Flavour Components of Whiskey. III. Ageing Changes in the Low-Volatility Fraction

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The low-volatility wood-originating compounds isolated from whiskey by vacuum fractional distillation were analysed by high-resolution gas chromatography and mass spectrometry (GC-MS). Three phenolic esters previously unreported in whiskey were identified and confirmed by synthesis. Formation profiles for sixteen compounds were established in whiskeys aged for periods from 1.5 to 10 years in second-fill heavy-charred American Bourbon barrels. These profiles indicated significant increases for several compounds, especially in the older whiskeys. Ratios of aromatic phenolic aldehydes, and similar ratio changes during ageing, were different from reported data relating to other wood types and treatments. Further preparative separation by high-pressure liquid chromatography (HPLC) of the wood fraction followed by GC-MS allowed retention and mass spectral characterisation of additional compounds originating from wood. Sensory investigation indicated different and unique contributions from the HPLC cuts. Spiking of the three phenolic esters into a young whiskey gave a detectable increase in maturation intensity.

Freshly distilled whiskey is colourless with a pungent aroma and harsh taste. The practice of storage in oak casks modifies and significantly improves the sensory properties of the product. Maturation of distilled spirits in oak barrels takes place slowly and therefore over many years. The mechanisms involved in this barrel contribution include direct extraction of wood components, decomposition of wood components, and reaction of wood components both with each other and with components of the distillate (Nishimura & Matsuyama, 1989). Some of these reactions occur in the already complex matrix of the unaged whiskey with resultant difficulties for analysis of the new compounds produced and related subsequent changes.

The approach of this work was to attempt to interpret some of these complex changes by first isolating the relevant low-volatility compounds as a distinct fraction from the whiskey (MacNamara *et al.*, 2001a). A similar approach was used to isolate the high-volatility compounds from whiskey and to investigate their changes with ageing (MacNamara *et al.*, 2001b). In both cases the vacuum fractional distillation procedure separates either the high- or low-volatility compounds free from both the dominant ethanol and the complex fusel compounds. This allowed subsequent chromatography to be tailored to the specific compounds in each fraction.

When the low-volatility compounds of interest are isolated in this way, the increases in concentration of dominant and trace compounds can be measured for natural barrel-aged whiskey. A different approach towards the identification of oak wood aroma compounds involved the extraction of such compounds from oak wood chips and shavings in model solutions. In one study over one hundred compounds were identified from the steam distillate of methanol extracts of white oak shavings (Nishimura *et al.*, 1983). Extraction of volatile and non-volatile compounds by 60% ethanol from oak hardwood shavings was also investigated (Nykänen, *et al.*, 1984). Maximum extraction occurred after three months and, with the aid of subsequent analysis, carbohydrates and a range of carboxylic acids were identified.

In both of these studies the presence of ß-methyl-γ-octalactone was not reported even though the isomers of this compound had previously been identified in spirits stored in oak casks (Suomalainen & Nykänen, 1970). The *cis* and *trans* isomers were also shown to be major constituents of oak wood (Masuda & Nishimura, 1971) and subsequent work confirmed the presence of these compounds in spirits stored in oak wood (Nishimura & Masuda, 1971; Guymon & Crowell, 1972). Organoleptic thresholds of both isomers have been established in 30% alcohol solution and a positive correlation has been established by a scale method, involving ranking for aroma and taste evaluation, between desirable aged flavour and lactone content for ten commercial whiskeys (Otsuka *et al.*, 1974). Other studies have shown that production of lactones is substantially enhanced by thermal oxidation of lipid precursors during charring or toasting of wood (Maga, 1989), and no such treatment was indicated in both of the previously mentioned studies where lactones were not reported. Therefore care must be taken with data from model solution experiments, as they may not fully represent the natural ageing process in barrels. Isolating the wood compounds by vacuum fractional distillation from barrel whiskey at different ages as was proposed for this study allows a more accurate and authentic representation of the chemical changes to be established.

