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THE NATURE AND FATE OF NATURAL RESINS IN THE GEOSPHERE. VI¹.

Analysis of Fossil Resins from Axel Heiberg Island
Canadian Arctic.

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¹ For Part V of this series, see Anderson, 1995 (Chapter #, This Volume).

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Abstract

Ambers are well known and abundant in terrestrial sediments all over the world; however, due largely to the absence of definite morphological characteristics, the precise botanical origin of most amber samples, are at best, often a matter of speculation. This has severely restricted the usefulness of amber in paleobotanical and paleoecological interpretations. The molecular composition and structural characteristics of fossil resins however, may preserve evidence of their botanical origin, which could be of great value in both geochemical, paleobotanical, and paleoenvironmental studies. The remains of a number of exceptionally well-preserved Taxodiaceae-dominated swamp-forest communities have been identified in the sediments of the middle Eocene (45 million years old) Buchanan Lake Formation of Axel Heiberg Island, Canadian Arctic Archipelago. The amber collected from these ancient *in situ* forests provides a unique opportunity to characterize these resins chemically and taxonomically. Resinite associated with *Metasequoia*, *Pinus* and *Pseudolarix* has been characterized using Pyrolysis-Gas Chromatography-Mass Spectrometry. This method provides a direct analysis of the molecular structure and composition of the resin. In several cases, both bleed resin and cone-resin samples have been characterized. The results of these analyses are presented and discussed. The implications of these results for the botanical origins of other ambers represented in the fossil record (including succinite) will also be discussed.

Introduction

Ambers, the "fossilized" resins of vascular plants, are often common constituents of fossiliferous deposits, and due to their potential value as biological markers they are currently receiving considerable attention from scientists in a number of earth science disciplines. With the application of modern analytical techniques, a large number of fossil resins have now been characterized and considerable detail of the (macro)molecular structures of these materials has been established (1-7). There is, however, very little data available concerning the analysis of fossil resins which can be unambiguously assigned to specific extinct or relict species. This is due to the fact that (i) in most cases the structural characteristics of fossil resins are not necessarily diagnostic of specific species and (ii) well-preserved identifiable macrofossil remains (e.g., wood and seed cones) with resinite still present within the tissues is uncommon. In rare instances however, fossil resins occur in association with identifiable plant remains and in such cases, information concerning the structural characteristics of the resins produced by these fossil representatives can be obtained.

Baltic Amber, and related Class Ia resinates are an extraordinarily abundant resource which have been mined throughout and before recorded history. By some estimates, reserves of Baltic Amber may be as great as 4.8×10^8 kg (8, 9), and this does not include microscopic resinite fragments which undoubtedly add significantly to this figure. The species of tree(s) which produced this exceptional

resource, however, is unknown and represents, perhaps arguably, one of the great mysteries of the organic geosciences.

On Axel Heiberg Island, one of the northernmost islands in the Canadian Arctic Archipelago, a succession of exquisitely preserved fossil forests of Eocene age (ca. 45 million years) were discovered in sediments of the Buchanan Lake Formation (Figure 1) (10-13). Macrofossil remains containing resinite and unassociated resin "balls" are common throughout these deposits. In this paper we describe the analytical results of a number of resinites from this site and discuss the implications of these data for the origin of succinite and related resinites which are exceptionally abundant in the Baltic region.

Speculation on the Botanical Nature of the "Amber Trees"

Scientists have been attempting to identify the species of tree responsible for the production of the Baltic Amber for over 150 years. Resin-bearing fossil woods from the Baltic region were first reported as an unidentified species of *Pinus* by Aycke in 1835 (14). Göppert (15) subsequently identified this wood as an extinct species of conifer showing affinity with living representatives of the family Pinaceae and named these specimens *Pinites succinifer*. Since then, interest in the plant remains associated with Baltic amber has produced several names for these resin-bearing woody fragments (e.g., *Abies bituminosa* (16), *Pinites succinifer* (17), *Taxoxylum electrochiton* (18), *Pityoxylon succiniferum* (19), *Picea succinifera* (20), *Pinus succinifera* (21, 22), *Pinus* (23), *Pinus halepensis* (24), and *Agathis* (25-28), but little has been added to resolving the true identity of the resin-producing tree(s) and its relationship with living conifers.

On-the-whole, analysis of the anatomical and morphological features of the plant remains associated with Baltic Amber indicate the amber was produced by an extinct member of the Pinaceae. However, using spectroscopic analyses, (especially infrared spectroscopy), a number of workers (25, 29) have shown that the spectroscopic characteristics of resin produced by *Agathis australis* and Baltic Amber are similar. This has been widely interpreted as evidence for a phylogenetic affinity between Baltic amber and resins produced by members of the Araucariaceae, especially *Agathis* (25, 28-31).

Removal of succinic acid from the Baltic Amber by alkaline hydrolysis gave a product with an infrared spectrum that was nearly identical with *A. australis* resin (25, 29), and succinylation of *A. australis* resin gave a product with an infra-red spectrum comparable to that of Baltic Amber (27). Based on these results, it has been suggested by a number of workers that Baltic Amber may be derived from the resin of an extinct Araucarian species, probably related to *Agathis*.

These analyses however, demonstrate only that the gross structural characteristics of these products are similar. Py-GC-MS analyses have shown that the macromolecular structures of Class Ia ambers (including succinite) are derived from resins based on polymers of *regular* labdanoid diterpenes, including communic acid, communol, and biformene. Various analyses of living (32) and fossil (2, 3, 26, 29) *Agathis* resins indicate these resins are also based on a *regular* polylabdanoid

macromolecular structure, and therefore, provide results similar to those obtained for Class Ia ambers. However, no known extant *Agathis* resin has been shown to contain succinic acid - a diagnostic component of Succinite. Furthermore, in addition to *Agathis* (family Araucariaceae) a significant number of species belonging to the Cupressaceae (33-35), and Taxodiaceae (including *Metasequoia*, see 36, 37, and data presented below) produce resins based on *regular* polylabdanoid macromolecular structures, but lack succinic acid. Because the macromolecular structures of the resins from any of these genera are based on comparable mixtures of *regular* labdanoid diterpenes, spectroscopic analysis of the applicable resins of each of these genera will give results essentially similar to those obtained by spectroscopic analysis of *Agathis* or Baltic Amber. Therefore, based on results derived from spectroscopic analyses it is impossible to support the notion that Baltic amber is derived from *Agathis* or an *Agathis*-like ancestor.

In addition, it is also important to note when considering the question of the relationship of *Agathis* with the amber producing trees that, unequivocal fossil remains of *Agathis* are restricted to the Southern Hemisphere (38, 39).

