Pyrolytic formation of polycyclic aromatic hydrocarbons from sesquiterpenes

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Abstract

The products of the pyrolysis of four sesquiterpenes, β-caryophyllene, α-cedrene, longifolene and valencene, have been examined. Pyrolysis was carried out at 300, 400 and 500 °C, the products determined by GC-MS and then examined for similarities and differences using multivariate data analysis. Analysis showed that longifolene was most resistant and caryophyllene least resistant to pyrolysis with cedrene and valencene occupying intermediate positions. While the compounds were largely unchanged at 300 °C, polycyclic aromatic hydrocarbons (PAHs) were major components of the pyrolysates at 400 and 500 °C. No less than nine of the sixteen EPA priority pollutants were present in the pyrolysates at the higher temperatures.

Keywords

Pyrolysis, sesquiterpene, polycyclic aromatic hydrocarbon, β-caryophyllene, α-cedrene, longifolene, valencene, PAH.

1. Introduction

Sesquiterpenoids are products of the terpenoid, or isoprenoid, pathway and have been identified in many plants. This biosynthetic pathway is a requirement for photosynthesis since both chlorophyll and carotenoids, the pigments involved in light harvesting, depend on the availability of geranylgeranyl pyrophosphate or its equivalent for their assembly (Bogorad, 1976 and Britton, 1976). All green plants must therefore contain at least transiently the C-15 precursor, farnesyl pyrophosphate, which is also the precursor for the sesquiterpenoids which are commonly identified in these organisms.

The sesquiterpenoids are the most varied in structure of the terpenoids and even forty years ago over 1000 members of the category were identified as belonging to 30 main skeletal classes and some 70 less common types (Devon & Scott, 1972). New skeletons and individual compounds continue to be reported (Fraga, 2011). This diversity results from a variety of sesquiterpene synthases which utilize farnesyl pyrophosphate as a precursor for cyclisation, methyl shifts, hydride shifts, Wagner-Meerwein rearrangements etc. in different combinations to produce everything from acyclic to tetracyclic structures which are then liable to changes in oxidation level and functionalisation (Degenhardt, Köller & Gershenzon, 2009).

Sesquiterpenoids are important components of many spices where they contribute to both the taste and aroma (Parthasarathy, Chempakam & Zachariah, 2008). In this way they are deliberately introduced to the food chain in addition to their occurrence in minor amounts in a fortuitous manner in other foods. Indeed, genetic manipulation to increase plant sesquiterpenoid biosynthesis with a view to improving plant traits and crop protection has recently been reviewed (Yu & Utsumi, 2009). A good example of this approach is to be found in a study of sesquiterpenoids in rice (Cheng et al., 2007).

A previous study (Christy, Lian & Francis, 2011) showed that the pyrolysis of steroid hormones resulted in the formation of polycyclic aromatic hydrocarbons (PAHs) and that the pyrolysates varied according to the steroid involved. It was decided to extend this work to sesquiterpenes on the basis of their being common components in foods and the fact that they might contribute in a similar way to the formation of PAHs. Most sesquiterpene skeletons are either bicyclic or tricyclic and two compounds of each type were included in this study. Caryophyllene and valencene have bicyclic structures while cedrene and longifolene have tricyclic structures (Figure 1). The choice of sesquiterpene hydrocarbons rather than of oxygen-containing sesquiterpenoids was intended to simplify the results.

Initial experiments showed that the pyrosylates contained major amounts of PAHs, the carcinogenic and mutagenic properties of which have been established (Wornat, Braun, Hawiger, Logwell & Sarofim, 1990). Mechanisms for the PAH induced mutogenesis and tumorigenesis have been proposed and in most cases the first step is the oxidation of the PAH by cytochrome 450 enzymes to provide electrophilic species, diolepoxides, that then react to form DNA adducts which can induce both preneoplastic and tumorigenic mutations (Chakravarti et al., 2008). The mutagenicity of the adducts has been related to their relative repair efficiencies in mammalian cells (Lagerqvist et al., 2011)

While the amounts of spices added to individual foods subjected to roasting, frying, grilling and other forms of heat treatment may be limited, the continuing exposure to such foods over extended times must clearly be a cause for concern. It has been shown that lifetime rather than recent intake of cooked meat and the PAHs therein increase the risk of breast cancer (Steck et al., 2007). Lifetime consumption of meat and cooking practices has shown that regular consumption of well-done red meat increases the risk of prostrate cancer (John et al., 2011) Higher cooking temperatures and longer cooking times are known to increase mutagenicity in cooked meat (Barrington et al., 1990). While the temperatures met with in normal cooking methods should not exceed 300 °C, the occurrence of local hot spots under non-ideal conditions and/or open flame cooking make it interesting to study the effects at this and higher temperatures. The aim of this work was thus to establish which PAHs and in what amounts these were formed at temperatures of 300, 400 and 500 ^{o}C. It was also regarded as being important to see to what extent the sesquiterpene structure affected the PAH formation.

