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Research Article

Isolation of Cellulosic Material from Drumstick Pulp and Outer Shell of Watermelon and preparation of their acetate and carboxymethyl derivatives.

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Abstract

From the pulp of drumstick (*Moringa oleifera*) and peel of water melon (*Citrullus lantus*) the cellulosic material has been isolated. The acetate and carboxymethyl derivatives of the isolated cellulosic material have been prepared. These derivatives have been characterized by titrimetric method. and IR spectral study. Successful conversion of cellulosic material of the pulp of drumstick and peel of watermelon into their acetate and carboxylmethyl derivatives, suggests their alternative and commercial utilization.

Keywords: *Morings oleifera* (Drumstick), *Citrullus lantus* (Watermelon), cellulose, holocellulose, α-cellulose, degree of substitution, carboxymethyl cellulose (CMC), Infrared spectroscopy (IR).

I. INTRODUCTION

Bangladesh is blessed with various types of fruits and vegetables. Some parts of these vegetables are used and some parts are treated as waste materials. *Moringa oleifera* is the most widely cultivated species of the genus Moringa. It is a fast-growing, drought-resistant tree, native to the southern foothills of the Himalayas in northern India, and widely cultivated in tropical and subtropical areas where its young seedpods and leaves are used as a vegetable. The immature seedpods are called “drumsticks” which is popular as vegetable in Asia and Africa. Watermelon (*Citrllus lanatus*) is one of the familiar summer fruits in Bangladesh. It grows in lowland and may covers an area of cultivation. Its flesh is commonly bright red in color and it is used as part as fruit. *Citrllus lanatus* is a plant species in the family Cucurbitaceae, a vine-like (scrambler and trailer) flowering plant originally from southern Africa. Watermelon is locally known as “Tarmuj”. The fruits have two parts interior flesh are the edible part while the outer shell (ie peel) are the non-edible part. The non-edible part of the fruit like peel usually light green or white in color and also used as vegetable.

Cellulosic materials are the key step of the present civilization. These are used in different form in our daily life. Now, it becomes very important to find out the sources of cellulosic materials in most economic way. Outer skin and the inner (edible) parts of the fruits and vegetables are also the sources of cellulose. So, the diversified uses of the different cellulosic sources may be explored for the development of present civilization as well as the economic condition.

Now a days isolation of cellulose followed by their derivatization such as acetates, nitrates, sulfate, carboxymethyl cellulose have great demand both in textile and pharmaceutical industry[1]. So, this paper deals with the isolation cellulosic material from drumstick and outer skin of watermelon and their derivatization.

II. MATERIALS AND METHODS.

Solvents and chemicals: All the solvents used in the present work were analytical (E.Merck and BDH) and were distilled before use.

Sample collection and preparation: The sample drumstick and watermelon were collected from the local market of Dhaka city. The edible part of drumstick and outer skin of watermelon were separated, cut into small pieces and dried in air and finally in an electric oven at 45°C. After drying, the dried drumstick edible and outer skin of watermelon were grinded with grinder mill. The dried powders were stored separately for further investigation.

Extraction of the dried materials: Measured quantity of the dried powder of drumstick (40.0g) and skin of watermelon (40.5g) were extracted with (250 mL) of *n*-hexane under reflux condition for 30 minutes. After refluxing the content of the flasks were allowed to cool at room temperature and filtered. The whole process was repeated twice and the residues were dried in the air and these were marked a "extractive free powder". The percentages of extractive and extractive free powder were given in Table 1.

Delignification of extractive free powder: The extractive free powders of the drumstick pulp (30.4g) and watermelon skin powder (35.3g) were suspended separately in water (150 mL) in a conical flask and their delignification were carried out following the standard method[2]. The resultant delignified powders obtained were termed as "hollocellulose" and the percentages of hollocelluloses were given in (Table 1).

Isolation of alpha-cellulose: Each of hollocellulose powder of drumstick (10.3 g) and watermelon skin (10.2g) was treated separately with 17.5% aqueous sodium hydroxide solution in a 500 mL round bottomed flask under nitrogen atmosphere for 4 hours over magnetic stirrer with constant stirring to obtain the α-cellulose[3]. The percentages alpha celluloses obtained were given in (Table1).

Preparation of cellulose acetate: Acetate derivatives of each of the hollocellulose and alpha-cellulose of the drumstick pulp and watermelon skin were prepared[4] following the standard procedures. The percentages of yields of the acetate derivatives were given in Table-1.

Preparation of carboxymethyl cellulose derivatives: Measured amounts of hollocellulose and alpha-cellulose of the drumstick pulp and watermelon skin were separately converted into their carboxymethyl cellulose (CMC) derivative following the standard procedure[5]. The percentages of yields were given in Table-1.

