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Review paper

Pectin, Sources and its Food and Pharmaceuticals Applications: An Overall Review

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ABSTRACT

Pectin, a complex structural heterogeneous polysaccharide widespread in terrestrial plants cell walls, About one-third of the dry substance in the cell walls of higher plants is made up of pectin, a complex mixture of polysaccharides. Pectin polysaccharides, in addition to proteins, make up practically the whole middle lamella and cellulose is absent. Pectin contributes between 2 and 35% of the weight of plant cell walls and cellulose is absent. Pectin contributes between 2 and 35% of the weight of plant cell walls and is crucial for the development defense and control of ion and water exchange as well as plant growth. Pectin is a naturally occurring component of fruits and vegetables. In addition to being a natural part of fruits and vegetables, pectin also contributes to the soluble fibre in the human diet. There is evidence that soluble fibre is healthy, although not being digested by the upper gastrointestinal system. Pectin is used to make a variety of products, such as edible and biodegradable films, adhesives, paper substitutes, foams and plasticizers, surface modifiers for clinical devices, materials for biomedical implantation, and drug delivery systems.

Keywords: Pectin, polysaccharide, lamella, fibre, human diet, natural, plant growth

As a result of population growth and changing eating habits, including a rise in people shifting vegetarian diets, fruits and vegetables have population growth dramatically recently. Indian is the second largest producer of fruits and about 25-30 % waste created during the processing of fruits. Now a days food industries are increasing and grow fast due to busy life of people's they want less time consumable production like RTE, RTC type Food products.

Pectin, a complex structural heterogeneous polysaccharide widespread in terrestrial plants cell walls, About one-third of the dry substance in the cell walls of higher plants is made up of pectin, a complex mixture of polysaccharides. Pectin levels are highest in the middle lamella of cell walls and gradually drop as one move from the primary wall towards the plasma membrane (Kertesz, 1951). The primary compartment of parenchyma cells is the central vacuole, which is large and encompassed by cytoplasm that likes gel. Around this complex, cellulose, hemicellulose, and pectin are found in the thin (0.1–10 m) and semi-rigid cell wall, which is vital because it provides the plant cell with structural

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support (Darvill *et al.* 1980). In order to hold adjacent cells together and create the tissue, the colloidal middle lamella is placed in between their primary cell walls (Thakur *et al.* 1997). Pectin polysaccharides, in addition to proteins, make up practically the whole middle lamella (Guillemin *et al.* 2005) and cellulose is absent. Pectin contributes between 2 and 35% of the weight of plant cell walls (Madlav and Pushpalatha, 2002) and is crucial for the development defense and control of ion and water exchange as well as plant growth (Ukiwe and Alinnor, 2011). Fig. 1 shows the Structure of primary plant cell wall.

Pectin is a naturally occurring component of fruits and vegetables. In addition to being a natural part of fruits and vegetables, pectin also contributes to the soluble fibre in the human diet. There is evidence that soluble fibre is healthy, although not being digested by the upper gastrointestinal system (Maxwell *et al.* 2012).

Pectin is present in all fruit, however the amounts vary greatly. The most pectin-rich fruits are apples and oranges, and pectin from each of these fruits is utilised in industry to thicken a wide range of good. Pectins are commonly used as a gelatinizer, thickening, stabiliser, or fat replacement in the food industry for jams, jellies, fruit drinks, acidified milk, and ice creams. (Dongmei *et al.* 2021). In addition, pectin is used to make a variety of products, such as edible and biodegradable films, adhesives, paper substitutes, foams and plasticizers, surface modifiers for clinical devices, materials for biomedical implantation, and drug delivery systems (Roy *et al.* 2017; Sriamornsak, 2016 Mada, 2022). Pectin from different sources does not have the same gelling ability due to changes in these characteristics since the capacity of pectin to form gel depends on the molecular size and degree of esterification (DE). Commercial pectin is currently made nearly solely from apple pomace or citrus peel, both of which are leftovers from the production of juice (or cider). Pectin makes up 15–20% of the dry matter in apple pomace. 20–30% of citrus peel is present. Citrus and apple pectins are similar in many ways when it comes to applications. Apple pectins are frequently darker than citrus pectins, which are typically light tan or cream in colour. Alternative sources include mango trash, sunflower heads (seeds used to make edible oil), and sugar beetroot waste from the production of sugar (Udonne *et al.* 2016). Pectin is one of the most valuable products which can be obtained from various sources commercial pectin are primarily extracted from citrus peel such as lime peel, apple pomace, orange, ect.

