of anhydrous ammonia. After allowing a reaction time of several minutes, the pulp is spread in a thin layer to allow the excess ammonia to evaporate. If the product is allowed to stand in a warm place and with adequate ventilation, it will lose its ammoniacal odor in an hour or two. This purging of the ammoniacal odor is complete and does not recur even on storage in a closed container. The resulting product has the same consistency as the original pulp, has a light yellow color, and a crude protein content of 25 to 30%.

Larger batches of this product were made in connection with the preparation of hesperidin (10). This material had part of its ammonia soluble solids removed and a crude protein content of about 18%. Tests on the palatability of this material were conducted and it was found that its acceptability was equal to that of untreated citrus pulp.

This pulp is by far the most acceptable from a palatability standpoint of the ammoniated pulps produced so far. The necessity of ammonia recovery apparatus will make the cost of this material higher than those produced with close to the stoichiometric amount of gaseous ammonia.

The production of ammoniated citrus pulp that is palatable is only one step in the commercialization of this product. The economics of the process remain undetermined. Both the cost of production on a commercial scale and the price of the finished product to the dairy or cattle trade have not yet been determined. Speculation as to the price that this product could command has been in the vicinity of $1.00 per ton per percent added crude protein, but this will not be proven until pilot plant quantities are available for test marketing.

BIBLIOGRAPHY
6. Maurer, R. H., George W. Ochs, Everett M. Burdick, A New Citrus Pulp and Method for Producing It., The Border Scope, 7-10 October (1951)

II. EXTRACTION OF HESPERIDIN FROM DEHYDRATED, LIMED, CITRUS PULP

James M. Bonnell
Tropicana Products, Inc.
Bradenton

During the period, several years ago, when interest was high regarding hesperidin, our interest was drawn towards the investigation of means of solvent extraction of hesperidin from dehydrated, limed, citrus pulp. The usual methods of preparation of hesperidin from citrus peel (1), (2) involve handling of the wet peel, large quantities of rather dilute press water, the filtering of large quantities of press water, precipitation of the hesperidin with hydrochloric acid, filtering of the precipitated hesperidin from the large volume of liquid, and finally the disposal of the dilute press water. A solvent extraction of the hesperidin from the dry pulp produced for cattle feed would simplify its manufacture.

Hesperidin is only slightly soluble in water, dilute acids, and the usual organic solvents such as alcohol, acetone, hydrocarbons, etc. It is soluble in basic solvents such as dilute alkali, pyridine, amines, dimethylformamide, etc. The usual extraction of hesperidin from citrus peel involves the treatment of the peel with an excess of calcium hydroxide with perhaps the addition of some sodium hydroxide. This affects the solution of the hesperidin which is then precipitated from the clarified liquor and recovered. The filtering of aqueous liquors from citrus peels is difficult and is slow even with liberal use of filter aids. Due to the fact that calcium hydroxide is used in the process, it is necessary to use the expensive hydrochloric acid to precipitate the hesperidin so as not to contaminate the product with calcium sulfate, which would also precipitate if sulfuric acid is used.

The extracted pulp should be useful for cattle feed. The wet peel, that has been treated with an excess of calcium hydroxide,
can be used as cattle feed but it is of poor quality and is usually mixed with untreated peel before drying. The expense of the organic solvents for hesperidin, the difficulty of complete removal of the solvents from the pulp, and their toxic character and obnoxious odors have prevented their use as solvent extractants.

Liquid anhydrous ammonia, referred to subsequently as liquid ammonia, was a solvent that had never been tried for the extraction or solution of hesperidin, and a solvent that offered attractive possibilities. Liquid ammonia has been used for a number of years as a solvent and reactant in organic synthesis. The latent heat of evaporation is 327 cal./g, which is high. Water has a latent heat of evaporation of 541 cal./g. Liquid ammonia, because of its high latent heat of evaporation can be handled at its boiling point exactly as water can be handled at its boiling point. An efficient fume removal system is necessary because of the irritating nature of ammonia gas. The cooling effect of the boiling of liquid ammonia allows liquid ammonia to be drawn directly from a cylinder at room temperature. Losses of ammonia can be minimized by cooling the cylinder and apparatus with dry ice before operation, but it has been found to be much simpler to allow the vaporization of the ammonia to do its own cooling.

Liquid ammonia offers two other advantages. It is a rather cheap material, costing $82.50 per ton in tank car lots. This reflects a price of slightly over 4c per pound, or 22c per gallon. The specific gravity of liquid ammonia is 0.65 at −10°C. The cattle feed resulting from such an extraction should be enhanced in value due to part of the ammonia being fixed in the feed so producing an ammoniated cattle feed.

