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Changes in Carbonyl Compounds in the French Bean as a Function of Cooking and Enzyme Treatment

Selim Kermasha,* Frederik R. van de Voort, and Maurice Metche

The changes in the volatile and total carbonyl compounds in the French bean prior to cooking and after cooking and the subsequent application of endogenous enzymes were investigated. Carbonyl compounds were extracted from treated beans and prepared as DPNH derivatives, which were quantitated both gravimetrically and spectrophotometrically. Gas chromatographic analysis showed that thermal treatment of the beans resulted in increased levels of both volatile and total carbonyl compounds, with a corresponding decrease in longer chain carbonyl compounds. These changes were accentuated by the incubation of the whole cooked beans in the presence of an enzyme extract obtained from germinated beans. Mass spectroscopic analysis indicated the appearance of two dienals (C_{10} and C_{11}) as a result of enzyme treatment. It would appear that enzyme treatment of the cooked bean resulted in changes similar to the cooking of the beans for a prolonged period of time.

The French bean is an important food source because of its relatively high oil and protein content. Cultivated in France, and other regions of the world, it is consumed directly or futher processed in a manner similar to the better known soybean. Flavor is an important factor in the acceptability of any food product, and the authors have been involved in an ongoing study to understand the chemistry of flavor compounds in the French bean. For example, the French bean, like other oil-bearing seeds, suffers from the development of off-flavors during storage and enzymatic mechanisms are considered to be involved.

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French bean lipase has been characterized (Kermasha et al., 1986a), its activity followed during development, maturation (Kermasha et al., 1986b), and the storage of the full-fat flour (Kermasha et al., 1986c). French bean lipoxygenase was subsequently characterized (Kermasha and Metche, 1986), and it was shown that linoleic acid hydroperoxide could be converted to ketols by the French bean hydroperoxide isomerase (Kermasha et al., 1986d).

Carbonyl compounds, especially the volatiles, are known to be contributers to the flavor development in foods (Arai et al., 1967; Buttery et al., 1971; Franzen and Kinsella, 1974; Gardner, 1975; Solms et al., 1973). The flavor of fresh foods results from compounds normally present in vivo and others produced by enzymatic degradation during harvesting and processing. The flavor of cooked foods is due to a complex sequence of enzymatic and chemical reactions, i.e. Maillard reaction/Strecker degradation, taking place as a function of temperature, mositure, and the rate of heating, generally producing a consistent result if the process is carried out in a standardized manner (Hewitt et al., 1956; Salem et al., 1967; Rooney et al., 1967). The enzymatic mechanism is short-lived during the cooking process of the whole bean, as the thermal energy generally denatures the enzymes before significant changes can take place. Although the original enzymes that generate flavor are destroyed during cooking/thermal processing, the addition of endogenous enzymes back to its processed source will allow it to act on any excess precursor to regenerate its characteristic flavor (Chase, 1974). This use of endogenous enzymes added after processing to develop flavor is commonly termed the "flavorese" concept (Richardson, 1976).

The aim of this work was to determine, quantitatively and qualitatively, changes in volatile and total carbonyl compounds assumed to be associated with flavor as a function of cooking and the addition of endogenous flavorese enzyme to the cooked French bean seed.

MATERIALS AND METHODS

Materials. Certified mature French bean (*Phaseolus vulgaris*) seeds of the cultivar Roi des Verts obtained from Vilmorin, France, were used throughout this study. To obtain the enzyme extract, mature seeds were treated with 0.1% $HgCl_2$ solution, washed, sown in trays lined with vermiculite, placed in a controlled environment chamber (25 °C; 45% RH), and allowed to germinate over a period of 5 days. A crude enzyme extract was prepared as required by blending 5-day-old germinated cotyledons with 0.9% sodium chloride solution (1:3, w/v) for 2 min, and a clear extract was obtained after centrifugation of the homogenate at 48000*g* for 30 min. The thermal treatment of beans was carried out, in duplicate, under standardized conditions, i.e., a 1:10 ratio of seeds to water maintained at a preselected temperature for a specified time (Figure 1). The heat-treated product was then cooled immediately under cold tap water for 10 min and drained.