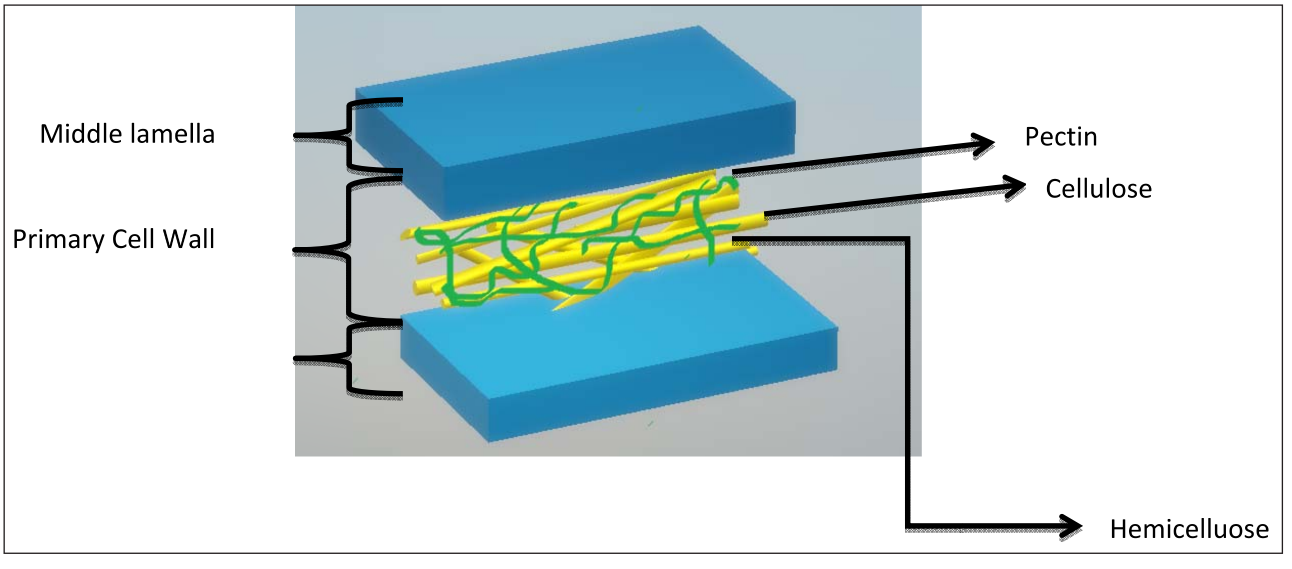

Fig. 1: Structure of primary plant cell wall

Pectin is composed of methylated ester of polygalacturonic acid connected together by α-1 → 4 linkages of as shown in Fig. 2 (Purandare, N. 2021) When pectin was first synthesized, its carboxyl groups are heavily methylesterified, but as it matures, the pectin methyl esterase enzyme depolymerizes these esters. The American Chemical Society has divided the pectic compounds into four different categories: (1) Protopectin, (2) Pectic acid, (3) Pectinic acid, and 4) Pectin.

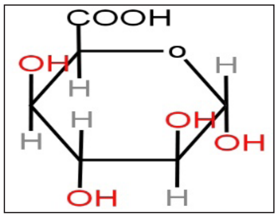

Fig. 2: D-galacturonic acid

1. Protopectin

The parent substance, typically protopectin, has no gel-forming qualities and is comparatively insoluble. The interior of plant cell walls frequently contain protopectin (Kameshwar *et al.* 2018).

