

Appendices

Table 1. Conditions for purification of starches and yield (%).

Starch code	Solvent	Reaction time (day)	Temperature (°C)	Yield (%)
Hylon VII	DMSO	3	20	96.9
Hylon V	DMSO	3	20	96.2
Abrastarch	DMSO	3	20	99.0
Amioca	DMSO	3	20	100

Table 2. Conditions for alkali treatment of starches.

Sample No	Starch code	Starch weight (g)	NaOH (M)	Reaction time (h)
1	Hylon VII	1.08	0.05	16
2	Abrastarch	1.08	0.05	16
3	HylonVII	1.62	0.1	16
4	Hylon V	1.62	0.1	16
5	Abrastarch	1.62	0.1	16
6	Amioca	1.62	0.1	16
7	Hylon VII	2.70	0.5	16
8	Hylon V	2.70	0.5	16
9	Abrastarch	2.70	0.5	16
10	Amioca	2.70	0.5	16
11	Hylon VII	5.40	1.0	16
12	Hylon V	5.40	1.0	16
13	Abrastarch	5.40	1.0	16
14	Amioca	5.40	1.0	16
15	Hylon VII	1.62	1.5	16
16	Hylon V	1.62	1.5	16
17	Abrastarch	1.62	1.5	16
18	Amioca	1.62	1.5	16
19	Hylon VII	5.40	2.0	16
20	Hylon V	5.40	2.0	16
21	Abrastarch	5.40	2.0	16
22	Amioca	5.40	2.0	16
23	Hylon VII	6.75	2.5	16
24	Hylon V	6.75	2.5	16
25	Abrastarch	6.75	2.5	16
26	Amioca	6.75	2.5	16
27	Hylon VII	8.10	3.0	16
28	HylonV	8.10	3.0	16
29	Abrastarch	8.10	3.0	16
30	Amioca	8.10	3.0	16
31	Hylon VII	10.8	4.0	16
32	Hylon V	10.8	4.0	16
33	Abrastarch	10.8	4.0	16
34	Amioca	10.8	4.0	16
35	Abrastarch	0.54	1.0	88
36	Abrastarch	0.81	1.5	88

**Project
title**

Starch granule deconstruction and modification under
homogeneous aqueous conditions