Pyrolysis may be defined as the transformation of materials by heat treatment and a variety of techniques are used to accomplish this under controlled conditions (Voorhees, 1984). While the initial process in pyrolysis involves the cleavage of molecules into smaller unstable species which over time react in a process called pyrosynthesis to form molecular products of greater mass (Lee, Novotny & Bartle, 1981). It is this latter process that results in the formation of PAHs and investigation into the mechanisms involved remains under active investigation (Shukla & Koshi, 2010).

2. Materials and methods

2.1. Samples, pyrolysis and GCMS analysis

β-Caryophyllene, α-cedrene, logifolene and valencene were obtained from commercial sources. All solvents were of HPLC quality and used as received.

The ampoules used were made from borosilicate glass and the main body had approximate internal dimensions of 17 x 80 mm with a wall thickness of 1.2 mm. Ampoules had initially an extension which provided access to the body of the ampoule through a narrow neck. Each sample was prepared by introducing the compound (3-4 mg.) to be pyrolysed through the extension to the ampoule, replacing the air in the ampoule with nitrogen and then closing it by melting the neck to provide a gas-tight seal. The use of a nitrogen atmosphere in the ampoule prevents oxidation and thus simplifies the analysis of the pyrolysate.

Sealed ampoules were placed directly into an electric oven preheated to the intended pyrolysis temperature, 300, 400 or 500 ^{o}C where they were allowed to remain for a period of 4 h. After this time the ampoules were removed and cooled in the dark overnight. The cooled ampoules were carefully opened and extracted with 1 ml portions of hexane. Hexane has been shown to be a suitable solvent for PAHs (García-Falcón, Cancho-Grande & Simal-Gándara, 2005; Khatmullina et al., 2012) and preliminary experiments indicated that this solvent dissolved all of the pyrolysates in the present case.

The GC-MS analysis was carried out on a Hewlett Packard (HP) 5890 series II gas chromatograph connected to a HP 5971A quadrupole mass spectrometer. The components were separated on a 30 m x 0.25mm I.D fused silica column coated with 0.25 μm 100% dimethyl polysiloxane stationary phase. The oven was programmed from 50 ^{o} C, after a 5 minutes hold time, at 4^{o} C /min up to 250^{o} C where the temperature was held for a further 10 minutes. Adjustments were made to the program to improve resolution where required.

The total ion chromatograms of the pyrolysates were acquired using the HP G1034C chemstation program. The peaks in the total ion chromatogram were then identified using a mass spectral library (NIST 98). Library identifications were further investigated and confirmed by examining and comparing the fragmentation patterns obtained with the suggested molecular structure.

2.2. Data Analysis

The large number of compounds in the pyrolysates makes it extremely difficult to carry out comparisons between the different starting materials and different temperatures used. Similarities, dissimilarities and relationships between the products formed were thus identified by means of principal component analysis (PCA), a chemometric technique, the theoretical basis for which can be found elsewhere (Christy, Ozaki & Gregoriu, 2001).

The peaks in the total ion chromatograms from all pyrolysates were area-integrated and recorded. A table was then prepared utilising the component peak areas as variables and the pyrolysis temperatures as samples. This table was then used to obtain information about the products found in the pyrolysates and as a data matrix for the multivariate data analysis which was carried out using the SIRIUS multivariate data analysis programme (Kvalheim & Karstang, 1997) on the data matrix of area percentages of the components. Since the table already contains the percentage data for the individual components found in the total ion chromatograms pre-processing of the data was unnecessary. Additional analysis was carried out after grouping compounds into classes according to structural criteria.

3. Results

3.1. General

The gas chromatograms obtained increased in complexity according to the pyrolysis temperature involved. At the one extreme the chromatogram obtained for valencene after applying the conditions of pyrolysis at 300 ^{o}C showed only unchanged starting material, while at the other the chromatogram obtained on pyrolysis of longifolene at 500 ^{o}C, reproduced in Figure 2, included some 100 different peaks.

PAHs were not observed in any of the pyrolysates at 300 ^{o}C, or in that of longifolene at 400 ^{o}C. In all other cases considerable amounts of PAH were found in the pyrolysates. Table 1 shows the polycyclic aromatic hydrocarbons present in greater than 0.1 % of the total pyrolysates. Compounds identified by the EPA as priority pollutants are italicised in the table.

Table 2 provides the amounts of substituted and unsubstituted PAHs found in the pyrolysates at the different temperatures. The increased formation of unsubstituted PAHs at higher temperatures is significant since these are known to carry greater mutagenic activity (Wornat, M. J., Braun, A. G., Hawiger, A., Logwell, J. P. & Sarofim, A. F., 1990).

3.2. Chemometric results

Analysis of the total data matrix using temperatures as samples and peak areas as variables revealed that two principal components could explain 98.9 % of the total variance. A scoreplot showing the scores of all of the samples is shown in Figure 3. It is immediately obvious that the objects are divided into two groups along the x-axis (PC 1). All objects at 500 ^{o}C plus caryophyllene at 400 ^{o}C are collected loosely on the right side of the plot, while the remaining objects are tightly grouped to the left of the origin. This may be interpreted as reflecting the fact that while all compounds are extensively decomposed after pyrolysis at 500

^{o}C, caryophyllene alone is seriously changed by pyrolysis at 400 ^{o}C. There appears to be only limited difference in the final products of the pyrolysis of the different compounds at 500 ^{o}C.

