

STUDY OF VOLATILE COMPONENTS IN THE PYROLYZATES OF COCOA POWDER TOBACCO PRODUCTS FLAVORANT

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담배향료로 쓰이는 코코아분말의 열분해 생성물에 관한 연구

박준영, 김옥찬, 나도영, 장희진, 김용태

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초 록

담배향료로 사용하는 코코아 분말을 Cigarette smoking condition인 distillation-pyrolysis zone과 high temperature zone 중에서 4개의 온도 350°C, 550°C, 650°C, 850°C를 선택하여 열분해 장치를 이용하여 열분해하였고, 열분해생성물은 CS₂ trap과 charcoal tube로 포집하여 GC/MS분석에 이용하였다. 분석결과 650°C에서 열분해가 가장 잘 이루어졌고 수율 역시 가장 높았다. 열분해의 주요 성분은 주로 hydrocarbon과 phenolic화합물이 90% 이상을 차지하였고 그 외에 소량의 aldehyde, ketone, pyrazine도 검출되었다. 열분해 온도에 따라서 성분의 변화를 보면 decane, styrene, tridecane, m-cresol, 4-ethylphenol등은 증가하였고, hexadecane, tetradecane등은 감소하였다. 또 o-cresol, 2-ethylphenol등은 함량변화가 거의 없었다.

* 이 논문은 제44차 TCRC(미국개최)에서 구두로 발표한 내용의 일부를 논문으로 정리한 것임.

ABSTRACT

The pyrolytic behavior of cocoa powder, a flavorant of tobacco smoking products, was examined by determining its pyrolyzate constituents. Cocoa powder was pyrolyzed of two cigarette smoking conditions : distillation-pyrolysis zone(350°C, 550°C) and high temperature zone(650°C, 850°C). Pyrolyzate was flushed from the tube by N₂ gas into CS₂ trap in dry ice-acetone cooled bath and charcoal tube and its constituents were analyzed by GC/MS. As results, the major components of pyrolyzates were identified as hydrocarbon and phenolic compounds. In addition to these, aldehyde, ketone, pyrazin in very small amount. Component changes were observed with temperature increase ; decane, styrene, tridecane, m-cresol, 4-ethylphenol were increased while hexadecane, tetradecane were decreased. o-cresol and 2-ethylphenol were constant in amounts despite temperature change.

INTRODUCTION

The importance of cocoa powder as a casing material for tobacco is well known¹⁾. It has long been used in flavor formulations of tobacco smoking products. Virtually all blended cigarettes of the American type employ casing materials such as sugar and/or fruit extracts, licorice, and cocoa. These materials are used to mellow nicotine harshness and to enhance the flavor of tobacco²⁾.

The cocoa powder consists of protein, amino acids, the astrigent tannin-like, polyhydroxyphe-nols, starch, sugar, cocoa butter fat, miscellaneous cell wall constituents, and the bitter principles, theobromine and caffeine. Cocoa butter is composed almost entirely of fatty acid triglyceride, which possess novel physical properties prized in chocolate candy manufacture³⁾.

In tobacco smoking products, the organoleptic properties of cocoa butter are that of a smoothing, yet substantially enhanced, tobacco flavor which we propose is owing to entrapment of tobacco flavor volatiles by agglomeration in the cocoa butter aerosol droplets in the smoke mainstream. A similar effect is observed with the major tobacco hydrocarbon, neophytadiene, which possesses no specific flavor properties.

Much attention has been focused on the study on the volatile components in cocoa since 1964⁴⁻⁹⁾. Major emphasis in these studies has been put on the analysis of the basic(pH) fraction of cocoa volatiles which possess a roasted, nutty, chocolate type aroma and on the comparison of cocoa volatiles with known volatiles in tobacco and tobacco smoke.

It is interesting to note that many volatile constituents of cocoa are, in the majority, identical or analogous to either natural tobacco or tobacco smoke constituents.

As may be noted, numerous studies of the volatile components of cocoa powder have been reported, but only a few papers have dealt with the pyrolysis of cocoa powder.

Schlotzhauer has reported results on the pyrolysis of cocoa powder in which the cocoa butter fat yielded stearic and palmitic acid at temperatures which might be encountered in a burning cigarette¹⁰⁾. Therefore it would be important to investigate the volatile pyrolysis product of cocoa powder. Contribution to the smoke composition of tobacco products containing cocoa powder depends on the composition and quantity of cocoa powder added, and the proportion of additive subjected to distillation and/or pyrolytic reactions within the temperature gradient developed during the smoking process.