**Experimental:**

The first point to be checked was the solubility of hesperidin in liquid ammonia. The absolute solubility was not determined but it was found that hesperidin is very soluble in liquid ammonia. Solutions with as high as 28% by weight of hesperidin in liquid ammonia have been prepared. The solution is yellow in color, the color approaching black as the concentration of hesperidin is increased. The hesperidin appears to be in the form of the chalcone as the product recovered from evaporation of the ammonia is soluble in water with a yellow color and hesperidin may be precipitated when the pH of the solution is adjusted to 4-4.5. A sample of dehydrated, limed, citrus pulp was exhaustively extracted with liquid ammonia. Fifty grams of citrus pulp containing 9% moisture were placed in the thimble of a Soxhlet extractor. The thimble was placed in the Soxhlet extractor but the condenser was not attached. Liquid ammonia was added from a beaker until the unit siphoned. This was repeated until no yellow color was observed in the extract. Approximately 1000 ml. of liquid ammonia were used for this extraction. Evaporation of the ammonia yielded 19 grams of material which were dissolved in 150 ml. of water. The extracted pulp, after evaporation of the ammonia, weighed 37 grams and showed only a trace of yellowing in the white albedo portions of the peel. The water solution of the extract was adjusted to a pH of 4.5 with sulfuric acid and allowed to digest for two hours on the steam bath. The precipitated hesperidin was filtered and dried yielding 0.47 grams of product, or slightly more than 1% on the dry weight of the pulp used. The resulting peel contained 15.2% crude protein and the extract contained 72% crude protein on a basis of dry solids.

A trial was next conducted to determine the minimum amount of ammonia needed to effect the extraction. From these experiments it was determined that between two and three times the weight of the pulp in liquid ammonia was necessary to extract 95% of the hesperidin. The smaller amount of ammonia removed considerably less of the ammonia soluble solids. This resulted in smaller yields of extract but larger yields of extracted pulp without materially changing the yield of hesperidin. The extracted peel from these runs contained between 18% and 20% crude protein. It should be noted here that the pulps used were pulps with the molasses added back before drying.

To evaluate the effect of using peel without add-back molasses, the feed mill ran a commercial size run of pulp with no molasses. Fifty grams of this pulp containing 3% moisture were treated in the same manner and yielded about 6 grams of extract after removal of the ammonia, about 47 grams of extracted pulp at 14.6% crude protein, and 0.51 grams of hesperidin. The hesperidin produced from this run again represented about 1% of the weight.
of the starting material and was pure white in color as recovered from the extract. The hesperidin had a melting point of 251.5°C, corrected as opposed to a literature value of 252°C. The hesperidin produced from the peel containing added molasses was generally darker in color varying from light gray to light brown.

The success of the extraction on a small scale indicated investigation of the process on a large scale. A 500 gallon ammonia tank was procured and a 4" pipe line was run to the roof of the building. A location was selected so that the apparatus could be operated from any direction so that the prevailing wind would remove the ammonia vapors from the reaction. A fifty gallon stainless steel tank with a bottom drain value was mounted on a platform scale. The extract was placed in a 55 gallon barrel which was heated by steam. A pump and Sparkler filter were used to recover the precipitated hesperidin.

A typical run from this series was made with 70 lbs. of pulp at 10% moisture. To this pulp were added 100 lbs. of liquid ammonia during a period of 30 minutes. The extract was drained into the barrel and the pulp rinsed with an additional 5 lbs. of ammonia. The combined extracts were evaporated with steam until the temperature reached 70°F. At this point the evaporation was stopped, 20 gallons of water were added, and the pH adjusted to 4.5 with sulfuric acid. This required about 2.5 lbs. of acid. The acidified extract was heated to 130 to 140°F. with steam and allowed to digest overnight. The precipitated hesperidin was filtered, using Sparkler filter. This run yielded 280 grams of hesperidin, or 1%, based on the dry pulp used. The extracted pulp had a crude protein content of 18%. The pulp was spread on plastic film on the roof in a sunny location and lost all traces of ammoniacal odor in 3 to 4 hours.

Using this apparatus, over 2500 lbs. of ammoniated pulp and 25 lbs. of hesperidin were produced. This pulp was tested for palatability and was accepted as readily as untreated citrus pulp.

