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Review

Role of Agar in Neutaceuticals

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Abstract

As a food and gelling agent, agar, a gelatinous polysaccharide found in the cell walls of numerous red algae, is widely used. Due to its lower molecular weight, greater water solubility, and superior absorption efficiency, the hydrolysate of agar, oligosaccharides (AOs), exhibits a far wider range of biological activities. Under various preparation conditions, it is shown that AOs with varying structure and degree of polymerization, such as series of agaro-oligosaccharides and neoagaro-oligosaccharides, can be produced. Furthermore, the biological activities of AOs are intimately and variably related to the composition and structure. The objective of this review is to give a comprehensive overview of the production, structural properties, and biological activity of AOs in order to offer a foundation for the usage of AOs as marine natural products used in the nutraceutical, cosmetic, and pharmaceutical industries.

Keywords: Bioactivity, application, preparation, agar oligosaccharides.

INTRODUCTION

According to the US Pharmacopeia, agar can be defined as a hydrophilic colloid extracted from certain seaweeds of the Rhodophyceae class. It is insoluble in cold water but soluble in boiling water. A 1.5% solution is clear and when it is cooled to 34-43°C it forms a firm gel which does not melt again below 85°C. It is a mixture of polysaccharides whose basic monomer is galactose. These polysaccharides can be sulphated in very variable degrees but to a lesser degree than in carrageenan. For this reason the ash content is below those of carrageenan, furcelleran (Danish agar) and others. Although it is often kept between 2.5 and 4%, an ash concentration of no more than 5% is acceptable for agar. Similar to Gelidium pacificum, which exploited agar shortage, agar is the phycocolloid of most ancient origin. In Japan, Minoya Tarozaemon is credited with discovering agar in 1658, and the first time it was produced is marked by a monument called Shimizu-mura. The product, known as tokoroten at the time, was first produced and marketed as an extract in solution (hot) or gel form (cold) for immediate use in the vicinity of the factories. It has been known as kanten since the early 18th century, when it began to be industrialized as a dry and stable product.

The word "agar-agar", however, has a Malayan origin and agar is the most commonly accepted term, although in French- and Portuguese-speaking countries it is also called gelosa.[1] Recently, Japan has shifted to complete modern technology plants for the production of uniform agar production. The times when World War second was at peak, countries with sufficient supply of *Gelidum sesquipedale* that is v sed by Japanese industries. Agar developing and manufacturing enterprises were built by Portuguese and Spanish people after researching about the process of agar development from *Gelidium sesquipedale*. Agar replacements from different seaweed extracts were also made by European countries that had scarcity of agarophyte algae. For maintaining the prime quality of agar, mostly Red Algae *Gelidium amansii* is employed for agar extraction. Frau fanny Eilshemiushesse a German housewife was the first person who suggested her husband to use agar as growth media to sustain bacterial growth for the further study in biotech and microbiology labs as a replacement for gelatin . During the end of 19thcentury agar is used in laboratories significantly less than it is used in food the majority of countries imported agar from Japan while agar is currently produced in a number of countries other than Japan. Araki's groundbreaking work on agars chemical structure revealed that the major component responsible for gelation is agarose after this discovery the use of agar as gelling agent increase in the scientific and research areas . Sincethen, any research work related to agarose gels is directly applied to agar gels as well. Seaweeds are also known as the "Medical Food of the Twenty-First Century". Mostly the raw material comes form the natura sea weed beds which are utilized to make agar, alginates, and seaweed liquid fertiliser in India. In the marine states of Tamil Nadu, Kerala, Karnataka, Andhra Pradesh, and Gujarat, there are around 25 agar and 10 algin factories located in various locations. Red algae like Gelidiella acerasa, Gracia riaedulis, G. crassa, G. faliilera andG. vecasa are now used to make agar, whereas brown algae like Sargassum spp., Turbinaria spp., and Cystoseira indica are used to make alginates and liquid seaweed fertilizer. Among these agarophytes, G. acerosa produces bacteriological grade agar, whereas Gracilaria species produce food quality agar[2]

Fig 1: AGAR [3]

