Investigating Grain-on Malt Whiskey Production Using Naked Barley

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The ability to produce malt whiskey using grain-on production methods may benefit American craft spirit producers who lack the capacity to separate grains from the wort prior to fermentation and distillation. Off-flavors thought to be derived from barley husk material have prevented distillers from producing whiskey made entirely from malt with grain-on production methods. In the present study, the impacts of using a huskless, naked barley to produce grain-on malt whiskey was investigated. New make spirit was produced at laboratory scale using malt from the covered barley variety Lightning and naked barley variety Buck. The level of esters, higher alcohols, and total polyphenols was measured in the new make spirit. Distillate made from naked barley malt (50% ABV) had a total fusel oil concentration of 2,767 mg/L while whiskey made from covered barley malt had a higher total fusel oil concentration of 3,128 mg/L. Ester levels between the two spirits were similar, with levels of ethyl acetate measuring 7.15 mg/L in the whiskey made from naked barley malt and 7.68 mg/L in the whiskey made from husked barley malt. No polyphenols were detected in either spirit. The new make spirit was also subjected to sensory analysis in the form of a triangle test and quantitative descriptive analysis. Panelists were able to detect a difference between the samples, and whiskey made from naked barley malt was perceived to have a reduction in cereal, feinty, and pungent character. Additionally, despite the naked barley being a GN producer, processing during malting reduced GN to a level associated with non-producing varieties.

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INTRODUCTION

Naked barley (*Hordeum vulgare*) has been studied as a raw ingredient for the production of malt whiskey due to the potential it has to increase extract yields while reducing shipping costs, spent grain quantities, and polyphenol levels [1, 2]. All of these advantages relate to the removal of the barley hull during threshing. The lack of an adhering hull is the phenotypic result of a recessive allele at the *nud* gene located on chromosome 7H [3, 4]. The lack of hull results in naked barley consisting of proportionally more starch, protein, and β-glucan than covered barley [5, 6]. Naked barley is typically used only for food and animal feed, as the hull is important for efficient lautering during production of most malt whiskey and beer [4]. In traditional production of malt whiskey, grains are processed with a roller mill and separated from the wort prior to fermentation, here the husk is required as it forms a vital filter bed [7]. This process differs from the production of American whiskeys where the majority of the mash bill is typically corn and rye, both of which lack a husk; grains are hammer milled and remain in the mash through to distillation [8]. Limitations exist to producing malt whiskies using grain-on techniques as fermenting on the husks results in over extraction of husk materials and produces undesirable grainy characteristics in the new make spirit [9].

The husk accounts for nine to 14 percent of the dried weight of covered barley [4, 10, 11] and is composed primarily of holocellulose, hemicellulose, and lignin [11, 12]. Absence of the husk results in a reduction of the total polyphenols present in barley [1, 13]. The absence of the husk may also increase the susceptibility of the embryo and acrospire to damage [14, 15]. The proportionally higher starch levels in naked barley result in increases in extract yield of three to five percent [14] and by tailoring malting procedures, malt extract and predicted spirit yield (PSY) can be optimized [16].

High quality malt can be obtained from naked barley by adjusting the steeping, germination, and kilning methods [14, 17]. Many studies have shown that naked barley requires a shorter steeping time than covered barley [2, 11, 16, 17]. One possible mechanism to explain this phenomenon is that removal of the husk allows the grain to swell more freely [11]. Shorter steeping cycles may result in time, water, and cost savings [15, 18]. Naked barley has been found to contain more nitrogen than covered barley grown under the same fertilization treatment [19]. Due to the higher nitrogen content, longer germination times are likely needed for naked barley to achieve peak PSY [19] and reduce β-glucan to acceptable levels [2]. Germination times of four and five days have been reported for optimal PSY [2, 15, 16]. Kilning naked barley malt at lower temperatures both initially and during curing is thought to slow enzyme inactivation and result in malt with reduced β-glucan levels and increased α-amylase activity [14]. High β-glucan levels can lead to increased wort viscosity [5, 14, 19] and decreased friability [20]. Increasing the steeping time and temperature during malting can lead to the reduction of β-glucan levels [21]. β-glucan levels in naked barley are elevated for two main reasons: (1) Removal of husk proportionally increases β-glucan, which is predominantly associated with endosperm cell wall tissues [19]. (2) Naked barley has been bred for food and not for malt production; elevated β-glucan levels are seen as a positive attribute in barley destined for human consumption [4]. Even when compared to acid-dehusked malt, naked malt was found to contain more β-glucan [5]. Embryo damage prior to malting may also contribute to elevated β-glucan levels because dead kernels do not modify.

