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Composition of Peats Used in the Preparation of Malt for Scotch Whisky Production—Influence of Geographical Source and Extraction Depth

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Peat is burned during malt kilning to provide flavor compounds in Scotch malt whisky. The aim of this work was to establish whether peats from different locations in Scotland are chemically distinct and could impart different flavors. Peat samples from four locations (Islay, Orkney, St. Fergus, and Tomintoul) were analyzed using Curie point pyrolysis in combination with gas chromatography−mass spectrometry (Py-GC-MS). Peat pyrolysates from Islay and St. Fergus were rich in lignin derivatives, while those from Orkney and Tomintoul had higher levels of carbohydrate derivatives. Also, Islay and Orkney peat pyrolysates were rich in nitrogen-containing compounds and aromatic hydrocarbons, respectively. The depth of peat extraction was found to have an additional effect on peat composition as the levels of carbohydrate derivatives reduced with increasing depth. Where peat is used in whisky production, the observed differences in peat composition could potentially impact flavor, an important consideration if the peat used for malt production is changed by either choice or necessity.

KEYWORDS: GC-MS; peat; pyrolysis; Scotland; whisky

INTRODUCTION

Some Scotch malt whiskies, particularly those from the island of Islay, are noted for their smoky flavors. These flavor compounds are derived from the burning of peat during the kilning of the malted barley. The constituents of this smoke or "peat reek" are adsorbed by the malt and impart characteristic flavors to the spirit that survive maturation to become key quality attributes for Scotch malt whiskies (*1*). The peat used by the Scotch whisky industry is currently sourced from various locations across Scotland, particularly from the northeast of the mainland and the islands of Islay and Orkney.

The chemical composition of peat is derived from a combination of plants and microorganisms, the soil−water quality, and the secondary substances produced during the decomposition process. Generally, it is the more persistent, less reactive structural elements such as lignin and cellulose that contribute to the solid structure of peat. In a previous study on the chemical composition of peat, the most significant chromatographic peaks identified were due to phenolic compounds related to lignin (*2*).

Lignin, the second most abundant polymeric organic substance in the world, is characteristic of the tissues of higher plants, gymnosperms, and angiosperms, where it typically occurs in the vascular tissues (*3*). The monomeric units from which lignin is biosynthesized have characteristic substitution patterns around the benzene ring. Lignin precursors are believed to be *p*-coumaryl, coniferyl, and sinapyl alcohols—the monolignols (**Figure 1**) (*4*). The relative proportions of these monomers in lignin vary between different vascular plant species (*5*). Gymnosperm (nonflowering plant) lignin is a polymer of coniferyl alcohol. Most angiosperm (flowering plant) lignin is a mixed polymer of coniferyl and sinapyl alcohols. Grass (angiosperm) lignin, however, is composed of a mixed polymer of coniferyl, sinapyl, and *p*-coumaryl alcohols. Additionally, in grass lignin, aromatic or cinnamic acids are esterified to the Cγ-hydroxyl group of the side chains in the lignin polymer (*5*).

Sphagnum mosses are examples of nonvascular plants that are characterized by a type of polyphenolic network that is different from the true lignin present in vascular plants (*6*).

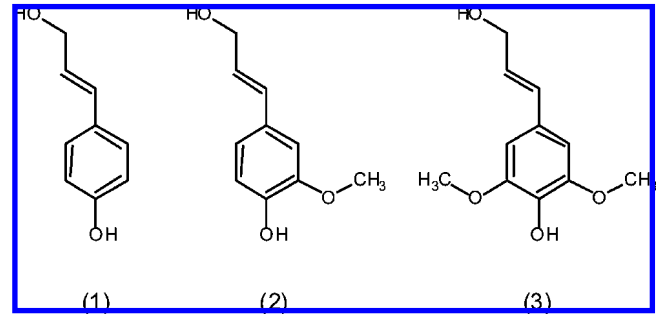

Figure 1. Lignin precursors. (1) *p*-Coumaryl alcohol, (2) coniferyl alcohol, and (3) sinapyl alcohol.

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Table 1. Geographical Locations of Peat Samples Used in This Study[a]

geographical location	OS National Grid reference	sample codes
Islay (Castlehill, Gartbreck, and Glenmachrie)	NR3650 (Castlehill), NR2858 (Gartbreck), NR3350 (Glenmachrie)	I1, I2, I3
Orkney	HY3806	O1, O2, O3
St. Fergus	NK0553	S1, S2, S3
Tomintoul	NJ2020	T1, T2, T3

[a] Peat samples were previously characterized by FT-IR (*8*).

Sphagnum-derived peat gives a high yield of *p*-hydroxyl phenolics relative to syringyl and guaiacyl phenols, resulting from a lack of mono- and dimethoxyl-substituted phenyl propene monomers in its polyphenolic network. This serves as an organochemical fingerprint of *Sphagnum (7)*.

