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Fructose and sucrose interactions with hydrolyzed aluminium(III)

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Abstract

The incorporation of fructose (a selected monosaccharide) and of sucrose (a selected disaccharide) into an aluminium hydroxide matrix was investigated at constant ionic strength, i.e. 0.6 M NaCl. The ratio of total sugar concentration to aluminium in solution (*N*) varied upto 75 in the 4.0–11.2 pH range. Solid phases were separated from solutions and characterized with chemical analyses, powder X-ray diffraction, IR and FT-IR spectra, ^{27}Al, ^{23}Na and ^{13}C NMR spectra. Soluble samples close to the precipitation boundary were examined with UV spectroscopy. Fructose showed very good ability of binding to $Al(OH)_3$, with aluminium to fructose in the solid equal to 3. Sucrose showed much weaker binding tendency to aluminium, with aluminium to sucrose being in this case equal to 13. In the Al(III)–carbohydrate adducts aluminium was found to be octahedrally coordinated. Sodium was found not as an NaCl impurity, but rather in an oxygen-coordinated chemical form. From ^{13}C NMR data it is suggested that fructose is bound to aluminium hydroxide matrix in β-pyranose and β-furanose forms. Sucrose is bound to the same matrix through its fructose part.

Introduction

The present investigation is a continuation of our work on the interaction of hydrolyzed aluminium(III) with naturally occurring organic ligands, such as oxalate [1], amino acids [2–5] and sugars. In addition to environmental reasons, this research could also be of medical interest as a consequence of the ascertained connections of aluminium(III) accumulation with some human neurological disfunctions and bone disorders. In particular, Al complexes with the deprotonated forms of maltol and kojic acid have been reported to be highly neurotoxic in preliminary toxicity studies [6].

We report here on the interaction of fructose and sucrose with hydrolyzed aluminium(III). Although, to our knowledge, the interaction of Al(III) with carbohydrates has not yet been described, an extensive literature about complexation of sugars with salts of alkali and alkaline earth metals and with iron(III) is available [7–14]. Precipitation and characterization of solid phases will be studied at various ligand to aluminium(III) ratios in solutions (*N*), at approximately constant pH and also at different pH values and at a constant *N* value.

Experimental

Materials

Stock solutions were prepared by dissolving $AlCl_3 \cdot 6H_2O$ (Merck), D(−)fructose, sucrose and NaOH (Kemika, Croatia) in bidistilled water. All chemicals were of reagent grade.

Preparation of solid phases and chemical analyses

Reactions of aluminium(III) with fructose and sucrose were studied in a constant ionic strength medium of 0.6 mol dm^{-3} NaCl. Precipitation conditions and results of analyses are described in Table 1 for fructose and in Table 2 for sucrose. In one series of experiments the aluminium(III) concentration and the pH were maintained constant, while the sugar to aluminium ratio, *N*, was varied. In another series of experiments, the concentration of aluminium and *N* were kept constant and the pH values were varied from 4.0 to 11.2.

The general procedure employed for batch preparation of samples was the following. Solutions of aluminium chloride, of sodium chloride and then of a carbohydrate were first mixed. The total volume of a sample was 0.10 dm^{-3}. The desired pH value was adjusted by adding dropwise a 1 mol dm^{-3} solution

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TABLE 1. Precipitation conditions and analyses of solids in the $AlCl_3$–NaOH–fructose system (0.6 M NaCl)

