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## **Chemical Characterization of Fossil Resins (“Amber”) – A Critical Review of Methods, Problems and Possibilities: Determination of Mineral Species, Botanical Sources and Geographical Attribution**

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With 5 Text-Figures

*Fossil Resins*  
*Amber*  
*Organic Minerals*  
*Infrared Spectroscopy*  
*Mass Spectrometry*  
*Gas Liquid Chromatography*

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## **Chemische Charakterisierung fossiler Harze („Bernstein“) – Eine kritische Übersicht der Methoden, Probleme und Möglichkeiten: Mineralbestimmung, pflanzliche Herkunft und geographische Zuordnung**

### Zusammenfassung

Neben der in manchen Fällen noch recht problematischen Unterscheidung einzelner Arten fossiler Harze gibt es zumindest noch zwei weitere Gründe für die chemische Bearbeitung dieser wichtigen Gruppe organischer Minerale: die Bestimmung ihrer pflanzlichen Herkunft und die geographische Zuordnung zu einem bestimmten Fundgebiet, wie sie von Prähistorikern und Archäologen immer wieder erwartet wird. Von den einzelnen chemischen Methoden werden neben der Infrarotspektroskopie auch Möglichkeiten und Anwendungsbeispiele für die Massenspektroskopie und vor allem für die verschiedenen Arten der Gaschromatographie aufgezeigt. Computergestützte, kombinierte Gaschromatographie/Massenspektroskopie wird als besonders aussagekräftige Möglichkeit für die Charakterisierung fossiler Harze vorgestellt.

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## Abstract

Apart from the problem of an exact distinction of single mineral species of fossil resins which is still uncertain in some cases, there are at least two more reasons for the study of this outstanding group of organic minerals: determination of the botanical origin and geographical attribution to a special area – a question rather often asked by archaeologists. Among chemical methods discussed, possibilities and applications not only for infrared spectroscopy but also for mass spectroscopy are given. In addition advantages of different varieties of gas liquid chromatography are discussed in greater detail. Computer-aided combined gas liquid chromatography/mass spectroscopy is shown to be the most promising method for the characterization of fossil resins at the moment.

## 1. Introduction

Fossil resins ("amber") are only for a very few countries of any economical importance at all; Austria has to be mentioned among those being rather "rich in poor occurrences" having in fact – according to our present state of knowledge – only one locality which is really rich in fossil resin: the Roßfeld strata (Early Cretaceous: Upper Valanginian/Hauterivian) near Golling, Salzburg. From this locality, having been accessible in the years 1979–1982, approximately 500–800 kg of fossil resin have been collected mainly by the activity of private collectors; there have even been found 30–50 specimens of about half a kilogram, the largest specimen having had a weight of 4,6 kg (SCHLEE, 1985).

This occurrence which is of great scientific interest not only because of its geological age but also because of a few inclusions having been detected (SCHLEE, loc. cit.), and also the many other localities having often yielded only tiny amounts of fossil resins but being of different geological age and being in different states of diagenetic transformation and being often also of different botanical origin are a reasonable basis to justify the study of such materials with methods of modern organic geochemistry in Austria too.

## 2. Mineral Names for Fossil Resins

Unfortunately there does still exist a considerable confusion in respect to the use of mineral names for fossil resins: "amber" can be regarded as the most prominent example in this respect. This term is used either as a general term for all fossil resins, or as a general term for all fossil resins coming from the Baltic area or as a synonym for succinite. There have also been attempts to classify fossil resins in amber, "amber-like resins" and resins being dissimilar to amber – a system having had much to do with the contents of succinic acid in the different resins.

Besides there does exist a steadily increasing amount of mineral names for different fossil resins; many countries have made contributions to this still growing list of names: gedanite, beckerite, stantienite, krantzite and glessite are examples from the Baltic area; ajkaite, telegdite and kiscellite have been described from Hungary; walchovite, muchite and neudorfite have been mentioned from localities in Czechoslovakia; or to add a few more "exotic" examples: ambrite from New Zealand, bacalite from Baja California, bucaramangite from Columbia, chemawinitite and/or cedarite from Canada, burmite from Burma, guayaquilite from Ecuador etc. More "Recent" examples to be found in the literature are: amekite from Nigeria (SAVKEVICH & ARUA, 1988) or goitschite, bitterfeldite, durglessite and pseudostantienite from the coal mine of Bitterfeld (Germany) as described by FUHRMANN & BORSCH (1986).

Modern mineralogical and organic geochemical research has established quite a number of such fossil resins as valid mineral species; beckerite, stantienite, glessite, krantzite and gedanite are such examples. Others have been recognized as junior synonyms and are therefore no valid mineral names any more: neudorfite and muchite are for instance synonyms of walchovite (STREIBL, VASICKOVA, HEROUT & BOUŠKA, 1976) or the above mentioned cedarite must be regarded as an invalid synonym of chemawinitite (CARPENTER et al., 1937). Some others (e.g. "bacalite") are of dubious origin (BUDDHE, 1935; LANGENHEIM, BUDDHE & JELINEK, 1965) and therefore no reasonable basis for further use or must be regarded as a general term for different fossil resins having only one thing in common: the geographical origin. Examples of this last kind are the "rumaenite" as a general term for resins coming from Rumania or also "ajkaite" for all resins from Ajka (Hungary; pers. information from Prof. S. SAVKEVICH, St. Petersburg).

Other mineral species of fossil resins mentioned above are restudied right now (e.g. those from Bitterfeld by KOSMOWSKA-CERANOWICZ and KRUMBIEGEL).

