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Comparison of Pyrolytic Components in Lamina and Midrib of Flue-Cured Tobacco Leaves

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ABSTRACT : This study was conducted to compare the volatile components of lamina(cutter group) and midrib of flue-cured tobacco leaves by two analytical methods, Curie-Point pyrolysis and Purge & Trap headspace technique. The pyrolysis of lamina and midrib part of tobacco leaves was performed at the temperature of 330℃, 650℃, and 920℃ by Curie-Point Pyrolyzer, and 33 compounds were identified in the pyrolyzates by GC/MSD. The composition of the components identified showed a quite difference between lamina and midrib. However, the amount of the pyrolyzed products from the both of lamina and midrib was increased with temperature inerease except that of acetic acid, furfural, and nicotine. The content of phenolic compounds including phenol, 4-methyl phenol, and 3-methyl phenol was higher in midrib than in lamina, while that of furan compounds such as 2,3-dihydrobenzofuran, 5-hydroxymethyl furfural, was high in lamina. Interestingly, acetamide, 2-propenamide and 3-acetoxy pyridine were not defected in the pyrolyzates of lamina. By Purge & Trap headspace technique, 28 volatile components were identified in both lamina and midrib. The composition of the identified compounds and their chromatograpic patterns also showed the complete difference between the two. The content of solanone, β-damascone, β-damascenone, and megastigmatrienones, key components of tobacco aroma, was much higher in lamina than in midrib. The results indicate that lamina contains much more carbonyl compounds known to enhance the smoke taste of cigarette, whereas midrib takes nitrogenous and phenolic compounds, which are known to cause a deteriorate effect of smoke such as irritation

Key words : **Pyrolyzer, Purge & Trap, Volatile components, Tobacco.**

The taste of cigarette smoke is characterized by various factors such as leaf tobacco and additives. Leaf tobacco among these plays a pivotal role in determining the taste of a cigarette. However, the aroma characters of leaf tobacco can be altered during the combustion and the cigarette taste is specified by the smoke, which is a combustion products. Therefore, the evaluation of volatile components of leaf tobacco before and after burning is important in cigarette manufacturing because it provides a useful information for the improvement of cigarette quality and the reduction of an irritation of cigarette smoke.

Tobacco leaves are separated into the lamina part and the midrib one at the first before making cigarettes, In general, the lamina part of flue-

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cured tobacco leaves has been known to get various ingredients for flavor, while the midrib part contains the compounds forming a cellulose taste during the combustion (Johnstone and Plimmer 1959; Ishiguro *et al.*, 1975). Such a sensory character of the smoke derived from each parts of tobacco leaf, therefore, might be caused from the difference in the composition of components related with taste of the cigarette smoke.

Since Williams(1862) has found isoprene in the pyrolyzates of rubber, several papers related to the pyrolysis study of tobacco leaves have been published (Lam 1956; Scblotzbauer 1985). However, there was no paper comparing the volatile components of lamina and midrib of flue-cured tobacco before and/or after burning. The studies on pyrolysis of leaf tobacco have been limited because of an absence of a suitable tool for the pyrolysis of samples. The crucial feature of pyrolysis is the necessary to achieve the rapid and highly reproducible heating in the rate and final temperature. So far, three modes, Curie-Point type, filament type, and microfurnace type have been used. Among these, Curie-Point pyrolyzer takes an advantage of a rapid heating rate and precise control of temperature, which is achieved by a device of the ferromagnetic alloy(Irwin and Winewordner 1993). Purge & Trap headspace technique is another method able to identify the volatile components in the samples under the low temperature without burning them. These two techniques have provided us to analyze the volatile components of lamina and midrib parts of tobacco leaves.

Therefore, the aim of the present study is to compare the components in the pyrolyzates and in the volatile mixture obtained by Purge & Trap headspace from raw materials of lamina and midrib by two techniques.

MATERIAL AND METHODS

Tobacco samples : Lamina(cutter group) and midrib of flue-cured tobacco cultivated in korea were used. The lamina used is C1L grade, and midrib is sample expanded after cutting

Pyrolysis : Five mg of lamina and midrib were pyrolyzed in pyrofoil with Curie-Point pyrolyzer (JHP-3S of Japan Analytical Industry Co., Ltd.) connected directly to a gas chromatograph. Pyrolysis was conducted in helium for 5 sec at 330, 650, and 920℃, respectively, and the pyrolyzed products captured in a quartz tube were introduced into the gas chromatography.

