EUROPEAN PROJECT RESPONSE to challenges in forensic drugs analyses

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Synthetic cannabinoids - characteristic MS fragmentation patterns and FTIR spectra of some cumyl-indole, cumyl-indazole and cumyl-azaindole carboxamide analogues

S. Klemenc*, T. Gostič

Ministry of the Interior Police, National forensic Laboratory (NFL), Ljubljana, Slovenia

INTRODUCTION

Several multi-kilogram seizures from three different groups of new cumyl-type synthetic cannabinoids were confiscated in Slovenia in late 2014 and 2015. Pure forms of substances as well as liquid and herbal preparations (delivered from China) were confiscated.

Substances were identified and structure elucidated by means of GC-MS, HPLC-TOF, NMR. FTIR –ATR spectra of pure compound were scanned as well. Analytical data were reported for the first time worldwide through the REITOX EWS (early warning system) - to the European Monitoring Center for Drugs and Drugs Addiction (EMCDDA).

In this work we wish to stress the main differences in MS fragmentation patterns and comparison of FTIR spectra of fluorinated and non fluorinated indole, indazole and azaindlole analogues. Results reported here were obtained from studies of compounds in “pure form” (liquids and solids).

METHODS (GC-MS and FTIR)

Approximately 1mg of sample was dissolved in CH2Cl2 : MeOH (volume ratio 9:1). Liquid samples (cca 1mg) were diluted by 1 ml of solvent mixture as above. Microliter aliquots have been analysed by GC-MS (analytical parameters are available on request). Perkin Elmer FT-IR spectrometer (Frontier) with DTGS detector and ATR module (UATR Diamond/KRS5) were applied for direct measurements of samples. Spectra were acquired in the range form 400 cm-1 to 4000 cm-1, spectral resolution was 4 cm-1.

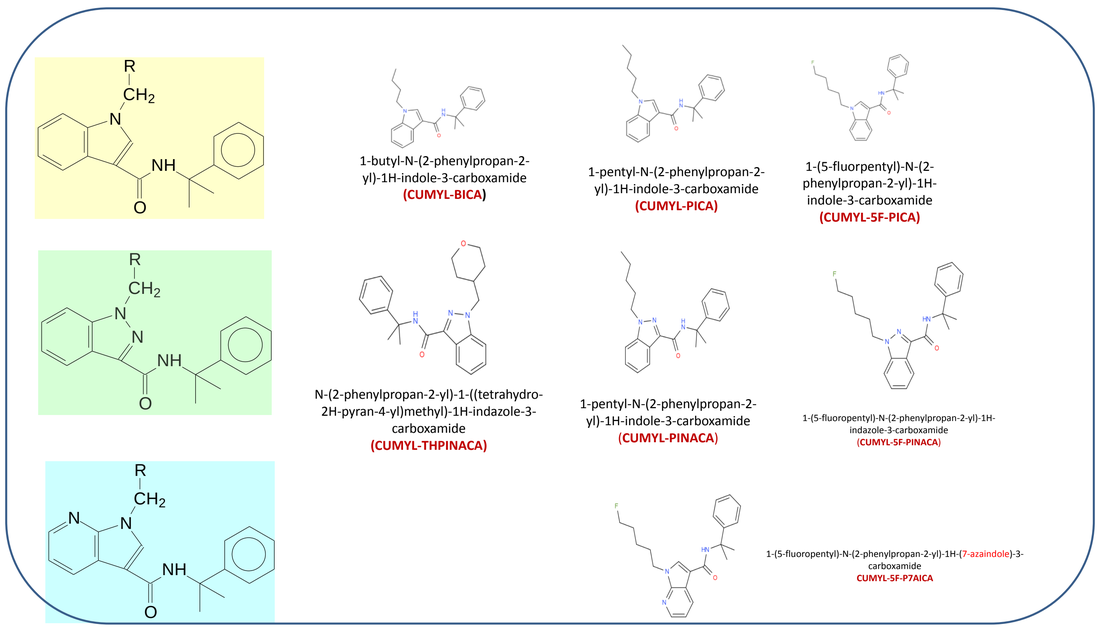

Figure 1: Compounds identified structures:(I) -indole, (II) – indazole and (III) azaindole cumyl -carboxamides

MS – ANALYSES & FRAGMENTATION PATTERNS

MS spectra of selected compound from classes I, II, III are sown on Figure 2. Typical fragment ions are labeled for each class. Formation of the base peak ions (B+) can be formally explained by initial ionization at the indole nitrogen or on the carboxamide oxygene, which leads to the α cleavage next to the carbonyl group (i.e. C-NH bond) and loose of cumyl imine radical (see example for indole compound Fig. 3). The m/z formation of ions 144 for indoles and 145 for indazoles and azaindole could be explained by further rearrangements (hydrogen transfer) and bond cleavage of the indole/indazole/azaindole side chain (tail). (see Figure 3). The proposed simplified mechanisms of formation of m/z ions 173 for indole example is shown in Figure 3a.