The role polyphenols play in beer is well understood. Polyphenols contribute to astringency and bitterness [22]. Total polyphenol levels decrease as the husk fraction in the wort decreases [1]. Reducing polyphenols leads to a reduction in harsh bitter flavors [23]. Milling conditions impact the extraction of polyphenols. Extraction is reduced if the husk remains largely intact [24], while fermenting on fine husk particles can lead to off flavors [9]. Phenols are leached from the husk during mashing [12], and increased contact between grist and wort increases extraction [25, 26]. The level of fatty acids in wort also increases with prolonged husk contact [27, 28].

Malt whiskey made from naked barley may have reduced levels of ethyl carbamate. Ethyl carbamate is a carcinogen found in distilled spirits and has been regulated in many countries around the world [29]. Ethyl carbamate is primarily derived from the epiheterodendrin (EPH) found in malted barley [30]. EPH — a glycosidic nitrile (GN) — is produced in the acrospires of germinating barley [31]. The amount of EPH a barley produces is variety specific, with some varieties producing no measurable levels [30]. While Scotland has committed to only approve barleys that are non-producers of EPH for whiskey production [30], LCS Odyssey is currently the only variety on the American Malting Barley Association's (AMBA) list of recommended barleys that is a non-producer [32]. In naked barley, the unprotected acrospire is removed during deculming. The removal of the acrospire during the deculming of naked barley may reduce the level of EPH in the malt and may lower the level of ethyl carbamate in the new make spirit. This may prove to be an important advantage in the American market.

Within the industry, there has been an expectation that whiskey produced using naked barley would contain lower overall concentrations of polyphenolic compounds as compared to spirit derived from typical husked barley, but these potential differences have not yet been addressed in the published literature. Differences have been expected to arise from the removal of the husk and acrospire, and from other physicochemical differences (grain composition, total nitrogen, barley metabolites) that have previously been identified in naked barley varieties [33, 34] many of which are known to contributory to aroma-active volatile compounds such as esters and higher alcohols. The present research evaluates the compositional and sensorial impacts for use of naked barley during production of malt whiskey.

METHODS

MALT PROCESSING

The naked barley variety Buck (Figure 1a) and covered variety Lightning (Figure 1b) were grown at Goschie Farm (Silverton, Oregon) and harvested in 2019. Both varieties were malted using Oregon State University's pilot malting system in 91kg batches. The thousand corn weight of the finished malt was 30.2g for Buck and 49.4g for Lightning on a dry weight basis.

Malting conditions were optimized for each variety (Table 1), based on grain quality data and the work of Craine et al. [35]. The Lightning cultivar was subjected to shorter steeps and longer air rests to compensate for water sensitivity (Water sensitivity: Lightning 38 percent, Buck three percent; Germinative energy: Lightning 99 percent, Buck 98 percent; measured using ASBC Methods of Analysis Barley-3C). The steep out moisture content was 47% for Buck and 42% for Lightning. The barley was sprayed with water every six hours during the first day of germination in order to reach a target moisture content of 49% for Buck and 47% for Lightning, requiring one and three sprays respectively. Grain was turned every six hours throughout germination. Moisture content at the end of germination was 46.4% for Buck and 44.7% for Lightning. To determine that suitable modification had been achieved, grains were checked manually for steely ends. Analysis of the malt was conducted by Hartwick College Center for Craft Food and Beverage (Oneonta, New York) using American Society of Brewing Chemists (ASBC) Methods [36]. Hartwick College also analyzed the glycosidic nitrile levels in the malt samples using Analytica EBC method 4.21 [37]. Full Pint was used as a negative control for glycosidic nitrile while Copeland was used as a positive control.

FIGURE 1 Malted barley samples a) Buck naked barley malt b) Lightning covered barley malt.

TABLE 1 Malting regime for Buck and Lightning barley.

	BUCK			LIGHTNING		
	STEEPING					
	TIME (H)	TEMP. (°C)		TIME (H)	TEMP. (°C)	
Steep 1	10	16		5	18	
Air rest 1	12	16		16	16	
Steep 2	10	16		5	18	
Air rest 2	10	16		15	16	
Steep 3	6.5	16		5	18	
	GERMINATION					
	TIME (H)	TEMP. (°C)		TIME (H)	TEMP. (°C)	
Conditions	120	18		96	18	
	KILNING					
	TIME (H)	AIR-ON TEMP. (°C)	AIR-OFF TEMP. (°C)	TIME (H)	AIR-ON TEMP. (°C)	AIR-OFF TEMP. (°C)
Stage 1	10	50	43	10	50	43
Stage 2	3	60	56	3	60	56
Stage 3	3	65	61	3	65	61
Stage 4	2	70	64	2	70	65
Stage 5	2	80	71	2	80	71
Stage 6	5	90	78	5	90	79