Assignment of *Pinites succinifera* to the Pinaceae is based on morphological and anatomical data and its association with *Pinus*-like cones and needles in the "Blue Earth" sediments. The Blue Earth sediments are marine in origin and all of the plant fossils associated with these sediments are allochthonous and represent materials that have been transported, perhaps a considerable distance from the site in which the trees originally grew. If organic connections between the wood and *Pinus*-like cones and needles existed, they would have inevitably been broken during transport. Without organic connection, the association of *Pinites succinifera* with *Pinus*-like cones and needles, especially in allochthonous deposits is essentially meaningless.

Using anatomical and morphological features, Conwentz (20) assigned the wood associated with the Baltic Amber to *Pinus succinifera*, but indicated the wood possessed morphological features common to both *Pinus* and *Picea*. In a reinvestigation of the "amber tree" wood, Schubert (22) unequivocally concluded that the amber trees belonged to the genus *Pinus*, based on morphological features of the bark and the presence of calcium oxalate crystals in the wood parenchyma cells. However, calcium oxalate crystals are not unique to the genus *Pinus* and occur in the wood of living species of *Ginkgo* (maidenhair tree), *Abies* (fir) and *Pseudolarix* (golden larch) (40).

Although anatomical, morphological, and chemical features of the resinites and resin-bearing woods from the Baltic region provide good evidence that the identity of the amber producing tree is a member of the Pinaceae, it has generally been thought that the tree is an extinct species of *Pinus* (14, 21-24). Scientists have always considered the resin-producing capability of common or economically important living species to be significant in their attempt to identify the resin-producing tree. Rather than systematically analyzing the resin produced by each living species of conifer, at least within the Pinaceae, the search has been limited to a few species, such as *Pinus palustris*, *P. caribaea*, and *P. elliottii*, that are able to produce considerable amounts of resin (41). Consequently, species of uncommon or relictual genera such as *Keteleeria*, *Cathaya*, and *Pseudolarix* have never been considered as a possible source of the amber.

Experimental

Samples. The collection site, which is informally referred to as the fossil-forest site is located east of the Geodetic Hills at 79°55'N, 89°02'W on eastern Axel Heiberg Island (Figure 2). The sediments are comprised of interbedded sandstone, mudstone, siltstone, and lignite sequences. Autochthonous leaf-litter mats and mummified wood are commonly associated with the coal seams and represent the *in situ* forest-floor remains of poorly drained, low energy meander plain swamps (Figure 3) (11-13, 42, 43). Megafossil diversity and abundance data from a number of litter mats indicate *Metasequoia* (dawn redwood) and *Glyptostrobus* (Chinese swamp cypress), both members of the conifer family Taxodiaceae (redwood family), were the dominant vegetational constituents of these regional swamp forest communities (11, 42).

Extensive late Cenozoic and Quaternary erosion has resulted in widespread exposure of the fossils contained within the leafy litter mats. Unassociated resinite "balls" as large as 4 cm in diameter (Figure 4) and resinite associated with wood (Figure 5), cones and cone scales (Figures 6-8) were collected from a number of localities.

Analytical Procedures. Pyrolysis-gas chromatographic-mass spectrometric analyses were carried out as follows: Resinite (0.5-1mg) was placed in a quartz pyrolysis tube and pyrolysed using a CDS pyroprobe pyrolyser directly coupled to the injection port of an HP 5890 (II) GC. All pyrolyses discussed in this report were carried out at 480°C in the presence of excess tetramethyl ammonium hydroxide (TMAH) (2). It is noteworthy that for these analyses it was necessary to crush the resinites rich in succinic acid in order to obtain useful analyses. Pyrolysis of the larger pieces resulted in incomplete methylation of the succinic acid and poor chromatographic behavior of the monomethyl succinate fraction. The resulting pyrolysate was then chromatographed using a 60m DB-1701 capillary GC column programmed as follows: Initial temp. = 40°C, initial time = 1.5 min., ramp rate = 4°C/min., final temp. = 280°C, and minimum final time = 18.5 min. The pyrolysate was chromatographed directly into the ion source of an HP 5971 mass selective detector. Peak assignments were based on interpretation, comparison with literature data, and comparison and co-elution with authentic standards whenever possible. Additional details of the techniques used in these analyses have been reported elsewhere (2). Details of the mass spectra of previously unreported compounds are given in Appendix I.

Results and Discussion

The primary aim of this study was to characterize fossil resins associated with well-defined paleobotanical remains. This objective was derived, in part, from preliminary analysis of unassociated resinites collected at the Axel Heiberg Island site, and forms part of a larger, more general global survey of the structural characteristics of fossil resins (3-5, 7).

Py-GC-MS analysis of the unassociated resinites indicated that most were closely comparable in structural and compositional characteristics, and therefore almost certainly derived from a common botanical source. Representative data for three of these unassociated resinites are illustrated in

Figure 9. The most significant find in these data is the presence and abundance of succinic acid (observed as its dimethyl ester) in the pyrolysates of most of these samples (see Figure 9 a, b). Succinic acid is a major constituent of Succinite and related Baltic Ambers, but is only rarely reported in other ambers (44). The presence of succinic acid in these resinites, and the potential for locating other succinic acid-containing resinites in unambiguous association with identifiable macrofossil remains suggested a possibility for identifying the botanical source for Baltic Amber, and was, therefore, of great interest.

Our initial efforts focused on collecting and analyzing resinite samples which could be unambiguously associated with identifiable fossil woods. Ultimately, four samples identified as *Metasequoia* (Hayashi, K., Ehime University, personal communication 1994) with large resinite-filled cysts were collected and analyzed. Py-GC-MS results from two of these samples are illustrated in Figure 10. Data for the remaining samples were closely comparable with those illustrated in Figure 10. The pyrolysates of all four samples, which are typical of relatively immature Class Ib resinites, contain characteristic bicyclic products derived from communic acid and communol moieties within their macromolecular structures. A number of readily assignable mono- and diterpenoids which were undoubtedly occluded within the macromolecular network are also observed. Disappointingly, none of these resinites contained any trace of succinic acid. Nevertheless, comparison of these data with those obtained for the unassociated resinite illustrated in Figure 9c suggests this unassociated resinite was likely derived from *Metasequoia*.