In present study, cocoa powder was pyrolyzed at two cigarette smoking conditions ; distillation pyrolysis zone¹⁵⁾ and high temperature zone. For each condition, two pyrolysis temperature were selected ; 350°C and 550°C for distillation zone and 650°C and 850°C for high temperature zone. The pyrolysis products were distilled by steam distillation apparatus in order to obtain the volatile compound and distilled products have been analyzed and identified on GC and GC/MS. Relative yields of pyrolytic products were determined by measuring the corresponding peak areas on gas chromatogram.

As will be noted, our experimental conditions were different from those of earlier workers. Therefore, as might be expected, some of the products we report were either not generated or overlooked in previous work, while others were identical to those reported by the earlier workers cited above.

The results of these studies should be of interest, not only to the tobacco industry but also to the food industry, since the compounds discussed are also abundant in food stuffs. Consequently, the thermal reactions reported may also occur in foods during cooking or processing.

MATERIALS AND METHODS

Cocoa powder for in tobacco formulation was obtain from a commercial source for these studies. The pyrolysis was performed in a vertical quartz tube inserted into a furnace equipped with automatic temperature controller and pyrometer. Nitrogen flow through the pyrolysis system was maintain at 30ml/min. Oven was pre-heated to give desired temperature(350, 550, 650, 850+10°C at the center of the heated zone). Products were flushed from the tube by the nitrogen into CS₂ traps consisting of an uncooled trap, three dry ice-cooled cold fi-

ngers and charcoal tube. The pyrolyzate was distilled by the SDE method for 4hr. Ether solution obtained from distillating was dried and concentrated.

The residue was analyzed and identified by GC and GC/MS

Gas chromatographic analysis

Gas chromatography was carried out on a HP-5880A model. The temperature program used was as follows ; started with a column temperature of 50°C for 5min, the heated at a rate of 2°C/min to 220°C and maintained at 220°C for 60min. The column used was fused silica capillary column supelco wax 10 with the i.d. of 60mx0.32mm. The temperature of both detector and injector on point heater was 250°C respectively, Detector was FID.

The analysis of GC/MS

Hitachi 80-B instrument was used. The same GC conditions as above were used, with He as carrier gas. Significant operating parameters of the MS during EIMS were : ionization voltage ; 70 eV ; accelerating voltage ; 3000V.

RESULTS AND DISCUSSION

A 15g sample was used for pyrolysis. The yields of total pyrolyzate are shown in Table 1.

Table 1 shows that pyrolyzate yields were constant throughout the whole temperature ranges but relatively lower at 350°C and that the pyrolysis temperatures of 550°C and 650°C, are considered to be favorable for the most effective performance of the pyrolysis. The GC chromatogram also shows that only a little pyrolysis took place at 350°C. The chromatogram of the pyrolysis products was clear at 550°C, 650°C, but at 350°C the chromatogram was not clear. Accordingly, pyrolysis can best performed at 550°C, 650°C.

Table 1. The yield of total pyrolyzate

| pyrolysis temp. sample | 350°C | | 550°C | | 650°C | | 850°C | |
|------------------------|-------------------|------------------|-------------------|------------------|-------------------|------------------|-------------------|------------------|
| | pyrolysis product | after distilling | pyrolysis product | after distilling | pyrolysis product | after distilling | pyrolysis product | after distilling |
| cocoa powder | 1.98g (13.2%) | 0.1g (0.6%) | 3.74g (24.9%) | 0.56g (3.7%) | 3.78g (25.2%) | 0.62g (4.1%) | 2.48g (16.5%) | 0.46g (3.07%) |

