PREPARATION AND INFRARED STUDY OF CELLULOSE BASED AMPHIPHILIC MATERIALS

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Carboxymethyl cellulose acetate butyrate (CMCAB) was prepared for the first time from alpha cellulose extracted from sugarcane bagasse. Also, carboxymethyl cellulose (CMC) and carboxymethyl cellulose acetate (CMCA) were prepared and analyzed by FTIR, XRD and TEM. FTIR analysis indicated that, in addition to the main characteristic bands of alpha cellulose, CMC showed new characteristic absorption bands at 1599.7 and 1414.5 cm^{-1}, which were associated with the anti-symmetric and symmetric stretching vibrations of COO$^-$, respectively. Also, strong sharp absorption peaks were noted at 1743.3 for carbonyl C=O, at 1639.2 for CMCA and at 1748.16 and 1640.16 cm^{-1} for CMCAB which indicate the formation of an ester. As detected from the IR spectra, the crystallinity index of cellulose exhibited a higher value than that of CMC. XRD analysis confirmed that CMC crystallinity was reduced remarkably in comparison with that of cellulose. This decrease may be attributed to the chemical reaction steps that contributed to the breakdown of chemical and physical bonds between the cellulose fibers. The results confirmed that valuable amphiphilic CMCAB was effectively prepared in this study.

Keywords: bagasse, cellulose ester, cellulose ether, amphiphilic cellulose, IR, carboxymethyl cellulose acetate butyrate

INTRODUCTION

Cellulose is the most abundant natural polymer in nature. Different renewable sources can yield cellulose based on chemical or biological processes. Carboxymethylation is one of the most important functionalization processes for cellulose in which the primary and/or secondary OH groups are substituted by carboxymethyl groups. Carboxymethylation can be achieved through cellulose activation by NaOH. Consequently, the activated cellulose is reacted with monochloroacetic acid to convert it to carboxymethyl cellulose (CMC).[1-2]

Cellulose is a promising biopolymer to prepare amphiphilic materials, which can be used for many potential applications.[3] Functionalization of cellulose can provide amphiphilic materials that exhibit stimuli-response properties towards pH and temperature.[3-4] Amphiphilic polymers have been utilized in various applications, such as stabilizers for colloidal systems through surface interaction. Amphiphilic cellulose derivatives are composed of hydrophobic and hydrophilic moieties. The hydrophilic moiety enables polymer solubility in aqueous solvents, while the hydrophobic moiety enables the formation of polymeric micelles in aqueous solvents due to hydrophobic interactions. Polymeric micelles can be used as carrier for poorly soluble compounds, where the hydrophilic shell maintains the stability of a poorly soluble compound as a dispersion.[5-6]

Carboxymethyl cellulose acetate butyrate (CMCAB), which is a mixed cellulose ester, is an example of amphiphilic polymer.[7] CMCAB can be synthesized by activation of CMC by sulfuric acid to form free acid CMC-H, which is washed with demineralized water and then with acetic and butyric acids, respectively. Subsequently, the slurry is catalytically esterified by acetic and butyric anhydride in one step. The temperature is raised gradually until complete dissolution of CMC. Hydrolysis is the final step: magnesium acetate tetrahydrate is dissolved in water and acetic acid to form a partially substituted CMCAB, which is washed with water and filtered

as a white solid.[8-10] The aim of the present work is to synthesize valuable carboxymethyl cellulose acetate butyrate from available cheap wastes, such as sugarcane bagasse, and to analyze it in order to illustrate the introduction of new functional groups to cellulose during etherification and esterification reactions.

EXPERIMENTAL
Materials
Sugarcane bagasse was obtained from Quena Company for Paper Industry, Egypt. The chemicals used were of analytical grades and were employed without further purification.

Extraction of cellulose from sugarcane bagasse (SCB)
SCB was hydrolyzed with 1.5% HCl, based on the raw material, using a liquor to material ratio of 1:10 at 120 °C for 2h. The prehydrolyzed bagasse was treated with 20% NaOH (based on SCB), using a liquor to material ratio of 1:7 at 170 °C for 2h. The residual lignin of the pretreated bagasse was removed by bleaching with sodium chlorite. Mercerization of cellulose was carried out by 17.5% NaOH to remove the traces of lignin and other constituents. The chemical composition of the obtained pulp was the following: 94.2% α-cellulose, 0.3% lignin, 3.4% hemicellulose and 0.4% ash.