Attempts to collect additional bled resinite samples associated with identifiable fossil woods of other species were unsuccessful. However, numerous *Pinus* (pine), and *Metasequoia* cones, and *Pseudolarix robusta* and *P. wehrlii* (golden larch) cone scales were collected, and many of these retained small resinous inclusions within the resin canals (Figures 6-8). As noted by Langenheim (30), it is important to take into account the nature of the resin producing organ in assessing the results of comparative studies of resins and ambers. In the present study, it has been found that the structural and compositional characteristics of each of the cone and cone-scale resinites analyzed was directly comparable to those of either (i) one of the associated or unassociated bled resinites, or (ii) known modern and fossil bled resins from other sites. Hence, by analysis of the known cone and cone-scale resinites and associated bled resinites, it is possible to unambiguously identify the source of each of the unassociated bled resins. The results of analysis of resinite samples from *Pinus* and *Metasequoia* cones, and *Pseudolarix* cone scales are illustrated in Figure 11.

Data obtained from the *Pinus* cone resinites indicate the presence of abietane, pimarane and isopimarane skeleton diterpenoids - typical of many living pine resins and closely comparable with other Class V resinites (2, 3). The results for *Metasequoia* cone resinites show a typical distribution of diterpenoid and diterpenoid-derived products, and characteristic bicyclic acids derived from communic acid monomers (presumably at least partially incorporated into a polymeric structure, although both *cis*- and *trans* communic acid methyl esters are observed in the pyrolysate). These data are consistent with those obtained for the *Metasequoia* bled resinites illustrated in Figure 10 and the unassociated resinite illustrated in Figure 9c, now also assigned to *Metasequoia*.

Data for the *Pseudolarix* cone-scale resinites, illustrated in Figure 11, indicate succinic acid is a major component of these resinites. These resinites also contain small amounts of bicyclic hydrocarbons derived from labdanoid structures present within the resinite, and significant amounts of abietane skeleton diterpenoids, including methyl ether analogues of abietol and dehydroabietol. These results are consistent with those obtained for a large number of the unassociated resinites collected and analyzed from the Axel Heiberg Island site and those illustrated in Figure 9a and b. These data indicate that the unassociated resinites are likely to have been derived from *Pseudolarix*.

It is noteworthy that *Pseudolarix* resinites are the most abundant of the unassociated resins found at the Axel Heiberg Island site, despite the fact that macrofossil evidence indicates *Pseudolarix* was a uncommon member of the original vegetational mosaic (43, 45). This suggests that *Pseudolarix*, at least in this environment, was a relatively copious resin producer.

At least two distinct species of *Pseudolarix* were contemporaneous in a number of high-latitude forest communities, including those present at the fossil forest site (45). Species discrimination is based on differences in the length and morphology of the bract subtending the cone scale (Figure 12). One species, *Pseudolarix robusta*, a short-bracted form, is similar in appearance to the living species *P. amabilis* and may be closely related. The second species, *P. wehrlii*, a long-bracted form, appears to represent an extinct lineage. Relative macrofossil abundance data indicates that *P. robusta* was more abundant than *P. wehrlii*. For the purposes of comparison with the bleed-resinite data, cone-scale resinite from both *P. wehrlii* and *P. robusta* were collected and analyzed. The results of these analyses are illustrated in Figure 13.

Based on the results illustrated in Figure 13, it is apparent that *P. wehrlii* is likely to have been the source of the unassociated *Pseudolarix* resinites. Although resinites of both *P. robusta* and *P. wehrlii* contain succinic acid, it is clear that this acid is only a minor component in the *P. robusta* resinite, whereas it is the predominant product in *P. wehrlii* resinite. Moreover, the two abietane skeleton methyl ethers (observed in significant abundance in the unassociated *Pseudolarix* resinites) are major components in the pyrolysate of the *P. wehrlii* resinite, but are very minor components or are absent in the pyrolysate of *P. robusta* resinite.

Given the presence of succinic acid and characteristic labdanoid derived bicyclic products in the pyrolysates of these *Pseudolarix* resinites, comparison of these ambers with succinite is inevitable. In order to address the question of the relationship, if any, between these *Pseudolarix* derived resinites, succinite, and related Baltic Ambers, a number of comparative analyses were undertaken. It was apparent from the preliminary comparative analyses that significant differences exist between the *Pseudolarix* resinites characterized here and typical Class Ia resinites. These differences were initially observed as inconsistencies between the chromatographic behavior of products identified by mass spectrometry as characteristic bicyclic alcohols and methyl ethers. These inconsistencies suggest differences between the polylabdanoid macromolecular structure of these *Pseudolarix* resinites and normal Class Ia resinites. Therefore, in order to establish the precise nature of these products, and hence establish the precise structural characteristics of the macromolecular structures of the *Pseudolarix* resinites, a series of co-pyrolysis experiments were completed to compare the

behavior of the *Pseudolarix* derived products with analogous products from other, well characterized, resinites.

Partial results from these analyses are illustrated in Figure 14. These data compare the chromatographic behavior and distributions of C_{15} bicyclic alcohols observed in the pyrolysate of unassociated *Pseudolarix* resinites with those observed in experiments in which *Pseudolarix* resinite was co-pyrolysed with representative Class Ia, Ib and Ic resinites. The results indicate that the C_{15} alcohols seen in the pyrolysates of the *Pseudolarix* resinites are identical with those derived from Class Ic resinites. These characteristic alcohols are known to be derived from ozol, and are epimeric with the analogous communol derived C_{15} alcohols observed in Class Ia and Ib resinites. Similar results are obtained from analysis of the distributions of C_{14} alcohols and analogous C_{14} and C_{15} bicyclic methyl ethers. (Characteristic bicyclic hydrocarbons derived from *regular* and *enantio* biformene precursors are enantiomeric and hence are not resolvable on normal chromatographic phases.) This result clearly differentiates these *Pseudolarix* resinites from Succinite and other Class Ia resinites which are derived from polylabdanoid structures based on *regular* labdanoid diterpenes, and hence precludes *Pseudolarix* as a direct source for Baltic Amber.

This observation inevitably raises the question: "*What relationship, if any, exists between the Pseudolarix resinites characterized in this study, and succinite and other Class Ia ambers*". The fact that both the *Pseudolarix* resinites described here and Class Ia resinites, are derived from polylabdanoid resins, and both incorporate significant amounts of succinic acid, strongly suggests that some relationship is likely. Although the precise nature of this relationship cannot be determined based on the limited data presently available, a number of possibilities exist, and the relative merits of each are worthy of discussion.

1. It is possible that one of the two known fossil species of *Pseudolarix* existed throughout the circumpolar regions during the Paleogene (ca. 65-22 million years) and that distinct ecotypic populations existed; the Axel Heiberg Island population producing the *enantio* polylabdanoid resin and the Baltic population producing a *regular* Class Ia resin.

