

THERMAL STABILITY AND DEGRADATION OF CHITOSAN MODIFIED BY SUCCINIC ANHYDRIDE

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ABSTRACT

Chitosan succinimide polymer was prepared and characterized using microanalysis and IR spectroscopy. Thermal analysis of the formed polymer showed a decrease in stability in comparison with chitosan. Thermal degradation of the polymer was carried out and the degradation products were identified by GC-MS technique. Accordingly, it seems that the mechanism of the degradation of chitosan succinimide is characterized by elimination of low-molecular weight radicals. Combination of these radicals and random scission mechanism along the backbone chain are the main source of the degradation products.

INTRODUCTION

It was found that chitosan at high temperature in air undergo degradation [Austin (1975) and Kurila(1998)]. Thermal analysis with a derivatograph showed that this polymer cannot withstand temperature higher than 200 - 220°C [Ravi Kumer (2000) and Mahavinio et al. (2004)]. It was reported the reaction of chitosan with same cyclic oxygenated compounds with the aim of synthesis of same new chitosan derivatives [Tirkistani (1998) and Tirkistani (1998)]. Thermal stabilities of these derivatives has been studied.

In this paper, thermal stability of chitosan succinimide polymer is reported by thermogravimetric analysis. Thermal degradation of the modified polymer is studied using GC-MS apparatus.

EXPERIMENTAL

Materials:

Chitosan (Aldrich Chemical Co., Inc.) was used without further purification. Succinic anhydride (BDH Chemical Ltd.) was purified by standard procedure. All other chemicals and solvent were purified by standard procedure.

Preparation of the Polymer:

An equimolar ratio of chitosan and succinic anhydride were fused for 30 min., then 50 ml of glacial acetic acid was added to the reaction mixture and refluxed for 2h. The excess acetic acid was removed by distillation. The reaction mixture was cooled to room temperature and washed with diethyl ether and ethanol to remove the unreacted succinic anhydride. The formed polymer was filtered off and dried in an oven at 40°C for several days.

Analytical Techniques:

Infrared Spectroscopy (IR):

Spectra of the polymer samples were recorded on a Pye Unicam SP 2000 spectrometry in the form of KBr discs.

Microanalysis:

Elemental analysis of the modified polymer sample was performed by microanalysis unit at King Abdel Azzez University.

Thermal Gravimetric Analysis (TG):

TG measurements were made with a Mettler TG 3000 apparatus. Finely powdered (~ 10 mg) samples were heated at 10° / min in a dynamic nitrogen atmosphere (30 ml / min), the sample holder was boat-shaped, 10 mm × 5 mm × 2.5 mm deep and the temperature measuring thermocouple was placed 1 mm from the sample holder.

TG was also used for the determination of rates of degradation of the polymer in the initial stages of decomposition. The activation energies were calculated by application of the Arrhenius equation.

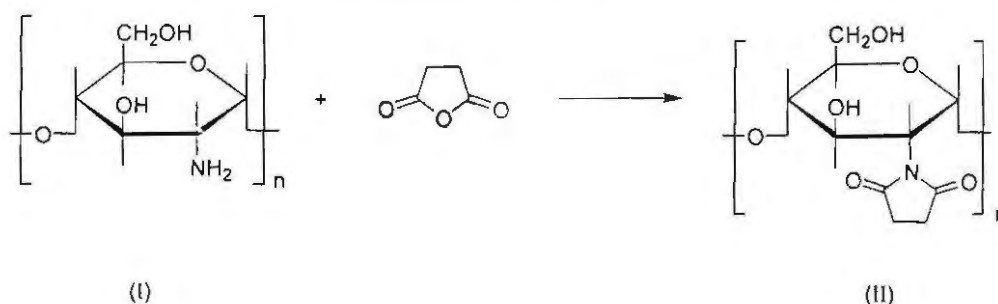
Thermal degradation of the polymer:

Samples of ~50 mg were heated under vacuum from ambient temperature to 500°C. The volatile degradation products were collected for qualitative analysis by using GC-MS technique. A Saturn GC 3400 with a fused quartz capillary column of 30 m × 0.25 mm coated with methylsilicon, under programmed heating condition from 40 to 200 °C was used for the identification of the condensable degradation products. The GC is interfaced with a Varian mass spectrometer.

