Qalaee (Stannum) metallic origin element, its chemical compounds, action, therapeutic uses, adverse effect and pharmacological activity studies: A Review

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Abstract

Qalaee is Unani name of tin (stannum), which is a metallic element, belongs to group 14 of periodic table. Atomic number of tin is 50 and its atomic mass is 119. Qalaee (Tin) consist two types of compounds, inorganic tin compounds and organic tin compounds. Several toxic and adverse effect studies of Qalaee (stannum) have been reported such as, Respiratory Effects, Gastrointestinal Effects, Haematological Effects, Renal Effects, Dermal Effects, Ocular Effects, Immunological and Lymph reticular Effects, Neurological Effects, Cardiovascular Effects, Body weight effect and reproductive effects. Some studies on different pharmacological activities of tin also reported like, antibacterial activity, anticancer activity and anti-parasitic activity. In traditional system of medicine Qalaee is used in the form of Kusta or Bhasm for various disorders such as spermatorrhoea, excessive nocturnal emission, premature ejaculation and Syphilis etc. Its important Unani formulation is Kusta qalaee.

Keyword: Qalaee (Stannum), Action and Therapeutic use, adverse effect, Pharmacological action.

Introduction

Qalaee is a metallic element which is commonly known as tin. It belongs to group 14 of the periodic table, along with C, Si, Ge and Pb. The element has an atomic number of 50, an atomic mass of 119, and tin naturally occurring isotopes, the largest number of all elements (\(^{112}\)Sn, \(^{114}\)Sn to \(^{120}\)Sn, \(^{122}\)Sn and \(^{124}\)Sn), of which \(^{112}\)Sn, \(^{114}\)Sn and \(^{120}\)Sn are the most abundant at 32.97%, 24.01% and 14.24% respectively of its mass.1 Qalaee (Tin) shows intermediate characteristics in its chemistry between that of Ge and Pb. Qalaee (Sn) is a naturally occurring heavy metal in the earth’s crust, at an average concentration of 2 mg/kg. For that reason, it is also present in many soils as a result of bedrock degrading naturally. Less than 1 mg/kg to 200 mg/kg are typical quantities of Sn in uncontaminated soils. Sn exists in two oxidative states: stannous (+2) and stannic (+4). 2. Qalaee is a soft, white, silvery metal that is insoluble in water. Aerosol, food, and drink cans are lined with tin metal. It can be found in pewter, brass, bronze, and many soldering supplies. Tin is a metal that may mix to create a wide range of combinations, for this reason, it is also present in many soils as a result of bedrock degrading naturally. An inorganic tin compound is formed when tin is mixed with oxygen, sulfur, or chlorine. The earth’s crust contains trace levels of inorganic tin compounds. They are also present found in food additives, toothpaste, soaps, fragrances, and colors. Further, tin and carbon can combine to generate organotin compounds. These compounds are used in making plastics, plastic pipes, paints, food packages, pesticides, wood preservatives, and rodent (rats and mice) repellents. There can be qalaee (Sn) metal as well as Tin compounds, both inorganic and organic, in the soil, water, and air close to their native locations in rocks, mines, and manufacturing sites. Organic tin compounds are often man-made substances that don’t arise
naturally in the environment. The time each tin compound stays in air, water, or soil differs from compound to compound. It is softer than gold but harder than lead. It is malleable and ductile with less elasticity and bends with a cracking sound. Qalaee is obtained by heating tin stone with charcoal. Qalaee is puried by heating it over fire and when it melts it is poured into the milk of Calotropic giga. In other process the qalaee is melted and poured into the juice of Vitex negunda and mixed with zard chobe, this process is repeated three times. According to Unani classical literature, Qalaee is two types (1) Misraka (Impure) which is dirty white in appearance. Its main impurities are arsenic and sulphur (II) Khanj (Pure) which is soft bright and cold readily fusible. Only pure qalaee is recommended for medicinal purpose. Qalaee is used in various ailments such as spermatorrhoea, excessive nocturnal emission, premature ejaculation and Syphilis.