No. of sample	Concentration in solution		pH	Aged days	Chemical analyses of precipitates (%)					Al/fructose
	$AlCl_3$ (mM)	Fructose (mM)			Al	C	H	Na	*LOI*[a]	
1	20	40	5.4	2	30.04	2.96	5.54	–[b]	43.24	27.0
2	20	100	5.9	2	23.13	3.76	3.46	0.17	56.30	16.4
3	10	100	5.0	5	34.17	8.63	3.40	–	35.43	10.6
4	20	200	5.7	2	21.15	4.18	3.38	0.13	60.03	13.5
5	20	300	6.4	2	20.17	8.06	5.47	–	61.90	6.7
6	20	500	5.2	2	20.35	8.56	5.06	–	61.55	6.3
7	20	800	5.5	2	19.98	10.74	5.31	–	62.25	5.1
8	20	1000	5.7	2	17.80	12.92	5.08	–	66.36	3.7
9	20	1500	5.7	1	17.84	13.11	5.61	–	66.28	3.6
10	20	500	4.4		soluble					
11	20	500	5.9	2	19.08	10.23	4.95	0.56	63.94	5.0
12	20	500	6.5	2	19.82	10.29	4.43	0.08	65.56	5.1
13	20	500	7.3	2	18.81	14.89	5.13	–	64.45	3.4
14	20	500	7.6	2	20.25	13.57	4.25	0.32	61.72	4.0
15	20	500	7.9	2	19.48	17.14	5.39	1.45	63.17	3.0
16	20	500	8.4	2	18.64	15.44	3.03	1.08	64.77	3.3
17	20	500	9.4		turbid, dissolves					
18	20	500	9.9		soluble					
19	20	500	10.5		soluble					
20	20	500	7.9	17	20.94	12.34	5.28	0.52	60.13	4.5
21	20	500	6.5	17	20.43	10.60	4.91	0.14	61.38	5.1
22	20	500	7.6	17	19.99	12.85	4.83	0.26	62.21	4.2
23	20	500	8.4	17	18.73	15.98	4.70	1.54	63.84	3.2

[a] *LOI* = loss on ignition. [b] Not measured.

of sodium hydroxide. Total concentrations of precipitation components and the ageing times are indicated in Tables 1 and 2. The solids were separated by filtration through a Millipore filter, washed with ethanol to remove traces of NaCl and dried at room temperature in air over silica gel. The solid phases were chemically analyzed by conventional methods, i.e. sodium by flame photometry after dissolving weighed amounts of solid in hydrochloric acid and aluminium as aluminium oxide by weighing the residual sample after the combustion of the solid phase in an oxygen stream and accounting for the amount of Na_2O so formed.

Methods

IR spectra were recorded with a Perkin-Elmer spectrophotometer model 580 B and FT-IR model 1720, using KBr discs.

UV spectra were recorded with a Perkin-Elmer spectrophotometer model 124.

^{27}Al and ^{23}Na NMR spectra were recorded in solid state on MSL 400 in a 4 mm DB-MAS probe spinning at a speed in excess of 10 MHz and collected with high power decoupling.

^{13}C NMR spectra of fructose and Al–fructose adduct were recorded at 22.5 MHz on a Jeol FX 90 Q Fourier-transform spectrometer at room temperature in 5 mm o.d. tubes. The sweep width was 5200 Hz, pulse width 7 μs, pulse delay 1 s and digital resolution 1.27 ppm/point. Chemical shifts were measured relative to that of internal 1,4-dioxane, set at 67.4 ppm downfield of that of tetramethylsilane. The spectra of sucrose and Al–sucrose adducts were recorded with a Varian Gemini 300 Fourier-transform spectrometer at room temperature in 5 mm o.d. tubes at 75 MHz. The spectral width was 20000 Hz, pulse width 7.0 μs, pulse width (90°) 13.0 μs, pulse delay 3.0 s. Chemical shifts were measured relative to CD_3COOD set at 20.0 ppm.

Sodium was determined using a Carl Zeiss flame photometer.

X-ray powder diffraction patterns were recorded with a Philips PW 1050 X-ray diffractometer (Cu Kα radiation).

pH values were measured with a Radiometer 26 pH-meter, using a combined GK 2322 C electrode, calibrated by Titrisol buffers.

Results and discussion

Composition of precipitates

It was found that both fructose and sucrose can be embedded in aluminium hydroxide matrix.

TABLE 2. Precipitation conditions and analyses of solids in the $AlCl_3$–NaOH–sucrose system (0.6 M NaCl)

