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(Research Article)

Studies on Physico-Chemical Properties of Rice Bran Wax and its Comparison with Carnauba Wax

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ABSTRACT

Rice bran wax is a natural vegetable wax and is a value added by product of Rice bran oil refineries. It is hard nontacky wax and contains higher fatty alcohols and esters which make it comparable to Carnauba wax. In the present work, studies are carried out on Rice bran wax for various physico-chemical properties like solubility, melting point, specific gravity, moisture content, saponification value, acid value, ester value, hydroxyl value, unsaponifiable matter, Iodine number etc. The observed values are compared with the reported data of Carnauba wax. It can be concluded from the results that most of the physico-chemical properties of Rice bran wax are similar to that of Carnauba wax and that's why Rice bran wax may prove to be suitable substitute for Carnauba wax in various cosmetics and pharmaceutical products. This kind of data will also help in standardization and evaluation of Rice bran wax.

Key Words: Rice bran Wax, Carnauba wax, Rice bran oil,Acid value, Ester value, Iodine value.

INTRODUCTION

Rice (*Oryza sativa*) is one of the most important grains in the world. India is second largest producer of Rice in the world. The outer covering of rice kernel after removing the husk is called Rice bran. It is valuable byproduct of rice milling industry because it contains 12-25 % of oil depending on quality[1].

The oil extracted from Rice bran is called Rice bran oil and is available in both grades (i.e. edible and non edible). Rice bran wax is hard non tacky wax and is the byproduct of Rice bran oil refinery. Its presence is 2-5 % in Rice bran oil. It is recovered as sludge wax and further processed to slack wax, pressed wax. This form is solvent extracted to produce pure wax which is further refined and bleached to procure hard wax of food or cosmetic grade. It is white to yellowish in color and can be made available in flakes form also[10].

The chemical constituents of Rice bran wax are mainly saturated monoesters (C-46 to C-60) of long chain fatty acids (C-22 to C-26) and long chain fatty alcohols (C-26 to C-30). Main esters are myricyl cerotate (43-45 %), ceryl cerotate (21-22 %) and Isoceryl isocerotate (9-10 %). The refined and bleached Rice bran wax has melting point78-82°c, Saponification value 70-120 and iodine value 4 to 10. It can be used in many industries like polishes, leather, crayons, candle making, shoe creams, paper coating, carbon paper, lubricants etc. Its major consumption is in food industries as constituents of chocolate enrobers, vegetable coating, and wax emulsion for fruit preservation. Recently lot of research work is done on Rice bran wax for its use in pharmaceutical and cosmetics products. It has chemical constituents and physicochemical properties similar to that of Carnauba wax which is drawing interest of researchers for using this wax in various pharmaceutical products like tablets, ointment bases, suppositories and cosmetic products like moisturizing lotions, lipsticks, creams etc. Lots of work is done in USA, China and Japan but most of those are patented. It can also be used in Novel Drug Delivery Systems (NDDS) which is currently hot research and development area of pharmaceutical industries. RBW can be used in producing Octacosanol which is believed to enhance athletic performance. It can also be used to produce Triacontanol which is plant growth stimulants[9, 10].

MATERIALS AND METHODS

Material
Pure Rice Bran Wax (RBW) was obtained from Space Lab, Nasik as a gift sample.

Appearance
Appearance of RBW was observed by visual inspection.

Solubility
10.2 mg of sample was dissolved in 100.0 ml of water.

Melting Point
Dried a small quantity of the finely powdered RBW at a temperature considerably below its melting point. Transfered a portion to a dry capillary tube and packed the powder by tapping on a hard surface so as to form a tightly packed column 4 to 6 mm in height. Attached one of the tubes to a thermometer graduated in 0.5°C so that the substance is close to the bulb of the thermometer. Introduced the thermometer with the attached tube into a beaker so that the distance between the bottom of the beaker and the lower part of the bulb of the thermometer is 1 cm. fill the beaker with water to a depth of 5cm. Increased the temperature of the water gradually at a rate of 1 c/min. The temperature at which the substance begins to rise in the capillary tube was regarded as the melting point. Repeated the operation with the other 4 capillary tubes and calculated the result as the mean of the 5 readings[3].

