^{1}H qNMR of Alcoholic Cider – Detailed Chemical Component Distribution

By John C. Edwards, Ph.D., Process NMR Associates, LLC, 87A Sand Pit Rd, Danbury CT, 06810 USA

email: john@process-NMR.com tel: +1 (203) 241-0143 web: www.process-nmr.com blog: www.nmrblog.com

Background: ^{1}H quantitative NMR (qNMR) has been utilized to assess the small molecule and carbohydrate chemistry of a large number of home-brewed and commercial alcoholic (hard) ciders. A quantitative chemistry distribution of the products of the various fermentations that occur in cider making was obtained. Malolactic fermentation as well as fermentation by saccharomyces and other wild yeasts occurs in the cider-making process which traditionally occurred without the intentional addition of yeast by the cider-maker. The distribution of small molecules produced by the yeast and bacterial metabolomes at work in the process can yield information of the sensory perception of ciders produced by the many variations of the cider making process that exist today. An investigation of the residual sugar chemistry of commercial ciders gives some indication of the process of back-sweetening some commercial cider products with sugar or unfermented juice additions after fermentation is complete. Dry ciders are readily characterized by their low residual sugar concentrations. A range of ciders are produced ranging from sweet draft cider fermented with saccharomyces yeast (fermentation arrested or back sweetened), to dry cask and bottle conditioned ciders (all or most of the sugar allowed to ferment), to very dry styles such as those found in the Basque region of Spain, brewed with wild yeasts where fermentation is taken to an extreme resulting in complete conversion of sugars to alcohol as well as glycerols to 1,3 propandiol.

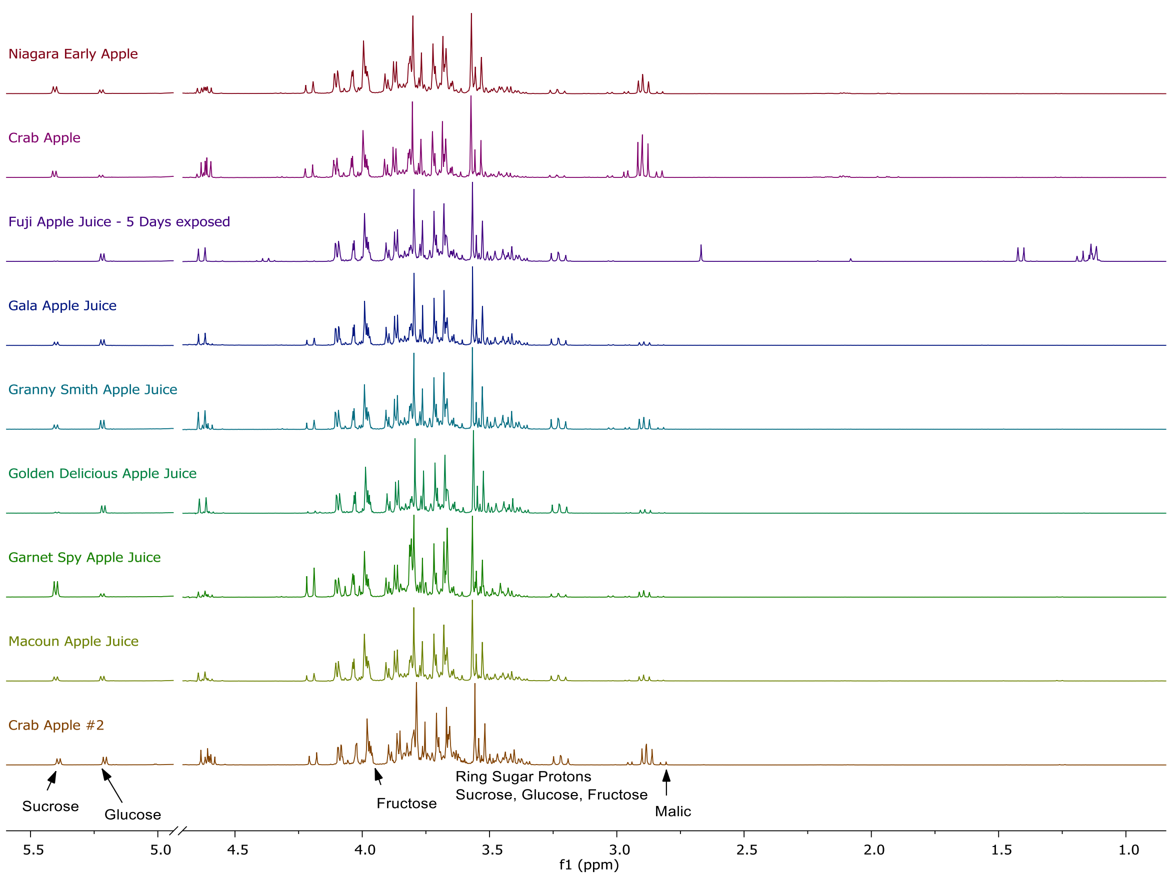


Figure 1: Component chemistry variability in common store-bought apples.

The kinetics of both sugar to ethanol fermentation as well as malolactic fermentation can be followed readily and time based brewing decisions calculated. Fermentation products caused by Enterobacter or wild yeasts can also be detected, particularly from the concentration of 2,3-butandiol which is formed directly by bacteria or by saccharomyces yeast that consume diacetyl during the fermentation process.

Another aspect of NMR analysis is the ability to quantify the important chemical components in apple juices pressed at the beginning of the cider-making process. Detailed sugar chemistry distributions can be quantified as well as amino acids, malic acid, and other organic acid concentrations can be readily obtained. Figure 1 shows the relatively large variation of sugar, amino acid, tannin, and malic acid concentrations that occur between commonly available grocery apples. Figure 2 shows the sugar and organic acid region of the ^{1}H NMR spectrum of the same series of apple juices with the vertical expansion that allows observation of amino acid and tannin concentrations. The amino acid information is informative concerning the nitrogen available to the yeast during the fermentation process. We are currently following the consumption of amino acids during fermentation as well as the introduction of amino acids from lysis of yeast.

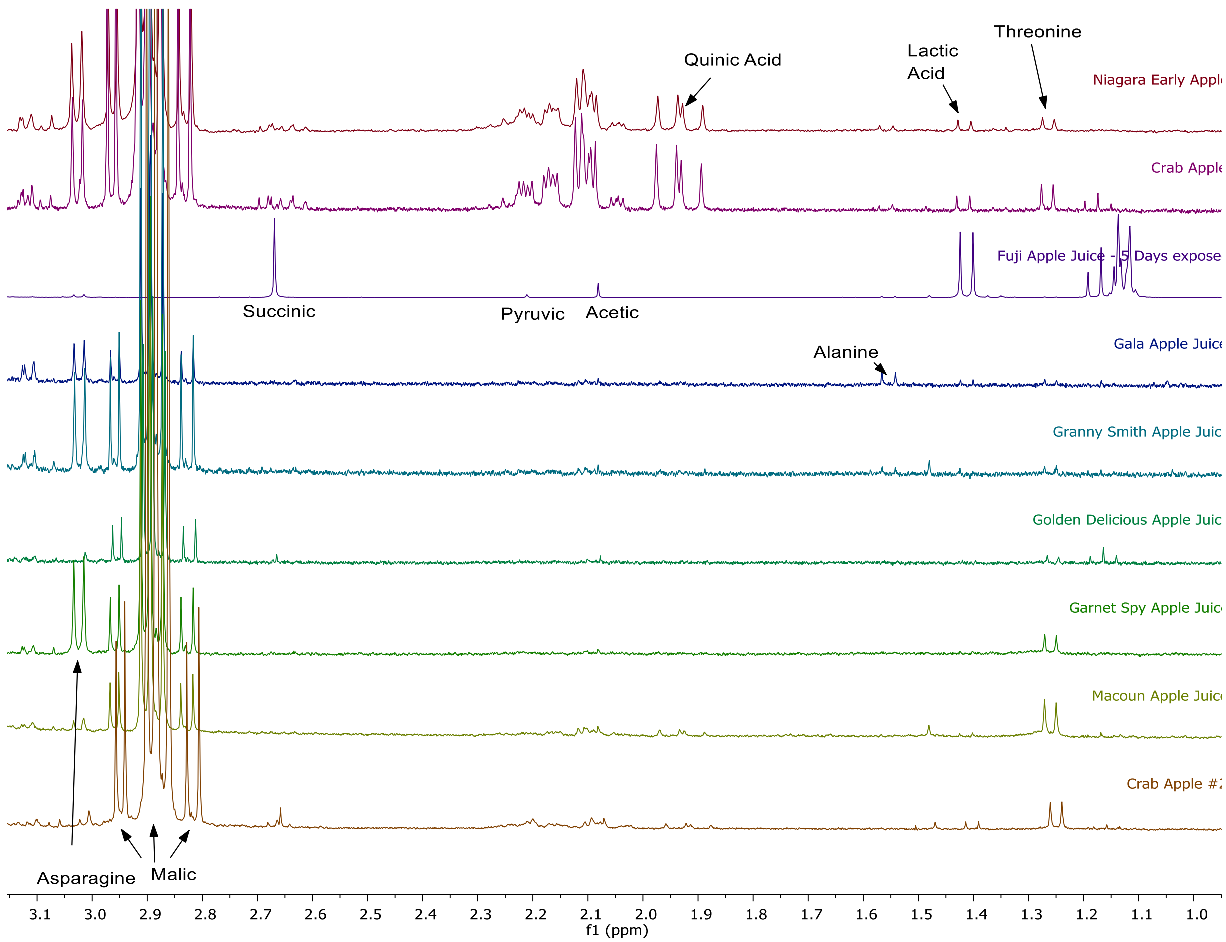


Figure 2: Amino acid and organic acid region of the ^{1}H NMR spectrum. Showing the presence of tannins such as quinic acid and chlorogenic acid. Amino acids such as asparagine, threonine and alanine are observed as well as malic acid, lactic acid, succinic acid and acetic acid.

Figure 3 shows what can happen when a freshly pressed apple juice (in this case Fuji) is improperly stored at room temperature and exposed to peel of the apples for 5 days. The malic acid is completely converted to lactic acid by exposure to lactobacillus. A considerable concentration of succinic acid is also formed which will lead to off-flavor. This demonstrates the usefulness of a non-targeted analysis such as NMR in the observation of quality problems with starting raw materials such as apple juice.

