Angels' share challenge

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We would like to invite you to participate in the Analytical Challenge, a series of puzzles to entertain and challenge our readers. This special feature of "Analytical and Bioanalytical Chemistry" (ABC) has established itself as a truly unique quiz series, with a new scientific puzzle published every other month. Readers can access the complete collection of published problems with their solutions on the ABC homepage at <http://www.springer.com/abc>. Test your knowledge and tease your wits in diverse areas of analytical and bioanalytical chemistry by viewing this collection.

In this challenge, flavorants are the topic. And please note that there is a prize to be won (a Springer book of your choice up to a value of €100). Please read on ...

Meet the angels' share challenge

The small portion of wine or distilled spirit that is lost during long aging in wood barrels is known as the "Angels' share" (if this "nip" is larger than two percent per year, the alertness of the tax collectors will awaken). Many flavoring compounds are extracted from the wood of the barrels during this time. In fact, several hundred flavorants have been detected in these complex beverages, including a gamut of alcohols, carbonyl compounds, carboxylic acids and their esters, terpenes, nitrogen-containing and sulfur-containing compounds, tannins and other polyphenolic compounds, and oxygen-containing heterocyclic compounds [1].

In this challenge we are looking for such a compound which occurs in whiskies, cognac, rum, and also old wine. The complexity of this subject is grand, which is why this challenge will be limited to whisky.

The flavor and color of whisky arises due to three reasons: the distillation, the cask maturing, and additives. During distillation, the flavor develops in part because of the presence of fermentation products, for example acetals, ketones, esters or aldehydes, and higher alcohols. Most of these compounds contribute to the hangover (veisalgia) and will not be given closer attention here. The additional flavor and color of whisky depends strongly on local regulations. For instance, a Scotch whisky may contain no additives other than the caramel coloring (E150a). Last, the presence of "our" flavorant in whisky is because of the aging process.

Laws in several jurisdictions require that whisk(e)y must be aged in wood barrels. Similar regulations exist for brandy, sherry, and cognac. In addition to the length of aging, the volume of the barrels and their storage location, the type of wood and its provenance also play an important role in the quality of the end product. The type of the wood used for barrels will be kept a secret in this challenge. This tree is a symbol of strength and endurance and a national tree of many countries. In Greek mythology it was sacred to Zeus and in Norse mythology it was sacred to Thor, and a legend goes that the Christianization of Germany was marked by the felling of this sacred tree by an Anglo-Saxon missionary in 723. Today, both the common name and the botanical (Latin) name of this tree features in the trivial names of "our" compound.

The barrels for aging alcoholic beverages are made from European and American trees. The choice between

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these two kinds of tree is especially important for wine producers. For maturing of whisk(e)y, different rules are prescribed by law. As an example, the “straight whiskey” must be stored in the United States for at least two years in new, charred wood containers; “Bottled in Bond” Bourbon whiskey liquor must age for four years whereas all Scotch whisky must be aged in wood barrels for at least three years and one day [2]. Therefore, it seems that only the fanciers of fresh distilled whisk(e)y, named “new spirit”, “moonshine”, or “poitin” underestimate the value of our flavor compound. All other consumers enjoy spirits matured in wood casks. Misleadingly, the maturing of Scotch whisky in a “new cask” does not mean the use of a fresh unused cask. In Scotland, the “first fill” typically describes maturing in an American cask formerly used to mature bourbon whiskey. Recently, a new trend, the so-called “finishing” has gained in popularity with the product known as “double matured” or “wood-finished”. Here, the spirit spends further time in a second cask, usually one that has been used to mature fortified wine, sherry, port wine, Madeira, or even standard wines. However, this may still not be the end of the life of a wood cask. For example, the pepper mash used to make Tabasco sauce is aged for three years in used whiskey barrels (Fig. 1).

The challenge

From the scientific literature, it appears that our compound was first reported at the end of the 1960s. For convenience, it was first christened after the peak number in the gas chromatogram of red wine flavorants. Shortly after the first description it was found that four possible stereoisomers can exist, and in the aftermath a few authors incorrectly assigned the naturally occurring isomer. The pure stereoisomers were obtained on a preparative scale in the mid-1980s and their sensory properties can now be analyzed with greater accuracy. However, only two diastereomers will be of interest in this challenge. Both of these diastereomers are found in spirits that have been aged in wood containers and their odor is described as “weedy”, “hay”, “celery”, “spicy” for one of them, and “sweet”, “cinnamon”, “fatty” for the other. The organoleptic description of the mixture of both diastereomers is “coconut” and “green”.

