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## Occurrence, Chemical Characteristics, and Paleontology of the Fossil Resins from New Jersey

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### ABSTRACT

The chemical characteristics, geographic and stratigraphic occurrence, and insect inclusions of various fossil resins from New Jersey are presented. Distinctions are made between amber and fossil resin, the latter being the more general term, and each is defined. Most of the fossil resins lie within the Cretaceous band in the Atlantic Coastal Plain, but a unique Tertiary form is probably of *Liquidambar* or other hamamelidaceous origin, as based on Fourier transform infrared diffraction and pyrolysis gas chromatography, which have revealed that the material is composed mostly of polystyrene. The Cretaceous resins (true terpenoid

amber) are araucariaceous in origin, as based on chemistry. It has been determined by scanning electron microscope that the carbonized fossil wood found with the amber is coniferous, shows very fine detail, but does not have features diagnostic for the Araucariaceae. Dark red and clear yellow forms of the Cretaceous amber exist, the former of which appears to be an oxidized state of the latter. Despite the rarity of the amber, several interesting new insect inclusions have been found, which have affinities with various living and amber faunas.

### INTRODUCTION

Fossil resins from the Atlantic Coastal Plain of the United States have been reported in the literature for more than 150 years, the

first account being given by Troost (1821). Since then only three old anecdotal reports have dealt exclusively with the material, and

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several other, but much more recent, reports have dealt in part with chemistry of or inclusions in fossil resins from this region. This report is an attempt to synthesize all that is known on the fossil resins with a great deal of new data. It is the insect inclusions that initially stimulated Grimaldi to collect and study the material, particularly since all the published reports indicated that fossil resins from this region were Cretaceous. This period apparently was a time when many modern insect taxa made their debut. The present analysis seemed pressing as well due to the varied nature of the insect inclusions: compared to modern families, some are undoubtedly plesiomorphic, such as *Sphecomyrma* (Formicidae), others are modern (such as *Trigona prisca* [Apidae: Meliponinae]), and others have Baltic amber and/or Gondwanan affinities. A comprehensive study on the resins is needed to put such fossils into a meaningful paleontological context. Throughout the text we refer to both amber resins and fossil resins, the latter of which is a more general term. In the broadest sense, a fossil resin is any plant exudate of a respectable age, say one million years old or more. Specifically, amber is a polymeric, terpenoid fossil resin, which thus excludes some materials such as the polystyrene type of fossil resin from New Jersey that is treated later in this paper. Most fossil resins are amber; this is because terpenoids are rather resistant to natural decay and readily form extensive polymers that render them virtually chemically inert. Thus, terpenoid resin fossilizes readily.

Troost's (1821) report was stimulated by the finding of what presumably was a large piece of fossil resin found with lignite and pyrite in clay from Cape Sable near the Magothy River, Maryland. This resin contained what he described as perhaps a gall made by "lac coccids." The location of the specimen has not been traced, which apparently would have been in his large, private, mineral collection, now at the Louisville Museum of History and Science, but which is not there. Kunz (1883) likewise was intrigued by a large ( $20 \times 6 \times 1$  in.) piece of fossil resin, found at "Kirby's Marl Pit" in glauconitic sand at Harrisonville, New Jersey. But this apparently may not have been the largest piece ever found, for there is reference in that report to

"the largest specimen of amber . . . ever seen, found on the shore of Raritan Bay [New Jersey], deposited in the museum at Berlin, Germany." This was probably the Humboldt Museum, but no such specimen now resides there. Kunz's specimen was unusual in that it was opaque, cut "like horn," and upon polishing gave "a pearly lustre." Knowlton (1896) also found the fossil resin from Cape Sable to lie among lignite in clay. His observations on the lignite led to the conclusion that, because of a lack of compound medullary rays and large resin tubes, the lignite, and thus the source of the fossil resin, was not from a pine (*Pinus*), but most likely *Sequoia* or *Cupressinoxylon*. An origin of the material at Charleston (formerly Kreischerville), Staten Island, New York, from a species of *Pinus* was the hypothesis proposed by Hollick (1905), even though purported fossils of *Sequoia*, *Juniperus*, and *Dammara* were also found there. Later, Hollick and Jeffrey (1909) reported that "in all such cases [of finding amber in situ in lignite] . . . the correlated wood was . . . *Pityoxylon statenense*." Cross sections of the lignite revealed large resin canals. These authors placed *Pityoxylon* in the Abietinae, or the pines. Hollick found the resin among lignitic clays, and was the first to report on several forms of the material from this one locality in Staten Island. These forms were mostly drop-shaped, transparent yellow or red, some being opaque or grayish white. Large amounts of the fossil resin were reported as having been found by workers mining clay in the clay brick pits on Staten Island around the turn of the century.

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the AMNH. Edward Johnson, Curator of Science at the Staten Island Institute of Arts and Sciences, loaned the amber specimens deposited in that collection by Arthur Hollick. Alan Goldstein, Curator of Science at the Louisville Museum of History and Science, checked through Troost's collection (which is deposited there) for the large piece of amber reported from Ann Arundel County, Maryland. Paul Whalley, British Museum (Natural History), made available his unpublished notes on the Lebanese amber. Penny Dillon and Ralph Johnson were instrumental in showing one source of the amber, and Jim Brown very kindly provided the amber specimens from Marlboro, New Jersey. Frank Carpenter, MCZ, Harvard, loaned specimens of Canadian amber for study. Darlene Judd provided assistance with regard to *Tvetenia*. Jean Langenheim, George Poinar, and Alexander Shedrinsky also provided valuable critiques of the manuscript.

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#### GENERAL CHARACTERISTICS OF THE FOSSIL RESINS

Based on color, hardness, fractal features, and shapes there are basically three types of fossil resins from New Jersey and surrounding areas in the Atlantic Coastal Plain. One is deep red (fig. 1), permeated with needlelike fractures (much like ice). It fractures very easily and conchoidally, and the resultant broken form often produces a rounded and polished surface. Some pieces of this type are cylindrical, others are drop-shaped, most are round or amorphous. The other type is a very clear yellow, possessing fewer internal fractures, and it is commonly cylindrical and drop-shaped, occasionally amorphous. The yellow form has few conchoidal fractures. The drop shapes are similar to those seen on exuded

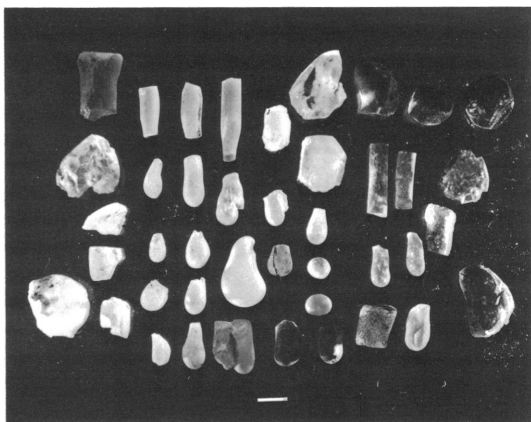


Fig. 1. Examples of the yellow (left half) and red (right half) forms of the amber from New Jersey, with representative shapes. Note the drop-and-stream shapes of some pieces. Taken from the Sayre-Fisher Pits, Sayreville, Middlesex Co. (map site 5, fig. 4). Scale is 1 cm.

streams of resin running down the bark of pines and other conifers. When found on an exposed, washed surface of lignitic clay, both color forms occur in about equal proportions in sizes between 1 mm and about 2 cm in diameter, but they may be larger within the clay matrix where weathering would not fragment the pieces. Because the clay is so fine and dense it was virtually impossible to screen for the amber by washing. The third type of fossil resin (fig. 2) can occur in rather large slabs; it is an opaque yellowish-white and has a composition like soft plastic (fig. 2). This no doubt is the type to which Kunz (1883) referred.

One of us (D.G.) has collected fossil resin at the Sayre-Fisher Pits in Sayreville, and at Oschwald's Pits, near Cheesequake State Park, where at least the red and yellow forms of the material were found together in clay permeated with a lignite resembling charcoal, except that it was highly compressed. The material was never found in situ embedded in the lignite. The fossil resin is found sporadically at certain sites in this clay layer, and even then is not abundant.

Samples of the carbonized wood collected with resin at three sites were dried and split either in cross section or longitudinally, mounted on SEM stubs, sputter coated with gold, and the fine structure of the vessels ex-