Table 2. Pyrolysis product of cocoa power

| PEAK NO. | COMPOUND NAME | AREA % | | | |
|----------|-------------------------|--------|-------|-------|-------|
| | | 350°C | 550°C | 650°C | 850°C |
| 1 | Acetaldehyde | 0.39 | 0.06 | 0.21 | 0.88 |
| 2 | Octane | — | 0.15 | 0.21 | — |
| 3 | Octene-1 | — | 0.10 | 0.25 | — |
| 4 | Nonane | — | 0.54 | 0.92 | 0.13 |
| 5 | Nonene-1 | — | 0.39 | 1.13 | 0.19 |
| 6 | Nonene* | — | 0.07 | 0.12 | 0.02 |
| 7 | Nonene* | — | 0.05 | 0.10 | t |
| 8 | Decane | — | 0.85 | 1.42 | 1.54 |
| 9 | Decene-1 | — | 0.73 | 2.07 | 0.80 |
| 10 | Decene* | — | 0.05 | 0.14 | t |
| 11 | Toluene | — | 0.36 | 0.69 | 0.10 |
| 12 | Decene* | — | 0.12 | 0.20 | 0.08 |
| 13 | Undecane | — | 1.23 | 1.81 | 0.70 |
| 14 | Undecene-1 | — | 1.33 | 3.12 | 1.47 |
| 15 | Ethyl benzene | — | 0.08 | 0.27 | 0.11 |
| 16 | Undecene* | — | 0.38 | 0.45 | 0.24 |
| 17 | Undecene* | — | 0.06 | 0.07 | 0.04 |
| 18 | Undecene* | — | 0.18 | 0.27 | 0.15 |
| 19 | 2-heptanone | — | 0.01 | 0.03 | 0.03 |
| 20 | Dodecane | — | 1.59 | 1.96 | 1.08 |
| 21 | Dodecene-1 | — | 0.95 | 1.91 | 1.46 |
| 22 | Dodecene* | — | 0.31 | 0.40 | 0.28 |
| 23 | Styrene | 0.44 | 1.01 | 1.80 | 2.22 |
| 24 | Ethyl toluene | — | 0.05 | 0.10 | 0.06 |
| 25 | Tridecane | — | 2.00 | 2.15 | 2.38 |
| 26 | 2,5-dimethylpyrazine | 2.1 | 0.65 | 0.69 | 0.28 |
| 27 | Tridecene-1 | 3.21 | 1.21 | 1.59 | 1.35 |
| 28 | Tridecene* | 0.22 | 0.25 | 0.52 | 0.44 |
| 29 | Tetradecane | — | 2.42 | 1.56 | 1.32 |
| 30 | 2,3,5-trimethylpyrazine | 1.02 | 0.12 | 0.15 | 0.15 |

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| PEAK NO. | COMPOUND NAME | AREA % | | | |
|------------------|-----------------------|--------|-------|-------|-------|
| | | 350℃ | 550℃ | 650℃ | 850℃ |
| 31 | Indane | 2.24 | 0.21 | 0.24 | 0.15 |
| 32 | Pentylbenzene | — | 0.27 | 0.38 | 0.24 |
| 33 | Tetradecene-1 | 1.53 | 1.90 | 1.71 | 1.89 |
| 34 | Tetradecene* | 1.18 | 0.27 | 0.30 | 0.24 |
| 35 | Pentadecane | — | 4.92 | 2.62 | 3.11 |
| 36 | Pyrrole | 1.11 | 0.84 | 1.06 | 0.37 |
| 37 | Pentadecene-1 | 0.89 | 3.38 | 1.96 | 2.43 |
| 38 | Pentadecene* | 0.49 | 1.05 | 0.66 | 0.62 |
| 39 | Pentadecene* | 0.27 | 0.65 | 0.44 | 0.45 |
| 40 | Hexadecene | — | 2.54 | 1.09 | 0.78 |
| 41 | Hexadecene-1 | 0.45 | 1.83 | 0.86 | 1.53 |
| 42 | Hexadecene* | 6.62 | 0.90 | 0.59 | 0.71 |
| 43 | Heptadecane | — | 5.22 | 1.68 | 2.73 |
| 44 | Heptadecene* | — | 1.15 | 0.53 | 0.86 |
| 45 | Heptadecene-1 | 0.07 | 4.28 | 1.76 | 2.37 |
| 46 | Heptadecene* | 0.60 | 1.08 | 0.61 | 0.66 |
| 47 | Heptadecene* | 0.38 | 0.96 | 0.44 | 0.69 |
| 48 | Heptadecene* | 0.05 | 0.86 | 0.32 | 5.97 |
| 49 | Octadecane | 0.89 | 0.91 | 0.22 | 0.26 |
| 50 | Octadecene-1 | — | 0.32 | 0.18 | 0.36 |
| 51 | Octadecene* | — | 0.30 | 0.99 | 0.17 |
| 52 | Octadecene* | 0.06 | 0.41 | 0.18 | 1.16 |
| 53 | Nonadecane | — | 0.34 | 0.47 | 1.17 |
| 54 | 2,6-dimethylphenol | — | 0.28 | 0.09 | 1.12 |
| 55 | o-cresol | 0.45 | 2.68 | 2.58 | 2.77 |
| 56 | Phenol | 10.84 | 2.32 | 3.38 | 4.77 |
| 57 | 3-phenylpropionitrile | 1.41 | 0.31 | 0.37 | 0.37 |
| 58 | 2-ethylphenol | 0.39 | 0.85 | 0.81 | 0.73 |
| 59 | 2,5-dimethylphenol | — | 0.47 | 0.67 | 0.78 |
| 60 | 2,4-dimethylphenol | 0.20 | 0.95 | 1.07 | 1.08 |
| 61 | Heneicosane | 2.38 | 1.11 | 1.56 | 2.07 |
| 62 | m-cresol | 0.55 | 0.65 | 1.18 | 1.76 |
| 63 | 4-ethylphenol | 1.18 | 1.28 | 1.43 | 1.59 |
| 64 | Methylpalmitate | 1.17 | 0.50 | 0.10 | 0.16 |
| 65 | 2-heptadecanone | 0.11 | 0.62 | 0.25 | 0.50 |
| 66 | Indole | 5.78 | 1.50 | 1.29 | 3.39 |
| 67 | Skatole | 0.92 | 0.40 | 0.20 | 0.58 |
| Unknown compound | | 50.35 | 34.19 | 39.42 | 31.91 |