A good example for the use – or should one rather say "abuse"? – of a mineral name for a fossil resin is also given by the so-called "copaline" from the area of Vienna. This mineral name had been used by STARKL (1883) for a fossil resin from the Satzberg area (SE slope of this hill, area of Hütteldorf, Vienna) on the basis of comparison with resin material from the Highgate Hill near London. As well for this "Highgate Resin (=copalite)" as for the fossil resin from the Satzberg area a chemical composition had been suspected similar to copal resins – therefore the name. Later authors have then used the name "copaline" for a distinctly different fossil resin in the surrounding of Vienna: for the resin found near Gablitz, Vienna Woods, Lower Austria. The resin from Gablitz is of Eocene age – the resin from the Satzberg has been of Cretaceous age: the first is hardly soluble in carbon disulfide the latter one was (according to STARKL) perfectly soluble in this solvent ... – a typical example for a mineral name of a fossil resin having been transferred from one find to another one and giving rise to considerable confusion. Moreover: to restudy material from the Satzberg area has turned out to be impossible: there is obviously no material available from this locality in our collections at Vienna.

## 3. Goals for Chemical Studies of Fossil Resins

All the confusion still existing in respect to the use of mineral names for fossil resins and the problems in connection with old and/or insufficient descriptions of organic minerals like fossil resins in general would already justify detailed and extended studies of such materials using

methods of modern organic (geo-) chemistry. But there are two more problems which are and have been a reason to resume chemical studies of fossil resins always and always again.

These two problems are the determination of the botanical origin of fossil resin material, i.e. the identification of chemical fossils in the resins which can help on the basis of (palaeo-)chemotaxonomy to establish the botanical origin of a find and on the other side the determination of the geographical origin of a fossil resin being for instance found among archaeological materials.

This latter aspect has a rather great importance in connection with the reconstruction of trading routes ("Bernsteinstraßen") for prehistoric times.

#### 4. Botanical Origin of Fossil Resins

One of the main goals for studies of fossil resins has always been the question concerning the type of plants which might have produced fossil resins. Besides "classical" methods of palaeobotany rather sophisticated methods had been used to identify the botanical origin already very early.

As an example for the first type of publications from more recent years SCHUBERT's publication "Neue Untersuchungen über Bau und Leben der Bernsteinkiefern" (1961) can be mentioned; as an outstanding, really thorough study using methods of modern organic and analytical chemistry THOMAS (1969) can be mentioned. He gave a detailed study of the chemistry of resins occurring in different species of the genus *Agathis* as well as their different biosynthetic pathways. He described and analysed not only Recent and "subfossil" resins but extended his studies to fossil resins of different geological age from New Zealand (Miocene – Cretaceous). On a broad basis of comparisons of resin acid patterns for these samples he could determine a botanical origin from the genus *Agathis* for most of them. Substances (different resin acids and their corresponding alcohols) were characterized in addition by the use of nuclear magnetic resonance and by mass spectroscopy.

Another example for chemotaxonomy applied to fossil material worth mentioning may be given: FRONDEL (1969) showed with a rather high degree of reliability that a few fossil resins can be regarded as fossil elemi-resins. She proved the occurrence of amyrrin (a pentacyclic triterpenes, see Fig. 3) by means of thin layer chromatography respectively by means of X-ray diffraction; because of their contents of crystalline amyrrin elemi-resins are said to yield a distinct pattern.

According to observations by FRONDEL the occurrence of this terpene could be proved for glessite from the Baltic area, for Highgate Resin (= "copalite") from the Blue clays of London (Eocene) and for guyaquillite, a resin of unknown geological age from Ecuador. Realizing nevertheless that amyrrins do occur in quite a number of plant families, the only family producing resins and amyrrins as well are the Burseraceae, genera of which are not only known to produce frankincense (genus: *Boswellia*), myrrh (genus: *Commiphora*) but also the so-called elemi-resins (genera: *Protium*, *Bursera*).

As a third example for chemotaxonomy applied to fossil resins the investigations done by GRANTHAM & DOUGLAS (1980) for retinellite (a fossil resin from the Oligocene of Great Britain) and for ionite (a resin from the Pliocene of

California) can be given. By means of gas chromatography and mass spectroscopical comparisons with authentic material they could establish the occurrence of special terpenes (alpha-cedrene, cuparene etc.) which are said to be characteristic for the family Cupressaceae. Therefore these fossil resins can be regarded as products of a fossil representative of this family.

The most common method however having been used for many years to establish the botanical origin of resins has been the infrared spectroscopy (e.g. BECK, WILBUR & MERET, 1964; LANGENHEIM, 1964, 1965, 1966, 1969 etc.). Though this method has a lot of advantages and merits (see below) it has nevertheless sometimes been regarded as far too reliable in respect to the determination of the botanical origin of resins. It has at any case helped to establish the botanical origin of resin from Chiapas (Mexico) and possibly also for resins from the Dominican Republic: both can now be regarded with high reliability as being of Angiosperm origin (*Hymenaea* having been the resin-producing tree). A certain number of botanical affinities claimed only on the basis of infrared spectra alone must obviously remain dubious nevertheless.

Determination of botanical origin of fossil resins will remain a rather difficult problem in many cases for the future. Diagenetic alteration of the material and the unknown biochemistry of Mesozoic plants will help to maintain this challenge for the future especially in respect to "old" (in the geological sense of the word) and therefore most interesting resin samples.

But even in respect to the "well-known" Baltic amber (=succinite) surprises in respect to its biochemistry are possible: the paper by GOUGH & MILLS (1972) as well as observations of our own are hints in the direction that the "classical amber-tree" has obviously had a biochemistry similar to Araucariaceae!

