Volatile Constituents of Commercial Canned Pumpkin Puree (ex *Cucurbita moschata*) by Dynamic Headspace Analysis

by

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(Dedicated to the memory of E. D. Alford, who died on January 7th, 2015. A career mass spectroscopist and President of Alford Consulting, he was well known to those in the flavor & fragrance industry for his unique ability to unravel the most difficult GC-MS analyses.)

Summary

The main source of commercial pumpkin puree is from the Dickinson pumpkin cultivar of *Cucurbita moschata* ('Libby's Select') produced by the Nestlé Food Company. The town of Morton, near Peoria in central Illinois (USA), is the location of the Libby's® pumpkin processing plant which cans more than 85 percent of the world's pumpkin puree each year (1).

Pumpkin pie and pumpkin bread have historically been favorite autumn and early winter sweet desserts often consumed during the Thanksgiving and Christmas seasons in the USA and Canada. Generally, spices consisting of cinnamon, clove, nutmeg and ginger (and often vanilla extract) are used to provide the characteristic flavor.

In recent years, a variety of popular "pumpkin flavored" products (notably Starbucks® "Pumpkin Spice Latte" and Pumpkin Spice Frappuccino® Blended Coffee), have been introduced as specialties for the fall season. In most cases, these type products contain a "pumpkin spice flavor", but no real pumpkin.

We previously reported on the volatile constituents of the "raw pumpkin" (Connecticut Field cultivar of *Cucurbita pepo* L.) which is the classic Halloween pumpkin used for jack o'lanterns (2). In this paper, utilizing the same type of headspace technique, we look at a "partial" analysis of the volatile constituents of canned pumpkin puree.

Experimental:

Plant Name: *Cucurbita moschata* ('Libby's Select') – a Dickinson pumpkin cultivar.

Source: Commercial canned pumpkin puree (LIBBY'S® 100% Pure Pumpkin); purchased at Walmart in Louisville, KY, November 2014

Sample Analysis:

SAMPLE 8.D: A 4-5 gram sample of the Libby's® canned pumpkin puree was placed in 16 fl. Oz. glass jar fitted with a metal lid having both inlet and outlet gas tubes. The inlet tube was connected to a helium tank and the outlet tube connected to a stainless tube with Swagelok nuts & ferrules attached. The top of the tube was fitted with a 1/4'" Swagelok union with the top nut hole diameter increased to allow the easy introduction of a Agilent injection port liner (Agilent part 5181-3316) and sealed with an injection port O-Ring. The injection port liner had been packed with 100 mg of Tenax TA (20-35 mesh) (glass-wool plugs on top and bottom) and previously baked out at 260^{o}C for 2.5 hours. Helium (30 cc/min) was introduced into the bottom of the glass jar containing the pumpkin sample. The sample was purged for 100 minutes trapping the volatiles on the Tenax injection port liner. The Tenax liner was then placed directly into the GC injection port for thermal desorption of the volatiles onto the GC column.

GC and GC/MS: The GC-MS was an Agilent 7890A/5975C High Performance combination. An Agilent 60m X 0.32mm I. D. fused silica column coated with a 0.25 micron film thickness of HP-5MS (HP part No. 19091S-416M), a DB-5 equivalent column, was used in all analyses. The column was held isothermally at 30^{o}C for 1.5 minutes, then programmed from 30^{o}C to 260^{o}C at 2^{o}C/min, with a final hold time of 28.5 minutes to give a total analysis time of 145 minutes. The Injection port was held at 260^{o}C. Helium Carrier Gas was used with a flow rate of 3.403 ml/min. Split ratio of 15:1.The Mass spectrometer was scanned in the EI mode from 26m/z to 350m/z using 70eV ionizing voltage. Additionally, FID chromatograms were obtained and a PFPD detector was employed for sulfur compound detection. Percentages are FID percentages, corrected for known experimental artifacts, but without correction for response factors. Analysis was done on the Agilent MS Enhanced Chemstation program Version E.02.02.1431.

Component Identification: Identifications were based on mass spectra from the Wiley 6 and NIST 05 MS libraries as well as from the authors MS library. Standard classic (isothermal) Kovats Indices (KI) based on n-Alkanes (3) were calculated using the formula:

$$Ix = 100n + 100[\log(tx) - \log(tn)] / [\log(tn+1) - \log(tn)]$$

Additionally Linear Retention Indices (LRI), sometimes referred to as the Arithmetic Index (AI), based on n-alkanes using the methodology of Van den Dool and Kratz (4) were calculated using the formula:

$$LRIx = 100n + 100(tx - tn) / (tn+1 - tn)$$

Where available, retention time comparisons were used employing primarily the Retention Indices compilations of the NIST Mass Spec Data Center (5), as well as those of Boelens (6) and Adams (7). Both the calculated Kovats KI and the LRI retention indices are provided in our tables because some of the reported literature does not specify which RI calculations were actually employed. The NIST and Adams values used for comparison were both the van den Dool and Kratz temperature programmed LRI values and the Kovats (KI) values. The Boelens values in the ESO 2000 (Update 2006) database that were derived from the literature do not specify the method of RI calculation. In most cases the RI values by both methods are quite

