Characteristics And Features Of The Expert Research
On α-Bromovalerophenone (2-bromo-1- phenylpentan-1-one)

Abstract. The research paper discusses methods of expert research on objects containing α-bromovalerophenone. Recently, there has been an increase in the facts of detection of places of unregulated (illegal) manufacture of PVP psychotropic substance with the seizure of large amount of initial reagents for its synthesis. One of these substances, which is used for the synthesis of PVP as well as pentedrone psychotropic substance, is α-bromovalerophenone. Identification of α-bromovalerophenone by methods of qualitative color reactions, thin-layer chromatography (TLC), gas chromatography with mass-selective detection (GC-MS), molecular spectroscopy in the ultraviolet region of the spectrum, and also by X-ray fluorescence spectral analysis (XRF) is outlined.

Key words: α-bromovalerophenone, synthetic cathinones, qualitative chemical reactions, thin-layer chromatography, gas chromatography, chroma-mass spectrometry, forensic examination.

Research Problem Formulation. Recently, structural derivatives of cathinone which are increasingly common among objects of forensic examination have become widely distributed at the market for illegal sale of drugs in Ukraine. Mephedrone (4-MMC, 4-methylmethcathinone), methylene (3,4-methylenedioxy-N-methylcathinone), PVP (α-pyrrolidinopentiophenone), MDPV (3,4-methylenedioxypyrovaleron), butylone (b-keto MBDB), pentedrone (α-methylaminovalerophenone) are the most common and studied synthetic cathinones.

Analysis of Essential Researches and Publications. As a rule, chemical synthesis of cathinones is a simple, two-phase process. At the first stage, the synthesis of α-bromoketone takes place, followed by nucleophilic substitution
with a relevant amine, with formation of the cathinone free base, which can further be converted into a number of salts.

One of such substances that is used for the synthesis of especially dangerous psychotropic substances which circulation is prohibited (α-PVP and pentedrone) is α-bromovalerophenone.

There are several ways of synthesizing -bromovalerophenone, which take place within one stage. One of these ways is photochemical reaction of -halogenation of carbonyl compounds. Another method of synthesis is the reaction of valerophenone with copper bromide (II).

In conformity with the List of Narcotic Drugs, Psychotropic Substances and Precursors approved by Resolution of the Cabinet of Ministers of Ukraine No. 770 dated May 6, 2000, Table I, List No. 2, α-bromovalerophenone is classified as a particularly dangerous psychotropic substance which circulation is prohibited.

However, in literary sources available on the Internet, there is no reference to the facts of human consumption of this substance. Instead, there is evidence that this substance poses a significant damage to a human, since when it evaporates, highly toxic vapors are released possessing strong lachrymatory and irritating properties.

α-Bromovalerophenone is widely available for purchase on the Internet. Many suppliers from countries in Asia (especially China), some countries in Europe and North America offer to purchase 2-bromo-1-phenylpentan-1-one both in small (from 0.100 g to 1 g) and in large (up to 5 tons) quantities. The declared purity of the compound is about 98%.

In view of its easy availability, it can be assumed that illegal import of α-bromovalerophenone into the territory of Ukraine takes place for further synthesis of certain substances of the cathinone series. Due to chemical structure, this substance can be used for the synthesis of particularly dangerous psychotropic substances which circulation is prohibited: -PVP or pentedrone.

In literary sources, 2-bromovalerophenone is mentioned as a precursor that was seized during raids on laboratories for production of α-PVP and pentedrone. This information is supported by the report from the World Health Organization, in which relevant synthesis schemes of the specified psychotropic substances are provided.

General characteristics and main physical and chemical properties of α-bromovalerophenone. -Bromovalerophenone is an organic substance that is a aromatic ketone derivative. It is used in the pharmaceutical industry for production of medicines having calming effect on the nervous system. It is also used in the perfumery industry as a component of some flavorants. It is primary raw material for creation of substances that slow down the speed of chemical reactions (inhibitors).

3. 3Perelik narkotychnykh zasobiv, psykhotropnykh rechovyn i prekursoriv, zatverdzhennyy Postanovoyu Kabinetu Ministiriv Ukrainy № 770 vid 06.05.2000 [in Ukrainian].
α-Bromovalerophenone is an extremely toxic and physiologically dangerous substance.

