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Synthesis of glycosides of [$^2H_7$]-geraniol for its use as an internal standard in analysis of bound terpenes in wines

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Wine volatile and flavor compounds consists of several hundred of constituents, representing different classes and of various concentrations and odor thresholds. Wine flavor compounds originate from grapes, fermentation process, as well as from ageing process.
Terpenes form an important group of compound responsible for specific aroma of Muscat, Gewürtztraminer and some other aromatic wines. They come from grapes and are present in wines in both free and bound (as glycosides) form. Free forms can be released from their non-volatile precursors (glycosides) in a result of mild acidic hydrolysis that undergoes in wine during production and storage. Monoterpene alcohols present in wines can also undergo transformations during winemaking.
For the quantitation of terpenes in wine, which are usually present in concentration of few to hundreds ppb, there is a need of reliable methods, preferably using isotopomers of these compounds as internal standards. No such compounds are commercially available. Moreover, no deuterated glycosides of monoterpenes were reported in literature to be synthesized for their use in quantitative analysis.
Presented work shows synthesis of deuterated geraniol and nerol (according to Pedersen *et al*, 2003) and the subsequent synthesis of their glycosides based on the reaction of β-D-glucopyranose penta-O-acetate bromide with terpenes using method of Koenigs-Knorr (Banoub & Bundle, 1978). In the synthesis of deuterated geranio a mixture of [$^2H_7$]-geraniol and $^2H_7$]-nerol is obtained in a proportion of 4:1, which is then used for further reactions. All products and intermediates were characterized by mass spectrometry [GC/MS (EI)], analyzed after hydrolysis and derivatization of intact glycosides. Obtain glycosides can be used for SIDA (Stable Isotope Dilution Analysis) of bound terpenes in wines.

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Speciation of selenium in Polish diet suplements

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Selenium is found in organisms as a trace element though it is indispensable to their correct functioning. It is supplied in organic form, mainly as selenomethionine and selenocysteine, as well as inorganic form, as selenate (Se(VI)) and selenite (Se(IV)). However, various selenium derivatives of sulphuric amino acids have been detected in plants and animals [1]. Selenium facilitates assimilation of vitamin E and regulates its physiological functions. This element is indispensable in the work of the heart muscle and blood vessels, stimulates the immune system and retards tissue aging processes. Besides taking part in enzymatic reactions protecting cells from the effects of free radicals, selenium has immunodulatory, anti-inflammatory and antiviral effects. It protects the organism from poisoning by heavy metals, e.g. Fe, Cd or Pb, by forming metal selenides with them. It has also been found to have anticarcinogenic (antitumor) properties, so it plays an important role in the prevention of neoplasmic diseases [2]. In organisms selenium plays mainly a biochemical role, as a component of enzymic proteins. There is no more comprehensive evidence for potential protection against tumours by different diet components than that which concerns selenium [3]. In over 90% of scientific research on the anticarcinogenic effects of selenium, selenite(IV) or selenomethionine (Se-Met) are used. It has been proved that Se-Met is much less toxic than inorganic selenium compounds [4]. Organisms take in selenium primarily with their food, but in the world, deficiency of selenium in diet is more common than its abundance and is often compensated through selenium-enriched food supplements. The easy access to supplements, also available at the chemist's and supermarkets, makes their use uncontrolled and potentially dangerous, because the range of concentration between deficiency and toxicity is very narrow and strongly depends on the chemical form in which the metal is present [5, 6]. Many commercial formulations label only the total selenium content and not the speciation forms.Speciation methods present in literature are mainly based on various kinds of HPLC technique interfaced with ICP and mass spectrometry detection [6–8], HPLC MS/MS [6] and GC-MS [9]. The aim of this work was to determine qualitatively and quantitatively different speciation forms of selenium in Polish food supplements by HPLC MS/MS methods.

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