PREPARATION OF SUGAR SYRUP FROM CASHEW APPLE (*Anacardium occidentale*, LINN).

By M. Srinivasan.

The cashew is a hardy tree that thrives well in many parts of India, especially on the west coast, where it is largely grown for its valuable nut. After the removal of the nut, there remains the fleshy and succulent portion, the cashew apple, more popularly known as the cashew fruit. This apple is soft and sweet and possesses a strong aroma. It has, besides, an astringent principle which curtails its use as an edible fruit. The juice of the apple can be fermented either to yield a beverage, or to produce vinegar (Rama Iyer, *Scientific Reports, Agricultural Research Institute*, Pusa, 1930, 55). The production of the fruit is, however, far in excess of the demand, and being readily perishable, the available supply is largely wasted.

In a previous communication (Subrahmanyan, Report to the Director of Industries, Madras, 1932—unpublished) it was pointed out that though alcohol could be obtained from cashew apple by fermentation, the cost of its preparation does not warrant large scale production, and hence the juice could be more usefully converted into syrup. The present paper relates to a systematic enquiry on the utilisation of cashew apple for the preparation of sugar syrup.

EXPERIMENTAL.

Materials.—Several consignments of cashew apple were obtained through the courtesy of the Honorary Secretary, District Advancement Association, South Kanara, to whom the author's thanks are due. When received in Bangalore, however, these fruits were found to have mostly decayed. The apples were, therefore, bought from the local Palace Orchards. They were brought to the laboratory immediately after plucking and used for the experiments.

Examination of the Fruit.—Total solids were determined according to Hughes and Maunsell (*Analyst*, 1934, **59**, 231). The apples were cut into thin slices and a known weight (1 to 2 g.) weighed from a squat type of weighing bottle into a tared platinum dish (100 c.c.). Hot distilled water was added to distribute the sample evenly over the bottom of the dish, and placed on a water-bath till almost dry, the last traces of water being removed by heating in a vacuum oven at 100° till the weight was constant. To find out the extreme variations, two samples, (1) unripe (pale-yellow in colour and hard to feel), and (2) fully ripe (red and soft) were analysed. The former yielded

48 per cent. and the latter 14·9 per cent. of total solids on the fresh weight of the apple.

Sugars.—About 10 g. of sample was refluxed with 200 c.c. of 95 per cent. alcohol for about one hour. The alcoholic extract was filtered and the residue washed twice with alcohol. From the combined filtrates, alcohol was distilled off at a low temperature (50°). The residue left in the flask was dissolved in hot water, transferred to a 500 c.c. measuring flask, and made to volume. 25 c.c. of the solution were clarified with 2 to 3 c.c. of normal lead acetate solution, made upto 100 c.c. and filtered. 50 c.c. of the filtrate were deleaded with sodium phosphate, made upto 100 c.c., and again filtered. Sugar was estimated according to Bertrand in 20 c.c. portions of the filtrate.

Another aliquot was inverted, and the resulting sugars estimated as before, there being practically no difference in value before and after inversion (Table I).

TABLE I.

Sugar content of cashew apple.

Condition of Fruit	Reducing sugar per cent. (as invert sugar on fresh weight of the apple)	
	Before inversion	After inversion
Unripe	4·1	4·3
Half ripe	5·3	5·3
Ripe	7·0	7·0
Fully ripe	7·2	7·2

The above results show that the sugar content of the cashew apple depends on the extent of its ripeness. The unripe apple has the minimum sugar content, while the ripe one has the maximum, others between these stages having corresponding intermediate values.

At none of the stages of ripeness was there any evidence of cane sugar being present. The origin of reducing sugars in the apple would, therefore, appear to be a highly interesting line of enquiry.

Experiments with the juice.—The juice obtained by pressing the minced cashew apple through cloth (*vide infra*) was turbid. On examination under the microscope, it was found to be teeming with micro-organisms. It was further characterised by powerful reducing action, which was greatly diminished, however, by ærating the warm juice (50°) for half an hour. This behaviour suggests the presence of ascorbic acid—vitamin C (Watt, *Commercial Products of India*, p. 65) in the juice.

