Exudates from the Asterids: Characterization by Nuclear Magnetic Resonance Spectroscopy[1]

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Abstract: Exudate samples from the asterid clade of the flowering plants have been collected and analyzed by nuclear magnetic resonance spectroscopy. Examination of carbon-13 nuclei in the solid state provides characterization of the exudates in the bulk. Examination of hydrogen nuclei by one and two dimensional methods provides further characterization. Six orders and 15 families are represented in the 78 samples analyzed. The exudates include 46 resins, 10 gums, 14 gum resins, 2 kinos, 5 balsams, and 1 unaffiliated. Balsams represent a newly characterized class of exudates from the genus *Styrax*.

Key Words: plant exudates, resins, gums, gum resins, kinos, balsams, asterids, nuclear magnetic resonance spectroscopy, NMR

Flowering plants have been classified by the Angiosperm Phylogeny Group (2009) largely on the basis of molecular (DNA) criteria while building on traditional morphological analysis. The three largest clades of flowering plants are the magnoliids, the monocots, and the eudicots. We have been examining exudates of the entire plant kingdom, but in particular those of the eudicots, or true dicotyledonous plants. This clade comprises plants that are tricolpate, that is, whose pollen grains exhibit three colpi or grooves along the polar axis. This group is monophyletic, whereas the traditional grouping of dicotyledonous plants with two embryonic leaves, which includes both magnoliids and eudicots, are polyphyletic. The eudicots comprise core eudicots, the vast rosid clade, and the asterid clade. In the Cronquist system, the latter two clades were known as the Rosi-dae and the Asteridae. We have reported extensively on the exudates of the rosids (Lambert et al. 2007, Lambert et al. 2009, Lambert et al. submitted), and we report herein the first comprehensive investigation of the exudates of the asterids.

The asterids include some 70,000 species in about 100 families and 13 orders (Donoghue et al. 1998, Bremer 2005, Angiosperm Phylogeny Group 2009). APGIII further divides the asterids into two subclades, the lamiids (or euasterids I) and the campanulids (or euasterids II), with the orders Cornales and Ericales basal to these groups. Major recent taxonomic changes based on DNA

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analysis include moving the Apiales from the rosids to the asterids and placing the former order of Rubiales within Gentianales. Floral characteristics of many asterids include fused petals, smaller numbers of stamens attached to the corolla, and zygomorphic flowers, i.e., those with bilateral symmetry (with only a plane of symmetry) rather than with radial symmetry (with a center of symmetry). All asterids share the morphological characteristic of having a single layer or integument on the embryo.

Many plants exude sticky material as the result of damage or disease, and this viscous material often solidifies with time. Such materials have found religious, medicinal, and other practical and symbolic uses by humans. Exudates come in a variety of molecular forms, including resins that are based on terpene building blocks, gums that are based on carbohydrates, gum resins that contain the elements of both these components, kinos that are based on phenolic constituents, and a few minor classes (Lambert et al., 2008; Lambert et al., submitted). Resins and gums have been treated exhaustively by Langenheim (2003) and by Nussinovitch (2010), respectively. Mills and White (1994) provide a useful overview of many exudates and related materials in the context of museum objects.

Exudates are produced most famously and most profusely by conifers and rosids (Langenheim, 2003). Although there are about the same number of species in the rosid and the asterid clades, fewer species by far of the asterids produce exudates. Langenheim (2003) lists several resin-producing asterid orders and families, pointing out that resin-producing trees are rarer in the asterids than resin-producing shrubs. She notes that the Asteraceae are the richest resin producers in the asterids. Gums are rarer in the asterids than in the rosids. In his compilation of gums, Nussinovitch (2010) lists only 12 asterid species that produce gum exudates out of over 220 described, or ca. 5% of the total.

It is our purpose in this study to determine the molecular classes of exudates produced by the asterids and to explore whether the molecular identities are related to their taxonomic classification. We use nuclear magnetic resonance (NMR) spectroscopy to accomplish these analyses. We restrict our study to exudates that fully solidify. For the direct study of solid exudates in the bulk, carbon-13 (13C) NMR analysis is the method of choice because it characterizes the entire sample spectroscopically. Other important methods include mass spectrometry, which provides very useful information but not on the complete bulk. Preparation requires powdering of the sample but is otherwise nondestructive. None of the sample is lost, and the entire material is analyzed. NMR analysis of solids utilizes the specialized techniques of cross polarization (CP) and magic angle spinning (MAS), along with proton decoupling (Lambert and Mazzola 2004). In addition, we examine the proton (1H) spectra, which requires dissolution and hence some sample selection.

Methods

Sample Collection and Preparation. Samples were collected from public and private botanical gardens or arboreta with permission of the institutions. The species and their sources are provided in Table 1. Samples were removed from the plant surface by hand or with the help of a knife without any harm to the plant such as causing an incision. Typically, samples of 1-5 g were collected. The material was powdered or dissolved for NMR analysis but was fully recoverable as a powder. Original and powdered samples will remain in the laboratory at Trinity University for continued experiments but can be made available on request.

In preparation for solid state 13C experiments, samples were ground into a fine powder and were loaded into a Varian 5 mm general purpose Zirconia rotor sealed with Vespel caps. Each sample load optimally required about 160 mg of material, although smaller sample sizes were possible (as little as 50 mg) and required larger scan numbers. For solution state ^{1}H spectra, approximately 55 mg of powdered exudate (as prepared for ^{13}C analysis) was transferred to a small, glass vial. About 1 mL of deuterated chloroform-d6 or dimethyl sulfoxide (DMSO-d6) was added to each vial. The contents was stirred at room temperature and allowed to sit overnight. The supernatant was pipetted out and transferred to the NMR tube.

Data Acquisition. Solid state ^{13}C NMR data were recorded on a 400 MHz Varian NMR System with a 5 mm T3 PENCIL probe. The magic angle spinning rate was set to 5000 Hz. The cross polarization (CP) pulse sequence was used for normal proton decoupling. For interrupted decoupling (dipolar dephasing), a 50 μs delay was applied in the ^{1}H channel just before the 180° pulse in the ^{13}C channel. We used adamantane to adjust the Hartmann-Hahn matching condition for normal CP experiments and to adjust the observation pulse and the delay time for dipolar dephasing. A typical parameter set was as follows: spectrum frequency 100.544 MHz, spectral width 50 kHz, pulse width 3.4 μs for the 90° pulse for both ^{1}H and ^{13}C, delay time 5 s, contact time 2 ms, acquisition time 20.5 ms, and scan number 256. Solid state ^{13}C spectra were referenced to an external adamantane peak at δ 38.3 and were converted to tetramethylsilane at δ 0.0.

Most proton spectra were obtained on a Varian Inova-500 NMR spectrometer at room temperature without spinning. Typical one-dimensional parameters were as follows: spectral width 12,000 Hz, pulse width 60°, delay time 1.0 s, acquisition time 1.0 s, and scan number 4. Spectra were referenced in $CDCl_3$ to TMS. Typical two-dimensional parameters without pulsed field gradients were as follows: spectral width 12,000 Hz, pulse width 90°, delay time 1.0 s, scan number 4, acquisition time 0.17 s, and increment number 256.

Results and Discussion

Figure 1 presents a phylogenetic tree of the orders of the asterids, including the family Boraginaceae, which is not affiliated with an order in APGIII. Of the 13 orders, sampled six plus the Boraginaceae, which are depicted in red, with a total of 78 exudate samples (Table 1, located after the Literature Cited section). Unsampled orders (in blue) tend to be small and rarely produce exudates. Our discussion follows the phylogenetic order of Figure 1.

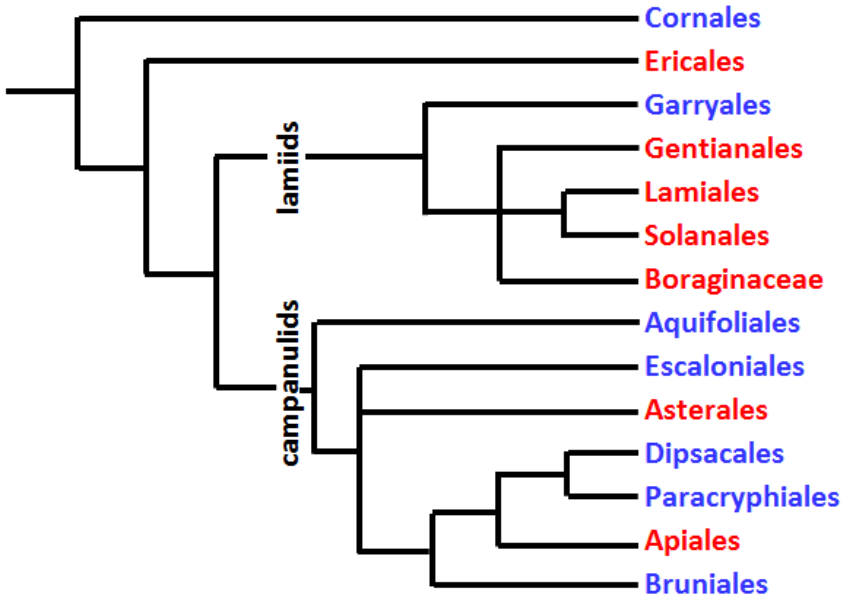

Figure 1. Phylogenetic tree of the asterids. The third through sixth orders from the top plus the unaffiliated family Boraginaceae are members of the subclade lamiids or euasterids I, and the lower seven orders are members of the subclade campanulids or euasterids II. Sampled orders are in red and unsampled orders in blue. Several other unaffilated families were not sampled and are not included.

Ericales. This large order is basal to the euasterid groups and contains 22 familes and about 8,000 species. We have examined 22 samples from five families, 10 genera, and 14 species (plus two samples identified only by genus). Economically important members of the Ericales include tea, blueberry, cranberry, kiwi, persimmon, Brazil nut, azalea, rhododendron, and phlox, which occur variously as trees, bushes, vines, and herbaceous plants. The geographical range extends from the tropics to the Arctic.

Ebanaceae. This family comprises some 800 species from three genera, of which ebony and persimmon probably are the most famous. In the tropics and subtropics, the plants are primarily evergreen, although some plants are

deciduous in temperate zones. We have analyzed the NMR spectra of two samples from *Diospyros virginiana*, the American persimmon. The spectra indicate that both materials are gums. Because gums are poorly soluble and have low volatility, they are best examined by ^{13}C NMR spectroscopy directly on the bulk solid, using the CP/MAS techniques. The ^{13}C spectra of gums obtained in this fashion are characterized by a strong peak at δ ca. 75 from the carbohydrate carbons attached to a single oxygen (C—O) and a weaker peak at δ ca. 105 from the anomeric carbons, which are attached to two oxygen atoms (O—C—O) (see Figure 2 of *Lucuma* sp. from another family of the Ericales). In common carbohydrates, all saturated carbon atoms are attached to at least one oxygen. The region of the ^{13}C spectrum from about δ 40 to 100 is referred to as the electron-withdrawing group (EWG) region because the carbon resonances all have been shifted by the effect of an electronegative atom or group attached to the resonating carbon, oxygen in this case. The higher frequency of the anomeric carbon thus arises from the combined effect of two oxygen atoms. Gum spectra therefore characteristically have two broad peaks in the ratio of about five to one. Nussinovitch (2010) does not have *D. virginiana* in his compendium but does include the gum of *D. mespiliformis* from Africa and notes the importance of *Diospyros* gums as wood adhesives.

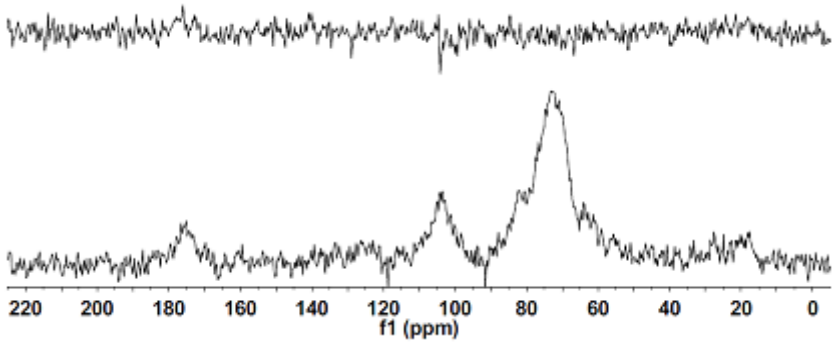

Figure 2. The ^{13}C NMR spectra of *Lucuma* sp. of the Sapotaceae. For the lower spectrum, all protons were decoupled from carbon-13. In the upper spectrum, the technique of dipolar dephasing was used to select primarily quaternary carbons (absent in gums). These spectra are representative of gums.

