

Whiskey Composition: Formation of Alpha- and Beta-Ionone by the Thermal Decomposition of Beta-Carotene

Alpha- and β -ionones have been detected in distilled alcoholic beverages by gas chromatography and were shown to result from the thermal decomposition of β -carotene. Both compounds were found in extracts of distillates from cooked corn and in extracts of a number of alcoholic beverages. The ionones were generated in small amounts along with toluene,

xylylene, 2,6-dimethylnaphthalene, and ionene when β -carotene was heated at 188° C. for 72 hours. Traces of α - and β -ionone were found also when pure β -carotene was heated in water for 30 minutes followed by steam distillation of the mixture. The ionones were not present in measurable quantity in unheated carotene or the oil fraction of corn.

Mulik and Erdman (1963), and Day and Erdman (1963) have shown that β -carotene decomposes at 188° C. in an oxygen-free environment to yield toluene, *m*-xylene, 2,6-dimethylnaphthalene and ionene (1,1,6-trimethyl-1,2,3,4-tetrahydronaphthalene). Hirose *et al.* (1963) found α -ionone and unidentified aliphatic and aromatic hydrocarbons in a corn fusel oil fraction. The origin of these compounds was not explained.

The authors have detected alpha ionone in 29 extracts and β -ionone in 33 extracts representing aged and unaged Bourbons, rye, malt, Scotch, Irish, and Canadian whiskeys, grape brandy, and grain fusel oils (unpublished data). The present work was carried out to determine if thermal degradation of β -carotene could lead to the ionones found in liquor extract concentrates.

The premise that the ionones in alcoholic distillates could be derived from β -carotene or Vitamin A in grain was tested by simulating conditions which prevail in distillery mash cooking, extraction of raw, ground corn, heating a β -carotene-water mixture to 100° C, and thermal degradation of β -carotene in the presence of air at 188° C.

EXPERIMENTAL

A Varian Aerograph Model 1200 with hydrogen flame detector was used. A $\frac{1}{8}$ -inch diameter \times 10-foot stainless steel column was packed with 10% SE-30 on 60/80 mesh Chromosorb W-AW. The column exit was fitted with a 1-to-1 splitter. Operating conditions were: Helium carrier gas flow, 25 ml. per minute; column temperature was programmed at 4° per minute from 110° to 250° C. with balance of runs at 250° C.; injector and detector temperatures were 280° C.

Solvents used were analyzed and found to contribute no detectable volatiles.

Corn Mash Extract. One hundred-fifty grams of U. S.

Number 2 corn, 0.1 gram of ground distillers' barley malt, and demineralized water were cooked at 100° C. for 15 minutes. The starch was converted to sugar by treatment with commercial fungal diastase preparation at 55–60° C. for 30 minutes. The converted mash was diluted with an equal volume of water and was steam-distilled to yield 250 ml. This distillate was extracted three times with 50 ml. of 1,1,2-trichlorotrifluoroethane (DuPont Freon 113). The extract was dried over anhydrous sodium sulfate and the solvent evaporated under reduced pressure without heat.

Raw Corn Extracts. Two samples of U. S. Number 2 corn were ground with pulverized dry ice in a Wiley mill to pass a 1-mm screen and extracted with dichloromethane. The extracts were dried and concentrated as described above. Two microliters of each of the oil residues were analyzed by GLC.

β -Carotene Degradation. Beta-carotene (synthetic, General Biochemicals, Inc.) was recrystallized from benzene. A solution of the recrystallized β -carotene in dichloromethane was injected into the gas chromatograph. No ionones were detected either by peak response or by odor at the splitter exit.

Ten milligrams of β -carotene in 200 ml. of distilled water were heated in each of two screw-capped borosilicate glass tubes, one for 30 minutes, the other for 3 hours at 100° C. Each suspension was steam-distilled until 250 ml. of distillate were collected. The distillates were extracted with Freon, and the extracts dried as described above.

Thermal degradation of β -carotene, as described by Day and Erdman (1963) was carried out except that no precautions were taken to exclude air from the system. The β -carotene contained in a sealed bomb was heated for 72 hours at 188° C. The benzene was removed under vacuum and the residue, dissolved in 2 ml. of *n*-pentane (Fisher, Cert., P400). A 1- μ l. portion was used for GLC.

Retention times were determined for authentic α - and β -

Table I. Products of Thermal Decomposition of β -Carotene Separated and Identified by Gas Chromatography in Various Extracts

Source	Toluene ^a	<i>m</i> -Xylene ^a	2,6-Dimethylnaphthalene	Ionene	α -Ionone	β -Ionone
Raw corn extract	—	—	—	—	—	— ^b
Cooked corn distillate	—	—	—	—	+	+
Liquor extracts	—	—	—	—	+	+
Grain fusel oil extracts	—	—	+	—	+	+
β -Carotene heated in benzene (72 hrs. at 188° C.)	+	+	+	+ ^d	+ ^d	+ ^d
β -Carotene heated in water (30 min. at 100° C.)	—	—	—	+ ^c	+	+
Compound retention time, min.	1.8	2.8	14.0	14.1	15.9	17.7

^a Tentative identification based on retention time corresponding to that of authentic compound.

^b Trace of odor at GLC splitter probably due to degradation of carotene in injection port.

^c Peak at correct retention time but not confirmed.

^d Confirmed by GLC-mass spectrometry.

ionones, ionene, *m*-xylene, toluene, and 2,6-dimethylnaphthalene. Mass spectra were taken of the first three compounds. Authentic ionene was prepared by the method of Bogert and Fourman (1933). Its structure was verified by NMR spectroscopy.

RESULTS AND DISCUSSION

A summary of the products of thermal decomposition of β -carotene identified by gas chromatography in various extracts is shown in Table I. The Freon extract from the cooked corn mash distillate showed peaks for α - and β -ionones in the positions noted for the authentic compounds. The violet-like odor, which is characteristic of the ionones in dilute solution, was noted at the exit of the 1-to-1 column effluent splitter simultaneously with the peak records. A number of other unidentified peaks were also observed in this fraction.

The virtual absence of ionones *per se* in raw corn was demonstrated by the GLC analysis of the oily fractions obtained by dichloromethane extraction. A very slight ionone odor was detected simultaneously with a very small peak corresponding to the retention time of β -ionone. A number of other unidentified peaks in small amounts were detectable under these conditions.

Alpha- and β -ionones were found in distillations from suspensions of β -carotene heated to 100° C. for 30-minute and 3-hour periods. A peak with a retention time corresponding to that of ionene was seen but was not confirmed as that compound.

The thermal degradation of β -carotene in benzene at 188° C. and in the presence of air yielded toluene, *m*-xylene, ionene, and α - and β -ionones. The last three compounds were confirmed by GLC-fast scan mass spectrometry. The presence of 60 GLC peaks indicated that the ionones were minor products of the reaction.

These experiments show that degradation of carotene in

cereal grains under mild heat conditions can account for trace amounts of α - and β -ionones found in distilled beverages. To our knowledge, this is the first report showing that α - and β -ionones result from this reaction. Additional amounts of ionones *per se* in cereal grains may be present. Other possible sources of these compounds which are being investigated are the yeast fermentation, chemical transformations during aging, and the charred oak barrel in which aging takes place.

The formation of ionones from β -carotene at 100° C. and at 188° C. and the presence of 2,6-dimethylnaphthalene and the ionones in a fusel oil extract (unpublished data) indicate that carotene may be the common source of these aromatic compounds. The finding of aromatic hydrocarbon degradation products of carotene in alcoholic beverages is interesting in that such reactions may also take place in heat processing of many foods whose raw materials contain carotene.

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