Thermal Behavior Analysis of Two Synthesized Flavor Precursors of *N*-alkylpyrrole Derivatives

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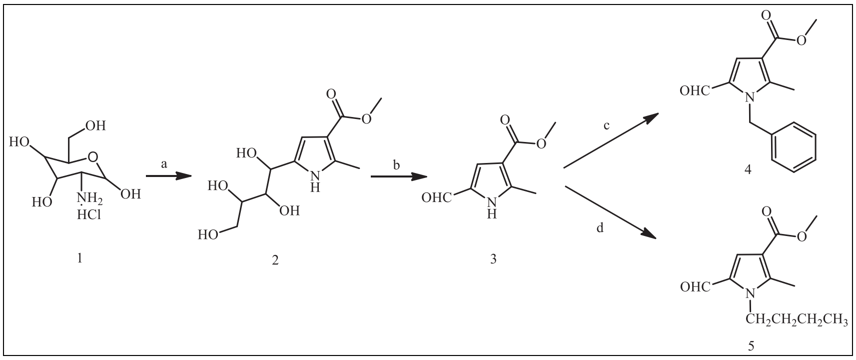

To expand the library of pyrrole-containing flavor precursors, two new flavor precursors—methyl *N*-benzyl-2-methyl-5-formylpyrrole-3-carboxylate (NBMF) and methyl *N*-butyl-2-methyl-5-formylpyrrole-3-carboxylate (NUMF)—were synthesized by cyclization, oxidation, and alkylation reactions. Thermogravimetry (TG), differential scanning calorimeter, and pyrolysis–gas chromatography/mass spectrometry were utilized to analyze the thermal degradation behavior and thermal degradation products of NBMF and NUMF. The TG-DTG curve indicated that the maximum mass loss rates of NBMF and NUMF appear at 310 and 268°C, respectively. The largest peaks of NBMF and NUMF showed by the differential scanning calorimeter curve were 315 and 274°C, respectively. Pyrolysis–gas chromatography/mass spectrometry detected small molecule fragrance compounds appeared during thermal degradation, such as 2-methylpyrrole, 1-methylpyrrole-2-carboxylic acid methyl ester, limonene, and methyl formate. Finally, the thermal degradation mechanism of NBMF and NUMF was discussed, which provided a theoretical basis for their application in tobacco flavoring additives.

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INTRODUCTION

Because of the antioxidant activities [1] and the special flavor properties, pyrrole-containing compounds are widely used in food-stuff industry [2,3], medicine [4,5], pesticides [6], and polymeric materials [7]. Some of these pyrrole derivatives are thought to provide powerful flavors and aromas; for instance, pyrrole-2-carboxaldehyde contributes sweet and corn-like odor, and 2-methylpyrrole shows bread and coffee flavor, while 2-acetylpyrrole has caramel-like flavor [8]. Previous studies indicated that bread, beef, coffee, cigarette, and other toasted food all contain pyrrole derivatives [9–13]. These pyrrole derivatives are generated from a series of complex reactions such as Maillard reaction [8,14], which usually contribute to the formation of characteristic caramel, popcorn, and nut aromas [15–17]. Because of their remarkable flavor properties, pyrrole derivatives recently received widespread attention in the food industry. Pyrroles with characteristic flavors are exploited as flavor additives in food and tobacco processing [1,18]. However, compared with other heterocyclic compounds, such as pyrazines, only a relatively small amount of pyrrole additives have been applied to food-related systems [1]. Besides, these pyrrole aromas are highly volatile, and their fragrances are easily lost. Therefore, our research interests are focused on the synthesis and possible applications of nonvolatile precursor of pyrrole derivatives.

To the best of our knowledge, the 2-formylpyrrole contributes to the roasted flavor [19]. Meanwhile, 2-formylpyrroles are important intermediates in the preparation of pyrrole derivatives [20]. Thus far, a series of synthetic methods for pyrrole heterocyclic compounds related to 2-formylpyrrole core were reported by chemists [21]. However, the further applications of these products were not been reported. On the basis of the previous reports and our early work [22], methyl *N*-benzyl-2-methyl-5-formylpyrrole-3-carboxylate (NBMF) and methyl *N*-butyl-2-methyl-5-formylpyrrole-3-carboxylate (NUMF) of 2-formylpyrrole derivatives, the new flavor precursor compounds, were synthesized. The thermal behavior analysis of NBMF and NUMF was discussed.