Sources:
Qalaee is rarely found in a free state, it is mostly found as oxide or tin stone or in combination with Sulphur as sulphide. It is abundant in Burma, Tenasserim and Malacca. China, Indonesia, Peru, Bolivia, Brazil, and Australia are the largest producers of qalaee (Sn); Malaysia and Thailand also produce a signi cant amount of the metal. Qalaee occurs naturally in the Earth's crust, with an average concentration of approximately 2–3 mg/kg.

Vernacular Names:
Arabic; Rasas, Abruz, Kasdir, Bengali; Bana, Burma; Khaimaphyn, Duk; Kathali, English; Tin, Pewter-calx, Gujrati; Kalai, Hindi; Kathal, Rang, Konkan; Tavaray, Malayalam; Kalanga, Timah, Persian; Urzis, Sanskrit; Vanga, Ranga, Trapu, Sindhi; Sudu-iyam, Tamil; Tagram, Telangana; Vendi Sisam, Urdu; Qalaee.

Mijaz (Temperament): Sard and Tar third degree, Cold and dry.

Doses: 3-4 Grain, 125-250 mg, 1-2 Ratti; 6, 125 mg.

Important Unani formulation: Kusta qalaee 9 Safooof qalaee.

A`fal (Action) in Unani classical literature:
Daf`i-Dagh al-Dam (Antiphlogistic), Daf`i-Tufayli (Antiparasitic), Anti viral, Daf`i-Jarafim (Antibacterial), Daf`i-Santan (Anti-cancer), Mubhi (Aphrodisiac), Muqawwi (Tonic), Qaṭīl-i-kirm-i- Shikham (Antihelmintic), Urinary disorder, Majzuﬁ (Desicative), Mulattif (Sedative), Mohallil (Resolvent), Muqawwi-i-chashm (Eye tonic) Qābīd (Astringent) Mughalliz-i-Mani.

Therapeutic Uses in Unani Classical Literature:
Du`f al-Bah (Sexual weakness), Sur`a al-Inzāl (premature ejaculation), Riqqat-e-Mani and Kathra al-Iltilām (excessive nocturnal emission), Ananat, (Impotence), Āṭshak (Syphilis), Buthīr Labaṇiyu (Acne vulgaris), Iṣṭikha (Paralysis), Jīryān or Sālo-n-i-Mani (Spermatorrhoea), Jamir (Anthrax), Juzam (Leprosy), Kami-e-Lazzat (Sexual debility), Leishmaniasis, Nafs-al-Dam (Hemoptyis), Qabd (Constipation), Sha`īra (Stye), Sill (Phthisis), Su`-al-Hađm (Dyspepsia), Sozākh (Gonorhoea), Yanqāḏ (Jaundice), Ziq al-Nafas (Asthma), Amra-ḍ-i-Chashm (Eye diseases), Bawāsīr (Haemorrhoid), Jarab (Scabies), Mushţahi (Appetizer), Nazla (Catarrh), Sayalān al-Rahim (Leucorrhoea), Surhādā (Erysipelas), Zayābīs (Diabetes), Sur`a al-Inzāl (Premature ejaculation), Waj`a al-Mafasil (Rheumatoid arthritis).

Chemical Compounds of Qalaee (Tin):
Potassium stannate (Dibotassium tin trioxide) K₂SnO₃, Potassium stannate (Potassium stannate trihydrate) KSn(OH)₄, Sodium stannate (Disodium tin trioxide) Na₂SnO₃, Sodium stannate (Sodium stannate trihydrate) Na₂Sn(OH)₃, Tin bromide (Tin tetrabromide; stannic bromide) SnBr₄, Tin chloride (Tin tetrachloride; stannic chloride) SnCl₄, Tin chloride monohydrate (Tin dichloride-di-iodide) SnClI₂, Tin dibromide (Tin dibromide; stannic bromide) SnBr₂, Tin dichloride (Tin dichloride; stannic chloride) SnCl₂.