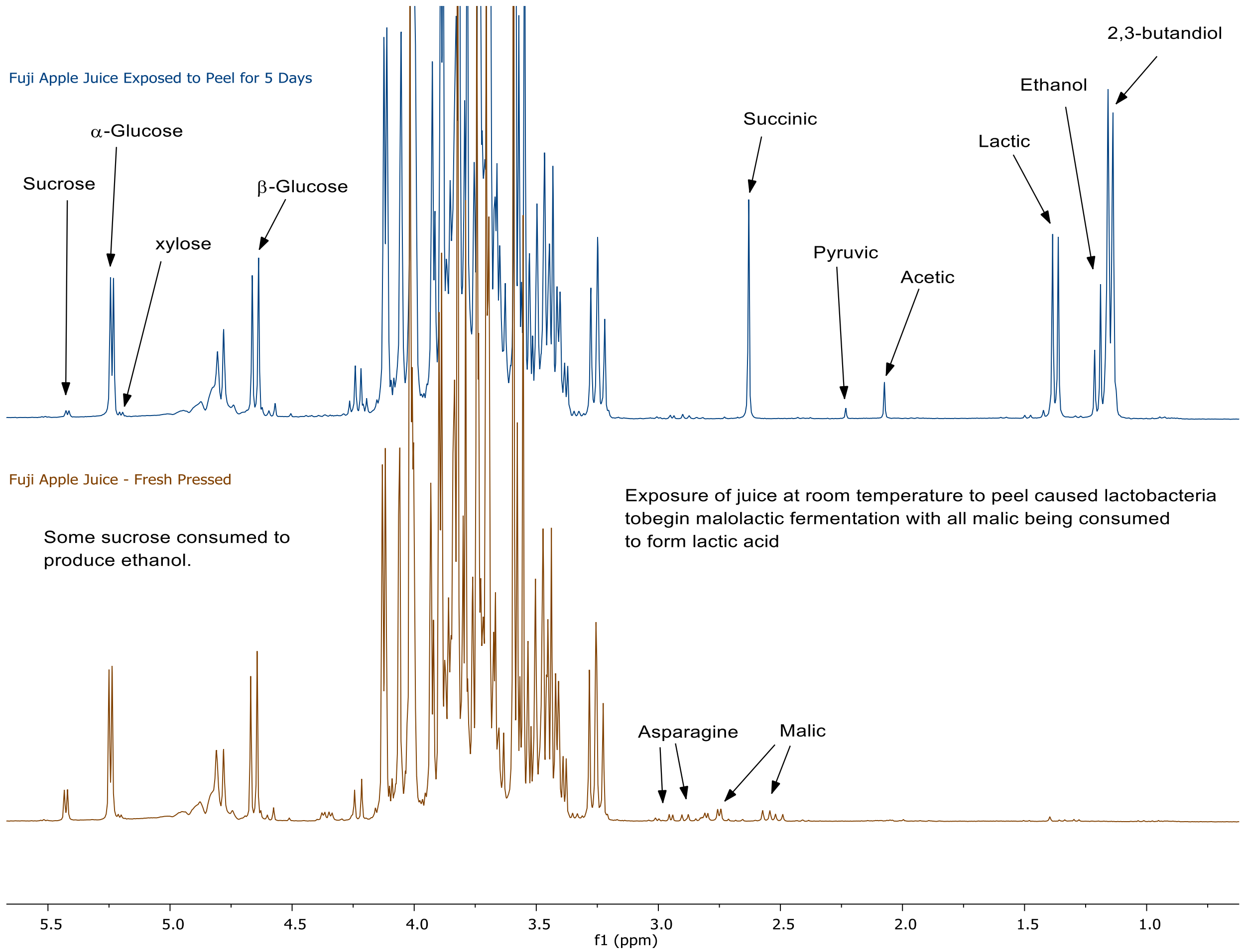
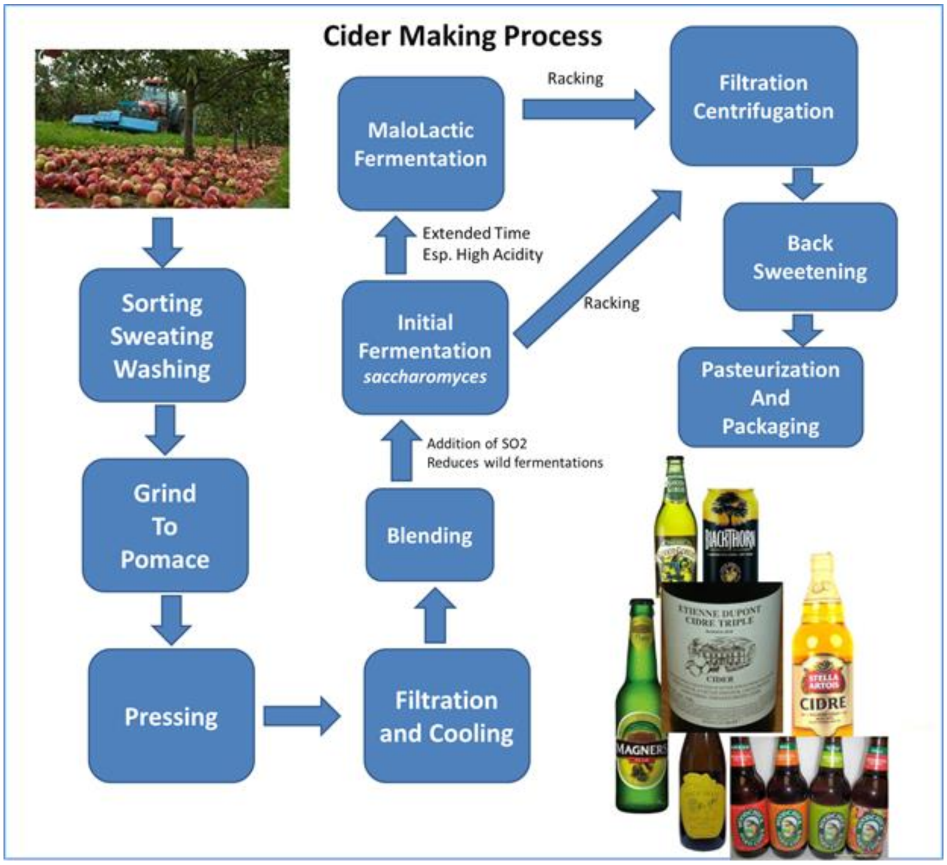


Figure 3: Comparison of the sugar and organic acid/alcohol/amino acid region of the ^{1}H NMR spectrum of fresh pressed Fuji apple juice and the same juice stored at room temperature for 5 days and without filtering of apple peel and cellulose.

Scheme 1 shows a generalized flow diagram of the cider-making process. There are many variations of this process that revolve around 1) the presence of a malolactic step, 2) whether back-sweetening will be performed, 3) whether the sample is pasteurized or the yeast activity curtailed by addition of sorbate, 4) will the cider be matured in wood or bottle conditioned.



Scheme 1: A general outline of the cider making process for production of sweeter ciders. In drier cider production or bottle conditioned ciders the back-sweetening and pasteurization steps may be skipped.

Sample Preparation:

The only sample preparation step to be taken is a de-gassing procedure which we perform by repeated agitation in a vortex mixer. This is obviously not necessary for freshly pressed or stored apple juice.

Original sample analysis – 175µl of cider was added to a 5mm NMR tube followed by 100µl of internal standard solution prepared such that the concentration was 10mg per 100µl. Finally, 475ml of D_2O was added to the sample and the tube capped and agitated for 10 seconds.

Freeze dried samples – 1000µl of cider was placed in a 2 dram vial and freeze dried in a Virtis Benchtop K and the entire dried sample was then dissolved in 650ml of D_2O and 100µl of maleic acid internal standard solution (10mg/100ml) added and the sample agitated before transfer to a 5mm NMR tube.

Standard Material:

Maleic Acid (99.0%) – Aldrich – Lot#SLBC1970V - 10mg/100µl solution in D_2O (99.9%D)

Experimental:

^{1}H NMR experiments were carried out on a Varian Mercury MVX-300 equipped with a 5mm Varian ATB probe operating at a resonance frequency of 299.67 MHz, and on a Varian Mercury 300 equipped with a 5mm Varian 4-Nucleus probe operating at 299.94. Experiments were performed with a p/3 pulse with an

8 kHz spectral width collecting 64k over an 8 second acquisition time and with a 7 second relaxation delay. For original cider samples 128 transients were co-averaged and for freeze dried samples 64 scans were co-averaged. All data was post-processed using Mestrelab MNova software version 10.0.1-14719.

In the final data processing the maleic acid resonance at 6.4 ppm was normalized to 10 so that a direct calculation could be made of all measured components on a mg/L basis

NMR Assignments:

^{1}H NMR yields complex spectra that comprise of the overlapping spectra of individual small molecules found in alcoholic (and non-alcoholic) beverages. Figure 4 shows the ^{1}H NMR spectra of a number of components that are formed during fermentation. Each of the spectra is fully assigned with the protons of the molecule indicated in the spectra by number or letter. Also provided is the number of protons that each NMR peak represents. The peaks are split into various patterns called quartets, triplets, doublets, or multiplets. These splitting patterns are caused by interactions of the nuclear spins on adjacent carbons. They allow assignments to be verified by number of nearest neighbor interactions. Figure 5 shows a stacked series of spectra obtained on individual pure amino acids that are also found in juices and alcoholic beverages. Figure 6 shows the ^{1}H NMR pure spectra of the three main sugar components of ciders, sucrose, glucose and fructose. The integrations that are utilized to quantify the sugar components are indicated in this figure. For fructose it is necessary, in the presence of sucrose, to utilize certain resonances that are not overlapped by glucose or sucrose resonances. These resonances are indicated in the figure as well as the number of protons that the peaks represent in the fructose molecule.

A number of example cider spectra are provided in Figures 6-10 with molecular assignments indicated on the spectrum.

When ^{1}H NMR spectra of cider beverages are analyzed it is the chemical shift position and the splitting pattern that is used to identify a signal from a component molecule. The integrated signal intensity of the peak is utilized to quantify the relative intensity of that peak compared to the intensity of an internal standard peak (in this case 10 mg of maleic acid (singlet peak at 6.4 ppm)). The molar ratios of the unique integrated component signals compared to the maleic acid signal allows a weight to volume concentration to be calculated based on molecular weights, peak areas and the known weight of maleic acid in solution.

Calculations: This study centered on commercial hard ciders taken off the shelf at quality beverage centers. At this point in the study we have not attempted to follow fermentation chemistry or product consistency. Rather we have focused on the finished product and what small organic acid, fusel alcohol, tannin, and residual/back blended sugar chemistry can be readily quantified by a rapid screening NMR analysis.

The following volatile components were always obtained on the fresh cider sample as the freeze drying process would compromise the amount present: ethanol, acetic acid, fusel alcohols (isobutanol, isopentanol (isoamyl alcohol), and 1-propanol). The calculation utilized to quantify these components was:

$$\text{Component mg/L} = 0.99 * 10\text{ mg} * ((I_{comp} / N_{comp}) / 50) * (Mw_{comp} / 116.1) * (1{,}000{,}000 / 175) \qquad \text{Eq. 1}$$

Where, wt of maleic acid = 10mg, I_{comp} = Integration of component resonance, N_{comp} = number of protons integrated, I_{MA}/N_{MA} = 50 (MA integral set as 100), Mw_{comp} = molecular weight of component molecule, MW of Maleic Acid = 116.1 amu, the 1,000,000/175 factor rectifies the volumetric component of the calculation to allow mg/L to be calculated. 0.99 represents the 99% purity of the maleic acid standard.

The following non-volatile components were always obtained on the freeze dried sample: lactic acid, acetic acid, succinic acid, malic acid, citrate, fructose, glucose, sucrose, glycerol, quinic acid. The calculation utilized to quantify these components was:

$$\text{Component mg/L} = 0.99 * 10\text{ mg} * ((I_{comp} / N_{comp}) / 50) * (Mw_{comp} / 116.1) * (1{,}000{,}000 / 1{,}000) \quad \text{Eq. 2}$$

Where, wt of maleic acid = 10 mg, I_{comp} = Integration of component resonance, N_{comp} = number of protons integrated, I_{MA}/N_{MA} = 50 (MA integral set at 100), Mw_{comp} = molecular weight of component molecule, MW of Maleic Acid = 116.1 amu, the 1,000,000/1,000 factor rectifies the volumetric component of the calculation to allow mg/L to be calculated. 0.99 represents the 99% purity of the maleic acid standard.

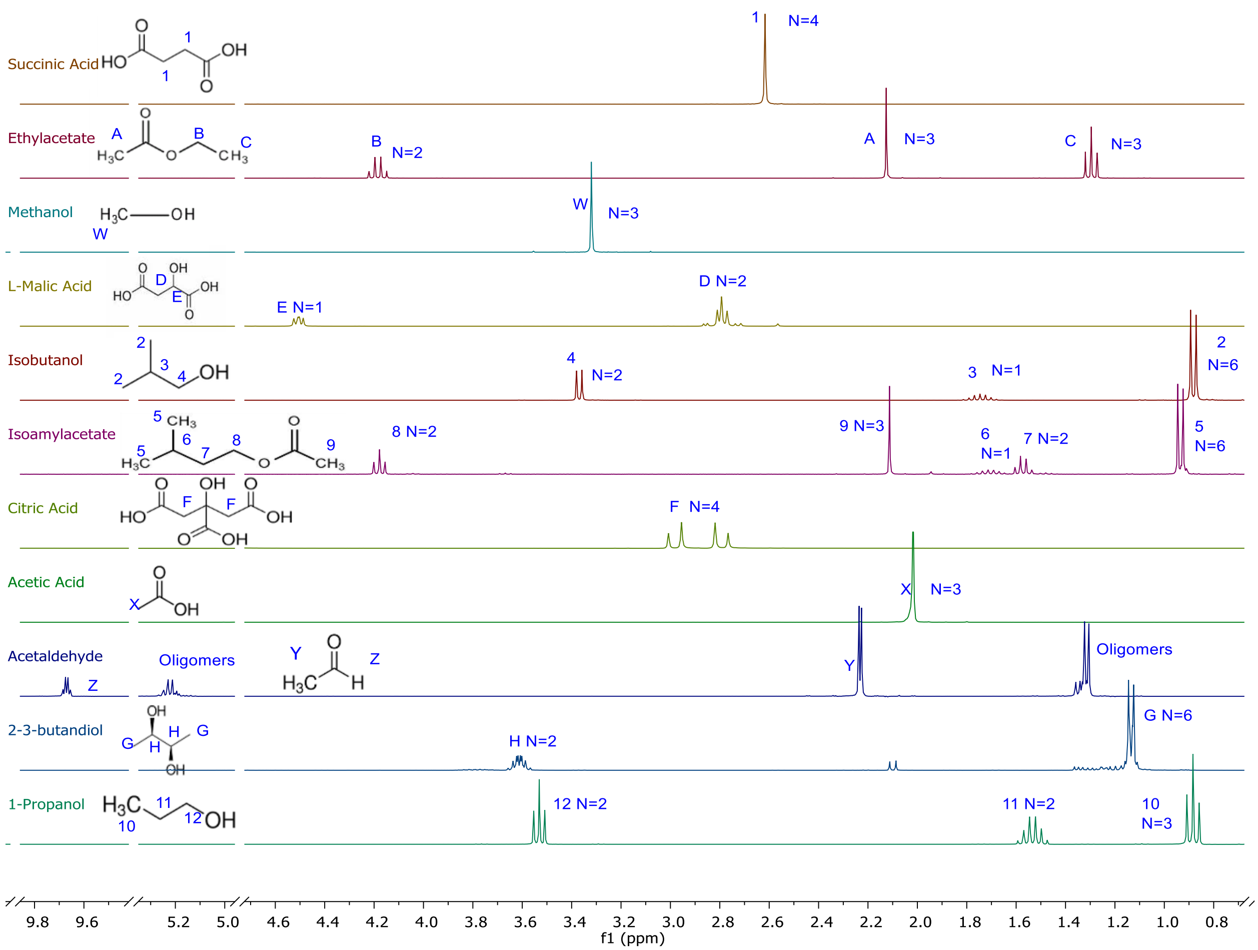


Figure 4: [1]H NMR spectra of individual molecular components found in fruit juices and fermented beverages. Molecular assignments of the various NMR peaks representing proton chemistries present in each molecule are show along with the mole number of protons that each peak represents. These pure component spectra are utilized to identify and quantify the components present in the complex mixture that is the beverage.

