

# Detecting Corn Syrup in Barley Malt Extracts

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## ABSTRACT

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Methods for detecting corn syrup in barley (*Hordeum vulgare* L.) malt extract were evaluated. Twelve samples representative of commercially available 2-rowed and 6-rowed malting barleys were malted. Extracts prepared from the finely ground malts were analyzed for  $^{13}\text{C}/^{12}\text{C}$  ratios, expressed as  $\delta^{13}\text{C}$ , and concentrations of protein and sugars. The  $^{13}\text{C}/^{12}\text{C}$  ratios were sufficiently different to distinguish corn syrup from malt extract. By calculating the mean values for the barleys, it was determined that a  $\delta^{13}\text{C} > -24.3\text{‰}$  indicated that the malt extract had been adulterated with corn syrup (99% confidence). Protein concentrations  $<4.5\%$  (2-rowed

malt) or  $<5.0\%$  (6-rowed malt) of the extracts also indicated probable adulteration with corn syrup, which is devoid of protein. Because of differences in sugar concentrations between the malt extracts and corn syrup, carbohydrate analysis also indicated probable mixtures. These findings were confirmed by analysis of extracts from composite 2-rowed and 6-rowed barley malts that had been mixed with known quantities of corn syrup. The regressions for  $\delta^{13}\text{C}$ , protein concentration, and most sugar concentrations against percent dilution with corn syrup in the mixtures were significant.

Malt extract is produced from malted barley and used in the formulation of foodstuffs, where it serves as a source of sweetener, flavor, color, and enzymes (Bamforth and Barclay 1993). There are economic incentives to adulterate malt extract, which is relatively expensive, with corn syrup, which is relatively cheap. To control this practice and protect the consumer, methods are needed to detect the presence of corn syrup in malt extract. This research evaluated three potential methods for detecting the presence of the adulterant: stable carbon isotope ratio analysis (SCIRA), protein analysis, and carbohydrate analysis. SCIRA is based on the principle that the  $^{13}\text{C}/^{12}\text{C}$  ratio of organic materials derived from plants that use the  $\text{C}_4$  photosynthesis pathway is higher than that from  $\text{C}_3$  plants. Corn is a  $\text{C}_4$  plant and barley is a  $\text{C}_3$  plant. SCIRA has previously proven effective for detecting corn syrup adulteration of honey, maple syrup, and fruit juices (White and Doner 1978; Doner and Bills 1982; Doner 1991). The protein analysis method works by detecting the dilution of the malt extract proteins when corn syrup, which is devoid of protein, is added. Carbohydrate analysis detects the altered levels of glucose, sucrose, maltose, maltotriose, and maltotetraose that are caused by the addition of corn syrup. Any one of the three methods has the potential to detect the presence of corn syrup in malt extracts. Whether the methods will work in actual practice depends on variation among barleys and accuracy of measurements.

The objectives of this study were to determine the feasibility of using these three different methods to detect the adulteration of malt extract by corn syrup. Furthermore, by analyzing artificial mixtures we showed the relationships between the percentage of the adulterant and protein and sugars concentrations and  $\delta^{13}\text{C}$ . Through statistical analysis, we determined the lowest concentration of corn syrup that can be detected in these mixtures.

Although SCIRA has been used effectively for detecting corn syrup adulteration in honey, maple syrup and fruit juices, it has not been demonstrated by scientific testing to work for malt extracts. Furthermore, we wanted to evaluate other tests such as protein and carbohydrate analyses and compare them with SCIRA, which requires highly skilled technicians and expensive instrumentation. Protein analyses can be performed more easily with less expense using

one of several available standard techniques. Likewise, the sugars can be analyzed by standard HPLC separations or by one of several enzymatic assays.

## MATERIALS AND METHODS

**Materials.** Twelve samples of malting barley grown in 1998 were obtained. The samples were representative of the commercially important 2-rowed ['Conlon' (North Dakota), 'Harrington' (Montana, Washington, Idaho), 'Crystal' (Idaho), 'B1202' (Idaho)] and 6-rowed ['Morex' (North Dakota, Saskatchewan), 'Stander' (North Dakota, Minnesota), 'Robust' (North Dakota, Minnesota)] barleys. Crystal and B1202 were obtained from Darrell Wesenberg, USDA, ARS, Aberdeen ID. The other cultivars were obtained from Scott Heisel, American Malting Barley Association, Milwaukee WI, who had assembled them from various plant breeders for pilot-scale malt quality evaluation. Four commercial 42DE corn syrup samples were obtained from ADM Corn Processing (Decatur IL), Cerestar (Hammond IN), A.E. Staley (Decatur IL), and Corn Products International (Bedford Park IL). All of the syrups had nearly identical specifications (Table I).