Respiratory Effects
Inorganic Tin Compounds. People who are exposed to stannic oxide dust or fumes can develop stannosis, a benign form of pneumoconiosis.

Adverse Effects Study of Qalaee (Stannum):

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nausea and vomiting occurred among all the members of a family of five who were exposed at home to tributyltin oxide contained in paint for mildew control. Saary and House (2002) stated that a man had burning in his sub sternum and epigastric area along with flatulence a few hours after inhaling powdered trimethyltin chloride. Two months after exposure, the stomach ache was still present.

Haematological Effects

Fatty degeneration was observed at necropsy in animals killed after a 95-day exposure period to 4-6 mg/m³ (0.30–0.45 ppm) tributyltin chloride. The histopathology of rats exposed to 2 mg tin/m³ (0.41 ppm) as a combination of tributyltin bromide (0.39 ppm) showed liver shrinkage and mild necrosis, di butyl tin dibromide (0.02 ppm), and hydrocarbon impurities for up to 80 days as part of a study of reproductive function. In females, the length of exposure enhanced liver cell atrophy. If tin exposure was halted before sacrifice, some recovery was visible. The recovery is less complete the longer the exposure period.

Renal Effects

Autopsy of the one chemical worker who died following exposure to the combination of the methyl tin salts revealed shock kidneys (i.e., proximal tubule degeneration), which represents severe tubule damage. The urine of the other five exposed males contained significantly higher concentrations of tin, with the most adversely impacted having the highest levels. Inhalation exposure of mice to a concentration of 5.65 mg tin/m³ (1.16 ppm) as a mixture of tributyltin bromide (1.1 ppm), di butyl tin dibromide (0.06 ppm), and hydrocarbon impurities for 7 hours/day over 6 days produced pathological changes in the kidney.

Animal necropsies showed extra-medullary haemato poiesis and mild degenerative changes in the glomeruli, convoluted tubules, and collecting tubules. More extensive kidney pathology was observed in rats exposed to 2 mg tin/m³ (0.41 ppm) as a mixture of tributyltin bromide (0.39 ppm) and di butyl tin dibromide (0.02 ppm) for 2 hours/day for 80 days. Kidney damage consisted of extensive congestion and swelling of the renal tubular epithelium.

Dermal Effects

According to the WHO study in 1980 Contact with inorganic tin salts produces mild irritation of the skin and mucous membranes. However, no specific studies were located regarding dermal effects in humans and animals after inhalation exposure to inorganic tin compounds.

Mice exposed to a butyl tin mixture (30 parts tributyltin bromide to 1 part dibutyl tin dibromide) during inhalation experiments by Igarashi in 1959 showed dermal effects, including skin reddening and dilated blood vessels in the nose, feet, and tail. Direct contact with the chemical may have produced these effects.

Ocular Effects

During the last month of a 95-day inhalation study of tributyltin chloride in female rats by Gholke in 1969, inflammatory eyes and nasal mucous membranes were seen. For six hours a day, five days a week, the animals were exposed to doses of 4-6 mg/m³ (0.30–0.45 ppm).

Immunological and Lymph reticular Effects

There are no studies on the immunological effects of inhaling inorganic tin or organotin compounds on humans or animals. However, after 14 days of exposure to a butyl tin mixture, rats showed signs of lymph node atrophy.

Neurological Effects

A research conducted by Rey et al. in 1984 gives some details on the neurobehavioral alterations that occur in people who are exposed to organotin chemicals (trimethyl tin chloride and dimethyltin dichloride). Six chemical workers were exposed to methyltins primarily through inhalation; the study details their experiences with headache, tinnitus, deafness, memory impairment, disorientation, aggression, psychotic and other severe neuropsychiatric behaviour, syncope, and loss of consciousness as exposure symptoms. One of the subjects passed away. After exposure, the two surviving workers with the highest urine tin levels experienced fixed neurological impairments that persisted for more than six years. The three surviving survivors went back to work, although they suffered from memory loss that lasted for six months. Other investigators have documented cases similar to this one.

