Pigment Composition and Color of Conventional and Veri-Green Canned Beans

Joachim H. von Elbe,* Alvin S. Huang, Ernest L. Attoe,[1] and W. Kenneth Nank[1]

Qualitative pigment differences between conventional and Veri-Green (VG) processed canned green beans were determined. Pigments in conventional processed beans were pheophytins and pyropheophytins, typical of the pigments found in heat-processed green vegetables. The green color of VG processed beans was attributed to the formation of zinc complexes, specifically the formation of the metallochlorophyll complexes, Zn–pheophytin *a* and Zn–pyropheophytin *a*. Large differences in Hunter color value $-a$ (green) were observed between conventional and VG processed beans. Hunter color values of VG processed beans approached the color values of fresh beans.

INTRODUCTION

The retention of the bright green color of vegetables during heat processing has long been the goal of research in the canning industry. The degradation of chlorophyll involves a number of reactions. The olive green color of canned vegetables has been attributed to the formation of pheophytin (Campbell, 1937). Recently it has been shown that not only the formation of pheophytins is involved but also the formation of pyropheophytins (Schwartz et al., 1981; Schwartz and von Elbe, 1983). Other heat-initiated changes in green vegetables are the isomerization of chlorophylls and the activation of the enzyme chlorophylase. Isomerization of chlorophylls will occur at room temperature, but more rapidly during heating, e.g. blanching (Strain, 1954; Bacan and Holden, 1967; Schwartz, et al., 1981). The heat activation of chlorophylase in vegetables and its effect in chlorophyll were first studied by Jones et al. (1962). Some green vegetables show considerable formation of chlorophyllides and some pheophorbides during low-temperature (60–70 °C) blanching treatment (Buckle and Edwards, 1970; Clydesdale and Francis, 1968).

A number of attempts have been made to preserve chlorophylls during heat processing through the application of pH control (Blair and Ayres, 1943; Gupte et al., 1964), high-temperature short-time processing (Tan and Francis, 1962), or a combination of these two factors (Gupte and Francis, 1964; Buckle and Edwards, 1970; Clydesdale et al., 1970; Malecki, 1978). Other improvements in color have involved the production of the more heat-stable chlorophyllides (Loef and Thung, 1965). Clydesdale and Francis (1968) combined pH control and the formation of phytol-free pigments to improve the color of spinach. The improvement in color was limited by insufficient production of chlorophyllides.

Regreening of vegetables has been observed and attributed to the formation of metallochlorophyll complexes. Zinc and copper complexes of chlorophyll derivatives have been shown to be responsible for the green color of canned okra (Fischbach, 1943; Fischbach and Newburger, 1943) and brussel sprout samples (Swirski et al., 1969). Sweeney and Martin (1958) reported that the addition of zinc chloride to cooked broccolli caused the regreening process to occur. Metallo complex formation appears to involve chlorophyll derivatives and occurs in the presence of 1–2 ppm of Cu, and 10–20 ppm of Cu was required for complete complex formulation with pheophytin in pea puree. The formation of Zn complexes requires a minimum of 25 ppm, and 100 ppm is required for complete complexation (Schanderl et al., 1965a,b). The application of high-performance liquid chromatography to separate zinc and copper complexes of pheophytin has been demonstrated by Schwartz (1984). Copper pheophytin complexes are commercially manufactured as food colorants and permitted for use in some European countries (Humphrey, 1980). Recently a process, Veri-Green, to enhance the appearance of canned green vegetables was introduced by the Continental Can Co. The process applies new internal coating of metal cans and/or new process technology to preserve the green color of vegetables (Andres, 1983).

The present investigation was made to determine qualitative pigment differences between conventional and Veri-Green (VG) processed canned green beans.

MATERIALS AND METHODS

Canned samples of green beans processed by conventional methods and the VG process were supplied by Continental Can Co. Green beans were packed during the 1982 and 1983 growing seasons. They were analyzed for pigment composition and color.

Determination of Color Data. Samples (approximately 50 g) were pureed and placed in a 6-cm-diameter glass dish to depth of not less than 2 cm. The sample dish was placed on the light port of a Hunter Lab Model D-25A-9 colorimeter. The instrument was standardized on a white plate, and accuracy was checked with standard green ($Y = 43.2$, $X = 36.4$, $Z = 44.1$). The sample dish was covered to avoid stray light. The L, a, and b values were recorded, and derived functions for hue (h), saturation (C), and total color differences (ΔE) were calculated: $h = \arctan(b/a)$; $C = (a^2 + b^2)^{1/2}$; $\Delta E = [(L_1 - L_2)^2 + (a_1 - a_2)^2 + (b_1 - b_2)^2]^{1/2}$.