Purge & Trap Headspace : To extract the volatile components from lamina and midrib, 50g of the samples were put into a column, and purged with nitrogen gas at flow rate of 60ml/min for 20 hours at 60℃(Fig. 1). Volatile components were adsorbed at Tenax trap, which was packed with Tenax-GR(1g). At this time, moisture contained in the trap was removed by using a cooling condenser. Tenax-GR from Tenax trap was moved to sample tube of Headspace sampler (JHS-100A of Japan Analytical Industry Co., Ltd.). The volatile components in the sample tube were purged out from matrix by helium at 250℃, and then purged volatile components were adsorbed in adsorption tube, which was cooled at -30℃. Adsorption tube was thermally desorbed for 20 sec, and then volatile components were injected into gas chromatography.

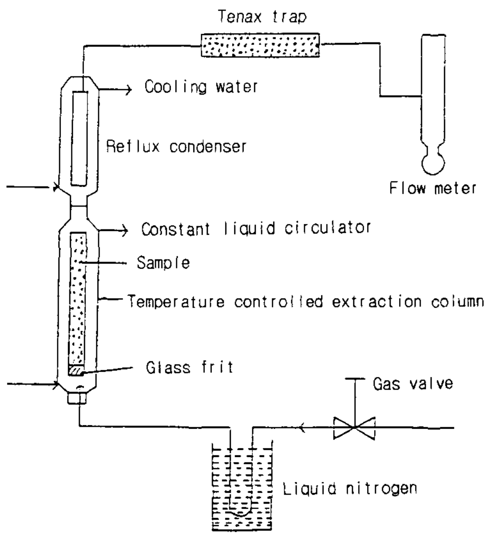

Fig. 1. Schematic diagram of the purge & trap headspace trapping method

Gas Chromatography-Mass Selective Detector (GC/MSD) : GC/MSD was performed with HP-5890/5970B. The temperature of injector and interface parts was 250℃, respectively. A 60m capillary column coated with PEG was used for the chromatography. Helium was used as a carrier gas with flow rate of 4mℓ/min. The oven temperature of GC was programmed from 50℃ to 220℃ by increasing 3℃/min. Ion source energy of 70eV and electron multiplier of 2200V were utilized. The components were identified on the basis of computer matching with combined Wiley 138.

RESULTS AND DISCUSSION

Pyrolysis products

Total ion chromatograms of pyrolysis products from lamina and midrib at the temperature of 330℃, 650℃, and 920℃ are shown in Fig. 2. The chromatograms of two samples showed a quite different pattern each other at the corresponding temperature and the amount of pyrolysis products was higher in lamina than in midrib. From fig. 2, we identified 33 compounds including 4 carbonyl compounds, 11 nitrogenous compounds, 7 furans, 5 hydrocarbons, 3 phenols, 2 acids and 1 alcoholic one. Total amount of the compounds identified in the pylolyzates from the both samples was increased with temperature, but that of some components such as acetic acid, furfural, and nicotine was decreased. Interestingly, acetamide, 2-propenamide and 3-acetoxy pyridine were found only in the pyrolyzates of midrib.

The content of phenolic compounds including phenol, 4-methyl phenol, and 3-methyl phenol was also increased in the both parts of tobacco leaf gradually with temperature from 330℃ to 920℃, and showed higher content in midrib than in lamina similarly with the results of Ishiguro's study (Ishiguro *et al*., 1975).

Furan compounds such as 2,3-dihydrobenzofuran, 5-hydroxymethyl furfural, which were derived generally from sugars during the pyrolysis of leaf tobacco, were not found in the pyrolysates of midrib and neophytadiene was detected only in the lamina. Such a difference in the content of volatile components of the pyrolyzed products might be caused from the difference of chemical composition of leaf tobacco such as sugar, cellulose, proteins, and lignin (Johnstone and Plimmer 1959; Phillips and Bacot 1953). Especially, lignin, which is a source of phenolic compounds during its combustion, is much more in the midrib of flue-cured tobacco compared to the lamina (Schlotzhauer *et al.*, 1985; Serban 1998).