A biplot from the principal component analysis combining a score plot and a loading plot of the pyrolysis products at 400 ^{o}C is shown in Figure 4a. The data for unchanged material was excluded from this analysis to avoid domination of the results. The two principal components identified explained a total of 98.9% of the variance. PC 1 clearly separates caryophyllene from the other compounds and can thus be identified with the fact that the pyrolysis has proceeded further in this case than for the other compounds. Cedrene is clearly associated with variable 57 and well separated from the other components along PC 2.

No unchanged starting material was present in the pyrolysates at 500 ^{o}C. A biplot including a score plot and a loading plot of the pyrolysis products at 500 ^{o}C is also provided in Figure 4b. PC 1 separates valencene and cedrene from each other where variable 89 is associated with valencene while variable 47 is connected to cedrene. Caryophyllene and longifolene are separated from the other compounds along PC 2 and are associated with the variables 40 and 41.

The results of pyrolysis were also examined by classifying the products of pyrolysis into a total of 17 structural groups. The first of these groups corresponded to acyclic compounds, while the groups 2-15 were based on the main ring structure present in each case (see Table 3). The final two groups were group 16 which consisted of rearranged sesquiterpoid structures ($C_{15}H_{24}$) while group 17 was assigned to unchanged starting material. A biplot using starting compound as samples and integrated group peak areas as variables was prepared for each individual temperature. While the biplots at 300 and 400 ^{o}C provided little additional information, that for 500 °C was somewhat more informative and is reproduced as Figure 5. This showed that caryophyllene had a central position on the plot and also fell close to many of the variables. Longifolene, valencene and cedrene on the other hand are found at positions towards the edge of the plot at well separated angular positions. Longifolene (variable 14), valencene (variables 6 and 9) and cedrene (variable 4) were clearly associated with particular variables.

4. Discussion

4.1. General

The results of the principal component analysis may be discussed in relation to Table 1 which examines the PAHs found at the different temperatures. The finding of very large conversions to PAH at 500 °C is disturbing in view of the fact that these compounds are known to be carcinogenic (Luch, 2005). Even the results from the pyrolysis of the compounds other than longifolene at 400 °C are disquieting. Figure 1 indicates clearly that caryophyllene is much more sensitive to pyrolysis than the other sesquiterpenes examined since it reacts at 400 °C while the others appear to be much less affected at this temperature. A further conclusion from Figure 4 is that in general terms there is little difference in the pyrolysates obtained at 500 °C, although the valencene pyrolysate is somewhat separated and thus somewhat different from the others.

The fact that caryophyllene is more sensitive to pyrolysis parallels similar findings that this compound is among the most sensitive sesquiterpenes to ozonolysis (Shu & Atkinson, 1994). Caryophyllene has long been known to be readily rearranged under a variety of conditions (Aebi, Barton, Burgstahler & Lindsey, 1954; Schulte-Elte & Ohloff, 1971; Parker, Raphael &

Roberts, 1965) and a general review on the chemistry of cayophyllene is available (Collado, Hanson & Macias-Sanchez, 1998).

The caryophyllene pyrosylate at 400 °C is well separated from the other compounds along PC 1 (Figure 5a) corresponding to the much greater conversion seen in Table 2. The identification of cedrene with variable 57 may be related to the fact that the compound contains a cyclohexene ring annealed to two five member rings. The original data show that variable 57 (2-methyl-6-(p-tolyl)hept-2-ene) is produced at 300 °C (0.21 %) and at 400 °C (9.10 %) but was absent at 500 °C. It was not observed in any of the other pyrosylates.

Figure 5b shows the results of the PCA at 500 °C and indicates that PC 1 separates valencene and cedrene from each other where variable 89 (benzcycloheptatriene) is associated with valencene, while variable 47 (ethyl-methylbenzene) is connected to cedrene. PC 2 separates caryophyllene and longifolene from the other compounds and indicates their association with variables 40 and 41 (dimethylbenzene and trimethylbenzene).

Since unsubstituted PAHs are known to be more dangerous to life than the substituted compounds a table indicating the amounts of both substituted and unsubstituted compounds is provided (Table 3). It is immediately clear that as the temperature is increased the amounts of unsubstituted PAHs increases in both absolute amount and proportion, thus demonstrating the deleterious effects of increasing pyrolysis temperatures.

4.2. Mechanism

The formation of PAHs from organic materials have been the subject of investigations over a number of years and it has been shown that almost any organic compound or mixture of compounds can provide PAHs under suitable conditions (Badger, Donnely & Spotswood, 1965; Cypres, 1987; Wornat, Sarofim & Longwell, 1987). Three mechanisms are currently thought to contribute to some degree in the production of PAHs (Slavinskaya & Frank, 2009; Shukla, Miyoshi & Koshi, 2010; Shukla & Koshi, 2010; Ross et al., 2011). These mechanisms are known by the acronyms HACA (Hydrogen Abstraction Carbon Addition), MAC (Methyl Addition Cyclisation) and PAC (Phenyl Addition Cyclisation), and are believed to act in concert to provide PAHs.