According to Fortemps et al. (1978) two chemists who had been exposed to dimethyl tin dichloride and trimethyltin chloride vapours on occasion for roughly three months suddenly acquired a state of mental disorientation with generalized epileptic seizures. The individuals had reported experiencing headaches, discomfort in several organs, and psychological disorders such disorientation, memory loss, sleeplessness, anorexia, and memory errors before the acute episode. Both patients fully recovered after being taken out of exposure.

A study conducted by Ross et al. in 1981, to examine the frequency of neurological symptoms in 22 male workers who had been exposed to trimethyltin spillage one month earlier (there was likely some inhalation and cutaneous exposure). Comparison of individuals with lesser exposure to those with higher exposure revealed that the former group had a considerably higher incidence of specific symptoms like depressive episodes and fits of fury and temper tantrums, as well as general symptoms like forgetfulness, exhaustion and weakness, and loss of motivation. After the collision, certain symptoms lasted for at least three years.

Cardiovascular Effects

Rats were fed stannous chloride at dietary amounts ranging from <10 to 315 mg/kg/day for 13 weeks, and the relative heart weights of the male rats were larger than the controls. Both the impact and the related histopathology findings were not dose-dependent. The observation’s relevance is unclear on its own. Heart weights did not alter following four weeks of exposure to the same doses.

Endocrine Effects

Furthermore, it brought about alterations that were consistent with the activation of ACTH production and secretion, which led to adrenal hypertrophy. Thyroxin (T4) and thyrotrophin (TSH) levels in the serum were much lower, while the staining intensity of TSH cells was higher, indicating that tributyltin oxide obstructed TSH release, leading to thyroid hypofunction. Given that the drop in circulating T4 was significantly more dramatic than the drop in TSH, it is possible that tributyltin oxide directly affects the thyroid. Within 14 days, the majority of the acute effects seemed to be reversible. Rats given a daily dose of 6 mg/kg were shown to exhibit symptoms of thyroid hypofunction, enhanced adrenal function, and hypophysis weight.

In the duration of six weeks, Wistar rats were given diets containing 0, 1, or 4 mg of tributyltin oxide/kg/day during a study conducted by Krajnc et al. in 1984. Serum levels of T4 and TSH were substantially decreased while luteinizing hormone (LH) was significantly elevated throughout treatment with 4 mg/kg/day. A glucose tolerance test revealed unimpressive results, despite the fact that both exposure
levels reduced blood insulin levels. This finding raises the possibility that a significant reduction in feed intake was the cause of the serum insulin decrease. The levels of corticosterone and follicle-stimulating hormone (FSH) did not vary significantly. Thyrotropin-releasing hormone (TRH) was administered at a dose of 4 mg/kg/day. This resulted in a modest reduction in TSH release, but an increase in LH and FSH release. At 4 mg/kg/day, but not at lower levels, flattening of the thyroid follicles’ epithelial lining was observed by light microscopy. Treatment of the pituitary with 4 mg/kg/day of tributyltin oxide resulted in a decrease in the number and intensity of TSH-immunoreactive cells, an increase in the number of cells staining for LH, and no noticeable improvement in the staining for GH, FSH, or ACTH-producing cells. Concluded that the pituitary-adrenal axis was not stimulated by tributyltin oxide treatment, which lasted for six weeks. In a two-year dietary trial including tributyltin oxide in Wistar rats, blood levels of TSH, LH, FSH, insulin, T4, and free thyroxin (FT4) at doses up to 2.1 mg/kg/day showed no significant modifications at 12 or 24 months.

Body Weight Effects

Oral investigations of inorganic tin compounds indicated reductions in body weight, dietary intake, and water consumption. Studies in which rats were given acute and intermediate doses of stannous chloride and other inorganic tin compounds (≥7.9 mg tin/kg/day) showed decreases in body weights and reduced food intake.

