Chemistry of PLANT GUMS *and* MUCILAGES

and Some Related Polysaccharides

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and R. MONTGOMERY

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AND SOME RELATED POLYSACCHARIDES

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GENERAL INTRODUCTION

American Chemical Society's Series of Chemical Monographs

By arrangement with the Interallied Conference of Pure and Applied Chemistry, which met in London and Brussels in July, 1919, the American Chemical Society was to undertake the production and publication of Scientific and Technologic Monographs on chemical subjects. At the same time it was agreed that the National Research Council, in cooperation with the American Chemical Society and the American Physical Society, should undertake the production and publication of Critical Tables of Chemical and Physical Constants. The American Chemical Society and the National Research Council mutually agreed to care for these two fields of chemical progress. The American Chemical Society named as Trustees, to make the necessary arrangements of the publication of the Monographs, Charles L. Parsons, secretary of the Society, Washington, D. C.; the late John E. Teeple, then treasurer of the Society, New York; and the late Professor Gellert Alleman of Swarthmore College. The Trustees arranged for the publication of the ACS Series of (a) Scientific and (b) Technological Monographs by the Chemical Catalog Company, Inc. (Reinhold Publishing Corporation, successor) of New York.

The Council of the American Chemical Society, acting through its Committee on National Policy, appointed editors (the present list of whom appears at the close of this sketch) to select authors of competent authority in their respective fields and to consider critically the manuscripts submitted.

The first Monograph of the Series appeared in 1921. After twenty-three years of experience certain modifications of general policy were indicated. In the beginning there still remained from the preceding five decades a distinct though arbitrary differentiation between so-called "pure science" publications and technologic or applied science literature. By 1944 this differentiation was fast becoming nebulous. Research in private enterprise had grown apace and not a little of it was pursued on the frontiers of knowledge. Furthermore, most workers in the sciences were coming to see the artificiality of the separation. The methods of both groups of workers are the same. They employ the same instrumentalities, and frankly recognize that their objectives are common, namely, the search for new knowledge for the service of man. The officers of the Society therefore combined the two editorial Boards in a single Board of twelve representative members.

Also in the beginning of the Series, it seemed expedient to construe rather broadly the definition of a Monograph. Needs of workers had to be recognized. Consequently among the first hundred Monographs appeared works in the form of treatises covering in some instances rather broad areas. Because such necessary works do not now want for publishers, it is considered advisable to hew more strictly to the line of the Monograph character, which means more complete and critical treatment of relatively restricted areas, and, where a broader field needs coverage, to subdivide it into logical subareas. The prodigious expansion of new knowledge makes such a change desirable.

These Monographs are intended to serve two principal purposes: first, to make available to chemists a thorough treatment of a selected area in form usable by persons working in more or less unrelated fields to the end that they may correlate their own work with a larger area of physical science discipline; second, to stimulate further research in the specific field treated. To implement this purpose the authors of Monographs are expected to give extended references to the literature. Where the literature is of such volume that a complete bibliography is impracticable, the authors are expected to append a list of references critically selected on the basis of their relative importance and significance.

PREFACE

Plant gums and mucilages have been known and in use since very early times, reference being made to them in the Bible; and they seem to have been of commercial value for several thousand years, especially in India, Asia, Africa, Australia, and China. These natural products were later exported to Europe where their use in industry has never ceased to expand. They were used as food by the natives of Africa, Asia, India and Australia as far back as historical records go. The use of the seaweed gums by the natives of the coastal regions of France, Wales, Ireland, Scotland and Scandinavia in food and in medicinal preparations represents an art whose origin cannot be traced.[1]

The word "gum" was probably applied originally to plant exudates, which thickened and hardened on exposure to air. For this reason it had been applied to the water-insoluble resins as well as to the gums proper, which either imbibe or dissolve in water.[2] One of the earliest uses of the word was by Herodotus about 450 B.C., who recorded that the embalmers in Egypt used gum rather than glue for coating the linen in which corpses were clothed. Herodotus uses the word κομμι, from which gum is derived, and it should be noted that this is a foreign and not a native Greek word.

In spite of the tremendous quantity of gums and mucilages employed in industry, a real insight into the chemistry of these substances has been obtained only during the last twenty or thirty years. It is, therefore, not surprising to find even at the present time that the use of gums and mucilages is indeed much more of an art than a science, although certain empirical scientific controls have been employed in the industrial use of gums.

In general, the gums and mucilages were, and still are, used either as they are found in nature or as aqueous extracts of parts of plants. The utilization of these complicated polysaccharide polymers is clearly at the very beginnings of what will eventually come to pass when their chemistry is more fully understood. Modifications and numerous derivatives of gums will be made in ever-increasing numbers in the not too distant future, so that a more extensive and efficient use may be made of these raw materials.