Synonym	Agaragar[4]
Biological Source	Agar is obtained from the cell walls of red algae (Rhodophyceae) such as *Gelidium amansii, Gracilaria verrucosa, Pterocladia lucida, Gelidiella acerosa.*
Family	*Gelidiaceae and Gracilariaceae* (under Rhodophyceae – red algae).
Geological Source	Mainly found in Japan, China, Sri Lanka, India (coastal regions of Tamil Nadu & Gujarat), Philippines, Chile, South Africa, and Mediterranean countries.
Morphological Characters	Agar occurs as thin, membranous, translucent strips or sheets
Colour	White to Pale Yellowish
Chemical Constituents	Agarose (linear polymer of D-galactose and 3,6-anhydro-L-galactose) – responsible for gel strength.[5]

COLLECTION OF AGAR

The red algae are grown in rocks in shallow water or on the bamboos by placing them in the ocean. Collection of the algae is usually made in summer (May and October). The bamboos are taken out and the seaweeds are stripped off. Algae are dried, beaten with sticks and shaken to remove the sand and shell attached to them. Then the entire material is taken to high altitude, washed with water and bleached by keeping them in trays in the sunlight, sprinkling water and rotating them periodically. The agar is then boiled; one part of algae with 50 parts of water acidified with acetic acid or dilute sulphuric acid. The hot extract is subjected for coarse and fine filtration using cloth to remove the large and small impurities present in them. The filtered extract is then transferred into wooden trough which on cooling forms a jelly like mass. The mass thus obtained is then passed through screw press to obtain strips of agar. These strips contain water and to remove the water present in them, the agar strips are placed in open air to get the benefits of the Japanese climate. During this season, Japan has a very warm day and the nights are very cold with a temperature less than 0°C. As a result of this climate the water present on top of the strips are converted into ice at night, and during day they are reconverted to water and the excess water present in them are removed. Then, these strips are again dried in the sunlight in trays.Modern method of deep freezing is being utilized in the preparation of agar in recent development of technology. The algae which is collected is washed in running water for a day and then extracted firstly with dilute acid in steam heated digester and then with water for 30 min, the hot solution so obtained is cooled and deep freezed in an ice machine. The water present in the agar is converted to ice and these masses are powdered, melted and filtered in rotary vacuum filter. The moist agar is dried using dry air and powdered agar is obtained.[6]

PREPARATION OF AGAR

The alga *A. plicata* was pre-treated by ultrasound of 20 KHz in the Citric acid-sodium citrate buff er solution (pH 5.0) in a ratio of 1:30 (w/v) for 2 min. The alga was hydrolysis by cellulase of 10 U/kg at the temperature of 50°C for 4 h. Then the alga was treated by 0.18% of NaClO with a pH value of 5.39 for 10 min. The solutions were discarded and the alga was washed to neutral with water. The alga was then treated in an autoclave with 1.2% alkali solution in a ratio of 1:30 w/v for 2 h at 121°C. The solution was collected by fi ltration and followed by gelation at room temperature, frozen at -20°C for 20 h, and thawed. Finally, the gel was dried at 60°C.[7]

PROPERTIES OF AGAR

Agar gels due to the presence of the agarose fraction in the crude agar at typical concentrations between 0.5% and 2.0%. Unlike carrageenan agar does not require the presence of any particular ions to gel. One of the classic uses of agar is for the preparation of microbial plates where the combined properties of low syneresis, ion independent and a low set temperature make agar ideal. Agar has a uniquely large hysteresis between its melting and setting temperature[8]. Typically agar need to be heated above 90^0C to form a good solution and depending on the seaweed source the setting temperate can be as low as 30^0C and is typically between 30-45^0C for a 1.5% solution. To overcome the very high dissolution temperature of agar several companies manufacture a form of agar that has been specially dried to allow the agar to dissolve at lower temperatures. According to Rees agar forms antisymmetric double helices on cooling that hydrogen bond to form clumps of helices. These clumps can then form larger groupings that from a large porous gel structure[9]. Agar is known to form a very porous gel and the pore size can be roughly measured by assessing the size of particulates that are excluded from the gel in a gel permeation experiment .It has been shown that agar gels can allow molecules up to 30M daltons in size to percolate through it structure. An agar gel as the unusual property of behaving like a sponge. An agar gel of a particular shape can be dried and upon rehydration it will swell to its original size and shape. Agar synergy's are not as commercially important as they are for xanthan or carrageenan and tend to be rather small in magnitude. Gelidium agar is known to form a small synergistic interaction with locust bean gum that is not seen in products based on gracilaria. Agar forms a synergistic interaction with sucrose and is used in some confectionery products. Tannic acid on the other hand may actually inhibit gelation. Agar is reasonably acid stable compared to other polysaccharides and does not show any protein reactivity. Agar can be used in acidic dairy products such as yoghurts where carrageenan would cause excessive flocculation due to the protein reactivity of the carrageenan. Recently a synergy has been reported between low gel strength agar and guar gum in patent by Rachid Lebbar of Setexam Agars all have negative optical rotations whereas carrageenans are positive. This can be used to distinguish the two when identification is tricky. Sulphate level is often used and whereas a low sulphate level would indicate an agar you cannot definitively say that a high sulphate level is always a carrageenan.[10]