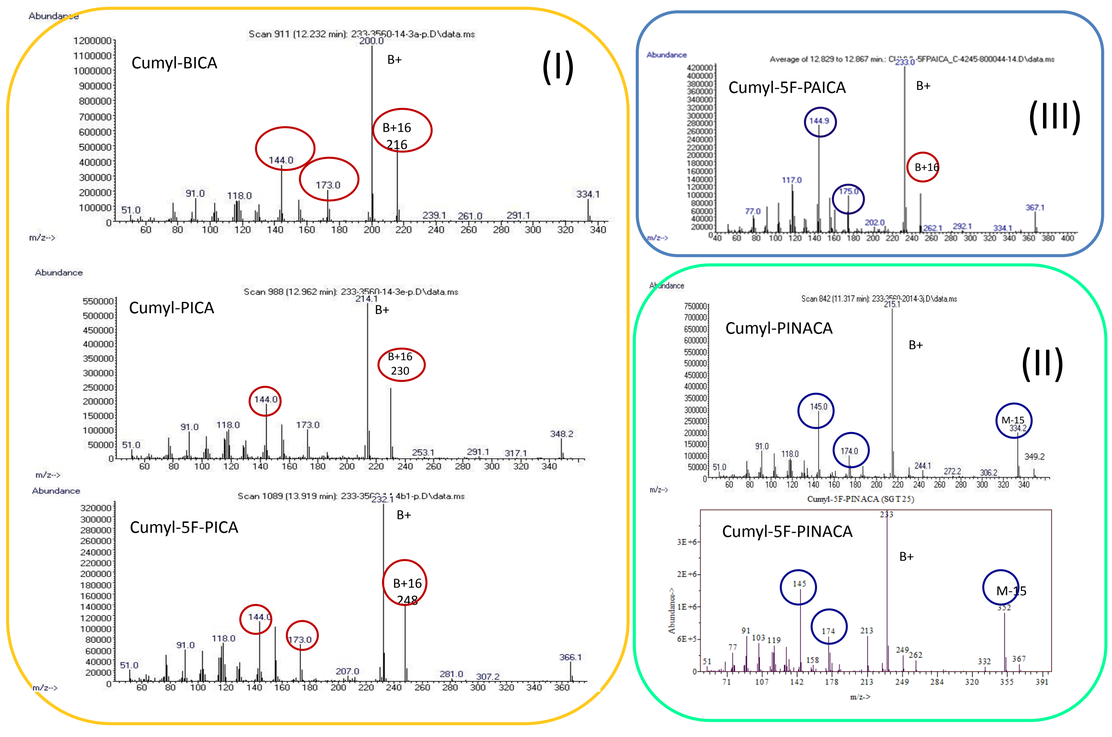

Figure 2: MS spectra: indole (I), indazole (II) and azaindole cumyl (III) carboxamides

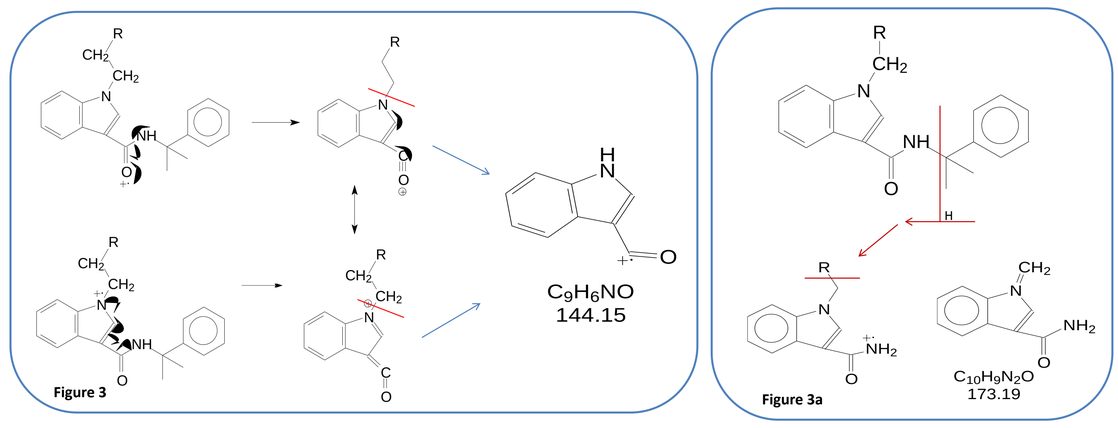

Figure 3

Figure 3a

For cumyl indole and azaindole compounds we observed strong B+16 ions. The formation of these could be explained by McLafferty rearrangement. Proposed mechanism is shown at Figure 4. B+16 fragments are almost absent in indazole species. Indazole compounds (only) show strong M-15 ion, which indicates the lose of CH3 group from cumyl substituent. In all spectra we observed ion 91 and group (tropilium ion) ions m/z 116 to 119 which are characteristic fragments of cumyl cation alpha-metyhlstyrene. The source of this ions is the cumyl part of investigated substances.