**MAFF
project code**

NF0510

37	Abrastarch	1.08	2.0	88
38	Hylon VII	1.62	3.0	72
39	Hylon V	1.62	3.0	72
40	Hylon V	13.51	5.0	40

Table 3. Reaction conditions for starch modification

Reaction No	Starch weight (g)	NaOH (M)	Catalyst	Acyl chloride	Reagent (mol)	Time (h)	Temperature (°C)
M1	6.75	2.5	None	Acetyl	0.5	1	RT
M2	6.75	2.5	DMAP	Acetyl	0.5	1	RT
M3	6.75	2.5	TEA	Acetyl	0.5	1	RT
M4	6.75	2.5	Pyridine	Acetyl	0.5	1	RT
M5	6.75	2.5	DIEA	Acetyl	0.5	1	RT
M6	6.75	2.5	None	Butyryl	0.5	1	RT
M7	6.75	2.5	Pyridine	Butyryl	0.5	1	RT
M8	6.75	2.5	TEA	Butyryl	0.5	1	RT
M9	10.8	4.0	None	Butyryl	0.5	1	RT
M10	6.75	2.5	None	Hexanoyl	0.5	1	RT
M11	6.75	2.5	Pyridine	Hexanoyl	0.5	1	RT
M12	6.75	2.5	TEA	Hexanoyl	0.5	1	RT
M13	6.75	2.5	DIEA	Hexanoyl	0.5	1	RT
M14	6.75	2.5	None	Heptanoyl	0.5	1	RT
M15	6.75	2.5	Pyridine	Heptanoyl	0.5	1	RT
M16	6.75	2.5	TEA	Heptanoyl	0.5	1	RT
M17	6.75	2.5	DIEA	Heptanoyl	0.5	1	RT
M18	6.75	2.5	None	Octanoyl	0.5	1	RT
M19	6.75	2.5	Pyridine	Octanoyl	0.5	1	RT
M20	6.75	2.5	TEA	Octanoyl	0.5	1	RT
M21	6.75	2.5	DIEA	Octanoyl	0.5	1	RT
M22	10.8	4.0	None	Octanoyl	0.5	1	RT
M23	6.75	2.5	None	Nonanoyl	0.5	1	RT
M24	6.75	2.5	Pyridine	Nonanoyl	0.5	1	RT
M25	6.75	2.5	TEA	Nonanoyl	0.5	1	RT
M26	6.75	2.5	DIEA	Nonanoyl	0.5	1	RT
M27	6.75	2.5	None	Decanoyl	0.5	1	RT
M28	6.75	2.5	None	Lauroyl	0.5	1	RT
M29	6.75	2.5	Pyridine	Lauroyl	0.5	1	RT
M30	6.75	2.5	TEA	Lauroyl	0.5	1	RT
M31	6.75	2.5	None	Palmitoyl	0.5	1	RT
M32	6.75	2.5	None	Stearoyl	0.5	1	RT
M33	6.75	2.5	Pyridine	Stearoyl	0.5	1	RT
M34	6.75	2.5	TEA	Stearoyl	0.5	1	RT
M35	6.75	2.5	DIEA	Stearoyl	0.5	1	RT
M36	10.8	4.0	None	Stearoyl	0.5	1	RT
M37	6.75	2.5	None	Lauroyl	1.5	1	RT
M38	6.75	2.5	None	Lauroyl	1.5	1	40
M39	6.75	2.5	None	Heptanoyl	3.0	1	RT
M40	6.75	2.5	None	Octanoyl	3.0	1	RT

M41	6.75	2.5	Pyridine	Octanoyl	3.0	1	RT
M42	6.75	2.5	TEA	Octanoyl	3.0	1	RT
M43	6.75	2.5	DIEA	Octanoyl	3.0	1	RT
M44	6.75	2.5	None	Octanoyl	3.0	4	RT
M45	6.75	2.5	None	Nonanoyl	3.0	1	RT
M46	6.75	2.5	None	Decanoyl	3.0	1	RT
M47	6.75	2.5	None	Decanoyl	3.0	4	RT
M48	6.75	2.5	None	Lauroyl	3.0	1	RT
M49	6.75	2.5	Pyridine	Lauroyl	3.0	1	RT
M50	6.75	2.5	TEA	Lauroyl	3.0	1	RT
M51	6.75	2.5	DIEA	Lauroyl	3.0	1	RT
M52	6.75	2.5	None	Lauroyl	3.0	1	40
M53	6.75	2.5	None	Lauroyl	3.0	4	RT

Hylon VII was used in the reactions. * = no product recovered; † = no carbonyl signal observed in the range 1740–1750 cm⁻¹

Table 4. Calculated DS-values based on elemental analysis, and yield of acylated starches

Acyl chloride	Starch code	Theoretical C %	Measured C %	Theoretical DS-value	Actual DS-value	FT-IR (cm ⁻¹)	Yield (%)
Hexanoyl	Hylon VII	51.18	46.562	0.5	0.13	1749	74
	Hylon V	51.18	47.078	0.5	0.17	1749	74
	Abrastarch	51.18	45.931	0.5	0.12	1749	75
	Amioca	51.18	46.785	0.5	0.15	1749	75
Heptanoyl	Hylon VII	52.29	48.964	0.5	0.25	1749	78
	Hylon V	52.29	48.823	0.5	0.24	1749	79
	Abrastarch	52.29	49.566	0.5	0.29	1749	78
	Amioca	52.29	49.586	0.5	0.29	1749	76
Octanoyl	Hylon VII	53.33	49.054	0.5	0.23	1749	78
	Hylon V	53.33	49.547	0.5	0.27	1749	79
	Abrastarch	53.33	49.365	0.5	0.24	1749	76
	Amioca	53.33	47.918	0.5	0.16	1749	72
Nonanoyl	Hylon VII	54.31	50.547	0.5	0.27	1749	74
	Hylon V	54.31	50.404	0.5	0.26	1749	74
	Abrastarch	54.31	49.427	0.5	0.21	1749	74
	Amioca	54.31	49.969	0.5	0.24	1749	72
Decanoyl	Hylon VII	55.23	46.355	0.5	0.10	1749	67
	Hylon V	55.23	46.111	0.5	0.10	1749	66
	Abrastarch	55.23	45.669	0.5	0.10	1749	67
	Amioca	55.23	45.922	0.5	0.10	1749	63