High-pressure liquid chromatography (HPLC) is usually the technique of choice for analysing the low-volatility compounds produced during ageing (Lehtonen, 1984). However, since it

offers limited resolution and suffers from lack of a routine universal detector, high-resolution gas chromatography – mass spectrometry (GC-MS) was selected as a better alternative to analyse the isolated lower-volatility flavour compounds in aged whiskey. In addition, programmed temperature vaporisation (PTV) followed by chromatography on a stable high-temperature column was selected for the elution of low-volatility compounds previously not amenable to gas chromatography. Despite the limitations of HPLC, it still appears very useful as a technique to segregate the principal wood-originating compounds prior to GC-MS analyses. Thus it is believed that the above integrated analytical strategy would allow the characterisation of both abundant and trace compounds formed during ageing. Such analysis of premium whiskeys aged for long periods of time in order to develop significant maturation flavour should permit a better understanding of compound development during maturation and may allow the achievement of greater effects in less time with important implications for production costs.

MATERIALS AND METHODS

Material

Whiskey at 1.5, 3, 5 and 10 years old was used for both GC-MS investigations of low-volatility compounds and formation profiles for selected compounds over the full time range. The 10-year-old sample was also used for additional GC-MS analysis after a further preparative chromatographic procedure. All samples were from standard once-used American Bourbon barrels and at strengths between 60% and 65% vol/vol ethanol, depending on the natural evaporation loss during ageing. These samples at various ages were composites of twelve aliquots from similar casks at the same age.

Sample preparation

The general whiskey vacuum fractional distillation separation has been described previously (MacNamara *et al.*, 2001a).

Essentially, the distillation removes the matrix ethanol together with those volatile and fermentation compounds that partition into the first four fractions, leaving the compounds of interest in an aqueous fraction 5. Two 250 mL aliquots of fraction 5 from the 10-year-old whiskey were each continually extracted overnight with 60 mL of Freon 11/Dichloromethane (90%/10%). The organic layers were bulked and subsequently concentrated in a Kuderna Danish apparatus to 1 mL. This extract was further fractionated by preparative HPLC and the fractions obtained were assembled into composites, re-extracted as above and concentrated for GC-MS analysis. Triplicate 50 mL portions of the whiskey fraction 5 at the different ages were similarly extracted and concentrated after addition of 6 ppm 2, 3, 4-trimethoxy benzaldehyde as internal standard. These extracts were analysed by simultaneous GC-MS and GC-FID to quantitatively determine concentration increases of the selected compounds with time. For quantification the area ratio of each peak of interest to the internal standard at the different ages was used to give amounts relative to the known added amount of the internal standard.

Preparative high pressure liquid chromatography

The apparatus was a Waters Maxima 820 (Waters Corporation, Milford, MA., USA) with gradient capability and an SM400 multi UV/VIS detector set at 254nm and 2.0 AUFS. The column was a 250 mm x 10 mm Lichrospher RP-18 (Merck Gmbh, Darmstadt, Germany) with a 10 mm particle size. An ethanol/water gradient was used starting from 10% ethanol and increasing at 1.5% ethanol/min to 100% ethanol. A further period of 15 min at 100% ethanol was used to clean the column. Thirty injections were made using the concentrate from 500 mL of the 10-year-old fraction 5. The injection volume was 20 µL per run with 36 fractions per run collected on a time basis.

Gas chromatography-mass spectrometry

The GC-MS analyses of the 10-year-old fraction 5 concentrate and similar concentrates of its HPLC composites were performed on a Hewlett-Packard 5890 GC coupled to a 5971 Mass Selective Detector (Hewlett-Packard, Palo Alto, CA., USA). The column used was a chemically bonded XTI5 fused silica capillary (50 m x 0.25 mm i.d. x 0.25 df, Restek, Bellefonte, PA., USA) directly interfaced to the ion source of the mass selective detector. The oven temperature was programmed from 60°C at 2°C/min to 300°C, where it was held for 10 min. Linear temperature programmed retention indices were calculated using the same conditions after injection of a mixture of C9 to C26 alkanes. The mass selective detector was operated in scan mode at a detector setting of 1600 V and an ionisation voltage of 70eV. The scan range was 25-400amu, and spectra were acquired at 2 scans/sec. Helium was used as carrier gas at 1 mL/min. 1 µL of each sample was injected in splitless mode using a programmed temperature injector (CIS-3, Gerstel Gmbh) with an empty deactivated vigreux glass liner. The injector temperature was programmed from 40°C at 10°C/sec to 300°C. The splitless time was 1 min. Mass spectra and retention indices of authentic compounds were used for identification. Compounds were either purchased (Sigma-Aldrich, Poole, Dorset,UK) or were available from internal collections. Ethyl homovanillate, ethyl syringate and ethyl homosyringate were synthesised as described later.

