



Thermal behaviour of selected flavour ingredients and additives under simulated cigarette combustion and tobacco heating conditions

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ABSTRACT

An experimental method of pyrolysis–gas chromatography/mass spectrometry (Py–GC/MS) is proposed to evaluate the fate of selected flavour compounds in low-temperature (300 °C) tobacco heating conditions. The thermal behaviour of five flavouring compounds (citronellol, menthol, tartaric acid, cinnamic acid, and guaiacol) was studied under conditions to simulate low-temperature tobacco heating at 300 °C, and compared with results obtained using simulated cigarette-combustion conditions with a temperature programme up to 900 °C. The impact of oxygen and nitrogen atmospheres on the thermal transfer and breakdown patterns was also investigated.

It was established that the four flavouring compounds of high volatility (citronellol, menthol, cinnamic acid, and guaiacol) evaporated to a high degree (88–100%) during the low- and high-temperature experiments, as well. Guaiacol was the most stable compound under the test conditions; only 0.3% decomposition was detected at 900 °C with the oxidative atmosphere. Thermal decomposition reactions were substantially less extensive at the low-temperature heating conditions than with the high-temperature pyrolysis and simulated cigarette combustion. Citronellol and cinnamic acid produced about 1.5% decomposition products, while menthol produced 0.8%. In general, dehydrogenation reactions were more pronounced in the oxidative atmosphere, while aromatisation was significant in the nitrogen atmosphere, and at high temperatures. More oxo-compounds and less aromatic hydrocarbons were formed in the oxidative atmosphere.

Other types of reactions took place with tartaric acid, due to its low volatility. Extensive formation of light carboxylic acids was observed at the low temperature, and cyclic compounds were also formed in addition to carbon oxides and water under both nitrogen and oxidative atmospheres. Intermolecular reactions are proposed to explain these observations. At high temperatures the pyrolysis products of tartaric acid were the same as at low temperatures, but in the oxidative atmosphere more carboxylic acids and less aldehydes were formed than in pure nitrogen.

These results demonstrate the flavour compound's thermal stability depends strongly on the exact thermal history (heating temperature, heating duration and gas atmosphere) that they are exposed to. The information obtained will be of interests in understanding the thermal behaviour of these and other flavour compounds used in tobacco heating products.

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1. Introduction

Tobacco products such as cigarettes contain a range of ingredients that are essential for physical integrity, engineering/manufacturing as well as consumer acceptability [1]. The use

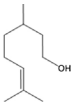
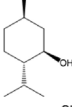
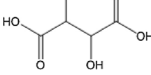
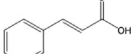

of ingredients in tobacco products is regulated in most developed countries. Both “positive” and “negative” ingredient lists have been proposed to either permit or to restrict certain types of ingredients used. European Union's scientific advisory committee, SCENIHR (Scientific Committee on Emerging and Newly Identified Health Risks), has defined an “ingredient” as “tobacco, an additive, as well as any substance or element present in a finished tobacco product or related products, including paper, filter, ink, capsules and adhesives”. It classifies an “additive” as being “a substance, other

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Table 1

The main characteristics of the test materials.

Materials	CAS-Number	Chemical structure	Melting point (°C)	Boiling point (°C)
Citronellol	106-22-9		−7 (−20)	225
Menthol	89-78-1		42–45	212–216
Tartaric acid	87-69-4		168–174	decomposes
Cinnamic acid	140-10-3		132–136	350
Guaiacol	90-05-1		27–29	204–206

than tobacco, that is added to a tobacco product, a unit packet or to any outside packaging” [2]. In practice, additives can be applied during tobacco processing (e.g., cutting, expansion), or during reconstituted tobacco manufacture; by either paper-based or bandcast processes. There are further opportunities for the addition of humectants, casing and flavouring compounds during cigarette manufacturing and also during the packaging of the cigarettes.

Extensive research has been carried out to understand and to model the thermal behaviour of ingredients or additives during cigarette smoking [3–11]. Baker et al. [5,6,11] used a pyrolysis technique that simulated the thermal decomposition of tobacco inside a burning cigarette and studied the levels of thermal decomposition for 291 volatile and non-volatile ingredients. The results were then compared to mainstream smoke chemistry results obtained from cigarettes with these ingredients added at elevated levels compared to commercial usage. The only classes of ingredients with a noticeable impact on the smoke chemistry were several sugars added as tobacco casing ingredients. The chemistry changes did not cause significant differences in responsive in vitro assays targeting both genotoxicity and cytotoxicity, as well inhalation toxicity in rodents. Subsequent studies from other laboratories support these findings [12–14]. For example, a series of in vitro and in vivo studies to evaluate the potential effects of tobacco flavouring and casing ingredients have not discovered consistent differences in toxicological effects between smoke generated from cigarettes containing these ingredients against reference or control cigarettes [12]. Gen-

erally these studies show that the relationship between tobacco leaf composition and smoke components is complex. The current scientific understanding on complex chemistry does not permit a full assessment on each individual component's contribution to the final outcome [15]. Tobacco as a natural agricultural product also has variations in chemical compositions depending on crop year and agricultural practices. Additional analytical characterisations including targeted and untargeted approaches have to be taken when evaluating the effect of a single ingredient in the context of this complex matrix.

Nevertheless, tobacco regulators have called for more research on the pyrolysis behaviour of ingredients. For example, in the European Union, the Tobacco Products Directive 2014/40/EU sets out the rules and regulations on reporting the composition of tobacco products, including those used as ingredients contained in tobacco products [16]. The European Union's scientific advisory committee, SCENIHR, has recently published its “Preliminary Opinion on Additives used in Tobacco Products”, concluding that “Data on pyrolysis of most of the individual additives are scant” and calls for more pyrolysis studies on individual and complex flavour additives to be carried out [2,17]. The US Food and Drug Administration (FDA)'s Center for Tobacco Products (CTP) also considered extensive pyrolysis, smoke chemistry and biological evidence in its evaluation of menthol's role in mentholated cigarettes in US [18].

Many tobacco regulations (e.g., the Tobacco Products Directive 2014/40/EU) not only cover machine-made cigarettes, they also

Table 2

Pyrolysis and GC/MS experimental conditions for low-temperature heating and simulated cigarette combustion conditions.

Pyrolysis conditions	Low-temperature heating	High-temperature heating
Pyroprobe heating programme	300 °C (held 300 s)	300 °C (held 5 s)–30 °C/s–to 900 °C (held 5 s)
Atmospheres	100% nitrogen or 9% oxygen in nitrogen	100% nitrogen or 9% oxygen in nitrogen
Sample size	60 µg in 2 µL ethanol solution on quartz wool except tartaric acid: 600 µg as received	
Pyrolysis gas flow	276 mL/min (4.6 mL/s)	
Pyrolysis interface temperature	250 °C	
GC/MS operating conditions	Low-temperature heating	High-temperature heating
Oven programme	40 °C (held 3.5 min)–10 °C/min–to 240 °C–20 °C/min–to 280 °C (held 5 min ^a)	40 °C (held 7 min)–10 °C/min–to 240 °C– 20 °C/min– to 280 °C (held 5 min)
Solvent delay	7 min ^a	3.5 min
Column	DB 1701 (30 m length, 0.25 mm i.d., 0.25 µm)	
Injection mode	Split (split flow: 276 mL/min)	
Carrier gas	He at 1 mL/min flow	
Mass range	29–400 Da	
MS ionization mode	El 70 eV	

^a Additional experiments were performed with tartaric acid using 75 s hold time and 3.3 min solvent delay.

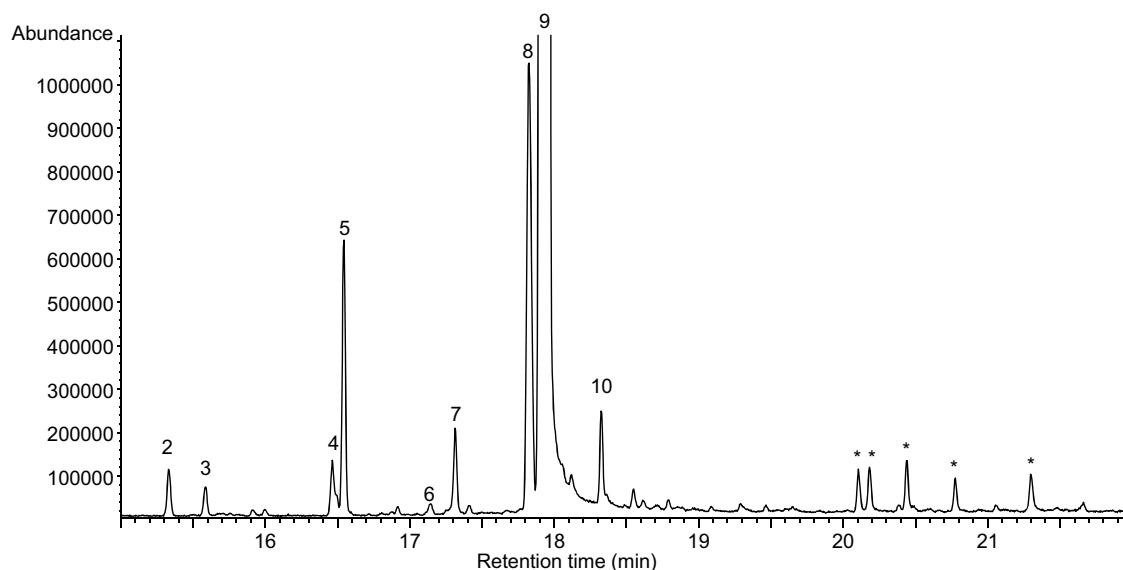


Fig. 1. Py-GC/MS total ion chromatogram of citronellol at 300 °C in oxidative atmosphere. Numbered peak identities are given in Table 3. * denotes impurities.