Specific Gravity
Selected a scrupulously clean, dry pycnometer that previously has been calibrated by determining its weight and the weight of recently boiled water contained in it at 25°C. Melted the substance and filled the pycnometer with it. Adjusted the temperature of filled pycnometer to 25°C and weighed. Subtracted the tare weight of the pycnometer from the filled weight. The specific gravity is the quotient obtained by dividing the weight of sample contained in the pycnometer by the weight of water contained in it, both determined at 25°C.

Moisture Content

Standardization of the reagent
Placed about 36 ml of dehydrated methanol in the titration vessel and added sufficient KF reagent to give the characteristic end-point. Added quickly 150 to 350 mg of sodium tartrate accurately weight by difference and titrated to end-point. The water equivalence factor F in mg of water per ml of reagent is given by the formula[4];

$$Factor = \frac{Wt.of\ DST\ X\ 0.1566}{B.R.}$$

Procedure
After determination of factor added 0.5 g RBW accurately to the titration vessel. Stirred for 1 minute and titrated against the electrometric end-point using KF reagent.

$$Moisture\ content = \frac{B.R.X\ Factor\ X\ 100}{Wt.of\ sample}$$

Saponification Value
Weighed 2 g of the RBW into a 200 ml flask, added 40.0 ml of the ethanolic solution of potassium hydroxide and boiled under a reflux condenser for 2 hour, rotating the contents frequently. While the solution was hot, titrated the excess of alkali with 0.5 M hydrochloric acid using phenolphthalein solution as indicator. Repeated the operation without RBW. Calculated the Saponification Value from the expression 28.05 v/w where v is the difference, in ml, between the titrations and w is the weight, in g, of substance taken[3, 4];

$$Saponification\ value\ (Is) = \frac{28.05\ X\ Diff.}{Wt.of\ sample}$$

Acid Value
Dissolved 10.00 g of RBW in 50 ml a mixture of equal volumes of ethanol (96 %) and light petroleum, previously neutralized with 0.1 M sodium hydroxide, using 0.5 ml of phenolphthalein solution as indicator.

Heated to about 90°C to dissolved the RBW. When the substance has dissolved, titrated with 0.1 M sodium hydroxide until the pink color persists for at least 15s (n ml of titrant). When heating has been applied to aid dissolution, maintained the temperature at about 90°C during the titration[3]

$$Acid\ Value\ (IA) = \frac{5.610\ X\ n}{Wt.\ of\ Sample}$$

Ester Value

The ester value was calculated by following formula;

$$Ester\ value\ (IE) = saponification\ value - Acid\ value$$

Hydroxyl Value

Introduced 2.0 gm of RBW into a 150 ml acetylating flask fitted with an air condenser. Added 5 ml of acetic anhydride solution and attached the air condenser. Heated the flask in a water- bath for 1 h keeping the level of the water about 2.5 cm above the level of the liquid in the flask. Withdrawn the flask and allowed it to cool. Added 5 ml of water trough the upper end of the condenser. Added sufficient pyridine to clear cloudiness and the volume added was noted. Shaken the flask and replaced it in the water- bath for 10 min. Withdrawn the flask again and allowed to cool. Rinsed the condenser and the walls of the flask with 5 ml of alcohol, previously neutralized to phenolphthalein solution .Titrated with 0.5 M alcoholic potassium hydroxide using 0.2 ml of phenolphthalein solution as indicator (n2 ml of 0.5 M alcoholic potassium hydroxide). Carried out a blank test under the same conditions (n2 ml of 0.5 M alcoholic potassium hydroxide) [3, 4].

$$Hydroxyl\ value\ (IoH) = \frac{28.05\ X\ (n2 - n1)}{Wt.\ of\ Sample} + Acid\ Value$$