The production of PAHs from sesquiterpenes by the above mechanisms requires their breakdown by bond scissions, among others to 1- and 2- carbon species. Some specific support for initial bond scission of the required type may be found in the fact that at 300 and 400 ^{o}C cedrene provided 2-methyl-6-(p-tolyl)-hept-2-ene which might be formulated by such bond cleavage and partial aromatisation (see Figure 2b). This might be taken together with the finding in the 500 ^{o}C pyrolysate of cedrene to further bolster this suggestion. However, the generality of such fission to smaller fragments is accepted as a formation mechanism for PAH from many materials and is thus not controversial.

However, it should be remembered that the aromatisation of sesquiterpenes by heat fusion in the presence of sulphur or selenium was much used to establish both carbon skeletons and substitution patterns (Nigam & Levi, 1964; Stahl & Müller, 1974). Thus some aromatisation may be occurring without prior fragmentation and this should be borne in mind.

5. Conclusions

Sesquiterpenes produce PAHs on pyrolysis at 400 and 500 ^{o}C. At the lowest temperature studied, 300 ^{o}C, no PAHs were formed although some rearrangement was observed. The temperature required for pyrolytic reactions to occur varies between sesquiterpenes with caryophyllene clearly being the most susceptible of the compounds examined. Longifolene, on the other hand was most resistant to pyrolysis. Increasing the pyrolysis temperature from 400 to 500 ^{o}C not only increased the amounts of PAHs formed, but also led to an increasing proportion of the more dangerous unsubstituted PAHs.

The pyrolysates at 500 ^{o}C show much similarity and two factors may be contributing to this: the known propensity of the sesquiterpenes to rearrange and the fact that pyrosynthesis requires breakdown to low weight species prior to reassembly.

It is apparent from the present results that the presence of sesquiterpenes in spices and other vegetable food products and the resulting PAH production represent a real risk factor when both high temperatures and long cooking/heat treatment times are involved in the preparation of food.

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Figure Captions

Figure 1. (a) Structures of the sesquiterpenes in the present study. (b) Indication of how bond scission might lead to variable 57. (c) Variables found to correlate with specific pyrolysis substrates. (d) Ring systems (group variables) found in pyrolysates at 500 °C.

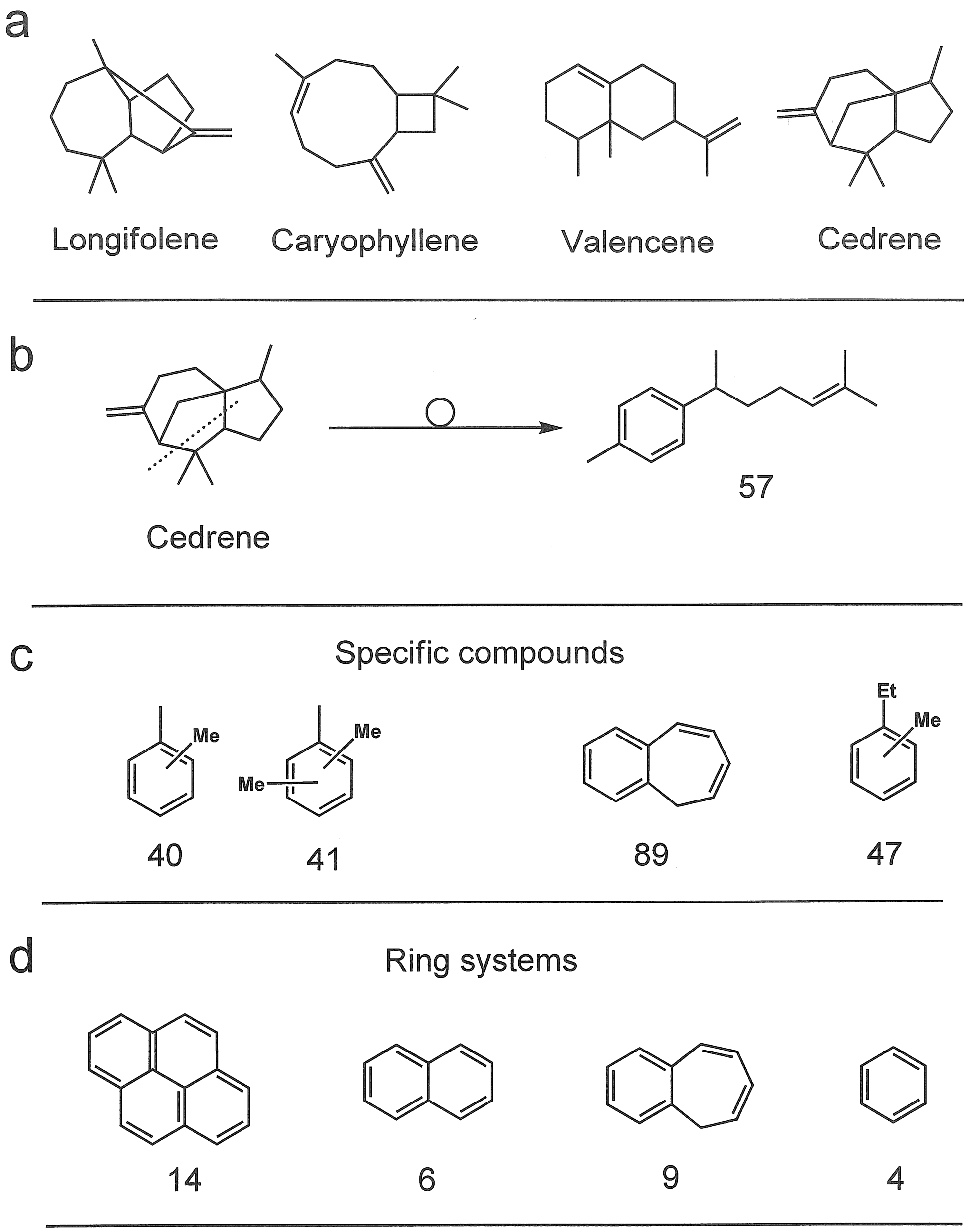
Figure 2. Total ion chromatogram (TIC) for longifolene pyrolysed at 500 °C.