Simultaneous mass spectrometric and flame ionisation detection

The MS and FID analyses on the triplicate fraction 5 concentrates at various ages were performed using the same GC-MS conditions as above, but with a split injection of 1/10 to ensure resolution of all compounds for quantification. At the column exit a micro crosspiece (Gerstel Gmbh) with individual fused silica segments to MS and FID was used to achieve the simultaneous detection. Quantification was obtained from the FID signal with spectral confirmation from the MS signal.

Synthesis of phenolic esters

Ethyl syringate and ethyl homovanillate were synthesised from the corresponding commercially available acids by esterification with p-toluene sulfonic acid in the presence of an excess of ethanol. Homosyringic acid was synthesised via a rhodanine complex from syringaldehyde (Fischer & Hibbert, 1947; Tanner & Osman,1987) and esterified as above. The following IR, NMR and MS data are in agreement with the proposed structures.

Ethyl homovanillate

GC data: non polar index: 1645 (on XTI-5), polar index: 2721 (on FFAP).

Spectroscopic data:- ^{1}H-n.m.r. (400MHz) δ ($CDCl_3$): 1.23 (3H, t, -$OCH_2\underline{CH_3}$, J=7.4Hz), 3.5 (2H, s, -CH_2-), 3.83 (3H, s, -OCH_3), 4.12 (2H, q, -$O\underline{CH_2}CH_3$, J=7.4Hz), 5.73 (1H, s, -OH), 6.74 (1H,dd, 6-H, J=2, 8.36 Hz), 6.78 (1H,d, 2-H, J=2Hz), 6.83 (1H,

study. In this regard, for Bourbon in heavy charred new barrels, maximum amounts of phenolic aldehydes will be immediately released into the spirit from degraded lignin beneath the heavy char layer, and their relative ratios could be different from phenolic aldehydes produced in once-used Bourbon barrels by the slower acidic ethanolysis mechanism. This also agrees with the substantial differences, both in absolute levels of phenolic aldehydes and in the vanillin/coniferaldehyde and syringaldehyde/sinapaldehyde ratios reported for uncharred wood soaked in 60% ethanol, in comparison to similarly treated charred wood (Nishimura *et al.*, 1983). In the Cognac study the wood type was also different and initial charring of the wood was not employed. An additional complicating factor is that the Cognac was initially matured for one year in new oak, and then transferred to used casks for further ageing (Puech *et al.*, 1984). In a separate study on Armagnac in Limousin oak the increase in the ratios of vanillin to coniferaldehyde and syringaldehyde to sinapaldehyde did not materialise until after fifteen years of ageing (Puech, 1981). This is not in agreement with the previously mentioned Cognac study, where a regular decrease over fifty years was presented. However, the Armagnac results are in agreement with data presented here and may imply that if whiskey is left sufficiently long in cask, such a similar increase in these ratios may occur. Normal commercial whiskey is not usually matured for more than twelve years.

Relative levels and ratios of the aromatic aldehydes at various stages of ageing were also clearly different in a comparasion of aged Armagnac and Rum (Puech *et al.*, 1977). In this case the additional factor of climatic condition was cited, in addition to different wood type and pretreatment. In rum-producing countries warehouses are generally heated during winter to produce an average temperature of 20°C to 25°C (Kervegant, 1946), and this temperature increase will cause an acceleration in oxidation reactions (Mourgues *et al.*, 1973). Therefore, characteristic analytical profiles of aged distilled spirits must be interpreted in terms of the different variables of wood type, wood pre-treatment, barrel history in the re-usage cycle, and the climatic conditions for storage during maturation. There is a possibility here for commercial producers to use such profiles to aid authentication of their own products in the market place.

HPLC separation of fractions

Separation of the fraction 5 extract from the 10-year-old whiskey according to the HPLC procedure previously described is represented in Fig. 4.

Thirty-six fractions were collected per run, comprising an initial zero fraction, thirty-four fractions during elution of compounds and a final fraction. The opinion of experienced whiskey tasters was that the zero and final fractions had little sensory interest and these were excluded from further investigation.