2. Pectic acid

Pectic acid which lacking gelling ability, is created from pectin by enzymes hydrolyzing a methyl ester group from the pectin molecule. In plant tissues, protopectin-the water-insoluble precursor of pectin- is changed into water-soluble pectin by a process known as limited depolymerization. Protopectinase (PPase) is the enzyme responsible for hydrolyzing or dissolving protopectin to release water-soluble pectin and, as a result, causing the separation of the plant cells (Sakamoto *et al.* 1993). Pectic acid, are water-soluble pectic compounds containing less methoxyl groups. Salts of pectic acid are also known as pectates.

3. Pectinic acid

Pectinates, long polygalacturonans with around 75% methylated galacturonate units, are the name given to the salts of pectinic acids.

4. Pectin

Pectin or pectinic acid are the these are requires for gel formation soluble forms of pectin polymers. In pectin or polymethyl galacturonate polysaccharide, methanol is used to esterify about 75% of the carboxyl groups (Kameshwar *et al.* 2018).

Pectin is regarded as an additive E440 by the EFSA and the Joint Food and Agriculture Organization/World Health Organisation Expert Committee on Food Additives (JECFA) in cases when it has a proportion of GalA more than 65%. According to Mortensen *et al.* 2017, there is no set daily intake restriction because it is regarded as safe. Pectin is generally recognised as a safe food component. According to European Union regulation (EC 1333/2008), it may be used under "quantum satis" conditions, meaning that it must be used at a level that is not greater than the necessary amount in accordance with good manufacturing practise. The Joint FAO/WHO Expert Committee on Food Additives (JECFA) assigned pectin a "not specified" recommended daily intake; the US Food and Drug Administration (FDA) recognizes it as GRAS, or generally recognised as safe (Cindio *et al.* 2016).

HISTORY OF PECTIN

Pectin has a long history as an ingredient in food. The preparation of fruit jellies was carried out long time before the discovery of pectin. In the year 1790, Louis Nicolas Vauquelin initially isolated this chemical from the tamarind fruit. He showed that the expressed juice of tamarinds and other fruits solidified when left rest to a transparent jelly, which may be purified by draining off the juice and washing.

In the year 1825, Henri Braconnot coined the word "pectin" from the Greek word "pektikos". (Braconnot *et al.* 1825) which means to solidify or coagulate (Dominiak, 2014). He defines the pectin as the gelatinous substance in fruit that gave them the ability to form jeillies on boiling with sugar and he created artificial jelly for the first time. Also Barconnot identified that sugar, small amount of acid to "break up the pectates" and accurate pH is required. Fruit tissues contain pectic compounds that are principally responsible for the fruit juice ability to gel. The central lamellae of plant and fruit cells are known to contain a high concentration of pectins.

The pectin was extracted from apple peelings by the colonists of New England to make their own pectin. The Cobourg, Ontario, steel and armaments complex was converted into the first Pectin manufacturing plant in the British. Empire in 1919 by the Fairport (Douglas, 1913), New York-based Douglas Pectin Co. the first four years. In 1923, pectin was supplied to retail customers for use at home under the brand name Certo after being sold to industrial processors in Canada and the UK. When first originally sold as a liquid extract, pectin is now frequently used as a dried powder. That is more convenient to handle and store than a liquid.

The Morris 1933, pectin is primarily found in apples. According to the United States Department of Agriculture (1923), 5,400 tonnes of pectin are thought to be generated annually in the United States from the 54,000 tonnes of apples that are pressed there Pectin, which makes up around 35% of the bulk of dicotyledonous plant cells and belongs to the family of complex polysaccharides, is present in lower concentrations in grasses (between 2-10%) (Tanhatan *et al.* 2008) and woody tissues (5%) (Voragen *et al.* 2009).

Structure of pectin

Pectins, which are regarded as soluble fibre, are complex polysaccharides found in the main cell wall of plants. D-galacturonic acid is the principal constituent of the pectin molecule (Fig. 2), Pectin composed of D-galacturonic acid (GalA) α-(1→4) linked to form molecule of backbone interrupted by (1,2)- linked β-L-Rhamnose (Rha).

