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Synthesis of Polyol Esters of Lower Fatty acid and Their Flavoring in Tobacco

Zeng Shitong

Zhengzhou Tobacco Research Institute of CNTC

中国烟草总公司郑州烟草研究院
ZHENGZHOU TOBACCO RESEARCH INITITUTE OF CNTC

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- Experiment
- Results and discussion
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Background

- Organic acids in tobacco
- Polyol esters in tobacco
- Advantages of polyol ester of lower fatty acid as tobacco flavorant
- Synthesis of ester

Experiment

➢ Preparation of $TiSiW_{12}O_{40}/TiO_2$

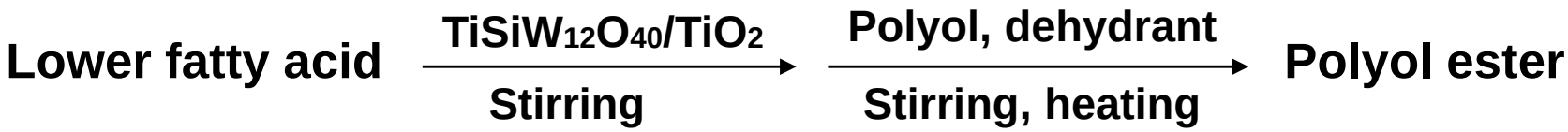
$$TiCl_4 \xrightarrow[\text{Filtrating, washing, drying}]{NH_3 \cdot H_2O} Ti(OH)_4$$

$$H_4SiW_{12}O_{40} \cdot xH_2O \xrightarrow[\text{Heat}]{H_2O} Ti(OH)_4 \xrightarrow[\text{4 h}]{} \xrightarrow[\text{Drying, grinding}]{-H_2O}$$

$$\xrightarrow[\text{300℃, 3h}]{\text{activating}} TiSiW_{12}O_{40}/TiO_2$$

Experiment

➢ Synthesis of polyol esters of lower fatty acid



Lower fatty acids: acetic acid, butyric acid, isobutyric acid, isovaleric acid, caproic acid

Polyols: glycerol, xylitol, glucose

Dehydrant : cyclohexane

Experiment

➢ Characterization and evaluation

FT-IR

MS

GC/MS

Py/GC/MS

Flavoring evaluation

Results and discussion

➢FT-IR

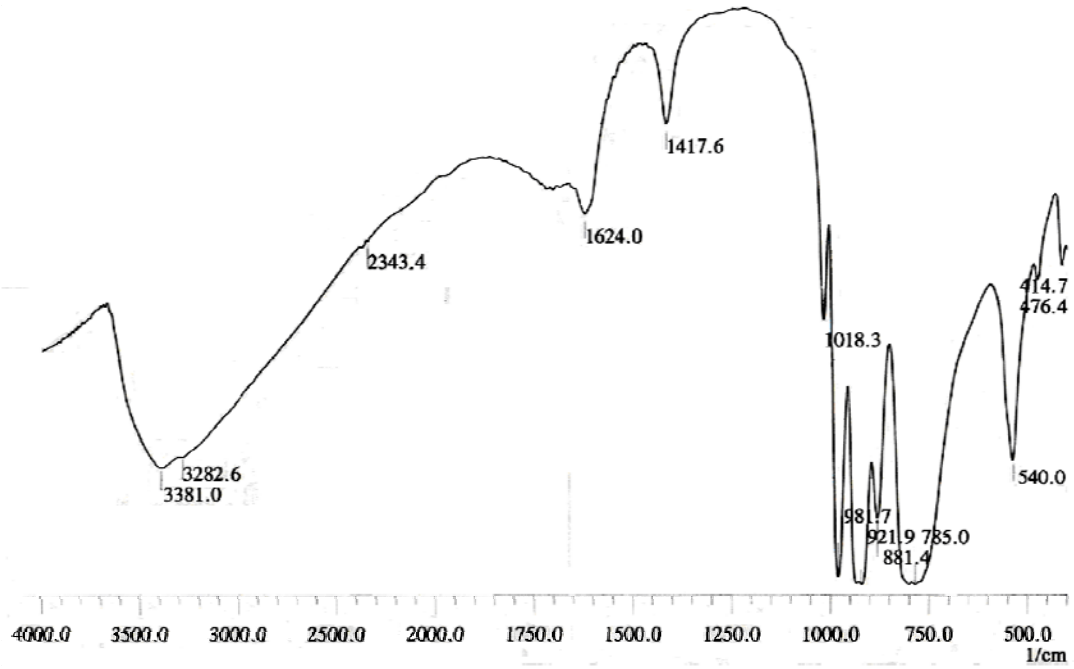


Fig.1 IR spectrum of $TiSiW_{12}O_{40}/TiO_2$

Results and discussion

➢ Synthesis of polyol esters of lower fatty acid

Table1 Reaction conditions and results

Reactants	Mol ratio	Catalyst amount %	Dehydrant amount ml	Reaction temperature ℃	Reaction time h	Product state	Yield %
Acetic acid /glucose	20：1	2	8	100	3	White crystal	41
Isobutyric acid /glucose	13：1	2	8	100	3	Viscosity oily matter	34
Iospennoic acid /glucose	11：1	2	8	100	3	Viscosity oily matter	23
Butyric acid /xylitol	15：1	2	8	100	3	Viscosity oily matter	68
Isobutyric acid /xylitol	15：1	2	8	100	3	Viscosity oily matter	55
Iospennoic acid /xylitol	13：1	2	8	100	3	Viscosity oily matter	50
Hexanoic acid /xylitol	12：1	2	8	100	3	Viscosity oily matter	61
Butyric acid /glycerol	20：1	2	8	100	3	Viscosity oily matter	72