Analysis of the juice.—The following is a proximate analysis of the juice, the analytical methods employed being those recommended by A.O.A.C. (1931) for fruits and fruit products:—pH, 4·2 to 4·6; titratable acidity, 6·7 c.c. (N acid); density, 1040; total solids, 10·6 per cent.; and ash, 0·36 per cent.—all on volume basis.

On being moistened with water, the ash was found to be alkaline to litmus. It also yielded a positive test for phosphorus.

The sugars were estimated by reduction (Bertrand) and polarization methods, both before and after inversion.

TABLE II.

Sugar (as invert sugar) per 100 c.c. of the juice.

Sample	Before clarification g.	After clarification		$[\alpha]_D^{26}$
		Before inversion g.	After inversion g.	
1	9·6	9·2	9·7	−16·0
2	9·5	9·1	9·9	,,
3	10·0	9·5	9·9	,,

The small increase in the total sugar value after inversion indicates that there is very little cane sugar even in the juice. The reducing sugars correspond on an average to 95 per cent. of the total solids, or 98 per cent. of the organic solutes present in the juice.

Nature of sugars.—The specific rotation $[\alpha]_D^{26} = -16°$ of the cashew juice after clarification indicates the presence of invert sugar, $[\alpha]_D^{20} = -20°$. In further confirmation of the presence of invert sugar in the medium, the clarified juice gave positive colour reactions both for glucose and fructose, while the osazone prepared therefrom was purely that of glucose (equally of fructose).

Other constituents of the juice.—As indicated in a previous communication (Subrahmanyan, *loc. cit.*), the juice contained considerable quantities of tannins, organic acids and an astringent principle. It had also the penetrating odour of the whole apple, and was pale yellow in colour. The odour was removed by vigorous boiling of the juice. The colour was traced to the pigments extracted from the outer skin of the apple during mincing and pressing. The extracted pigments were of the nature of anthocyanins, as evidenced by the characteristic pink colour the juice developed on the addition of concentrated hydrochloric acid.

Preparation of Syrup.

The methods employed to prepare sugar syrup from cashew apple were those usually adopted in obtaining raw sugars from cane or beet. Such methods involved (1) extraction of juice from the apple, (2) defecation and clarification of the juice by heat, chemicals or filtration, (3) concentration of the clarified juice by fire, steam or vacuum evaporation, and (4) purification (curing) of the resulting product.

Extraction of juice from cashew apple.—Working with small numbers of the apples, it was found that a very simple but efficient method of expressing the juice was to mince the fruits and squeeze the resulting mass through folds of cloth. An aluminium mincer was used for the purpose. This method of extraction gave fairly uniform yields of juice as shown by Table III. Use of iron-ware was found undesirable, since it yielded a bluish-black extract, the colour being due to the reaction between the metal and the acids and tannins of the juice.

Table III.

Yield of juice from cashew apple.

Condition of the apple	Number	Yield of juice c.c.	Yield of juice per apple c.c.
Fully ripe, weighing 75·8 g. ..	1	55	55
Unripe, weighing 255 g. ..	7	90	13
Collection, ripe (major portion), half-ripe and unripe ..	100	2,400	24
,,	1,150	27,200	24
,,	1,300	29,000	22

It may be seen from the above that when a representative collection (including fruits at various stages of ripeness) is crushed, the average yield of juice may be reckoned at 20 to 25 c.c. per apple.

The state of ripeness of the cashew apple not only regulates the yield of juice, but so controls the efficiency of pressing. Thus, in case of the fully ripe, soft apple, it was found that squeezing the minced mass through cloth extracted 85 per cent. of the total sugars, while in case of the hard, unripe one, only 70 per cent. was expressed, demonstrating the need for greater pressure in the latter case. Leaching with water, however, removed most of the residual sugars from both the pressed cakes. On a commercial scale, a more efficient pressing could be carried out with the aid of machinery; but it is very necessary, for reasons already mentioned, that the juice should, under no circumstance, come directly into contact with iron. Nickel-plated iron presses, or wooden ones could be used.

