Dhaka Univ. J. Sci. 60(1): 77-78, 2012 (January)

Investigation on Orange Peel: Derivatization of Isolated Cellulosic Material and Analysis of the Fatty Acids Composition

Md. Rabiul Islam, Tanvir Muslim and Md. Azizur Rahman*

Department of Chemistry, University of Dhaka, Dhaka-1000, Bangladesh

Received on 14. 03. 2011. Accepted for Publication on 18. 06. 2011

Abstract

Isolation of cellulosic material from the waste material, orange *(Citrus sinensis)* peel has been carried out. The isolated cellulosic material has been converted into its acetate ester. The acetate derivative has been characterized by titrimetric method and IR spectra. The fatty acid composition of the orange peel has also analyzed by GLC. Successful conversion of agro-waste into its acetate derivative and the fatty acid composition suggest an alternative use of this waste material.

Key words : Orange peel, cellulose acetate, fatty acids

I. Introduction

The outer part or the skin of an orange is called orange peel. In our country the orange peel is a waste material. Its proper utilization may help to have a friendly environment as well as it may help to add our economic development. Orange peel may be used as a source of cellulose for isolation of its cellulosic material. The derivatization of isolated cellulosic material may remove the waste disposal problem and earn economic importance. The important cellulose derivative, cellulose acetate has versatile commercial uses. The extraction of oil from orange peel and its characterization may suggest the feasibility of its utilization. Literature survey reveals that almost no work has been done on derivatization of cellulosic material isolated from orange peel and analysis of fatty acids composition of orange peel. So, this paper deals with the isolation of cellulosic material and extraction of oil from orange peel, preparation of cellulosic acetate from the cellulosic material and characterization of cellulose acetate and the extracted oil.

II. Experimental

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

Sample collection and preparation: The sample was collected from different places of Dhaka city. It was first cut into small pieces, dried in open air and finally dried in the oven at 45ºC. After drying, the dried plant material was grinded with grinder mill and stored at room temperature to carry out all the experiments.

Extraction of dried orange peel powder: Dried orange peel powder (78.2 g) was extracted with (500 ml) petroleum ether (b.p. 40-60ºC) under reflux condition for 30 minutes. After refluxing, the content of the flask was allowed to cool at room temperature and filtered. The residue was dried in the air. This residue was marked as "extractive free powder" of orange peel. The percentage of yield of the petroleum ether extract was found to be 12.19.

Delignification of extractive free powder[1]: The extractive free powder of orange peel (20 g) was suspended in water (200 mL) in a conical flask and heated at 70-80ºC with constant stirring for 30 minutes in a magnetic stirrer. Sodium chlorite (2 g) and glacial acetic acid (15 mL) was added drop wise into the flask. The addition of sodium chlorite and acetic acid were repeated four times. The percentage of yield of holocellulose obtained from the extractive free powder of orange peel was 40.0.

Preparation of cellulose acetate[2]: Holocellulose (1.08 g) obtained from orange peel was taken in a round bottomed flask (250 ml). The whole content of the flask was placed in a magnetic stirrer for frequent stirring at 80ºC for about 1 hour. After stirring, it was placed in a water bath at 60ºC. A mixture of acetic anhydride (10 mL) and concentrated H_2SO_4 (0.4 mL) were added to it drop wise from a dropping funnel for about 30 minutes keeping the temperature 90-100ºC. After the addition of the mixture from the dropping funnel to the sample, the content of the flask was kept in water bath for another 30 minutes at the same temperature. At first a clear solution was obtained at the bottom of the flask which was then turned into a crudy white precipitate on the addition of distilled water. The precipitate was centrifuged and washed with distilled water. It was centrifuged again. Finally, the precipitate was washed with ethanol and then dried in air and the yield cellulose acetate was found to be 50.9%.

Determination of degree of substitution (DS)[3]: Degree of substitution of the prepared cellulose acetate was determined by titrametric method. Cellulose acetate (0.10 g) was taken in a conical flask (250 ml). Sodium hydroxide (0.25 M, 5.00 mL) and ethanol (5.00 mL) were added to it.

* Corresponding author.

The mixture was allowed to stand for 24 hours. Then hydrochloric acid (0.24 M, 10.0 mL) was added to the mixture and allowed to stand for 30 minutes. The mixture was then titrated with sodium hydroxide solution (0.25 M) using phenolphthalein as an indicator. The degree of substitution of cellulose acetate was found to be 12.6%.

Infra red (IR) spectroscopic analysis of holocellulose and cellulose acetate: The IR spectrum of holocellulose and cellulose acetate of the sample of orange peel were recorded in KBr pellets using a Shimadzu IR-470 Spectrophotometer. Characteristic peaks for holocellulose were obtained at 3400 2890 and 1040 cm^{-1}, and the characteristic peaks for cellulose acetate were found at 1780, 1220, and 1040 cm^{-1} respectively.

Isolation of free and bound fatty acids[4, 5]: The free and bound fatty acids were isolated from the petroleum ether extract. The amounts of free and bound fatty acids were found to be 73.0 % and 27.0 %, respectively.

Analysis of free and bound fatty acids[4, 5]: The free fatty acids (0.168 g) and bound fatty acids (0.168 g) of isolated from orange peel were converted[4] into their methyl ester and these were analysed using GLC.

III. Results and Discussion

The agro waste orange peel contains about 40.0 % cellulosic material which is comparable with the cellulosic material of other sources. The yield of cellulose acetate (50.9 %) obtained from orange peel was satisfactory compared with the yield obtained from the other sources. The of DS of the prepared cellulose acetate was estimated using titrametric method and the result was found to be 12.6 %, which reveals that the cellulosic material obtained from orange peel has been partially acetylated. In infrared spectral analysis of the holocellulose peaks were found at 3400, 2890 and 1040 cm^{-1} indicating the presence of O-H stretching, C-H stretching and C-O stretching of sugar unit, but no distinct peak for C=O stretching was found. On the other hand IR spectra of cellulose acetate indicated the strong absorption peak of >C=O of acetate group at 1780 cm^{-1} and weak absorption peak of C-O stretching of acetyl group at 1220 cm^{-1}. The DS determination and IR spectral analysis indicated the successful acetylation of cellulosic material obtained from orange peel.

The free and bound fatty acids of orange peel were isolated[4, 5] from the petroleum ether (b.p-40-60ºC) extract. These were converted to their methyl ester and analyzed by GLC. Oleic acid and palmitic acid were identified as free fatty acids having their relative percentage 92.7 and 7.3, respectively. Analysis of bound fatty acids indicated the presence of oleic acid (57.2 %), palmtic acid (38.6 %), stearic acid (4.1 %) with trace amount of behenic and lignoceric acids. Both the free and bound fatty acids of orange peel contain high proportion of oleic acid. This acid is a component[6] of butter, soybean, cotton and corn oil. On the other hand the saturated acids namely palmitic and stearic acids are very low proportion. These results indicate that the oil extracted from orange peel has the quality of edible oil.

IV. Conclusion

This finding suggest that the cellulosic material of the agro-waste, orange (*Citrus sinesis*) peel may successrfully and satisfactorily be converted into cellulose acetate to explore its multipurpose commercial uses and if it is feasible to extract the oil of orange peel on a large scale, the oil may be commercially used.

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