Characterization of the lignocellulosic material
The yield and the percentage chemical constituents, such as ash, lignin and α-cellulose, were determined according to standard methods.[11]

Synthesis of sodium carboxymethylcellulose (CMC)
CMC was synthesized from SCB cellulose according to the procedure described by Browning.[12] The degree of substitution of the carboxyl group in CMC was conducted by potentiometric titration according to the standard method.[13]

Synthesis of carboxymethylcellulose acetate (CMCA)
CMCA was prepared from the obtained CMC with a DS of 0.45 by the same esterification method used for the preparation of CMCAB from CMC.[10]

Synthesis of carboxymethylcellulose acetate butyrate (CMCAB)
Starting from CMC with the DS of 0.45, the preparation of the CMCAB was accomplished by five consecutive steps: transformation of CMC-Na to the free acid form, activation of CMC (CMC-H), esterification, hydrolysis & neutralization and precipitation & filtration, as described in detail elsewhere.[10]

Fourier transform infrared spectroscopy (FTIR)
Infrared spectra were recorded with a JASCO FT/IR, Nicolet, Model 670 in the region from 4000 to 400 cm^{-1}. The relative absorbance of different bands was determined *via* the baseline correction method for making a comparative study of the spectra. The band at 1645.95 cm^{-1}, which is attributed to O-H bending from absorbed water, was chosen as an internal standard to determine the relative absorbance.

X-ray diffraction (XRD)
The crystallinity was analyzed using X-ray diffraction. Diffraction patterns were obtained using a Bruker D8 Advance X-ray diffractometer (Germany). The diffraction patterns were recorded at a voltage of 40 kV with a current of 40 mA, using copper (Kα) radiation (1.5406 Å). Specimens were prepared from cellulose or cellulose derivatives by pressing tablets with a thickness of 1 mm after freeze-drying the samples. Scans were taken over a 2θ (Bragg angle) range from 5 to 80°. The crystallinity index (CrI) was calculated as follows:

$$Cr.I. (\%) = (Sc/St) \cdot 100 \qquad (1)$$

where Sc is the area of the crystalline domain; St is the area of the total domain.[14]

Transmission electron microscopy (TEM)
The morphology and particle size of CMCAB were characterized using TEM (JEOL, JEM-1230 electron microscope).The sample was prepared by evaporation of one drop of CMCAB suspended in distilled water placed on a carbon coated copper grid.

Gas chromatography (GC)
GC/MS analysis was performed using a Thermo ScientificTrace GC Ultra/ISO single Quadrupole MS TG-5MS fused silica capillary column (30m, 0.251mm, 0.1mm film thickness). For GC/MS detection, an electron ionization system with ionization energy of 70 eV was used. Helium gas was used as carrier gas at a constant flow rate of 1ml/min. The injector and MS transfer line temperature was set at 280°C. The acetyl and butyryl weight percents were determined by the hydrolysis GC method.[8]

Gel permeation chromatography (GPC)
GPC measurements were performed on an Agilent 1100 Series Gel Permeation Chromatography System, Germany. The measurements were conducted at ambient temperature, using tetrahydrofuran (THF) as mobile phase at a flow rate of 10 ml/min. The CMCAB sample (0.01 g) was dissolved in 2ml of solvent, and then filtrated by a 0.45 micro syringe filter. The obtained sample was placed in the GPC device for measurements.

RESULTS AND DISCUSSION
Characterization of the lignocellulosic material and cellulose derivatives

The characterisation of the lignocellulosic material is presented in Table 1. The chemical composition of the cellulose extracted from bagasse exhibits about 94.2% α-cellulose. This high content shows that bagasse is a competitive source of pure cellulose.

