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## STRUCTURAL CHANGES IN *Peganum harmala* L. INDUCED BY GAMMA RADIATION

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## СТРУКТУРНЫЕ ИЗМЕНЕНИЯ В *Peganum harmala* L., ВЫЗВАННЫЕ ГАММА-ИЗЛУЧЕНИЕМ

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**Abstract.** For the first time, the qualitative and quantitative alkaloid composition of *Peganum harmala* L. was thoroughly studied by identifying IR and radiothermoluminescence spectra. In order to identify alkaloids, a new combined and improved IR spectroscopy and radiothermoluminescence methods with high resolution were proposed. It is shown that the content and ratio of different types of alkaloids in the stems and seeds of *P. Harmala* differ significantly. More precisely, harmine prevails in the seeds, and peganine in the stems. In terms of the content and ratio of alkaloid components, *P. harmala* growing in the Absheron has a number of advantages compared to the same plants growing in the Masalli and Ismaili regions. It was found that when *P. Harmala* samples were irradiated, the IR spectra were transformed. More precisely, in the region of small doses ( $0.5 < D_{\gamma} \leq 25$  Gy), the intensities of the absorption bands of alkaloids were redistributed, the intensities of the absorption bands of harmine and harmaline increased, and on the contrary - the intensities of the absorption bands of peganine and pegadinine decreased. A further increase in the irradiation dose from 25 to 50 Gy led to a decrease in the intensities of all absorption bands. It was assumed that structural changes in the dose range of  $25 < D_{\gamma} \leq 50$  Gy are associated with partial decomposition of alkaloids.

**Аннотация.** Впервые качественно-количественный состав алкалоидов *Peganum harmala* L. был детально изучен путем выявления ИК- и радиотермолуминесцентных спектров. Для выявления алкалоидов предложены новые комбинированные и усовершенствованные методы ИК-спектроскопии и радиотермолуминесценции с высоким разрешением. Показано, что содержание и соотношение различных видов алкалоидов в стеблях и семенах *P. Harmala* существенно различаются. Точнее, в семенах преобладает гармин, а в стеблях пеганин. По содержанию и соотношению алкалоидных компонентов *P. Harmala*, произрастающая в

Апшероне, имеет ряд преимуществ по сравнению с такими же растениями, произрастающими в Масаллинском и Исмаиллинском районах. Установлено, что при облучении образцов *P. Harmala* происходит трансформация ИК-спектров. Точнее, в области малых доз ( $0.5 < D\gamma \leq 25$  Гц), произошло перераспределение интенсивностей полос поглощения алкалоидов, возросли интенсивности полос поглощения гармина и гармалина, и наоборот – снизились интенсивности полос поглощения пеганина и пегадина. Дальнейшее увеличение дозы облучения от 25 до 50 Гц привело к снижению интенсивностей всех полос поглощения. Структурные изменения в диапазоне доз  $25 < D\gamma \leq 50$  Гц связаны с частичным распадом алкалоидов.

**Keywords:** *Peganum harmala*, alkaloid composition,  $\gamma$ -radiation, IR spectroscopy, radiothermoluminescence.

**Ключевые слова:** *Peganum harmala*, алкалоидный состав,  $\gamma$ -излучение, ИК-спектроскопия, радиотермолюминесценция.

Azerbaijan has a rich flora. Over 4,500 species of flowering plants are widespread in Azerbaijan, including both rare and endangered ones. Almost all types of vegetation common in the world are found in a relatively small area, which are united into 125 orders and 920 genera. Plant species found in Azerbaijan make up 66% of the total number of species growing in the Caucasus. Along with species widespread in the Caucasus and other regions, the Azerbaijani flora includes plant species that grow only in Azerbaijan. Low-growing plant types are found on the mountain peaks of alpine meadows, on steep hills, and slightly less on saddle-shaped passes compared to subalpine glades. Alpine carpets consist of two groups of formations: true alpine carpets (caraway, plantain, lady's mantle, dandelion) and alpine carpets on rocky terrain (sibbaldia, bellflower). Azerbaijan is also a country rich in medicinal plants. One of these plants is *Peganum harmala*. The plant contains a huge range of alkaloids [1].

Therefore, it has a wide range of medicinal properties. The therapeutic effect of this plant is due to the presence of  $\beta$ -carboline alkaloids in its composition, such as peganine, harmine, harmaline and their derivatives [2].

The pharmacological activity of alkaloids varies widely depending on their structure. Among them are analgesics - narcotics (morphine, codeine), powerful stimulants of the central nervous system (strychnine, brucine), mydriatic - pupil dilators (atropine, hyoscyamine) and miotic - pupil constrictors (physostigmine, pilocarpine) [3].