RESULT AND DISCUSSION**Characterization of Chitosan Succinimide Polymer:**

The IR spectrum of chitosan shows a broad band at 3423 cm^{-1} due to OH and NH_2 groups. The bands at 1655 and 1321 cm^{-1} due to the amino group. There are bands at 1458, 1423, 1379 and 1078 cm^{-1} due to O-C-O group. These bands are in good agreement with the IR spectrum of chitosan reported [Muzzarella et al.(1972)]. Microanalysis of $\text{C}_6\text{H}_{11}\text{O}_4\text{N}$ (calcd. C, 44.7; H, 6.8; N, 8.7 %. Found C, 44.62; H, 9.4; N, 8.67%).

The reaction of chitosan I with succinic anhydride gives the corresponding chitosan succinimide polymer II.



The IR spectrum of chitosan succinimide polymer II shows a band at 1720 cm^{-1} attributed to the carbonyl group. Also, the IR spectrum of the modified polymer shows the absence of the anhydride bands at 1800 and 1760 cm^{-1} , indicating the involvement of amino group in modification of chitosan. Microanalysis of II ($\text{C}_{10}\text{H}_{13}\text{O}_6\text{N}$) (calcd. C, 49.4; H, 5.3; N, 5.8%. Found C, 49.61; H, 5.26; N, 6.02%).

Thermal Methods of Analysis**Thermogravimetry (TG):**

TG curve of chitosan is shown in Figure 1. There are two degradation stages in chitosan polymer. In the first stage, weight loss starts at ~ 220 °C and continues to 320 °C with 50% weight loss. The maximum rate of weight loss, shown by derivative equipment associated with TG apparatus, occurs at 295 °C. The second stage reaches a maximum at ~ 470 °C with a weight loss percentage of $\sim 40\%$.

There are two degradation stages in the chitosan succinimide polymer as shown in Figure 2. The first stage starts at ~ 180 °C with a weight loss percentage of $\sim 40\%$. The maximum rate of weight loss percentage of $\sim 50\%$. TG curves reveal that the thermal stability of chitosan polymer is greater than chitosan succinimide polymer.

The effective activation energies of the thermal degradation of chitosan and chitosan succinimide polymers were determined from the temperature dependence of the chain rupture rate. The rate constant of the thermal degradation plotted according to the Arrhenius relationship (Figure 3). The activation energies of degradation of chitosan and chitosan succinimide polymers were found to be 52.2 and 34.8 kJ/mole, respectively. It is clear that the activation energies are in the same order of the stabilities.

Thermal Degradation of Chitosan Succinimide Polymer:

50 mg of chitosan succinimide polymer was heated under vacuum from ambient temperature to 500 °C. The degradation products were injected into the GC-MS apparatus. Figure 4 shows the GC trace of the thermal degradation products of polymer sample. Table 1 represents the degradation products which were identified by mass spectroscopic apparatus. Some of the peaks could not be identified because of their small size or due to the unclear mass spectra. From Figure 4, peak 3 at retention time 8.51 min having m/e 99 as shown in the mass spectrum, corresponding to 2,5-diketo-tetrahydropyrrole III. Peak 6 at 9.59 min having m/e 115 due to 2,5-diketo-1-hydroxytetrahydropyrrole IV.

