

Note

Thermal Decomposition Products of Starch and Its Derivatives

Masaru SHIMADA and Mitsuo DEKI*

Introduction

It needs hardly be said that starch seems to have an important role by the fact that starch or its derivatives are used widely not only as food additives which may be added directly to foods but as raw material for glucose, "mizu-ame" (millet jelly) and brewery industries. Starch is one of polysaccharides in which ether linkages are formed by glucopyranose at C1 ~ 4 and/or C1 ~ 6, so it has 2 ~ 4 hydroxy groups in one glucose unit. As the derivatives can be easily synthesized by reaction with these hydroxy groups, the starch derivatives have been used as a mean for the analysis of chemical structure of starch itself.

On the other hand, oxidized starch, phosphoric derivatives, and hydroxyalkyl derivatives are used much as paste, adhesives in fiber industry and additives in food industry, the amount of consumption for these industries is steadily increasing every year. Furthermore, since the starch for raw material in Japan maintains the same level in production, and the supply of the starch derivatives must depend upon a foreign market; thus, the import of the starch derivatives is increasing gradually.

The starch derivatives used in fiber and food industries, which requires special properties from the point of gelatination temperature, viscosity, adhesivity and so forth, are of low substitution and most of the imported starch derivatives meet these properties because of being with low substitution. It is, however, very difficult to distinguish the derivatives from starch by X-ray diffractions and IR spectra. Specially, as for the low substituted phosphoric starch used as food additives, it has become even more difficult to distinguish them from nontreated starch. Considering these circum-

stances the thermal decomposition products of the starch derivatives were studied. In this paper the thermal decomposition products of the starch derivatives have been compared by GC and compositions of volatile components were detected by GC-MS.

Experimental

Materials and methods

Materials:

Starch and its derivatives used in this experiment were as follows; corn starch, acetate starch [degree of substitution (D.S.)0.1] and hydroxypropyl starch(D.S. 1.0).

Apparatus and pyrolysis procedure:

The apparatus used for pyrolysis is shown in Fig.1. The furnace consists of a glass tube and a coiled heater wound around the glass tube. Temperature of the furnace was maintained by means of an automatic controller.

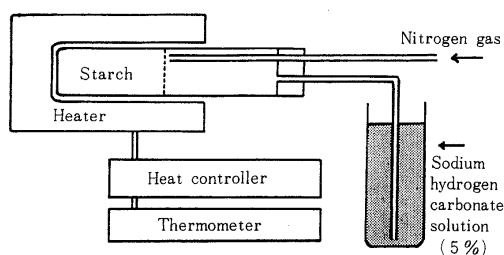


Fig.1 Apparatus for thermal decomposition

Sample(1g) was put into a decomposition tube and the tube was then placed in the furnace, kept at 500 or 650 beforehand, for two minutes with flow of nitrogen gas through the tube. Pyrolysis products were

*Central Customs Laboratory, Ministry of Finance, 531, Iwase, Matsudo-shi, Chiba-ken, Japan

absorbed in a solution of sodium hydrogen carbonate (5%). The carbonate solution was extracted with chloroform in a separate funnel, and the chloroform solution being freed from acidic components was dehydrated, and used for GC and GC-MS analysis. The acidic fraction was out of consideration in this experiment.

Gas chromatography and mass spectrometry combined with gas chromatograph:

For gas chromatography of the pyrolysis products, a Shimadzu GC-5APF gas chromatograph with a 3mm X 4m glass column packed with 3 % polyethyleneglycol 20M on 80/100 mesh Chromosorb WAW was used. The injection port of the gas chromatograph was set at 280 °C, and the column oven was temperature-programmed from 50 °C at 6 °C/min. Helium flow rate was 60ml/min.