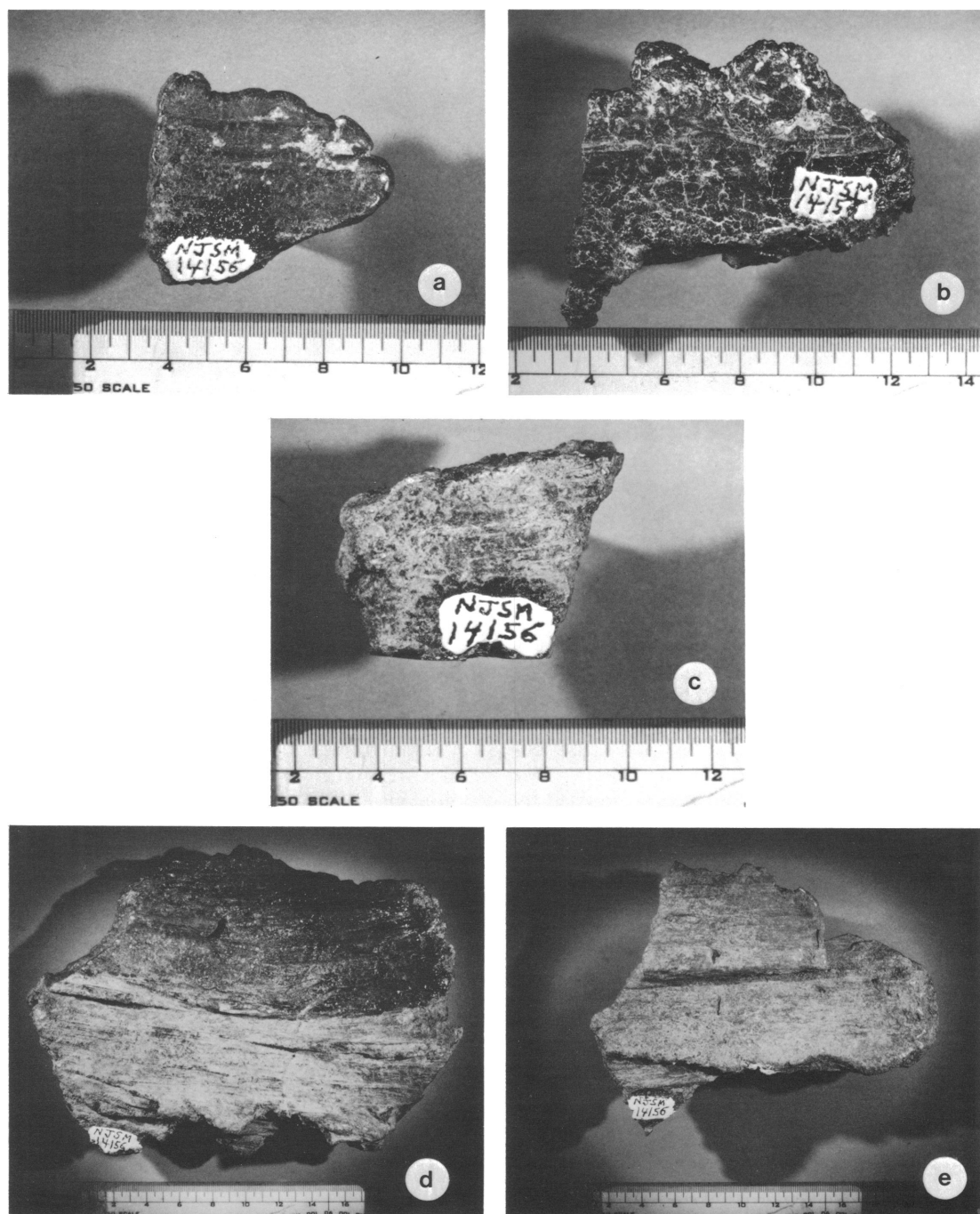
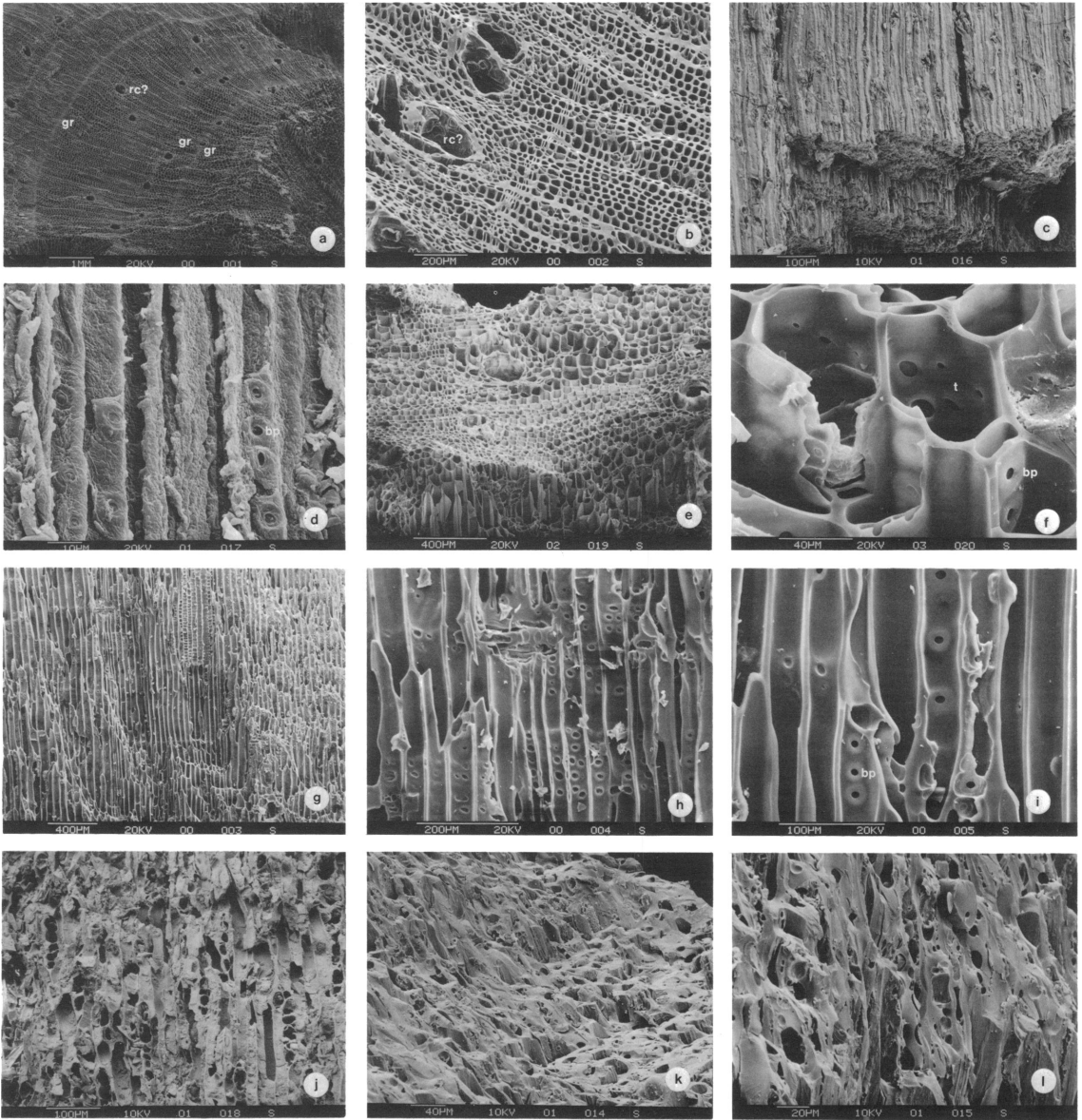


Fig. 2. Specimens of the polystyrene (*Liquidambar*) fossil resin type, from Inversand Marl Pit, Sewell, Gloucester Co., N.J. (D. Parris, coll.) (map site 16, fig. 4).

aminated at 10 kV beam current (fig. 3a-l). Preservation of fine structure in the carbonized wood varied from excellent (resembling

fresh, living wood) to much less so. The presence of bordered pits on the radial walls of the tracheids, and the homogeneously small-



**Fig. 3.** Scanning electron micrographs of fossil woods collected with Cretaceous ambers. a–j. Carbonized wood from the Atlantic Coastal Plain, U.S.A.: a–d. Oswald's Pits (map site 6, fig. 4). a. transverse section. b. detail of section in a. c. tangential longitudinal section of different piece than in a, b. d. detail of section in c. e–i. specimens from Sayre Fisher Pits (map site 5, fig. 4). e. transverse-longitudinal section, oblique view. f. oblique view of transverse section in detail. g. tangential longitudinal section. h, i. detail of section in g. j. tangential longitudinal section of specimen from Outerbridge Crossing (map site 2, fig. 4). k, l. lignite from the Aptian, lower Cretaceous, of Lebanon (specimen courtesy of Mr. Fadi Acra), oblique tranverse (k) and longitudinal sections. Abbreviations: bp, bordered pit; gr, growth ring; rc?, resin canal?; t, tracheid.

diameter, linearly arranged longitudinal tracheids, indicate that the fossil wood is coniferous (fig. 3a–j, especially d, h, i), which

corroborates Knowlton's (1896) early observations. The better preserved samples showed some growth rings (fig. 3a, b). Bordered pits

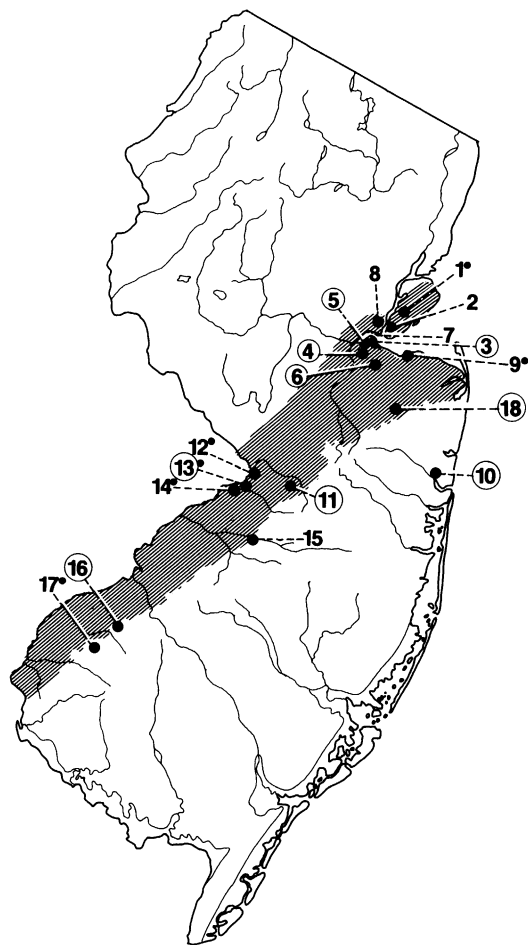


Fig. 4. Distribution of fossil resins in the Atlantic Coastal Plain of New Jersey and Staten Island. Hatched area is Cretaceous, taken from maps by the New Jersey State Geological Survey (1984). Numbers refer to the localities given in text: those that are circled are sites for which samples were analyzed using ir spectroscopy in this study; site numbers followed by a dot were samples analyzed by ir spectroscopy in Langenheim and Beck (1968).

were uniseriate and rarely oppositely paired, which contrasts with the characteristic alternate tracheid pitting (in usually two to four rows) seen in the Araucariaceae (e.g., Pool, 1929). Moreover, resin canals were present, which rules out the Araucariaceae, but which corroborates the findings of Hollick and Jeffrey (1909). Penny (1947) described the stem wood of *Araucarioxylon* as having a tracheal

pitting "identical with that seen in modern species of *Agathis* and *Araucaria*." Taxodiacean fossils from the Cretaceous of New Jersey are *Geinitzia* and *Sequoia* (Penny, 1947).

Although exact identity of the lignite must await detailed botanical study, the SEM has revealed several things. First, there may have been mixing of amber and lignite of two or more botanical sources in the original deposits, since the spectroscopy indicates an araucariaceous origin. Alternatively, perhaps a primitive conifer produced a resin similar to *Agathis*; in which case, the chemistry described below and the original hypotheses of Hollick and Jeffrey would correspond. These samples were compared to true lignite collected with amber from the Aptian, lower Cretaceous, of Lebanon (courtesy of Mr. Fadi Acra), which is much more mineralized and with substantially less preserved detail than the New Jersey material. Gross structure of the Lebanese amber resembles very closely the transparent yellow form of the amber from the Atlantic Coastal Plain.

#### OCCURRENCE AND STRATIGRAPHY

Fossil resin specimens for comparison were acquired by collecting at exposed sections in Staten Island and New Jersey, and by borrowing specimens from the New Jersey State Museum, Trenton, the Mineralogy Department at the AMNH, the Staten Island Institute of Arts and Sciences, and from the Mineralogy Collection of Columbia University (now owned by the AMNH). Based on actual museum specimens and on reports in the literature, a total of 18 sites in New Jersey and Staten Island were found to have yielded fossil resins (six additional sites, from Cape Cod to North Carolina were reported, but these were not confirmed in this study with museum specimens).

The following are the fossil resin localities (New Jersey and Staten Island localities are numbered: see map, fig. 4; AMNH = American Museum of Natural History; NJSM = New Jersey State Museum; HBM = Harvard Botanical Museum; USNM = United States National Museum, Smithsonian Institution; USGS = U.S. Geological Survey [the last three depositories as cited by Langenheim and

Beck, 1968]). **New York:** STATEN ISLAND: 1. Charleston (formerly Kreischerville) (Hollick, 1905; Jeffrey and Chrysler, 1906; Hollick and Jeffrey, 1909); 2. Outerbridge Crossing (AMNH, no numbers). **New Jersey:** MIDDLESEX CO.: 3. South Amboy, Isaac Inslee's Pit (NJSM 4641); 4. Parlin, Crossman's Clay Pits (AMNH 39411); 5. Sayreville, Sayre-Fisher Pits (AMNH, various pieces); 6. Cheesequake, Oswald's Pits (AMNH, various pieces); 7. "on shore, Raritan Bay" (Kunz, 1883); 8. Woodbridge, Valentine's Clay Pit (Hollick, 1905). **MONMOUTH CO.:** 9. Cliffwood Beach Bluffs (Berry, 1906; Wilson et al., 1967); 10. Squankum, Marl Pits (AMNH C89828). 11. Ellisdale (NJSM 14154, 14155). **BURLINGTON CO.:** 12. Bordentown (USGS 95367); 13. Kinkora (AMNH C88712-88720; USNM 5610); 14. Roebling (USNM R7289); 15. Pemberton (Langenheim and Beck, 1968, no number). **GLOUCESTER CO.:** 16. Sewell, Inversand Marl Pit (NJSM 14156, 14157); 17. Harrisonville, Kirby's Marl Pit (AMNH, no number; Kunz, 1883; Hollick, 1905; USNM C163); Gloucester Co. (no other locality) (AMNH 39412). Recently added is the following locality: **MONMOUTH CO.:** 18. Marlboro, Big Brook (AMNH, no numbers). Other localities in the Atlantic Coastal Plain (but which are not placed on the map in fig. 4) are the following: **Delaware:** St. Georges (USNM 82552). **Maryland:** Cape Sable, Magothy River (Troost, 1821; Berry, 1906; Knowlton, 1896; USNM 72871). **Massachusetts:** Martha's Vineyard, Gay Head (Finch, 1824). **North Carolina:** Charleston (USNM R7317); "Marl beds" (no other locality) (Kunz, 1883). **Washington, D.C.:** (Langenheim and Beck, 1968; no number).