Pigment Analysis. All samples were drained, and 50 g of beans was blended with an equivalent weight of acetone for 2 min. This mixture was filtered through Whatman #1 and #42 filter paper and washed with acetone until the filtrate (250–300 mL) was colorless. Pigment extracts were analyzed for chlorophyll and their derivatives by using high-performance liquid chromatography (HPLC) (Schwartz and von Elbe, 1983). Duplicate 25-μL samples were injected for each extract.

RESULTS AND DISCUSSION

Figure 1a is a typical HPLC chromatogram of chlorophyll derivatives found in conventional processed green beans. The pigments were identified as pheophytin *b*, *b'* (Pb, Pb'); pyropheophytin *b* (PYb); pheophytin *a*, *a'* (Pa, Pa') and pyropheophytin *a* (PYa). This result is in agreement with previously reported findings (Schwartz et

Department of Food Science, University of Wisconsin—Madison, Madison, Wisconsin 53706.

[1]Present address: Continental Can Co., Oak Brook, IL 60521.

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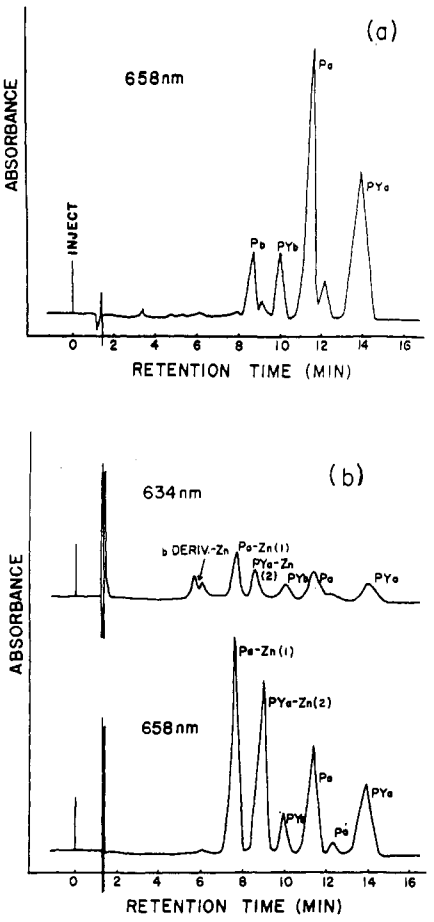

Figure 1. Chromatogram of canned green bean pigments: a = conventional process; b = Veri-Green process.

al., 1981; Schwartz and von Elbe, 1983).

Typical chromatograms detected at 634 and 658 nm of a green bean sample canned by using the VG process are shown in Figure 1b. The peaks detected at 658 nm were identified representing the pigments PYa, Pa', Pa, PYb, and two unknown pigments marked as peaks 1 and 2. The pigment represented by peak 2 has a retention time similar to that of Pb (Figure 1a). It is concluded, however, that the pigment represented by peak 2 cannot only be Pb, because the concentration represented by the size of the peak far exceeds the concentration of Pa. A concentration of Pb greater than Pa is contrary to reported results. Chlorophyll *a* and *b*, the precursors of Pa and Pb, are usually found with each other in green plants at a ratio of 2:1 = *a*:*b* (Jackson, 1976).

When zinc acetate was added to the pigment extract, the green color increased along with an increase in peak sizes 1 and 2 and a decrease in peak sizes Pa and PYa. The result suggested that zinc complexes, specifically zinc–pheophytin *a* (Zn–Pa) and Zn–pyropheophytin *a* (Zn–PYa) are the major metallochlorophyll complexes responsible for the green color in VG processed beans.

