twelve year long collaboration. First, there seems to be a simple classification of plant exudates into various molecular types: gums, resins, gum-resins, kinos, and other exudates. Herein, we provide examples of plants that live in arid zones and their exudates. The gymnospermous families Pinaceae (Figure 1), such as pines, spruces, and firs, and Cupressaceae (Figure 2), which include the cypresses, produce resins. Resins are exudates rich in terpenes whose chemical building block is a 5-carbon molecule called isoprene. Resins are water insoluble; hence they have a greater likelihood of surviving deep time.

Another common desert plant group whose exudates are resinous is the angiospermous family Euphorbiaceae, or spurges (Figure 3). Although the exudate of these plants is colloquially called "latex," this material is chemically a resin. Interestingly, during JASB's visit to Balboa Park (San Diego, California), honey bees, *Apis mellifera* L., were only seen harvesting exudates on the areas containing the somewhat sticky material, not in the newly oozed material or in the dried up, injured areas.

The family Fabaceae, or legumes, which includes many desert plants such as mesquite, *Prosopis* spp., and the *Acacia* spp., is the only plant family studied thus far with a full complement of plant exudates. This family includes numerous species of enormous economic importance. Representative examples of these plants were discussed and illustrated recently (Lambert et al., 2009, Santiago-Blay and Lambert 2010).

The family Rosaceae is also well represented in arid regions of the world. *Prunus ilicifolia* (Figure 4) is native to the chaparral

Figure 1. *Pinus torreyana* Parry ex Carrière, one of the rarest pines in the world, a resin producer, and closeup of exudate

Figure 2. *Cupressus guadalupensis* S. Watson, a cypress endemic to Guadalupe Island (Baja California, Mexico) and southern California (USA), a resin producer

Figure 3. *Euphorbia* spp. (Euphorbiaceae) Note a honey bee collecting exudates.

Figure 4. *Prunus ilicifolia* (Nutt. ex Hook. & Arn.) Walp. (Rosaceae) and close-up of exudate

communities of California (USA) and Baja California (Mexico). All tested members of the genus *Prunus* are gum producers. The basic chemical units of gums are the monosaccharides. When produced, gums are water soluble; hence they are less to be represented in the fossil record.

Figure 5. *Eucalyptus sideroxylon* A. Cunn. ex Wolls (Myrtaceae), a kino producer and close-up of exudate

The family Myrtaceae, particularly *Eucalyptus,* produces kinos (Figure 5). Kinos are exudates rich in aromatic components, such as phenol.

Second, if an exudate is a resin, its carbon 13 spectrum often is characteristic of its botanical provenance at the family level (Lambert, et al., 2005; Lambert et al. 2010). This has been helpful in ascertaining the origin of samples whose botanical origin is unknown or questionable.

Third, in the case of the Pinaceae, proton NMR can not only separate the seven tested genera but it has also allowed us to group species within each of the genera on the basis of the characteristic of their spectrum (Lambert et al. , 2007; Lambert, Kozminski, and Santiago-Blay, 2007).

In addition to the chemical makeup of plant exudates worldwide, we have received or made anecdotal observations, some of which we herein summarize.

Use of exudates by birds. Canaries, *Serinus canaria* L., have been seen feeding on the exudates produced by the leaves of star fruit, *Averrhoa carambola* L. (Oxalidaceae) (Cary to Santiago-Blay, personal communication, August 2009). Also, birds have been seen drilling the trunk and imbibing the exudates produced by *Pittosporum* spp. (Pittosporaceae, Figure 6). Interestingly, birds have also been seen collecting nesting material filled with conifer exudates and actually using the material to build a nest in a suburb of the Greater Washington DC region although author JASB has not been able to receive all the details from the person who made the observations.

Figure 6. *Pittosporum* sp. (Pittosporaceae) with feeding marks produced by birds at the Boyce Thompson Arboretum, Superior, Arizona. Human collectors of plant exudates, such as JASB, often only get the material left over by the birds.

Speed of production and beginning of polymerization. We often wonder (and are commonly asked) how much exudate plants produce per unit time. Recently, one of us (JASB) estimated exudate production from a single wound of a legume tree to 1-2 ml in 24 hours. The process of polymerization begins right after the exudates oozes from the plant and hardening is relatively fast. For instance, in the island of Kauai (the westernmost inhabited island in the Hawaiian archipelago), JASB noticed the liquid exudates from a freshly cut frond of a tree fern began to get sticky in 30 minutes. Likewise, the fresh exudate of some South African cycads becomes solid to the touch in approximately two weeks (Labandeira to Santiago-Blay, personal communication).

