THE EXUDATE GUMS AND THEIR STRUCTURAL RELATIONSHIP TO OTHER GROUPS OF PLANT POLYSACCHARIDES

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The exudate gums are complex acidic polysaccharides produced by trees either spontaneously or after mechanical injury. Each polysaccharide contains three or more constituent sugars including D-glucuronic acid (or its 4-methyl ether) and/or D-galacturonic acid. Highly branched structures are invariably encountered and since each constituent sugar may be present in furanose or pyranose ring forms may have different configurations at its glycosidic linkages, and may be involved in a variety of types of linkage, the elucidation of the detailed molecular structure of the exudate gums provides one of the most challenging problems in organic chemistry.

Many plant gums consist almost entirely of polysaccharides and consequently the problem of isolating these substances free from other materials, especially from other natural macromolecules, is often relatively simple compared with that of the isolation of other plant polysaccharides which are present as cell-wall components. The additional problem of obtaining polysaccharides in a sufficiently homogeneous form for detailed chemical examination cannot be considered at length on this occasion. Suffice it to say that three types of polymer heterogeneity have been recognized amongst the polysaccharide constituents of the exudate gums. First, there are those gums, such as gum tragacanth[1] and *Khaya senegalensis* gum[2,3], in which two polysaccharide components of entirely different structural type are present. Secondly, at the other end of the scale, there is the kind of micro-heterogeneity found in *Combretum leonense* gum[4] in which polysaccharide subfractions show small differences in composition but no differences in the nature of the structural units or in the linkages between them. Thirdly, heterogeneity of an intermediate type has been encountered recently in *Anogeissus leiocarpus* (formerly *A. schimperi*) gum[5,6]. This gum contains two discrete polysaccharide components which are sufficiently different to permit fractionation on a preparative scale. Structural investigations so far carried out indicate that the two polysaccharides contain many of the same structural units but in markedly different relative proportions.

To an increasing extent complex plant polysaccharides may be classified in terms of families of related molecular species in which the members of each group contain common structural units, most frequently the sequences of sugar residues in the interior chains, but differ considerably in the nature and number of other units attached as side-chains. This type of structural classification of polysaccharides, often of diverse origins, has been applied to many of the cell-wall polysaccharides of higher plants[7,8], the xylan group

providing the most fully authenticated example. I wish today to extend this type of classification to three groups of polysaccharides amongst the exudate gums of which sufficient is known to permit reasonably detailed structural formulations. In the case of two of these groups this kind of systematization serves to emphasize the structural relationship between certain of the exudate gums and other types of plant polysaccharides.

The presence in many gum polysaccharides of a variety of glycosidic linkage which undergo cleavage at markedly different rates has permitted the use of controlled acid hydrolysis for relatively selective fragmentation. This type of graded hydrolysis, which was first used over twenty-five years ago by the late F. Smith in studies on gum arabic, and by E. L. Hirst and J. K. N. Jones in studies on damson and cherry gums[9], still forms the basis for the controlled fragmentation of gums. The power of this method of approach has been greatly extended during more recent years by modern chromatographic methods for the separation of oligosaccharides, and the general procedure is outlined in *Figure 1.* More recently, alternative methods of fragmentation have been exploited; these include acetolysis, which often results in markedly different "cracking patterns" from those of partial hydrolysis in aqueous solution, and the Smith degradation of sequential periodate oxidation, borohydride reduction, and mild acid hydrolysis of resulting acyclic acetals, which provides a powerful method for the isolation of those portions of the molecule which are resistant to oxidative glycol cleavage. Advantage has also been taken of changes in the relative rates of cleavage of different glycoside bonds consequent on structural modifications in polysaccharides such as reduction of or oxidation to hexuronic acid residues. In all phases of the examination of complex macromolecules, from the polysaccharides themselves to oligosaccharides as degradation products, the classical methylation procedure has continued to be widely exploited for the determination of sites of substitution, the more especially since gas chromatographic methods have been developed for the identification of mixtures of methyl glycosides of methylated and partially methylated sugars.

Gum acid

↓ "Autohydrolysis" *or* 0·01N-acid at 100° → L-arabinose (*ex* L-Ara*f* 1 . .)

Degraded arabinose-free gum + **oligosaccharides** (*ex* R→L-Ara*f* 1 . .)

↓ *ca.* 0·2N-acid at 100° for 1 h → L-rhamnose (*ex* L-Rha*p* 1 . .)