Determination of degree of substitution (DS): Degree of substitution of the prepared acetate derivatives of hollocelluluse and alpha-cellulose of both samples were determined by titrametric method[6]. The degrees of substitution of these acetate derivatives of hollocellulose and alpha-cellulose were calculated using the following equation and the results are given in Table-2.

$$\%\ \text{of AG} = \frac{[(V_{bi} + V_{bt})\mu_b - V_a \times \mu_a]43 \times 100}{m_{ca} \times 1000}$$

where

V_{bi} = vol. of sodium hydroxide added

V_{bt} = Vol. of sodium hydroxide spent in the titration

m_{ca} = Weight of acetate derivatives taken

μ_b = Strength of sodium hydroxide solution

μ_a = Strength of hydrochloride solution

V_a = Volume of hydrochloric aced added to the system

molar mass of acetyl group = 43

Calculation

Strength of sodium hydroxide used = 0.24 M

Strength of hydrochloric acid used = 0.24 M

Infra-red (IR) spectroscopic analyses hollocellulose, alpha-cellulose and the derivatives of their acetate and carboxymethyl cellulose: The IR spectra of hollocellulose, alpha-cellulose, the derivatives of the acetate and carboxylmethyl cellulose of the pulp of drumstick and peel of watermelon were recorded separately in KBr pellets using a Shimadzu IR-470 spectrophotometer. Characteristics absorption peaks for hollocellulose, alpha-cellulose and the derivatives of their acetate and carboxymethyl cellulose were identified and the absorption pattern was mentioned in Table 3.

III. RESULTS AND DISCUSSION

The drumstick and watermelon were collected locally; skin of watermelon and the pulp of drumstick were separated. The pulp of the drumstick and peel of watermelon were cut into small pieces, dried and powdered. The powdered were separately extracted with *n*-hexane. The extractive free powders were separately delignified. Alpha-celluloses were separated from the delignified powders. Each of the hollo- and alpha-cellulose were separately acetylated and carboxy methylated. Degrees of substitution of the acetate derivatives were determined and IR spectral study of the hollo- and alpha-cellulose and the derivatives of their acetate and carboxymethyl cellulose were carried out.

The amount of *n*-hexane extract (Table-1) in drumstick pulp (6.54 %) and the peel of watermelon (1.98%), was found to be very low; This, indicates that these materials contain very small amounts of soluble organic materials. It was observed that the hollocellulose in drumstick pulp (Table-1) is 43.8% and the same in the peel of watermelon is 54.7%. The corresponding alpha-celluloses are 20.9% and 26.4% in drumstick pulp and in the peel of watermelon, respectively. This results (Table-1) reveals that, both the pulp of drumstick and peel of watermelon may be used as sources of cellulosic materials, which are comparable to the other agro waste materials[7,8,9]. The degree of substitution of the acetate derivatives (Table-2) of the hollocellulose and the corresponding alpha-cellulose are 3.32 % and 14.45 % for drumstick pulp and it was 14.34 % and 3.63 % for the peel of watermelon, respectively. These results reveal that the cellulosic materials obtained from both these two sources have been partially acetylated.

In infra-red spectral analysis (Table-3) of the hollocellulose shows the absorption peaks at around 3442, 2918 and at 1057 cm^{-1} indicating the presence of O–H stretching, C–H stretching and C–O stretching of glucose unit, but no distinct peak for C=O was found. On the other hand, IR spectra of acetate derivatives of hollocellulose in both the cases indicated the strong absorption peak of >C=O for acetate group at around 1731-1754 cm^{-1} and the absorption peak of C–O stretching of acetyl group at 1227-1236 cm^{-1}. The other characteristic peaks due to C–O stretching of skeletal backbone were observed in both hollocellulose and its acetate derivative at 1047-1057 cm^{-1}. The characteristic strong peaks of O–H stretching for both hollocellulose and their acetate derivatives means that the inner portion has many free –OH groups left in acetate derivatives means partial acetylation achieved during the derivatization.

The IR spectral analysis of alpha-cellulose and its acetate derivatives (Table-3) possess the strong absorption bands at around 3438, 3446 and 3450 cm^{-1}, due to the presence of large number of –OH groups in the fractions. The acetate derivative possess the distinct strong absorption band for >C=O group at around 1735-1743 cm^{-1} with the other characteristic peak of C–O stretching of skeletal backbone at 1071-1091 cm^{-1}. The C–H stretching band of acetate derivatives of hollocellulose and alpha-cellulose was observed with strong intensity at 2920, 2923 and 2961 cm^{-1}, except the CMC derivative of α-cellulose in case of watermelon.

The IR spectral analysis of the carboxylmethyl cellulose derivatives of hollocellulose and alpha-cellulose (Table-3) shows the strong absorption bands at 1611, 1622 1626 and 1633 cm^{-1} due to the asymmetric stretching and that of 1380, 1415, 1420 and 1426 cm^{-1} for symmetric stretching of the carboxylate ion that present in the CMC derivatives of hollocellulose and alpha-cellulose, respectively. The presence of these peaks are also giving the information of successful derivatization of these two fractions. The C–H stretching band of carboxymethyl cellulose derivatives of hollocellulose was observed with strong to moderate intensity at 2926 and 2923 cm^{-1} in both the materials but such absorption band is absence in the derivatives of alpha-cellulose in both the cases. The >C=O stretching band of acetyl group was not detected in alpha-cellulose but it appears as strong peak at 1735 and 1743 cm^{-1} in the derivatives of carboxylmethyl cellulose, which is the indication of successful acetylation of the sample. The DS and IR spectral analysis indicated the successful acetylation of the cellulosic materials obtained from the pulp of drumstick and the peel of watermelon.