**Malting.** The grain samples were cleaned on a Carter Dockage tester and only the seeds that were retained on a 5/64" screen were malted. Samples (170 g, db) were steeped at 16°C for 24–48 hr to bring them to 45% moisture by alternating 4 hr of wet steep with 4 hr of air rest. The steeped samples were then placed in a germination chamber for five days at 17°C and 100% rh with periodic rotation. The germinated grain (green malt) was kilned for 24 hr at 0.5 hr from 25 to 49°C, 9.5 hr at 49°C, 0.5 hr from 49 to 54°C, 4.0 hr at 54°C, 0.5 hr from 54 to 60°C, 3.0 hr at 60°C, 0.5 hr from 60 to 68°C, 2.0 hr at 68°C, 0.5 hr from 68 to 85°C, and 3.0 hr at 85°C. This procedure follows from that originally described by Burger and LaBerge (1987) but has been substantially modified to produce malts that are as similar as possible to those produced under commercial conditions. It is used routinely to produce malts from thousands of breeders' samples each year for the purpose of evaluating the quality of these selections.

The malts were ground with a Miag laboratory cone mill (Buhler, Inc., Plymouth, MN) that was adjusted so that 10% of the grist remained on a standard 8" series #30 525- $\mu\text{m}$  sieve after 3 min of shaking on a mechanical barley grader with tapping as described in Malt-4 (ASBC 1992). The malted barleys were analyzed with a battery of quality tests to ensure that the malt was of satisfactory quality. These analyses, which are described in the ASBC Standard Methods (ASBC 1992), included measuring the malt extract percentage (Malt-4), wort color, wort clarity, wort protein (Wort-17), total protein (Barley-7C), diastatic power (Malt-6C), and wort  $\beta$ -glucan levels (Wort-18).  $\alpha$ -Amylase activities were determined on a Skalar SAN plus System (Skalar Inc., Norcross, GA) by

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heating the extract to 73°C to inactivate any  $\beta$ -amylase present, after which the remaining activity was measured as described for diastatic power. Free amino N was measured using a ninhydrin reagent (Wort-12). Two-rowed (Harrington) and 6-rowed (Morex) check samples were malted and analyzed along with the 12 experimental samples.

**Malt extracts.** The finely ground samples were extracted using the Malt-4 procedure, except that all of the weights and volumes specified for the procedure were halved. Also, at the conclusion of the conversion step (1 hr at 70°C) the temperature was elevated to 75°C for 30 min to inactivate any remaining  $\alpha$ -amylase. The densities of the filtered extracts were measured with a Mettler/Paar density meter (Anton Paar USA, Ashland, VA), and the amounts of total dissolved solids in the filtrates were calculated using the equations described in Malt-4. Extracts were frozen and stored at -20°C for subsequent analyses.

**Protein analysis.** The soluble protein concentrations of the malt extracts were measured in duplicate by the combustion method (AOAC 1995) using a Mitsubishi TN-05 total nitrogen analyzer (Tokyo, Japan). This instrument measures sample N levels by cata-

lytic oxidative pyrolysis and chemiluminescence. The percent protein was calculated as  $N \times 6.25$  expressed on a total solids basis.

**Carbohydrate analysis.** Sugars in the malt extracts were separated on a Dionex CarboPac PA1 column (4  $\times$  250 mm). The elution solvents used were A: 100 mM NaOH, and B: solvent A containing 600 mM Na acetate. The elution gradient profile during the 30-min separation was from 99.5% A/0.5% B to 43% A/57% B over 20 min, followed by 10 min of 99.5% A/0.5% B. The separated sugars were detected with a gold electrode 0.3 sec into the 1-sec pulsed cycle (E1 = 0.05V [0.4 sec], E2 = 0.75V [0.2 sec], E3 = -0.15V [0.4 sec]) at a potential of 0.05V, with a pulsed electrochemical detector. The sugar concentrations are reported as percentages of the total soluble solids of the extracts. There was no indication that sucrose or any other sugar was unstable during the analysis or prior period of storage.