——→ **Neutral (galactose-containing) oligosaccharides**

↓ *ca.* N-acid at 100° for 4-6 h

D-galactose + **Aldobiouronic acid** (*e.g.*, β-D-G*p*A 1→6 D-Gal)

Figure 1. Graded acid hydrolysis of gums

We may consider first the galactan group of exudate gums in which each polysaccharide contains a branched core of β-D-galactopyranose residues

mutually joined by 1→3′ and 1→6′ linkages. The distribution of the two types of linkage is such that those of the 1→3′ type predominate in the interior chains whilst those of the 1→6′ type are concentrated in the outer chains. Gum arabic, one of the best known exudate gums, produced by trees of *Acacia senegal* (Leguminosae, Mimosaceae) in the Sudan, although one of the most complex known polysaccharides,was the first gum of this type in which the nature of the galactan core was established. The main structural features of the gum, which are based on the application of the general methods previously outlined, are summarized in *Figure 2.* It must be emphasized, however, that this highly branched type of structure does not provide a unique representation of this complex polysaccharide, and, if anything, is an over-simplification.

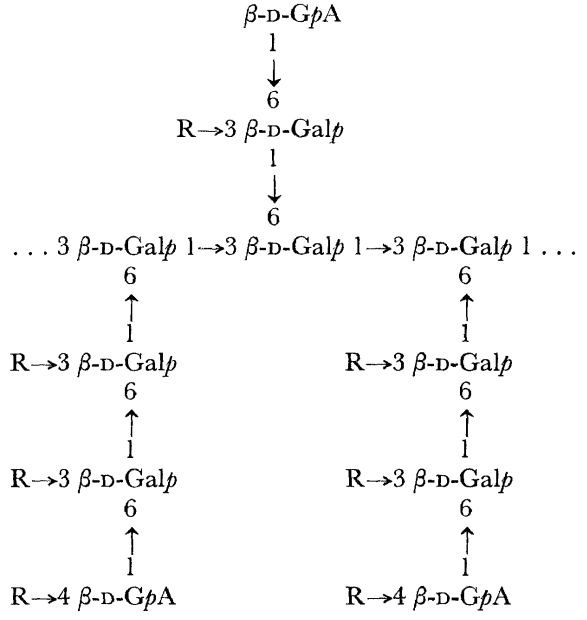


Figure 2. Gum arabic, where R = L-Ara*f* 1 . . . , L-Rha*p* 1 . . . , α-D-Gal*p* 1→3 L-Ara*f* 1 . . . , or occasionally β-L-Ara*p* 1→3 L-Ara*f* 1 . . .

Of the various acid-labile units (R) in the outer chains of gum arabic only the L-rhamnopyranose residues have been placed with certainty. Although L-rhamnopyranosidic linkages are readily hydrolysed in aqueous solution, they are sufficiently resistant to cleavage by acetolysis to permit the isolation by this procedure of oligosaccharides with intact L-rhamnosidic linkages. Thus, acetolysis of carboxyl-reduced arabic acid, followed by deacetylation of the products, led to the isolation of 4-*O*-α-L-rhamnopyranosyl-D-glucose and *O*-α-L-rhamnopyranosyl-(1→4)-*O*-β-D-glucopyranosyl-(1→6)-D-galactose (see *Figure 3*)[10].

Gums containing the same type of basal structure have been recognized from other *Acacia* species and from a number of botanically unrelated trees. These polysaccharides vary to some extent in the degree of branching in the galactan core and also differ in the sites of attachment of the peripheral

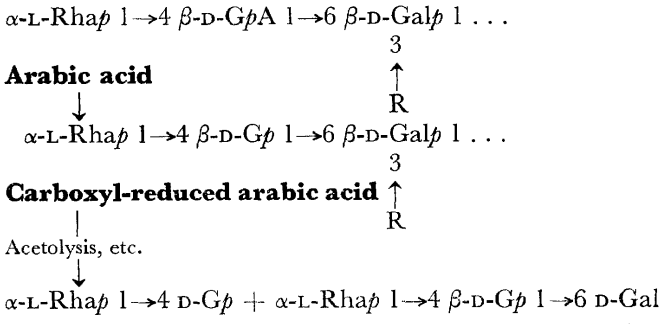


Figure 3. Location of L-rhamnopyranose end groups in arabic acid

L-arabinofuranose and L-rhamnopyranose residues and in the nature of the more complex substituted L-arabinofuranose units. Polysaccharides containing a highly branched galactan core are also found in the wood of many coniferous trees, especially of larches. These polysaccharides generally possess somewhat less highly ramified structures and contain a lower proportion of sugar residues other than D-galactose, than do the exudate gums. On structural grounds, however, there is no clear line of demarcation between the two groups of polysaccharides. *Table I* indicates the similarities