Table 5. Modification of Hylon VII in buffered solutions

Sample No	Starch weight (g)	Buffer	Catalyst	Octanoyl chloride (mol)	FT-IR (cm ⁻¹)	Recovery (%)
1	5.0	Aldrich buffer (pH 10)	None	3.0	—	—
2	1.77	1M NaC ₆ H ₅ SO ₄ /1M NaOH	None	3.0	—	—
3	1.77	1M NaC ₆ H ₅ SO ₄ /1M NaOH	Pyridine	3.0	1749	34
4	3.54	1M NaC ₆ H ₅ SO ₄ /1M NaOH	Pyridine	1.5	1754	51
5	7.08	1M NaC ₆ H ₅ SO ₄ /1M NaOH	Pyridine	0.75	1759	64
6	3.54	2M NaC ₆ H ₅ SO ₄ /2M NaOH	Pyridine	1.5	1754	56
7	3.54	1M NaC ₆ H ₅ SO ₄ /2M NaOH	Pyridine	3.0	1738	34
8	3.54	1M NaC ₆ H ₅ SO ₄ /2M NaOH	DMAP	3.0	1738	38
9	5.39	3M NaC ₆ H ₅ SO ₄ /3M NaOH	Pyridine	3.0	1754	67
10	1.73	0.25M Na ₂ B ₆ O ₇ /1M NaOH	None	3.0	—	—
11	1.73	0.25M Na ₂ B ₆ O ₇ /1M NaOH	Pyridine	3.0	—	—
12	1.16	0.5M NaHCO ₃ /1M NaOH	None	3.0	—	—
13	1.16	0.5M NaHCO ₃ /1M NaOH	Pyridine	3.0	—	—
14	1.45	0.5M Na ₂ HPO ₄ /1M NaOH	Pyridine	3.0	—	—

Table 6. Modification of Hylon VII in water/solvent system

Reaction No	Starch weight (g)	Alkaline concentration	Acyl chloride	Reagent (mol)	FT-IR (cm ⁻¹)
1	1.0	3.0 M NaOH	Acryloyl	3.0	—
2	1.0	5.0 M KOH	Acryloyl	3.0	—
3	1.0	3.0 M NaOH	Methacryloyl	3.0	—
4	1.0	3.0 M NaOH	Lauroyl	0.5	—

Table 7. The molecular mass distribution of native and treated starches.

