

# Organic geochemical evidence for pine tar production in middle Eastern Sweden during the Roman Iron Age

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## Abstract

Several funnel-shaped features of unknown function were discovered at excavations related to a new stretch of the highway E4 in middle Sweden during 2002–2003. These features could be sub classed into two categories: large funnel-shaped pits dated to 600–1100 AD (Vendel period – Viking Age) and small funnel-shaped pits dated to 240–540 AD (late Roman Iron Age – Migration period) respectively. Soil samples were analysed for diterpenoids derived from abietic acid (mainly retene, abietic acid, dehydroabietic acid and methyl dehydroabietate) by Gas Chromatography-Mass Spectrometry (GC-MS) in order to test the hypothesis that the features might be connected to pine tar manufacture. For comparison, samples from historically known pine tar and charcoal production features were analysed. The resinous fraction in the larger funnel-shaped features were very similar to those of the historical pine tar and charcoal production features, while the composition in the small funnel-shaped pits was dominated by retene and methyl dehydroabietate. The biomarker, methyl dehydroabietate, could be identified in several of the soil samples from the funnel-shaped pits. We suggest that both of these features have been used for pine tar production, which makes the smaller funnel-shaped features the oldest known tar production features in Europe.

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## 1. Introduction

The investigation of wood tar products in residues found in association with ships was one of the first successful applications of organic analysis on archaeological material [25,17]. Since then several successful studies in order to identify different products of distilled wood of both *Pinaceae* (e.g. spruce and pine) and *Betulaceae* (e.g. birch) origin have been carried out (e.g. [3–5,9–11,13–15,20,22,28,30]). The analyses have so far been made on materials that have been identified to be or assumed to be some kind of resin, tar or pitch. In this study we have concentrated on soil samples.

Tar derived from Scots pine (*Pinus sylvestris*) was an essential export product in Sweden during the Hanseatic period and continued to be so until modern times. This was particularly significant during the 17th and 18th century when the merchant fleets and navies of Europe needed large amounts of pine tar. A main source was the pine forests of the kingdom of Sweden-Finland and the common name ‘Stockholm tar’ for pine tar from many different areas was a well-known product. It is, however, undoubted that tar of *Pinaceae* origin was produced in the area during prehistoric times, but how and to what extent has been an unsolved question. The main objective of this study is to learn how pine tar/pine pitch was produced during earlier periods in middle Sweden. The chemical analytical technique used is gas chromatography-mass spectrometry (GC-MS) on lipid extracts

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from soil samples collected from possible production features in order to study pine tar production methods.

## 2. Biochemical markers of wood tars

Triterpenoid resinous compounds originating from birch bark tar have been detected in several archaeological contexts from the Mesolithic and later periods (e.g. [1,27,2,35]). GC-MS analysis of archaeological tar of birch origin has demonstrated that the triterpenoid betulin (lup-20(29)-ene-3 $\beta$ ,28-diol) is retained as a major component (e.g. [20,30]). However, betulin is not a biomarker for birch tar since it is present in untreated birch bark as well ([20]).

Diterpenoids are the predominant constituents of higher plant resins and supportive tissue, especially in conifers, such as pine and spruce. Diterpenoid acids such as abietic acid and dehydroabietic acid have for long been known to be the major constituents in conifer resin [34]. During distillation of resinous conifer wood some of the acids will react with methanol and become methylated. The transformation from abietic acid to methyl dehydroabietate is illustrated in Fig. 1. Methyl dehydroabietate is thus related to dry distilled *Pinaceae* and is hence a suitable biomarker for this substance [26]. The four diterpenoids retene, abietic acid, dehydroabietic acid and methyl dehydroabietate are all major components in pine tar and have been chosen as key compounds in this study. Since this study mainly treats soil samples it should be noted that dehydroabietic acid, derived from the rapid conversion of abietic acid, is relatively common in sediment, especially in the northern hemisphere where conifers are abundant, and is stable over geological time periods [31].

## 3. Archaeological background

During the seasons 2002–2003 several sites were excavated in the province of Uppland, in connection with an expansion and a new stretch of the highway E4

between Uppsala and Mehedeby (Fig. 2). Features of a previously unknown function were identified at several of the investigated sites during the first year. These features displayed similar characteristics in shape, dimension and filling. After topsoil stripping the features appeared as dark coloured circles with a diameter between 0,5–1,3 m. At first some of them were interpreted as postholes due to their shape or as circular hearths due to their dark filling. However, the distinct shape and the similarities between several features indicated that this kind of feature must have had a particular function. As seen in Fig. 3 the top part was funnel-shaped with vertical edges below forming a cylindrical shape at the bottom.

Subsequent excavations the following year revealed features with clear resemblance in shape but much larger in size. A low circular bank consisting of soil from the digging out of the cylinder encircles the funnel. The bank has an outer diameter of 7–9 m. The funnel had a diameter of ca. 2 m and depths of up to more than 2 m. The bank and the depression in the centre were visible prior to excavation, as seen in Fig. 4. Another difference, apart from the sizes of the small and large features, was the location in the landscape. The smaller funnel-shaped pits are found on the present farmland at the same location as the Early Iron Age settlements, while the larger features are found in the woodland quite far from the closest settlement of any period.