(*) : the position of double bond is unidentified.

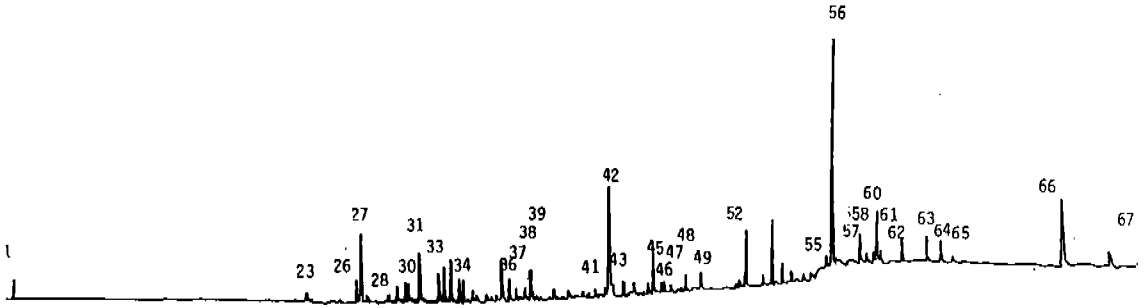


Fig. 1. The GC chromatogram of pyrolysis products at 350°C

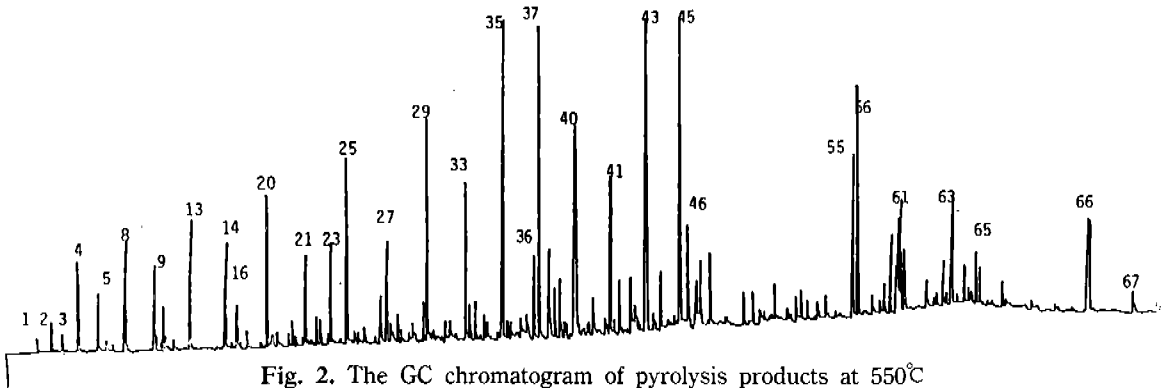


Fig. 2. The GC chromatogram of pyrolysis products at 550°C

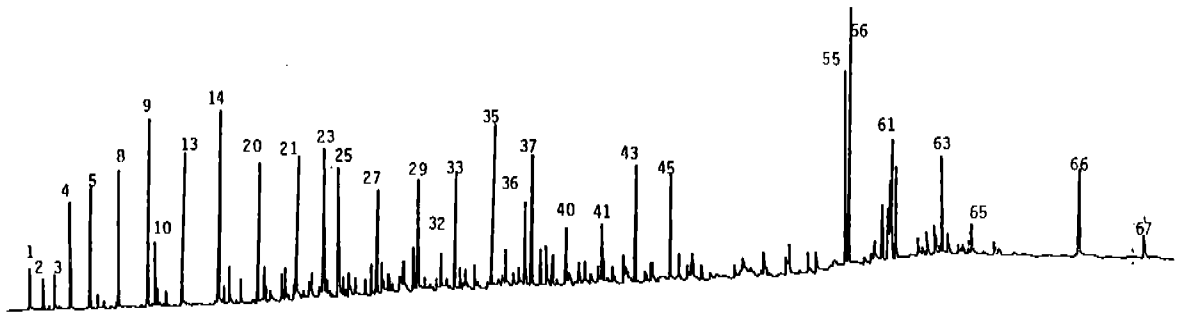


Fig. 3. The GC chromatogram of pyrolysis products at 650°C

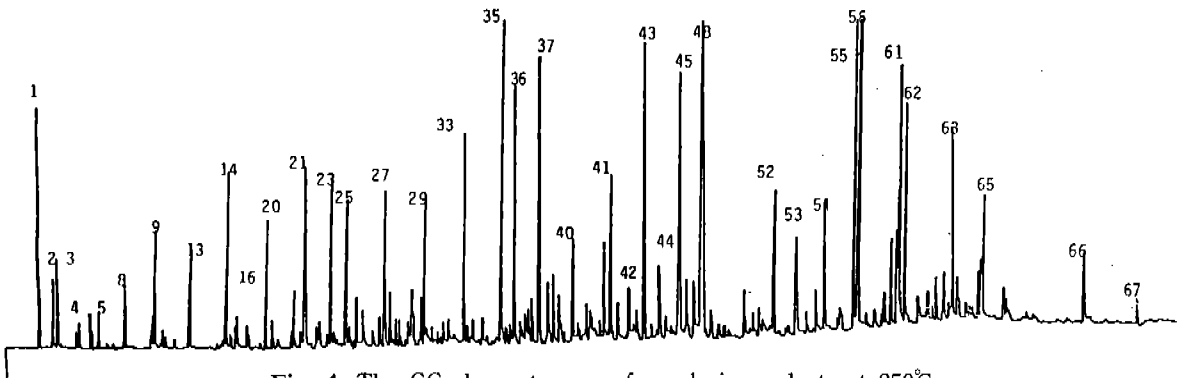


Fig. 4. The GC chromatogram of pyrolysis products at 850°C

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| PEAK NO. | COMPOUND NAME | AREA % | | | |
|------------------|-----------------------|--------|-------|-------|-------|
| | | 350°C | 550°C | 650°C | 850°C |
| 31 | Indane | 2.24 | 0.21 | 0.24 | 0.15 |
| 32 | Pentylbenzene | — | 0.27 | 0.38 | 0.24 |
| 33 | Tetradecene-1 | 1.53 | 1.90 | 1.71 | 1.89 |
| 34 | Tetradecene* | 1.18 | 0.27 | 0.30 | 0.24 |
| 35 | Pentadecane | — | 4.92 | 2.62 | 3.11 |
| 36 | Pyrrrole | 1.11 | 0.84 | 1.06 | 0.37 |
| 37 | Pentadecene-1 | 0.89 | 3.38 | 1.96 | 2.43 |
| 38 | Pentadecene* | 0.49 | 1.05 | 0.66 | 0.62 |
| 39 | Pentadecene* | 0.27 | 0.65 | 0.44 | 0.45 |
| 40 | Hexadecene | — | 2.54 | 1.09 | 0.78 |
| 41 | Hexadecene-1 | 0.45 | 1.83 | 0.86 | 1.53 |
| 42 | Hexadecene* | 6.62 | 0.90 | 0.59 | 0.71 |