Results and discussion

➢MS analysis

Table2 MS analysis results of polyol esters of lower fatty acid

Products	Molecular ion peak (m/z)
glucose acetate	311.2 371.3 413.3
glucose isobutyrate	325.4 395.3 483.4 553.4
glucose isopentyrate	269.2 353.4 437.4 455.4 539.4
xylitol butyrate	297.3 367.4 455.4 570.4 640.4
xylitol isobutyrate	227.3 297.3 367.4 455.4 570.4
xylitol isopentyrate	241.2 343.5 359.4 427.4 459.3 542.8 626.5
xylitol caproate	255.4 353.7 371.7 413.8 469.8 584.8
glycerol butyrate	255.2 325.3 399.4 469.4 543.4

Results and discussion

➢GC/MS analysis

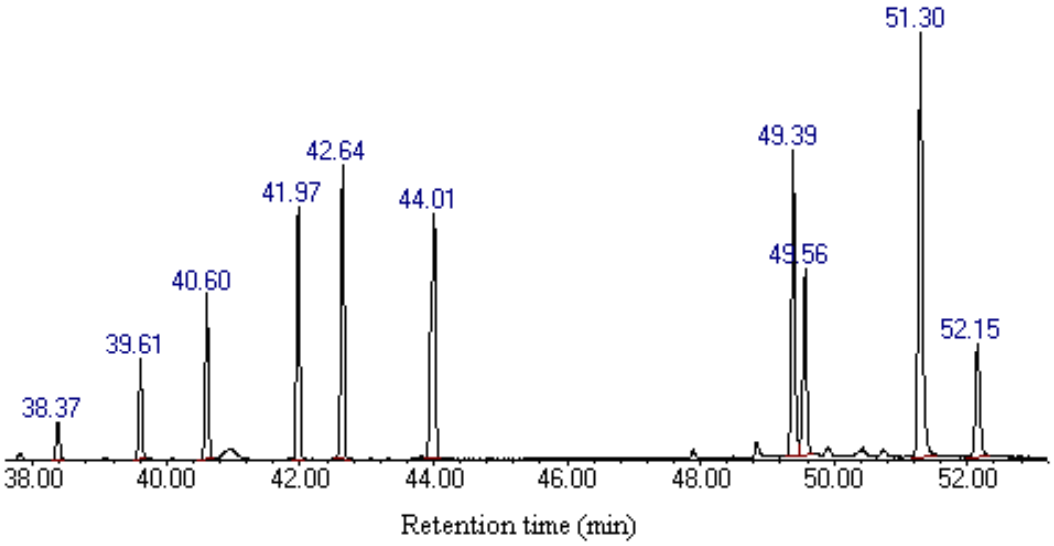


Fig.2 GC/MS results of glucose isobutyrate

Table 3 Composition of glucose isobutyrate

Retention time min	component	Relative area %
38.37 39.61 40.60	Glucose biisobutyrate	12.4
41.97 42.64 44.01	Glucose triisobutyrate	35.0
49.39 49.56 51.30	Glucose tetraisobutyrate	44.9
52.15	Glucose pentaisobutyrate	6.2
total		98.5