### 3.1. Early pine tar-production in Scandinavia

From historical times there are several methods of pine tar production known in the area, all using internal heating. The terminology of the methods appears somewhat confusing since several similar terms are used for different methods and the terms differ between regions. The development of production methods of larger quantities is often described as starting with the tar ‘grave’ (Sw. tjärgrav), which, sometimes, also is referred to as tar ‘dale’ (Sw. tjärdal). The tar ‘grave’ consisted of, as

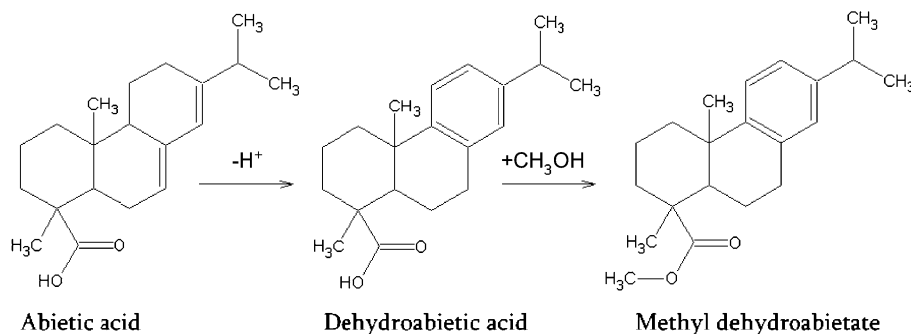


Fig. 1. Abietic acid is a main component in resins of *Pinaceae* origin. Abietic acid can convert into dehydroabietic acid through dehydrogenation and isomerisation reactions. Dehydroabietic acid is, apart from being a major constituent in pine resin, also relatively common in sediment in areas where *Pinaceae* has grown. During distillation of pine resin some of the dehydroabietic acid will react with methanol and form methyl dehydroabietate, which is a main component in tars of *Pinaceae* origin and a biomarker for distilled dehydroabietic acid.

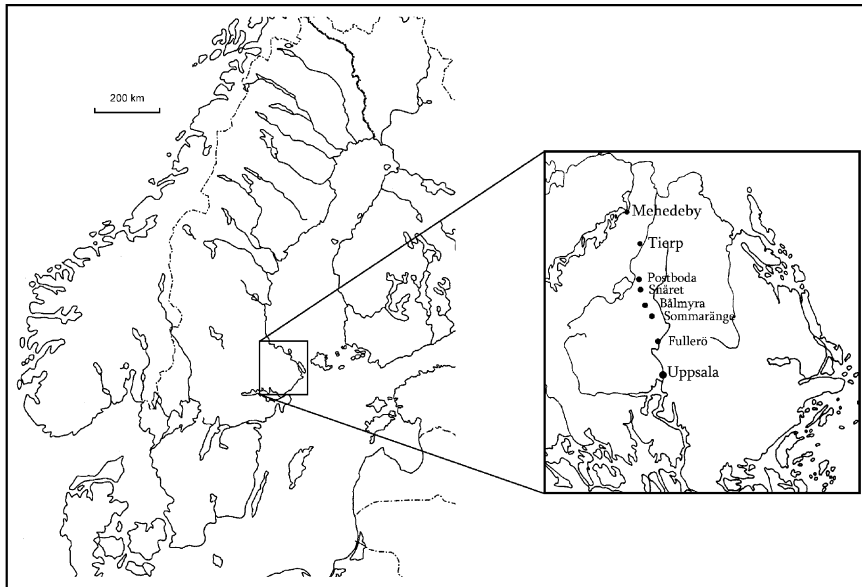


Fig. 2. Map of the study area.

the name implies, an oblong, shallow ditch that was dug in a slope. The resinous pinewood was placed in the ditch and covered with peat and soil. It was then ignited in its upper part to cause the produced tar to flow down to a vessel at the other end of the tar ‘grave’. A supposed later method, known from Finland, is described by N. E. Villstrand [36], who gives an account of a funnel-shaped pit used for pine tar production. The tar ran down the sides of the pit to the bottom where the tar could be collected after the coal had been removed. This method should have come into use, towards the end of the Middle Ages, at the latest [36]. A very similar production technique is the bog-tar kiln known from Trøndelag in Norway [18]. These pine tar kilns were situated in bogs and the cylinder where the tar is collected was filled with water. The dates of the bog-tar kiln are concentrated to the 17th–18th century. However, one kiln is, through an artefact, dated back to the 12th century. The descriptions

of both the Finnish and the Norwegian tar pit seem very similar to the larger funnel-shaped pits from the excavations in Uppland. An improvement of the enclosed tar pit took place when a dugout log was placed at the tip of the funnel, which functioned as a channel for the running tar and made it possible to collect the tar during distillation. This kind of construction is referred to as tar ‘dale’ in Swedish, just like the tar ‘grave’, something that causes confusion. But the proper tar ‘dale’ differs from the tar ‘grave’ in the fact that the tar wood is placed in a pit on a slope rather than in a ditch. One side of the tar ‘dale’ is often strengthened or built up as shown in the schematic illustration of a tar ‘dale’ in Fig. 5. The tar ‘dale’ is the best-documented production technique (see Fig. 6) and dominated the tar production at least from the 16th century until the industrial production appears. However, this dating is approximate and the technique was probably introduced earlier.