FUNCTIONAL ROLE OF AGAR

Agar-Agar is a very unique naturally occuring polymer that is increasingly favoured over the synthetic polymers and is being explored as a raw material alternative for medicinal applications. It is widely sought after in the pharmaceutical sector due to its remarkable inherent qualities, such as the strength of the gel generated from Agar-Agar. Agar was used to create an injectable and phase-changeable composite hydrogel for treating cancers with chemo and photothermal treatment. Chemotherapeutics and antibiotics may be loaded into this composite hydrogel and then released. Furthermore, an agar-based nanocomposite film was shown to be effective in preventing Listeria monocytogenes growth. Agar and polysaccharide blends are also gaining popularity in the pharmaceutical industry. Agar-Agar is primarily used in pharmaceuticals as a gelation, stabilization, and thickening agent. Agar-agar is also commonly used for purgative purposes and as a surgical aid. Researchers have worked hard to develop Agar-based products like as composite hydrogels, nanocomposite films, and other materials for application in the pharmacological industry[11]

1. Hydrocolloid Matrix for Delivery Systems

Agar functions as a hydrocolloid an edible biopolymer that forms stable gels capable of encapsulating and protecting bioactive compounds, or nutraceuticals. Its matrix can shield sensitive ingredients from degradation and facilitate controlled release at the target site. Hydrocolloids like agar have been proposed as effective delivery vehicles due to their ordered microstructure and the ability to embed and protect bioactive molecules such as curcumin .[12]

2. Texturizer, Gelling & Stabilizer

Commonly used in food formulations, agar creates firm, thermo-reversible gels even at low concentrations (~0.2–1.5%). This makes it ideal for shaping the texture and mouthfeel of nutraceutical products such as gummy supplements. It produces firm, brittle gels that melt only at high temperatures (<85 °C), lending thermal stability .In vegan gummy studies, agar helped provide structure, elasticity, and chewiness; when combined with guar gum, it matched the texture quality of gelatin-based gummies .[13]

3. Dietary Fiber & Prebiotic Potential

Human enzymes cannot digest agar, which is approximately 80% dietary soluble fiber. One of the best sources available, it makes its way to the colon, where it may be partially fermented by the gut flora, which could be beneficial to digestive health. solute dietary fiber in meals, which aids in bulking and regulating intestinal transit. Agar and its derivatives, such agaran, have nutraceutical qualities such as antioxidant, anti-inflammatory, and others. antiviral, antibacterial, anticoagulant, and even anticancer properties. They may also influence blood sugar levels and aid immune function.

4. Enhancing Bioactivity via Combinations

Agar's structural functionality can be harnessed alongside other bioactive-rich compounds. For instance, incorporating antioxidant-rich pectin from fireweed into agar gel enhanced colon-targeted release and had potential benefits for populations with swallowing difficulties. The study highlighted how agar provides the mechanical framework while pectin contributes functional antioxidant activity. The resulting gel could aid antioxidant delivery in the colon.[14]