In addition to lignin, cellulose and hemicelluloses also make a significant contribution to peat composition. Cellulose acts as the main structural component of plant cell walls and can be characterized as a linear high-molecular-weight polymer built up exclusively of β-D-glucose (anhydroglucopyranose) units (*3*). Hemicelluloses are found in close association with cellulose in the cell wall. Hemicelluloses differ from cellulose by inclusion of various sugar units, by much shorter molecular chains, and by a branching of the chain molecules (*3*). Five neutral sugars, glucose, mannose, and galactose (the hexoses) and xylose and arabinose (the pentoses), are the main constituents of hemicelluloses. Some hemicelluloses additionally contain uronic acids. Simple sugars, amino acids, and other water-soluble components of the living tissues are present in low concentrations in peat or may even be entirely absent.

Earlier work using Fourier-transform infrared spectroscopy (FT-IR) has shown that peat from different geographical locations in Scotland is chemically distinct (*8*). This technique, however, does not provide details of chemical composition. Here, we used Curie point pyrolysis in combination with gas chromatography and mass spectrometry (Py-GC-MS) to show that peat varies in several classes of key flavor compounds according to geographical location.

MATERIALS AND METHODS

Samples. Samples were collected from the same depth at four geographical locations; three representative samples were selected from each location (**Table 1**). At sites where peat was cut along banks [Orkney and Islay (Glenmachrie)], it was also possible to take samples from different depths to assess the effect of depth on peat composition. These depth profiles were positioned where the peat banks were at their deepest. At Orkney, five samples were taken, from just below the surface to the bottom of the bank at 30 cm intervals (Op0−Op4). At Islay, four samples were taken, from about 10 cm below the surface to about 30 cm from the bottom of the bank, at 25 cm intervals (Ip0−Ip3).

Sample Preparation. Peat samples were air-dried to a moisture content of <20% before initial reduction to a soil-like consistency using a Bosch AXT Rapid 180 garden shredder (Robert Bosch Limited, United Kingdom). Samples were then ground to a fine dust using a SPEX 6700 freezer/mill (Glen Creston Limited, United Kingdom). Samples (300 mg) of the finely ground peat were suspended in 5 mL of UHQ water and homogenized. One or two drops of peat suspension were applied onto a ferromagnetic wire using a microcapillary tube. The Curie point temperature of the wire was 610 °C (*9*). Wires were dried at room temperature while being rotated constantly to ensure an even coating of the sample around the wire. All samples were analyzed in duplicate.

Analytical Instrumentation. Pyrolysis was performed using a Horizons instruments Curie point pyrolyzer (Horizon Instruments Ltd., United Kingdom). Each prepared sample was connected to the probe of the pyrolyzer and manually inserted into the radio frequency coil. The pyrolyzer was then allowed to equilibrate for a few minutes. Pyrolysis heating was initiated and held for 3 s during which time the wire reached its Curie point temperature. The pyrolysate then passed onto the column within the gas chromatograph.

GC-MS was performed on a Hewlett-Packard 5890 series II gas chromatograph coupled to a 5971 mass spectrometer (Agilent Technologies UK Limited, United Kingdom). The column used was a 30 m × 0.25 mm ZB5 ms capillary column with a film thickness of 0.5 μm (Phenomenex, United Kingdom). Analysis was carried out in split mode. The carrier gas was He, the head pressure was 11 psi (giving a flow of approximately 1 mL min^{-1} at 100 °C), and the split flow was 5 mL min^{-1}. The inlet temperature was maintained at 250 °C throughout the analysis. The initial oven temperature was 40 °C, held for 1 min, increasing to 280 at 6 °C min^{-1} with a final hold time of 9 min. The mass spectrometer was operated in the electron impact mode, and ions from 35 to 400 amu were scanned at a rate of 2 scans per second. The GC line temperature was maintained at 310 °C throughout the analysis.

All peak quantifications were made on integrated single ion peaks to diminish coelution problems. To account for differences in sample size, peak area data were normalized by dividing the peak area by the total identified peak area in each chromatogram.

Compound identities were obtained initially by comparison of their mass spectra with those found in the National Institute of Standards and Technology (NIST) library (version 2.0) (Gaithersburg, United States). To support the identification of compounds by their mass spectra, linear retention indices were calculated for all compounds using the *n*-alkanes as reference substances (*10*). The columns used for the calculation of linear retention indices were a 30 m × 0.25 mm ZB5 capillary column with a film thickness of 0.5 μm (Phenomenex) and a 30 m × 0.25 mm RTX-200 capillary column with a film thickness of 0.25 μm (Restek, United Kingdom).

Statistical Analysis. Analysis of variance (ANOVA) and principal component analysis (PCA) were performed using Unistat statistical software (version 5.0) (Unistat Ltd., United Kingdom). Statistically significant differences were determined at ($P < 0.05$).

RESULTS

Identification of Pyrolysis Products. In total, 106 pyrolysis products were identified in the pyrolysates produced from the peat samples (**Table 2**). The compounds were broadly split into the following classes: phenolic compounds, carbohydrate derivatives, aromatic compounds, and nitrogen-containing compounds. The phenolic compounds were further divided into specific lignin markers (guaiacols and syringols) and less specific phenolic compounds (henceforth referred to as phenols) such as catechols and phenols themselves. The aromatic compounds refer to those compounds of an aromatic nature that could not be included in one of the other classes.