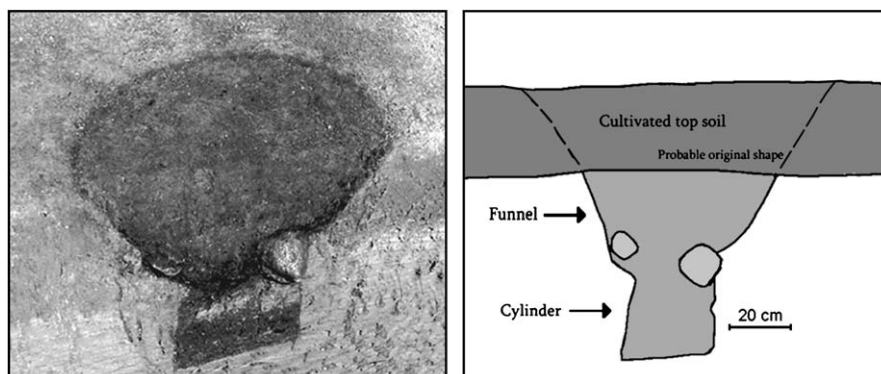


Fig. 3. Small funnel-shaped feature A4177 from Sommaränge.

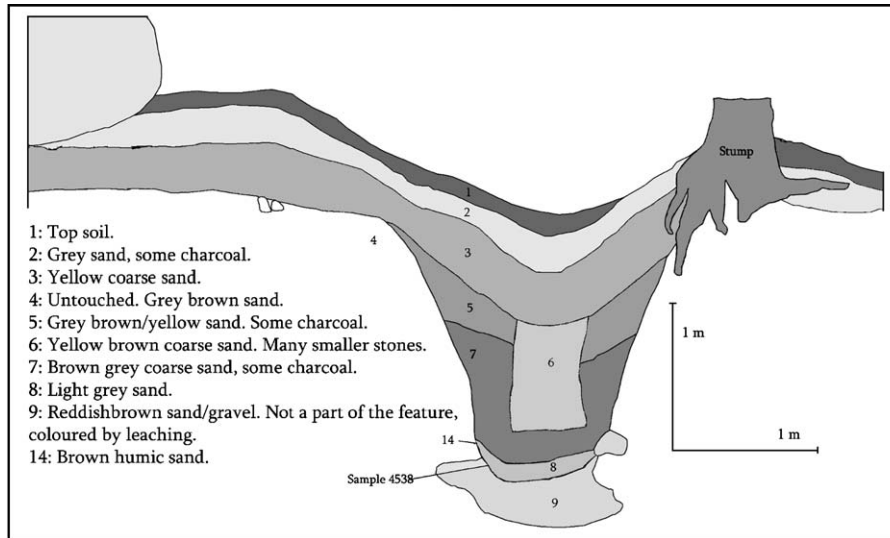


Fig. 4. Large funnel-shaped feature from Postboda. Sample 4538 taken from the thin layer at the bottom of the feature.

#### 4. Material

If in fact the funnel-shaped features were used for pine tar production, the biomarkers for destructively distilled *Pinaceae* could be expected to be present in the soil from the features. To be able to find methyl dehydroabietate in the soil stipulates that the filling in the features originate from the primary function of the feature and not from a secondary refilling of soil from surrounding cultural layer. The filling in the smaller funnel-shaped pits differed clearly from the filling in other features (both primary and secondary filling) at the settlement. This made us assume that the filling of the investigated features was related to the actual features, possibly by being refilled with the remaining material after the produced product had been removed and collected.

All analysed soil samples are shown in Table 1. The samples of the larger funnel-shaped pits were collected

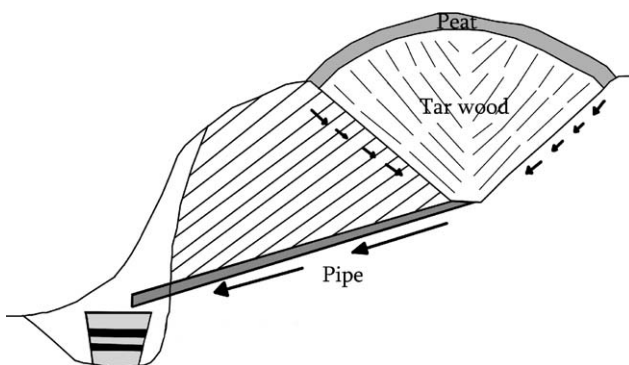


Fig. 5. Schematic illustration of a tar 'dale'. The hatched area to the left of the tar pit might be constructed in several different ways. It is often built up by a raked wooden construction or strengthened in some other way. The arrows show the flow of the pine tar.

from four features at the three sites Postboda, Bålmyra and Snåret. The samples of the small funnel-shaped pits come from two features in Fullerö [8] and from three features in Sommaränge [6]. Five samples were analysed from the large features and eight samples from the small features. As reference material soil samples from known historical pine tar and charcoal production features as well as soil samples from cultural layers and from other features from Iron Age settlements were analysed. The comparative material from known historical pine tar and charcoal production features were collected from: One tar 'dale', two charcoal stacks and one charcoal keep. The tar 'dale' was expected to provide a comparative soil for pine tar production. The charcoal stacks and possibly the charcoal keep might also provide comparative soil since the remaining material, the leftovers in the bottom, might have methylated even though that was not the intention with the feature. Reference soil samples were collected from two hearths and from a kiln from the Iron Age settlements in Fullerö and Sommaränge. In addition eleven soil samples from cultural layers from three Iron Age settlements (Tuna, Vendel parish, Up; Kyrsta, Årentuna parish, Up; Fullerö, Gamla Uppsala parish, Up) were analysed. In order to get a comparative material the solvent extractable components of modern pine tar and pine resin from *Pinus sylvestris* have also been analysed.