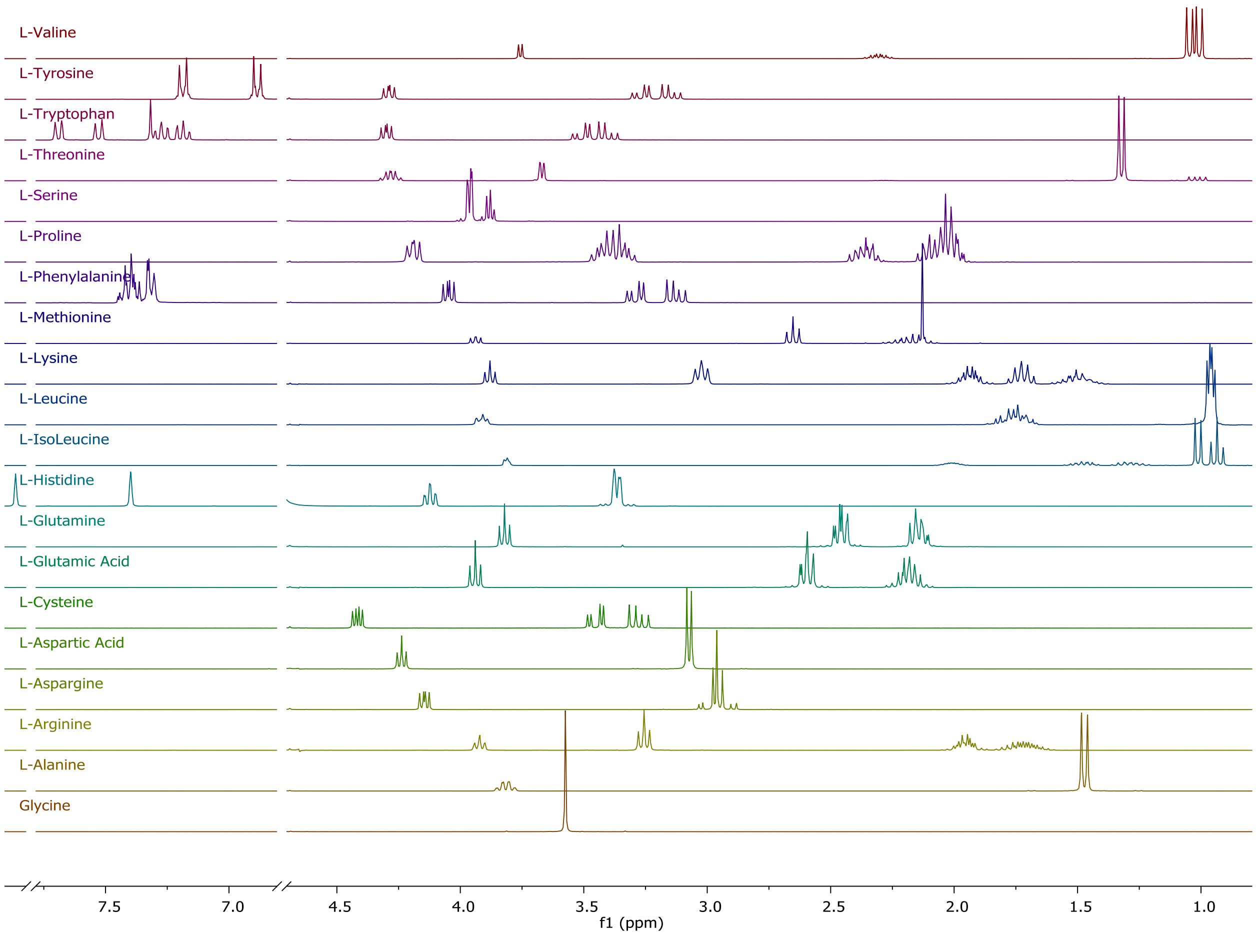


Figure 5: ^{1}H NMR spectra of pure amino acids that can be present in fruit juices and fermented beverages. Amino acids are often consumed by yeast and bacteria and for the basic building blocks for cell reproduction.

Results and Discussion: Figure 6 shows the ^{1}H NMR spectrum of Magners cider a popular Irish cider produced by Bulmers. From this spectrum we have calculated the ethanol, fusel alcohols (isobutanol, isopentanol, 1-propanol), methanol, and acetic acid concentrations. In all cases we have listed the calculated ethanol value from NMR analysis as well as the alcohol content provided by the manufacturer on the label. It is accepted that the label value of non-bottle conditioned ciders will be within 0.5% of the actual value as the alcohol content is typically calculated from the original and final gravity of the juice and cider. Figure 7 shows the same sample after freeze drying. In Figure 7 we show the ^{1}H NMR spectrum of the freeze dried cider which is utilized to quantify all other non-volatile components of the sample – lactic acid, malic acid, succinic acid, citric acid, acetic acid, quinic acid, sucrose, glucose, fructose, glycerol (in dry ciders where the glycerol signals are not obscured by sugar signals), 2,3-butandiol, 1,3-propandiol, sorbate additive, epicatechins, chlorogenic acid, valine, alanine, asparagine, isoleucine, threonine, ethyl acetate, acetaldehyde.

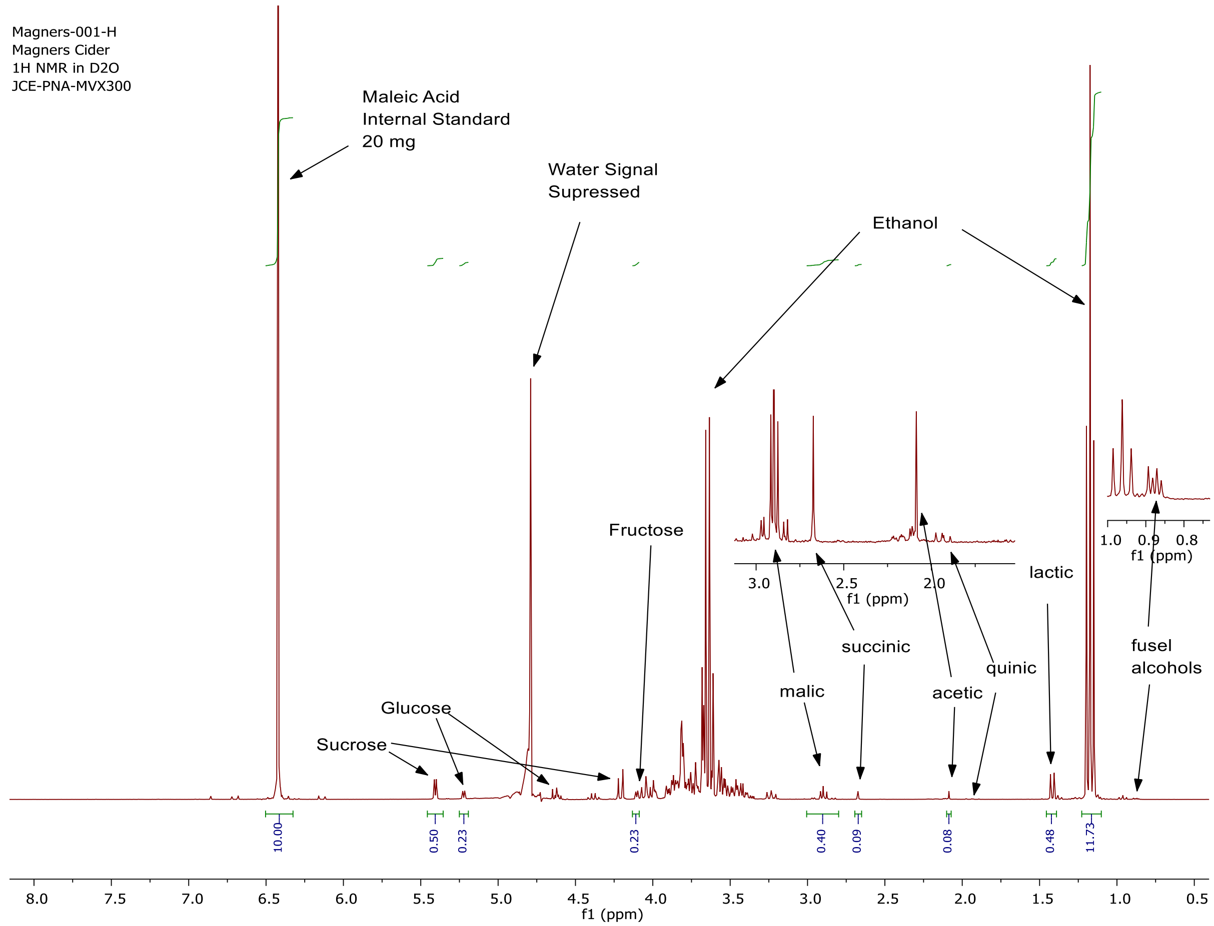


Figure 6: Magners Cider – assignments of the components quantified in the [1]H qNMR analysis – spectrum was obtained with water suppression on a 175ml aliquot of freshly degassed cider. This sample was the excpetion to the rule in the experimental process in that 20 mg of maleic acid was added to the sample. Sucrose, glucose and fructose are observed in the sample and relatively high quinic acid indicating considerable tannin content.

For each of the ciders we have calculated the organic acid concentrations (malic, lactic, citric, acetic, succinic) – see Table II. The distribution of organic acids in the 60 ciders analyzed is summarized in Figure 11. The ethanol concentration was obtained in mg/L, and %ABV – and we have also listed the ethanol content as stated on the label of the cider product bottles – also see Table II. Table III shows the calculated residual sugar distribution (fructose, glucose, sucrose) for all 60 cider samples and the distribution is illustrated in Figure 12.

A further step in the analysis was taken by calculating the calories in the cider products that arise from the residual sugars (4 Cal/g), the ethanol (7 Cal/g), and the organic acids (3 Cal/g). The calculated calorie values are shown in Table IV and summarized in Figure 14. The NMR analysis does not observe proteins due to their high molecular weight and the concentration of fats appears to be below the detection limit of the NMR experiment. Thus, the calorie calculation does not include a contribution from proteins or fats, which would appear to be a negligible contribution. Figure 15 shows a table block chart of the calorie content of a 12 oz serving of each of the 60 commercial ciders that were analyzed.

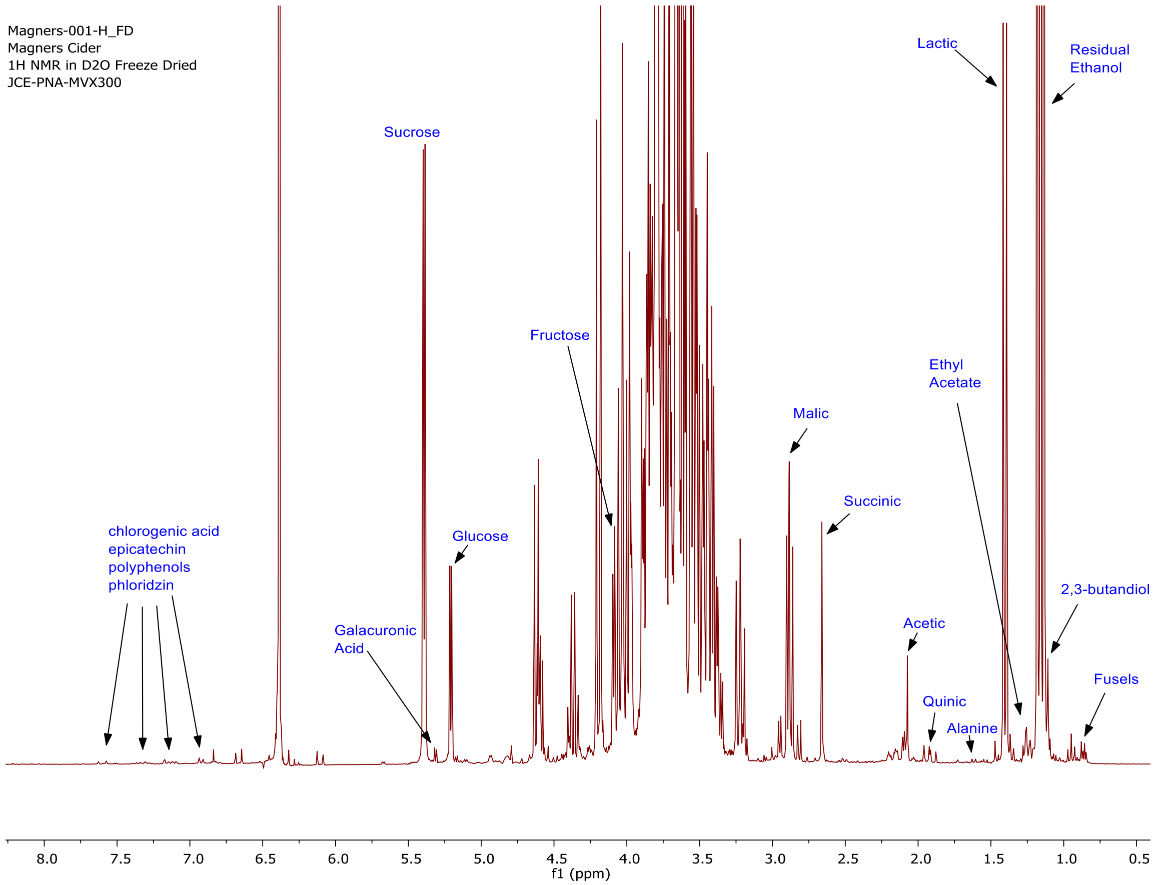


Figure 7: ^{1}H NMR spectrum of freeze dried Magners Cider. Assignments of chemical components included.