Pyrolysis–gas chromatography/mass spectrometry (Py-GC/MS) is an efficient way to identify compounds evolved during pyrolysis of organic matter [23]. Thermogravimetry (TG) and differential scanning calorimeter (DSC) are methods for analyzing thermal changes in samples during pyrolysis. Py-GC/MS, TG, and DSC have been widely used in thermal studies in many fields [24–28], such as cigarette [29], wines [30], wood [31], French cider [32], and crude oils [33]. The thermal behavior and decomposition mechanism of the two compounds NBMF and NUMF have not been reported in former literature. The aim of this study is to investigate the pyrolysis behavior of alkylpyrroles through TG, DSC, and Py-GC/MS analysis. The initial material compound 2-methyl-5-formyl-3-pyrrolecarboxylic acid methyl ester was synthesized by cyclization reaction, and NBMF and NUMF were both obtained by oxidation and alkylation reaction. Their structures were analyzed by proton nuclear magnetic resonance spectroscopy (^{1}H NMR and ^{13}C NMR), infrared (IR) spectroscopy, and high-resolution mass spectroscopy (HRMS). Then TG, DSC, and Py-GC/MS were used to investigate the thermal property of NBMF and NUMF. The purpose of studying the pyrolysis behavior of NBMF and NUMF was to initially assess the effect of its application to tobacco additives. According to previous literature [34], the key controllable variables in experiments to mimic smoking are temperature and pyrolysis atmosphere; in order to simulate the cigarette burning process, this experiment sets the pyrolysis temperature range at 300–900°C. The thermal stability, pyrolysis products, and degradation mechanism of NBMF and NUMF were discussed in this paper.

EXPERIMENTAL

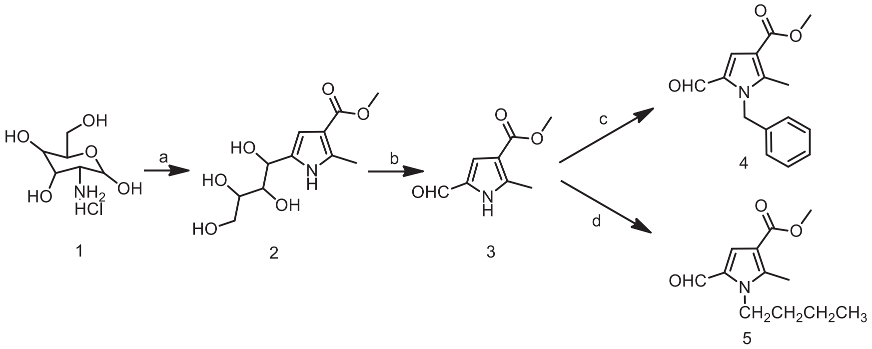
Materials. The reagents used in this study were analytically pure and purchased from Tianjin Kemer Chemical Reagent Co., Ltd. (China). Analytical thin-layer chromatography (TLC) using glass slides pre-coated with silica gel (GF254, Merck, China). Column chromatography was performed on a glass column (3 cm i.d. × 60 cm) filled with silica gel (0.03–0.06 mm, Qingdao Ocean Chemistry Factory, China).

Synthesis. The major concern about this study is the development of new, flavor precursor compounds of pyrrole derivatives. As shown in Scheme 1, compounds **2**, **3**, **4**, and **5** were synthesized. The precursors 2-methyl-5-1′2′3′4′-tetrahydroxybutyl-3-carboxylic acid methyl ester pyrrole (compound **2**) and the 2-methyl-5-formyl-3-carboxylic acid methyl ester pyrrole (compound **3**) were achieved according to the formerly reported procedure [35]. Compound **2** was synthesized by the cyclization reaction, and compound **3** was obtained by the oxidation reaction of compound **2** with an excess of $NaIO_4$ [22]. The synthesis of pyrrole flavor precursors **4** and **5** by using benzyl chloride and 1-bromobutan, respectively, was all ended within 24 h.