##### 4.1. Dating of the analysed features

When the large funnel-shaped pits were found they were believed to be contemporary with the tar 'dale', i.e. from historical times. The results from the radiocarbon dating, shown in Table 2, place them, however, in an interval between the years 680–1160 AD, that is,



Fig. 6. Depiction of a tar 'dale' (Juvelius, 1747). Essential tools and the drain with the tar barrel are depicted explicitly [24]. Edited after reproduction by Ulf Lundin/The Royal Library.

the Vendel period – Viking Age/medieval time. A stone from one of the large funnel-shaped pits was dated by optically stimulated luminescence (OSL) [21]. The result gives a date for the last heating of the stone to the years  $944 \pm 70$  AD. The dating of the small funnel-shaped pits are earlier and the radiocarbon dating lies in the interval of the years 240–540 AD, which is the later Roman Iron Age-Migration period. One of the radiocarbon dating from a small funnel-shaped pit dates back to the years 800–200 BC, but a single sample has to be treated very cautiously, especially when the main part is so well grouped.

The tar 'grave' is dated back to the years 1030–1210 and the tar 'dale' to 1300–1430, which is a rather early dating for the tar 'grave'. The best pine tar wood, containing high amounts of resinous acids, consists of old stumps and roots. If this kind of material was used, it would give a radiocarbon date much earlier than the actual utilization of the tar production feature. However, the pieces of charcoal selected for radiocarbon dating from both the small [12] and the large [21] funnel-shaped pits derives from young trees representing a short radiocarbon event. The radiocarbon dating from the small funnel-shaped pits also corresponds with the

Table 1

The symbol ○ indicates that some of the analysed compounds have been identified in the sample. Methyl dehydroabietate was not present in the sample marked with the symbol ⊙

Sample	Category	Feature	Location	Comment
upmu2559 ○	Charcoal stack		Bålmyra	
upmu3665	Reference	Next to 3444	Snåret	
upmu3669 ○	Funnel-shaped pit	3444	Snåret	Layer 9
upmu3670 ○	Funnel-shaped pit	3444	Snåret	Layer 5
upmu4278 ○	Charcoal keep	4128	P8	Inside the wall
upmu4538	Funnel-shaped pit	3851	Postboda	From bottom layer
upmu4541 ○	Funnel-shaped pit	3883	Postboda	
upmu4562 ○	Reference	Next to 3851 & 3883	Postboda	
upmu4798 ○	Tar 'dale'	4712	P60	
upmu6937 ○	Charcoal stack	4802	L173	
upmu50044 ○	Funnel-shaped pit	57.1	P57	
so19077	Small funnel-shaped pit	10333	Sommaränge	
so19081	Small funnel-shaped pit	10317	Sommaränge	From the funnel
so19106 ○	Small funnel-shaped pit	4177	Sommaränge	From the lower part of the funnel
so19111 ○	Small funnel-shaped pit	4177	Sommaränge	From the cylinder
so20027	Hearth	19184	Sommaränge	
so35213	Cultivation layer		Sommaränge	
so35214	Under cultivation layer		Sommaränge	
fu.A4961	Low temperature oven	4961	Fullerö	
fu5620 ○	Small funnel-shaped pit	3061	Fullerö	From the funnel
fu5621 ○	Small funnel-shaped pit	3061	Fullerö	From the cylinder
fu5622	Reference	Next to 3061	Fullerö	From the section
fu5629 ○	Small funnel-shaped pit	3052	Fullerö	From the funnel
fu5630 ○	Small funnel-shaped pit	3052	Fullerö	From the cylinder
fu5631	Reference	Next to 3052	Fullerö	
fu.A5654	Hearth	5654	Fullerö	
ky115959	Cultural layer		Kyrsta, Up	
ky115971	Cultural layer		Kyrsta, Up	
ky115984	Cultural layer		Kyrsta, Up	
ky126344	Under Cultural layer	Glacial clay	Kyrsta, Up	
ve124	Cultural layer		Vendel, Up	
ve126	Cultural layer		Vendel, Up	
ve206 ○ ⊙	Cultural layer		Vendel, Up	
ve249 ○ ⊙	Cultural layer		Vendel, Up	
ve701 ○ ⊙	Cultural layer		Vendel, Up	

general dating for the settlements where they have been found. The raw material for the Swedish-Finnish pine tar production of the 17th and 18th centuries consisted mainly of resin-soaked stems from relatively young pine trees. This can be accomplished by debarking the pine trees during a period of three to four years in order to accelerate the lightwood formation of the trees [19]. The use of young pine trees was as a result of the increasing demand for pine tar, and the peasants, who performed the burning, were either too impatient or too poor to wait for the stumps to mature naturally [36]. A similar demand or lack of suitable material cannot be presumed to have existed during the Iron Age. However, to use pre-treated young pine trees as well as old stumps and roots for effective pine tar manufacture

has proven to be a possible mode of procedure. Altogether this gives rather positive indications that if the small funnel-shaped pits were used for pine tar production they were used during the Roman Iron-Age.

