



Chlorhexidine: An Ally to Trust

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ABSTRACT

Chlorhexidine has been the most commonly prescribed antiseptic agent in the dental field and it is the main component of mouthwash. It has an antibacterial activity with a broad spectrum of action and it has been used to reduce plaque, gingival inflammation, and bleeding.(1) And it is considered a safe compound, with the least systemic side effects. It is available in different formulations. The aim of the article is to provide a complete review of the history, mechanism of action, characteristics, application, and problems associated with the use of chlorhexidine.

Keywords: Anti-microbial Agent, Chlorhexidine, Disinfection, Substantivity.

Introduction

Dental plaque is the primary etiologic factor responsible for gingivitis and periodontitis.¹ Mechanical plaque control using toothbrushes, interdental brushes, and dental floss prevents the occurrence of gingivitis.² Chlorhexidine, characterized by cationic properties, is a bisbiguanide formulation. As a strong base, chlorhexidine is most stable when in the form of salts, with digluconate salt being the most common due to its water solubility.³

Chlorhexidine has been used in a variety of healthcare settings. It is often used as a topical antiseptic for wound care and skin preparation before procedures. It has also been used as a

mouthwash for oral hygiene and as a pre-operative rinse.⁴

Chlorhexidine works by damaging the cell walls of microorganisms, leading to their death.² It also disrupts the formation of biofilms. It can cause some side effects, such as staining of teeth, allergic reactions in some individuals, and rarely anaphylactic shock. Its low toxicity profile makes it a safe option for healthcare professionals and patients alike. This drug is utilized for both the treatment and prevention of infections, particularly those affecting the skin, mouth, or throat. Additionally, it serves as a skin cleanser prior to injections or small surgical procedures.⁵

It was first used for controlling plaque by Schroeder in 1969 and is known for its broad-spectrum anti-microbial properties. Chlorhexidine is accessible in three forms: digluconate, acetate, and hydrochloride. Its exceptional substantivity allows it to stand out among other chemical components.⁵

History of Mouthwash

The Chinese are credited with the earliest known reference to mouth rinsing dating back to 2700 B.C.E, where it was recommended to rinse with the urine of a child. During the Roman period, mouth rinsing became popular with the upper classes as an adjunct to mechanical cleansing. Recommendations included using salty water in an uneven number of mouthfuls, a mixture of salt, alum, and vinegar as advocated by Hippocrates, and a variety of other mixtures including honey, oil, beer, dill, anise seed, and pure white wine. Europeans regarded "therapeutic rinsing" as especially popular until the early 18th century. Mouth rinsing also had a religious connection, as the Talmud contained instructions for rinsing the mouth between meals to remove food remnants and prevent the admixing of meat and milk products, which violated the dietary laws. By the 16th century, mechanical tooth cleaning and mouth rinsing had established themselves as common practices.^{4,6}

The Zene Artzney, a 1530 publication in Germany, provided advice on preserving teeth, such as rinsing the mouth with burnt alum mixed with vinegar or myrrh boiled in wine. The text also suggested washing the mouth with wine or beer after eating to prevent decay and bad odour. W.D. Miller supported his Chemo-parasitic theory of tooth decay by noting that certain areas of the teeth cannot be reached by antiseptics or may not react strongly enough to them.^{4,6}

Structure

Belonging to the biguanide family, chlorhexidine is composed of hydrophilic and hydrophobic groups and is synthesized from proguanil. It is known as a bisbiguanide antiseptic and is comprised of two chlorophenyl rings and two biguanide groups that are connected by a hexamethylene bridge. This compound is a strong base and has two positive charges on each side of the bridge when pH levels rise above 3.5.⁷

Most studies and oral formulations use the digluconate salt, manufactured as a 20% V/V concentrate, as it is water-soluble. In contrast, the acetate salt is also water-soluble, but the hydrochloride salt has very low solubility in water.⁷