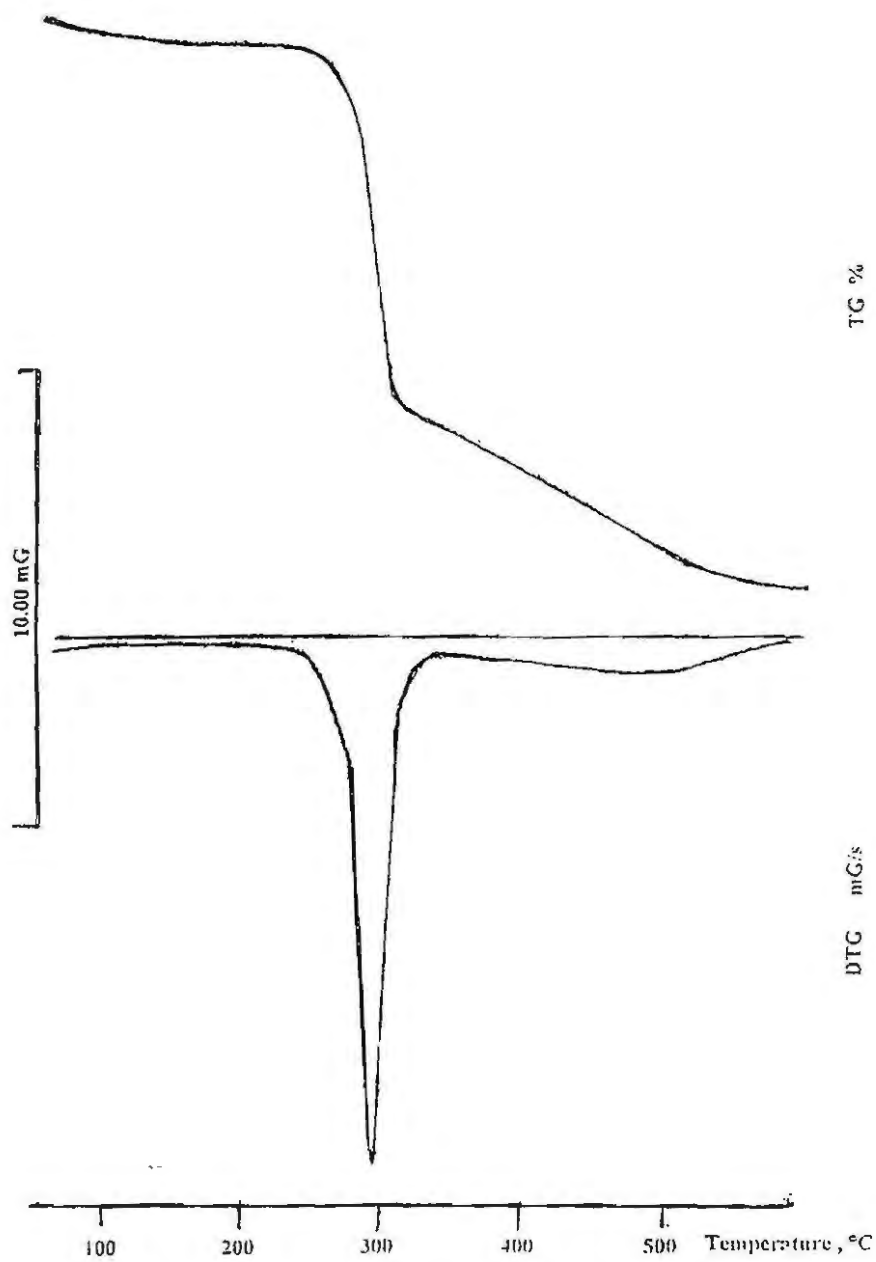


Figure 1: TG curve of chitosan

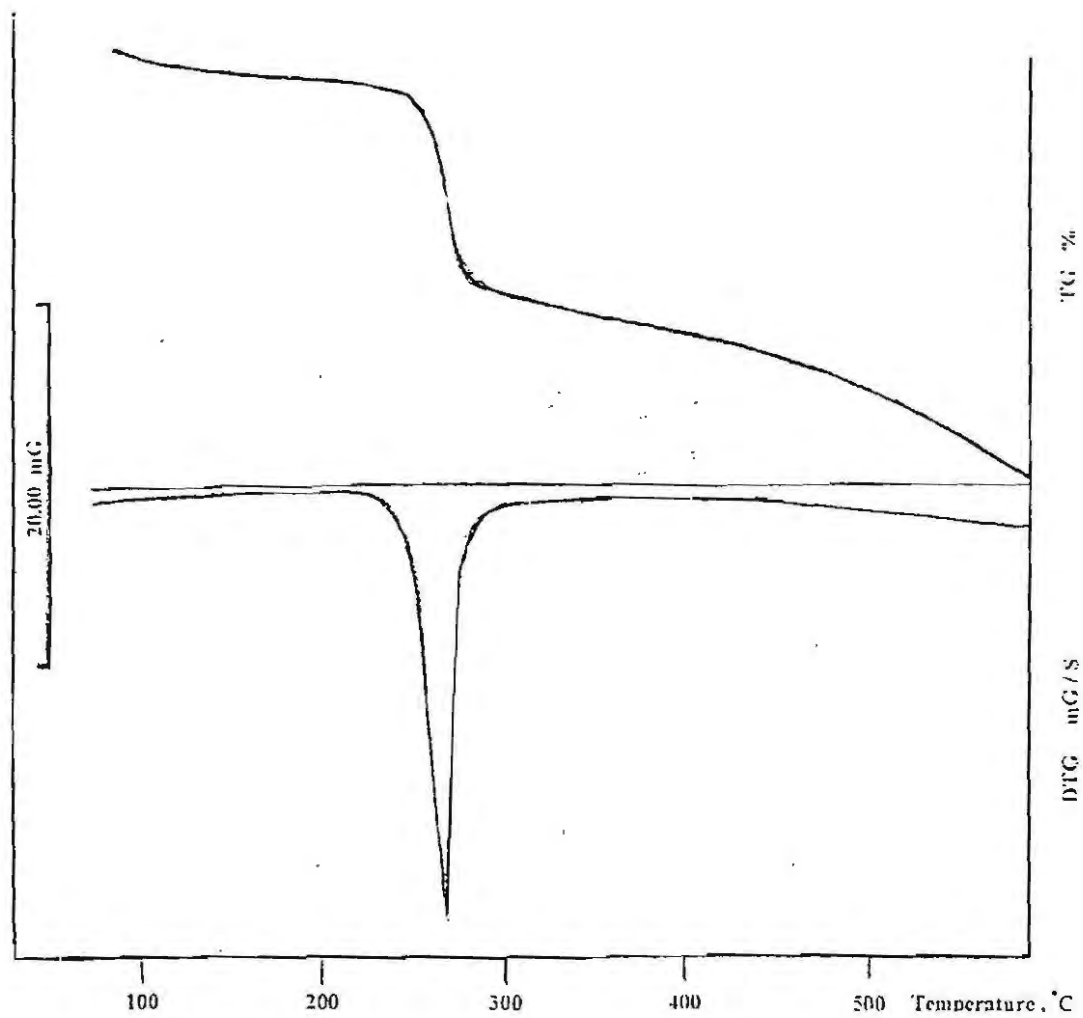