## 5. Method

### 5.1. Extraction and derivatisation

The soil-samples consisted of about 5 g dried and sieved soil. As an internal standard (IS) 10 µg n-hexatricontane (C36) was added. The soil was extracted with chloroform/methanol (2:1, v:v) followed by sonication, sedimentation and centrifugation. The extracts

Table 2  
Radiocarbon dates from features mentioned in the text and from related features. Calibrated according to [33]

Feature	Radiocarbon age BP	Calibrated (1sigma)	Context	Laboratory no.	Material
A18479	1730 ± 45	240–390 AD	Small funnel shaped pit	Ua-20901	Spruce
A14153	1650 ± 45	260–530 AD	Small funnel shaped pit.	Ua-20902	Pine
A14153	1585 ± 45	420–540 AD	Small funnel shaped pit	Ua-20903	Pine
A4177	1655 ± 40	260–440 AD	Small funnel shaped pit	Ua-20904	Pine
A18290	1615 ± 40	400–540 AD	Small funnel shaped pit	Ua-20905	Spruce
A3061	1740 ± 45	130–420 AD	Small funnel shaped pit	Ua-26671	Pine
A3080	2360 ± 50	800–200 BC	Small funnel shaped pit	Ua-26672	Pine
A3071	1750 ± 40	130–410 AD	Small funnel shaped pit	GrN-27809	Pine
A2582	570 ± 30	1300–1430 AD	Tar 'dale'	Poz-4731	Pine
A2702	915 ± 30	1030–1210 AD	Tar 'grave'	Poz-4643	Pine
A3444	1230 ± 30	680–890 AD	Large funnel shaped pit	Poz-4649	Pine
A3883	975 ± 30	990–1160 AD	Large funnel shaped pit	Poz-4729	Pine
A57:2	1185 ± 30	770–960 AD	Large funnel shaped pit	Poz-4646	Pine
A57:1	1145 ± 30	780–990 AD	Large funnel shaped pit	Poz-4716	Pine

(2.5–3.0 ml) were transferred to vials and evaporated by a stream of nitrogen after which the lipids were redissolved into a concentration of 10 mg ml<sup>-1</sup> through sonication in chloroform. A known amount (50–100 µl) of the lipid-solution was treated with *bis*(trimethylsilyl)-trifluoroacetamide (BSTFA) with 10% (v) trimethylchlorosilane (at 65° for 30 minutes). The excess derivatising agent was removed by a gentle stream of nitrogen after which the samples were redissolved into *n*-hexane.

### 5.2. Instrumental analyses/GC-MS

The GC-MS analyses were conducted on a Hewlett-Packard (HP) Model 6890 GC equipped with a SGE BPX5 capillary column (15 m × 0,25 mm × 0,25 µm). The oven temperature was held at 50°C for two minutes, ramped at 10°C min<sup>-1</sup> to 360°C and held there for 15 minutes. Helium was used as carrier gas, held at a constant flow of 2 ml min<sup>-1</sup>. Injection was done by pulsed splitless technique at 350°C with a pulse pressure of 17,6 Psi. The GC was coupled to a HP 5973 Mass Selective Detector, by an interface with a temperature of 350°C. Scanning in the range of *m/z* 50–700, providing 2,26 scans sec<sup>-1</sup>. Fragmentation of separated compounds was done by electronic ionisation (EI) at 70 eV, with an ion source temperature of 150°C. Chromatograms and mass spectra obtained were analysed with the HP-Chemstation A.003.00 software. To identify the compounds of interest in the total ion-chromatograms, ion-chromatograms of several characteristic ion-fragments of each specific compound were extracted in order to verify their presence or absence in comparison to the distributions of our authentic reference samples. To obtain the relative abundance of the compounds, their corresponding peaks in the total ion chromatogram (TIC) were integrated. The absolute abundance in the soil was quantified in relation to the peak-area of the internal standard.

## 6. Results

The TIC for the resin fraction of the pine tar sample is shown in Fig. 7. The dominating component is dehydroabietic acid with lesser amounts of other diterpenoids; methyl dehydroabietate, abietic acid, retene and isomers of pimaric acid, in descending order. The *n*-alkanoic acids C<sub>16</sub> and C<sub>18</sub> are also prominent. Some of the selected diterpenoids could be detected in eighteen of the thirty-five soil samples. Methyl dehydroabietate was a constituent in fifteen of these as shown in Table 1. The relative abundance of the four selected compounds is shown in Fig. 8. The selected components abundance of the TIC is presented in Table 3. The distribution of the selected components in the pine tar sample is 56% dehydroabietic acid, 18% methyl dehydroabietate, 15% abietic acid and 11% retene. Together these constituted 55.9% of the solvent extractable content. The pine resin sample was dominated by abietic acid (46%) and dehydroabietic acid (51%) but did also contain small quantities of both retene (1%) and methyl dehydroabietate (2%).

Methyl dehydroabietate was present in all four of the comparative soil samples from the historical pine tar and charcoal production features. However, abietic acid was generally missing and was only present in sample upmu4278 (7%), which indicates a higher degree of transformation from abietic acid into dehydroabietic acid in the comparative soil samples compared to the pine tar sample. Additionally, retene constituted a larger part in the comparative soils while dehydroabietic acid was equivalent in two samples and noticeably less in upmu6937 and upmu4278.