For all except one locality (at Squankum, Monmouth Co., New Jersey), the deposits occurred within the Cretaceous band in New Jersey or on its southern edge. South of the Cretaceous strata are Tertiary and north of it are Jurassic and older exposed strata. Thus, the fossil resins from Staten Island and New Jersey are mostly Cretaceous, and the sources of the unusual plasticlike, polystyrene fossil resin are no older than Tertiary or at the Cretaceous-Tertiary boundary.

Berry (1906: 137) mentioned that "a secondary feature of the Magothy Formation is

the occurrence of amber . . ." which suggests the amber from the Atlantic Coastal Plain to be entirely from this geological formation. As discussed below, this is an unreliable assumption. Some of the fossil resin samples in figure 4 have been associated with stratigraphic units based on lithology. Eventually there must be a palynological or foraminiferal study of the lignitic matrices in which the material occurs. The following papers were consulted in assigning stratigraphic positions to the seven fossil resin deposits discussed below that have some sort of vertical sampling data: Christopher, 1977, 1982; Dorf, 1952; Perry et al., 1975; Petters, 1976; Sirkin, 1986; Wolfe, 1976. Work on the Raritan Formation is mostly palynological, as foraminiferans are rare. Richards (1958) provides a history of early studies on the New Jersey Cretaceous.

The geologically oldest known fossil resin deposits in New Jersey are at Woodbridge (site 8) and Sayreville (site 5). These belong to the Woodbridge Clay Member in the lower Raritan Formation (or palynological zone IV of Christopher [1982] and Sirkin [1986]), which is considered by these and other authors as being middle Cenomanian, an age of about 95 m.y.b.p. Perry et al. (1975) assigned this clay member to the upper Cenomanian. The amber-bearing lignitic clay at the Sayre-Fisher Pit lies just below the South Amboy Fire Clay and Old Bridge Sand Members of the Magothy Formation (Metz, 1978, 1985; sensu Wolfe and Pakiser, 1971). The next oldest sites appear to be the sites at Cliffwood (site 9) (Cliffwood beds of the upper Magothy Formation) and at Oswald's Pits (site 6) (Merchantville Formation—see fig. 5), both generally considered to be Santonian, but the latter considered to be late Campanian by Wolfe (1976) and Perry et al. (1975). According to the late Cretaceous dates provided by Wolfe (1976), which are based on radiometric and stratigraphic methods and cited hereafter, these sites would be about 80 m.y. old. As discussed by Michener and Grimaldi (1988a), the site from Kinkora (no. 13) is possibly from the upper Magothy, and thus may be of a similar age.

The youngest known fossil resin deposits in the New Jersey Cretaceous are at Ellisdale (site 11), Marlboro (site 18), and Sewell (site



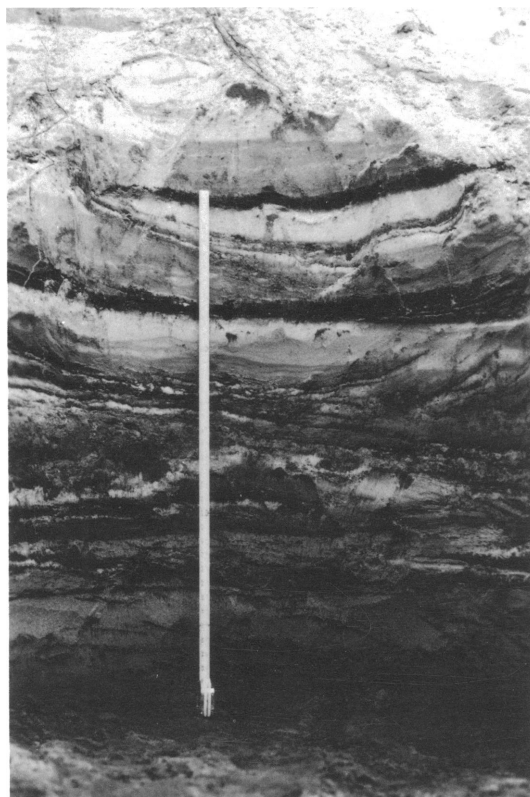


Fig. 5. Section through alternating layers of carbonized fossil wood (black) and fine sand, lying just above one of the clay layers (on floor of section) of the Merchantville Formation, taken at Oschwald's Pits, near Cheesequake State Park, Middlesex Co. (map site 6, fig. 4). Ruler is extended to 3 ft.

16). The Ellisdale fossil resin is in the Marshalltown Formation (late Campanian), and the Marlboro fossil resin is in the Wenonah-Mt. Laurel Sands Formation (late Maestrichtian [Koch and Olson, 1977; Petters, 1976] or late Campanian [Perry et al., 1975; Wolfe, 1976]), both being about 70 m.y. old. The Sewell specimens come from the "Main Fossiliferous Layer" of the Hornerstown Formation, which is the latest Maestrichtian and possibly extending into the Paleocene (Koch and Olson, 1977; Olson and Parris, 1987; Parris, 1986), about 65 m.y. old.

#### CHEMICAL FEATURES AND RESIN ORIGINS

Gies' (1907) study on the elemental composition of fossil resin from Charleston, Stat-

en Island, New York, yielded results that fall within the range of that published for the Baltic amber, and as such it is uninformative in describing characteristics of the New Jersey amber. He did, however, report on the possible presence of succinic acid, which was formed after distillation (see also a copy of the letter sent to Hollick by Gies, pp. 11–12 in Hollick and Jeffrey [1909]). Distillation of amber yields several crystalline products, one of which can be succinic acid derivatives, so it is possible that Gies had always identified such solids as "succinic acid." In fact, as described below, there is no indication at all that succinic acid occurs in the fossil resins from New Jersey. Clearly, the methods of choice in chemically analyzing fossil resins are now x-ray diffraction (Fron del, 1967), nuclear magnetic resonance spectroscopy (Lambert and Frye, 1982; Lambert et al., 1985), pyrolysis mass spectrometry (Poinar and Haverkamp, 1985), pyrolysis gas chromatography (e.g., Stout et al., 1988), and infrared (ir) spectroscopy (summary in Beck, 1986).

The most comprehensive prior treatment of the New Jersey and other Coastal Plain fossil resins was in the large study by Langenheim and Beck (1968). Specimens analyzed in that study with ir spectroscopy were from one locality in State Island and six in New Jersey (Kreischerville, now named Charleston, erroneously placed in that study on Long Island) (see map, fig. 4). Infrared spectroscopy allows the classification of fossil and recent resins by the measurement of differential absorption of ir spectra by various functional radicals. Langenheim and Beck made two major conclusions on the New Jersey fossil resins. One, most, but not all, New Jersey amber was similar to that from other areas of the Atlantic Coastal Plain (e.g., Maryland and Delaware) and to the Cretaceous amber from Manitoba, Canada (the Kreischerville fossil resin was most similar to the Cretaceous amber from the Arctic Coastal Plain of northern Alaska). Second, a distinctive "amber" from Harrisonville and Pemberton, New Jersey had a "composition similar to that of the European fossil resin siegburgite which has been related to *Liquidambar* by chemical studies in which cinnamic acid and styrene were isolated . . ." (p. 86). The similarity was due specifically to the presence of monosubstituted benzenoid hy-



drocarbons. According to Langenheim (1969), the significance of this finding was that this was only one of two localities for which an angiosperm fossil resin was known from the Cretaceous. However, it is indeed interesting to note that the four sites in our study for which the *Liquidambar* fossil resin was found or reported are actually either Tertiary (site 10, at Squankum), or at the Cretaceous–Tertiary boundary (sites 15, 16, 17).

Broughton (1974) analyzed fossil resins from four localities in the Atlantic Coastal Plain, among other North American deposits. His ir spectra showed there to be a distinctive shoulder at  $5.8\ \mu\text{m}$  for resins from the following localities: Black Creek Formation (upper Cretaceous) of North Carolina, Yorktown Formation (Miocene) of North Carolina, and the Raritan Formation (upper Cretaceous) of Sayreville, New Jersey (site number 5 of this study). The Atlantic Coastal Plain fossil resins were found to be distinct (by lacking the  $5.8\ \mu\text{m}$  peak) from the material from the Eocene of Arkansas and the upper Cretaceous of Manitoba, Canada (however, differential thermal analyses showed the New Jersey material to be more similar to that from Arkansas than to other Atlantic Coastal Plain ambers). Based on ir spectra, Broughton put the Arkansas material closest to the amber from the Simojoval Formation (upper Oligocene to lower Miocene of Chiapas, Mexico). The latter, no doubt, has originated from the Neotropical tree *Hymenaea* (Leguminosae) (Langenheim, 1969). Saunders et al. (1974), however, also used ir spectra in their analyses of the Arkansas fossil resin (with very similar results), but stated that the botanical source of it was possibly *Shorea* (Dipterocarpaceae).

It is quite apparent that acid fossil resins from the Atlantic Coastal Plain and from the Gulf Coastal Plain have different botanical origins. Yet, physically, the fossil resins from Arkansas occur in the three types that are similar to that in New Jersey: a clear yellow form (type 1 of Saunders et al. [1974]; the type described above); a deep red, highly fractured form (type 2 of Saunders et al. [1974]); and a form described as having a “brittle rubber consistency” (Saunders et al., 1974) and being an “unidentified related natural wax” (Broughton [1974] type B). This last type is chemically not the same as the *Liquidambar*

fossil polystyrene described below. The dark red, fractured form is probably a highly oxidized state of the clear yellow material, as we have found for the New Jersey amber. The results of Langenheim and Beck (1968) and Broughton (1974) are tested here using a more refined, Fourier transform infrared (FTIR) diffractometer (by C. W. Beck), and pyrolysis gas chromatography (PYGC) and PYGC-mass spectroscopy (by J. Boon), using various samples from additional sites (map, fig. 4; also see Appendix for description of the individual samples tested using FTIR).

### THE INFRARED SPECTRA

**HYDROCARBON RESINS.** The FTIR spectra in the present study confirm the earlier assignments and allow a more definite and specific identification of seven specimens from five localities as essentially pure polystyrene. They include two samples from Harrisonville (AMNH [no number] and USNM C163), one from Pemberton (USNM 81704), two from “Poke Hill” (specific locality unknown) (AMNH 17350 and 17350A), and one each from Sewell (NJSM 14157), and one each from Sewell (NJSM 14157) and Squankum (AMNH C89828). The infrared spectrum of the Sewell sample (fig. 6a) shows its identity with a film of modern, synthetic, atactic polystyrene (fig. 6b). All 20 major absorptions agree in wavelength and relative intensity, including five aromatic carbon-hydrogen stretching modes between  $3103$  and  $3001\ \text{cm}^{-1}$ , four summation bands of the carbon-hydrogen out-of-plane deformation modes between  $1943$  and  $1746\ \text{cm}^{-1}$ , four ring-breathing modes between  $1601$  and  $1453\ \text{cm}^{-1}$ , and seven aromatic carbon-hydrogen deformation modes between  $1070$  and  $540\ \text{cm}^{-1}$ . The wavelengths of the 16 fundamental modes of synthetic polystyrene and the New Jersey hydrocarbon resins are listed in table 1. One specimen from Poke Hill (AMNH 17350) shows the same perfect agreement with the polystyrene bands. The other hydrocarbon resins listed in table 1 lack some of the weaker absorptions of the polystyrene reference spectrum, notably the lower and higher carbon-hydrogen stretching bands, the weakest ring-breathing band at  $1584\ \text{cm}^{-1}$ , and the weakest in-plane deformation band at  $1070\ \text{cm}^{-1}$ . They are visually disappointing, as seen in a representative example of the raw spec-