Table 2 shows that the yield of CMC increased with increasing NaOH concentration. The reaction of cellulose with monochloroacetic acid under alkaline conditions causes the substitution of the cellulose hydroxyl group with the carboxymethyl group of higher molecular weight.[12] The DS of CMC, as shown in Table 2, increased directly with NaOH concentration and reached the highest value of 1.1 at a NaOH concentration of 40% (w/v). This is due to the fact that the crystalline region in cellulose was changed to amorphous, and thus, the hydroxyl groups of the anhydroglucose unit could be easily accessed by the monochloroacetic acid. However, the DS started declining at higher concentrations of NaOH (>40%), which could be caused by the formation of sodium glycolate as a by-product and also to the degradation of the cellulose polymer.[12]

The obtained CMCA has the DS of the CM group of 0.26 and 2.27% acetate. Table 3 shows the characterization of the synthesized CMCAB. From the GPC data, the weight average molecular weight and the number average molecular weight were determined as 13028 and 1555, respectively. Polydispersity, defined as Mw/Mn was calculated as 8.4. From the GC data, acetate and butyrate, %, were determined in accordance with the standard methods.[15] It is obvious that the carboxymethylation degree decreased after esterification because of the severe reaction conditions. Different acetate and butyrate contents of CMCAB could be obtained by adjusting the ratio of acetic anhydride and butyric anhydride during the esterification reaction. A higher DS of the butyrate groups, compared to that of the acetate groups, in CMCAB was attained because mixed esterification by acetic and butyric acid took place at the same time using the excess of butyric acid.

FT-IR spectroscopy

Figure 1 exhibits the FT-IR spectra of cellulose, CMC, CMCA and CMCAB. Cellulose showed characteristic bands at 3482.81, 2897.52, 1370.18, 1034.62 and 898.66 cm^{-1}, related to O-H stretching, CH_2 stretching, C-H bending, C-O-C pyranose ring vibration and β-glycosidic linkage between the glucose units in cellulose, respectively.

Table 1
Characterisation of the lignocellulosic material

Amount of component, %	Bagasse	Prehydrolysis	Pulp	Bleached pulp	α-Cellulose extraction
Wax and resin	0.99	-	-	-	-
Lignin	23.6	22.2	5.2	1.5	0.3
Hemicellulose	19.7	19.6	19	18.6	3.4
α-cellulose	54.1	62.9	75.1	78.8	94.2
Hollocellulose	73.8	82.6	94.1	97.4	97.6
Ash	2.1	0.5	0.6	0.5	0.4
Yield	-	99.5	97	82	56

Table 2
Percentage yield and DS of CMC synthesized with various NaOH concentrations

NaOH,%	Yield, %	DS
20	99.3	0.45
25	135.1	0.69
30	140.0	0.76
40	185.3	1.10
50	175.4	0.87

Table 3
Properties of CMCAB

Analysis	Value
Acetyl (GC)	4.75%
Butyryl (GC)	24.04%
DS CM	0.24
Mw	13,028
Mn	1,555
Mw/Mn	8.4
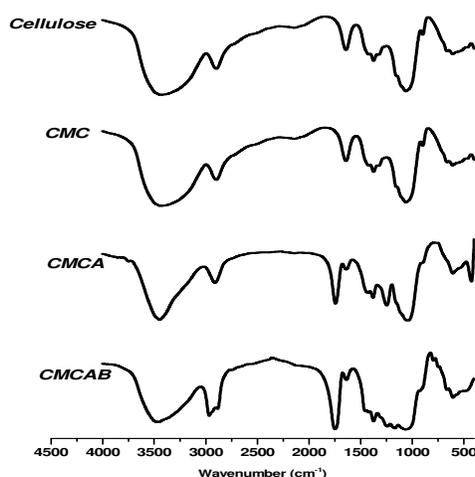
Figure 1: IR spectra for cellulose, CMC, CMCA and CMCAB

In addition to the main characteristic bands of cellulose, CMC showed new characteristic absorption bands at 1599.7 and 1414.5 cm^{-1} (with relative absorbance of 1 and 0.99, respectively), which correspond to the anti-symmetric and symmetric stretching vibrations of COO$^-$, respectively.

