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CASE REPORT

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‘Flying high?’—Jump from a height in a ‘Spice’ high?: A case report on the synthetic cannabinoid 5F-MDMB-P7AICA

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Abstract

Regarding the high potency of synthetic cannabinoids (SC), many intoxications and fatal cases are reported in literature. Here, we report on a fatality with 5F-MDMB-P7AICA contributing to the occurrence of death. A 31-year-old man died 10 h after he fell from the rooftop of a house. Police investigations revealed that he had consumed a ‘legal high’ herbal blend some hours earlier. An initial toxicological screening for new psychoactive substances (NPS) was negative. One year after, the analysis of confiscated drug samples revealed the SC 5F-MDMB-P7AICA being unknown at the time of the first investigations. Hence, post-mortem specimens were retrospectively analysed for 5F-MDMB-P7AICA and its dimethylbutanoic acid (DBA) metabolite. Lung, liver, kidney and bile fluid (BF) of the decedent were analysed following solid-phase extraction and standard addition, heart blood (HB) and peripheral blood (PB) by fully validated liquid–liquid extraction and protein precipitation methods. Additionally, hair specimens were analysed to examine a possible chronic consumption of the SC. All specimens were analysed by liquid–chromatography tandem mass spectrometry. 5F-MDMB-P7AICA was detected in HB (0.69 ng/ml), PB (1.2 ng/ml) and hair. DBA was found in HB (46 ng/ml) and PB (5.7 ng/ml) and could additionally be identified in liver and kidney (approximately 4–5 ng/g), lung (approximately 12 ng/g) and BF (approximately 60 ng/g). Compared with the parent compound, much higher concentrations of DBA were quantified. This case shows that drugs found at the scene can provide helpful initial information for further toxicological screenings in biological samples, especially when there is evidence of NPS consumption.

KEYWORDS
5F-MDMB-P7AICA, ester hydrolysis, fatal case, synthetic cannabinoid

1 | INTRODUCTION

Originally synthesized as pharmaceuticals and for research purposes, synthetic cannabinoids (SCs) have emerged on the European drug market from 2008 on and in 2021 still represent the largest class of new psychoactive substances (NPS) monitored by the EMCDDA.[1] SCs show a high functional activity at the cannabinoid receptors CB 1 and CB 2.[2–5] Compared with Δ^9-tetrahydrocannabinol, SCs often act as full agonists with sometimes higher binding affinities at the CB 1 receptor and even higher potencies, resulting in unpredictable toxicodynamic

effects (e.g. tachycardia, confusion, hallucinations and vomiting).[5–7] Therefore, serious adverse health effects have been observed after the consumption of SCs. Consequentially, many intoxications as well as fatalities related to the use of SCs have been reported so far.[2,8,9]

The indazole-based synthetic cannabinoid (SC) 5F-ADB (Figure 1a), also known as 5F-MDMB-PINACA, is considered to be one of the most present SCs in association with intoxications and fatalities.[10–13] In 2016, 5F-ADB was covered in Germany by the narcotics law. As a consequence, 5F-MDMB-P7AICA (Figure 1b; methyl-2-{[1-(5-fluoropentyl)-1H-pyrrolo[2,3-b]pyridine-3-carbonyl]amino}-3,3-dimethylbutanoate, also labelled as MDMB-5F-P7AICA or 7′N-5F-ADB) emerged on the drug market in 2017. 5F-MDMB-P7AICA contains a 7-azaindole core structure (Figure 1b) not regulated in most countries at this time. Recently, several studies have been published regarding the toxicokinetic properties, stability and potency of this substance.[14–18] In these studies, 5F-MDMB-P7AICA dimethylbutanoic acid (DBA; Figure 1c) was found to be the main metabolite. Additionally, Richter et al[18] firstly reported on one authentic human intoxication after suspected consumption of 5F-MDMB-P7AICA and provided analytical results in plasma. However, until now, only one fatal case associated with 5F-MDMB-P7AICA has been reported. In this case, a man died after having smoked fentanyl combined with a herbal blend using a bucket bong.[19] Prior to this, he had additionally smoked a joint. Toxicological screening revealed 17 SCs, including 5F-MDMB-P7AICA, in blood and hair samples of the decedent.[19] In conclusion, the occurrence of death was attributed to the cardiovascular effects of SCs on the previously damaged heart and a respiratory depression due to fentanyl.