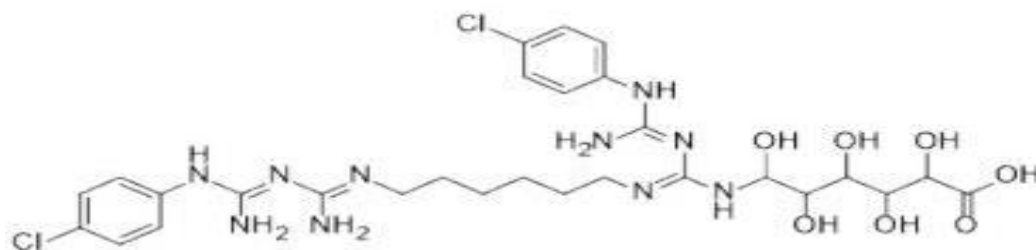


Figure 1: chemical structure of chlorhexidine.

Chlorhexidine is available in three forms⁵:

1. Digluconate - Most commonly used, and Water soluble.
2. Acetate - Water soluble.
3. Hydrochloride salts - sparingly water soluble.

By formulating chlorhexidine with gluconic or acetic acid, water soluble digluconate or diacetate salts can be produced despite chlorhexidine's insolubility in water. The resulting solutions are colourless and odourless, although they possess an unpleasant bitter taste. When applied externally, the N-chlorinated derivative of chlorhexidine can covalently bond to proteins in the skin and mucous membranes, producing a long-lasting antimicrobial effect with minimal systemic absorption, even if accidentally ingested.⁸

Low molecular weight substances, such as potassium and phosphorous, will permeate out of the cell at a concentration of 0.2%, whereas at a concentration of 2%, the cytoplasmic contents precipitate, leading to chlorhexidine -induced bactericidal effects and ultimately, cell death.⁸

Chlorhexidine- Products

The products are^{8,9}:

1. **Mouth Rinses:** Chlorhexidine mouth rinses are available in both 0.2% and 0.12% concentrations, with similar efficacy at appropriate doses. Rinsing time ranges from 30 to 60 seconds depending on the antiseptic's absorption rate to oral surfaces, although individual variations may occur.
2. **Gel:** Chlorhexidine gel is available in various concentrations, including 0.2%, and 0.12%, and comes in the form of trays or toothbrushes. When applied once a day, the gel has therapeutic effects, such as minimizing oral malodor and chlorhexidine staining.
3. **Sprays:** Physically and mentally handicapped patients have shown positive acceptance towards 0.1% and 0.2%

sprays, which have comparable plaque inhibition properties to 0.2% mouthwash.

4. **Toothpaste:** Due to its potential interaction with anionic components found in toothpaste and competition for oral retention sites, Chlorhexidine in dentifrices received limited attention.²⁴
5. **Varnishes:** Chlorhexidine varnishes are used for prophylaxis against root caries.
6. **Sugar free:** Chlorhexidine in the form of chewing gum contains 20mg of chlorhexidine diacetate.

Mechanism of Action

Chlorhexidine is most stable as a salt due to its strong base nature. The original salts used, acetate and hydrochlorite, were replaced by the highly water-soluble digluconate in 1957. Within the pH range of 5 to 8, aqueous solutions of chlorhexidine are stable. The optimal pH range for its antimicrobial activity is between 5.5 to 7.0, which coincides with the pH of body tissues and surfaces.^{9,10}

The drug's bactericidal effect is achieved through the cationic molecule binding to extra-microbial complexes and negatively charged microbial cell walls, disrupting the osmotic equilibrium of the cells. At low concentrations, leakage of low molecular weight substances such as potassium and phosphorous leads to a bacteriostatic effect. However, at higher concentrations, Chlorhexidine precipitates and/or coagulates bacterial cell cytoplasm, leading to protein cross-linking and ultimately, cell death. This leaves cell debris in the root canals which can be removed through thorough irrigation with distilled water.^{10,11}

