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Microwave-promoted hydrolysis of plant seed gums on alumina support

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Abstract—Using a catalytic amount of potassium persulfate (1.48×10^{-4} M), eight different seed gums were fully hydrolyzed on alumina support under microwave irradiation. The hydrolysis time varied between 1.33 and 2.33 min depending upon the seed gum structure. The used solid support could be easily separated from the hydrolyzates and recycled. However, under microwave field in an aqueous medium, the same amount of persulfate was unable to hydrolyze the seed gums. Solid-supported microwave hydrolysis has been compared with the microwave-enhanced aqueous hydrolysis (using $K_2S_2O_8$ or 0.1 N H_2SO_4) and also with the conventional hydrolysis procedures.

Keywords: Seed gums; Microwave irradiation; Potassium persulfate; Alumina

1. Introduction

Constituent monosaccharides of any polysaccharide material are detected and isolated by its complete hydrolysis, followed by chromatographic separation of the resulting sugars. Polysaccharides require hydrolysis under the mildest conditions[1] to avoid any possible degradation of the sugars. Conventionally, complete hydrolysis of a polysaccharide to its constituent monosaccharides involves strong acids like trifluoroacetic acid[2] or sufficiently prolonged hydrolysis time.[3]

As microwave (mw) irradiation[4–8] is emerging as an efficient source of thermal energy, and constitutes a very original procedure for the heating of materials, in ways different from the classical ones. Microwaves can heat reactants selectively, directly, and without thermal inertia and heat exchange with the medium.[9] Several reports on hydrolysis reactions under microwave irradiation are available. Starch,[10] sucrose,[11] colominic acid,[12] polymide 6,[13] proteins,[14] and chitosan[15] have been hydrolyzed with acids in aqueous media under microwave irradiation. Effect of inorganic salts on the hydrolysis of starch[16] and chitosan[15] was also studied. Our group has reported[17] microwave-promoted hydrolysis of the seed gums in an aqueous medium under mild, acidic conditions. In the present study, we for the first time report on the microwave-accelerated complete hydrolysis of the seed gums on an alumina support using a catalytic amount of potassium persulfate. Eight different seed gums like *Ipomoea quamoclit* (IQ),[17] *Cassia abbreviata* (CA),[18] *Cassia javanica* (CJ),[18] *Cassia reticulata* (CR),[18] *Ipomoea dasyperma* (ID),[19] *Ipomoea hedracea* (IH),[20] *Ipomoea campanulata* (IC),[21] and *Cyamopsis tetragonolobus* (guar gum; GG)[22] were used in the study.

2. Results and discussion

The complete hydrolysis of *Cassia marginata* on alumina support using potassium persulfate was studied under conditions of microwave irradiation. Hydrolysis of the seed gum was monitored at different exposure times and persulfate concentrations at 100% microwave power (Tables 1 and 2). Minimum persulfate concentration

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Table 1. Hydrolysis of CM gum on Al_2O_3 support under 100% microwave power at different exposure times with fixed persulfate concentration[a]

Sample no.	Solid-supported microwave hydrolysis						Hydrolysis with 2 N H_2SO_4 for 48 h
	Without HQ			With HQ (20 mg)			
	Exposure (s)	pH after exposure	Cu_2O[b] (mg)	Exposure (s)	pH after exposure	Cu_2O[b] (mg)	Cu_2O[b] (mg)
1	20	6	—	20	6	—	68
2	40	4	—	40	4	—	
3	60	2	50	60	3	—	
4	80	2	65	80	3	—	
5	100	2	65	100	3	—	

[a] Hydrolysis of the CM gum (80 mg) at Al_2O_3 (200 mg) under 100% microwave power at different exposure time with 1.48×10^{-4} M $K_2S_2O_8$.
[b] Weight of Cu_2O obtained on gravimetric estimation of the hydrolyzates.