Preparation of Carbonyl Compounds. *Phaseolus* seeds were blended in a Waring blender with 350 mL distilled water (2 min) and transferred to a 1-L round-bottomed flask equipped with a mechanical stirrer. Magnesium sulfate (30 g) was added, and the flask was placed in a 35 °C water bath and connected to a distillation apparatus having a dry ice cold trap (−70 °C) attached. The volatile components released, in the presence of gentle stream of nitrogen and under vacuum, were collected over a 24-h period behind the dry ice trap in a mixture of 2,4-dinitrophenylhydrazine (DNP) solution (0.9 M in 2 N HCl) and benzene (1:1, v/v). The volatie carbonyl compounds were then separated from the benzene phase, as 2,4-dinitrophenylhydrazone derivatives (DNPH). Total carbonyl compounds were prepared from separate extracts as DNPH derivatives as described by Halvarson (1972). Volatile and total carbonyl compounds were prepared in duplicate.

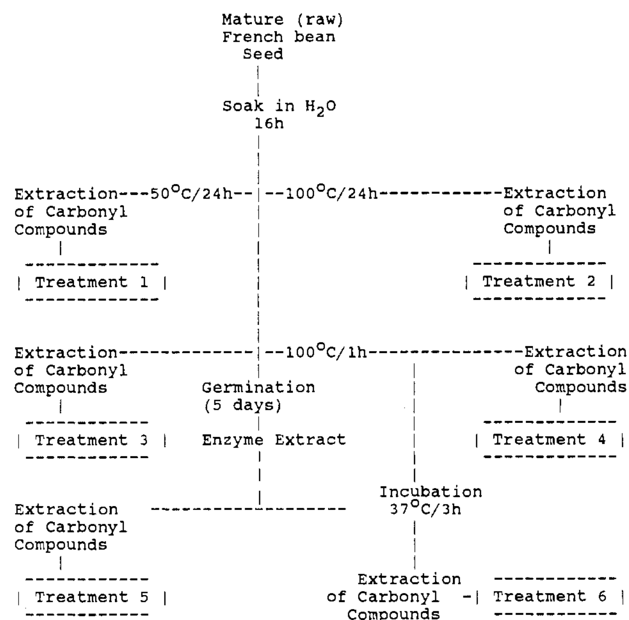

Figure 1. Schematic diagram of the treatments the French bean underwent prior to analysis for volatile and total carbonyl compounds.

Quantitation of Carbonyl Compounds. Two methods were used to quantitate the DNPH-derivatized carbonyl compounds. One procedure involved the evaporation of benzene under vacuum, collecting the DNPH derivatives and quantitating them gravimetrically as a percentage relative to the weight of beans. The second method involved the spectrophotometric measurement of DNPH derivatives at 340 nm, with a PYE Unicam SP-1800 spectrophotometer, as suggested by Lohman (1958). The initial calibration for spectrophotometric measurements was performed with three representative carbonyl compounds of different chain lengths: acetone (C_3), capronaldehyde (C_6), and methylnonyl ketone (C_{11}). DNPH derivatives were quantitated as a percentage, based on the average value of spectrophotometric measurement of standard compounds, relative to the weight of the beans. Quantitation of volatile and total carbonyl compounds was performed in duplicate.

Gas Chromatography–Mass Spectroscopy. The DNPH derivatives of carbonyl compounds were initially separated and purified by preparative TLC (Kermasha et al., 1986d). Gas chromatography (GC) of the DNPH derivatives of carbonyl compounds was then carried out as described previously by Kermasha et al. (1986d). Identification of individual DNPH derivatives was based on retention times of purchased standards (Fuka Chemical Co.), the quantitation initially based on detector response relative to the concentration of each individual standard and, later, via an internal standard for the analytical runs. Gas chromatography–mass spectroscopy (GC–MS) analysis of the DNPH derivatives of carbonyl compounds was also performed according to procedures described previously by Kermasha et al. (1986d).