For further evidence to show that Zn complexes were responsible for the green color, Pa and PYa were isolated and purified (Schwartz et al. 1981). Zinc acetate was added to each of the solutions, and complex formation was monitored over time. Addition of zinc acetate to Pa resulted in the formation of peak 1 while the addition to PYa resulted in the formation of peak 2. It is concluded that peak 1 is the metallo complex Zn–Pa, and peak 2, Zn–PYa. The formation of Zn–PYa over time is shown in Figure 2. Detection at 634 nm, the maximum light absorption of zinc–pheophytin *b*, showed what is believed to be the

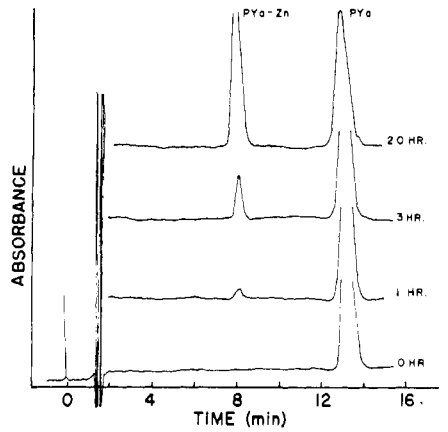

Figure 2. Chromatograms showing the formation of pyropheophytin *a*–zinc complex (Zn–PYa) in ethanol from pyropheophytin *a* (PYa) over time.

Table I. Hunter Color Values of Green Beans

sample	*L*	*a*	*b*	*h*	*C*	ΔE
beans fresh	40.6	−13.6	20.7	56.7	24.2	
Con—1983[a]	38.6	−2.2	19.5	83.6	19.6	11.6
VG—1983	41.7	−4.6	20.2	77.2	20.7	9.1
Con—1982	38.2	−2.2	19.5	83.6	20.3	11.6
VG—1982	37.8	−7.4	19.2	68.9	20.0	7.0

[a] Con = conventional processed; VG = Veri-Green processed.

presence of small amounts of zinc complexes of *b* derivatives (Figure 1b). The reason for this result may be attributed to the lower amounts of *b* derivatives available (Berezin and Koifman, 1970).

The color of fresh and processed green beans in terms of Hunter color values is given in Talbe I. There was little difference among samples in the *L*, *b*, and the calculated saturation value (*C*). Large differences were noted in the $-a$ (greeness), *h* (hue), and ΔE (total color difference) values. Fresh green beans had a $-a$ value of 13.6 and a calculated hue value of 56.7. All VG processed beans more closely approached these values when compared to the beans canned with a conventional process. The greatest $-a$ value was observed in VG processed beans that were subjected to long storage periods (1 year or longer). The greener color is attributed to the greater amount of Zn complex formation over time. This result is further illustrated in comparing the calculated ΔE value between fresh and VG processed beans canned in 1982 and 1983. The ΔE value for beans processed in 1983 was 9.1 while the difference decreased to 7.0 for beans processed in 1982. This decrease in ΔE clearly shows regreening of the beans over time.

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Registry No. ZnP, 15739-11-4; Pa, 603-17-8; Pa', 75598-38-8; Pb, 3147-18-0; PYa, 14409-87-1; ZnPYa, 15333-64-9; PYb, 77331-75-0.

LITERATURE CITED

Andres, C. *Food Processing* **1983**, *44* (3), 49.
Bacan, M. F.; Holden, M. *Phytochemistry* **1967**, *9*, 115.
Berezin, B. D.; Koifman, O. I. *Russ. J. Phys. Chem.* **1970**, *44*, 677.
Blair, J. S.; Ayres, T. B. *Ind. Eng. Chem.* **1943**, *35*, 85.
Buckle, K. A.; Edwards, R. A. *J. Food Technol.* **1970**, *5*, 173.
Campbell, H. *Food Res.* **1937**, *2*, 55.
Clydesdale, F. M.; Fleischman, D. L.; Francis, F. J. *Food Prod. Dev.* **1970**, *4* (5), 127.

Clydesdale, F. M.; Francis, F. J. *Food Technol.* **1968**, *22*, 793.
Fischbach, H. *J. Assoc. Off. Agr. Chem.* **1943**, *26*, 139.
Fischbach, H.; Newburger, S. H. *J. Assoc. Off. Agric. Chem.* **1943**, *26*, 134.
Gupte, S. M.; Francis, F. J. *Food Technol.* **1967**, *18*, 1645.
Gupte, S. M.; El-Bisi, H. M.; Francis, F. J. *J. Food Sci.* **1964**, *29*, 379.
Humphrey, A. M. *Food Chem.* **1980**, *5*, 57.
Jackson, A. H. In "Chemistry and Biochemistry of Plant Pigments"; Goodwin, T. W., Ed.; Academic Press: New York, 1976; Vol. I, Chapter 1.
Jones, I. D.; White, R. C.; Gibbs, E. *Food Technol.* **1962**, *16* (3), 96.
Loef, H. W.; Thung, S. B. *Z. Lebensm.-Untersuch Forsch.* **1965**, *126*, 401.
Malecki, G. J. U.S. Patent 4 104 410, 1978.
Schanderl, S. H.; Marsh, G. L.; Chichester, C. O. *J. Food Sci.* **1965a**, *30*, 312.
Schanderl, S. H.; Marsh, G. L.; Chichester, C. O. *J. Food Sci.* **1965b**, *30*, 317.
Schwartz, S. J. *J. Liquid Chron.* **1984**, *7*, 1673.
Schwartz, S. J.; Woo, S. L.; von Elbe, J. H. *J. Agric. Food Chem.* **1981**, *29*, 533.
Schwartz, S. J.; von Elbe, J. H. *J. Food Sci.* **1983**, *48*, 1303.
Strain, H. H. *J. Agric. Food Chem.* **1954**, *2*, 1222.
Sweeney, J. B.; Martin, M. *Food Res.* **1958**, *23*, 2635.
Swirski, M. A.; Allauf, R.; Guimard, A.; Cheftel, H. *J. Agric. Food Chem.* **1969**, *17*, 799.
Tan, C. T.; Francis, F. J. *J. Food Sci.* **1962**, *27*, 232.