General procedure for the synthesis of methyl *N*-benzyl-2-methyl-5-formylpyrrole-3-carboxylate. Anhydrous K_2CO_3 (0.621 g, 4.5 mmol), benzyl chloride (0.189 g, 1.5 mmol), and TBAB (0.023 g, 0.07 mmol) were added into compound **3** (0.167 g, 1 mmol) in acetonitrile (6 mL) in sequence, and then the mixed solution was stirred for 24 h at 55°C. The reaction was monitored by TLC with petroleum ether : ethyl acetate (5:1, v : v). Then, the solution was evaporated to dryness, and the residue was treated with ethyl acetate (4 × 10 mL) and water (4 × 10 mL); the organic phase was separated. The mixed organic layers were dried over anhyd Na_2SO_4, then filtered, and evaporated. The crude products were finally purified by chromatography of petroleum ether and ethyl acetate (5:1, v : v) to give NBMF as a yellow oil. Yield: 0.218 g (85%). Spectrums of NBMF were given in the supporting information (including NMR, IR, and HRMS). ^{1}H NMR (400 MHz, $CDCl_3$) δ: 2.51 (s, 3H, CH_3), 3.83 (s, 3H, CH_3), 5.67 (s, 2H, CH_2), 6.97 (d, 2H, J = 8.04 Hz, CH=CH), 7.22–7.31 (m, 3H, 3CH), 7.40 (s, 1H, C=CH), 9.51 (s, 1H, O=CH). ^{13}C NMR δ: 11.13 (CH_3), 48.43 (CH_3), 51.26 (CH_2), 114.52 (C), 126.16 (CH), 128.81 (CH), 136.43 (C), 130.7 (C), 145.11 (C), 164.57 (C), 179.36 (O=CH). IR (KBr) ν = 783 (C–H), 1667 (C=C), 1670 (O=CH), 1253 (C–O–C), 3476 (C=O) cm^{-1}. HRMS calcd for $[M+H]^+$ 258.1130, found $[M+H]^+$ 258.1133.

General procedure for the synthesis of methyl *N*-butyl-2-methyl-5-formylpyrrole-3-carboxylate. Compound **5** (NUMF): Replacing benzyl chloride with *n*-butyl bromide (0.163 g, 1.2 mmol), other processes were the same as above. The reaction mixture was stirred at 55°C for 12 h, and the reaction was monitored by TLC with petroleum ether : ethyl acetate (7:1, v : v); when reaction completed, the mixture was also extracted and dried by the same operations as above. The crude product was chromatographed on a silica gel column with petroleum ether : ethyl acetate (10:1, v : v) to give an orange-yellow oil. Yield: 0.18 g (81%). Spectrums of NUMF were given in the supporting information (including NMR, IR, and HRMS). ^{1}H NMR δ: 0.95 (t, 3H, J = 7.28 HZ, CH_3), 1.26–1.41 (m, 2H, CH_2), 1.61–1.69 (m, 2H, CH_2), 2.59 (s, 3H, CH_3), 3.82 (s, 3H, CH_3), 4.31 (d, 2H, J = 7.64 Hz, CH_2), 7.38 (s, H, CH=C), 9.45 (s, 1H, O=CH). ^{13}C NMR δ: 10.76 (CH_3), 13.61 (CH_3), 19.74 (CH_2), 32.57 (CH_2), 45.09 (CH_2), 50.98 (CH_3), 113.78

Scheme 1. Synthetic routes of **4** (methyl *N*-benzyl-2-methyl-5-formylpyrrole-3-carboxylate) and **5** (methyl *N*-butyl-2-methyl-5-formylpyrrole-3-carboxylate). (a) H_2O, $NaHCO_3$, methyl acetoacetate 25°C. (b) H_2O, $NaIO_4$, −4°C. (c) Benzyl chloride, MeCN, TBAB, K_2CO_3, 55°C. (d) *n*-Butyl bromide, MeCN, TBAB, K_2CO_3, 55°C.



(C), 126.35 (CH), 130.36 (C), 144.03 (C), 164.4 (C), 178.84 (O=CH). IR (KBr) ν = 2964 (C–H), 1670 (O=CH), 1250 (C–O–C), 3497 (C=O) cm^{-1}. HRMS calcd for $[M+H]^+$ 224.1286, found $[M+H]^+$ 224.1285.