Although nobody knows exactly how many species produce exudates, we would like to study any exudate produced by any plant in the following named families: the gymnospermous families Cephalotaxaceae, Cupressaceae (we need to examine all the endemic Old World genera), Ephedraceae, Ginkgoaceae, Gnetaceae, Phyllocladaceae, Podocarpaceae, Sciadopityaceae, Taxaceae, Welwitchiaceae; the angiospermous families, Acanthaceae, Aceraceae, Achariaceae, Achatocarpaceae, Acistrocladaceae, Actinidiaceae, Adoxaceae, Aextoxiceae, Aizoaceae, Akaniaceae, Alismataceae, Alliaceae, Aloaceae, Alsinaceae, Alstroemeriaceae, Altingiaceae, Amaranthaceae, Amaryllidaceae, Amborerllaceae, Abrosiaceae, Amygdalaceae, Annonaceae, Apocynaceae, Aponogetonaceae, Apostasiaceae, Aquifoliaceae, Araliaceae, Arecaeceae, Aristolochiaceae, Asclepiadaceae, Asparagaceae, Asteraceae, Asteranthaceae, Austrobaileyaceae, Avicenniaceae, Balanitaceae, Balanophoraceae, Balsaminaceae, Barbeyaceae, Barringtoniaceae, Basellaceae, Bataceae, Begoniaceae, Berberidaceae, Betulaceae, Bignoniaceae, Bixaceae, Bombacaceae, Boraginaceae, Brassicaceae (or Cruciferae), Bretschneideraceae, Bromeliaceae, Brunelliaceae, Bruniaceae, Brunoniaceae, Buddlejaceae, Burmanniaceae, Butomaceae, Buxaceae, Byblidaceae, Byttneriaceae, Cabombaceae, Cactaceae, Callitrichaceae, Calycanthaceae, Calyceraceae, Campanulaceae, Canellaceae, Cannabinaceae, Cannaceae, Capparidaceae, Caprifoliaceae, Cardiopteridaceae, Caricaceae, Cartonemataceae, Caryocaraceae, Caryophyllaceae, Cassythaceae, Celastraceae, Centrolepidaceae, Cephalotaceae, Ceratophyllaceae, Cercidiphyllaceae, Chenopodiaceae, Chloranthaceae, Chrysobalanaceae, Cichoriaceae, Circaeasteraceae, Cistaceae, Clethraceae, Clusiaceae, Cneoraceae, Cochlospermaceae, Cochicaceae, Columelliaceae, Combretaceae, Commelinaceae, Connaraceae, Convolvulaceae, Cordiaceae, Coriariaceae, Cornaceae, Corsiaceae, Corylaceae, Corynocarpaceae, Crassulaceae, Crossosomataceae, Crypteroniaceae, Cucurbitaceae, Cunoniaceae, Cuscutaceae, Cyanastraceae, Cyclanthaceae, Cymodoceaceae, Cyperaceae, Cyrillaceae, Daphniphyllaceae, Datiscaceae, Degeneriaceae, Desfontainiaceae, Dialypetalanthaceae, Diapensiaceae, Dichapetalaceae, Dichondraceae, Diclidantheraceae, Didiereaceae, Dilleniaceae, Dioncophyllaceae, Dioscoreaceae, Dipentodontaceae, Dipsacaceae, Dodonaeaceae, Donatiaceae, Dracaenaceae, Droseraceae, Dysphaniaceae, Ebenaceae, Ehretiaceae, Elaeagnaceae, Elaeocarpaceae, Elatinaceae, Empetraceae, Epacridaceae, Ericaceae, Eriocaulaceae, Erythropalaceae, Erythroxylaceae, Euphorbiaceae, Eupomatiaceae, Eupteleaceae, Fagaceae, Flacourtiaceae, Flagellariaceae, Fouquieriaceae, Francoaceae, Frankeniaceae, Fumariaceae, Garryaceae, Geissolomataceae, Gentianaceae, Geosiridaceae, Geraniaceae, Gesneriaceae, Globulariaceae, Gomortegaceae, Gonystylaceae, Goodeniaceae, Greyiaceae, Grossulariaceae, Grubbiaceae, Gunneraceae, Guttifereae, Gyrocarpaceae, Haemodoraceae, Haloragaceae, Heliotropiaceae, Hernandiaceae, Heteropyxidaceae, Himantandraceae, Hippocastanaceae, Hippuridaceae, Hoplestigmataceae, Humberticeae, Humiriaceae, Hydnoraceae, Hydrangeaceae, Hydrocharitaceae, Hydrocotylaceae, Hydrophyllaceae, Hydrostachyaceae, Hypericaceae, Hypoxidaceae, Icacinaceae, Illecebraceae, Illiciaceae, Iridaceae, Irvingiaceae, Iteaceae, Ixonanthhaceae, Juglandaceae, Julianaceae, Juncaceae, Juncaginaceae, Koeberliniaceae, Krameriaceae, Lacistemataceae, Lactoridaceae, Lamiaceae (or Labiatae), Lardizabalaceae, Lauraceae, Lecythidaceae, Leeaceae, Leitneriaceae, Lemnaceae, Lennoaceae, Lentibulariaceae, Lepidobotryaceae, Lilaeaceae, Limnanthaceae, Limoniaceae, Linaceae, Lissocarpaceae, Loasaceae, Lobeliaceae, Loganiaceae, Loranthaceae, Lowiaceae, Lythraceae, Magnoliaceae, Marcgraviaceae, Medusagynaceae, Melastomataceae, Meliaceae, Melianthaceae, Menispermaceae, Moraceae, Moringaceae, Musaceae, Myoporaceae, Myricaceae, Myristicaceae, Myrsinaceae, Nepentaceae, Nyctaginaceae, Nymphaeaceae, Ochnaceae, Olacaceae, Oleaceae, Oleraceae, Orchidiaceae, Pandanaceae, Papaveraceae, Passifloraceae, Pedaliaceae, Penaeaceae, Phormiaceae, Piperaceae, Plantaginaceae, Poaceae, Portulacaceae, Primulaceae, Proteaceae, Puniaceae, Resedaceae, Rhamnaceae, Rhizophoraceae, Rosaceae (any genus except *Prunus*), Rubiaceae, Rutaceae, Sabiaceae, Salicaceae, Samydaceae, Sapindaceae, Sapotaceae, Schisandraceae, Scrophulariaceae, Simaroubiaceae, Solanaceae, Styracaceae, Symplocaceae, Tamaricaceae, Theaceae, Thymelaceae, Tiliaceae, Ulmaceae, Urticaceae, Winteraceae, Verbenaceae, Violaceae, Viscaceae, Vitaceae, and Xanthorrhoeaceae. Note, not all of these families may have genera with exudates-producing species. We wish to request readers to contact us if they wish to make exudates of those and other plant families available for study.