Some alkaloids, such as ephedrine, epinephrine, exhibit adrenergic activity, exciting the sympathetic nervous system, and thereby stimulating cardiac activity and increasing blood pressure [4, 5].

Different organs of *P. harmala*, depending on the development phase and place of growth, have different qualitative properties and are widely used in traditional folk medicine. In particular, in the treatment of bronchial asthma [6], radiculitis, osteochondrosis [7], to normalize blood pressure, insomnia [8], as well as in the treatment of various skin diseases [9], the use of a drug based on *P. harmala* gave encouraging results.

Preparations prepared on the basis of *P. harmala*, in addition to anti-inflammatory, diuretic, diaphoretic, also have diuretic, sedative, analgesic and antiseptic effects [10].

*P. harmala* also has a stimulating effect on the central nervous system, lowers blood pressure, increases breathing, relaxes the muscles of the intestines, heart and dilates peripheral vessels [11].

*P. harmala* is also recognized by official medicine. The pharmaceutical industry produces a drug based on this plant, which is called harmine hydrochloride. The alkaloid harmine of the above-ground part or seeds of this plant in the form of hydrochloric salt is used in the treatment of some diseases of the central nervous system (shaking palsy, consequences of epidemic inflammation of the brain - encephalitis, Parkinsonism) [12, 13], and other alkaloids, having a neuroprotective property, can affect the nervous system [14].

*P. harmala*, containing some alkaloids, which, due to their physiological activity and being strong poisons, are also used in medicine [15]. Preparations based on *P. harmala* also have antidiabetic, antihyperlipidemic [16, 17] and antileishmanial properties [18].

Preparations made from *P. harmala* plants with different alkaloid contents in the countries of Central Asia, India, Russia, and Iran, in addition to traditional medicine, are used in different clinical purposes. In these countries, neoplasms are mainly obtained from plants containing  $\beta$ -carboline alkaloids [19].

Recently, *P. harmala* has also found application in the treatment of a number of “serious” diseases. Research by various authors has shown that some isolated components of this plant exhibit cytotoxic [15, 20] and anticancer effects [11]. In particular, the use of these components revealed cytoplasmic vacuolization of cells [21]. It is assumed that drugs based on these components are a valuable sensitizer and in the future may find wide application as key regulators of cancer cells [22].

It should be noted that, despite the wide use of alkaloids in modern therapeutic practice, their potential capabilities have not yet been fully revealed. Therefore, the search for new drugs based on medicinal plant raw materials containing alkaloids, as well as the production of new drugs with improved pharmacotherapeutic indicators based on existing drugs should take a worthy place in future research work.

Based on the literature on the pharmacotherapeutic effects of medicinal plants published in recent years, it can be concluded that targeted chemical or physical modification of alkaloid molecules, with the aim of synthesizing new derivatives of alkaloid-bearing natural compounds, will be a prerequisite for creating effective drugs with pharmacological action. Based on these considerations, it can be noted that the use of medicinal plants in industrial medicine, i.e. the transition from traditional medicine to industrial medicine, is of great relevance.

Here it is necessary to mention one important fact. It is known that external factors such as high and low temperatures, electromagnetic field, radiation background of the area of plant growth, as well as its surface pollution caused by atmospheric aerosols and microorganisms, play a significant role in the formation of the qualitative composition of the plant. Considering that the era in which we live is characterized by high electromagnetic radiation, as well as a daily increase in the number of locally contaminated zones with various radionuclides, in the presented work we tried to study the structural changes caused in *P. harmala* under the influence of radiation.

### Materials and methods

The medicinal plant *P. harmala* from the Absheron, Ismayilli and Masalli regions of the Republic of Azerbaijan was chosen as the research object.

*P. harmala*, which belongs to the *Zygophyllaceae* family, is a perennial wild herbaceous plant with a strong specific smell, lush flowering and many useful substances. The plant is successfully used for medical purposes, observing precise dosages, since the plant is poisonous. The leaves and seeds are the most toxic.

