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Identification and derivatization of selected cathinones by spectroscopic studies

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ABSTRACT

In this study we identified three novel hydrochloride salts of cathinones 2-(pyrrolidin-1-yl)-1-(5,6,7,8-tetrahydronaphthalen-2-yl)pentan-1-one (1a) (TH-PVP), 2-(methylamino)-1-(2-methylphenyl)-1-propanone (1b) (2-MMC) and 1-(4-chlorophenyl)-2-(methylamino)propan-1-one (1c) (4-CMC). Their properties have been examined through combinations of GC–MS, IR, NMR, electronic absorption spectroscopy and single crystal X-ray diffraction method. NMR solution spectra showed readily diagnostic H-1 and C-13 signals from methyl, *N*-methyl and carbonyl groups. Additionally the use of thionation and amination reactions for identification of selected cathinones was presented.

1. Introduction

The classical cathinones are a series of bioisostere compounds containing α-aminopropiophenone moiety. They are the derivatives of cathinone, a natural amphetamine-like alkaloid, which is the major pharmacologically active constituent extracted from fresh leaves and stems of *Catha edulis* Forsk, Celastraceae (Khat) [1]. The first described synthesis of cathinones was published in 1928 [2]. Independent to Hyde et al. in 1929 Saem de Burnaga Sanchez reported the synthesis of mephedrone as an example of cathinone [3]. Until now over 97 individual substances were reported to United Nations Office on Drugs Crime (UNODC) up to July 2015 [4]. The cathinones are expected to act as a central nervous system stimulants by promoting the release of monoamine neurotransmitters such as catecholamines and likely inhibiting their reuptake [5]. Their pharmacological profiles were closely resemble to that of amphetamine's acting on central nervous system and subsequent sympathomimetic effects. Frequently cathinones with chiral atom centre show differing potencies for every enantiomeric form [5]. The postulated metabolic phase I pathways of cathinones are through the *N*-dealkylation in particular demethylations, followed by the *O*-methylation and reduction of the keto moiety to alcohols, and the oxidation of the tolyl moiety to the corresponding alcohols or carboxylic acids [6,7]. Until now there is only the Zimmerman test suitable for identification of synthetic cathinones, which provides a clear and unambiguous response for both the hydrochloride and hydrobromide salts in most cases.

Recently we have already presented five novel cathinones and their hydrochloride salts. They were characterized by FTIR, UV–vis, multinuclear NMR spectroscopy and four by single crystal X-ray diffraction method [8]. The current work focused on characteristic reactions for the identification of keto fragment in cathinone constitution and three novel representatives of the compounds in their hydrochloride salt form through the combination of IR, NMR, GC–MS, electronic absorption spectroscopy and single crystal X-ray diffraction method.

2. Experimental

2.1. Apparatus

NMR spectra were obtained with Bruker Avance 400 operating at 400.13 MHz (^{1}H) and 100.5 MHz (^{13}C) at 21 °C; chemical shifts referenced to ext. TMS (^{1}H, ^{13}C); coupling constants are given in Hz.

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The ^{1}H and ^{13}C NMR calculations were performed with the ACD Labs NMR Predictor v.7 program. For GC–MS a Gas Chromatograph Agilent Technologies 7890A with MS 5975 EI/CI MSD with autosampler 7693 with capillary column Agilent HP-5MS (30 m × 0.25 mm × 0.25 μm) was used. FTIR spectra were recorded on a Perkin Elmer spectrophotometer in the spectral range 4000–450 cm^{-1} with the samples in the form of KBr pellets. Electronic spectra were measured on a spectrophotometer Lab. Alliance UV–Vis 8500 in the range 500–180 nm in CH_2Cl_2 solution. Melting points were determined on MPA100 OptiMelt melting point apparatus and uncorrected.

2.2. Materials

All experiments were carried out in an atmosphere of argon. The analyzed hydrochloride salts of **1a**, **1b** and **1c** were confiscated in 2015 by the police in the Upper Silesia region of South Poland and delivered to our laboratory for spectroscopic examination.

