

Chemical Transformations and Spectral Characterization of Lutergerinine and Its Derivatives

Robert Vincent Allen*, Benjamin Kyle Harper, Gregory Yale Anderson, Zachary Ryan Sullivan & Daniel Keith Smith

Department of Applied Sciences, Midlands State University, Birmingham, UK

ABSTRACT

In this work, we studied the IR, UV, PMR and mass spectra, chemical transformations of lutergerinin and its derivatives of homoproporphine alkaloids of time-lapse. According to the given spectral data, this compound is assigned to the homoproporphine base group with a spiro cyclohexanol ring. When establishing the structure of lutergerinine, its various spectral data and numerous chemical transformations were studied. The most important of them can be considered following with the action of acetic anhydride and acetic acid sodium from the base obtained O, N-diacetyl derivative, indicating the presence in it of a hydroxyl group and tetrahydroisoquinoline core. Heating of lutergerinin acid solutions led to the formation of α -diketone, the structure of which is confirmed by the preparation of dioxime. In the reaction of acetalization of the base, ketal was obtained. The reduction of lutergerinin hydrazine by hydrate forms a pyrazalin derivative, which undergoes catalytic decomposition and is converted to a compound containing a cyclopropane ring in its structure. It was found that their samples mainly differ in the composition of the strong base fractions.

KEYWORDS: Colchicum Luteum Baker, alkaloids, the homoproporphine base, lutergerinin

1. INTRODUCTION

Colchicum yellow (Colchicum Luteum Baker) is a widely distributed colchicine-containing plant in Central Asia [1]. The main alkaloids of the leaves and stems of this plant are tropolone compounds - colchicine and kolhamin. In plants, the homoproporphine base found was also found: luteidin, luteicin, luteinin, collutin, lutergerin [2,3,4,5,6].

Colchicins and botanical closely related species of liliaceae are known to be highly poisonous. Being pasture weeds, they often, especially in early spring, cause cattle poisoning [7]. There are also known cases of human poisoning [8].

The main symptom of colchicine poisoning is vomiting with diarrhea. Large doses cause increasing paralysis of the central nervous system and respiration. It also acts slowly through the skin. Alkaloid toxicity when ingested is detected over time. Therefore, it is believed that the products of its oxidation in the body have a poisonous effect [9].

Despite the toxic properties, autumn crocus are among the oldest medicinal plants. In particular, autumn crocus yellow, growing on the slopes of the Himalayas (India), was exported to the countries of the Middle East and Western Europe as a good remedy for gout [10]. This plant in India is harvested to this day [11].

Thus, alkaloids in leaves and stems of autumn crocus yellow are somewhat studied, while in other parts of plants, such as flowers, seeds, fruit boxes, tubers and their membranes, they remain unexplored.

Our goal is to isolate alkaloids from the leaves and stems of the plant. To obtain the extract with alkaloids used 3% acetic acid. At the same time, 0.45% alkaloids of neutral character were obtained, of which they reliably identified colchicine. In a mixture of basic alkaloids (0.03%), compounds containing no tropolone ring were found.

In addition, a small amount of an unknown base 1 was obtained from the mother liquor after the extraction of neutral and basic phenolic alkaloids.

2. MATERIALS AND METHODS

UV spectra were recorded on an SF-4A spectrometer in methanol, IR spectra were recorded on a UR-10 two-beam spectrometer in KBr, and the PMR spectra were measured on a Varian XL-100 instrument in CDCl₃.

Individuality and authenticity of substances controlled by BH methods. Radtrac HD on paper of the brand Filtrak was performed using mobile phases: n-butyl alcohol-hydrochloric acid-water, 50: 7.5: 13.5 (system 1) and: p-butyl alcohol - 5% CH₃COOH (1: 1, organic part) (system 2). The spots of the substances were shown by the modified Dragendorff reagent and iodine vapors.

Alkaloid exudation. 5,1 kg of crushed yellow croissant collected in Surkhandarya and Samarkand regions in different years and periods of flowering, extracted five times with 3% acetic acid. Fractions of alkaloids were obtained by the previously described method [14].

Neutral alkaloids	- 22,97 г (0,45%)
Phenolic alkaloids	- 4,59 г (0,09%)
Alkaloids sour character	- 2,04 г (0,04%)
Basic alkaloids	- 7,14 г (0,14%)
Phenolic - basic alkaloids	- 4,57 г (0,09%)
The amount of fractions of alkaloids	- 41,31 г (0,81%)

The allocation of luteidin

The fraction of phenolic basic alkaloids consists mainly of a compound with R_f 0,56 and minor compounds with R_f 0,16; 0,28 and 0,66. By the value of R_f , the main alkaloid corresponds to luteidin.