Small aliquots of the intermediate thirty-four fractions were then analysed by GC-MS and based on these results the fractions were combined into four composite fractions in order to achieve the maximum segregation of the dominant 2-phenyl ethanol, whiskey lactones and the four phenolic aldehydes. After extraction and GC-MS analysis these composites give the traces in Fig. 5.

From this figure it is clear that the phenolic aldehydes, 2-phenyl ethanol and the whiskey lactones were substantially segregated into separate composites, allowing cleaner mass spectra of the minor components.

Preparative HPLC has also been used previously for concentrating flavour compounds from distilled spirits (Piggott *et al.*, 1992). However, this study simply involved initial dilution of 200 mL of the spirit to 5% ethanol followed by pumping of the diluted solution through the HPLC column to enrich flavour com-

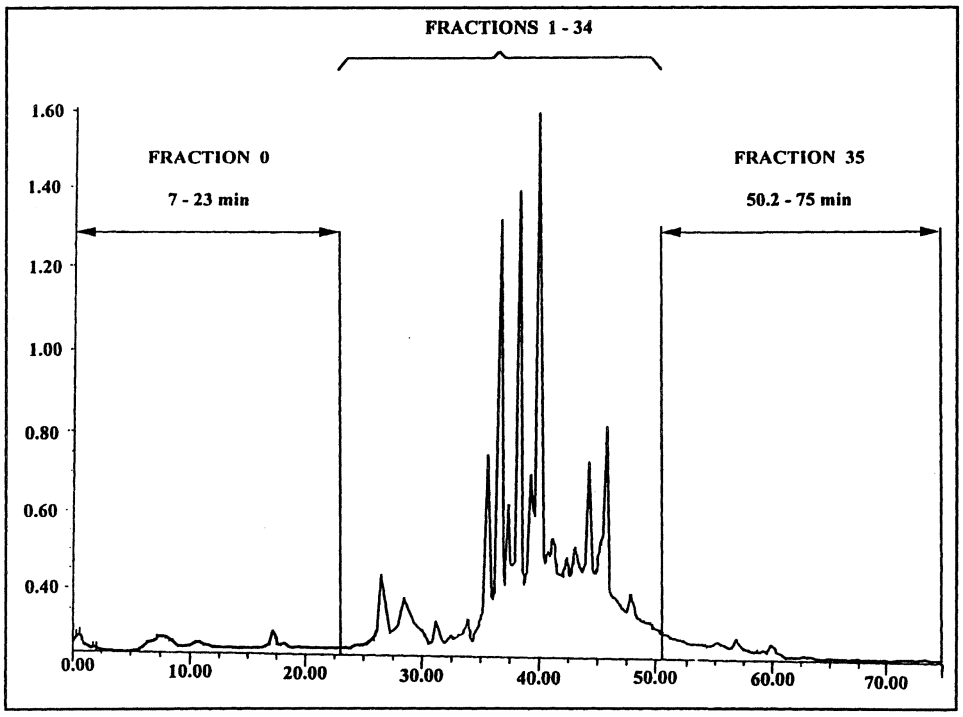

FIGURE 4

HPLC-UV [1)] trace of fraction 5 concentrated extract [2)]. [1)] Ethanol-water gradient. [2)] 36 cuts per injection as indicated.