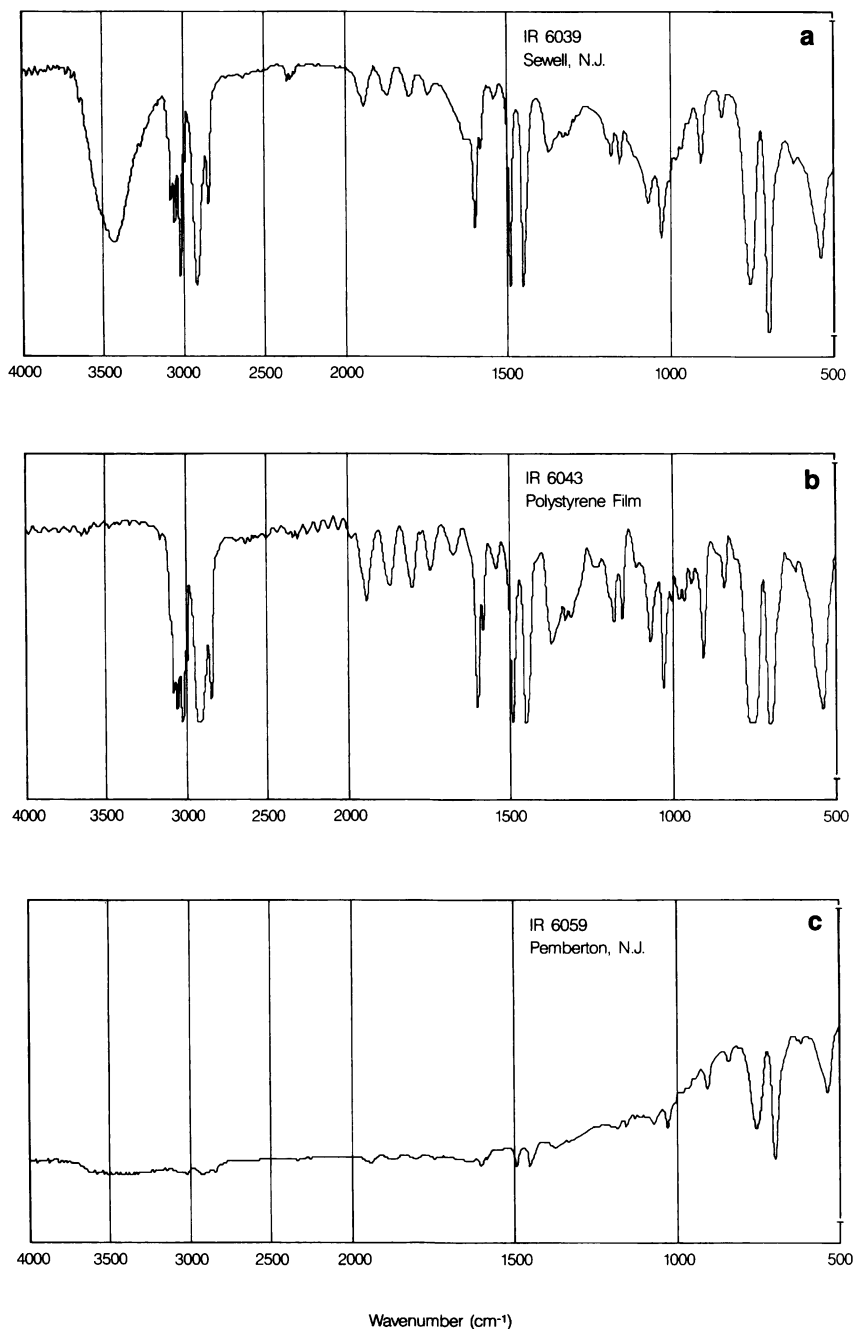


Fig. 6. Fourier transform infrared spectra of two fossil (a,c) and one synthetic (b) hydrocarbon resins. See text for description.

trum of USNM 81704 from Pemberton, shown in figure 6c, but computer enhancement and the computer-produced peak list leave no doubt that all of them consist of

polystyrene with only one extraneous band, i.e., the broad hydroxyl absorption just below 3500  $\text{cm}^{-1}$ , which is due to free water not present in the synthetic polystyrene film.

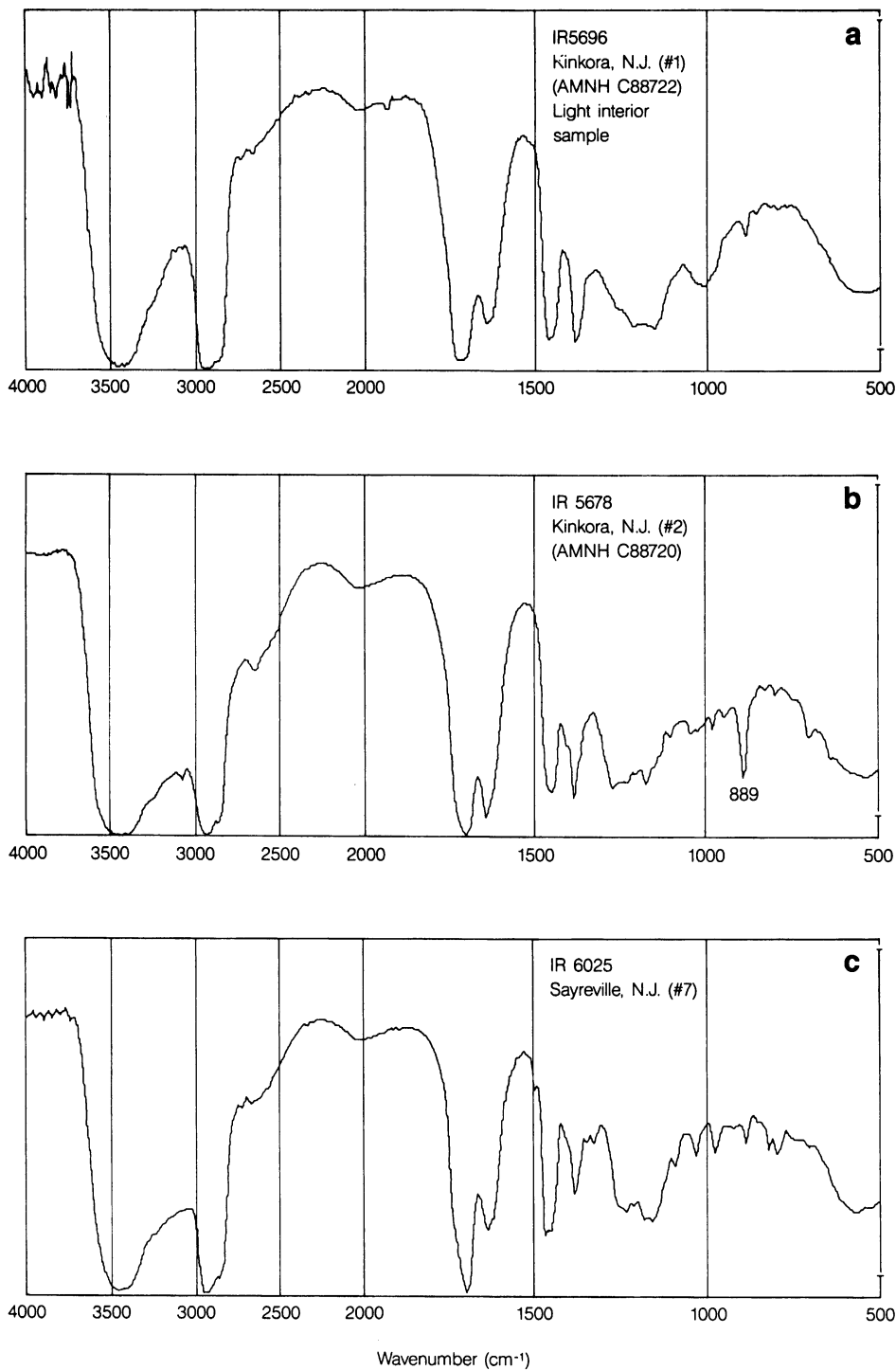


Fig. 7. FTIR spectra of three representative samples of New Jersey Cretaceous fossil acid resins.

TABLE 1  
Hydrocarbon (Polystyrene) Resins

Sample	IR No	Aromatic CH Stretching	Ring Breathing	In plane Deformation	Out of plane Deformation
Polystyrene	6043	3103 3082 3060 3025 3002	1602 1584 1493 1452	1070 1029	907 843 756 699 540
HARRISONVILLE					
AMNH no No.	6041	3024	1601 1494 1453	1029	908 843 758 699 539
	6042	3083 3061 3027 3002	1602 1584 1494 1453	1070 1029	907 842 757 698 540
USNM C-163	6056	3068 3026	1602 1584 1494 1453	1069 1029	907 842 757 698 540
	6057	3082 3059 3026	1602 1584 1494 1453	1068 1029	907 842 757 698 539
PEMBERTON					
USNM 81704	6058	3049	1602 1494 1453	1070 1029	907 843 757 698 540
	6059	3050	1602 1494 1453	1071 1029	907 842 757 698 540
POKE HILL					
AMNH 17350	6054	3103 3083 3060 3026 3001	1602 1584 1494 1453	1069 1029	907 843 757 698 540
	6055	3103 3082 3060 3026 3002	1602 1584 1494 1453	1070 1029	907 842 757 699 540
AMNH 17350B	6019	3053	1602 1492 1451	1070 1029	907 842 757 699 541
	6020	3080 3022	1602 1494 1453	1070 1029	907 842 757 699 540
SEWELL					
NJSM 14157	6039	3103 3082 3060 3026 3002	1602 1584 1494 1453	1069 1029	907 842 757 698 540
	6040	3103 3082 3060 3026 3002	1602 1584 1494 1453	1069 1029	907 842 757 698 540
AMNH C-89828	16021	3060 3025	1600 1494 1453	1030	908 842 758 699 541
	16022	3070 3025	1602 1494 1453	1071 1029	907 842 757 698 541

TABLE 2  
Acid Resins

Location	Sample	IR No	Unsat	Methylene	Methyl	Vinyl Hydrogen				
Bordentown	Smithsonian 95367	6048	1633	1456	1382	798				
Bordentown	Smithsonian 95367	6049	1635	1456	1382	798				
Cheesequake	OP-1	5690	1643	1451	1382	976	888	850	821	795
Cheesequake	OP-1	5691	1638	1455	1382	975	888	849	820	793
Cheesequake	OP-2	5692	1637	1467	1451	1385	977	922	889	821
Cheesequake	OP-2	5693	1636	1467	1451	1385	977	923	889	821
Cliffwood	Smithsonian no #	6050	1634	1455	1383	978	889	796		
Cliffwood	Smithsonian no #	6051	1634	1455	1383	978	890	795		
Ellisdale	NJSM 14155	5680	1636	1467	1451	1384	975	923	888	819
Ellisdale	NJSM 14155	5681	1637	1467	1451	1384	974	925	889	821
Kinkora	AMNH C88720 (K-2)	5678	1643	1450	1386	980	946	889	825	796
Kinkora	AMNH C88720 (K-2)	5679	1642	1457	1386	980	947	889	699	
Kinkora	AMNH C88722 (K-1)	5696	1642	1456	1384	888 856 795				
Kinkora	AMNH C88722 (K-1)	5697	1637	1457	1385	889				
Kinkora	AMNH C88722 (K-1)	6033	1636	1456	1382	819				
Kinkora	AMNH C88722 (K-1)	6034	1633	1456	1382	979	817 795			
Kinkora	Smithsonian C 5610	5686	1635	1456	1385					
Kinkora	Smithsonian C 5610	5687	1634	1456	1384					
Marlboro	AMNH no #	6060	1632	1466	1451	1385	977	921	888	795
Marlboro	AMNH no #	6060A	1631	1466	1451	1385	977	888	793	
Parlin	AMNH 39411	6052	1632	1466	1451	1386	977	889	796	
Parlin	AMNH 39411	6053	1636	1458	1386	795				
Parlin	AMNH 39411 (P-1)	5694	1643	1466	1451	1385	977	924	888	816
Parlin	AMNH 39411 (P-1)	5695	1636	1466	1451	1385	978	925	888	795
Poke Hill	AMNH 17350A	5700	1639	1457	1386					
Poke Hill	AMNH 17350A	6018	1643	1457	1386					
Poke Hill	AMNH 17350A	6035	1638	1457	1386					
Poke Hill	AMNH 17350A	6036	1636	1457	1385					
Roebbing	BM-NH 1925.488	6046	1636	1456	1382	980	891	858	815	796
Roebbing	BM-NH 1925.488	6047	1643	1456	1381	982	890	859	817	798
Roebbing	Smithsonian R7289	6044	1637	1456	1381	980	890	856	793	
Roebbing	Smithsonian R7289	6045	1636	1456	1382	986	888	788		
Sayreville	SF- 2	6023	1636	1455	1383	977	888	795		699
Sayreville	SF- 2	6024	1637	1455	1383	977	888	793		
Sayreville	SF- 2	6029	1638	1467	1451	1384	975	922	889	847
Sayreville	SF- 2	6030	1642	1467	1451	1384	975	923	889	821
Sayreville	SF- 3	6037	1636	1452	1384	977	888	795		
Sayreville	SF- 3	6038	1637	1451	1382	976	888	847	795	
Sayreville	SF- 4	5682	1638	1456	1384	978	888			
Sayreville	SF- 4	5683	1637	1456	1383	977	888	793		
Sayreville	SF- 5	5684	1636	1467	1451	1385	976	924	888	820
Sayreville	SF- 5	5685	1631	1466	1451	1386	977	888	796	
Sayreville	SF- 5	6031	1643	1466	1386	978	887	858	822	795
Sayreville	SF- 5	6032	1636	1461	1386	979	888	822 794 745		
Sayreville	SF- 7	6025	1632	1467	1451	1384	977	921	889	821
Sayreville	SF- 7	6026	1636	1467	1451	1384	976	922	889	822
Sayreville	SF-10	6027	1639	1461	1386	978	887	858	822	797
Sayreville	SF-10	6028	1632	1461	1386	979	887	822 794 746		
South Amboy	NJSM 4641	5698	1636	1451	1385	976	853 821 794			
South Amboy	NJSM 4641	5699	1636	1451	1385	976	852 793			

