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Heat assisted sample introduction and determination of cannabinoids by dielectric barrier discharge ionization mass spectrometry

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ABSTRACT

DBDI-MS equipped with an appropriate sample heater was employed to analyze directly 8 seized synthetic cannabinoids in botanical matrices. The heater allowed for a pronounced increase of the quality of acquired spectra, allowing for much easier identification of cannabinoids, as compared to standard DBDI source without heating device. A few hundred micrograms of herbal material was sufficient for easy detection of cannabinoids content in the samples. These designer drugs are difficult to identify in a conventional way due to their association with complex plant matrices during manufacturing (to mask active and illicit ingredients) and so requires time consuming extraction and sample preparation before analysis. The ability for fast and direct analysis of the so-called "legal highs" can be a useful supporting tool for an initial and rapid identification of compounds present in this type of species, and can partially replace GC/MS technique for fast screening.

1. Introduction

In recent years, many herbal mixtures containing new cannabis alternatives have been introduced to the illegal drug market, mainly through Internet [1,2]. Many countries have taken legal actions to control this market, but new derivatives or analogs are constantly introduced, circumventing legal regulations, and thus are coined as "legal highs" or "designer drugs". Synthetic cannabinoids are known by a variety of names, such as "Spice" or "K2," and sometimes are referred to as "synthetic marijuana" or "fake marijuana" because they are sold with claims that their effects mimic those of marijuana. Synthetic cannabinoids are usually sprayed onto the surface of herbal products, and sold in that form. They have been reported to cause a variety of side effects like anxiety [3], vomiting [4], tachycardia [5], hallucinations [6], nonresponsiveness [7], and many others [8]. The routine screening tests are not currently designed for identification of synthetic cannabinoids and this causes high demand for analyses of this type of compounds. Synthetic cannabinoids have been studied by many mass spectrometry methods, such as GC–MS [9], LC–ESI-MS [10], MALDI [11] or DART [12]. Each method has its own advantages or drawbacks. The main advantage of the method used in the present study is a possibility for direct and rapid analysis of cannabinoids in herbal matrices. Original construction of the heat assisted DBDI allows to obtain MS and MS/MS data of a very good quality within seconds and without derivatization or presence of any solvent. From this point of view, only DART MS can be comparable with DBDI source. DBDI source has been developed in 2007 [13] and since then it has been used for many applications. It was applied for pesticide testing [14], for detection of amino acids, water-soluble vitamins, and nonpolar compounds like polycyclic aromatic hydrocarbons and functionalized hydrocarbons [15], explosives [16], and to detect both minor and trace components (free fatty acids, phenolics and volatiles) in raw, untreated olive oil [17]. DBDI was also coupled to HPLC for detection of pesticides, polycyclic aromatic hydrocarbons,

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Table 1
Structures of all cannabinoids analyzed and proposed formulas for the main fragmentation ions.

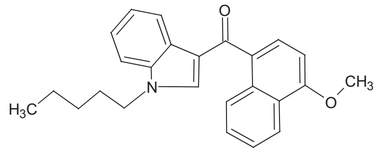
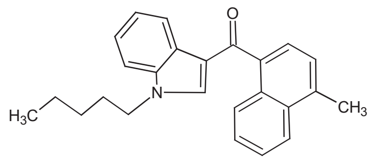
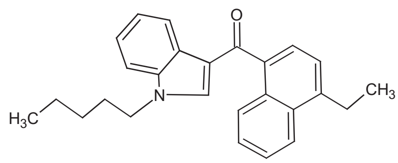
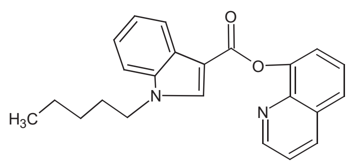
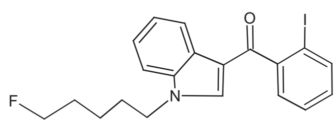
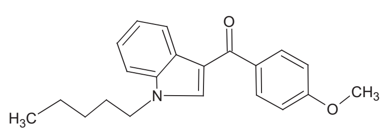
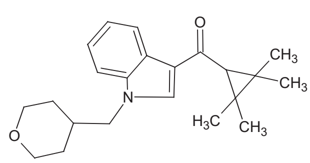
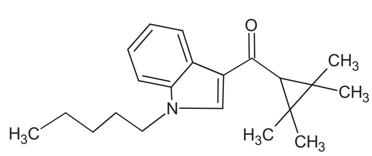
Name Formula M_w [Da]	Structure	MS/MS fragments (observed m/z)	Proposed formula of the fragment
JWH-081 $C_{25}H_{25}NO_2$ 371.19		157.1 185.1 214.1	$C_{11}H_9O^+$ $C_{12}H_9O_2{}^+$ $C_{14}H_{16}NO^+$
JWH-122 $C_{25}H_{25}NO$ 355.19		141.1 169.1 214.1	$C_{11}H_9{}^+$ $C_{12}H_9O^+$ $C_{14}H_{16}NO^+$
JWH-210 $C_{26}H_{27}NO$ 369.21		155.1 183.1 214.1	$C_{12}H_{11}{}^+$ $C_{13}H_{11}O^+$ $C_{14}H_{16}NO^+$
PB-22 $C_{23}H_{22}N_2O_2$ 358.17		214.1	$C_{14}H_{16}NO^+$
AM-694 $C_{20}H_{19}FINO$ 435.05		230.9 309.1	$C_7H_4IO^+$ $C_{20}H_{20}FNO^+$
RCS-4 $C_{21}H_{23}NO_2$ 321.17		135.2 186.1 265.0	$C_8H_7O_2{}^+$ $C_{13}H_{16}N^+$ $C_{17}H_{15}NO_2{}^+$
A-834,735 $C_{22}H_{29}NO_2$ 339.22		125.3 242.1 322.2	$C_8H_{13}O_2{}^+$ $C_{15}H_{16}NO_2{}^+$ $C_{22}H_{28}NO^+$
UR-144 $C_{21}H_{29}NO$ 311.22		125.1 214.0 294.2	$C_8H_{13}O_2{}^+$ $C_{14}H_{16}NO^+$ $C_{21}H_{28}N^+$

Fig. 1. Schematic diagram of DBDI source with sample heater.