| 43 | Heptadecane | — | 5.22 | 1.68 | 2.73 |
| 44 | Heptadecene* | — | 1.15 | 0.53 | 0.86 |
| 45 | Heptadecene-1 | 0.07 | 4.28 | 1.76 | 2.37 |
| 46 | Heptadecene* | 0.60 | 1.08 | 0.61 | 0.66 |
| 47 | Heptadecene* | 0.38 | 0.96 | 0.44 | 0.69 |
| 48 | Heptadecene* | 0.05 | 0.86 | 0.32 | 5.97 |
| 49 | Octadecane | 0.89 | 0.91 | 0.22 | 0.26 |
| 50 | Octadecene-1 | — | 0.32 | 0.18 | 0.36 |
| 51 | Octadecene* | — | 0.30 | 0.99 | 0.17 |
| 52 | Octadecene* | 0.06 | 0.41 | 0.18 | 1.16 |
| 53 | Nonadecane | — | 0.34 | 0.47 | 1.17 |
| 54 | 2,6-dimethylphenol | — | 0.28 | 0.09 | 1.12 |
| 55 | o-cresol | 0.45 | 2.68 | 2.58 | 2.77 |
| 56 | Phenol | 10.84 | 2.32 | 3.38 | 4.77 |
| 57 | 3-phenylpropionitrile | 1.41 | 0.31 | 0.37 | 0.37 |
| 58 | 2-ethylphenol | 0.39 | 0.85 | 0.81 | 0.73 |
| 59 | 2,5-dimethylphenol | — | 0.47 | 0.67 | 0.78 |
| 60 | 2,4-dimethylphenol | 0.20 | 0.95 | 1.07 | 1.08 |
| 61 | Heneicosane | 2.38 | 1.11 | 1.56 | 2.07 |
| 62 | m-cresol | 0.55 | 0.65 | 1.18 | 1.76 |
| 63 | 4-ethylphenol | 1.18 | 1.28 | 1.43 | 1.59 |
| 64 | Methylpalmitate | 1.17 | 0.50 | 0.10 | 0.16 |
| 65 | 2-heptadecanone | 0.11 | 0.62 | 0.25 | 0.50 |
| 66 | Indole | 5.78 | 1.50 | 1.29 | 3.39 |
| 67 | Skatole | 0.92 | 0.40 | 0.20 | 0.58 |
| Unknown compound | | 50.35 | 34.19 | 39.42 | 31.91 |