Figure 2 and all ^{13}C representations herein contain two spectra, taken under different conditions of decoupling. The lower spectrum was recorded under the normal conditions whereby all protons have been decoupled from carbon. In the upper spectrum, the technique of dipolar dephasing (or interrupted decoupling) was used to select only quaternary carbons (those lacking attached protons) and some rapidly moving carbons such as in methyl groups. As carbohydrates usually lack these functionalities, there are no resonances in the dephased

spectrum. The two decoupling techniques are used to provide distinct spectral fingerprints. The absence of resonances in the dephased spectrum, for example, is a diagnostic for gums.

Fouquieriaceae. This monogeneric family contains the ocotillos, an iconic group of plants common in the drylands of Mexico and the American Southwest. A single exudate sample from *Fouquieria shrevei* proved to be a resin. Resins may be analyzed by a number of techniques, including NMR spectroscopy and mass spectrometry (MS), because of their good solubility and volatility. We use ^{13}C NMR spectroscopy to examine resins in the bulk and ^{1}H to examine them in solution. The two methods often are complementary, and for many cases unique information is provided by both nuclides. Resin solubility is variable, so that any insoluble residue is unexamined by ^{1}H NMR spectroscopy. In the case of *F. shrevei*, the ^{13}C spectrum is dominated by saturated carbons (those not involved in multiple bonding), with resonances in the region δ 10-50 (Figure 3). The largest peak is at δ 32, and two other, substantial peaks are at δ 18 and 38. There are two small peaks in the EWG region, a sharp peak at δ 51 and a broad peak at δ ca. 75. The latter peak coincides with the C—O resonance of carbohydrates. There is little or no resonance, however, at the anomeric position δ ca. 105. In the absence of a confirming anomeric peak, we conclude that there is no gum component in the sample. Although resins exhibit considerable variety in the appearance of their resonances in the saturated NMR region, Figure 3 is representative of the resin class of exudates. Other resins also are expected to exhibit resonances primarily in the saturated region, but the details of the fine structure can differ considerably. In the spectrum of *F. shrevei* with dipolar dephasing (upper spectrum in Figure 3), the large peak at δ 32 and the small peaks in the EWG region have disappeared, and the only remaining peaks are those at δ 18 and 38.

The ^{1}H spectrum of *F. shrevei* also is representative of the resin class (Figure 4). The region of hydrogens attached to saturated carbons (δ 0.5-2.1, the saturated region) contains the greatest concentration of peaks, as expected for terpenoid hydrocarbons. In addition, there are a few small peaks in the region of hydrogens attached to saturated carbons that bear electron-withdrawing groups (such as hydroxyl, alkoxyl, or carbonyl) (δ 2.2-5.0, the EWG region) and in the region of hydrogens attached to alkenic carbons (C==CH, δ5.0-6.5, the alkenic region). The only significant peak in the region of hydrogens attached to aromatic carbons (δ 6.5-8.5, the aromatic region) is the fortuitous solvent peak from chloroform. The electron-withdrawing effect of three chlorine atoms suffices to push the resonance into the aromatic region.

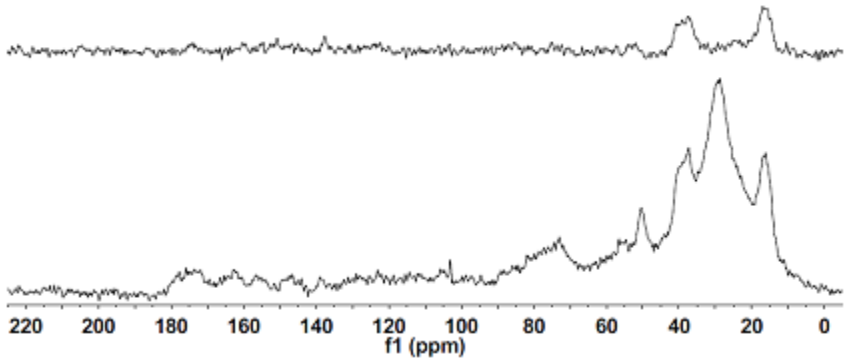

Figure 3. The ^{13}C spectra of *Fouquieria shrevei*, with normal decoupling at the bottom and with dipolar dephasing at the top. These spectra are representative of resins.

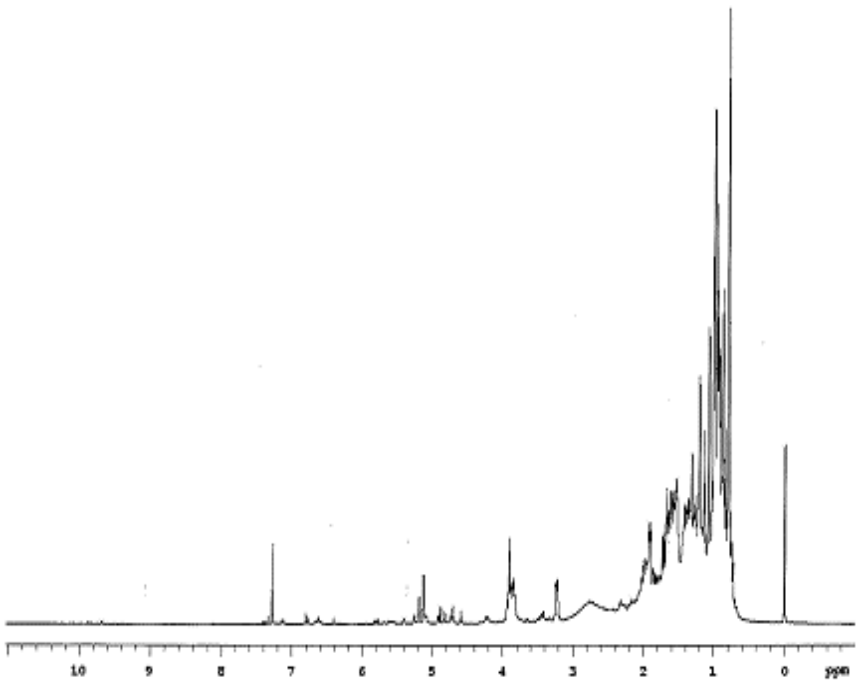

Figure 4. The 1H spectra of *Fouquieria shrevei*. This spectrum is representative of resins.

Sapotaceae. The Sapotaceae include some 800 species of evergreen trees and shrubs, which often produce edible fruit, particularly from the genera *Manikara* and *Pouteria* studied here. The family name derives from the Nahuatl (the language of the ancient Aztecs and many current residents of central Mexico) word *Tzapotl*, which has generally been anglicized to the common name *sapota*. The family includes the genus *Palaquium*, also studied here, well known for the exudate named gutta-percha. This material was used widely as an insulator in electronic applications (now largely replaced by synthetics) and in surgical devices such as dental implants. More obscure uses included as cores of golf balls (along with the exudate from *M. bidentata*), molded jewelry, canes, and furniture, although its popularity has declined with the rise of synthetic polymers.

We have examined exudates from two subfamilies of the Sapotaceae. The Sapotoideae are represented by ten samples from five genera and six species (plus one sample identified only by genus). The sample from *Isonandra acuminata* proved to be a resin with a ^{13}C spectrum somewhat similar to that of *Fouquieria shrevei* (Figure 3). In the case of *I. acuminata*, the peak at δ 32 is reduced to a height equal to those at δ 18 and 38, the small peak at δ 51 is absent, and a new peak is present at δ 168. The two spectra look almost identical under conditions of dipolar dephasing, except for addition of the new peak at δ 168. This peak is in the carbonyl region (δ 160-220, in which the functionality C==O resonates). Since most such carbon atoms have no attached protons, they persist stongly with dipolar dephasing.

Several other Sapotoideae samples are resins, with ^{13}C spectra that grade away from that of *I. acuminata*, but with some some similarities. Figure 5 illustrates this resin type, from *Manilkara zapota* (sample from the Field Museum; sources are specified in the text only in cases of multiple samples of a given species). The saturated region contains the two strong peaks at δ 18 and 38, but the peak at δ 32 for *I. acuminata* is much reduced in intenstiy. The spectra in Figure 5 are sharper than those in Figure 3. As a result, the broad peak around δ 38 in Figure 3 has split into three well defined peaks at δ 37, 41, and 43. With dipolar dephasing, the four strong, saturated peaks at δ18, 37, 41, and 43 survive, so that the dephased spectra in Figures 3 and 5 are almost identical, except for the differences in resolution. This same resin pattern is found for all the samples of *M. zapota*, as well as for *Mimusops* sp. and *Palaquium sumatranum*. For reference, we will call this spectral pattern the sapota resin pattern (Figures 3 and 5).

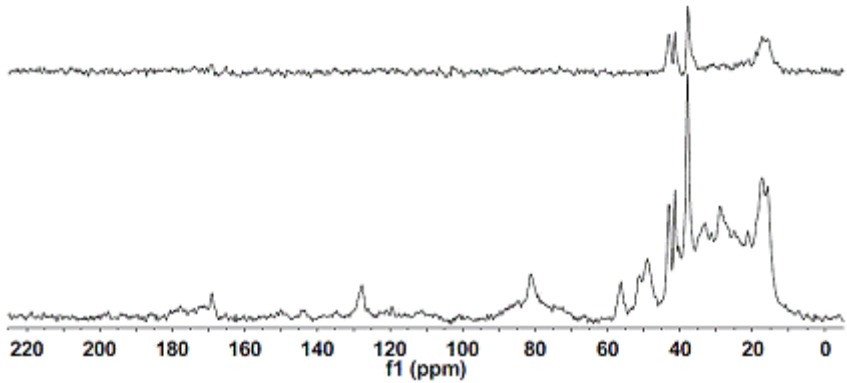

Figure 5. The ^{13}C spectra of *Manilkara zapota* from the Field Museum, with normal decoupling at the bottom and with dipolar dephasing at the top. These spectra are representative of most sapota resins.

The ^{13}C spectra of *Manilkara bidentata* (Figure 6) and *Palaquium gutta* (sample 5450 from the Harvard University Farlow Herbarium, a sample of gutta-percha) grade further away from these. The saturated region still dominates, but the entire region consists of a single, very broad peak with intensities decreasing from right to left. There is a broad peak in the EWG region from δ 70 to 90. The appearance is not gum-like, as those resonances rarely extend to a frequency above δ 80, and there is little evidence of an anomeric peak δ ca.105. Consequently, we do not believe there is a gum component. The ^{13}C spectrum of our second sample of *P. gutta* (sample 5229 from the Harvard University Farlow Herbarium) has all these characteristics, but its peaks generally are much sharper. We shall return to the broad spectral type of Figure 6 in the context of the Apocynaceae, for which it appears more frequently. Because the saturated resonances for these three samples, typical of resins, are accompanied by significant peaks in the EWG and unsaturated regions, we have classified them as resins (other), in which the parenthetical notation signifies the presence of additional peaks beyond the norm for resins.

There is one gum sample in the Sapotoideae, as the ^{13}C spectra of the sample of *Madhuca longifolia* have the gum pattern of Figure 2.

We have three samples from the subfamily Chrysophylloideae. The sample from *Lucuma* sp. gave the typical ^{13}C spectra of a gum (like Figure 2). The samples from *Pouteria procera* and *P. campechiana* gave ^{13}C spectra very much like those of *Manilkara zapota*, *Mimusops sp.*, and *Palaquium sumatranum* in the saturated region (the sapota resin pattern). Indeed, all ten resins from the Sapotaceae gave relatively similar ^{13}C spectra, with the variations outlined above. The two *Pouteria* samples additionally had small peaks in the

unsaturated region. The two spectra were remarkably alike, despite disparate sources.