Reproductive Effects

A significant percentage of research on the reproductive effects of some organotin chemicals has been done on rats, while there is also some information available regarding mice. The pregnant dams in the majority of rat trials received doses at different points during their pregnancies, and Cd 20 sacrifices were made. The frequency of resorptions and dead foetuses per litter as well as the percentage of post-implantation loss were considerably enhanced in pregnant Wistar rats treated with dosages of ≥7.5 mg di butyl tin dichloride/kg/day on Gds 7–15. Rat mortality was similarly induced by these dosage levels. Reproductive or maternal effects were not significantly affected by daily doses of 5 mg/kg. In a related investigation, the rate of dead or resorbed foetuses was considerably raised by doses of 15 mg di butyl tin diacetate/kg/day given on the global distribution system 7–17; however, a lower dose of 10 mg/kg/day was without significant reproductive effects.

Thymus involution, while a sensitive indicator of maternal toxicity, may not be connected to the manifestation of reproductive effects. Maternal thymus weight was reduced by 54% at a dose of 5 mg/kg/day, and body weight was significantly reduced at 15 mg/kg/day. These findings suggest that the adverse reproductive effects observed at 15 mg/kg/day may have been secondary to maternal toxicity. The highest dose tested, 10 mg/kg/day, was maternally toxic (reduced weight gain and food consumption) in a more recent study using di butyl tin dichloride administered on Gds 6–15, but it had no significant impact on any reproductive parameter, including total implantations, mean implantations/litter, total early resorptions, mean early resorptions/litter, total late resorptions, and mean late resorptions/litter.

Rats have been utilized in the study to evaluate the effects on reproduction of a mixture of tributyltin bromide (81.2%) and other substances, including di butyl tin dibromide (Iwamoto 1960). The rats were given acute and intermediate-duration doses of 2 mg tin/m3 (0.41 ppm), which is equivalent to 0.39 ppm tributyltin bromide and 0.02 ppm di butyl tin dibromide. After 4 weeks to 3 months of exposure, pregnancy rates were much lower; however, when exposure was stopped, pregnancy rates reverted to levels close to control. In independent investigations, histopathological assessments were conducted after various exposure times (14–80 days) and recovery intervals. Males indicate no alterations, while females showed atrophy of the glandular uterus as early as 14 days after exposure. Every effect was inverted throughout the recovery period. This research indicates some impairment of female reproductive systems may occur after inhaling a mixture of butyl tin compounds, even though the results weren’t sufficiently clear.

Pharmacological Activity:

Antibacterial activity

Kashta-e-qalaee in its nanoparticulate form showed potent bactericidal action against most gram positive strains and a small number of gram negative bacteria, according to a 2015 study by Umair et al. The two types of bacteria with the highest bactericidal activity were Corynebacterium xerosis and Streptococcus mutans. It is quite clear that Streptococcus mutans and dental caries are related. Kashta-e-qalaee may be suggested for use in dental powders, amalgams, dental implants with tin as one of the constituents, chewable or dispersible antibacterial pills, dusting powder, or ointments for infections caused by Candida xerosis. The research findings indicate that kashta-e-qalaee exhibits noteworthy antibacterial action against Corynebacterium xerosis and Streptococcus mutans.

Anti-tubercular activity

According to Kovala-Demertz and Hussain et al., tuberculosis (TB) is a chronic infectious disease that kills millions of people annually and is caused by the tubercle bacillus. The World Health Organization reported that one-third of the world’s population is infected with the bacteria. Some organotin (IV) complexes could be used to inhibit the growth of tubercle bacillus, similar to common anti-TB agents like isoniazid and rifampicin. SnPh3L inhibited as much as 98% of M. tuberculosis H37Rv at a concentration of 6.25μg/mL, with a minimum inhibitory concentration value of 0.39 μg/mL. At the same concentration, SnBu2L2 inhibited 92% of the M. tuberculosis. As a result, both compounds were considered promising anti-TB agents. Other organotin complexes were also screened against M. tuberculosis H37 Rv to determine their potential as anti-TB agents.