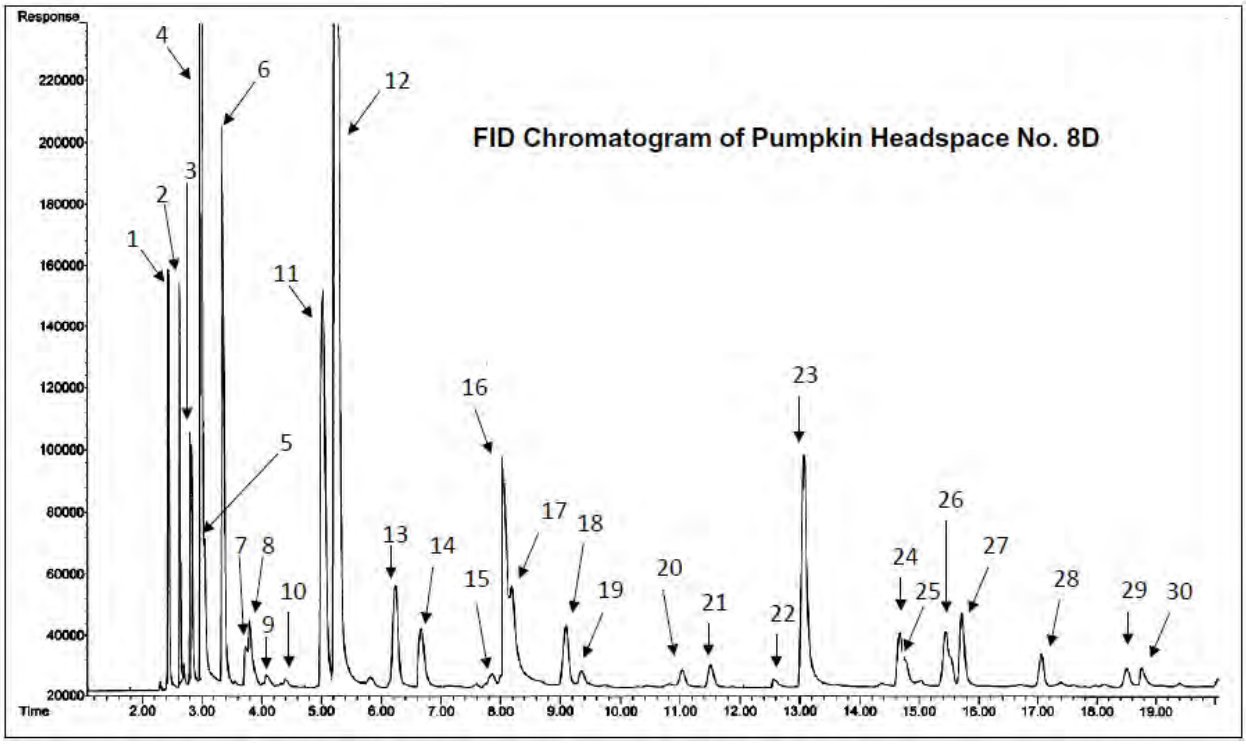
similar, but can vary by 1-9 units. As with all such reported retention index values, those below 500-700 KI/LRI must be considered as somewhat approximate as such values are subject to greater instrumental experimental fluctuations.

Special note: Due to the untimely death of one of the authors (E.D. Alford), only a partial analysis is reported as not all of the results beyond 23 R.T. minutes were available for this article. However, sufficient data for the major volatiles reported is provided.

Results:

Figure 1 illustrates the GC headspace profile of sample 8.D while Table1 provides the detailed analysis with both Kovats retention indices and the Linear retention Indices (LRI).

Figure 1



1. Metthanol; **2.** Ethanol; **3.** 2-Propanone + Furan; **4.** Dimethyl sulfide; **5.** Methyl acetate; **6.** 2-Methylpropanal; **7.** Diacetyl; **8.** 2-Butanone; **9.** Ethyl acetate; **10.** 2-Methylpropanol; **11.** 3-Methylbutanal; **12.** 2-Methylbutanal; **13.** Pentanal; **14.** 3-Hydroxy-2-butanone; **15.** 2-Ethylbutanol (TID); **16.** Dimethyl disulfide + Pyridine; **17.** 1,2-Propanediol; **18.** Toluene; **19.** 1-Pentanol; **20.** Hexanal; **21.** 2-Methyltetrahydrofuran-3-one; **22.** 2-Methylpyrazine; **23.** Furfural; **24.** (Z)-3-hexenol; **25.** 1,4-Dimethylbenzene; **26.** 1,3-Dimethylbenzene; **27.** 1-Hexanol; **28.** 1,2-Dimethylbenzene; **29.** 2-Acetylfuran + Methional; **30.** 2,5-Dimethylpyrazine