Table 2. Hydrolysis of CM gum on Al_2O_3 support with different persulfate concentrations and 100% microwave power and hydrolysis in an aqueous solution and 100% microwave power[a]

Sample no.	Solid-supported microwave hydrolysis			Aqueous microwave hydrolysis	
	$K_2S_2O_8$	pH after exposure	Cu_2O[b] (mg)	pH after exposure	Cu_2O[b] (mg)
1	9.25×10^{-6} M	7	—	4	—
2	1.85×10^{-5} M	6	—	3	—
3	3.7×10^{-5} M	4	30	2	—
4	7.39×10^{-5} M	2	40	2	—
5	11.09×10^{-5} M	2	55	2	—
6	1.48×10^{-4} M	2	66	2	—
7	1.85×10^{-4} M	2	66	2	2.01
8	2.22×10^{-4} M	2	66	2	8.85

[a] Hydrolysis of CM gum (80 mg) with different persulfate concentration at Al_2O_3 (200 mg); in 25 mL H_2O at 100% microwave power and 1.33 min exposure.
[b] Weight of Cu_2O obtained on gravimetric estimation of the hydrolyzates.

and time required for the complete hydrolysis of *C. marginata* at 100% microwave power were 1.48×10^{-4} M and 1.33 min, respectively. Using potassium persulfate (1.48×10^{-4} M) at 100% microwave power, all the seed gums under study could be fully hydrolyzed on alumina support between 1.33 and 2.33 min, and the results were found to be reproducible. Complete hydrolysis time for all the seed gums are recorded in Table 3. The use of the recovered alumina as a solid support in the hydrolysis experiments gave the same results as before (Table 3). Paper chromatography (solvent A) of the complete hydrolyzates of all the seed gums revealed the presence of galactose (R_f 0.15) and mannose (R_f 0.21). Constituent monosaccharides from the hydrolyzates (separated by column chromatography) were identified to be D-galactose and D-mannose by their melting points, co-chromatography with authentic samples and by preparation of derivatives:[21] D-Galactose, mp 163 °C, $[\alpha]_D^{30}$ +80 (water); D-galactose phenylhydrazone, mp 153 °C; D-mannose, mp 131 °C, $[\alpha]_D^{30}$ +14 (water); D-mannose phenylhydrazone, mp 198 °C.

No hydrolysis was observed when aqueous solutions of the seed gums were exposed to microwaves in the presence of 1.48×10^{-4} M persulfate, indicating that the reagents immobilized on the porous solid support have advantages over the conventional solution-phase reaction as shown by enhanced reaction rates, and higher yields than those reported in other solid-supported reactions.[7] In an aqueous medium, even with 2.22×10^{-4} M persulfate, only partial hydrolysis could be observed (Table 2).

When the same seed gums were hydrolyzed with 0.1 N sulfuric acid (under aqueous conditions) under 100% microwave power, complete hydrolysis was observed between 1.45 and 7.66 min (Table 2). All the seed gums[17–23] under study possess a linear chain of β-(1→4)-linked D-mannopyranosyl units to which D-galactopyranosyl side chains are attached through an α-(1→6) linkage. It is clear that with the increase in β linkages hydrolysis time increased as expected. Due to the peripheral position[17–23] of the α-linked galactopyranosyl units in the seed gums and the weaker nature of the α linkages compared to β, seed gums having higher mannose content (β linkages) had higher hydrolysis time. Hydrolysis of the seed gums by conventional method (2 N H_2SO_4, 48 h) also furnished the same monosaccharides. Identities and configurations of the monosaccharides were confirmed by co-chromatography with authentic samples and the preparation of derivatives.

In a control experiment, gravimetric estimation of a known mixture of galactose and mannose, before and after microwave exposure, gave the same results, revealing that they do not degrade under the microwave conditions (Table 4). Gravimetric estimation of monosaccharides in the complete hydrolyzates of the seed gums hydrolyzed by the conventional method and under microwaves gave same results, showing their