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Cydonia vulgaris Pers.: A review on diversity, cultivation, chemistry and utilization

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ABSTRACT

Cydonia vulgaris Pers. is the cultivated and economically important species of genus Cydonia. Cydonia vulgaris Pers. (Cydonia oblonga Miller) is a small shrub belonging to the family Rosaceae and is a native to Southwest Europe and Minor Asia. The plant is commonly called Quince. The Cydonia vulgaris is commonly medicinally used as demulcent, in treatment of asthma. Other usages of the plant are as a source of flavor in marmalade, liqueur, candies, brandy, jelly and preserves. There are three varieties of the tree namely Cydonia vulgaris Pyriformis, Cydonia vulgaris Maliformis and Cydonia vulgaris Lusitanica. The present review highlights the plant, its variety, cultivation, chemistry and utilization of this medicinal plant.

Key words: *Cydonia vulgaris, Cydonia oblonga*, mucilage, chemistry, utilization.

INTRODUCTION

Cydonia vulgaris Pers. (*Cydonia oblonga* Miller) is a small shrub belonging to the family Rosaceae and is a native to Southwest Europe and Minor Asia. [1] It is a small tree with bright golden yellow pome fruits, when mature. The bark is smooth and brown approaching to black. The leaves are roundish or ovate, dusky green above and whitish underneath.

Table I: Synonym of *Cydonia vulgaris* Pers. in various countries [2]

Sr. No.	Synonym	Country
1	Quince-tree, Quince bush	Britain and Anglo-America
2	Armud	Russia
3	Marmeleiro	Portuguese
4	Membrillo	Spain
5	Cotogno, Melo Cotogno, Pero Cotogno	Italy
6	Quittenbaum	Germany
7	Coigner	France

The fruit of *C. vulgaris* Pers., known as Quince, resembles an apple, but differs in having many seeds in each carpel. The fruits are globular, oblong or pear shaped form of rich yellow or orange colored when ripe of an austere taste and emitting a peculiar and pleasant smell. [2, 3] The seeds called bihidana, are in great use medicinally, and highly valued as demulcent tonic. It mainly grows in Europe, Persia, Afghanistan, in India it grows in Kashmir in Himalayan valley. [2, 4]

The other synonyms used for Quince seed are given in Table I and II.

Table II: Names of plant in various languages of India [5]

SR. NO	LANGUAGE	NAME
1	Sanskrit	Amritphala
2	Hindi	Bihi
3	Tamil	Shimaimathala
4	Telugu	Simadanimma
5	Kannada	Simedalimbe
6	Kashmir	Bamsutu, Bam-tsuntu

Varieties

Generally in botanical works there are five or more varities of this species but Mr. Thompson of London Horticulture Society's Garden, has judiciously remarked that there are in reality only the three following,

1. *Cydonia vulgaris* Pyriformis. Pear shaped Quince, Coignassier pyriforme of the French which may be considered as the normal form of the species. For ornamental purpose this variety and the apple-shaped quince are much to be preferred to the Portugal Quince.
2. *Cydonia vulgaris* Maliformis. Apple-shaped quince, Coignassier a fruit pomiforme, Coignassier male of the French. This variety requires to be continued by extension, because it is found that seedling plants of both this and the preceding variety are not quite true to their kinds. They most frequently produce pear-shaped fruit.
3. *Cydonia vulgaris* Lusitanica. *Lusitanian or Portugal quince*, Coignassier de Portugal of the French. This variety has broader leaves and larger fruits than two preceding and being of a more vigorous growth, it is better adapted for stocks to graft upon. It is not so good a bearer as either of the other two varities, and the fruit is not so of deep orange but is considered the best for marmalade as its pulp turns to fine purple, when stewed or baked and becomes much softer and less austere. [2]

Geography and history

The quince is supposed to have been originally a native of sidon a city of ancient Crete, now the island of Candia, but it is much more probable that it was only first brought into notice in that city. It is considered at present as indigeneous to the south of France, particularly on the borders of the Garrone, and to Germany on the bank of Danube. By some the tree is thought to be indigenous to Britain, and Phillips states in his, "Pomarium Britaniccum," that quince grow in such abundance in some parts of the Wealds of Sussex, as to enable private families to make quince wine in quantities of from one hundred to two hundred gallons in a season".