Preservation of juice.—Since the cloth-filtered juice, abounding in microflora, began to ferment rapidly, it was necessary to sterilise it, either by treating with chemicals (sulphur-dioxide), or by heating in steam under pressure. In following the first method, about 35 litres of the filtered juice, contained in a 50-litre carboy, were treated with sulphur-dioxide, the carboy plugged with cotton, and preserved in ice room (−2°). The second method consisted in sterilising a similar carboy, containing about 30 litres of the juice, directly in an autoclave for 10 mins. at 15 lbs. After sterilisation, the carboy was allowed to cool in the autoclave. After cooling there was a deposit of some debris, while the supernatant was clear but orange-red in colour, due to partial caramelisation of sugars. Along with the carboy for sterilisation in the autoclave, were kept each time six conical flasks (500 c.c.), containing cashew juice, with which preliminary trials were conducted.

The juice, sterilised and preserved by the above methods, formed the material for the preparation of sugar syrup.

Defecation.—Preliminary analysis having shown that the cashew juice contains mainly invert sugar, the usual methods of defecation of cane juice could not be adopted. Great care was necessary in adopting lime as a defecator, since even a slight excess of it resulted in caramelisation of the sugars present. Though calcium carbonate has been often used in place of lime for defecating sugar juices, it was found in the present instance, that addition of calcium carbonate even in quantities far in excess of the amount needed to neutralise the juice, did not completely remove the acids, thus resulting in insufficient precipitation of albuminoids and tannins. While the use of lime was thus indispensable, still an excess of it had to be carefully avoided, to prevent caramelisation of sugars and redissolution of coagulated impurities.

Behaviour of cashew juice on addition of lime.—On adding increasing quantities of milk of lime to cashew juice and shaking, the juice, fresh or steam sterilised, turned reddish-black. Addition of 20 per cent. of the total quantity of lime calculated to bring the medium to neutrality, brought about this initial colour change. Addition of a greater portion of the balance darkened this colour, and imparted a turbidity to the juice. When all the lime was added, the turbidity culminated in a sudden coagulation. The separated mass dispersed evenly through the medium, imparted to it a dull grey appearance. On now stopping both the addition of lime and shaking, a clear supernatant tinged slightly greenish yellow, was formed. This supernatant, neutral to litmus, was found to filter easily through filter paper, and even better, through cloth (by gravity), giving a clear filtrate. When lime was in excess, the filtrate was coloured yellow.

The correct amount of lime would have been added to the cashew juice, only when the coagulum in the juice precipitates down completely, giving a pale yellow, easily filterable supernatant, almost immediately after shaking is discontinued. The filtrate will now be found neutral. The coagulum on the filter, containing a mixture of tannins, albuminoids and colouring matter, will be slimy and chocolate coloured.

Thus it should be possible, with some experience, to accurately neutralise the acidity in cashew juice, and thereby remove tannins and albuminoids by lime treatment, even without the adventitious aid of special indicators, the necessary colour change being shown by the pigments present in the juice.

The quantity of lime required to neutralise the juice was found to be about 0·2 g. per 100 c.c. of juice. Lime was used in the form of milk, and the reaction was conducted in the cold.

Clarification.—The filtrate from the above, sweeter than before due to removal of acids, tannins and astringent principle, but containing more calcium salts in solution, had now to be clarified. This had to be carried out before beginning to concentrate the juice; otherwise, the calcium salts would be precipitated and dispersed evenly through the syrup rendering it turbid, and difficult to be decalcified by filtration, or otherwise. Further, such a syrup would acquire a bitter taste which is ascribed to the calcium ion. According to Paine, Keane and McCalip (*J. Ind. Eng. Chem.*, 1928, **20**, 262), calcium salts are more detrimental to metabolism than generally recognised. So, most of the calcium salts were removed from the defecated juice by using sulphur-dioxide, carbon-dioxide or phosphoric acid. The removal of calcium from solution as insoluble salts of these three acids was almost complete. A greater portion of the residual calcium was removed from the final syrup by filtration (see *infra*).

