

The nature and fate of natural resins in the geosphere—II.* Identification, classification and nomenclature of resinites

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Abstract—A classification scheme for resinites is proposed. Most resinites may be classified, on the basis of structural characteristics, into one of four classes. In order to exclude the effects of structural changes which reflect differences in the relative maturity of different samples, classifications are based on the structural character of the original resin from which the resinite was derived. In all samples characterized to date, this may be reasonably inferred from analytical data concerning the structure and composition of the individual sample. Class I resinites, which are by far the most abundant form of resinite in the geosphere, are derived from resins based primarily on polymers of labdatriene (diterpenoid) carboxylic acids, especially communic or ozic acids. Class II resinites are derived from resins based on polymers of sesquiterpenoid hydrocarbons, especially various isomers of cadinene. Class III resinites are natural polystyrenes. Class IV resinites are the least well characterized of the four resinite classes defined, but appear to be largely non-polymeric materials, dominated by sesquiterpenoids based on the cedrane carbon skeleton. Resinites belonging to Class I are further subdivided into three sub-classes on the basis of details of their composition. Class Ia resinites, which include succinite and related “Baltic ambers”, are derived from resins based primarily on communic acid and incorporate significant amounts of succinic acid into their macromolecular structure. Class Ib resinites are also derived from resins based primarily on communic acid, but do not contain succinic acid. Class Ic resinites are derived from resins based primarily on labdatrienoic acids of the *enantio* series, especially ozic and/or zanzibaric acids. The structure, origin, and identification of resinites of each class are discussed. The effects of maturation on the structure of Class I resinites, and the consequences of these changes for the recognition and classification of this form of resinite are also briefly discussed.

Key words—resinite, amber, classification, pyrolysis, PY–GC–MS, NMR, maturation

INTRODUCTION

Sedimentary organic matter derived from the resins of higher plants is normally referred to by the general 34, petrographic classification “resinite”, or by the common name for these materials, “amber”. The existence of a number of chemically distinct forms of resinite is readily apparent from the literature (Gough and Mills, 1972; Mills *et al.*, 1984; Thomas, 1969, 1970; Brackmann *et al.*, 1984; van Aarssen *et al.*, 1990; Grimaldi *et al.*, 1989; Grantham and Douglas, 1980), and is widely recognized amongst scientists concerned with the characterization of these materials. The existence of distinct groups of resinites with specific geographical and/or botanical affinities has also been recognized (Paclt, 1953; Broughton, 1974), as has the need for an established convention for differentiation of resinites of distinct structural character (Meuzelaar *et al.*, 1991). To date however, no such convention has been established. A previous attempt to develop a classification system for resinites based on botanical origin (Paclt, 1953), has not

proven to be generally useful, due to the high level of uncertainty concerning the precise botanical origins of many resinites. (Since publication of this report (Paclt, 1953), considerable progress has been made in determining the botanical origins of a number of resinites (Langenheim and Beck, 1985). However, considerable uncertainty concerning the botanical origins of many resinites still exists. Due to (i) the structural similarity of many modern resins from different species, and (ii) the effects of maturation—briefly described later; it seems unlikely to the present authors that any classification system based solely on botanical origin will ever be generally applicable.) Herein, we propose a global classification system for resinites based on the structural characteristics and composition of these materials. An earlier report of the preliminary form of this classification system for resinites has appeared elsewhere (Anderson and Winans, 1991a). This paper is intended to report the scope and basis of the proposed classification system; to extend the system to incorporate an additional resinite class not described in our preliminary report; and to describe experimental parameters, as far as they are thus far defined, for the classification of resinites. Specific details of the results of analysis of individual resinite samples will be reported separately.

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EXPERIMENTAL

In some samples, surface oxidation was significant due to prolonged storage in air after recovery from the parent coal or sediment. Therefore, in order to minimize the effect of oxidative weathering, all analyses were carried out using samples taken from freshly exposed surfaces.

Pyrolysis-Gas Chromatographic-Mass Spectroscopic (Py-GC-MS) analyses were carried out using a CDS Pyroprobe pyrolysis system fitted to an HP 5890 GC which was directly coupled to an HP 5970 MSD. Pyrolysis temperature was typically = 480 °C, although additional studies using $T_{py} = 300^{\circ}\text{C}$ and $T_{py} = 540^{\circ}\text{C}$ were also undertaken. Simultaneous pyrolysis methylation (SPM) procedures were employed in order to methylate acidic products and thereby facilitate GC separation of pyrolysate components (Challinor, 1989, 1991). 60 m × 0.25 mm (i.d.) DB-1701 and DB-5 capillary columns, programmed as follows, were used for all analyses described herein: $T_{(\text{initial})} = 40^{\circ}\text{C}$ (1.5 min), ramp rate = 4 °C/min, $T_{(\text{final})} = 280^{\circ}\text{C}$ (DB-1701) $T_{(\text{final})} = 310^{\circ}\text{C}$ (DB-5) Helium carrier gas was used for all analyses. Additional details of the experimental procedures employed, and the basis for these is given elsewhere (Anderson and Winans, 1991b).

Cross polarization/magic angle spinning (CP/MAS) ^{13}C NMR spectra were obtained using a Bruker CXP-100 NMR spectrometer, operating at a field of 2.3 T (25.18 MHz for ^{13}C). Approximately 250 mg of sample was packed into a 300 μl ceramic sample rotor which was spun at about 4 kHz. The

operating conditions used in CP experiments included a spectral width of 10 kHz, a 90° proton pulse width of 4.5 μs (corresponding to a 60 kHz proton decoupling field), an acquisition time of 30 ms, and a total acquisition of 2–4 K transients. Contact time studies carried out on one resinite sample indicated that employing a single contact time of 2 ms allowed good quantitative estimates of the distribution of C functional groups. Chemical shifts are reported in ppm relative to tetramethylsilane (TMS), with *tetrakis*(trimethylsilyl)silane (Muntean *et al.*, 1988) used as a secondary reference material.

RESULTS AND DISCUSSION

Scope and basis of the proposed classification system

The classification system herein proposed is intended to recognize and delineate the existence of a number of discrete forms of resinite in the geosphere, and to provide a basis for uniform nomenclature of structurally related resinites. The proposed classification system is summarized in Table 1. For the purposes of this system, resinites are defined as solid, discrete organic materials found in coals and other sediments in macroscopic or microscopic form, which are derived from the resins of higher plants. This definition, therefore, specifically excludes paraffinic waxes and related materials which are also sometimes referred to as *lipid*- or *wax*-resinite (Stach *et al.*, 1982), and resin-derived organic materials which have become dispersed at a molecular level, and hence, no longer exist in the form of observable discrete bodies.