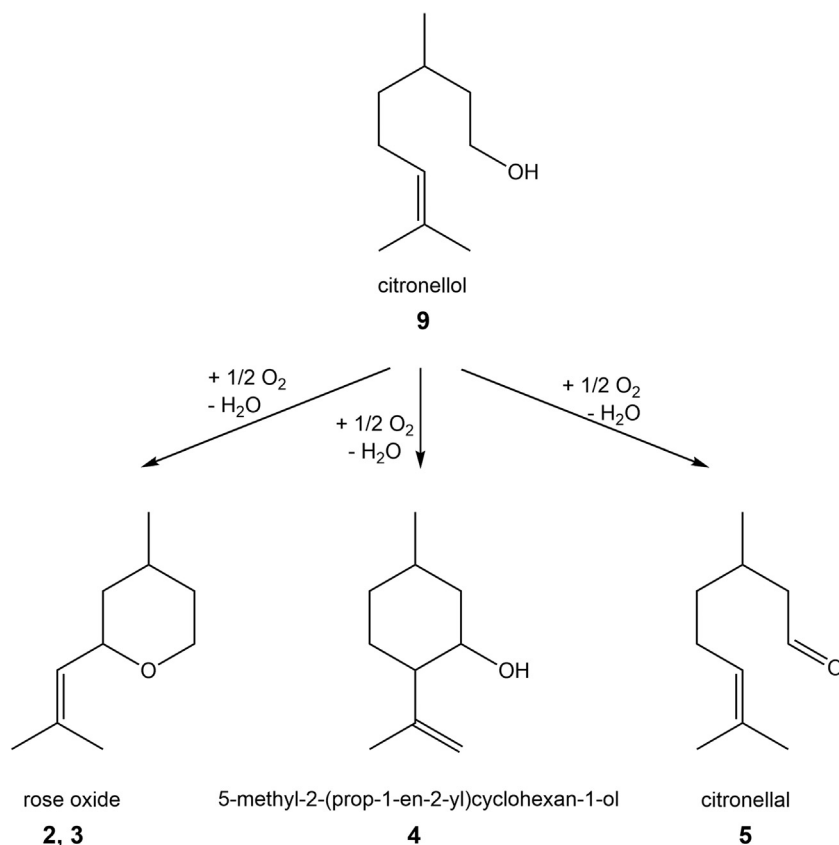
include so-called novel tobacco products. One type of novel tobacco product utilises tobacco heating technology (or heat-not-burn) in order to reduce or avoid those toxicants mainly produced by high-temperature pyrolysis and combustion of tobacco. Two broad types of tobacco heating products have been marketed so far. The first type has the appearance of a conventional cigarette and uses a charcoal tip as the heat source [19]. During use, the charcoal tip is lit without causing the rest of the tobacco rod to burn. Puffing on the product leads to air being heated by the charcoal tip and this heated air then passes through the tobacco rod to release aerosol agents (e.g., glycerol), tobacco aroma and flavouring compounds. The second type of tobacco heating product is based on consumer electronics, i.e., based on a re-chargeable battery and a heating chamber which hosts a tobacco rod. During use, the tobacco rod is heated to significantly below the pyrolysis temperature of a burning cigarette [20]. For both types of tobacco heating products, the main part of the aerosol comes from added aerosol agents such as glycerol. Heating tobacco to around 200–300 °C is sufficient to release nicotine but not sufficient to lead significant pyrosynthesis of tobacco-derived aerosol agents. To compensate for the difference in tobacco aroma, flavouring agents are usually added to this type

of product. The heating rates and temperatures in tobacco heating products are generally lower and less aggressive as compared to those experienced in a burning cigarette. On the other hand, the tobacco is subjected to a longer heating time in these novel tobacco products as the tobacco is not consumed during burning as it is in a cigarette. There is therefore a significant thermophysical difference between conventional cigarettes and tobacco heating products, which may cause different thermal behaviours for the added flavour ingredients. So far, there is a shortage of published studies to help understand and to compare flavouring compound thermal behaviour in this novel tobacco category.

In this work, pyrolysis experiments were performed on five single flavour compounds, selected to represent a wide range of chemical and thermophysical properties. The focus of the work was to evaluate the effects of atmosphere and heating temperature on the composition and relative amount of volatile decomposition products. The 5 compounds studied are citronellol, menthol, tartaric acid, cinnamic acid, and guaiacol. By using both a previously published simulated cigarette-combustion temperature, with a final holding temperature at 900 °C, and a proposed tobacco heating temperature profile peaking at 300 °C, their transfer and thermal breakdown patterns were systematically recorded and analysed.

Table 3
Product distribution of citronellol under four thermal conditions (TIC area%) and the composition of the test material.

Peak No.	Compounds	Purity test Area (%)	Heating conditions			
			300 °C (300 s)		300 °C (5 s)–30 °C/s–900 °C (5 s)	
			N ₂ Area (%)	9% O ₂ in N ₂ Area (%)	N ₂ Area (%)	9% O ₂ in N ₂ Area (%)
1.	Toluene				0.13 ± 0.05	
2.	Rose oxide (<i>cis</i> or <i>trans</i> -4-methyl-2-(2-methylprop-1-en-1-yl) tetrahydro-2H-pyran)	0.05 ± 0.01	0.10 ± 0.04	0.24 ± 0.04	0.35 ± 0.11	0.14 ± 0.05
3.	Rose oxide (<i>cis</i> or <i>trans</i> -4-methyl-2-(2-methylprop-1-en-1-yl) tetrahydro-2H-pyran)	0.03 ± 0.01	0.06 ± 0.02	0.14 ± 0.03	0.22 ± 0.07	0.09 ± 0.03
4.	5-Methyl- 2-(1-methylethenyl)-cyclohexanol		0.02 ± 0.01	0.36 ± 0.14	0.06 ± 0.02	0.15 ± 0.07
5.	Citronellal (3,7-dimethyloct-6-en-1-ol)	0.22 ± 0.01	0.21 ± 0.02	1.67 ± 0.53	0.48 ± 0.01	0.80 ± 0.38
6.	2-Isobutyl-4-methyltetrahydro-2H-pyran			0.10 ± 0.05	0.09 ± 0.02	
7.	3,7-Dimethyl-1-octanol	0.43 ± 0.01	0.54 ± 0.01	0.47 ± 0.03	0.46 ± 0.05	0.36 ± 0.04
8.	Rhodinol (3,7-dimethyloct-7-en-1-ol)	3.66 ± 0.02	4.04 ± 0.06	3.44 ± 0.09	4.31 ± 0.29	3.19 ± 0.23
9.	Citronellol (3,7-dimethyloct-6-en-1-ol)	94.55 ± 0.29	94.21 ± 0.18	93.06 ± 0.43	92.95 ± 0.17	94.78 ± 0.63
10.	3,7-Dimethyl-1,6-octadien-3-ol	1.06 ± 0.13	0.80 ± 0.05	0.52 ± 0.05	0.96 ± 0.04	0.50 ± 0.06



Scheme 1. Proposed reaction pathways of citronellol heated under oxidative atmosphere.

2. Experimental

2.1. Materials

Citronellol (>95%), menthol (99%), tartaric acid (99.5%), *trans*-cinnamic acid (>99%), and guaiacol (>98%) were purchased from Sigma-Aldrich Co. (Hungary). Citronellol, menthol, *trans*-cinnamic acid, and guaiacol were made up in ethanol working solutions to a concentration of 30 mg/mL. Each of the analysed solutions was

prepared fresh on the day of the experiment. Tartaric acid was pyrolysed as received because tartaric acid undergoes esterification reaction in ethanol solution. The main characteristics of the compounds are listed in Table 1.

The carrier and pyrolysis gases of 99.995% (n/n) purity were obtained from Messer Hungarogáz Kft., Hungary. Helium was used as a carrier gas for the GC/MS. The experiments were performed either in nitrogen atmosphere or in a gas mixture of 9.34% (n/n) oxygen and 90.66% (n/n) nitrogen.

Table 4
Product distribution of menthol under four thermal conditions (TIC area%) and the composition of the test material.

Peak No.	Compounds	Purity test Area (%)	Heating conditions			
			300 °C (300 s)		300 °C (5 s)–30 °C/s–900 °C (5 s)	
			N ₂ Area (%)	9% O ₂ in N ₂ Area (%)	N ₂ Area (%)	9% O ₂ in N ₂ Area (%)
1.	Toluene				0.13 ± 0.02	0.06 ± 0.01
2.	1-Methyl-3-(2-methyl-2-propenyl)-cyclopentane				0.13 ± 0.06	0.13 ± 0.06
3.	<i>Trans</i> -2-Menthene (<i>trans</i> -3-methyl-6-(1-methylethyl)-cyclohexene)			0.24 ± 0.04	0.14 ± 0.03	0.56 ± 0.23
4.	3-Menthene (4-methyl-1-(1-methylethyl)-cyclohexene)				0.69 ± 0.07	2.05 ± 0.87
5.	1-Methyl-3-(2-methyl-1-propenyl)-cyclopentane					0.31 ± 0.14
6.	<i>cis</i> -2-Menthene (<i>cis</i> -3-methyl-6-(1-methylethyl)-cyclohexene)					0.10 ± 0.05
7.	Menthene isomer					0.14 ± 0.06
8.	3-Methylcyclohexanone					0.04 ± 0.02
9.	1-Methyl-4-(methylethyl)-benzene					0.12 ± 0.06
10.	Menthone (2 <i>S</i> ,5 <i>R</i>)-2-isopropyl-5-methylcyclohexan-1-one			0.63 ± 0.39	0.06 ± 0.01	1.41 ± 0.84
11.	Isomenthol (1 <i>S</i> ,2 <i>R</i> ,5 <i>R</i>)-2-isopropyl-5-methylcyclohexanol	0.20 ± 0.01	0.31 ± 0.01	0.20 ± 0.02	0.27 ± 0.02	0.20 ± 0.01
12.	Isomenthone (2 <i>S</i> ,5 <i>S</i>)-2-isopropyl-5-methylcyclohexan-1-one					0.27 ± 0.23
13.	Menthol (1 <i>R</i> ,2 <i>S</i> ,5 <i>R</i>)-2-isopropyl-5-methylcyclohexanol	99.23 ± 0.04	98.94 ± 0.03	98.35 ± 0.34	98.05 ± 0.06	94.14 ± 1.85
14.	Neoisomenthol (1 <i>R</i> ,2 <i>R</i> ,5 <i>R</i>)-2-isopropyl-5-methylcyclohexanol	0.57 ± 0.03	0.75 ± 0.02	0.59 ± 0.02	0.67 ± 0.01	0.48 ± 0.03