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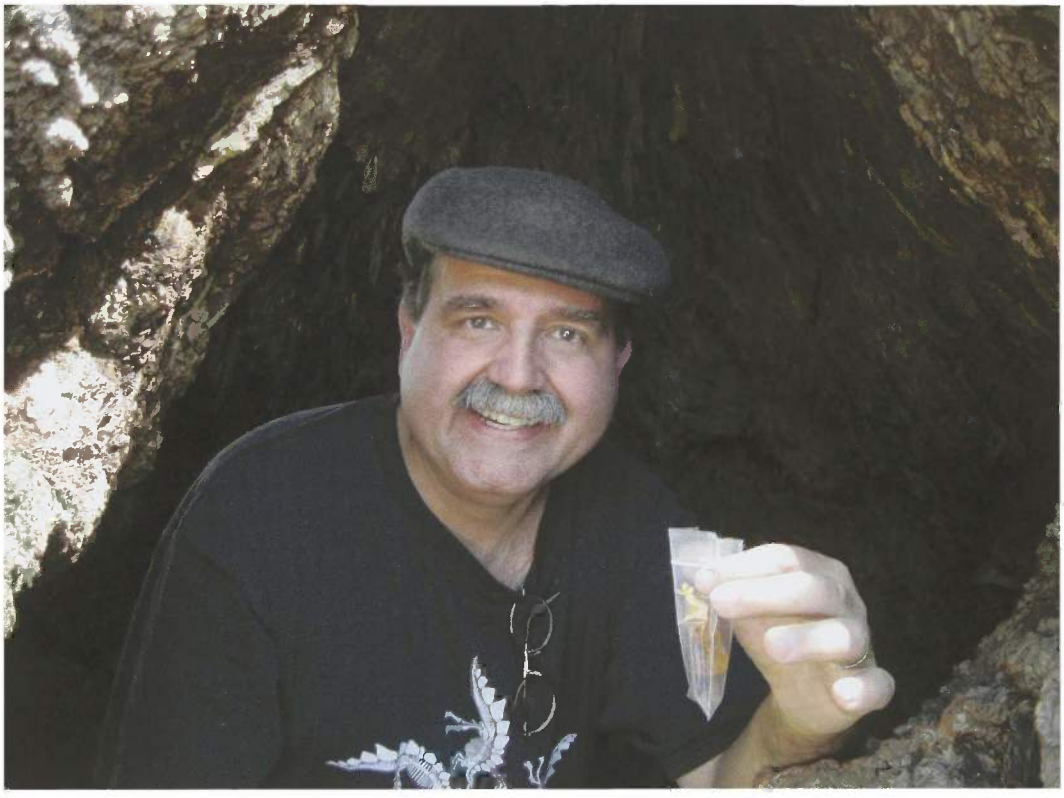

Author JASB holding collected exudate in zip lock bag