



NATURAL OPIUM PRODUCTS IN THE MODERN STRUCTURE OF DRUG POISONING (LITERATURE REVIEW AND RESULTS OF DRUG SCREENING FOR 1990-2020)

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ABSTRACT. Despite the rapid increase in synthetic drug use in the United States, the European Union, and many other parts of the world, narcotic and psychoactive substances of natural origin remain relevant to toxicologists.

Aim. To analyze the results of drug screening of opium drugs in 1990-2020 and their impact on the formation of acute unintentional poisoning among the adult population of Kyiv.

Materials and Methods. A retrospective analysis of the reports of the toxicological laboratory of the Kyiv City Clinical Emergency Hospital for 1990-2020 on the results of chemical-toxicological screening for drug content in persons diagnosed with "Acute drug poisoning" (ICD-10: T40.0-T40.3). Methods used: Immuno-chromatographic analysis (ICA), thin layer chromatography (TLC) and gas-liquid chromatography with mass spectral detection (GC/MS).

Results. According to official data in Ukraine in 2019, the substances that caused people to seek medical help are distributed as follows: opioids – 68.53%; cannabinoids – 6.84%; cocaine – 0.08%; hallucinogens – 0.04%; other drugs – 24.51%. Among those who died as a result of drug poisoning, the proportion of opiates T40.2 (codeine, morphine) was 16%; opium T40.0 – 4%; methadone T40.3 – 23%; other drugs T40.4 (pethidine) – 2%, which together is 45%. According to the results of chemical-toxicological screening for opiate content, it was found that the first step in the average annual growth rate is occupied by: buprenorphine (+7.95%), morphine (+7.6%) and heroin (+6.04%). The number of positive tests decreased in the group of opiates - "shirka" (-9.38%) and opium alkaloids (-2.55%). Over the last 10 years, there has been a progressive increase in the annual number of positive tests for methadone content (+39.3%) at $R^2=8904$, which indicates a high stability of the growth rate.

Conclusions. Opiates continue to occupy an important segment in the structure of drugs, where their positions for the period 1990-2020 strengthened buprenorphine, morphine and heroin against the weakening of the position of opium ("shirka") and opium alkaloids; at the same time there is a rapid increase in the proportion of semi-synthetic and synthetic opioids. These changes necessitate continuous improvement of methods of chemical and toxicological studies of opium products, clinical diagnosis and prevention of related poisonings.

Key Words: opiates, drugs poisoning.

Introduction. Despite the rapid increase in synthetic drug use in the United States, the European Union, and many other parts of the world, narcotic and psychoactive substances of natural origin remain relevant to clinical toxicologists.

A review of scientific sources related to the field of drug control (UNODS, EMCDDA) suggests that opiates remain a significant segment in the structure of drugs in the United States, Canada, the United Kingdom and some EU countries, unfortunately, Ukraine is no exception.

Today, a wide range of standardized research methods are used in the laboratory diagnosis of acute poisoning and intoxication caused by drug use. Modern technology of chemical-analytical

research includes preliminary identification of group affiliation of narcotic substances ("dry" chemistry), carrying out of confirmatory researches using methods of thin-layer chromatography, gas chromatography (flame-ionization or mass spectrometry); methods of spectrophotometry, photometry; immunochemical methods of analysis, high performance liquid chromatography, etc.

The choice of methods and techniques for chemical and toxicological analysis depends on the objectives of the study, economic opportunities and qualifications of laboratory staff.

The method of toxicological screening for qualitative detection and quantification of opium

alkaloids and their derivatives in biological fluids of the human body is key for the toxicologist in making decisions regarding the diagnosis, treatment, prevention and examination of drug poisoning.

The aim of the work is to analyze the results of screening for opium drugs, its dynamics in 1990-2020 and the impact of opiates on the formation of acute unintentional poisoning among the adult population of Kyiv.

Materials and Methods. A retrospective analysis of the reports of the toxicological laboratory of the Kyiv City Clinical Emergency Hospital for 1990-2020; the structure and dynamics of positive tests for the content of narcotic substances determined during chemical and toxicological screening in patients treated with the diagnosis: "Acute drug poisoning" (ICD-10: T40.0-T40.3) were studied. Methods used: immunochromatography, thin layer sorbent chromatography (TLC) and gas-liquid chromatography with mass spectral detection (GC/MS).

