

Composition of Kiln-Produced Tar

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Abstract

In Norway there is a living tradition for softwood tar production in a kiln. Kiln-productions has been documented with respect to choice of wood, design, burning and collection of the tar. Tar samples were collected at intervals during burning, analysed and characterised with GC-MS. The tar fractions from an early stage of the production are different from the fractions from a later stage, probably as a result of the heat and the relatively reducing conditions under which the production takes place.

Introduction

Kiln (also called heap, pile og pit) produced softwood tar is specified by the Directorate for Cultural Heritage (in Norway: Riksantikvaren) as the only material which may be used as coating material for the remaining 28 stavechurches. It is therefore of interest to examine in detail the production of kiln produced tar, together with an examination of the resulting tar products.

The design and building of a kiln and the production of tar herefrom has been discussed in detail elsewhere [Egenberg 1993, 1997], together with a tentative identification of the resin acids and neutral components. We feel, however, that there is a need for a more specific identification of the tar products, specifically the diterpene and diterpene derivative components and present these results in connection to a well documented kiln burning. Samples have been taken at intervals during tar burning and analysed by gas chromatography/mass spectrometry (GC/MS). Furthermore we want to discuss our results in relation to a recent article [Beck et al. 1997] in which the temperature influence on the production of diterpene resin acids and neutrals is presented and to discuss the relevance of the use of separate analysis for resin acid methyl esters formed during the tar burning.

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Materials and Methods

Temperature measurements in the kiln were collected on a Yokogawa 12 channel hybrid writer. Thermoelements, type K. Viscosity was measured on a Cannon-Fenske Viscometer.

Preparation of tar samples (0.1-1.0 mg) was done in 50µl of a 10% KOH (w/v) solution (in 1:1 methanol/water) which were left overnight at room temperature. The solution was neutralised with 100µl of a 6M HCl solution in water and immediately extracted with 175µl of redistilled diethyl ether and transferred to a new vial. The diethyl ether was evaporated off and a diazomethane/diethyl ether solution added to the vial. The sample was concentrated under a stream of N₂ gas before analysis.

Diazomethane/diethyl ether solution was prepared according to Glastrup (1998).

Gas chromatograph: Injector: SPI, init. temp. 40°C, 1 min., ramp rate 200°C/min to 310°C, held at 310°C for 55 min. GC oven: init. temp. 40°C, 1 min., ramp rate 10°C/min to 190, ramp rate 4°C/min to 310°C, held at 310°C for 10 min. Column: J & W, BP-5, i. d. 0.18 mm, coating 0.4 µm. Carrier gas: He at 22 psi.

MS detector: Saturn 3, tuned through autotune.

Results and conclusion

The process of tar production is probably an effect of wood being heated in a reducing atmosphere and a complex combination of steam distillation of the non polymer component of the wood, a partial hydrolysis or degradation of the polymer content, together with liquefying of the resin, resulting in a running off of the tar fraction. The production is a balance of having an almost open fire on top of the kiln, together with the running off of an easily ignitable organic mixture through and below the kiln. The production therefore demands skilled tar burner personnel in order to maintain an open fire on top and keeping the top as insulated as possible against the surrounding air by covering with turf and slabbing the ash cover.

After 4-5 hours the tar starts to run. The tar runs slowly in the beginning of the process, more quickly in the middle, and again more slowly at the end. It is also more viscous in the beginning and in the end than in the middle of the production. The tar gradually gets darker throughout the process.

The kiln burning described here consisted of 32 cubic metres of pine wood, it burned for 40 hours and produced 1200 litres of tar.

As a result of the above mentioned heating and subsequent steam distilling/extraction of the non polymer components of the wood, tar fractions are collected in barrels over time. The composition of tar depends on the quality of the wood used, and on the region where the wood has grown, thus leading to a further variability. Depending on the time when the fraction was collected, the tar contains various amounts of water which separates after a couple of days. The water contains components as acetic acid, methanol acetone and phenols.

