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Review Article

A Comprehensive Review of Tropane Alkaloids: Atropine from Origin to Biological Activity

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ABSTRACT

Tropane alkaloids (TAs) are a distinct class of secondary metabolites primarily found in the Solanaceae family, characterized by a unique bicyclic tropane ring. Among them, atropine is one of the most extensively studied and clinically significant compounds. This comprehensive review explores atropine's origin, chemical classification, biosynthesis, extraction, identification, and pharmacological properties. Derived biosynthetically from ornithine and phenylalanine, atropine is synthesized via a complex pathway that includes the intermediates littorine and hyoscyamine. Though not naturally present in free form, atropine is obtained through the racemization of hyoscyamine during extraction from plants like Atropa belladonna and Datura species. Chemically, atropine functions as a potent anticholinergic agent, acting primarily on muscarinic receptors, and demonstrates significant biological activities. Clinically, atropine is used to manage bradycardia, myopia progression, smooth muscle spasms, and gastric disorders, showing high efficacy with manageable side effects under medical supervision. Advances in structural elucidation, biosynthetic pathway analysis, and pharmacological profiling continue to support atropine's relevance in modern medicine. However, due to its strong pharmacological effects, appropriate dosing and regulatory oversight remain critical. Overall, atropine exemplifies the therapeutic potential and complexity of natural product-based drug discovery.

INTRODUCTION

Natural Products:

Natural products are the chemical ingredients synthesized by living organisms via semisynthetic or synthetic methods. Since ancient times natural sources are being utilized by human beings as a

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primary source for food, shelter, and curative remedies and since the last few decades tremendous research has been carried out on natural herbs for the search and development of novel therapeutic agents beneficial for human health without or with least side effects. Commonly, the term natural product is considered the other name for secondary metabolites. These secondary metabolites are the organic ingredients that exert various pharmacological effects on human health, but do not contribute directly in various process like reproduction, growth, development, etc. Nutraceuticals, cosmetics, and pharmaceuticals are the main industries in which natural ingredients are purposely used as the main constituents. These are basically small molecules with some structural changes and are less than 3000 Da in molecular weight.

The relative study of natural products inspires scientists to isolate, identify, and characterize active compounds from natural plants and further use them to develop pharmacologically active molecules. However, natural ingredients are extremely cumbersome to isolate and very challenging to synthesize. Natural products are frequently regarded as an initial point for drug discovery in chemical synthesis, from which synthetic derivatives can be synthesized with upgraded efficiency, safety, and purity. Natural products include alkaloids, steroids, terpenoids, amino acids, proteins, carbohydrates, lipids, nucleic acids, vitamins, hormones, insect and plant growth regulators, natural pigments and dyes etc. [1]

Problems With Synthetic Drugs:

Potency, Cost, Side effects, Requires close supervision of clinician, Resistance, Unavailability, Stability. [12]

Classification Of Natural Products:

Natural products chemistry has originated from mankind's curiosity about colour, taste odour, and cures for human, animal and plant diseases.

Primary And Secondary Metabolites:

Plants produce an enormous variety of natural products with highly diverse structures. These products are commonly termed "secondary metabolites" in contrast to the "primary metabolites" which are essential for plant growth and development. The term natural product is applied to materials derived from plants, microorganisms, invertebrates and vertebrates, which are fine biochemical factories for the biosynthesis of both primary and secondary metabolites.

Secondary metabolites play ecologically significant roles in how the living organisms deal with their surroundings and therefore are important for their ultimate survival. They were formerly regarded as "waste products" without physiological function for the plant. With the emergence of the field of chemical ecology about 30 years ago, it became evident, however, that these natural products fulfil important functions in the interaction between plants and their biotic and abiotic environment. They can serve, for example, as defence compounds against herbivores and pathogens, as flower pigments that attract pollinators, or as hormones or signal molecules. In addition to their physiological function in plants, natural products also have a strong impact on human culture and have been used throughout human history as condiments, pigments, and pharmaceuticals.