The plant has a powerful, two- or three-headed taproot up to 2-3 meters long and up to 10 cm thick, which helps to penetrate the soil and provide the plant with moisture and nutrients. The stems

are bare and green, grow to a height of 30 to 80 centimeters and branch out. The leaves are sessile, alternate. The flowers can be yellow or white, singly on peduncles or up to three at the ends of branches. The calyx is five-partite, almost to the very base. The corolla of 5 petals elliptical shape and length approximately 1.5-2 centimeters. The flower has 15 stamens. The fruit is 6-10 millimeters in diameter and looks like a spherical capsule with three nests and partitions. The seeds are angular, numerous, brown or brownish gray in color, about 3 - 4 m long. One plant produces up to 120 thousand seeds. The weight of 1000 seeds is 2.5-3 g [23] (Figure 1).

*P. harmala* is not very demanding to growing conditions. It grows on saline, clayey soils and sands, near wells on desert pastures, along cattle drives, on rocky areas, on wastelands. Often forms pure thickets at an altitude of 450 - 3700 m [23]. In Azerbaijan, it grows in semi-desert areas. The most well-known are the Absheron, Ismailli and Masalli species of *P. harmala*, which differ in alkaloid content [24, 25].



Figure 1. General appearance of the *P. Harmala* (1 - root, 2 - stem, 3 - leaves, 4 - flowers, 5 - fruit, 6 - seed)

Pre-sowing  $\gamma$ -irradiation of the seeds of this plant was carried out using a  $^{60}\text{Co}$  source. Irradiation was carried out using a remote control of the radiation source in special concrete chambers that ensured protection of the working personnel. The dose rate of the source was 1.03 Gy/s. The absorbed dose was calculated using spectrometry (absorption band of  $\text{Fe}^{3+}$  ions with a maximum at 305 nm) and considering the electron densities of the dosimetric solution and the sample under study. Depending on the nature of the study, irradiation of the samples was carried out both at room temperature and at liquid nitrogen temperature.

Experiments on determining the quantitative and qualitative alkaloid composition of *P. harmala* were conducted using dry samples of this plant. To obtain dry plant samples, a method of low-temperature microwave processing was used. Microwave drying and fermentation of the plant was carried out on a laboratory installation, which included a container with a cry solvent, a microwave oven and a source of UV radiation.

A quartz vessel with green raw *P. harmala* (seeds, stems and leaves) was immersed in a volume of liquid nitrogen, cooled to a temperature of 77 K for 5-15 min, then placed on a



microwave oven conveyor and subjected to electromagnetic microwave field treatment at a frequency of 400-1000 MHz with generator power varying from 45 to 55 kW.

Microwave heating was carried out with simultaneous blowing with air previously purified from carbon dioxide and treatment with light with a wavelength of 400-700 nm and an intensity of 1 mW/cm<sup>2</sup>. The choice of the spectral range of 400-700 nm is since the band of residual chlorophyll is at 665 nm, and photo irradiation of *P. harmala* in this region does not lead to deterioration in the quality of the medicinal plant.

The method of drying *P. harmala* proposed by us allowed us to obtain dry samples of a yellowish hue. The desired effect was achieved since the plants were irradiated with light of a wavelength causing photo oxidation of the green pigments contained in them. At the same time, simultaneous blowing with air purified from carbon dioxide sharply suppressed natural photochemical processes in the seeds, stems and leaves of the plant, and the frequency of the electromagnetic field used ensured the necessary duration of processing and drying of the preparation.

The essence of this method is that because of intensive absorption of electromagnetic waves, dielectric heating of the plant (material with low thermal conductivity and heat resistance) occurs. In this case, photo- and thermochemical reactions occur both on the surface and throughout the entire volume. The electromagnetic field, in addition to local thermal action, also initiates the uniform flow of photochemical reactions, which is of no small importance for obtaining high-quality products. Additional UV irradiation accelerates the decomposition of residual chlorophyll.

It should be noted that the combined drying method proposed by us is currently the only way to obtain high-quality raw material. At the same time, a balance is achieved between the processes of yellowing and moisture release (hydration) in different organs of *P. harmala*. Structural changes occurring during heat treatment of *P. harmala* were studied using differential thermal analysis. To record thermo grams of seeds, stems and leaves, the samples were crushed and filled into a ceramic crucible. Thermal analysis in combination with weight and differential gravimetric analysis was carried out using a derivatograph (Q-Derivatograff, MOM, Hungary). The heating mode selected was: temperature range 300–127 K, heating rate 5 K/min. Aluminum oxide (Al<sub>2</sub>O<sub>3</sub>) was used as a standard. To study the structural changes in *P. harmala* samples caused by  $\gamma$ -irradiation and microwave field treatment, we used our improved traditional IR spectroscopy technique based on measuring the transmission spectra of translucent pressed tablets. For this purpose, a special optical cell was developed and manufactured, allowing IR studies of the original and treated samples under vacuum  $P=10^{-6}$  Pa in a wide temperature range: from  $T=300$  K (room temperature) to 923 K.