Here, we report on a second fatal case with 5F-MDMB-P7AICA contributing to the occurrence of death, in contrast to the fatality yet reported not mediated via a somatic impact on circulation or respiration but most probably via modification of the mental condition resulting in a fatal accident.

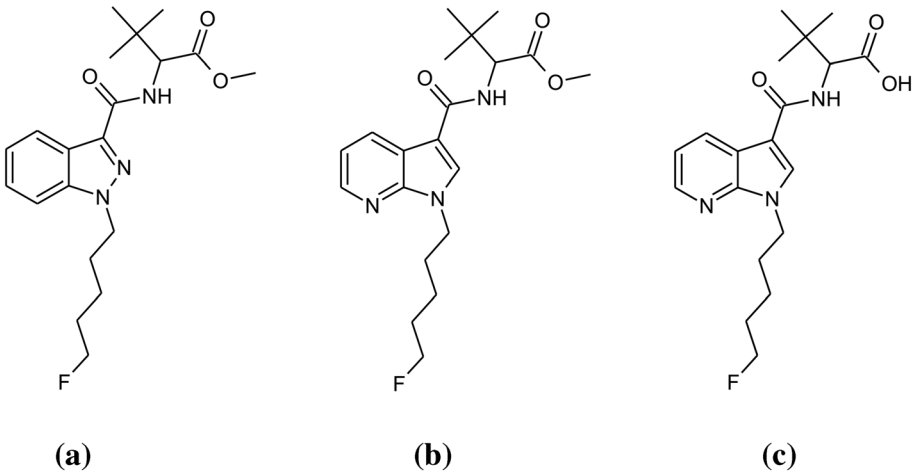
2 | CASE REPORT

Following the case history, a 31-year-old man fell from the rooftop of a house after he consumed a ‘legal high’ herbal blend. The man died 10 h after admission to the hospital. The autopsy was performed 4 days after death and revealed lethal multiple trauma, which mainly involved head and thorax and composed of skull fractures, subarachnoid haemorrhage, multiple rib fractures, contusion of the lung and haematothorax. Toxicological analysis performed with regard to the history revealed therapeutically administered pharmaceuticals (propofol, midazolam and lidocaine); furthermore, a subtherapeutic concentration of morphine and a very low concentration of benzoylecgonine in peripheral blood (PB). Additionally, blood alcohol analysis was negative. However, an extensive screening for NPS, especially SCs, was carried out, no respective substances could be found.

About 1 year after that incident, in the context of a further police investigation involving the deceased, ‘legal high’ herbal blends, a half-smoked joint and several cigarette butts (Figure 2), which were seized in the apartment of the decedent, were analysed. After preparation of the seized samples (see Supporting Information), 5F-MDMB-P7AICA

(a) (b)

FIGURE 2 Seized herbal material (a) and a half-smoked joint (b) found in the decedents apartment [Colour figure can be viewed at wileyonlinelibrary.com]



(a) (b) (c)

FIGURE 1 Molecular structures of 5F-MDMB-PINACA (5F-ADB) (a), 5F-MDMB-P7AICA (b) and 5F-MDMB-P7AICA dimethyl butanoic acid metabolite (c)

was detected via gas chromatography–mass spectrometry (GC-MS) analysis (Figure S1). The total ion count gas chromatogram as well as the selected ion traces of five characteristic fragment ions (FI) of one seized herbal blend is depicted in Figures S2 and S3. At the time of the first investigations, this SC had been completely unknown, and thus, 5F-MDMB-P7AICA had not been included in the screening method. Therefore, tissues (lung, liver and kidney), body fluids [bile fluid, PB, heart blood (HB)] and hair specimens of the decedent collected during autopsy were retrospectively analysed to assess a potential consumption of 5F-MDMB-P7AICA that might have contributed to the fatality.

3 | MATERIALS AND METHODS

3.1 | Chemicals and reagents

Chemicals and reagents used for analysis are described in detail in the Supporting Information.