No. of sample	Concentration in solution		pH	Aged days	Chemical analyses of precipitates (%)					Al/sucrose
	$AlCl_3$ (mM)	Sucrose (mM)			Al	C	H	Na	*LOI*^{a}	
1	20	40	6.0	5	26.44	3.84	4.90	–^{b}	50.01	36.8
2	20	200	6.0	2	28.63	3.07	4.68	–	45.89	49.8
3	20	500	6.2	5	24.43	4.43	5.03	–	53.82	29.4
4	20	800	5.9	5	25.36	4.48	4.60	0.13	52.05	27.7
5	20	1000	6.2	5	22.81	6.92	4.94	–	56.89	18.0
6	20	1200	6.2	5	22.07	9.12	3.97	–	58.28	13.0
7	20	1400	6.4	5	22.50	7.69	4.81	–	57.46	15.0
8	20	200	4.5	2	soluble					
9	20	200	6.0	2	28.63	3.07	4.68	0.12	45.89	49.8
10	20	200	6.9	2	28.05	4.52	4.59	0.09	46.97	33.1
11	20	200	8.3	2	28.16	6.55	4.57	0.12	46.77	23.0
12	20	200	9.0	2	26.77	7.54	3.82	0.25	43.72	19.0
13	20	200	10.0	2	30.75	8.52	3.94	1.31	40.87	19.3
14	20	200	9.9	2	28.28	11.56	4.12	0.95	45.86	13.0
15	20	200	10.0	2	35.45	5.98	3.83	0.89	35.45	30.0
16	20	200	11.2	2	soluble					
17	20	200	11.2	50	30.25	6.83	4.10	1.84	41.35	33.6
18	20	500	4.0	2	soluble					
19	20	500	4.9	2	25.16	3.41	4.68	–	52.44	40.0
20	20	500	6.2	2	27.29	5.40	4.49	–	48.41	27.0
21	20	500	7.2	2	26.02	6.69	4.56	0.04	50.81	21.0
22	20	500	8.2	2	26.84	9.22	3.82	0.19	49.26	16.0
23	20	500	9.0	2	25.16	9.73	3.55	0.14	52.44	14.0
24	20	500	10.0	2	27.55	9.90	3.52	0.60	47.50	14.3
25	20	500	11.0	9	27.92	7.61	4.75	1.10	46.43	20.0

^{a}*LOI* = loss on ignition. ^{b}Not measured.

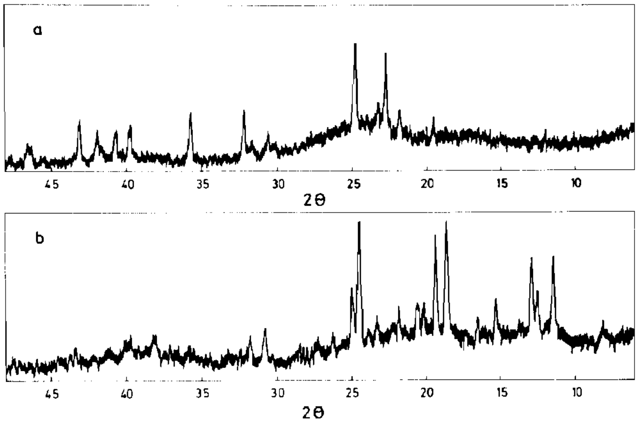

Fig. 1. X-ray diffraction of powder of: (a) sample 13, Table 2, having the composition $(AlOOH)_{19}(Na^+L^-)\cdot 10H_2O$, where L = sucrose; (b) sample 6, Table 2, having the composition $Al_{13}(OH)_{39}L\cdot 10H_2O$, where L = sucrose.

Results of chemical analyses in Tables 1 and 2 were used to calculate the molar ratio of aluminium to fructose and aluminium to sucrose in each solid sample. In both cases this ratio gradually decreased, either by increasing the excess of ligand or by increasing the pH. The lowest value, 3, in the case of fructose was obtained for sample 15 (Table 1). The deduced formula is $Al_{12}(OH)_{36}(Na^+L^-)L_3\cdot 2H_2O$, where L = fructose. Analytical data are in reasonable agreement with the theoretical ones (C, 16.80; H, 5.07; Al, 18.89; Na, 1.34; *LOI*, 62.49%).