To the present authors, this scenario seems unlikely for two reasons. First, there are no reports of ecotypic populations of a species, or even closely related species, producing qualitatively different resins. Although distinct populations of a species may produce distinguishable resins (30) the differences are quantitative rather than qualitative. That is, rather than significant differences in the macromolecular structure, the structural and compositional characteristics of the resins are limited to differences in the relative abundances of specific components or incorporation of components with small structural modifications such as double bond isomers or differing degrees of oxidation. Second, *Pseudolarix* does not appear in the Baltic region until the latest Oligocene/early Miocene (ca. 22 million years) (45).

2. A third species of *Pseudolarix*, endemic to the Baltic region, evolved and produced a *regular* polylabdanoid resin that incorporated succinic acid into its macromolecular structure.

This scenario is not supported by the known fossil record. Of the nearly seventy reports of *Pseudolarix* fossils in the literature only two distinct species have been recognized (45). It seems unlikely that a large population of a third species of *Pseudolarix* could have existed in and around the Baltic region for millions of years without leaving evidence of its occurrence.

3. Succinite and related Class Ia resins were produced by an unknown species of vascular plant which has subsequently evolved and given rise to one or more living representatives that no longer have the ability to produce resins that incorporate succinic acid into their macromolecular structure.

The suggestion that Baltic amber may be derived from an extinct species of *Agathis* is based on this concept. A specific discussion of difficulties with the *Agathis*/araucarian origin of Baltic amber has already been provided above. In general however, in the absence of additional data from species specific resinites, it is not possible to determine whether any living species producing resins based on regular polylabdanoid structures ever had ancestral species that produced resins incorporating succinic acid. It is possible that evolutionary pressures have caused this characteristic to be lost, but at least in the cases of the resinites characterized in this study, the basic structural characteristics of the *Pseudolarix*, *Pinus*, and *Metasequoia* resinites appear to have been conserved, at least, over the last 45 million years.

4. That polylabdanoid resinites incorporating succinic acid into their macromolecular structure independently evolved twice.

Labdane diterpenoids are relatively complex molecules, which require considerable biosynthetic "dexterity" in their natural preparation. It is, therefore, highly unlikely that resins based on polylabdanoid macromolecular structures have evolved twice. There is a greater possibility that the characteristic of incorporation of succinic acid may have evolved independently in two distinct lineages, but even this possibility seems remote.

5. *Pseudolarix* and the species which produced the Baltic Amber are derived from a common ancestor which probably produced a non-specific polylabdanoid resin (i.e., including both *regular* and *enantio* labdanoids) and which incorporated succinic acid into the macromolecular structure of the resin..

This interpretation seems most reasonable, at least in the opinion of the present authors. Given that both the Baltic Amber tree and *Pseudolarix* existed in the high latitudes of the Northern Hemisphere at about the same time, and that both produced resins based on polylabdanoid macromolecular structures, and that both incorporated succinic acid into these structures it seems reasonable to suggest that a phylogenetic relationship between these taxa exists.

Given the very small number of resinites, especially pre-Tertiary resinites, which have been characterized at a molecular level, it is not surprising that examples of an appropriate "precursor" resinite (non-specific polylabdanoid incorporating succinic acid) have not been identified in the

fossil record, although at least one example of a fossil resin incorporating both *regular* and *enantio* labdanoids is known (7).

Conclusions

The compositional and structural characteristics of fossil *Pinus*, *Metasequoia*, and *Pseudolarix* resins collected from the middle Eocene deposits on Axel Heiberg Island, have been characterized using Py-GC-MS. Bled and cone resinites from *Metasequoia* were found to be typical of Class Ib resinites, and those of *Pinus* were found to be typical of Class V resinites and closely comparable with living pine resins.

The *Pseudolarix* resinites characterized in this study, however, were found to be a previously unknown form of polylabdanoid resinite. These samples were shown by Py-GC-MS to be based on a polylabdanoid macromolecular structure incorporating substantial amounts of succinic acid. However, unlike succinite and related Baltic Ambers (which can be described in an identical manner) which are derived from resins incorporating communic acid, communol, and analogous *regular* labdanoids, the labdanoid precursors incorporated into the polymeric structures of these samples are based on ozol and related *enantio* labdanoids.

The presence of succinic acid and the fact that both succinite and *Pseudolarix* resinites are derived from polylabdanoid resins, strongly suggests that a phylogenetic relationship exists between *Pseudolarix* and the species of trees which originally produced succinite. However, the precise nature of this relationship can not be unambiguously determined based on the data presently available. Given the differences in the configurations of the labdanoid diterpenes present in the polymeric structures of these two resinites, it is unlikely that succinite was produced by *Pseudolarix*. Nevertheless, it is possible that *Pseudolarix* and the trees which produced the original source resin for Baltic Amber were related, possibly through a common ancestor. Additional analysis of contemporary and fossil resins, especially those associated with well-defined paleobotanical remains may help to further resolve this question.

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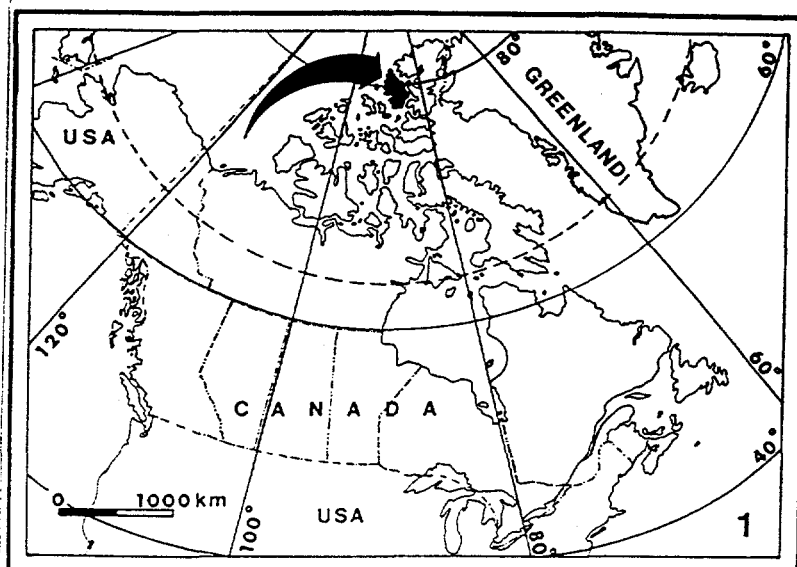
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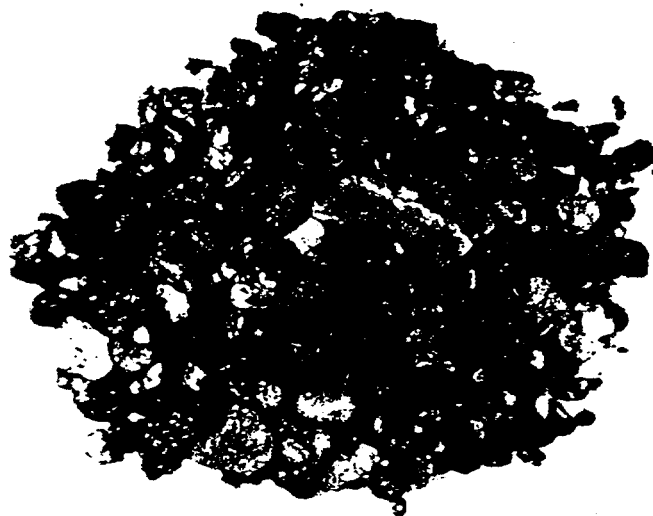
Figure Captions