For the purpose of comparative analysis of the structure of drugs of natural origin, the data of official reports of the United Nations Office on Drugs and Crime (UNODS), the European Center for Drugs and Drug Addiction (EMCDDA) and the sources of the scientific library PubMed were used. Methods of system, comparative and content analysis are used. Statistical analysis was performed using Statistica 12.6 (Windows 10/7).

This study is part of the research work "Scientific substantiation of safety for human health of pesticides and agrochemicals, new technologies, substances, materials, products, environmental facilities, food and food raw materials; development of appropriate medical criteria and indicators (sanitary and epidemiological); sanitary-chemical, toxicological-hygienic assessment, regulation, rationing "(state registration number - 0112U001133), on the topic:" Establish causal links in the formation of modern household toxicosis and justify the modification of artificial detoxification technologies for socially significant poisons and their mixes". The research was carried out in accordance with the Helsinki Declaration of the World Medical Association "Ethical principles of medical research with human participation as an object of study" (1964) and approved by the local ethics committee.

Results. According to the EMCDDA, global and European trends in the structure of drugs have changed significantly over the past 25 years, but,

as many decades ago, the use of opium-based products is a major factor in health damage. At the beginning of 2020, deaths from opioid overdoses (natural and synthetic) accounted for 82% of all fatal drug poisonings in the European Union. Among opium products, heroin is the most common among consumers, but others, such as methadone, buprenorphine, tramadol, and fentanyl derivatives, also have significant weight in the illicit market [1-3]. At the end of 2018, the prevalence of opioid use with a high risk of overdose among adults (aged 15–64) was estimated at 0.4% of the total population of the European Union, which is equivalent to 1.3 million people. Three quarters (75%) of this number were in the five most populous countries of the European Union (Germany, Spain, France, Italy, Great Britain). In these countries, the most common opioids (other than heroin) were: improperly used methadone, buprenorphine, fentanyl, codeine, morphine, tramadol and oxycodone. The main routes of application were: injectable - 34%; smoking / inhalation - 47%; swallowing - 3%; inhalation - 15%; otherwise - 1%. The following substances were present in the structure of requests for medical assistance in case of overdose or poisoning: heroin - 83.6%; other opioids - 16.4%; of them fentanyl - 0.4%, buprenorphine - 4%; methadone - 5%; others - 7% [1, 4-6].

Opioids also accounted for a significant share of opioid users in Poland, where 27% of respondents reported using compote (heroin made from poppy straw), and in Cyprus, where 39% of users reported using oxycodone as a priority [1].

Ukraine does not participate in the European monitoring of drug poisoning, but carries out state monitoring of drugs and psychoactive substances, which is reflected in the reports of the State Service of Ukraine for Medicines and Drug Control and information from specialized institutions of the Ministry of Health of Ukraine. According to the results of the analysis of the drug situation in Ukraine according to open sources, the structure of substances that caused people to seek medical help: opioids – 68.53%; cannabinoids – 6.84%; cocaine – 0.08%; hallucinogens – 0.04%; other drugs – 24.51%. Among the drugs seized during 2018, the top 5 include the following substances: cannabis; poppy straws; amphetamine; cocaine; methadone.

Analyzing the cases of deaths from poisoning by psychoactive substances, it was found that the proportion of deaths from poisoning by opi-

oids T40.2 (codeine, morphine) was 16%; from opium T40.0 – 4%; from methadone T40.3 – 23%; other synthetic drugs T40.4 (pethidine) – 2%, which together account for 45% of all deaths related to the use of psychoactive substances; other unspecified drugs T 40.6 accounted for 43%. Among the deceased, in whom the fact of the presence of a psychoactive substance in the biological material was established, opioids accounted for 27.9%. Among the dead, people aged 25-44 years (76.1%) were male – 84.8%, female – 15.2% [7].

Emergency medical care in cases of drug poisoning in Kyiv is carried out at the pre-hospital stage by emergency medical care teams, and at the inpatient stage in the toxicological center. The Kyiv Toxicological Center (hereinafter – KTC) has existed since 1986, it consists of a toxicology department with 30 beds, a department of intensive care and extracorporeal detoxification with 6 beds and a toxicology (chemical-analytical) laboratory. On average, 2,500 adult patients with acute poisoning of chemical etiology are hospitalized in the KTC per year, 1,500 patients are provided on an outpatient basis, round-the-clock telephone consultations and outpatient visits to other hospitals in Kyiv are provided. Toxicological laboratory is a specialized chemical-analytical laboratory that works around the clock and annually performs about 25-30 thousand studies of biological material (blood, urine, gastric contents) for the presence of toxic substances.