The quince was known to Greeks and Romans and both nations held it in high estimation. Columella says, "Quince not only yields pleasure, but health". He speaks of three kinds – the "Struthian," the "Must Quince", and the "Orange Quince". Pliny mentions many kinds, some growing in Italy and others in Cultivation so large that they weighed and boughs, on which they grew, down to the ground. He also says that some were of a green and others of a golden colour the latter of which were called Chrysomela. The only kind that was eaten raw, he states to have been raised by grafting the large quince upon the stock of a small variety called Struthala. "All kinds of this Fruits," continues he, are grown in boxes and placed within the waiting chambers of our great personages in which men wait to salute these personages as they come forth every morning". It appears from the same author that the quinces were used to decorate the images of the god which were placed in sleeping chambers round the beds, whence it follows that the Romans did not think that there was anything either injurious or unpleasant in their smell. He gives directions for preserving the fruits by excluding the air from them, or boiling them in honey or by plunging them in boiling honey a practice in use with this and others fruits in Genoa, at the present day. He also writes much on the medicinal qualities of this fruits. "Quinces", says he when eaten raw if quite ripe are good for those who spit blood or are troubled with hemorrhage. The juice of raw quinces states to be sovereign remedy for the swollen spleen, dropsy and the difficulty of taking breath. The fresh or dried flowers are good for inflamed eyes. The root was used as charmed against Scrofula.

The date of the introduction of the quince into Britain is unknown. Gerard mentions it as growing in gardens and orchards and as being planted often time in hedges and fences belonging to gardens and Vineyards, from which we may infer that it was by no means rare in his times and indeed in all probability it has existed in England from the time to Romans.

The largest recorded tree of this species in Britain is a Randorshine at Maeshlough castle which is twenty-one feet in height with a trunk ten inches in diameter and an ambitus or spread of branches of twenty-two feet.

The quince was probably introduced into the North American colonies at the early periods of their settlements. It is very generally cultivated for its fruit and is usually planted in clumps of bushes rather than as individual trees or shrubs. Of late however orchards of it have been formed on the rich loamy spots of Long Island and other parts of the country, and doubtless in time their owners will derive a handsome profit. [2]

Chemical Constituents

The powerful and characteristic odour of Quince fruit has attracted considerable attention as a source of flavour in recent years, particularly appreciated in marmalades, candies, fruits, sweets and brandy.

Two ionone glycosides, β-D gentiobioside and β-D glucopyranoside of (3R), 3-hydroxy-β-ionone along with 2,7-dimethyl-8 hydroxy-4(E), 6(E)-octadienoic acid and its diol have been isolated from the fruit. The aglycone, 3-hydroxy- β ionone yields a number of volatile C_{13} nor-isoterpenoid degradation products, including (E) – 3, 4-dihydro- β ionone and 1, 1, 6 – trimethyl – 1, 2 – dihydronaphthalene. The presence of C_{15} – carotenoid metabolites, (S) – abscisic alcohol, trans abscisic alcohol – β – D- glucopyranoside and (4R, 1'E, 3'E)- 4(5'- hydroxy-3'methyl - 1',3' – pentadienyl) 3, 5, 5 – trimethyl – 2- cyclohexen – 1 – one – β – D glucopyranoside together with trace amount of C_{12} – terpenoids, viz. quince oxepine and quince oxepanes (Cis and Trans) is also reported in fruits. Besides, marmelo oxide having a strong, characteristic quince dour is reported in fruits. [6- 9]

The nor-isoprenoids contribute to overall flavour impression of the fruit. The juice from ripe fruits contains C_{13} nor-isoprenoids, viz. 3-hydroxy – and 4- hydroxy – β- ionols, 3 – hydroxy – 7,8 – dihydro – β ionol, 3 – oxo – α – ionol, 4 – oxo – β – ionol, 3 – hydroxy – 4 – hydroxy – and 5 -6 – dihydroxy – β ionones, vomifoliol, dehydro vomifoliol and 7, 8 – dihydro vomifoliol together with (2S, 5S)- (-) and (2S, 5R) – (+) – theaspirones. The presence of 4 – hydroxy – 7, 8 – dihydro – β ionol, a natural precursor of theaspiranes which are widely used in flavour industry, is also reported in quince fruit juice. Theaspiranes are not present in original volatiles but are formed at natural pH of the fruit pulp i.e. in acidic conditions (pH 3.5 – 3.8) from a labile precursor. The industrially quince quince fruit constituents are found to be vitispiranes, bicycle [4.3.0] nonane derivatives, 3, 4 didehydro – β – ionol, metastigma – 4, 6, 8 – trine – 3 – ones and theaspirones. [10, 11]