In our experiments, the optical cell was connected to a vacuum unit used to clean the samples from adsorbed atmospheric gases and contaminants, as well as to dehydroxylate their surface.

For radiothermoluminescence analysis, tablets were made from finely ground samples of this plant and inserted into special metal holders with holes necessary for the passage of irradiation. Radio thermoluminescence curves of  $\gamma$ -irradiated and microwave-treated *P. harmala* samples were obtained in the temperature range of 80–450 K.

### Results and discussion

Among the spectral methods for studying the molecular structure and composition of objects of plant origin and bio systems, the most informative is the method of IR spectroscopy. This method allows us to obtain more accurate data on the functional and structural groups that make up plants, to trace the structural changes that occur in plants because of the influence of various environmental factors and to identify their features.

To study the structural features, IR absorption spectra of *P. harmala* growing in three different regions of Azerbaijan (Absheron, Masalli and Ismayilli regions) were obtained. The listed

regions are characterized by a unique climate, differences in soil and radiation background. Since the regions we selected belong to different geographical regions of our republic and differ greatly in soil cover. Being located in different climatic zones, they also differ in climatic conditions of the area. Let us recall that the listed areas belong respectively to the type of dry subtropical climate, to the zone of humid subtropical climate, to the type of moderate dry subtropical climate zones. The soils in these areas are sandy-clayey, chestnut and gray, respectively.

It is known that the content of alkaloids in plants often fluctuates depending on climatic conditions, time of collection, stages of biological development of plants, and the specifics of its cultivation. However, in most cases, the highest content of alkaloids is determined during the period of budding and flowering of plant objects. It varies from insignificant amounts (traces of alkaloids) to 2-3% of the total mass of dry plant material [25].

Based on this, the content of alkaloids was determined during the period of budding and flowering of this plant. Considering that different parts of *P. harmala* (both underground and aboveground - roots, stems, leaves, seeds) differ in the composition of the content of alkaloids, we conducted a comparative molecular IR spectroscopic study of the structure of its individual parts. IR absorption spectrum was obtained from samples that were prepared in the form of tablets pressed in a solid matrix. To obtain more detailed information, relatively thin films of *P. harmala*, without a binder, were studied. Figure 2 shows the IR absorption spectra of the seeds and stems of this plant (curves 1 and 2, respectively) in the frequency ranges of 4000–2000 and 2000–650  $\text{cm}^{-1}$ , which include the main molecular-structural features of chemical compounds.

As can be seen from the figure, the most intense bands appear in the regions of 1800-1500, 1500-1250 and 1250-1000  $\text{cm}^{-1}$ . When interpreting the absorption bands, we relied on reference data on the IR spectra of organic molecules and alkaloid-bearing plants. In the region of 1800-1500  $\text{cm}^{-1}$  there are carbonyl-containing  $\text{C}=\text{O}$  (1750-1700  $\text{cm}^{-1}$ ),  $\text{C}=\text{C}$  and  $-\text{N}=\text{C}$  groups (1690-1500  $\text{cm}^{-1}$ ) in aromatic cycles. The presence of aromatic  $\text{C}=\text{C}$ ,  $-\text{N}=\text{C}$  and carbonyl-containing  $\text{C}=\text{O}$  groups, including aceto groups ( $\text{CH}_3-\text{CO}-\text{CH}_2$ ) is associated with the alkaloids that are part of this plant.