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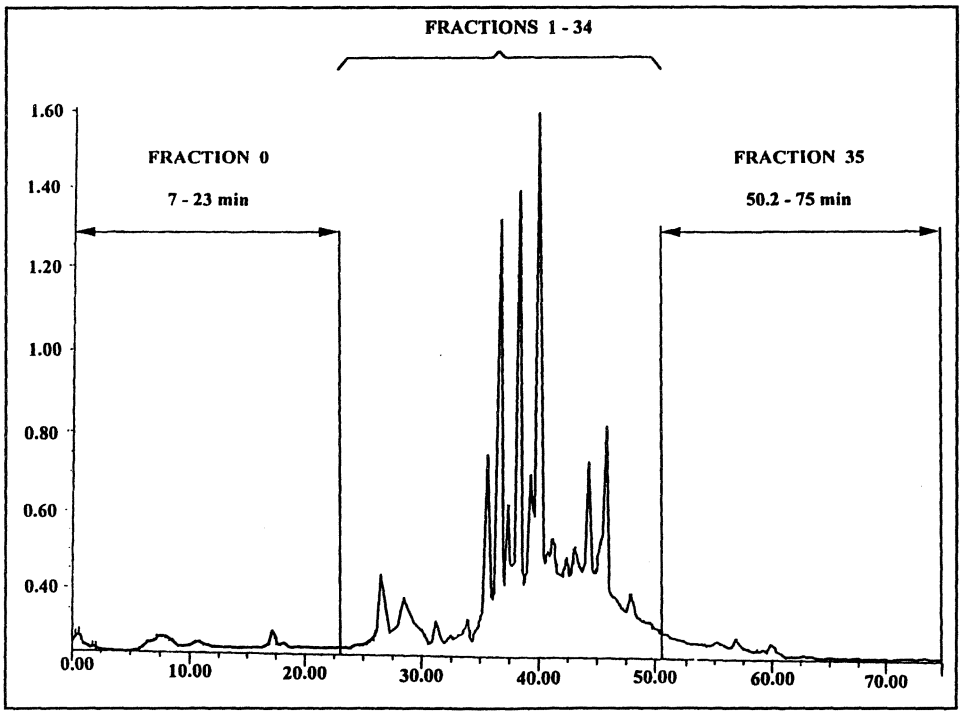

FIGURE 4

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'ional compounds found in aged whiskey after distillation and preparative liquid chromatography.

o.	Compound	Ret.[a] Index	Mass Spectral Data [c]
	Propiovanillone [b]	1609	151(100), 180(55, M^+), 123(49), 108(25), 52(17), 65(16), 77(13), 51(10)
	Homosyringyl ethyl ether [b]	1714	167(100), 168(57), 212(47, M^+), 123(23), 153(20), 95(15), 107(13), 77(12), 53(11)
	Propiosyringone [b]	1850	181(100), 210(43, M^+), 182(20), 153(18), 67(13), 108(13), 123(12), 138(10)
	Butyl vanillate [b] (principal loss of m/z 73)	1874	151(100), 123(17), 152(11), 149(10), 224(4, M^+)
	2-Ethoxy-(4 hydroxy-3,5 [b] dimethoxy-phenyl)-ethyl acetate	2035	211(100), 123(42), 95(16), 212(12), 140(10), 155(10), 167(9), 284(9, M^+)
	3-Ethoxy-3(4-hydroxy-3-methoxy phenyl) methyl propanoate [b]	2064	181(100), 182(18), 153(14), 67(11), 123(10), 108(10), 254(9, M^+)
	Vanillic acid derivative	2093	151(100), 207(11), 123(10), 152(9), 252(6, M^+)
	Possible isomer of peak 36 (principal loss of m/z 73)	2108	181(100), 182(16), 154(21), 179(15), 153(12), 254(9, M^+)
	Syringic acid derivative	2493	182(100), 85(96), 167(85), 181(72), 81(54), 83(40), 57(26), 154(25), 168(25), 237(17), 310(11, M^+)
	Vanillic acid derivative	2567	151(100), 123(18), 274(11, M^+), 108(9), 152(8), 243(6)
	Unknown	2694	272(100, M^+), 211(24), 168(20), 136(19), 197(17), 273(17), 207(15)

ɔrogrammed retention indices.

ɔture.

lance in brackets. Suggested molecular ion is the highest mass detected in the electron impact mass spectrum.

me either through extraction from the wood or ions in the aqueous ethanol medium.

ilar compounds not found in this study has been y heating of oak wood with absolute alcohol in /drochloric acid (Puech, 1984), or after pyroly- forage material (Ralph & Hatfield, 1991). droxypropiosyringone, vanilloylmethylketone, illone and syringylmethylketone. However, as was discussed earlier, constitutes classical represents an extreme treatment in compari- lic ethanolysis which occurs during natural d would be expected to produce different akdown pathways (Puech, *et al.*, 1978). terial represents a situation more similar to ourbon casks than to the once-used casks dy. In new charred barrels the main mech- f aromatic compounds is thermal degrada- reas in the once-used variety mild acidic y the dominant route (Nishimura *et al.*,

f sub-fractions

radient was used for the HPLC separa- ct, it was possible to examine the result- and taste. Table 4 summarises the opin- iskey taste panel.

t have been partitioned into the differ- upport the descriptions. The phenolic ohol, and the isomeric lactones were 1, 3 and 4, respectively. The sensory characteristics of these compounds are well documented and were reflected in the assessors' comments. None, or only trace amounts, of these dominant aroma-contributing compounds partitioned into composite 2, and subsequently allowed the indicated positive maturation characteristics to be assigned to composite 2 without interference or masking from other compounds.