**SCIRA.** Samples ( $\approx$ 15 mL) of the malted barley extracts and corn syrups were frozen in glass screw-capped test tubes, packed in frozen CO<sub>2</sub>, and shipped by overnight express to Geochron Laboratories (Cambridge, MA) for analysis. The samples were combusted and the <sup>13</sup>C/<sup>12</sup>C ratios were analyzed by mass spectrometry; a  $\delta^{13}$ C

**TABLE I**  
Corn Syrup Composition (%)<sup>a</sup> and Carbon Isotope Ratios

Corn Syrup	DE	Total Solids	Dextrose	Maltose	Maltotriose	Higher Saccharides	$\delta^{13}$ C ‰
ADM 42/43	42	80.7	19	14	12	55	-10.4
Cerestar C*Sweet 01160	42	80.3	19	14	12	55	-10.8
Staley 1300	43	80.3	19	14	13	54	-10.5
Corn Products Int. Globe 011420	43.9	80.6	19.1	14.1	11.3	55.5	-10.5

<sup>a</sup> DE = dextrose equivalent. Manufacturers data, except for <sup>13</sup>C.

**TABLE II**  
Quality Analysis of Two-Rowed and Six-Rowed Malts

Cultivar and Origin	Rows	Kernel Wt (mg)	On 6/64'' (%)	Barley color (Agtron)	Malt Extract (%)	Wort Clarity <sup>a</sup>	Barley Protein (%)	Wort Protein (%)	S/T <sup>b</sup> (%)	Diastatic Power (°ASBC)	$\alpha$ -Amylase (20° DU)	$\beta$ -Glucan (ppm)	Free Amino N (ppm)
B1202 ID	2	42.6	92.4	49	79.6	1	14.3	5.13	37.3	109	57.0	284	200
Crystal ID	2	42.3	88.3	59	79.6	2	14.5	5.54	39.6	138	67.5	325	221
Conlon ND	2	42.1	98.6	52	80.9	1	13.5	5.55	43.3	107	79.6	333	227
Harrington ND	2	39.2	83.2	58	79.0	2	12.8	4.80	39.5	82	56.1	334	184
Harrington WA	2	36.3	71.9	60	79.5	2	12.7	4.83	39.9	84	53.5	351	183
Harrington MT	2	31.2	58.2	84	80.1	1	12.1	5.39	46.9	110	70.2	208	214
Morex ND	6	30.4	53.7	62	80.0	1	12.9	6.16	50.3	147	80.4	139	271
Morex SK	6	33.3	69.3	76	79.6	1	12.5	5.11	43.0	140	69.9	205	215
Stander MN	6	35.0	85.2	43	79.8	1	13.3	6.37	50.6	123	74.8	384	292
Stander ND	6	33.0	72.0	59	80.7	1	13.3	6.74	53.6	163	90.0	208	317
Morex MN	6	33.9	76.6	42	78.3	1	14.1	5.82	43.2	132	55.7	459	237
Robust ND	6	32.4	60.6	57	79.8	1	14.3	6.32	46.4	173	61.7	290	274
Morex malt check	6	30.6	68.6	72	80.2	1	12.7	5.91	49.3	125	76.1	187	279
Harrington malt check	2	37.5	88.7	60	80.1	1	12.8	4.81	39.7	92	58.8	638	193

<sup>a</sup> 1 = clear, 2 = slightly hazy, 3 = hazy.

<sup>b</sup> 100 (Wort protein/total malt protein).

**TABLE III**  
Stable Carbon Isotope Ratio Analysis, Protein (by Combustion), and Sugar Analyses of Worts from Two-Rowed and Six-Rowed Malts

Cultivar and Origin	Rows	$\delta^{13}$ C (‰)	Protein (%)	Sugar (mg/mL)				
				Glucose	Sucrose	Maltose	Maltotriose	Maltotetraose
B1202 ID	2	-24.8	5.26	8.32	5.06	44.44	8.41	2.05
Crystal ID	2	-25.0	5.60	8.81	5.31	42.30	8.27	1.52
Conlon ND	2	-26.6	5.40	8.45	5.48	42.41	8.85	1.73
Harrington ND	2	-24.9	4.67	7.52	4.71	42.03	8.57	2.61
Harrington WA	2	-25.8	4.67	7.66	4.38	40.75	8.47	2.45
Harrington MT	2	-24.5	5.23	7.71	5.39	43.33	8.74	1.80
Morex ND	6	-26.6	5.77	8.61	5.72	41.20	8.76	1.45
Morex SK	6	-23.9	4.97	7.75	6.16	45.40	8.11	1.47
Stander MN	6	-27.2	6.24	9.37	4.66	42.26	8.93	1.74
Stander ND	6	-26.7	6.64	9.91	5.64	43.79	9.18	1.28
Morex MN	6	-26.8	5.71	7.57	3.83	43.24	8.01	1.94
Robust ND	6	-27.1	6.27	8.20	4.80	43.98	8.21	1.72
Morex malt check	6	-25.1	5.61	9.40	5.70	46.69	10.17	1.66
Harrington malt check	2	-24.2	4.82	7.41	4.07	46.40	9.79	2.20