The amount of pyridine derivatives and phenolic compounds was much higher in midrib than in lamina. These components are well known as negative factors in irritation or impact of cigarette smoke. So, in order to reduce the irritation and/or cellulose taste of cigarette smoke, it is necessary to develop a technique able to eliminate or to mask the undesirable effects caused by these compounds.

Volatile Compounds

The Purge & Trap method has been considered by several investigators recently as a tool for the analysis of aroma components. In this study, we applied this method using a specific device designed by ourselves to analyze the volatile compounds of lamina and midrib. The compounds extracted by Purge & Trap were analyzed by a GC/MSD attached with Headspace sampler(JHS-100A).

As shown in Figure 3, the pattern of chromatograms of volatile compounds obtained by GC/MSD also differed quitely between lamina and midrib. The data in Table 2 show 28 compounds identified from the chromatograms. The major compounds of those were carbonyl compounds, acidic compounds, alcohols, furans, and hydrocarbons. The amount of alcoholic compounds was relatively high in the lamina, but that of acidic compounds was high in the midrib, respectively. Especially, acetic acid content was high significantly in midrib, as its peak area %, the lamina and midrib showed 1.1 and 33.0 %, respectively.

Aroma compounds also showed much different patterns each other. The ketoisophorone, β-damascone, and β-ionone were detected only in