METHODS

Structure identification. ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker spectrometer (Bruker, Rheinstetten, Germany) at 400 MHz. The ^1H NMR and ^{13}C NMR chemical shifts were referenced to tetramethylsilane signals. Mass spectra (MS) were recorded on a high-resolution mass spectrometer (Waters Micromass Q-TOF Micro TM, Agilent, USA). Functional groups were recorded on a Fourier transform infrared spectrophotometer (Nicolet iS50, Thermo Nicolet Co, Waltham, MA, USA), and sample and spectroscopic-grade potassium bromide powder were pressed into a 1 mm wafer for Fourier transform infrared analysis. For each sample, scanning range was from 4000 to 400 cm^{-1} and a resolution of 4 cm^{-1}.

Thermal analysis. The TG and DSC analyses were recorded on a simultaneous thermal analyzer (STA 449 F3, Netzsch, Germany). The sample mass was kept about 10 mg each time, and spectral pure Al_2O_3 was used as a reference. Purified nitrogen was used as carrier gas at a flow rate of 60 mL/min to afford an inert atmosphere for pyrolysis. Then the sample was heated from 30 to 900°C at 10°C/min.

Pyrolysis–gas chromatography/mass spectrometry analysis. Pyrolysis–gas chromatography/mass spectrometry analysis used in this study had a Pyroprobe (5250T, CDS, USA) that was coupled to a GC/MS (7890A/5975C, Agilent, USA). About 1 mg sample was settled into a quartz tube between two threads of quartz wool. The pyrolysis chamber was heated to 900°C at 20°C/ms with a hold time of 10 s, while the initial temperature of the pyrolysis interface was set to 300°C with a hold time of 1 s. The pyrolysis atmosphere was helium, and the final pyrolysis products were detached and determined by the GC/MS.

The chromatographic separation was using a HP-5MS fused silica capillary column (60 m × 250 μm × 0.25 μm df, Agilent). The injector temperature was kept at 300°C. The oven program started at 50°C for 1 min and was heated to 220°C at a constant 3°C/min with a final hold time of 15 min. Then the oven program was continuously heated to 280°C at the rate of 10°C/min and held at 280°C for 10 min. The split ratio was 50:1 of helium carrier gas with the flow rate at 1 mL/min. The transfer line temperature, ion source temperature, and quadruple temperature were 300, 230, and 150°C, respectively. The mass spectrometer scan ranges between 30 and 500 amu and sets to an ionization energy of 70 eV. The solvent delay time was 3.6 min. Recognition of the pyrolysis products was accomplished by using a NIST 11 library and their MS. Each pyrolysis was carried out at least in duplicate. Before each set of replicates, the quartz tube and wool were analyzed as a blank to ensure that there was no carryover between samples.

Thermal analysis of methyl *N*-benzyl-2-methyl-5-formylpyrrole-3-carboxylate and methyl *N*-butyl-2-methyl-5-formylpyrrole-3-carboxylate sample. TG-DTG curves represent the relationship between sample temperature change and mass loss. TG-DTG curves of NBMF and NUMF are shown in Figures 1 and 2, respectively. It can be seen from Figure 1 that NBMF has three thermal degradation stages: in the first stage from 30 to 200°C, the mass of sample showed a slow mass loss trend with a loss of 3.07%. Then it was observed that 200–320°C stage was the main degradation stage, and there was a sharp decrease in mass loss of 99.91%. In this stage, the largest mass loss rate occurred at 310°C.

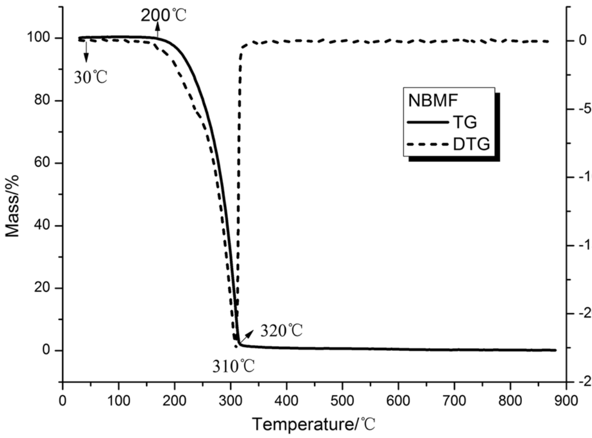


Figure 1. Thermogravimetry (TG) and derivative TG (DTG) curves of methyl *N*-benzyl-2-methyl-5-formylpyrrole-3-carboxylate (NBMF).