The tar production described here comes from a kiln constructed in Gudbrandsdalen, at Skjåk, and constructed from finely cleaved root stumps of *Pinus silvestris* (L.). The kiln was built by two carriers of the tradition, Gudmund Øyberg and Asbjørn Fallingen. To follow the tem-

perature during burning, the kiln was equipped with eight thermosensors, positioned evenly and in such a way that temperatures could be measured in the top, middle and bottom. The maximum measured was 972°C in the top of the kiln, whereas the temperature at the bottom, run-off point for the tar, did not exceed 100°C over most of the process. Fig. 1 shows the average of all the temperatures measured and the time of the collected and analysed samples. Skjåk A is taken at the very beginning of the tar production, Skjåk 4 and 7 exemplify the main production period where the tar flows easily from the kiln, Skjåk 9 is late in the production and finally Skjåk 11 is taken after the production has stopped and the fire about to be extinguished. Table 1 shows the viscosity of the five fractions.

To examine the content more thoroughly the samples were analysed by GC/MS. Preparation of samples was done by basic hydrolysis, followed by neutralisation and extraction with ether. This sample preparation procedure does not - as any other preparation procedure - pretend to extract or analyse all components found in tar. Before analysis the acids were converted to their respective methyl esters. The method is commonly used in museum analysis of oils and resins, and does favour relatively non polar neutral or acidic, non polymeric components. No attempt was done to make a prior separation of free and already methylated resin acids.

The GC/MS analysis shows a composition which at a glance resembles colophony. The components are mainly diterpenes, but especially for the early fractions, in the early part of the chromatogram, the A region (See fig. 2), small amounts of mono- and sesquiterpenes are still seen in the sample. In the same region of the chromatogram small amounts of components which belong to the mono-, di- or trioxxygenated benzenes may be seen, notably components as guaiol and vanillin (lignin is today a major raw material for the production of vanillin). These latter components are also found in non-coniferous tars such as beech and birch tar [Reunanen et al. 1996], where they may be the major products found by GC/MS analysis. These are not specific to conifer tar but are degradation products from lignin in wood.

Later in the chromatogram, the B region, (See Fig. 2-3), the main components of softwood tar are found. These are mainly the familiar diterpenes also found in colophony. Typically the major peak is dehydroabietic acid, and in earlier fractions from the tar production, even components which are attributed to a less oxidised products of colophony, like neoabietic acid, abietic and palustric acid are seen (See Table 2 and Fig. 3). The components have been identified on the basis of Nielsen (1998) and authentic samples from JF. Zinkel and R White. In later fractions from the tar production the complexity of the resinous components decreases, and now the main component is exclusively dehydroabietic acid. There are, however, other components which are unique to tar found in the analysed fractions. Retene is found, which has previously been described as characteristic to softwood tar. Furthermore, two components which have previously been attributed to isomers of dehydro-4-epiabietylal [Egenberg 1993, Glastrup 1995] (Cas. nr.: 24035-50-5) are found. Today we are more convinced that these are two isomers of 1,4a-dimethyl-7-isopropyl-1,2,3,4,4a,9,10,10a.alpha.-octahydrophenanthrene (Cas. nr.: 19407-18-2), also called norabietatrienes. These data are in agreement with Mills and White (1987) and Reunanen et al. (1989). The former has a molecular ion of 284, which is not seen in the spectra, the latter has a molecular ion of 256, which is shown, (See Fig. 4). The spectra of the two norabietatriene isomers are very similar. Initially the two components appear in low concentration but increase together with retene in the later samples, and are some of the few dominant components found in the end of a softwood tar production (See Table 2). The change in the nature and in concentration of the com-