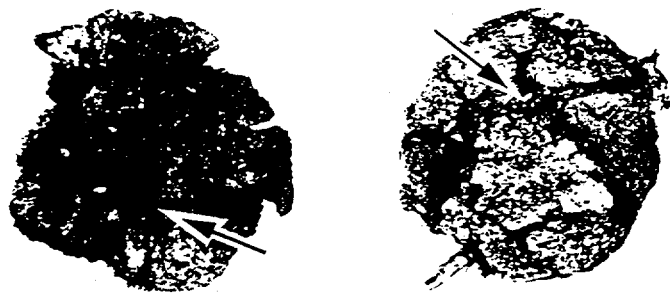
1. Map of Canada showing the location of Axel Heiberg Island in the Canadian Arctic.
2. A view of the Axel Heiberg Island site. The black bands (arrows) are coal seams that represent the remains of swamp forest communities.
3. A coal seam showing the portion of the seam from which forest-floor litter mats containing well-preserved fossil plants commonly occur.
4. Unassociated resinite "balls".
5. *Metasequoia* wood with an exposed resin-filled cyst, X 1.6.
6. *Metasequoia* cones showing extruded resin (arrows), X 1.6.
7. *Pinus* cones showing extruded resin (arrows), X 2.0.
8. *Pseudolarix* cone scales showing resin still contained within the resin canals (arrows), X 2.0.
9. Py-GC-MS total ion chromatograms illustrating the distributions of products observed in pyrolysates of three Unassociated resinite "balls". Based on analysis of associated resinites from the same site (see main text) these are identified as follows: A and B unassociated *Pseudolarix* resinite; and C unassociated *Metasequoia* resinite.
10. Representative Py-GC-MS total ion chromatograms obtained by analysis of *Metasequoia* wood resinite.
11. Py-GC-MS total ion chromatograms illustrating the product distributions observed in the pyrolysates of cone scale resinites of: *Pinus*; *Metasequoia*; and *Pseudolarix*.
12. Cone scales of *Pseudolarix robusta*, a short bracted species (left) and *P. wehrlii*, a long bracted species (right).
13. Comparison of the distributions of products observed in PY-GC-MS analysis of cone scale resinites of *Pseudolarix robusta* and *Pseudolarix wehrlii*.
14. Partial Py-GC-MS chromatograms illustrating the distribution of C₁₅ bicyclic alcohols in the pyrolysates (and co-pyrolysates) of *Pseudolarix* resinite and representative Class Ia, Ib and Ic. resinites from other sites.

Figures.

**THE NATURE AND FATE OF NATURAL RESINS IN THE GEOSPHERE. VI.
ANALYSIS OF FOSSIL RESINS FROM AXEL HEIBERG ISLAND
CANADIAN ARCTIC.**