The object of the study was selected drug poisoning in adults (18 years and older), the subject of the study – opium-based drugs that gave positive tests during toxicological screening of the biological environment of persons seeking medical care with a diagnosis of "drug poisoning".

From the beginning and throughout the study period, immunochromatographic analysis (IHA) was used to determine the group affiliation of drugs during screening. Highly sensitive test strips based on monoclonal antibodies were used, which allowed to detect both native compounds (eg, morphine, codeine) and some metabolites (eg, 3 β -morphine-glucuronide). When testing urine samples with a content 25% below or above the established threshold of detection (cut-off) in some cases there were fuzzy results (category of "unconfirmed" results).

In order to exclude errors after obtaining a positive result in the determination of opium alka-

loids, it was mandatory to use confirmatory chemical and toxicological analysis by other more specific methods (thin layer chromatography (TLC) and gas-liquid chromatography with mass spectral detection (GC/MS)).

When using the HTSS method, silica gels were used as sorbents, this method was also used for additional purification of certain substances, their isolation and detection, and in a modified form and to confirm the study of opiates (cut-off 200 $\mu\text{g/l}$). The limit of detection of opiates (heroin, codeine, β -codeine, meconic acid, 6-Monoacetylmorphine (6-MAM), morphine, oripavin, papaverine, thebaine) by thin layer chromatography – 0.5-1 mg/liter. Densitometric method was used to quantify the content of opiates during HTSC, and a calibration graph was used to quantify the content of opiates, codeine and papaverine were chosen as standards.

After 2001, the GC/MS method (Aligent 6850/5973N, manufactured by Aligent Technologies, HP-5MS quartz capillary column) was used to search for and quantify the group affiliation of narcotic substances. Identification of all detected substances was performed by comparing the retention times of the characteristic ions of the test substances with the library data. When detecting characteristic ions with a reliability of more than 75%, the conclusion was made about the detection of opium alkaloids and their derivatives. The limit of detection of opiates by GC/MS is 5.0 ng / ml ($\mu\text{g/l}$).

Fig. 1 and 2 show the structure of opiates and opioids identified in patients with drug poisoning, petal diagrams clearly show the differences manifested by a gradual decrease in the proportion of opiates and with an increase in the proportion of opioids in the structure of poisoning.

Fig. 3-8 show data on the number of positive tests obtained during the year based on the results of urine tests of patients with drug and psychotropic poisoning. The dynamics of indicators with different rates of growth and decline throughout the study period are reflected by the coefficients R-square (R^2) of the logarithmic approximation (trend lines). During the entire study period, opium alkaloids showed a negative average annual growth rate of 2.55%, and unstable dynamics of change in the indicator – $R^2=0.3574$ (Fig. 3). Positive tests for opiate content (cases associated with the injection of poppy straw extract, or "shirka") also had a negative average annual growth rate – -9.38% with a

high rate of $R^2=0.9105$, which demonstrates the stability of the dynamics of the indicator (Fig. 4).

The number of positive tests for morphine content revealed an average annual growth rate of 7.6%, with a high value of $R^2=0.7024$, which confirms the stability of growth dynamics (Fig. 5). The number of positive tests for heroin content showed an average annual growth rate of 6.04%, with a low rate of $R^2=0.2546$, which indicates the instability of the change during the study period (Fig. 6).

Thus, according to the results of the study of the dynamics of positive tests for opiate content, morphine (7.6%) and heroin (6.04%) took the first place in terms of the average annual growth rate. Instead, a decrease in the number of positive tests occurred in the groups of opiates (minus 9.38%) and opium alkaloids (minus 2.55%).

Positive tests for buprenorphine (semi-synthetic opioid) had an average annual growth rate of 7.95%, and $R^2=0.3053$ indicates the instability of changes in the indicator during the study period (Fig. 7). It is important to note that over the last 10 years there has been a progressive increase in the annual number of positive tests for methadone (semi-synthetic opioid) with an average annual growth rate of 39.3% at $R^2=0.8904$, which indicates the stability of the indicator (Fig. 8).