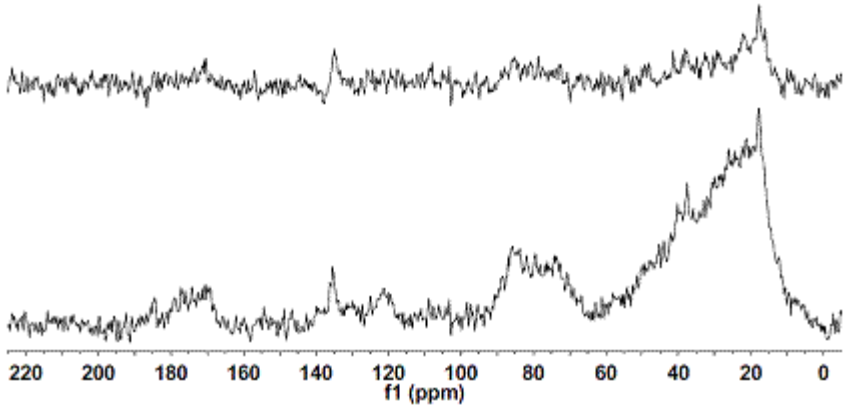

Figure 6. The ^{13}C spectra of *Manilkara bidentata*, with normal decoupling at the bottom and with dipolar dephasing at the top.

Styracaceae. This family comprises 11 genera and about 160 species, most of which belong to the genus *Styrax*. These ornamental plants of this predominantly Northern Hemisphere family, usually shrubs and small trees, are known for their decorative white flowers. Their exudates often are called benzoin resin, used in perfume and herbal medicine. The so-called resin is harvested from various species of the genus *Styrax*, of which we have examined five samples from two species. Exudates from the genus *Styrax* have an ancient history. They have been known by many names, including benzoin, benzoin resin, styrax resin, balsamic resin, gum benzoin, gum benjamin, Sumatra benzoin, and Siam benzoin. They also have been called balsamic resins, which is a term used to describe exudates whose principal components are benzoic acid ($C_6H_5CO_2H$) and cinnamic acid ($C_6H_5CH{=}{=}CHCO_2H$). Langenheim (2003) has discussed these materials extensively. In a case of linguistic convergence, the ambiguous term *benzoin* also refers to a specific chemical compound [$C_6H_5CHOH(C{=}{=}O)C_6H_5$]. The word comes from the Arabic phrase *luban jawi*, meaning "frankincense from Java." This substance was referred to as early as ca. 1350 by Ibn Bututa (Oxford English Dictionary 2009). The initial syllable "lu" was lost, and *ban jawi* evolved into *benzoin*. The acid extracted from it thus became known as benzoic acid, from which all the chemical and common names with the "benz" root have evolved, including benzene, the parent of all aromatic compounds, and *benzin*, the German word for gasoline or petrol.

As we shall see, *Styrax* exudates give ^{13}C and ^{1}H spectra that are neither terpenoid nor saccharidic. Consequently, the terms *resin* and *gum* are inappropriate in this context. Thus benzoin resin, styrax resin, balsamic resin,

gum benzoin, and gum benjamin are inadmissible terms for this class in a technical context. The existing term *balsam* most properly refers to materials with a characteristic odor that derives from its main constituents, benzoic and cinnamic acids. We prefer the term *balsam* to *benzoin* for the *Styrax* exudates, because of the latter's ambiguity with the compound of the same name. Balsams also should be distinguished from phenolic exudates called "kinos," derived from eucalypts and many other sources. *Styrax* exudates (balsams) have been used since antiquity as incense (in the Russian Orthodox Church), perfume, antiseptic, and as a general folk medicine.

Figure 7 presents the ^{13}C spectra for the sample of *Styrax benzoides*. The spectra of the other four samples (all *S. benzoin*) are identical, peak for peak, but all their resonances are slightly broader. The spectra in Figure 7 with normal decoupling resemble those of no previously studied exudate. It is not a resin or a gum resin, as it lacks significant saturated resonances. It is not a gum, as it lacks the characteristic resonances at δ 75 (there is an EWG peak at δ 81, but this is out of the normal gum range). The pattern of unsaturated and carbonyl peaks does not resemble the phenolic pattern in kinos (discussed below), the xanthone pattern of xanthics, or the guaiacol pattern of guaiacs (minor exudate classes not observed among the asterids). It is not found in the spectra of any of the unclassified rosid samples (Lambert et al., submitted).

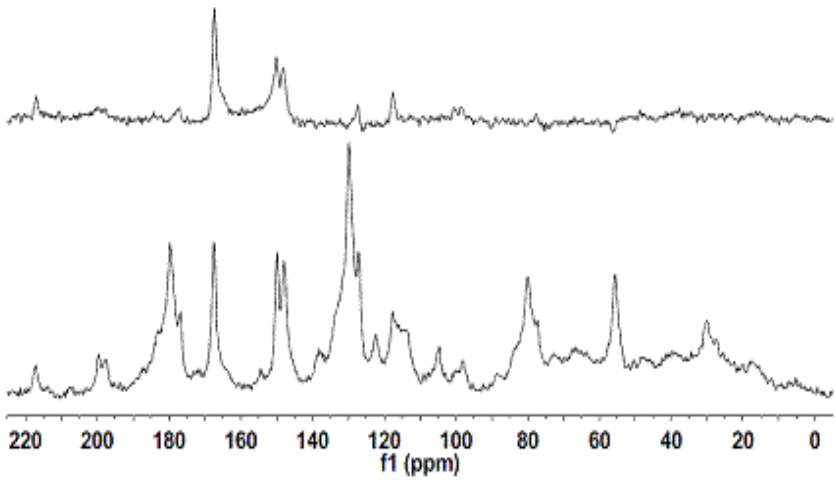

Figure 7. The ^{13}C spectra of *Styrax benzoides* (sample 271836 from the Field Museum), with normal decoupling at the bottom and with dipolar dephasing at the top. These spectra are representative of balsams.

Because *Styrax* exudates are known to contain benzoic and cinnamic acids, we compared the spectra of these compounds with that in Figure 7 and found

good consonance. The aromatic resonances for both acids fall in the well populated region near δ 130. The double bond carbons of cinnamic acid occur at δ 117 and 147, which are observed in Figure 7. There are two large carbonyl peaks in Figure 7, at δ 168 and 180, the former of which is close to those of benzoic and cinnamic acid. Small peaks at higher frequency than δ 190 are spinning side bands. There also are two peaks in the EWG region, at δ 54 and 81, which could come from other carboxylic acids. Anisic acid (4-methoxybenzoic acid), for example, has its methoxy resonance at δ 55. The resonance at δ 180 is unusual, because it occurs in the carbonyl region but disappears with dipolar dephasing (carbonyl resonances normally persist). Two types of carbonyl functionalities, however, contain a hydrogen atom attached to the carbonyl carbon: aldehydes and formates. The resonance acts more like that of an aromatic aldehyde (Ar—CHO) than of a carboxylic acid. Because aldehydic carbonyls have an attached proton, they are selected out by dipolar dephasing. The resonance of benzaldehyde itself occurs at δ 192, but substitution can alter its position.

The ^{1}H spectra of the five balsams also are consistent with the known content. Figure 8 illustrates the 1D 1H spectrum of a balsam from *Styrax benzoin* (sample 1002 from the Field Museum). The characteristic pair of doublets for the CH==CH protons of cinnamic acid are visible at δ 6.5 and 7.8, with the aromatic resonances clustered at 7.4-7.5. The resonances of benzoic acid and similar systems also cluster around δ 7.5. In addition, saturated resonances presumably from aromatic side chains are present. The broad peaks in the regions δ ca. 3.8 and 6.8 occur in all five balsam spectra, but we can only hypothesize about their structural source. All five ^{1}H spectra generally are similar, but the relative intensities of the peaks vary from species to species. The most intense peak in the 2D COSY spectrum for S. benzoin (Figure 9) occurs at δ 6.5/7.8 and corresponds to coupling between the alkenic cinnamic acid protons. We suspect that the cross peak (and the corresponding 1D resonances) at 7.6/8.2 comes from another aromatic carboxylic acid with an unsaturated side chain, but we have not identified it. In COSY spectra, all peaks are represented by the contour of their bases. The 1D spectrum occurs on the diagonal of the spectrum, and the off-diagonal or cross peaks result from coupling between two protons.

Theaceae. This family is best known for the genus *Camellia*, which contains not only the camellia flower but also the common tea plant, *C. sinensis*. The sole representative in this study is a sample of *C. sinensis*. Its ^{13}C spectra are typical of a resin, with only small, broad resonances outside the saturated region. The sample definitely does not contain significant amounts of ellagic acid, a polyphenol often associated with theaceous plants.

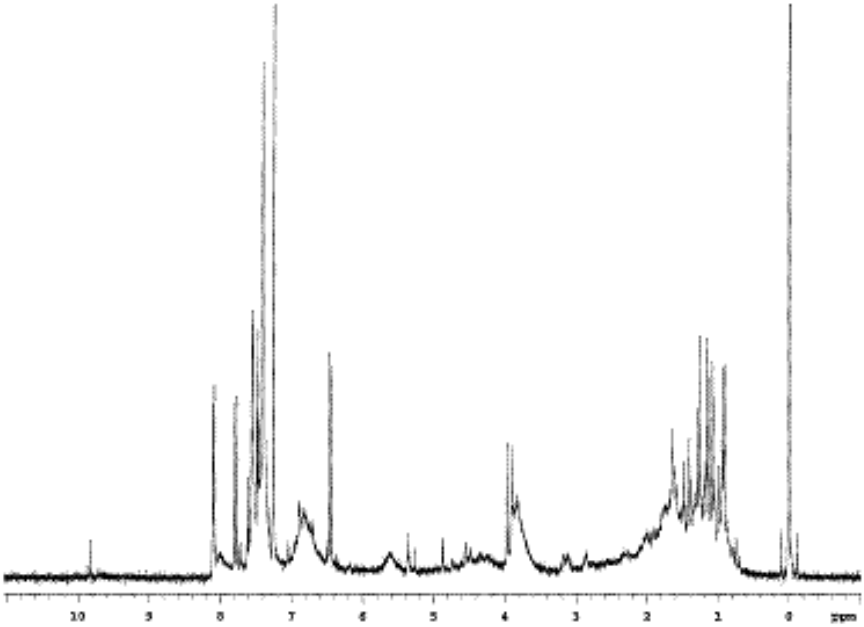

Figure 8. The ^{1}H spectrum of *Styrax benzoin* (sample 1002 from the Field Museum). This spectrum is representative of balsams.

Gentianales. This order is our first in the subclade known as the lamiids or the euasterids I. The lamiids comprise four orders and several unassigned families such as the Boraginaceae (Figure 1). The Gentianales constitute the largest of these orders and are the most exudate rich, by our experience. This order contains five families, 1,100 genera, and 17,000 species, including coffee, gardenia, and frangipani. We have obtained 15 samples from two families.

Apocynaceae. The dogbane family contains about 400 genera and 2,000 species. Well known members include periwinkle, oleander, frangipani, and liana. We have examined eight samples from this family, two from the subfamily Asclepiadoideae and six from the subfamily Rauvolfioideae. The ^{13}C spectra of *Asclepias speciosa* (Figure 10) is typical of a resin. It is very similar to seven resins in the Sapotaceae (Figure 5). This spectral pattern, which we have called the sapota resin pattern, therefore includes lamiids as well as basal asterids. It also is seen in the spectra of *Couma utilis* and *Parahancornia amapa* of the subfamily Rauvolfioideae. The latter two are somewhat different from the sapota type with normal decoupling but quite similar with interrupted decoupling.