3.2 | Buffers, stock solutions, quality controls (QC), calibration standards and calibrators for standard addition

The preparations of buffers, standard stock solutions, QCs and calibration standards of 5F-MDMB-P7AICA and DBA used in the present work were in accordance to those already described elsewhere[17,20] and are described in the Supporting Information, respectively.

3.3 | Sample preparations of herbal blends, blood and tissue specimens

Until analysis, all tissues and body fluids collected during autopsy were stored in a freezer at −20°C, and hair specimens as well as herbal blends were kept at room temperature, respectively. Analyses were performed about 2 years after the autopsy.

3.3.1 | Herbal blends

The detailed sample preparation of the seized herbal blends can be found in the Supporting Information.

3.3.2 | Blood specimens

Preparation of HB and PB was carried out using validated methods based on a liquid–liquid extraction and a protein precipitation already reported in a previous study.[17] The respective validation parameters as well as the sample preparations are described in detail in the Supporting Information, respectively.

3.3.3 | Tissue specimens

For detection and quantification of 5F-MDMB-P7AICA and the DBA in the tissue specimens (liver, lung and kidney) and the bile fluid of the decedent, a standard addition method was used as recommended by national and international guidelines.[21,22] The samples were prepared analogous to already published preparation of pig tissue samples for the detection of SCs, with the modification that no enzymatic hydrolysis was performed.[20] Analysis was performed by a liquid chromatography–tandem mass spectrometry (LC-MS/MS) system. Detailed information on the respective sample preparation is depicted in the Supporting Information.

3.3.4 | Hair samples

For quantification, a one-point calibration using a blank hair sample was performed. In brief, the blank hair sample and two segments a 5 cm of the decedent's hair were pulverized, and the substances were extracted using ethanol. The subsequent analysis was performed using a LC-MS/MS system. The respective sample preparation of the hair samples can be found in the Supporting Information.

3.4 | Instrumental apparatus

The detailed conditions used for the GC-MS and LC-MS/MS methods are described in the Supporting Information, respectively.

4 | RESULTS

GC-MS analysis of the seized herbal material, cigarette butts and the half-smoked joint yielded a molecular ion at *m/z* 377.2 with FI at *m/z* 289.1, 233.2 and 145.0 (Figure S1).

The post-mortem analysis of the autopsy specimens revealed 0.69 ng/ml 5F-MDMB-P7AICA in HB and 1.2 ng/ml in PB, respectively. An amount of 5.7 ng/ml DBA was found in PB and 46 ng/ml in HB (Table 1). In the analysed tissues and bile fluid, only the ester hydrolysed DBA metabolite, and no parent compound could be identified, displaying the highest concentration in bile fluid. The corresponding values (calculated concentrations, slope and intercept) are shown in Table 1. The respective fragment ion traces of the analytes in PB of the decedent are shown in Figure S4.

Analysis of the hair segments led to the detection of 5F-MDMB-P7AICA. In the proximal segment about 70 pg/mg and in the distal segment about 80 pg/mg of 5F-MDMB-P7AICA were found. On the contrary, no DBA could be detected in any of the samples.

5 | DISCUSSION

Considering the GC-MS analysis, 5F-MDMB-P7AICA was identified in every seized material by the molecular ion at *m/z* 377.2 with the

TABLE 1 Concentrations of 5F-MDMB-P7AICA dimethylbutanoic acid in lung, liver, kidney, bile, heart blood (HB) and peripheral blood (PB) [ng/g or ng/mL] as well as slope, intercept and regression coefficient (r^2) used for quantification

	5F-MDMB-P7AICA dimethylbutanoic acid			
Specimen	**Concentration**	**Slope (a)[a]**	**Intercept (b)[a]**	**r^2**
Lung	12[b]	0.0824	0.4787	0.9569
Liver	4[b]	0.0752	0.2775	0.9953
Kidney	5[b]	0.096	0.4585	0.9977
Bile	38[b]	0.3474	13.308	0.8976
HB	46[c]	-	-	-
PB	5.7[c]	-	-	-

[a]y = ax+b; concentration x can be calculated as minus value.
[b]approximated concentration.
[c]fully validated method.

simultaneous presence of the most abundant FI at *m/z* 233.2, indicating a cleavage at the amide. An additional loss of the fluorinated alkyl chain resulted in the FI at *m/z* 145.0. The unaltered 7-azaindole core structure was identified by the presence of the FI at *m/z* 117.0 (Figure S1). The identification of 5F-MDMB-P7AICA was confirmed by comparison to the reference substance regarding retention time and fragment abundances.