PRODUCTION OF NEW MAKE SPIRIT

Mashing, fermentation, and distillation was carried out in triplicate for all samples following a random production order. Malt was milled using a hammer mill with a 0.198cm screen. Infusion mashing was completed in a 38L insulated beverage dispenser. Mashing consisted of a single conversion step at 65°C. Malt (3kg) was combined with strike water (12kg) at 68°C. The liquefaction enzyme Hitempase 2XL (Kerry Ingredients, Co. Cork, Ireland; a *Bacillus licheniformis* derived α-amylase) was added at a rate of 0.535ml/L and the mashes were allowed 60 minutes for conversion [38]. After stirring to combine, samples were left unagitated for the duration of mashing. On average, the mash dropped 3°C during conversion. Mashes were cooled to 21°C±1°C using a copper immersion wort cooler. Water was added to standardize the original gravity to a specific gravity of 1.061. All fermentations were carried out in 19L HDPE fermenters sealed with lids that had been perforated with one 3mm hole to allow off gassing. At the onset of fermentation, 0.35ml/L of Bioglucanase GB (Kerry Ingredients, Co. Cork, Ireland; *Trichoderma longibrachiatum* derived β-glucanase) [39], 0.35ml/L of Amylo 300 (Kerry Ingredients; fungal amyloglucosidases)[40], 0.71ml/L of FermCap S (Kerry Ingredients; Dimethylpolysiloxane) [41], and 0.57g/L of M type yeast was added. Specific gravity, pH, and temperature was measured at the start of fermentation and daily throughout the four-day fermentation period. Wash was filtered through a fine mesh before analysis. Wash yield ranged from 15.9 to 17L. The resulting wash was double distilled using a 3L glass benchtop pot still. Copper mesh (15g) was added to the vapor path to catalyze reactions with sulfur. Heat was applied using a 100B TM112 heating mantle (Glas-col LCC, Terre Haute, Indiana) controlled by an Aldrich Digitrol II temperature controller (Millipore Sigma, St. Louis, Missouri) set to 96°C. For stripping distillations, 3L of wash was distilled until the distillate run-off dropped below an alcohol by volume (ABV) of five percent. The average flow rate of distillate from the condenser was 7.5 ml/min. Three stripping runs were performed for each fermentation and combined ahead of the spirit distillation. For the spirit distillations, 100ml of distillate was collected as heads (foreshots) and discarded. A hearts (main cut) fraction was collected until the ABV dropped below 50%, at which point the run was concluded without the collection of tails. Vapor temperature at the top of the still and ABV was recorded at five-minute intervals after the onset of runoff for both stripping and finishing distillations. ABV was measured using an Anton Paar DMA 35 density meter (Anton Paar, Graz, Austria). For each trial group, new-make spirits from the three replications were combined for analysis.

ANALYSIS OF NEW MAKE SPIRIT

The new make spirit was subjected to both analytical and sensory analysis. A spectrum of tests included the determination of polyphenol, higher alcohol, and ester concentrations and was completed by Brewing and Distilling Analytical Services (Lexington, Kentucky). Total polyphenols were assessed using the colorimetric — spectrophotometric method described by ASBC Methods of Analysis Beer-35 [42]. New make was assessed in duplicate at dilutions of 50% ABV and 5% ABV. Higher alcohols and esters were measured using gas chromatography with flame-ionization detection (GC/FID); new make was diluted to 50% ABV and assessed in duplicate.

Sensory analysis included a triangle test and quantitative descriptive analysis, these were used to assess overall sensory differences and more granular spirit aroma profile attributes respectively. For both tests, samples were bottled and provided to panelists with instructions for remote assessment. Sensory analysis guidelines laid out by Jack (2003) were followed, including diluting all samples to 20% ABV. Samples were presented as 50ml aliquots labeled with three-digit codes that were generated randomly. Triangle testing was carried out following methodology of the British Standards Institute [43] as has been done in recent studies [44]. Testing was completed by 32 individual assessors. The group of assessors was composed of professionals and academics with beverage or barley breeding experience. Quantitative descriptive analysis for the new make was carried out using methods described in ISO 6564:1985 [45]. Sensory attributes were selected from previous descriptive analysis studies of new make malt whiskey [46, 47]: pungent, phenolic, feinty, cereal, estery, oily, sulfury, and clean. The panel consisted of eight distillers with experience tasting new make spirits. Assessors were asked to nose and taste the samples. Assessors were asked to rank the chosen attributes on a scale of 0-5 (Table 2) [45]. A Scotch whiskey flavor wheel [8] was provided to panelists to help focus descriptions.