Physical and chemical properties: transparent colorless or pale yellow oily liquid, density: 1.31 g/cm³; boiling point: 282.267°C (at a pressure of up to 1 atm); fire point: 42.5 °C, refractive index: 1.5418.

The substance is a hydrophobic compound, insoluble in water, but soluble in most organic solvents such as methanol, isopropanol, hexane, ethyl acetate, dichloromethane and acetone.

Research aim. The paper aims to develop an optimal research scheme that would enable to reliably identify the α-bromovalerophenone substance with further determination of its quantitative content, applying the set of approaches tested in practice and physicochemical methods.

Main Content Presentation.

Research materials and methods. The research was carried out during 2020–2022 on the basis of the laboratory of the Materials, Substances and Products Research Department (MSPRD) of the Cherkasy Research Expert Forensic Center of the Ministry of Internal Affairs of Ukraine. Identification of α-bromovalerophenone includes research by the following methods:

- qualitative analytical reactions;
- X-ray fluorescence spectral analysis;
- thin layer chromatography;
- gas chromatography with mass selective detection;
- molecular spectroscopy in the ultraviolet region of the spectrum;
- gas chromatography with flame ionization detection.

Qualitative analytical reactions. In terms of chemical composition, α-bromovalerophenone contains carbonyl (keto-) group in its composition, belonging to the class of bromoketones, and therefore shows chemical properties that are characteristic of ketones.

Carbonyl compounds may be identified by reaction with 2,4-dinitrophenylhydrazine (2,4-DNPH). Almost all aldehydes and ketones form solid colored (yellow or orange-red) 2,4-dinitrophenylhydrazines.

Identification of α-bromovalerophenone by methods of qualitative color reactions, thin layer chromatography (TLC), gas chromatography with mass selective detection (GC-MS), molecular spectroscopy in the ultraviolet region of the spectrum, and also by X-ray fluorescence spectral analysis (XRF), is outlined.
The availability of α-bromovalerophenone, both through purchases on the Internet and through the use of simple synthesis schemes carried out in one or several stages, every year increases the chance of finding this substance in forensic examination objects.

The process of qualitative identification of α-bromovalerophenone in the objects of study includes:
- preliminary study by the method of qualitative analytical reactions and X-ray fluorescence analysis;
- research by thin layer chromatography (TLC);
- research by instrumental methods, in particular gas chromatography with mass selective detection (GC-MS), spectroscopy in the ultraviolet region of the spectrum and gas chromatography with flame ionization detection (GC-FID).

Quantitative determination of the content and mass of α-bromovalerophenone in the objects of study is carried out by GC-MS or GC-FID methods, using a calibration curve or an external standard method without constructing a calibration curve.

The conditions of the methods and operating modes of the devices given in the article have sufficient sensitivity and selectivity and allow accurately determining α-bromovalerophenone in the composition of objects of study. It should be noted that the specified list of tools, methods and methodologies of research is not exhaustive. The forensic expert should be guided by the availability of relevant literature and appropriate analytical equipment while research. In accordance with this, one or another method of studying substances should be used. These methods are subject to mandatory verification before laboratory use.

The obtained research results allow recommending this technique for implementation in forensic expert practice.

Key words:
- α-bromovalerophenone,
synthetic cathinones, qualitative chemical reactions, thin-layer chromatography, gas chromatography, mass spectrometry, forensic examination.

Reagent. Dissolving 2,4-dinitrophenylhydrazine in 60 cm of 85% phosphoric acid by heating on water bath. The solution is diluted with 40 cm3 of 95% ethanol and must be filtered. The resulting solution is stable during long-term storage.

Performing reaction. We add 3 cm3 of the reagent to 1-2 drops of studied solution dissolved in 2 cm3 of 95% ethanol (methanol, methyl cellosolve, dimethylformamide (but not in any case acetone!). The mixture is vigorously stirred, if a precipitate does not immediately form, leave for another 15 minutes. In the course of reaction, a yellow as well as orange-red precipitate may be formed (depending on reaction conditions).

The mentioned reaction shows the existence of a carbonyl (aldehyde or ketone) group in studied substance. The reaction is not specific.

Halogen determination. The Beilstein test. A qualitative method for determination of halogens (excluding fluorine) in a sample, which is based on the formation of volatile copper halides coloring colorless flame in green. Due to its simplicity, it is widely used for rapid analysis of organic halogen compounds.