A number of ionone – related compounds have been reported in quince essential oil. They are not original volatiles of fruit but are formed during technological processes such as heating degradation of acid labile and non volatile precursor compounds. The major important C_{13} – norisoterpenoids formed on the heat treatment at normal pH (pH 3.5) of the quince juice are; 2, 2, 6, 7 – tetramethyl bicycle [4.3.0] nona – 4,7, 9 (1) – triene, 3, 4 – didehydro – β – ionol and 2, 2, 6, 7 – tetramethyl bicycle [4.3.0] nona – 4, 9 (1) – dien – 8 – ol. The natural precursor of these compounds have been characterised as 3 – hydroxy – β – ionol – β – D – gentiobioside. [12]

The fruit juice (pH 3.0) from Japan contained glucose, 1.98; fructose, 454; sucrose, 0.91; malic acid, 1.29; polyphenol, 0.59%; besides vitamin C, 29; calcium, 350.0; pectin, 175.8 ppm. A juice sample from Poland was similar to citrus juice in the level of monosaccharides (1.90% vs. 1.82 %), total sugars (2.06% vs. 1.96%), protein (0.56% vs. 0.47%), pectin (0.32% vs. 0.32%) and thiamine (0.035% vs. 0.044%). It has a higher content of ascorbic acid, β- carotene, and phenolic compounds but lower percentage of citric acid. However, as compared to pomegranate and grape fruit juices, it contains higher percentage of citric acid, pectin, ascorbic acid, phenols and mineral elements. The fruit paste can be used as a partial substituent for sugars in pastries. Vinegar with good flavour can be prepared from the fruit juice. The fruit pectin (yield 0.53% fresh weight) is similar to that of apple. It has high galacturonic acid content (6.78%). [13]

In Greece, a tea prepared by boiling dry seeds in water is given in cystitis. The kernel oil is used for massage. The major water soluble polysaccharide in mucilage of seeds has been identified as a partially O – acetylated (4 – O – methyl – D – glucorono) – D – xylan having a proportion of glucoronic acid residues. [14, 15]

Quince seeds contains 3β-(18-hydroxylinoleoyl)-28 hydroxyurs-12-ene, 3β-linoleoylurs-12-en-28-oicacid, 3β-oleoyl-24-hydroxy-24 ethylcholesta-5, 28 (29)-diene, tiglic acid 1-O- β-D-glucopyranoside and 6,9-dihydroxymegastigmasta-5,7-dien-3-one 9-O-b-D-gentiobioside. [16] (2E, 4E)-2, 7-Dimethyloctadiene-1, 8-diol, (2E, 4E, 7Z)-2,7 dimethyldecatriene-l,lO-diol and (4E,6E)- 2,7-dimethyl 8 hydroxyoctadienoic acid, three acyclic precursors of the marmelo oxides, of the marmelolactones and of quince oxepine respectively, as well as three acyclic C_{l0} compounds ((3E)-2,7 dimethyloctene-1,X-diol, (2E, 4E)-2,7. Dimethyl 8 hydroxyoctadienoic acid and *(2E, 4E)-2,7-* dimethyloctadienedioic acid) were isolated from the glycosidic fraction of quince fruit *(Cydonia oblonga* Miller). Quince brandy contains a number of mixed acetals of aliphatic and aromatic aldehydes, C_{13} nor-isoterpenoids, substituted C_{12} hydro oxipenes and marmelo oxide derivatives. [17]