Pectin can be made up of up to 17 different monosaccharides with more than 20 different connections (Chan Choo, Young, & Loh, 2017; Ndeh *et al.* 2017) Pectin is an acidic hetero-polysaccharide that is heterogeneous and complex, and depending on the extraction process and source material, usually has a molecular mass of 50,000–150,000 g/mol (Dongowski *et al.* 1997). The structure of pectin shows three methyl ester forms (-$COOHCH_3$) for every two carboxyl groups (-COOH), therefore it has 60% degree of esterification. The substituted residues at C-4 with neutral and acidic oligosaccharide side chain that can be linked either to the rhamnose group or galacturonic acid group the most composed of D-Galactose, L-Arabinose, D-Xylose and less common sugar are D- Glucose, D-Mannose.

Plants include three distinct pectin domains: homogalacturonan (HG), rhamnogalacturonan I (RGI), and rhamnogalacturon II (RGII). In addition, due to their similar structural similarities to HG, xylogalacturonan (XGA) and apiogalacturonan (AGA) are frequently regarded as pectin 1, 4-D-galacturonic acid (GalA) is the primary backbone residue of pectin. Fig. 3 shows the structure of D-galacturonic acid. Fig. 4. shows the three distinct pectin domains available in plants: homogalacturonan (HG), rhamnogalacturonan I (RGI), and rhamnogalacturon II (RGII).

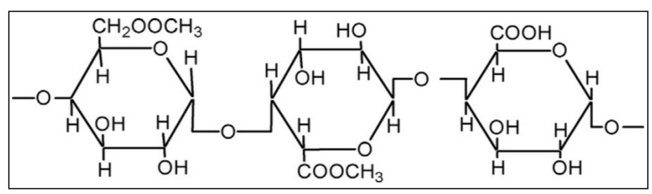

Fig. 3: Structure of pectin

1. Homogalacturonan

HG is made up only of GalA units, some of which have had their carboxyl groups esterified with acetyl or methanol groups. For instance, the pectin backbone of HG is made up of at least 72 to 100 D-galacturonic acid residues in the cases of apple, citrus, and sugar beetroot (Thibault *et al.* 1993).

2. Rhamnogalacturonan I

GalA and 1, 2-L-rhamnose repeating residues make up RGI. For pectins isolated from suspension-cultured sycamore cell walls, the length of the RGI backbone ranges from 100 to 300 repeating units (Talmadge *et al.* 1973). According to Renard, Crepeau,