Figure 3. Scoreplot for showing the scores of samples of the sesquiterpenes pyrolysed at temperatures of 300, 400 and 500 °C. Identities of samples as follows: 1 – cedrene (300), 2 – valencene (300), 3 – longifolene (300), 4 – caryophyllene (300), 5 – cedrene (400), 6 – valencene (400), 7 – longifolene (400), 8 – caryophyllene (400), 9 – cedrene (500), 10 – valencene(500), 11 – longifolene (500), 12 – caryophyllene (500).

Figure 4. (a) Bi-plot, combined score plot and loading plot, of samples pyrolysed at 400 °C. (b) Bi-plot, combined score plot and loading plot, of samples pyrolysed at 500 °C. Variables refer to individual compounds.

Figure 5. Bi-plot, combined score plot and loading plot, of samples pyrolysed at 500 °C. Variables refer to structural groups.

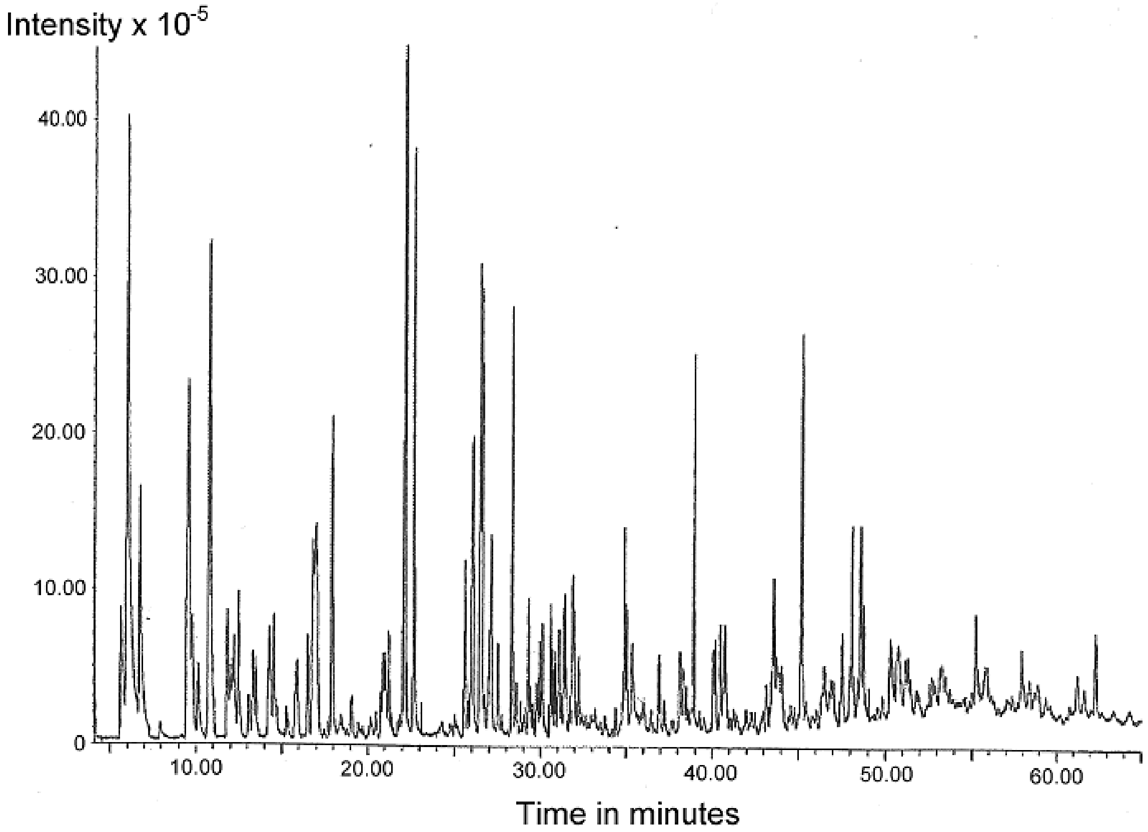
Fig. 1



Specific compounds

Ring systems

Fig. 2


Intensity x 10^{-5}
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30.00
20.00
10.00
0
10.00
20.00
30.00
40.00
50.00
60.00
Time in minutes