ACID RESINS. The 50 FTIR spectra of 20 specimens listed in table 2 have carbonyl absorptions over the range of 1695–1723  $\text{cm}^{-1}$ . Since ketone and aldehyde groups can be dis-

counted as principal functionalities in terpenoid resins, this identifies all of these samples as free carboxylic acid resin rather than as carboxylate esters which absorb at higher

wavelengths ( $1730\text{--}1750\text{ cm}^{-1}$ ). It is tempting to divide these carboxylic carbonyl absorptions into two groups (cf. table 2 for corroboration): 18 spectra with carbonyl bands between  $1708$  and  $1723\text{ cm}^{-1}$  which are certainly saturated carboxylic acids, and 32 spectra with carbonyl absorptions between  $1695$  and  $1704\text{ cm}^{-1}$  which may be conjugated unsaturated carboxylic acids. Unfortunately, this distinction cannot be made with certainty for several reasons: (1) the literature values for saturated and conjugated carboxylic carbonyl absorptions overlap by  $5\text{ cm}^{-1}$  at  $1700\text{--}1705\text{ cm}^{-1}$  (Bellamy, 1975); (2) in the New Jersey spectra, the gap between the highest presumably conjugated ( $1704\text{ cm}^{-1}$ ) samples is of the same order of magnitude ( $4\text{ cm}^{-1}$ ) and falls across the overlap; and (3) the reproducibility of the carbonyl bands in duplicate spectra of the New Jersey specimens is also of that order of magnitude. Thus the duplicate spectra of the specimen from Cheesequake State Park absorb at  $1698$  and  $1703\text{ cm}^{-1}$ , respectively; and the duplicate spectra of the samples from South Amboy and from Cliffwood, with carbonyl absorptions at  $1703$  and  $1708\text{ cm}^{-1}$ , respectively, straddle the narrow gap between saturated and conjugated carboxylic acids. While it can be said with confidence that the fossil resins with carbonyl absorptions consistently above  $1710\text{ cm}^{-1}$  (Bordentown, Kinkora [AMNH C88722], and Poke Hill) are saturated acid resins, the classification of the other specimens as conjugated acid resins is only probable, although the probability is quite high for the specimens with carbonyl absorptions consistently below  $1700\text{ cm}^{-1}$  (Ellisdale, Cheesequake [AMNH OP-2], Sayreville [AMNH SF-2, 3, 5, 7, 10], Marlboro, and Parlin [AMNH 39411]). Figure 7 shows three representative spectra for the acid resins.

As table 2 shows, the carbon-oxygen single-bond region of the spectra, which has been of prime diagnostic value in classifying ester resins like Baltic amber (Beck, 1986), is of little use: there appears to be no reliable correlation between the wavelength of the carboxyl-carbonyl band and the pattern of the six other carbon-oxygen bands listed in the fifth column of the table.

Useful structural information can, however, be obtained from the out-of-plane vi-

nylic hydrogen deformations at wavelengths below  $1000\text{ cm}^{-1}$ . Eight such absorptions are tabulated in the last column of table 2 and they indicate virtually every possible substitution pattern of an ethylenic bond. Of the most prevalent, the band at  $974\text{--}986\text{ cm}^{-1}$  (mean value of  $978\text{ cm}^{-1}$ ), which is present in 38 of the 50 spectra, is characteristic of a monosubstituted ethylene; the band at  $788\text{--}798\text{ cm}^{-1}$  (mean of  $795\text{ cm}^{-1}$ ), which is present in 40 of the 50 spectra, identifies a trisubstituted ethylene. The botanically most significant vinyl deformation band, present in 37 of 50 spectra, occurs at  $887\text{--}891\text{ cm}^{-1}$  (mean value of  $888\text{ cm}^{-1}$ ) and is due to an unsymmetrically disubstituted ethylene, i.e., to the structure  $\text{RRC}=\text{CH}_2$ . It could be argued that the New Jersey samples without the exocyclic absorption band at  $888\text{ cm}^{-1}$ , and especially those without any vinylic deformation bands, might have different botanical origins, but these exceptional spectra are more likely due to well-known diagenetic changes. Double bonds in general, and sterically exposed terminal double bonds in particular, are highly sensitive to oxidation. Baltic amber beads in aerobic archaeological deposits, for example, suffer a rapid loss of their unsaturation, which may completely disappear in just a few thousand years. This oxidation is invariably and understandably accompanied by a progressive darkening of the color from the original bright yellow to dark red. Since the New Jersey specimens that show little or no spectroscopic evidence for unsaturation (Bordentown [USNM 95367], Kinkora [USNM C5610], Poke Hill [AMNH 17350A], South Amboy [NJSM 4641]) are those that also exhibit the darkest colors, it is almost certain that they are merely weathered samples of the same botanical origin as the better preserved yellow material.

#### PYROLYSIS GAS CHROMATOGRAPHY

Resin samples analyzed were a Baltic succinite from Kaliningrad (USSR) and New Jersey resins AMNH 39411, AMNH C88720, and AMNH C89828. The synthetic polystyrene was a commercially available extruded polystyrene foam. The hydrocarbon mixture used for determination of the relative retention time of the n-alkanes was isolated from a crude Oman oil.

**CURIE POINT PYROLYSIS GAS CHROMATOGRAPHY.** The analytical pyrolysis was performed in the FOM-3LX pyrolysis unit (Boon et al., 1987) especially designed for capillary gas chromatography using the principle of Curie point pyrolysis (Meuzelaar et al., 1982). Aliquots of the resin samples (microgram amounts) were loaded on ferromagnetic wires from suspensions in water. After evaporation of the suspension fluid, each sample wire was inserted into a glass liner, flushed with argon, and placed into the pyrolysis unit (see fig. 8 for a schematic). The pyrolysis took place in a helium flow (ca. 3 ml/min), which also served as the carrier gas in the gas chromatograph. Rapid heating of the sample to its Curie point (610°C; 4 sec total heating time; temperature of the ceramic tube in the unit 180°C) was done with a 1 megahertz electromagnetic field using a Fischer 9425 power supply unit. Volatile compounds produced by pyrolysis were swept into the capillary GC column of a Carbo Erba 4200 gas chromatograph and separated on a 50 m fused silica column (ID 0.32 mm) coated with a 0.4 film of CP SIL-5 (Chrompak International). A cryogenically cooled oven was programmed from 5 to 325°C at a rate of 4°C/min. The flame ionization signal (F.I.D.) was transferred both to a recorder and to a Nelson Analytical 3000 data system. The relative retention time scale was calibrated with a hydrocarbon reference mixture introduced as an emulsion of carboxymethyl cellulose and water on a Curie point wire and analyzed under the same conditions. Pyrolysis products were identified with PYGCMS under similar conditions of analysis using a JEOL DX-303 double focusing mass spectrometer on line with the JEOL DA-5000 data system. Mass spectra were obtained at 70 eV (3.0 kV acceleration voltage,  $m/z$  50–600, cycle time 1.0 sec).

**PLATINUM FILAMENT PYROLYSIS BY DCI-MS.** DCI-(Desorption Chemical Ionization) MS was done on fossil resin sample AMNH C89828 and a piece of synthetic polystyrene with a JEOL DX-303 mass spectrometer using a combined EI/CI source. The samples were dissolved in dichloromethane and an aliquot of the suspension was applied to the platinum wire (length 1.2 cm; diameter 100  $\mu$ m) of the direct desorption probe, whereaf-

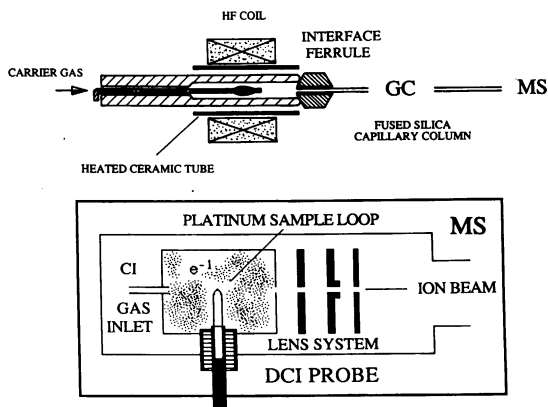


Fig. 8. Schematic diagram of the pyrolysis units for Curie point pyrolysis GC(MS) and platinum filament pyrolysis in the ion source under chemical ionization conditions (DCI-MS).

ter the suspension liquid was evaporated. In-source pyrolysis (see the schematic in fig. 8) was achieved by programming of the heating current from 0 to 0.7 A at 2.0 A/min. Chemical ionization of the pyrolysis products was achieved using  $\text{NH}_3$  as the reagent gas, which was ionized by an electron beam of 250 eV at a pressure (above the pump) of ca.  $7 \times 10^{-4}$  Pa. Magnetic scans were recorded under the following conditions: acceleration voltage 3.0 kV; mass range  $m/z$  50–1000; cycle time 1.0 sec. The spectra were recorded and processed using a JEOL DA-5000 computer system.

**ANALYTICAL PYROLYSIS.** This is a micro-scale process of thermal dissociation, in which weak bonds in a polymeric material are broken and rearranged to neutral molecules often representing monomeric and oligomeric units in the polymer system (Montaudou and Puglisi, 1987). These dissociation products are analyzed by gas chromatography or introduced into or even generated in the mass spectrometer itself, resulting in molecular and fragment ion distributions. Both approaches have been used in this study: the GC allows the separation of many isomers on the monomer and submonomer level but the transmission of oligomeric compounds is limited. The mass spectrometer has a higher transmission for oligomers and directly analyzes molecular properties as distributions of ions.