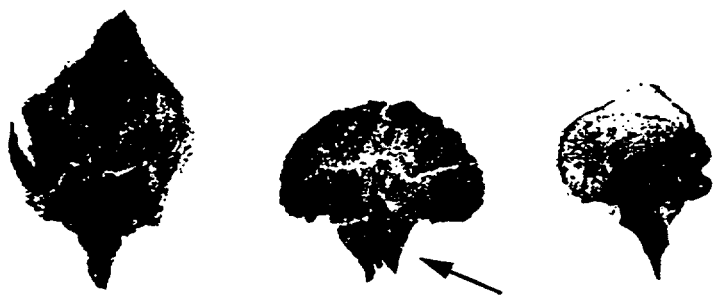




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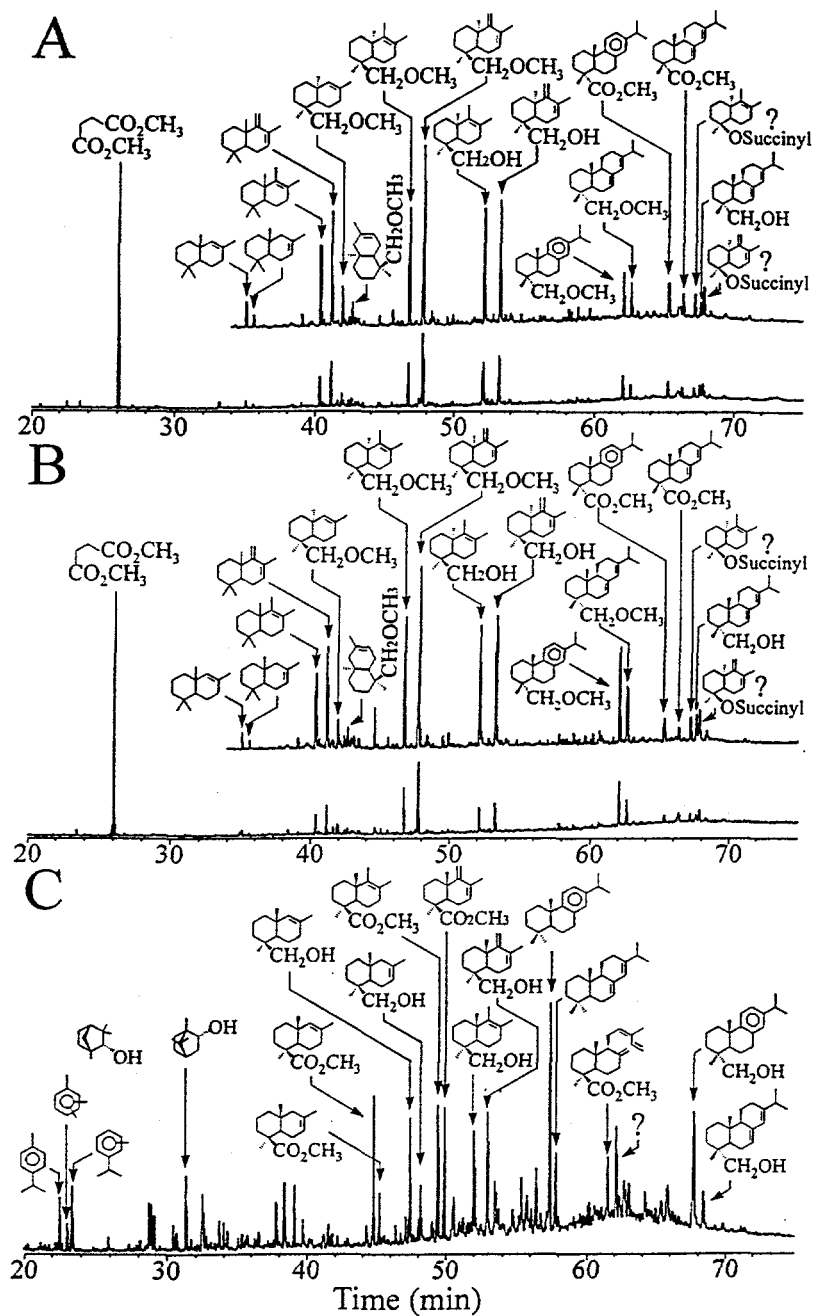
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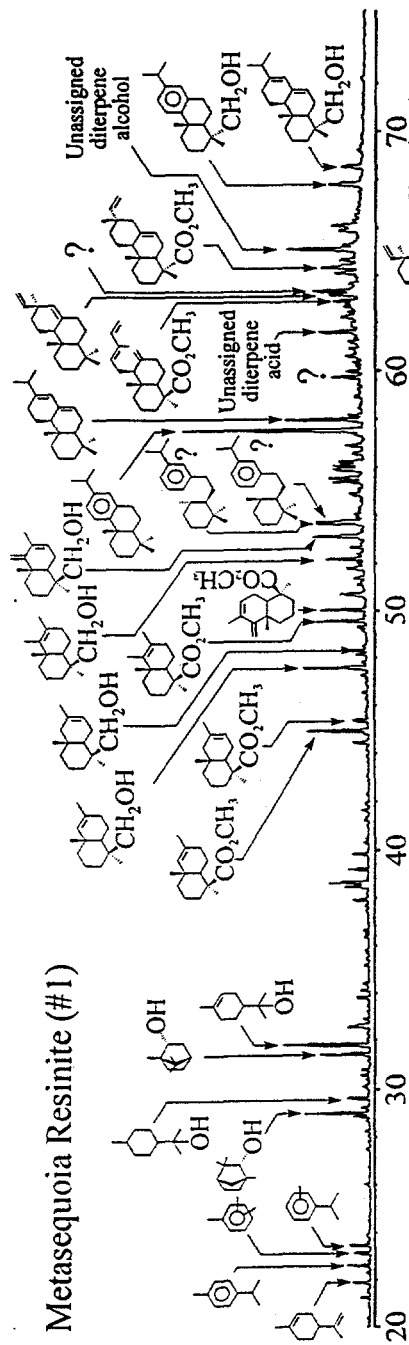
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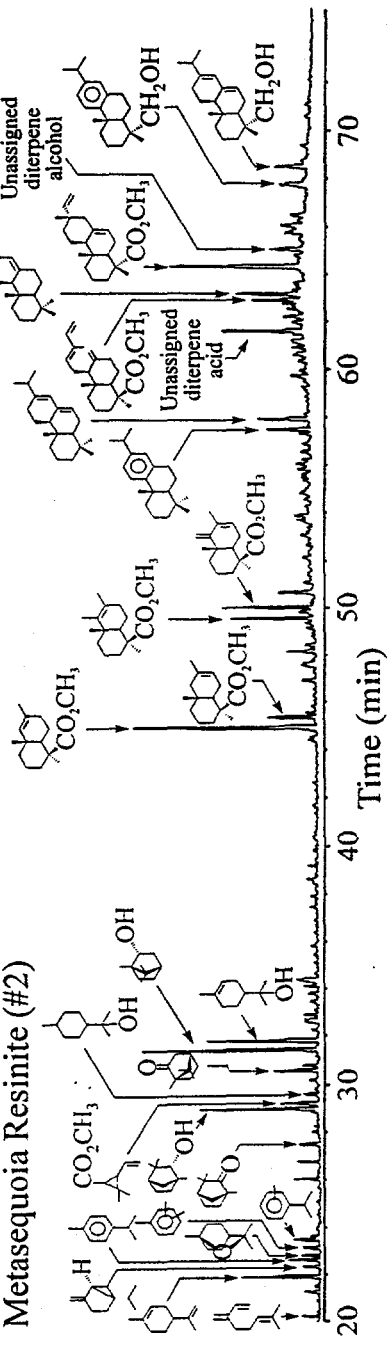
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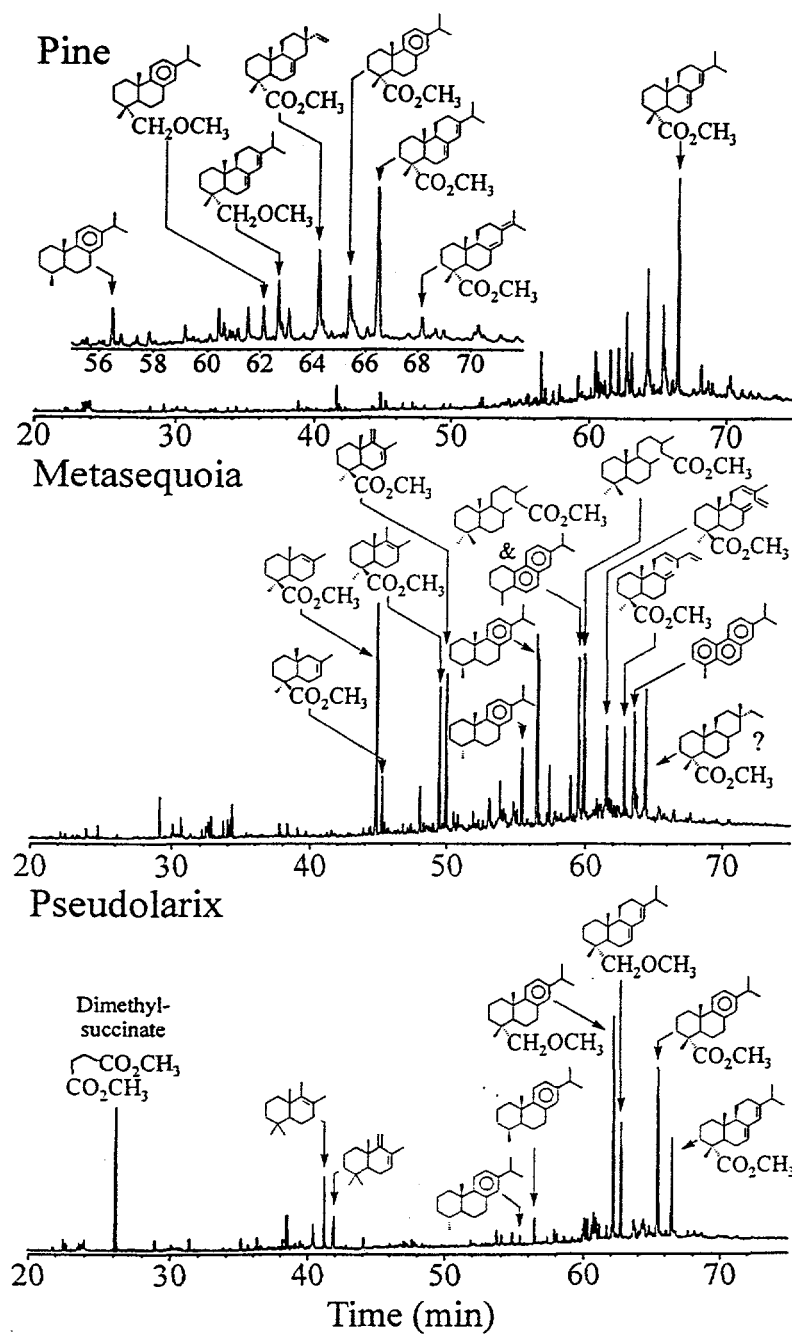