(*) : the position of double bond is unidentified.

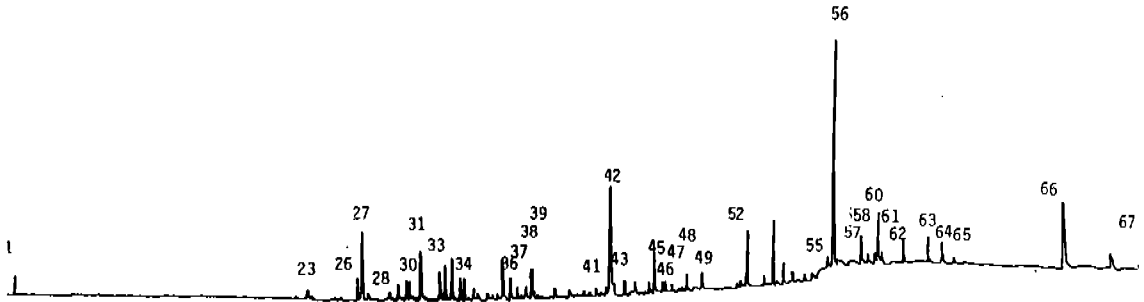


Fig. 1. The GC chromatogram of pyrolysis products at 350°C

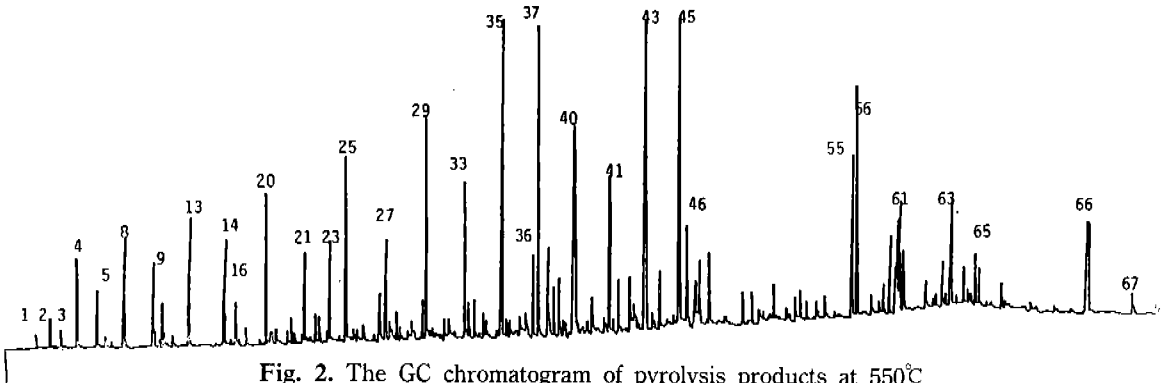


Fig. 2. The GC chromatogram of pyrolysis products at 550°C

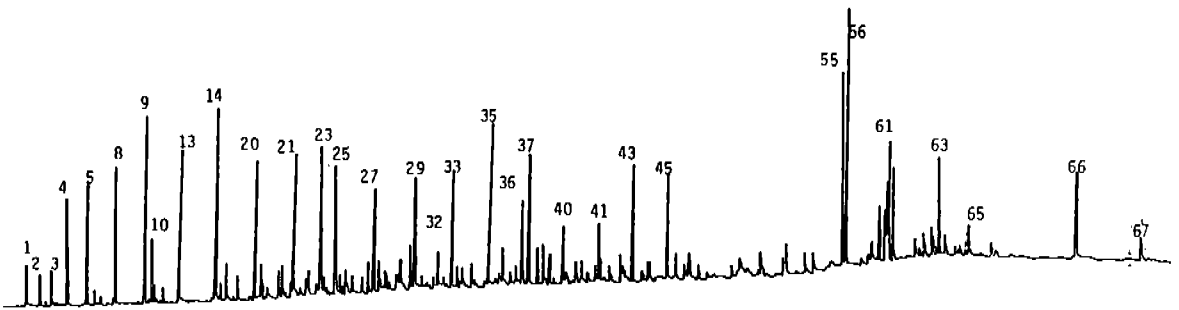


Fig. 3. The GC chromatogram of pyrolysis products at 650°C

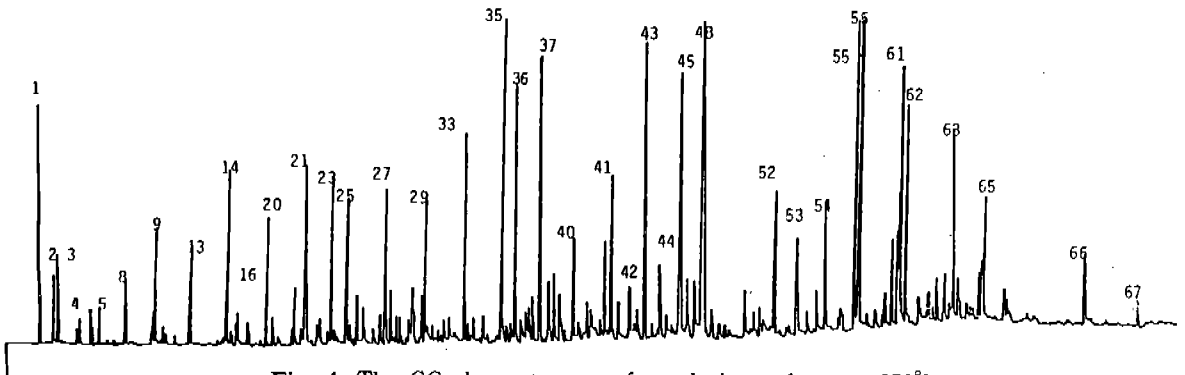


Fig. 4. The GC chromatogram of pyrolysis products at 850°C

The GC chromatograms of these pyrolyzates are shown in Figure 1,2,3 and 4. The results of GC and GC/MS analyses are shown in Table 2.

The GC and GC/MS analysis of pyrolysis products show that the main parts are saturated and unsaturated aliphatic hydrocarbons. In addition to these, phenol, ketone, pyrazine and aldehyde were found to be present in very small amounts. Overall above 150 components were detected as pyrolysis products, although all were not identified. Of these, 67 components were positively identified and were tentatively characterized. The ratios of identified to unidentified components at the pyrolyzate temperature of 350°C, 550°C, 650°C and 850°C pyrolyzates analyzed are as follows ; at 350°C - 33 identified (comprising 49.7% w/w of the pyrolyzates), unidentified (50.3%) ; at 550°C - 67 (65.8%), (34.2%) ; at 650°C - 67 (60.6%), (39.4%) ; at 850°C - 65 (68.1%), (31.9%).