Table 1

Class I	All Class I resinites are derived from resins based on polymers of (primarily) labdatriene carboxylic acids.
Class Ia	Derived from resins based primarily on polymers of communic acid (I), partially copolymerized with communol. Significant incorporation of succinic acid, probably as a cross linking agent is characteristic. (Mills <i>et al.</i> , 1984/85; and others) <i>Examples:</i> Succinite (Baltic Amber), and many other (primarily) European ambers.
Class Ib	Derived from resins based primarily on polymers of communic acid (I), with varying degrees of copolymerization with communol. Succinic acid is absent. (Thomas, 1969, 1970) <i>Examples:</i> New Zealand resinites, Victorian Brown Coal resinites, and many others.
Class Ic	Derived from resins based primarily on polymers of ozic acid (IIa) and/or zanzibaric acid (IIb).* (Cunningham <i>et al.</i> , 1983; Mills and White, 1987) <i>Examples:</i> Resinities from Mexico and Dominican Republic, (some) African resinities, (Zanzibar, Kenya) <i>Nearest equivalent modern resins:</i> (includes Classes Ia, Ib and Ic). Various "Copals", esp. Manila Copal/Pontianak, Kauri Resin, Sandarac, Brazil Copal, Congo Copal <i>Most probable bonical affinities:</i> † <i>Araucariaceae</i> (esp. <i>Agathis</i>), <i>Leguminosae</i> (esp. <i>Hymenaea</i> , <i>Copaifera</i>), <i>Cupressaceae</i> , <i>Taxodiaceae</i> , and others.
Class II	Derived from resins based on polymer of bicyclic sesquiterpenoid hydrocarbons, esp. cadinene. Triterpenoid, including di-sesquiterpenoid component may also present probably mostly as occluded materials. (van Aarssen <i>et al.</i> , 1990, 1991; Meuzelaar <i>et al.</i> , 1991). <i>Examples:</i> Utah resinities, (some) Indonesian resinities. <i>Nearest equivalent modern resin:</i> "Damar". <i>Most probable botanical affinity:</i> † <i>Dipterocarpaceae</i> (esp. <i>Shorea</i>).
Class III	Basic structural character is Polystyrene (Grimaldi <i>et al.</i> , 1989; Langenheim, 1969). <i>Examples:</i> (some) New Jersey resinities, (some) German resinities (Siegburgite). <i>Nearest equivalent modern resin:</i> "Storax" (Sometimes = <i>Styrax</i>). <i>Most probable botanical affinity:</i> † <i>Hammelidaceae</i> (esp. liquidambar).
Class IV	Basic structural character is sesquiterpenoid, especially based on the Cedrane (IX) skeleton. Apparently non-polymeric (Streibl <i>et al.</i> , 1976; Grantham and Douglas, 1980). <i>Examples:</i> Bovey-Tracy retinilite, Ionite, Moravian resinities. <i>Nearest equivalent modern resin:</i> Unknown. <i>Most probable botanical affinity:</i> † Unknown.

*See discussion in text.

†Based on nearest equivalent modern resins.

(The term "resin" as used herein refers to modern plant resins.)

The purpose of the present study is to provide a rational basis for the recognition and classification of resinates on the basis of the nature of their organic molecular structure. This system does not attempt to address classification of modern plant resins. It is apparent from the limited diversity of the nature of resinates (described below and summarized in Table 1) that many forms of natural resins are unable to persist in the environment and/or survive diagenetic processes in a recognizable form. Hence, only resins which persist in the geosphere are described by this classification system. Furthermore, only resinates which are known from more than one deposit or site are included in the scheme. Unique samples are regarded as reflecting specialized depositional and/or sedimentary environments which are not generally representative, and are therefore not at present described by this classification system, which is intended to be general in scope. It is likely however, that as the number of samples subjected to detailed chemical analyses increases, additional forms of resinite will be recognized, and it may therefore become necessary in the future to revise and extend the system outlined in Table 1.

No attempt is made to classify resinates on the basis of provenance i.e. geographic origin. A large body of data concerning identification of the provenance of resinite (amber) samples, primarily for archaeological purposes, has been reported by other workers using a variety of analytical techniques [i.r.: Beck, 1986 (and references cited therein); Broughton, 1974; NMR: Lambert and Frye, 1982; Lambert *et al.*, 1985, 1988, 1989, 1990; Py-MS: Poinar and Haverkamp, 1985; Py-GC: Shedrinski *et al.*, 1987/88, 1989, 1989/90/91]. However, much of the data and many of the analytical techniques described herein may also be relevant for the purposes of provenance analysis.

Like all forms of sedimentary organic matter, the structure and composition of resinates undergo systematic changes over the course of geologic time. The rates at which these processes proceed are almost certainly strongly temperature dependent, and therefore, the structure and composition of any given resinite will depend on: (i) the structure and composition of the original resin from which the resinite is derived; and (ii) the age and thermal history of the sample. For this reason, it is inappropriate to describe structural changes in resinates as a function of the "age" of the sample. Rather, it is more appropriate to describe changes in the structure and composition of these materials as a function of "maturity", which reflects both age and thermal history, as is usual in discussions of the structural changes which occur in other types of sedimentary organic matter (e.g. Tissot and Welte, 1984).

As a consequence of changes in the structures and compositions of resinates due to the effects of maturational "forces", it is not reasonable to develop a

classification system for resinates which is based solely on structural or compositional characteristics as they presently occur, since such differences may reflect nothing more than differences in the level of maturity of samples of closely similar origin. We have found however, that even up to quite high levels of maturity, the degree of structural character retained by resinates is sufficient to reasonably establish the nature of the original resins from which distinct classes of resinates have developed. The classification system described in Table 1 is, therefore, based on the principal structural character of the original resin from which any given resinite has been derived.