computed value was compared to that of a PDB (fossil belemnite from the PeeDee Formation in South Carolina) standard:  $\delta^{13}\text{C}\text{‰} = 1,000 [(^{13}\text{C}/^{12}\text{C}_{\text{sample}})/(^{13}\text{C}/^{12}\text{C}_{\text{standard}}) - 1]$ .

**Mixtures.** Duplicate composite mixtures of 2-rowed and 6-rowed malts were prepared by mixing equal amounts of each of the six 2-rowed and six 6-rowed malts. These composite samples were ground and extracted as described above. These extracts (worts) contained  $9.94 \pm 0.01\%$  solids. Each of the four corn syrups was diluted with deionized water to a solids concentration equal to that of the malt extracts, and then equal volumes were combined to form a composite corn syrup mixture. Malt extract and corn syrup mixtures were prepared in the ratios 0/100, 25/75, 50/50, 75/25, and 100/0, two sets for the 2-rowed composite and two for the 6-rowed composite. These mixtures were analyzed by SCIRA and for concentrations of protein, sugars, and several other components as described above.

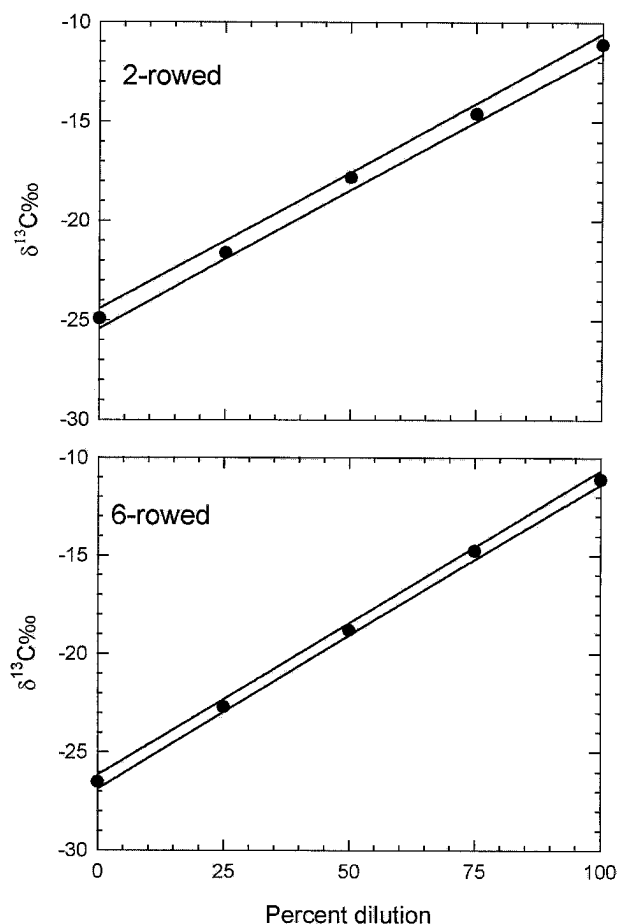
**Statistical analysis.** The Univariate procedure (SAS Institute, Cary, NC) was used to determine whether the six 2-rowed and six 6-rowed malts were samples from normally distributed populations based on the SCIRA, protein, and carbohydrate data. The variances for the 2-rowed and 6-rowed sample populations were tested for homogeneity, and the means compared by *F* test (if the variances were homogeneous) or *t* test (for unequal variances). If the sample means were not different, the 2-rowed and 6-rowed samples were combined into a single group for further analysis. The probabilities that a given  $\delta^{13}\text{C}$  value, protein level, or carbohydrate composition would be obtained from an unadulterated sample was determined from the confidence intervals computed from the six 2-rowed, six 6-rowed, or twelve combined malts, assuming that these malt samples are representative of the populations of malts that are available commercially. The data obtained from the mixtures were analyzed by regression analysis and the regression coefficients, prediction intervals, *F* statistics, and  $r^2$  values from the analyses of variance were determined. Significant regression coefficients indicated that the  $\delta^{13}\text{C}$  values, protein concentrations, and carbohydrate concentrations of the mixtures were determined by fractional compositions.