The following general trends in product distribution were observed. Firstly the level of pyrolysis product increased with temperature ; decane, styrene, tridecane, nonadecane, 2,5-dimethylphenol, 2,4-dimethylphenol, m-cresol, 4-ethylphenol. Secondly the level of pyrolysis product decreased with temperature ; hexadecane, tetradecane. Thirdly the level of pyrolysis product increased at the temperature up on 650°C but declined at higher pyrolytic temperature : octane 23 components. others have not shown clear trend.

The most common classes of compounds detected are shown in Table 3.

Table 3 shows that the major components of pyrolyzates are aliphatic hydrocarbons. Of these olefins were found to be present in very large amounts.

A.A. Craveiro reported that pyrolysis of fatty acid afforded a mixture of n-alkane and 1-alkene as the major products. The formation of a complete series of n-alkane and 1-alkene is consistent with the generation of the radicals, RCOO (A) and RCH₂CO (B) from triglyceride molecule. Radical A on decarboxylation would lead to the formation of R. This radical, on disproportionation and successive eliminations of ethylene molecules, would be responsible for the odd series of n-alkane and 1-alkenes present in the mixture. Radical B, by loss of ketene (CH₂=CO), disproportionation, and successive eliminations of ethylene molecule, would generate the n-alkanes and 1-alkenes with an even number of carbon atoms¹¹.

E.B. Higman reported that pyrolysis of tristearin was observed on GC/MS consisted of C7 to C17 alkanes and alkenes extending from C7 to C21 compound¹².