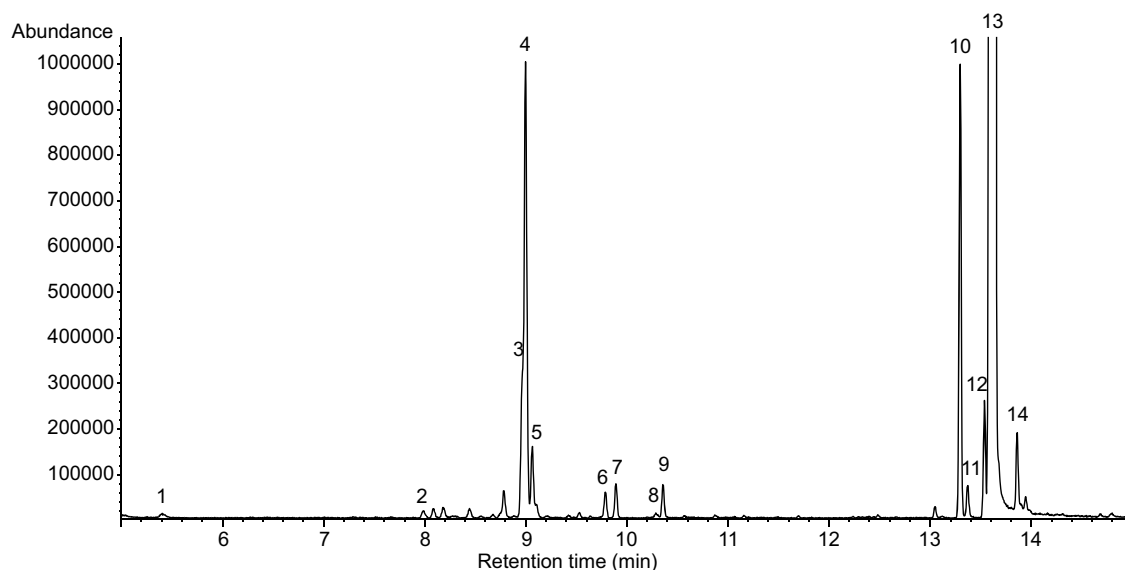


Fig. 2. Py-GC/MS total ion chromatogram of menthol at 900 °C in oxidative atmosphere. Numbered peak identities are given in Table 4.

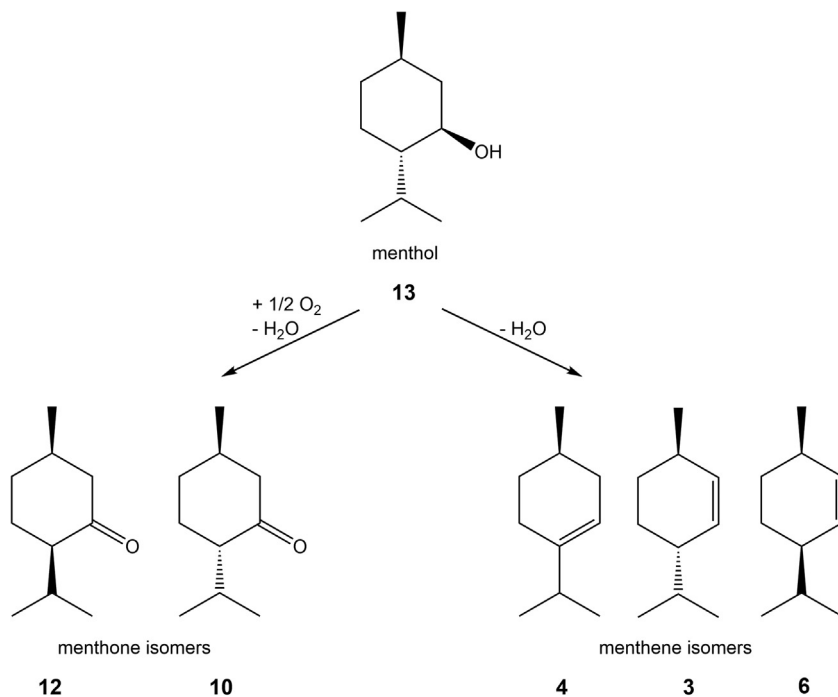
2.2. Pyrolysis-GC/MS

Py-GC/MS analyses have been carried out using a Pyroprobe 2000 (CDS Analytical, Oxford, PA, USA) pyrolyzer equipped with a platinum coil and a quartz sample tube. A 2.0 μ L aliquot of solution was dispensed onto a piece of quartz wool placed in a quartz tube and it was rested for 5 min at room temperature to allow the evaporation of majority of the solvent. Solution was applied to quartz wool because it simulates tobacco strand structure. The quartz tube was placed in the Pyroprobe, at room temperature, which was then inserted into the pre-heated (250 °C) pyrolysis chamber. The pyrolysis chamber was flushed by the applied gas mixture using 276 mL/min flow rate. The volatile products of the pyrolysis were purged on-line to an Agilent 6890 GC/5973 MSD

system (Agilent Technologies, Palo Alto, CA, USA). At the end of the pyrolysis programme, the pyrolysis gas flow was closed and He carrier gas supplied to the GC/MS.

The identification of the pyrolysis products was based on NIST mass spectral library and literature data. The percentages of the compounds were estimated using the peak areas of the total ion current chromatograms. The pyrolysis and GC/MS operating conditions for the low-temperature and high-temperature heating, under both inert and oxidative atmosphere, are summarised in Table 2.

In the present work only partial analysis of the pyrolysis products could be performed. This is because product gases (e.g. CO, CO₂, H₂O and small organic molecules) co-eluted from the GC with the nitrogen and oxygen gaseous medium. As the ion chamber of



Scheme 2. Proposed formation of menthone and menthene isomers from menthol.

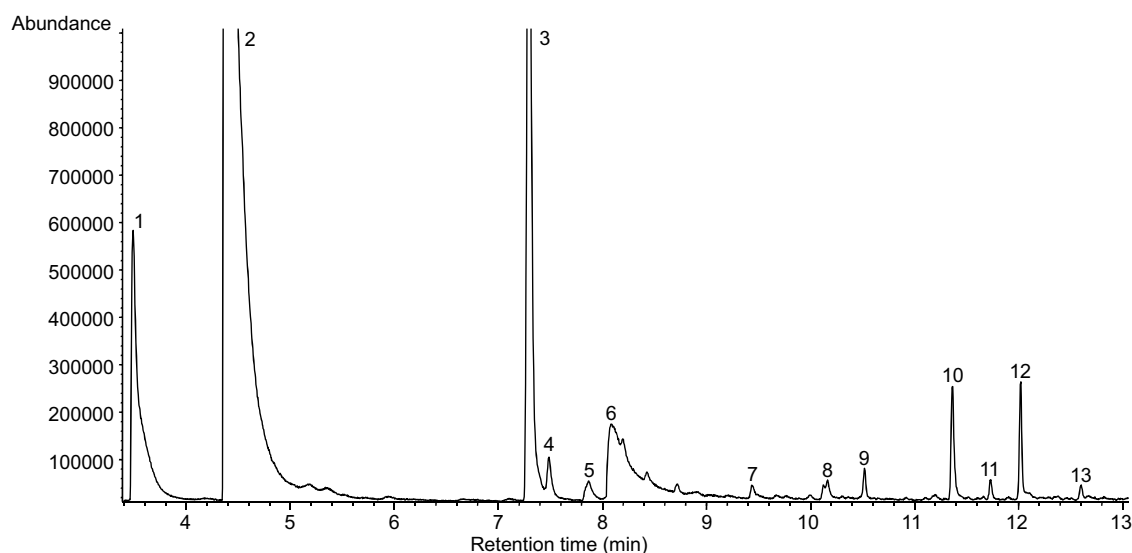
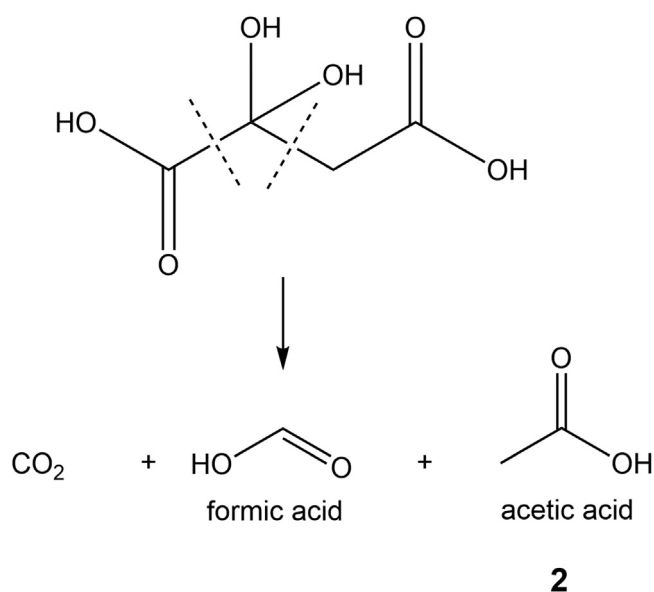


Fig. 3. Py-GC/MS total ion chromatogram of tartaric acid at 900 °C in inert atmosphere. Numbered peak identities are given in Table 5.



Scheme 3. Proposed formation of acetic and formic acid from 2,2-dihydroxybutanedioic acid probably produced by an intramolecular rearrangement of tartaric acid [26].

the mass spectrometer had to be protected from these gases, only the reaction products of longer retention time could be analysed.