3 g of the phenol base alkaloid fraction was treated with a small amount of dry acetone, at which 0,86 g was obtained. Crystals of the compound with R_f 0,56 and so on. Pl. 230-232°C. According to the melting point and the PMR spectral data - isolated base identified with luteidine.

The allocation of lutherginin. In the mother liquor after crystallization of luteidine, there are, in addition to the same alkaloid (R_f 0,42, system 2), compounds with R_f 0,28; 0,16 and 0,14. The first two of them were chromatographically identified with luteicin and luteinin, respectively. When treating this mixture with water, 0,07 g of a substance with R_f 0,14 was isolated, which differs in physical constants and spectral data from known alkaloids.

This new base turned out to be Lutherginin. M.p. 226-228°C.

Results and discussion

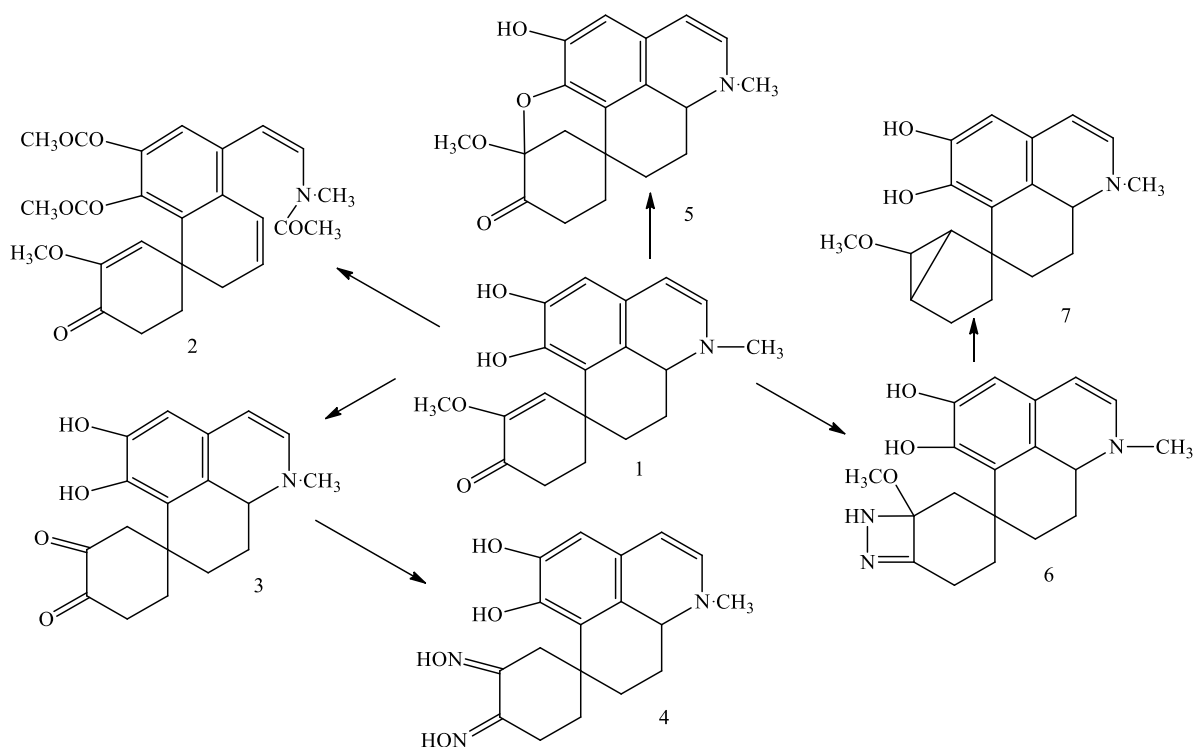
The composition of the base 1 $C_{19}H_{21}O_4N$ Lutherginin has absorption maxima at 230 and 272 nm in the UV spectrum. In alkaline solutions, the absorption maxima undergo a bathochromic shift (by 8 nm), which indicates the presence of a phenolic hydroxyl group at the base. A color reaction with ferric chloride confirms the UV spectrum data. The infrared spectrum of the base contains absorption bands at 1677, 1667, 1616, 1601 and 3535-3540 cm^{-1} , indicating the presence of an aromatic ring, an enone moiety, and a hydroxyl group. In the mass spectrum of the base has peaks of the main ions with m/z 329 (M^+ 37 %), 314, 304, 286 (M^+ 40%), 258, 242, 233 (M^+ 49, 100%), 231, 217, 182 and 180.