Figure 2: TG of chitosan succinimide polymer

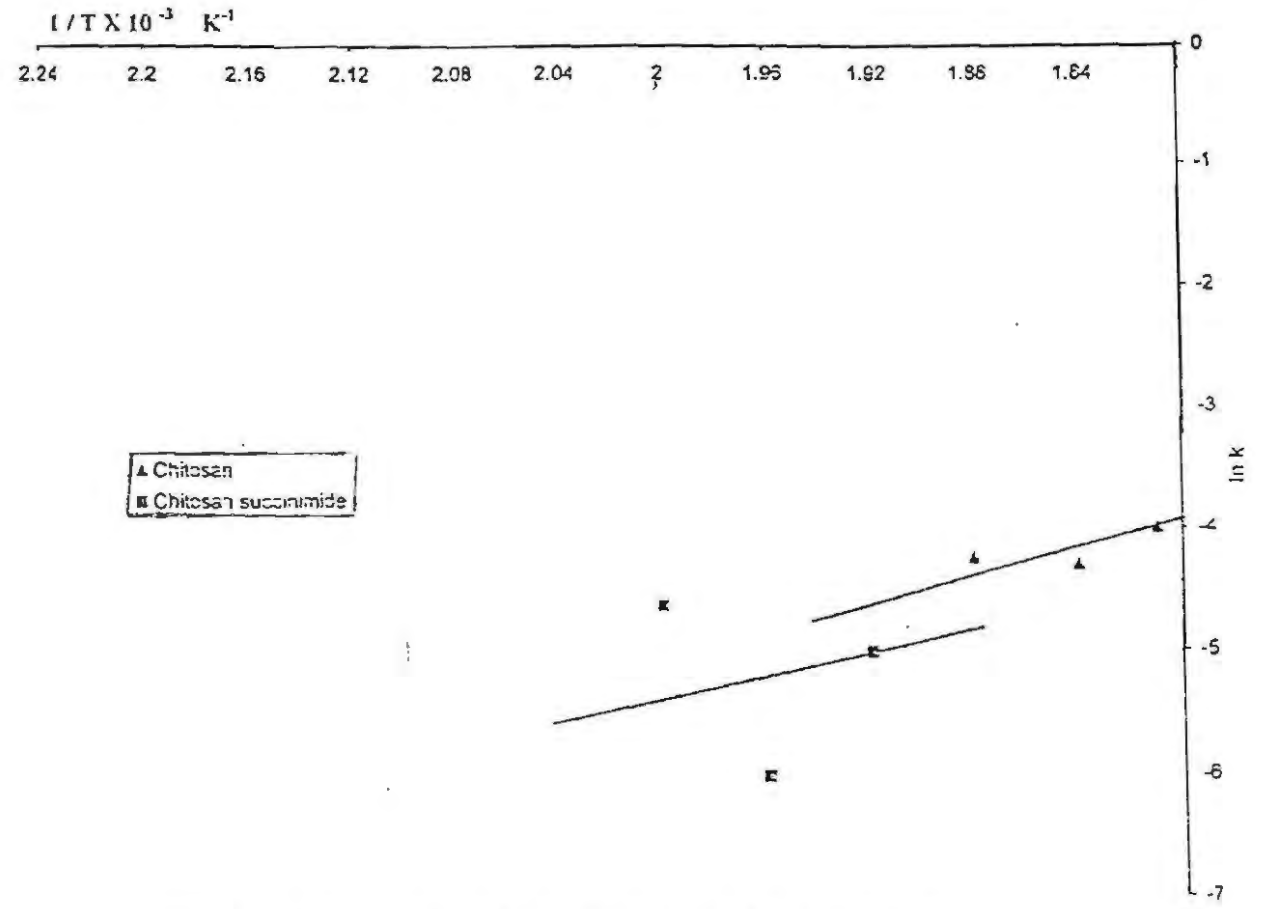


Figure 3: Arrhenius plots of the rate constants of degradation of chitosan and chitosan succinimide polymers