2.2.1. Pyrolysis conditions to mimic a low-temperature tobacco heating

The representative heating temperature range for the current low-temperature tobacco heating products is between 150–300 °C. This reflects the heater temperature, while the actual temperature experienced by the bulk of tobacco materials may be lower and variable throughout the heating period, and may vary from one heating system to another. It is therefore difficult to prescribe a “standard” heating profile for all tobacco heating products. However, for the purpose of evaluating the thermal stability of a flavour compound during the low-temperature heating, it is reasonable to assume an isothermal temperature profile that envelops the anticipated temperature ranges and heating rates. In this study, a 300 °C isothermal temperature was applied in order to mimic the heat-

ing conditions of the low-temperature tobacco heating products. The information obtained would be considered applicable to evaluate thermal stability for heating systems with heater temperatures up to a maximum 300 °C. The length of the isothermal period was 5 min, according to an estimated typical average length of the usage of a relevant tobacco product. After 5 min of heating, the pyrolysis gas flow was closed off and then He carrier gas supplied to the GC. As the carrier gas left the ion source in an additional ca. 1.7 min (the dead time of the GC), a total of 7 min of solvent delay was set to protect the MS filament and multiplier. No MS data was obtained during this time. Further experimental parameters are summarised in Table 2.

For tartaric acid, initial experiments demonstrated that significant decomposition occurred and a few products eluted in the first 7 min of the chromatogram. In order to obtain the information about the yields of these compounds, additional experiments were carried out using only 75 s of isothermal heating and 3.3 min solvent delay.

2.2.2. Pyrolysis conditions used to simulate a burning cigarette

The pyrolysis conditions used to simulate a burning cigarette have been described previously [5,6]. They were developed to represent the averaged thermophysical and thermochemical conditions for a burning cigarette. In this work almost all the parameters were set as described by Baker and Bishop [5]. However, there were some differences due to necessity and practicality. In order to measure low molecular weight volatile products, the shortest possible solvent delay was set at 3.5 min. Without a CIS injector as used by Baker et al. [5,6] to manage the pyrolysis gas flow, approximately triple sample weights were applied to reach the similar intensity in the chromatogram.

The detailed description of the parameters can be found elsewhere [5,6]. Briefly, the mixed gas of 9% O₂ in N₂ was considered appropriate to represent a range of oxidative and reductive gas atmospheres. A ramped temperature programme targeting the main pyrolysis region of the burning coal was found important to allow a balanced occurrence of evaporative transfer and pyrolytic decomposition. An initial temperature of 300 °C held for 5 s represented the “smouldering” state just prior to a puff, this was then followed by heating at 30 °C/s to 900 °C then held at this temperature for 5 s.

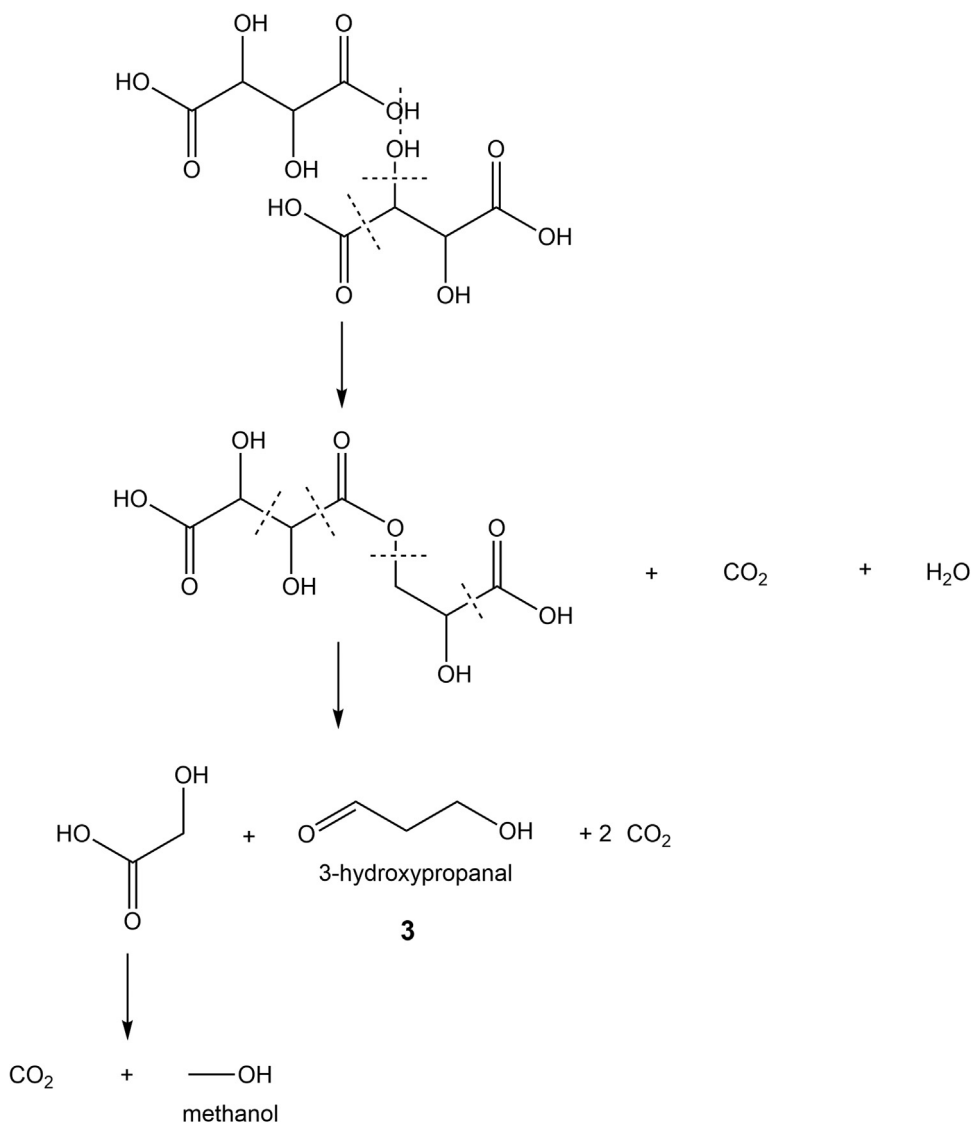
Table 5
Product distribution of tartaric acid under four thermal conditions (TIC area%).

Peak No.	Compounds	Heating conditions			
		300 °C (75 s)		300 °C (5 s)–30 °C/s–900 °C (5 s)	
		N ₂ Area (%)	9% O ₂ in N ₂ Area (%)	N ₂ Area (%)	9% O ₂ in N ₂ Area (%)
1.	Ethandial + 2-hydroxyacetaldehyde	3.40 ± 0.08	5.72 ± 0.59	8.60 ± 1.17	8.05 ± 0.55
2.	Acetic acid	61.48 ± 1.00	61.84 ± 1.40	62.17 ± 2.55	65.48 ± 0.34
3.	3-Hydroxypropanal	10.12 ± 0.47	13.10 ± 0.51	15.36 ± 1.59	11.73 ± 0.60
4.	Fumaraldehyde (but-2-ene-1,4-dione)	1.55 ± 0.07		0.98 ± 0.11	0.70 ± 0.01
5.	2H-Furan-3-one			0.55 ± 0.09	0.46 ± 0.07
6.	Pyruvic acid (2-Oxopropanoic acid) + acetic acid anhydride	19.28 ± 1.12	14.89 ± 2.05	7.73 ± 1.14	9.44 ± 0.98
7.	1-Acetoxy-2-propanone			0.26 ± 0.02	
8.	2,5-Furandione			0.28 ± 0.06	0.37 ± 0.03
9.	5-Methoxypent-4-enoic acid methyl ester	0.18 ± 0.01	0.20 ± 0.03	0.46 ± 0.13	0.41 ± 0.24
10.	2(5H)-Furanone-5-carbaldehyde	1.81 ± 0.20	1.72 ± 0.46	1.72 ± 0.11	1.35 ± 0.08
11.	3-Methyl-2,5-furandione	0.61 ± 0.03	0.61 ± 0.30	0.32 ± 0.05	0.36 ± 0.05
12.	1,2-Ethandioldiacetate + 3,4-dihydro-6-methyl-2H-pyran-2-one	1.57 ± 0.10	1.92 ± 0.11	1.37 ± 0.12	1.54 ± 0.01
13.	Phenol			0.20 ± 0.01	0.11 ± 0.01

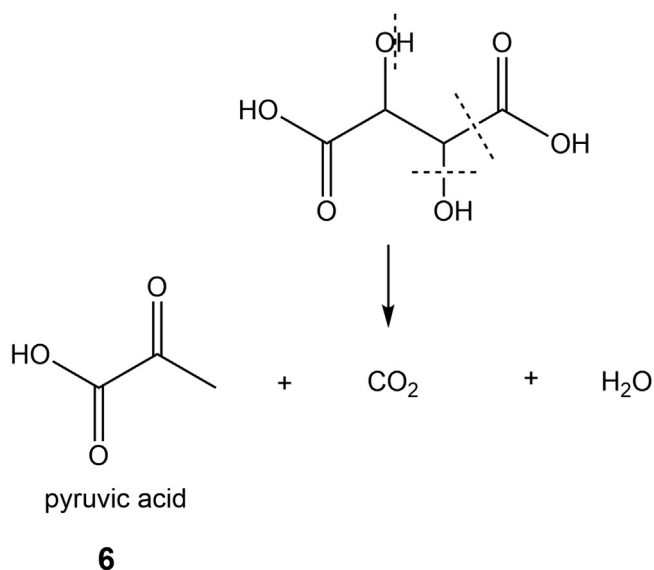
2.3. GC/MS purity test

GC/MS analysis of the test materials was performed to check for contaminants that would produce artifactual peaks. The analy-

sis was performed by Agilent 6890A/5973 GC/MS equipment. 1 µL sample in ethanol solution of 30 mg/mL concentration was separated on a DB-1701 capillary column (30 m × 0.25 mm, 0.25 µm



Scheme 4. Proposed formation of 3-hydroxypropanal and methanol from tartaric acid.



Scheme 5. Proposed formation of pyruvic acid (2-oxopropanoic acid) from tartaric acid.

film thickness). The range of m/z 29–400 was scanned by the mass spectrometer in EI mode at 70 eV.

Since tartaric acid did not evaporate (decomposed instead), GC/MS purity analysis of this compound was not possible.