Composition of Peat from Different Geographical Locations. Py-GC-MS analysis of samples from the four geographical locations was carried out, and the peak area data for the 106 identified compounds were normalized. To eliminate redundant data, an ANOVA was carried out on the normalized peak area data to determine those compounds that were having a significant effect on the separation of the four geographical locations. In this way, the number of compounds was reduced from 106 to 92 (compounds **2**, **18**, **33**, **41**, **43**, **44**, **55**, **60**, **61**, **66**, **73**, **74**, **77**, and **95** were removed). PCA was then carried out using normalized peak area data for the 92 significant compounds. Using geographical location as a factor, ANOVA carried out on the principal component values showed that the PCA model produced three components, explaining 85.38% of variance, which significantly differentiated peat samples from the four locations.

The data for the first two principal components are plotted in **Figure 2**. By examining the PCA loadings for this plot, it

Table 2. Compounds Detected by Py-GC-MS of Peat Samples

peak no.	compound class[a]	compound name	RT[b]	RI (ZB5)[c]	RI (RTX-200)[c]	QI[d]	MW[e]	Identification[f]
1	C	acetic acid	2.25	674	815	60	60	MS, RI
2	A	benzene	2.81	657	<800	78	78	MS, RI
3	C	2,3-pentanedione	3.31	700		100	100	MS
4	C	2,5-dimethylfuran	3.46	706	<800	96	96	MS, RI
5	C	vinylfuran	3.78	721		94	94	RI
6	N	1-methyl-1*H*-pyrrole	4.07	737		81	81	MS, RI
7	N	pyridine	4.25	742	891	79	79	MS, RI
8	N	pyrrole	4.32	751	857	67	67	MS, RI
9	A	toluene	4.71	766	834	91	92	MS, RI
10	C	(2*H*)-furan-3-one	5.42	805	1027	84	84	RI
11	C	3-furaldehyde	5.81	812		95	96	MS, RI
12	N	2-methylpyridine	5.92	826	950	66	93	MS, RI
13	C	furfural	6.28	832	1048	96	96	MS, RI
14	A	ethylbenzene	7.07	863	926	91	106	MS, RI
15	N	methylpyridine 2	7.11	868	1034	66	93	MS
16	C	acetol acetate	7.15	869		116	116	MS, RI
17	C	5-methyl-2(3*H*)-furanone	7.19	867		98	98	MS, RI
18	A	xylene 1	7.31	871	938	91	106	MS
19	C	cyclopentenedione 2	7.58	877		96	96	MS
20	C	cyclopentenedione 3	7.68	881		96	96	MS
21	A	styrene	7.92	893	977	104	104	MS, RI
22	A	xylene 2	7.95	896	970	91	106	MS
23	C	2-methyl-2-cyclopentene-1-one	8.25	907	1127	67	96	MS, RI
24	C	(5*H*)-furan-2-one	8.33	918	1279	55	84	MS, RI
25	C	2-acetylfuran	8.50	911	1137	110	110	MS, RI
26	A	methoxybenzene	8.61	918		108	108	MS, RI
27	C	2-hydroxy-2-cyclopenten-1-one	8.82	926	1129	98	98	MS
28	C	5-methyl-2(5*H*)-furanone	9.10	934	1314	55	98	MS
29	C	3-methyl-2,5-furandione	9.26	949		68	112	MS
30	C	5-methylfurfural	9.86	965	1213	110	110	MS, RI
31	C	2*H*-pyran-2-one	10.07	973		68	96	MS, RI
32	P	phenol	10.34	986	1088	94	94	MS, RI
33	A	benzofuran	10.95	1000	1117	118	118	MS, RI
34	C	4-hydroxy-5,6-dihydro-(2*H*)-pyran-2-one	11.05	1004		114	114	RI
35	C	3-hydroxy-2-methyl-2-cyclopentene-1-one	11.41	1025	1260	112	112	MS, RI
36	C	cyclotene	11.71	1037	1251	112	112	MS, RI
37	C	2-acetyl-5-methylfuran	11.93	1039	1290	109	124	MS, RI
38	C	2,3-dimethyl-2-cyclopenten-1-one	12.01	1043	1311	67	110	MS, RI
39	C	4-methyl-5*H*-furan-2-one	12.14	1052	1331	69	98	MS
40	A	indene	12.35	1049	1150	115	116	MS, RI
41	P	*o*-cresol	12.44	1058	1161	108	108	MS, RI
42	N	2-pyridinecarbonitrile	12.74	1069		104	104	MS, RI
43	A	acetophenone	12.93	1070	1294	105	120	MS, RI
44	P	*m*-/*p*-cresol	13.05	1081	1194	107	108	MS, RI
45	C	methylfuroate	13.32	1092	1343	95	126	MS
46	G	guaiacol	13.46	1096	1271	109	124	MS, RI
47	C	maltol	14.14	1122	1379	126	126	MS, RI
48	C	2-methyl-5-hydroxy-(4*H*)-pyran-4-one	14.70	1142		126	126	MS
49	P	2-ethylphenol	14.74	1140	1239	107	122	MS, RI
50	N	benzyl nitrile	14.92	1143	1422	117	117	MS, RI
51	P	dimethylphenol 1	15.08	1152	1263	107	122	MS
52	C	2,3-dihydro-3,5-dihydroxy-6-methyl-4(*H*)-pyran-4-one	15.09	1153		144	144	MS, RI
53	P	dimethylphenol 2	15.14	1152	1263	107	122	MS
54	A	3-methyl-1*H*-indene	15.27	1155	1251	115	130	MS
55	A	4-ethyl-1,2-dimethylbenzene	15.31	1158	1237	119	134	MS
56	P	4-ethylphenol	15.54	1171	1283	107	122	MS, RI
57	G	4-methoxy-3-methylphenol	15.92	1183	1234	123	138	MS
58	C	3,5-dihydroxy-2-methyl-(4*H*)-pyran-4-one	16.22	1197	1388	142	142	MS, RI
59	G	methylguaiacol	16.27	1199	1387	123	138	MS, RI
60	P	pyrocatechol	16.34	1210	1345	110	110	MS, RI
61	A	2,3-dihydrobenzofuran	16.70	1211	1344	120	120	MS, RI
62	A	dihydrobenzofuran 2	16.96	1223	1355	120	120	MS
63	P	unknown phenolic 1	17.22	1239		110		MS
64	C	5-hydroxymethylfurfural	17.25	1238		97	126	MS, RI
65	P	ethylmethylphenol	17.44	1242	1348	121	136	MS
66	A	2-coumaranone	17.57	1250	1412	134	134	MS
67	P	propenylphenol 1	17.84	1258		134	134	MS
68	P	4-propylphenol	17.96	1262	1378	136	136	MS
69	P	methylbenzenediol	17.96	1269	1409	124	124	MS
70	P	3-methoxy-1,2-benzenediol	18.05	1272	1480	140	140	MS
71	G	ethylguaiacol	18.46	1287	1472	137	152	MS, RI
72	N	indole	19.00	1303	1503	117	117	MS, RI
73	A	2-methyl-2,3-dihydrobenzofuran	19.08	1306	1433	134	134	MS
74	A	2-methylnaphthalene	19.21	1306	1451	142	142	MS, RI