TABLE 2 Quantitative descriptive analysis scale.

SCORE	PERCEPTION
0	Not present
1	Just recognizable
2	Weak
3	Moderate
4	Strong
5	Very strong

RESULTS AND DISCUSSION

PRODUCTION CONSIDERATIONS

Malt was produced from both Buck and Lightning barley (Table 3). It was necessary to malt each variety under differing conditions (Table 1) to achieve acceptable modification and friability. In the finished malts, differences were seen in the levels of extract yield, β-glucan, protein, and diastatic power (DP). As expected, Buck malt had elevated extract yield (89.3% compared to 82.2%) and β-glucan levels (102 mg/L compared to 44mg/L). The likely causes for these results was the proportional increase in starch due to the removal of the husk. No processing issues (scorching or foaming) were seen in the lab scale trials due to elevated β-glucan levels. Protein levels differed between Buck (8.8 percent) and Lightning (10.6 percent), but the associated free amino nitrogen (FAN) levels for Buck (140 mg/L) and Lightning (172mg/L) were within the AMBA specified range of 140-190mg/L [48]. Diastatic power also differed but use of exogenous enzymes during mashing and

TABLE 3 Quality analysis of Buck and Lightning malt. A single replication was run for each quality parameter following ASBC methods.

QUALITY PARAMETER	BUCK	LIGHTNING
Moisture Content (%)	5.0	4.2
Friability (%)	96.4*	98.2
Extract (%)	89.3	82.2
Color (°SRM)	1.35	1.44
β-glucan (mg/L)	102.0	44.0
Total Protein (%)	8.8	10.6
Soluble Protein (%)	3.92	4.59
S/T (%)	44.5	43.3
FAN (mg/L)	140.0	172.0
DP (°L)	77.0	120.0
Alpha Amylase (DU)	45.0	46.4
Filtration	Normal	Normal
Clarity	Hazy	Clear
pH	5.78	5.81

*Completed by Oregon State University.

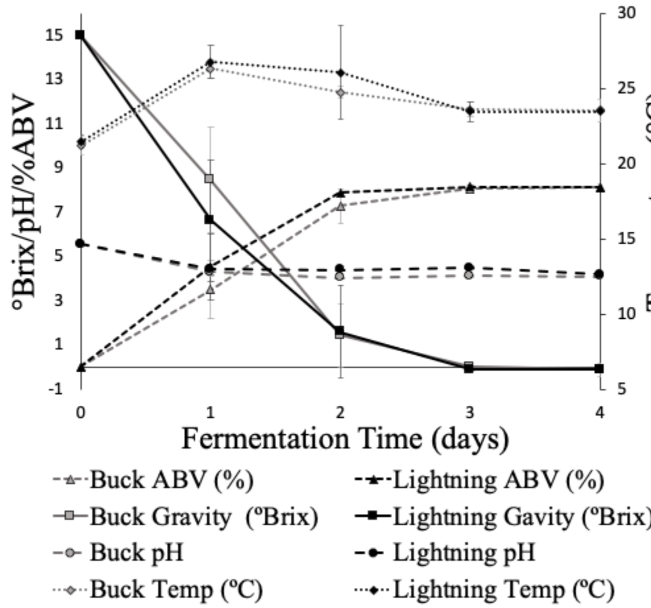

FIGURE 2 Fermentation profile for Lightning covered barley malt and Buck naked barley malt. Results are the mean of triplicate analyses ± standard deviation.

fermentation perhaps reduced impact on processing.

The specialized malting parameters needed to create high quality malt from naked barley may increase costs. In alignment with previous research by Edney and Langrell (2004), the malt produced for this project needed five days to modify completely. Drum malting naked barley may be problematic since the embryo and acrospire are more susceptible to damage [14]. In addition, premiums are often paid to growers for malt barleys that yield less than feed barleys [11]. Buck barley showed yields that were lower than covered barley (6,485 kg/ha compared to an average of 7,022 kg/ha for the covered checks). However, when yields were adjusted by 12 percent to account for husk removal, Buck yielded slightly more than the covered barleys studied [6]. The premiums that Buck will command are currently unknown.

Fermentations with these malts followed similar trajectories (Figure 2). Both malts resulted in a wash with an average final alcohol content of 8.1±0.2 % ABV. There was no statistical difference between the two groups. A two-tailed T test with a p-value of 0.001 showed a significant difference in the wash volumes between the varieties with Buck malt washes averaging 16.9L and Lightning malt washes averaging 16L. Wash volumes differed due to standardization of the original gravity.