In general, the subsequent toxicological examination of the authentic post-mortem blood specimens of the decedent revealed low concentrations of the parent compound and high concentrations of the DBA in HB and PB (Table 1). This rather low concentration or absence of the parent substance in blood specimens is reported to be quite common for SCs, even in cases of fatal intoxications.[23] A rapid in vivo hydrolysis of SCs containing an ester structure as well as the rather low dosages of SCs with high potencies might lead to low concentrations of the parent substance in blood.[23] Comparison of the results obtained in HB and PB showed that the concentration of 5F-MDMB-P7AICA was higher in PB than in HB. Conversely, the concentration of the ester hydrolysed metabolite was much higher in HB than compared with PB. Regarding the higher concentrations of 5F-MDMB-P7AICA in PB as compared with HB, one might speculate that a resuscitation procedure shortly before death might have led to a distribution from heart to peripheral compartments, as already reported by Ferreirós et al.[24] Nevertheless, explanations of this discrepancy remain speculative as neither the dose nor the frequency of consumption is known in this authentic case.

Considering already published data, only one fatal case with a contribution of 5F-MDMB-P7AICA was reported until now.[19] In this case, a man died immediately after he had consumed a bucket bong. In toxicological analysis, 13 ng/ml of 5F-MDMB-P7AICA was found in post-mortem blood specimens. However, comparison with data obtained in the present fatal case is difficult, since apart from fentanyl, several other SCs were also detected in this case, so a mixed intoxication with leading relevance of the toxic effects of fentanyl was considered.[19] In contrast to this fatal case with the immediate occurrence of death, the decedent in the present case survived for about 10 h allowing for further metabolism of the SC.

In addition, Richter et al reported on plasma concentrations after a suspected intake of 5F-MDMB-P7AICA in routine toxicological analysis.[18] In this case, plasma specimens (plasma a and b) were obtained from one human at two different points of time. In plasma a 183 + 10 ng/ml and in plasma b 177 + 28 ng/ml of 5F-MDMB-P7AICA were quantified, respectively.[18] Thus, compared with the data obtained in the present fatal case, substantially higher concentrations of the parent compound could be detected. Even if dosage and time of intake were unknown, it is nevertheless feasible that consumption of 5F-MDMB-P7AICA had probably taken place shortly before blood draw. In addition, a standard of unknown purity was used in the study conducted by Richter et al.[18] At last, as in the present case, the decedent survived for about 10 h and autopsy and the sample collection were performed after a post-mortem interval of 4 days, the results could not be compared with those obtained by Richter et al.[18]

Until now, a few in vivo toxicokinetic studies on 5F-MDMB-P7AICA are available. Recently, Doerr et al reported on the distribution of 5F-MDMB-P7AICA in tissue and blood specimens found in a systematic toxicokinetic pig study 8 h after inhalative administration of a 200 μg/kg body weight dose.[25] The distribution of the parent substance between PB and HB reported by Doerr et al is in line with that found in the herein reported fatal case. Nevertheless, this finding could not be confirmed regarding the DBA. Concerning the tissue distribution, the results obtained in the animal study are partly in line with the data obtained in the present fatal case.

With respect to the analysis of the solid tissues as well as the bile fluid of the decedent, 5F-MDMB-P7AICA could not be detected in any of the analysed specimens. In contrast, high concentrations of the DBA metabolite were found in all solid tissues as well as body fluids, particularly in bile fluid (Table 1). This observation is not surprising and in good agreement with previous studies on SC, which also reported on high concentrations of the metabolite in bile fluid, suggesting an enterohepatic circulation process and a biliary excretion.[20]

Regarding the generally much higher concentrations of the DBA metabolite, several explanations should be considered. As already known for the isomer 5F-ADB,[26] a time- and/or temperature-dependent instability during the storage time of the specimens of more than 2 years should be taken into account. However, in a recently published in vitro stability study during storage and smoking of the SC 5F-MDMB-P7AICA,[17] an instability of the parent compound could only be observed in samples stored at RT over 12 months. On the contrary, storage at −20 and 4°C seemed to contribute to the stability of 5F-MDMB-P7AICA. Thus, the remarkably high concentration of the metabolite in the decedents blood stored at −20°C could not be explained by a degradation of 5F-MDMB-P7AICA due to ester hydrolysis during the storage time.