Hylon VII	MW ₁	MW ₂	MW ₃
Control	(2.412 +/- 0.079)×10 ⁷ (3%)	(2.907 +/- 0.154)×10 ⁵ (5%)	
Control/DMSO	(1.675 +/- 0.060)×10 ⁷ (3%)	(8.594 +/- 0.398)×10 ⁵ (4%)	
2.5 M NaOH/DMSO	(2.046 +/- 0.075)×10 ⁷ (3%)	(7.239 +/- 0.329)×10 ⁵ (4%)	
2.5 M NaOH	(2.663 +/- 0.085)×10 ⁷ (3%)	(4.847 +/- 0.180)×10 ⁵ (3%)	(2.57 +/- 0.195)×10 ⁵ (%)
4 M NaOH	(2.079 +/- 0.067)×10 ⁷ (3%)	(5.033 +/- 0.203)×10 ⁵ (4%)	(6.367 +/- 0.888)×10 ⁴ (13%)
Hylon V	MW ₁	MW ₂	MW ₃
Control	(1.827 +/- 0.067)×10 ⁷ (8%)	(7.189 +/- 0.325)×10 ⁵ (4%)	
Control/DMSO	(1.957 +/- 0.062)×10 ⁷ (3%)	(5.332 +/- 0.218)×10 ⁵ (4%)	
2.5 M NaOH/DMSO	(2.142 +/- 0.074)×10 ⁷ (3%)	(6.901 +/- 0.313)×10 ⁵ (4%)	
2.5 M NaOH	(2.801 +/- 0.100)×10 ⁷ (3%)	(7.332 +/- 0.371)×10 ⁵ (5%)	
3 M NaOH	(2.278 +/- 0.068)×10 ⁷ (3%)	(1.113 +/- 0.053)×10 ⁶ (4%)	(7.619 +/- 0.887)×10 ⁵ (11%)
5 M NaOH	(2.141 +/- 0.077)×10 ⁷ (3%)	(5.872 +/- 0.325)×10 ⁵ (5%)	
Abrastarch	MW ₁	MW ₂	MW ₃
Control	(3.804 +/- 0.132)×10 ⁷ (3%)	(3.935 +/- 0.162)×10 ⁶ (4%)	
Control/DMSO	(3.093 +/- 0.103)×10 ⁷ (3%)	(4.008 +/- 0.207)×10 ⁶ (6%)	
2.5 M NaOH/DMSO	(3.196 +/- 0.21)×10 ⁷ (3%)	(1.134 +/- 0.181)×10 ⁷ (15%)	
2.5 M NaOH	(3.380 +/- 0.327)×10 ⁷ (7%)	(6.959 +/- 5.057)×10 ⁶ (72%)	
4 M NaOH	(2.013 +/- 0.070)×10 ⁷ (3%)	(9.874 +/- 0.584)×10 ⁵ (5%)	(3.145 +/- 0.466)×10 ⁵ (14%)

Amioca	MW ₁	MW ₂	MW ₃
Control	(3.471 +/- 0.156)×10 ⁷ (4%)		
Control/DMSO	(4.364 +/- 0.181)×10 ⁷ (4%)		
2.5 M NaOH/DMSO	(3.412 +/- 0.165)×10 ⁷ (4%)		
2.5 M NaOH	(3.627 +/- 0.129)×10 ⁷ (5%)		
4 M NaOH	(1.876 +/- 0.339)×10 ⁵ (5%)	(5.876 +/- 0.339)×10 ⁵ (%)	

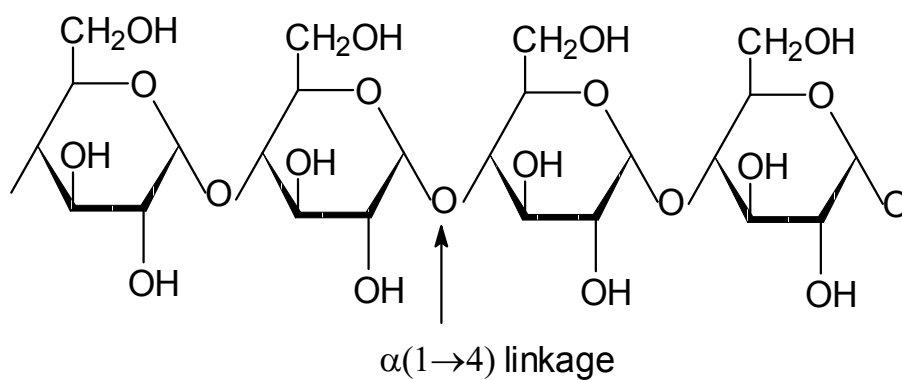
Measurement conditions: 60 sec microbomb (0.1 g/20 ml solutin), mobile phase 0.1 M KSCN and flow rate 0.5 mg/ml. All measurements were carried out at room temperature using HEMA Bio Column.

Table 8. The radius of gyration (R_g) of native and treated starches.