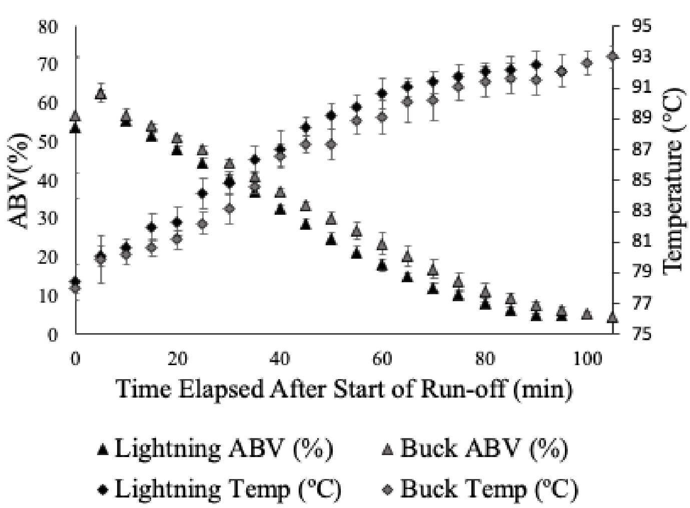

FIGURE 3 Temperature and ABV profiles during stripping distillation for Lightning and Buck barley malts. Results display mean measurement ± standard deviation. Nine replicates were conducted for each test group.

During the stripping distillations (Figure 3), distillate from Lightning malt mashes were consistently collected at a lower proof than distillate collected from Buck malt mashes. This resulted in the temperature at the top of the still reading higher at any given point during the distillation for Lightning, and the stripping distillations concluding 10 minutes earlier than Buck stripping distillations. Buck malt washes produced significantly more liters of absolute alcohol (LAA) during stripping runs (Table 4). Finishing distillations proceeded similarly (Figure 4); From 9L of wash, Buck malt produced on average 0.5 LAA of new make spirit compared to

0.45 LAA for Lightning malt — a significant difference (P = 0.003) (Table 4).

Previous research on naked barley has touted increased yields as one of the primary benefits [2]. Results from this experiment are aligned with previous works. Producing new make spirit from naked barley using grain-on methods resulted in an 11 percent increase in LAA (Table 4). This increase in efficiency may offset premiums associated with procuring and malting naked barley. The size and production capabilities of a distillery that is interested in producing malt whiskey will also impact the economics of using naked malt.

For a distillery with low throughput and no separation capabilities — as may be expected for a craft distillery producing several different styles of American whiskey — the capital cost of installing separation and milling equipment to produce malt whiskey using traditional methods may be high. In this case, paying a premium for naked barley may well be justifiable. Conversely, if the capital costs are more reasonable or the operation is large or focused solely on making malt whiskey, using naked barley may not be the most economical option.

TABLE 4 Yield data collected during stripping and finishing distillations. Low wines originating from the same fermentation were aggregated. Low wine data is presented as the average amount collected from each of the three fermentations ± standard deviation. New make data is the average from the three finishing runs ± standard deviation.

	BUCK	LIGHTNING
Low Wines volume (ml)	2166±53	2081±45
Low Wines %ABV	31.9±0.8	30.5±0.4
Low Wines LAA	0.69±0.1	0.64±0.2
New Make volume (ml)	696±6	627±19
New Make %ABV	72.4±0.1	72.3±0.1
New Make LAA	0.50±0.03	0.45±0.1

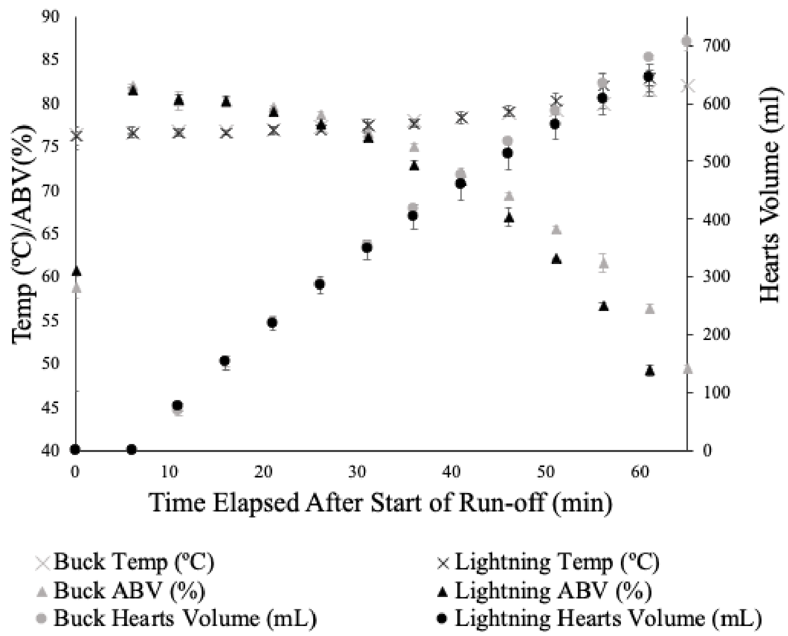

FIGURE 4 Average temperature, ABV, and spirit volume collected during finishing distillations for Lightning covered barley malt and Buck naked barley malt. Error bars show standard deviation. Three replications were conducted for each test group.