Treatment Protocol. Figure 1 presents a schematic diagram of the treatments the French bean underwent in order to obtain separate analytes for which volatile and total carbonyl compounds were characterized and quantitated. Treatments 1 and 2 correspond to carbonyl com-

Table I. Percent of DNPH Derivatives of Volatile and Total Carbonyl Compounds Present in Raw and Heat-Treated French Bean Seeds as Assessed by Gravimetric and Spectrophotometric Methods

	DNPH[a,b]			
	gravimetric		spectrophotometric[c]	
treatment (no.)	volatile	total	volatile	total
mature (raw) seed (3)	0.12	4.18	0.11	4.68
50 °C, 24 h (1)	0.18	5.19	0.13	5.41
100 °C, 1 h (4)	0.19	5.38	nd[d]	nd
100 °C, 24 h (2)	0.21	6.01	0.19	6.26

[a] Percent of each DNPH derivative relative to the dry weight of the beans. [b] Relative standard deviation (RSD) within ±5%. [c] Average based on three calibrations. [d] Not determined.

Table II. Spectrophotometric Determination of Percent DNPH Derivatives of Volatile and Total Carbonyl Compounds at 340 nm as a Function of the Calibration Standards Employed

treatment (no.)	acetone (C_3)	capronaldehyde (C_6)	methyl nonyl ketone (C_{11})	av (calcd)
	Volatile Carbonyls[a,b]			
mature seed (raw) (3)	0.07	0.11	0.14	0.11
50 °C, 24 h (1)	0.08	0.12	0.17	0.13
100 °C, 24 h (2)	0.10	0.14	0.21	0.19
	Total Carbonyls			
mature seed (raw) (3)	3.01	4.54	6.41	4.68
50 °C, 24 h (1)	3.67	4.81	7.75	5.41
100 °C, 24 h (2)	4.11	5.19	8.75	6.26

[a] Percent of each DNPH derivative relative to the dry weight of the beans. [b] Relative standard deviation (RSD) within ±5%.

pounds extracted from beans heated for 24 h at 50 and 100 °C while treatment 3 represents raw beans. Treatment 4 assesses the carbonyl compounds extracted from beans heated at 100 °C for 1 h whereas treatment 5 indicates carbonyl compounds obtained from the enzyme extract of germinated seed. Incubation at 37 °C for 3 h of cooked beans (100 °C, 1 h) with the crude enzyme extract resulted in treatment 6. Volatile and total carbonyl compounds were prepared as DNPH derivatives, purified by TLC, and subjected to GC–MS analyses as described previously. The raw bean (treatment 3) was considered a reference to which the subsequent treatments were compared.

RESULTS AND DISCUSSION

Initially the overall effects of the thermal treatments on the volatile and total carbonyl compounds relative to the raw French bean were considered in light of the methodologies available to carry out this analysis. Table I presents the relative percentages of DNPH derivatives due to volatile and total carbonyl compounds obtained as a function of time and temperature as determined by both gravimetric and spectrophotometric methods. Two methods were used, as each has some limitations. The average values presented in Table I for the spectrophotometric method were derived from the data in Table II using 340-nm and selected calibration standards.

As one would expect, the calculated carbonyl levels, for the same treatment, were directly proportional to the chain length of the standard. A further complication is that the λ_{max} for DNPH derivatives ranges between 331 and 358 nm (Lohman, 1958), which is an additional variable in this approach to quantitating carbonyl compounds. Since the calculated carbonyl compound levels (Table II), for the same treatment, were directly proportional to the chain length of the standards and since it was difficult to consider any one compared as a reference, a calibration curve was based on the average response to the three standards