The growth rate of positive tests for the content of semisynthetic and synthetic opioids indicates significant changes in the structure of opium drugs occurring in recent years. These changes necessitate continuous improvement of chemical and toxicological research methods, clinical diagnostics and approaches to the use of antidotes and detoxification methods.

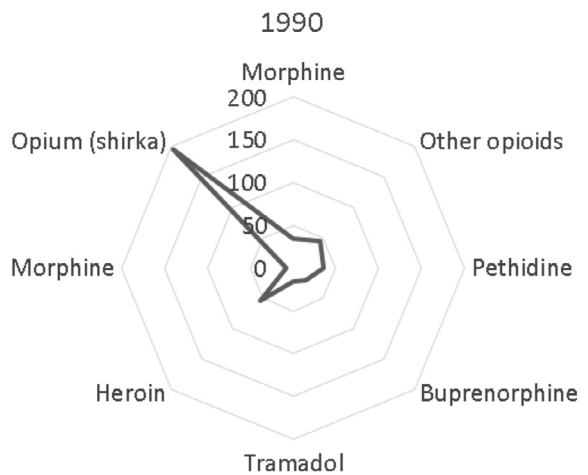


Fig. 1. The structure of opiates and opioids identified in the urine of persons who sought medical help for poisoning by drugs and psychotropic substances in 1990 (research methods: rapid testing, IHA, TLC).

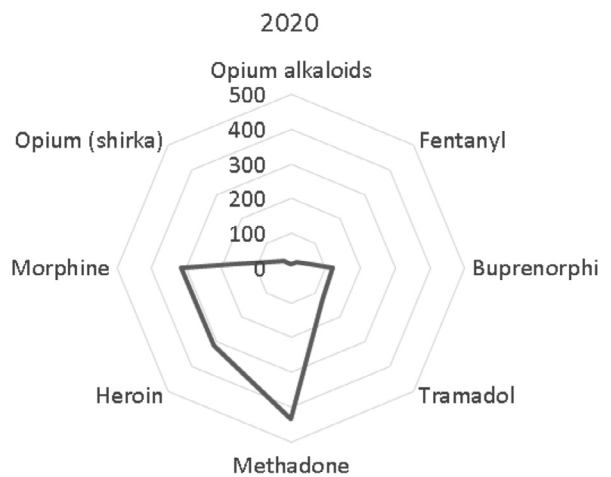


Fig. 2. Structure of opiates and opioids identified in the urine of persons seeking medical care for poisoning by drugs and psychotropic substances in 2020 (research methods: rapid testing, GC/MS).

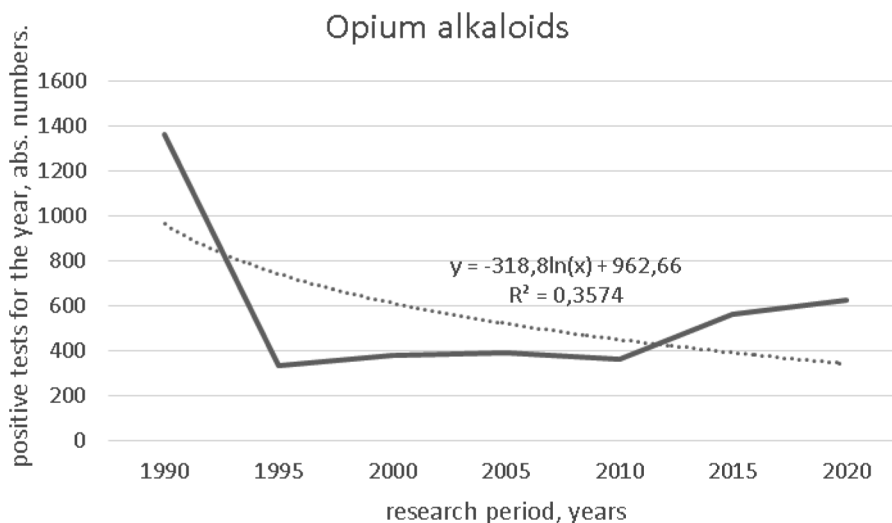


Fig. 3. The number of positive tests for the content of opium alkaloids (codeine, thebaine, papaverine, etc.), according to the KTC in the period 1990-2020.