Although the first report of the compound isolated it “in amounts so small that only a relatively poor infrared spectrum could be obtained”, here the reader

Fig. 1 Part of the filling station in the whisky museum in the Dallas Dhu distillery in Scotland. The last barrel was filled here with a single malt Scotch whisky on March 16, 1983 and in 1988 it was re-opened to the public (photo R. Meusinger)

has the luxury set of spectra for structural analysis of this flavorant. The infrared spectrum (Fig. 2), the electron-impact mass spectrum (Fig. 3), and the NMR spectra (Figs. 4 and 5) were obtained from a synthetic mixture of the two diastereomers (courtesy of Dr Hans-Georg Schmarr, Head of Wine Analysis and Microbiology, Center for Wine Research, Neustadt/Weinstrasse, Germany).

Although irrelevant in IR and MS spectra, both diastereomers are distinguishable in the NMR spectra. All NMR spectra were obtained in CDCl_3 . In Fig. 4 the 500-MHz ^1H NMR, DEPT-135, and ^{13}C NMR spectra of a nonequivalent mixture of both diastereomers are given. In the ^1H NMR spectrum the integral value of the low-field shifted signal of the major component at 3.93 ppm was set to 1.0. The signals with unambiguous assignment to the major and minor components are colored red and blue, respectively. The chemical shift

Fig. 2 Infrared spectrum (liquid film)

Fig. 3 Electron-impact mass spectrum. Note the parent peak at m/e 156 and the base peak at m/e 99

Fig. 4 500-MHz ^1H NMR (top), DEPT-135 (middle, CH_3 and CH positive and CH_2 negative signals), and ^{13}C NMR (bottom) spectra of a synthetic mixture of both diastereomers of the compound in CDCl_3 relative to tetramethylsilane. The major and minor components are colored red and blue, respectively

Fig. 5 Two-dimensional ^1H -correlated COSY (top) and TOCSY spectra and the ^{13}C heteronuclear single bond (HSQC) and multiple bond (HMBC) correlation spectra (bottom)

region in the ^{13}C NMR spectrum is divided for the sake of clarity.

Figure 5 shows a set of two-dimensional NMR spectra. In addition to the ^1H -correlated COSY spectrum the TOCSY (TOtal Correlated SpectroscopY) spectrum is also given. Whereas the COSY experiment generally correlates protons via geminal or vicinal spin coupling, the TOCSY method can, in principle, give a total correlation of all protons of a chain with each other. In the pictured spectrum up to nine signals may be assigned to a single diastereomer; these emanate from the most low-field shifted ^1H NMR signals. The same color coding was used here as in the one-dimensional spectrum. Further, the ^{13}C heteronuclear single bond (HSQC) and multiple bond (HMBC) correlation spectra are shown in the same figure. Here the direct couplings ($^1J_{\text{H-C}}$) and couplings over two ($^2J_{\text{H-C-C}}$) and/or three ($^3J_{\text{H-C-C-C}}$) covalent bonds are indicated. All spectra are truncated for clarity in both dimensions. For easier interpretation, note the DEPT spectrum in the F1 projection of the HSQC spectrum. In the HMBC spectrum the cross peaks of the two ^1H methyl signals at 0.94 ppm and 1.07 ppm are particularly remarkable, because each indicates markedly different correlations with one CH_2 and two CH carbons, respectively. The reason for this is the different stereochemical arrangement of the aliphatic neighboring groups.

Can you identify the compound described in this challenge? Salud!

References

1. Maarse H (1991) "Volatile Compounds in Foods and Beverages". CRC Press. ISBN 0-8247-8390-5
2. "The Scotch Whisky Regulations 2009: Guidance for Producers and Bottlers". Scotch Whisky Association. 2 December 2009. Retrieved 24 September 2012

We invite our readers to participate in the Analytical Challenge by solving the puzzle above. Please send the correct solution to abc-challenge@springer.com by December 1, 2013. Make sure you enter "Angels' share challenge" in the subject line of your e-mail. The winner will be notified by e-mail and his/her name will be published on the "Analytical and Bioanalytical Chemistry" website at <http://www.springer.com/abc> and in the journal (volume 406/issue 7) where the readers will find the solution and a short explanation.

The next Analytical Challenge will be published in 406/1, January 2013. If you have enjoyed solving this Analytical Challenge you are invited to try the previous puzzles on the ABC homepage.