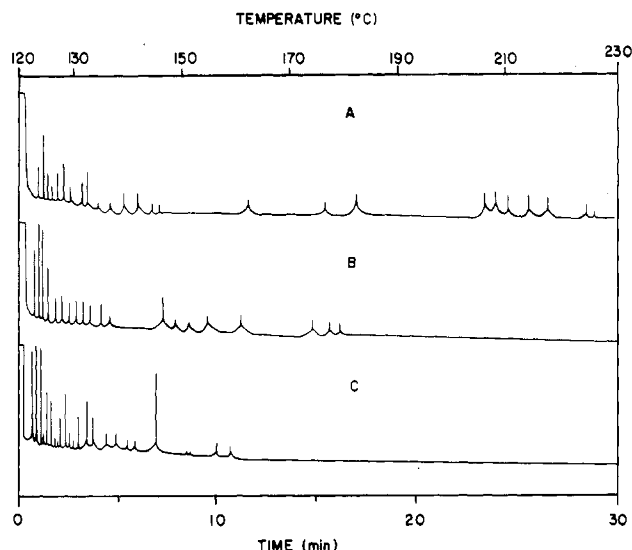

Figure 2. Gas chromatographic profile of DNPH derivatives of volatile carbonyl compounds in the French bean: (a) raw bean; (b) beans cooked at 100 °C for 1 h; (c) cooked bean incubated at 37 °C for 3 h with crude enzyme extract.

(C_3, C_6, C_{11}) and the midpoint of the carbonyl absorbance range (340 nm).

The gravimetric method suffers from the possible presence of DPNH impurities, which might affect the values obtained and does not discriminate between the types of carbonyl compounds present. On the other hand, the gravimetric method is likely to be more accurate, as the chain length and wavelength variables are not present. Overall, the trends obtained by both methods agree to a large extent in that there is a formation of carbonyl compounds as a function of time and temperature. On the basis of gravimetric data (Table I) there is a significant increase in carbonyl compounds (57% for volatile and 28% for total) over the first 1 h of heating at 100 °C and a subsequent smaller increase (17% for volatile and 15% for total) over the next 23 h, indicating that most of the changes take place within 1 h at 100 °C.

Changes in Volatile Carbonyl Compounds. In order to follow some of the changes taking place as a function of the thermal treatments given to the French bean, the DNPH derivatives of the volatile carbonyl compounds were purified by TLC and then analyzed by gas–liquid chromatography. Parts A and B of Figure 2 illustrate typical gas chromatograms obtained for the raw and cooked (100 °C, 1 h) beans. Table III identifies and quantitates selected ketones and aldehydes present or absent in the chromatograms of the selected treatments of beans. In terms of its gas chromatographic profile (Figure 2), it is clear that major changes take place when the bean is cooked, specifically a reduction in the long-chain carbonyl compounds with a concomitant increase in the short-chain carbonyl compounds, which is furhter accentuated when the cooked seed was incubated with the enzyme extract. On the basis of GC retention time data (Table III), a variety of aldehydes and ketones were tentatively identified and shown to be present in the treated and untreated samples. Depending on the treatment, formaldehyde, acetaldehyde, acetone, *n*-propionaldehyde, isobuturaldehyde, methyl ethyl ketone, *n*-butyraldehyde, methyl propyl ketone, valeraldehyde, glutaraldehyde, capronaldehyde, and (hydroxymethyl)furfural were present. The quantitative GC data demonstrate that the number of voltile carbonyl compounds increased as a function of temperature as initially indicated by both the gravimetric and spectrometric methods (Tables I and II). The for-

Table III. Partial Identification and Quantitation of DNPH Derivatives of Volatile Carbonyl Compounds as a Function of Thermal Treatment of the French Bean

carbonyl compd	DNPH,[a,b] %, at treatment (no.)			
	raw (3)	50 °C, 24 h (1)	100 °C, 1 h (4)	100 °C, 24 h (2)
formaldehyde	nd[c]	12	14	15
acetaldehyde	4	10	12	13
acetone	10	11	13	14
n-propionaldehyde	1	4	7	8
isobutyraldehyde	nd	nd	nd	1
methyl ethyl ketone	2	3	4	6
n-butyraldehyde	7	nd	1	1
methyl propyl ketone	9	5	6	6
valeraldehyde	8	6	4	3
glutaraldehyde	6	4	2	2
capronaldehyde	5	nd	1	1
(hydroxymethyl)furfural	nd	5	8	9
total ident area, %	52	60	70	79
total no. of peaks	25	18	20	22
volatile carbonyl compd,[d] %	0.120	0.180	0.189	0.210

[a] Area percent of each DNPH carbonyl derivative relative to the total area. [b] Relative standard deviation (RSD) within ±5%. [c] Not detected. [d] Percent of each DNPH derivative relative to the dry weight of the beans as reported in Table I.