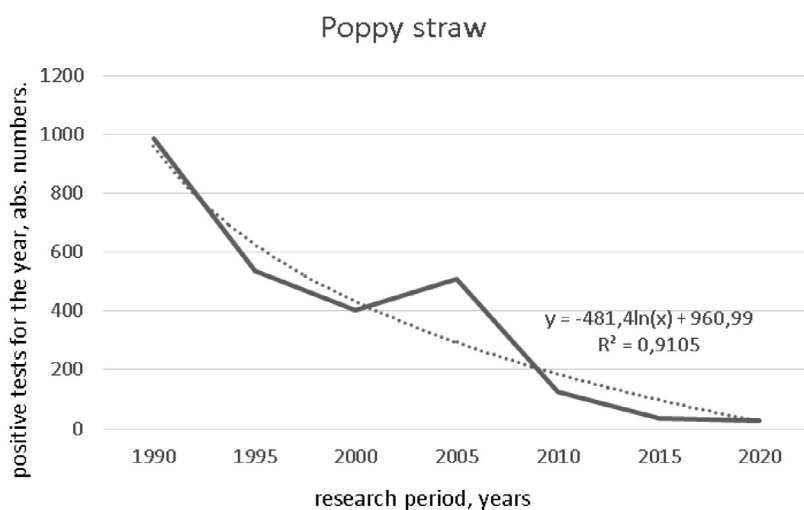


Fig. 4. Number of positive tests for opiates (poisoning tests due to injection of poppy straw extract, or "shirka"), according to the KTC in the period 1990-2020.

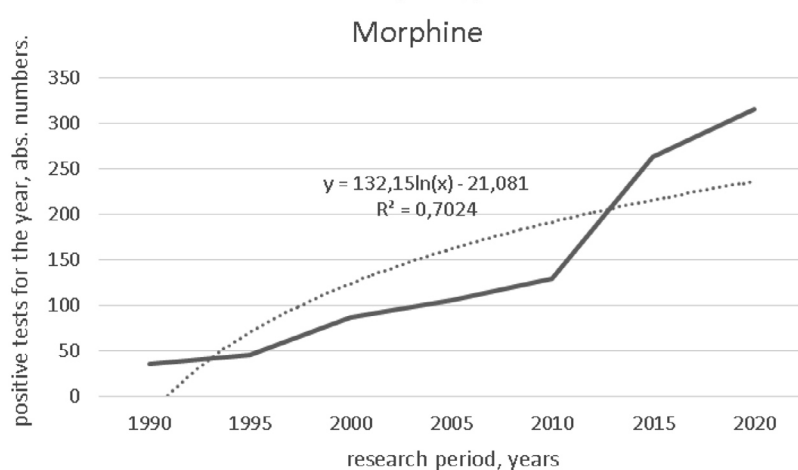


Fig. 5. The number of positive tests for morphine, according to the KTC in the period 1990-2020.

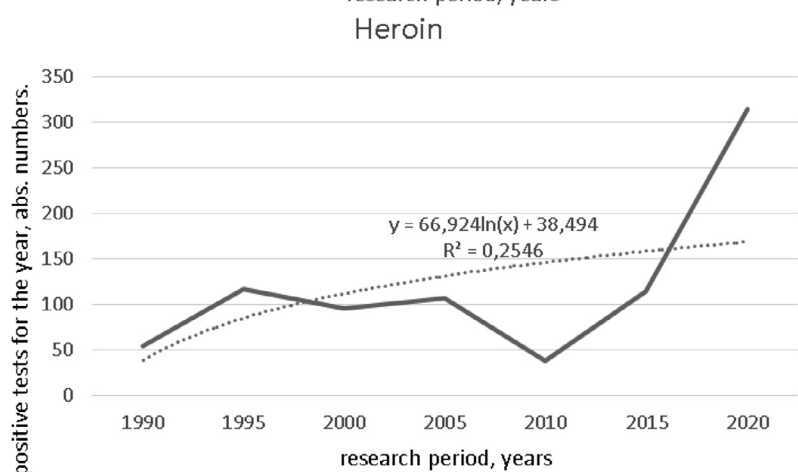


Fig. 6. The number of positive tests for heroin, according to the KTC in the period 1990-2020.

Discussion. When analyzing sources of scientific information related to drugs, it is important to take into account some terminological features. In this study, we follow the current United Nations glossary on drugs and crime (UNODS) [4].

In many sources of information, including official ones, the term "opioids" the authors combine both natural (opiates) and synthetic (opioids) drugs that act mainly on the μ -receptors of the central nervous system. Therefore, we suggest paying attention to some interpretations of

the key terms proposed by UNODS.