Table 2. Continued

peak no.	compound class[a]	compound name	RT[b]	RI (ZB5)[c]	RI (RTX-200)[c]	QI[d]	MW[e]	Identification[f]
75	G	vinylguaiacol	19.43	1324	1530	150	150	MS, RI
76	A	1,3-dimethoxybenzene	19.53	1325		138	138	MS, RI
77	A	1-methylnaphthalene	19.61	1325	1464	142	142	MS, RI
78	P	propenylphenol 2	20.06	1345	1493	134	134	MS
79	S	syringol	20.25	1358	1608	154	154	MS, RI
80	G	eugenol	20.41	1365	1546	164	164	MS, RI
81	G	propylguaiacol	20.65	1374	1562	137	166	MS, RI
82	P	4-ethylcatechol	21.00	1392	1544	123	138	MS
83	N	3-methyl-1*H*-indole	21.30	1396	1594	130	131	MS, RI
84	G	vanillin	21.51	1410	1738	151	152	MS, RI
85	G	*cis*-isoeugenol	21.64	1415	1602	164	164	MS, RI
86	P	4-acetylphenol	22.43	1447	1736	121	136	MS, RI
87	S	methylsyringol	22.46	1454	1714	168	168	MS, RI
88	G	*trans*-isoeugenol	22.66	1458	1675	164	164	MS, RI
89	G	unknown guaiacyl isomer 1	23.39	1489	1718	147		MS
90	G	acetovanillone	23.49	1498	1843	151	166	MS, RI
91	G	unknown guaiacyl isomer 2	23.51	1496	1737	147		MS
92	G	methylvanillate	24.13	1526		151	182	MS, RI
93	S	ethylsyringol	24.18	1533	1791	167	182	MS, RI
94	G	guaiacylacetone	24.38	1541	1930	137	180	MS, RI
95	A	dibenzofuran	24.46	1534		168	168	MS, RI
96	S	vinylsyringol	25.10	1573	1852	180	180	MS, RI
97	G	guaiacyl propanaldehyde	25.58	1593	1916	180	180	RI
98	S	propylsyringol	25.98	1616	1880	167	196	MS, RI
99	S	methoxyeugenol	26.86	1660	1920	194	194	MS, RI
100	S	syringaldehyde	27.11	1669	1848	182	182	MS, RI
101	S	unknown syringyl monomer 1	27.60	1693	1958	192		MS
102	S	unknown syringyl monomer 2	27.73	1701	1971	192		MS
103	S	propenylsyringol	27.94	1709	1999	194	194	MS
104	S	acetosyringone	28.54	1744	2175	181	196	MS, RI
105	S	syringylpropanone	29.17	1781	2251	167	210	RI
106	S	syringyl propanaldehyde	30.28	1836	2239	210	210	MS, RI