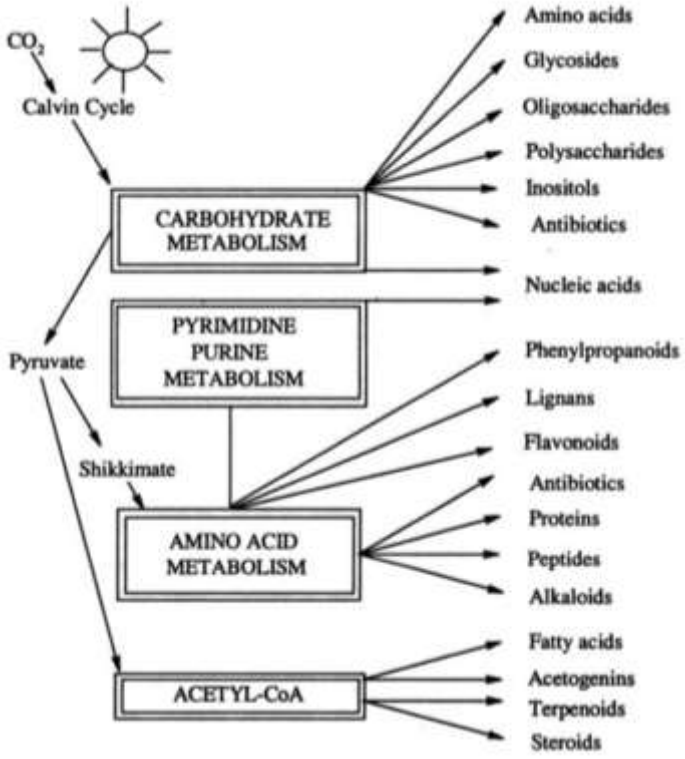


Figure 1

The secondary metabolite compounds are classified into four different groups according to their biosynthetic origin: alkaloids, phenylpropanoids, polyketides, and terpenoids. [1]

Alkaloids:

Alkaloids are classically defined as being plant derived, pharmacologically active, basic compounds derived from amino acids that contain one or more heterocyclic nitrogen atoms. [2] Alkaloids are mainly biosynthetically derived from amino acids resulting in variety of chemical structures, mostly isolated from plants . Alkaloids can be found in about 20% of plant species in small qualities and their production (including in biotechnology), extraction and processing remain major areas of research and development. Alkaloid biosynthetic pathways can be manipulated genetically for example in order to achieve higher production levels of alkaloids.

There is a need for drug discoveries from natural sources to result in a more diversified medicine portfolio for human use. Furthermore, natural products are more likely to resemble endogenous metabolites and biosynthetic intermediates compared to synthetic compounds which can be recognized as substrate by active transporters. Despite the changes in discovery strategies and most notably the emergence of medicines derived from molecular biology, there remains a need to develop natural product-based medicines which has shown great success as a strategy.

Alkaloids play an essential role in both human medicine and in an organism's natural defence. Alkaloids make up approximately 20% of the known secondary metabolites founds in plants. In plants, alkaloids protect plants from predators and regulate their growth. Therapeutically, alkaloids are particularly well known as anaesthetics, cardioprotective, and anti-inflammatory agents. Well-known alkaloids used in clinical settings

include morphine, strychnine, quinine, ephedrine, and nicotine. As of 25 October 2020, 27,683 alkaloids were included in the Dictionary of Natural Products (DNP) with 990 hits of newly reported or reinvestigated alkaloids from nature between 2014 to 2020. [3]

Classification Of Alkaloids:

1. **Classification Established Upon The Biogenesis:**

From a structural perception, alkaloids can be classified, based on their molecular precursor, structures, and origins or on the biological pathways used to obtain the molecule. There are three central types of alkaloids: (1) true alkaloids, (2) protoalkaloids, and (3) pseudoalkaloids. True alkaloids and protoalkaloids are produced from amino acids, whereas pseudoalkaloids are not derived from these compounds.

True Alkaloids:

This type of alkaloids are obtained from amino acids and they share a nitrogen-containing heterocyclic ring. They are highly reactive in nature and have potent biological activity. They form water-soluble salts, and many of them are crystalline in nature, which conjugates with acid and forms a salt. Almost all true alkaloids are bitter in taste and solid, except nicotine, which is a brown liquid. Various amino acids like L-phenylalanine/L-tyrosine, L-ornithine, L-histidine, L-lysine are the main sources of true alkaloids. Cocaine, morphine, quinine are the common true alkaloids found in nature.