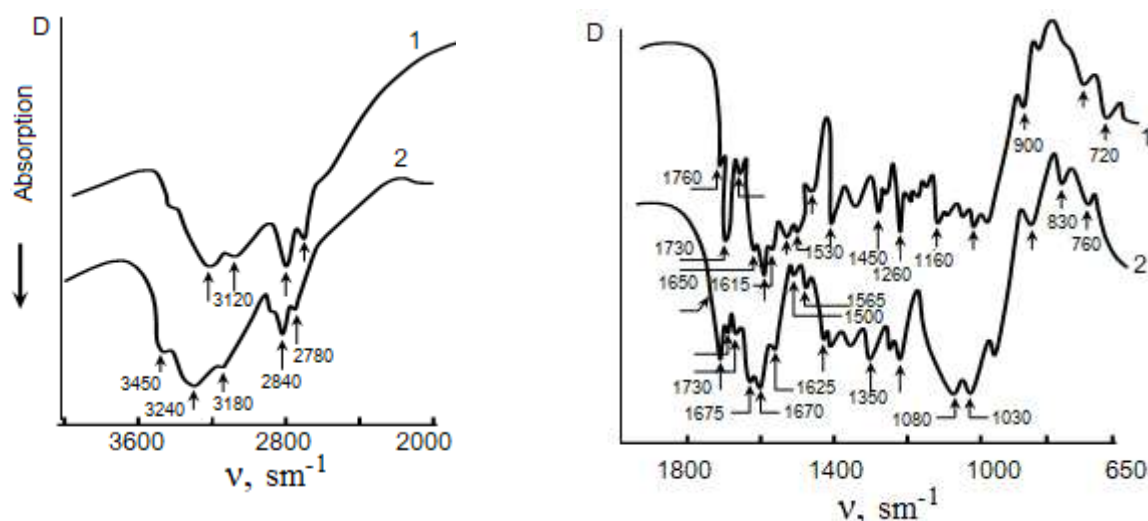


Figure 2. IR absorption spectra of *P. harmala* (1 – seeds, 2 – stems)

The region of 1800-1500  $\text{cm}^{-1}$  has the finest structure and is characterized by a set of nearby absorption bands caused by different types of alkaloids. It is known that the bands in the region of 1800-1200  $\text{cm}^{-1}$  characterize various valence vibrations of groups with multiple bonds ( $\text{C}=\text{O}$ ,  $\text{C}=\text{C}$ ). Here are also located the bands caused by deformation vibrations of the  $\text{C}-\text{H}$  bond and other

groups. Conjugation with a double bond or aromatic ring leads to a shift of the bands to the region of lower wave numbers (up to  $1660\text{ cm}^{-1}$ ). The band  $1720\text{ cm}^{-1}$  corresponds to carboxyl groups, which, as can be seen from the figure, are also present in *P. harmala* samples.

When the carboxyl group is converted into the ionic form, this band almost disappears, and two new bands ( $1555$  and  $1400\text{ cm}^{-1}$ ) appear, which correspond to the asymmetric and symmetric valence vibrations of the carboxylate ion. The type of hydroxyl groups present in the compound can be determined from the acetylation spectrum of harmine derivatives. The absorption of the carbonyl group in phenol acetates appears in the region of  $1765\text{ cm}^{-1}$ , and in acetates of non-conjugated alcohols —  $1760\text{ cm}^{-1}$ . In addition, in the region of  $1700$ – $1660\text{ cm}^{-1}$  the absorption of the valence vibrations of carbonyl groups in quinoid structures appears. In the region of  $1626$ – $1608\text{ cm}^{-1}$ , ethylene  $\alpha$ -,  $\beta$ -double bonds absorb. In the spectra, this vibration sometimes appears as a weak shoulder on the intense band of  $1600\text{ cm}^{-1}$ , caused by vibrations of the aromatic ring [26].

The skeletal vibrations of the aromatic ring include four bands. These bands are bands corresponding to the frequency intervals  $1605$ – $1595$ ,  $1515$ – $1505$ ,  $1490$  and  $1450$ – $1420\text{ cm}^{-1}$ . The bands  $1470$ – $1460\text{ cm}^{-1}$  are attributed by many authors to asymmetric deformation vibrations of aliphatic C–H bonds. Note that the band  $1430\text{ cm}^{-1}$  is attributed to scissor vibrations of  $\text{CH}_2$  groups associated with the carbonyl group, as well as to skeletal vibrations of the aromatic ring. The intensity of this band is insensitive to the influence of external factors. The spectral region of  $1800$ – $1200\text{ cm}^{-1}$  is characterized by a set of nearby absorption bands, related mainly to various types of alkaloids in the composition of the studied plant. This is evidenced by the presence of carbonyl-containing C = O ( $1750$ – $1700\text{ cm}^{-1}$ ), C = C and nitrogen-containing – N = C groups ( $1690$ – $1500\text{ cm}^{-1}$ ) in aromatic cycles. And the bands at  $1600$ ,  $1580$  (conjugated rings),  $1500$  and  $1450\text{ cm}^{-1}$  are characteristic of the ring itself. Considering the complex chemical composition and reference data on the IR spectra of individual *P. harmala* alkaloids presented in Figure 2, the absorption bands with frequencies of  $1725$ ,  $1700$ ,  $1690$  and  $1625\text{ cm}^{-1}$  were assigned to harmine, peganidine, harmaline and peganine, respectively. The peaks corresponding to these compounds are also clearly visible in Figure 3.