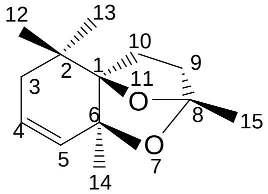
The isolation of four new flavonol glycosides and nine new R-ionolderived glycosides together with the known 3-oxo-α-ionol 9-*O*-*β*-D-apiofuranosyl-(1→6)-*β*-Dglucopyranoside, vomifoliol 9-*O*-*β*-D-glucopyranoside (roseoside), and vomifoliol 9-*O*-*β*-Dapiofuranosyl- (1→6)-*β*-D-glucopyranoside from the MeOH extract of the aerial parts of *C. vulgaris* Pers. (Rosaceae). [18] The $CHCl_3$-MeOH extract of *Cydonia vulgaris* Pers. (Rosaceae) was shown to contain four new sesterterpene esters, namely 24, 25-*O*-diacetylvulgaroside, 25-*O*-acetylvulgaroside, 24-*O*-acetyl-25-*O*-cinnamoylvulgaroside, and 25-*O*-cinnamoylvulgaroside. [19]

Quince leaves presented a common organic acid profile, composed of six constituents: oxalic, citric, malic, quinic, shikimic and fumaric acids. [20]

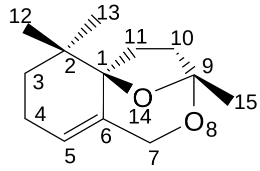
Phytochemistry

Two new ionone-type compounds (**1** and **2**) were Isolated from quince brandy (*Cydonia oblonga* Miller) and their structures deduced from spectroscopic data and confirmed by synthesis ^{13}C- ^{1}H-NMR and MS data as well as olfactive properties of **1** and **2** are given.

In the analysis of the brandy of quince fruit (*Cydonia oblonga* Miller), the two novel acetals **1** and **2** with an ionone skeleton were identified.



1



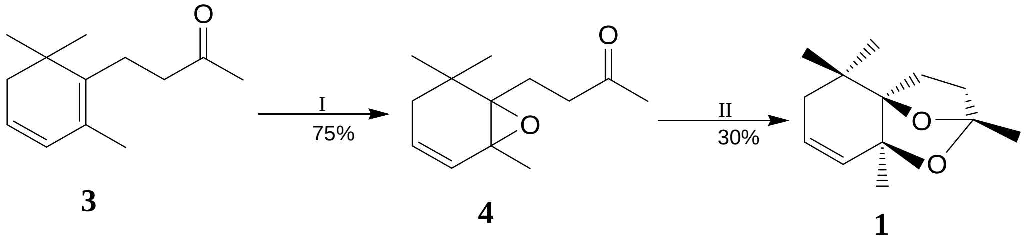
2

The extract, prepared by continuous extraction of the diluted brandy with ether, was separated on silica gel (60, Merck, 0.040-0.063, 230-400 mesh) with pentane/ether = 9/l. The two new acetals were in a fraction with an R_f 0.17 (pentane/ether = 9/l). On GC (Capillary column, Supelcowax, 60 m,0.25 mm ID 80-220˚C 5˚/mm, 1.5 kg He) 1 eluted after 18'20" and 2 after 23'40". The ^{1}H-NMR spectrum (Bruker WH 360, $CDC1_3$, ppm, J in Hz) 0f compound 1 showed four tertiary methyl groups (δ=0.97, 1.13, 1.77, 1.52), two of which seemed to be adjacent to oxygen, two olefinic protons of one double bond (δ = 5.36, 5.53) attached to, a quaternary centre on one side and a methylene group on the other side, (δ_A=1.74, δ_B=2.28) The number of hydrogen atoms and the mass spectral data (Finnigan 4021 C, 70 eV, m/e, % of base peak) suggested a $C_{13}H_{20}O_2$, compound (four parameters). The R_f was in accord with a diether or an acetal, and in the NMR no hydrogen atoms adjacent to oxygen were visible Thus the structure shown was in good agreement with spectral data and was confirmed by synthesis. The relative stereochemistry shown with the oxygen atoms in Cis configuration was the more stable one and was corroborated by nOe (irrad H_3-C(14) → increases H^1-C(9), H -C(10) and H_3-C(13), irrad H_3-C(13) → increases H^1-C(l0) and H_3-C(14)).

The ^{1}H-NMR spectrum of **2** revealed three methyl groups as singlets (δ = 0.93, 1.01, 1.48), and AB system at δ_A= 4.07 (J=13) and δ_B= 4.45 (J=13 with fine splitting), suggesting a cyclic CH_2-group attached to oxygen, and a vinyl proton at δ=5.48. The number of hydrogen atoms together with the mass spectrum (m/e = 208) suggested a $C_{13}H_{20}O_2$ compound having four parameters The R_f on TLC was in agreement with the acetal structure. The much larger synthetic sample also allowed measurement of a ^{13}C spectrum.