As seen in table 1 methyl dehydroabietate was identified in four out of five samples from the larger funnel-shaped pits, and in six out of eight soil samples from the smaller funnel-shaped pits. The composition in the larger funnel-shaped pits is similar to that from the pine tar comparative soil samples. The resinous fraction in

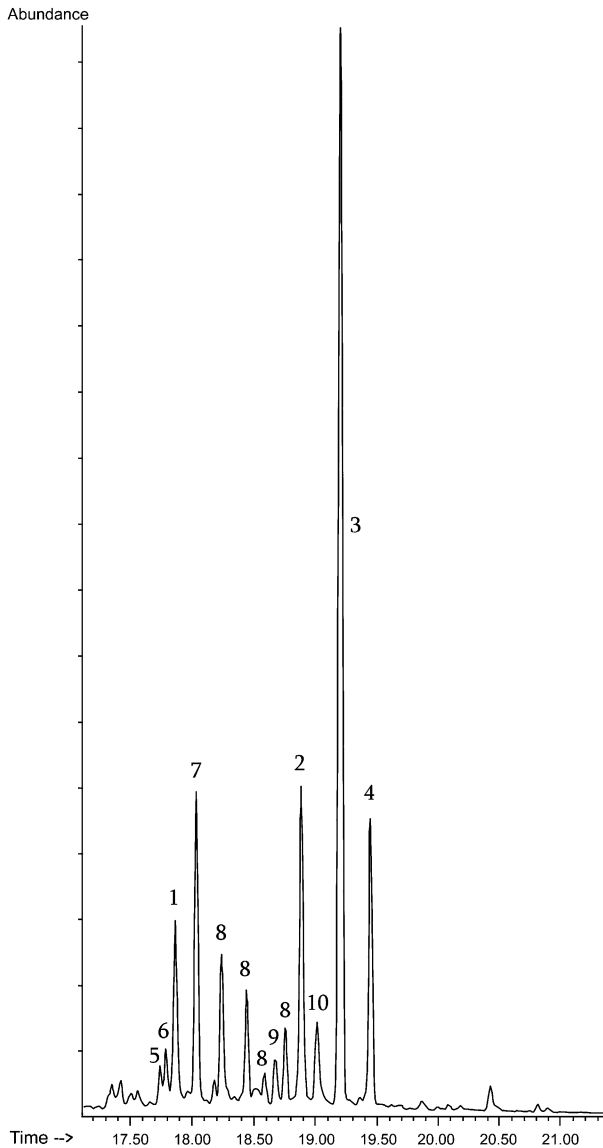


Fig. 7. Chromatogram showing the resin acid region of the pine tar sample. 1) retene; 2) methyl dehydroabietate; 3) dehydroabietic acid; 4) abietic acid; 5) *n*-alkanoic acid C<sub>18:2</sub>; 6) *n*-alkanoic acid C<sub>18:1</sub>; 7) *n*-alkanoic acid C<sub>18</sub>; 8) pimaric acid, Isomer (m/z 374); 9) 2-methyl retene; 10) abieta-6,8,11,13-tetraen-18-oic acid. The *n*-alkanoic acid C<sub>16</sub> is not shown in the selected region.

the small funnel-shaped pits constitutes a very small part of the solvent extractable content compared to the large funnel-shaped pits (Table 3), and the diterpenes were dominated by methyl dehydroabietate and retene. Traces of dehydroabietic acid could be detected in three of the eleven samples from Iron Age settlement layers (Table 1).

The triterpenoid allobetul-2-ene, indicating *Betula*, was detected in four samples: sample upmu4541 and upmu4538 from the larger funnel-shaped pits and fu5620 and fu5630 from the smaller features. The layer, where the sample upmu4541 was taken was identified as birch bark during the excavation.

## 7. Discussion and conclusion

The presence of Methyl dehydroabietate in four out of five samples from the large funnel-shaped pits, and in six out of eight soil samples from the smaller funnel-shaped pits and the similarities in composition between the funnel-shaped features and the features of known pine tar production show that the funnel-shaped features most probably were used for pine tar production.

The preservation capacity of methyl dehydroabietate in soil for at least 1700 years, as demonstrated here, makes it a good biomarker for destructively distilled *Pinaceae* also in soil from archaeological features. The presence of methyl dehydroabietate is, however, not a direct marker showing that the pine tar production has taken place where the indicator is found. Rather, it indicates the presence of pine tar and can be present where pine tar has been spilled or kept. Methyl dehydroabietate can also be produced unintentionally, as in the charcoal stacks. It is also present in smoke from campfire burning of pine wood [32] as well as in pine resin although in small amounts (Fig. 7).

The dehydroabietic acid in the soil samples from the cultural layer from Vendel parish, most probably derives from the vegetation. The present vegetation at the site is grass. This is however due to human influence and it is very likely that pine has grown at the site at some time. Evidence is both the presence of dehydroabietic acid, and because of its location situated on an esker where the unadulterated vegetation is expected to contain pine. The absence of dehydroabietic acid in the cultural layers from the Iron Age settlement in Årentuna parish is not surprising since the composition of the long chain *n*-alkanols, *n*-alkanes and *n*-alkanoic acid all in all indicates a grass land vegetation, since the land uplift made the area solid land (c. 2000 B.C.) until present times [23].