Performing reaction. Dip heated copper wire into sample substance and introduce into the colorless flame of spirit lamp. The blue-green coloration of alcohol (colorless) flame indicates the presence of chlorine or bromine in the composition, and the green color: iodine.

X-ray fluorescence analysis (XRF). In order to determine the presence of halogens in the molecule of substance, it is possible to carry out research on the method of X-ray fluorescence spectral analysis. The liquid is placed in a special cuvette (pay particular attention to safety precautions when working with acrid substances and respiratory tract irritants!). The research was conducted with the use of energy dispersive X-ray fluorescence spectrometer SERP-01 of ElvaX-L modification or similar, under the following conditions:

<table>
<thead>
<tr>
<th>primary radiation</th>
<th>Ti;</th>
</tr>
</thead>
<tbody>
<tr>
<td>voltage at the anode of the tube</td>
<td>45 kV;</td>
</tr>
<tr>
<td>tube current</td>
<td>40 µA;</td>
</tr>
<tr>
<td>range of analyzed elements</td>
<td>from 12Mg to 92U;</td>
</tr>
<tr>
<td>filming time</td>
<td>60 sec.</td>
</tr>
</tbody>
</table>

The decoding of the spectra and calculation of the relative quantitative elemental composition by the method of fundamental parameters are performed with the help of the device software.

As a result of conducted research, it was established that studied liquid contains bromine.

Research using the method of thin layer ascending chromatography (TLC). To perform research, weighed sample is dissolved in methanol (or any other organic solvent) in the ratio of about 1:100. Obtained solution as well as standard sample solution are placed near the starting line of the chromatographic plate.

Chromatography was carried out within the following systems: xylene; petroleum ether (fraction 80-110 °С) – diethyl ether (4:1); octane – benzene (5:1). Approximate values of ratio of fronts (Rf) on Merck TLC Silica gel 60 F254 plates are presented in Table 1.

The given values may vary depending on environmental conditions, batches of reagents, chromatographic plates, volume of chromatographic bath, and other factors.
Table 1
Approximate values of $R_f$ on Merck TLC Silica gel 60 $F_{254}$ plates

<table>
<thead>
<tr>
<th>System of solvents</th>
<th>$R_f$ value for α-bromovalerophenone</th>
</tr>
</thead>
<tbody>
<tr>
<td>Xylene</td>
<td>0.62</td>
</tr>
<tr>
<td>petroleum ether – diethyl ether</td>
<td>0.50</td>
</tr>
<tr>
<td>octane – benzene</td>
<td>0.31</td>
</tr>
</tbody>
</table>

After lifting the start line of solvent to the finish line, plates were taken out from chambers, dried at room temperature or in a stream of warm air until the solvents smell completely disappeared.

Visualization of obtained results: 1. detection in the UV region of the spectrum (254 and 312 nm); 2. spraying with Dragendorf’s reagent; 3. spraying with the 2,4-DNPH reagent as well as separating qualitative analytical reactions indicated above.

Liquid-gas chromatography with mass selective detection (GC-MS). For qualitative determination of α-bromovalerophenone by gas chromatography with mass selective detection, you must dissolve weighed sample (liquid) in methanol in a ratio of about 1:100. The obtained sample was studied under the following conditions (the screening method):