#### 5. Determination of the Geographical Origin

AGRICOLA (1546) is reported to have been the very first scientist isolating succinic acid (in the form of its anhydride) from amber by dry distillation (ROTTLÄNDER, 1970). With HELM (1877) the determination of the succinic acid content in fossil resins became a matter of utmost importance in respect to chemical characterization of fossil resins and especially in respect to the determination of the geographical origin of the material. The question concerning the geographical origin had been asked by archaeological sciences; many finds of amber products in Greece, Italy and wherever gave rise to the question concerning the geographical origin and – obviously even more fascinating – concerning the trading routes ("Bernsteinstraßen") for amber. An extensive literature in archaeology is concerned with finds of amber products, as listed (for the older literature) for instance by SCHMID (1931). HELM had obviously started his studies with the preconceived opinion that only Baltic amber contained succinic acid. Even rather early criticism (e.g. HEDINGER, 1903), emphasizing already that the composition of fossil resins from different localities could be quite different and on the other hand that even the composition of resins from one locality could be different as well, resulted in the statement that opposing to HELM's standpoint no geographical attribution could be made on the basis of succinic acid content. Nevertheless this "tradition" to regard succinic acid not only as characteristic for Baltic amber (= succinite) and a

few other resins (as later admitted) survived for some time. The last remainder of this idea survives still in our days: the preconceived opinion that chemical analysis of a fossil resin may be able to give information about the geographical origin.

Nowadays usually infrared spectroscopy is used for this purpose; often the results achieved read like these: there is a "Baltic shoulder" in the infrared spectrum, therefore it is succinite, therefore it must come from the Baltic area. For a considerable time it had really been ignored that succinite can also be found elsewhere. One example is shown in Fig. 1 (spectrum 2): this sample had been given to me as "walchovite" from Walchov. Already its general appearance, colour, transparency etc. having been distinctly different from authentic walchovite, the infrared spectrum showed finally the "Baltic shoulder" – the material being succinite without any doubt, succinite found at Walchov, why not? One of many examples for the occurrence of succinite far outside the Baltic area. Why should there always be only one species of a fossil resin at one locality? Even in the "classical" area of fossil resins, in the Baltic there are quite a number of different mineral species of fossil resins. Considerations like these show that the chemical characterization, i.e. the determination of a single mineral species can never be sufficient and reliable enough to determine any geographical origin.

The background for many studies like these has been the reconstruction of the above-mentioned trading routes for amber (= "Bernsteinstraßen"). About the detailed geography of these ancient trading routes there are different opinions. One must also realize that amber in the strict sense of succinite could have been brought from the North Sea, from the western part of the Baltic Sea and finally of course from the Samland peninsula. At least four different routes have been suggested:

- 1) Transport by ships from the North Sea and perhaps even from the Baltic Sea
- 2) From "Massilia" following the Rhône valley towards the Rhine valley etc.
- 3) From Aquileia via Pannonia (Carnuntum!) towards the Baltic Sea
- 4) From the Black Sea starting from the Greek colony of Olbia (FREISING, 1977).

There exists an extensive literature on this subject; the oldest publication concerning this problem is usually said to be a publication by SPOWSKI (1877). For further details see for instance BECKER (1941) or PITTIONI (1985).

Concluding these few remarks about the determination of the geographical origin one must once more emphasize that it is only possible to determine by chemical and physicochemical methods a mineral species like succinite or whatever and according to the present state of knowledge it is not possible to make geographical attributions in general. The widespread occurrence of succinite makes such a goal hopeless from the very first beginning. For a discussion of this problem see SAVKEVICH (1981). There is nevertheless the possibility for those resins (e.g. the sime-tite from Sicily) which occur in a rather restricted area only to draw geographical conclusions on the basis of the identification of a special mineral species; or one has – being aware of the fact that in Europe succinite has so far only been detected "north of the Alps" – to restrict to the simple statement that this or that archaeological object was made of material from "north of the Alps" – leaving no possibility to discern between succinite from England, the North Sea the Baltic area or whatever. Such restrictions

seem necessary even if they are "a disservice to European archaeology" as stated by BECK (1982).

## 6. The Chemical Structure of Fossil Resins

There exists surprisingly little modern chemical literature dealing with the structure of the "amber molecule" resp. dealing with the chemical structure of fossil resins in general.

For Baltic amber ROTTLÄNDER (1969) has suggested the following way of formation: abietic acid is the substance from which the reaction starts, a substance which is first suffering dimerization yielding diabetenic acid. This product is characterized among others by an exocyclic double bond which is transformed by addition of a water molecule to a primary alcohol function. Thus a bifunctional molecule – being acid and alcohol as well – is formed, which according to ROTTLÄNDER's standpoint easily undergoes polycondensation thus giving a molecule of high molecular weight which together with its oxidation products is regarded as the main component of Baltic amber. ROTTLÄNDER has offered rather convincing proofs for this theory by means of products of model experiments starting with pure abietic acid being compared with material which he had received after removal of the coloured substances in succinite by treatment with pyridine. Both these products showed infrared spectra which were practically identical.

Quite a different structure for Baltic amber has been suggested by GOUGH & MILLS (1972): according to a short remark in their publication they regard amber as a product similar to one yielded by copolymerization of communic acid and the corresponding alcohol, extensive cross-linking and acylation of the hydroxylgroups with succinic acid being additional features of the structure suggested.

On the other side ROTTLÄNDER (1970) has emphasized that succinic acid can not be bound by ester linkages because the acid can't be set free by acid hydrolysis.

Thus it would be probably a futile hope to expect the "perfect identification" of the chemical structure of fossil resins for the near future; in fact one must probably realize that a "formula" for fossil resins could never be expected to be established at all. Perhaps the idea that a fossil resin is a statistical polymer, formed partly by polycondensation, partly by polymerisation, being partly oxidized would not be far from truth. Probably fossil resins can thus only be regarded as "statistical copolymers", for which the main characteristics to be established would be:

- 1) molecular weight
- 2) type of monomer(s)
- 3) type of bonding (e.g. percentage of poly-condensation)
- 4) degree of oxidation etc.

Fossil resins offer therefore problems in respect to their chemical characterization rather similar to problems offered for instance by lignins – but there is some hope, that they are perhaps not quite as "evil" as other statistically constructed substances of high molecular weight like humic acids or (worst of all!) kerogen.

Facing this situation restricts quite automatically methods and possibilities for chemical characterization and shows moreover that beyond a special limit chemical

studies may become impossible or even a waste of time i.e. without any further essential chemical information to be expected.