In Figure 8 we show another European Cidre manufactured by Stella Artois. This cider does not contain any residual sucrose and has a much lower lactic acid concentration and higher malic than the Magners cider product. Many commercial cider products are fermented to produce ethanol and then the fermentation is arrested by addition of SO_2, sorbate or by filtering the yeast out of the cider. The dry cider that is produced by the fermentation is then sweetened by addition of sugars or fresh apple juice. In many malolactic fermentation is not allowed to proceed. The Stella product seems to be typical of this approach whereas the Magners cider appears to be allowed to begin malolactic fermentation which is then arrested and sweetener added. These draft style ciders are often curtailed at the end of the initial fermentation and are not allowed to develop a malolactic fermentation. Malic acid is still substantially present and little to no lactic acid is observed.

If a non-sweet dry cider is desired the cider is not sweetened at the end of the initial alcohol fermentation stage. This yields a finished cider with little to no observable sugar. A second stage of fermentation (malolactic) can also be initiated when the initial saccharomyces fermentation is near completion or when the cider is racked of it's lees and placed in a secondary fermenter. This malolactic fermentation can occur spontaneously in warm conditions or when the cider is brought into contact with barrels containing lactic acid bacteria (LAB) or will occur when the cider maker innoculates the cider with LAB. The conversion of malic acid to lactic acid in this process is desirable as it mellows the acidity of the cider also contributes tastes (such as clean barnyard aroma) and mouthfeel. In Figure 9 we

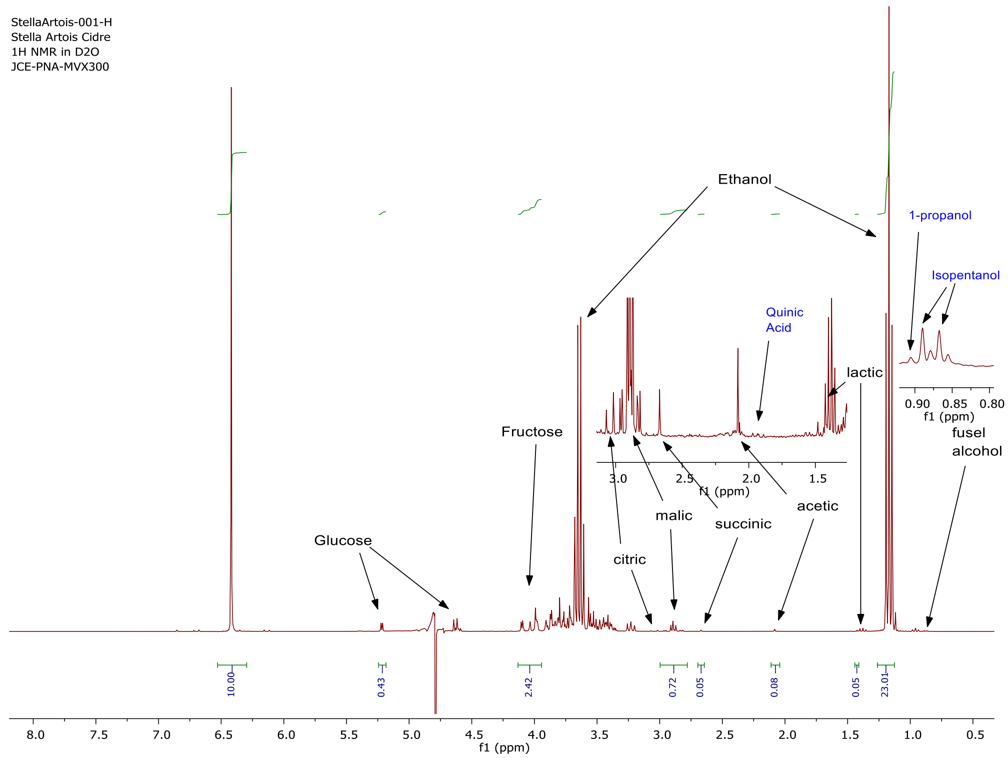


Figure 8: ¹H NMR spectrum of Stella Artois Cidre with assignments of the components quantified.

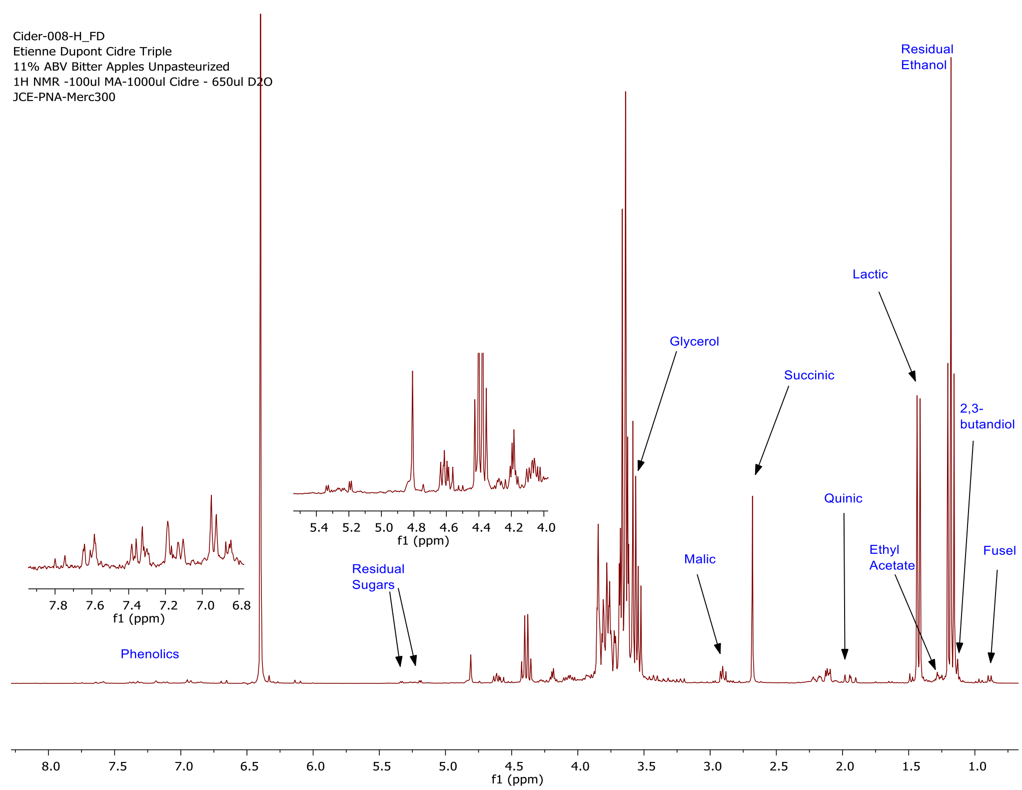


Figure 9: ¹H NMR spectrum of the freeze dried sample of Etienne Dupont Cidre Triple which shows very low residual sugar content as well allowing easy observation and quantitation of glycerol in the sample. Also demonstrates high quinic acid and polyphenol concentrations.

show the spectrum of a dry cider that has fermented to the point that there is very low residual sugar concentration. Malolactic fermentation has occurred leading to a large decrease in the amount of malic acid in the cider which is counterpointed by a rise in lactic acid content. When sugar signals are eliminated from the NMR spectrum it becomes much easier to identify the glycerol resonances that are usually obscured by sugar signals. It is possible to accurately quantify glycerol content in these dry ciders.

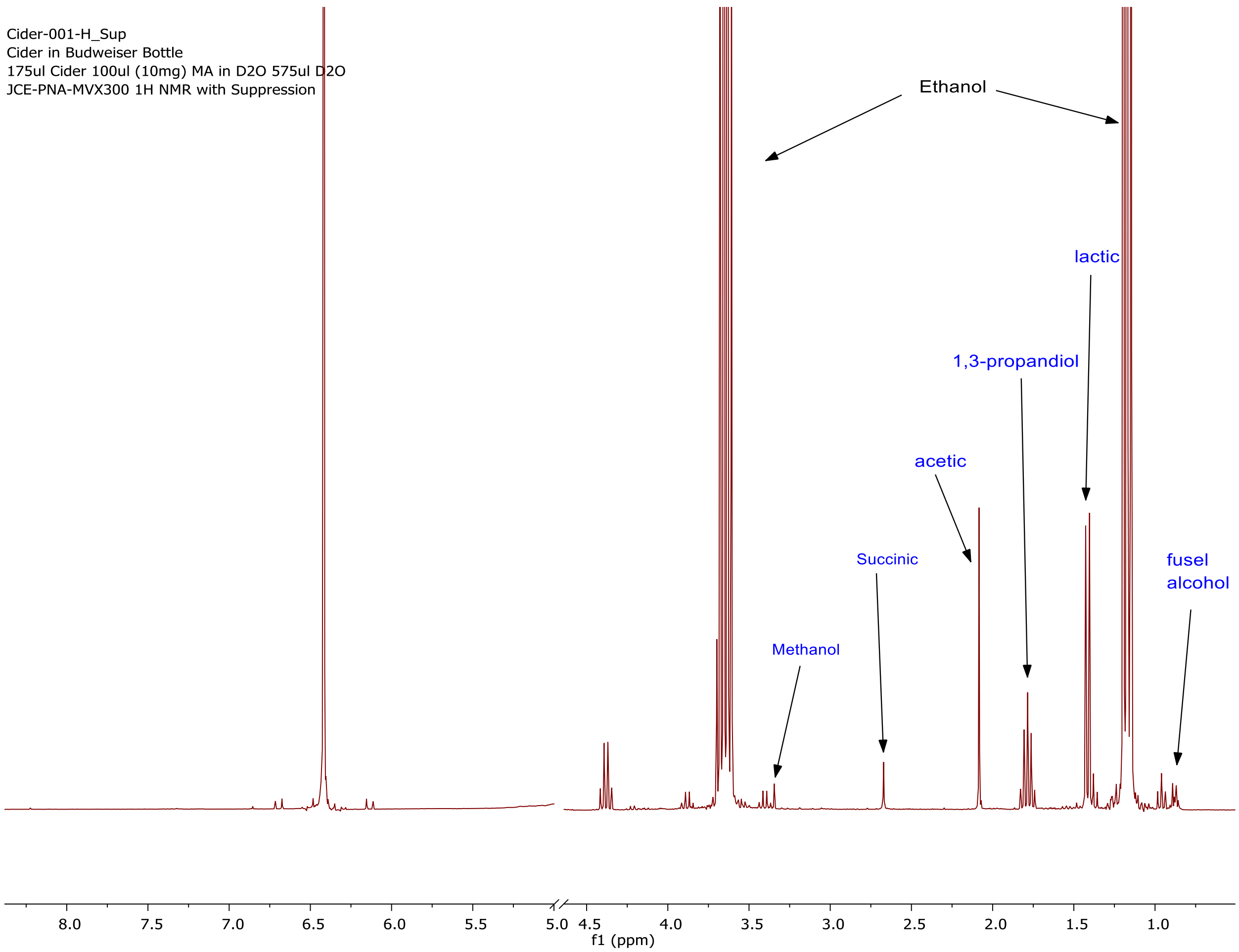


Figure 10: ^{1}H NMR spectrum of a Spanish (Basque Style) cider that is fermented to final dry state where all sugars, malic acid and even some glycerol is consumed by the yeast producing alcohol, lactic acid and 1,3-propandiol, respectively.

In Spain a very dry cider (sidra) is produced based on predominantly wild yeast and the cider is allowed to age in large barrels where it undergoes complete malolactic fermentation. The yeast involved in producing this cider also continue to ferment an extra step when the sugars have been consumed and they begin converting the glycerol produced in the initial fermentation into 1,3-propandiol. This lends a strong astringency to the cider. Figure 10 shows a spectrum of one such cider.