Acetal **1** was synthesized from the known ionone **3** in two steps (Scheme 1) Peracetic acid epoxidation with a NaOAc buffer followed by careful neutral work-up allowed isolation of epoxyketone **4** (75% yield) Winter halter et al 3, under slightly different conditions, did not obtain this epoxide which is extremely acid-labile and is unstable even with silica gel at room temperature. Dilute sulfuric acid in acetone transformed epoxide **4** directly into Acetal **1** (30% yield, remainder polymers).

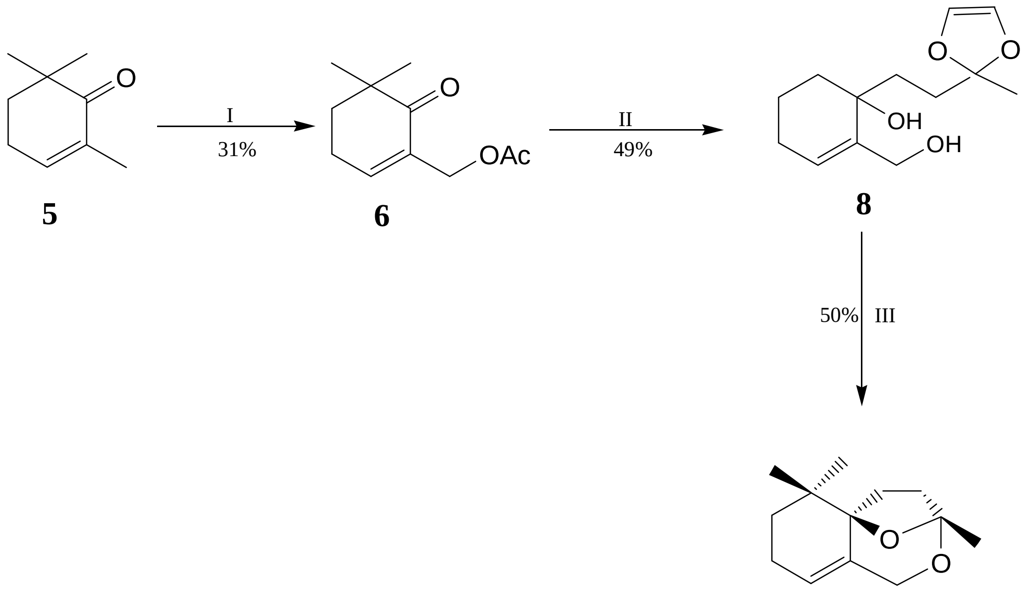
Scheme I

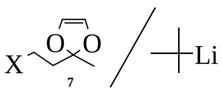


Reagents 1) 40% AcOOH in AcOH/CH_2Cl_2/NaOAc/20°/4h
2) Aq. In H_2SO_4-ACETONE 1 1/2h rt

Acetal **2** was prepared in three steps *(Scheme 2)* 2,6,6-Tnmethyl-2-cyclohexenone **5** was oxidized with SeO_2 to yield, in agreement with Sharpless mechanism, acetoxyketone **6** as the main product which was isolated in pure form by column chromatography. Reaction of **6** with an organollthlum reagent (prepared from 2-(2-bromoethyl)-1, 3-dioxalan by metal-halogen exchange with tert butyllithium, gave the key intermediate **8** possessing the correct carbon skeleton with all oxygen functions at the right place. It is not stable in the GC and was purified by column chromatography (49% yield). Mild acid treatment of **8** cleaved the ethylene glycol acetal and formed the internal acetal **2** which was isolated by bulb-to-bulb distillation at 100-l10˚/14 Torr (50% yield). [21]

Scheme II



Reagents
1) SeO_2/AcOH-Ac_2O_3 1/7 h reflux
2)  */THF-EtO_2-pentane 2511/-95°/1h, then addition of 6/-90°/1h/RT*
3) Aq.70% $HClO_4$-H_2O-THF 335 /R1/3