Also, strong sharp absorption peaks were noted for carbonyl C=O at 1743.3 and 1639.2 (with relative absorbance of 1.98 and 1.0, respectively) in the spectrum of CMCA, and at 1748.16 and 1640.16 cm^{-1} (with relative absorbance of 2.23 and 1.0, respectively) in the spectrum of CMCAB, which illustrate the formation of an ester, as more carboxylic groups were introduced. The relative absorbance of C=O is increased upon esterification. The shift of the characteristic CMC band at 1599.66 cm^{-1} to higher values for CMCA and CMCAB also indicates the formation of an ester.[15]

Meanwhile, compared with the characteristic peaks at 2901 cm^{-1} and 2911 cm^{-1} (with relative absorbance of 0.997 and 1.36, respectively) in the spectra of CMC and CMCA, there were stretching vibrations assigned to methylene CH$_2$ and methyl-CH3 at 2884.99 and 2966.95 cm^{-1} (with relative absorbance of 1.1 and 0.95, respectively) for CMCAB, demonstrating the existence of the ester, acetyl and butyryl. In addition, the asymmetric stretching vibration of C-O-C can be remarked at 1245.79, 1037.52 and 904.45 cm^{-1} in the spectrum of CMCA, and at 1240.97, 1168.65 and 1064.51 cm^{-1} in the spectrum of CMCAB, which further proves the existence of the ester. Moreover, the broad peak at 3445.21 cm^{-1} of the CMC hydroxyl group, with relative absorbance of 1.31, shifted after esterification to 3447.13 cm^{-1} in the spectrum of CMCA, with relative absorbance of 0.68, and to 3531.99 cm^{-1} in that of CMCAB, with relative absorbance of 1.1.[9]

The OH stretching vibration appearing at 3482.81 cm^{-1} characteristic of cellulose decreased and shifted to lower frequency (3445.21 cm^{-1}) in the spectrum of CMC. The peak associated with CH stretching appeared at 2897.5 cm^{-1} in the case of cellulose, but shifted to higher frequency (2901.28 cm^{-1}) after carboxymethylation. The change of the absorbance value of the OH

stretching vibration may be due to intermolecular hydrogen bonding, which decreased upon carboxymethylation.[16-17]

Table 4
Characteristic IR bands of cellulose

Wavenumber (cm⁻¹)	Assignment	Relative absorbance
3482.81	Strong hydrogen-bonded O-H stretching vibration	3.59
2897.52	C-H stretching	1.74
1645.95	O-H bending from absorbed water	1
1428.99	CH_2 bending of pyranose ring	2.12
1370.18	C-H bending	2.56
1034.62	C-O-C pyranose ring vibration	2.42
898.66	β-glycosidic linkage between glucose units in cellulose	1.08
662.43	O-H out-of-plane bending	2.07

Table 5
Characteristic IR bands of CMC

Wavenumber (cm⁻¹)	Assignment	Relative absorbance
3445.21	O-H stretching	1.31
2901.38	Stretching vibration of methine (C-H)	3.37
1599.66	C=O group	1
1414.53	Anti-symmetric and symmetric stretching vibration peak of COO	0.99
1369.21	C-H bending	0.99
1060.66	C-O-C stretching	1.21

Table 6
Characteristic IR bands of CMCA

Wavenumber (cm⁻¹)	Assignment	Relative absorbance
3447.13	Unsubstituted O-H group	0.68
2911.02	COOH of acetyl group and methyl –CH_3 of CMCA	1.36
1743.33, 1639.2	Asymmetric and symmetric C=O coupled stretching, respectively	1.98, 1
1379.82, 1434.38	Symmetric and asymmetric vibrations of CH_3	1.79, 1.65
1434.38	CH_2 band	1.65
1245.79, 1037.52, 904.45	Asymmetric stretching vibrations of C-O-C in ester	2.03, 2.52, 1.02

Table 7
Characteristic IRbands of CMCAB

Wavenumber (cm⁻¹)	Assignment	Relative absorbance
3531.99	Unsubstituted O-H group	1.1
2966.95	COOH dimer group and methyl –CH_3 of CMCAB	0.43
2884.99	Methylene –CH_2 of CMCAB	0.03
1748.16, 1640.16	Asymmetric and symmetric C=O coupled stretching, respectively	2.23, 1
1375	C-CH_3 of acetyl	1.22
1240.97, 1168.65, 1064.51	Asymmetric vibrations of C-O-C to prove the existence of an ester	1.66, 1.96, 2.36

The usual absorption of the OH stretching vibration of cellulose at 3445.21 shifted to higher values in the case of both CMCA and CMCAB (mixed esterification), at 3447.13 and 3531.99 cm^{-1}, respectively, due to an increase in intermolecular hydrogen bonding.

