

# Detection of $\Delta^9$ -Tetrahydrocannabinolic acid in human urine and human blood serum by LC/MS/MS and GC/MS

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**Background:**  $\Delta^9$ -Tetrahydrocannabinolic acid ( $\Delta^9$ -THCA) is the precursor of  $\Delta^9$ -Tetrahydrocannabinol ( $\Delta^9$ -THC) in hemp plants. During smoking, the non-psychoactive  $\Delta^9$ -THCA is converted to  $\Delta^9$ -THC, the main psychoactive component of marijuana and hashish. Although the decarboxylation of  $\Delta^9$ -THCA to  $\Delta^9$ -THC was assumed to be complete – so no  $\Delta^9$ -THCA should be detectable in urine and blood serum of cannabis consumers – we found  $\Delta^9$ -THCA in urine and blood serum samples collected from roadside testing of driving under the influence of drugs.

**METHODS:** *LC-MS/MS analysis:* Urine and blood serum samples were prepared using solid-phase extraction (Macherey-Nagel, Chromabond C18, 500 mg). Analysis of urine samples was performed on a Luna phenylhexyl analytical column (Phenomenex, 50 mm  $\times$  2 mm, I.D. 3  $\mu$ m) using gradient elution. For detection of  $\Delta^9$ -THCA the mass spectrometer with turboionspray source) was operated in multiple reaction monitoring mode using the following transitions: 357  $\rightarrow$  313, 357  $\rightarrow$  245, 357  $\rightarrow$  191. For further identification reference compound  $\Delta^9$ -THCA was obtained from Dr. F. Dussy (Institute of Legal Medicine, Basel, Switzerland).

*GC/MS-analysis:* After solid-phase extraction of blood serum, cannabinoids were converted to trimethylsilyl derivatives and analyzed on a DB-5 capillary column with an Agilent GC-MSD 5973. The presence of  $\Delta^9$ -THCA was screened for by mass chromatography with selected ions ( $m/z$  487, 213, 324) followed by library search (Pfleger/Maurer/Weber GC/MS library of drugs).

**RESULTS AND CONCLUSIONS:**  $\Delta^9$ -THCA could be detected in urine and blood serum samples of several cannabis consumers. However, its detectability seems to depend on the time span between consumption and blood sampling. Other criteria might be the  $\Delta^9$ -THCA content of the cannabis product, the frequency of abuse and interindividual differences during metabolism and elimination.

**KEYWORDS:**  *$\Delta^9$ -Tetrahydrocannabinolic acid,  $\Delta^9$ -Tetrahydrocannabinol precursor, LC-MS/MS, GC/MS*

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