ETHYL CARBAMATE IN NAKED MALT

The glycosidic nitrile levels (Table 5) found in Buck malt were less than 0.5 g/tonne, the level at which barley varieties are said to be non-producers. The Lightning malt tested in line with low producers (between 0.5-1.5 g/tonne). Levels of glycosidic nitrile in Buck malt are similar to the levels seen in the variety Odyssey, the only EPH non-producing malt variety available in the United States [49]. The acrospire of germinated Buck barley was identified as an EPH producer using the methods of Cook and Oliver [50]. The removal of the acrospire during deculming likely contributed to the malt testing lower in glycosidic nitrile. Lightning has glycosidic nitrile levels similar to the widely used varieties such as CDC Copeland, USDA Endeavor, and AC Metcalfe [49].

Although levels of ethyl carbamate in whiskey are not currently regulated in the United States, it is a known carcinogen. Maximum levels have been set in Canada (150 ppb), Germany (400 ppm), and the Czech Republic (150 ppb) [30]. The reduction of ethyl carbamate associated with naked malt may allow producers to take advantage of new export markets and protect themselves against the possibility of future regulations.

TABLE 5 Glycosidic nitrile levels in Buck and Lightning malt. Sample GN producer status was defined as: Non-producer (<0.5 g/tonne), Low-producer (0.5-1.5g/tonne), High-producer (>5g/tonne). A single replication was conducted for each sample.

	GLYCOSIDIC NITRILE (G/TONNE)	PRODUCER STATUS
Buck	0.2	Non-producer
Lightning	1.4	Low-producer

SENSORY DIFFERENCES

While distilling malt whiskey from naked barley may offer increased efficiency and reduction of ethyl carbamate, evidence from the triangle test, analytical analysis, and quantitative descriptive analysis point to differences between new make spirit made from naked and covered barley. In the triangle tests, 18 of 32 participants correctly identified the sample that was different from the others. This corresponds to an α-risk of 1 percent [43]. This indicates strong evidence of an apparent difference. It has been shown that beers made from different barley varieties have perceptible variations in sensory attributes [33, 51]. However, the impact of variety on flavor is less significant than the impact of malting and yeast type [51]. Importantly for this study, the level of phenolic compounds may vary substantially between barley varieties [52]. In comparing the flavor of malt whiskies made from a naked and covered barley, some flavor differences may be due to varietal differences.

TABLE 6 Analysis of new make spirit at 50% ABV. Values are presented as the average of duplicate analysis.

NMS VOLATILE COMPONENT	BUCK	LIGHTNING
Acetaldehyde (mg/L)	7.15	7.68
Ethyl Acetate (mg/L)	23.1	24.6
Methanol (mg/L)	n.d.	12.4
n-Propanol (mg/L)	138.8	274.65*
Isobutanol (mg/L)	777.1	846.5
1-Butanol (mg/L)	3.8	3.66
Active and Iso-amyl Alcohol (mg/L)	1846.8*	2003.7*
Furfural (mg/L)	n.d.	n.d.
Total Fusel Oils (mg/L)	2766.5	3128.3
Total Polyphenols (mg/L)	n.d.	n.d.

n.d. = not detected
* = outside of instrument's calibration range

Analysis of the new make spirit (Table 6) indicated that the whiskies had similar levels of acetaldehyde, ethyl acetate, and 1-butanol. Whiskey made from Lightning was higher in methanol, n-propanol, isobutanol, active and iso-amyl alcohol, and total fusel oils. Polyphenols and furfural were not detected in either sample.