ponents reflects the conditions found in the kiln during burning. The diterpenes undergo isomerisation, decarboxylation and partial aromatisation during heating. This results in the formation of dehydroabiatic acid as the main component. However, conditions are not very oxidative and components as 7-oxo-dehydroabiatic acid and 15-hydroxy-7-oxo-dehydroabiatic acid, which would be found in a heavily oxidised colophony, are virtually absent in all fractions. Instead the formation of the completely aromatized and decarboxylated component retene is seen, and the decarboxylated components, the two isomers of norabietatrienes, rise in concentration as the process continues. The presence of 1,2,3,4-tetrahydroretene has previously been reported [Mills and White 1987, Beck et al. 1997] and is indeed present, however in absolutely minor concentrations. From an identification point of view, these findings relate to a tar which has been recently produced. In older tar, dehydroabiatic acid would be expected to be further oxidised and to a large extent converted to 7-oxodehydroabiatic acid and 15-hydroxy-7-oxodehydroabiatic acid.

It has recently been demonstrated [Beck et al. 1997] that the “resin acids”:“neutral resin acids derivatives” ratio could be used as a measure of the temperature at which the tar was produced. The temperature dependence is in agreement with our findings as we find an increased amount of neutrals in comparison with the resin acids. In our results, the ratio changes from 30 to 3 and in the same period the temperature increases, on the average, from about 50°C in the earliest sample to about 350°C in the end.

The retort type should be possible to distinguish from the kiln type by the total amount of resin acids, based on a statement by P. Clason (1930) that kiln burned softwood tar contains 40%, whereas retort type tar contains only 14%. In a relatively thorough report, Romslo (1952) examines several types of retort and kiln burned tars and he states that at least two types, Bolinder and Johnson, retorts give “a high content of fatty and resin acids, 45 - 50%”, other types give “30 - 35% of fatty and resin acids”. As the content of fatty acids is undoubtedly low in softwood tar, we therefore question whether it is possible to distinguish between retort and kiln burned tar on the basis of the resin acid content.

Comparison of our results with Beck et al. (1997), shows that tar production of resin under experimental conditions can give a substantially more oxidised product compared with samples taken from a kiln. In our results virtually no 7-oxo-dehydroabiatic acid methyl ester or 15-hydroxy-7-oxo-dehydroabiatic acid methyl ester (<2%) was found in any of the five fractions. In the results presented by Beck et al. (1997) the maximum amount found is at least 20% at 350°C.

In recent years it has been stated that the presence of resin acids methyl esters in tar is an indication of tar production based on wood and not on pure resin, because of the methanol formed from the wood which esterifies during the process [Beck et al. 1997]. We have, however, analysed tar samples from viking ships which were extracted under neutral conditions and silylated [Aasen, Egenberg and Lundanes, unpublished]. These samples showed no content of resin acids methyl esters, but on the other hand it seems rather unlikely that tar production at that time, for that purpose, would be based on collection of resin and not on tar production on wood. Besides, methyl esters are, under acidic or basic conditions, subject to hydrolysis, and as methanol would surely evaporate during time, the process would be expected to proceed towards the free acids. Presence of methyl esters therefore suggest that tar production has

been based on wood, but the absence does not indicate that the tar has been produced from resin.

Retene is unique to softwood tar production. This is, however, not the case for the two norbornadienes, which can also be found in colophony (Glastrup, unpublished), but are absent in the analysis of fresh resin extracted from wood. As colophony is the solid residue from the production of turpentine, it is tempting to believe that the formation of the two isomers are characteristic to softwood resin which has been heat treated.

Acknowledgement:

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	Viscosity
Skjåk A	9,161
Skjåk 4	3,463
Skjåk 7	1,749
Skjåk 9	1,059
Skjåk 11	4,084

Table 1: Viscosity and colour of the five analysed fractions from Skjåk. All measured viscosity units are in mm²/s (cSt). Numbers given are the average of two independent analysis.