The chemistry of gums and mucilages has been reviewed (2–7) from time to time, but there is no comprehensive treatise on the subject. An attempt is made herein to bring together what is known of the chemistry of plant gums and mucilages, to indicate some of the procedures that may be adopted for studying these and other polysaccharides to stimulate new researches in what can only be described as a fascinating field of organic chemistry, and also to promote new ideas for their industrial application. A brief consideration of the vast petrochemical industry that has arisen from the study of the fundamental chemistry of aliphatic and aromatic compounds will indicate something of the future possibilities of carbohydrate chemistry as it applies to polysaccharide gums and other related carbohydrate polymers. It is hoped that this work will be of some interest to those investigating the chemistry of gums and mucilages and to those engaged in their industrial use.

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CONTENTS

CHAPTER 1

FUNCTION AND ORIGIN OF GUMS

Gum Exudates

Gum exudates are produced by a surprisingly large number of plants. Exposed to the air and allowed to dry, the exudates form clear, glassy masses which are usually colored from dark brown to pale yellow. It is seldom that colorless exudates are encountered, although some samples of gum tragacanth are almost white. Various parts of the plant may secrete gum. In some cases, the secretion is hardly discernible, but in others, such as the trees producing commercial gums, copious quantities are produced

More than a hundred species of *Acacia* of the *Leguminosae* family produce gums (1), some of them in such large amounts that the supply supports a world-wide industrial market. Gums are also secreted by a number of species of *Astragalus*, which provide the hitherto highly valued gum tragacanth. Likewise, many species of *Prunus* produce gums in large amounts, but they do not seem to be valued as highly as the others mentioned above. Similar gum exudates are produced by the genera *Albizzia, Banhinia, Caesalpinia, Ceratonia,* and *Pithecolobium.* The plant families *Anacardiaceae, Combretaceae, Meliaceae, Rosaceae* and *Rutaceae* are also known for their capacity for producing gums (30).

There is no agreement as to the origin of gum exudates. Some subscribe to the theory (1,2) that they are a product of normal plant metabolism, while others suggest that they arise from a pathological condition. Some evidence favors the latter view, for it has been recognized that healthy *Acacia* trees, grown under favorable conditions of moisture, soil and temperature, do not produce any gum; when grown under the adverse conditions offered by high elevation, heat and lack of moisture, the secretion of gum is favored (3). The gums are thought by others to be formed as a result of an infection of the plant by micro-organisms (4). The plant is believed to synthesize the gum exudates in order to seal off the infected section of the plant and prevent further invasion of the tissue (5–8). It is not yet clear whether the carbohydrate gums are formed at the site of the injury or whether they are generated elsewhere in the plant and then transported to the injured site.

The phenomenon of gum production has also been attributed to fungus growth on the plant with the liberation of fungal enzymes which then proceed to synthesize the complex polysaccharide gums.

It is of interest to note that certain fungi contain enzymes which convert gums into their component sugars. For example, the parasite *Stereum purpureum*, which causes a disease (lead disease), induces plum trees to produce a considerable amount of gum at the place where the parasite grows (6). Lutz (9,10) has proceeded from this observation and claims that the *Stereum purpureum* fungus has a slow but definite hydrolytic action on cherry gum and that the component sugars are generated. The fungus *Asterula gummipara* Vuill., isolated from the trunks of *Acacia verek*, completely liquefied cherry gum in three months. Other fungi, such as, *Xanthochrous hispidus, Polyporus sulfureus*, and *Coriolus versicolor* had no effect on cherry gum.

In this connection it is to be noted that an enzyme extracted from *Turbo cornutus* is capable of hydrolyzing the seaweed gum obtained from *Chondrus ocellatus*, while agar and carrageenin are hydrolyzed by the organism *Bacillus gelaticus* found in sea water. Similarly, the mucilage found in the root of *Hydrangea paniculata* is cleaved by *Bacillus mesentericus vulgatus*. An organism growing on rotting agar has recently been shown to secrete an enzyme which hydrolyzes agar to give a disaccharide, neoagarobiose.

In certain cases, gum formation by *Acacia* trees has been attributed to the action of bacteria (3,11). However, no one appears to have succeeded beyond doubt in stimulating gum formation in *Acacia* trees by inoculation, although it has been reported that inoculation of peach trees with *Bacterium acaciae* isolated from the exudate of *A. binervata* trees produced gummosis (12). Such an achievement as this would be important not only scientifically, but also from a commercial standpoint; this possibility should be examined. The gums are evidently produced in greatest quantity by injured trees, growing under unfavorable conditions, namely, at elevated, hot and dry locations. The theory that gum exudation is caused by infection of the trees is not supported by the observation that *Acacia* trees continue to survive and indeed propagate, even though they are supposed to be diseased and are growing under unfavorable climatic conditions. More recently it has been reported (31) that gum formation can be produced by the injection of ascorbic acid into the culms of *Arundo donax* and *Phalaris tuberosa*.