On the basis of the results of these studies, it is clear that the homologous series of alkane and alkene obtained from pyrolysis of cocoa powder were generated by the thermal degradation of cocoa butter.

Table 3. The most common classes of pyrolysis product

(%)

| pyrolysis temp. | | 350°C | 550°C | 650°C | 850°C |
|-----------------------|--------|-------|-------|-------|-------|
| compound | | | | | |
| aliphatic hydrocarbon | alkane | 3.3 | 23.8 | 17.7 | 17.3 |
| | alkene | 16 | 25.2 | 23.8 | 26.6 |
| aromatic hydrocarbon | | 2.7 | 2 | 3.5 | 2.9 |
| phenol | | 13.6 | 9.5 | 11.2 | 14.6 |
| others | | 14 | 5 | 4.4 | 6.7 |

Table 3. also shows that phenol as present in considerable amount.

In the tobacco smoke, the presence of phenols along with PAH, is physiologically significant¹³⁾. In the present study, phenols were detected in the pyrolysis products but PAH was absent from the pyrolyzate.

The pyrolytic formation of phenols from the carbohydrate has been observed by Schlotzhaur et al.,¹⁴⁾. Therefore, as might be expected, the phenols that were produced are most likely derived from cocoa powder carbohydrates.

We concluded that addition of cocoa powder to tobacco products in quantities normally utilized for flavoring purposes would significantly enhance the phenolic content of tobacco smoke. In addition, tobacco flavor was enhanced synergistically, resulting from entrapment of tobacco flavor volatile by agglomeration in the hydrocarbon aerosol droplets obtained from the pyrolysis product of cocoa powder.

CONCLUSION

Cocoa powder was pyrolyzated at two cigarette smoking conditions. Pyrolyzates yield was constant throughout the whole temperature ranges but relatively low at 350°C.

The major pyrolysis products of cocoa powder are saturated and unsaturated aliphatic hydrocarbons. In addition, phenol, ketone, pyrazine and aldehyde were present in very small amounts. It is clear that the homologous series of alkane and alkene were generated by the thermal degradation of cocoa butter, and phenols are most likely derived from cocoa powder carbohydrate.

REFERENCES

1. Harller, G.C. and Leffeingwell, G.C., 32nd Tobacco Chemist Conference Montreal(1978)
2. Leffingwell, J.C., E. Bernasek and H.J. Young, R.J. Reymonds Tobacco Co.(1972)
3. Meursing, E.H., Cocoa powders for industrial processing. Scnd Ed., Holland, Cacaofabriek De Zaan B.V., publishers(1976)
4. Vitztum, O.G., P. Werkhoff and P. Hubert, Volatile components of roasted cocoa : basic fraction, J. Food science, 40, pp 911-916(1975)
5. Dietrich, P.E. Lederer, M. Winter and M. Stoll. Surl'arome du cocoa. I, Helv. Chim. Acta., 47 pp 1581-1590(1964)
6. Marion, J.P., F. Muggler-Chavan, R. Viani, J. Bricout, D. Reymond and R.H. Egli, The composition of chocolate aroma, Helv. Chim. Acta., 50, pp 1509-1516(1967)
7. Van Praag, M., H.S. Stein and M.S. Tibbetts, Steam volatile aroma constituent of roasted cocoa beans, J. Agr. Food. Chem., 16, pp 1005-1008(1968)
8. Van der wal, B., G. Sipmer, D.K. Kettenes and A. Th. J. Semper, Some new constituents of roasted cocoa, Rec. des Trav. Chim. despays-bas., 87, pp 238-240(1968)
9. Stoll, M., P. Dietrich, e. Sundt and M. Winter, Surl'arome du cocoa, II., Helv. Chim Acta., 50, pp 2065-2067(1967)
10. Schlotzhaur, W.S., Fattyacids and phenols from pyrolysis of cocoa powder, a tobacco product flavorant, tobacco science III, pp 1-2(1978)
11. J.W. Alencar, P.B. Alves, and A.A. Craveiro Pyrolysis of tropical vegetable oils J. Agric. Food. Chem. 31(6) 1270-1275(1983)
12. E.B. Higman, Irwin Schmeltz, and O.T. Chortyk Products from the pyrolysis of triglyceride at 400°C J. Agr. Food. Chem., 21(2) 202-204 (1973)

13. Wynder, E.L., Hoffmann, D., Tobacco and tobacco smoke p 231, Academic press, New York 1960
14. Schlotzhauer, W.S., Schmeltz., Tobacco Sci. 11, 31(1967)
15. Philip Morris Science Symposium, pp 47(1975)