Cultivation
Soil and Situation:
The quince prefers a moist but free soil near water and a situation rather opened but sheltered. In dry soils neither the tree nor the fruit will attain the large size, and in situation exposed to high wind the fruit is liable to fall before mature. The finest specimen of quince-trees in Britain are said to be found in old orchards adjoining ponds; it being customary formerly to plant a quince-

tree in every apple orchard. If the soil be too dry or meager, an artificial one may be prepared as recommended for the *Gordonia lasianthus* or a hole may be excavated for each tree to a depth of ten or twelve feet of the surface and the remainder with rich loamy earth or mould. Such a preparation is well worthy of the expense in every garden where this tree will not otherwise grow. [2]

Propagation and Culture:

The quince may be as readily propagated from seeds as the apple and pear, but the quickest mode of raising plants is by layers. It will also grow by cuttings, planted in autumn in moist sandy soil. The trees when planted as standards should be situated about ten feet apart and once set out, require but little attention, beyond that of removing suckers from the roots and side shoots from the main stems. To have the fruit of large size the head of the tree should be kept open by thinning out the shoots; and the fruit ought also to be thinned out, leaving no more on the tree than it can well mature. The tree is of moderately rapid growth, when young, acquiring in four or five years, a height of six or eight feet, and in ten or twelve years it attains an elevation of fifteen feet after which it continues to increase chiefly in the width of its head. [2]

Morphology of quince seed

Quince seeds are ovoid and flattened, about 5 to 10 mm long, 2 to 5 mm. wide and 2 mm thick. The two larger flattened surfaces meet in a straight acute edge on one side and are united by a strongly arched rounded surface on the other side. They frequently adhere to one another in small irregular masses, being usually arranged in two more or less regular rows, and cemented together by dry mucilage, which is visible in the form of whitish flakes on the surface of the seeds. This mucilage is derived from the cells of the epidermis of the seed-coat. The seeds are pointed at one end, where the hilum appears as a minute paler spot, and are obtuse at the distal or chalazal end; the raphe is evident as a paler line extending from the hilum along the acute ridge to the chalaza. Within the mahogany-brown testa is a very narrow endosperm surrounding a straight embryo composed of two piano-convex whitish cotyledons and a small radical. **(Figure II)** The kernel possesses a taste resembling that of bitter almonds but much fainter. The seed-coats, when chewed are mucilaginous constituents. The seeds contain about 15% of fixed oil in the cotyledons together with proteins and probably a small amount of amygladin and emulsion, which yield the odour and taste resembling that of bitter almond when they are crushed with water. [3]