Concentration.—Concentration of the defecated and clarified cashew juice was conducted in enamelled iron vessels. The vessels containing the juice were heated in one instance over a ring burner, and in another over a water-bath, the contents of the vessel in either case being kept well stirred during concentration. The burner took about 5 hours, and the water-bath 8 hours to concentrate 20 litres of the juice to the same syrupy consistency (70–80 per cent. sugars). From the intensity of colour, it appeared that caramelisation had occurred to about the same extent in both the cases, thereby showing that water-bath offered no special advantage over the quicker direct fire, as a means of concentration.

Extent of concentration.—The gravity, as determined by the hydrometer, is a useful measure of the sugar content of the defecated and clarified juice at any moment during the process of concentration. A more practical, though less accurate, method is to judge the sugar concentration from the consistency of the syrup. This was the guiding factor in preparing the syrup from cashew juice. Concentration of the juice was continued upto a point when the resulting hot viscous syrup, taken at the end of a glass rod, poured slowly at first, then formed a thread as it cooled, and finally broke off from the edge—the sort of test that confectioners adopt in the preparation of fruit jellies. Such a syrup was found to assume a semi-solid state on cooling, corresponding to a sugar strength of about 80 per cent.

Filtration of the syrup.—With the increase in the concentration of the juice, there was correspondingly greater amount of turbidity, due to separation of the residual calcium salts. This sediment in the final concentrated syrup was filtered off with the aid of a water heated Hirsch funnel attached to the top of a Witt's apparatus. The bottom of the Hirsch funnel was covered with a filter paper. The wide bell jar portion of the Witt's apparatus contained the receiver (wide-mouthed bottles for large quantities and sample tubes for smaller quantities of the syrup) in which the syrups were to be finally stored. The Witt's apparatus was connected to an ordinary water pump, while the funnel was kept hot by heating the water in the jacket. The turbid syrup was poured into the funnel, and under the influence of suction and heat, it filtered through easily. A further modification of the method contemplated is to use in place of the filter paper covering the Hirsch funnel, a bed composed of alternate layers of paper pulp, and some other porous materials like kieselguhr or Supercell, as has been recommended for filtering fruit juices and plant extracts (Hall and Baier, *J. Ind. Eng. Chem. Anal. Edn.*, 1934, **6**, 208).

Properties of the syrup.—The syrup obtained according to the above procedure was in every instance cherry red in colour. A sample, obtained by boiling down the original juice as such to a syrupy consistency without defecation, was found to have a mixed taste of jaggery on the one hand, and acids and tannins on the other. Another sample, defecated but containing the calcium salts precipitated in the final stages, had the same colour as the first sample, but less turbid and tasted better. Removal of calcium salts and other suspended impurities from the latter sample resulted in a clear syrup though equally coloured.

The colour in all these cases was mostly due to the presence of caramel. When the starting material for the preparation of syrup was the sulphur-dioxide treated juice, the resulting syrup had a bright colour, though it had the unpleasant residual taste of the preservative. On the other hand, using steam sterilised juice, the caramel originally present in it was concentrated during heating, yielding a dark coloured syrup resembling treacle.

Curing.—A few experiments were tried to refine the coloured syrups. The usual method of dissolving a small quantity of raw sugars in water, and agitating the resulting solution with various decolourising carbons did not result in any improvement. The following decolourising carbons were tried:—Norit, bone or blood charcoal, paddy husk and cocoanut shell charcoals. On passing the mixture through a small basket centrifuge, a clear centrifugate was obtained, but the original dark colour of the syrup persisted. Preliminary treatment with porous materials like kaolin, kieselguhr or pumice did not also improve the colour. Next, the caramelised juice was concentrated to about 60 per cent. of its original volume, and then defecated in the hope that the defecation scum would carry down with it at least a part of the caramel. The results were again not satisfactory. Defecation by normal lead acetate, followed by the removal of lead by hydrogen sulphide, did not also result in any advantage.