IV. CONCLUSION

This finding suggests that the drumstick pulp and peel of watermelon may be used as cellulosic sources and the isolated celluloses may also be successfully and satisfactorily converted into different types of cellulosic derivatives to explore its Multipurpose commercial uses.

Table 1
Percentage of extractive, hollocellulose, alpha-cellulose and the derivatives

* Sample materials	Extracts	Extractive free powder	Hollocellulose Obtained	α-cellulose obtainrd	Acetate Derivatives		CMC derivatives	
					hollocellulose	α-cellulose	hollocellulose	α-cellulose
Drumstick % Obtained	6.54	88.7	43.8	20.9	6.9	9.4	35.0	20.0
Watermelon % Obtained	1.98	91.8	54.4	26.4	8.6	21.4	39.2	25.1

*** On the basis of raw powder**

Table 2
Degree of substitution of the acetate derivatives of hollocellulose and ~-cellulose of drumstick pulp and peel of watermelon

Acetate derivatives	Vol. of NaOH (0.25 M) added V_{bi} (mL)	Vol. of EtOH added (mL)	Vol. of HCl (0.24 M) added V_a (mL)	Vol. of NaOH (0.25 M) spent in titration V_{bt} (mL)	DS of acetates derivatives (% AG)
Hollocellulose of Drumstick pulp	5.0	5.0	10.0	5.4	3.32
α-cellulose of Drumstick pulp	10.0	10.0	20.0	12.9	14.45
Hollocellulose of Peel of watermelon	5.0	5.0	10.0	7.1	14.34
α-cellulose Peel of watermelon	5.0	10.0	10.0	5.5	3.63

Table 3
Comparative IR study of hollocellulose, ~-cellulose and the derivatives of their acetate and CMC of drumstick pulp and peel of watermelon

Types of vibration	Hollocellulose	Derivatives of hollocellulose		α-cellulose	Derivatives of α-cellulose	
		Acetates	CMC		Acetates	CMC
O–H stretching	DS: 3442.03 (S)	DS: 3487.36 (S)	DS: 3441.07 (S)	DS: 3450.71 (S)	DS: 3446.85 (S)	DS: 3443.96 (S)
	WM: 3437.21(S)	WM: 3447.82 (S)	WM: 3427.56 (S)	WM: 3438.17 (S)	WM: 3438.17 (S)	WM: 3441.07 (S)
C–H stretching	DS: 2918.35 (S)	DS: 2961.75 (S)	DS: 2926 06 (S)	DS: N.O.	DS: 2923.27 (S)	DS: N.O.
(sp^3)	WM: 2921.24 (S)	WM: 2920.28 (S)	WM: 2923.17 (M)	WM: N.O.	WM: N.O.	WM: N.O
C=O stretching	DS: N.O.	DS: 1754.29 (S)	DS: N.O.	DS: N.O.	DS: 1735.0 (S)	DS: 1735.0 (S)
of acetyl gr.	WM: N.O.	WM: 1731.14 (S)	WM: N.O.	WM: N.O.	WM: 1743.68 (S)	WM: 1738.86 (S)
CH_3 bending	DS: N.O.	DS: 1377.20 (S)	DS: N.O.	DS: N.O.	DS: 1380.09 (S)	DS: N.O.
of acetyl gr.	WM: N.O.	WM: 1366 .59 (S)	WM: N.O.	WM: N.O.	WM: 1423.49 (S)	WM: N.O.
C–O stretching	DS: N.O.	DS: 1236. 39 (S)	DS: N.O.	DS: N.O.	DS: N.O	DS: N.O.
of acetyl gr.	WM: N.O.	WM: 1227.71 (S)	WM: N.O.	WM: N.O.	WM: N.O	WM: N.O.
C–O stretching	DS: 1057.01 (S)	DS: 1047.36 (S)	DS: 1060.87 (S)	DS: N.O.	DS: 1071.48 (S)	DS: 1068.58 (M)
skeletol	WM: 1057.0 (S)	WM: 1051.22 (S)	WM: 1063.10 (S)	WM: N.O.	WM: 1091.73 (S)	WM: 1111.02 (M)
Assymetrical Strecching of	DS: N.O.	DS: N.O.	DS: 1626.98 (S)	DS: N.O.	DS: N.O.	DS: 1622.16 (S)
carboxylate ion	WM: N.O.	WM: N.O.	WM: 1633 74 (S)	WM: N.O.	WM: N.O.	WM: 1611.55 (S)
Symetrical Strecching of	DS: N.O.	DS: N.O.	DS: 1380.09 (S)	DS: N.O.	DS: N.O.	DS: 1415.78 (S)
carboxylate ion	WM: N.O.	WM: N.O.	WM: 1420.60 (S)	WM: N.O.	WM: N.O.	WM: 1426.38 (S)

***Not observed: N.O.; DS drumstick and WM means water melon**

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