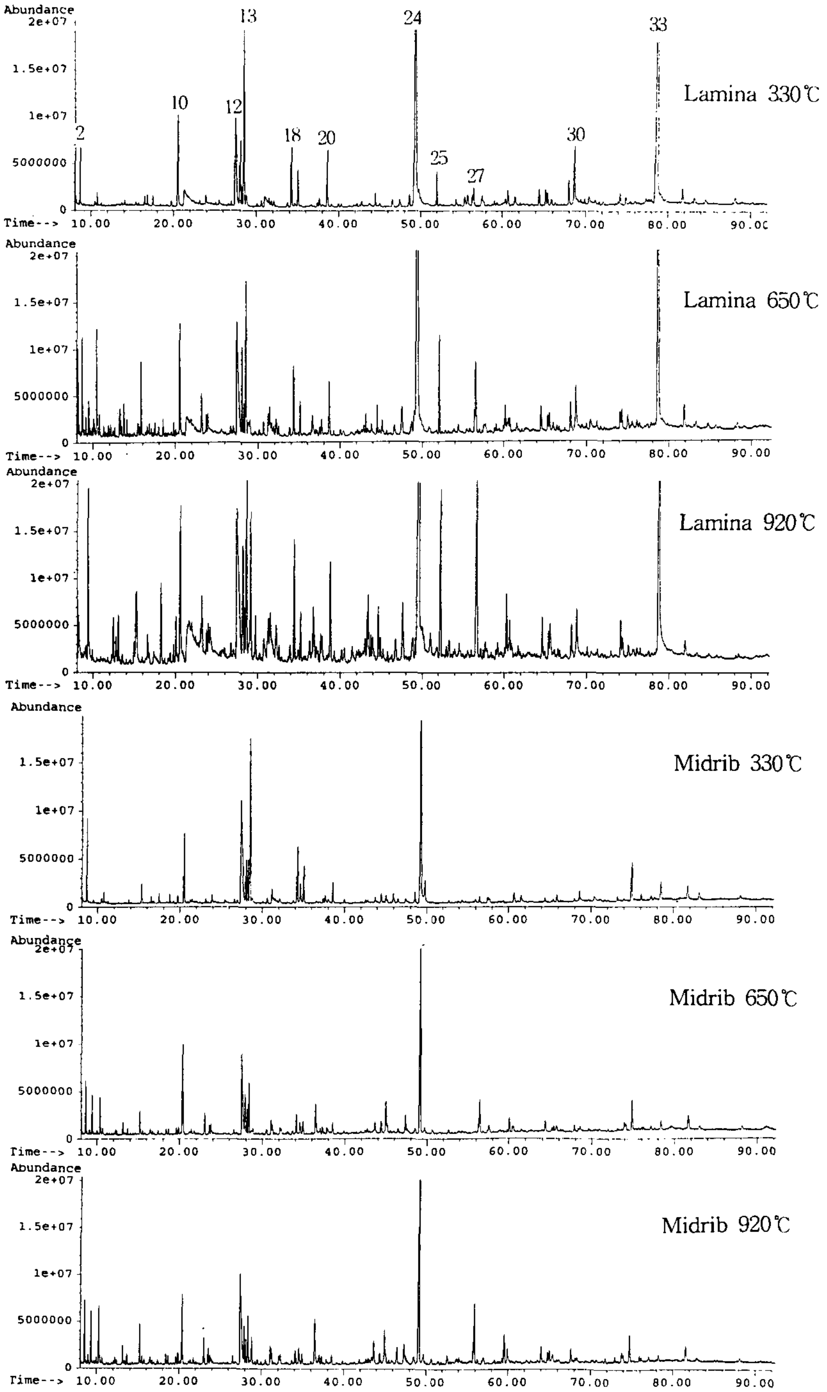

Fig. 2. Total ion chromatograms of pyrolysis products in the lamina and midrib at 330℃ 650℃, and 920℃

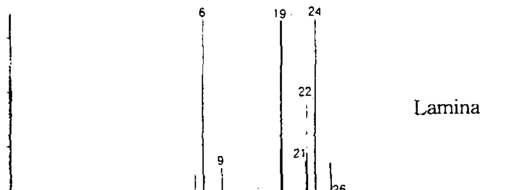

Fig. 3. Total ion chromatograms of volatile compounds in the lamina and midrib

the lamina. The key components of tobacco aroma such as solanone, β-damascone, β- damascenone, and megastigmatrienones, were much higher in lamina than in midrib. These com- pounds are well known as components enhancing smoke taste of cigarette (Lloyd *et al.,* 1976).

Comparison of Pyrolytic Products and Volatile Compounds

As compared the data of the pyrolysis products(Table 1) and volatile compounds obtained by Purge & Trap from the samples without burning (Table 2), the key aroma components of tobacco such as solanone, β-damascone, β-damascenone, β-ionone, and megastigmatrienones were much higher in the volatile mixture extracted by Purge and Trap. These components have been known to be derived from leaf tobacco directly by volatilization. The reason why these components are not identified in the pyroylsis products is not clear, however, their relatively low concentration can be considered as a possibile reason (Wakeham 1972; Weeks 1985).

In general, although the smokers can readily recognize the aroma characteristics of these components even at very low level via their sensory organs such as the palate and tongue, our results suggest that the Purge & Trap method might be more reliable than pyrolysis one in the comparing volatile components of the samples.

Another interesting feature of this study is to identify the 7 compounds such as furans and furfural etc, which were found commonly in the both methods. These compounds are known to be formed from sugar and others in leaf tobacco (Roberts 1988). It has been reported that the content of carbonyl compounds, acids, and alcohols is high in leaf tobacco rather than in smoke, and that of furans, nitrogenous, and phenolic compounds is relatively high in the smoke (Roberts 1988). Our results was well agreeable to this.

The pH of cigarette smoke is one of the major factors influencing the irritation and impact of the smoke, and the content of acids and nitrogenous compounds can affect its pH. Specially, nitrogenous compounds, which were able to increase pH of the smoke, showed a high content in the pyrolyzates of midrib indicating the smoke generated from this part of tobacco leaf coued give more irritant to smokers. Therefore, such deteriorating properties of the smoke derived from the midrib might be improved by the decrease of smoke pH through addition of some organic acids to the midrib as an additive.

SUMMARY

This study was conducted to compare the volatile components of lamina(cutter group) and midrib of flue-cured tobacco leaves by two analytical methods, Curie-Point pyrolysis and Purge & Trap headspace technique.