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Nutrient Characteristics and Glycoalkaloid Content of Potato Distiller Byproducts

Linda J. Kling, Rodney J. Bushway,* Ralph M. Cleale,[1] and Alfred A. Bushway

Nine potato distiller byproducts were analyzed for nutrient composition. Estimates of feeding value to livestock were determined. Proximate analyses of the byproducts showed all the products to have a fair amount of crude protein, but amino acid determination revealed a large portion of the crude protein to consist of nonprotein nitrogen. The products were good sources of lysine and methionine. The products were high in ash content, which would limit their potential feeding value. The carbohydrate portion of the byproducts was highly available as determined by proximate analyses and digestibility studies. Estimates of net energy for lactation were found to be comparable to other distiller byproducts, but the determination of true feeding value must await feeding trials to determine palatability and productivity. The glycoalkaloid content of the byproducts raises concern of the products palatability to livestock.

INTRODUCTION

The quantity of potato waste products from potato processing plants is tremendous. These waste products are currently being used as fertilizer or are being dried and used as cattle feed. An additional potential use of these waste products is as a source of fermentable carbohydrates in the production of gasohol (gasoline and alcohol mixture as a fuel source).

The purpose of this study was to determine the nutrient composition and estimate the potential feeding value of the byproducts that result from the production of ethanol from the fermentation of potato waste products. Several combinations of potato waste products and oat grain were tested for ethanol yield, and the feeding value of the subsequent distiller byproducts was estimated from nutrient composition and digestibility data. Because glycoalkaloids are naturally occurring toxicants present in all potatoes and potato products (Hansen, 1925; Renwick, 1972; Mun et al., 1975; Keeler et al., 1976; Renwick et al., 1984), the potato distiller byproducts were analyzed for their glycoalkaloid content.

Departments of Animal and Veterinary Sciences (L.J.K., R.M.C.) and Food Science (R.J.B., A.A.B.), University of Maine, Orono, Maine 04469.

[1]Present address: Department of Animal Science, University of Nebraska, Lincoln, NE 68583.

MATERIALS AND METHODS

Materials. Nine samples of potato distiller byproducts were obtained from pilot distillation projects performed by Biochem. Technology (Malvern, PA 19355) for Johnson Products, Inc. (Boston, MA 02210). The constitution of the nine potato waste fermentation mash samples is depicted in Table I. The components of the fermentation mash are primarily byproducts of the french fry potato industry. Cull potatoes are potatoes of insufficient quality to be processed as french fries. Peel waste is material from the steam peelers; filter cake waste is the solid residue from the filtered processing water. Screen waste is composed of potato slices that are too small to be fried; whereas, french fried waste is composed of fried potatoes of insufficient quality to meet quality control standards. Drum waste is waste material from the drying of potato flour.

Samples of the byproduct residue resulting after the distillation of ethanol were received in the air-dried state. Protein (Kjeldahl N), fat (ether extract), ash, moisture, crude fiber, and available carbohydrate analyses were performed according to the AOAC methods (1984).

Amino Acid Analyses. Amino acid analyses were performed by the University of Maryland. The method of hydrolysis was an adaptation of the procedure of Moore and Stein (1963). Fat-free dried samples (20–200 mg) were hydrolyzed with 6 N HCl under nitrogen for 24 h and for 72 h. Kontes hydrolysis tubes were used, and no sample transfers were made. Norleucine was added as an internal

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