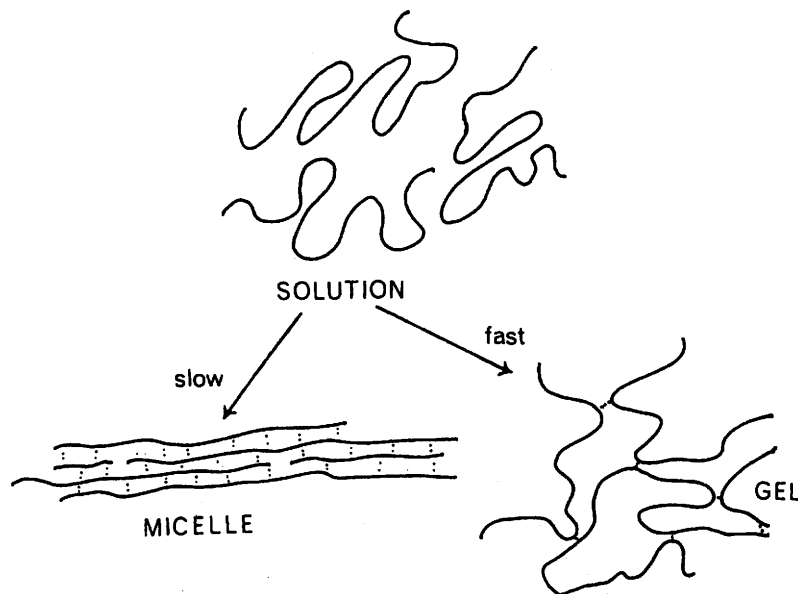
Hylon VII	RW ₁	RW ₂	RW ₃
Control	(48.1 +/- 2.0) (4%)	(37.3 +/- 4.3) (11%)	
Control/DMSO	(43.9 +/- 2.4) (5%)	(36.9 +/- 3.7) (9%)	
2.5 M NaOH/DMSO	(44.9 +/- 2.2) (4%)	(36.2 +/- 2.8) (7%)	
2.5 M NaOH	(50.3 +/- 1.9) (3%)	(44.9 +/- 2.5) (5%)	(56.2 +/- 3.1) (5%)
4 M NaOH	(46.7 +/- 1.9) (4%)	(39.7 +/- 2.7) (6%)	(50.7 +/- 8.6) (15%)
Hylon V	RW ₁	RW ₂	RW ₃
Control	(45.7 +/- 2.4) (5%)	(38.5 +/- 3.2) (8%)	
Control/DMSO	(47.4 +/- 2.1) (4%)	(42.0 +/- 2.9) (7%)	
2.5 M NaOH/DMSO	(51.1 +/- 1.9) (3%)	(48.3 +/- 2.4) (5%)	
2.5 M NaOH	(52.7 +/- 2.3) (4%)	(50.6 +/- 3.1) (6%)	
3 M NaOH	(47.7 +/- 2.0) (4%)	(48.1 +/- 2.9) (6%)	(50.7 +/- 6.6) (13%)
5 M NaOH	(48.0 +/- 2.3) (4%)	(38.6 +/- 3.6) (9%)	
Abrastarch	RW ₁	RW ₂	RW ₃
Control	(52.2 +/- 2.0) (3%)	(49.6 +/- 2.1) (4%)	
Control/DMSO	(52.0 +/- 2.0) (3%)	(50.2 +/- 2.1) (4%)	
2.5 M NaOH/DMSO	(50.3 +/- 2.0) (4%)	(50.3 +/- 2.2) (4%)	
2.5 M NaOH	(51.1 +/- 3.4) (6%)	(52.8 +/- 2.8) (5%)	
4 M NaOH	(48.1 +/- 2.1) (4%)	(48.2 +/- 3.1) (6%)	(53.8 +/- 7.8) (14%)
Amioca	RW ₁	RW ₂	RW ₃
Control	(52.9 +/- 2.4) (4%)		
Control/DMSO	(55.1 +/- 2.1) (3%)		
2.5 M NaOH/DMSO	(53.7 +/- 2.1) (3%)		
2.5 M NaOH	(52.1 +/- 2.1) (4%)		
4 M NaOH	(41.7 +/- 7.7) (18%)	(57.6 +/- 5.0) (5%)	