No Component:	Cas. nr.	Ret. time	Skjåk A (%)	Skjåk 4 (%)	Skjåk 7 (%)	Skjåk 9 (%)	Skjåk 11(%)
1 Palmitic acid methyl ester	112-39-0	21.50	0.5	0.5	0.5	0.6	0.6
2 Norabietane 1	19407-18-2 ?	22.99	0.6	1.1	2.1	2.6	3.6
3 Norabietane 2	19407-18-2 ?	23.70	0.8	1.5	2.8	3.5	4.6
4 Linoleic acid methyl ester	112-63-0	24.70	1.0	0.9	0.7	0.5	0.2
5 Oleic acid methyl ester	112-62-9	24.81	1.3	-	-	-	-
6 Methyl cis-secopimarate isomer	35482-10-1 ?	26.43	0.3	0.4	0.4	0.5	-
7 Methyl cis-secopimarate isomer	35482-10-1 ?	26.84	0.5	0.6	0.7	0.9	0.9
8 Retene	483-65-8	27.59	1.8	3.1	4.6	7.3	14.8
9 Pimaric acid methyl ester	3730-56-1	28.02	5.7	4.4	4.2	2.6	1.1
10 Sandaracopimaric acid methyl ester	1686-54-0	28.35	0.9	0.7	0.7	0.5	0.2
11 Isopimaric acid methyl ester	1686-62-0	29.16	2.6	1.9	1.6	1.0	-
12 Palustric acid methyl ester	3310-94-9	29.29	5.6	3.6	2.6	-	-
13 Dehydroabietic acid methyl ester	1235-74-1	29.96	53.4	61.4	66.5	72.1	71.4
14 Abietic acid methyl ester	127-25-3	30.89	18.0	14.2	10.7	5.7	1.9
15 8,11,13,15-abietatetraenoic acid methyl ester		31.82	1.6	1.6	0.3	0.8	0.2
16 Neoabietic acid methyl ester	3310-97-2	32.01	3.8	2.7	1.7	0.6	0.1
17 7-oxo-dehydroabietic acid methyl ester	17751-36-9	34.51	1.2	1.0	-	0.8	0.4
Total			99.6	99.6	100.1	100	100
Resin acids			96.4	93.9	90.6	86.6	77.0
Neutrals			3.2	5.7	9.5	13.4	23.0
Resin acids:Neutrals ratio			30.1	16.4	9.5	6.5	3.4

Table 2. The diterpene and related components found in the tar, their concentrations and retention time. Note the total of norabietane 1 and 2, retene and dehydroabietic acid methyl ester adds up to 56.6% in Skjåk A and to 94.4% in Skjåk 11, illustrating the tendency against fewer components. It is also characteristic that the Resin acids:Neutrals ratio decreases with the increasing temperature of the kiln. The amounts of resin acids and neutrals are calculated from the TIC of the analysed peaks.