A sample of fossil polystyrene (AMNH C89828, from Squankum, N.J.) was com-



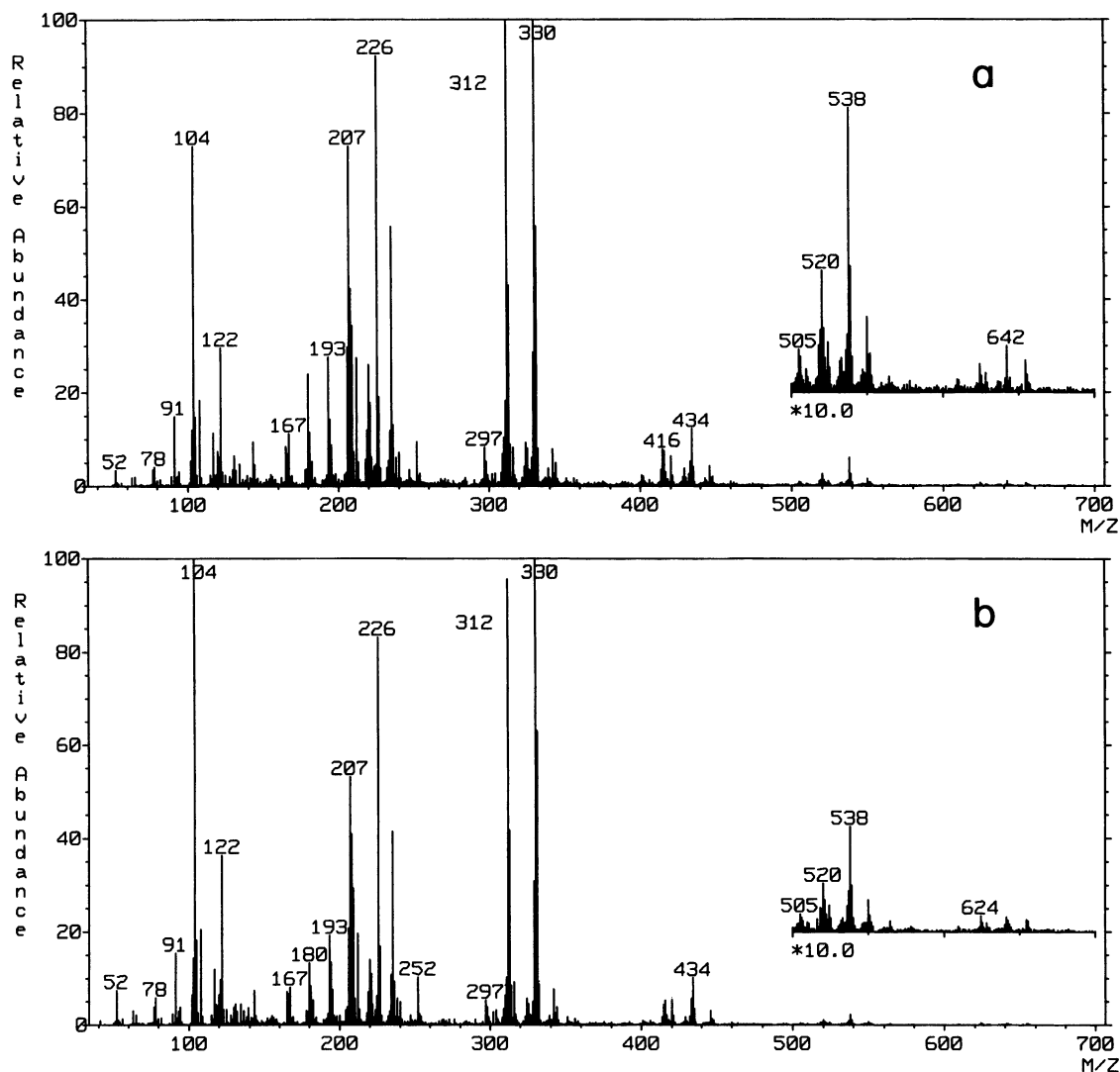


Fig. 9. Ammonia chemical ionization pyrolysis mass spectra from a Tertiary polystyrene (a) (sample AMNH C89828) and a modern polystyrene foam (b), showing the great similarity in composition.

pared with recent synthetic polystyrene foam and with several other resin samples by PYGC and PYMS. Figure 9 shows pyrolysis mass spectra of the recent and fossil polystyrene, obtained under ammonia chemical ionization conditions in order to preserve the molecular weight distribution of the pyrolysis products. Mass  $m/z$  104 and 122 are the molecular ion and the ammonium adduct ion of styrene, the monomeric pyrolysis product of polystyrene. Higher molecular weight oligomers can be deduced from  $m/z$  208 and 226

(styrene dimer), 312 and 330 (styrene trimer), 416 and 434 (styrene tetramer), 520 and 538 (styrene pentamer), etc. The spectra of recent and fossil polystyrene are very similar in ion distribution, but not identical. The two samples show identical heating profiles—a sharp peak with a width of 4 sec—which point to high purity and very similar composition of the two samples. Figure 10e shows the pyrolysis gas chromatogram of the fossil polystyrene sample, with major peaks for styrene, styrene dimer, styrene trimer, and a number

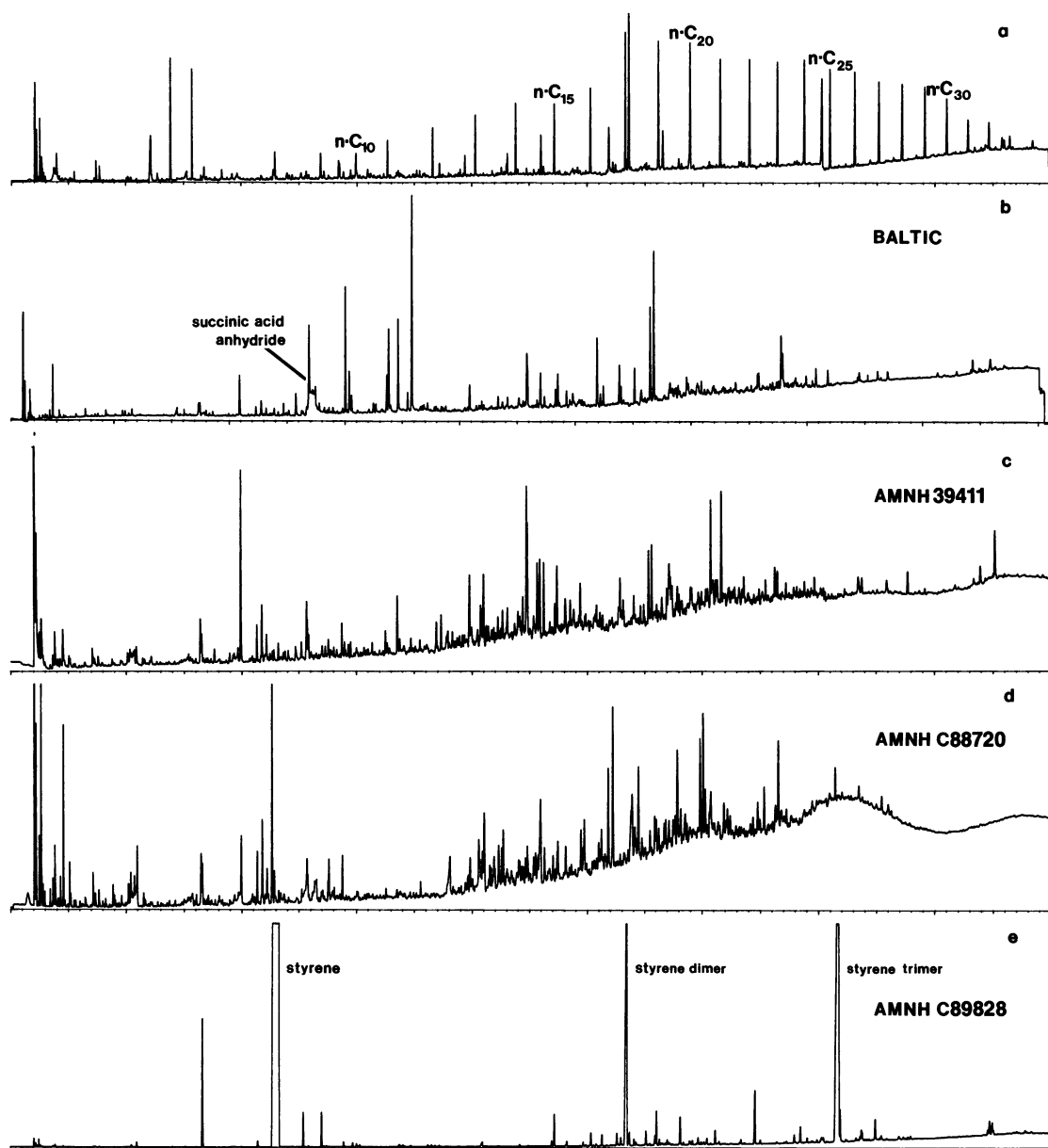


Fig. 10. Pyrolysis gas chromatograms of (a) a hydrocarbon reference mixture, (b) Baltic amber from Kaliningrad (USSR), (c) New Jersey Cretaceous fossil acid resins, AMNH 39411, (d) AMNH C88720, and (e) the Tertiary New Jersey polystyrene sample AMNH C89828. The regular series of n-alkanes ranging from C10 to C32 in the reference mixture serves as a relative retention time scale for the chromatograms.

of isomeric compounds with low relative abundance. PYGCMS of this sample did not show any non-styrene related compounds.

The gas chromatograms of the other fossil resins (fig. 10b, c, d) are in striking contrast

with the fossil polystyrene pyrolysate. In the case of the true ambers, one deals with a random polymer and condensate of terpenoid hydrocarbons, alcohols, and acids (Mills et al., 1984/85). Because of the unique hydro-

carbon composition of the Tertiary fossil polystyrene, the term *amber* in this study, again, should be reserved solely for the Cretaceous, terpenoid, coniferous fossil resins. The pyrolysis of ambers such as AMNH 39411 and AMNH C88720 leads to complex mixtures of terpenoid compounds with no apparent regularity. The pyrolysis products can be classified as terpenoid hydrocarbons on the basis of their mass spectra, but the compounds are difficult to identify without the appropriate standards. A worldwide survey of fossil resins by Tom et al. (1988) with the same technique has shown that each sample has a unique PYGC fingerprint, but that samples of the same botanical origin and from the same deposit share the most similarity in their traces. Conclusions conflict to some extent with earlier data of Poinar and Haverkamp (1985) based on Curie point PY-EIMS data, a technique that tends to underestimate the importance of terpenoid stereoisomers. On the basis of the PYGC data, one can say that the two amber samples analyzed from New Jersey either have a different botanical origin, they differ in depositional history or conditions, or both. There is presently not enough comparative PYGC data available, however, to postulate a botanical source of this amber. Comparison of the PYGC fingerprints of these resins with the Baltic sample (fig. 10b) shows that they are not at all related in botanical origin because of their entirely different terpenoid profiles. The Baltic ambers (succinites) release succinic acid, which is present as succinic acid anhydride in the PYGC. This compound is not present in the New Jersey ambers analyzed.

### BOTANICAL CONCLUSIONS

The presence of polystyrene and its derivatives, as seen in the FTIR and PYGC and PYMS results, shows this material to be fossil storax (= styrax = sweet gum), a product of the genus *Liquidambar* (family Hamamelidaceae). *Liquidambar orientalis* is native to the Near East and yields Levant storax, while *L. styraciflua* is the source of American storax, also called copalm balm. Modern storax contains less than 1 percent free styrene, but its major constituents, cinnamic acid and its esters, are readily decarboxylated to styrenes

that then polymerize, the polymer of which apparently resists biodegradation for up to 65 or 70 million years. Styrene was originally shown to occur in the fossil resin material, sieburgite, by Klinger and Pitschki (1884), and our data indicate a similar type of fossil resin from a different location. The purity of the fossil sample on the basis of all our chemical results is truly remarkable for a resin of geochemical origin. The fact that no mixed condensate was formed points to a very pure precursor substance or excretion product, which may have reacted catalytically to this kind of polymer immediately after its release. Future research will compare the exudates from living *Liquidambar* with the fossil material.

The ancient Egyptians used Levant storax for impregnating burial gauze so as to better preserve the corpse, and other uses were as an incense and a treatment for venereal disease. The chief center of production of American storax is Honduras, and the tree species yielding it is native to the Atlantic Coast from Connecticut to Central America. According to Peattie (1950), American storax, when first exuded, is "semitransparent and yellowish brown, but on exposure to air it hardens into a rosin-like and darker solid. From pioneer times it was used in the South [U.S.] for the treatment of sores and skin troubles, for chewing gum, for catarh, and in the treatment of dysentery . . ." (p. 310). The center of production in the United States was Clarke County, Alabama. The pollens of *Liquidambar* and *Altingia* (almost structurally inseparable) are known from the Paleocene of Europe and the Rocky Mountains, U.S.A., and by numerous Eocene records in Japan and Europe, but no Cretaceous records exist (Muller, 1981). There is no megafossil evidence of *Liquidambar* in the deposits of the Atlantic Coastal Plain, but, as the spectra show, the range of the genus during the Tertiary included this area as well.