Table 9. The intrinsic viscosity of the native and acylated starches

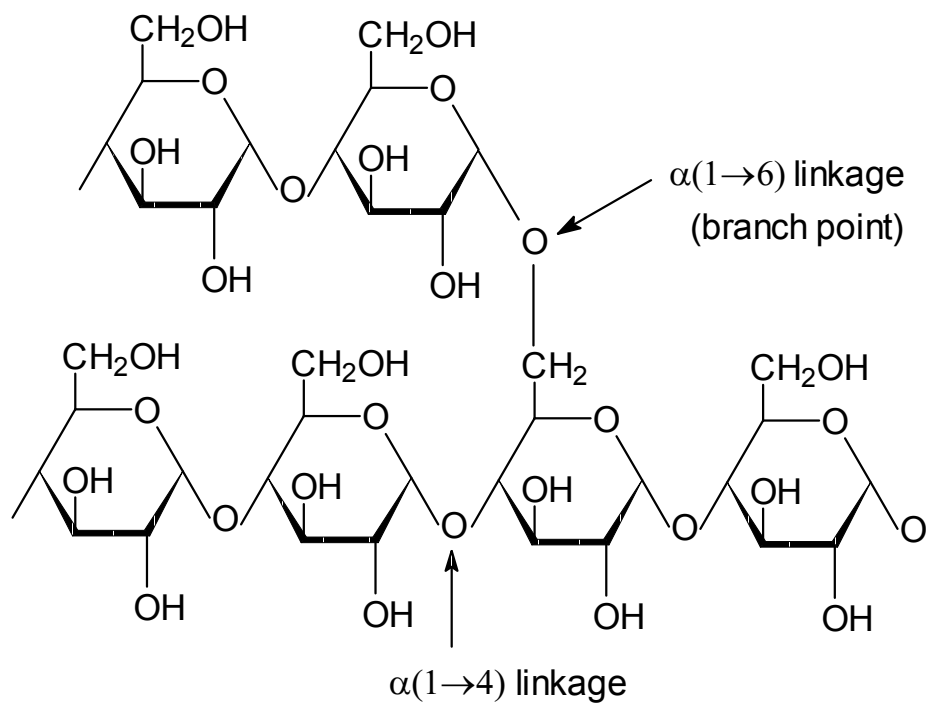
Sample	Intrinsic viscosity
Abrastarch (native)	90
Abrastarch (hexanoyl)	91
Hylon V (native)	85
Hylon V (hexanoyl)	65
Hylon VII (native)	40
Hylon VII (decanoyl)	51
Hylon VII (nonanoyl)	40
Hylon VII (octanoyl)	40
Hylon VII (heptanoyl)	42
Hylon VII (hexanoyl)	40



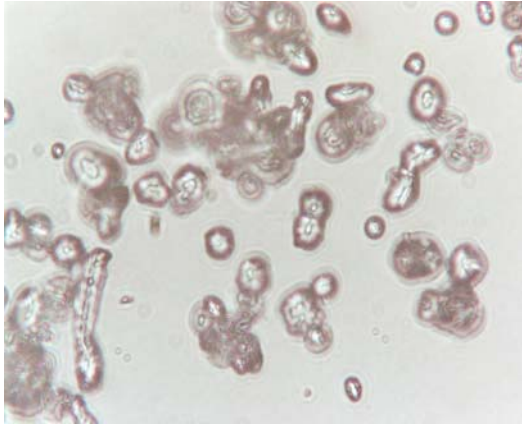
Scheme 1. Structure of amylose.



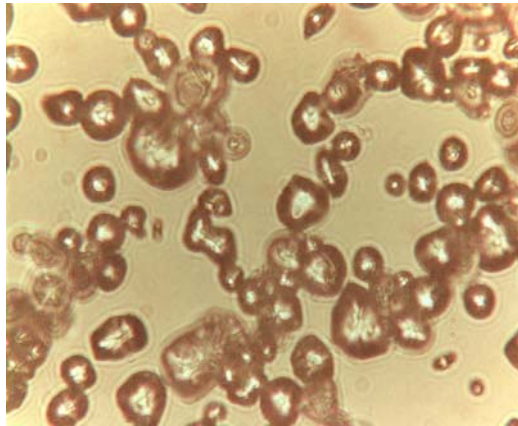
Scheme 2. Behaviour of amylose molecules when a concentrated aqueous solution is cooled (according to Greenwood, 1970).