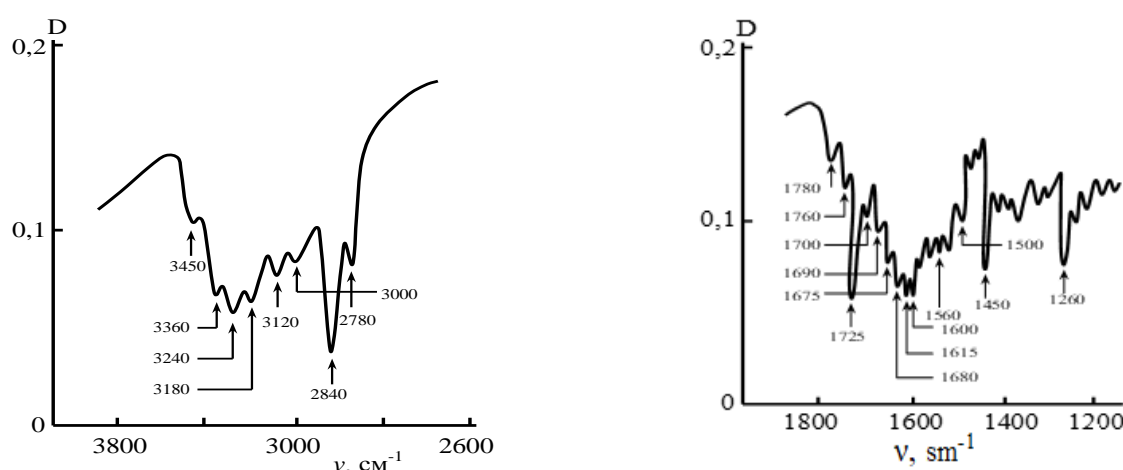


Figure 3. IR absorption spectra of *P. harmala* in the frequency ranges of  $3800$ – $2600$  and  $1800$ – $1200\text{ cm}^{-1}$

Figure 3 shows a fragment from the spectrum of a thin film of *P. harmala* in the region of  $3800$ – $1200\text{ cm}^{-1}$ , where the characteristic bands corresponding to the functional C = O, C = C, – N = C groups and associated with the presence of alkaloids are located in the region of  $1800$ – $1200\text{ cm}^{-1}$ .

The bands at 1600, 1580 (conjugated rings) 1500, 1450  $\text{cm}^{-1}$  are characteristic of the aromatic ring itself, which together with the band of valence vibrations = C – H near  $\sim 3000 \text{ cm}^{-1}$  makes it easy to recognize the aromatic structure (benzene ring). The absorption bands in the region of valence vibrations of –OH, –NH and alkyl  $\text{CH}_3$ ,  $\text{CH}_2$ , CH - groups with different around also testify in favor of alkaloids. The bands with frequencies of 3120, 3180, 3240, 3360 and 3450  $\text{cm}^{-1}$  refer to OH or NH groups. The bands with maxima of 2840 and 2780  $\text{cm}^{-1}$  are characteristic of aceto ( $\text{CH}_3$  – CO –  $\text{CH}_2$ ) – and aldehyde ( $\text{HC} = \text{O}$ ) – groups. = C – O – groups absorb in the region 1270-1200  $\text{cm}^{-1}$ , and bands 1040-1100  $\text{cm}^{-1}$  and 1100-1070  $\text{cm}^{-1}$  are associated with valence C – O – groups (ethers) and a five-membered heterocycle, respectively.

In the region of 988-960  $\text{cm}^{-1}$ , deformation vibrations of the C – H bond with a double bond in the trans position are manifested. The low intensity of this band in the spectrum indicates a small number of double bonds in the structure of *P. harmala*. Out-of-plane deformation vibrations of the C – H bonds of the aromatic ring of varying degrees and nature of substitution are manifested in the region of 900-720  $\text{cm}^{-1}$ . In the samples of the studied plant, two bands were manifested, characterizing the vibrations of one or two hydrogen atoms – in the region of 880-850  $\text{cm}^{-1}$  and 855-800  $\text{cm}^{-1}$ . Based on the above, the content of alkaloids in two organs (seeds and stems) of this plant was determined. Data on the content (both quantitative and qualitative) of alkaloids of *P. harmala*, determined by the IR spectra of the samples, are presented in the Table.