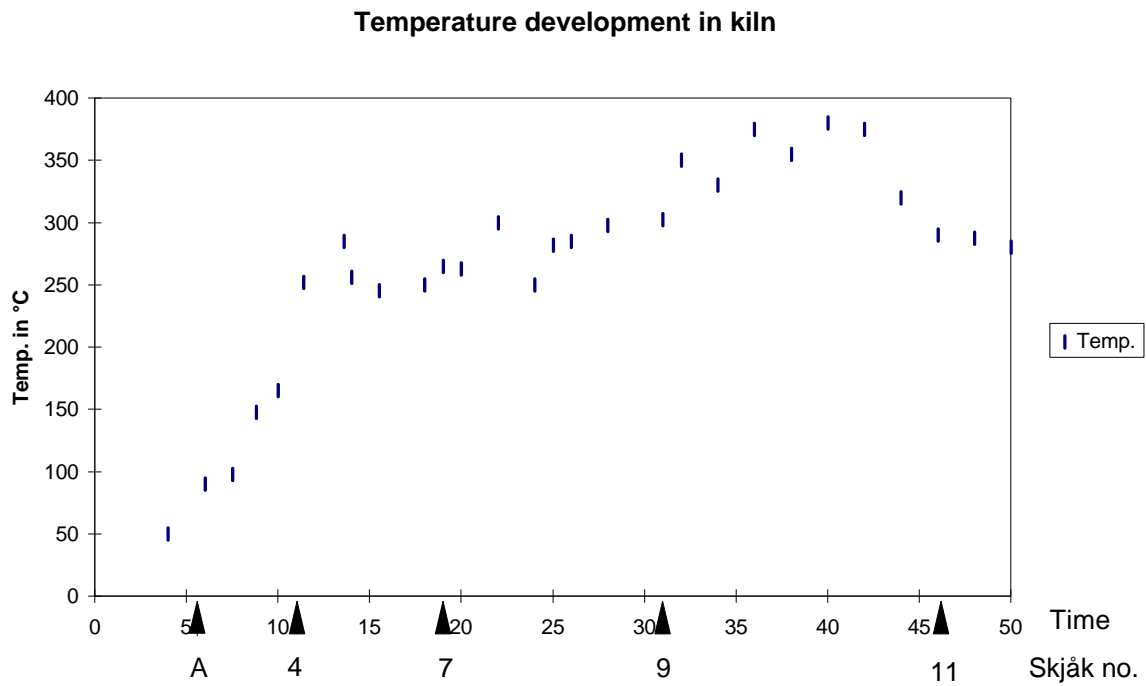


Figure 1. The temperature development in the kiln during burning. The temperatures given are the average of 8 independent sensors in the kiln. Also the time at which the five analysed samples were taken are indicated.

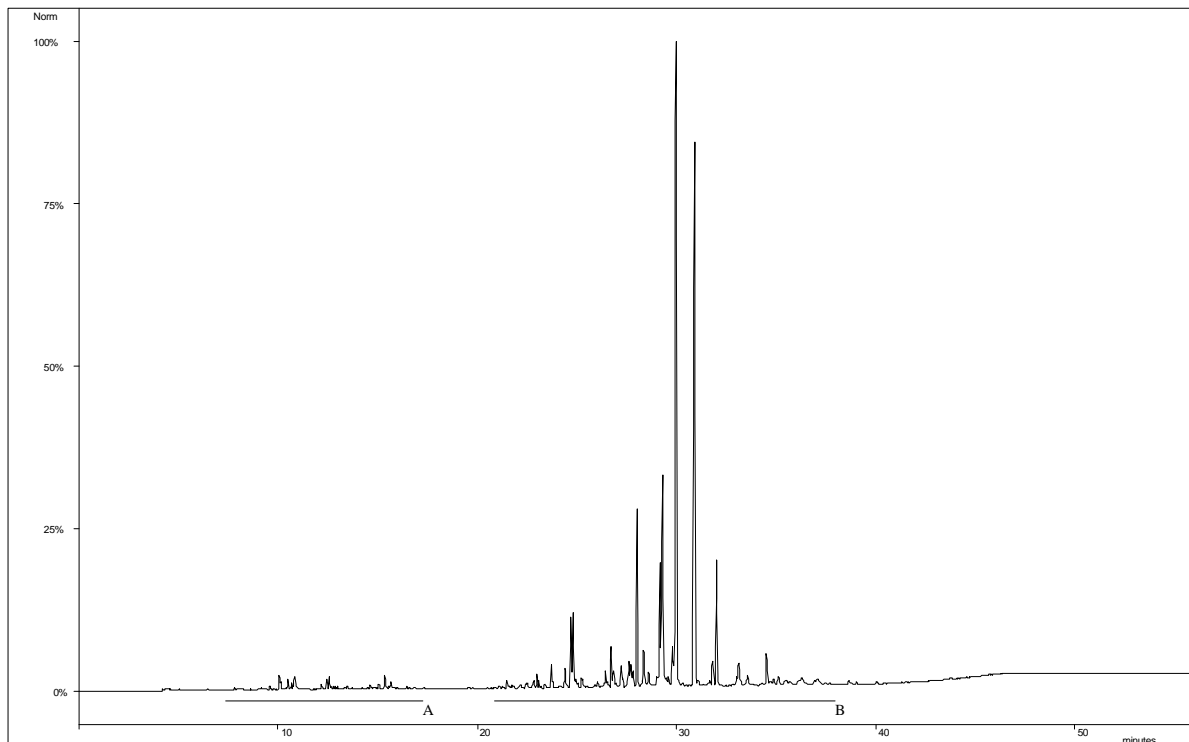


Figure 2. Chromatogram of “Skjåk A”. A is the region in which the mono- and sesquiterpenes and the substituted benzenes are found. B is the region of the diterpenes, together with few other components.