<table>
<thead>
<tr>
<th>Gas chromatograph</th>
<th>Agilent Technologies (6890N model)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample injection mode</td>
<td>with flow split</td>
</tr>
<tr>
<td>Split of carrier gas flow</td>
<td>20:1</td>
</tr>
<tr>
<td>Sample size</td>
<td>1 μl</td>
</tr>
<tr>
<td>Temperature program of chromatograph thermostat</td>
<td>100 ºC (keep for 3 min.), heated at 100ºC/min. to 300 ºC (keep for 10 min.)</td>
</tr>
<tr>
<td>Carrier gas</td>
<td>Helium</td>
</tr>
<tr>
<td>Flow of carrier gas through column</td>
<td>1.2 ml/min.</td>
</tr>
<tr>
<td>Supply of carrier gas</td>
<td>Continuous</td>
</tr>
<tr>
<td>Column</td>
<td>J&amp;W, HP-5MS, Cat. Nº 19091S-433</td>
</tr>
<tr>
<td>Length, diameter, thickness of coating</td>
<td>30.0 m * 0.250 mm * 0.25 μm</td>
</tr>
<tr>
<td>Mass selective detector (MSD)</td>
<td>Agilent Technologies (Model: 5975B inert MSD)</td>
</tr>
<tr>
<td>MSD mode of operation</td>
<td>on total ion current (SCAN) scanning range of 39 to 450 amu</td>
</tr>
<tr>
<td>Delay for solution yield</td>
<td>3.00 min.</td>
</tr>
<tr>
<td>Quadrupole temperature</td>
<td>150ºC</td>
</tr>
<tr>
<td>Ionization source temperature</td>
<td>230 ºC</td>
</tr>
<tr>
<td>Injector temperature</td>
<td>250 ºC</td>
</tr>
<tr>
<td>Interface temperature</td>
<td>280 ºC</td>
</tr>
</tbody>
</table>

When using other devices (from other manufacturing companies), operating conditions may differ depending on mass detector settings, the type of column used, etc.

Identification of substances is carried out by the retention time of substance and by its mass spectrum.
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Chromatogram analysis was performed using software-based instrument, in this case MSD Productivity ChemStation Revision D.03.00.611 SP1, with application of the NIST Mass Spectral Library and the Cayman Spectral Library.

The retention time of α-bromovalerophenone was RT = 7.299 min. and may vary depending on the software instrument, chromatography operating conditions, etc.

Library mass spectrum of the α-bromovalerophenone substance is presented in Figure 3.

Figure 3. Mass spectrum of α-bromovalerophenone from the Cayman Spectral Library

The main ions: 105; 77; 161; 51; 106; 78; 50; 120; 145 and 198

Spectroscopy in the UV region of the spectrum. To identify molecular composition of studied substance, research was conducted using the method of molecular spectroscopy in the ultraviolet region of the spectrum in the following conditions:

<table>
<thead>
<tr>
<th>Device</th>
<th>HELIOS gamma THERMO ELECTRON</th>
</tr>
</thead>
<tbody>
<tr>
<td>cuvette width</td>
<td>1.0 cm</td>
</tr>
<tr>
<td>spectral index</td>
<td>0.5 nm</td>
</tr>
<tr>
<td>scanning speed</td>
<td>200 nm/min.</td>
</tr>
<tr>
<td>wavelength range</td>
<td>200-400 nm</td>
</tr>
</tbody>
</table>

In order to do this, weighed substance (liquid) was dissolved in methanol, placed in cuvettes, and the spectrum was recorded under the above conditions.

The molecular spectrum of the studied substance in the UV region of the spectrum is shown in Figure 4.

At the end of chromatographic research, chromatograms were analyzed using the device software.

The α-bromovalerophenone mass is determined according to calibration curve. For this purpose, its concentration in samples is quantified with the help of the device software.
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Roman Tsinda,
Wiaczesław Pasiecznik,
Dmytro Szinkarenko,
Walentyna Gordijczuk

W artykule omówiono metody eksperckiego badania obiektów zawierających w swoim składzie α-bromowalerofenon. Ostatnio nastąpił wzrost faktów wykrycia miejsc nieuregulowanej (nielegalnej) produkcji substancji psychotropowej PVP wraz z zajęciem dużej liczby początkowych odczynników do jej syntezy. Jedną z takich substancji, która służy do syntezy PVP, a także substancji psychotropowej pentedronu, jest α-bromowalerofenon. Opisana identyfikacja α-bromowalerofenonu metodami jakościowych reakcji barwnych, chromatografii cienkowarstwowej (TLC), chromatografii gazowej z selektywnym detektorem mas (GC-MS), spektroskopii molekularnej w zakresie ultrafioletu widma, a także rentgenowskiej analizy widmowej fluorescji (XRF).

Dostępność α-bromowalerofenonu, zarówno poprzez zakupy w Internecie, jak i poprzez stosowanie prostych schematów syntezy przeprowadzanych w jednym lub kilku etapach, z każdym rokiem zwiększa możliwość przedostania się substancji na przedmiot badań kryminalistycznych.