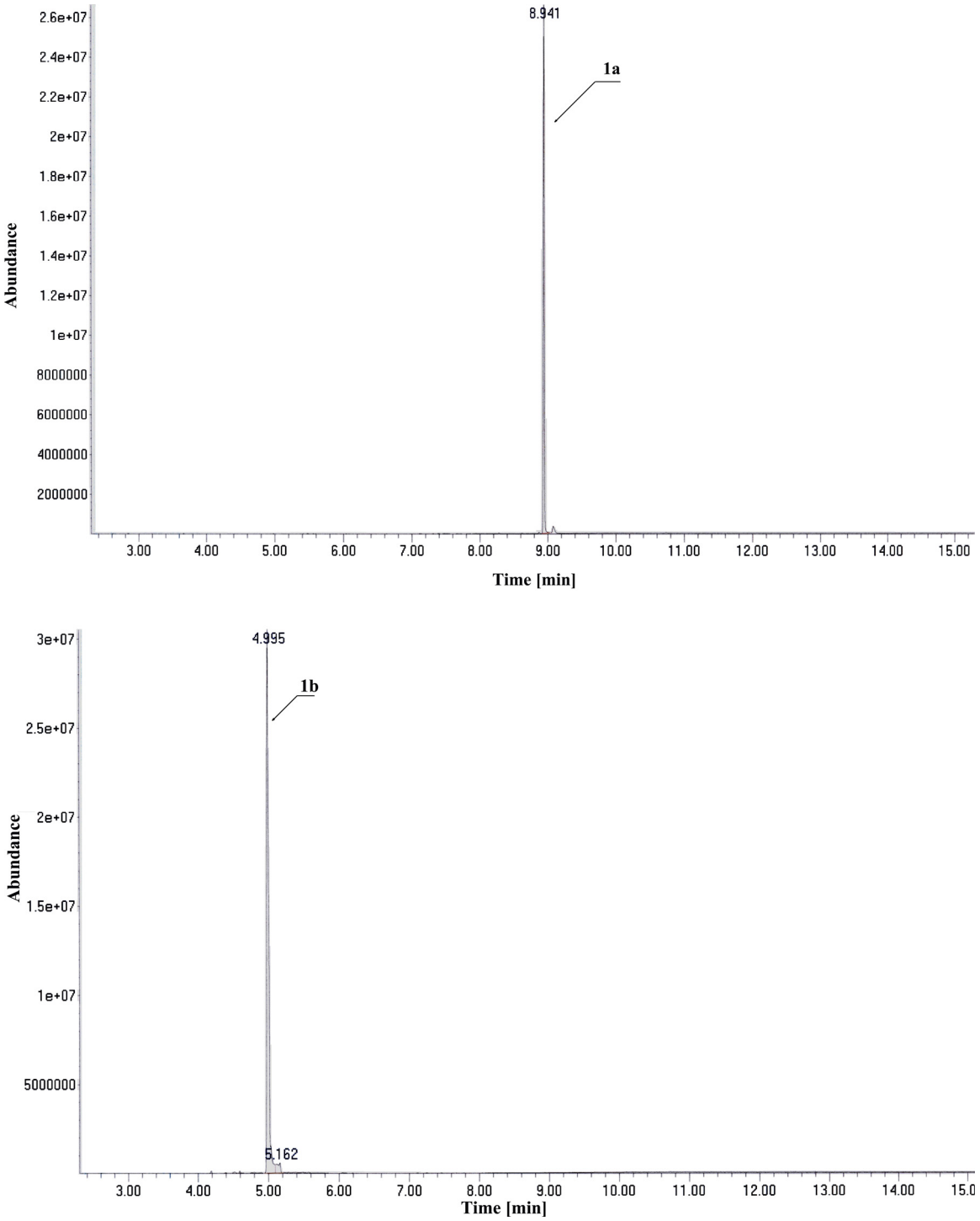

Fig. 1. Chromatograms of the confiscated cathinones **1a**, **1b** and **1c**.