The exocyclic double bonds seen in the FTIR are typical features of acid resins with a labdane skeleton, which in turn are characteristic of fossil and recent copals derived from *Agathis* (Araucariaceae). The acid resin nature of the Cretaceous amber from New Jersey is corroborated with the PYGC. The acid resins of New Jersey can therefore be

assigned to a botanical source within that family. The Araucariaceae are presently distributed from southern South America to northern Australia, New Zealand, and the Indo-Pacific to the Malaysian peninsula (Whitmore, 1980). Fossil species of *Agathis* are known from the Oligocene and Miocene of New Zealand and Australia, and the Tertiary of Antarctica. Apparently, more primitive fossil genera of Araucariaceae were quite extensively distributed around the world. They are known from the Jurassic of several localities in the Northern hemisphere and from numerous records from the Cretaceous (Seward and Ford, 1906; Townrow, 1969; Stockey, 1982). Penny (1947) described a wood of *Araucarioxylon* as being common in the Magothy Formation of New Jersey, as well as having found cones of *Protodammara speciosa* Hollick and Jeffrey (which he believed to be an *Agathis*).

### INCLUSIONS

Inclusions in the amber from New Jersey are curious in that despite their rarity, at least two of the most important insect fossils have been found here, both of them social insects. Nearly 300 red and yellow pieces of amber from the Sayre-Fisher Pits and Oswald's Pits, Middlesex County have been examined, along with about 50 pieces collected by Hollick on Staten Island, New York, but only one yielded a partial fungus gnat (Diptera: Sciaroidae; AMNH SF-1; fig. 11). The oldest known amber sciarids are undescribed from the Aptian of Lebanon (P. Whalley, personal commun.).

Specimen AMNH SF-1 is most similar to *Sciara defectuosa* Meunier, in Baltic amber, as based on comparison to Meunier's (1904) illustrations. The venation of both species is distinctive, in particular an incomplete first medial (M) vein and a loss of the second medial. The venation of these two species shares the complete loss of vein  $M_2$  and loss of the proximal portion of  $M_1$ , with another fossil sciaroid, an undescribed species from the Upper Cretaceous amber of Cedar Lake, Manitoba, Canada (MCZ specimen no. 6927). Specimen MCZ 6927, however, is even more modified in venation:  $R_{4+5}$  is incomplete proximally and runs very close (almost

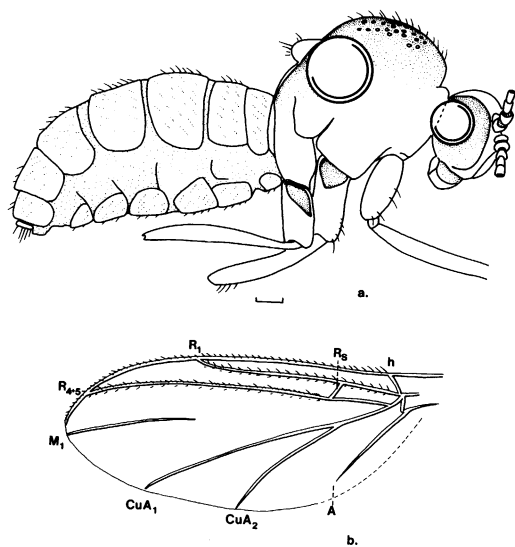


Fig. 11. Sciaroidae (Diptera) inclusion in amber from the Sayre-Fisher Pits, Sayreville (AMNH SF-1). **a.** Lateral view of body showing all portions intact in the fossil. The piece was found fractured along one side of the specimen, so this view of the specimen is actually along the inner surface of the bodywall. **b.** Reconstructed wing of fossil, taken from portions of both wings. Veins: A, anal;  $CuA_1$ , anterior cubitals; h, humeral;  $M_1$ , first medial;  $R_1$ , radials;  $R_5$ , radial sector. Scale is 0.10 mm.

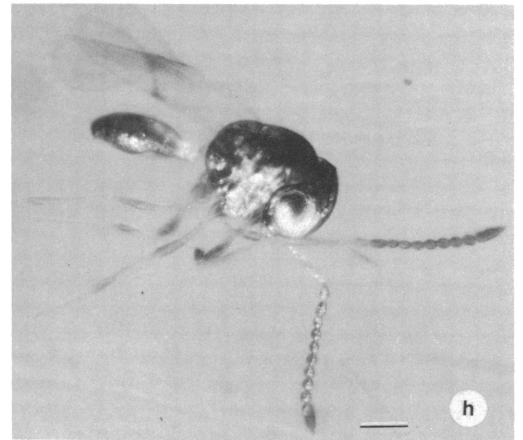
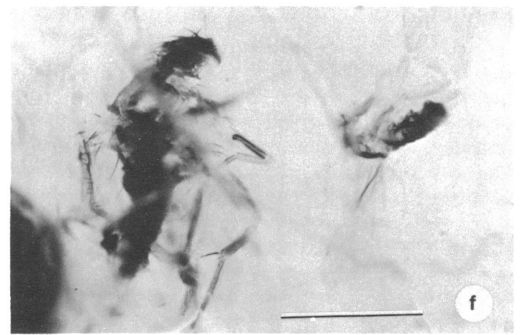
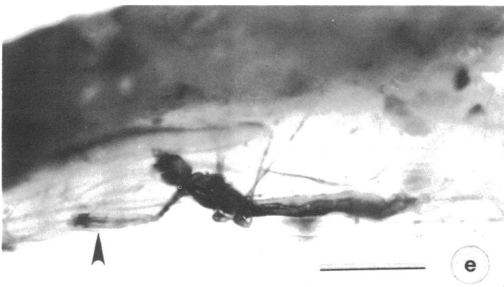
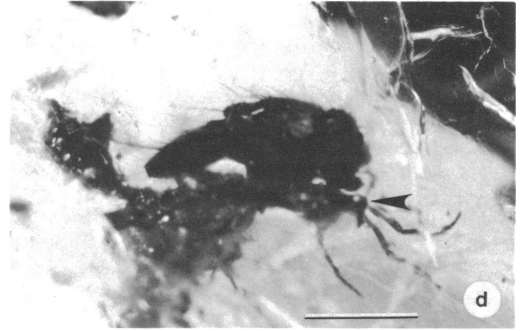
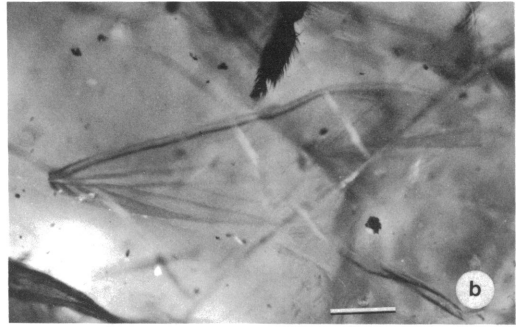
touching) to  $R_1$ ;  $R_5$  is lost, and the point where the fork of  $CuA_1$  and  $CuA_2$  lies is considerably distal to that in the other amber species, in fact lying at the level of the apex of  $R_1$ . MCZ 6927 has the dorsal eye bridge of sciarids, and the well-developed apical tibial spurs seen in the Mycetophilidae. The only other sciaroids with a similar venation are the manotine Mycetophilidae, in which veins  $M_1$  and  $M_2$  are always present, albeit also incomplete. Other important venational features of the New Jersey amber specimen are the presence of vein  $R_5$  (common to most sciarids and mycetophilids), the fork of  $CuA_1$  and  $CuA_2$  near the level of vein  $R_5$ , and microtrichia that occur only on the radial veins and not on the medial or anterior cubitals. Unfortunately, the distal portions of the legs are not preserved in AMNH SF-1, for the spination of these parts of the legs are taxonomically very important. Relationships of these enigmatic sciaroids to living genera is still uncertain, but a chronological similarity of



Fig. 12. Two males of a species of orthocladiine Chironomidae (Diptera) in amber from the Sayre-Fisher Pits, Sayreville (PU 88892a, b). Scale is 1.0 mm.

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Fig. 13. Some inclusions from piece no. AMNH C88720 from Kinkora, N.J. a. entire piece; large insect near center is meliponine bee, *Trigona prisca*. b. Isoptera (termite) wing. c. Coleoptera (Curculionidae) and Acarina (mite, at upper left of weevil, see arrow). d. Muscomorphan fly, arrow points to acute bend in proboscis, which indicates that the fossil may be a milichiid. e. Lateral view of nymphal



emesine Reduviidae (Heteroptera), arrow points to raptorial forelegs. f. Two species of Phoridae (Diptera), at left is badly preserved specimen (undetermined), at right is *Metopina*. g. Lateral view of *Dohrniphora*? (Phoridae), the genus of which is partially characterized by the peculiar, long rostrum. h. A tiny parasitoid wasp, Scelionidae (Hymenoptera). Scale in each is 1.0 mm, except for h, which is 0.10 mm.

the Baltic, Canadian, and New Jersey ambers is suggested by their presence in these ambers.

In a piece (Princeton University 88892) collected by Mr. Gerard Case also at the Sayre-Fisher Pits (map site 5, fig. 4) were three small nematoceros Diptera, which have been separated. In one section is a male Ceratopogonidae, probably a species of *Culicoides* (PU 88892a) (identified by W. L. Grogan, personal commun. 1987). In two other pieces (PU 88892b, c) are two males of a species of orthoclaadiine Chironomidae in *Tvetenia* or a very closely related genus, such as *Eukiefferiella* or *Paratrissocladius* (fig. 12). *Tvetenia* is mostly a holarctic genus of approximately 15 species, but its limits and that of *Eukiefferiella* (sensu Saether and Halvorsen, 1981) need to be sorted out. Chironomidae (and especially Ceratopogonidae, because of their minute size) are well represented in ambers around the world, probably the most exciting described thus far being *Libanoclites*, a podonine from the Aptian amber of Lebanon (Brundin, 1976). Biogeographic patterns and generic affinities of the Cretaceous chironomids are reviewed by Ashe et al. (1987), who indicate that a Triassic origin of the family is reasonable. This age seems unjustified in the light of any discernible patterns based on vicariance and drift of continents during this time.

Until 1975, the oldest and morphologically most primitive known ant was *Sphecomyrma freyi*, found in amber for Cliffwood Beach bluffs, N.J. (Wilson et al., 1967) (map site 9, fig. 4) (but see Dlussky, in Rasnitsyn [1975], and Dlussky [1983]). The Russian evidence is from Coniacian-Santonian amber of the Magadan region in eastern Siberia and the Taymyr Peninsula, and compression fossils from the Turonian of southern Kazakhstan. In compression fossils it is virtually impossible to confirm the presence of several important ant synapomorphies, such as the metapleural gland. Most of the names for the taxa in the Russian deposits have been synonymized with the genus *Sphecomyrma* (Wilson, 1987). Most recently, Dlussky (1987) has completed the study of the fossil formicoids in the collection at the Paleontological Institute, USSR, including the description of a primitive new genus of ant. Thus, he in-

cludes 4 genera, 3 of them from the Taymyr amber (the other, *Sphecomyrma*, from New Jersey and Canadian Cretaceous amber), placed in the family Sphecomyrminae (Dlussky's ranking), the sister-group to the true ants, the Formicidae. He stated that in all of them the metapleural gland is well developed. To Dlussky, the true ants did not appear until the Paleocene. Wilson (1987) provided evidence that within the Cretaceous diversity of these primitive ants there are three recognizable castes, so Dlussky's genera may actually just represent polymorphism. Despite the fact that the Sphecomyrminae were social, their primitive morphological features indicate that the Cretaceous was a very important period in the evolution and appearance of Formicidae.