Figure I: Quince seeds

Figure II: Quince fruits

Microscopy of quince seed

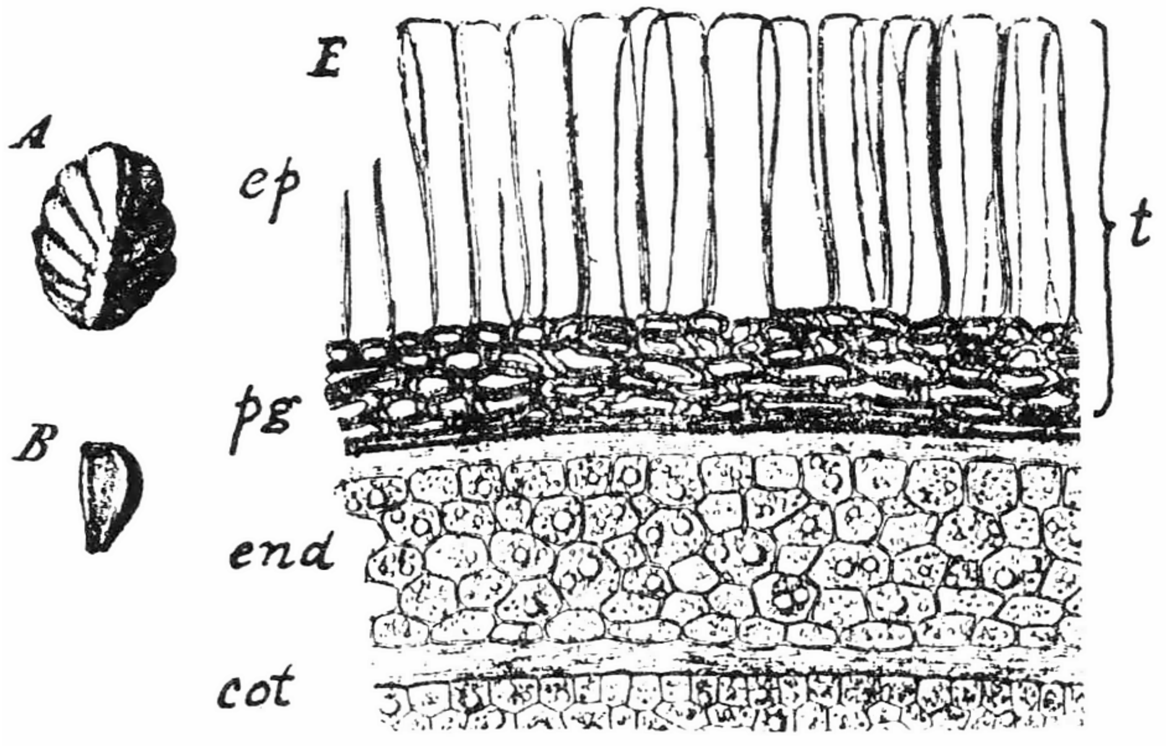


Figure III: Microscopy of Quince seeds [3]

Quince Seed — Cydonia oblonga Mill. A, seeds adhering by mucilage × 1; B, a single seed × 1 **;** *C, transverse section of B x 1; a seed x 3; B, transverse section x 190. cot, cotyledon* **;** *end, endosperm; ep, epidermis containing mucilage; pg, pigment layer; t, testa.*

Preparation of quince seed gum:

For the preparation of the gum the seeds were first extracted with alcohol and with ether, or with 50 % alcohol-ether. Subsequently 500 g were treated with 3 liters and then with 1 L of water, during a total period of 24 hours. The resultant mucilage was drained from the seeds on a Buchner funnel and filtered through cloth. The gum was precipitated with several volumes of alcohol, dehydrated with alcohol and acetone, and pressed in a hydraulic press. The neutral gum is readily soluble in water and contains about 6% ash, 25 % SiO_2, 15 % R_2O_3, and 16 % CaO, and 8 % MgO, with a considerable amount of phosphate. The ash also gives a strong flame test for potassium. To obtain a gum with less ash, precipitation was carried out in a solution containing about 1 % hydrochloric acid. The coagulum was collected, dissolved in dilute alkali, and again precipitated from a slightly acid solution. The dehydrated acidic gum was no longer soluble in water except with the addition of dilute alkali. The carefully washed gum had a neutralization equivalent corresponding to the uranic acid content as estimated by the Lefevre carbon dioxide method [22]. When the gum was prepared by precipitation in an acidified solution, it was possible to separate arabinose and a more soluble gum fraction from the concentrated liquors; this more soluble gum contained about 30 % uranic acid and 52 % pentose. No study was made of the supernatant liquor from the neutral gum. [23]

Uses:

It has been reported that the leaves and fruits of Quince have some positive effects in the medical treatment of various conditions, including cardiovascular diseases, hemorrhoids, bronchial asthma, and cough. Pomes of Quince, known in Italy as 'cotogna' apple, have hard flesh of high flavor, but very acid, and these are largely used for marmalade, liqueur, jelly and preserves. [3]

Quince fruit is recognized as a good, cheap and important dietary source of health-promoting compounds, due to its biologically active constituents which are characterized by their antioxidant, antimicrobial and anti-ulcerative properties [24-31]. It has protective effect against oxidative hemolysis of human erythrocytes. [32]

Quince seed mucilage has a wound healing activity. [33]

Cydonia oblonga Miller leaves have been used, after decoction or infusion, in folk medicine for their sedative, antipyretic, anti-diarrheic and antitussive properties and for the treatment of various skin diseases. [34]

CONCLUSION

Cydonia vulgaris Pers. as a large spontaneous plant have a wide range of applications in the traditional medicine. Recently, the pharmacology and chemistry of this plant have been extensively studied. Chemical studies of the different parts of Cydonia vulgaris Pers. have shown the presence of many beneficial compounds. The mucilage content in the seed has also importance. So in future the swelling properties can be explored in different possible ways.

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