The PMR spectrum indicates the presence in it of the N-methyl group (2,37 ppm), one O-methyl group located in the aromatic ring (3,78 ppm) and in the olefinic double bond (3,51 ppm), protons of two hydroxyl groups (6,08 ppm) of aromatic and olefinic protons (single proton singlets at 6,6 and 5,79 ppm). Lutherginin represents a tertiary base but also demethylated the position from C2. A less likely alternative structure is the double bond isomer position C7-C8.

According to spectral data, lutherginin was assigned to a group of homoporphyrine bases from which are contained in a number of colchicine-containing plants of the lily family including *Colchicum luteum* [12].

1- SCHEME

STRUCTURE AND TRANSFORMATION OF LUTERGININ



When establishing the structure of lutergerinine, its various spectral data and numerous chemical transformations were studied. The most important of them are the following (Scheme 1.): with the action of acetic anhydride and acetic acid sodium, the O, N – diacetyl derivative (2) was obtained from the base, indicating the presence of a hydroxyl group in it and the tetrahydroisoquinoline core. Heating of lutergerinine acidic solutions led to the formation of α -diketone (3), the structure of which is confirmed by obtaining dioxime (4). In the reaction of acetalization of the base, ketal (5) was obtained. Reduction of lutergerinine hydrazine by hydrate (according to Kizner) [13] forms a pyrazalin derivative (6), which undergoes catalytic decomposition and is converted into a compound containing a cyclopropane ring (7) in its structure.

It was found that their samples mainly differ in the composition of the strong base fractions.

3. CONCLUSION

- As a result of a comparative study of the amount of plant alkaloids from different growing areas, it was revealed that they differ in the qualitative composition of fractions of strong bases.
- According to the spectral data and chemical transformations, lutergerinine is assigned to the homoproporphinic base group.

REFERENCES

- [1] Юсупов М.К., Садыков А.С. Исследование алкалоидов *Colchicum Luteum* Baker. Науч. тр. Ташкентск. гос. ун-та. Им.В.И.Ленина. Естеств. науки, 1962, вып.203, с. 3-14.
- [2] Мухамедьярова Н.Л., Юсупов М.К., Левкович М.Г., Асланов Х.А., Садыков А.С. Строение лутеидина. – Химия природ.соедин., 1976, №3, с. 354-359.
- [3] Юсупов М.К., Мухамедьярова Н.Л., Асланов Х.А., Строение лутеидина. – Химия природ.соедин., 1976, №3, с. 359-363.
- [4] Мухамедьярова Н.Л., Юсупов М.К., Асланов Х.А., Садыков А.С. Строение и абсолютная конфигурация коллутина. Химия природ.соедин., 1975, №6, с. 758-761.
- [5] Мухамедьярова Н.Л., Левкович М.Г., Юсупов М.К. О строении лутеидина. тр. Ташкентск. гос. ун-та. Им.В.И.Ленина. Естеств. науки, 1976, вып.513, с. 111-115.
- [6] Аликулов Р.В. [и др.]. Строение лутергина // *Universum: Химия и биология* : электрон. научн. журн. 2019. № 6(60).
- [7] Кармышева Н.Х. Безвременник желтый – причина тяжелых отравлений скота на горных пастбищах истоков р.Сайрамсу. – Изв.АН КазССР, серия биол. наук, 1963, №2, с.16-19.
- [8] Clarke E.G.C. The forensic Chemistry of Alkaloids. Colchicine. – In Manske R.H.F., Holmes H.L. The Alkaloids. Chemistry and Physiology. V.XII. N.-Y.: Acad.Press, 1970, p.526.
- [9] Генри Т.А. Химия растительных алкалоидов. – М.: Изд-во ГНТИ химич. лит-ры. 1956. с.904.

- [10] Сало В.М. Растения и медицина. – М.: Изд-во «Наука», 1968, с.69-77.
- [11] Губанов И.А., Рабинович И.М., Гладких А.С. Возделывание лекарственных и эфиромасличных растений в Индии. – Растит. Ресурсы, 1968, т.4, №3, с.410-428.
- [12] Юсупов М.К., Садыков А.С. Исследование алкалоидов *Colchicum Luteum* Bak. - тр. Ташкентск. гос. ун-та. Им.В.И.Ленина. Естеств. науки, 1962, вып.203, с. 3-14.
- [13] Серрей А. Справочник по органическим реакциям. М.: ГНТИ хим. лит. 1955. С.136
- [14] Аликулов Р.В., Юсупов М.К. Химия природ.соедин., 1993, с. 862.