## 7. Short Survey of Methods

### 7.1. Infrared Spectroscopy

The method having found the most general application for the characterization and identification of fossil resins is without any doubt the infrared spectroscopy (for examples see Fig. 1). The advantages of this method are rather obvious: by the use of potassium bromide pellets in which the resin sample is dispersed the whole sample is characterized and not only a special, soluble fraction like with other methods (see below). The problem that practically all fossil resins show low solubility in usual solvents, a fact which restricts the application of many an analytical possibility, becomes thus unessential. A further advantage of this method is the low amount of material needed for yielding a spectrum: with modern equipment a few mg are quite sufficient. The disadvantages of the method are identical with problems generally involved in the infrared spectroscopy of polymers. Sometimes even very strong absorptions even if they can be attributed to special functional groups etc. are not useful for the characterization or for the distinction between different mineral species of fossil resins. Characteristic and "valuable" absorptions can be weak because of low "concentrations" within the sample or because of some other reason and may thus be easily "drowned" in other absorption bands. Nevertheless the interpretation of such spectra can mostly be done rather easily on a broad basis of studies published. The first author who had claimed the possibility to discern between copals and amber has been HUMMEL (1958), whose spectra of Baltic amber show the typical "Baltic shoulder", a distinct feature for the infrared spectrum of succinite, consisting of an absorption at  $1160\text{ cm}^{-1}$  and the "shoulder" between  $1160$  and  $1260\text{ cm}^{-1}$  (see Fig. 1, spectrum 2), being usually regarded as an absorption caused by polyester structures. An other characteristic, but usually rather weak set of absorptions at  $888$ ,  $1640$  and  $3080\text{ cm}^{-1}$ , is attributed to the "out-of-plane-bending" of an exocyclic double bond as it is coming into existence for instance by dimerization of abietic acid.

For more details see LANGENHEIM & BECK (1968), RÖTTLÄNDER (1969), SCHLÜTER (1978).

On a rather broad basis of data BECK & al. (1964) could show that by means of infrared spectroscopy "Baltic amber" can be identified and discerned from other fossil resins with a high degree of certainty. By means of computer-based studies BECK could show (1966, quoted in SCHLÜTER) that succinite can be identified with 97 % reliability. SAVKEVICH, who had started to work with infrared spectroscopy at the same time as BECK, criticized that there is no possibility to discern "Baltic material" from other resins by this method, but – this is an important distinction! – that only the possibility to discern between succinite and other mineral species of resins exists. The geographical attribution of amber finds remain therefore problematical (see above).

Another outstanding example of evaluation of infrared spectra of resins has already been mentioned above: the determination of the botanical origin of fossil resin from Chiapas (Mexico) by LANGENHEIM (1966) on a really broad basis of data with a high degree of reliability.

Thus infrared spectroscopy will remain for the future one of the most important methods for a quick characterization of fossil resins and for the identification of succinite and some other resin species. Nevertheless one must realize the limits of this method which one can perhaps summarize in the simple slogan: different infrared spectra indicate different mineral species of fossil resins, but identical spectra need not always mean identical fossil resins. The higher the geological age of a sample is, the more similar the infrared spectra obviously are.

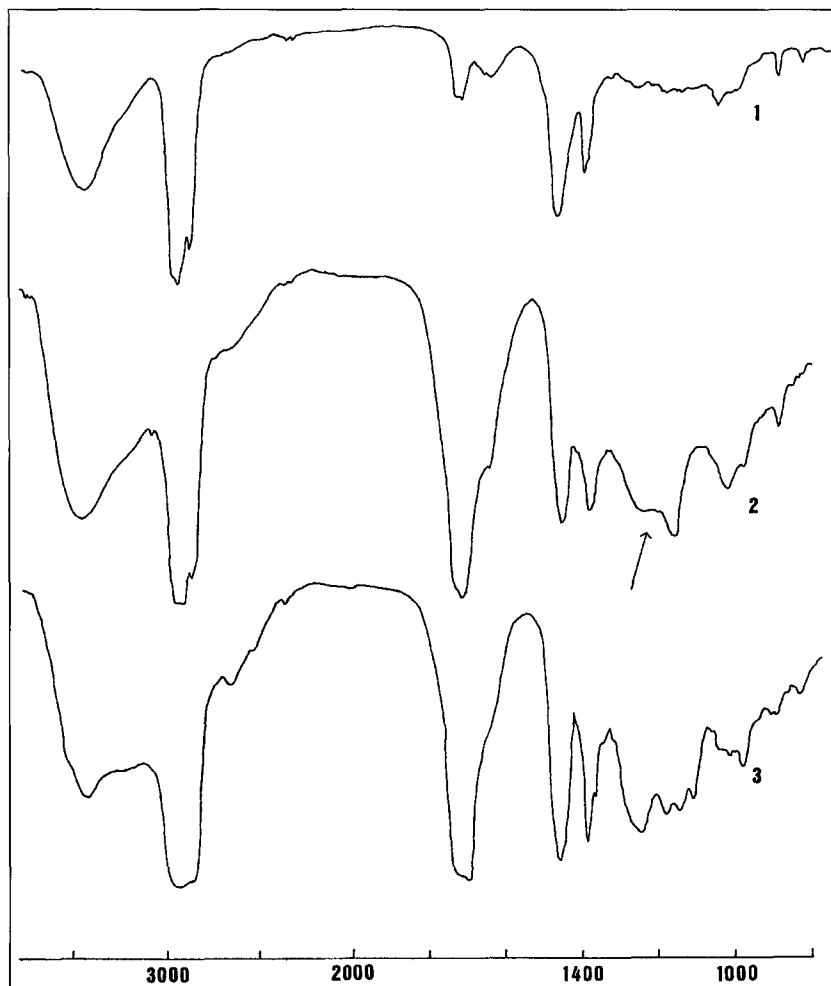


Fig. 1.  
Infrared spectra of fossil resins (Abscissa: wave-number in  $\text{cm}^{-1}$ ).