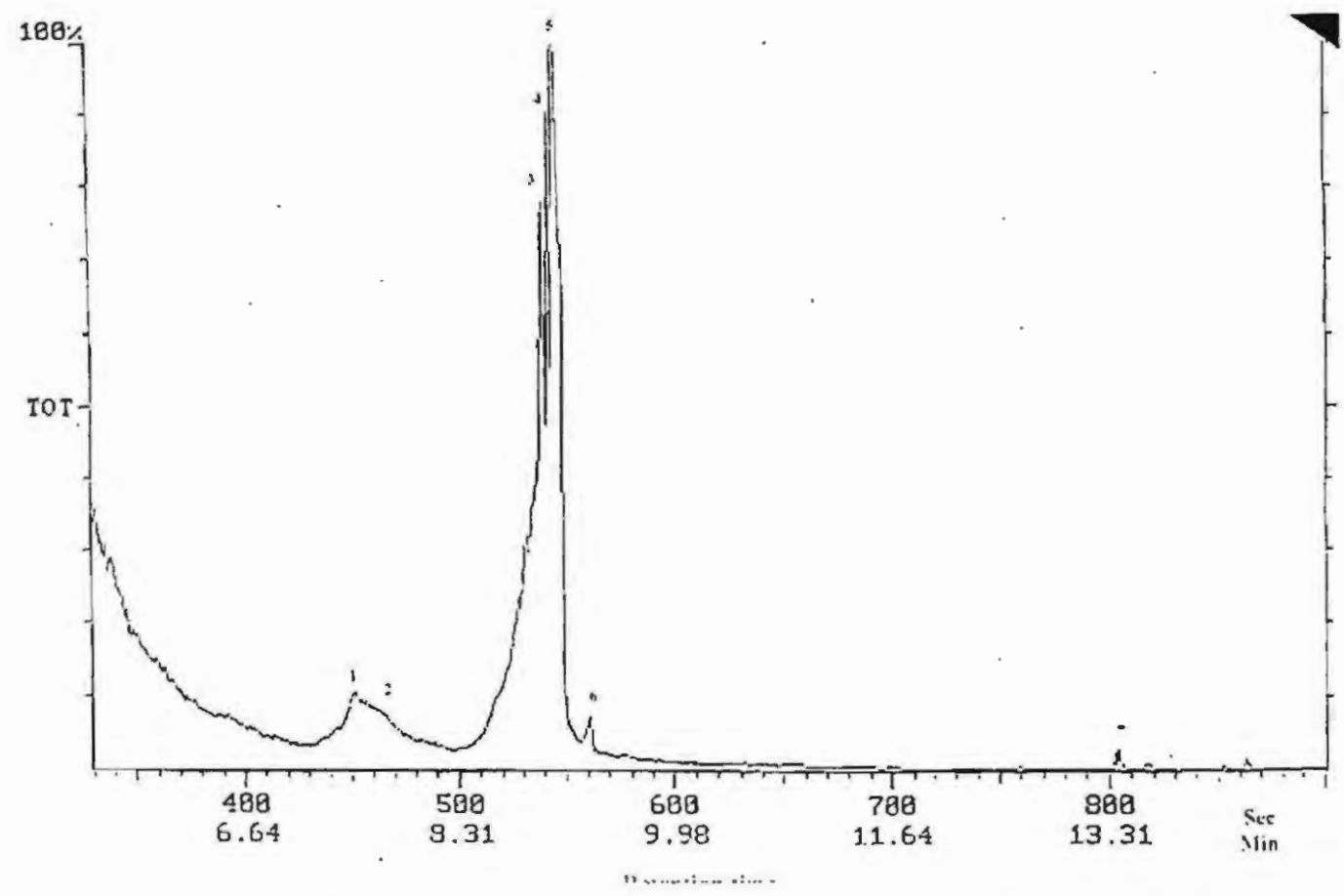
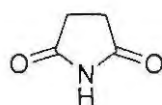


Figure 4: GC curve of the degradation products of chitosan succinimide polymer

Table (1): GC-MS of the degradation products of chitosan succinimide polymer.

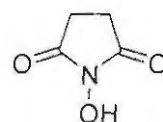
Peak No.	Retention Time, min	Major MS Fragment	Suggested Structures (most probable)
1	7.49	84, 61, 47	5-Hydroxy-1,3-pentadiene
2	7.69	95, 70, 47	Cyclohex-1-en-6-ol
3	8.51	99, 83, 61, 47	2,5-Diketotetrahydropyrrole
4	8.70	102, 83, 61, 47	4,5-Dihydropent-1-ene
5	9.44	112, 83, 56, 42	6-Hydroxy-2,4-hexadienal
6	9.59	115, 99, 86, 48	2,5-Diketo-1-hydroxytetrahydropyrrole
7	13.38	148, 132, 114, 61, 47	3,5,6-Trihydroxyhexanal



(III)

Peak 3
(m/e = 99)