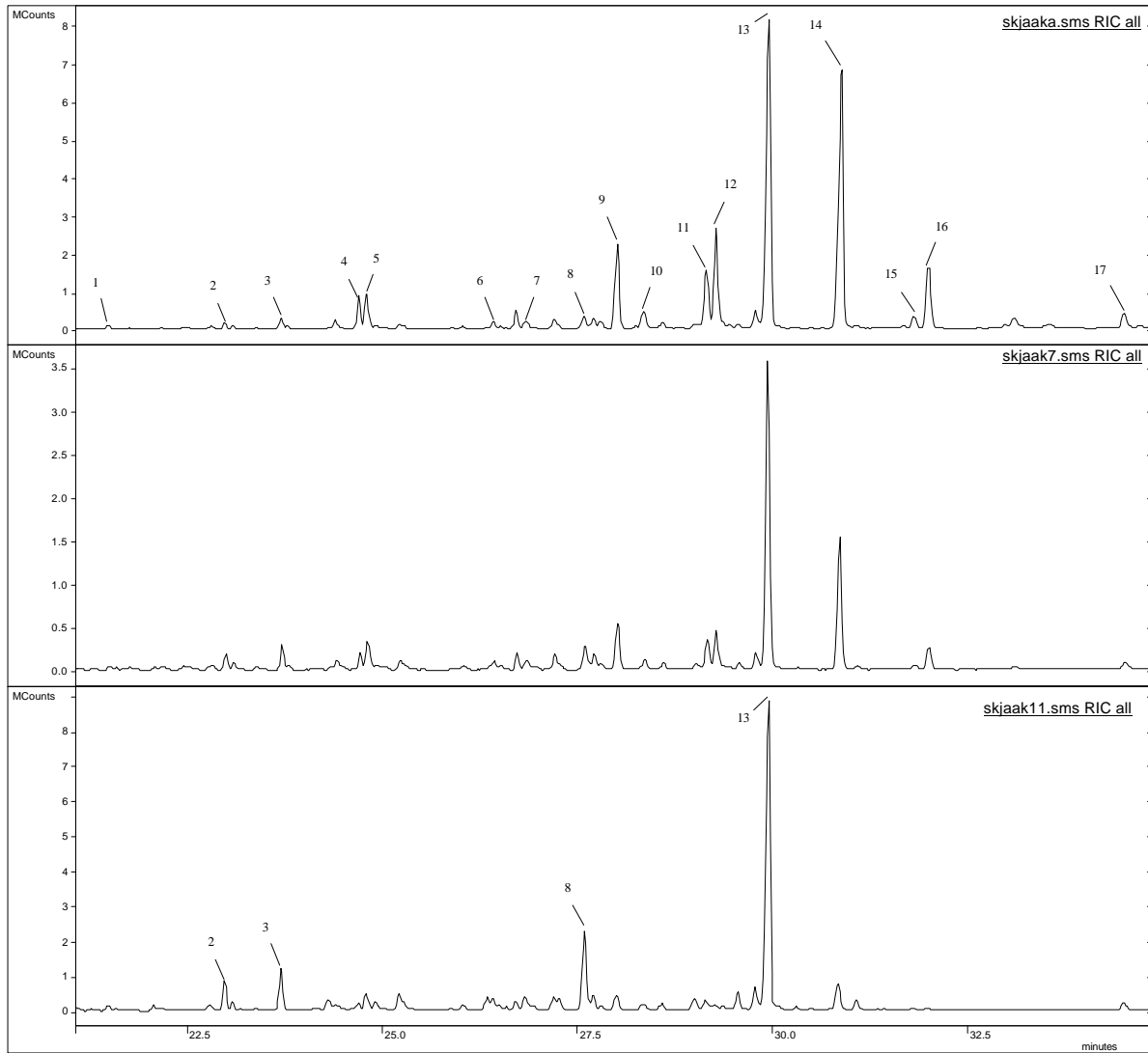
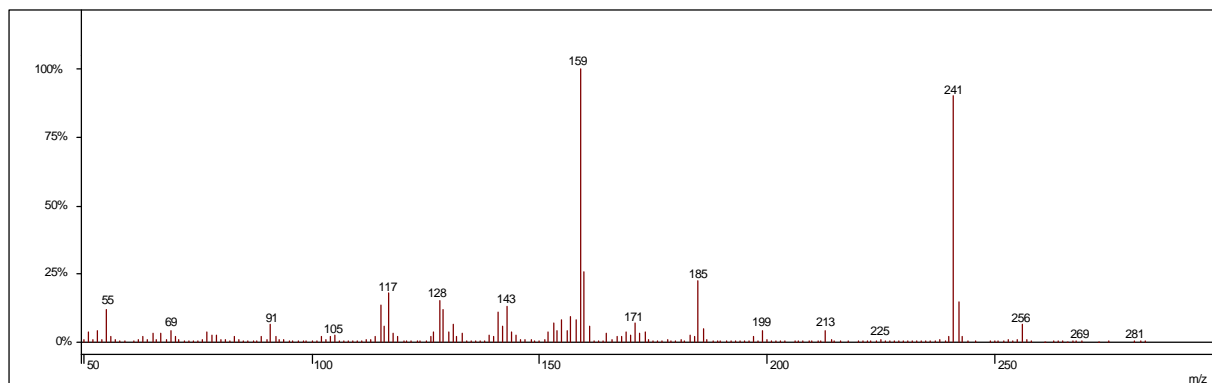