## RESULTS

The carbohydrate concentrations of the four corn syrups were nearly identical, according to the manufacturers' specifications (Table I). The dextrose equivalents were 42–43.9 and the total solids were 80.3–80.6%. The dextrose, maltose, maltotriose, and higher saccharides concentrations were nearly the same among the four syrups. Carbon isotope ratios were also very similar, ranging from  $-10.4$  to  $-10.8$   $\delta^{13}\text{C}\text{‰}$ . The mean  $\delta^{13}\text{C}\text{‰}$  for the corn syrups was  $-10.5$ , and the 95 and 99% confidence intervals were  $-0.3$  and  $-0.6$ , respectively. There was no detectable protein in the corn syrups.

Malting quality analyses of the 12 barley samples and malts showed that, for the most part, they were typical of 2-rowed and 6-rowed

malting barleys that are commercially available (Table II). Among the 2-rowed barleys, the MT Harrington kernels were thinner than normal. All samples had similar malt extract percentages of 79.0–80.9%. The barley protein levels of three of the barleys (B1202, Crystal, and Conlon) were higher than the  $<13.5\%$  commercially acceptable level. The ND and WA Harrington malts were low in diastatic power; Crystal, Conlon, and MT Harrington samples contained slightly high  $\alpha$ -amylase activity levels. Among the 6-rowed barleys, the ND and SK Morex and Robust kernels were thinner than



**Fig. 1.** Stable carbon isotope ratio analysis of malt extracts diluted with various percentages of corn syrup. Lines indicate 95% prediction intervals. Regression equation for two-rowed:  $S = -11.08 - 0.138 E$  ( $r^2 = 0.999$ ); for six-rowed:  $S = -11.02 - 0.155 E$  ( $r^2 = 0.999$ ), where  $S = \delta^{13}\text{C}$  (‰) and  $E = \%$  dilution with corn syrup.

**TABLE IV**  
Mean Values and Confidence Intervals (CI) for Wort Analyses

	Two-Rowed Malts			Six-Rowed Malts			Combined <sup>a</sup>		
	Mean	95% CI	99% CI	Mean	95% CI	99% CI	Mean	95% CI	99% CI
$\delta^{13}\text{C}\text{‰}$	-25.3	-0.8	-1.3	-26.4 <sup>b</sup>	-1.3 <sup>b</sup>	-2.1 <sup>b</sup>	-25.9	-0.7	-1.0
Wort protein, %	5.14	0.40	0.63	5.93	0.61	0.96	...	...	...
Sugar, mg/mL									
Glucose	8.08	0.55	0.86	8.57	0.97	1.52	8.32	0.48	0.68
Sucrose	5.05	0.45	0.71	5.13	0.90	1.42	5.09	0.41	0.58
Maltose	42.54	1.31	2.05	43.31	1.53	2.40	42.92	0.86	1.21
Maltotriose	8.55	0.23	0.36	8.53	0.51	0.80	8.54	0.23	0.32
Maltotetraose	2.03	0.45	0.71	1.60	0.25	0.40	1.81	0.25	0.36
Glucose-sucrose	1.60	0.12	0.18	1.70	0.30	0.47	1.65	0.14	0.19
Maltose-glucose	5.28	0.34	0.53	5.11	0.65	1.02	5.20	0.31	0.43
Maltose-sucrose	8.45	0.66	1.04	8.65	1.62	2.55	8.55	0.72	1.01
Maltotetraose-sucrose	0.41	0.13	0.20	0.33	0.11	0.14	0.37	0.07	0.11

<sup>a</sup> Data for both two-rowed and six-rowed malts were combined when there was no significant difference in the means by analysis of variance or *t*-test.