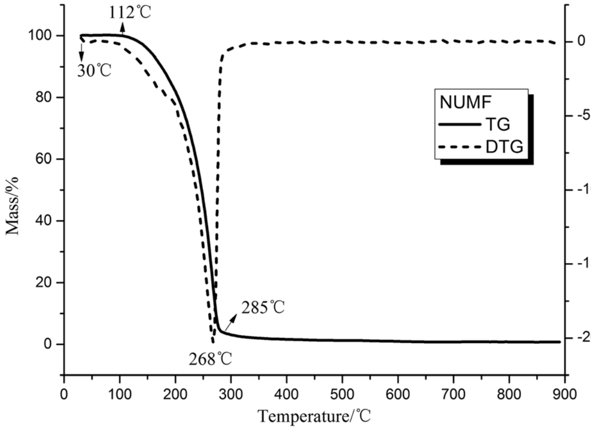


Figure 2. Thermogravimetry (TG) and derivative TG (DTG) curves of methyl *N*-butyl-2-methyl-5-formylpyrrole-3-carboxylate (NUMF).

In the last stage from 320 to 900°C, the TG and DTG curves tend to be stable, and the mass of NBMF was still 0.10% of its original mass, indicating that the compound NBMF is completely decomposed.

Figure 2 shows that NUMF has three thermal degradation stages. The initial degradation stage was from 30 to 112°C, with mass loss of 0.65%. The second stage was the main thermal mass loss of NUMF in the temperature range from 112 to 285°C, with a mass loss of 99.26%, and the largest mass loss rate appeared at 268°C. Finally, from 285 to 900°C, the NUMF decomposes completely. The TG and DTG curves tend to be stable, and the quality of the NUMF is still 0.74% of its original mass.

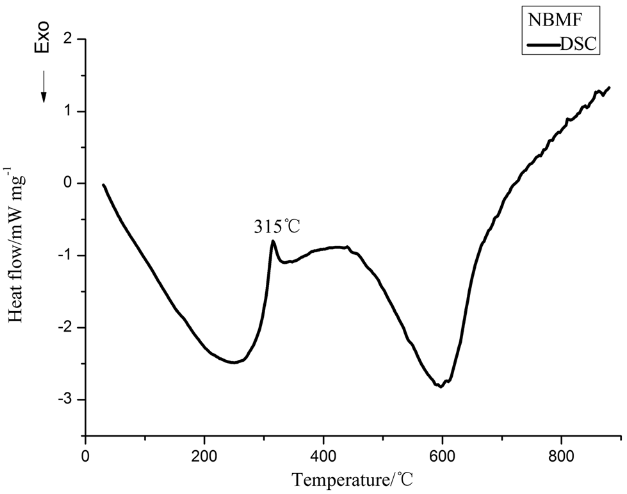


Figure 3. Differential scanning calorimeter (DSC) curve of methyl *N*-benzyl-2-methyl-5-formylpyrrole-3-carboxylate (NBMF).

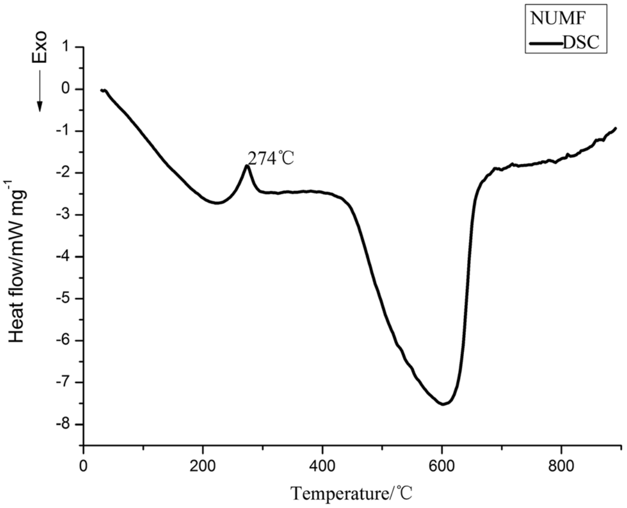


Figure 4. Differential scanning calorimeter (DSC) curve of methyl *N*-butyl-2-methyl-5-formylpyrrole-3-carboxylate (NUMF).