In addition, the relative absorbance of the OH group of CMCA and CMCAB (0.68 and 1.1, respectively) was found to be lower than that of cellulose (3.59), which proves the substitution of the free OH groups of cellulose by ester groups.

Tables 4-7 show the relative absorbance of different bands (the ratio of the absorbance of the investigated bands to the band at 1061.62 cm^{-1}, which corresponds to C-O-C and remained nearly constant for all the samples).[18] The absorbance intensities at 1420-1430 cm^{-1} and 900 cm^{-1} are characterized by the amount of crystalline and amorphous structure of cellulose, respectively.[17] The ratio between these two bands was defined as the empirical crystallinity index, or as proposed by Nelson and O'Connor, the lateral order index (LOI).[19]

Measuring the crystallinity indices revealed the higher crystallinity index of cellulose, due to the fact that the fibers are more compact in the case of cellulose I, compared to cellulose II. Upon carboxymethylation, the crystallinity index decreased because of the transformation of crystalline cellulose to amorphous cellulose by NaOH treatment. The increase in crystallinity and H-bonding of CMCAB might be due to the decomposition of the amorphous parts of CMC during the modifications. The H-bonding of CMCA is in-between those of CMCAB and

cellulose, but still higher than that of CMC, due to the decomposition of the amorphous parts of CMC during the modifications.[20]

From the IR spectra, the mercerization depth (M_D) was determined from the following relation:[21]

$$M_D = \frac{A1375}{A1325}$$

(2)

In general, the mean hydrogen bond strength (A_{OH}/A_{CH}) must increase after alkaline treatment in carboxymethylation, but, in this case, it decreased because of the lower alkaline percentage used during CMC preparation.[22]

XRD analysis

The crystallinity of cellulose was related to inter- and intra-molecular hydrogen bonding. Cellulose I can be transformed to cellulose II by treatment with an aqueous sodium hydroxide solution. The major difference between cellulose I and II is due to the hydrogen bonding between the cellulose chains. Cellulose II has an antiparallel orientation between the chains, which has a direct influence on the structure of the cellulose crystallites, as demonstrated by X-ray diffraction (Table 9). As may be noted in Figure 2, the XRD pattern for cellulose shows reflections at 11.96, 20.08 and 21.63° 2θ, the splitting in the reflection bands at 20.08 and 21.63° 2θ, indicating that cellulose II is obtained after sodium hydroxide treatment.[23] In the case of CMC (Fig. 2), slightly broader reflections may be observed at 10.31, 20.13 and 22.45° 2θ. The reflection at 10.31° 2θ represents the patterns of the amorphous CMC.

Table 8
Crystallinity index, mean H-bond strength and mercerization depth of different samples

Sample	Crystallinity index A_{1425}/A_{900} (LOI)	Mean H-bond strength (A_{OH}/A_{CH})	Mercerization depth (1375cm^{-1}/1325cm^{-1})
Cellulose	1.96	2.06	-
CMC	0.82	0.39	0.45
CMCA	1.62	0.5	-
CMCAB	2.44	2.56	-

Table 9
X-ray crystallinity index of cellulose, CMC, CMCA and CMCAB

Sample	CrI, %	ΔCrI, % *
Cellulose II	61.02	-
CMC	25.56	-58.11
CMCA	38.94	-36.18
CMCAB	66.67	9.26