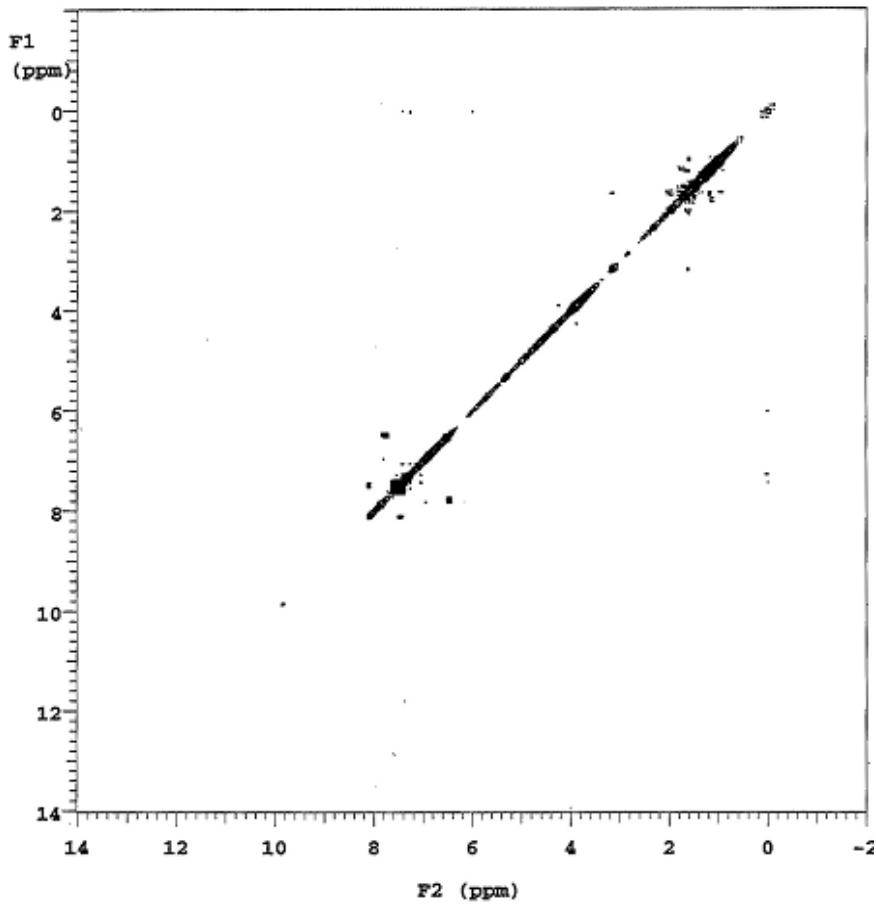

Figure 9. The 2D COSY spectrum of *Styrax benzoin* (sample 1002 from the Field Museum). This spectrum is representative of balsams.

The sample of *Dyera costulata* of the subfamily Rauvolfioideae has a ^{13}C spectrum characteristic of a gum resin. This class of exudates contains both gum and resin constituents, and their spectra reflect the content accordingly (see Figure 11 for a typical gum resin spectra, in this case of *Convolvulus scammonia* of the Convolvulaceae from the National Herbarium Nederland). The resin resonances occur as always in the saturated region between about δ 10 and 50 and the gum resonances occur as the usual pair at about δ 75 and 105. Comparison of the relative intensities of the two groupings provides a qualitative measure of the amounts of gum and resin. In the case in Figure 11, there are similar amounts of gum and resin. For *D. costulata* there is much more resin than gum, and the resin portion of its spectrum is typical of the sapota type.

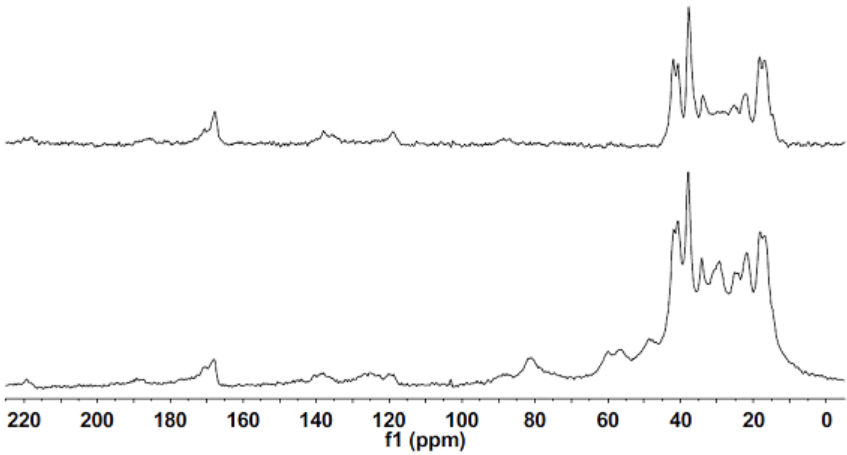

Figure 10. The ^{13}C spectra of *Asclepias speciosa*, with normal decoupling at the bottom and with dipolar dephasing at the top.

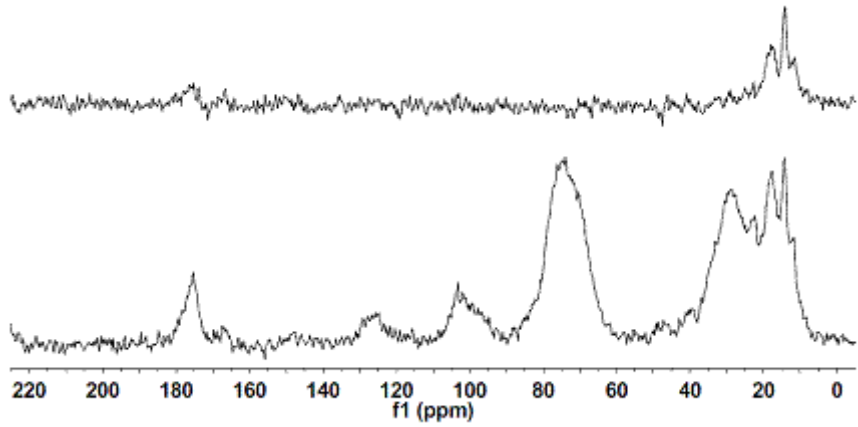

Figure 11. The ^{13}C spectra of *Convolvulus scammonia* of the Convolvulaceae (from the National Herbarium Nederland), with normal decoupling at the bottom and with dipolar dephasing at the top. These spectra are representative of gum resins.

We noted earlier that the sample of *Palaquium gutta* (sample 5229 from the Harvard University Farlow Herbarium) gave a resin spectrum rather different from that of the sapota type. Two samples from the Apocynaceae proved to have nearly identical ^{13}C spectral patterns to that of this sample of *P. gutta*: *Landolphia kirkii* (Figure 12) and *Willughbeia* sp. The saturated region is quite different from that of the sapota pattern, and in addition there are significant

resonances in the EWG and unsaturated regions. The EWG pattern is very different from that of gums. The two small, sharp peaks in the unsaturated region at δ 127 and 136 occur reproducibly with all three exudates. The smaller peaks in the carbonyl region are spinning sidebands of the unsaturated resonances and may be ignored (the lower frequency, matching spinning sidebands are superimposed on top of the resonances in the EWG region). Because of the additional peaks in the EWG region, we have classified these spectra as "resin (other)." The unusual pattern is repeated in multiple species and suggests that there are interesting underlying molecular components, which need to be identified by mass spectral techniques. The ^{1}H spectrum of *L. kirkii* (Figure 13) is typical for resins, with the strongest peaks in the saturated region and smaller peaks in the EWG region. The ^{1}H spectrum supports the fundamentally resinous nature of the exudate.

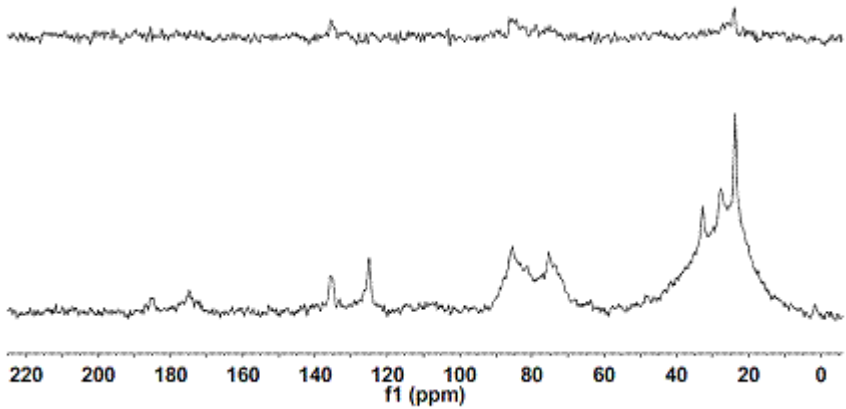

Figure 12. The ^{13}C spectra of *Landolphia kirkii*, with normal decoupling at the bottom and with dipolar dephasing at the top. These spectra are unusual for resins.

The ^{13}C spectra of *Urceola elastica* (Borneo caoutchouc) from the subfamily Asclepiadoideae and of *Landolphia gummifea* from the subfamily Rauvolfioideae are dominated by resinous peaks in the saturated region, which are broad and undefined, grading down from a maximum at δ 20 to zero at δ 60. This pattern was noted previously for the exudates of *Manilkara bidentata* (Figure 6) and of *Palaquium gutta* (sample 5450 from Harvard University Farlow Herbarium). The smaller peaks in the EWG region have some resemblance to gums, but the resonances in the C—O region are doubled, as they are in Figure 12. Instead of the single peak normally seen with gums at δ ca. 75, there are two peaks at δ 75 and 84, with no significant peak in the anomeric region. Although a similar pattern is seen in the just-discussed spectra illustrated in Figure 12, the peaks here are much broader. The samples

producing sharp peaks like that of Figure 12 and broad peaks like that of Figure 6 may represent two varieties of a distinct resinous molecular type.

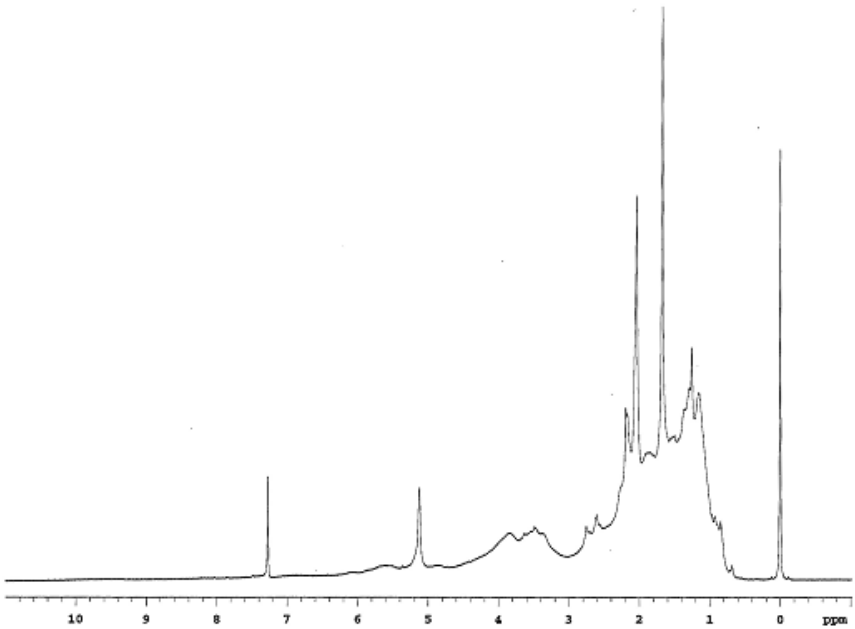

Figure 13. The ^{1}H spectrum of *Landolphia kirkii*.

Rubiaceae. The coffee or madder family contains 600 genera and 13,000 species in three subfamilies, including economically important plants such as coffee, quinine, and gardenia. We have examined seven samples, including three from the subfamily Ixoroideae: *Elaeagia utilis*, *Gardenia brighamii*, and *Gardenia gummifera*. The exudates of these three species have nearly the same spectrum with dipolar decoupling (which follow the sapota pattern) but exhibit differences with normal decoupling. The spectrum of *G. gummifera* with normal decoupling is the same as that of *Dyera costulata* of the Apocynaceae, a gum resin with much more resin than gum. The saturated region of the spectrum of *G. brighamii* is the same as that of *G. gummifera* but entirely lacks gum peaks in the EWG region, so it is a pure resin. The spectrum of *E. utilis* is nearly identical in almost every detail with that of *Fouquieria shrevei* of the Fouquieriaceae, the first resin discussed herein (Figure 3). As noted before, the saturated region with normal decoupling resembles that of the sapota pattern, except that it additionally has a very large peak at δ 34, which disappears with dipolar dephasing to give the standard dephased sapota pattern.