Class I resinates

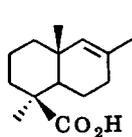
On the basis of data reported in the literature (Langenheim, 1969, 1990; Thomas, 1969, 1970; Mills *et al.*, 1984/85; Beck, 1986 and references cited therein; Cunningham *et al.*, 1983; Lambert and Frye, 1982; Lambert *et al.*, 1985, 1988, 1989, 1990; Anderson *et al.*, 1989), and also on the results of the authors' own studies (described in part herein and Anderson *et al.*, unpublished results) it is apparent that Class I resinates are by far the most widespread and abundant form of resinite in the geosphere. The structure and composition of a number of resinates belonging to this class have received considerable attention (Beck *et al.*, 1965; Mills *et al.*, 1984/85; Thomas, 1969, 1970; Cunningham *et al.*, 1983; Mills and White, 1987) and it has been established that resinates of this class are derived from resins based primarily on polymers of labdatriene diterpenoid carboxylic acids, especially various isomers of: communic acid (I), and ozic acid (IIa) and/or zanzibaric acid (IIb) (see Scheme 1) Appendix Note 1. Modern resins based on these compounds are produced, often in significant amounts, by a number of plant taxa, including; but not restricted to; *Araucariaceae*, *Leguminosae*, and *Cupressaceae*. These modern resins have been investigated by a number of workers, and hence, considerable detail of the formation and structure of polymers of these compounds has been reported (Carman *et al.*, 1970; Carman and Deeth, 1971; Thomas, 1966, 1969, 1970; Cunningham *et al.*, 1983; Gough, 1964). Initial polymerization of these compounds occurs primarily across the terminal olefinic group located in the side chain, resulting in the formation of a general polymeric structure of the type illustrated in Scheme 2 (Carman *et al.*, 1970). In fresh modern resins, these compounds normally occur in conjunction with other diterpenoids, with the result that varying amounts of other materials (e.g. communol, communal, biformenes, and others) are incorporated into the polymeric structure on hardening of the resin (Carman and Dennis, 1967; Carman *et al.*, 1970; Carman and Deeth, 1971; Thomas, 1966, 1969, 1970). Hence, Class I resinates are *not* derived from resins based on pure or totally consistent polymers. However, in all cases so far characterized, the predominant



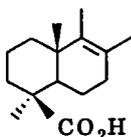
I Communic acids

IIa R'=H Ozic acids

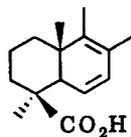
IIb R'=OH Zanzibaric acids



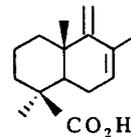
III



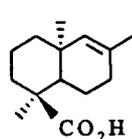
IV



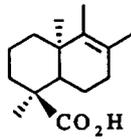
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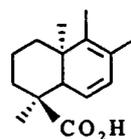
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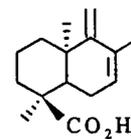
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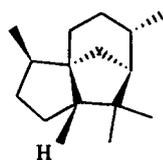
VII



OR



VIII



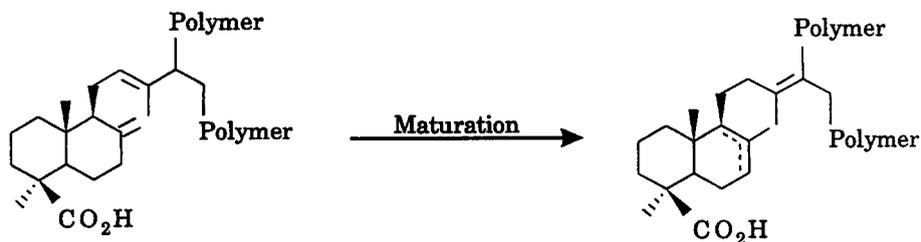
IX

Scheme 1

monomers appear to be labdatriene carboxylic acids (I, IIa, IIb).

All Class I resinites also contain at least a small proportion of non-polymeric material occluded within their macromolecular structure (Thomas,

1969, 1970; Mills *et al.*, 1984/85; Allan, 1975; and numerous others). This typically includes monoterpenes and diterpenes. Occluded diterpenes appear to be predominantly based on the abietane and pimarane skeletons, but may also include unpolymerized lab-



Scheme 2

danoids. Triterpenes may also be present in small amounts, but evidence for this class of compounds, in this class of resinite, is at present somewhat ambiguous. It has been suggested that this material, which is generally extractable in organic solvents, may act primarily as natural plasticizer, or in fresh resins, may aid in viscosity control (Thomas, 1969, 1970; Cunningham *et al.*, 1983). As is observed in modern resins, we have observed that the amount and composition of non-polymeric material present in Class I resinites is highly variable, and therefore is not useful for classification purposes. These occluded materials, especially the more volatile monoterpenoids, appear to be progressively lost with increasing maturity.

As indicated above, resinites are subject to structural and compositional changes as a consequence of the effects of increasing degree of maturation. It is not the purpose of this report to describe in detail the results of studies aimed at determining the nature of the effects of maturation on Class I resinites. However, insofar as these changes affect the identification and classification of individual resinite samples, a brief summary of the nature of these effects is necessary.

The most readily apparent effect of maturation on the structure of Class I resinites is loss (by isomerization) of exomethylene functionality. This type of structure is readily identified by solid-state ^{13}C NMR

and i.r. spectroscopy and hence, labdatriene based resins and immature Class I resinites may readily be recognized and identified by these types of spectroscopic analysis (^{13}C resonances at 108 and 148 ppm, and i.r. absorbance at 887 cm^{-1} are highly specific for exomethylene structures). (See, for example, spectra A and B of Fig. 1; Lambert *et al.*, 1985; Beck *et al.*, 1965; Beck, 1986 and references cited therein; and Anderson *et al.*, 1989.) On the basis of presently available data, it appears that the occurrence of detectable levels of these structures in sedimentary organic matter is unique to Class I resinites, and therefore, evidence for such structural character strongly indicates a Class I resinite. With increasing maturity however, exomethylene structure is progressively "lost" due to isomerization to more thermodynamically favourable isomers. This effect is illustrated in Fig. 1, which shows the solid state ^{13}C spectra of four Class Ib resinites obtained from coal fields in New Zealand. Loss of exomethylene resonances (108 and 148 ppm) with increasing maturity (measured here in terms of the rank of the coals from which these samples were obtained), is clearly apparent in these spectra. However, the total relative abundance of olefinic carbon observed in the spectra illustrated in Fig. 1 is approximately equal for all samples, which indicates that the observed loss of intensity from exomethylene resonances is predomi-