Protoalkaloids:

This type of alkaloids contains a nitrogen atom, which is derived from an amino acid but is not part of the heterocyclic ring system. L-Tryptophan and L-tyrosine are the main precursors of this type of alkaloids. Yohimbine, mescaline, and hordenine are the main alkaloids of this type. They are used in various health disorders, including mental illness, pain, and neuralgia.

Pseudoalkaloids:

The basic carbon skeleton of pseudoalkaloids is not directly derived from amino acids; instead, they are connected with amino acid pathways where they are derived from by amination or transamination reaction from forerunners or post cursors of amino acid. Non-amino acid precursors can also produce pseudoalkaloids. They can be phenylalanine or acetate derived. Capsaicin, caffeine, ephedrine are very common examples of pseudoalkaloids.

2. **Classification Established Upon The Ring Structure:**

This is the most comprehensively established classification, based on the presence of a basic heterocyclic nucleus in their structure.

Tropane Alkaloid:

This category of alkaloids has tropane (C4N skeleton) nucleus. They are abundantly found in the Solanaceae family. They are derived from ornithine and acetoacetate. Structurally, pyrrolines are the precursor of these type of alkaloids Cocaine, atropine, scopolamine, and their derivatives are widely studied since the 19th century because of their enormous pharmacological actions.

Pyrrolizidine Alkaloids:

The pyrrolizidine nucleus is distinctive of this group of alkaloids. They occur in the plants from Asteraceae and Fabaceae family. These alkaloids enter into the food chain and become antifeedants

for the animals who eat them. Senecionine is the popular alkaloid of this type.

Piperidine Alkaloids:

Piperidine nucleus is the basic ring system of this group of alkaloids. Monocycle compounds with the C5N nucleus is the important feature of true piperidine alkaloids. Presence of odour is the common feature of piperidine alkaloids. They exert chronic neurotoxicity. Many of them are originated from plants. Although piperidine itself is a lysine-derived alkaloid, some of the piperidine alkaloids also derived from acetate, acetoacetate, in an analogous fashion to the simple pyrrolidine alkaloids. Lobeline is one of the important alkaloids in this group.

Quinolines Alkaloid:

This type of quinolone-nucleus-containing alkaloid is achieved exclusively from the bark of the Cinchona plant. But a variety of simple heteroaromatic quinolines are also isolated from various marine sources (4,8-quinolinediol from cephalopod ink and 2-heptyl-4 hydroxyquinoline from a marine pseudomonad). The major alkaloid of this specific group is cinchonine, cinchonidine, quinine, and quinidine.

Isoquinoline Alkaloids:

Isoquinoline alkaloids are an extremely large group of alkaloids mostly occurring in higher plants, but few groups are also isoquinolinoid marine alkaloids. Isoquinoline nucleus is the basic structural feature. These groups of alkaloids have huge types of medicinal properties like antiviral, antifungal, anticancer, antioxidant, antispasmodic, and an enzyme inhibitor.

Morphine and codeine are the major and widely studied isoquinoline alkaloids. They are derived from tyrosine or phenylalanine.

Indole Alkaloids:

This is the largest and most interesting alkaloid group derived from tryptophan. Although structural diversity varies according to the terrestrial and marine source, classical research studies have been carried out on alkaloids from both origins and the fungal source. Polyhalogenation is a common feature of these alkaloids.

Steroidal Alkaloids:

1,2-Cyclopentane phenanthrene ring system is the characteristic of this type of alkaloids. They are typically originated from higher plants, which belong to Liliaceae, Solanaceae, Apocynaceae, Buxaceae families, but some are also isolated from amphibians too.

Imidazole Alkaloid:

The imidazole ring structure is the characteristic of this type of alkaloid. The imidazole ring of these alkaloids is previously made at the stage of the precursor, so they are an exemption in the transformation procedure of structures. This type of alkaloids contains numerous structurally different examples, particularly among marine and microbial alkaloids. They display a wide array of biological activities and significant pharmaceutical potential. Pilocarpine is the most pharmaceutically significant imidazole alkaloid.