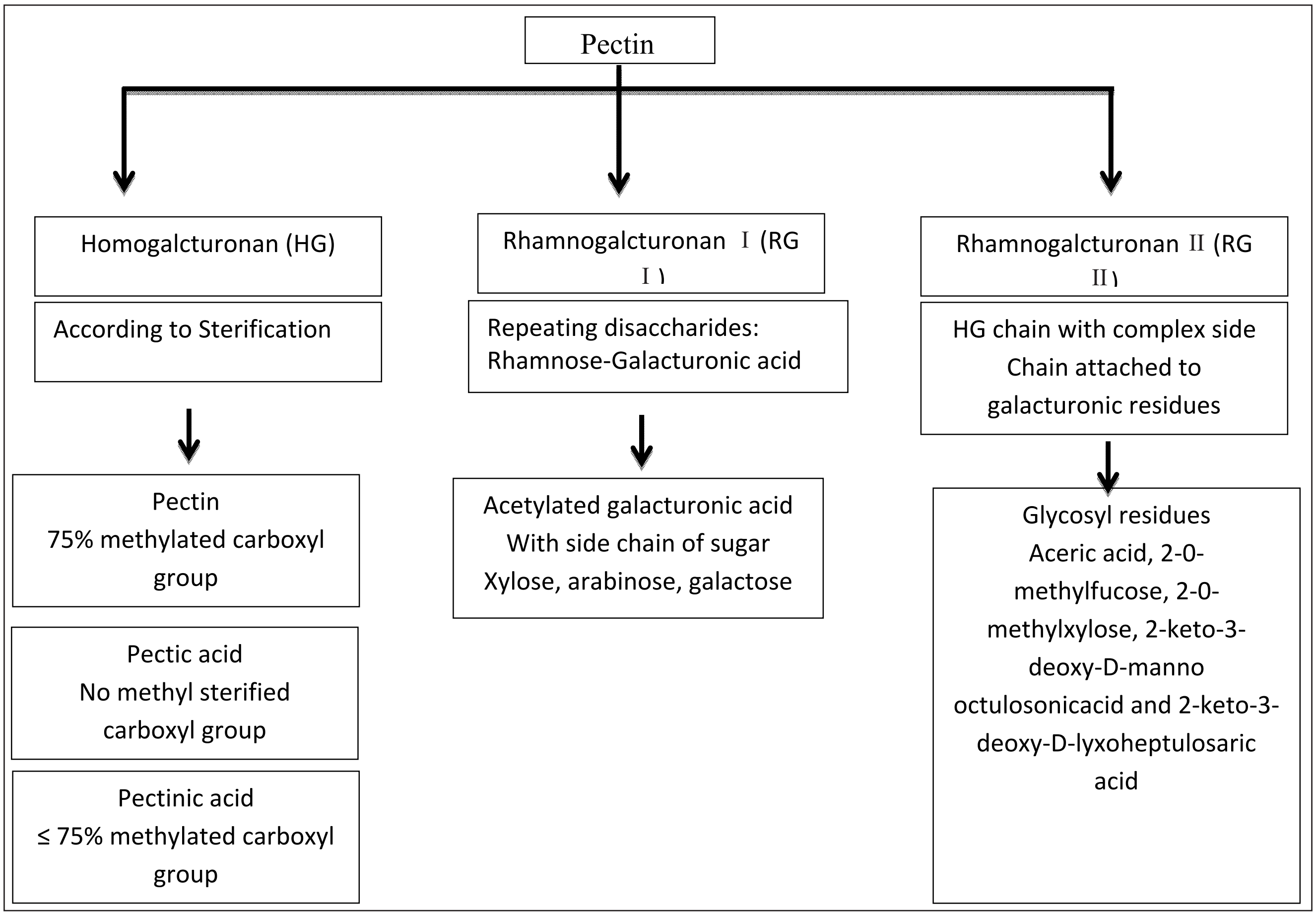

Fig. 4: Three distinct pectin domains available in plants: homogalacturonan (HG), rhamnogalacturonan I (RGI), and rhamnogalacturon II (RGII)

and Thibault 1995, sugar beets have a substantially shorter RGI, consisting of only 20 residues of this disaccharide. At C-4 of the rhamnose residues, side chains are attached that contain galactose and/or arabinose residues. One sugar residue per side chain or combination chains of arabinans, galactans, or arabinogalactans make up the side chain.

3. Rhamnogalacturonan

Similar to HG, the backbone of RGII is made up of GalA residues, however RGII's backbone is heavily branched and has side chains at the C-2 and C-3 positions. A few examples of the side chains are xylose, arabinose, apiose, fucose, galactose, rhamnose, aceric acid, glucuronic acid, and galacturonic acid. These pectin domains are thought to be covalently linked (Coenen *et al.* 2007) because they are difficult to separate without the use of chain-cleaving enzymes like endopolygalacturonase (Zhan, 1998) or chromatographic fractionation (Ignatyeva *et al.* 2015).