The DSC curves of NBMF and NUMF are shown in Figures 3 and 4, respectively. The peak temperature of DSC curve was recorded by apparatus. The strong endothermic peaks of the two samples appeared at 315 and 274°C, respectively. In general, the results in the DSC curves were consistent with the results in the TG-DTG curves.

Pyrolysis–gas chromatography/mass spectrometry analysis of methyl *N*-benzyl-2-methyl-5-formylpyrrole-3-carboxylate and methyl *N*-butyl-2-methyl-5-formylpyrrole-3-carboxylate samples. The thermal stability of the sample, the heat loss associated with the mass loss, and the mass loss can be reflected by the TG-DTG-DSC. However, thermal degradation products need to be further detected by Py-GC/MS. In order to simulate the combustion process of cigarettes, pyrolysis conditions were performed in an oxygen-free atmosphere

Table 1

Pyrolysis products of methyl *N*-benzyl-2-methyl-5-formylpyrrole-3-carboxylate.

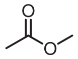
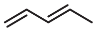
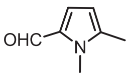
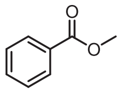
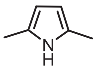
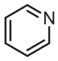
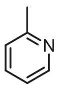
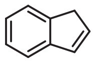
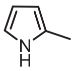
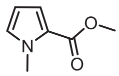
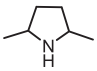
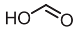
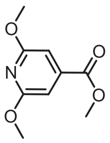
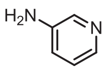
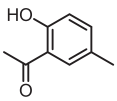
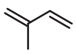
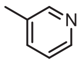
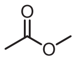
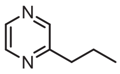
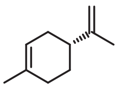
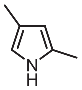
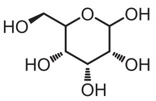
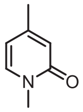
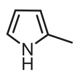
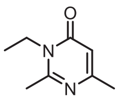
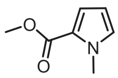
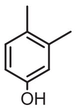
Peak	RT/min	Pyrolysis products	Structure	Match	Relative content/%
1	5.9019	Methyl acetate		87	1.14
2	6.5449	1,3-Pentadiene		91	0.14
3	9.1721	1,5-Dimethyl-1*H*-pyrrole-2-carbaldehyde		95	5.33
4	12.7482	Methyl benzoate		95	0.78
5	15.9901	2,5-Dimethyl-1*H*-pyrrole		91	5.35
6	17.1588	Pyridine		94	1.63
7	18.6646	2-Picoline		97	1.56
8	26.9378	Indene		95	0.69
9	32.7927	2-Methyl-1*H*-pyrrole		94	3.83
10	41.2558	Methyl-4-methylpyrrole-2-carboxylate		89	10.74
11	49.4842	2,5-Dimethylpyrrolidine		86	12.82
12	54.6518	Formic acid		97	11.76
13	71.6385	Methyl-2,6-dimethoxyisonicotinate		87	19.73
14	74.1295	3-Aminopyridine		90	12.50
15	83.8082	2′-Hydroxy-5′-methylacetophenone		88	10.00

Table 2

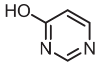
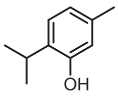
Pyrolysis products of methyl *N*-butyl-2-methyl-5-formylpyrrole-3-carboxylate.