Egenberg and Glastrup [16] have studied the composition of kiln-produced pine tar from different stages of the burning process with different burning temperature. In the sample with the lowest temperature did retene and methyl dehydroabietate constituted 55.2%, and at the highest temperature 86.2%. In the same study abietic acid diminished from 18% to 1.9% with the increase in temperature. The samples were methylated prior to the analysis which means that the methyl dehydroabietate comprises both methylated dehydroabietic acid and any original methyl dehydroabietate, and that the difference in composition between them cannot be distinguished. The tendency of fewer dominating components corresponding to higher production temperature is, however, clear. Reunanen et al. [29] have investigated the chemical composition of pine tar from a barrel preserved in a marine environment. The samples from the outer part of the barrel contained tetrahydroabietic acid and 18-norabieta-8,11,13-triene (decarboxylated dehydroabietic acid) as the major components, whereas dehydroabietic acid



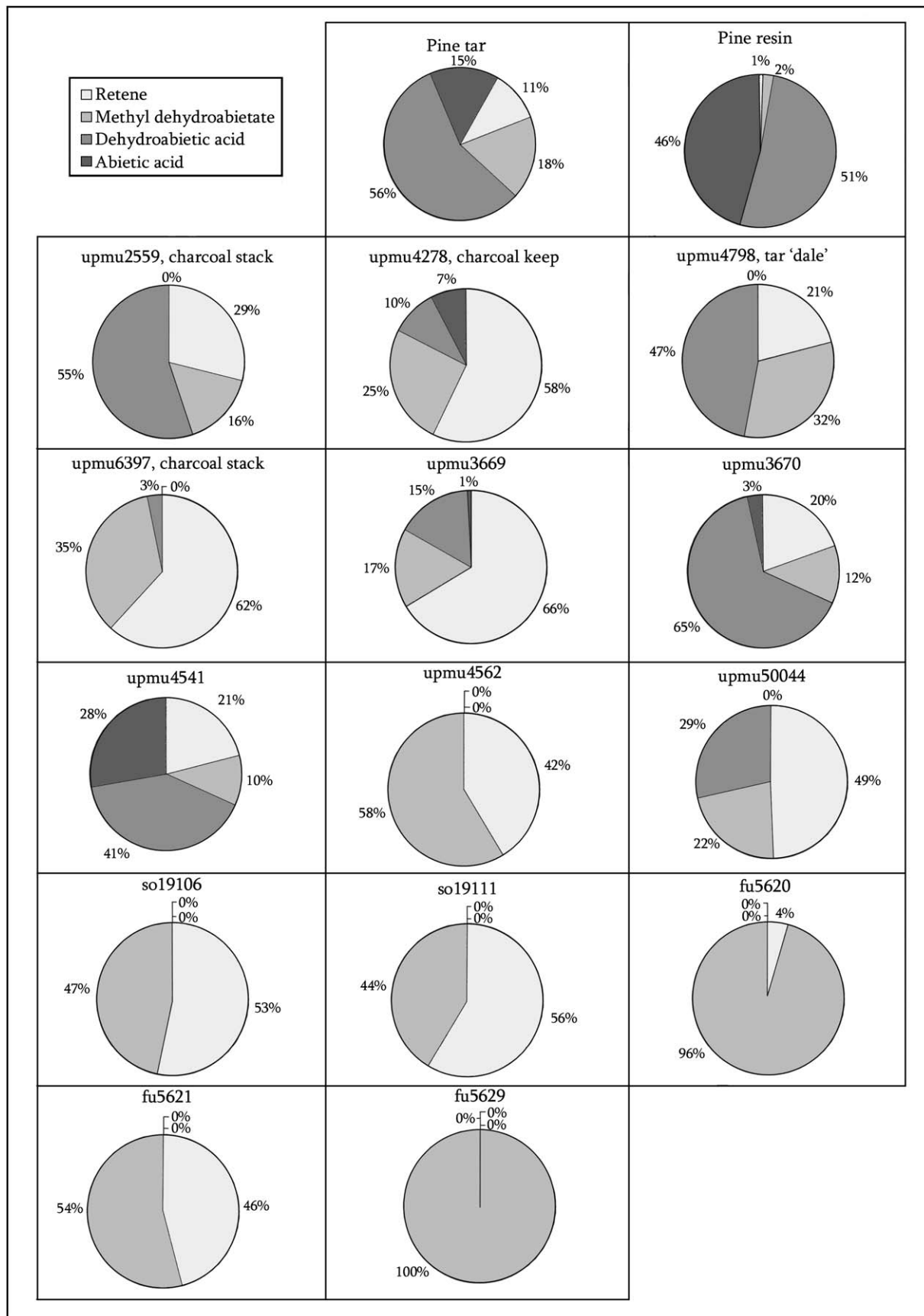


Fig. 8. The relative abundance of the four components retene, methyl dehydroabietate, dehydroabietic acid and abietic acid.