Anti-cancer activity

Barot, 2009, USA, provided a detailed description of the structural, biological, and synthetic studies of organotin polyethers (Sn-O). Organotin polyethers (Sn-O) were categorized in his report into four groups: hydroquinone and its derivatives, methylene spacer series, four polyethylene glycols (PEG) series, and miscellaneous derivatives. These polymeric medications’ biological effects have been investigated using Balb-3T3 fibroblast mouse embryonic cells as well as other cell lines. PEG polymers significantly inhibited the growth of Balb-3T3 cells, which was indicated by the 50% growth inhibition (GI50) values of the polymers on the cells, which were less than half of the value of cisplatin. Furthermore, because the DTT poly ethers could suppress cancer cell lines at certain concentrations but had no effect on healthy cells, the cell line data further demonstrated the safety of the series. The human colon cancer cell line HT29 and the MCF-7 cell growth were both successfully suppressed by the compounds in the methylene spacer series. Based on the GI50 values, the anti-cancer properties of the polymeric compounds were found to be on par with or superior to those of cisplatin. In general, hydroquinone and its derivatives exhibited lower toxicity. In comparison to cisplatin, their GI50 values for the...
human fetal lung normal cell line, WI-38, were five to fifty times greater. The ethylene glycol derivatives were used to treat similar cell lines. For the normal WI-38 cell line, the GI50 values of these derivatives (e.g., 2-butylene-1, 4-diol polyether) were greater than those of cisplatin and Bu2SnCl2. Moreover, 2,5-dimethyl-3-hexyne-2,5-diol polymers and DBT dichloride demonstrated strong promise for preventing cancer cells with the lowest GI50 values when tested in the PC-3 (human prostate cancer) cell line38.

**Anti-parasitic activity**

The parasitic zoonosis known as amoeba sickness was studied by Michalik et al. The infection's agony has drawn attention to the need for disease therapy. Trimethyl tin (TMT) can be used to treat amoeba illness and damage microtubules. Examined the impact of TMT on cell morphology, viability, and pinocytic activity using Dictyostelium discoideum, TMT at 5, 10, and 20 μM reduced the activity of endocytic cells. Furthermore, the shape of amoebae was modified by 20 μM TMT, causing them to become rounder and separate from the substratum39.

**Conclusion**

*Qulaee* (Stannum) is metallic element, tin have two types, inorganic tin and its compounds, organic tin and its compounds. They are also present found in food additives, toothpaste, soaps, fragrances, and colours. Tin and carbon can combine to generate organotin compounds. Tin used in industries. And these compounds are used in making plastics, plastic pipes, paints, food packages, pesticides, wood preservatives, and rodent (rats and mice) repellents. Long terms intake tin and tin compound by air, water, food, drugs etc. Over concentration of tin and its compound in the animal and human body have much adverse and toxic effect produce likes, **Respiratory effect**: stenosis, and pneumoniosis. **Gastrointestinal Effects**: stomach-ache, **Haematological Effects**: necrosis of the liver, Atrophy of the liver, **Renal Effects**: proximal tubule degeneration, swelling of the renal tubular epithelium, **Dermal Effects**: irritation, **Ocular Effects**: Inflamed eyes and nasal mucous membranes, **Immunological and Lymph reticular Effects**: lymph node atrophy, **Neurological Effects**: headache, tinnitus, deafness, impaired memory, disorientation, aggressiveness, psychotic and other severe neuropsychiatric behaviour, syncope, and loss of consciousness, mental confusion with generalized epileptic seizures, **Cardiovascular Effects**: no change in the heart weight. **Endocrine Effects**: TSH, LH, FSH, insulin, T4, or free thyroxin (FT4) was significantly increased. **Body Weight Effects**: decreases in body weights, **Reproductive Effects**: atrophy of the glandular uterus, increased the incidence of dead or resorbed foetuses, maternal toxicity. *Qulaee* have been found **pharmacological activity**: Antibacterial activity, Anti-tubercular activity, Anti-cancer activity, Anti-parasitic activity.

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Dr. Amir and Dr. Mohd Tauseef Alam participated in article writing and other authors participated in article reading and proofing.

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