The lowest value, 13, in the case of sucrose was obtained for samples 6 and 14 (Table 2). The deduced formula of the sample 6 is $Al_{13}(OH)_{39}L\cdot 10H_2O$, where L = sucrose. Analytical values are in reasonable agreement with the theoretical ones (C, 9.37; H, 5.27; Al, 22.84; *LOI*, 56.85%). The deduced formula of sample 14, isolated at high pH, is $(AlOOH)_{26}(Na^+L^-)L\cdot 10H_2O$, where L = sucrose. The experimental values are in reasonable agreement with the theoretical ones (C, 11.78; H, 3.63; Al, 28.68; Na, 0.94; *LOI*, 45.80%). The observed lower reactivity of sucrose compared to that of fructose is similar to the observations of Davis and Deller [15] dealing with iron(III). In fact, they proposed that the ability of fructose to chelate iron(III) is related to the dihydroxy acetone structure found in the open chain fructose molecule, which forms with iron a stable six-membered ring structure. However, these authors didn't give any experimental evidence in support of this proposal. As in the case of fructose, an aluminium to ligand ratio equal to 3 was found in

TABLE 3. IR and FT-IR absorption bands (cm^{-1}) of ligands and Al compounds with possible band assignments

Fructose	$Al_7(OH)_{21}L_2 \cdot 8H_2O$ Sample 9[a]	$Al_9(OH)_{27}(Na^+L^-)L_2 \cdot 2H_2O$ Sample 23[a]	Assignments	Sucrose	$Al_{13}(OH)_{39}L \cdot 10H_2O$ Sample 6[b]	$Al_{20}(OH)_{60}(Na^+L^-)$ Sample 25[b]	Assignments
3383vs	3400s,b	3420s,b	ν(O–H)	3563m	3434s,b	3434s,b	ν(O–H)
				3392s,b			
3020w			ν(C–H),	3014w			ν(C–H),
3000w			$\nu(CH_2)$	2994w			$\nu(CH_2)$,
2960w				2984m			(CH_2)
2940w	2940w	2940w		2942m	2933sh	2955sh	
2905w		2900					
1639m	1645m	1650m	$\delta(H_2O)$		1642	1642	$\delta(H_2O)$
1475w	1470sh		δ(COH), (OCH),				
			(CCH)				
1460w		1460sh	$\delta(CH_2)$	1461w	1462sh		$\delta(CH_2)$
1430m	1420w	1420m	δ(COH) + δ(CCH)	1435m	1432w	1419m	δ(COH)
1400m			δ(OCH) + δ(COH)				
			δ(CCH)				
1340m			$\delta(CH_2)$	1367w			δ(COC),
1270m		1265sh	δ(CCH) +	1347m	1347sh		δ(COH)
1250sh			δ(COH)	1323w	1333sh		
1180w			δ(OCH) +	1280m			δ(COH),
			δ(CCH)				δ(CCH)
1160m			ν(CO) + ν(CC),	1240m			δ(CCH)
			ν(CCC)	1209m			
1060s	1060w	1065m	ν(CO)		1125sh	1136sh	δ(COH)
				1072m	1055w	1057w	ν(CO)
985s	980sh	980sh	ν(CO) +	991m	994w	999w	δ(CCH),
			δ(CCO)				δ(CH)
930m	950sh	940m	ν(CO),	943m	929w	929w	
			δ(CCH)	910m			
880m		860sh		868m		866sh	δ(CH) + δ(COH)
820m			δ(CH)	850			δ(CH), ν(CC)
790m			δ(CCO) +	733w			δ(CCO)
			δ(CCH)				
690m			δ(CCO) +	683m			δ(OCO)
			δ(OCO)	643w			δ(CCO)
	580m,b	570m,b	ν(Al–O)	584w			δ(CCC)
560m			ν(CO)	552w			
					567m,b	599m,b	ν(Al–O)
390m				473m			
	352w	350sh	ν(Al–O)	403m			
325m							

s = strong, m = medium, w = weak, sh = shoulder, b = broad. [a]See Table 1. [b]See Table 2.

the aluminium–hydroxo–oxalate [1], aluminium–hydroxo–leucine [2] and aluminium–hydroxo–valine adducts [5].

UV spectral characteristics of soluble complexes

It is known [16] that precipitation of aluminium hydroxide occurs in the 4.2–11.2 pH range for a total concentration of aluminium equal to 20 mM. In the presence of fructose solubilization takes place at pH 9.4 (samples 17–19, Table 1). With sucrose, the solubility boundary is not shifted. UV spectra of soluble aluminium complexes with fructose and with sucrose are extremely simple and not very informative. There is a red shift of only about 10 nm, which is pH dependent. This shift was observed for aluminium–fructose from 209 nm (sample 10, Table 1) to 219 nm (sample 19, Table 1) and for aluminium–sucrose from 202 nm (sample 8, Table 2) to 212 nm (sample 16, Table 2). According to Williams and Fleming [17] this shift can be due to a deprotonation reaction.