Metasequoia Resinite (#1)

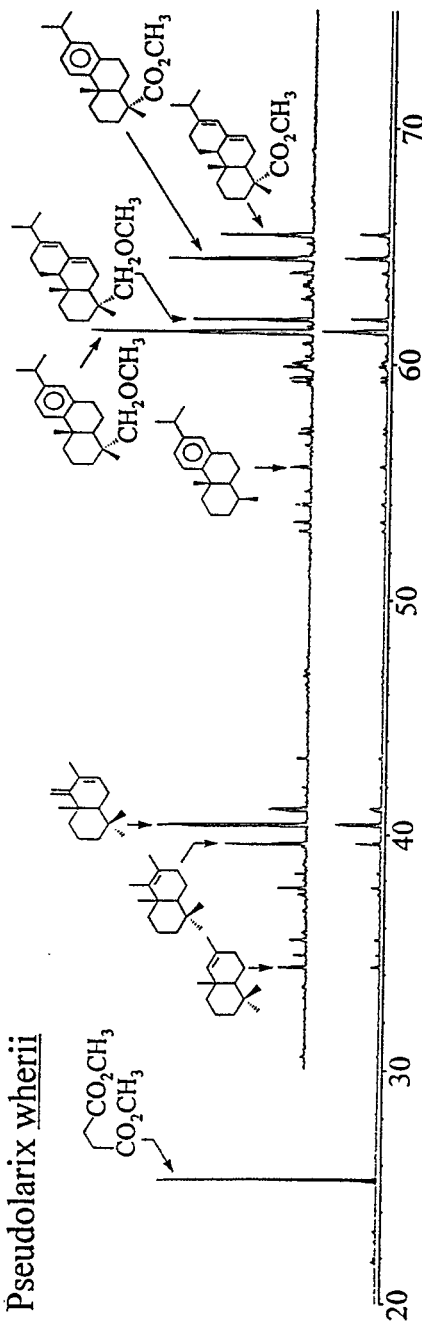


Metasequoia Resinite (#2)