Purine Alkaloids:

Purine is the nitrogenous base of nucleotide (building block of DNA and RNA), which consist of purine ring and pentose sugar along with another base pyrimidine. Caffeine, Theophylline and Theobromine are typical examples of purine alkaloids. They are popular as plant alkaloids, but they can be also originated in marine organisms with substituted purines (e.g., Phidolopin) and a

variety of terpenoid-purine alkaloids, such as the age lines and others.

Pyrrolidine Alkaloids:

Pyrrolidine (C4N skeleton) nucleus constitutes the basic nucleus of pyrrolidine alkaloids. Many pyrrolidine alkaloids are known from plants. Hygrine (biosynthesized from ornithine), ficine (where the pyrrolidine ring is involved to a flavone nucleus), and brevicolline (wherein it is attached to a β-carboline unit) are some examples of this type of alkaloids. [4]

Tropane Alkaloids:

Tropane alkaloids (TA) are valuable secondary plant metabolites which are mostly found in high concentrations in the Solanaceae and Erythroxylaceae families. The TAs, which are characterized by their unique bicyclic tropane ring system, can be divided into three major groups: hyoscyamine and scopolamine, cocaine and calystegines. Although all TAs have the same basic structure, they differ immensely in their biological, chemical and pharmacological properties. Scopolamine, also known as hyoscine, has the largest legitimate market as a pharmacological agent due to its treatment of nausea, vomiting, motion sickness, as well as smooth muscle spasms while cocaine is the 2nd most frequently consumed illicit drug globally.

Tropane alkaloids (TAs) are a specific class of alkaloid and can be more specifically defined as all molecules that possess a tropane ring system.

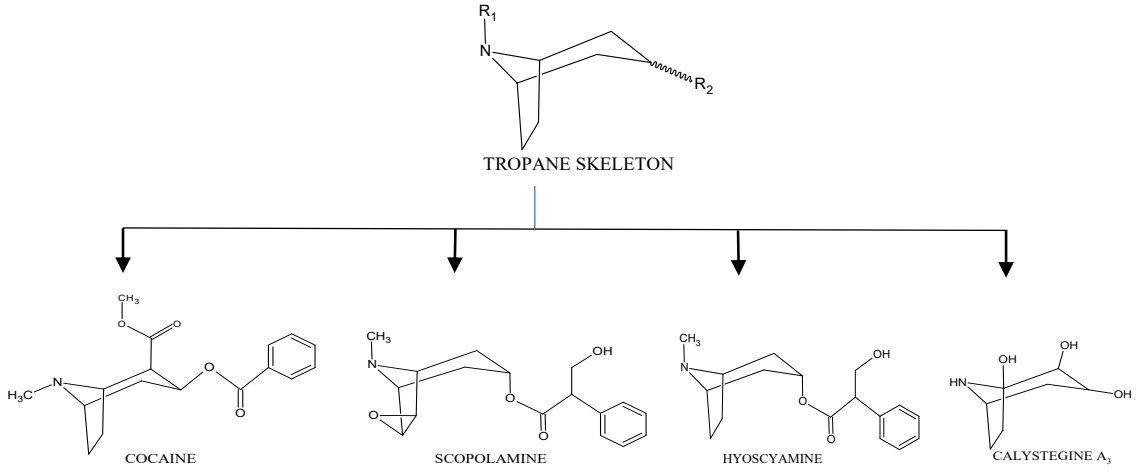


Figure 1

Although all TAs have a high degree of structural similarity due to their tropane ring, the pharmacological effects of these compounds differ significantly. Cocaine and hyoscyamine/scopolamine are able to pass the blood-brain barrier and commit dose-dependent hallucination and psychoactive effects. Calystegines do not cause these effects due to their polarity as well as hydrophilicity and consequent inability to pass this barrier. [5]

Atropine:

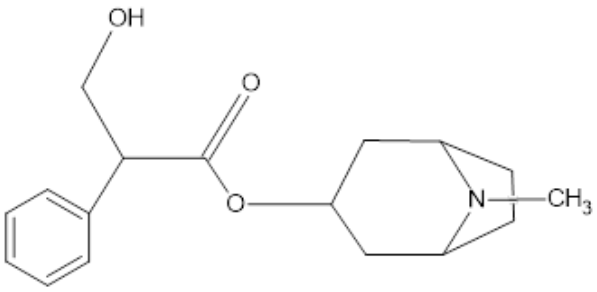


Table 1: Properties of Atropine.