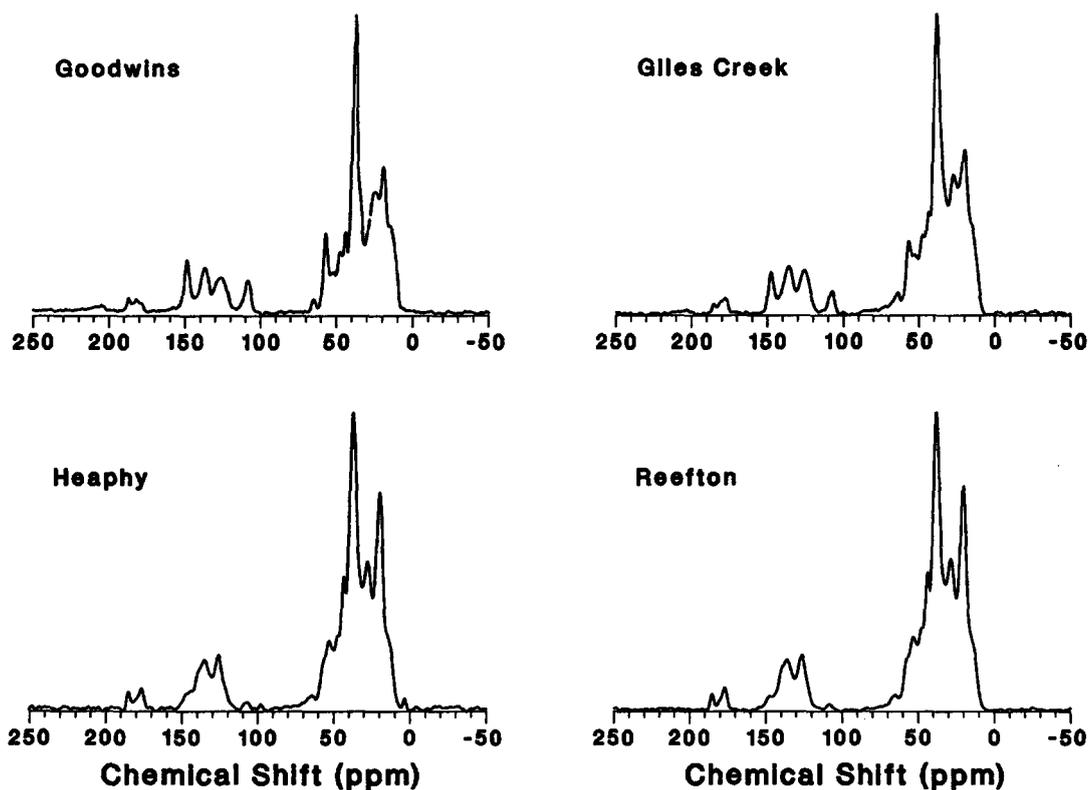


Fig. 1. Cross polarization/magic-angle spinning solid-state ^{13}C NMR spectra of four Class Ib resinites obtained from coal fields in New Zealand. Spectra are plotted in order of increasing maturity (based on coal rank): Goodwins (lignite A) < Giles Creek (lignite B) < Heaphy (sub-bituminous) \approx Reefton (sub-bituminous).

nantly due to isomerization to more stable, olefinic structures, as illustrated in Scheme 2. Similar loss of exomethylene character with increasing maturity has also been described by other authors for Class Ic resinates from the Dominican Republic (Lambert *et al.*, 1985). Corresponding loss of i.r. absorbance at 887 cm^{-1} is also observed in the FTIR spectra of these samples, and has been reported by Mustoe (1985) upon heating of Class I resinates from north western North America, and subsequently by Hwang and Teerman (1988), and Vassallo *et al.* (1991) in similar experiments with other Class I resinates. Hence, whilst evidence for exomethylene functionality is highly characteristic of immature Class I resinates, the absence of such evidence does not necessarily indicate an alternative classification, since these structures are progressively lost as a function of increasing maturity and are virtually absent in "mature" samples of Class I resinates.

Additional evidence concerning the nature of the effects of increasing maturation on the structure and composition of Class I resinates can be obtained from the composition of their pyrolysates. Figure 2 illustrates the Py-GC-MS total ion chromatograms of the same series of resinite samples described in Fig. 1. Data from these chromatograms suggests that in addition to isomerization of exomethylene functionality, maturation of Class I resinates also involves isomerization of the trisubstituted olefin located in the side chain of polycommunic acid (and other polyabdatrienes) to the adjacent, more thermodynamically stable, tetrasubstituted position (also illustrated in Scheme 2). This effect is crudely illustrated by the ratio of three characteristic bicyclic acids derived from the A/B ring system of polycommunic acid (III, IV and V) by cleavage of the side-chain. (Note: in Class Ic resinates, the corresponding *enantio-* compounds VI, VII and VIII are observed.) The ratio of these acids in the pyrolysates of Class I resinates is apparently controlled, at least in part, by the position of the olefinic structure located in the monomer side-chain, by pyrolytic β -bond scission. It is also likely that formation of these acids will be affected by location of the isomerized exomethylene group; studies aimed at clarifying this issue are in progress. The ratio of these compounds, viz, III/(IV + V), obtained from the data illustrated in Fig. 2, is illustrated in Fig. 3. The formation of these acids is clearly maturity dependent, and therefore reflects changes in the structural nature of the resinite as a function of increasing maturity.

Maturation effects probably also account for variation in the compositions of New Zealand resinates reported by Thomas (1969, 1970). Thomas concluded that compositional differences in the samples which he characterized probably reflected different botanical origins. The data illustrated in Figs 2 and 3, however, indicate that the compositional differences reported by Thomas may well reflect differences in the maturity of the different

samples rather than different botanical origins, since the occurrence of compounds III-V in all of these resinates clearly suggests a common Class I origin.

The observation of compounds III-V in the pyrolysate of any given sample is highly characteristic of resinates derived from polycommunic acid based resins, and has been used in the present study as a primary classification parameter. (Note: these compounds have also been observed in pyrolysates obtained by off-line pyrolysis; van Aarssen and deLeeuw, 1991.) Resinates derived from resins based on structure IIa give the corresponding compounds VI-VIII, which may be distinguished from III-V on the basis of chromatographic behaviour (compounds VI-VIII elute at slightly longer retention times than the corresponding enantiomeric compounds III-V under the conditions used in this study—see Fig. 4). The mass spectra of compounds VI-VIII are indistinguishable from those of compounds III-V, which have been described in detail elsewhere (Anderson and Winans, 1991b).

Sub-classification of Class I resinates

Based on current data from the literature (Mills *et al.*, 1984/85; Cunningham *et al.*, 1983; Thomas, 1966, 1969, 1970; and others) and on the results of studies undertaken by the authors (described in part herein), at least three distinct forms of Class I resinates can be recognized. For some purposes it is useful to distinguish these distinct sub-classes as discrete groups, as described in Table 1. Py-GC-MS data for each of these sub classes is illustrated in Fig. 4. Both Class Ia and Ib resinates are derived from resins based on labdatrienes of the "regular" configuration (i.e. $1S[1\alpha,4\alpha,5\alpha,8\alpha\beta]$) Appendix Note 2, especially various isomers of communic acid, often partially co-polymerized with communol and possibly small amounts of other compounds. Class Ia resinates are distinct from Class Ib resinates in that Class Ia resinates incorporate significant amounts of succinic acid into their polymeric structure, presumably as a cross-linking agent between communol units (Gough and Mills, 1972; Mills *et al.*, 1984/85; and numerous others). These resins may be recognized by the presence in their pyrolysates of succinic acid (observed as dimethyl succinate in the data illustrated in Fig. 4), in addition to compounds III-V. Class Ia resinates include, but are not restricted to, succinite and numerous other related European resinates (ambers), probably derived from a common botanical source, and which are extremely abundant and extensively documented. It is, therefore, useful to differentiate Class Ia and Ib resinates for solely practical considerations. Class Ib resinates are also derived from resins based on polycommunic acid, and hence are identified by the presence of compounds III-V in their pyrolysates, but contain no succinic acid. This sub-class includes Australian, New Zealand and many North American resinates, in addition to