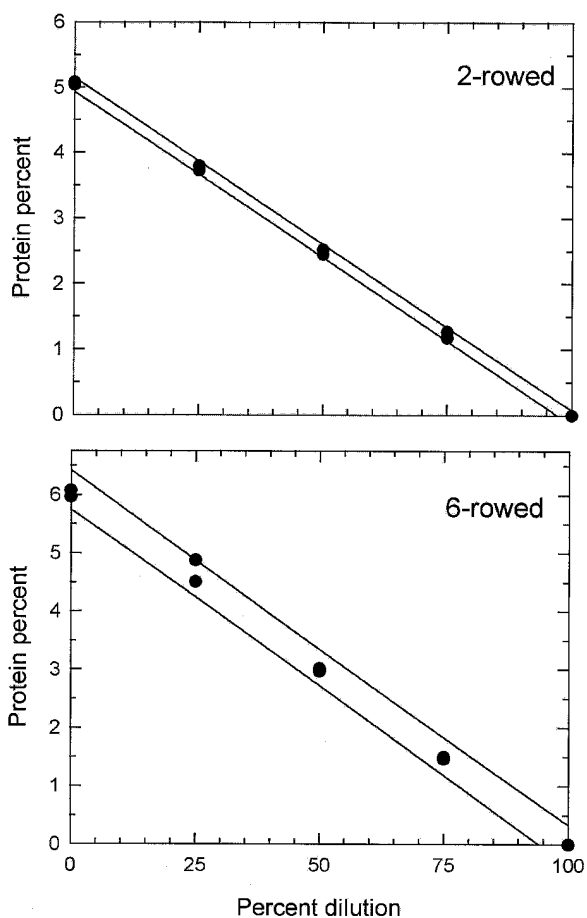
<sup>b</sup> Omitting data for Morex SK, which was an outlier, the values for the mean, 95% CI, and 99% CI were  $-26.9$ ,  $-0.3$ , and  $-0.5$ , respectively.

desired. The MN Morex sample yielded a low malt extract percentage, and the MN Morex and Robust samples contained high barley protein levels. The  $\alpha$ -amylase activity levels of all of the samples, except MN Morex, were high. The MN Stander and Morex diastatic power levels were lower than preferred, while those of ND Stander and Robust were slightly higher. Although some of the barley and malt quality parameters fell outside of ideal ranges, none were unusual.

Table III shows the results of SCIRA and protein and sugar analyses in worts from each malt. Tests for normality using the Univariate procedure of SAS indicated that the six samples each of the 2-rowed and 6-rowed malts were normally distributed for wort protein. The  $\delta^{13}\text{C}$  values of the 2-rowed malt samples were normally distributed, but within the six 6-rowed malt samples, the  $\delta^{13}\text{C}$  value for SK Morex was an outlier that was higher (less negative) than the others. The sugar concentrations were normally distributed within the 2- and 6-rowed groups and as a combined group of all 12 barleys.

We computed the mean values and the 95 and 99% confidence intervals for  $\delta^{13}\text{C}$ , wort protein, and sugar compositions and ratios for the 2-rowed and 6-rowed malts (Table IV). When there was no significant difference between the mean values for the 2-rowed and 6-rowed malts, the data for all 12 barleys were combined for computing the means and confidence intervals.

The SCIRA and wort protein analyses of the mixtures of the corn syrup composite with extracts prepared from the malt composites are presented in Figs. 1 and 2. Each graph shows the 95% prediction intervals. There is a significant linear relationship between the percent dilution of the extracts and the protein concentrations and  $\delta^{13}\text{C}$ . The regression equations are all highly significant,  $r^2 >$



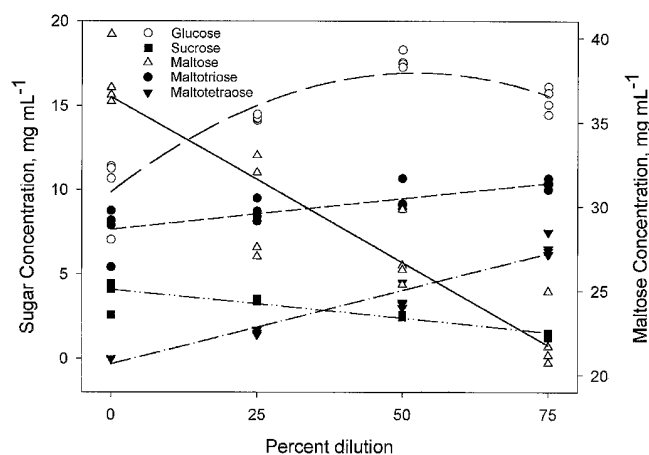
**Fig. 2.** Protein concentrations of malt extracts diluted with various percentages of corn syrup. Lines indicate 95% prediction intervals. Regression equations for two-rowed:  $P = -0.0357 + 0.0508 E$  ( $r^2 = 0.999$ ); for six-rowed:  $P = -0.0171 + 0.0611 E$  ( $r^2 = 0.997$ ), where  $P$  = protein concentration and  $E$  = % dilution with corn syrup.