Effect of phenolic esters on young whiskey aroma

The interesting composite 2 contained the three phenolic esters in addition to the compounds described in Table 3. Therefore it was decided to investigate the effect of addition of these three esters to a young whiskey to determine if maturation character increased.. Control samples were the original 3-year- and 10-year-old whiskeys. Initially sixteen judges were used, but in an initial screening judges who were not able to detect the 10-year-old product or those who did not rate the 10-year-old highest in maturation characteristics were excluded. Table 5 represents the results of the tasting after three months using the twelve remaining judges.

The maturation intensity of the 3-year-old whiskey, as well as the same sample spiked with two levels of the three phenolic esters (amounts found in the 10-year-old whiskey and double this level), were ranked significantly lower than that of the 10-year-old whiskey. This illustrates that these three esters, even at double the level found in a 10-year-old whiskey, did not account for the higher maturation odour intensity of the 10-year-old product. However, at double the level found in the 10-year-old whiskey, they caused a significant increase in the maturation odour intensity of the 3-year-old whiskey. This intensification of the maturation odour to some extent demonstrates that these esters are in

TABLE 4

Description of HPLC composites by an experienced whiskey panel.

Sample	Description
Composite 1 HPLC Cuts 1 – 20	Sweet, woody aroma. Strong vanillin note. Dull wood taste.
Composite 2 HPLC Cuts 20 – 25	Spicy delicate aroma. Intense taste characteristics similar to well-aged whiskey.
Composite 3 HPLC Cuts 26 – 30	Rose-like aroma. Also fatty ester type notes. Fatty bland taste.
Composite 4 HPLC Cuts 31 –34	Intense sweet coconut aroma. Little taste.

TABLE 5

Maturation intensity rankings on young whiskey, young whiskey after spiking and old whiskey.

Sample	Maturation intensity (Mean)
3-Year-Old Whiskey	38,85^{c}
3-Year-Old Whiskey+ Level 1 Spike	46,54^{bc}
3-Year-Old Whiskey + Level 2 Spike	49,54^{b}
10-Year-Old Whiskey	72,69^{c}

* LSD (p = 0.05) = 10.08.

fact making a contribution to the odour intensity, although not significantly at the lower level of spiking.

Although these esters may contribute significantly to the aroma intensity of aged whiskey, this contribution should also be evaluated together with several other aroma impact components previously reported and also found in this study.

CONCLUSIONS

Vacuum fractional distillation followed by GC-MC analysis allowed construction of practical profiles of ageing changes during maturation of whiskey in second-fill heavy-charred Bourbon oak barrels. There is evidence to suggest that these ageing patterns may be related to wood type, its pre-treatment and fill history. Ratios of certain aromatic phenolic aldehydes were different from similar published data relating to other wood types and other treatments. Ratios of syringyl and guaiacyl phenolic aldehydes decreased rather than increased over ten years of ageing. These observations are fundamentally linked to a unique balance of extraction mechanisms, which in turn is related to the wood type and fill history of the barrel. An appreciation of the relative contribution of these maturation parameters can be used to investigate and improve the ageing flavour of whiskey.

A combination of vacuum fractional distillation and preparative HPLC allowed the maturation flavour of whiskey to be segregated into composites. This approach isolated a unique group of compounds, free from the known dominant aroma-contributing components, and these compounds were shown to be partially significant for maturation character.

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Errata

MacNamara, K., Van Wyk, C.J., Brunerie, P., Augustyn, O.P.H. & Rapp, A., 2001. Flavour components of whiskey. III. Ageing changes in the low-volatility fraction. S. Afr. J. Enol. Vitic. 22, 82-92.