[a] Letter indicates class of compound: C, carbohydrate-derived (*11*); G, guaiacols; S, syringols; P, phenols; N, nitrogen-containing compounds; and A, aromatics. [b] RT, retention time (minutes). [c] RI, retention index. [d] QI, quantitation ion. [e] MW, molecular weight. [f] Identification method: comparison with library mass spectrum (MS) and comparison with literature retention index data (RI) (*12*−*17*).

was found that PC 1, which described 60.11% of the variance, mainly separated samples according to the ratio of carbohydrate derivatives to guaiacols, syringols, and phenols (**Figure 2** and **Table 3**). St. Fergus and Islay samples, located on the positive side of PC 1, were characterized by high percentages of guaiacols, syringols, and phenols in the pyrolysate. Tomintoul and Orkney samples, located on the negative side of PC 1, were characterized by relatively high proportions of carbohydrate derivatives in the pyrolysate. Furthermore, the samples from Tomintoul were found to yield a significantly higher proportion of carbohydrate derivatives than the samples collected from Orkney.

Unlike the specific, lignin-derived phenolic compounds (guaiacols and syringols), the phenols were less well clustered. While the majority of these compounds colocalized with the lignin-derived phenolic compounds, three were found to locate to the negative side of PC 1 [phenol (**32**), 2-ethylphenol (**49**), and 4-acetylphenol (**86**)]. Phenol and 2-ethylphenol were characteristic of the Orkney peat pyrolysates, while 4-acetylphenol characterized the Tomintoul pyrolysates.

The distribution of the subclasses of phenolic compounds was examined quantitatively (**Table 3**). First, there was a difference in the ratio of lignin derivatives (guaiacyl and syringyl compounds) to phenols. The highest ratio of lignin compounds to phenols was obtained from St. Fergus peats, and the lowest was obtained from Tomintoul. Second, lignin derivatives were further divided into guaiacyl and syringyl derivatives, and the distribution of these two subclasses was determined (**Table 3**). The pyrolysate with the highest lignin content (St. Fergus) was also found to have the highest syringyl compound content.

The second principal component, describing 15.93% of the variance, generally separated Tomintoul and St. Fergus peats on the negative side from Islay and Orkney peats on the positive side. One exception was O3, which was more similar to Tomintoul peats than the other Orkney peats. Compounds from two classes had a particularly high positive effect on this component. The first class was the nitrogen-containing compounds, with the exception of 1-methyl-1*H*-pyrrole (**6**), which was relatively abundant in the St. Fergus peat pyrolysate. The second class was the aromatic compounds, with the exception of 1,3-dimethoxybenzene (**76**), which was relatively abundant in the St. Fergus peat pyrolysate.

Carbonyl lignin derivatives, notably guaiacyl derivatives, were also found to be higher in Orkney and Islay peat pyrolysates. The ratio of acetovanillone (**90**) to *trans*-isoeugenol (**88**) has previously been used as a descriptor for the amount of lignin oxidation undergone in peat (*18*). This ratio was highest in the Orkney and Islay sample pyrolysates (**Table 3**).

Figure 3a shows the separation of Islay samples from the rest on PC 3. Additionally, S1 was quite distinct from S2 and S3 on this component. Explaining 9.34% of the total variance, this was a relatively important separation. The differentiation of the Islay samples was found to be due to a relative abundance of particular compounds in the Islay pyrolysates, notably dihydrobenzofuran 2 (**62**) (**Figure 3b**). S2 and S3 yielded relatively low levels of these compounds as compared to S1.

Impact of Extraction Depth on Composition. Samples taken from depth profiles at two locations, Orkney and Islay (Glenmachrie), were also analyzed using Py-GC-MS. Normalized peak areas were obtained for the 92 significant compounds