Table 3  
Content in µg per g soil and the percentage of the selected compounds of the total content

Sample	Retene	Abietic acid	Dehydroabietic acid	Methyl dehydroabietate	Total µg/g	% of total
upmu2559	2.48 µg/g /5.6%	-	4.69 µg/g /10.6%	1.37 µg/g /3.1%	42.15	19.3
upmu3669	32.76 µg/g /15.1%	0.46 µg/g /0.2%	7.93 µg/g /3.7%	8.26 µg/g /3.8%	215.38	22.7
upmu3670	6.77 µg/g /5.1%	1.15 µg/g /0.9%	22.43 µg/g /16.9%	4.10 µg/g /2.5%	130.70	26
upmu4278	7.47 µg/g /5.8%	0.97 µg/g /0.8%	1.33 µg/g /1%	3.35 µg/g /2.6%	127.34	10.2
upmu4541	1.99 µg/g /1.2%	2.61 µg/g /1.5%	3.83 µg/g /2.2%	0.98 µg/g /0.5%	169.85	5.5
upmu4562	0.07 µg/g /0.1%	-	-	0.1 µg/g /0.1%	59.54	28
upmu4798	0.88 µg/g /1.1%	-	1.96 µg/g /2.5%	1.31 µg/g /1.7%	76.30	5.3
upmu6937	64.69 µg/g /5.5%	-	3.11 µg/g /0.3%	37.29 µg/g /3.2%	1182.1	8.9
upmu50044	197.28 µg/g /5.2%	-	113.57 µg/g /3%	87.37 µg/g /2.3%	3791.73	10.5
so19106	0.57 µg/g /3.8%	-	-	0.50 µg/g /3.4%	12.93	7.2
so19111	0.17 µg/g /0.2%	-	-	0.13 µg/g /0.1%	100.49	0.3
fu5620	0.33 µg/g /0.1%	-	-	7.41 µg/g /3.2%	232.12	3.3
fu5621	0.40 µg/g /0.3%	-	-	0.46 µg/g /0.4%	118.27	0.7
fu5629	-	-	-	0.19 µg/g /0.1%	274.07	0.1
ve206	-	-	0.05%	-	-	0.05
ve249	-	-	0.07%	-	-	0.07
ve701	-	-	0.05%	-	-	0.05
Pine resin	0.09%	6.83%	7.61%	0.33%	-	14.86
Pine tar	5.98%	8.22%	31.85%	9.86%	-	55.91

and abietic acid were minor ones. The tar from the interior part was, however, similar to authentic tar extracts. The observed difference might be due to long term microbial degradation/modification of abietic type resin acids in the surface layer of the tar [29]. The reason for the composition with a complete domination of retene and methyl dehydroabietate in the older funnel-shaped feature is uncertain. It could possibly derive from a higher burning temperature, as demonstrated by [16]. It is, however, a more plausible explanation that the low absolute amounts of diterpenoids and the absence of dehydroabietic acid and abietic acid are due to diagenesis.

The result from this study gives support to the hypothesis that both the large and the small funnel-shaped pits have been used for pine tar production. The very similar composition of the historical pine tar and charcoal production features and the larger funnel-shaped pits are striking and are strong indications of pine tar manufacture. The reason for the differing composition in the older small funnel-shaped pits is most likely due to diagenesis. The resemblance in shape between the large and the small funnel-shaped pits also supports the hypothesis that they are used for the same practice. Altogether this accounts for the most plausible explanation that these features are associated with pine tar manufacturing. This makes the small funnel-shaped pits the oldest known production features of tar of *Pinaceae* origin in Europe and the large funnel-shaped pits the earliest evidence for large scale pine tar manufacture in Sweden. Since the present analysis was carried out and the small funnel-shaped pits were recognised as a new find category, this kind of feature has been recognised at several excavations, as well as in reports from earlier excavations.

One possible interpretation of the presence of allobet-*ul*-2-ene in four of the samples is that the features might have been used also for birch tar production. There are also some similarities between the small funnel-shaped pits and features used for birch tar production from the central European area (western Slavic settlement area), known from c. 600 AD (e.g. [7,37]). This, so-called double pot technique, was externally heated with a perforated ceramic vessel filled with wood or bark from which the produced tar dripped down into a vessel beneath. However, the fact that allobetulene is present in birch bark and the absence of any similar ceramic vessels from the excavated sites contradict this hypothesis regarding the features of this investigation. It is more likely that the allobetulene in the samples upmu4541 and upmu4538 provide information of how the larger funnel-shaped pits were constructed. The sample upmu4541 is taken from a layer that was interpreted as birch bark already during the excavation. The upmu4538 sample is taken from the bottom of the feature (Fig. 4). The explanation of the allobetulene is probably that these features were lined with birch bark to prevent leaking of the pine tar. This is a practice that is known also from historical times. It is quite plausible that the presence of allobetulene in the smaller funnel-shaped pits (fu5620 and fu5630) are traces of the same practice rather than being indications of birch tar production.

The change that can be seen in the pine tar production – from the small scale settlement related production during the Late Roman Iron Age to the forest set large scale production during the late Vendel period and Viking Age – also reflects a change in the society's relation to pine tar production. While the early one is aimed for self-subsistence and was conducted at the

farm, the later one relates to a large-scale production, possibly for trading. This change can also be viewed in other archaeological materials. Trade became to some extent more specialized and significant during the Viking Age. Maybe pine tar was already then an important trade goods in the area, as an early predecessor to the Stockholm tar.

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