The oldest known bee, the meliponine *Trigona prisca* (in piece no. AMNH C88720), is from Kinkora, New Jersey (Michener and Grimaldi, 1988a) (fig. 13a). It is very closely related to the living species *Trigona cilipes*, which occurs from Brazil to Panama. Geological ages of the bees have important implications for the ages of advanced angiosperms (Michener and Grimaldi, 1988b). Prior to this the oldest known bees were from the Baltic amber. The large piece (12 × 17 × 12 mm) in which it occurs contains 14 inclusions, representing 10 arthropod families. Besides the bee, the inclusions are three Phoridae (Diptera: one being *Metopina*, another is perhaps *Dohrniphora*, fig. 13f, g), one weevil (Coleoptera: Curculionidae, fig. 13c), one Scelionidae (Hymenoptera, fig. 13h; very similar to *Ibris* from Baltic amber [Szabo and Oehlke, 1986]), one nymphal emesine Reduviidae (Heteroptera, fig. 13e), two gall midges (Diptera: Cecidomyiidae), one spiderling (Araneae), two mites (Acarina), one termite wing (Isoptera, fig. 13b), and a small muscomorphan fly which, because of the geniculate proboscis (other features are not obvious) is probably in the Milichiidae or a close relative thereof. The milichiid is only the second instance of the Muscomorpha Diptera in the Mesozoic. This is also the oldest record for the Emesinae, which is a dominantly tropical group. *Metopina* contains approximately 33 described and undescribed species, most of which are Neotropical, Palearctic, with a few Old World tropical species (only two are



Nearctic). *Metopina* has also been found in the Oligomiocene ambers of the Dominican Republic and Chiapas, Mexico (Grimaldi, 1989).

All the insect inclusions thus far have been found in the clear yellow amber. It is doubtful that any will be found in the polystyrene fossil resin because it is so opaque, and the dense fractures inside the red amber also obscure the interior of each piece. The emesine, the

meliponine bee, and to a lesser extent *Metopina*, demonstrate some geographical extinction of tropical elements from the New Jersey Cretaceous, which corroborates the paleobotanical evidence. The sciaroids have affinities with species in the Baltic (Oligocene to Eocene) and Canadian (upper Cretaceous) amber. D. Grimaldi is at present collecting and examining additional New Jersey amber for insect inclusions.

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## APPENDIX

## Samples Analyzed by FTIR

- South Amboy (Middlesex Co.), 40°29'N, 74°17'W (map site 3). NJSM no. 4641, collected in Isaac Inslee's Pit, are translucent, small red (2.5 YR 5/8, using the Munsell Soil Color Chart) pieces in a lignitic clay matrix. Duplicate FTIR spectra (nos. 5698 and 5699) identify it as an acid resin (table 2).
- Parlin (Middlesex Co.), 40°47'N, 74°32'W (map site 4). The AMNH specimen (no. 3941) from Crossman's Clay Pit is red (2.5 YR 4/8) and semiopaque to translucent. Four FTIR spectra (nos. 5694, 5695, 6052, and 6053) identify it as an acid resin (table 2).
- Sayreville (Middlesex Co.), 40°28'N, 74°21'W (map site 5). All the samples from this location were collected by D. Grimaldi in the Sayre-Fisher Clay Pits. SF-2 contains portions that are transparent with a few brown inclusions, is very hard and brittle, with a yellow (2.5 Y 8/8) exterior and a lighter yellow (2.5 Y 8/6) interior. Another part of the same sample is also transparent and brittle, but dark red (2.5 YR 3/6) in color. Four FTIR spectra (two of each color) are essentially identical (nos. 6023, 6024, 6029, and 6030) and are those of an acid resin (table 2). SF-3 is red (2.5 YR 4/6), transparent, and brittle. Duplicate FTIR spectra (nos. 6037 and 6038) identify it as an acid resin (table 2). SF-4 is brittle and dark red (2.4 YR 3/6). The spectra (nos. 5682 and 5683) are those of an acid resin. SF-5 includes pieces with a thick, tan, weathered crust under which the sample is transparent, brittle, and yellow (2.5 Y 8/8) to pale yellow (2.5 Y 8/4). Four FTIR spectra (nos. 5684, 5685, 6031, and 6032) show it to be an acid resin (table 2). The FTIR spectra of SF-4 and SF-5 have been discussed in Michener and Grimaldi (1988a). SF-7 is brittle, transparent to translucent, and yellow (10 YR 7/8) with an almost colorless interior. Two FTIR spectra (nos. 6025 and 6026) identify it as an acid resin. SF-10 has much the same appearance as SF-7, but is more opaque and lighter in color (10 YR 8/6). It is also an acid resin from its FTIR spectra (nos. 6027 and 6028; table 2).
- Cheesequake (Middlesex Co.), 40°40'N, 74°36'W (map site 6). The resin was found in Oswald's Pit near Cheesequake State Park. Two samples from the AMNH collection were analyzed. OP-1 is very brittle with a yellowish brown crust (10 YR 5/6); its interior is translucent and reddish yellow (7.5 YR 6/8). OP-2 is yellow (2.5 YR 8/6), brittle, and translucent. Duplicate FTIR spectra of OP-1 (nos. 5690 and 5691) and of OP-2 (nos. 5692 and 5693) identify them as acid resins (table 2).
- Cliffwood (Monmouth Co.), 40°42'N, 74°23'W (map site 9). The sample was obtained in 1963 from the Roebling Collection of the Smithsonian Institution. It carries no inventory number. The label reads "Cliffwood Brick Company Pits; collected by E. W. Berry, 1905" and Berry published on the specimen (Berry, 1906; also Wilson et al., 1967). The material is translucent, brittle, and red (10 R 4/6). A dispersive infrared spectrum has been published (Langenheim and Beck, 1968). Duplicate FTIR spectra (nos. 6050 and 6051) show it to be an acid resin (table 2).
- Squankum (Monmouth Co.), 40°11'N, 74°18'W (map site 10). AMNH no. C89828 is from a marl pit. It is opaque and mottled, with a darker yellowish brown (1 YR 5/4) crust and a lighter yellow (10 YR 8/6) interior. The material is extremely tough and had to be sampled with a sapphire file. Duplicate FTIR spectra (nos. 6021 and 6022) show it to be polystyrene (table 1).
- Ellisdale (Monmouth Co.), 40°12'N, 74°37'W (map site 11). The sample is from Quarry B of Bob's Run (no. 14155 in the NJSM). It is brittle, transparent, and yellow (2.5 YR 8/6). FTIR spectra (nos. 5680 and 5681) have been discussed but not published in Michener and Grimaldi (1988). They identify the sample as an acid resin (table 2). A second specimen (NJSM 14154), was not analyzed.
- Bordentown (Burlington Co.), 40°08'N, 74°43'W (map site 12). A specimen in the Smithsonian Institution (USNM 95367), was contributed by the USGS in 1912. It is brittle, opaque, agated, and reddish yellow in color (5 YR 6/8). Macroscopically it resembles Moravian retinite called walchowite (Beck et al., 1978). A dispersive spectrum has been published (Langenheim and Beck, 1968). Duplicate FTIR spectra (nos. 6048 and 6049) show it to be an acid resin (table 2).
- Kinkora (Burlington Co.), 40°13'N, 74°75'W (map site 13). A sample from the American Museum of Natural History, no. C88722, is opaque and reddish yellow (5 YR 6/8), like walchowite. The interior is somewhat paler. Four FTIR spectra (nos. 5696, 5697, 6033, and 6034) show it to be an acid resin. Another sample, also from the AMNH, no. C88720, is very different in appearance: it is transparent and yellow (5 Y 8/6); the interior is very light and clear yellow. Duplicate FTIR spectra (nos. 5678 and 5679) show carboxylic acid absorptions, but at significantly lower wavelengths than the previous sample (table 2). The sample, a bee inclusion, and the spectra have been discussed in Michener and Grimaldi (1988a). A third sample from this location is in the Canfield Collection of the Smithsonian Institution, no. C5610. It again looks very much like walchowite: opaque, brittle, and reddish yellow (exterior 5 YR 6/8; interior 5 YR

- 6/6). A dispersive infrared spectrum has been published (Langenheim and Beck, 1968). It, too, is an acid resin (duplicate FTIR spectra nos. 5686 and 5687; table 2).
- Roebing (Burlington Co.), 40°01'N, 74°46'W (map site 14). The label of no. 1925.488 in the British Museum (Natural History) reads "Amber. Ambrosine . . . from Cretaceous formation at Roebing, N.J., Burlington Co. Exchange from Colonel Washington A. Roebing, 1925" and also bears the corrections "Evidently retinite. Shephard's 1870 ambrosine is from Charleston, S.C.," written by A. J. Spenser. The opaque and yellow (10 YR 7/8) specimen is an acid resin (spectra 6046 and 6047; table 2). A specimen in the Roebing Collection of the Smithsonian Institution, USNM no. R7289, is also opaque but reddish yellow in color (5 YR 6/8) and resembles walchowite. Three dispersive infrared spectra have been published earlier (Langenheim and Beck, 1968). It is an acid resin (FTIR spectra 6044 and 6045; table 2).
- Pemberton (Burlington Co.), 39°59'N, 74°41'W (map site 15). USNM no. 81704 is mottled reddish yellow (7.5 YR 6/6) to brown (7.5 YR 5/4) with opaque yellow (10 YR 8/6) inclusions. Its dispersive infrared spectrum has been published and discussed earlier (Langenheim and Beck, 1968). Duplicate FTIR spectra (nos. 6058 and 6059 [fig. 6c]) identify it as polystyrene (table 1).
- Sewell (Gloucester Co.), 39°75'N, 75°14'W (map site 16). NJSM no. 14157 is from the Inversand Marl Pit. It is fibrous, tough, and heterogeneous in appearance, the color mostly yellowish brown (10 YR 5/4). Duplicate FTIR spectra (nos. 6039 [fig. 6a] and 6040) identify it as polystyrene (table 1).
- Harrisonville (Gloucester Co.), 39°42'N, 75°17'W (map site 17). A sample from Kirby's Marl Pit in the AMNH (no inventory no.) is of a very tough, heterogeneous material with colors ranging from brownish yellow (10 YR 6/6) to dark yellowish brown (10 YR 4/4) containing highly reflective transparent ("glassy") portions. The find was published by Kunz (1883) and is mentioned by Hollick (1905) in his paper on amber from Kreischerville (now Charleston), Staten Island. Duplicate FTIR spectra (nos. 6041 and 6042) show that the transparent portions are essentially pure polystyrene (table 1). Another sample of the same find is in the Canfield Collection of the Smithsonian Institution, USNM no. C163. It is a small, transparent, light brownish-gray piece (10 YR 6/2). A dispersive infrared spectrum has been published (Langenheim and Beck, 1968). Duplicate FTIR spectra (nos. 6056 and 6057) also identify it as polystyrene (table 1).
- Marlboro (Monmouth Co.), 40°19'N, 74°15'W (map site 18). The AMNH specimen from Marlboro, Big Brook (no inventory number) was collected by Mr. Jim Brown, and amateur paleontologist. It is transparent and pale yellow (2.5 Y 8/8), with an almost colorless interior. Duplicate FTIR spectra (nos. 6060 and 6060A) identify it as an acid resin (table 2).
- "Poke Hill," no coordinates known (not on map). Sample with this origin was first collected in 1963, in the AMNH (no. 17350). It is opaque, has a fibrous structure, and is so tough that the sample for analysis had to be taken by filing. Its color is yellow (2.5 Y 8/4 to 2.5 Y 8/6). Duplicate FTIR spectra (nos. 6054 and 6055) identify it as polystyrene (table 1). Currently there are two separate samples with this inventory number in the AMNH collection: AMNH 17350A is dark reddish brown (2.5 YR 3/4) and transparent; it is an acid resin (FTIR spectra 5700, 6018, 6035, and 6036; table 1). Specimen no. 17350B resembles the one taken in 1963. It is very heterogeneous, with light yellow (2.5 Y 8/8) clear inclusions in a darker brownish yellow matrix (10 YR 6/8). The material is very tough. Samples for duplicate FTIR spectra (nos. 6019 and 6020) were taken of the clear inclusions and identify them as polystyrene (table 1).

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