Molecular Formula	$C_{17}H_{23}NO_3$
Molecular Weight	289.4 g/mol
SMILES	CN1[C@@H]2CC[C@H]1CC(C2)OC(=O)C(CO)C3=CC=CC=C3
IUPAC Name	[(1R,5S)-8-methyl-8-azabicyclo[3.2.1]octan-3-yl] 3-hydroxy-2-phenylpropanoate
Melting Point	91.791
Boiling Point	269.853

Isolation Of Atropine:

Atropine occurs in several solanaceous plants these include species of Atropa, Datura, Hyoscyamus, Duboisia, Mandragora and Scopolia. It is claimed that atropine does not occur as such in the plants, but 2-hyoscyamine present in plants, and during extraction process, 2-hyoscyamine undergoes racemization to give atropine.

One of the best methods for the isolation of atropine is as follows. The powdered drug is thoroughly moistened with an aqueous solution of sodium carbonate and extracted with ether or benzene. The alkaloidal bases are extracted from the solvent with water acidified with acetic acid. The acid solution is then shaken with ether as long as the latter takes up colouring matters. The alkaloids are precipitated with sodium carbonate, filtered off, washed and dried. The dried precipitate is dissolved in ether or acetone, dehydrated with anhydrous sodium sulphate and filtered. The filtrate is concentrated, cooled, when crude hyoscyamine and atropine crystallize from the solution. The crude crystalline mass resulted is filtered off and dissolved in alcohol, sodium hydroxide solution is added and the mixture is allowed to stand until racemization of hyoscyamine to atropine is completed (as indicated by the absence of optical activity). The crude atropine is purified by crystallisation from acetone.

Identification Tests of Atropine:

The following identification tests are mentioned in the British Pharmacopoeia of 1963(70)–

1 mg of atropine is added to 4 drops of fuming nitric acid and the mixture is evaporated to dryness on a water bath; a yellow residue is obtained. 2 ml of acetone and 4 drops of a 3% w/v solution of potassium hydroxide in methyl alcohol are added to the cooled residue; a deep violet colour is produced.

Other identification tests are as follows :-

The Gerrard Reaction

To about 6 mg of atropine, 1 ml of 2% solution of mercuric chloride in 50% aqueous methanol is added; a deep red colour is produced.

To a trace of atropine in an evaporating dish, drops of the p-dimethylaminobenzaldehyde reagent are added as well as 0.4 ml of water. The resulting mixture is heated on a boiling water bath; an intense red colour is produced which changing to Permanent cherry red on cooling.

Physiological Test:

Induction of mydriasis

An aqueous, alcohol free solution of atropine or its sulphate is dropped into the conjunctival sac of the eye and held so that non is lost by overflow of tears. It will cause dilation of pupil of eye in 1 hour. [6]

Chemistry:

Tropane alkaloids are a class of organic compounds found naturally in plants, particularly within the Solanaceae family. They are characterized by the presence of a tropane ring system within their molecular structure. This bicyclic ring system consists of a piperidine ring fused to a pyrrolidine ring, with a nitrogen atom bridging the two rings. The nitrogen atom is also typically attached to a methyl group.

Here's a more detailed look at their chemistry:

Key Features:

Tropane Ring: The defining structural feature is the tropane ring, a bicyclic system with a nitrogen bridge.

Nitrogen Atom: The nitrogen atom in the tropane ring is usually tertiary (containing a methyl group).

Alkaloids: They are classified as alkaloids because they contain nitrogen and are derived from amino acids.

Solanaceae Family: Many tropane alkaloids are found in plants of the Solanaceae family, which includes familiar plants like tomatoes, potatoes, and tobacco.

Stereochemistry: Tropane itself is a symmetrical molecule, but many tropane alkaloids have chiral centers (asymmetric carbons) leading to different stereoisomers.

Biological Activity: Some tropane alkaloids have pharmacological properties, acting as anticholinergics or stimulants.

Examples:

Atropine: A well-known tropane alkaloid found in plants like deadly nightshade (Atropa belladonna). Scopolamine: Another tropane alkaloid with anticholinergic and sedative effects.