Of our four samples from the subfamily Cinchonoideae, two are resins and two are kinos. The resinous ^{13}C spectra of *Exostema caribaeum* are sapota-like,

with an additional peak at δ 56 and a number of small peaks at higher frequencies (a messy spectrum probably containing unknown impurities). The ^{13}C spectra of *Neolaugeria densiflora* were very weak, due to small sample size, but sufficient to indicate the resin pattern. Two samples of *Uncaria gambir*, respectively from the Field Museum and the Harvard University Farlow Herbarium, proved to be kinos (Figure 14 for the sample from the Field Museum). These plants, and their processed extracts, are known as *gambier*, with applications as drugs, dyes, and tanning. Kino exudates are most widely associated with eucalyptus and related trees (Lambert et al. 2007). They are characterized by high phenolic content. The spectrum in Figure 14 with normal decoupling exhibits the classic kino pattern, with the two most distinctive peaks in the unsaturated region (from arene carbons) at δ 145 and 155. In our original study of kinos, we described several varieties. These samples most closely resemble Class C, as represented, for example, by *Eucalyptus rubida*. *Gambier* now is seen to be a kino, closely related to exudates of eucalypts (which in Australia are called gum trees in another example of common usage that is not scientifically admissible). These two samples proved to be the only kinos observed among the asterids, whereas about 12% of the rosids are kinos (Lambert et al., unpublished).

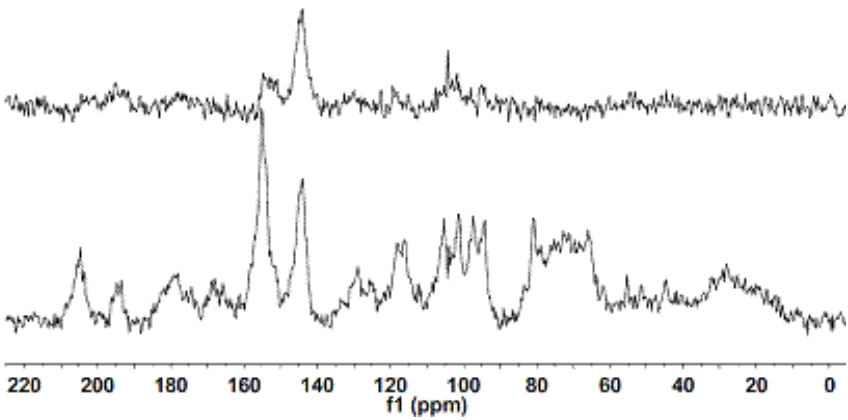

Figure 14. The ^{13}C spectra of *Uncaria gambir*, with normal decoupling at the bottom and with dipolar dephasing at the top. These spectra are representative of kinos.

Lamiales. The 20 families and 11,000 species of this order include olive, lilac, ash, teak, lavender, snapdragon, mint, and rosemary. We have examined six samples from this order.

Bignoniaceae. This family contains some 120 genera and 700 species and ranges from creepers to trees. Our single sample is from *Crescentia cujete* or the calabash tree. The ^{13}C spectra (Figure 15) contain the fingerprint of a resin,

with all significant resonances in the region δ 15-50. The distinctive pattern in the saturated region, with at least eight strong peaks, is like that seen in Figures 3 and 5 as the sapota type but with a few additional peaks.

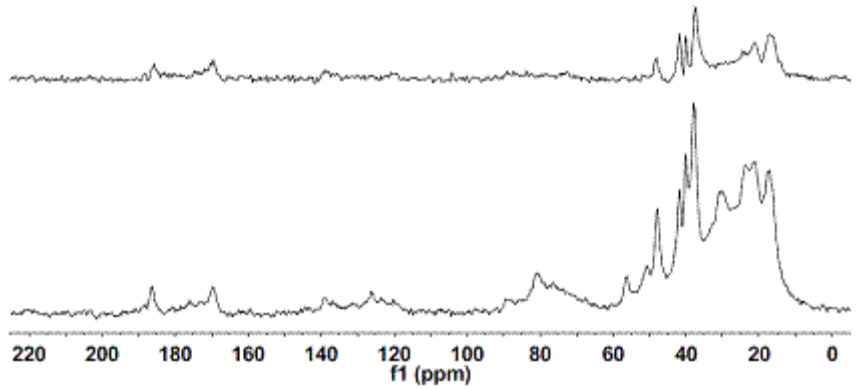

Figure 15. The ^{13}C spectra of *Crescentia cujete*, with normal decoupling at the bottom and with dipolar dephasing at the top.

Oleaceae. The olive or lilac family contains 24 genera and around 600 species. Our four samples are from only one of its four tribes (the Oleeae). The sample of *Fraxinus* sp. (not identified by species but thought to be *F. americana*) gave the ^{13}C pattern of a resin, with a broad set of resonances without well defined peaks between δ 15 and 50. The highest peak is at δ ca. 20, and the resonances decrease to higher frequency. This pattern has been described before as the broader version of the spectra illustrated in Figure 12 and includes the exudates from *Manilkara bidentata* (Figure 6), *Palaquium gutta* from Harvard University, *Urceola elastica*, and *Landolphia gummifea*. The sample of *F. angustifolia* gave a very unusual ^{13}C spectrum, which contains only a single broad peak in the C—O region at δ 70. Such a spectrum corresponds to no exudate category ("other" in the table). The sample was somewhat suspect, as it may have been processed. The spectrum must remain unidentified and unclassified until confirmed by another sample of the same species.

We have two samples of *Olea europaea*, the common olive tree. They gave identical ^{13}C spectra, containing primarily strong resin peaks in the region δ 15-40. It is noteworthy that the four peaks in this region are very similar to the four lowest frequency peaks of *Crescentia cujete*. The other four (higher frequency) peaks observed for *C. cujete*, however, are absent. In addition, the ^{13}C spectrum of *O. europaea* contains three broad peaks at about δ 76, 120-140, and 170-190 (the peaks in the carbonyl region likely are spinning sidebands of the peaks in the unsaturated region). Similar patterns were observed in four rosids (Lambert

et al., submitted) and may represent unusual impurities. Because the spectra of *O. europaea* exhibit predominantly the resin pattern, with impurities, we classify it as resin (other).

Verbenaceae. We have examined a single sample from the verbena family, which contains about 35 genera and 1,200 species. The sample of *Clerodendrum splendens* (flaming glorybower vine) gave ^{13}C spectra characteristic of a gum.

Solanales. This order contains five families, of which the largest and most important are the Solanaceae and the Convolvulaceae. The Solanales include many well known herbs, woody epiphytes, shrubs, and trees, such as potatoes, tomatoes, peppers, tobacco, petunias, belladonna, and datura. We have found no exudates from the Solanaceae. All of the exudates we have examined from this order are from the Convolvulaceae.

Convolvulaceae. The morning glory family, with 57 genera and some 1,600 species, is best known for the sweet potato and the morning glory. We have obtained five samples from three genera and three species. All five proved to be gum resins with nearly constant ^{13}C NMR spectra. Figure 11 for *Convolvulus scammonia* (from the Field Museum) is typical of these materials. This vining plant, called scammony, produces typical morning glory flowers and a juice from its root that, when dried, is used medicinally. The amounts of gum and resin are seen from Figure 11 to be approximately comparable. The saturated region contains three major peaks, and the EWG region contains only the two gum peaks. There is a minor peak in the unsaturated region at δ 126 and a minor peak in the carbonyl region at δ 175. This same pair of peaks is replicated in the other four samples, including the species *Ipomoea purga* and *Operculina turbethum* (both considered types of morning glory vines). With dipolar dephasing, the only surviving peaks are the lowest frequency saturated group (δ 15-17) and a weakened carbonyl resonance. The constancy of the spectra across three genera is remarkable.

Borignaceae. This family does not belong to an order in the APGIII classification but is sister to the other lamiid orders. Some classifications attribute it to the order Boraginales. The family contains some 150 genera and 2,000 species, including forget-me-nots and heliotropes. Our single sample of *Cordia sinensis* gave ^{13}C spectra typical of a gum.

Asterales. This order is our first in the subclade called campanulid or euasterid II, which contains a total of seven orders (Figure 1). We have examined exudates from two of these orders, including six from the Asterales. Of the 11 families of the Asterales, we have examined samples from the two largest.

Asteraceae. The largest family of the Asterales is the Asteraceae, with 1,600 genera and 23,000 species, including the sunflower, lettuce, sage (source of absinthe), and chrysanthemum. We have examined six samples from four genera and five species. The desert shrubs *Artemisia spinescens* (a sagebrush,

one sample) and *Encelia farinosa* (brittlebush, two samples from different sources) produced nearly identical ^{13}C spectra, illustrated in Figure 16 for the sample of *E. farinosa* from the Desert Botanical Garden.

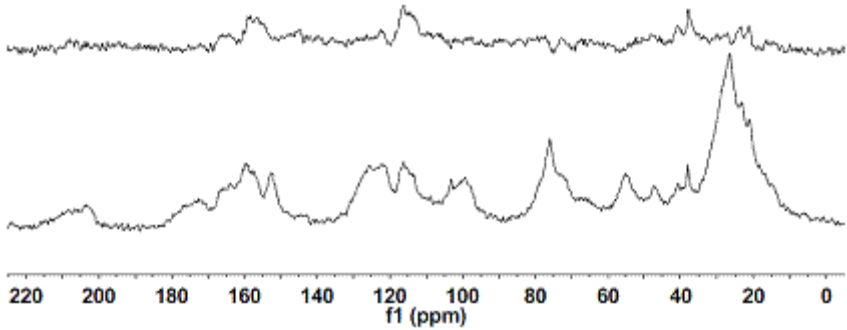

Figure 16. The ^{13}C spectra of *Encelia farinosa* from the Desert Botanical Garden, with normal decoupling at the bottom and with dipolar dephasing at the top.

A Spanish name for *E. farinosa* is *incienso* because its exudate was used as incense in the Spanish missions in the colonial period of the New World. The strongest peaks are in the saturated region and are characteristic of resins, but there are weaker peaks in all the other regions. The distribution is somewhat similar to spectra of exudates called xanthics from the genus *Garcinia* of the Clusiaceae, which contain xanthones. The molecular structures of the constituents of the exudates from *E. farinosa*, however, have not been identified. The ^{1}H spectrum (Figure 17, also the sample from the Desert Botanical Garden) provides further structural information. As with the ^{13}C spectrum with normal decoupling, the strongest peaks in the ^{1}H spectrum fall in the saturated region. The remaining ^{1}H peaks parallel the ^{13}C peaks. The strong ^{1}H peak at δ 3.8 in the EWG region corresponds to the similar ^{13}C peak at δ 76. Had the ^{13}C peak been from a gum, the functionality would not have appeared in the ^{1}H spectrum, because of poor solubility of gums in chloroform. The peaks in the ^{1}H alkenic region at δ 5.0-6.5 correspond to those in the ^{13}C unsaturated region at δ 100-150. It is noteworthy that the aromatic region in the ^{1}H spectrum is nearly empty (only very small peaks around δ 7.8), so that we can conclude that aromatic constituents are not important in this spectrum (eliminating, for example, phenols, xanthones, and arene acids, respectively associated with kinos, xanthics, and balsams). All the resonances in the ^{13}C unsaturated region, therefore, can be assigned to alkenic rather than aromatic carbons. Finally, there are several peaks in the ^{1}H spectrum in the vicinity of δ 12.4, indicative of carboxylic acids, although not large. The strongest cross peak in the 2D COSY spectrum (Figure 18) is at δ 5.4/6.3, indicating coupling between alkenic protons, whose resonances are clearly visible in the 1D spectrum. Because the

strongest component in the spectrum is resinous, we are classifying these three exudates as resins (other). Nonetheless, we recognize that further study of the molecular structures may reveal that the materials provide a new class of exudates.

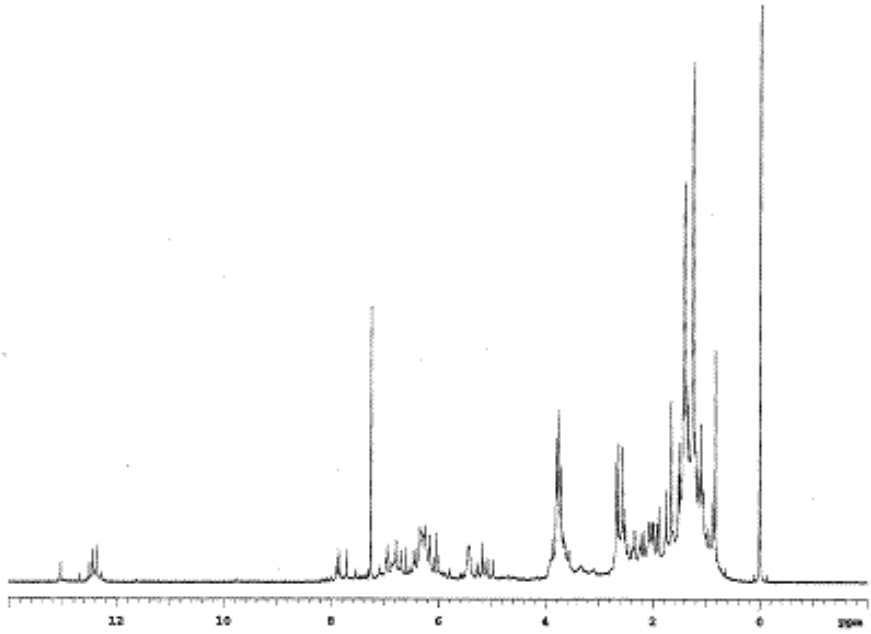

Figure 17. The ^{1}H spectrum of *Encelia farinosa* from the Desert Botanical Garden.