Mass spectrometric measurements were carried out on a Shimadzu LKB9000 connected with a gas chromatograph. Gas chromatographic conditions for GC-MS were set up to be the same as those of gas chromatographic measurements mentioned above except the length of column. Column for GC-MS was 3m in length. The ion source temperature was held at 270 °C during the GC-MS runs. The mass spectra were obtained at 70 eV of electron energy, 3.5 kV of accelerating voltage, and 60 µA of trap current.

Results and discussion

Conditions of thermal decomposition

Bryce et al.¹⁾ found carbon dioxide, acetaldehyde, furan, acetone and 2-methylfuran as the main compounds in thermal decomposition products from pyrolysis of starches at 300 °C in a stream of nitrogen and analyzed directly by a gas chromatograph, and indicated that there exists no differences by kinds of starches, however, in case of jute hemicellulose, some differences were observed for low boiling compounds.

Shimizu et al.²⁾ studied aroma of starch roasted at 300 ~ 500 °C. In order to evaluate the influence of decomposition temperature, pyrolyzates at various temperature were analyzed in this experiments. As a result, the pyrolyzates of corn starch decomposed at 400 °C showed markedly the abundance of permanent gas and, on the contrary, there was no peak in high boiling region in the gas chromatogram. This behavior was the same as decomposition products of hydroxypropyl starch with low substitution and acetate starch.

In case of pyrolysis at over 500 °C, many peaks were observed, as shown in Fig.2, and at 650 °C, it was characteristic showing many peaks in low boiling region. Reproducibility of decomposition products was good, and GC patterns indicated good reproducibility as shown in Fig.3.

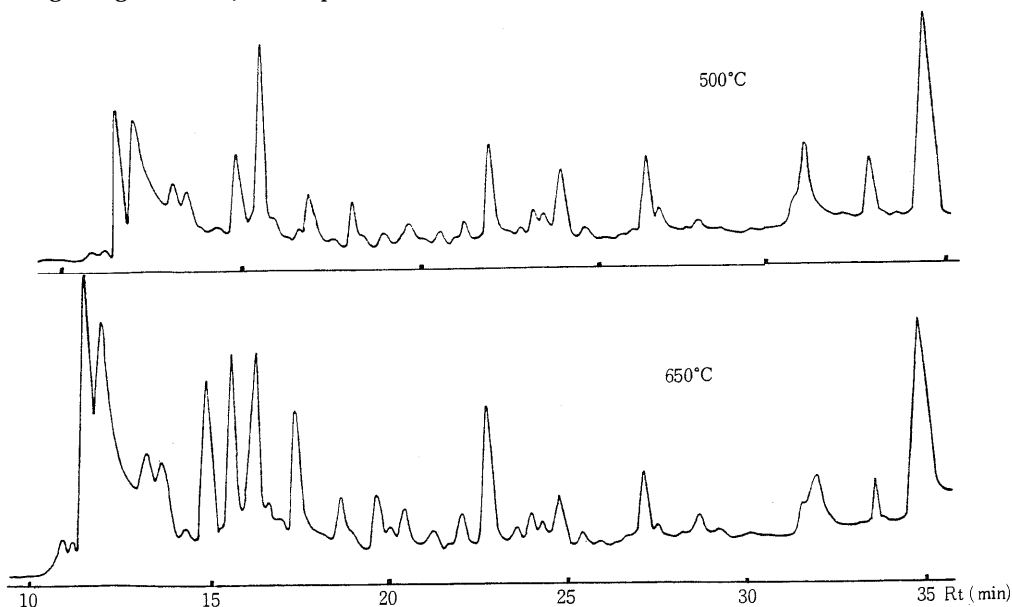


Fig.2 Temperature dependence on pyrolyzation (corn starch pyrolyzate without chloroform extraction)