Table IV. Percent of DNPH Derivatives of Volatile and Total Carbonyl Compounds Present in Treated French Bean Seeds as Assessed by the Gravimetric Method

treatment (no.)	DNPH[a,b]	
	volatile	total
mature (raw) seed (3)	0.12	4.18
100 °C, 1 h (4)	0.19	5.38
enzyme extract (5)	0.07	2.30
100 °C, 1 h & enzyme treated (6)	0.27	6.52

[a] Percent of each DNPH derivative relative to the dry weight of the beans. [b] Relative standard derivation (RSD) within ±5%.

mation of (hydroxymethyl)furfural appears to be a direct result of thermal treatment.

Treatment with Enzymatic Extract. The flavorese concept, i.e. the addition of an active enzyme extract obtained from the tissue of the source material, is a method of modifying or producing additional flavor compounds in the processed end product. The effect of incubating cooked beans at 37 °C for 3 h with an active enzyme extract obtained from a dry old bean sprout was assessed chemically via the determination of volatile and total carbonyl compounds.

Table IV provides data that compare the relative levels of carbonyl compounds to that of cooked and raw beans and the enzyme extract itself. The latter was analyzed to make sure that the extract itself did not contribute significantly to the results. Both volatile and total carbonyl compounds increased significantly when seeds treated at 100 °C for 1 h were incubated with crude bean enzyme extract for 3 h (Table IV). Clearly, a major increase takes place in both volatile and total carbonyl compounds, in fact more than observed in the case of boiling the beans for 24 h (Table I). The GC profile of carbonyl compounds also changed after this treatment (Figure II). The enzyme-treated cooked bean volatile carbonyls (Table V) showed trends similar to that observed for the cooked bean itself (Table III), but substantially accentuated. The quantitative results (Table V) demonstrate that the incubation of cooked beans with the enzyme extract resulted in increase of the number of carbonyl compounds with a concomitant increase in the shorter carbonyl compounds such as formaldehyde and acetaldehyde. The increase in levels of aldehyde compounds such as isobutyraldehyde, valeraldehyde, and capronaldehyde as well as an increase

Table V. Partial Identification and Quantitation of DNPH Derivatives of Volatile Carbonyl Compounds as a Function of Selected Treatments of the French Bean

carbonyl compd	DNPH, rel %,[a,b] at treatment (no.)			
	raw (1)	100 °C, 1 h (4)	enzyme extr (5)	100 °C, 1 h enzyme treated (6)
formaldehyde	nd[c]	14	6	16
acetaldehyde	4	12	8	15
acetone	10	13	15	2
n-propionaldehyde	1	7	2	3
isobutyraldehyde	nd	nd	6	2
methyl ethyl ketone	2	4	2	11
n-butyraldehyde	7	1	10	1
methyl propyl ketone	9	6	3	8
valeraldehyde	8	4	1	3
glutaraldehyde	6	2	16	2
capronaldehyde	5	1	5	2
(hydroxymethyl)furfural	nd	8	nd	18
total ident area, %	52	70	74	83
total no. of peaks	25	20	18	25
volatile carbonyl compd,[d] %	0.120	0.180	0.067	0.271

[a] Area percent of each DNPH carbonyl derivative relative to the total area. [b] Relative standard deviation (RSD) within ±5%. [c] Not detected. [d] Percent of each DNPH derivative relative to the dry weight of the beans as reported in Table I.