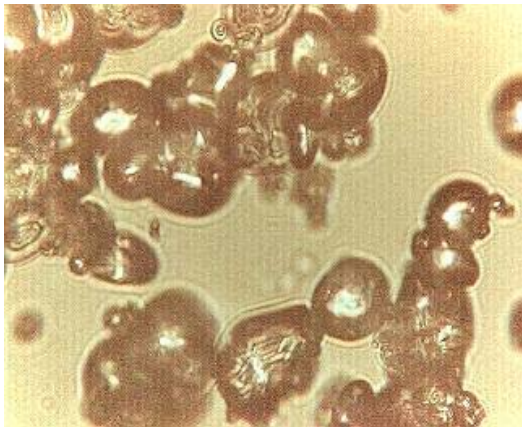
Scheme 3. Structure of amylopectin.



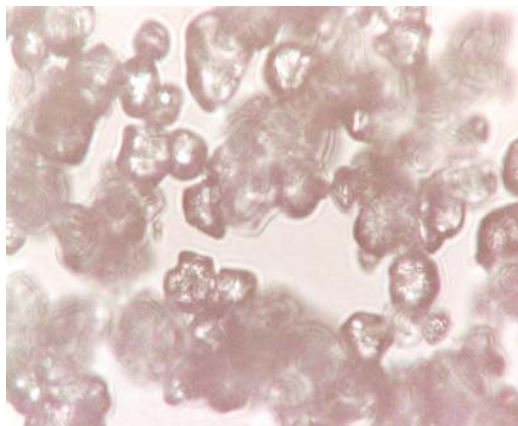
a



b

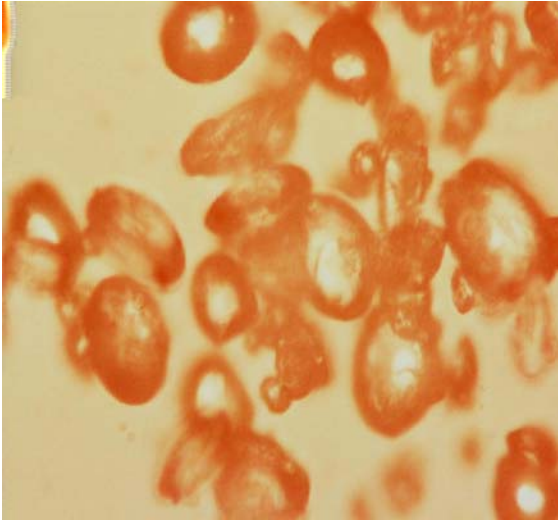
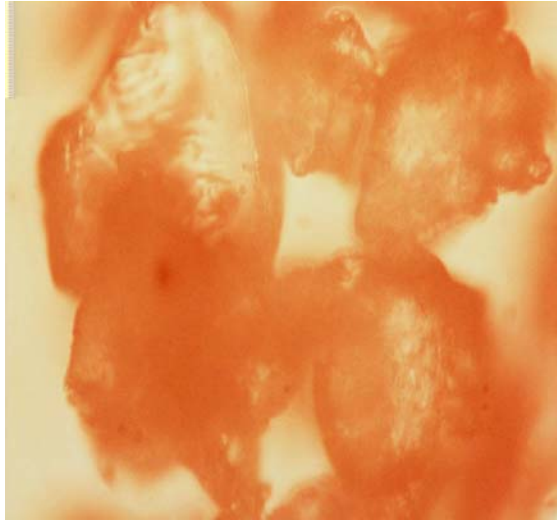
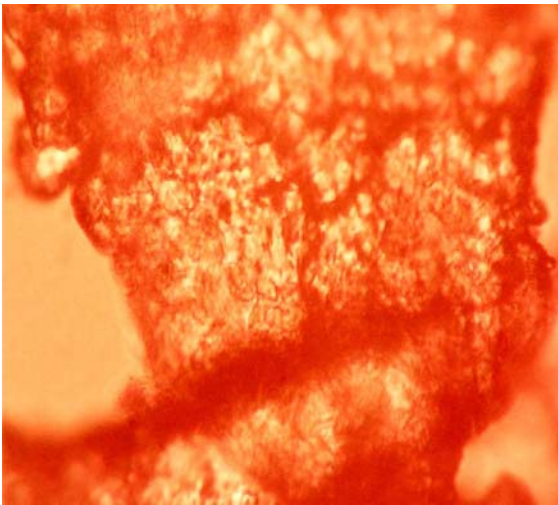
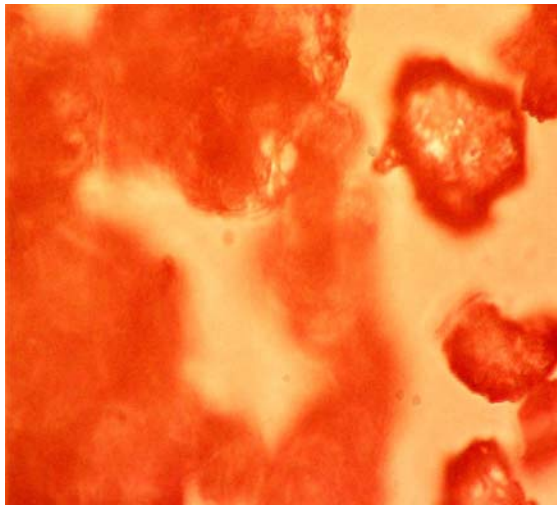