Proces jakościowej identyfikacji α-bromowalerofenonu w obiektach badań obejmuje:
- wstępne badania metodą jakościowych reakcji analitycznych i analizy fluorescji rentgenowskiej;
- badania metodą chromatografii cienkowarstwowej (TLC);
- badania metodami instrumentalnymi, w szczególności chromatografią gazową z detekcją selektywną masę (GC-MS), spektroskopią w zakresie nadfioletu widma oraz chromatografią gazową z detekcją płomieniowo-jonizacyjną (GC-FID).

Determınation of α-bromovalerophenone mass according to calibration curve. To determine quantitative content of α-bromovalerophenone in the submitted object, we should dissolve two weighed samples (liquids) in exact quantities of methanol. Obtained solutions are analyzed by chromatography using flame ionization detection under the following conditions:

<table>
<thead>
<tr>
<th>Gas chromatograph</th>
<th>Shimadzu GC 2010 Pro AF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample injection mode</td>
<td>with flow split 20:1</td>
</tr>
<tr>
<td>Sample size</td>
<td>1 ml</td>
</tr>
<tr>
<td>Temperature program of chromatograph thermostat</td>
<td>100 ºC (keep for 1 min.), heated at 25ºC/min. to 275 ºC (keep for 2 min.)</td>
</tr>
<tr>
<td>Carrier gas</td>
<td>Helium</td>
</tr>
<tr>
<td>Flow of carrier gas through column</td>
<td>1.2 ml/min.</td>
</tr>
<tr>
<td>Supply of carrier gas</td>
<td>Continuous</td>
</tr>
<tr>
<td>Column</td>
<td>Rxi-5-MS, Cat. № 13423</td>
</tr>
<tr>
<td>Length, diameter, thickness of coating</td>
<td>30.0 m * 0.250 mm * 0.25 µm</td>
</tr>
<tr>
<td>Detector</td>
<td>flame ionization (FID)</td>
</tr>
<tr>
<td>FID mode of operation:</td>
<td></td>
</tr>
<tr>
<td>temperature</td>
<td>280 ºC</td>
</tr>
<tr>
<td>hydrogen flow rate</td>
<td>40 ml/min.</td>
</tr>
<tr>
<td>airflow rate</td>
<td>400 ml/min.</td>
</tr>
</tbody>
</table>

The percentage content of substance in each sample is determined. The average value of two parallel samples is taken as the final value.

Figure 4. UV spectrum of α-bromovalerophenone recorded in A mode.

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Determination of α-bromovalerophenone mass with application of the external standard method without constructing calibration curve. Samples as well as conditions for chromatography are prepared under the aforementioned conditions. What is more, chromatography of a standard sample with a precisely defined concentration is also carried out under the specified conditions.

Peak areas of substance and standard are determined using the software. Percentage content of substance in each sample is quantified. The average value of two parallel samples is taken as the final value.

It should be stressed that there are other methods outlined in specialized literature on forensic science which also help to obtain accurate results and can be applied at the discretion of forensic expert. In a specific case, depending on capabilities of a laboratory, other research methods can be chosen, but their combination should comply with international practice.

Conclusions
1. Availability of α-bromovalerophenone, both due to purchases on the Internet and the use of simple synthesizing schemes carried out in one or more stages, increases the chance of finding this substance in forensic examination objects.
2. The process of qualitative identification of α-bromovalerophenone in studied objects includes:
   - preliminary study by the method of qualitative analytical reactions and X-ray fluorescence analysis;
   - research by thin layer chromatography (TLC);
   - research by instrumental methods, in particular gas chromatography with mass selective detection (GC-MS), spectroscopy in the ultraviolet region of the spectrum and gas chromatography with flame ionization detection (GC-FID).
3. Quantitative determination of the content and mass of α-bromovalerophenone in the objects of study is carried out by GC-MS or GC-FID methods, using a calibration curve or the external standard method without constructing a calibration curve.
4. The conditions of the methods and operating modes of the devices given in the article have sufficient sensitivity and selectivity and allow accurately determining α-bromovalerophenone in the composition of studied objects.

It should be noted that the specified list of tools, methods and methodologies of research is not exhaustive. The forensic expert should be guided by the availability of relevant literature and appropriate analytical equipment while research. In accordance with this, one or another method of studying substances should be applied. These methods are subject to mandatory verification before laboratory use.

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