The term "opium" defines the coagulated juice of the opium poppy (plants of the species *Papaver somniferum* L. The plant grows well in many countries with temperate climates and is a source of a number of psychoactive substances (alkaloids), the main of which are morphine and codeine [8].

In percentage, the main alkaloids of *Papaver somniferum* L. are distributed as follows: morphine 3.1-19.2%; codeine 0.7-6.6% thebaine 0.2-

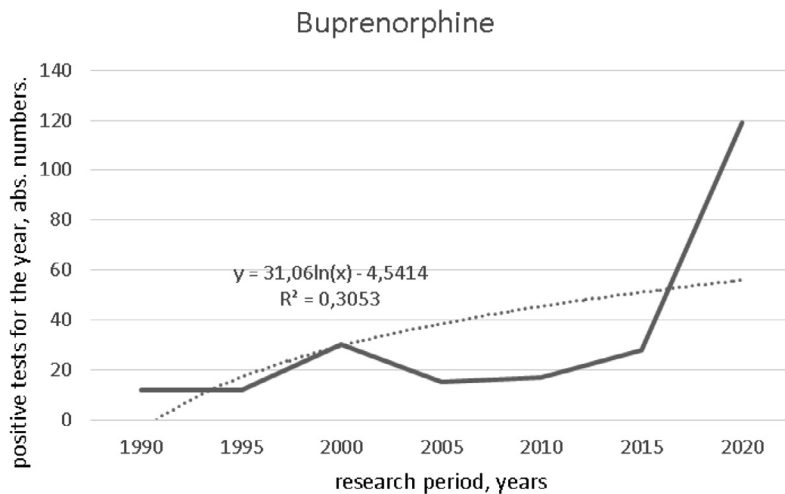


Fig. 7. The number of positive tests for the content of buprenorphine (semi-synthetic opioid), according to the KTC in the period 1990-2020.

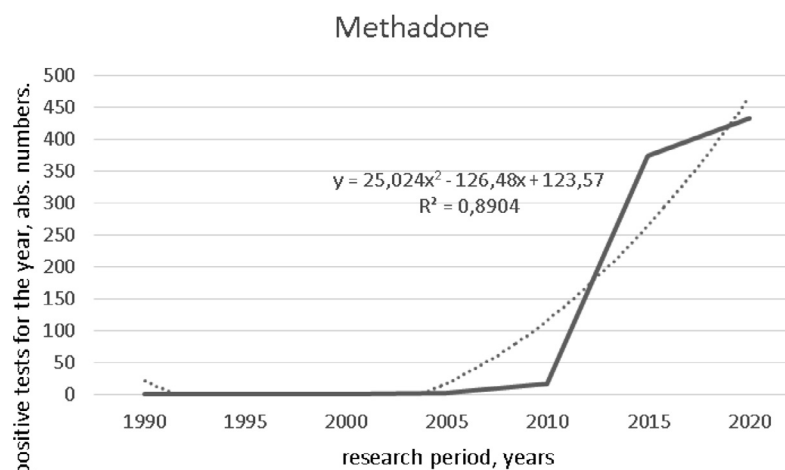


Fig. 8. The number of positive tests for methadone (semi-synthetic opioid), according to the KTC in the period 1990-2020.

10.6%; papaverine <0.1-9.0%; noscapine 1.4-15.8%. Raw opium is obtained from immature boxes of opium poppy. Milk juice of opium poppy is collected from the surface of the box, on which it acts as a result of shallow incisions. Raw opium is of market value, which in its fresh form is a heterogeneous sticky (resin-like) mass of dark brown color, containing particles of opium poppy boxes, which eventually hardens and becomes brittle.

The term "poppy straw" defines all parts (except seeds) of cut opium poppy, including the dried upper part of the stem and box of the poppy plant. Poppy straw concentrate: a material obtained as a result of the process of concentration of alkaloids contained in its composition, as a result of which a substance is created that becomes the subject of illegal trade.

The term "opiates" defines alkaloids of natural origin contained in the plant *Papaver somniferum* L., such as morphine, codeine, thebaine, etc. Instead, the term "opioids" is often used. However, opioids are chemical compounds of artificial origin that are derived from opiates but are not opiates.

Opium, poppy straw concentrate, morphine and heroin are included in List I of the 1961 Single Convention on Narcotic Drugs [9].

