

dry ether solution; the hydrogen chloride salt of 1-phenyl-4-aminobutadiene was precipitated from this solution. It is apparent that the acid amide of styrylacrylic acid has undergone a rearrangement to give 1-phenyl-4-aminobutadiene.

Summary

1. The method of preparation of 1-phenyl-4-aminobutadiene and of 1-phenyl-4-anilidobutadiene is described.
2. Both of these amines absorb hydrogen chloride in the 3,4-positions.
3. 1-Phenyl-4-anilidobutadiene absorbs both chlorine and bromine in the 3,4-positions.
4. The significance of these reactions of aliphatic amino conjugated compounds to the problem of substitution in the benzene ring is indicated.

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The Effects of Glucose and Fructose on the Sucrose Content in Potato Slices

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The opinion seems to be held by many¹ that desiccation of starch containing plant tissues, such as leaves and potato slices, increases the sucrose content. Schroeder and Horn² studying the increase in sucrose on drying *tropæolum* leaves as well as the changes in the amount of reducing sugar present in the leaves, reached the conclusion that starch is converted into sucrose in the desiccation of the leaves in a more direct way than through the reducing sugars as an intermediate stage. Ahrns³ more or less repeated the work of Schroeder and his co-workers using starch bearing leaves of several plants, and also reached the conclusion that the conversion of the starch to sucrose in the desiccation of leaves is independent of the reducing sugars present.

Waterman⁴ studied the phenomenon of starch to sucrose by drying potato slices at temperatures from 30 to 50°, and like the above-mentioned investigators expressed the opinion that starch is changed to sucrose during the drying process, in some direct way, probably by the aid of enzymic action. Following Waterman, de Wolff⁵ studied the starch to sucrose reaction when potato slices are subjected to desiccation. He too looked upon the reaction as one independent of the reducing sugars present.

(1) M. W. Onslow, "The Principles of Plant Biochemistry," The University Press, Cambridge, 1931, p. 55; R. A. Gortner, "Outlines of Biochemistry," John Wiley and Sons, New York, 1929, p. 535.

(2) H. Schroeder and T. Horn, *Biochem. Z.*, **130**, 165 (1922); H. Schroeder and F. Herman, *ibid.*, **235**, 407 (1931).

(3) W. Ahrns, *Bot. Archiv.*, **5**, 234 (1924).

(4) H. I. Waterman, *Chem. Weekblad.*, **11**, 332 (1914).

(5) C. J. de Wolff, *Biochem. Z.*, **176**, 225 (1926); **178**, 36 (1926).

Contrary to the conclusions reached by Schroeder and his co-workers and by Ahrns, in the case of leaves, and also contrary to the view held by Waterman and de Wolff that starch is changed directly into sucrose when these plant tissues are dried, the results obtained in this Laboratory show that reducing sugars, in the form of glucose and fructose, play a dominating role in the formation of sucrose in potato slices, and that desiccation is only incidental. By dipping the slices in aqueous glucose or fructose solutions and then permitting them to remain in the moist condition, without any desiccation or loss of moisture whatever, in contact with air, even a larger increase in sucrose content results than when the slices are dried without dipping them in the hexose solution. The formation of sucrose by simply drying leaves and potato slices is probably also due to reducing sugars present in the tissue or formed during the desiccation.

In connection with the effect of reducing sugars on the sucrose content of potato slices it was found that slices dipped in galactose, maltose or glycerin solutions instead of glucose or fructose solutions showed only a small increase in sucrose. Similarly freshly cut slices, dipped in distilled water, instead of in a glucose solution, or not dipped at all, when exposed in the wet condition to air gave only slight increases in sucrose. These small increases are very likely due to wounding. Hopkins⁶ has shown that when potato tissues are wounded by cutting, the respiration is increased and along with it a slight increase in sucrose content occurs. This inability of galactose, maltose and glycerin to increase the sucrose content recalls the observations made by Meyer⁷ who found leaves of several kinds of plants were able to form starch when floated on aqueous solutions of sucrose, glucose or fructose, but only in one or two instances did he observe any starch formation when the leaves were floated on galactose, or glycerin solutions. Similarly, Parkin⁸ found in the case of narcissus and iris leaves that maltose, in contrast to sucrose, glucose and fructose, gave rise to only very little starch formation.