As smoking is the most common route of administration of SC, a possible pyrolysis of 5F-MDMB-P7AICA during smoking should be considered as alternative explanation for the high DBA metabolite concentrations. Again, in a smoke test conducted by Walle et al,[17] no relevant pyrolysis could be found during smoking of 5F-MDMB-

P7AICA. Hence, the high concentrations of the DBA metabolite in the tissues and body fluids of the decedent in the authentic case could not be explained by a pyrolysis during smoking either.

Since a thermal instability of 5F-MDMB-P7AICA during storage or smoking could not be substantiated, alternative reasons for the high tissue and body fluid concentrations of the DBA have to be taken into consideration. With regard to common user habits, a chronic consumption over a long time might have led to an accumulation of the DBA metabolite. To examine this issue, the hair of the decedent collected during the autopsy was analysed. As mentioned before, only the parent compound and no DBA metabolite could be detected in both segments. However, the absence of the DBA metabolite does not definitively contradict a chronic consumption of 5F-MDMB-P7AICA. As this metabolite shows hydrophilic properties due to the carboxylic acid unit in its chemical structure, it is possibly not stored in hair. It has additionally to be mentioned restrictively that the analytical hair method used in this study was not specifically developed for the substances examined in the present case. Hence, the recovery of the DBA metabolite was not known. In this context, it should further be mentioned that hair may be contaminated due to sidestream smoke.[27]

In fact, the high amount of 5F-MDMB-P7AICA detected in every hair segment of the decedent might be consistent with chronic consumption, suggesting that the high DBA concentration in tissues and body fluids of the decedent may be due to an in vivo ester hydrolysis by carboxylesterases and a following storage and accumulation in tissues and bile fluid. A possible renal failure of the decedent may also have prevented the excretion of the DBA metabolite, resulting in a higher blood concentration and a subsequent accumulation in tissue specimens.

A further discussion regarding concentrations of the constitutional isomer 5F-ADB and its metabolite can be found in the Supporting Information.

Considering all findings, the deceased was under the influence of 5F-MDMB-P7AICA at the time of death. However, the fatal consequences of the drug were not mediated by a direct toxic impairment of, for example, the respiratory or circulatory system, but rather by a fatal accident after consumption of the synthetic drug. As already known for SC, they can also have an impact on psyche after consumption, triggering, for example, psychosis and hallucinations.[9] In this context, a few fatal cases after jumping from heights in connection with the consumption of SCs were already reported in literature.[9] Hence, in the presented case, the psychoactive effects of 5F-MDMB-P7AICA might possibly have contributed to the fatality. However, since no one observed the mental state of the deceased prior to the fatal incident as well as the jump, an accidental fall might not be ruled out with absolute certainty.

6 | CONCLUSIONS

Presently, a second fatality with a contribution of 5F-MDMB-P7AICA to the occurrence of death is reported. Low concentrations of the parent compound could only be found in PB and HB, whereas high concentrations of the DBA metabolite were additionally detected in every tissue examined. In the hair specimens of the decedent, only 5F-MDMB-P7AICA could be found. Considering the results, a chronic consumption potentially combined with a final renal failure was possibly indicated.

In the present fatal case, 5F-MDMB-P7AICA was assessed to have contributed to the occurrence of death. Different to fatalities already reported in literature for, for example, 5F-ADB, the SC did not act via impairment of somatic formation like circulation of respiration. As it was already reported for several SCs, in this case, the fatality might be caused via a change of the mental conditions, resulting in a fatal jump off the roof. Nevertheless, as no one has seen the jump from the height, an accident cannot be disproved with absolute certainty.

The case also impressively shows that analysis of drugs found at the scene represents a useful tool to obtain initial indications of potentially consumed substances in connection to death and might be helpful for further toxicological screenings in biological matrices.

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DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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SUPPORTING INFORMATION

Additional supporting information can be found online in the Supporting Information section at the end of this article.

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