It has previously been suggested that polyphenols extracted from the husk during mashing and fermentation would be present in the new make spirit made from covered barley and that they would contribute to bitter and astringent off-flavors. In the present research, results do not support this hypothesis as polyphenols were not detected in either new make spirits (Table 6) and QDA analysis (Figure 5) indicates that spirit derived from husked barley was elevated in phenol character as compared to that produced using naked barley. Husk is not the sole source of phenolic compounds in barley and other tissues may potentially contribute to phenolic sensory characteristics, for instance hydroxycinnamic acids (ρ-coumaric and ferulic acids) can be derived from plant cell walls found throughout the barley grain, from here they can be extracted during mashing [53]. Through enzymatic or thermal reactions, these phenolic compounds with high flavor thresholds (such as ferulic acid) can be decarboxylated to compounds with low flavor thresholds (such as 4-vinyl guaiacol)[54]. 4-vinyl guaiacol is considered a desirable volatile in rye whiskies that contributes to the characteristic spiciness common to these spirits [55]. ρ-coumaric acid, ferulic acid and vanillin are respectively converted to 4-ethylphenol, 4-ethylguaiacol and 4-methyl-guaiucol by various strains of yeast and bacteria (Suomalainen and Lehtonen, 1979)[56]. For example, *Brettanomyces* yeast strains will convert phenols from malt into volatiles such as 4-ethylguiacol (Clove/smoky aroma) and 4-ethylphenol (smoky/phenolic aroma) (Vanderhaegen et al., 2003). As bacteria and wild yeast are often encouraged during whiskey fermentation through the use of wooden fermenters and unsterilized washes (Reid et al., 2020), these phenol-derived volatiles are likely to be found in new make whiskey. Strains of distiller's yeast are also known to produce 4-vinyl guaiacol [57] — the strain used in this experiment being a common choice for distillers [57, 58]. Interestingly, it has been found that mixed cultures of yeast and lactic acid bacteria result in less volatile

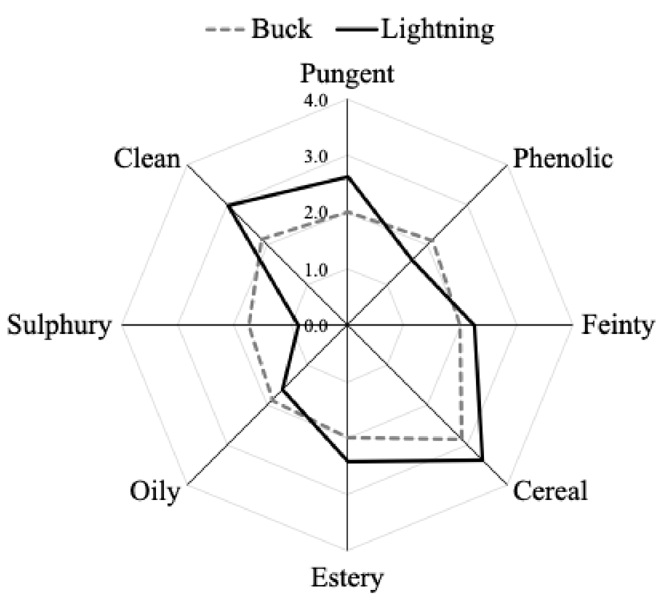

FIGURE 5 Quantitative descriptive analysis of whiskies made with Buck and Lightning malt. Results are the average of rankings by eight individual assessors.

phenols at the end of fermentation than do pure strains of yeast [56]. Rye varietal trials conducted by Michigan State University (East Lansing, MI) found a positive correlation between protein levels in different rye varieties and the levels of 4-vinyl guaiacol in new make rye whiskey [55]. The levels of 4-vinyl guaiacol and other phenolic-derived volatiles in new make spirit from this experiment were not tested. Further investigation into the levels of these compounds is needed to determine how they influence the flavor differences observed in this experiment. Furfural is another flavor active compound derived from cell wall and husk material [27, 59]. At levels between 20 and 30 mg/L, furfural has been said to add sweet, grainy, and nutty flavors in malt whiskey and is thought to influence the hotness of a spirit [59]. Typical levels seen in Scotch whisky are 1.5-9.95mg/L Similar to polyphenols, furfural was not detected in the new make spirit (Table 6). Previous studies have indicated that furfural levels in whiskey are derived from wood during maturation [60], with levels increasing rapidly during the first six months [61]. Quantitative Descriptive Analysis (QDA) (Figure 5) indicated that Cereal was the most intense attribute in both samples; the average rating for cereal character was 2.9 in new make made from Buck malt and 3.4 in whiskey made from Lightning malt.

Bathgate (2016) notes that excessive concentrations of amino acids and hydrolysed lipids in grain-on fermentations likely result in different higher alcohol profiles. He notes that whiskies made using these techniques have grainy, vegetal, and sulphury notes [9]. New make spirit made from Buck malt had lower levels of total fusel oils (2766.5 mg/L) than new make spirit made from Lightning malt (3128.3 mg/L)(Table 6) and reduced cereal, feinty, and pungent characteristics (Figure 5). Lightning new make spirit had n-propanol levels (274.65 mg/L) within the previously observed range of 180-605 mg/L [62] but higher levels of isobutanol (846.5mg/L) than had previously been observed (280-470 mg/L) [62]. Buck malt whiskey tested lower than the previously observed range for n-propanol (138.8mg/L) and higher than the range for isobutanol (777.1 mg/L).