- 1) Resin from the Roßfeld strata (Upper Valanginian/Hauterivian) near Golling (Salzburg), Material: Dr. HERNDLER.
- 2) Resin from Walchow near Obora (CSFR) – "Baltic shoulder" (arrow) helps to identify this sample as succinite. Material: Dr. WEITSCHAT.
- 3) Simetite, Sicily – Spectrum enables to discern this resin from succinite, Material: Prof. STEININGER, resp. V. FECOROTTA and ROMEO.

## 7.2. Mass Spectroscopy

Mass spectroscopy would offer an additional possibility for the characterization of the whole resin sample; nevertheless this method has found only very limited application until now. The reason is rather obvious: the usual method based on electron impact ionization yields a high degree of fragmentation resulting in spectra which are not very informative and offer sometimes only a low chance to discern fossil resins on this basis. Such spectra can be called "debris spectra": many (usually small) fragments, no distinct molecular ion peaks, a low chance to identify characteristic peaks.

Nevertheless there exists one variety of mass spectroscopy which can be successfully used: field ionization, as applied to the study of fossil resins by MISCHER & al. (1970). Using this method, molecular ion peaks are formed to a considerable extent, very good spectra with a low amount of "molecular debris" offer a fair chance for comparisons. By this method the above-mentioned authors could even discern between succinite and (the rather similar) rumenite. This method has nevertheless one important disadvantage: the high price of the equipment. Thus it will always be restricted to a very few laboratories. The "standard" student of resins will have only the chance to try his luck with the above-mentioned "debris spectra" like BANDEL & VAVRA (1981) – or decide for the use of other methods.

Similar (financial) restrictions exist in respect to nuclear magnetic resonance of solid samples, as already applied to fossil resins too (SAVKEVICH, 1970) and in respect to other "more sophisticated" methods.

A fair chance nevertheless does exist for the application of mass spectroscopy to identify single compounds of low molecular weight by standard equipment as used for instance already by THOMAS (1969) or by GRANTHAM & DOUGLAS (1980).

## 7.3. Pyrolysis and Thermolysis

There do exist at least two more methods to characterize the whole resin sample; one of them is pyrolysis in combination with gas liquid chromatography, the other one thermolysis and thin layer chromatography of the thermolysis products.

The combination of pyrolysis and gas liquid chromatography has been applied for fossil resins already by MISCHER & al. (1970) or by STREIBL & al. (1976) and also by SORG & KREBS (1986). Results are

quite promising and show that by this technique there exists a fair additional chance for "finger-printing" of fossil resins. Thus SORG and KREBS could discern succinite, fossil resins from Bitterfeld, the Dominican Republic and from Columbia.

Thermolysis seems to offer an additional approach by extending the possibilities of thin layer chromatography ("TLC"). TLC has of course been applied to fossil resins always and always again, but the fact that only the soluble part of a resin could be characterized by this method puts always an unpleasant limit to this rather simple analytical technique. Therefore VAVRA & VYČUDILÍK (1976) tried to apply the so-called TAS-method according to STAHL (equipment available from DESAGA) to the study of fossil resins. The results seem quite promising and will find application in future also for the TLC of other substances of high molecular weight in organic geochemistry. Moreover it's a method "for the small purse" – which is also an aspect worth mentioning.

## 7.4. Gas Liquid Chromatography

Soluble fractions of fossil resins were already characterized by means of gas liquid chromatography in the above-mentioned publication by STREIBL & al. (1976); derivatives of resin acids (methyl esters) have been identified by this method already by THOMAS (1969) or by GOUGH & MILLS (1972) etc. An additional variety of this method having the advantage of being really simple and easy is the gas liquid chromatography of silylation products in a soluble fraction

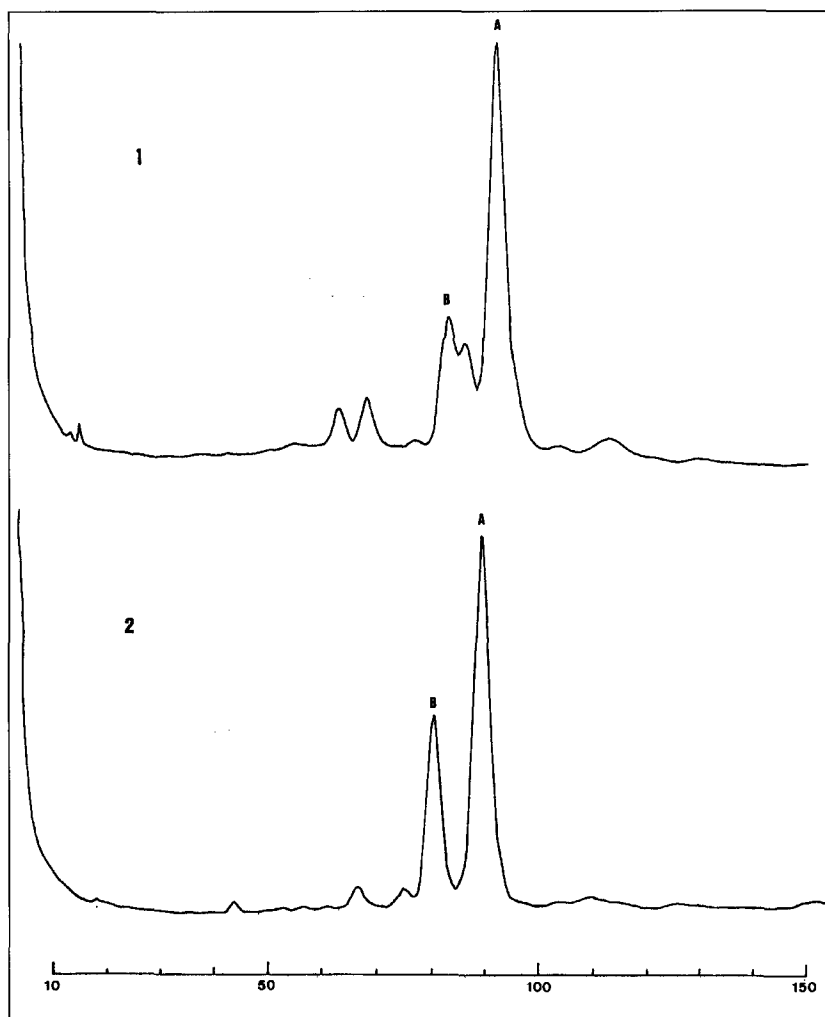


Fig. 2.  
Gas liquid chromatograms (detector response versus retention time in minutes) of a silylated pyridine-soluble fraction of:

1) Rosthornite, Eocene, Carinthia.