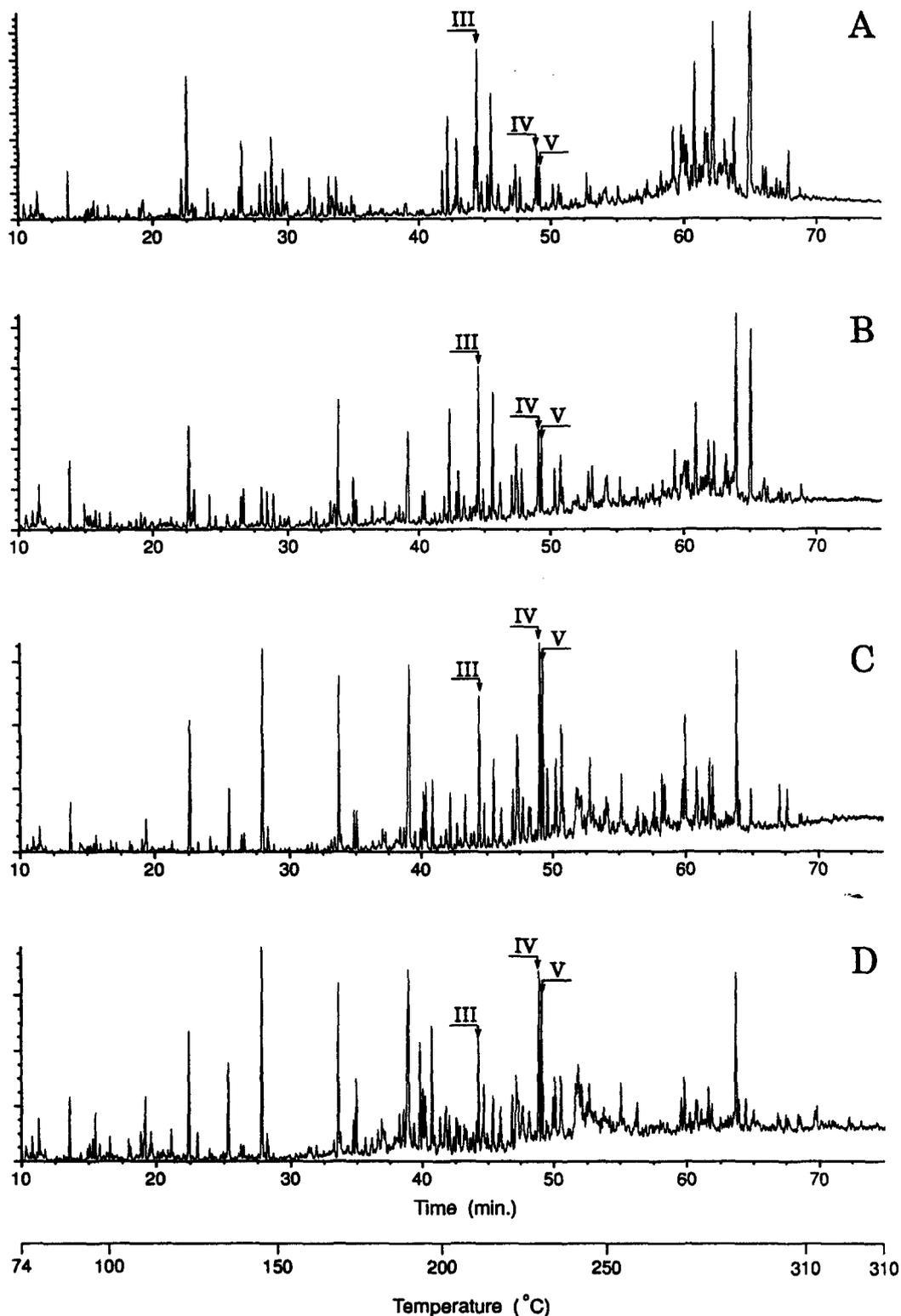


Fig. 2. Total ion chromatograms obtained by Py-GC-MS analysis of New Zealand resinites. Samples are identical to those described in Fig. 1: A—Goodwins; B—Giles Creek; C—Heaphy; D—Reefton. Characteristic bicyclic acids, determined as their corresponding methyl esters, are indicated. Data were obtained using a 60 m DB-5 capillary GC column (see: Anderson and Winans, 1991b). $T_{py} = 480^{\circ}\text{C}$ in all cases. For identification of selected peaks, see Scheme 1.

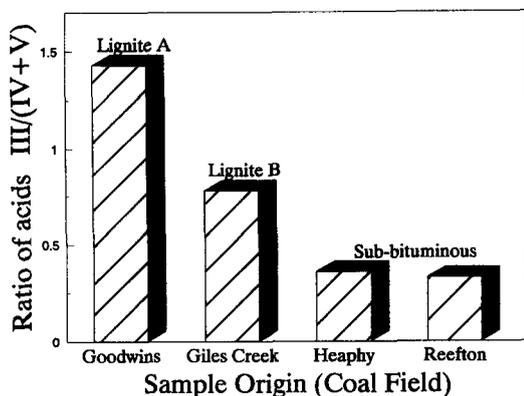


Fig. 3. Ratio of characteristic trimethyl/tetramethyl bicyclic acids [III/(IV + V)], determined as their corresponding methyl esters, in the pyrolysates (Py-GC-MS) of four New Zealand resinites. Samples are identical to those described in Fig. 1. Data are taken from Fig. 2.

resinites from numerous other locations around the globe.

Class Ic resinites are derived from resins based on labdatirenes of the alternate *enantio* configuration (1R-[1 α ,4 $\alpha\beta$,5 β ,8 $\alpha\alpha$]) especially polyozic acid (Mills and White, 1987) and/or polyzanzibaric acid (Langenheim, 1990; Cunningham *et al.*, 1983). These resinites may be distinguished from Class Ia and Ib resinites on the basis of the occurrence of compounds VI-VIII (and the absence of III-V) in their pyrolysates.