Peak	RT/min	Pyrolysis products	Structure	Match	Relative content/%
1	5.8963	1-Dimethylethene		88	0.03
2	6.4236	Butane		97	0.05
3	6.5458	Isoprene		94	0.08
4	9.1688	3-Picoline		94	0.20
5	12.7385	Methyl acetate		93	0.49
6	18.6585	2-Propylpyrazine		97	0.98
7	25.9852	D-Limonene		98	3.16
8	29.9954	2,4-Dimethylpyrrole		88	0.53
9	48.827	D-Allose		84	9.49
10	52.0075	1,4-Dimethyl-1,2-dihydropyridine-2-one		88	11.93
11	56.5207	2-Methyl-1*H*-pyrrole		83	14.78
12	56.6034	3-Ethyl-2,6-dimethyl-4(3*H*)-pyrimidinone		90	5.23
13	59.239	Methyl-4-methylpyrrole-2-carboxylate		90	17.08
14	61.7261	3,4-Dimethylphenol		85	5.36

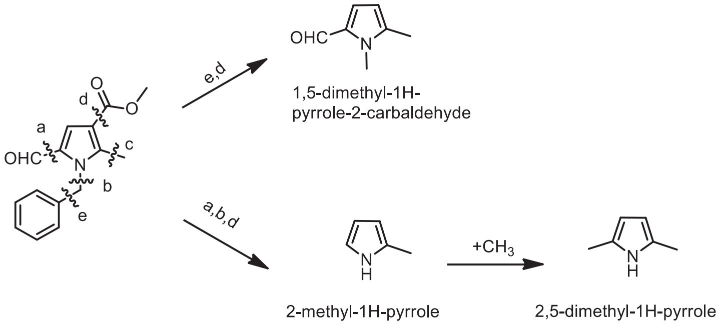
(*Continues*)

Table 2

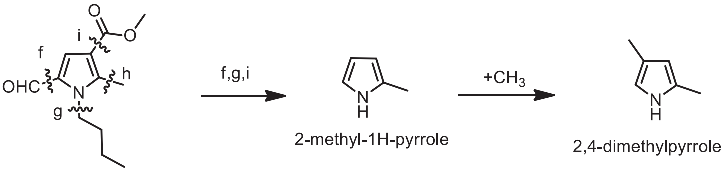
(*Continued*)

Peak	RT/min	Pyrolysis products	Structure	Match	Relative content/%
15	62.8939	4-Pyrimidinol		85	13.80
16	79.4611	Thymol		96	10.81

Scheme 2. Proposed pyrolysis pathways for methyl *N*-benzyl-2-methyl-5-formylpyrrole-3-carboxylate.



Scheme 3. Proposed pyrolysis pathways for methyl *N*-butyl-2-methyl-5-formylpyrrole-3-carboxylate.



at a temperature from 300 to 900°C. The major pyrolysis products of NBMF and NUMF were listed in Tables 1 and 2.

Among pyrolysis products, 1,5-dimethyl-1*H*-pyrrole-2-carbaldehyde, 2,5-dimethyl-1*H*-pyrrole, 2-methyl-1*H*-pyrrole, methyl-4-methylpyrrole-2-carboxylate, 2,5-dimethylpyrrolidine, 2,4-dimethylpyrrole, 2-methyl-1*H*-pyrrole were the flavor compounds we expected. Besides, the methyl-4-methylpyrrole-2-carboxylate and 2-methyl-1*H*-pyrrole were the common pyrolysis compounds of NBMF and NUMF. All compounds were formed by thermal degradation or rearrangement during high-temperature conditions.

Table 1 shows that NBMF mainly produced 15 important compounds. It was observed that 1,5-dimethyl-1*H*-pyrrole-2-carbaldehyde, 2,5-dimethyl-1*H*-pyrrole, 2-methyl-1*H*-pyrrole, methyl-4-methylpyrrole-2-carboxylate, and 2,5-dimethylpyrrolidine were generated by NBMF degradation under pyrolysis conditions. Among which 2,5-dimethylpyrrolidine accounted for the largest proportion (12.82%), followed by methyl-4-methylpyrrole-2-carboxylate (10.74%), 2,5-dimethyl-1*H*-pyrrole (5.35%), 1,5-dimethyl-1*H*-pyrrole-2-carbaldehyde (5.33%), and 2-methyl-1*H*-pyrrole (3.83%). The relative amount of pyrolysis derived pyrrole compounds of NBMF was 38.07%.