FAN values between 150-180 mg/L are typically specified for malt destined for whiskey production [7]. Increased levels of FAN are associated with increased production of higher alcohols and esters during fermentation [33]. The Lightning malt used for this experiment fit within the acceptable range at 172 mg/L while the Buck malt used was just below acceptable levels at 140 mg/L (Table 3). Accordingly, Lightning produced higher levels of higher alcohols and esters (Table 6). Along with lower FAN levels in general, naked barley may have reduced levels of specific amino acids that are required by yeasts [63]. While reduction in specific amino acids may limit fermentability, no such issue was observed during this trial — both varieties had a terminal specific gravity of 1.0 (Figure 2). Naked barley malt had reduced FAN and elevated β-glucan as compared to husked malt, this suggests reduced modification of endosperm. It is interesting that the naked barley malt had a higher extract potential (89.3%) than husked malt (82.2%), perhaps as a result of the increased proportion of endosperm tissue. Isoamyl alcohol makes up 40-70 percent of the higher alcohols in alcoholic beverages [64]. Both whiskies in this study fall in that range with active and isoamyl alcohol representing 64 percent of total fusel oils in whiskey made from Lightning malt and 66 percent in whiskey made from Buck malt (Table 6). High levels of isoamyl alcohol are perceived as off flavors [57] and may have translated into the increased perception of feinty and pungent character in the whiskey made from Lightning malt (Figure 5). During maturation, the concentration of fusel oils in the whiskey is relatively unchanged; increases are accounted for by varying volatility of distillate components and evaporation from the barrel [65].

While ester levels (Table 6) measured similarly between the two malts — 23.1mg/L for Buck and 24.6 mg/L for Lightning — whiskey made from Lightning was perceived to have more ester character (Figure 5); assessors ratings averaged 2.4 for Lightning and 2.0 for Buck. Esters contribute solvent-like and fruity character to spirits [66]. Previous research has shown that there isn't a direct relationship between chemical composition and perceived flavor due to interplay between compounds and masking effects [67]. Removal of the husk may contribute to a reduction in ester production by reducing the level of beneficial microorganisms. At low levels, bacteria may improve spirit quality [68]. Lactic acid bacteria found on grain surfaces can contribute to the acidification of mash and have a positive effect on whiskey flavor [58, 69, 70]. Specifically, lactic acid bacteria have been shown to increase fruity, floral, and sweet aromas in new make malt whiskey [44].

Whiskey made from Buck barley was perceived to have more prominent sulphur character (Figure 5). The amino acid metabolism of yeast produce sulphur aromas that contribute to the heaviness of a spirit [57]. Sulphur compounds have vegetal, rotten egg, and rubbery aromas [71]. Fermentation temperature, yeast strain, and yeast pitching rate may influence the production of sulphur during fermentation [72]. Sulphur levels are reduced due to reactions with copper in the still [71] — spirits made using a stainless steel still had higher concentrations of dimethyl trisulphide (DMTS) than spirits made using a copper still [47]. Since a glass still with a limited amount of copper packing was used in this experiment, it is unsurprising that some sulphur character is present in the new make whiskey. New make spirit from a copper pot still would likely have lower levels of DMTS and other sulphur compounds. Sulphur character can be further reduced with maturation in heavily charred barrels [71].

CONCLUSIONS

Increased extract yield was achieved in the new make spirit produced from naked barley using grain-on production methods. This aligns with previous studies that have used naked barley to make spirits from filtered worts. Concentration of GN in naked barley was similar to that expected of non-producing barley varieties, perhaps as a result of acrospire removal during malt processing. New make spirit made with naked barley using grain-on techniques had lower levels of higher alcohols than new make spirit made with covered barley under the same conditions. A difference in flavor between the two new make spirits was perceptible on a sensory basis but interestingly whiskey produced using naked barley was not perceived to be reduced in phenolic character as compared to whiskey made from husked barley. Future research is needed to assess the source of perceived differences. Producing malt whiskey from naked barley using grain-on production methods may allow American craft distillers to efficiently produce high quality spirit without investing in new production equipment. The reduced GN levels seen in naked barley malt may open export markets in regions that regulate ethyl carbamate in spirits.

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CONFLICTS OF INTEREST

The authors declare no conflict of interest.

CRediT STATEMENT

Jamie Burns — Conceptualization; Investigation; Writing — original draft

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