In our preliminary report of these results we described Class Ic resinites as being derived from resins based on polyzanzibaric acid (Iib) (Anderson and Winans, 1991a). This conclusion was based on the results of studies carried out by Langenheim and coworkers (Langenheim, 1990; Cunningham *et al.*, 1983). Mills and White (1987) have offered the alternative suggestion that these resinites are based on polyozic acid (IIa), but neither present nor cite evidence in support of this contention; presumably this assertion is based on unpublished results obtained by these authors. The observation of compounds VI-VIII in Py-GC-MS data obtained from a number of Class Ic resinites characterized by the authors (data described herein and unpublished results) tends to support the polyozic acid hypothesis, but does not rule out the possibility that these resinites are derived from a copolymeric (zanzibaric acid + ozic acid) resin. By analogy with resinites based on labdanoids of the regular series, it seems likely to the present authors that the primary monomers of Class Ic resinites are ozic acids. However, given the co-occurrence of zanzibaric acid and *iso*-ozic acid in at least one species (*viz.*, *Hymenaea verrucosa*, Hugel and Ourisson, 1965; Martin and Langenheim, 1974), it appears likely that copolymeric resins and resinites that are based on varying proportions of both of these monomeric materials probably exist, and therefore, that analyses of Class Ic resinites are likely to reflect this. The data

described by Cunningham *et al.* (1983) appears to be consistent with this suggestion. As has been suggested above in the case of Class Ia and Ib resinites, other suitable compounds are also likely to be incorporated into the polymeric structures of these resinites.

Class II resinites

Class II resinites have been elegantly characterized by van Aarssen and co-workers (van Aarssen *et al.*, 1990, 1991), and Meuzelaar *et al.* (1991), as well as others (Mills and Werner, 1955; Brackmann *et al.*, 1984; Shigemoto *et al.*, 1987). Most of the principal structural characteristics of these materials now appear to have been established. These resinites, which are much less common on a global scale than Class I resinites, are derived from resins which are based on polycadinene structures (van Aarssen *et al.*, 1990, 1991), and this structural character appears to have been largely preserved in the samples so far characterized. Analogous modern resins, sold commercially as "damar", are produced in (sometimes) large quantities by trees belonging to the taxa *Dipterocarpaceae*.

Several workers have noted the existence of a number of distinct forms of Class II resinites from coal deposits located in central Utah (Crelling *et al.*, 1991 and references cited therein; Meuzelaar *et al.*, 1991; Yu *et al.*, 1991). Crelling and co-workers (1991) have described four distinct forms of resinite, which they differentiate on the basis of fluorescence characteristics, from these coals. Yu and co-workers (1991) also describe four distinct forms of resinite from the same coals, but differentiate these on the basis of colour. These distinctions do not, however, indicate the presence of distinct resinite classes. The results of the chemical and spectroscopic analyses reported by these authors, especially Meuzelaar and co-workers (1991) and Yu and co-workers (1991), indicate that the structural characteristics of all of these resinites are closely comparable. The data reported by these authors strongly indicate that all of these resinites are based on polymers of sesquiterpenoid hydrocarbons related to cadinene, and are, therefore, Class II resinites. The different fluorescence characteristics described by Crelling and co-workers probably reflect differences in the nature and abundance of occluded materials, especially triterpenoids (see Meuzelaar *et al.*, 1991), which are deposited as a component of the original resin (Mills and Werner, 1955; Mills, 1956; Brewis and Halsall, 1961; Cheung and Yan, 1972). Such differences may reflect distinct (albeit related) botanical origins of the resinites, or possibly seasonal variations in resin composition. Depositional and post depositional conditions are also likely to be important in determining the fluorescence characteristics of these resinites, although their co-occurrence suggests that differences of maturity are unlikely to be a predominant factor. The differences of colour described by