X-ray and IR spectral characteristics of solid samples

All samples obtained upon reaction of Al(III) with fructose (Table 1) and most of those with sucrose (Table 2) are amorphous as seen from X-ray diffraction patterns. Some samples with sucrose exhibit microcristallinity as illustrated in Fig. 1 for sample 6 (spectrum b) and for sample 13 (spectrum a) from Table 2. The different X-ray diffraction patterns of adducts precipitated from the acid region (sample 6) and from the alkaline one (sample 13), suggest different structures. Single crystals could not be obtained for structural analyses.

IR spectra will be qualitatively described using the assignments of Tajmir-Riahi, who studied the adducts of sugars with alkali, alkaline-earth and zinc-group metal ions [18–21].

The IR spectra of fructose and its Al compounds (samples 9 and 23 from Table 1) were recorded in the region of 4000–200 cm^{-1} and the FT-IR spectra of sucrose and its Al compounds (samples 6 and 25 from Table 2) were recorded in the 4000–370 cm^{-1} region. IR and FT-IR data indicating positions of all absorption bands of ligands and of selected isolated adducts are presented in Table 3.

The broad absorption band at ≈3400 cm^{-1} (related to the water OH stretching vibrations) and a medium band at ≈1640 cm^{-1} (due to the water bending mode) are assigned to the bonded H_2O molecules in the isolated compounds. The sugar OH stretching vibrations at ≈ 3400 cm^{-1} are overlapped by the OH stretching vibrations of coordinated H_2O molecules. Some of C–H stretching vibrations at ≈2900 cm^{-1} can be observed in the spectra of Al compounds as weak bands or as a shoulder. COH and COC bending modes of the free sugar in the 1470–1170 cm^{-1} region exhibited considerable intensity changes and shiftings in the spectra of the Al–sugar compounds. These changes may be indicative of the involvement of the sugar hydroxyl groups in metal–sugar bonding. Other strong absorption bands in the 1160–930 cm^{-1} region assigned to the C–O stretching vibrations in the sugar also showed major alterations after the bonding to the aluminium hydroxo matrix; this observation can be related to the coordination of the metal ions through the sugar oxygen atoms. The bands of sugar skeletal deformations C–O–C and C–C–C in the region of 650–400 cm^{-1} are overlapped with a strong and broad band at ≈580 cm^{-1} which can be attributed to Al–O stretching vibrations as described by Tarte [22]. This author suggested that the bands in the wave number range 680–500 cm^{-1} are characteristic of 'condensed' AlO_6 octahedra. The weak band at ≈380 cm^{-1} could be attributed to M–O stretching vibration as in the case of aluminium tris(3-hydroxy-4-pyronates) described by Finnegan *et al.* [6], although this assignment is tentative.

The bands at ≈580 and ≈370 cm^{-1} are present in the spectra of amorphous $Al(OH)_3$ isolated at various pH values (5.2, 6.8, 7.8 and 11.0) and used as blanks.

^{27}Al and ^{23}Na NMR spectral characteristics

Only selected samples were studied by these techniques and the relevant data are collected in Table 4. The details about the NMR measurements were described in the literature for aluminium [23] and sodium [24]. The ^{27}Al spectra all show a pronounced peak in the 8–4 ppm range, meaning that AlO_6 units are present in the samples. It is interesting to note that octahedral coordination is found even upto pH 11.2 in the sucrose adducts. This observation is in agreement with the data of Horvath *et al.* [25] for pure aluminium hydroxide prepared at the same high pH value. There is no evidence for the existence of a tetrahedrally coordinated aluminium ion in our compounds, which would have a peak near 80 ppm according to Müller *et al.* [23].

TABLE 4. ^{27}Al and ^{23}Na chemical shifts (ppm) of selected samples from Tables 1 and 2 measured by high-power NMR methods

Sample no.	^{27}Al	^{23}Na
21^{a}	5.89	
15^{a}	4.12	−6.35
23^{a}	6.40	−5.61
5^{b}	5.44	
11^{b}	6.47	
15^{b}	7.88	−5.84
17^{b}	5.50	−10.08

^{a}See Table 1. ^{b}See Table 2.