Unsaponifiable Matter

To 2.0 to 2.5 g of RBW contained in a 250 ml flask, added 25 ml of 0.5 M ethanolic potassium hydroxide and boiled under a reflux condenser in a water - bath for 1 hour, swirling the contents frequently.Washed the contents of the flask into a separating funnel with the aid of 50 ml of water and while the liquid was slightly warm, extracted by shaking vigorously with three 50 ml quantities of peroxide free ether, rinsing the flask with the first quantity of ether. Mixed the ether solutions in a separating funnel containing 20 ml of water. Gently rotated separating funnel for a few minutes without violent shaking, allowed the liquids to separate and discarded the aqueous layer. Washed the ether solution by shaking vigorously with two 20 ml quantities of water and then treated with three 20 ml quantities of 0.5 M potassium hydroxide, shaking vigorously on each occasion, each treatment was followed by washing with 20 ml of water. Finally washed with successive 20 ml quantities of water until the aqueous layer was no longer alkaline to phenolphthalein solution. Transfered the ether extract to a weighed flask rinsing the separating funnel with peroxide free ether, distiled the ether and added 3 ml of acetone to the flask. With the aid of a gentle current of a air removed the solvent completely from the flask which was almost immersed in boiling water and hold obliquely and rotated. Dried to constant weight at a temperature not exceeding 80° C and dissolved the content of the flask in 10 ml of freshly boiled ethanol (96 %) previously neutralized to phenolphthalein solution. Titrated with 0.1 M ethanol sodium hydroxide using phenolphthalein solution as indicator. Calculated the Unsaponifiable matter as a percentage of the substance [3, 4];

$$Unsaponifiable\ matter\ \left(\%\frac{w}{w}\right) = \frac{Wt.\ of\ residue\ X\ 100}{Wt.\ of\ Sample}$$

Free Fatty Acid

Boiled 250 ml of ethanol (96 %) to remove carbon dioxide, added 0.5 ml of phenolphthalein solution, allowed to cool to 70°C and neutralized with 10g Sodium hydroxide to 100 ml of the neutral ethanol, added 10 g of the RBW and dissolved it quickly by heating under a reflux condenser. Cooled to 70°C and titrated at 70°C with 0.1 M sodium hydroxide (Not more than 0.2 ml is required. If the solution is still pink added in a thin stream 5 ml of hot barium chloride solution previously neutralized to phenolphthalein solution, mix thoroughly and titrate with 0.1 M hydrochloric acid until the pink color disappears not more than 1.0 ml is required).

Iodine Value

Taken 1.0 g substance into a 250 ml flask fitted with a ground glass stopper and previously dried or rinsed with glacial acetic acid, and dissolved it in 15 ml of chloroform. Added very slowly 25.0 ml of iodine bromide solution. Closed the flask and kept it in the dark for 30 min. shaking frequently. Added 10 ml of a 100 g/l solution of potassium iodide and 100 ml of water. Titrated with 0.1 M sodium thiosulphate shaking vigorously until the yellow color was almost discharged. Added 5 ml of starch solution and continued the titration by adding the 0.1 M sodium thiosulphate drop wise until the color was discharged (n1 ml of 0.1 M sodium thiosulphate). Carried out a blank test under the same condition (n2 ml of 0.1 M sodium thiosulphate) [3, 4].

$$Iodine\ value\ (Ii) = \frac{1.269\ X\ (n2 - n1)}{Wt.\ of\ Sample}$$

RESULTS AND DISCUSSION

The Rice Bran Wax was characterized for various properties and specification set as per pharmacopoeial guidelines. The results of rice bran wax obtained was found to be nearly similar to the standards values of carnauba wax and shown in Table-1. On the basis of results obtained it can be suggested that the Rice bran wax is a suitable substitute for carnauba wax and it can be used as coating agent, as a base in cosmetic preparation and in some extent it can be used as release retardant agent in sustained release dosage form.

CONCLUSION

Rice bran wax is presently used in many general industries. It is also used by food industries; it has very good potential to be used in pharmaceutical and cosmetic industries. It can replace partially in most of the products and fully in some of the products to carnauba wax. Carnauba wax is not produced in India. It is imported from Brazil hence RBW can save lot of foreign currency for India.

Table-1: Comparison of Observed values of RBW and Standards value of Carnauba Wax[2, 5]

Sr. No.	Tests	Observed values of Rice Bran Wax	Standards value of Carnauba Wax
1	Solubility	Insoluble in water, soluble in ether, ethanol and isopropyl alcohol	Insoluble in water, soluble in ether, ethanol
2	Melting point	80.5 °c	78 °c to 88° c
3	Specific gravity	0.912	0.990- 0.999 at 25° c
4	Moisture content	0.074 % w/w	019 % w/w
5	Saponification value	80.88	78-95
6	Acid value	2.848	NMT 12
7	Ester value	78.04	68-85
8	Hydroxyl value	19.62	---
9	Unsaponifiable matter	40 % w/w	50-55 % w/w
10	Iodine value	10	5.0-14.0

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