Cocaine: A tropane alkaloid known for its stimulant properties.[7]

Biosynthesis Of Atropine:

The initial stages of Atropine biosynthesis is identical to that that of all tropane alkaloids. Arginine and Ornithine metabolism leads to the formation of Putrescine, Putrescine is methylated to form N-Methyl putrescine by the enzyme N putrescine Methyltransferase. N-Methyl putrescine is converted to N-methylpyrrolinium by spontaneous cyclization. N-methylpyrrolinium serves as the branch point for tropane synthesis. The biosynthesis of Atropine starting from L-Phenylalanine first undergoes a transamination forming Phenyl pyruvic acid which is then reduced to Phenyl lactic Acid. Coenzyme A then couples Phenyl-lactic acid with Tropine forming Littorine, which then undergoes a radical rearrangement initiated with a P450 enzyme forming hyoscyamine aldehyde. A dehydrogenase then reduces the aldehyde to a primary alcohol making Hyoscyamine, which upon racemization forms atropine. [8]

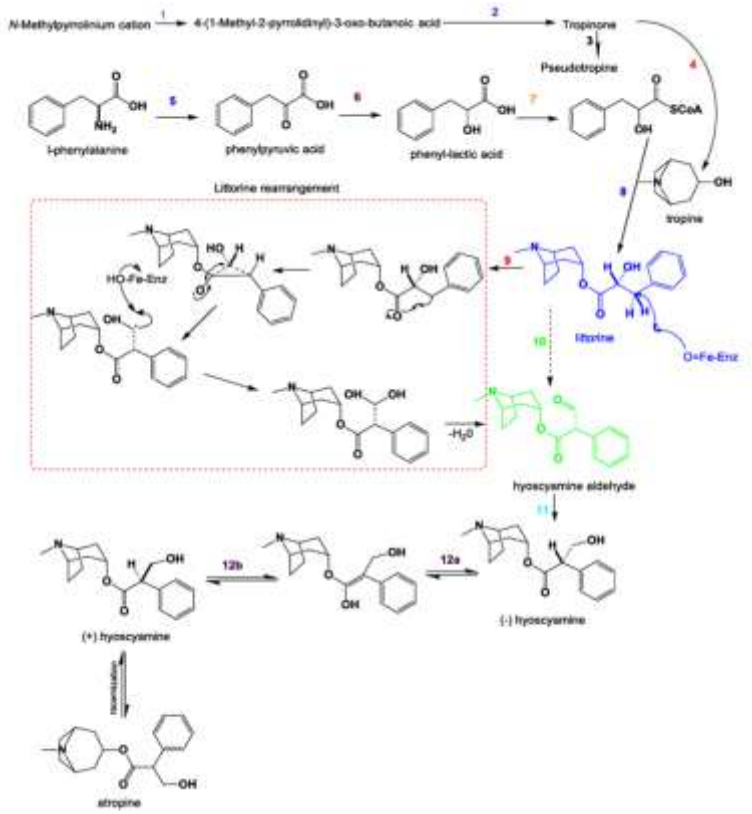


Figure 2: Fig 5: Atropine biosynthesis, starting with the L-phenylalanine; 1 = polyketide synthase; 2 = cytochrome P450 enzyme; 3,4 = tropinone reductase I/II; 5 = L-phenylalanine deaminase; 6 = D-phenyl lactate dehydrogenase; 7 = phenyl lactate CoA-transferase 8 = littorine synthase; 9 and 10 = cytochrome P450 littorine mutase/monooxygenase; 11 = unidentified alcohol dehydrogenase; 12a and 12b = hyoscyamine 6β hydroxylase

Biological Activities:

1. Anticholinergic Activity:

In their clinical study, Dr. Melvin M. Scheinman, David Thorburn, and Dr. Joseph A. Abbott investigate the therapeutic utility and safety of intravenous atropine in 56 patients diagnosed with acute myocardial infarction (AMI) complicated by sinus bradycardia (SB). Fifty-six patients with acute myocardial infarction complicated by sinus bradycardia (SB) were treated with intravenous atropine and monitored in a coronary care unit. Atropine decreased or completely abolished premature ventricular contractions (PVCs) and/or bouts of accelerated idioventricular rhythm in 27 of 31 patients (87%) and brought systemic blood pressure up to normal in 15 of 17 patients (88%) with hypotension. In addition, atropine administration was associated with improved atrioventricular conduction in 11 of 13 patients (85%) with acute inferior myocardial infarction associated with 20 or 3° atrioventricular block. Seven patients developed ten significant adverse effects: ventricular tachycardia or fibrillation in three, sustained sinus tachycardia in three, increased PVCs in three, and toxic psychosis in one. These major adverse effects correlated with either a higher initial dose of atropine (i.e., 1.0 mg as compared with the usual 0.5 or 0.6 mg) or a total cumulative dose exceeding 2.5 mg over 21/2 hours. Atropine is the drug of choice for management of patients with SB and hypotension and is effective in the treatment of ventricular arrhythmias as well as conduction disturbances in patients with inferior myocardial infarction.

Serious adverse effects, however, preclude use of atropine without careful medical supervision. [9]

2. Anti-myopia Activity:

In this review article, Dr. Pei-Chang Wu, Meng-Ni Chuang, Jessy Choi, Huan Chen, Grace Wu, Dr. Kyoko Ohno-Matsui, Dr. Jost B Jonas, and Chui Ming Gemmy Cheung investigate the escalating global prevalence of myopia and explore the clinical use of atropine eye drops in its control—particularly in children. The prevalence of myopia is increasing globally. Complications of myopia are associated with huge economic and social costs. It is believed that high myopia in adulthood can be traced back to school age onset myopia. Therefore, it is crucial and urgent to implement effective measures of myopia control, which may include preventing myopia onset as well as retarding myopia progression in school age children. The mechanism of myopia is still poorly understood. There are some evidences to suggest excessive expansion of Bruch's membrane, possibly in response to peripheral hyperopic defocus, and it may be one of the mechanisms leading to the uncontrolled axial elongation of the globe. Atropine is currently the most effective therapy for myopia control. Recent clinical trials demonstrated low-dose atropine eye drops such as 0.01% resulted in retardation of myopia progression, with significantly less side effects compared to higher concentration preparation. However, there remain a proportion of patients who are poor responders, in whom the optimal management remains unclear. Proposed strategies include stepwise increase of atropine dosing, and a combination of low-dose atropine with increase outdoor time. [10]

3. Antispasmodic And Analgesic Activity:

In a systematic review and meta-analysis conducted by Xian Lin, Hao Chen, and Yi-Nan Lin, the clinical efficacy and safety of atropine combined with omeprazole for the treatment of acute gastritis were evaluated across 11 randomized controlled trials involving 1,053 patients. This study analysed 11 articles from the literature with a total of 1,053 subjects. The combination of atropine and omeprazole significantly improved the clinical outcomes of patients with acute gastritis compared to patients treated with combined anisodamine and omeprazole (control group). The effective rate of combined atropine and omeprazole treatment was 1.21 times higher than that observed with the control group, and the incidence of adverse reactions was 0.41 times that of the control group. Atropine combined with omeprazole significantly alleviated the clinical symptoms of the patients. The total treatment time was shortened by 0.57 days, duration of abdominal pain was shortened by 2.82 days, duration of diarrhoea was reduced by 1.99 days, and the duration of nausea and vomiting was shortened by 2.68 days compared to the control group. The combination of atropine with omeprazole in the treatment of acute gastritis demonstrated a high effective rate with few adverse reactions. [11]

CONCLUSION:

Tropane alkaloids represent a chemically diverse and pharmacologically significant class of natural compounds primarily found in the Solanaceae family. Their potent anticholinergic properties, exemplified by compounds such as atropine, scopolamine, and hyoscyamine, have made them invaluable in both traditional and modern medicine. Recent advances in analytical techniques, biosynthetic pathway elucidation, and synthetic biology have enhanced our understanding of these alkaloids, opening new avenues for their sustainable production and therapeutic innovation. Despite their well-

documented medicinal uses, tropane alkaloids also pose significant toxicological risks, underscoring the importance of careful dosage and regulatory control. Continued interdisciplinary research is essential to fully harness their therapeutic potential while minimizing associated risks, ultimately contributing to the development of safer and more effective alkaloid-based treatments.

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