Table II: Organic Acids and Ethanol Content of 60 Commercial Ciders Obtained by ^{1}H qNMR Analysis

Sample	Lactic Acid mg/L	Succinic Acid mg/L	Acetic Acid mg/L	Malic Acid mg/L	Ethanol mg/L	Ethanol % v/v	Label Ethanol %v/v
Homemade Cider #1	5528	494	1716	0	56256	7.1	-
Homemade Cider #2	6770	494	2504	0	64000	8.1	-
Homemade Cider #3	4878	465	730	0	51627	6.5	-
JK Scrumpy Famhouse Cider	2674	706	1274	4013	45766	5.8	6.0
Harpoon Craft Cider	237	378	79	6072	34428	4.4	4.8
Stella Artois Cidre	296	145	158	4752	34806	4.4	4.5
Etienne Dupont Cidre Triple	3156	1123	256	993	84603	10.7	11.0
Etienne Dupont - Cidre Bouche Brut de Normandie	3032	701	434	2310	51702	6.6	5.5
Crispin Hard Apple Cider	1537	319	769	2178	51082	6.5	5.8
Strongbow Gold Apple Cider	714	168	158	3708	42324	5.4	5.0
WoodChuck - Out on a Limb - Spitter Splinter	155	310	99	4158	42430	5.4	5.5
Woodchuck Gumption Hard Cider	124	244	79	5359	43322	5.5	5.5
Woodchuck 802 Hard Cider	135	193	99	3858	36939	4.7	5.0
Woodchuck Amber Cider	186	173	138	4366	37015	4.7	5.0
Thatcher's Green Goblin - Oak Aged English Cider	1314	457	99	1502	49070	6.2	6.6
Magners Pear Cider	72	239	138	393	37605	4.8	4.5
Magners Original Irish Cider	916	279	148	1947	35133	4.5	4.5
Doc's Draft Cider	3047	442	177	2368	40267	5.1	5.0
Blackthorn English Cider	445	320	256	3916	48738	6.2	6.0
ACE California Apple Cider	103	264	256	9876	41522	5.3	5.0
Docs Draft Gold Rush Hard Cider	512	783	256	6618	59478	7.5	7.2
Sarasola Original Basque Cider	4795	479	2240	0	50462	6.4	6.0
Pitchfork Cider	4976	546	905	59	57316	7.3	6.9
Cidre Breton Traditionnel	2179	322	371	1505	34378	4.4	4.5
Hudson Valley Farmhouse Cider Bourbon Barrel	3707	801	1071	528	72698	9.2	6.8
Maeves Hudson Valley Cider	5446	781	1055	1300	56833	7.2	6.5
NinePin CiderWorks Belgian Hard Cider	715	409	95	3432	57301	7.3	6.3
NinePin CiderWorks NY Hard Cider	142	598	146	5729	52025	6.6	6.7
IronWood Hard Cider	509	322	93	4145	47351	6.0	6.0
Samuel Smiths Organic Cider	928	267	156	3789	41649	5.3	5.0
Bad Seed Hard Cider	101	305	205	5967	61017	7.7	6.9
Bad Seed - Bourbon Barrel Reserve	266	662	124	6462	69096	8.8	6.5
Bad Seed Farmer Saison	95	462	213	5392	65092	8.2	6.9
DownEast Original Cider - Batch X	101	343	57	4633	50647	6.4	5.1
DownEast Original Cider - Batch Y	2643	325	327	1914	52070	6.6	5.1
DownEast Honey Cider	1857	421	81	99	29258	3.7	5.1
DownEast Cranberry Cider	30	206	65	3657	24969	3.2	5.1
Awestruck Eastern Dry Cider	77	613	183	3914	60706	7.7	6.8
Awestruck Cider - Pink	1209	662	264	3399	55617	7.0	6.8
Naked Flock - Lemon and Ginger	136	378	256	2515	41795	5.3	6.8
Naked Flock Hard Cider	1247	610	335	6907	59538	7.5	6.8
Citizen Cider - Dirty Mayor	95	534	177	5036	47957	6.1	6.9
Citizen Cider - The Full Nelson	532	520	134	4686	50868	6.4	6.9
Citizen Cider - Unified Press	171	514	65	5254	53298	6.8	6.8
Homemade - Baldwin Crisp Green RI	3426	865	424	640	57995	7.4	-
Angry Orchard - Straw Man	154	944	440	7768	86996	11.0	10.0
Angry Orchard - Stone Dry	118	409	128	2990	42194	5.3	5.5
Angry Orchard - Ginger Crisp	118	468	150	4917	39860	5.1	5.0
Angry Orchard Traditional Dry Cider	124	457	217	5198	43912	5.6	5.5
Angry Orchard Summer Honey	124	517	30	3366	42130	5.3	5.0
Angry Orchard Crisp Apple	101	424	146	4851	40771	5.2	5.0
Angry Orchard Green Apple	106	560	45	4442	43381	5.5	5.0
E.Z. Orchards - Roman Beauty	3329	738	584	172	36090	4.6	4.2
E.Z. Orchards - Hawkhaus	4916	700	223	627	53909	6.8	6.6
E.Z. Orchards - Poire	3163	604	375	733	47289	6.0	5.9
1911 Cider - Original	101	317	140	7993	51029	6.5	5.5

Table III: Residual Sugar, Glycerol, Fusel Alcohol, Sorbate, 1,3-Propandiol, and Quinic Acid Concentrations obtained by ^{1}H qNMR Analysis

Sample	Sucrose mg/L	Glucose mg/L	Fructose mg/L	1,3-Propandiol mg/L	Glycerol mg/L	Quinic Acid mg/L	Chlorogenic Acid mg/L	Isobutanol mg/L	Isopentanol mg/L	Sorbate mg/L	Citrate mg/L
Homemade Cider #1	0	0	0	3895	0	0	0	97	231	0	0
Homemade Cider #2	0	0	0	3671	0	0	0	68	145	0	0
Homemade Cider #3	0	6302	8175	0	4646	497	580	49	231	0	0
JK Scrumpy Famhouse Cider	403	10876	52790	0	NC	0	0	55	132	0	0
Harpoon Craft Cider	0	2514	24676	0	5892	348	397	61	116	0	0
Stella Artois Cidre	0	22883	21251	0	NC	314	275	24	58	0	0
Etienne Dupont Cidre Triple	295	745	0	0	6799	828	1343	73	174	0	0
Etienne Dupont - Cidre Bouche Brut de Normandie	0	652	15782	0	6176	563	809	49	116	0	0
Crispin Hard Apple Cider	2181	20754	2566	0	NC	0	0	49	116	0	0
Strongbow Gold Apple Cider	1002	51965	31303	0	4646	265	336	24	58	0	0
WoodChuck - Out on a Limb - Spitter Splinter	15975	10337	14877	0	7649	215	610	49	231	0	0
Woodchuck Gumption Hard Cider	35428	8847	15755	0	NC	397	549	49	87	0	0
Woodchuck 802 Hard Cider	1710	31197	23189	0	NC	99	183	24	29	0	0
Woodchuck Amber Cider	1710	48053	33209	0	NC	149	214	24	58	0	0
Thatcher's Green Goblin - Oak Aged English Cider	0	25982	14799	0	NC	281	549	49	116	0	0
Magners Pear Cider	0	29987	28445	0	NC	166	168	24	87	147	2896
Magners Original Irish Cider	16876	9206	7263	0	NC	151	253	27	52	0	0
Doc's Draft Cider	531	12572	24911	0	NC	298	214	49	145	221	0
Blackthorn English Cider	5659	18346	10803	0	NC	298	519	24	87	0	0
ACE California Apple Cider	0	13783	22698	0	NC	348	488	24	58	147	0
Docs Draft Gold Rush Hard Cider	0	838	937	0	4816	248	244	73	202	331	0
Sarasola Original Basque Cider	0	0	0	2465	312	0	0	41	62	0	0
Pitchfork Cider	0	373	0	0	NC	274	244	50	123	0	0
Cidre Breton Traditionnel	539	6971	31516	0	NC	520	419	16	32	0	0
Hudson Valley Farmhouse Cider Bourbon Barrel	0	745	0	0	NC	331	340	44	104	0	0
Maeves Hudson Valley Cider	505	6705	11504	0	1212	0	0	26	72	0	0
NinePin CiderWorks Belgian Hard Cider	0	10004	21576	0	1280	208	279	22	94	121	0
NinePin CiderWorks NY Hard Cider	0	9685	21286	0	997	189	253	35	98	114	0
IronWood Hard Cider	741	10324	20715	0	NC	95	113	17	48	74	0
Samuel Smiths Organic Cider	15664	6865	6393	0	NC	407	785	24	46	0	0
Bad Seed Hard Cider	0	0	0	0	907	199	122	17	56	0	0
Bad Seed - Bourbon Barrel Reserve	0	0	0	0	1207	369	410	68	174	0	0
Bad Seed Farmer Saison	0	905	0	0	1190	189	253	35	98	114	0
DownEast Original Cider - Batch X	1280	16231	41273	0	NC	293	384	51	202	136	0
DownEast Original Cider - Batch Y	4413	19264	41434	0	0	208	209	44	171	269	0
DownEast Honey Cider	0	18093	19547	0	NC	132	61	61	133	224	0
DownEast Cranberry Cider	0	17508	30990	0	NC	643	872	22	78	221	1201
Awestruck Eastern Dry Cider	6670	9526	8635	0	1127	218	340	54	174	0	0
Awestruck Cider - Pink	0	48107	39385	0	NC	615	610	68	188	0	0
Naked Flock - Lemon and Ginger	0	24053	20777	0	NC	454	227	36	93	210	889
Naked Flock Hard Cider	413	18160	30212	0	NC	166	168	24	58	147	0
Citizen Cider - Dirty Mayor	0	13091	27082	0	NC	416	183	46	150	158	747
Citizen Cider - The Full Nelson	0	4310	9370	0	810	246	270	46	148	136	0
Citizen Cider - Unified Press	0	9206	19784	0	1116	568	288	75	148	0	0
Homemade - Baldwin Crisp Green RI	842	2182	3983	0	1059	331	793	66	174	0	0
Angry Orchard - Straw Man	0	6120	9739	0	1439	492	854	100	272	0	0
Angry Orchard - Stone Dry	5726	4630	5690	0	799	189	384	51	81	0	0
Angry Orchard - Ginger Crisp	19268	18838	13856	0	NC	463	497	54	133	0	0
Angry Orchard Traditional Dry Cider	26173	10710	9254	0	NC	314	320	49	145	0	0
Angry Orchard Summer Honey	29374	9579	10041	0	NC	85	305	27	81	0	0
Angry Orchard Crisp Apple	36077	10004	9639	0	NC	293	305	27	74	0	0
Angry Orchard Green Apple	43521	9419	9405	0	NC	199	244	29	81	0	0
E.Z. Orchards - Roman Beauty	0	2022	22577	0	1082	445	497	39	93	0	0
E.Z. Orchards - Hawkhaus	0	0	0	0	941	397	436	49	124	0	0
E.Z. Orchards - Poire	0	1969	0	0	958	161	166	56	130	0	0
1911 Cider - Original	0	8035	18502	0	NC	331	331	41	130	258	0

Table IV: Calorie Values for 60 Commercial Ciders Broken Down Between Carbohydrates (4 Cal/g), Ethanol (7 Cal/g), Glycerol (4 Cal/g), and Organic Acids (3 Cal/g)