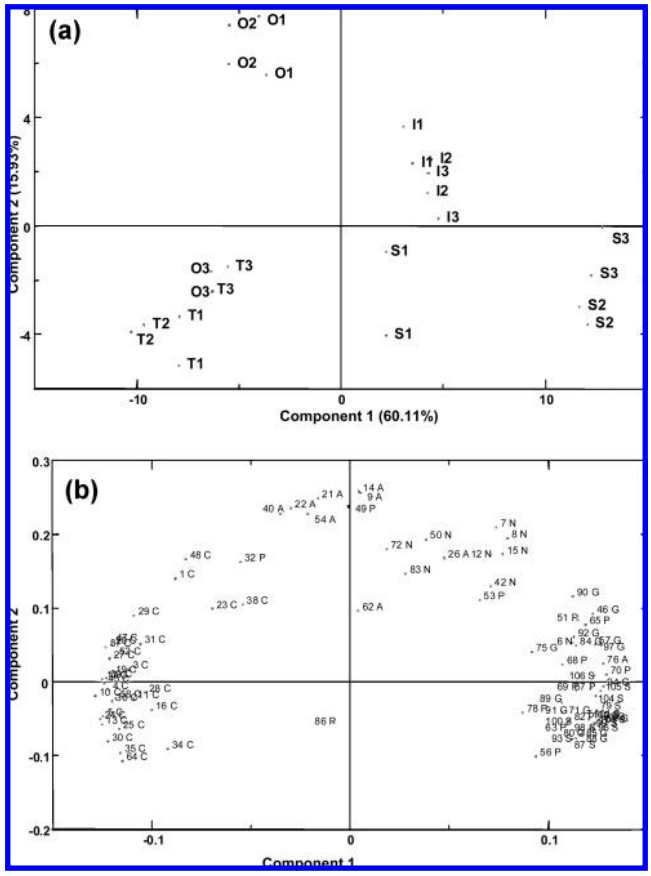

Figure 2. PCA of Py-GC-MS of peat from different geographical locations. (**a**) Score plot for PCs 1 and 2 (sample codes: **Table 1**). (**b**) Loadings plot for PCs 1 and 2 (number and letter codes: **Table 2**).

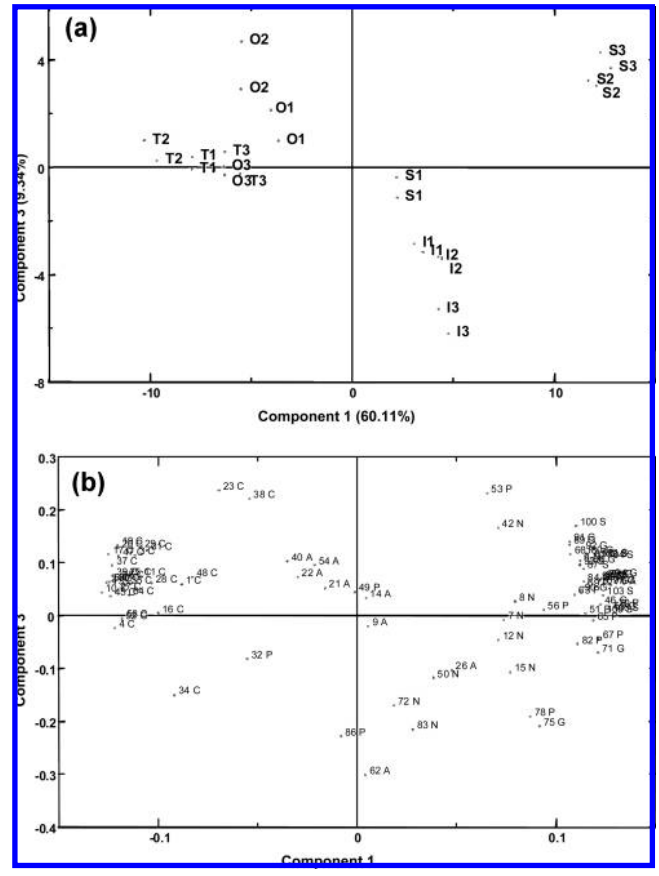

Figure 3. PCA of Py-GC-MS of peat from different geographical locations. (**a**) Score plot for PCs 1 and 3 (sample codes: **Table 1**). (**b**) Loadings plot for PCs 1 and 3 (number and letter codes: **Table 2**).

used for the characterization of peats from different geographical locations, and these were used to examine changes in composition with depth (**Table 4**).

A decrease in the carbohydrate content with increasing depth was detected in both profiles (**Table 4**). From the data in **Table 4**, it was apparent that the greatest reduction in carbohydrate content occurred in the upper 60 cm of the Orkney depth profile. Below this, carbohydrate losses were relatively small. With the reduction in the proportion of carbohydrates at increasing depth, there was a general increase in the proportions of the other classes of compound.

In the case of the Islay depth profile, the carbohydrate loss was greatest in the upper horizon of the peat profile, in this case, the upper 25 cm (**Table 4**). The proportion of guaiacols, phenols, and syringols increased with increasing depth. However, there were higher proportions of nitrogen-containing compounds and aromatic compounds in Ip1 and Ip2 as compared with Ip0 and Ip3.

To look at how variation in peat composition due extraction depth compared to the variation due to geographical location, the peak area data from the depth profile study were combined with the data from the geographical location study and analyzed using PCA (**Figure 4**). This analysis showed that, in the case of the Orkney depth profile, extraction depth had a relatively large impact on composition. The younger peat samples taken from the top of the depth profile, Op0 and Op1, were similar to the Tomintoul samples and O3. Op2 was more similar to O1 and O2. Older peat samples, Op3 and Op4, were similar to Islay samples.