Pin-Cushion Effect

The positively charged end of the CHX molecule binds to the tooth surface and the negatively charged end interacts with the bacterial membrane, which is termed a pin-cushion effect.¹⁰

Antibacterial action

CHX molecule has positive charges located on the nitrogen atoms situated on the sides of the Hexamethylene Bridge. At low concentrations, this molecule disrupts bacterial cellular transport by creating pores in the cellular membrane, while in higher concentrations, it penetrates the bacterial cell, leading to its lysis.¹⁰

Anti-plaque effect

Due to its substantivity, CHX is a highly effective antimicrobial agent for inhibiting plaque formation. This is because it blocks the acidic groups found on salivary glycoproteins and reduces protein adsorption on tooth surfaces. Additionally, CHX binds to bacterial surfaces, which leads to a reduction in plaque formation by causing agglutination factors in saliva to precipitate and displacing calcium. As a result, bacterial colonies are unable to form plaque.¹²

Bacteriostatic effect

The CHX molecule attracts the negatively charged bacterial cell surface and attaches to phosphate-containing compounds. This alters the integrity of bacterial cell membranes. The CHX molecule is further attracted toward the inner cell membrane and is bound to phospholipids. This bacteriostatic effect is reversible.¹³

Bactericidal effect

With an increase in concentration, CHX leads to a more severe damage of the membrane resulting in the coagulation and precipitation of the cytoplasm through the creation of phosphate complexes, leading to irreversible bactericidal properties.^{12,13}

Chlorhexidine Staining

The mechanisms proposed for chlorhexidine staining:

1. Degradation of the chlorhexidine molecule to release parachloraniline.
2. Catalysis of Maillard reactions.
3. Protein denaturation with metal sulfide formation.
4. Precipitation of anionic dietary chromogens.

There is no evidence of chlorhexidine degradation to release parachloraniline, either during storage or as a result of metabolic processes. Despite lacking parachloraniline groups, alexidine causes staining identical to that of chlorhexidine. Non-enzymatic browning reactions catalysed by chlorhexidine are a theoretical possibility, but cannot explain similar staining by other antiseptics and metal ions. The precipitation of anionic dietary chromogens by cationic antiseptics, such as chlorhexidine and polyvalent metal ions, is a well-supported explanation for staining phenomena. Cationic groups can also attach to dietary factors, such as polyphenols and tannins, and contribute to molecule and tooth surface staining. There is no direct evidence of protein denaturation produced by chlorhexidine interacting with exposed sulfide radicals and metal ions.¹²

Gold Standard

The superior degree of persistence at the tooth surface leads to a highly effective antiplaque effect, as well as a persistent bactericidal and bacteriostatic effect. This is due to the unique "Pin-Cushion" effect of chlorhexidine, where one charged end binds to the tooth surface while the other remains available to interact with approaching bacterial membranes resulting in a prolonged substantivity.¹³

Toxicology and Safety

Chlorhexidine's cationic nature reduces absorption through skin and mucosa, as well as the gastrointestinal tract, with primary excretion through feces; systemic toxicity from ingestion or topical application is not documented, and it is poorly absorbed by the GIT with an oral LD of 1800mg/kg. Even in intravenous infusion in animals, chlorhexidine is well tolerated, with an intravenous LD of 22mg/kg. While no teratogenic alterations have been found, neurosensory deafness may occur if introduced into the middle ear, and it should not be applied to the outer ear if the eardrum is perforated. Chlorhexidine as an oral

mouth rinse has been known to cause local side effects.¹²

1. Brown discoloration of the teeth and some restorative materials and the dorsum of the tongue (Dose dependent).
2. Taste perturbation (Concentration dependent).
3. Oral mucosal erosion.
4. Unilateral or bilateral parotid swelling. This is an extremely rare occurrence and an explanation is not available.
5. Enhanced supragingival calculus formation.¹³