The most likely function of gum formation is that the tree produces the gum in order to seal off the injured parts, not so much to prevent infection, but to prevent loss of moisture (13-16). Some support for this is forthcoming from the fact that gum tragacanth is produced by what can only be assumed to be healthy trees immediately after mechanical injury.

Whatever the exact origin and mode of formation of the gums may be, it is reasonable to believe that gum exudates are formed by some type of enzymic polymerization and not by direct chemical polymerization. If this is so, it is quite likely that the gums would contain entrapped enzymes that have escaped inactivation, since they are in close contact with the product elaborated and, under suitable conditions, these stranded enzymes would be capable of hydrolyzing the gums originally synthesized. There are numerous analogous examples which support this contention. For example, the enzymes which synthesize starch have been found in plants in contact with the synthetic polymer (starch) and after isolation they have been shown to be capable of reversing the synthetic polymerization and converting starch into α-D-glucosyl-phosphate in the presence of excess inorganic phosphate (17).

It was claimed long ago that cherry gum will undergo slow autolysis to give a mixture of reducing sugars (18) and that the enzyme present in cherry gum will hydrolyze plum gum but not gum arabic.

In refuting an earlier claim by Kosman (19) that an enzyme present in foxglove leaves was capable of hydrolyzing gum arabic, Reinitzer stated (20) that an enzyme capable of fermenting gum arabic was present only in gum arabic itself, cherry gum, a few of the rarer gums, and various stone fruits. Other investigators (21) disagreed, but relatively recently Lutz (22) has expressed the view that plant gums contain an enzyme which is capable of effecting autolysis under aseptic conditions. This is a point of considerable interest and should be investigated further.

A more recent viewpoint is that the stability of gum solutions to autolysis may be due to the presence of peroxidases which inactivate the degrading enzymes (23).

Another interesting feature, perhaps fortuitous, is that the gum exudates, such as those produced by the *Acacia* and mesquite trees, are chemically and structurally related to the pneumococcus polysaccharides which encapsulate and protect the pneumococcus organisms. These capsular polysaccharides are known to offer protection to the pneumococcus organisms and it is not unlikely that the injured trees produce gum, which acts in much the same manner as the capsular polysaccharide.

Gums and mucilages are said by some to arise from starch (25,26) while others suggest that they are produced at the expense of cellulose or hydrocellulose (27). The finding of traces of pentose oligosaccharides in certain gums has been taken to indicate their function as intermediate enzymic substrates in the synthesis of the gums (23). There seems to be no evidence which will enable this question to be decided at the present time. Perhaps some progress could be made if investigations were carried out into the relationship between the composition and structure of the gum and of the simple carbohydrates and carbohydrate polymers in various parts of the tree.

It is claimed that a histochemical examination of the gum exudations of the cherry (*Prunus cerasus*) tree indicates that the material first formed is composed entirely of hexoses. Afterwards the outer surfaces of the gum granule show the presence of uronic acid and pentoses. In none of these stages of exudation were the cell walls implicated in the gum formation which was claimed to be a "deviation" from normal metabolism (32).

Another interesting observation made recently in this connection (24) is that all the neutral sugars in plum gum are indeed present in the tissue of the tree in the free state. The D-glucuronic acid appears in the fruit just before gummosis occurs. It was further noted that the concentration of glucuronic acid in the mesocarp tissue was higher near the site of gummosis than at places farther removed from the site of gum formation. One other significant fact emerged, namely, that D-glucuronolactone is a good substrate for tissue regeneration and that its metabolism does not result in the formation of xylose; from this it has been tentatively deduced that pentoses do not arise from uronic acids by a process of decarboxylation.

The origin of the gum exudates represents a fascinating and challenging problem. The solution to it, coupled with the determination of the relationship between the various gum polysaccharides and the pneumococcus capsular polysaccharide would be of great value scientifically and might lead to the development of a synthetic vaccine for combatting pneumonia (28).

Plant Mucilages

What we have said thus far has been concerned with the gum exudates produced by trees that have not been intentionally injured, although they have been cultivated under unfavorable conditions. The so-called vegetable mucilages, which appear to have a much less complicated structure, are derived from the bark, roots, leaves, seeds, and in some cases, the flowers of the plants (7). They are products of normal plant metabolism and may serve as food reserves (14,29) in much the same manner as starch in many plants and glycogen in animals. The mucilages may arise from starch (25,26) and, in certain plants at least, they seem to act, as do the polysaccharides in succulent plants, (*Aloe*, *Euphorbiaceae*), as agents for holding water (13–15).