	Carbs	Ethanol	Organic Acids	Glycerol	Total Cal			
Sample	Cal/L	Cal/L	Cal/L	Cal/L	Cal/L	Cal/12oz	Cal/16Oz	Cal/ ImpPint
Homemade Cider #1	0	394	23	0	417	151	201	241
Homemade Cider #2	0	448	29	0	477	173	230	276
Homemade Cider #3	58	361	18	19	456	165	220	264
JK Scrumpy Famhouse Cider	256	320	26	NC	603	218	291	349
Harpoon Craft Cider	109	241	20	24	394	142	190	228
Stella Artois Cidre	177	244	16	NC	436	158	210	253
Etienne Dupont Cidre Triple	4	592	17	27	640	231	309	371
Etienne Dupont - Cidre Bouche Brut de Normandie	66	362	19	25	472	171	227	273
Crispin Hard Apple Cider	102	358	14	NC	474	171	229	274
Strongbow Gold Apple Cider	337	296	14	19	666	241	321	386
WoodChuck - Out on a Limb - Spitter Splinter	165	297	14	31	507	183	244	293
Woodchuck Gumption Hard Cider	240	303	17	NC	561	203	270	325
Woodchuck 802 Hard Cider	224	259	13	NC	496	179	239	287
Woodchuck Amber Cider	332	259	15	NC	606	219	292	351
Thatcher's Green Goblin - Oak Aged English Cider	163	343	10	NC	517	187	249	299
Magners Pear Cider	234	263	3	NC	499	181	241	289
Magners Original Irish Cider	133	246	10	NC	389	141	188	225
Doc's Draft Cider	152	282	18	NC	452	163	218	262
Blackthorn English Cider	139	341	15	NC	495	179	239	287
ACE California Apple Cider	146	291	31	NC	468	169	226	271
Docs Draft Gold Rush Hard Cider	7	416	25	19	467	169	225	271
Sarasola Original Basque Cider	0	353	23	1	377	136	182	218
Pitchfork Cider	1	401	19	NC	422	153	204	244
Cidre Breton Traditionnel	156	241	13	NC	410	148	198	237
Hudson Valley Farmhouse Cider Bourbon Barrel	3	509	18	NC	530	192	256	307
Maeves Hudson Valley Cider	75	398	26	5	503	182	243	291
NinePin CiderWorks Belgian Hard Cider	126	401	14	5	547	198	264	316
NinePin CiderWorks NY Hard Cider	124	364	20	4	512	185	247	296
IronWood Hard Cider	127	331	15	NC	474	171	228	274
Samuel Smiths Organic Cider	116	292	15	NC	423	153	204	245
Bad Seed Hard Cider	0	427	20	4	450	163	217	261
Bad Seed - Bourbon Barrel Reserve	0	484	23	5	511	185	246	296
Bad Seed Farmer Saison	4	456	18	5	483	174	233	279
DownEast Original Cider - Batch X	235	355	15	NC	605	219	292	350
DownEast Original Cider - Batch Y	260	364	16	0	641	232	309	371
DownEast Honey Cider	151	205	7	NC	363	131	175	210
DownEast Cranberry Cider	194	175	12	NC	381	138	184	220
Awestruck Eastern Dry Cider	99	425	14	5	543	196	262	315
Awestruck Cider - Pink	350	389	17	NC	756	273	364	438
Naked Flock - Lemon and Ginger	179	293	10	NC	482	174	232	279
Naked Flock Hard Cider	195	417	27	NC	639	231	308	370
Citizen Cider - Dirty Mayor	161	336	18	NC	514	186	248	298
Citizen Cider - The Full Nelson	55	356	18	3	432	156	208	250
Citizen Cider - Unified Press	116	373	18	4	512	185	247	296
Homemade - Baldwin Crisp Green RI	28	406	16	4	454	164	219	263
Angry Orchard - Straw Man	63	609	28	6	706	255	340	409
Angry Orchard - Stone Dry	64	295	11	3	374	135	180	216
Angry Orchard - Ginger Crisp	208	279	17	NC	504	182	243	292
Angry Orchard Traditional Dry Cider	185	307	18	NC	510	184	246	295
Angry Orchard Summer Honey	196	295	12	NC	503	182	243	291
Angry Orchard Crisp Apple	223	285	17	NC	525	190	253	304
Angry Orchard Green Apple	249	304	15	NC	569	206	274	329
E.Z. Orchards - Roman Beauty	98	253	14	4	370	134	178	214
E.Z. Orchards - Hawkhaus	0	377	19	4	401	145	193	232
E.Z. Orchards - Poire	8	331	15	4	357	129	172	207
1911 Cider - Original	106	357	26	NC	489	177	236	283

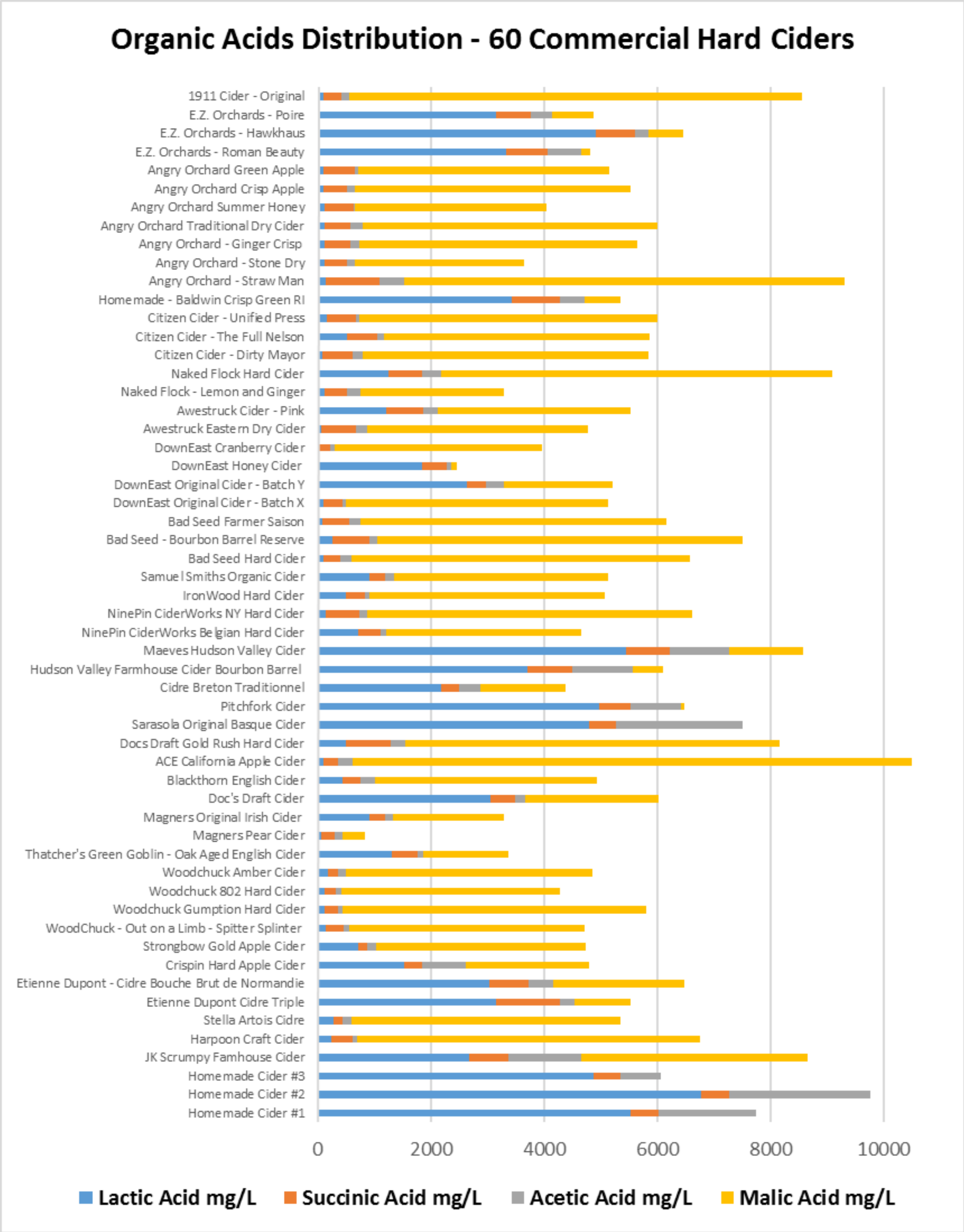


Figure 11: [1]H NMR Derived Distribution of Organic Acids in 60 Commercial Hard Ciders

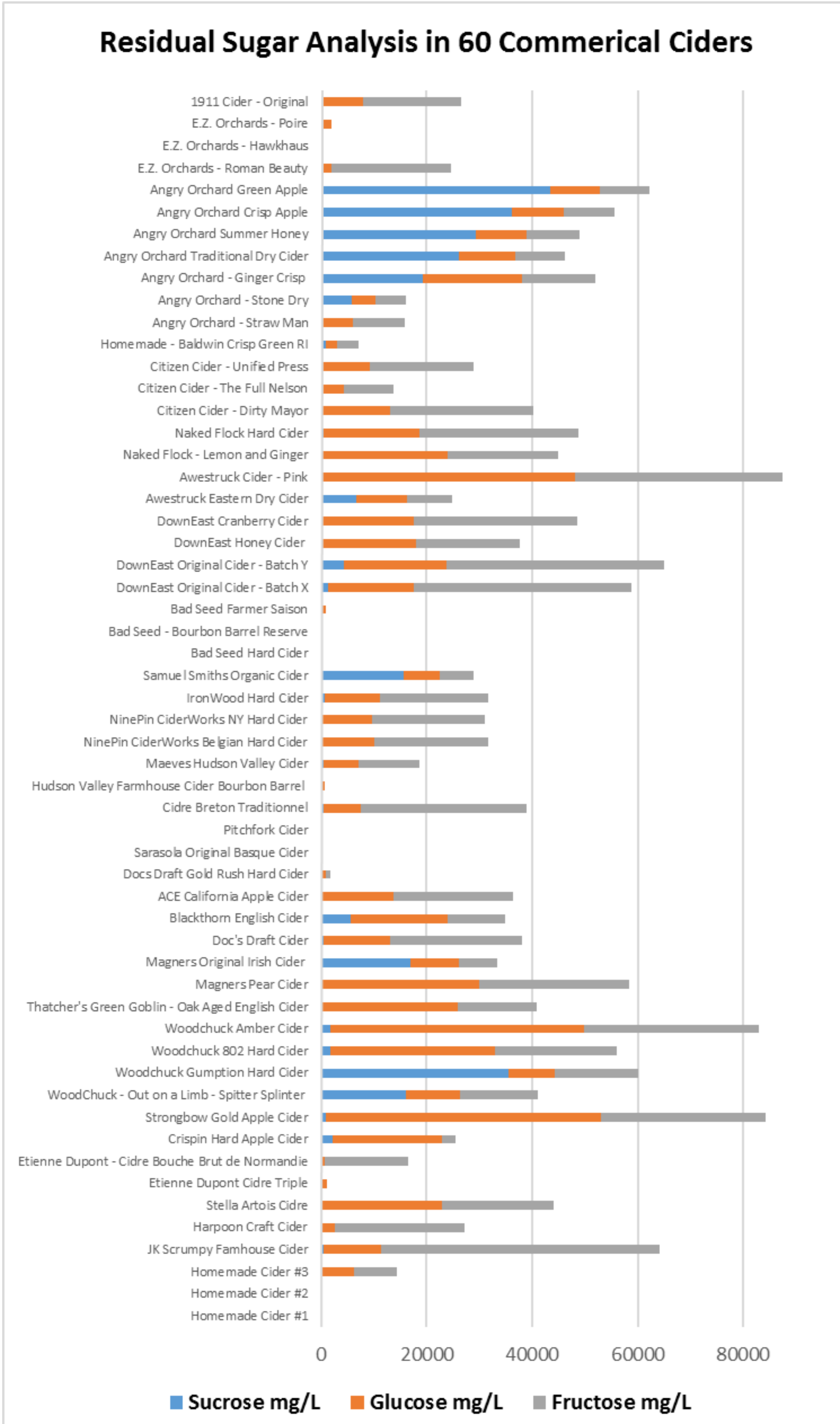


Figure 12: [1]H NMR Derived Distribution of Residual Sugars found in 60 Commercial Hard Ciders

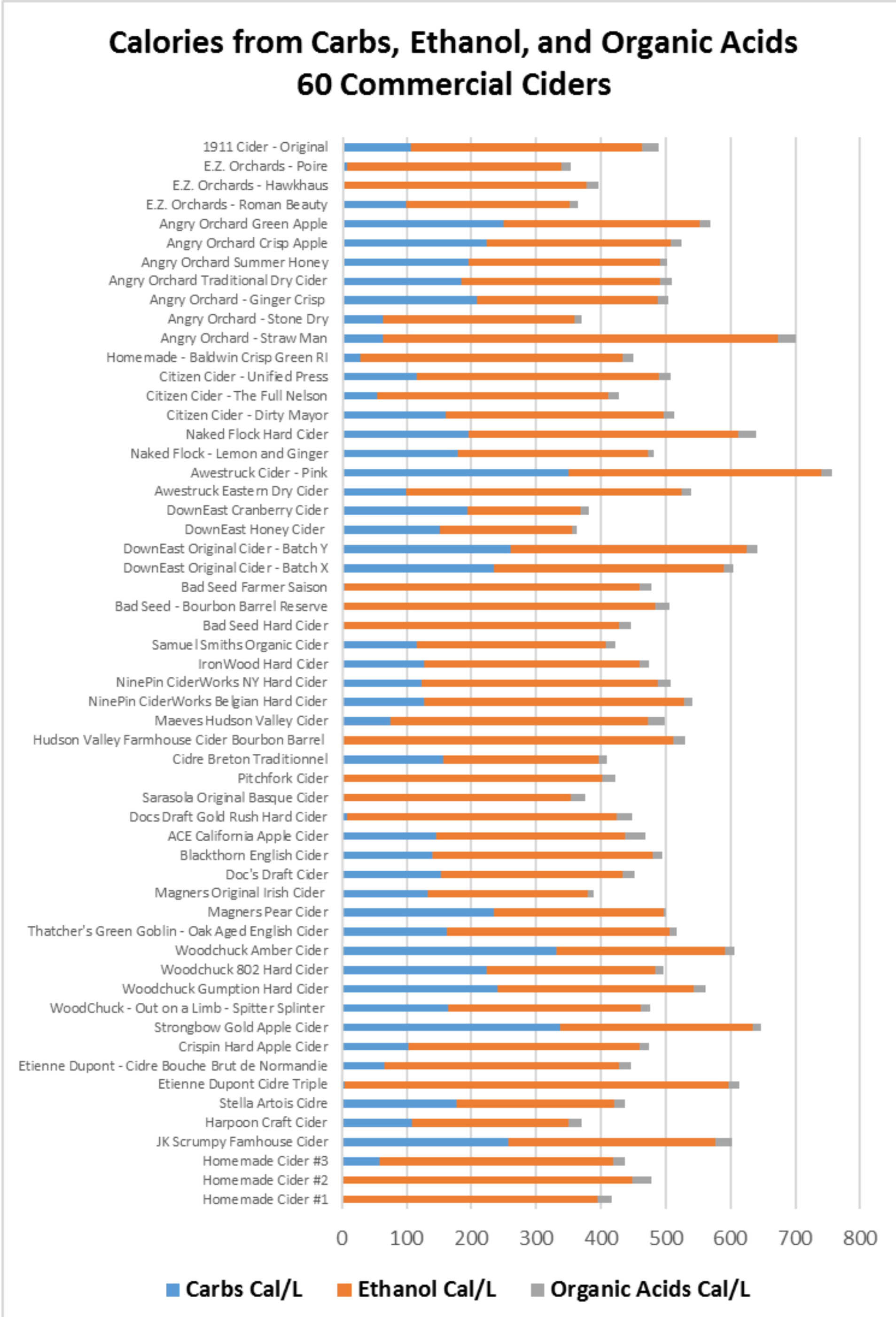


Figure 13: [1]H NMR Derived Calories Due to Residual Carbohydrates, Ethanol, and Organic Acids for 60 Commercial Hard Ciders