Table VI. Mass Spectroscopic Confirmation (+) of Components Present in Beans as Outlined in Figure 1.

carbonyl compd	treatment no.			
	1	4	5	6
acetone	+	+	+	+
acetaldehyde	+	+	+	+
2-hexenal	–	+	–	+
dienal (C_{10})	–	–	–	+
dienal (C_{11})	–	–	–	+

in some of ketones such as methyl ethyl ketone and methyl propyl ketone was also apparent. (Hydroxymethyl)-furfural, a component that appeared in the cooked bean, increased substantially with enzyme treatment. Acetadehyde and acetone, the dominant compounds indicated to be present by GC retention time data were confirmed by GC–MS of DNPH's having m/e 224 and 238, respectively (Table VI). GC–MS also indicated that 2-hexenal (m/e 278) appeared as a result of boiling beans for 1 h. Lumen et al. (1978) demonstrated the production of *trans*-2-hexenal from the oxidation of linoleic and linolenic acids in green beans; this compound was formed by lipoxygenase isoenzyme from soybeans (Grosch and Laskawy, 1975). The incubation of the beans with the enzyme extract led to the formation of two dienals (C_{10} and C_{11}) with m/e 332 and 346, respectively. Dienals in general are known to be flavor compounds (Maars and Visscher, 1985), and it is likely that these (Table V) may be part of the enzyme-generated flavor.

CONCLUSION

The data gathered in this study indicate that cooking of French beans results in important modifications in the profile and levels of carbonyl compounds, especially the volatiles. The results demonstrate that thermal treatment increased both volatile and total carbonyl compounds with a concomitant increase in the number of short-chain carbonyl compounds. Incubation of the beans with the enzyme resulted in changes that appeared to be similar to that of extended cooking. Two dienals were characterized by GC–MS as being formed when the cooked beans were treated with the enzyme extract.

Registry No. Me_2CO, 67-64-1; $BuCH_2CHO$, 66-25-1; MeCO-$(CH_2)_8Me$, 112-12-9; H_2CO, 50-00-0; AcH, 75-07-0; EtCHO, 123-38-6; *i*-PrCHO, 78-84-2; MeCOEt, 78-93-3; PrCHO, 123-72-8;

MeCOPr, 107-87-9; BuCHO, 110-62-3; $OHC(CH_2)_3CHO$, 111-30-8; PrCH=CHCHO, 505-57-7; (hydroxymethyl)furfural, 25376-49-2.

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Volatile Components of Mango Preserved by Deep Freezing

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Mango slices were stored for 14 months in a deep freeze at −15 °C and then analyzed for their volatile aroma components. Results were remarkably similar to those obtained for the fresh fruit, although the amount of the important constituent, car-3-ene, was slightly reduced. The plasticizer, di-2-ethylhexyl adipate, was also detected in the aroma isolate, originating by migration from the PVC film in which the fruit was wrapped while in storage.

In a previous paper we reported the results of analysis of the volatile flavor components of two cultivars of mango from Florida (MacLeod and Snyder, 1985). In addition, the effects of a limited range of storage conditions on the volatiles were also assessed, and it was found that storage of mango slices at −15 °C for 15 days provided results that were virtually identical with those for the fresh fruit. We now report data for mangoes stored similarly, but for a much longer period (over 1 year).

EXPERIMENTAL SECTION

All the mangoes used in this work (cultivar Tommy Atkins) were shipped by air freight to London from Miami, FL. Some were analyzed when fully ripe, and results have already been reported (MacLeod and Snyder, 1985). The remainder were stored for subsequent analysis as follows. Two whole mangoes were placed separately in plastic bags, the bulk of the air was removed, and the bags were sealed. A further two were first wrapped in clingfilm (thin plasticized PVC film designed specifically for such food storage) and then kept in plastic bags as described above. The final two mangoes were first sliced, the stones removed, and the slices, with skin still attached, then wrapped in clingfilm and placed in two plastic bags as described above. All samples were then stored in a deep freeze at −15 °C for 14 months. After thawing, the aroma volatiles of the sliced fruit were then analyzed exactly as described previously (MacLeod and Snyder, 1985).

RESULTS AND DISCUSSION

On thawing, the mangoes that had been stored whole in the deep freeze for 14 months were found to be unac-

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