Chlorhexidine also has a bitter taste, which is difficult to mask completely. For these reasons; the prolonged use of chlorhexidine should be avoided. It is useful for short periods of up to 2 weeks.⁴

Clinical Applications of Chlorhexidine

- As an adjunct to oral hygiene and professional prophylaxis.
- Post oral surgery in periodontal surgery or root planning.
- Patients with intermaxillary fixation and in patients who are under high risk of caries.
- Physically and mentally handicapped chlorhexidine sprays can be used.
- Medically compromised patients who are predisposed to oral candidiasis.
- Used to limit the bacteremia and operatory contamination by oral bacteria and as an adjunct to antibiotic prophylaxis.
- Sub gingival irrigation.
- Final irrigation before root canal obturation. management of denture stomatitis.
- Hypersensitivity, tooth decay, recurrent oral ulceration.
- Patients undergoing orthodontic treatment.
- Oral malodor [Halita is the name of a mouth rinse containing 0.05% of chlorhexidine , 0.05% cetylpyridinium chloride and 0.14% of zinc lactate].

- For surgical skin preparation.
- As a local drug delivery system(23) in the form of a bio - degradable chip to be used in the subgingival environment [periochip - 2.5mg of chlorhexidine is found to have an average drug concentration greater than 125 microgram per milliliter for 7 to 10 days.¹¹

Patients who are temporarily and moderately compromised with risk factors like poor oral hygiene, immune system suppression, and the accumulation of anaerobic bacteria (such as *Prevotella intermedia*, *Fusobacterium*, and *Treponema*), as well as stress, a lack of proper nutrition, and smoking 22, are more likely to develop necrotizing gingivitis (and, less commonly, necrotizing periodontitis). Inflammation and swelling of the gingiva are caused by bacteria that are associated with characteristic grey sloughing and halitosis. The first line of treatment involves improving oral hygiene and administering antibiotics like metronidazole or amoxicillin.²³ The current recommendations by NICE and SDCEP advocate mouthwashes like 0.12% or 0.2% CHX or 6% hydrogen peroxide as a supplementary treatment.²⁰

To prevent microbiologic contamination from entering the dental laboratory, it is highly advised to immerse all impressions in CHX of at least 0.2% concentration for a minimum of 10 minutes. Utilizing CHX as a disinfectant via either spray or immersion technique has been proven to effectively disinfect dental impression materials and prostheses, making it essential to perform this disinfection in the clinic.²⁰

Use in Other Branches

Chlorhexidine, with its antimicrobial properties, can be used throughout all stages of root canal treatment from disinfecting the operatory field to removing gutta-percha cones during retreatment. It can also be used as an intracanal medicament either alone or combined with others to model the main guttapercha cone.¹²

In addition, CHX is recommended as an alternative to NaOCl in cases of open apex, root resorption, foramen enlargement, root perforation, or in cases of allergy related to bleaching solutions due to its biocompatibility.

One of the main benefits of using CHX is that it does not affect the ability of root fillings to prevent fluid penetration into the root canal system through the apical foramen.¹²

Adjunctive uses of chlorhexidine products in the treatment of stage I-III periodontitis.¹³

Purpose of Interventions	Evidence Based Recommendations
Improve clinical outcome of subgingival instrumentation	<p>Chlorhexidine mouthwash may be used for a limited period of time, in periodontitis therapy, as an adjunct to mechanical debridement in specific cases.</p> <p>Locally administered sustained-release chlorhexidine may be considered for use as an adjunct to subgingival instrumentation in patients with periodontitis.</p>
Control of gingival inflammation in patients with periodontitis receiving supportive periodontal care	<p>If antiseptic dentifrice formulation is to be used adjunctively, products containing chlorhexidine, triclosan-copolymer, and stannous fluoride-sodium hexametaphosphate are suggested.</p> <p>If antiseptic mouthwash is to be used adjunctively, mouthwash containing chlorhexidine, essential oils, or cetylpyridinium chloride is suggested.</p>