The remaining three Asteraceae exudates also are resins. The spectrum of *Helianthus annuus* (the common sunflower) is typical of a resin, with only saturated resonances, somewhat different from the sapota pattern. We have examined two examples of the feverfew genus, *Parthenium tomentosum* and *P. argentatum*. The spectrum of *P. tomentosum* also is typical of a resin, again somewhat different from the sapota pattern. The congealed latex of *P. argentatum* is an alternative to natural rubber. Its ^{13}C spectra contain broad resonances typical of a resin, as well as a small, broad peak in the EWG region. Because this peak does not disappear with interrupted decoupling and is not accompanied by a peak at δ105, we do not classify this material as a gum resin. It in fact is very similar to the broad sapota pattern, illustrated in Figure 6 for *Manilkara bidentata*.

Apiales. This order comprises seven families and includes well known plants such as carrot, celery, ivy, and parsley. We have examined samples from three of the families.

Apiaceae. The parsley family, also called the Umbelliferae, contains about 400 genera and 3,700 species, including many herbs, spices, and other food plants, but also folk remedies and poisons: anise, carrot, celery, coriander, fennel, hemlock, and parsley. We have examined 13 samples from six genera and eight species. The spectra of almost all members of this family are complex, with resonances not characteristic of the known exudate types.

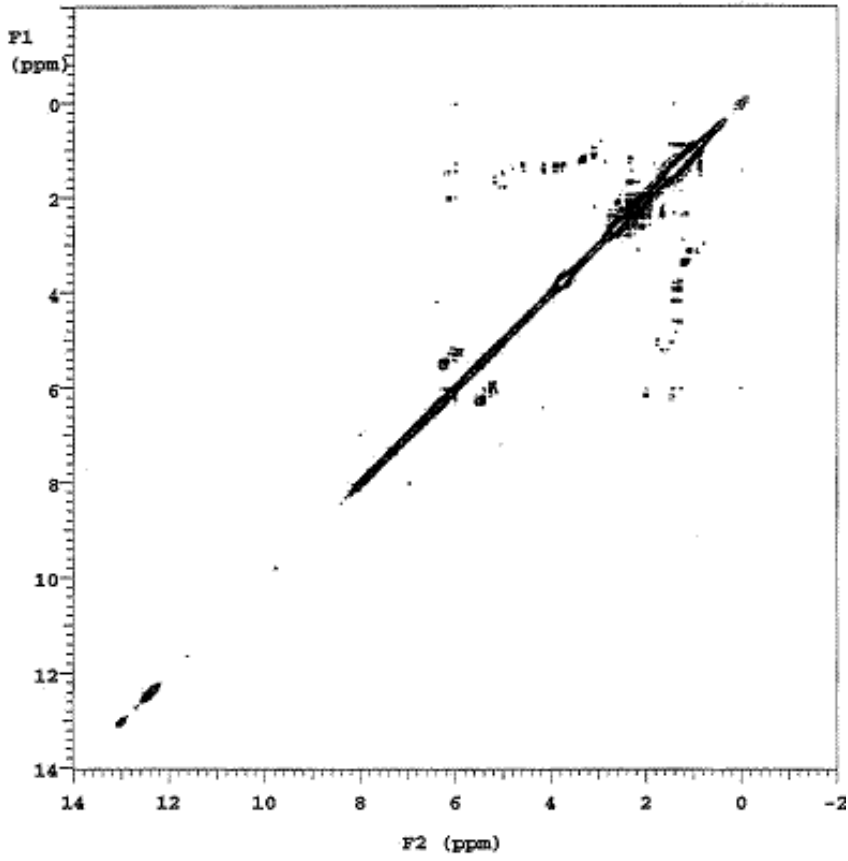

Figure 18. The 2D COSY spectrum of *Encelia farinosa* from the Desert Botanical Garden.

We have examined three samples of *Dorema ammoniacum* from three distinct sources (Field Museum, Harvard University Farlow Herbarium, and the American/National Museum of American History). This ancient material, called gum ammoniac, originally was associated with the gum from the Libyan temple of the Egyptian god Amun. The ^{13}C spectra are illustrated in Figure 19 for the

sample from the Harvard University Farlow Herbarium. The other two samples gave essentially the same spectra. There are clear resin resonances in the saturated region and possible gum resonances. In addition there are very appreciable contributions from resonances in the EWG, unsaturated, and carbonyl regions. The ^{1}H spectrum (Figure 20, also the sample from the Harvard University Farlow Herbarium) parallels the ^{13}C spectrum, with the strongest peaks in the saturated region, but also with significant peaks in the alkenic and aromatic regions and a small singlet in the carboxylic acid region. There are superficial similarities between the ^{1}H spectra of *Encelia farinosa* in Figure 17 and that of *D. ammoniacum* in Figure 20, but the details of the fine structure are quite different. The spectrum of *D. ammoniacum*, however, has significant aromatic resonances at δ 7.7-7.9 and δ 6.6-6.8, whereas that of *E. farinosa* has only minor aromatic resonances. Moreover, the largest cross peaks in the 2D COSY spectrum of *D. ammoniacum* (Figure 21) are at δ 6.9/7.8 and 6.6/7.7, representing coupling within aromatic rings. These peaks are absent in the 2D spectrum of *E. farinosa*. Thus the ^{13}C and ^{1}H spectra of *D. ammoniacum* present a new spectroscopic exudate pattern. The exudate of *Peucedanum galbaniflorum* gave almost the same ^{13}C spectra, with only minor differences. The dominance of the saturated peaks in both the ^{13}C and the ^{1}H spectra leads us to classify these materials as resins (other). The exudate evidently is composed of a well defined set of constituents produced by multiple genera and species in this family.

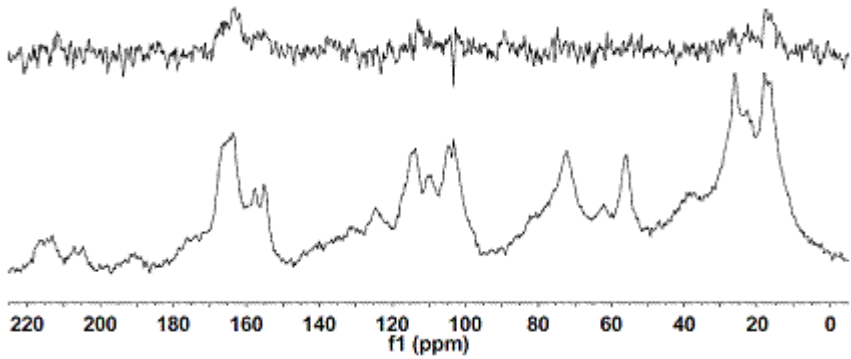

Figure 19. The ^{13}C spectra of *Dorema ammoniacum* from the Harvard University Farlow Herbarium, with normal decoupling at the bottom and with dipolar dephasing at the top.

The six samples of the genus *Ferula* come from three species. The exudates of *F. assafoetida* (Figure 22) and *F. foetida* gave ^{13}C spectra with strong resin resonances but even more resonances in the EWG, unsaturated, and carbonyl regions than for *D. ammoniacum*, with about 50% overlap of resonance positions. The spectra are similar but definitely not the same. We have three

samples of *F. gummosa* (synonym *F. galbaniflua*), an exudate called "galbanum" and mentioned both by Pliny and in the Book of Exodus. The three pairs of ^{13}C spectra are nearly identical, despite disparate sources from the Field Museum, Harvard University, and the National Herbarium Nederland. The question as to whether there is a gum component is unclear. There is a very large, broad peak at δ 65-90, not the usual appearance for gums. There are peaks in the anomeric region near δ 105, but the better description is that there are peaks for *F. assafoetida* and *F. foetida* over the entire region from δ 95 to 130, completely obscuring the anomeric region. For the three samples of *F. gummosa*, there are very small peaks in a less obscured anomeric region but not clear enough to make an unequivocal gum assignment. It is better to classify these samples of *F. gummosa* as resins (other), although they may be complex gum resins. The differences between these three ^{13}C spectra and those of *F. assafoetida* and *F. foetida* are a matter of degree. The latter two have very similar saturated (resinous) regions but differ from the other three by having very strong additional peaks in the unsaturated and carbonyl regions. In particular, a dominant peak at δ 148 is entirely absent in the spectra of the three samples of *F. gummosa.*

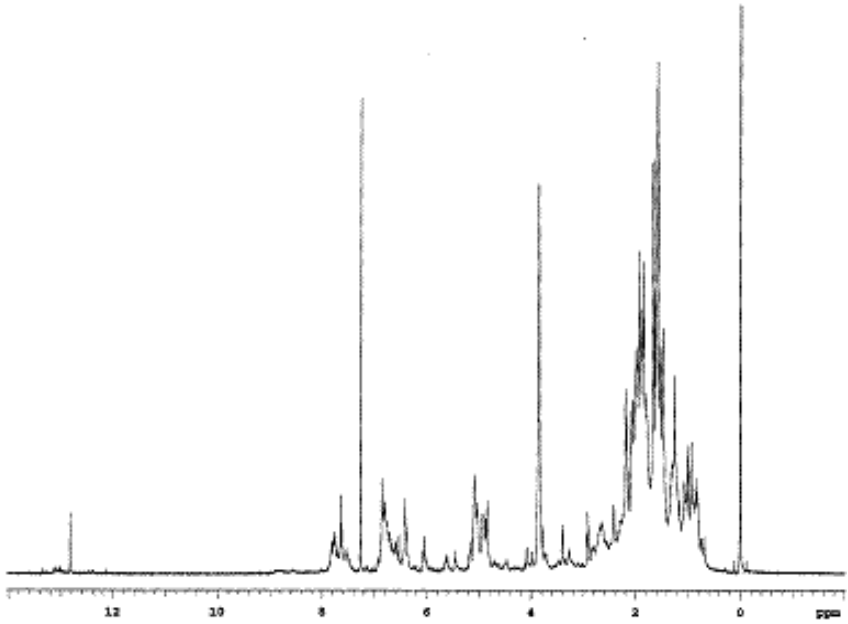

Figure 20. The ^{1}H spectrum of *Dorema ammoniacum* from the Harvard University Farlow Herbarium.

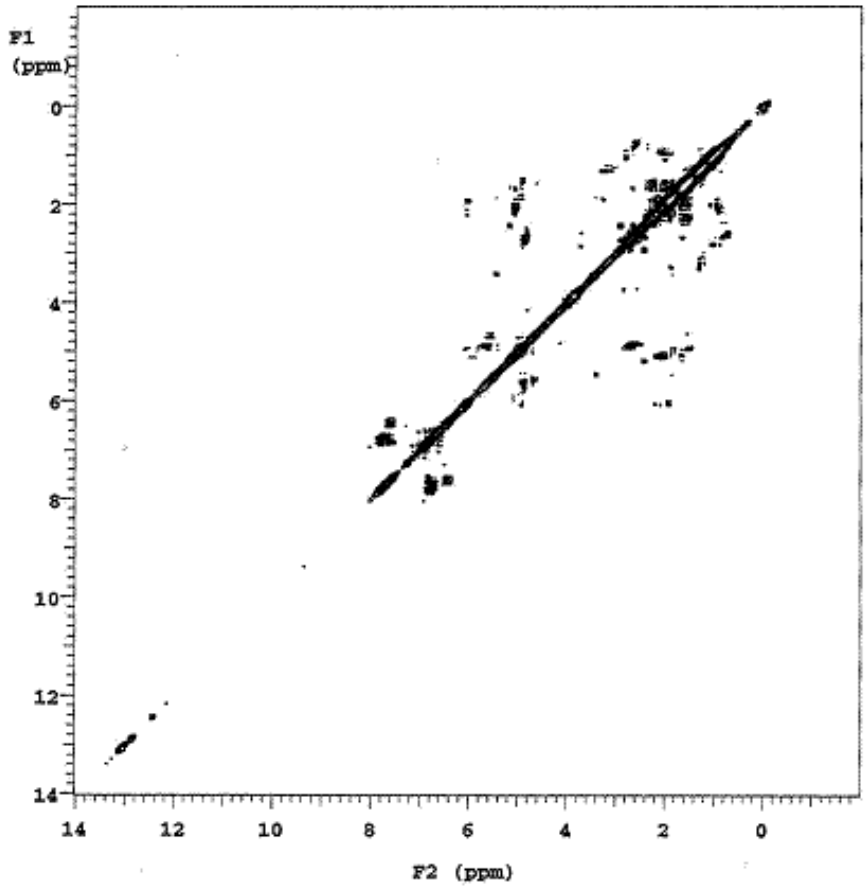

Figure 21. The 2D COSY spectrum of *Dorema ammoniacum* from the Harvard University Farlow Herbarium.