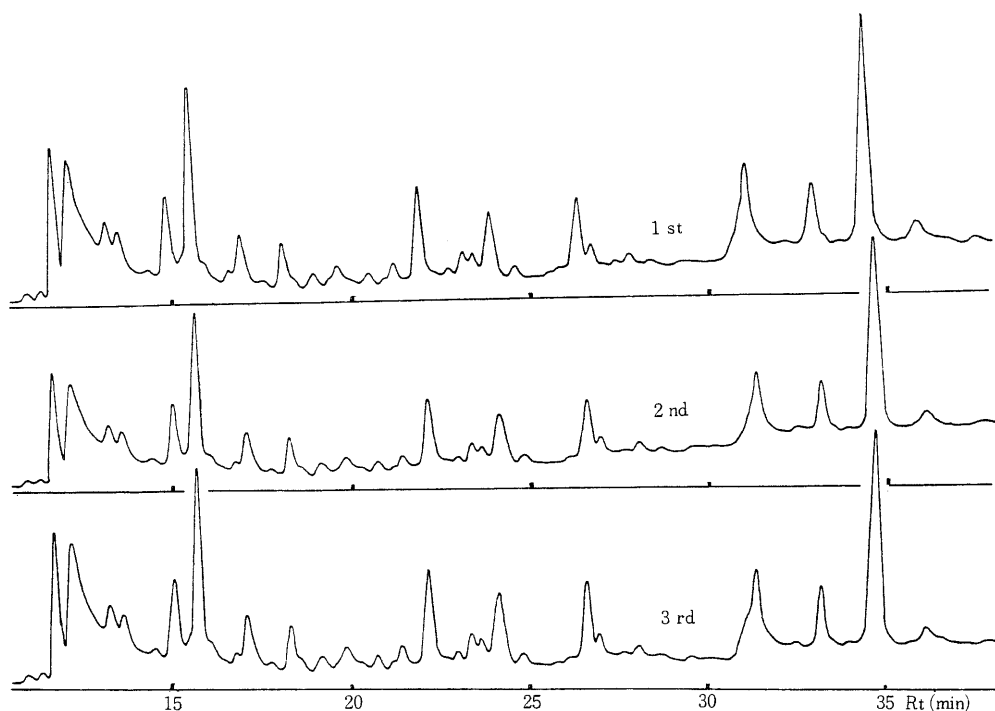


Fig.3 Reproducibility of gas chromatographic patterns (corn starch without chloroform extraction)

Pyrolysis patterns of starch and its derivatives

GC chromatograms of pyrolyzates of hydroxypropyl and acetate starch at 500 °C are shown in Fig.4. Qualitatively, the chromatograms from the pyrolysis of corn starch are identical to those from the pyrolysis of acetate starch and hydroxypropyl starch, but in GC pattern of hydroxypropyl starch, peak 2 and peak 3 are observed to be rather strong, and furthermore, in acetate starch the strongest among three. In addition, in acetate starch Peak 1 is very characteristic. This peak shows no appearance in both hydroxypropyl and corn starch pyrolyzates.

Determination of pyrolysis products by GC-MS spectrometry

In order to give agreeable flavour to foods, many studies on pyrolyzates of carbohydrates were carried out so far. Johnson et al.³⁾ have shown the 5-methylfurfural and furfural were produced from sucrose during thermal degradation process and estimated that 5-hydroxymethylfurfural could be precursor of 5-methylfurfural. Walter et al.⁴⁾ reported the presence of maltol

derivatives in glucose pyrolyzates after decomposition at 250 °C for 30 minutes. The final results of GC-MS analysis of corn, acetate and hydroxypropyl starch pyrolyzates are shown in Table 1.