2) Recent elemi-resin

Based on comparison with authentic material, peak A could be tentatively identified as alpha-amyrin and peak B as beta-amyrin (see Fig. 3). Identification has been confirmed by mass spectra meanwhile.

of fossil resins (VAVRA, 1982; VAVRA, 1990). About 30–100 mg of a sample of a fossil resin are treated with pyridine and “BSA” (a silylation reagent: bistrimethylsilylacetamide) at 120°C for one hour and then the supernatant solution is applied directly for gas liquid chromatography without any further separation or cleaning. The gas chromatograms thus achieved are of rather good quality, they can even be improved to a considerable extent if the chromatography is not performed at constant temperature, but by the use of a “temperature program”. Examples for such chromatograms are given (see Fig. 2, Fig. 4). Results achieved by the application of this method can be given in a few words. In addition to the above-mentioned infrared spectroscopy this method seems to offer a further chance for a fast but nevertheless rather detailed characterization and comparison of fossil (and Recent) resins. Qualitative comparison of the chromatograms under identical conditions by means of comparison of retention times can of course be improved by adding quantitative informations yielded by the use of a laboratory computer. Nevertheless the results thus achieved are not satisfying at least in one respect: identification of single peaks by comparison with authentic substances remains – as so often in gas chromatography – at least a little bit uncertain and (what is far more disturbing and annoying !) authentic substances are usually not available, resulting thus in comparison of unknown peaks of some resin sample with unknown peaks of an other sample.

In this respect the use of a mass-sensitive detector (i.e. a small quadrupole mass spectrometer) which is available in the author's laboratory since a few weeks will offer a decisive improvement of analytical facilities for the future (see below).

Nevertheless even the “simple” gas liquid chromatography as it has been available until now has yielded quite interesting results. Identification and comparison of single species of fossil resins, resulting even in a (faint) chance to discern between succinite and rumaenite (GHIURCA & VAVRA, 1990), comparison of resin samples from different localities from the Dominican Republic and in one case even a promising identification of the botanical source of a fossil resin from Austria: the “rosthornite” from Carinthia (Paleogene) could be identified as a fossil elemi-resin (see Fig. 2; see also VAVRA, 1990). Only this rather uncommon mineral as well as a sample of authentic glessite (from Bitterfeld, Germany) showed the occurrence of two amyryns (Fig. 3), with their typical, rather high retention times. Upon the basis of identical retention times as compared with Recent elemi-resins as well as by means of comparison with retention times of pure, authentic, commercially available amyryns these two substances could be identified in a preliminary way. Meanwhile mass spectra have proved that this assumption had been correct. Amyryns (see also above) do occur in many different plants, but among resin-producing plants the Burseraceae can be regarded as the only possible source for this type of resins. Burseraceae, now being restricted in occurrence to the tropical and subtropical zone have according to these results left fossil resins in the Eocene of Carinthia and in the Early Miocene of Bitterfeld as well. For Bitterfeld this result was not as unexpected as it seems. The sample studied having been identified (by Doz. KOSMOWSKA-CERANOWICZ, Warsaw, resp. by Dr. KRUMBIEGEL, Halle) as glessite was “suspicious” from the beginning, because of FRONDEL's identification of Baltic glessite as fossil elemi-resin (see above). Nevertheless our results give a far better and safer identification of the

amyryns now. Baltic glessite had unfortunately not been available for our studies. Special publications dealing with these interesting problems and consequences are in preparation.

### 7.5. Combined Gas Chromatography/Mass Spectroscopy

As suggested already above by the expression “mass-sensitive detector” the combination of gas liquid chromatography with mass spectroscopy – nowadays being one of the standard methods of organic geochemistry – will be one of the most promising methods for our future research in fossil resins.

In fact the application of this method to studies concerning fossil resins has been reported already in a few papers: GOUGH & MILLS (1972) used this method in their study of succinite for the identification of resin acids; URBANSKI & al. (1976) identified in this way volatile substances extracted from succinite with tetrahydrofurane; GRANTHAM & DOUGLAS (1980) have used the same method for the identification of single terpenes from fossil resins, on the basis of which they could suggest in a reasonable way the botanical origin of their samples. In fact this way of combined gas liquid chromatography and mass spectroscopy is not a new method in the field of amber research, but it has been applied until now only by a rather limited number of authors. Therefore its extended application in the future should yield a lot of promising results. The only disadvantage is of course the fact that only the soluble fractions of resins are studied and characterized by this method.