Concentration of the juice in vacuum, and other methods of preventing caramelisation of invert sugar present in the cashew juice, are now being tried. It is hoped that the results of these trials would form the subject of a later communication.

Uses.—The conversion of cashew apple juice into a syrup, containing eight times more invert sugar than the original juice, is a useful method of conserving the sugars in this apple, now running to waste. Once the juice has been converted to a syrup, this may be sold as such like the golden syrup, the melon and maple syrups, or used as raw material for the production of alcohol by fermentation. It may serve also as a bloomer to many syrups. Sold as an edible syrup, the quality might be improved by lending it a mild sub-acid taste. Syrups retaining the original aroma might also be prepared to cater to the tastes of people who like the cashew apple flavour.

The fact that cashew syrup contains mostly invert sugar enhances its value considerably. Invert sugar is in such great demand, being much used in the manufacture of artificial honey. Honey itself contains invert sugar to the extent of 65 to 80 per cent.

The water-holding capacity of invert sugar to the extent of 14 per cent., leaving it always syrupy, makes it indispensable for confectioners and bakers, while its easy assimilability, being a pre-digested sugar, renders it eminently suitable for inclusion in infant and invalid foods. Moreover, it is 25 per cent. sweeter than cane sugar (Biester, Wood and

Wahlin, *Amer. J. Physiol.*, 1925, **73**, 387). These remarks apply equally to cashew syrup, containing as it does mostly invert sugar.

Large quantities of invert sugar are required for use in confectionary. Since the total consumption of confectionary in India (including imports) amounts to several hundred tons per annum, there would appear to be prospects of a big demand for cashew syrup, if it could be produced in sufficiently large quantities.

Furthermore, special attention must be drawn to the use of invert sugar in tobacco industry as a "casing" for some cigarette tobaccos to hold the short tobacco with the long, and to keep moisture in the tobacco at the same time. Cashew syrups might thus be useful in this industry, the advancement of which is now being sponsored by the Imperial Council of Agricultural Research.

Cashew syrup may also serve as a useful source for levulose production. Levulose, it might be added, is of great medicinal value, because of the remarkable tolerance exhibited by diabetic patients, for which purpose it is now manufactured from Jerusalem artichoke.

If a biological assay confirms the finding that cashew juice contains vitamin C, the syrup may be so prepared as to include this vitamin.

SUMMARY.

1. By analytical methods it has been found that cashew apple contains invert sugar, about 7 per cent. on the fresh weight of the apple.

2. Each cashew apple yields on an average 20 to 25 c.c. of juice having 10·4 per cent. of total solids. Sugars alone account for 94 per cent. of the total solids in the juice. The remaining part is made up of acids, tannins, an astringent principle and pigments. Preliminary observations have also shown that the juice contains vitamin C.

The juice does not keep and ferments very readily, unless sterilised by heat, or treated with preservatives (SO_2) and cold.

3. The riper the fruit, the greater is its yield of juice and large the sugar content.

4. The usual methods of defecation and clarification of suga juices have been modified to suit this juice, which contains mostl invert sugar.

5. It has been found that pigments present in the juice facilitat the correct addition of lime, which is further aided by the finding tha at neutral pH, there is complete precipitation of albuminoids an tannins, and that the medium allows of easy filtration.

6. The removal of calcium salts appearing during concentration of the juice, even after preliminary precipitation of most of them as carbonate, sulphite or phosphate, is effected by filtration aided by heat and suction.

7. The uses of the resulting syrup are discussed.

In conclusion, the author wishes to thank Professor V. Subrahmanyan for guidance and Mr. B. N. Banerjee for helpful suggestions. He also wishes to acknowledge the grant of a scholarship from the Department of Industries, Madras, which enabled him to carry out this work.

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[Accepted, 6-8-1934.]

1390-34.—Printed at The Bangalore Press, Mysore Road, Bangalore City, by T. Subramania Aiyar, Superintendent.