STRUCTURE CLASSIFICATION OF PECTIN

Degree of methylation

At least 65% of the compound is galacturonic acid (GalA), which can either be free or methyl-esterified at the carboxyl groups at C-6 (Dongowski *et al.* 2006, Liang *et al.* 2012). Pectins can be classified according to their degree of methylation [DM] expressed as a percentage, which corresponds to the number of methylated carboxylic function per 100 unit of

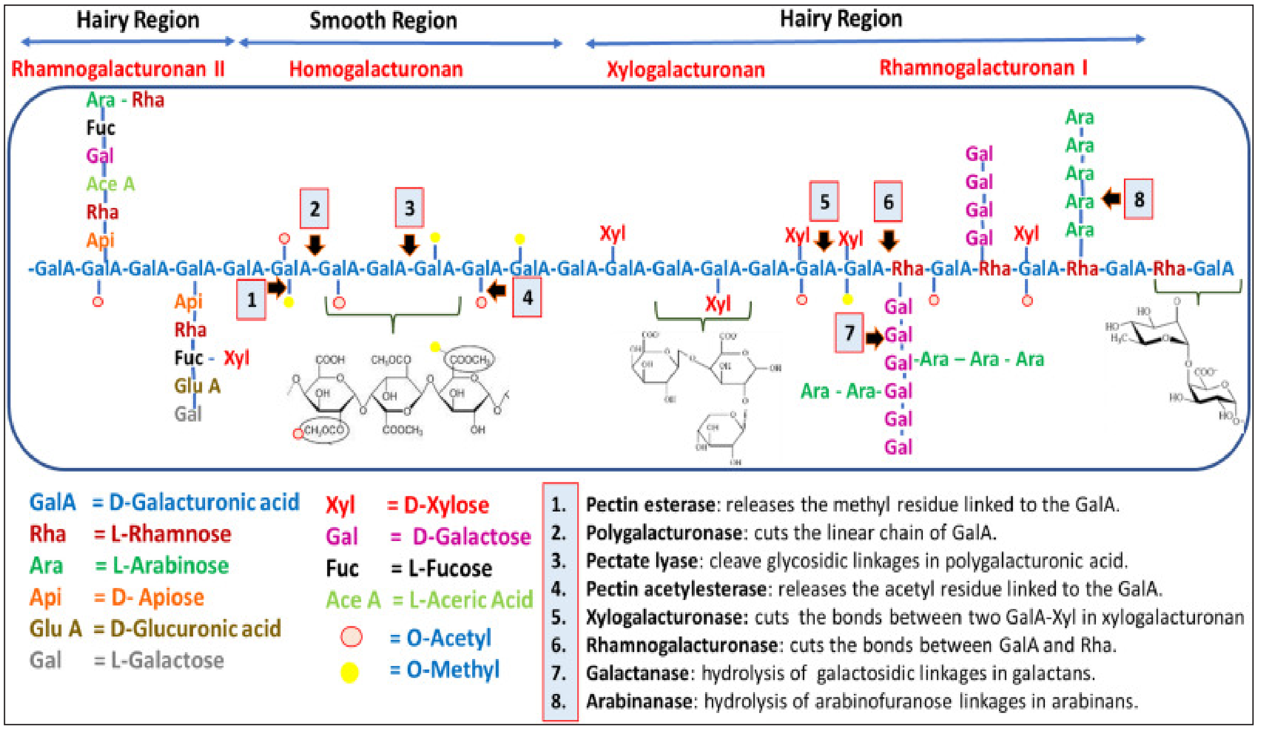

Fig. 5: Shows the structure of pectin comprises Homogalacturonan, Rhamnogalacturonan I and Rhamnogalacturonan II

galacturonic acid in the main chain. According to their degree of methylation, a distinction is made between: slow-methoxyl pectin (LMP) having the degree of esterification (DE) lower than 50%, and high-methoxyl pectin (HMP) when DE values are greater than 50% (Mesbahi, Jamalian & Farahnaky, 2005).

High - methoxyl (HM) pectin - with a DM >50%, mostly present in nature as native pectin.

Low – methoxyl (LM) pectin - with a DM < 50%. This LM pectin is only obtained after demethylation by enzymatic (methylesterases) or alkaline treatment of HM pectin. There are several unconventional sources of low methoxy pectin.