Acetone and aldehyde, of which Bryce et al. detected, were not discussed in this experiment. 2-Methylfuran, 5-methylfurfural, furfural and methyl furoate were detected. Mechanism for producing these compounds has recently been verified experimentally for thermal degradation products of glucose by Fagerson et al.⁵⁾ The presence of 3-ethylcyclopentene, methyl crotonate, phenyl propyl ether in corn starch pyrolyzates were estimated by the result of GC-MS. These compounds were also found in acetate and hydroxypropyl starch pyrolyzates, and moreover, from acetate starch pyrolyzates hexene, hexenone and ethylbenzene were identified. It is uncertain that these compounds are whether only from acetate starch or not. It must be studied using acetate starch with various substitution, but, they were not confirmed from corn starch and hydroxypropyl starch, however, they are characteristic in pyrolyzates of acetate starch. 2-Hydroxy-3-methyl-2-

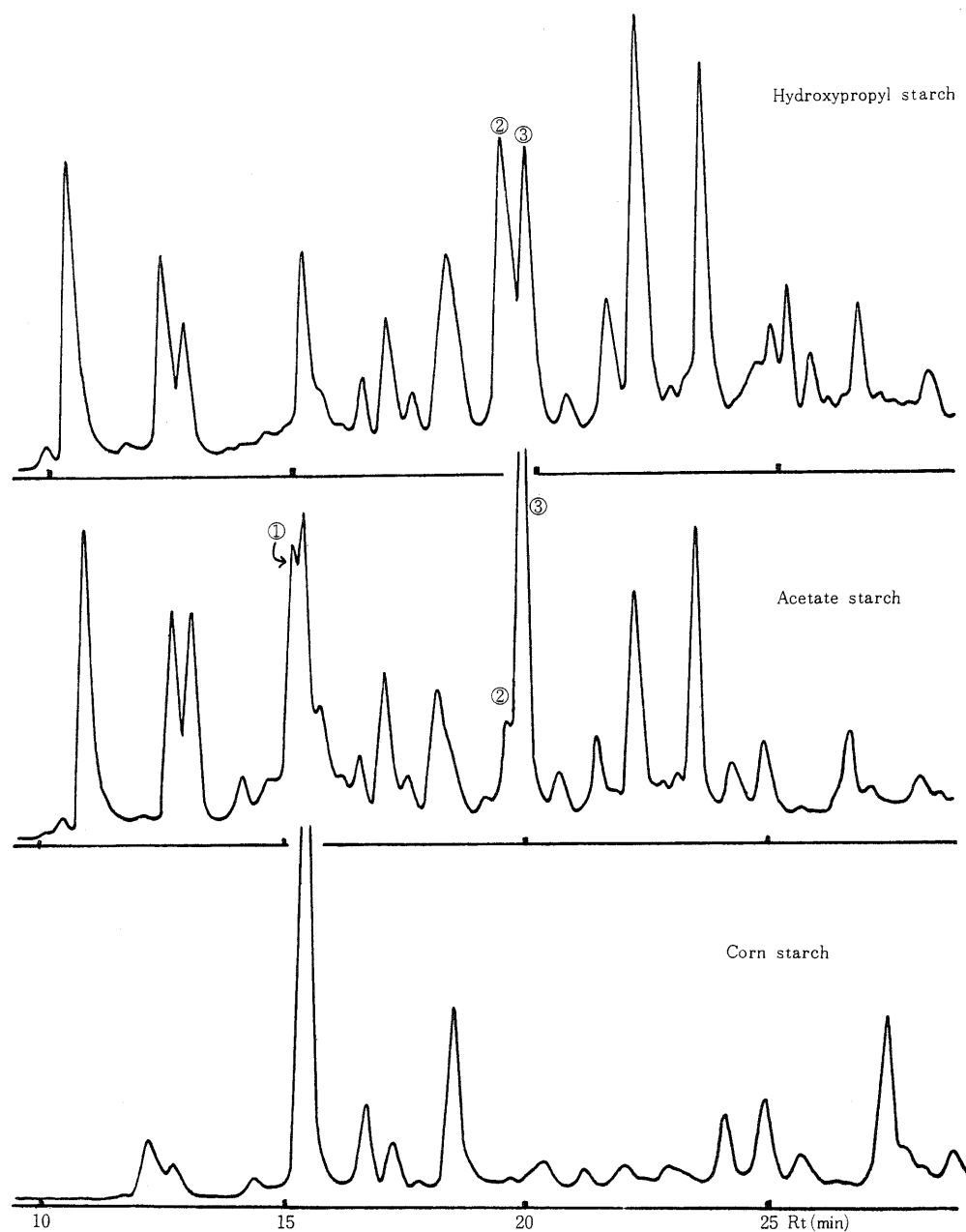
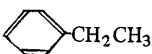
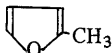