3. Results and discussions

3.1. Citronellol

Citronellol is a natural terpene alcohol occurring in many natural plant oils. It is one of the most widely used components in fragrances. Citronellol is also reported to be used as a raw material for rose oxide production.

Fig. 1 presents the pyrogram of citronellol at 300 °C in an oxidative atmosphere. Table 3 summarizes the amounts of the thermal decomposition products of citronellol formed under the four different experimental conditions and the results of the purity test. As the results show, the purchased citronellol contained several impurities; the intensities of the highest impurity peaks are included in Table 3 (peaks 7, 8, 10). The relative amounts of these impurities did not increase significantly under the various pyrolysis conditions indicating that these compounds did not form from citronellol during the thermal treatments.

Citronellal (CAS No. 106-23-0) was also identified as one of the impurities; however, the amount of this compound increased significantly, especially in the oxygen containing atmosphere at both low and high temperatures. The increased amount of citronellal most probably originated via dehydrogenation of the citronellol. The evolution of citronellal was most significant at 300 °C pyrolysis temperature in the oxidative atmosphere. This observation is in agreement with other thermo-oxidation studies in the literature. For example, Molinska et al. found [21] that during thermo-oxidation of citronellol at 80 °C in air the degradation was almost complete within the first 24 h, and citronellal was identified as one of the main thermo-oxidation products. Formation of citronellal was also found under 10 °C/min dynamic heating of citronellyl diesters in oxidative atmosphere by TG/FTIR [22]. The literature data and our results indicate that the dehydrogenation of citronellol is enhanced by oxygen. The general decomposition pattern based on the results obtained in this study and the literature is summarised in a reaction scheme shown in Scheme 1. As Scheme 1 proposed, dehydrogenation is accompanied by the release of water

in the presence of oxygen. At higher temperatures in the oxidative atmosphere the amount of the citronellal formed is less significant. This pyrolysis programme also contains 5 s of 300 °C isothermal heating period, which may be preferable for citronellal formation. At higher temperatures the formation of citronellal is less intensive.

According to the purity test results, the purchased citronellol contained rose oxide (concentration below 0.1%), this was released and observable during each of the pyrolysis experiment. Rose oxide (CAS No 16409-43-1) has *cis*- and *trans*-stereoisomers, which were separated on the GC column (Fig. 1, peaks 2 and 3), but they could not be distinguished on the basis of their EI mass spectra. The ratio of the *cis*- and *trans*-rose oxides is very similar under all the studied conditions. A key step in the manufacture of synthetic rose oxide is the peroxidation of citronellol by singlet oxygen through an ene-type mechanism [23]. Regarding our experimental results, rose oxide formed in small amounts both in the presence and absence of oxygen during the thermal decomposition reactions. Table 3 shows that the lower temperature (300 °C) and the presence of 9% of oxygen in the atmosphere promoted the formation of rose oxide, while at a higher temperature more rose oxide was formed in the absence of oxygen. The cyclisation reaction of citronellol through the formation of an oxygen-containing ring is believed to lead to the evolution of rose oxide. However, the cyclisation may also occur between two carbon atoms of citronellol giving rise to the release of 5-methyl-2-(1-methylethenyl)-cyclohexanol. This reaction is most significant at 300 °C in oxidative atmosphere. Scheme 1 summarizes the main thermal decomposition reactions of citronellol as described above.

At higher temperatures in the inert atmosphere the formation of a small amount of toluene was detected, indicating the scission of hydroxyl and propyl groups which led to aromatisation in the absence of oxygen.

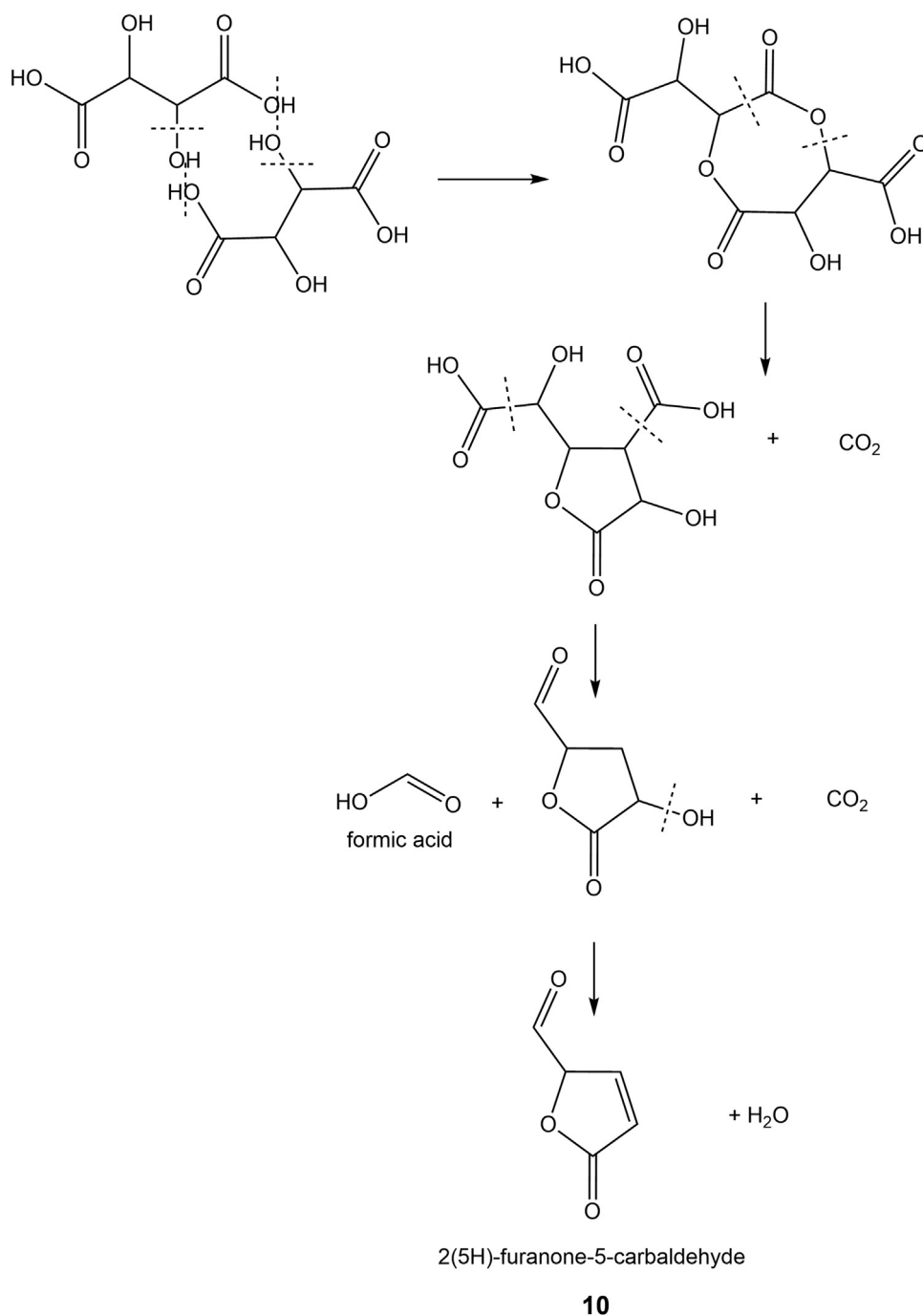
3.2. Menthol

Natural menthol can be obtained from peppermint or other mint oils and is extensively used in a wide variety of commercial applications including pharmaceuticals, tobacco products, confections and chewing gums. Menthol is an optically active substance in which eight stereoisomers or four racemic compounds exist: menthol, isomenthol, neomenthol and neoisomenthol. Among them only one specific form is present in natural peppermint oil, namely (–)-menthol. In Baker and Bishop's study [5], menthone and menthene were detected in the pyrolysate of menthol. Straight flash analytical pyrolysis of menthol has also been reported in the literature [10,24].

Table 4 summarizes the identified products of our menthol experiments. The pure menthol contained more than 99.2% (–)-menthol. Besides menthol, two other isomers were detected in small amounts; isomenthol (peak 11) and neoisomenthol (peak 14). By comparing the area% data, it may be concluded that the relative abundance of these two impurities did not change notably under the applied experimental conditions.

Menthone is an oxidation product of menthol, and it can be prepared by ozonization or other oxidation of menthol [25,26]. As Table 4 presents, menthone isomers (peaks 10 and 12) appeared in the pyrograms of menthol (Fig. 2). In the oxygen containing atmosphere the formation of 1.4% menthone was observed at the higher temperature, while about 0.6% was measured at 300 °C. In nitrogen atmosphere the evolution of menthone was not significant; it was only detected in a very low amount (0.06%) at the higher temperature, while it was under the detection limit at 300 °C. Accordingly, the supporting effect of oxygen on the formation of menthone can be confirmed.

As Table 4 presents, the number of decomposition products significantly increased at the higher temperature in the oxidative atmosphere. Numerous menthene isomers were identified. Dur-



Scheme 6. Proposed formation of 2(5H)-furanone 5-carbaldehyde from tartaric acid.