Use of Chlorhexidine in Covid-19 Patients (Oropharyngeal)

Chlorhexidine has proven to be effective in preventing postoperative infections, dental plaque, ventilator-associated pneumonia, and killing enveloped viruses due to its cationic nature. As SARS-CoV-2 is an enveloped virus, chlorhexidine has demonstrated effectiveness against it. Using a spray applicator to apply chlorhexidine directly to the posterior oropharynx improved the clearance of SARS-CoV-2 from the oropharynx significantly. This method eliminated the virus from the oropharynx in 86.0% of patients, whereas patients who used chlorhexidine as an oral rinse alone showed clearance in only 62.1% of cases.¹⁴

Although a small group of healthcare workers showed promising results in preventing SARS-CoV-2 infection with chlorhexidine, a formal analysis

was not conducted. Therefore, larger studies are required to determine the effectiveness of chlorhexidine in preventing COVID-19 among healthcare workers.

The authors propose that the use of chlorhexidine as an oropharyngeal rinse may serve two purposes:¹⁴

- To prevent viral spread from COVID-19 patients to others.¹⁴
- To prevent SARS-CoV-2 infection in the case of exposure to the virus.¹⁴

For prevention of viral spread from SARS-CoV-2-infected individuals to others, the authors recommend using chlorhexidine gluconate 0.12% mouthwash twice a day as follows:¹⁴

(1) Spray 1 ml to the nares.

(2) Rinse the throat thoroughly with 15 ml for at least 30 seconds.

(3) Use a spray applicator to spray the posterior throat three times (1.5 ml). This process may be continued until the virus is naturally cleared from the body, which takes approximately 2–3 weeks.

The authors recommend using the mentioned chlorhexidine regimen for 2-4 days as post-exposure prophylaxis but caution that it cannot be used to treat COVID-19 and strongly advise against trying to ingest chlorhexidine as a way to eliminate the disease.

Limitations and Adverse Effects¹²

- **Teratogenic Effects:** Although reproduction studies in rats and rabbits at doses up to 300 mg/kg/day and 40 mg/kg/day of CHX gluconate, respectively, found no harm to the fetus, there are no adequate and well-controlled studies in pregnant women available. As a result, the pregnancy category for CHX gluconate is designated as Category B.
- **Neurosensory Deafness:** One should avoid placing Chlorhexidine in the outer ear if the ear drum is perforated, as the introduction of the antiseptic into the middle ear can lead to complications.
- **Nursing Mothers:** Caution might be indicated when administering Chlorhexidine to a nursing woman, as it is unknown whether it is excreted in human milk and many drugs are known to be excreted in human milk.
- **Bacterial resistance:** Long-term oral use did not result in any reported resistance, super-infection by fungi, yeasts, or viruses. Although there was a slight shift in the flora towards less sensitive organisms, this effect quickly reversed upon discontinuing the use.

Conclusion

Chlorhexidine is indicated as an adjunct to mechanical methods in cases where plaque

removal is not adequate. The ineffectiveness of mechanical plaque control methods among the majority of the population is due to insufficient time spent on plaque removal and inconsistencies, leading to the need for chemical plaque control agents as supplementary measure. Chlorhexidine (CHX) is widely regarded as the foremost chemical agent for plaque control, with a structural formula comprising two symmetrical 4-chlorophenyl rings and two biguanide groups linked by a central hexamethylene chain.¹⁶

Using chlorhexidine mouthwash over an extended period of time may lead to brown discoloration of the teeth, which is its only downside.¹⁷ In conjunction with scaling and root planning, the adjunctive use of local delivery of drugs like chlorhexidine and tetracycline may enhance the results in isolated periodontal pocket sites that do not respond to conventional therapy.^{18,21}

While mechanical plaque control agents cannot effectively clean all areas of the mouth, mouthwashes such as CHX are able to access those difficult areas and have superior antiplaque properties.^{19,24}

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