Table

CONTENT OF INDIVIDUAL ALKALOIDS IN SEEDS AND STEMS OF *P. harmala*  
OF THE APSHERON REGION

Plant organs	Content, in %				Total alkaloids, in %
	Harmine	Harmaline	Peganine	Peganidine	
Absheron region					
Seeds	2.8	0.8	0.6	0.1	4.3
Stems	1.2	0.3	2.5	0.2	4.2
Ismayilli region					
Seeds	1.9	0.5	0.8	0.16	3.36
Stems	0.5	0.2	2.6	0.31	3.62
Masalli region					
Seeds	1.6	0.5	0.74	0.1	2.94
Stems	0.6	0.3	2.6	0.2	3.7

The analysis of the data presented in the table shows that *P. harmala* contains a sufficient amount of alkaloids. Moreover, these alkaloids mainly include harmine, harmaline, peganine, pegadinine. From the IR spectra it is clear that the seeds and stems of this plant also contain traces of such alkaloids as harmalol and peganol (these alkaloids are not listed in the table).

The results of our research confirm the fact that different organs of this plant are characterized by different alkaloid content. Moreover, different organs differ not only in quantity, but also in the quality of alkaloids. Comparison of IR spectra of seeds and stems shows that in all samples of *P. harmala* harmine predominates in seeds, and peganine in stems. In other words, if the seeds of this plant, regardless of the place of growth, contain a large amount of harmine, then its stems have the greatest amount of peganine [25].

In terms of harmine content, *P. harmala* of the Apsheron district ranks first (2.8%). Second place is occupied by P.Harmala of the Ismailli district (1.9%), and third place is occupied by *P. harmala* of the Masalli district, for which the harmine content in percentage terms is 1.6%.



Unlike the harmine content, peganine is present in approximately the same amount in all *P. harmala* samples. Since the peganine content in *P. Harmala* stems is approximately 2.5%, 2.6% and 2.6% of the total dry plant material mass for the Absheron, Ismailli and Masalli regions, respectively. All samples of *P. harmala* collected from different regions of our republic have a relatively small amount of peganidin in the seeds and stems. We assume that the data on the content of alkaloids can serve as a kind of biomarker for identifying *P. Harmala*. In other words, the amount of alkaloids can be used to determine the place of growth of this plant.

*Alkaloid content in  $\gamma$ -irradiated *P. harmala* samples.* Structural changes in  $\gamma$ -irradiated *P. Harmala* samples were also monitored in this case using IR absorption spectra. Figure 4 shows the IR absorption spectra of the initial (curves 1) and irradiated with  $\gamma$ -quanta at different doses (curves 2-3) *P. harmala* samples in the frequency range of 1800-1200  $\text{cm}^{-1}$ . The irradiation dose ranged from 0 to 50 Gy. The figure shows only irradiation doses of 10 and 50 Gy. The choice of these doses is due to the fact that 10 Gy and 50 Gy are the lower and upper limits of the interval of the stimulating dose for plant development. As can be seen from the presented spectra, when irradiating *P. harmala* samples, the IR spectra are clearly transformed. More precisely, in the region of relatively small doses ( $0.5 < D_\gamma \leq 25$  Gy), a redistribution of the intensities of the absorption bands of alkaloids occurs. More precisely, in this dose region, the intensities of the absorption bands of harmine and harmaline (1725 and 1690  $\text{cm}^{-1}$ ) increase. At the same time, the intensities of the absorption bands of peganine and peganidine (1700 and 1625  $\text{cm}^{-1}$ ) (curve 2), on the contrary, decrease. A further increase in the irradiation dose from 25 to 50 Gy leads to a decrease in the intensities of all absorption bands (curve 3).

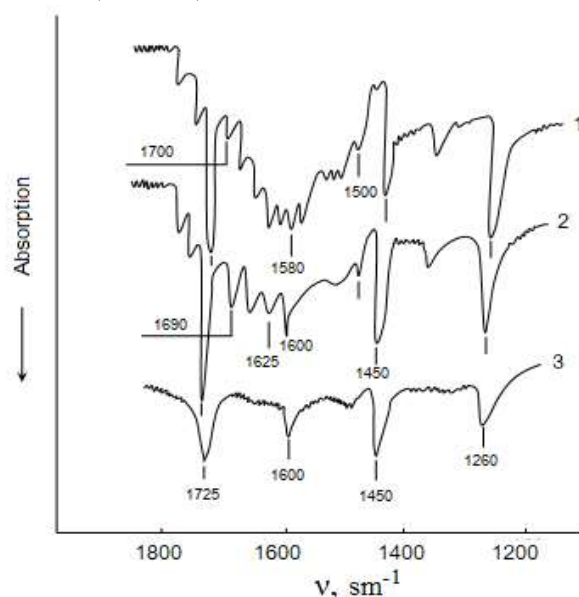


Figure 4. IR absorption spectra of *P. harmala* samples in the frequency range of 1800-1200  $\text{cm}^{-1}$  (1 – non-irradiated, 2 –  $\gamma$ -irradiated at a dose of 10 Gy and 3 –  $\gamma$ -irradiated at a dose of 50 Gy