2,5-Diketotetrahydropyrrole

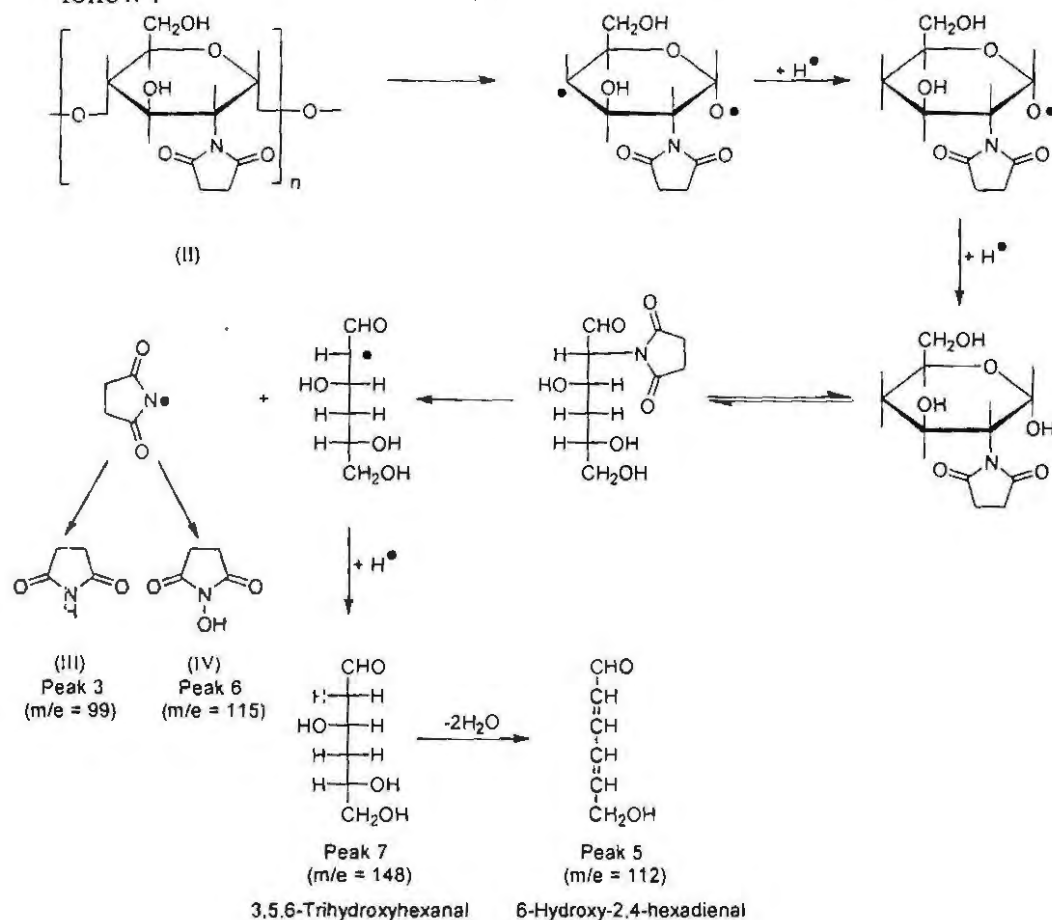


(IV)