In Table 2, there were 16 products listed. 2,4-Dimethylpyrrole, 2-methyl-1*H*-pyrrole, and methyl-4-methylpyrrole-2-carboxylate were produced from NUMF under pyrolysis conditions. Methyl-4-methylpyrrole-2-carboxylate has the largest relative amount of characteristic flavor compounds (17.08%). The relative contents of 2-methyl-1*H*-pyrrole (14.78%) and 2,4-dimethylpyrrole (0.53%) were sequentially decreased. The relative amount of pyrrole compounds produced by pyrolysis of NUMF was 32.39%.

The results demonstrated that flavor precursors NBMF and NUMF could generate characteristic flavor compounds under simulated cigarette burning conditions. Therefore, NBMF and NUMF could be used as flavor precursors under the high-temperature treatment. At the same time, the studies on the formation of characteristic pyrolysis products were significance for potential application of NBMF and NUMF as flavor additives in food stuffs and tobacco. It is speculated that the pyrolysis process of NBMF and NUMF under different time periods was as follows: In the initial stage, their side chains are broken, and a simple redox reaction occurred. The pyrolysis products of this stage were olefins, etc. With increasing temperature, these simple compounds were decomposed to small fragments, which were constantly rearranged and reacted to produce more complex structures of alcohols, esters, and pyrrole compounds.

Pyrolysis mechanism analysis. The pyrolysis mechanism was very complex and may be formed by complex reactions, such as dehydrogenation, addition, rearrangement, isomerization, and oxidation. Because the benzene ring and the C=O double bond both have strong thermal stability [36], the pyrolysis of NBMF and NUMF was mainly between the C–C single bond. On the basis of qualitative and quantitative relationship of pyrolysis products in pyrolysis process, it is speculated that the pyrolysis methods for NBMF and NUMF were shown in Schemes 2 and 3.

Scheme 2 shows the possible pyrolysis pathways of NBMF, the chemical bond d and e broken to produce the aroma compounds of 1,5-dimethyl-1*H*-pyrrole-2-carbaldehyde. Meanwhile, the chemical bonds a, b, and d of NBMF broke simultaneously, and 2-methyl-1-hydropyrrole was formed. Afterward, one methyl radical was captured in *C5* of 2-methyl-1-hydropyrrole to produce 2,5-dimethyl-1*H*-pyrrole. For NUMF, the pyrolysis process was similar to NBMF. The possible pyrolysis pathways are shown in Scheme 3. When the chemical bonds f, g, and i of NUMF ruptured, the 2-methyl-1-hydropyrrole was generated. After that, one methyl radical was captured in *meta*-position of 2-methyl-1-hydropyrrole to afford 2,4-dimethyl-1*H*-pyrrole. In addition, the above pyrolysis process also produces other compounds by rearranged or radicals reacted [37].

CONCLUSIONS

NBMF and NUMF were synthesized by cyclization, oxidation, and alkylation reactions, and their structures were confirmed by ^{1}H NMR, ^{13}C NMR, IR, and HRMS. The thermal behavior and decomposition compounds of NBMF and NUMF were discussed by TG, DSC, and Py-GC/MS analysis. TG-DTG curves showed that the temperature range of main mass loss of NBMF and NUMF was 200–320°C and 112–285°C, respectively. The maximum mass loss rates of NBMF and NUMF occurred at 310 and 268°C, respectively. The DSC curve indicated that the strongest endothermic peaks of NBMF and NUMF were at 315 and 274°C, respectively. Py-GC/MS analysis showed that there were some characteristic aromatic compounds produced such as 1,5-dimethyl-1*H*-pyrrole-2-carbaldehyde, 2,5-dimethyl-1*H*-pyrrole, methyl-4-methylpyrrole-2-carboxylate, 2,5-dimethylpyrrolidine, 2,4-dimethylpyrrole, and 2-methyl-1*H*-pyrrole. The production of these aromatic compounds was of great significance to the application of NBMF and NUMF in tobacco additives and food production.

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AUTHOR CONTRIBUTIONS

Xiaoming Ji designed the experiment and corrected the manuscript. Lvye Ai conducted synthetic experiments and wrote the manuscript. Miao Lai and Mengzhen Liu wrote a part of the manuscript and corrected it. Tianbao Ren and Mingqin Zhao assisted in analyzing the experimental results. All authors read and approved the final manuscript.

CONFLICT OF INTEREST

The authors declare no conflict of interest.

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