Table 1. Sugar residues in the outer chains of some gums and wood polysaccharides containing a branched galactan core

Source	*β-D-Glucuronic acid residues linked 1→6′ to D-galactose residues in outer chains*	*Peripheral units readily cleaved on mild hydrolysis*
	GUMS	
Acacia senegal [9,10] (gum arabic)	α-L-Rha*p* 1→4 β-D-GpA 1. . β-D-GpA 1. .	L-Rha*p* 1. L-Ara*f* 1. α-D-Gal*p* 1→3 L-Ara*f* 1. β-D-Ara*p* 1→3 L-Ara*f* 1.
Acacia pycnantha[11]	β-D-GpA 1. .	L-Rha*p* 1. L-Ara*f* 1. L-Ara*f* 1→3 L-Ara*f* 1.
Ferula spp.[12] (asafoetida gum)	β-D-GpA 1. . 4-Me β-D-GpA 1. .	L-Ara*f* 1.
Araucaria bidwillii[13]	β-D-GpA 1. . 4-Me β-D-GpA 1. .	L-Rha*p* 1. L-Ara*f* 1.
	WOOD POLYSACCHARIDES	
European, Western, and Japanese larches[14] (*Larix decidua, L. occidentalis, L. leptolepis*)		L-Ara*f* 1. β-L-Ara*p* 1→3 L-Ara*f* 1.
Mountain larch[15] (*L. lyallii*)	β-D-GpA 1. .	L-Ara*f* 1. β-L-Ara*p* 1→3 L-Ara*f* 1.
Maritime pine[16] (*Pinus pinaster*)	β-D-GpA 1. .	L-Ara*f* 1. β-L-Ara*p* 1→3 L-Ara*f* 1. α-D-Xyl*p* 1→3 L-Ara*f* 1.

in the nature (although not necessarily in the sites of attachment) of the sugar residues in the outer chains of some of the exudate gums and coniferous wood arabinogalactans.

One of the major problems awaiting solution in structural studies on polysaccharides of the galactan group is that of the unambiguous location of the various acid-labile peripheral units. One possible method of attack, presently under investigation, takes advantage of the susceptibility of 3-*O*-substituted sugars to degradation by alkali to form metasaccharinic acids. Since these polysaccharides contain interior chains of 3-*O*-substituted D-galactopyranose residues which carry side-chains attached at C–6, alkaline degradation should furnish a series of *O*-glycosyl saccharinic acids. In order to avoid unwanted complications arising from the formation of stereoisomeric saccharinic acids and to minimize the possibility of inadvertent autohydrolysis these acids have been degraded by treatment with hypochlorite at pH 5 to the corresponding 5-*O*-substituted 2-deoxy-D-*threo*-pentoses, and the separation and characterization of these oligosaccharides is under investigation. The degradative scheme is outlined in *Figure 4*[17].