$$* \ \Delta CrI\% = \frac{(CrI) \ modified \ cellulose - (CrI) \ pure \ cellulose}{(CrI) \ pure \ cellulose} * 100$$
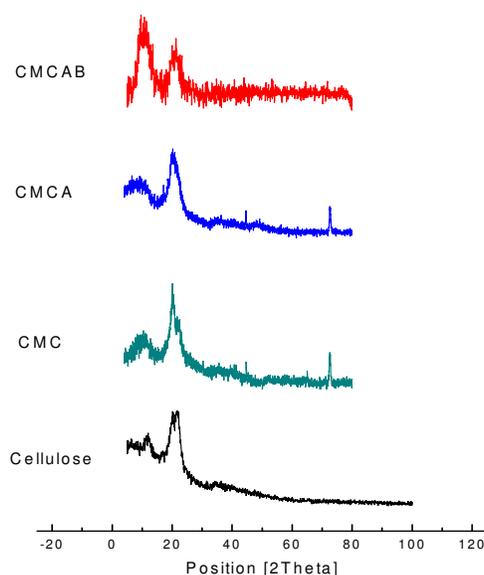
Figure 2: X-ray patterns of cellulose, CMC, CMCA and CMCAB
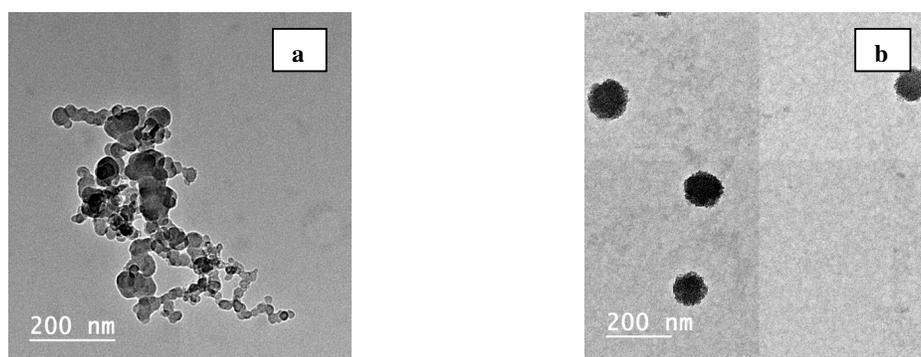
Figure 3: TEM images of (a) CMCA and (b) CMCAB

However, the CMCA exhibits the formation of a new reflection band at 44.58º 2θ, which is attributed to the acetate side chains. In addition, the double reflections in CMC at 20.13 and 22.45º 2θ are reduced to one reflection band at 20.26º 2θ.

In the case of CMCAB, the XRD pattern shows reflections at 12.91, 21.39 and 29.51º 2θ. In addition, a new reflection band at 28.36º 2θ is noticed, which can be attributed to the butyrate side chains.

XRD is most frequently used to measure the crystallinity of polymers. Table 9 illustrates the variation of the crystallinity index (CrI) as a function of different functionalizing groups of the ether and esters, as calculated from the X-ray patterns (Fig.2). It is clear that the CMC crystallinity is decreased, compared with that of cellulose (Table 9), because the mercerization reaction during CMC preparation leads to cleavage of the hydrogen bonds, which diminishes the crystallinity.[24] The increase in crystallinity of CMCA and CMCAB might be due to the decomposition of the amorphous parts of CMC during the reaction steps.[20] The maximum crystallinity value for CMCAB (66.67%) implies changes in the structural regularity of the main cellulosic chains upon mixed esterification.[25] The XRD crystallinity values agree with the crystallinity values calculated from the IR spectra.

TEM analysis

TEM images demonstrate that CMCA self-assembles into regular aggregates, oval in shape, with sizes ranging from 31 to 39.94 nm, with an average size 36.4 nm. CMCAB self-assembles into irregular aggregates, spherical in shape, with

sizes ranging from 93 to 122 nm and with an average size of 93 nm.

CONCLUSION

From sugarcane bagasse, alpha cellulose of 94.2% purity was extracted and utilized to prepare carboxymethyl cellulose, carboxymethyl cellulose acetate and carboxymethyl cellulose acetate butyrate. The cellulose and cellulose derivatives obtained were characterized by FTIR, XRD and TEM.

IR spectroscopy revealed that, in addition to the main characteristic bands of cellulose, CMC presented new characteristic absorption bands at 1599.7 and 1414.5 cm^{-1}, related to the anti-symmetric and symmetric stretching vibrations of COO$^-$, respectively. There were strong sharp absorption peaks of carbonyl C=O at 1743.3 and 1639.2 in the spectrum of CMCA and at 1748.16 and 1640.16 cm^{-1} in the spectrum of CMCAB, which demonstrate the formation of an ester. Also, stretching vibrations corresponding to methylene and methyl groups were noted at 2884.99 and 2966.95 cm^{-1} in the spectrum of CMCAB, so that the emergence of the acetyl and butyryl ester can be confirmed.

The measurement of the crystallinity confirmed that the crystallinity of CMC decreased, compared with that of cellulose, because of the mercerization reaction during CMC preparation. The crystallinity of CMCA and CMCAB increased due to the esterification reaction steps, which contributed to the decomposition of the amorphous parts of CMC during the reaction.

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