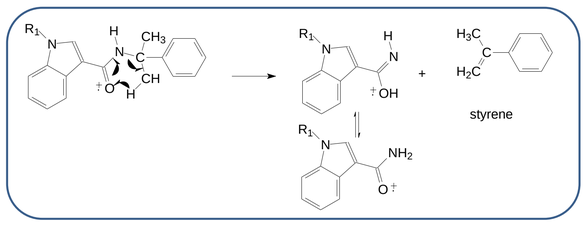

Figure 4: Formation of ions - Mc Lafferty rearangement

FTIR – ATR ANALYSES

FT-IR spectra for compounds classes (I) to (III) are shown and compared in Figures below. Spectra are similar and show strong absorbance bands corresponding to valence vibrations of carbonyl group around 1621 cm^{-1} (indole and azaindole carboxamides) and for indazole carboxamides around 1670 cm^{-1}. Despite the similarity of spectra they can be easily differentiated by mathematical comparison tools (based on cosine correlation coefficient).

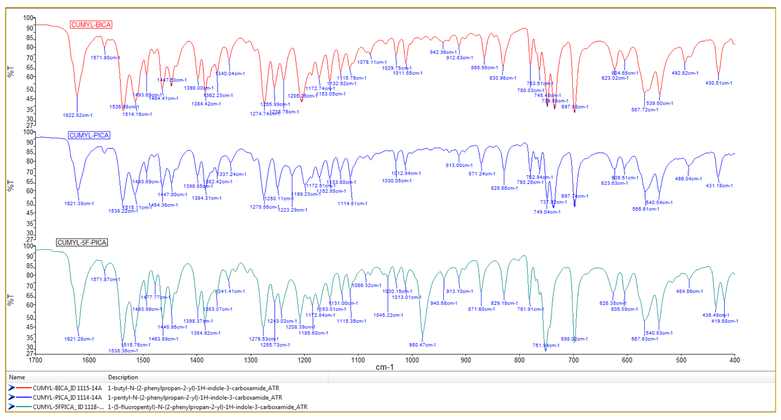

Figure 5: FTIR spectra of cumyl- indole carboxamides

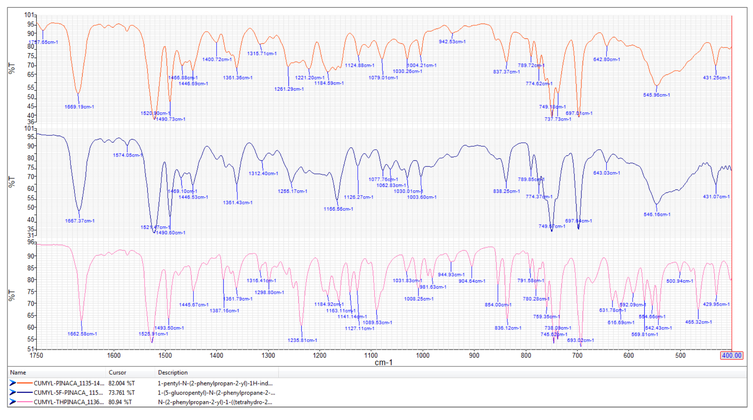

Figure 6: FTIR spectra of cumyl- indazole carboxamides

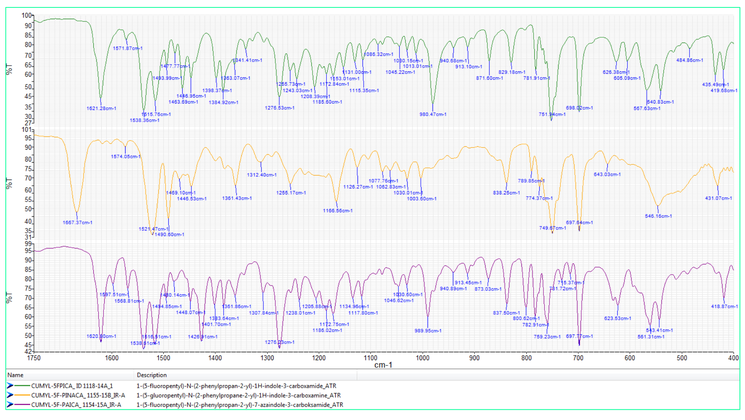

Figure 6: FTIR spectra of cumyl- indole, indazole and azaindole carboxamides, respectively

CONCLUSIONS

In this study brief overview of MS fragmentation patterns and FTIR characteristic for three novel classes of cumyl type synthectic cannabinoids have been given. Main differences have been highlighted.. Therefore , this report can support future forensic characterizations and identifications of upcoming structurally related novel NPS compounds .

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Corresponding author: Sonja Klemenc, e-mail : sonja.klemenc@policija.si

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