Morphine is the main alkaloid derived from opium or poppy straw. Color – from whitish to dark brown. Morphine can be compressed into briquettes, which are sold under different brands or names.

Heroin (diamorphine or diacetylmorphine) is a semi-synthetic opiate derived from morphine. There are two main types of heroin: the water-soluble salt of diacetylmorphine hydrochloride and the slightly water-soluble diacetylmorphine base. After injection, heroin is rapidly broken down in the blood to form active 6-monoacetylmorphine and then morphine, the most active metabolite of heroin.

Compared with morphine, heroin has a higher solubility in fats (due to the presence of two acetyl groups), overcomes the blood-brain barrier faster (usually within 15-20 seconds) and reaches a relatively high level of concentration in the brain after intravenous injection: the brain absorbs almost 70 percent of the administered

dose. As a result of oral administration, heroin decomposes mainly to morphine and has almost twice the potency of morphine and a powerful narcotic potential. The main methods of heroin use are injections, intranasal administration and inhalation by smoking.

The general term "opioids" refers to opiates and their synthetic analogues, which may be half or completely artificial, but similar in their action to morphine. Therefore, opioids are widely used as analgesics for acute and chronic pain, as well as anesthesia for surgery.

Synthetic opioids can differ significantly in structural terms and have significant potency. This group of drugs includes many different substances, including a number of derivatives of fentanyl, methadone, buprenorphine and AH-7921 and many others. The importance of synthetic opioids in the current structure of drug poisoning is so great that our separate study will soon be devoted to this topic.

Conclusions

According to the results of toxicological screening in 1990-2020, it was found that natural

opium products remain an important component of the spectrum of narcotic drugs that cause poisoning, and their structure has changed significantly during the study period.

1. It is established that the first step in the average annual growth rate is occupied by: buprenorphine (+7.95%), morphine (+7.6%) and heroin (+6.04%); negative indicators of average annual growth are shown by narcotic products based on poppy straw, or "shirka" (-9.38%) and opium alkaloids (-2.55%).

2. During 2010-2020, the average annual growth rate of positive tests for methadone reached a record (+39.3%) at $R^2=0.8904$; methadone clearly demonstrates the trend of consumers switching from natural products based on opium to the use of semi-synthetic and synthetic opioids.

3. The dynamic change of the spectrum of drugs, as an object of chemical analysis, necessitates the search for new methods of chemical and toxicological research and increase the material and technical level of specialized chemical and analytical laboratories.

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ПРОДУКТИ ПРИРОДНОГО ОПІУ В СУЧАСНІЙ СТРУКТУРІ НАРКОТИЧНИХ ОТРУЄНЬ (ОГЛЯД ЛІТЕРАТУРИ ТА РЕЗУЛЬТАТИ СКРИНІНГУ НА НАРКОТИКИ У 1990-2020 рр.)

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РЕЗЮМЕ. Незважаючи на стрімке збільшення обсягів споживання синтетичних наркотиків у США, країнах Європейського Союзу та багатьох інших регіонах світу, наркотичні та психоактивні речовини природного походження залишаються актуальним об'єктом дослідження токсикологів.

Мета. Аналіз результатів скринінгу на наркотики групи опію за 1990-2020 рр. та їхній вплив на формування гострих ненавмисних отруєнь серед дорослого населення м. Києва.

Матеріали та методи. Проведено ретроспективний аналіз звітів токсикологічної лабораторії Київської міської клінічної лікарні швидкої медичної допомоги за 1990-2020 рр. про результати хіміко-токсикологічного скринінгу на вміст наркотичних речовин у осіб з діагнозом: «Гостре наркотичне отруєння» (МКХ-10:T40.0-T40.3). Використано методи: імунохроматографічний аналіз (ІХА), хроматографія у тонкому шарі сорбенту (ТШХ) та газорідна хроматографія з мас-спектральним детектуванням (ГХ/МС).