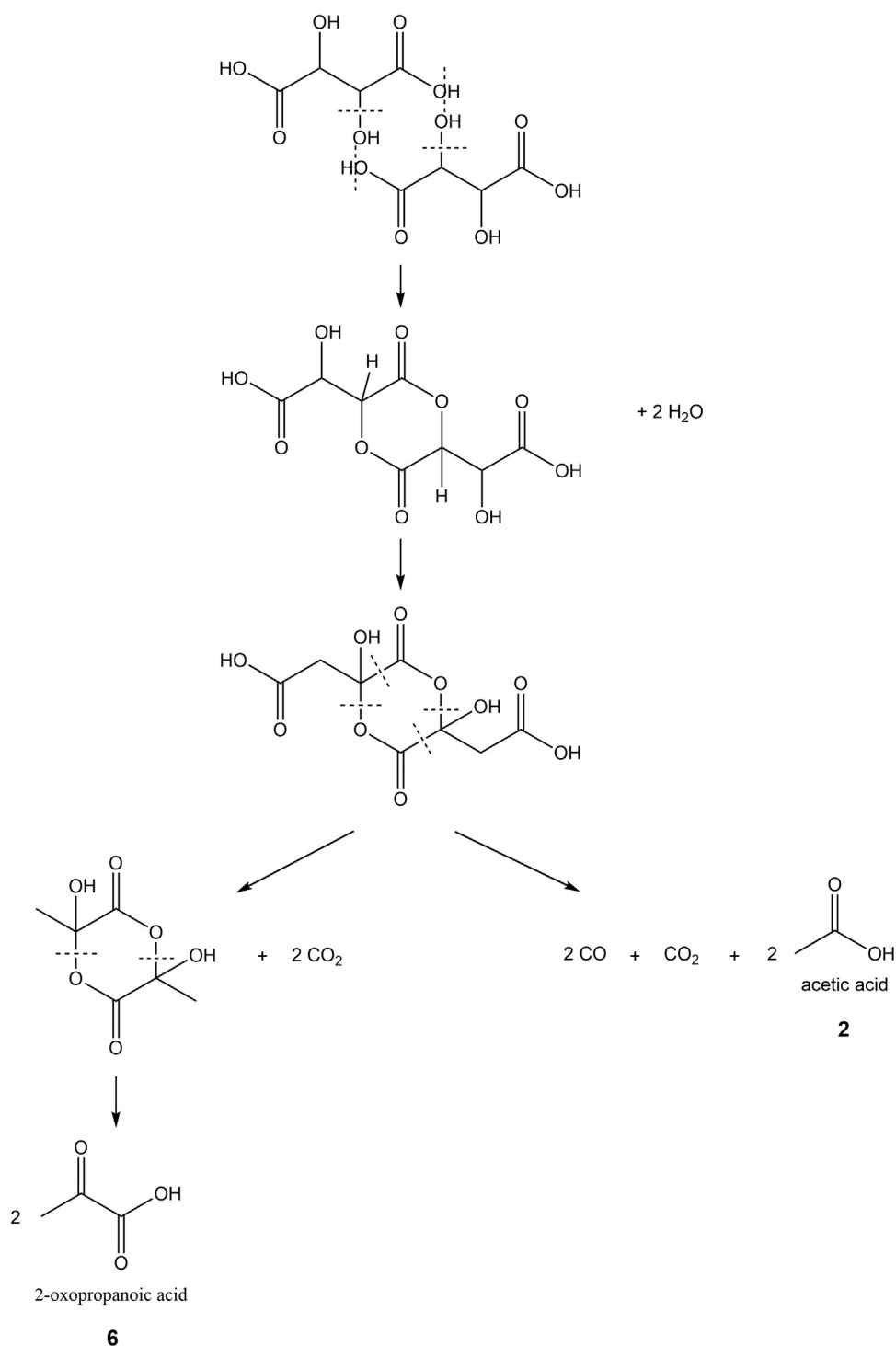
ing the pyrolysis of menthol, menthene is formed by elimination of one water molecule [10]. It seems that at the high temperature in our experiments the formation of 3-menthene (peak 4) was the most favourable. On the basis of the results it may be concluded that the presence of 9% of oxygen supported the elimination of water from the menthol molecule, as significantly more menthene was detected in the oxidative atmosphere under the simulated cigarette-combustion conditions than in the equivalent nitrogen atmosphere. At 300 °C in the oxidative atmosphere, only one menthene isomer was formed, while in the nitrogen atmosphere no menthene evolution was detected. Scheme 2 summarizes the main reaction routes of menthol decomposition.

At the higher temperature two aromatic compounds; toluene (peak 1) and 1-methyl-4-(methylethyl)-benzene (peak 9) were

detected in small amounts. Toluene appeared in both atmospheres, but the measured amount of this component was about double in the nitrogen atmosphere than in the presence of oxygen. Formation of 1-methyl-4-(methylethyl)-benzene was observed only in the oxygen-containing atmosphere.

3.3. Tartaric acid

Tartaric acid is an alpha-hydroxy-dicarboxyl acid which has three stereoisomers. The naturally occurring isomer is levotartaric acid that is present in many plants. Tartaric acid has several industrial applications and it is used in food industry as an antioxidant. Although tartaric acid is readily destroyed by heat and decomposes before boiling, its thermal breakdown has not been extensively



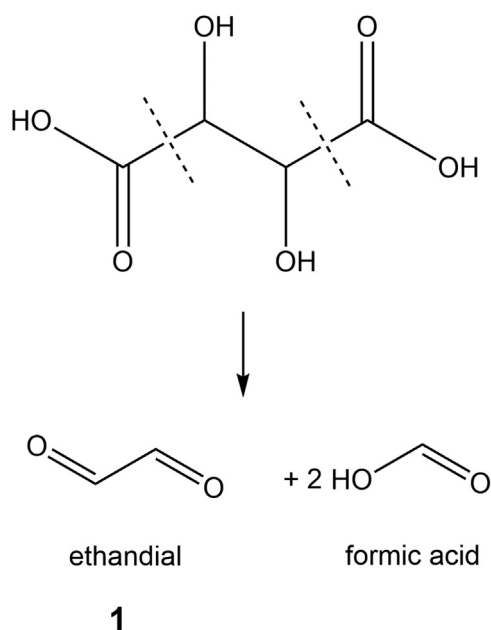
Scheme 7. Fragmentation of tartaric acid starting with the loss of water at the hydrogen bondings followed by a multistep rearrangement of hydrogen atoms and hydroxyl groups [26].

studied. Nevertheless, the early work of Chattaway and Ray published in 1921 [27] revealed the most important decomposition reactions occurring by heating tartaric acid. In the first stage of decomposition water is liberated, then carbon monoxide and carbon dioxide are produced, together with formic, acetic, and pyruvic acid [10]. Intermolecular reactions are proposed for the formation of these products. This is deemed probable due to the likely associations driven by hydrogen bonding between tartaric acid molecules in the molten state.

For the standard low-temperature experiments the heating time was 5 min with 7 min solvent delay. Ethandial, 2-hydroxyacetaldehyde and acetic acid elute below 7 min, so additional experiments were carried out using only 75 s of isothermal heating at 300 °C and 3.3 min solvent delay. No significant difference was observed in the product intensities of tartaric acid heated for 75 s and 300 s, indicating that most probably the whole of the tartaric acid sample decomposed during the first 75 s of the experiment at 300 °C under the applied conditions. For this reason Table 5

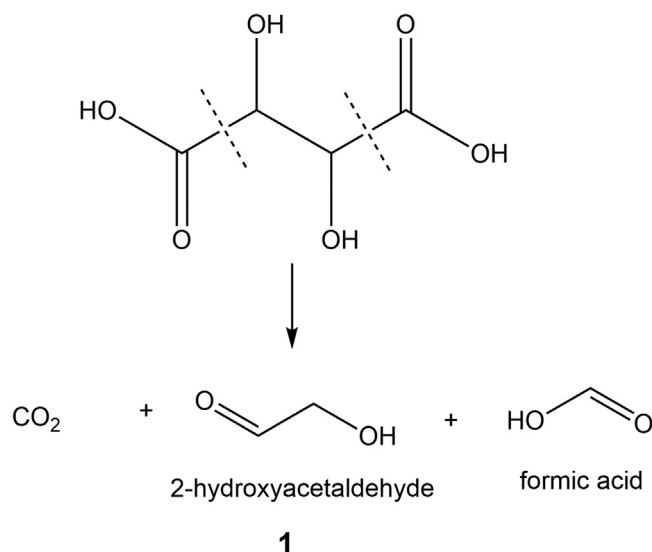
Table 6Product distribution of *trans*-cinnamic acid under four thermal conditions (TIC area%) and the composition of the test material.

Peak No.	Compounds	Purity test Area (%)	Heating conditions			
			300 °C (300 s)		300 °C (5 s)–30 °C/s–900 °C (5 s)	
			N ₂ Area (%)	9% O ₂ in N ₂ Area (%)	N ₂ Area (%)	9% O ₂ in N ₂ Area (%)
1.	Toluene				0.25 ± 0.08	
2.	Ethylbenzene				0.14 ± 0.05	
3.	Phenylethyne				1.41 ± 0.26	0.53 ± 0.30
4.	Styrene				5.40 ± 1.13	1.95 ± 1.56
5.	Benzaldehyde (+benzofuran)			1.02 ± 0.06		2.48 ± 1.36
6.	1-Propenylbenzene				0.16 ± 0.07	
7.	1-Propynylbenzene				0.17 ± 0.04	
8.	Phenylacetaldehyde			0.43 ± 0.02	0.07 ± 0.01	0.76 ± 0.41
9.	Acetophenone					0.20 ± 0.12
10.	Phenol					0.15 ± 0.07
11.	1,4-Dihydronaphthalene				0.09 ± 0.03	
12.	Naphthalene				0.28 ± 0.06	
13.	Ethyl cinnamate			0.11 ± 0.03	0.06 ± 0.01	0.24 ± 0.18
14.	<i>Trans</i> -cinnamic acid (3-phenylprop-2-enoic acid)	100.00	100.00	98.45 ± 0.07	88.60 ± 2.25	93.59 ± 3.90
15.	Stilbene (1,2-diphenylethene)				0.38 ± 0.07	0.11 ± 0.06
16.	3-Phenyl-1 <i>H</i> -indene				0.21 ± 0.03	
17.	1,4-Diphenyl-1,3-butadiene, or 1,2-dihydro-1-phenyl-naphthalene,				0.36 ± 0.08	
18.	1,2-Dihydro-4-phenyl-naphthalene				0.25 ± 0.06	
19.	1,2-Dihydro-phenyl-naphthalene isomer				0.13 ± 0.02	
20.	Phenanthrene				0.11 ± 0.01	
21.	1-Phenyl-naphthalene				0.71 ± 0.14	
22.	1-Phenyl-1 <i>H</i> -indene				0.27 ± 0.06	
23.	1,4-Diphenyl-1,3-butadiene isomer				0.13 ± 0.01	
24.	1,4-Diphenyl-1,3-butadiene isomer				0.13 ± 0.01	
25.	2-Phenyl-naphthalene				0.54 ± 0.08	
26.	1,4-Diphenyl-1,3-butadiene isomer				0.14 ± 0.02	

**Scheme 8.** Proposed formation of ethandial and formic acid from tartaric acid.

contains the results of experiments using the 75 s isothermal period only.