For the purpose of design of a continuous pilot plant and for making a cost analysis of the process, it was necessary to determine the heat of reaction of liquid ammonia and dry citrus pulp. An over-all heat of reaction figure including the heat evolved in reacting the water present with the ammonia, the cooling of the peel to liquid ammonia temperatures, and the actual heat of reaction of the peel and its components with the ammonia were determined. A Dewar flask was filled about one-half full of liquid ammonia and placed on a double pan trip balance and balanced. It was allowed to come to equilibrium with the ambient conditions and the rate of evaporation of ammonia from the flask was determined. This loss in weight was plotted versus time. After ten minutes had elapsed to develop an accurate base line, 25.0 grams of pulp were added to the flask. A proper adjustment for tare weight was made at this point so that the weight loss of ammonia could be calculated. The curve obtained from the average of 5 runs appears in Figure 1. The weight loss from the Dewar flask was at the rate of 1 gram per minute. On the addition of the 25.0 grams of pulp, a loss of 7.6 grams of ammonia occurred. After several minutes the rate of loss settled back to the starting rate of 1 gram per minute and the reaction was considered to be complete. The weight of ammonia lost was calculated by extrapolating the base line and taking the vertical distance to the line developed after the reaction was complete. The latent heat of evaporation of liquid ammonia is 327 cal./g. Thus 7.6 grams of lost ammonia represents 327 \times 7.6 calories or 2485 calories. This figure divided by 25 grams (the amount of pulp used) provides a heat of reaction of nearly 100 cal./g. (actual calculated figure was 99.5 cal./g.). For engineering calculations this is converted to 180 B.T.U./lb.

A cost estimate for the production of hesperidin by this process and based on the following assumptions, will be:

1. The plant is designed to run 500 lbs. of pulp per hour or 6 tons per day.
2. The yield of hesperidin is 1% of the dry weight of the pulp, or a total of 120 lbs. per day.
3. The ammonia gas from the process is recovered with an ammonia absorption type of apparatus with an overall loss of 12% including that remaining in the extract and neutralized with the sulfuric acid.
4. The plant will cost $75,000.00, will be operated for 300 days per year, and amortized over a period of 5 years.
The cost figures are based on the processing of 1 ton of pulp.

<table>
<thead>
<tr>
<th>Item</th>
<th>Quantity</th>
<th>Cost per 20 lbs. of hesperidin</th>
<th>Cost per lb. of hesperidin</th>
</tr>
</thead>
<tbody>
<tr>
<td>Steam</td>
<td>3000 lbs.</td>
<td>$1.00/1000 lbs.</td>
<td>$3.00</td>
</tr>
<tr>
<td>Power</td>
<td>25 H.P.</td>
<td>1.75/100 K.W.H.</td>
<td>0.35</td>
</tr>
<tr>
<td>Labor</td>
<td>4 hours</td>
<td>2.00/hr.</td>
<td>8.00</td>
</tr>
<tr>
<td>Ammonia</td>
<td>240 lbs.</td>
<td>0.04125/lb.</td>
<td>9.80</td>
</tr>
<tr>
<td>Sulfuric acid</td>
<td>240 lbs.</td>
<td>0.01 lb.</td>
<td>2.40</td>
</tr>
<tr>
<td>Amortization</td>
<td>20 lbs.</td>
<td>0.417/lb.</td>
<td>8.34</td>
</tr>
</tbody>
</table>

Overhead: 10%

Total estimated cost per 20 lbs. of hesperidin $31.89
Cost per lb. of hesperidin $1.75

5. The cost of the pulp will be an inplant accounting transfer from stock to the hesperidin plant and back into stock after processing.

In the estimates of the costs no account was made of the higher value of the ammoniated citrus pulp produced. A fair value for the increased protein content might be $1.00 per percent increase per ton of feed. This would bring $10.00 to $12.00 return per ton processed and further reduce the cost of the hesperidin.

A new process for the production of hesperidin from dehydrated, limed, citrus pulp has been developed. A high quality hesperidin can be produced by this method along with a very high quality ammoniated citrus pulp. Because of the properties of the solvent, the tedious and expensive steps of filtering water extracts of citrus peel have been eliminated and through the elimination of the use of calcium hydroxide, sulfuric acid may be substituted for expensive hydrochloric acid. Further economics that could be developed during pilot plant studies would probably lower the cost below the estimated figure of $1.75 per pound.

The reactions of citrus byproducts with liquid ammonia are of considerable interest and work is continuing in this field.

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SUGGESTED TRENDS IN THE AVOCADO AND LIME INDUSTRIES

Luther L. Chandler, Harold E. Kendall and C. F. Ivins

*Florida Avocado and Lime Commission*

Homestead

During the early fifties the intense enthusiasm of the burgeoning fruit juice industry brought a temporary wave of high prices and profits to Florida Lime Growers. Canners outbid each other for the fresh fruit, boosting prices up as high as $120.00 a ton or $3.30 a bushel. While these happy events were occurring to Florida limes a parallel situation was happening to the California lemon industry.

This prosperity was short lived, however. By 1954 the high prices attracted heavy sup-