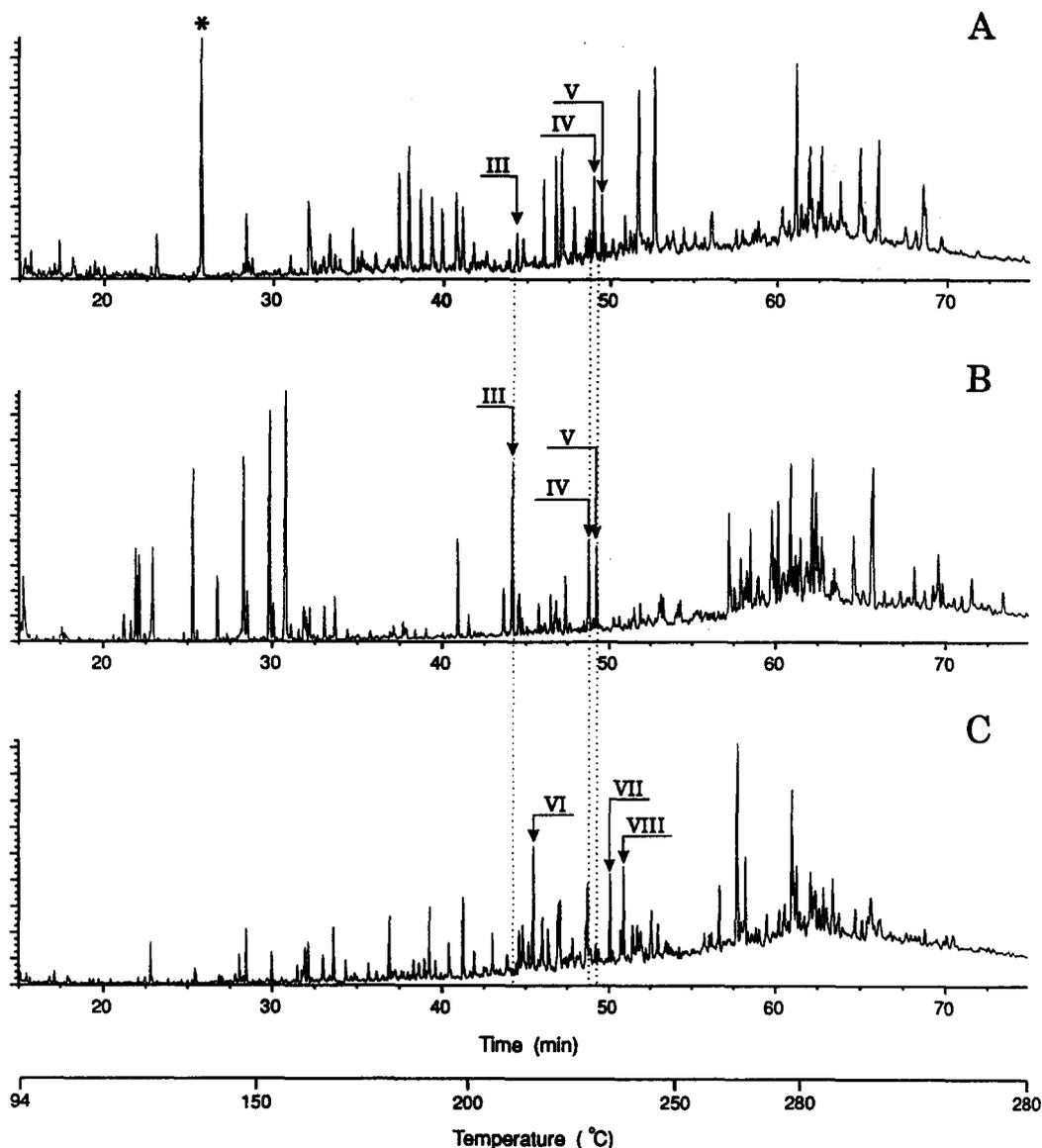


Fig. 4. Comparison of total ion chromatograms obtained by pyrolysis of typical samples of Class Ia, Ib and Ic resinites. A: Class Ia, Succinite, Baltic region, USNM # 353431; B: Class Ib, Victorian Brown Coal resinite (Yallourn seam); C: Class Ic, Zanzibar resinite, AMNH # H252. Data were obtained using a 60 m DB-1701 capillary GC column (see: Anderson and Winans, 1991b). $T_{py} = 480^{\circ}\text{C}$ in all cases. * = Dimethyl succinate. Chromatographic differentiation of compounds III–V and VI–VIII (determined as their methyl esters), is indicated.

Yu *et al.* (1991), most likely reflect differences in the extent of depositional or post-depositional oxidation, or may also be related to the factors described above.

Class II resinites and comparable modern resins can be readily distinguished from Class I resinites by Py–GC–MS (van Aarssen *et al.*, 1990; Anderson and Winans, 1991a) (see Fig. 5) and Py–MS (Brackmann *et al.*, 1984; Meuzelaar *et al.*, 1991). Infrared and NMR data are also characteristic, but in some cases may not provide definitive identification in the absence of other supporting data. Unlike Class I resinites, Class II resinites are substantially soluble in

organic solvents (Brackmann *et al.*, 1984; Bodily and Kopp, 1987; van Aarssen *et al.*, 1990; Yu *et al.*, 1991). No data is currently available on the maturation of Class II resinites.

Class III resinites

Class III resinites are naturally occurring polystyrenes (Grimaldi *et al.*, 1989; Langenheim, 1969) (see Fig. 5). Pyrolytic and spectroscopic data for these samples are totally characteristic of polystyrene, but given the frequency of occurrence of synthetic polystyrene samples in the environment, care is necessary to ensure the authenticity of individual samples. Class

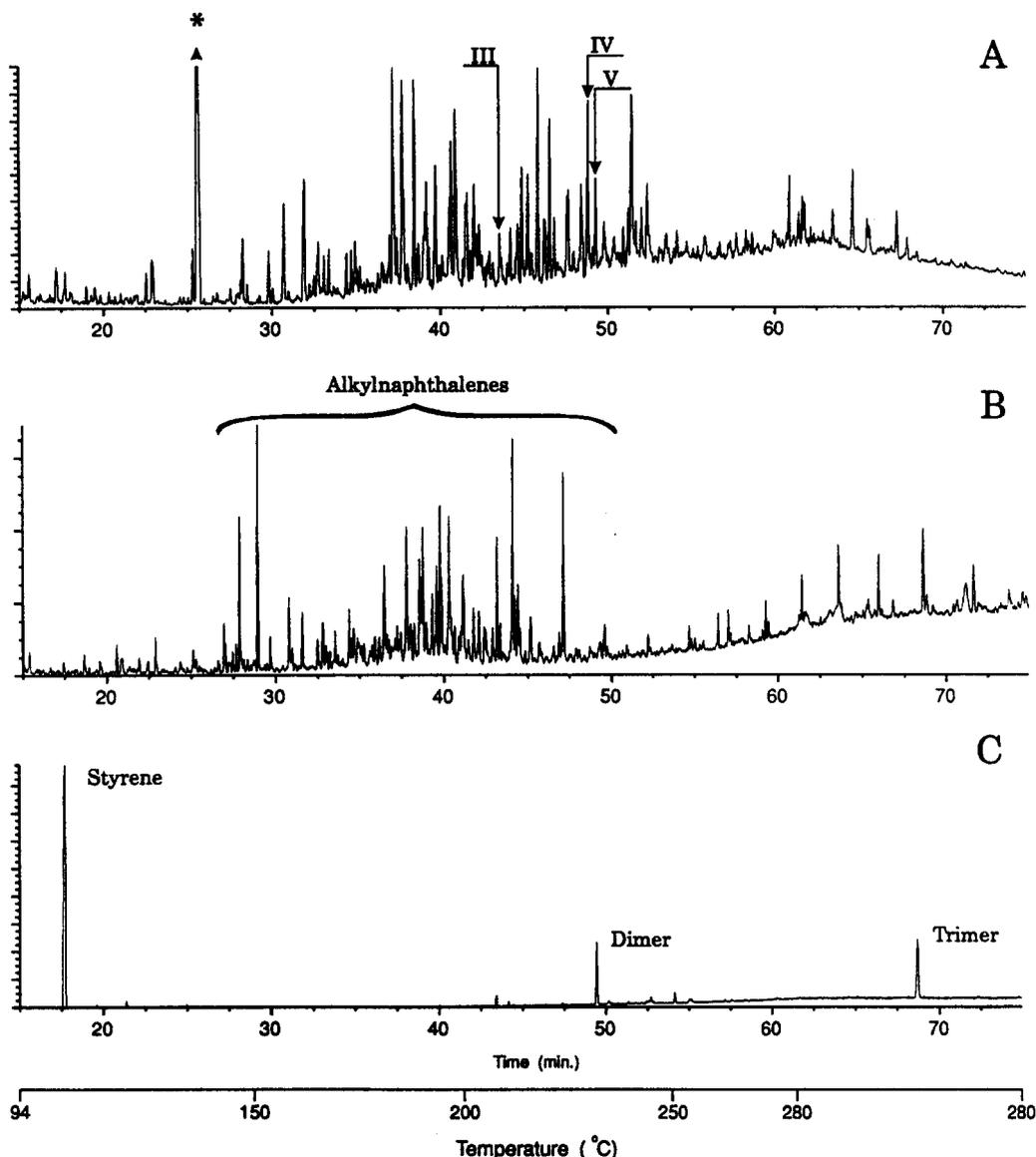


Fig. 5. Comparison of total ion chromatograms obtained by pyrolysis of samples of Class Ia, II and III resinites, demonstrating the ease of differentiation of these different classes of resinite by Py-GC-MS. No reliable samples of Class IV resinite were available to the authors for comparison. Samples: Class Ia, Bitterfeldite (Germany), AMNH # B3. $T_{py} = 480^{\circ}\text{C}$. * = Dimethyl succinate; Class II, Utah resinite (showing abundant alkylnaphthalene isomers, including especially cadinene derived and related structures); Class III, Sayerville resinite (New Jersey) NJSM # 14156. Data were obtained using a 60 m DB-1701 capillary GC column (see Anderson and Winans, 1991b). $T_{py} = 540^{\circ}\text{C}$ for Utah and Sayerville resinites.