The pyrolysis gas chromatogram obtained at ramped temperature programme from 300 to 900 °C is shown in Fig. 3. The total ion peak areas of pyrolysis-GC/MS chromatograms obtained under the four experimental conditions are summarised in Table 5. The relative amounts of the co-eluting compounds (in peaks 1 and 6) have been estimated based on their characteristic MS fragment ion intensities. Acetic acid and 3-hydroxypropanal were the dominating compounds produced both in pure nitrogen and in 9%

**Scheme 9.** Proposed formation of 2-hydroxyacetaldehyde and formic acid from tartaric acid.

oxygen/nitrogen atmospheres. The reactions leading to these compounds are presented in Schemes 3 and 4 respectively. Scheme 5 shows the proposed reactions for the formation of 2-oxopropanoic acid. Further, two smaller peaks (11 and 13) at longer retention times also appeared among the main products of tartaric acid. These cyclic compounds having more than four carbon atoms could not be decomposition products of tartaric acid. Their formation may be understood by considering that these larger compounds could be the products of two tartaric acid molecules associated by hydrogen bonding through the mechanism proposed in Scheme 6. The dominance of acetic acid and increased formation of 2-oxopropanoic acid among the reaction products at 300 °C could be understood by a similar decomposition of two attached tartaric acid molecules.

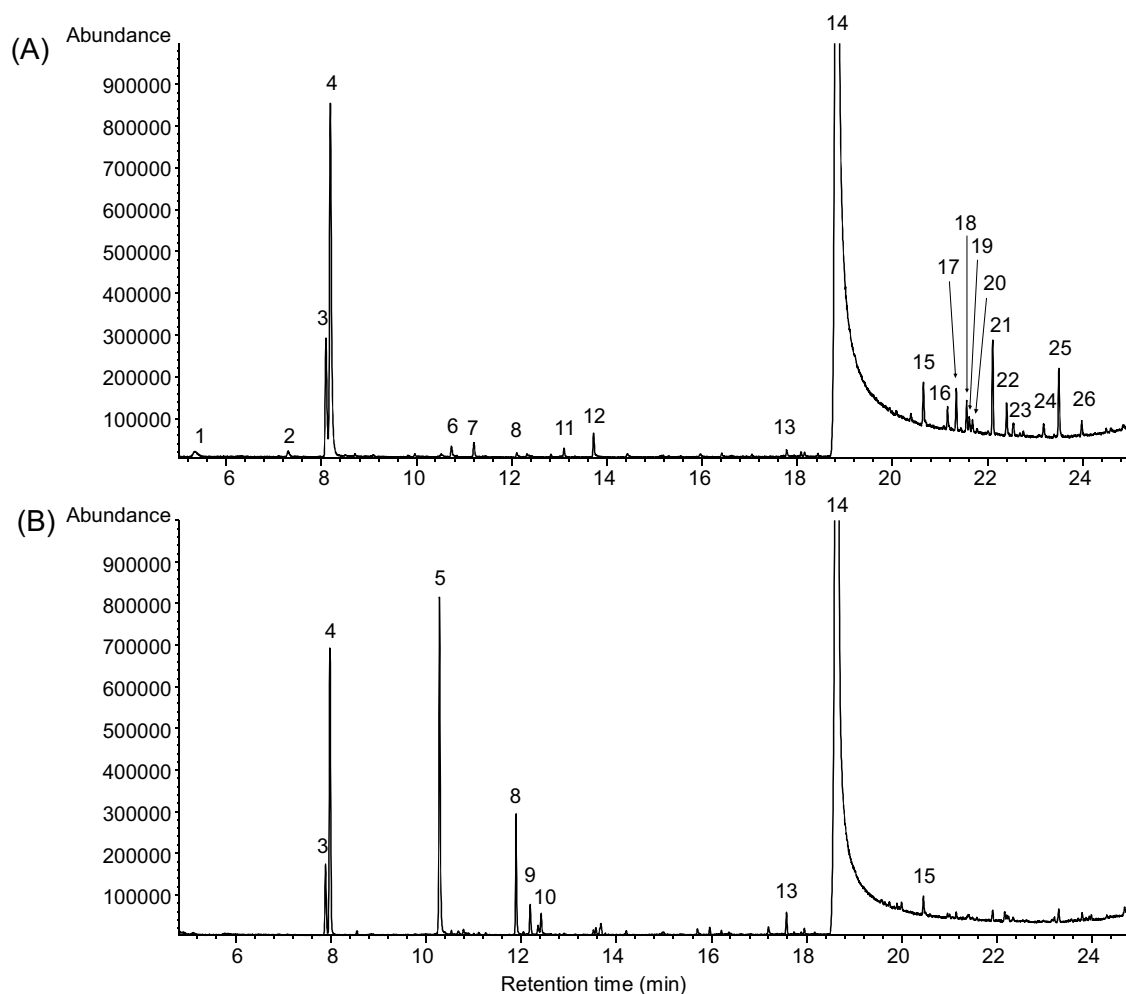
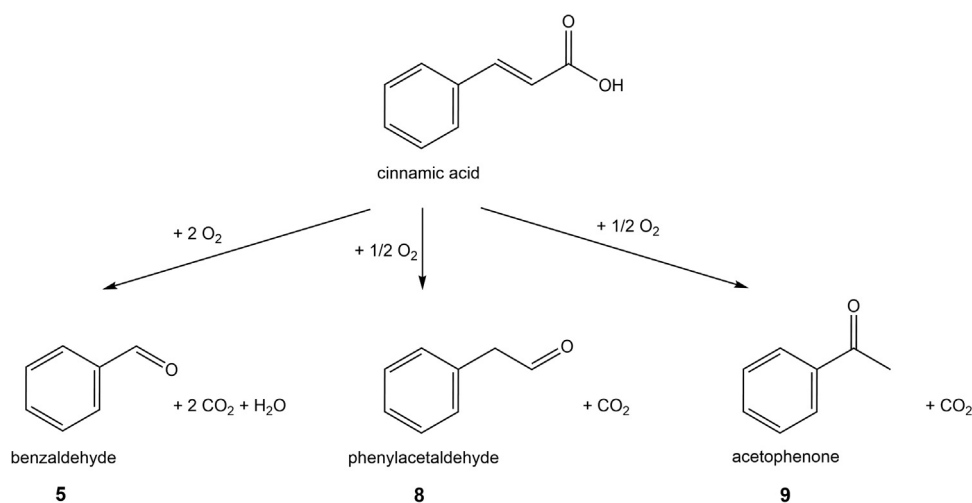


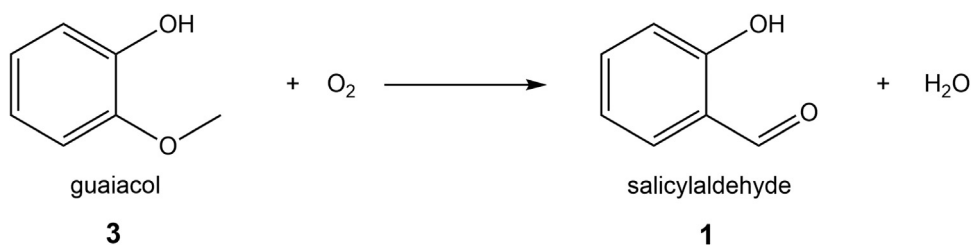
Fig. 4. Py-GC/MS total ion chromatograms of cinnamic acid at 900 °C in inert (A) and oxidative (B) atmospheres. Numbered peak identities are given in Table 6.



Scheme 10. Proposed decomposition pathways of cinnamic acid under oxidative atmosphere.

The fragmentation of tartaric acid starts with the loss of water followed by a rearrangement of hydrogen atoms and hydroxyl groups. The scissions of the intermediate product result in acetic acid or 2-oxopropanoic acid molecules as illustrated in Scheme 7. The first peak preceding acetic acid in the pyrograms represented two compounds: ethandial and 2-hydroxyacetaldehyde. Reactions leading

to these compounds are proposed in Schemes 8 and 9, respectively. The peak area data in the last two columns of Table 5 show that more acetic and 2-oxopropanoic acid, and less 3-hydroxypropanal and 2(5H)-furanone 5-carbaldehyde were produced when heating tartaric acid in the oxygen containing atmosphere than in pure



Scheme 11. Proposed formation of salicylaldehyde from guaiacol under oxidative atmosphere.

Table 7

Product distribution of guaiacol under four thermal conditions (TIC area%) and the composition of the test material.

Peak No.	Compounds	Purity test Area (%)	Heating conditions			
			300 °C (300 s)		300 °C (5 s)–30 °C/s–900 °C (5 s)	
			N ₂ Area (%)	9% O ₂ in N ₂ Area (%)	N ₂ Area (%)	9% O ₂ in N ₂ Area (%)
1.	Salicylaldehyde (2-Hydroxybenzaldehyde)					0.18 ± 0.08
2.	Phenol					0.02 ± 0.01
3.	Guaiacol	99.85 ± 0.02	99.83 ± 0.03	99.73 ± 0.07	99.79 ± 0.02	99.54 ± 0.12
4.	2-Methylphenol	0.15 ± 0.02	0.17 ± 0.03	0.18 ± 0.01	0.21 ± 0.02	0.13 ± 0.01
5.	Cinnamaldehyde (3-Phenylprop-2-enal)			0.07 ± 0.05		0.08 ± 0.03
6.	2,3-Dihydro-1(<i>H</i>)-inden-1-one			0.02 ± 0.01		0.05 ± 0.02

nitrogen. This could indicate that aldehydes were partially oxidised to acids by oxygen in the gaseous phase when heated at 900 °C.