The ^{1}H spectra of these five samples offer a more homogenous appearance, indicating their fundamental similarities (Figure 23 for the spectrum of *F. gummosa* from the Field Museum). All five have strong saturated (resinous) peaks. The alkenic region is relatively weak for the three samples of *F. gummosa* and somewhat stronger for those of *F. assafoetida* and *F. foetida*. Common to all five spectra, however, are four strong and very distinctive peaks in the aromatic region at δ 6.2, 6.8, 7.4, and 7.6 (Figure 23). The strongest cross peaks in the 2D COSY of these five samples (Figure 24) derive from coupling among these aromatic protons. Thus these five *Ferula* exudates have a common molecular base.

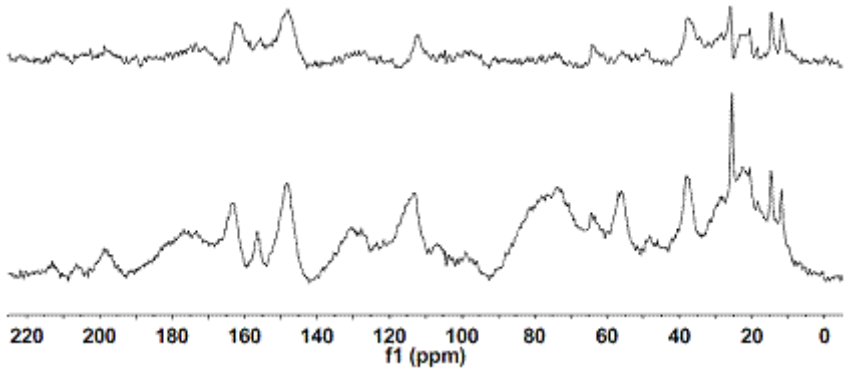

Figure 22. The ^{13}C spectra of *Ferula assafoetida*, with normal decoupling at the bottom and with dipolar dephasing at the top.

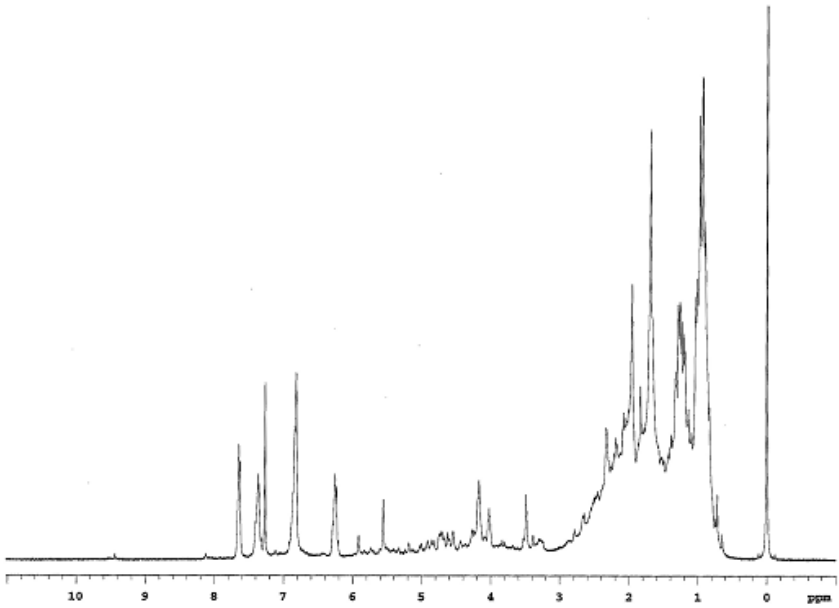

Figure 23. The ^{1}H spectrum of *Ferula gummosa* from the Field Museum.

A single sample of *F. persica* gave the typical gum resin ^{13}C spectrum, with much more resin than gum and small contributions from unsaturated and carbonyl resonances. The four distinctive peaks in the aromatic region of the other *Ferula* samples are completely absent, indicating a different molecular form. The saturated pattern also is somewhat different from those of *F. gummosa*. Moreover, the ^{1}H spectrum contains primarily saturated (resinous)

resonances, in contrast to the other *Ferula* species. The ^{13}C spectra of two samples of *Opopanax chironium* also is of a gum resin. The sample from Harvard University has slightly more gum than resin, whereas that from the National Museum of American History has much more gum than resin. The exudate from this species is known as sweet myrrh, to distinguish it from common myrrh from the rosid genus *Commiphora* (Lambert et al., submitted).

All of the samples from the Apiaceae described so far are from the subfamily Apioideae. They vary from gum resins to exudates containing largely resin but several other, smaller components. We have a single sample from the subfamily Azorelloideae, *Azorella compacta*. This very small plant, called *yareta*, is native to the Andes of South America. It is believed to grow only about 1.5 cm annually and can live for 3000 years. Its ^{13}C spectra are typical for a pure resin.

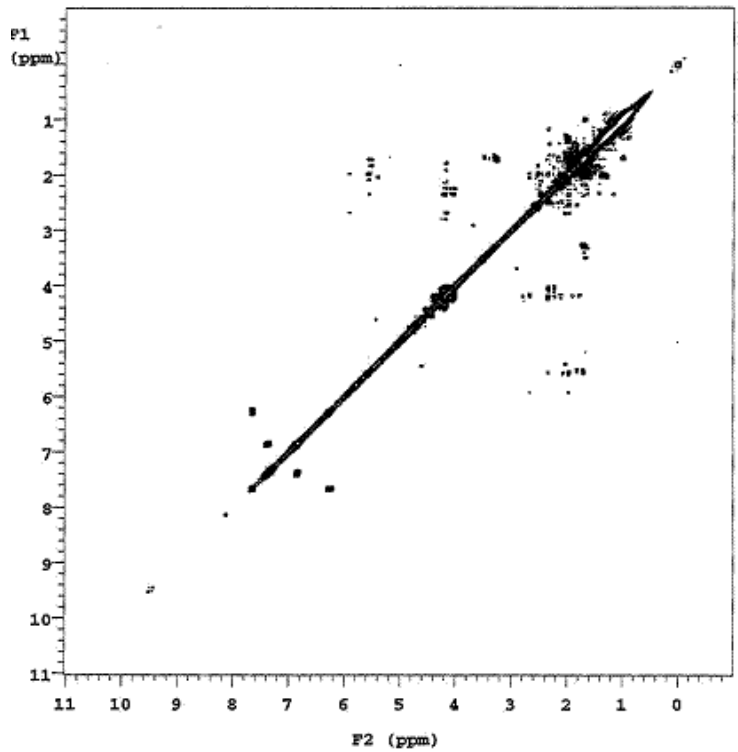

Figure 24. The 2D COSY spectrum of *Ferula gummosa* from the Field Museum.

Araliaceae. The ivy family contains 55 genera and 250 species, including, in addition to vines, a few trees and herbs such as ginseng. We have examined seven samples from seven different genera and species. All proved to be either

gums or gum resins. Whereas *Munroidendron racemosum*, *Pseudopanax crassifolius*, and *Reynoldsia sandwicensis* gave standard gum ^{13}C spectra, *Kalopanax septemlobus*, *Polyscias balfouriana*, *Schefflera actinophylla*, and *Tetraplasandra oahuensis* additionally have small but definite resin components, so that they are gum resins.

Pittosporaceae. This family contains about 10 genera and 200 species. Our three samples came from three different species of its primary genus, *Pittosporum*. The ^{13}C spectra of *P. pentandrum* are typical for a gum. The ^{13}C spectra of *P. tenuifolium* and *P. variegatum* are similar to each other and contain large resonances in the saturated region, indicative of a resinous component. In addition, for both species, there is a strong peak in the EWG region at δ 75, as well as a weaker peak at δ 82. There is no peak in the anomeric region at δ ca. 105, although each spectrum has a small peak at δ ca. 96. This pattern is not typical for a gum, even though all the peaks in the EWG region disappear with dipolar dephasing. Both spectra also have a small, complex set of resonances in the carbonyl region at δ 170-180. In the absence of definitive evidence for a gum, we prefer to render the classification as resin (other).

Conclusions

Although the asterids are not so prolific exudate producers as the rosids, some of the families, such as the Sapotaceae and the Apiaceae, are reasonably productive. We have harvested 78 exudate samples from 15 asterid families and analyzed them by ^{13}C and ^{1}H NMR spectroscopy. The pattern of asterid exudate molecular classes is somewhat different from that of the rosids. The asterid exudates proved to be 59% resins, 13% gums, 17% gum resins, 3% kinos, 7% balsams, and 1% unassigned. The balsams are a previously known but small class not usually listed, containing large proportions of aromatic carboxylic acids such as benzoic and cinnamic acids. In our previous examination of rosid exudates (Lambert et al., submitted), we found 40% resins, 33% gums, 12% gum resins, 8% kinos, no balsams, 3% minor classes (xanthics, guiaiacs), and 4% unassigned. Significantly more gums and kinos are found among the rosids, compensated by somewhat more resins among the asterids. The rosids contain some families that produce exclusively or almost exclusively gums (Rosaceae, Combretaceae, Meliaceae, Rutaceae, and the fabid subfamily Mimosoideae) and other families that produce exclusively kinos (Myrtaceae, including the genus *Eucalyptus*). In contrast, almost all the asterid families with multiple samples produce primarily resins or gum resins, with the exception of the Styracaceae, which produces only balsams.