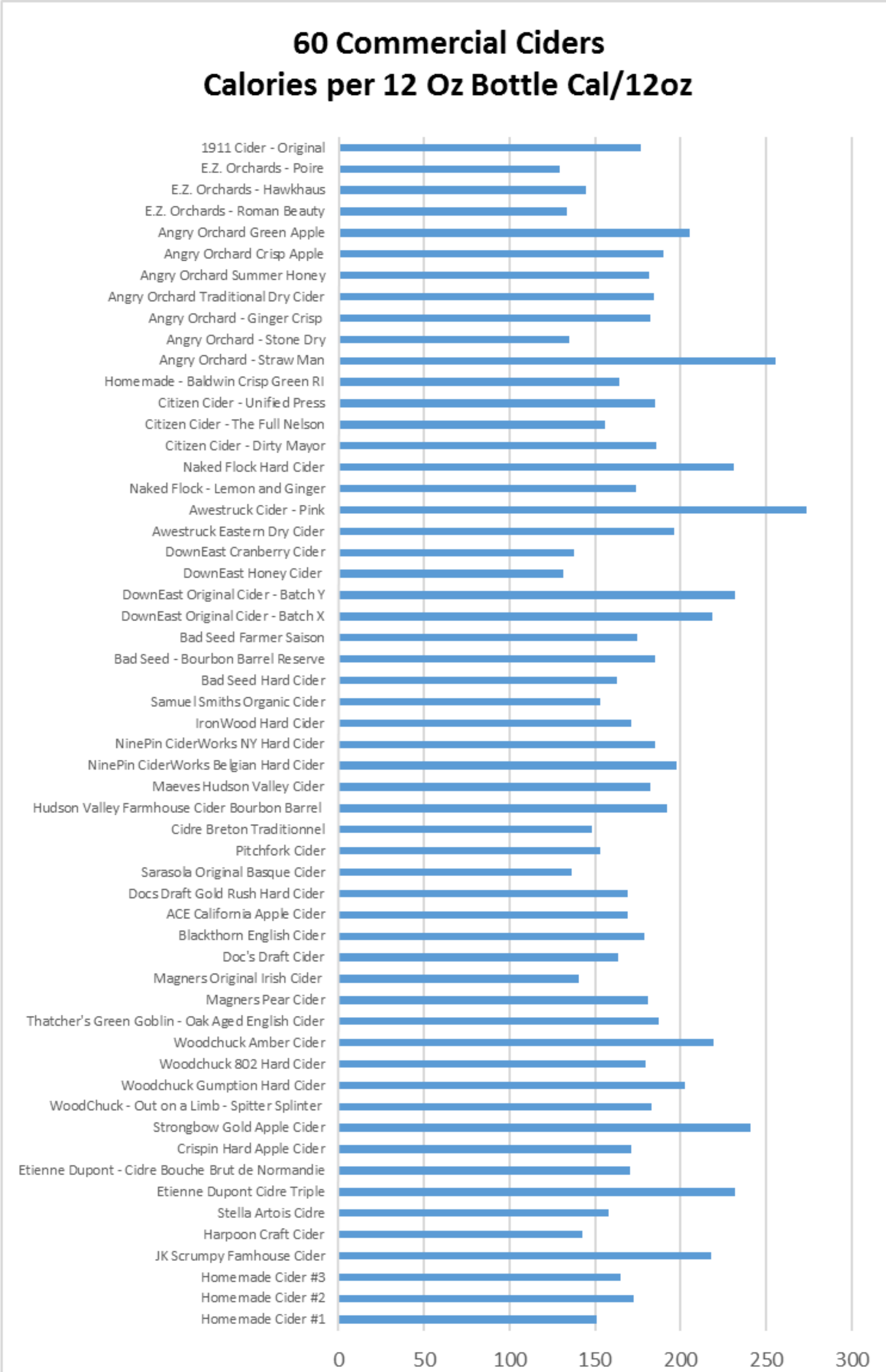


Figure 14: ^{1}H NMR derived calorie values for 12 ounce servings of 60 Commercial Ciders

Conclusion: ^{1}H NMR analysis can reveal very detailed chemical fingerprint information on apple juices and alcoholic ciders and can allow a critical understanding of the fermentation processes involved in producing artisanal ciders. For more information on how these analyses may improve your cider production processes from the orchard to the bottle contact John Edwards at Process NMR Associates for your analysis needs.

Relevant NMR References:

qNMR

"Validation of quantitative NMR", F Malz, H Jancke, J Pharm Biomed Anal, 38, 813–823, (2005)

"Quantitative ^{1}H NMR spectroscopy", S K Bharti, R Roy, Trends in Anal Chem, 35, 5-26 (2012)

"NMR-based plant metabolomics: where do we stand, where do we go?" H-K Kim, Y-H Choi, R Verpoorte Trends Biotech, 29(6), 267 (2011).

"Universal quantitative NMR analysis of complex natural samples", C Simmler, J G Napolitano, J B McAlpine, S-N Chen and G F Pauli, Current Opinion Biotech, 25, 51–59 (2014)

"Quantitative ^{1}H NMR: Development and Potential of a Method for Natural Products Analysis" G F Pauli, B U Jaki, D C Lankin, J. Nat. Prod., 68, 133-149 (2005)

Juices

"High-Field Proton NMR Studies of Apple Juices", P S Belton, I Delgadillo, A M Gil, P Roma, F Casuscelli, I J Colquhoun, M J Dennis M Spraul, Mag Res Chem, 35, S52-S60 (1997)

"Quantitative determination of (-)-epicatechin in cider apple juices by ^{1}H NMR", I Berregi , J I Santos , G del Campo , J I Miranda, Talanta 61 (2003) 139-145

"Use of the ^{1}H Nuclear Magnetic Resonance Spectra Signals from Polyphenols and Acids for Chemometric Characterization of Cider Apple Juices", G del Campo, J. I Santos, N Iturriza, I Berregi, A Munduate, J Agric Food Chem, 54, 3095−3100 (2006)

"Untargeted NMR-Based Methodology in the Study of Fruit Metabolites", A P Sobolev, L Mannina, N Proietti, S Carradori, M Daglia, A M Giusti, R Antiochia and D Capitani, Molecules, 20, 4088-4108 (2015)

"Quantitative determination of formic acid in apple juices by ^{1}H NMR spectrometry", I Berregi, G del Campo, R Caracena, J I Miranda, Talanta, 72, 1049–1053 (2007)

"Tracking the degradation of fresh orange juice and discrimination of orange varieties: An example of NMR in coordination with chemometrics analyses", C R de Oliveira, R L Carneiro, A G Ferreira, Food Chem, 164, 446–453 (2014)

"Quantitation determination of chlorogenic acid in cider apple juices by ^{1}H NMR spectrometry", I Berregi, J I Santos, G del Campo, J I Miranda, J M Aizpurua, Anal Chim Acta, 486, 269–274 (2003)

"NMR-based multi parametric quality control of fruit juices: SGF profiling", M Spraul, B Schuetz, P Rinke, S Koswig, E Humpfer, H Schaefer, Nutrients, 1, 148 (2009)

"Evolving window zone selection method followed by independent component analysis as useful chemometric tools to discriminate between grapefruit juice, orange juice and blends", M Cuny, G Le Gall, I J Colquhoun, M Lees, D N Rutledge, Anal Chim Acta, 597, 203 (2007)

"Fast NMR juice identification based on sugars and other plant metabolites from fruits", M Balan, A Nicolescu, C Deleanu, C Stavarache, M Ciobanu, Rev Roum Chim, 58(2-3), 175-182 (2013)

Cider

"Cider, hard and sweet: history, traditions, and making your own", Ben Watson, 2nd ed, Countryman Press, 2009

"Cider making, using & enjoying sweet and hard cider", Annie Proulx & Lew Nichols, 3rd Ed, Storey Publishing, 2003

"The new cider maker's handbook: a comprehensive guide for craft producers", Claude Jolicoeur, Chelsea Green Publishing, 2013

"Quantitative analysis of malic and citric acids in fruit juices using proton nuclear magnetic resonance spectroscopy", G del Campo, I Berregi, R Caracena, J I Santos, Anal Chim Acta, 556, 462–468 (2006)

"Quantitative determination of lactic and acetic acids in cider by ^{1}H NMR spectrometry", A Zuriarrain, J Zuriarrain, A I Puertas, M T Dueñas, I Berregi, Food Control, 52, 49–53 (2015)

"Glycerol metabolism in Lactobacillus collinoides: production of 3-hydroxypropionaldehyde, a precursor of acrolein", Nicolas Sauvageot , Kamila Gouffi, Jean-Marie Laplace, Yanick Auffray, Int J Food Microbiol 55, 167–170, (2000)

"Glycerol metabolism and bitterness producing lactic acid bacteria in cidermaking", G Garai-Ibabe, I Ibarburu , I Berregi , O Claisse , A Lonvaud-Funel , A Irastorza , MT Dueñas, Int J Food Microbiol, 121, 253–261, (2008)

"Quantitative determination of ethanol in cider by ^{1}H NMR spectrometry", A Zuriarrain, J Zuriarrain , M Villar ,I Berregi, Food Control, 50, 758-762, (2015)

Wine

"Application of One- and Two-Dimensional NMR Spectroscopy for the Characterization of Protected Designation of Origin Lambrusco Wines of Modena", G Papotti, D Bertelli, R Graziosi, M Silvestri, L Bertacchini, C Durante, and M Plessi, J Agric Food Chem, 61, 1741-1746 (2013)

"NMR metabolite fingerprinting in grape derived products: An overview", C Fotakis, K Kokkotou, P Zoumpoulakis, M Zervou, Food Res Int, 54, 1184–1194 (2013)

"NMR spectroscopy evaluation of direct relationship between soils and molecular composition of red wines from Aglianico grapes", P Mazzei, N Francesca, G Moschetti , A Piccolo, Analytica Chimica Acta 673 (2010) 167–172

"NMR investigation of acrolein stability in hydroalcoholic solution as a foundation for the valid HS-SPME/GC–MS quantification of the unsaturated aldehyde in beverages", M Kächele, Y B Monakhova, T Kuballa, D W Lachenmeier, Anal Chim Acta, 820, 112–118 (2014)

"Wine science in the metabolomics era", M E Alañón, M S Pérez-Coello, M L Marina, Trends Anal Chem, 74, 1–20 (2015)

"Amino acid uptake by wild and commercial yeasts in single fermentations and co-fermentations", N Barrajón-Simancas, E Giese, M Arévalo-Villena, J Úbeda , A Briones, Food Chem, 127, 441–446 (2011)

"Chemical Profile of White Wines Produced from 'Greco bianco' Grape Variety in Different Italian Areas by Nuclear Magnetic Resonance (NMR) and Conventional Physicochemical Analyses", M Caruso, F Galgano, M A C Morelli, L Viggiani, L Lencioni, B Giussani, F Favati, J Agric Food Chem, 60, 7-15 (2012)

"Metabolomic by ^{1}H NMR Spectroscopy Differentiates "Fiano Di Avellino" White Wines Obtained with Different Yeast Strains", P Mazzei, R Spaccini, N Francesca, G Moschetti, A Piccolo, J Agric Food Chem, 61, 10816-10822 (2013)

"An exploratory chemometric study of ^{1}H NMR spectra of table wines", F H Larsen, F van den Berg, S B Engelsen, J. Chemometrics, 20, 198-208 (2006)

"Sensory attributes of wine influenced by variety and berry shading discriminated by NMR metabolomics", S Rochfort , V Ezernieks , S E P Bastian , M O Downey. Food Chem, 121, 1296–1304 (2010)