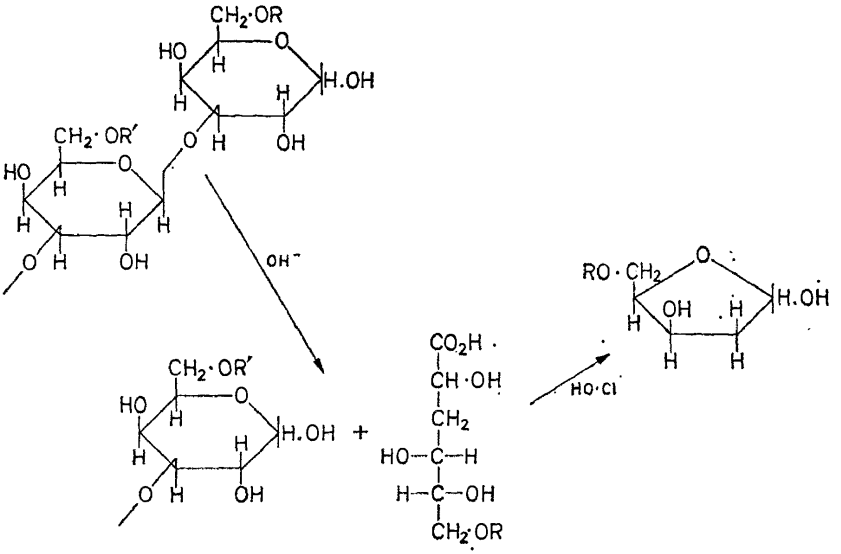


Figure 4. Alkaline degradation of 1→3′ linked galactans

The second group of exudate gums to which I wish to direct attention may be classified, in terms of the inner chains to which other units are attached as side-chains, as glucuronomannans. These gums, like those of the galactan group, usually contain acid-labile pentose residues on the periphery of the molecule and may be subjected to the same type of controlled hydrolysis to give degraded polysaccharides and various mixtures of neutral and acidic oligosaccharides. Gum ghatti of Indian origin from *Anogeissus latifolia* (Combretaceae) provided the first example of a polysaccharide in which clear evidence was obtained for the presence of interior chains of D-glucuronic acid and D-mannose residues, and some of the main structural

features of the gum are shown in *Figure 5*[18,19]. Since partial acid hydrolysis of the gum had yielded two polymer-homologous series of 1→6′ linked D-galactose-containing oligosaccharides, the one series with and the other without a 3-*O*-substituted L-arabinose reducing group, our first inclinations were to suppose that these units arose from main chains of β-D-galactopyranose residues interrupted at intervals by L-arabinose residues, and that units of the two aldobiouronic acids, 2-*O*-(β-D-glucopyranosyluronic acid)-D-mannose and 6-*O*-(β-D-glucopyranosyluronic acid)-D-galactose, were attached thereto as side-chains. Evidence for the type of structure shown in *Figure 5* came from fragmentation of the gum involving two successive degradations by Smith's procedure followed by partial acid hydrolysis which afforded a mixture of oligosaccharides including 6-*O*-β-D-galactopyranosyl-D-galactose, 3-*O*-β-D-galactopyranosyl-L-arabinose, and 3-*O*-L-arabinopyranosyl-D-mannose[20]. The proposed structure for gum ghatti is one in which these disaccharides have their origin in side-chains of 6-*O*-substituted β-D-galactopyranose residues linked *via* 3-*O*-substituted L-arabinopyranose to C–3 of D-mannopyranose residues in the interior structure of the gum. At present there are only indirect indications that some of these side-chains are terminated by D-glucuronic acid end groups, and thus provide the source of one of the two aldobiouronic acids, 6-*O*-(β-D-glucopyranosyluronic acid)-D-galactose, formed on partial hydrolysis. Evidence that the second aldobiouronic acid, 2-*O*-(β-D-glucopyranosyluronic acid)-D-mannose, originates from blocks of D-glucuronic acid and D-mannose residues rather than from isolated disaccharide units within the structure has been obtained recently by the isolation on partial hydrolysis of a tetrasaccharide containing alternating residues of the two sugars[21].

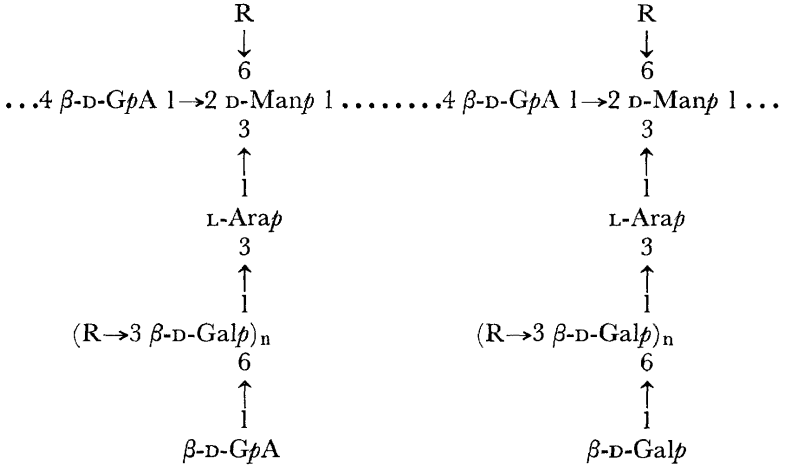
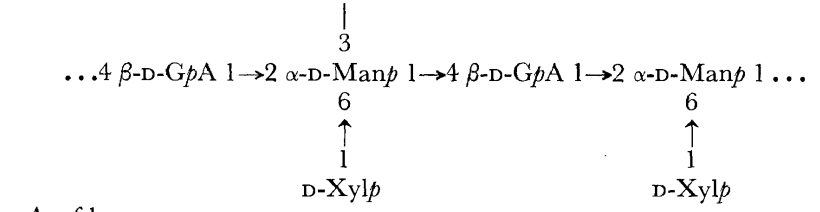


Figure 5. Gum ghatti, where the majority of sites indicated carry substituents R = L-Ara*f* 1 . . . , or less frequently, L-Ara*f* 1 → 2 L-Ara*f* 1 . . . , L-Ara*f* 1 → 3 L-Ara*f* 1 . . . or L-Ara*f* 1 → 5 L-Ara*f* 1 . . .