The observed feature of harmine, harmaline and their derivatives in the IR spectra of  $\gamma$ -irradiated *P. harmala* in the analytical region of alkaloids can be explained by structural conformational changes leading to an increase in the content of harmine and harmaline (in the region of relatively small doses –  $0.5 < D_\gamma \leq 25$  Gy) and to their partial decomposition (in the region of  $25 < D_\gamma \leq 50$  Gy).

The structural changes in *P. harmala*, caused by  $\gamma$  - radiation, studied in this work, open wide possibilities for its medical use. The data we obtained show that pre-sowing  $\gamma$ -irradiation of *P. harmala* leads to noticeable structural changes. To obtain more reliable information about the structural changes occurring during this, we considered it appropriate to study the structure of *P.*

*harmala*, the seeds of which were subjected to  $\gamma$  - irradiation also by the radio thermoluminescence method. The data obtained on these changes are presented in Figure 5.

Radio thermoluminescence curves show that irradiation with  $\gamma$ -quanta leads to the appearance of one intense peak at 175 K and 2 weak peaks at 320 K and 445 K in the spectrum of *P. harmala*.

We believe that the low-temperature broad peak (half-width  $T_{1/2} = 110$  K) at 175 K with energy activation  $E_a = 0.07 \div 0.10$  eV may be associated with both the presence of alkaloids in *P. harmala* and molecular water in the steric environment of the alkaloids. The broad low-temperature radio thermo luminescent peak with a maximum at 175 K has several features, since its spectral parameters (intensity and half-width) depend on the dose of  $\gamma$  -irradiation (curves 2 and 3).

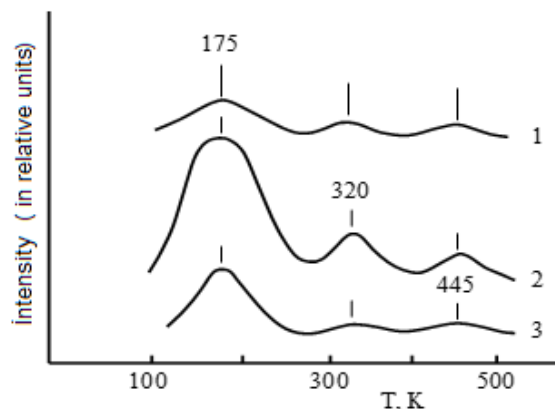


Figure 5. *P. harmala* radio thermoluminescence curves (1 – non-irradiated, 2 – irradiated at a dose of 25 Gy and 3 – irradiated at a dose of 50 Gy)

With an increase in the  $\gamma$ -irradiation dose from 0.5 to 25 Gy ( $0.5 < D\gamma \leq 25$  Gy), the intensity of the thermal emission peak increases by almost one order of magnitude. A further increase in the irradiation dose to 50 Gy ( $25 < D\gamma \leq 50$  Gy) is accompanied by a monotonic decrease in the intensity of this peak and its narrowing by  $\sim 2$  times (the half-width decreases by 60 K). In this case, the shape of the band remains unchanged and is close to Gaussian.

### Conclusion

By analyzing IR and radiothermoluminescence spectra, it is possible to identify the qualitative and quantitative alkaloid composition of *P. harmala* with high reliability. The combined and improved IR spectroscopy and radiothermoluminescence method with high resolution that we proposed allowed us to show that *P. harmala* contains a sufficient number of alkaloids. Moreover, these alkaloids mainly include harmine, harmaline, peganine and pegadinine. Traces of such rare alkaloids as harmalol and peganole are also found in the seeds and stems of this plant.

The fact that *P. harmala*, growing in the Absheron region, has a number of advantages in terms of the content and ratio of alkaloid components over the same plants growing in the Masalli and Ismaili regions, is of particular interest.

Our results that different organs (seeds and stems) of this plant are characterized by different alkaloid content, as well as the fact that these organs differ not only in quantity but also in quality of alkaloids, are in good agreement with the results of various authors obtained for other plants.

The results on the change in IR spectra for gamma-irradiated samples are also of some interest. Since these results, or rather the results on the change in the components of the chemical composition of *P. harmala* under the influence of radiation, can find application in medicine, or rather in the production of drugs based on this plant.

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