"Metabolic Influence of Botrytis cinerea Infection in Champagne Base Wine", Y-S Hong, C Cilindre, G Liger-Belair, P Jeandet, N Hertkorn, P Schmitt-Kopplin, J Agric Food Chem, 59, 7237-7245 (2011)

"A Thorough Study on the Use of Quantitative ^{1}H NMR in Rioja Red Wine Fermentation Processes", E Lopez-Rituerto, S Cabredo, M Lopez, A Avenoza, J H Busto, J M Peregrina, J Agric Food Chem, 57, 2112–2118 (2009)

"Comparison of Gas Chromatography-Coupled Time-of-Flight Mass Spectrometry and ^{1}H Nuclear Magnetic Resonance Spectroscopy Metabolite Identification in White Wines from a Sensory Study Investigating Wine Body", K Skogerson, R Runnebaum, G Wohlgemuth, J De ROPP, H Heymann, O Fiehn, J Agric Food Chem, 57(15), 6899-6907 (2009)

"Metabolomic Characterization of Malolactic Fermentation and Fermentative Behaviors of Wine Yeasts in Grape Wine" H-S Son, G-S Hwang, W-M Park, Y-S Hong, AND C-H Lee, J Agric Food Chem, 57(11), 4801-4809 (2009)

"^{1}H nuclear magnetic resonance-based metabolomic characterization of wines by grape varieties and production areas", H-S Son, K-M Kim, F Van den Berg, G-S Hwang , W-M Park, C-H Lee, J Agric Food Chem, 56, 8007 (2008)

"Metabolomic studies on geographical grapes and their wines using ^{1}H NMR analysis coupled with multivariate statistics", H-S Son, G-S Hwang, KM Kim, H-J Ahn, W-M Park, F Van Den Berg, J Agric Food Chem, 57, 1481 (2009)

"Use of modern nuclear magnetic resonance spectroscopy in wine analysis: determination of minor compounds", I J Kosir, J Kidric, Anal Chim Acta, 458, 77 (2002)

"Chemometric classification of Apulian and Slovenian wines using ^{1}H NMR and ICP-OES together with HPICE data", M A Brescia, I J Kosir, V Caldarola, J Kidric, A Sacco, J Agric Food Chem, 51, 21 (2003)

"Characterization of wines by nuclear magnetic resonance: a work study on wines from the Basilicata region in Italy", L Viggiani, M A C Morelli, J Agric Food Chem, 56, 8273 (2008)

"Classification of wines based on combination of ^{1}H NMR spectroscopy and principal component analysis", Y-Y Du, G-Y Bai, X Zhang, M-L Liu, Chin J Chem, 25, 930 (2007)

"^{1}H NMR-based metabonomics for the classification of Greek wines according to variety, region, and vintage. Comparison with HPLC data", M Anastasiadi, A Zira, P Magiatis, S A Haroutounian, A L Skaltsounis, E Mikros, J Agric Food Chem, 57, 11067 (2009)

"^{1}H NMR and chemometrics to characterize mature grape berries in four wine- growing areas in Bordeaux, France, G E Pereira, J P Gaudillere, C Van Leeuwen, G Hilbert, O Lavialle, M Maucourt, J Agric Food Chem, 53, 6382 (2005)

"^{1}H NMR-based metabolomic approach for understanding the fermentation behaviors of wine yeast strains", H-S Son, G-S Hwang, KM Kim, E-Y Kim, F van den Berg, W-M Park, Anal Chem, 81, 1137 (2009)

"Generalized 2D-correlation NMR analysis of a wine fermentation", G M Kirwan, S Clark, N W Barnett, J O Niere, M J Adams, Anal Chim Acta, 629, 128 (2008)

"*Time course of the evolution of malic and lactic acids in the alcoholic and malolactic fermentation of grape must by quantitative ^{1}H NMR (qHNMR) spectroscopy",* A Avenoz, J H Busto, N Canal, J M Peregrina, J Agric Food Chem, 54, 4715 (2006)

"NMR-based metabolomics in wine science", Y-S Hong, Magn Reson Chem, 49, S13 (2011)

"High- resolution NMR and diffusion-ordered spectroscopy of port wine", M Nilsson, I F Duarte, C Almeida, I Delgadillo, B J Goodfellow, A M Gil, J Agric Food Chem, 52, 3736 (2004)

"Quantitative NMR spectroscopy of binary liquid mixtures (aldehyde + alcohol) Part I: Acetaldehyde + (methanol or ethanol or 1-propanol)", S Jaubert, G Maurer, J Chem Thermo 68, 332–342 (2014)

Beer

"Composition of beer by ^{1}H NMR spectroscopy: effects of brewing site and date of production", C Almeida, I F Duarte, A Barros, J Rodrigues, M Spraul, A M Gil, J Agric Food Chem, 54, 700 (2006)

"Multivariate analysis of NMR and FTIR data as a potential tool for the quality control of beer ", I F Duarte, A Barros, C Almeida, M Spraul, A M Gil, J Agric Food Chem, 52, 1031 (2004)

"High-Resolution Nuclear Magnetic Resonance Spectroscopy and Multivariate Analysis for the Characterization of Beer", Ä I Duarte, A Barros, P S Belton, R Righelato, M Spraul, E Humpfer, A M Gil, J Agric Food Chem, 50, 2475−2481 (2002)

"Quantification of organic acids in beer by nuclear magnetic resonance (NMR)-based methods", J E A Rodrigues , G L Erny , A S Barros , V I Esteves , T Brandão , A A Ferreira , E Cabrita , A M Gil, Anal Chim Acta, 674, 166–175 (2010)

"NMR methods for beer characterization and quality control", J E Rodrigues, A M Gil, Magn Reson Chem, 49, S37–S45 (2011)

"Quality control of beer using high-resolution nuclear magnetic resonance spectroscopy and multivariate analysis", D W Lachenmeier, W Frank, E Humpfer, H Schafer, S Keller, M Mortter · M Spraul, Eur Food Res Technol, 220, 215–221 (2005)

"Probing beer aging chemistry by nuclear magnetic resonance and multivariate analysis", J A Rodrigues, A S Barros, B Carvalho, T Brandão, A M Gil, Anal Chim Acta, 702, 178–187 (2011)

"Quantification of Organic and Amino Acids in Beer by ^{1}H NMR Spectroscopy", L I Nord, P Vaag, J Ø Duus, Anal Chem, 76 (16), 4790–4798 (2004)

"*Application of Quantitative Nuclear Magnetic Resonance Spectroscopy to Biological Acidification of Barley Mashes",* A Dicaprio, J C Edwards, J Inst Brewing, 120(3), 207-211 (2014)

Beer Dextrins

"Separation and NMR structural characterisation of singly branched α-dextrins which differ in the location of the branch point", A Jodelet, N M Rigby, I J Colquhoun, Carb Res, 312, 139-151 (1998)

"*^{1}H NMR spectroscopy for profiling complex carbohydrate mixtures in non-fractionated beer*" B O Petersen , M Nilsson , M Bøjstrup , O Hindsgaul , S Meier, Food Chem, 150, 65–72 (2014)

"Development of brewing science in (and since) the late 19th century: Molecular profiles of 110–130 year old beers", A Walther, D Ravasio, F Qin, J Wendlan , S Meier, Food Chem, 183, 227–234 (2015)

"*Structural determination of some new oligosaccharides and analysis of the branching pattern of isomaltooligosaccharides from beer",* E Vinogradov, K Bock, Carb Res, 309, 57-64 (1998)

"NMR characterization of chemically synthesized branched α-dextrin model compounds", B O Petersen, M S Motawie, B Lindberg Møller, O Hindsgaul, S Meier, Carb Res, 403, 149–156 (2105)

Adjuncts – Hops, Malt, Honey

"Detection of honey adulteration by sugar syrups using one-dimensional and two-dimensional high-resolution nuclear magnetic resonance", D Bertelli, M Lolli, G Papotti, L Bortolotti, G Serra, M Plessi, J Agric Food Chem, 58, 8495 (2010)

"Identification of components of Brazilian honey by H NMR and classification of its botanical origin by chemometric methods", E F Boffo, L A Tavares, A C T Tobias, M M C Ferreira, A G Ferreira, LWT - Food Sci Tech, 49, 55-63 (2012)

"Fast and global authenticity screening of honey using ^{1}H-NMR profiling", M Spiteri, E Jamin, F Thomas, A Rebours, M Lees, K M Rogers, D N Rutledge, Food Chem, 189, 60-66 (2015)

"Characterization of Markers of Botanical Origin and Other Compounds Extracted from Unifloral Honeys", E Schievano, E Morelato, C Facchin, S Mammi, J Agric Food Chem, 61(8), 1747-1755 (2013)

"NMR Characterization of Saccharides in Italian Honeys of Different Floral Sources", R Consonni, L R Cagliani, C Cogliati, J Agric Food Chem, 60(18), 4526-4534 (2012)

"An improved NMR method for the quantification of alpha-acids in hops and hop products", A C Hoek, A C Hermans-Lokkerbol, R Verpoorte, Phytochem Anal, 12(1), 53-57 (2001)

"Characterization of reduced iso-α-acids derived from hops (Humulus lupulus) by NMR", L I Nord, S B Sørensen, J Ø Duus, Magn Reson Chem, 41(9), 660-670 (2003)

Sake

"NMR-Based Metabolic Profiling of Rice Wines by F2-Selective Total Correlation Spectra", M Koda, K Furihata, F Wei, T Miyakawa, M Tanokura, J Agric Food Chem, 60(19), 4818–4825 (2012)

Vinegar

"Traditional balsamic vinegar and balsamic vinegar of Modena analyzed by nuclear magnetic resonance spectroscopy coupled with multivariate data analysis", G Papotti, D Bertelli, R Graziosia, A Maietti, P Tedeschi, A Marchetti, M Plessi, LWT - Food Sci Tech, 60(2), 1017-1024 (2015)

"*Identification and quantification of the main organic components of vinegars by high resolution ^{1}H NMR spectroscopy*", A. Caligiani , D. Acquotti , G. Palla , V. Bocchi, Anal Chim Acta, 585,110–119 (2007)

^{1}H NMR studies on Italian balsamic and traditional balsamic vinegars", R Consonni, A Gatti, J Agric Food Chem, 52, 3446 (2004)

"NMR and chemometric methods: a powerful combination for characterization of Balsamic and Traditional Balsamic Vinegar of Modena", R Consonni, L R Cagliani, F Benevelli, M Spraul, E Humpfer, M Stocchero, Anal Chim Acta, 611, 31 (2008)

Spirits

"NMR metabolite profiling of Greek grape marc spirits" C Fotakis , D Christodouleas , K Kokkotou , M Zervou , P Zoumpoulakis , P Moulos , M Liouni , A Calokerinos, Food Chem, 138, 1837–1846 (2013)

"NMR metabolic fingerprinting and chemometrics driven authentication of Greek grape marc spirits", C Fotakis, M Zervou, Food Chem, 196, 760-768 (2016)

"Rapid Determination of Total Thujone in Absinthe Using ^{1}H NMR Spectroscopy", Y B Monakhova , T Kuballa, and D W Lachenmeier, Int J Spectroscopy, 2011, Article ID 171684, 5 pages (2011)

"Solute Effects on the Interaction between Water and Ethanol in Aged Whiskey", A Nose, M Hojo, M Suzuki, T Ueda, J Agric Food Chem, 52(17), 5359–5365 (2004)

"Hydrogen Bonding in Alcoholic Beverages (Distilled Spirits) and Water−Ethanol Mixtures", A Nose, T Hamasaki, M Hojo, R Kato, K Uehara, T Ueda, J Agric Food Chem, 5(18), 7074–7081 (2005)

"Structurability: A Collective Measure of the Structural Differences in Vodkas", N Hu, D Wu, K Cross, S Burikov, T Dolenko, S Patsaeva, D W Schaefer, J Agric Food Chem, 58(12), 7394–7401 (2010)

"Rapid Quantification of Ethyl Carbamate in Spirits Using NMR Spectroscopy and Chemometrics", Y B Monakhova, T Kuballa, Dirk W Lachenmeier, ISRN Anal Chem, 2012, Article ID 989174, 5 pages (2012)

"Authenticity of the Traditional Cypriot Spirit "Zivania" on the Basis of ^{1}H NMR Spectroscopy Diagnostic Parameters and Statistical Analysis", P Petrakis, I Touris, M Liouni, M Zervou, I Kyrikou, R Kokkinofta, C R Theocharis, T M Mavromoustakos, J Agric Food Chem, 53(13), 5293–5303 (2005)

"Investigation into the structural composition of hydroalcoholic solutions as basis for the development of multiple suppression pulse sequences for NMR measurement of alcoholic beverages", Y B Monakhova, S P Mushtakova, T Kuballa, D W Lachenmeier, Magn Reson Chem, 52, 755-759 (2014)

"Quantitative ^{1}H NMR Analysis of Egg Yolk, Alcohol, and Total Sugar Content in Egg Liqueurs", M Hohmann, V Koospal, C Bauer-Christoph, N Christoph, H Wachter, B Diehl, U Holzgrabe, J Agric Food Chem, 63(16), 4112–4119 (2015)