Результати. За офіційними даними, в Україні у 2019 р. речовини, що стали причиною звернення осіб за медичною допомогою, розподілені наступним чином: опіоїди – 68,53%; канабіноїди – 6,84%; кокаїн – 0,08%; галлюциногени – 0,04%; інші наркотики – 24,51%. Серед осіб, померлих внаслідок отруєнь наркотиками, частка опіатів Т40.2 (кодеїн, морфін) становила 16%; опій Т40.0 – 4%; метадон Т40.3 – 23%; інших наркотиків Т40.4 (петидин) – 2%, що разом становить 45%. За результатами хіміко-токсикологічного скринінгу на вміст опіатів встановлено, що першу сходинку за темпом середньорічного зростання посідають: бупренорфін (+7,95%), морфін (+7,6%) і героїн (+6,04%). Зменшення кількості позитивних тестів відбулося у групі опіатів – «ширки» (-9,38%) і алкалоїдів опію (-2,55%). Останні 10 років відбувається прогресивне зростання щорічної кількості позитивних тестів на вміст метадоноу (+39,3%) при $R^2=8904$, що свідчить про стабільність темпу зростання показника.

Висновки. Опіати продовжують займати вагомий сегмент у структурі наркотичних речовин, де свої позиції за період 1990-2020 рр. посіли бупренорфін, морфін і героїн на фоні послаблення позиції опію («ширки») та алкалоїдів опію; одночасно відбувається швидке збільшення частки напівсинтетичних і синтетичних опіоїдів. Зазначені зміни обумовлюють необхідність постійного удосконалення методів хіміко-токсикологічних досліджень продуктів опію, клінічної діагностики та профілактики пов'язаних з ними отруєнь.

Ключові слова: опіати, наркотичні отруєння.

ПРОДУКТЫ ПРИРОДНОГО ОПИЯ В СОВРЕМЕННОЙ СТРУКТУРЕ ОТРАВЛЕНИЙ НАРКОТИКАМИ (ОБЗОР ЛИТЕРАТУРЫ И РЕЗУЛЬТАТЫ СКРИНИНГА НА НАРКОТИКИ В 1990-2020 гг.)

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РЕЗЮМЕ. Несмотря на стремительное увеличение объемов потребления синтетических наркотиков в США, странах Европейского Союза и многих других регионах мира, наркотические и психоактивные вещества природного происхождения остаются актуальным объектом исследования для токсикологов.

Цель. Анализ результатов скрининга на наркотики группы опия за 1990-2020 гг. и их влияние на формирование острых непреднамеренных отравлений среди взрослого населения г. Киева.

Материалы и методы. Проведен ретроспективный анализ отчетов токсикологической лаборатории Киевской городской клинической больницы скорой медицинской помощи за 1990-2020 гг., результатов химико-токсикологического скрининга на содержание наркотических веществ у лиц с диагнозом «Острое наркотическое отравление» (МКБ-10:T40.0-T40.3). Применялись методы: иммунохроматографический анализ (ИХА), хроматография в тонком слое сорбента (ТСХ) и газожидкостная хроматография с масс-спектральным детектированием (ГХ/МС).

Результаты. По официальным данным в Украине в 2019 году вещества, ставшие причиной обращения за медицинской помощью, распределились следующим образом: опиоиды – 68,53%; каннабиноиды – 6,84%; кокаин – 0,08%; галлюциногены – 0,04%; другие наркотики – 24,51%. Среди лиц, умерших вследствие отравлений наркотиками, доля опиатов Т40.2 (кодеин, морфин) составила 16%; опий Т40.0 – 4%; метадон Т40.3 – 23%; других наркотиков Т40.4 (петидин) – 2%, что составило 45%. По результатам химико-токсикологического скрининга на содержание опиатов установлено, что первое место по темпу среднегодового роста занимают: бупренорфин (+7,95%), морфин (+7,6%) и героин (+6,04%). Уменьшение количества положительных тестов произошло в группе опиатов – «ширка» (-9,38%) и алкалоидов опия (-2,55%). За последние 10 лет произошел прогрессивный рост ежегодного количества положительных тестов на содержание метадоноу (+39,3%) при $R^2=8904$, что свидетельствует о стабильности темпа изменения показателя.

Выводы. Опии продолжают занимать весомый сегмент в структуре наркотических веществ, где свои позиции за период 1990-2020 гг. усилили бупренорфин, морфин и героин на фоне ослабления позиции опия («ширка») и алкалоидов опия; одновременно произошло увеличение доли полусинтетических и синтетических опиоидов. Указанные изменения определяют необходимость постоянного совершенствования методов химико-токсикологических исследований продуктов опия, клинической диагностики и профилактики связанных с ними отравлений.

Ключевые слова: опиаты, отравления наркотиками.

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