

Gas Chromatography and Mass Spectrometry in Honey Fingerprinting: The Occurrence of 3,4-dihydro-3-oxoedulan and (E)-4-(r-1',t-2',c-4'-trihydroxy-3',6',6'-trimethylcyclohexyl)-but-3-en-2-one

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Abstract : Owing to the attractive sensory properties and low odour thresholds, norisoprenoids (degraded carotenoid-like structures with 3,5,5-trimethylcyclohex-2-enoic unit) have been identified as aroma contributors in a number of different matrices. C₁₃-Norisoprenoids have been found among volatile organic compounds of various honey types as well as C₉/C₁₀-norisoprenoids or C₁₄/C₁₅-norisoprenoids. Besides degradation of abscisic acid (which produces, e.g., dehydrovomifoliol, vomifoliol, others), the cleavage of the C(9)=C(10) bond of other carotenoid precursors directly generates nonspecific C₁₃-norisoprenoids such as trans-β-damascenone, 3-hydroxy-trans-β-damascone, 3-oxo-α-ionol, 3-oxo-α-ionone, β-ionone found in various honey types. β-Damascenone and β-ionone smelling like honey, exhibit the lowest odour threshold values of all C₁₃-norisoprenoids. The presentation is targeted on two uncommon C₁₃-norisoprenoids in the honey flavor that could be used as specific or nonspecific chemical markers of the botanical origin. Namely, after screening of different honey types, the focus was directed on *Centaruea cyanus* L. and *Allium ursinum* L. honey. The samples were extracted by headspace solid-phase microextraction (HS-SPME) and ultrasonic solvent extraction (USE) and the extracts were analysed by gas chromatography and mass spectrometry (GC-MS). SPME fiber with divinylbenzene/carboxen/polydimethylsiloxane (DVB/CAR/PDMS) coating was applied for the research of *C. cyanus* honey headspace and predominant identified compound was 3,4-dihydro-3-oxoedulan (2,5,5,8a-tetramethyl-2,3,5,6,8,8a-hexahydro-7H-chromen-7-one also known as 2,3,5,6,8,8a-hexahydro-2,5,5,8a-tetramethyl-7H-1-benzo-pyran-7-one). The oxoedulan structure contains epoxide and it is more volatile in comparison with its hydroxylated precursors. This compound has not been found in other honey types and can be considered specific for *C. cyanus* honey. The dichloromethane extract of *A. ursinum* honey contained abundant (E)-4-(r-1',t-2',c-4'-trihydroxy-3',6',6'-trimethylcyclohexyl)-but-3-en-2-one that was previously isolated as dominant substance from the ether extracts of New Zealand thyme honey. Although a wide variety of degraded carotenoid-like substances have been identified from different honey types, this appears to be rare situation where 3,4-dihydro-3-oxoedulan and (E)-4-(r-1',t-2',c-4'-trihydroxy-3',6',6'-trimethylcyclohexyl)-but-3-en-2-one have been found that is of great importance for chemical fingerprinting and identification of the chemical biomarkers that can complement the pollen analysis as the major method for the honey classification.

Keywords : 3,4-dihydro-3-oxoedulan, (E)-4-(r-1',t-2',c-4'-trihydroxy-3',6',6'-trimethylcyclohexyl)-but-3-en-2-one, honey flavour, C₁₃-norisoprenoids

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