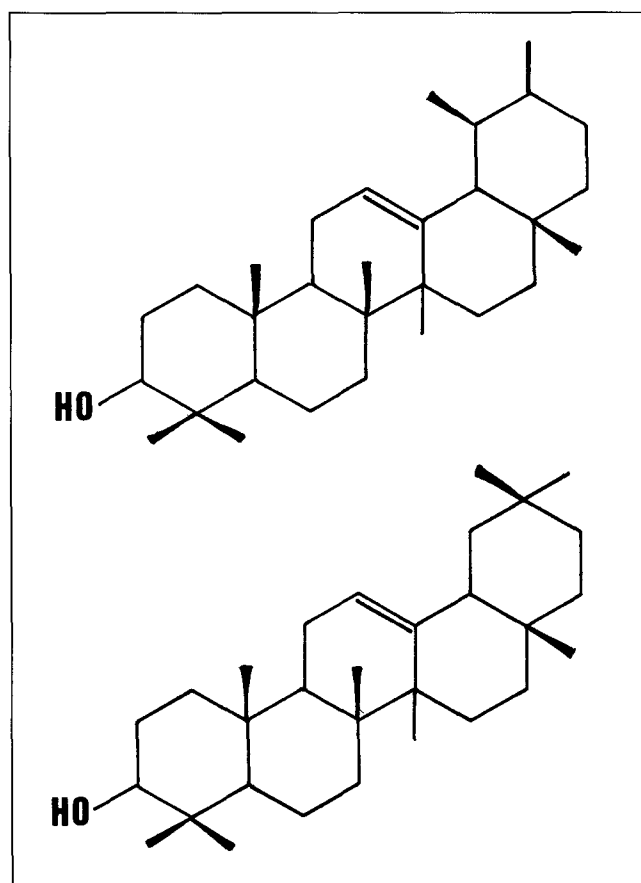


Fig. 3. Formulae of two pentacyclic triterpenes: alpha-amyrin (above) and beta-amyrin (below).

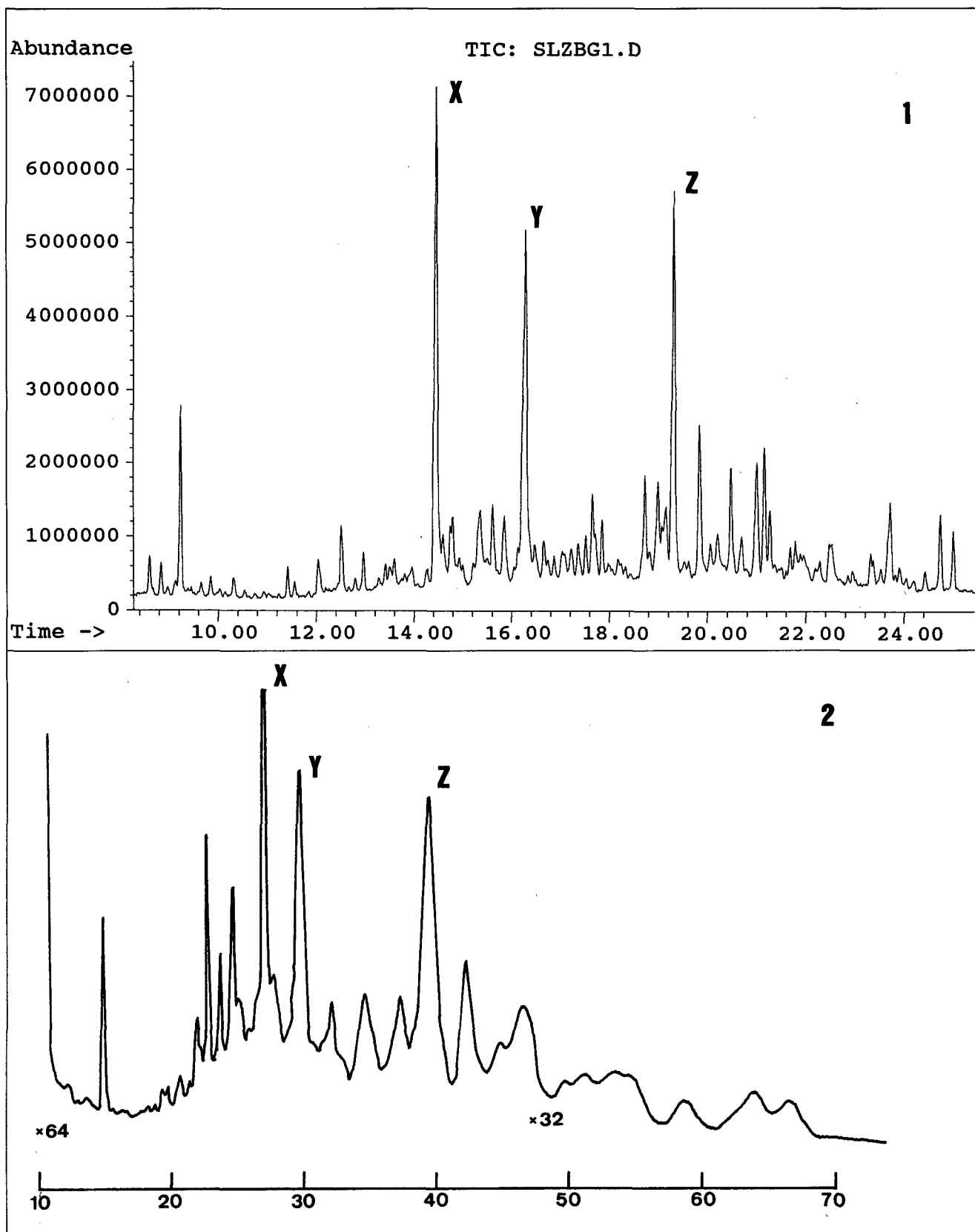


Fig. 4.

Comparison of two chromatograms of the silylated, pyridine-soluble fraction of resin from the Early Cretaceous of Golling, Salzburg.

1) Total ion chromatogram (ion abundance versus retention time in minutes) HEWLETT PACKARD 5890, series II gas chromatograph, MSD, carrier gas: helium, capillary column: HP-1 (cross-linked methyl silicone gum) 12 m x 0,2 mm x 0,33  $\mu$ m film thickness. Temp. program: 2 min 100°C, 6°C/min., final temp: 250°C..

2) Gas liquid chromatogram (detector response versus retention time in minutes) PERKIN ELMER 3920 B, FID, carrier gas: nitrogen, packed column: glass, 1,8 m, OV-11. Temp. program: 4 min at 100°C, 8°C/min., final temp.: 250°C. Attenuation as indicated: x64, x32.