Table 3. Relative Abundances of Pyrolysis Products from Peat from Different Geographical Locations

parameter	geographical location				*p* values[e]
	Islay[d]	St. Fergus[d]	Orkney[d]	Tomintoul[d]	
carbohydrate derivatives (%)	26.55 (5.7)	23.46 (23.0)	43.10 (6.6)	50.46 (6.0)	<0.0001
guaiacyl compounds (%)	20.57 (4.8)	23.55 (16.2)	14.33 (8.8)	11.11 (16.1)	<0.0001
syringyl compounds (%)	7.82 (10.2)	14.67 (36.2)	4.21 (19.8)	3.31 (13.4)	<0.0001
phenols (%)	14.56 (11.1)	12.82 (10.5)	12.30 (3.8)	11.60 (4.7)	0.0013
nitrogen-containing compounds (%)	3.23 (13.4)	2.50 (19.3)	2.81 (27.5)	1.19 (34.2)	<0.0001
aromatic compounds (%)	12.45 (8.3)	6.85 (13.2)	10.10 (15.7)	7.07 (8.5)	<0.0001
lignin derivatives: phenols[a]	1.97 (14.6)	2.96 (15.2)	1.51 (11.8)	1.25 (18.2)	<0.0001
syringyl: guaiacyl[b]	0.38 (8.4)	0.62 (32.3)	0.29 (16.8)	0.30 (13.1)	<0.0001
acetovanillone: *trans*-isoeugenol[c]	2.49 (12.1)	1.23 (14.5)	3.07 (44.8)	1.98 (6.8)	0.0018

[a] Ratio of total lignin-derived compound peak areas to total nonspecific phenols peak area. [b] Ratio of total syringyl compounds peak area to total guaiacyl compounds peak area. [c] Ratio of acetovanillone (**90**) peak area to *trans*-isoeugenol (**88**) peak area. [d] Figures in parentheses are the relative standard deviations for the six analyses of samples from each location. [e] *p* values from ANOVA using geographical location as factor.

Table 4. Pyrolysis Products of Peat from Different Depths at Two Sites: Orkney (Op0 to Op4) and Islay (Ip0 to Ip3)

sample no.	carbohydrate derivatives (%)	guaiacyl compounds (%)	syringyl compounds (%)	phenols (%)	nitrogen-containing compounds (%)	aromatics (%)
Op0 (0 cm)	51.73 (2.3)	15.39 (2.2)	4.93 (4.1)	6.50 (1.2)	1.54 (5.9)	6.81 (2.6)
Op1 (30 cm)	48.28 (2.6)	15.36 (6.4)	4.91 (2.0)	11.79 (11.0)	1.31 (1.8)	8.19 (4.6)
Op2 (60 cm)	33.34 (2.7)	16.56 (3.8)	5.79 (7.8)	16.75 (2.5)	2.99 (5.4)	10.55 (1.8)
Op3 (90 cm)	28.15 (3.4)	22.56 (5.8)	7.79 (4.1)	13.64 (1.0)	2.67 (3.8)	11.67 (1.6)
Op4 (120 cm)	23.14 (1.0)	20.76 (3.8)	6.83 (0.6)	17.28 (2.1)	3.08 (3.8)	13.37 (3.9)
Ip0 (0 cm)	43.47 (7.0)	18.52 (6.3)	5.48 (6.0)	10.25 (19.8)	2.45 (14.4)	10.53 (5.5)
Ip1 (25 cm)	26.87 (1.9)	21.56 (3.7)	7.67 (2.2)	15.12 (4.2)	3.79 (10.7)	12.33 (2.3)
Ip2 (50 cm)	23.29 (1.3)	20.82 (3.8)	7.11 (3.3)	17.78 (1.5)	3.08 (3.8)	12.43 (2.1)
Ip3 (75 cm)	20.42 (1.7)	23.62 (2.5)	10.46 (4.8)	16.88 (1.1)	2.27 (0.8)	10.86 (1.5)

sample no.	lignin derivatives: phenols	syringyl: guaiacyl	acetovanillone: trans-isoeugenol
Op0 (0 cm)	3.12 (1.5)	0.32 (1.9)	1.31 (2.9)
Op1 (30 cm)	1.73 (16.3)	0.32 (4.4)	2.16 (1.0)
Op2 (60 cm)	1.34 (7.4)	0.35 (4.0)	2.23 (6.8)
Op3 (90 cm)	2.23 (6.3)	0.35 (1.7)	2.22 (8.7)
Op4 (120 cm)	1.60 (5.1)	0.33 (3.1)	3.50 (4.4)
Ip0 (0 cm)	2.40 (25.8)	0.30 (0.3)	2.45 (5.7)
Ip1 (25 cm)	1.94 (7.5)	0.36 (1.4)	2.67 (5.1)
Ip2 (50 cm)	1.57 (5.1)	0.34 (0.6)	2.54 (2.7)
Ip3 (75 cm)	2.02 (4.3)	0.44 (2.3)	1.39 (2.2)

The Islay depth profile samples were less varied in composition than the Orkney samples (**Table 4**). Not surprisingly, therefore, with the exception of Lp0, they were all similar to the other Islay samples on the PCA plot shown in **Figure 4**. It was also noted that, with the exception of the Op0, Op1, and O3, all samples from the two island locations (Islay and Orkney) were separated on PC2 from the samples from the two mainland locations (St. Fergus and Tomintoul) regardless of extraction depth.