In the gas chromatograms obtained from heating tartaric acid at 300 °C for 75 s, the peak of 2-oxopropanoic acid was increased remarkably compared to the level observed on heating at 900 °C. The total ion peak area data in the first two columns of Table 5 show that the relative amount of acetic acid among the products did not change when varying the experimental conditions, but that of 3-hydroxypropanal was considerably lower when tartaric acid was heated in the nitrogen atmosphere at 300 °C for 75 s than under fast ramped heating to 900 °C. The amounts of the cyclic products of higher molecular mass were also increased to some extent. The observed changes could be explained considering the increased probability of intermolecular reactions between two tartaric acid molecules in the molten state, as discussed above.

3.4. Cinnamic acid

Cinnamic acid occurs naturally in a number of plants; the *trans* isomer is more common than the *cis*. It is a flavour component of cinnamon. The main decomposition reaction of cinnamic acid at 900 °C is the formation of styrene [10]. Jones and Schmelt studied the thermal decomposition of *trans*-cinnamic acid in a furnace under a nitrogen atmosphere [28]. The major conversion products were styrene, *trans*-styrene, phenanthrene, phenylanthracene and toluene. Fig. 4 presents the decomposition products of *trans*-cinnamic acid in the nitrogen and oxidative atmosphere at the final 900 °C temperature obtained from our study. Table 6 lists the identification and the intensity of the products under the various experimental conditions. No contamination was detected in the *trans*-cinnamic acid sample during the purity test. Pyrolysis at 300 °C in nitrogen atmosphere resulted in the evaporation of the sample with no decomposition products. The formation of numerous reaction products was observed during the thermal decomposition of cinnamic acid at 900 °C in a nitrogen atmosphere. The majority of the products were aromatic hydrocarbons; oxygen-containing compounds were only present in the pyrolysate in concentration below 0.1%. Apparently, the decarboxylation of cinnamic acid led to the formation of styrene and carbon dioxide in the first step of the decomposition. Therefore, styrene was the main reaction product in the inert atmosphere. Phenylethyne was

the next most abundant compound indicating the dehydrogenation of the alkenyl groups of cinnamic acid besides the decarboxylation. The complicated scission and recombination reactions of the alkenyl groups of cinnamic acid were confirmed by the formation of various alkyl-, alkenyl- and alkynylbenzenes as well as diphenylbutadienes. The complex aromatisation reactions of these aliphatic fragments with the benzene rings resulted in the evolution of several naphthalene derivatives.

As Fig. 4 and Table 6 show, the pyrogram of cinnamic acid was rather different in the oxidative atmosphere than in the nitrogen atmosphere using the same temperature programme up to 900 °C. The evolution of alkylaromatic products was significantly reduced; the yield of only 3 products was above 0.1% (styrene, phenylethyne, and stilbene). It appeared that decarboxylation took place in the oxidative atmosphere, since only one compound (ethyl cinnamate) kept the carboxyl group. The major products of the simulated cigarette-combustion experiment were aromatic oxo compounds. Scheme 10 illustrates that benzaldehyde, phenylacetaldehyde and acetophenone were likely to form via the reactions of oxygen with the double bond of cinnamic acid. At the same time, hydrogen transfer and decarboxylation took place. Similarly, benzaldehyde and phenylacetaldehyde represented the major products at the low-temperature (300 °C) heating experiment in oxidative atmosphere. In summary, decarboxylation of cinnamic acid was promoted by the presence of oxygen, since no decomposition occurred at 300 °C in nitrogen atmosphere.

3.5. Guaiacol

Guaiacol is a naturally occurring compound and it is a precursor of flavours (e.g., vanillin). Guaiacol is present in wood smoke; it derives from the pyrolysis of lignin. Its thermal decomposition has been studied as a lignin model compound in several papers relating to biomass pyrolysis [29–32]. As shown in Table 7 and Fig. 5, its thermal decomposition resulted in only a few products under the simulated combustion experiments due to the stability of the aromatic ring. Salicylaldehyde was the most significant product forming in the oxidative atmosphere when the sample was heated to the higher temperature (900 °C). Salicylaldehyde has been detected during the pyrolysis of methoxy-substituted lignin model compounds in vacuum [29] and during the pyrolysis of gua-

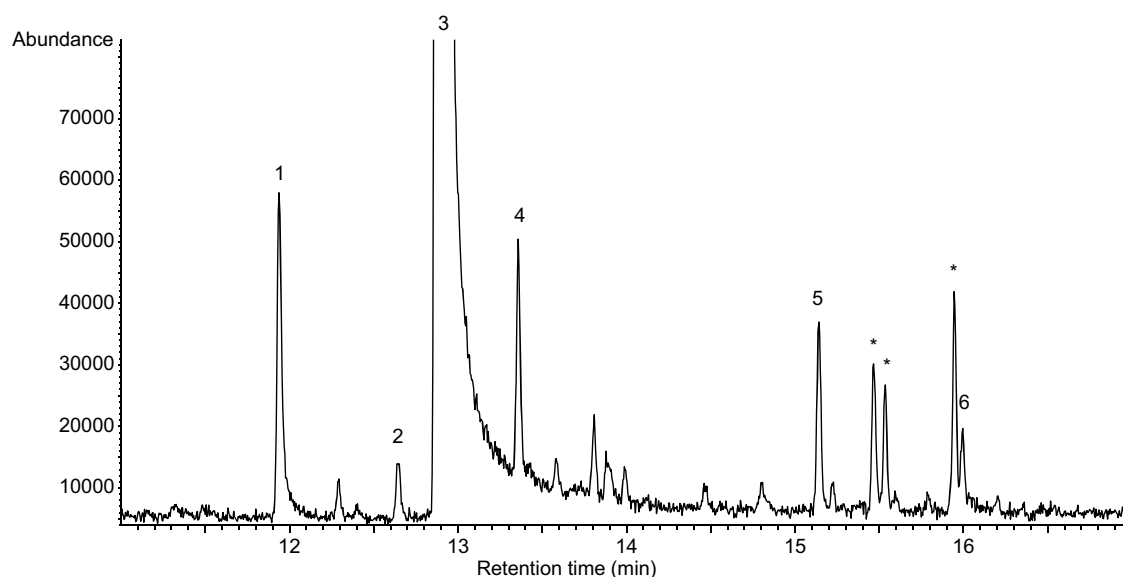


Fig. 5. Py-GC/MS total ion chromatogram of guaiacol at 900 °C in oxidative atmosphere. Numbered peak identities are given in Table 7. * denotes impurities.

iacol in helium atmosphere [30]. Britt et al. explained the aldehyde formation by hydrogen abstraction and rearrangement reactions [29]. In our simulated combustion experiment, the presence of oxygen appeared to enhance the hydrogen abstraction from the methoxy groups leading to aldehyde and water formation as shown in Scheme 11.

The guaiacol sample contained 2-methylphenol as an impurity, which might also be a decomposition product of guaiacol [30,31]. Slight increase in the intensity of 2-methylphenol could be observed that may be explained by the cleavage of methoxy groups and recombination of the formed phenol radicals with methyl groups. Small amounts of cinnamaldehyde and its cyclic derivative, 2,3-dihydro-1(*H*)-inden-1-one were released during the oxidative decomposition of guaiacol. These oxo derivatives could be formed by complex series of reactions of the substituents including scissions, recombinations and rearrangements. The comparison of the effects of atmospheres showed that the formation of carbonyl compounds was promoted by the presence of oxygen.

4. Conclusions

The thermal behaviour of five common flavour additives was studied under a range of four simulated low-temperature heating and model cigarette-combustion conditions by Py-GC/MS method in order to compare the decomposition pattern of the flavours. The experiments were carried out in both oxidative (9% oxygen in nitrogen) and pyrolytic (100% nitrogen) atmospheres to understand the effect of oxygen on the thermal transfer and breakdown patterns.

Citronellal, rose oxide and 5-methyl-2-(1-methylethenyl)-cyclohexanol were identified as the main decomposition products of citronellol. It was found that the formation of these citronellol derivatives was enhanced in the oxidative atmosphere at 300 °C isothermal heating. At higher pyrolysis temperature (up to 900 °C) the detected amount of rose oxide was higher in the nitrogen atmosphere as compared to the oxidative experiment, while formation of citronellal was increased in the oxidative atmosphere.

Under the model cigarette combustion conditions the most significant decomposition routes of menthol were the dehydration to menthene and the oxidation to menthone. In the nitrogen atmosphere and under the low-temperature heating conditions both processes were far less pronounced. The degree of the decomposition was around 5% under the simulated cigarette-combustion

conditions while it was below 1% at the 300 °C isothermal heating in the oxidative atmosphere.

The generation of acidic thermal decomposition products of tartaric acid was promoted in the oxidative atmosphere at high temperature, while aldehyde products were diminished. The relative amounts of 2-oxo-propanoic acid were considerably higher among the pyrolysis products at 300 °C than at 900 °C. This was interpreted by a process taking place in the melted tartaric acid at the low temperature in which pairs of tartaric acid molecules joined via water liberation are decomposing preferably to carboxylic acids and also to cyclic ketones.

Cinnamic acid behaved quite differently than tartaric acid due to its aromatic nature and volatility. In the nitrogen atmosphere, cinnamic acid decomposed via decarboxylation to styrene and several aromatic products at 900 °C, while no decomposition was observed at 300 °C. Although decarboxylation occurred in the oxidative atmosphere, as well, the most important products were aromatic aldehydes (e.g., benzaldehyde) and less aromatic hydrocarbons were formed. The degree of decomposition was significantly higher at 900 °C than at 300 °C (6.4% vs. 1.5%) in the oxidative atmosphere.

The final aromatic compound studied, guaiacol mostly evaporated under the applied heating conditions. The transformation of the methoxy groups into aldehyde groups was observed under the simulated cigarette-burning conditions; however only small amounts of oxo-compounds (below 0.1%) were detected under the low-temperature heating conditions.

This study shows that a detailed understanding of the thermo-physical conditions is necessary to evaluate the potential fate of a flavour compound under a defined thermal history. For the purpose of assessing the flavour thermal behaviour, it is necessary to combine their intrinsic thermochemical properties, the decomposition patterns and simulated pyrolysis results into account to form a more comprehensive understanding of their likely behaviour in final products.

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