Corresponding peaks in both chromatograms: X, Y, Z.



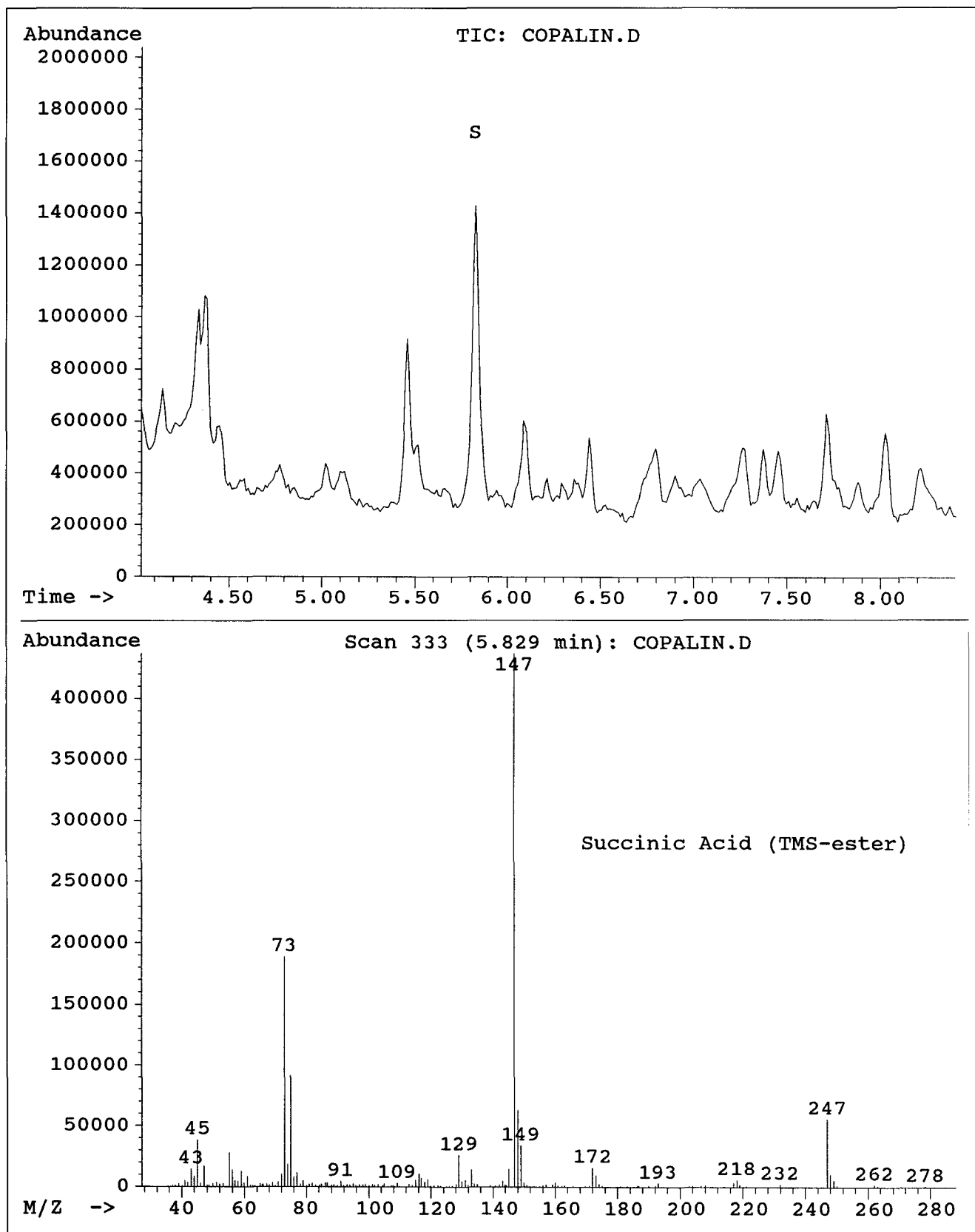


Fig. 5. Identification of single compounds in a silylated, pyridine-soluble fraction of a fossil resin ("copaline" from Gablitz, Eocene, Lower Austria) by combined gas chromatography/mass spectroscopy: part of the total ion chromatogram ("TIC", above) and mass spectrum of peak "S" (TMS-ester of succinic acid, below).

In respect to the author's laboratory facilities the introduction of this method has also had the consequence that gas chromatography using "packed columns" could now

be replaced by the technique using capillary columns – yielding far better separation possibilities. As an example results for the resin from Golling are given (Fig. 4). By

means of the use of packed columns (1, 8 m length) a separation of the soluble fraction could be achieved showing the presence of 15–20 single compounds; by the use of a capillary column (12 m length) more than 90 (!) substances could be separated. The far higher sensitivity by using a mass spectrometer as detector has of course also contributed to the increase of the number of peaks.

## 8. Future Aspects of Studies

By application of laboratory facilities as described above to as many fossil and Recent resins samples as possible a lot of detailed informations and results concerning Austria's organic minerals can be expected for the close future. The fact that questions as, for instance, identification of succinic acid in a fossil resin can now be answered with high reliability within a rather short time (see Fig. 5) will help to establish a compilation of data, which can also result for some cases in the identification of "chemical fossils" in fossil resins which can be a help for the determination of the botanical source of the sample.

The use of a computerized library of approximately 130.000 mass spectra ("Wiley-library" by HEWLETT-PACKARD) which can be searched automatically is a further valuable help for suggesting identifications of unknown compounds. Thus a rather extended knowledge for many fossil resins – at least as far as their soluble fractions are concerned – can be expected.

Establishment of a special library of mass spectra for direct identification of mineral species of fossil resins has also been initiated. First results also indicate that the fate of organic structures during diagenesis can be easily followed by means of this method too.

Finally studies of this kind shall not remain restricted to fossil resins: terpenes from soluble resin fractions of coals are to be included in our studies in the future hoping to establish additional data for coalification studies of organic substances.

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