0.99. The lines indicating the 95% prediction intervals can be used to predict the compositions of mixtures, based on a knowledge of either  $\delta^{13}\text{C}$  values or protein concentrations.

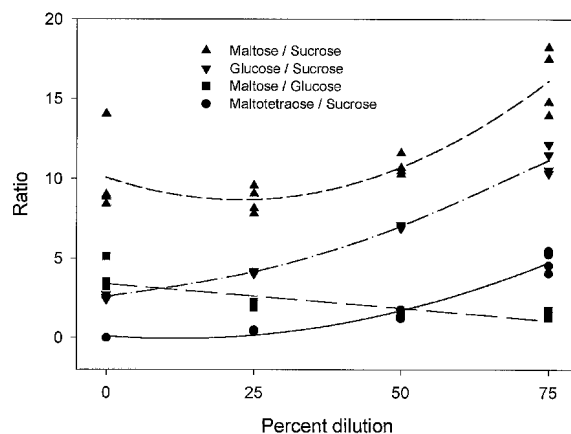
Significant linear or quadratic regressions were also obtained for all of the sugar concentrations (Fig. 3) and various ratios of sugar concentrations (Fig. 4). The concentrations of glucose, maltotriose, and maltotetraose increased, and those of sucrose and maltose decreased, as the percentage of corn syrup in the mixtures increased. Therefore, ratios of glucose, maltose, and maltotetraose to sucrose increased, and the ratio of maltose to glucose decreased as the percentage of corn syrup in the mixtures increased.

## DISCUSSION

The barley samples that we analyzed are representative of the barley cultivars that are available to commercial malt houses in the United States and were grown in environments where commercial barleys are produced. We did not preselect samples that had ideal quality parameters. Rather, we obtained samples that included the normal quality deviations that are expected in U.S. commercial malting barleys. Table II shows a range in the quality parameters among the 12 samples. Not all fell within the ideal range that the maltsters



**Fig. 3.** Sugar concentrations of malt extracts diluted with various percentages of corn syrup. Data from both composite two-rowed and six-rowed malt extracts. Linear (L) or quadratic (Q) regression equations were significant ( $P < 0.01$ ):  $r^2 = 0.85$  (Q),  $0.83$  (L),  $0.86$  (L),  $0.63$  (L), and  $0.97$  (Q) for glucose, sucrose, maltose, maltotriose, and maltotetraose, respectively.



**Fig. 4.** Ratios of sugar concentrations of malt extracts diluted with various percentages of corn syrup. Data from both composite two-rowed and six-rowed malt extracts. Linear (L) or quadratic (Q) regression equations were significant ( $P < 0.01$ ):  $r^2 = 0.69$  (L),  $0.76$  (Q),  $0.99$  (Q), and  $0.96$  (Q) for maltose-glucose, maltose-sucrose, glucose-sucrose, and maltotetraose-sucrose, respectively.

prefer. This range is normal, and lends credence to our assumption that these 12 barley samples are representative of the entire population of barleys that are malted in the United States.

The primary distinguishing feature between the malt extracts and corn syrup was the carbon isotope ratio, as determined by SCIRA. The  $\delta^{13}\text{C}$  of the malt extracts ( $-25.3$  and  $-26.4\text{‰}$  for 2-rowed and 6-rowed malts, respectively) were much lower than that for corn syrups (mean =  $-10.5\text{‰}$ ), and the confidence intervals were very tightly clustered. It can be concluded that any malt extract sample has been adulterated with corn syrup if the  $\delta^{13}\text{C}$  is greater than (less negative) the mean plus the 95 or 99% confidence intervals. This would be any  $\delta^{13}\text{C} > -24.5\text{‰}$  (95% CI) or  $-24.0\text{‰}$  (99% CI) for 2-rowed malts and  $> -26.1\text{‰}$  (95% CI) and  $-25.9\text{‰}$  (99% CI) for 6-rowed malts (using the confidence intervals computed from five 6-rowed barleys that fell within a normal distribution). This is illustrated in Fig. 1, where any value  $> -24.5\text{‰}$  (2-rowed) and  $> -26.1\text{‰}$  (6-rowed) lies outside the 95% prediction interval for pure malt extract. The data in Fig. 1 can also be used to predict the percent dilution of a malt extract sample that contains corn syrup if the  $\delta^{13}\text{C}$  is known. For example, a  $\delta^{13}\text{C}$  of  $-24.5\text{‰}$  for a 2-rowed malt extract indicates the presence of 0–7% corn syrup, and a  $\delta^{13}\text{C}$  of  $-26.1\text{‰}$  for a 6-rowed malt extract indicates the presence of 0–5% corn syrup. These are the minimum concentrations that can be detected with any degree of certainty using SCIRA.