Fig. 3

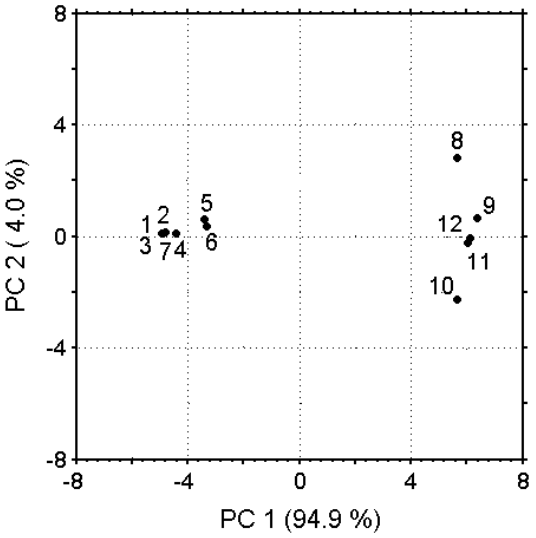


Fig. 4

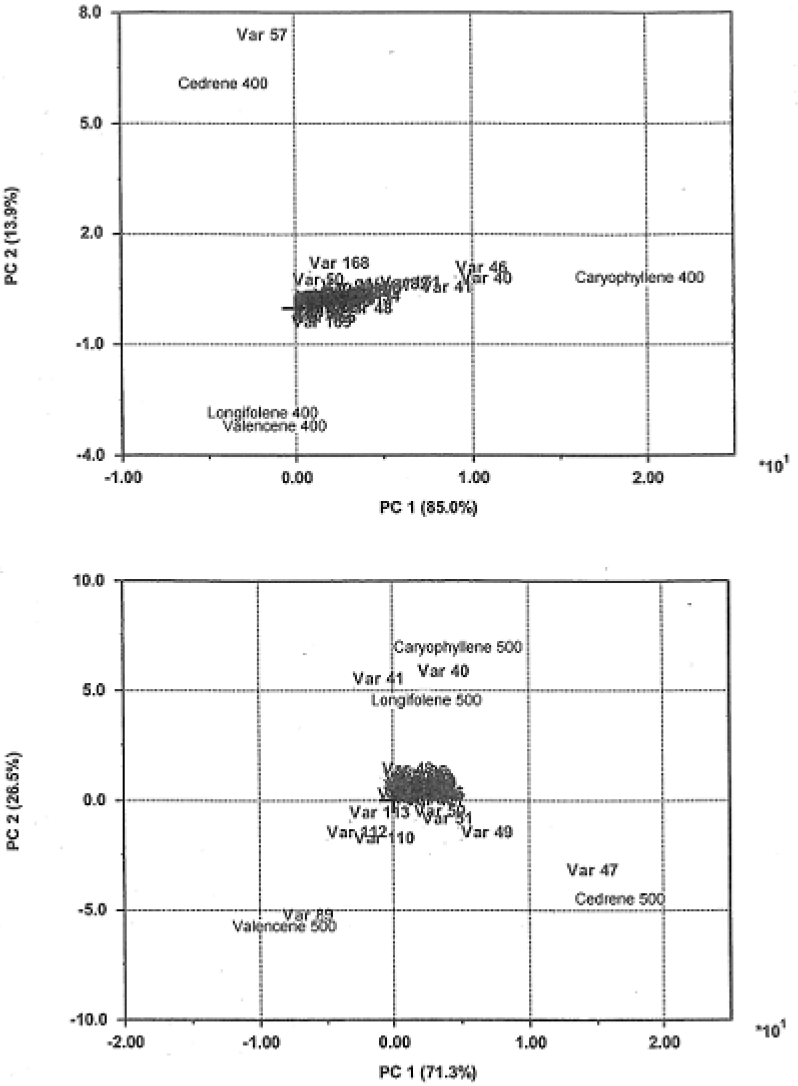
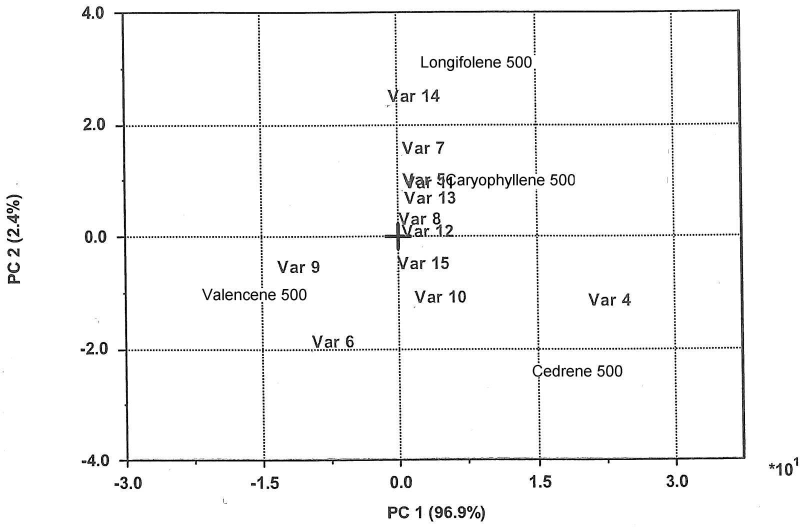