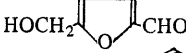
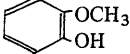

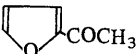
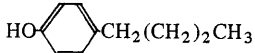
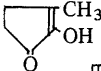
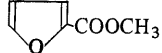
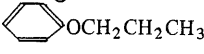
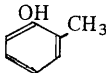


Fig.4 Gas chromatographic patterns of pyrolyzates

cyclopentene-1-one was detected from the pyrolyzates of acetate and hydroxypropyl starch, not from corn starch, but this compound was detected from aroma compounds of roasted starch by Shimizu et al.²⁾, so this compound did not seem to be characteristic for starch derivatives. Also, butyl phenol and 2-methyl furoate

were detected from hydroxypropyl starch pyrolyzates and both were confirmed in glucose decomposition products, so it does not seem that these are compounds only from starch decomposition products. But, these compounds were not identified from corn starch pyrolyzates which were dealt with the same treatment.

Table 1 Compounds found in pyrolyzates of corn starch and its derivatives

Compounds		Corn	Acetate	Ether*
3-Methyl-1-pentene	$\text{CH}_3\text{CH}_2\text{CH}(\text{CH}_3)\text{CH}=\text{CH}_2$	-	+	-
4-Methyl-3-pentene-2-one	$\text{CH}_3\text{COCH}=\text{C}(\text{CH}_3)\text{CH}_3$	-	+	-
Ethyl benzene		-	+	-
Methyl acetate	$\text{CH}_3\text{COOCH}_3$	-	+	+
2-Methyl furan		+	+	+
5-Methyl furfural		+	+	+
Furfural		+	+	+
5-Hydroxymethyl furfural		+	+	+
Guaiacol		-	+	+
3-Ethyl cyclopentene		+	+	+
cis-methyl crotonate	$\text{CH}_3\text{CH}=\text{CHCOOCH}_3$	+	+	+
2-Acetylfuran		-	+	+
p-Butyl phenol		-	-	+
n-Butyl crotonate	$\text{CH}_3\text{CH}=\text{CHCOOCH}_2(\text{CH}_2)_2\text{CH}_3$	-	+	+
Allyl crotonate	$\text{CH}_3\text{CH}=\text{CHCOOCH}_2\text{CH}=\text{CH}_2$	-	+	+
2-Hydroxy-3-methyl-2-cyclopentene-1-one		-	+	+
2-Methyl froate		-	-	+
Phenyl propyl ether		+	+	+
o-Cresol		-	+	+

* hydroxypropyl

Conclusion

Starch derivatives with low substitution are very difficult to distinguish raw starch from starch derivatives even by IR and NMR spectra. So, these starch derivatives were pyrolyzed. Thermal decomposition products were analyzed by GC and GC-MS. As a result, in addition to common compounds in starch and starch derivatives, hexene, hexenone, ethyl benzene, methyl acetate, guaiacol, 2-acetylfuran, n-butylcrotonate, allyl

crotonate, 2-hydroxy-3-methyl-2-cyclopentene-1-one, *o*-cresol and so on, in acetate starch (D.S. 0.1), and methyl acetate, guaiacol, 2-acetylfuran, *p*-butyl phenol, n-butyl crotonate, allyl crotonate, 2-hydroxy-3-methyl-2-cyclopentene-1-one, 2-methyl crotonate, *o*-cresol in hydroxypropyl starch (D.S. 1.0) were found. Also, the thermal decomposition products of acetate and hydroxypropyl starch were different from those of corn starch.

References

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