Another factor involved in the formation of sucrose noticed in the case of potato slices, which has not been mentioned by Waterman, or de Wolff, nor by Schroeder and Horn or Ahrns, in the case of leaves, is the effect of oxygen or air. When potato slices are dried in an atmosphere of nitrogen, no increase, or at least very little, in sucrose content occurs, and the same is true when the slices, dipped in a glucose solution, are stored wet in an atmosphere of nitrogen. This necessity of oxygen for the formation of sucrose seems to be like the dependence on oxygen noticed in the transformation of starch into sucrose in the ripening of fruit. Thus Bailey⁹ found when green bananas were coated with paraffin or immersed in oil so

(6) E. F. Hopkins, *Bot. Gazz.*, **84**, 75 (1927).

(7) A. Meyer, *Bot. Z.*, **44**, 104, 128 (1886).

(8) J. Parkin, *Trans. Roy. Soc. London*, **191B**, 35 (1899).

(9) E. M. Bailey, *THIS JOURNAL*, **34**, 1706 (1912).

as to keep the fruit from being in contact with air, the decrease in starch as well as the increase in sucrose ceased. Miss Hemperly in this Laboratory (unpublished) since then has observed the same, and Thornton¹⁰ finds that storing green bananas in an atmosphere of carbon dioxide prevents the starch from changing into sugar. The fact that oxygen is essential for changing reducing sugars in potato slices to sucrose shows that the reactions involved must be related in some way to aerobic respiration.

Experimental Procedure

1. **Variety of Potatoes Used.**—Mostly Irish Cobbler and Idaho Russets, all in the dormant condition.

2. **Slices.**—Tubers of fairly regular shape, about 10–15 cm. long and 5–7 cm. in diameter, were peeled and slices varying in thickness from 1 to 2 mm. cut from the middle portion of the tuber. Six slices weighing from 12 to 20 g. usually constituted an experimental sample.

3. **Slow Drying of Slices.**—Instead of drying the slices by warming them to about 30 to 40° over a low gas flame as was done by Waterman and de Wolff, the slices were usually dried at room temperature in a desiccator by means of anhydrous calcium chloride. For this purpose, the slices were distributed on a large perforated porcelain disk which constituted the shelf in the large 10-inch desiccator. Supported above the porcelain disk by means of three or four corks was a large watch glass containing the calcium chloride. By choosing the right amount of the drying agent it was possible to lower the weight of the sample from 15 to 75% in ten to twenty hours.

TABLE I

| Treatment | Orig. wt. of sample, g. | After storage, g. | Change in wt. during storage, % | Time of storage, hrs. | Orig. non-reducing sugar content, % ^a | Non-reducing sugar content after storage, % | Increase in non-reducing sugar, % |
|---|-------------------------|-------------------|---------------------------------|-----------------------|--|---|-----------------------------------|
| Idaho Russet Potatoes | | | | | | | |
| 20% Glucose ^b | 25.035 | 26.226 | + 4.0 | 18 | 0.16 | 0.83 | 420 |
| 20% Fructose ^b | 22.227 | 23.440 | + 5.0 | 22 | .13 | .90 | 590 |
| 20% Galactose ^b | 25.310 | 26.750 | + 5.0 | 18 | .16 | .25 | 56 |
| 20% Maltose ^b | 20.476 | 20.660 | + 0.9 | 21 | .15 | .35 | 133 |
| 20% Glycerin ^b | 14.640 | 13.040 | -10.0 | 22 | .12 | .07 | - 42 |
| 20% Distilled water ^c | 13.677 | 14.031 | + 2.6 | 19 | .26 | .43 | 65 |
| Irish Cobbler Potatoes Bought in the Open Market | | | | | | | |
| Untreated ^d | 23.754 | 22.805 | - 4.0 | 24 | .19 | .39 | 100 |
| 20% Glucose + N ₂ ^e | 16.438 | 14.434 | -12.0 | 19 | .15 | .29 | 93 |
| Air and CaCl ₂ ^f | 21.360 | 4.705 | -78.0 | 19 | .10 | .52 | 400 |
| N ₂ and CaCl ₂ ^g | 23.627 | 9.363 | -60.0 | 22 | .10 | .11 | 10 |