DISCUSSION

Py-GC-MS provided insights into differences in composition of peats from different locations in Scotland. It is important to note that while this technique shows how peats vary in composition, the process of peating during malt kilning differs from laboratory pyrolysis and will not necessarily yield the same compound species. Therefore, while Py-GC-MS can indicate what classes of compound may be affected when using different peats, the identities of specific compounds can only be determined by carrying out the industrial peating process.

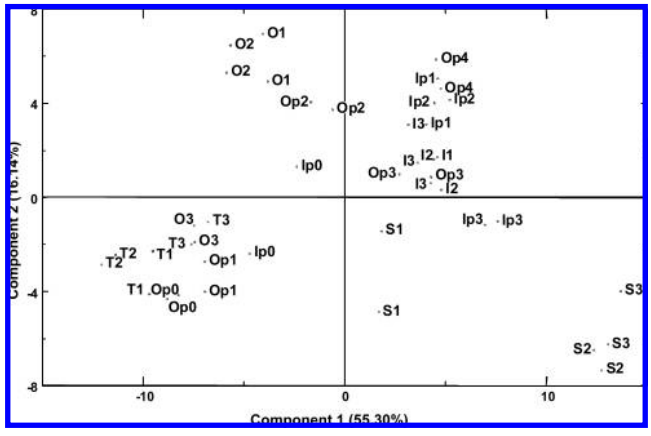

Figure 4. PCA of Py-GC-MS of peat from different geographical locations and different depths. Score plot for PCs 1 and 2 (sample codes: **Tables 1** and **4**).

Phenolic compounds such as phenols or guaiacols are known to be important for smoke flavor in Scotch malt whisky (*1*). The observed differences in the relative concentration of phenolic compounds produced from peats from different sources are industrially relevant and indicate that peats will vary in their contribution of these important flavor compounds (*19*).

We found that, in addition to yielding different total levels of phenolic compounds, peats from different locations also yielded different proportions of individual phenolic species. Different phenolic compounds have quite distinct aromas. For example, phenol has an aroma described as strongly phenolic, medicinal, antiseptic; guaiacol has an aroma described as aromatic, phenolic, burnt, woody, bacon, savory, smoky, and medicinal; and syringol has an aroma described as aromatic, phenolic, spicy, smoky, baconlike, sweet, medicinal, creamy, meaty, and vanilla (*20*). Whisky produced using peat from Tomintoul, for example, which had relatively high levels of phenols in the pyrolysate, may have a different aroma from whisky produced using St. Fergus peat with its high abundance of guaiacols and syringols.

Several guaiacyl-derived carbonyl compounds were more abundant in the pyrolysates produced from island samples relative to other lignin derivatives. Most notable in this respect was the relative increase in abundance of acetovanillone from the island peat. This compound has previously been identified as one that reflects an increase in lignin degradation, probably due to fungal action, which causes an increase in the relative abundance of lignin compounds containing a carbonyl group (*18*). Guaiacols that are vanillic in nature, such as acetovanillone, often have a vanilla aroma (*20*). The prominence of this type of compound from Islay and Orkney peat could again have an influence on whisky flavor.

With regard to carbohydrate derivatives produced by pyrolysis, compounds in this class are known to possess caramel and burnt flavor notes and so could contribute to the aroma of whisky (*19*). In wood smoke preparations, it has been reported that carbohydrate derivatives are responsible for the softening of the heavy aromas associated with phenolic compounds (*21*). This effect may be of relevance particularly in the case of Tomintoul

peat, which was found to give a relative abundance of carbohydrate derivatives.

Several nitrogen-containing compounds were found in the peat samples and were generally most characteristic of Islay peat. One potential source of nitrogen-containing compounds in peat is lignin-degrading fungi, which may have caused the elevation in oxidized lignin in the Islay peat. Although detected as relatively small peaks in the peat pyrolysates, compounds such as pyridines are known to have low odor thresholds and so could theoretically contribute to whisky aroma (*22*). Indeed, nitrogen-containing compounds such as pyridines have been detected previously in whisky at low levels (*23*, *24*).

Aromatic compounds were characteristic of Orkney samples O1 and O2, and these compounds may represent the products of lignin or other polyphenolic structure degradation (*9*). The potential impact of this class of compounds on whisky flavor is unclear. They do, however, indicate a difference in the composition of these peats, which could potentially affect flavor.

At those sites where peat is cut along banks, peat is extracted from all depths simultaneously, while at those locations where peat is extruded, the extraction depth will change over time. Extraction depth was found to have an additional influence on composition. FT-IR analysis was previously used to show that, with the possible exception of samples taken from the upper horizons of the depth profiles of both Orkney and Islay, peat from different depths showed chemical characteristics that were related to their geographical source (*8*). However, it must be noted that in terms of the compounds analyzed in this pyrolysis work, the composition of peat can alter significantly with depth. Therefore, the differences due to geographical location noted here can be affected by peat depth, particularly at locations were the peat is very deep.

In conclusion, while FT-IR can be used to distinguish between peats from different geographical locations, the pattern of the thermal degradation products detected by Py-GC-MS provides the chemistry responsible for this differentiation (*8*). Our results show the influence of source and depth on peat composition and indicate variations in compounds relevant to Scotch whisky flavor.

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