Degrees of Acetylation and Amidation

The degree of acetylation (DAC) is defined as the percentage of galacturonosyl residues esterified (on the hydroxyl group) with acetyl. Pectin having a high degree of acetylation (DAC upto 25%) do not have good gelling properties. Acetylation prevent of gel formation but increases the stabilizing and emulsifying effects of the pectins. Amidated pectins are synthetized through the reaction of pectin carboxymethyl group (-$COOCH_3$) with ammonia. The degree of amidation (DA) is the percentage of carboxylic groups in the amide form.

Sources of Pectin

Apple pomace and citrus fruit peels are both common and commercial sources of pectin. These are leftovers from several industries, like the apple pomace from the cider maker. Due to its high pectin concentration and desirable colouring qualities, orange peel has always been the material of choice for pectin synthesis. Citrus pectin is mostly obtained from the peel of orange, lemon, and lime. The levels of pectin in these various sources vary greatly, for example, the amounts found in sugar beet (10–20%), sunflower (15–25%), citrus peel (25–35%), and apple pomace (10–15%). The literature also reports on the pectin content of other fruits. The table 1 lists some prominent fruits along with how much pectin they contain.

Table 1: Conventional sources of pectin

Sl. No	Source name	%pectic substance
High percentage sources		
1	Apple pomace	1.5-2.5
2	Tamarind	1.71
3	Passion fruit rind	2.1-3.0
4	Lemon pulp	2.5-4.0
5	Orange peel	3.5-5.5
Low percentage sources		
1	Pineapple	0.04-0.13
2	Peaches	0.1-0.9
3	Carrot	0.2-0.4
4	Tomato fruit	0.2-0.6
5	Mango	0.26-0.42
6	Lychee	0.42
7	Passion Fruit	0.5
8	Apple	0.5-1.6
9	Strawberries	0.6-0.7
10	Carambola	0.66
11	Papaya	0.66-1.0
12	Banana	0.7-1.2

Karr. (1976), Renard and Thibault, (1993), Hodgson and Kerr, (1991), Nitin. (2017).

Agricultural wastes, such as mango peel, pomegranate peels, or sour cherry pomace, can be used as possible sources of pectin in the production process (Bagherian *et al.* 2011).

Commercial pectin is often made from sugar beetroot pulp (25% dry matter), apple pomace (15–18% dry matter), citrus peels (25% dry matter) and apple pomace (subproducts of their processing) (Panouille *et al.* 2005). 85.5% of commercial pectins come from citrus peel, 14% from apple pomace, and less than 0.5% from sugar beetroot pulp (Ciriminna *et al.* 2015).

These three sources make up the majority of the pectin in these products. Using hot mineral acids like HCl, H_2SO_4, or HNO3 (pH 1.5) at 85°C, industrial processes for the extraction of pectin are based on the thermal hydrolysis of citric peels, primarily from orange, lemon and lime, apple pomace and sugar beetroot pulp (Chen *et al.* 2021). The control of the extraction conditions is of great relevance for minimising the de-esterification and depolymerization of the polysaccharide and improving the functional Notably, these pectin extraction procedures result in considerable energy usage and substantial quantities of acidic industrial wastes (Panouille *et al.* 2006). As a result, recent research has looked towards using more environmentally friendly technologies to resolve these problems and improve yield extraction (Munarin F. *et al.* 2012; Stefani Cortes-Camargo, 2020).

Unconventional source of pectin

Due to their high production and advantageous physicochemical characteristics for a variety of uses in the food and pharmaceutical industries, citrus fruits and apples are widely recognised as the main sources of pectin extraction. However, new extraction sources have been sought in recent years that might serve as alternatives to overused sources and that also have the benefit of allowing the use of organic by-products, such as the case of hulls, husks, and seeds, from which pectins with particular physicochemical properties of high utility for numerous applications can be obtained.