^a The content of non-reducing sugar, hydrolyzed by invertase, contained in the freshly cut slices. ^b Slices dipped in 20% sugar solutions, then stored in desiccator containing air saturated with water vapor. ^c Slices dipped in distilled water and then stored in desiccator containing air saturated with water vapor. ^d Slices not dipped in any solution, just stored in desiccator containing air saturated with water vapor. ^e Slices dipped in 20% glucose and then stored in desiccator in an atmosphere of nitrogen. ^f Freshly cut slices stored in desiccator containing calcium chloride and dried slowly. ^g Freshly cut slices stored in desiccator containing calcium chloride and dried slowly in an atmosphere of nitrogen.

(10) N. C. Thornton, "Contributions from Boyce Thompson Institute," 3, 219 (1931).

4. **Storing the Slices.**—In order to show that no desiccation is necessary for the sucrose formation when the slices have been dipped in an aqueous glucose or fructose solution, it was necessary to keep the slices moist while being exposed to air. Instead of the watch-glass containing calcium chloride suspended over the slices on the porcelain disk, the bottom of the desiccator was covered with a layer of water. This kept the air sufficiently saturated with water vapor so that the slices suffered no appreciable change in weight on remaining in the desiccator for several hours.

5. **Dipping Slices in Hexose Solutions.**—The freshly cut slices were placed in 20% hexose solution, allowed to remain in the latter for two to three minutes, removed and either dried and stored as described in 3 or stored wet as indicated in 4.

6. **Determination of Sugars.**—The slices, after they had been stored in the desiccator for the desired length of time, or, in the case of the control samples, immediately after they were cut, were placed in 75 cc. of 95% ethyl alcohol and boiled on the water-bath for ten minutes. The slices were then removed from the alcohol, ground to a powder in a mortar and the ground material and alcohol used for washing the mortar returned to the original alcohol. The latter was then diluted by the addition of 25 cc. of water, placed in a flask and agitated in a shaking machine for two hours and filtered. The filtrate containing the dissolved sugars together with the alcohol washings was then distilled under reduced pressure at about 45° to remove the alcohol, the aqueous residue clarified by lead acetate and the reducing sugars determined, before and after inversion by yeast invertase, by means of copper reduction.¹¹

The following table is given to show the degree of precision in the determinations of the sucrose content. Six samples of potato slices were cut from the same potato, three for determining the sucrose content immediately after cutting the slices, and three for the sucrose content after dipping in 20% glucose solution and being stored for twenty-two hours in a desiccator containing moist air.

| | | | |
|---|------|------|------|
| Experiment number | 1 | 2 | 3 |
| Non-reducing sugar in fresh slices | 0.13 | 0.12 | 0.12 |
| Non-reducing sugar after dipped in glucose solution and stored wet for 22 hrs. | 1.15 | 1.11 | 1.09 |

Summary

1. Contrary to the conclusions of earlier investigators, it has been shown that dehydration of potato slices is not necessary in order to effect marked increases in sucrose content.

2. Evidence has been given that sucrose in the potato is synthesized from glucose or fructose, rather than, as has been supposed, in some more direct way from starch.

3. It has been shown that the presence of oxygen is necessary for the formation of sucrose in the potato slices.

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(11) Waterman, Ref. 4, isolated from the alcoholic extract of potato slices, dried at 35°, crystals of sucrose, m. p. 180°; 88 mg. dissolved in 20 cc. of water, gave a rotation in a 2-dcm. tube $[\alpha]_D +54^\circ$ (calcd. $+58^\circ$).