The pyrolysis of lamina and midrib parts of

Table 1. Comparison of pyrolysis products from the lamina and midrib of flue-cured tobacco at 330℃, 650℃ and 920℃

Peak No. Components	Peak area(%)					
	Lamina(℃)			Midrib(℃)		
	330	650	920	330	650	920
1. Acetonitrile	-	0.5	0.6	0.2	1.4	1.7
2. Methyl benzene	0.3	1.3	1.8	0.5	1.3	1.8
3. Ethyl benzene	-	0.3	0.4	0.2	0.5	0.7
4. Pyridine	0.1	0.1	0.7	1.0	1.0	1.3
5. Limonene	-	0.9	0.9	-	-	-
6. Styrene	-	0.3	0.7	0.2	0.3	0.3
7. 2-Methyl pyrazine	-	-	-	0.4	0.3	0.3
8. Acetoin	-	0.2	0.2	0.4	0.3	0.1
9. 3-Methyl pyridine	-	0.2	0.6	-	0.3	0.3
10. 1-Hydroxy-2-propanone	3.0	2.3	2.3	3.5	4.3	2.8
11. 2-Methyl-2-cyclopentenone	-	0.5	0.5	0.5	0.5	0.6
12. Acetic acid	5.2	4.2	4.8	11.3	7.1	7.4
13. Furfural	5.2	2.5	2.5	8.6	2.5	1.9
14. 3-Ethenyl pyridine	0.7	0.3	2.2	0.8	0.4	1.2
15. 2-Acetyl furan	0.2	0.3	0.5	0.3	0.3	0.2
16. 1H-Pyrrole	0.3	0.5	0.8	0.4	0.8	0.8
17. Propanoic acid	0.3	0.4	0.7	0.4	0.4	0.4
18. 5-Methyl furfural	1.7	1.2	1.4	2.8	1.1	0.6
19. Dihydro-2(3H)-furanone	0.2	0.4	0.3	0.5	0.5	0.4
20. Furfuryl alcohol	1.7	1.0	1.2	1.2	0.7	0.5
21. Acetamide	-	-	-	0.5	0.9	1.3
22. 3-Acetoxy pyridine	-	-	-	0.3	0.5	1.1
23. 2-Hydroxy-3-methyl-2--Cyclopentenone	0.5	0.9	1.1	0.4	1.4	1.3
24. Nicotine	18.2	12.6	8.9	18.9	15.2	15.8
25. Neophytadiene	0.8	1.5	2.2	-	-	-
26. 2-Propenamide	-	-	-	0.3	0.4	0.5
27. Phenol	0.7	1.4	3.2	0.3	1.8	3.2
28. 4-Methyl phenol	0.6	0.6	0.9	0.3	0.9	1.5
29. 3-Methyl phenol	0.4	0.4	0.6	0.2	0.4	0.9
30. 2,3-Dihydro-3,5-dihydroxy--6-methyl-4-pyrone	2.9	1.5	1.1	-	-	-
31. 2,3-Dihydro-benzofuran	0.4	0.6	0.5	-	-	-
32. 2(1H)-Pyridinone	0.3	0.3	0.3	2.9	2.0	1.5
33. 5-Hydroxymethyl furfural	19.5	9.7	6.1	-	-	-

Table 2. Comparison of volatile components from the lamina and midrib of flue-cured tobacco

Peak No. Components	Peak Area (%)	
	Lamina	Midrib
1. Hexanal	0.7	1.5
2. 1-Penten-3-ol	0.7	0.2
3. 3-Methyl-1-butanol	0.9	-
4. 2-Methyl-2-hepten-6-one	1.1	0.5
5. Acetic acid	1.1	33.0
6. Furfural	4.2	5.3
7. 2-Ethyl-1-hexanol	0.3	0.2
8. 2- Acetyl furan	0.4	0.2
9. Benzaldehyde	1.5	0.6
10. Linalool	0.9	-
11. Propanoic acid	0.2	0.7
12. Isobutyric acid	0.5	0.6
13. 5-Methyl furfural	0.5	0.9
14. 2-Butyl furan	1.9	-
15. L-Menthol	0.9	0.8
16. Acetophenone	0.5	0.2
17. 2-Furanmethanol	0.5	0.1
18. Ketoisophorone	0.9	-
19. Solanone	8.0	0.9
20. Pentanoic acid	0.7	0.5
21. β-Damascone	1.7	-
22. β-Damascenone	1.8	0.1
23. Caproic acid	0.2	0.5
24. Geranyl acetone	3.8	0.9
25. Benzyl alcohol	1.2	-
26. Neophytadiene	2.6	0.4
27. β-Ionone	0.9	-
28. Megastigmatrienone	1.8	0.1

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