8.0
5.0
2.0
-1.0
-4.0
PC 2 (13.9%)
-1.00
0.00
1.00
2.00
*10¹
PC 1 (85.0%)
Var 57
Cedrene 400
Var 168
Var 50
Var 46
Var 40
Var 41
Var 48
Var 169
Caryophyllene 400
Longifolene 400
Valencene 400
10.0
5.0
0.0
-5.0
-10.0
PC 2 (28.5%)
-2.00
-1.00
0.00
1.00
2.00
*10¹
PC 1 (71.3%)
Caryophyllene 500
Var 41
Var 40
Longifolene 500
Var 113
Var 112
Var 110
Var 51
Var 49
Var 47
Cedrene 500
Var 89
Valencene 500

Fig. 5


4.0
2.0
0.0
-2.0
-4.0
PC 2 (2.4%)
-3.0
-1.5
0.0
1.5
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*10^1
PC 1 (96.9%)
Longifolene 500
Var 14
Var 7
Var 5
Var 11
Caryophyllene 500
Var 13
Var 8
Var 12
Var 9
Var 15
Valencene 500
Var 10
Var 4
Var 6
Cedrene 500

Table 3. Substituted, unsubstituted and total PAH at 400 and 500 °C pyrolysates of longifolene, caryophyllene, valencene and cedrene.

Compound and pyrolysis temperature (°C)	Unsubstituted PAH	Substituted PAH	Total PAH	% of total PAH that is unsubstituted
Longifolene 400	0.0	0.0	0.0	----
Caryophyllene 400	1.3	14.9	16.1	8.1
Valencene 400	0.9	3.4	4.3	20.9
Cedrene 400	0.0	0.6	0.6	0.0
Longifolene 500	19.8	40.5	60.3	32.8
Caryophyllene 500	17.1	40.4	57.5	29.7
Valencene 500	32.8	44.9	77.6	42.3
Cedrene 500	12.7	36.7	49.4	25.7

Table 2. Compounds identified by structural groups in the pyrosylates of caryophyllene (K), cedrene (S), longifolene (L) and valencene (V) at pyrolysis temperatures of 300, 400 and 500 ^{o}C. Group structure type is based on the main skeleton of the compound. Group 16 refers to rearranged starting material, i.e. $C_{15}H_{24}$ compounds other than the original compound. Group 17 refers to unchanged starting material.

Group	Group structure type	300 ^{o}C				400 ^{o}C				500 ^{o}C			
		L	K	V	S	L	K	V	S	L	K	V	S
1	Acyclic		3.48				0.83						
2	Cyclopentene						0.93	0.32					
3	Cyclohexene		0.64				5.19	0.37					
4	Benzene				0.21	0.35	48.08	5.32	10.45	39.67	42.61	22.42	50.62
5	Azulene						0.80	0.12		1.73	1.09	0.39	0.79
6	Benzocycloheptatriene							0.81		9.13	7.76	19.46	7.23
7	Indene						9.56	2.09	0.58	8.26	7.28	6.31	6.53
8	Tetralin						2.09	0.17		0.18	0.06		
9	Naphthalene						4.09	1.34		18.37	18.98	31.78	13.57
10	Biphenyl								0.08	1.23	2.03	0.97	3.64
11	Fluorene									5.59	6.29	4.68	4.95
12	Fluoranthene									0.30	0.62	0.26	0.57
13	Anthracene/Phenanthrene									5.27	6.02	4.56	5.02
14	Pyrene									8.73	6.31	6.98	4.95
15	Tetracyclic PAH									1.54	0.96	2.15	2.13
16	Sesquiterpene		0.50	0.86	0.08	0.68	24.17	4.67	1.08				
17	Unchanged	100	95.37	99.14	99.71	98.97	4.26	84.79	87.77				

Table 1.

PAH compounds identified in the pyrosylates of caryophyllene (K), cedrene (S), longifolene (L) and valencene (V) at prolysis temperatures of 400 and 500 ^{o}C. Structural groups are indicated (Group) as are individual identification numbers (ID No.) as used in the multivariate data analysis. Molecular ions are indicated in brackets after the compound names. The numbers in the vertical columns indicate the percentage area of the peaks. The column for longifolene at 400 ^{o}C is empty but included for clarity.