Roots and tubers serve as sources of significant bioactive substances and store edible starchy elements in their stems, roots, rhizomes, corms, and tubers. Potentially beneficial polymers for food and medicine (Chandrasekara and Josheph Kumar, 2016). In root and tuber crops, pectins are one of the most crucial yet least studied polymers. The major cell wall and middle lamella of higher plants, as well as the sections of the plant that aren't woody, are both made up entirely of pectins (Srivastava and Malviya, 2011).

Current research on uncommon sources of pectins, which are hulls or husks, is shown in Table 2. These sources include cereal leaves (*Zea mays*), seeds of different fruits (*Nicandra physaloides* Linn., Gaertn, papaya, jackfruit, creeping fig, and sesame), as well as pods and seeds of legumes (soy, peas, faba beans, and riang). Additionally, its extraction procedures and other standout qualities are detailed.

Table 2: Non-conventional source of pectin

Sl. No.	Source name	Yeid of pectin
1. Hulls and Husks		
1	Almond hull	26.32%
2	Pistachio hull	32.3%
3	Cocoa pod husk	9.46%
2. Legumes (from seed and pods)		
1	Faba bean hull	14.86%
2	Riang pod husk	15.0%
3. Cereal		
1.	Zea mays husk	10.0%
4. Friut		
1	Jackfruit seeds sheats	35.52%
2	Nicandra physaloides Gaertn seeds	9.17-10.56%
3	Watermelon rinds	19.3%
4	Cubiu fruit	14.2%
5	Ponkan peel	25.6%
6	Pomegranate peel	8.5%
7	Jackfruit rinds	14.59%
8	Grapefruit peel	23.50%
5. Root and tuber crops		
1	Cassava bread	0.34-0.61
2	Cassava residue	0.1-0.5
3	Sweet potato	1.9-6.4
4	Potato pulp	14.34
5	Yam residue	4.32-15.88

Stefani et al. 2020.

Global Demand of Pectin

An estimated 40000 tonnes of pectins are consumed globally each year, with a 5% yearly increase rate. Citrus pomace and apple pomace are two sources of pectin used by the food industry, but they are insufficient to meet market demand (Willats *et al.* 2006; Ciriminna *et al.* 2015). The creation of novel food products and the demand for specialised hydrocolloids have caused a hunt for novel ingredients and stabilisers. In the food business, pectin is frequently employed as a gelling agent in a variety of items, including bakery fillings and confectionary goods (Willats and colleagues 2006). Its use has grown in recent years to include industries like cosmetics and pharmaceuticals. Due to the inclusion of proteins, ferulic acid, acetyl groups, and polyphenols, pectins have been revealed to have biological activity (Wang *et al.* 2016). This could further boost the demand for this product worldwide (Blanca *et al.* 2017). Fig. 6 shows the global pectin market by application (Nitin, 2018).

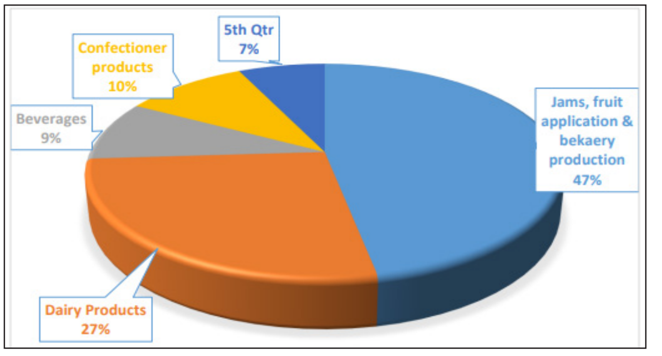

Fig. 6: Global pectin market by application (Nitin 2018)

CONCLUSION

Generally pectin is used in jams, jellies, yogurt, acid dairy drinks and confectionery. As it is vegan and having nutritional benefits, pectin is in high demand. Pectin is widely used as a texturizer, stabilizer, and emulsifier in a variety of food and other industries. It is also used as the sugar and fat replacer in low calorie food. Pectin is used for numerous application because it is safe, non-toxic product with low production cost, high availability (Martau *et al.*) and most important it's nutritional benefits.

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