5.Antioxidant Activity

Agar has moderate free radical scavenging activity. Hydrolysates of agar, produced through acid or enzymatic hydrolysis, show enhanced antioxidant properties. Enzymatic hydrolyzed oligosaccharides (NAOs) have stronger antioxidant activities compared to commercial agar products and algal polysaccharide extracts. However, the antioxidant activities of agar oligosaccharides obtained from acid treatment have conflicting results. Structural characteristics, such as molecular structure and weight, affect their antioxidant abilities. Higher hydrolysis degrees increase NAOs' scavenging capacity against radicals. Different agar oligosaccharides fractions vary in scavenging abilities towards different radicals. Factors like molecular mass and sulfate content influence enzymatic hydrolysates' antioxidant activities. Agar oligosaccharides with a degree of polymerization (DP) of 6 exhibit significant antioxidant effects against reactive oxygen species (ROS) in liver cells.[15]

6. Anti inflammatory Property

Earlier studies have indicated that agar oligosaccharides derived from agar, with a degree of polymerization (DP) of 2-4, can inhibit the production of pro-inflammatory cytokines such as TNF-α and the expression of inducible nitric oxide synthase (iNOS) in vitro. Agar oligosaccharides have also been found to suppress the production of other pro-inflammatory mediators like prostaglandin E2 (PGE2), and exhibit anti-inflammatory effects by stimulating the expression of heme oxygenase-1 (HO-1), an enzyme involved in the degradation of heme. HO-1 induction has been associated with the inhibition of TNF-α expression and neutrophil accumulation, effectively preventing intestinal inflammation. Agar oligosaccharides with AHGal (agarobiose) at the reducing end have shown better anti-inflammatory activity compared to NAOs (agarose) with d-galactose at the reducing end. Furthermore, agar oligosaccharides with DP of 2 or 4 have demonstrated higher anti-inflammatory activities, and the synergistic effects of different agar oligosaccharides fractions can contribute to their overall anti-inflammatory effectiveness. Further research is needed to fully understand the potential of agar oligosaccharides as candidates for preventing inflammatory diseases.[16]

7.Anti-Tumor activity

Agar oligosaccharides have shown anti-tumor activity in studies. They delayed tumor appearance and reduced tumor number by inhibiting prostaglandin E2 (PGE2) production in a mouse skin carcinogenesis model. Agar oligosaccharides also prevented gut dysbiosis and inhibited colon cancer in mice on a high-fat diet, decreasing p16 expression and increasing OGG1 expression. These findings highlight agar oligosaccharides' potential as anti-tumor agents. Further research is needed to study their absorption in the intestines, changes in metabolites, and impact on the intestinal microbial population in relation to colon cancer [17].

APPLICATION

Agars are widely employed in many fields, including the food business, dentistry, bacteriology, and biotechnology. [18] In order to predict the high product of agar in each application, it is necessary to better understand the diversity of its commercial goods and its physical and chemical properties. Keep in mind that neither Koch's agar nor today's agarose is necessarily the ideal agar for food applications. 'Many people believe that agar has only one texture: a brittle gel.' This isn't correct. By altering the weed source and processing, it is possible to build a broad range of agar textures, ranging from brittle to highly stretchy.

Agar in food application

Agar has a variety of uses, the most common of which is as a culinary component, which accounts for 80% of its use about 90% of the extracted agar is utilised in culinary items as a thickener and stabiliser in baked goods, a gelling agent in meats and fish items, and a texture improver in various dairy products such as yoghurt and cheese. [19]

Agar in pharmaceutical application

Agar-Agar is primarily used in pharmaceuticals as a gelation, stabilization, and thickening agent. Agar-agar is also commonly used for purgative purposes and as a surgical aid. Researchers have worked hard to develop Agar-based products like as composite hydrogels, nanocomposite films, and other materials for application in the pharmacological industry. [20]

CONCLUSION

Agar is a gelatinous substance usually obtained from red sea weeds. It is made up of two basic polysaccharides viz. agarose and agaropectin. The potential applicants of agar are pharmaceuticals, silkscreen printing, food and packaging industries. Plenty of methods have been identified in order to extract the agar but usage of synersis method have shown promising results among them due to its cost effectiveness and accuracy. In recent past, techniques have been developed to extract the agar with higher solubility with less amount of heat timings and a less temperature range while maintaining acceptable gel strengths. A wider scope can be seen in the recent time for more agar manufacturing process and its applications.

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