TABLE 5. ^{13}C NMR chemical shifts of ligands and Al complexes, sample 23, Table 1 and sample 22, Table 2

Compound		δ(ppm)					
		C-1	C-2	C-3	C-4	C-5	C-6
D-Fructose	β-Fru p	64.73	98.76	68.40	70.49	69.97	64.11
	β-Fru f	63.72	102.26	76.30	75.28	81.37	63.15
$Al_9(OH)_{27}(L^-Na^+)L_2 \cdot 2H_2O$	β-Fru p	64.79	98.67	68.45	70.54	70.09	64.28
(L = fructose)			98.93		71.28		
(Sample 23, Table 1)					71.90		
	β-Fru f	63.70	102.37	76.35	75.34	81.49	63.32
			102.76	76.69		82.06	
						82.82	
Sucrose	α-Glu	92.95	71.65	73.31	70.15	73.59	61.17
	β-Fru f	62.65	104.40	77.93	74.88	82.22	62.92
$Al_{16}(OH)_{48}L \cdot H_2O$	α-Glu	92.96	72.23	73.71	70.46	74.01	61.51
(Sample 22, Table 2)	β-Fru f	61.94	104.18	80.12	74.75	82.35	64.14

D-Fructose and $Al_9(OH)_{27}(L^-Na^+)L_2 \cdot 2H_2O$ dissolved in D_2O+HCl. Sucrose and $Al_{16}(OH)_{48}L \cdot H_2O$ dissolved in CD_3COOD.

No peak was detected near 62 ppm which was observed in an aqueous solution containing the $[Al_{13}(OH)_{24}O_4]^{7+}$ ion [26].

The ^{23}Na spectra show chemical shifts between −5.6 and −10.08 ppm. Similar shifts were observed [24] in sodium glutamate and sodium citrate, where sodium atoms are oxygen bonded. According to ref. 24 the local charge at the Na atom may be important in determining ^{23}Na chemical shifts. In sample 17 from Table 2, the ^{23}Na chemical shift is considerably shifted upfield compared to other samples. It indicates a longer Na–O bond distance than in other samples. It can also be concluded that the low sodium concentrations found do not come from an NaCl impurity, in which case a sharp line would be observed at about +7 ppm [24]. This conclusion is supported by the X-ray diffraction data, which do not contain peaks attributable to NaCl.

The sodium ion is very probably connected with the oxygen atom at the 1 position, which is known as the acidic site in the pentoses and hexoses [27].

Aluminium-induced chemical shifts in the ^{13}C NMR spectra of fructose and sucrose

Complexation of aluminium with fructose and sucrose was studied on two selected samples (sample 23, Table 1 and sample 22, Table 2) in order to obtain information about the possible binding sites for aluminium. As the ^{13}C chemical shifts of fructose and sucrose have been assigned previously [28, 29], these data were used to assign the carbon atoms of the two selected aluminium samples and to observe the changes.

^{13}C NMR results are given in Table 5. Solid aluminium samples had to be dissolved in acid to perform the measurement. Ligands were dissolved in the same way. It was found that fructose solution in D_2O+HCl is composed of β-pyranose and of β-furanose tautomeric forms. Sucrose was dissolved in CD_3COOD and remained stable, while in D_2O+HCl it was decomposed to glucose and to β-fructopyranose. In the aluminium fructose adduct (sample 23, Table 1) the changes in chemical shift took place at C-2 and C-4 of β-fructopyranose and at C-2, C-3 and C-5 of β-fructofuranose. These changes except at the C-5 atom can be related to the corresponding OH bonding to the hydrolyzed aluminium matrix. The intensive downfield shift of the C-5 atom may be related to the coordination of the oxygen atom in the fructose ring. Two signals of low intensity at 61.80 and 96.67 ppm remained unexplained. In the aluminium sucrose adduct (sample 22, Table 2) the main changes occurred at the C-3 and C-6 atoms in the fructose part. This is an indication that sucrose is bound to the aluminium hydroxide matrix through the fructose part, involving only sugar OH in the metal–ligand bonding.

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