Figure 5 on page 89 must be replaced by the following:

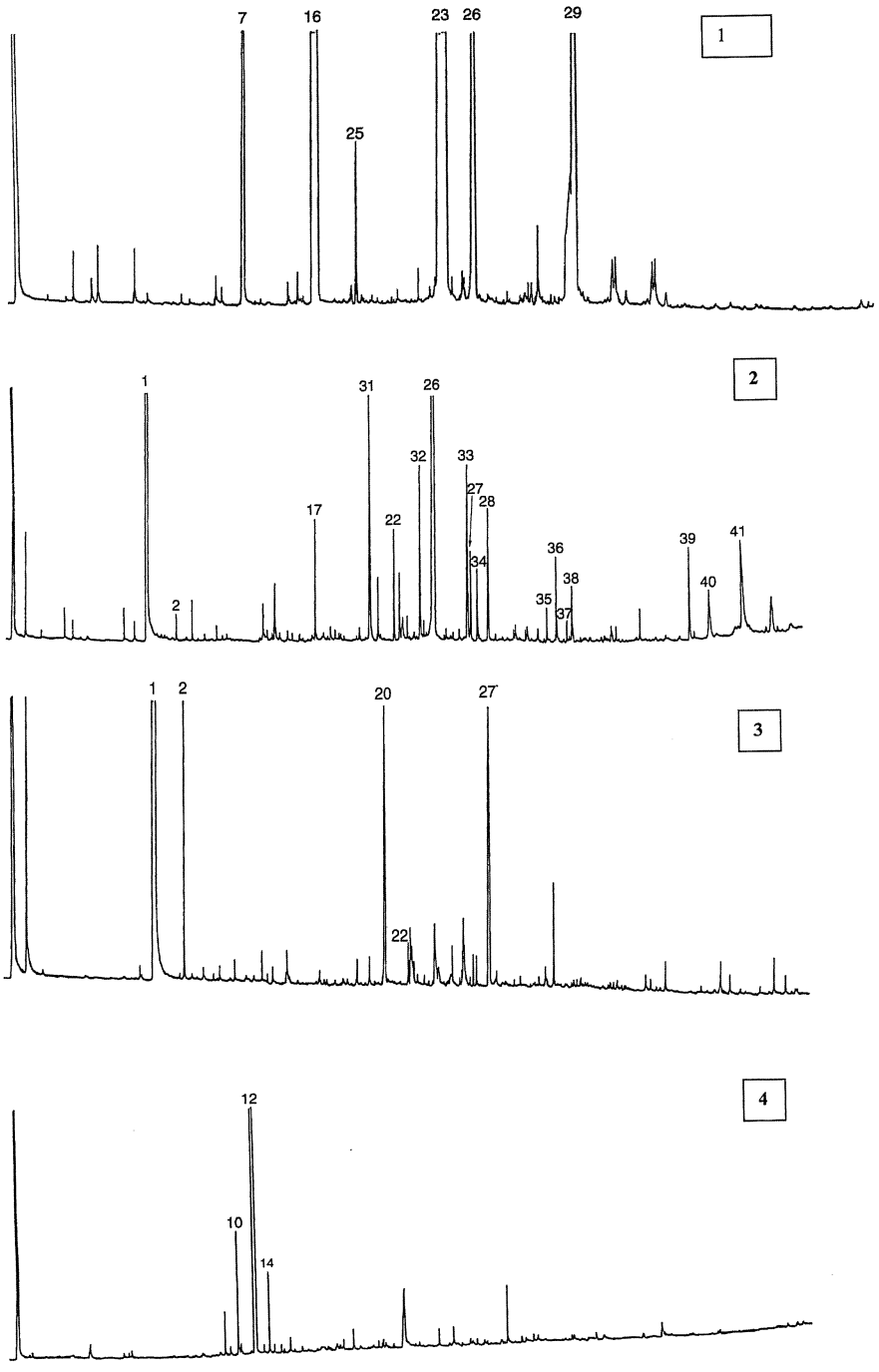

FIGURE 5

GC-MS traces [1–4] of extracts of composites after preparative HPLC separation of concentrated fraction 5 from 10-year-old whiskey. [1] HPLC cuts 1-20; [2] HPLC cuts 21-25; [3] HPLC cuts 26-30; [4] HPLC cuts 31-34. Peak identification in Tables 1 and 3.