c

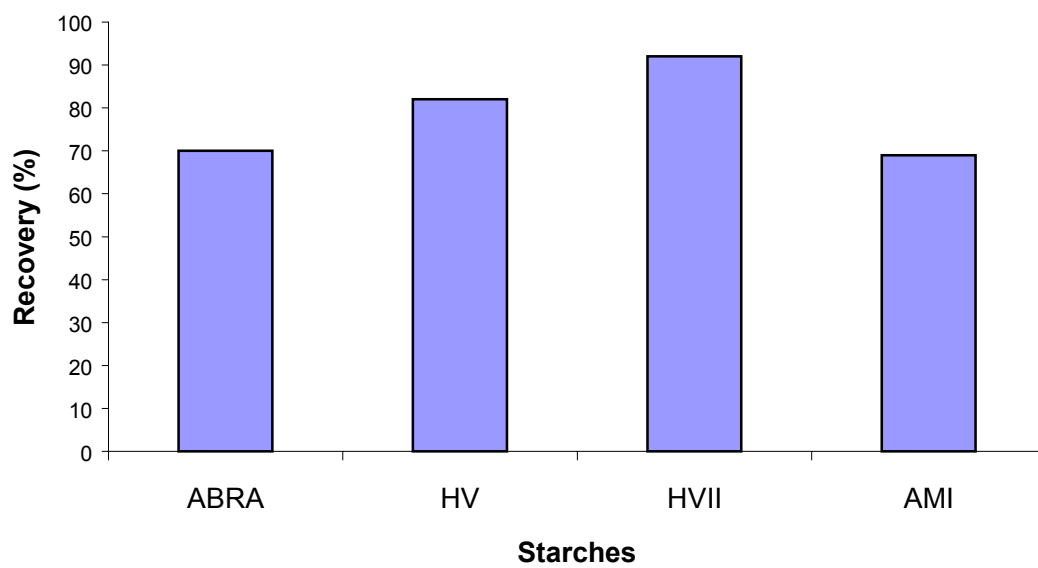


d

Scheme 4. Light micrographs of starch granules. Hylon VII (a); Hylon V (b); Abrastarch (c) and Amioca (d). All photographs are of the same magnification (400 ×).

**a****b****c****d**

Scheme 5. Light micrographs of Abrastarch granule changes after treatment, 0.05 M NaOH (**a**); 0.5 M NaOH (**b**); 1M NaOH (**c**) and 4 M NaOH (**d**). All photographs are of the same magnification (400×).



Scheme 6. The average recovery (%) of treated starches. ABRA (Abrastarch); HV (Hylon V); HVII (Hylon VII) and AMI (Amioca).