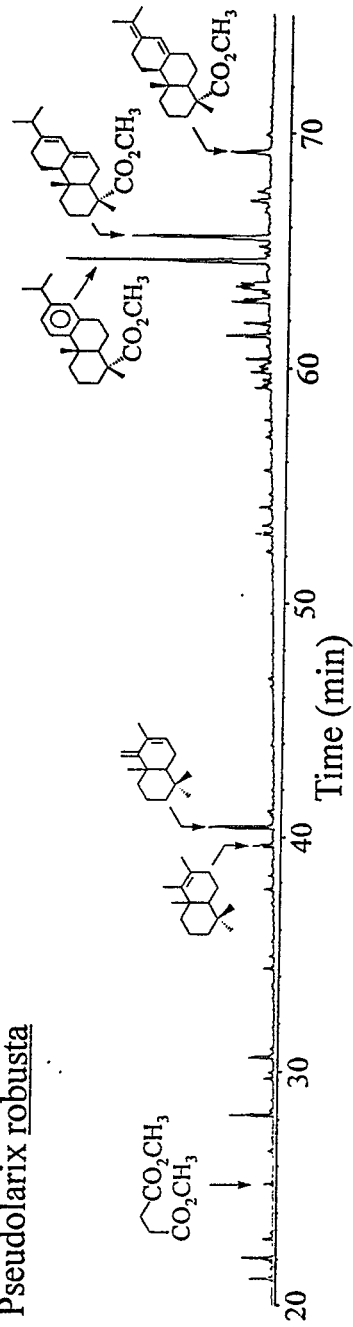


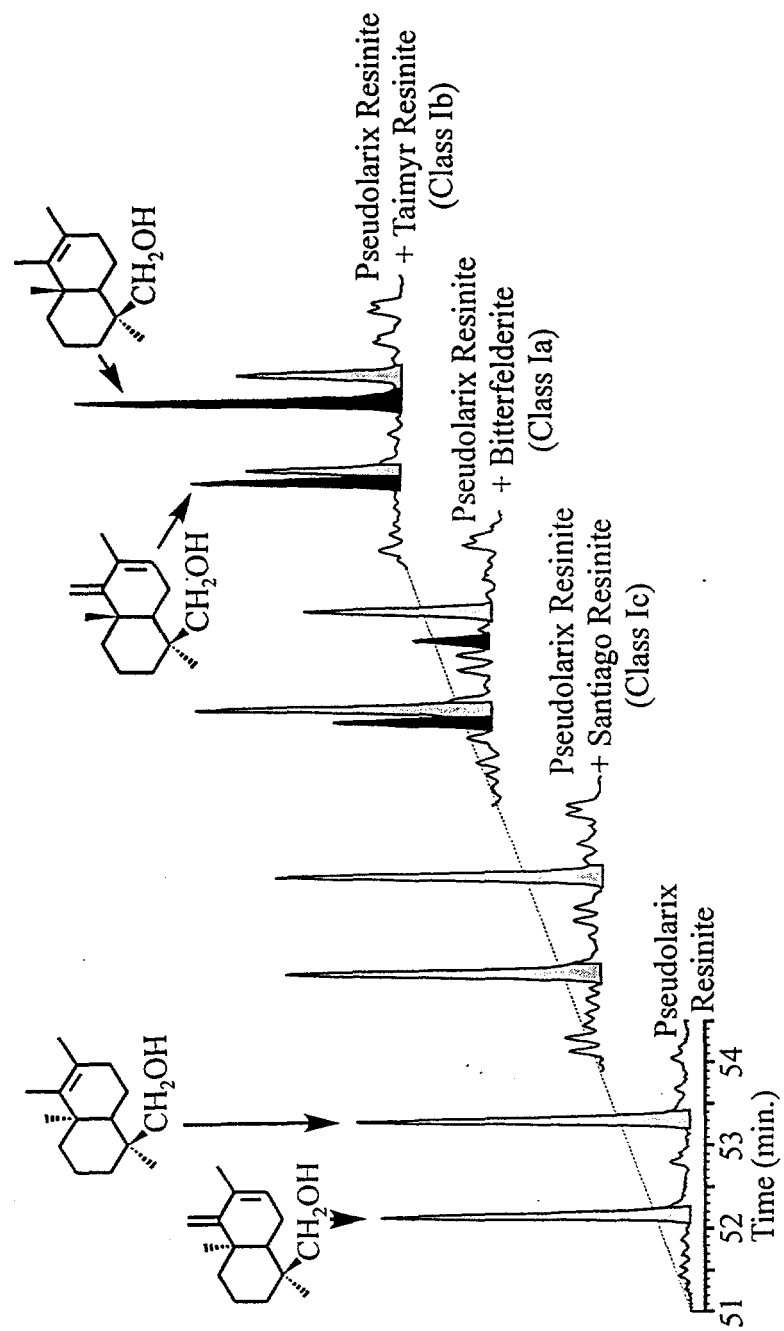


Pseudolarix wherrii



Pseudolarix robusta



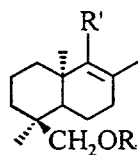


Appendix I

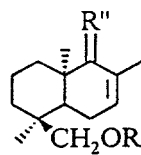
THE NATURE AND FATE OF NATURAL RESINS IN THE GEOSPHERE. VI. ANALYSIS OF FOSSIL RESINS FROM AXEL HEIBERG ISLAND CANADIAN ARCTIC.

Mass spectra of previously unreported compounds

Compound	MS Data and Assignment
I	222 (6), 207 (5), 190 (25), 177 (64), 175 (51), 161 (14), 147 (10), 133 (9), 122 (12), 121 (22), 119 (18), 107 (56), 105 (32), 95 (100), 93 (31), 91 (36), 81 (40), 79 (29), 77 (19), 69 (10), 67 (19), 55 (27), 53 (11), 45 (32), 41 (31). Naphthalene-1,2,3,4,4a,7,8,8a-octahydro-1-methoxymethyl-1,4a,6-trimethyl [1S, 4aS, 8aS]
II	222 (15), 190 (40), 177 (39), 175 (22), 161 (31), 133 (35), 121 (31), 120 (42), 119 (70), 109 (46), 107 (61), 105 (85), 97 (74), 95 (100), 93 (41), 91 (55), 81 (64), 79 (40), 77 (36), 69 (19), 67 (34), 65 (16), 55 (67), 45 (46), 41 (63). Naphthalene-1,2,3,4,4a,5,8,8a-octahydro-1-methoxymethyl-1,4a,6-trimethyl [1S, 4aS, 8aS]
III	236 (17), 221 (23), 204 (8), 191 (43), 189 (62), 175 (8), 161 (21), 149 (18), 148 (15), 147 (18), 135 (42), 133 (29), 121 (84), 119 (47), 109 (100), 107 (43), 105 (34), 95 (75), 93 (36), 91 (45), 83 (19), 81 (28), 79 (32), 77 (23), 69 (14), 67 (31), 65 (11), 59 (13), 57 (11), 55 (42), 53 (17), 45 (51), 41 (47). Naphthalene-1,2,3,4,4a,7,8,8a-octahydro-1-methoxymethyl-1,4a,5,6-tetramethyl [1S, 4aS, 8aS]
IV	234 (22), 219 (4), 202 (10), 189 (15), 108 (41), 173 (30), 161 (18), 159 (35), 147 (19), 146 (28), 145 (47), 133 (82), 132 (100), 131 (29), 120 (25), 119 (73), 117 (25), 107 (53), 105 (53), 98 (15), 97 (10), 95 (19), 93 (24), 91 (65), 81 (18), 79 (32), 77 (35), 67 (15), 65 (14), 55 (37), 53 (17), 45 (51), 41 (40). Naphthalene-1,2,3,4,4a,5,8,8a-octahydro-1-methoxymethyl-1,4a,6-trimethyl-5-methylene [1S, 4aS, 8aS]
V	336 (4), 204 (28), 189 (100), 175 (8), 161 (23), 148 (26), 147 (20), 135 (15), 134 (14), 133 (45), 121 (43), 119 (43), 115 (73), 109 (49), 107 (25), 105 (25), 95 (43), 93 (24), 91 (24), 83 (21), 81 (16), 79 (20), 67 (20), 59 (26), 55 (69), 41 (27). 1-Naphthalenemethanol-1,2,3,4,4a,7,8,8a-octahydro-1,4a,5,6-tetramethyl monomethyl succinyl ester [1S, 4aS, 8aS]
VI	334 (0), 203 (10), 202 (21), 187 (65), 173 (28), 159 (27), 146 (50), 145 (36), 133 (78), 132 (100), 120 (21), 119 (46), 117 (16), 115 (69), 107 (21), 105 (32), 95 (14), 93 (14), 91 (36), 79 (21), 77 (15), 59 (30), 55 (61), 41 (21). 1-Naphthalenemethanol-1,2,3,4,4a,5,8,8a-octahydro-1,4a,6-trimethyl-5-methylene monomethyl succinyl ester [1S, 4aS, 8aS]



I: $R=CH_3$, $R'=H$
 III: $R=CH_3$, $R'=CH_3$
 V: $R=CO(CH_2)_2CO_2CH_3$, $R'=CH_3$



II: $R=CH_3$, $R''=H_2$
 VI: $R=CH_3$, $R''=CH_2$
 VI: $R=CO(CH_2)_2CO_2CH_3$, $R''=CH_2$