Gum tragacanth is exuded from the stems and roots of the *Astragalus* trees immediately after incisions are made. This highly valued commercial gum is generated within the plant (13) at certain times of the year and, as it exudes, water is absorbed from the surrounding tissues. The gum eventually congeals and blocks the incision in much the same way that coagulated blood seals off a wound.

The fact that gum tragacanth is generated immediately after incisions are made in the bark of the tree leads to the view that the gum is already present in the tree, but in spite of this it does not appear to have been proved by sectioning and extracting to see what part of the tree generates the gum. Unlike the *Acacia* gums, gum tragacanth usually contains starch granules that were present in the plant cellular material.

An excellent source of mucilages composed of neutral sugar residues are the seeds of many *Leguminosae* such as the locust bean or carob bean (*Ceratonia siliqua* L.), guar (*Cyamopsis tetragonolobus*), Kentucky coffee bean *Gymnocladus dioica*), honey locust (*Gleditsia tricanthos*), and many others (see Tables II and III). Palm seeds also provide a neutral mucilaginous polysaccharide.

The seeds, especially those of the *Leguminosae*, are usually hard and some, for example the carob and Kentucky coffee beans, require considerable force to break them. The gum or mucilage is found as a hard vitreous layer on the inside of the seed coat. It can be removed either by a milling process, as is the case with the guar seed, or more efficiently but slowly, as in the case of the Kentucky coffee bean, by soaking the broken seeds in water to allow the mucilaginous material to swell, after which it can be mechanically removed.

Carob seed or locust bean gum is a valuable commercial gum in the food, textile, printing and ore-refining industries. Guar gum, another excellent seed mucilage, is also becoming an important commercial commodity and like carob gum, it can be used in place of the more expensive, though usually superior, gum tragacanth. The popularity of tamarind seed (*Tamarindus indica*) gum for industrial use is also growing. The consumption of these readily accessible, easily harvested, and cheaper gums is likely to continue to increase at the expense of gum tragacanth, except for specialized items.

Root Mucilages

The roots of certain plants such as Iles mannan (*Amorphophallus oncophyllus*) and konjak mannan (*A. konjak*), contain a polysaccharide which may be extracted with hot water or dilute alkali to give excellent mucilages that are useful in the paper and rubber latex industries. They are likewise normal metabolic products as is the mucilage extracted

Figure 1. Map showing the origin of the more important vegetable gums (1). 1. Gum arabic (*Acacia senegal* Willd.) 2. Other *Acacia* gums 3. Gum tragacanth (*Astragalus* Sp.) 4. Karaya gum or Indian tragacanth (*Sterculia urens* Roxb.) 5. Carob (locust) bean (*Ceratonia siliqua* L.) gum 6. Kutira (*Cochlospermum gossypium* DC) gum 7. Ghatti (*Anogeissus latifolia* Wall.) gum 8. Angico (*Piptadenia* Sp.) gum 9. Mesquite (*Prosopis juliflora* DC) gum 10. Guar (*Cyamopsis tetragonolobus*) gum 11. Iles mannan (from *Amorphophallus oncophyllus*) 12. Seaweed gums (Agar, carrageenin, algin, etc.) 13. Konjak mannan (from *Amorphophallus konjak*) Adopted from "Vegetable Gums and Resins," by F. N. Howes, published by Chronica Botanica Company, Waltham, Mass., 1949.

from asparagus roots which is reported to be of superior quality as far as viscosity is concerned.

Seaweed Gums or Mucilages

Although these substances have long been in use by people of the coastal areas of the world, only agar, a complex polysaccharide mixture produced almost exclusively by the Japanese from a variety of sea weeds by a somewhat lengthy and not well-understood extraction process, has occupied a permanent position as a commercial product of world-wide significance. In recent years, however, other sea-weeds have been examined and as a result two additional products, algin, a polyguluronomannuronic acid and carrageenin, a polyanhydrogalactosylgalactose sulfate, are being produced in quantity in Europe and North America for use in the food, textile, metallurgical, and other industries. The uses of these two products are expanding rapidly.

It is of some interest to note the origin of the more important commercial vegetable gums (see Figure 1) (1). The greatest production of gums which have to be collected by hand is to be found in those regions where labor is cheap. Even where hand labor is expensive, commercial development of certain gums becomes possible when mechanical devices can be used for harvesting the plants or plant products. Thus, sea-weed gums are being extracted in Europe and North America and guar gum is being produced on a small scale from beans grown in the United States where the seeds can be mechanically harvested and milled.

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