III resinites are uncommon in the geosphere, known current reserves being restricted to the Eastern U.S. and Germany (Grimaldi *et al.*, 1989; Langenheim, 1969). Analogous modern resins are produced by trees of the *Hammeliaceae* (especially liquidambar). No data are currently available on the maturation of Class III resinites, but the data illustrated in Fig. 5, which shows the total ion chromatogram (obtained by Py-GC-MS) of a late Cretaceous [approx. 65 Ma y.o. (Gallagher *et al.*, 1986)] Class III resinite sample, shows no evidence for significant alteration of the original polystyrene structure.

Class IV resinites

Class IV resinites are generally less well known and certainly less often characterized than resinites of other classes. Analyses have, however, been described by Streibl and co-workers (1976) and subsequently by Grantham and Douglas (1980). Resinites of this class have been shown by these workers to be largely soluble (non-polymeric?) materials comprised predominantly of sesquiterpenoid hydrocarbons and ketones, especially those based on the cedrane (IX) skeleton (Streibl *et al.*, 1976; Grantham and Douglas,

1980). Hence, given the physical character and chemical nature of the resinates described by these authors (Streibl *et al.*, 1976; and Grantham and Douglas, 1980), these materials satisfy the criteria set out earlier in this report, and are therefore included in the classification system herein proposed, as a discrete class of resinite. No data are available concerning the maturation of these materials.

Grantham and Douglas (1980) have suggested that resinates of this class may be derived from resins of the *Cupressaceae*. However, resins of this taxa have been shown to be dominated by communic acids (up to 70%) and related diterpenoids (Mangoni and Belardini, 1964, 1966; Mangoni and Caputo, 1967; Mills and White, 1987), and hence would be expected to give rise to Class I resinates. Further investigation is therefore required in order to establish the botanical origin of Class IV resinates.

Other resinates

As noted earlier, the classification system proposed herein is intended to be open ended so that additional forms of resinite may be added as indicated by additional analytical data. One form of resinite, that is not included in the present classification system, has been described in the literature. Frondel (1967a, b) has described resinite samples from several sites as "fossil elemi", which are reported to be based on, or at least contain, significant amounts of β -amyryn and related triterpenoids. The results of analysis of these resinates by the present authors however, indicate that this conclusion is in error. Details of the data on which this conclusion is based will be discussed in a forthcoming paper in this series.

Analytical techniques for the classification of resinates

In developing the classification system described above, extensive use has been made of data obtained by Py-GC-MS. We have found this analytical technique, which is rapid, requires only very small amounts of sample, and provides definitive data for classification, to be a very convenient procedure for this purpose. In some cases, e.g. Class III and immature Class I resinates (in which evidence for the presence of exomethylene structure is apparent); spectroscopic analyses (especially i.r., ^{13}C NMR) also provide unambiguous evidence for classification. However, we have found that in many cases, these techniques alone are insufficient to definitively differentiate between resinates for the purposes of classification. This is especially true in mature samples. (See for example spectra C and D of Fig. 1.) It is not our intention, however, to detract from the many excellent spectroscopic analyses which have been reported and which have contributed substantially to the present level of understanding of the structure and composition of many resinates [Beck *et al.*, 1965; Beck, 1986 (and references cited therein); Lambert and Frye, 1982; Lambert *et al.*, 1985, 1988, 1989, 1990]. However, at present not all resinates may be

definitively classified on the basis of spectroscopic data alone.

CONCLUSIONS

Understanding of the nature of sedimentary organic matter derived from the resins of higher plants has now evolved to a point where a number of chemically distinct forms of these materials have been recognized. In petrographic studies, the general classification "resinite" is still essential. However, in geochemical studies of resinates, it is desirable to indicate the basic structural character of the resinite(s) being described, in order to facilitate correlation with data obtained from comparable resinates from other sites. It is our intention that the classification system described above, will provide a convenient nomenclature for the description of the fundamental structural character of resinates. It is to be hoped that this will enhance recognition of the generally limited structural diversity of resinates.

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APPENDIX

Note 1

Although we have used this phraseology in previous reports (Anderson *et al.*, 1989, 1990, 1991a) it is, perhaps, not strictly correct to describe resinite samples as “based on polycommunic acid” when, in response to maturational “forces”, changes have occurred in the structure of the original resin resulting in formation of a “geopolymer”. Therefore, in view of the data described herein, and also in view of some degree of confusion as to our views concerning the structure of Class I resinates, we have now backed away from the use of this expression. In recent and immature samples such as those we have described previously, this expression is approximately accurate, but we now believe that it is inaccurate to use this expression as a generalized description of the structure of Class Ia and Ib resinates.

Furthermore, some authors appear to have interpreted “based on polycommunic acid” as identical with “polycommunic acid”. At no time have we ascribed to the view that Class Ia and Ib resinates are pure polycommunic acid. Depending on the composition of the original resin from which any given resinite is derived, the polymeric component of the resinite will incorporate varying degrees of other monomers, especially other labdanoids with suitable structural characteristics: e.g. biformenes, communol, communal, and potentially numerous others. It is our belief however, that as is observed in modern resins (Carman *et al.*, 1970), these compounds are less significant in the overall polymeric structure than various isomers of communic acid. This is in accordance with the views of other authors (Thomas, 1966, 1969, 1970; Mills *et al.*, 1984/85), whose work we have cited in our previous reports.

Note 2

Stereochemical conventions used in this report are based on the systematic names assigned to these compounds in **Chemical Abstracts** e.g. *trans*-Communic acid = 1-Naphthalenecarboxylic acid, decahydro-1,4a-dimethyl-6-methylene-5-(3-methyl-2,4-pentadienyl) [*1S*-(1 α ,4 α ,5 α ,(E),8 α β)], (CAS RN = 10178-32-2), *cis*-Ozic acid = 1-Naphthalenecarboxylic acid, decahydro-1,4a-dimethyl-6-methylene-5-(3-methyl-2,4-pentadienyl) [*1R*-(1 α ,4 α β,5β,(Z),8 α)], (CAS RN = 69427-96-9). These systematic names do not clearly reflect the diagrammatic conventions used by most authors for structural representations of labdanoid diterpenes, in which compounds of the “regular” series are drawn in the all β configuration, and compounds of the *enantio* series are drawn in the $\beta\alpha\alpha$ configuration, as illustrated in Schemes I and II. For a discussion of the nomenclature of diterpenoid resin acids, see Rowe, 1989.