Group	ID No.	Compound name	400 °C				500 °C			
			L	K	V	S	L	K	V	S
5	85	Azulene (128)		0.80			1.58	0.72		0.41
	87	7-Ethyl-1,4-dimethylazulene (184)						0.36	0.39	
	88	4,8-Dimethyl-6-phenylazulene (232)								0.27
6	89	Benzcycloheptatriene (142)			0.81		9.13	7.76	19.46	7.24
7	90	Indane (118)					0.71	0.39	0.71	
	91	Indene (116)					1.25	1.00	1.02	0.86
	92	X-Methylindane (132)		0.52			0.89	0.48	0.95	0.78
	93	X-Methylindene (140)		1.73			3.31	3.60	2.29	3.20
	94	X,Y-Dimethylindene (144)		3.62	0.54		1.63	1.35	1.02	1.59
	95	X,Y-Dimethylindane (146)		1.87	0.21		0.28	0.23		0.23
	96	X,Y,Z-Trimethylindane (160)		1.83	0.69	0.15				
	98	2-Ethylindane (146)					0.12	0.11		
	100	3-(2-Methylpropenyl)-1H-indene (170)			0.19					
	102	1,23-Trimethylindene (158)			0.21					

8	103	1,2-Dihydro-3-methylnaphthalene (144)					0.11			
	104	Tetrahydro-1,1,6-trimethylnaphthalene (174)		0.37						
	105	Tetrahydro-X,Y-dimethylnaphthalene (160)		0.39						
	106	1,4-Dihydro-1,4-methanonaphthalene (142)		0.49	0.17					
	108	Tetrahydro-tetramethylnaphthalene (186)		0.29						
	109	3-(1,1-Dimethylethyl)-1,2-dihydronaphthalene (186)		0.55						
9	110	*Naphthalene*(128)		0.46			0.60	1.58	5.37	0.85
	111	X-Methylnaphthalene (142)		0.40	0.18					
	112	X,Y-Dimethylnaphthalene (156)		0.55	0.46		10.14	8.80	14.36	7.33
	113	X,Y,Z-Trimethylnaphthalene (170)		2.49	0.49		4.50	4.91	7.85	3.13
	114	1,2,3,4-Tetramethylnaphthalene (184)			0.14				0.18	
	115	1-Ethylnaphthalene (156)					1.19	0.96	1.53	0.63
	116	X-Isopropenylnaphthalene (170)					0.11	0.44	0.34	0.51
	118	1-Isopropenylnaphthalene (168)		0.20			1.21	1.33	1.39	0.52
	119	1,2,5,6-Tetramethylacenaphthene (208)					0.10	0.32		0.27
	120	*Acenaphthene* (154)					0.44	0.55	0.54	0.33
10	125	Biphenyl (154)						0.16		0.11
	126	X-Methylbiphenyl (168)					0.57	0.58	0.18	1.22
	127	X,Y-Dimethylbiphenyl (182)						0.17		1.17
	128	α-Methylstilbene (194)					0.48	0.70	0.64	0.63
	130	o-Terphenyl (230)								0.11
	133	1-Tolyl-2-phenylethene (194)								0.33
	134	5,6,11,12-Tetrahydro-dibenzo[a,e]cyclooctene (208)						0.15		
11	137	*Fluorene* (166)					1.22	1.29	0.90	0.71
	138	X-Methylfluorene (180)					2.91	3.44	2.71	2.99
	139	2,3-Dimethylfluorene (194)					1.01	1.45	0.78	1.06
	140	Benz[a]fluorene (216), Benz[b]fluorene (216)					0.45	0.10	0.29	0.19
12	141	*Fluoranthrene* (202)					0.25	0.62	0.26	0.57
13	143	*Anthracene* (178) *Phenanthrene* (178)					0.85	0.90	0.86	0.32

	144	1-Methylanthracene (192) 2-Methylanthracene (192) 1-Methylphenanthrene (192) 2-Methylphenanthrene (192)					2.68	2.82	2.40	2.39
	145	X,Y-Dimethylanthracene (206) X,Y-Dimethylphenanthrene (206)					1.30	1.59	1.20	2.11
	147	2,3,5-Trimethylphenanthrene (220)					0.21	0.39		0.12
	149	Phenalene (166)					0.24			
	150	1a,9b-Dihydro-cyclopropa[1]phenanthrene (192)						0.25		
14	151	*Pyrene* (202)					2.21	1.08	2.33	0.84
	152	X-Methylpyrene (216)					3.85	3.52	3.31	2.50
	153	X,Y-Dimethylpyrene (230)					2.35	1.72	1.28	1.61
	154	*Benzo[a]pyrene* (252)					0.31			
15	156	X-Methylchrysene (242)					0.68	0.24	0.76	0.72
	157	Triphenalene (228)							0.32	
	158	2-Methyltriphenalene (242)						0.34	0.38	
	159	*Benz[a]anthracene* (228)					0.16	0.19	0.26	0.21
	160	1-Methylbenz[a]anthracene (242) 5-Methylbenzo[c]phenanthrene (242)							0.18	0.21
	161	7,12-Dimethylbenz[a]anthracene (256) 5,8-Dimthylbenzo[c]phenanthrene (256)					0.46	0.10	0.25	0.86