Results and discussion

➢ Py/GC/MS analysis

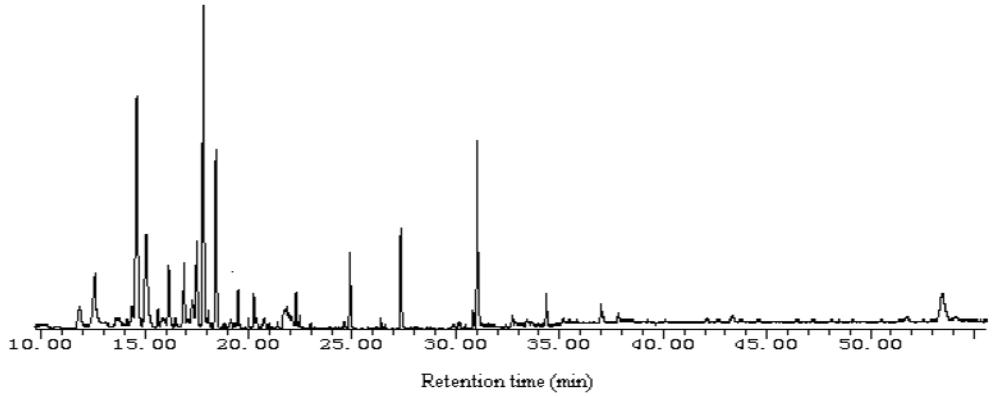


Fig.3 GC/MS spectrum of glucose isobutyrate pyrolysis products（400℃）

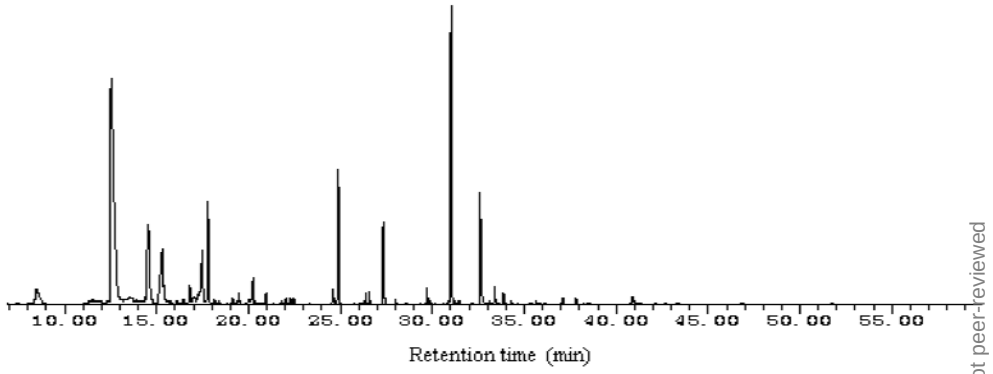


Fig.4 GC spectrum of glucose isobutyrate pyrolysis products（800℃）

Results and discussion

Table 4 pyrolysis products of glucose isobutyrate （400℃）

Retention time/min	Composition	Match degree/%
12.81	acetic acid	91
14.61	Benzaldehyde	95
15.15	isobutyric acid	95
15.63	1-methyl-4-(1-methylethyl)-3-cyclohexen-1-o	89
16.15	isophorone	91
16.89	1-Methyl-4-(1-methylethenyl) cyclohexanol	87
17.29	Phenylacetaldehyde	93
17.51	Acetophenone	93
17.82	Ethyl benzoate	95
20.27	4'-Methylacetophenone	95
22.30	Benzyl alcohol	96
22.47	Benzenepropanoic acid ethyl ester	97
27.35	Ethyl phenylacryate	98
31.03	Butyl phenylacryate	98
32.73	Benzoic acid	95
34.36	Di-iso-nonyl phthalate	85
37.01	Dibutyl phthalate	93

Results and discussion

Table 5 pyrolysis products of glucose isobutyrate （800℃）

Retention time/min	Composition	Match degree/%
12.52	acetic acid	95
14.52	Benzaldehyde	93
15.21	isobutyric acid	95
16.81	Methyl benzoate	93
17.48	Acetophenone	93
20.24	3'-Methylacetophenone	93
20.97	2-hydroxy-benzoic acid ethyl ester	95
22.04	Benzoic acid butyl ester	86
22.29	Benzyl alcohol	96
22.46	Benzenepropanoic acid ethyl ester	97
26.36	Methyl phenylacryate	92
26.58	Benzoylformic acid	86
27.34	Ethyl phenylacryate	98
29.73	2-Methyl-1-phenyl-1-propanone	86
31.02	Butyl phenylacryate	98
32.60	Benzoic acid	95
33.39	Benzophenone	95
40.88	3-Phenyl-2-propenoic acid	98

Results and discussion

➢ Flavoring evaluation

Polyol esters with satisfying flavoring effect:

glucose acetate
glucose isobutyrate
glucose isopentyrate
xylitol isopentyrate
xylitol caproate

Polyol esters with unsatisfying flavoring effect:

xylitol butyrate
xylitol isobutyrate
glycerol butyrate

Results and discussion

Table6 Tobacco flavoring evaluation of polyol esters of lower fatty acid

Polyol ester of lower fatty acid	Appropriate addition amount (ug/g)	Smoking results
glucose acetate	10	Diversity and quality of aroma, smoothness and softness of smoke increased; offensive odor and dryness decreased; after taste was improved.
glucose isobutyrate	20	Harmony and volume of aroma, smoothness and softness of smoke increased; irritancy decreased; after taste was improved
glucose isopentyrate	20	Harmony, diversity, quality and volume of aroma, smoothness and softness of smoke increased; dryness of smoke decreased.
xylitol isopentyrate	5	Harmony, diversity and volume of aroma increased; irritancy decreased.
xylitol caproate	5	Harmony, diversity, quality and volume of aroma, smoothness and softness of smoke increased; offensive odor, irritancy and dryness of smoke decreased.

Conclusion

- Synthesis of polyol esters of lower fatty acid can be effectively catalysed by $TiSiW_{12}O_{40}/TiO_2$, but without no site selectivity in esterification
- The synthesized products are mixed esters with different esterification degree
- polyol esters of lower fatty acid can release corresponding lower fatty acids and several other flavor components
- polyol esters of lower fatty acid can improve tabacco sensory quality