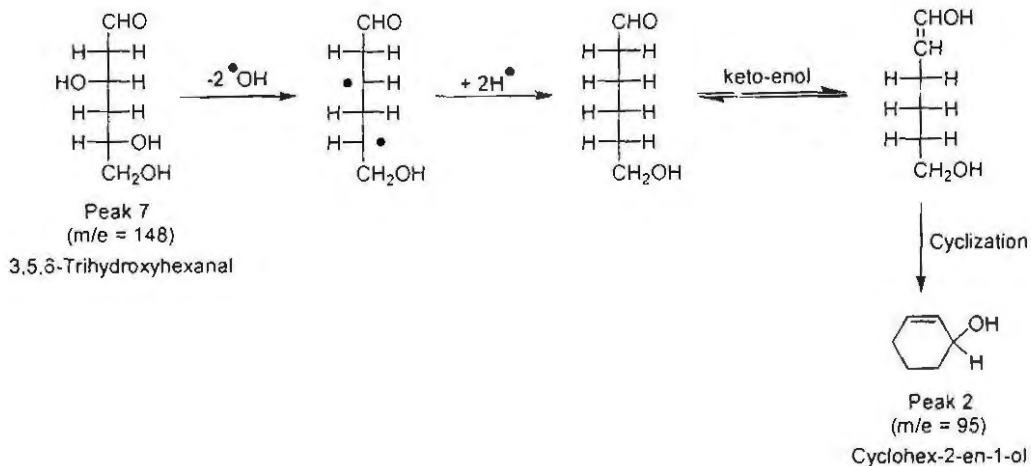
Peak 6
(m/e = 115)

2,5-Diketo-1-hydroxytetrahydropyrrole

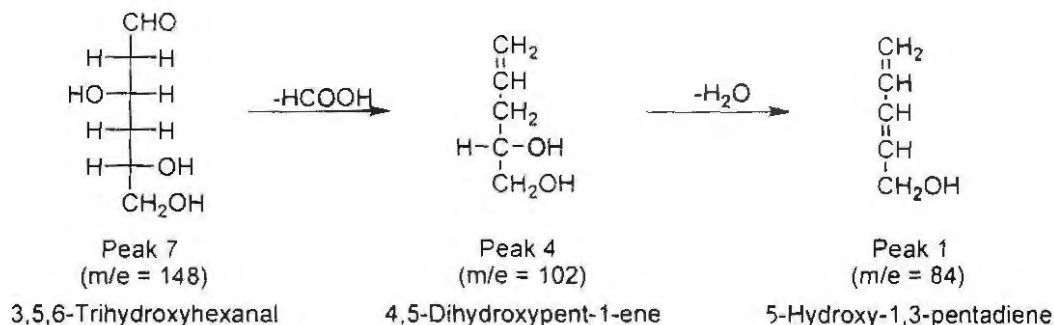
The mechanism of formation of these two compounds is represented as follow :



The aldehydic compound, namely. 3,5,6-trihydroxyhexanal was confirmed by mass spectroscopy. There is a composite peak having retention time between 8.51–9.59 min in GC curve of the degradation products of chitosan succinimide polymer, shown in Figure 4. 3,5,6-Trihydroxyhexanal may lose two molecules of water forming 6-hydroxy 2,4-hexadienal (peak 5). Cyclohex-2-en-1-ol (peak 2) was also obtained from 3,5,6-trihydroxyhexanal (peak 7) according to the following mechanism :



Also, 3,5,6-trihydroxyhexanal may lose formic acid to give 4,5-dihydroxypent-1-ene (peak 4) followed by losing water molecule to produce 5-hydroxy-1,3-pentadiene. The mechanism of formation of these two compounds may be represented as follows :



It seems that the mechanism of degradation of chitosan succinimide is characterized by elimination of low-molecular weight radicals, rather than monomer formation in the early stage of degradation, followed by random scission mechanism along the backbone chain. It seems that the break down of chitosan succinimide occurs mainly in the C-O bond producing radicals. These radicals abstract $\text{H}\cdot$ or $\cdot\text{OH}$ to produce these degradation products.

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المخلص العربي

هذا البحث يتناول دراسة التحليل الحرارى لبولى سكسيناميد الكيتوسان ومقارنتها بالكيتوسان كذلك استخدام مطياف الكتلة المتصل بالكروماتوجراف للتعرف على نواتج التكسير الحرارى للبوليمر المتكون ولقد اقترحت ميكانيكية لهذا التكسير اساسها تكوين شقوق ذات وزن جزيئى صغير سرعان ما تتحد لتكوين هذه النواتج كذلك تم قياس طاقة التنشيط لتكسير البولمرات المحضرة باستخدام معادلة أرهينيوس ووجد أنها تساوى ٣٤,٨ كيلو جول/مول.