Figure 3. The development in composition of the components of the diterpenes, the B region, from the samples “Skjåk A”, “Skjåk 7” and “Skjåk 11”. The names and concentrations of the components are found in table 2.

Scan 1380



Scan 1421

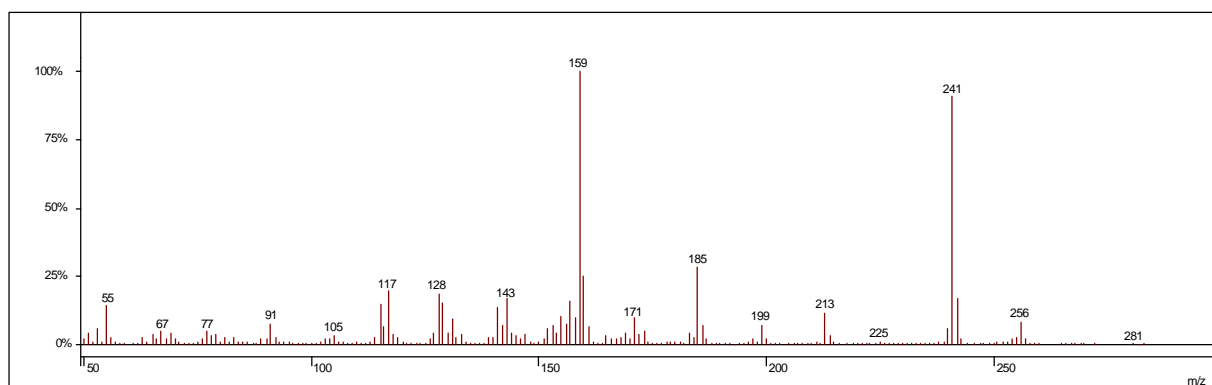


Figure 4. The mass spectra of the two norabietatriene components.