Table 1. - GC-MS Analysis of Canned Pumpkin Puree Headspace Sample 8.D

LRI - KI Lit.	HP-5MS (calc) Kovats RI	HP-5MS (calc) LRI	Compound	Actual R.T.	FID %	Ident.
368-404	400	400	Methanol	2.442	4.77	MS,RI
426-489	450	448	Ethanol[a]	2.629	2.30	MS,RI
491-503	494	493	2-Propanone[a]	2.804	1.40	MS,RI
NA	500	500	Furan	2.832	1.31	MS,RI
505-529	516	514	Dimethyl sulfide[a]	2.984	13.08	MS,RI
515-536	528	525	Methyl acetate	3.107	0.87	MS,RI
550-560	550	546	2-Methylpropanal[a]	3.337	9.59	MS,RI
585-613	586	584	Diacetyl[a,b,c]	3.751	0.41	MS,RI
589-606	591	589	2-Butanone[a]	3.812	0.76	MS,RI
605-628	609	608	Ethyl acetate[a,b,c]	4.081	0.12	MS,RI
614-635	626	622	2-Methylpropanol[a]	4.412	0.03	MS,RI
642-666	654	648	3-Methylbutanal[a,c]	5.026	10.33	MS,RI
640-670	663	658	2-Methylbutanal[a,c]	5.251	16.71	MS,RI
693-706	700	700	Pentanal	6.231	2.35	MS,RI
701-720	711	708	3-Hydroxy-2-butanone[a]	6.651	0.31	MS,RI
730-763	740	733	2-Methylbutanol[a,c] (TID)	7.833	0.06	MS,RI
730-756	744	737	Dimethyl disulfide[a] + Pyridine[c]	8.039	3.72	MS,RI
732-850	748	741	1,2-Propanediol[a]	8.234	3.49	MS,RI
761-776	766	760	Toluene[c]	9.123	1.45	MS,RI
758-781	771	765	1-Pentanol[a,b]	9.372	0.12	MS,RI
795-808	800	800	Hexanal[a,b]	11.045	0.15	MS,RI
804-810	808	806	2-Methyltetrahydrofuran-3-one[c]	11.455	0.58	MS,RI
820-836	827	823	2-Methylpyrazine	12.572	0.06	MS,RI
830-851	835	830	Furfural[a,b,c]	13.065	8.72	MS,RI
848-870	860	854	(Z)-3-hexenol[a,b,c]	14.711	1.05	MS,RI
856-875	861	856	1,4-Dimethylbenzene[d]	14.820	0.35	MS,RI
862-875	870	865	1,3-Dimethylbenzene[d]	15.420	0.77	MS,RI
858-888	876	871	1-Hexanol[a,b]	15.870	1.40	MS,RI
886-900	891	889	1,2-Dimethylbenzene[d]	17.070	0.58	MS,RI
906-915	911	909	2-Acetylfuran[c]	18.513	0.47	MS,RI
903-915	911	909	Methional[b]	18.538	0.05	MS,RI
906-920	914	912	2,5-Dimethylpyrazine[c]	18.762	0.35	MS,RI
965-975	971	967	Dimethyl trisulfide[a,b,c]	23.042	2.33	MS,RI
			Total % Identified		90.00	

TID = tentative identification

Compounds previously identified in:

a - Raw pumpkin headspace (Leffingwell et al. - Ref 2.)

b - Freshly cooked pumpkins [water/steam distilled] (Parliment et al. - Ref 8.)

c - Commercial canned pumpkin [water/steam distilled] (Parliment et al. - Ref 8.)

d - Possible artifact

Discussion:

As previously described (2), the presence of some green vegetative notes, e.g. (Z)-3-hexenol, is derived from the 13-lipoxygenase pathway from linolenic acid while the linoleic acid 13-lipoxygenase pathway produces hexanal and hexanol. However, the amounts are much lower in the canned puree than we found in the raw pumpkin (*Cucurbita pepo*).

And, in contrast to the raw pumpkin (2) and water/steam distillate of cooked pumpkin (8) analyses of *Cucurbita pepo* where 2-Methylbutanal and 3-Methylbutanal are nearly absent, these compounds are predominant and undoubtedly contribute to the flavor profile of canned pumpkin puree.

In addition to many of the constituents reported herein, Parliament et al. (8) in their study of a water/steam distillate of canned pumpkin also found phenylacetaldehyde which presumably would contribute to the flavor. Among other compounds they reported were 2,3-pentanedione and 2-methyl-2-pentenal which were not present in our partial analysis (which based on reported retention times should have been detected, if present).

Conclusions:

In comparison to the raw pumpkin (*Cucurbita pepo*) the relative amounts of the six-carbon aldehydes and alcohols are greatly reduced in the canned pumpkin puree of *Cucurbita moschata*.

As canned pumpkin is subjected to a high heat retorting process, it is not surprising to find items such as furfural, 2-methyltetrahydrofuran-3-one, 2-acetylfuran and some pyrazines. These are commonly found in numerous cooked food products. Similarly, the enhanced levels of 2 & 3-Methylbutanal are also common constituents of processed foods which may arise from the Strecker Degradation of isoleucine and leucine, respectively.

Notes: The authors declare they have no competing financial interests.

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