The protein concentration of an extract sample also can be used to determine whether corn syrup has been added, since the corn syrup is essentially devoid of protein. The protein test is less precise because the confidence intervals for the wort protein concentration are greater. Nevertheless, it is obvious that worts with protein concentrations  $< 4.74\%$  (95% CI) or  $4.51\%$  (99% CI) from 2-rowed malts or  $5.32\%$  (95% CI) or  $4.97\%$  (99% CI) from 6-rowed malts have been admixed with corn syrup. As with the carbon isotope ratio data, the graph of the regression of protein concentration against percent dilution can be used to predict the composition of an unknown sample (Fig. 2). The minimum concentrations of corn syrup in malt extracts that can be detected by protein concentration analysis are 10% for 2-rowed malt extract and 18% for 6-rowed.

Sugar concentration measurements may also help determine the presence of 42 DE corn syrup in malt extract because 1) corn syrup contains no sucrose, whereas malt extract contains  $\approx 5$  mg/mL; 2) corn syrup contains a lower concentration of maltose (14 vs. 43 mg/mL) and a higher concentration of glucose (19 vs. 8 mg/mL) than malt extract; 3) corn syrup contains higher concentrations of maltotriose and maltotetraose than malt extract; and 4) corn syrup has higher levels of maltodextrins with  $\text{DP} > 4$  than do malt extracts. Among these sugars, the maltose concentrations of malt extracts from the various barleys had the lowest coefficients of variation (CV) (2.9% for the 2-rowed barley malts, 3.4% for the 6-rowed, and 3.2% for the entire group of twelve). The CV values for the concentrations of the other sugars were 6.4–21.1%, indicating that there was considerable variation among the different malts.

When the sugar concentrations of the composite 2-rowed and 6-rowed malt extracts that had been diluted with various concentrations of corn syrup were regressed against percent dilution, significant linear or quadratic regressions were obtained for all sugar concentrations. Likewise, the combined data from both 2-rowed and 6-rowed malt extracts produced significant regressions for all sugar concentrations. The highest  $r^2$  values were for malto-

tetraose, even though this sugar is present in relatively low concentration. The ratios of some of the various sugars were calculated and subjected to regression analysis, and significant linear or quadratic regressions were obtained for maltose-glucose, maltose-sucrose, glucose-sucrose, and maltotetraose-sucrose. Glucose-sucrose ratios had the highest  $r^2$  values. These significant trends in sugar concentrations and ratios (Figs. 3 and 4) indicate that there is potential for using sugar analyses to determine the admixing of corn syrup into malt extracts. However, these regressions were obtained from only two malt extract samples (composite 2-rowed and 6-rowed malts). Had we made the dilution series with each of the 12 malt extract samples individually, the variability among samples may have reduced the probability of significant regressions.

Oligosaccharides with  $\text{DP} > 4$  are more concentrated in corn syrup than in malt extracts (data not shown). The differences in concentrations of these polymers might be developed as a diagnostic tool in laboratories that have HPLC instruments with pulsed electrochemical detectors.

It should also be noted that these results were obtained with 42 DE corn syrup, the cheapest and most readily available type. Corn syrup manufacturers can alter the sugar profiles of their products through enzyme selection and manipulation of processing conditions. Corn syrup refiners, for additional cost, can make a high maltose corn syrup that would more closely resemble the sugar profile of malt extract.

It is apparent from the lower  $r^2$  values, higher CV values among the barleys, and the possibility of using corn syrups with various sugar profiles that decisions about purity that are based on sugar analyses will be less precise and more subject to error than those based on SCIRA or protein analysis, where  $r^2 > 0.99$  were obtained. Nevertheless, a combination of techniques is now available that can be used to detect the presence of corn syrup in malt extracts.

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