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Table 1. Asterid Exudates Examined by Nuclear Magnetic Resonance Spectroscopy			
Number	**Family**	**Subfamily or Tribe**	**Genus/Species**
1331	Ebenaceae	Ebenoideae	*Diospyros virginiana*
367	Ebenaceae	Ebenoideae	*Diospyros virginiana*
1045	Fouquieriaceae		*Fouquieria shrevei*
844	Sapotaceae	Chrysophylloideae	*Lucuma* sp.
1373	Sapotaceae	Chrysophylloideae	*Pouteria campechiana*
1073	Sapotaceae	Chrysophylloideae	*Pouteria procera*
1077	Sapotaceae	Sapotoideae	*Isonandra acuminata*
1082	Sapotaceae	Sapotoideae	*Madhuca longifolia* (listed as *Bassia latifolia*)
1078	Sapotaceae	Sapotoideae	*Manilkara bidentata*
1337	Sapotaceae	Sapotoideae	*Manilkara zapota*
1008	Sapotaceae	Sapotoideae	*Manilkara zapota* (listed as *Achras sapota*)
1087	Sapotaceae	Sapotoideae	*Manilkara zapota* (listed as *Achras sapota*)
949	Sapotaceae	Sapotoideae	*Mimusops* sp.
1089	Sapotaceae	Sapotoideae	*Palaquium gutta*
1085	Sapotaceae	Sapotoideae	*Palaquium gutta* (listed as *Isonandra gutta*)
1086	Sapotaceae	Sapotoideae	*Palaquium sumatranum*
666	Styracaceae		*Styrax benzoides*
934	Styracaceae		*Styrax benzoin*
1081	Styracaceae		*Styrax benzoin*
1001	Styracaceae		*Styrax benzoin* (listed as *S. subdenticulara*)
1002	Styracaceae		*Styrax benzoin* (listed as *S. subdenticulara*)
1088	Theaceae	Theeae	*Camellia sinensis*
1358	Apocynaceae	Asclepiadoideae	*Asclepias speciosa*
1074	Apocynaceae	Asclepiadoideae	*Urceola elastica*
932	Apocynaceae	Rauvolfioideae	*Couma utilis*
1005	Apocynaceae	Rauvolfioideae	*Dyera costulata*
1075	Apocynaceae	Rauvolfioideae	*Landolphia gummifera*

Order	**Subclade**	**Exudate**	**Source**
Ericales	basal asterid	gum	Donald E. Davis Arboretum, Auburn AL, JASB
Ericales	basal asterid	gum	Coker Arboretum, Chapel Hill, NC, JASB
Ericales	basal asterid	resin	Desert Botanical Garden, Phoenix, AZ JASB
Ericales	basal asterid	gum	H. H. Rusby Collection, H. H. Rusby
Ericales	basal asterid	resin	Jardines Eneida, PR, D. Lugo, A. Vélez, S. Enriquez, JASB
Ericales	basal asterid	resin	Harvard University Farlow Herbarium, JASB
Ericales	basal asterid	resin	Harvard University Farlow Herbarium, JASB
Ericales	basal asterid	gum	Harvard University Farlow Herbarium, JASB
Ericales	basal asterid	resin (other)	Harvard University Farlow Herbarium, JASB
Ericales	basal asterid	resin	Agricultural Experimental Substation, Juana Díaz, PR, A. Vélez, I. Cabrera, JASB
Ericales	basal asterid	resin	Field Museum, Chicago, IL, JASB
Ericales	basal asterid	resin	Harvard University Farlow Herbarium, JASB
Ericales	basal asterid	resin	Field Museum, Chicago, IL, JASB
Ericales	basal asterid	resin (other)	Harvard University Farlow Herbarium, JASB (sample 5450 00206638)
Ericales	basal asterid	resin (other)	Harvard University Farlow Herbarium, JASB (sample 5229 00206433)
Ericales	basal asterid	resin	Harvard University Farlow Herbarium, JASB
Ericales	basal asterid	balsam	Scents of the Earth, Cape May, NJ
Ericales	basal asterid	balsam	Field Museum, Chicago, IL, JASB (sample 271837)
Ericales	basal asterid	balsam	Harvard University Farlow Herbarium, JASB
Ericales	basal asterid	balsam	Field Museum, Chicago, IL, JASB (sample 271836)
Ericales	basal asterid	balsam	Field Museum, Chicago, IL, JASB (sample 271836)
Ericales	basal asterid	resin	Harvard University Farlow Herbarium, JASB
Gentianales	euasterid I	resin	Chico State Herbarium, Chico, CA, L. Ahart, J. Dittes
Gentianales	euasterid I	resin (other)	Harvard University Farlow Herbarium, JASB
Gentianales	euasterid I	resin	Field Museum, Chicago, IL, JASB
Gentianales	euasterid I	gum resin	Field Museum, Chicago, IL, JASB
Gentianales	euasterid I	resin (other)	Harvard University Farlow Herbarium, JASB

Table 1. Asterid Exudates Examined by Nuclear Magnetic Resonance Spectroscopy (cont.)

Number	**Family**	**Subfamily or Tribe**	**Genus/Species**
1010	Apocynaceae	Rauvolfioideae	*Landolphia kirkii*
1006	Apocynaceae	Rauvolfioideae	*Parahancornia amapa*
1084	Apocynaceae	Rauvolfioideae	*Willughbeia* sp.
667	Rubiaceae	Cinchonoideae	*Exostema caribaeum*
1117	Rubiaceae	Cinchonoideae	*Neolaugeria densiflora*
933	Rubiaceae	Cinchonoideae	*Uncaria gambir*
1079	Rubiaceae	Cinchonoideae	*Uncaria gambir*
1076	Rubiaceae	Ixoroideae	*Elaeagia utilis*
604	Rubiaceae	Ixoroideae	*Gardenia brighamii*
1161	Rubiaceae	Ixoroideae	*Gardenia gummifera*
935	Bignoniaceae	Crescentieae	*Crescentia cujete*
1274	Oleaceae	Oleeae	*Fraxinus* sp. (*americana* ?)
1055	Oleaceae	Oleeae	*Fraxinus angustifolia*
1316	Oleaceae	Oleeae	*Olea europaea*
1317	Oleaceae	Oleeae	*Olea europaea*
516	Verbenaceae	Caryopterideae	*Clerodendrum splendens*
930	Convolvulaceae	Convolvuleae	*Convolvulus scammonia*
1152	Convolvulaceae	Convolvuleae	*Convolvulus scammonia*
1197	Convolvulaceae	Convolvuleae	*Convolvulus scammonia*
1200	Convolvulaceae	Ipomoeeae	*Ipomoea purga*
1194	Convolvulaceae	Merremieae	*Operculina turbethum*
937	Boraginaceae	Cordioideae	*Cordia sinensis* (listed as *C. rothii*)
1003	Apiaceae	Apioideae	*Dorema ammoniacum*
1083	Apiaceae	Apioideae	*Dorema ammoniacum*
1412	Apiaceae	Apioideae	*Dorema ammoniacum*
936	Apiaceae	Apioideae	*Ferula assafoetida*
1072	Apiaceae	Apioideae	*Ferula foetida*
928	Apiaceae	Apioideae	*Ferula gummosa* (synonym *F. galbaniflua)*

Order	**Subclade**	**Exudate**	**Source**
Gentianales	euasterid I	resin (other)	Field Museum, Chicago, IL, JASB
Gentianales	euasterid I	resin	Field Museum, Chicago, IL, JASB
Gentianales	euasterid I	resin (other)	Harvard University Farlow Herbarium, JASB
Gentianales	euasterid I	resin	Bosque Estatal de Guánica Guánica, PR, M. Canals
Gentianales	euasterid I	resin	Willard Sherman Turrell Herbarium, Oxford, OH, M. A. Vincent
Gentianales	euasterid I	kino	Field Museum, Chicago, IL, JASB
Gentianales	euasterid I	kino	Harvard University Farlow Herbarium, JASB
Gentianales	euasterid I	resin	Harvard University Farlow Herbarium, JASB
Gentianales	euasterid I	resin	Amy Greenwell Botanical Gardens, Captain Cook, Hawaii, HI, JASB
Gentianales	euasterid I	gum resin	National Museum of American History, JASB
Lamiales	euasterid I	resin	Field Museum, Chicago, IL, JASB
Lamiales	euasterid I	resin (other)	Salem, VA, JASB
Lamiales	euasterid I	other	Herbarium Mediterraneum Panormitanum. Palermo, Italy, G. Domina
Lamiales	euasterid I	resin (other)	Boyce Thompson Arboretum, Superior, AZ, JASB
Lamiales	euasterid I	resin (other)	Boyce Thompson Arboretum, Superior, AZ, JASB
Lamiales	euasterid I	gum	Smithsonian Greenhouses, Washington, DC, T. Mirenda, JASB
Solanales	euasterid I	gum resin	Field Museum, Chicago, IL, JASB
Solanales	euasterid I	gum resin	National Museum of American History, JASB
Solanales	euasterid I	gum resin	National Herbarium Nederland, Leiden, Netherlands
Solanales	euasterid I	gum resin	National Herbarium Nederland, Leiden, Netherlands
Solanales	euasterid I	gum resin	National Herbarium Nederland, Leiden, Netherlands
(none)	euasterid I	gum	Field Museum, Chicago, IL, JASB
Apiales	euasterid II	resin (other)	Field Museum, Chicago, IL, JASB
Apiales	euasterid II	resin (other)	Harvard University Farlow Herbarium, JASB
Apiales	euasterid II	resin (other)	National Museum of American History, JASB
Apiales	euasterid II	resin (other)	Field Museum, Chicago, IL, JASB
Apiales	euasterid II	resin (other)	Harvard University Farlow Herbarium, JASB
Apiales	euasterid II	resin (otjher)	Field Museum, Chicago, IL, JASB

Table 1. Asterid Exudates Examined by Nuclear Magnetic Resonance Spectroscopy (cont.)

Number	**Family**	**Subfamily or Tribe**	**Genus/Species**
1029	Apiaceae	Apioideae	*Ferula gummosa* (synonym *F. galbaniflua*)
1202	Apiaceae	Apioideae	*Ferula gummosa* (synonym *F. galbaniflua)*
927	Apiaceae	Apioideae	*Ferula persica*
1080	Apiaceae	Apioideae	*Opopanax chironium*
1410*	Apiaceae	Apioideae	*Opopanax chironium*
632	Apiaceae	Apioideae	*Peucedanum galbaniflorum*
484	Apiaceae	Azorelloideae	*Azorella compacta*
1269	Araliaceae	Aralioideae	*Kalopanax septemlobus* (listed as *K. pictus*)
277	Araliaceae	Aralioideae	*Munroidendron racemosum*
428	Araliaceae	Aralioideae	*Polyscias balfouriana*
960	Araliaceae	Aralioideae	*Pseudopanax crassifolius*
963	Araliaceae	Aralioideae	*Reynoldsia sandwicensis*
969	Araliaceae	Aralioideae	*Schefflera actinophylla*
967	Araliaceae	Aralioideae	*Tetraplasandra oahuensis*
1268	Pittosporaceae	Pittosporeae	*Pittosporum pentandrum*
854	Pittosporaceae	Pittosporeae	*Pittosporum tenuifolium*
859	Pittosporaceae	Pittosporeae	*Pittosporum variegatum*
600	Asteraceae	Asteroideae	*Artemisia spinescens*
1044	Asteraceae	Asteroideae	*Encelia farinosa*
1305	Asteraceae	Asteroideae	*Encelia farinosa*
673	Asteraceae	Asteroideae	*Helianthus annuus*
1110	Asteraceae	Asteroideae	*Parthenium argentatum*
1292	Asteraceae	Asteroideae	*Parthenium tomentosum*

Order	**Subclade**	**Exudate**	**Source**
Apiales	euasterid II	resin (other)	Harvard University Farlow Herbarium, JASB
Apiales	euasterid II	resin (other)	National Herbarium Nederland, Leiden, Netherlands
Apiales	euasterid II	gum resin	Field Museum, Chicago, IL, JASB
Apiales	euasterid II	gum resin	Harvard University Farlow Herbarium, JASB
Apiales	euasterid II		National Museum of American History, JASB
Apiales	euasterid II	resin (other)	Field Museum, Chicago, IL, JASB
Apiales	euasterid II	resin	San Pedro de Atacama, Chile, R. Farrar
Apiales	euasterid II	gum resin	Morris Arboretum, Philadelphia, PA, JASB
Apiales	euasterid II	gum	National Tropical Botanical Garden, Kauai, HI, JASB
Apiales	euasterid II	gum resin	Waimea, Oahu, HI, JASB
Apiales	euasterid II	gum	Strybing Arboretum, San Francisco, CA, P. R. Craig, JASB
Apiales	euasterid II	gum	Amy Greenwell Botanical Gardens, Captain Cook, Hawaii, HI, JASB
Apiales	euasterid II	gum resin	Limahuli Garden and Preserve, Haena, Kauai, HI, K. Winter. JASB
Apiales	euasterid II	gum resin	Amy Greenwell Botanical Gardens, Captain Cook, Hawaii, HI, JASB
Apiales	euasterid II	gum	Limahuli Botanical Garden, Kauai, HI, K. Winter, JASB
Apiales	euasterid II	resin (other)	Strybing Arboretum, San Francisco, CA, P. R. Craig, JASB
Apiales	euasterid II	resin (other)	UCSC Arboretum, Santa Cruz, CA, P. R. Craig, JASB
Asterales	euasterid II	resin (other)	Mojave Desert, CA, S. Ubick
Asterales	euasterid II	resin (other)	Desert Botanical Garden, Phoenix, AZ JASB
Asterales	euasterid II	resin (other)	Boyce Thompson Arboretum, Superior, AZ, JASB
Asterales	euasterid II	resin	New York Botanical Garden, Bronx, NY, C. D. Michener, JASB
Asterales	euasterid II	resin (other)	Harvard University Farlow Herbarium, JASB
Asterales	euasterid II	resin	Boyce Thompson Arboretum, Superior, AZ, JASB