More convincing evidence still for the presence in a polysaccharide of main chains composed of residues of D-glucuronic acid and D-mannose has been provided in recent studies on the gum from a botanically related tree,

Anogeissus leiocarpus (formerly *A. schimperi*), of West African origin. Our first investigations of this gum showed that it gave rise on partial hydrolysis to largely the same neutral and acidic oligosaccharides as gum ghatti, but that the relative amounts of the various oligosaccharides formed were substantially different in the two cases[5]. Further examination of this gum has shown that it contains two distinct but structurally related polysaccharide components[6]. The major component, leiocarpan A, which is selectively precipitated with cetyltrimethylammonium bromide, contains D-glucuronic acid, D-mannose, L-arabinose, and D-xylose as the main constituent sugars and a very low proportion (*ca.* 4 per cent) of D-galactose residues. The main structural features of the polysaccharide are outlined in *Figure 6*. The pentoses are largely present as single unit L-arabinofuranose and D-xylopyranose side-chains, and the main chains of D-glucuronic acid and D-mannose residues are much more readily exposed than in gum ghatti where these chains carry long side-chains and are hidden in the interior of the molecular structure. The D-galactose residues, although present in only low proportion, are probably present in the same type of side-chains as in gum ghatti since they give rise to the same oligosaccharides on partial hydrolysis. These side-chains in leiocarpan A, however, are probably shorter than in gum ghatti and attached much less frequently.



L-Araf 1...
L-Araf 1→3 L-Araf 1...
L-Arap 1→3 L-Araf 1...
β-D-GpA 1-(→6 β-D-Galp 1-)$_n$→3 L-Arap 1...
β-D-Galp 1-(→6 β-D-Galp 1-)$_n$→3 L-Arap 1...

Figure 6. Partial structures for leiocarpan A

Evidence for the nature of the interior chains in leiocarpan A and proof that residues of 4-*O*-substituted β-D-glucuronic acid and 2-*O*-substituted α-D-mannopyranose are present largely, if not exclusively, in a regularly alternating sequence has been obtained by the isolation from acetolysis of the carboxyl-reduced polysaccharide of the series of neutral oligosaccharides shown in *Figure 7*[22].

β-D-Gp 1→2 D-Man
α-D-Manp 1→4 D-Gp
Gp 1→2 Manp 1→4 Gp
Manp 1→4 Gp 1→2 Man
Gp 1→2 Manp 1→4 Gp 1→2 Man
Manp 1→4 Gp 1→2 Manp 1→4 Gp
Gp 1→2 Manp 1→4 Gp 1→2 Manp 1→4 Gp

Figure 7. Oligosaccharides from carboxyl-reduced leiocarpan A.

Several plant gums, including some from the *Prunus* genus (Rosaceae), give rise to the aldobiouronic acid, 2-*O*-(β-D-glucopyranosyluronic acid)-D-mannose, on partial hydrolysis, but it is not yet clear whether these gums can be properly regarded as members of the glucuronomannan family of polysaccharides. It is significant, however, that Zitko and his collaborators[23] in Bratislava have isolated a series of oligosaccharides composed of glucuronic acid and mannose units from the partial hydrolysis of apricot gum pointing to the presence of blocks of these units in some part of the structure of the gum. The glucuronomannan type of structure is at present unknown amongst plant polysaccharides other than the exudate gums.

We may turn finally to an entirely different group of exudate gums, named by reference to their interior or basal chains as galacturonans or galacturonorhamnans. It is perhaps more correct to consider these gums as members of three sub-groups between which there is partial structural overlap. These gums are noteworthy in containing residues of both D-galacturonic acid and D-glucuronic acid (or its 4-methyl ether). The former sugar units are located mainly in the interior chains, but the latter are found as terminal units in side-chains attached to a variety of different sugar residues. The first sub-group of gums of the galacturonorhamnan family is represented by gums of the *Sterculia* genus (Sterculiaceae) of widely different origins in India (*S. urens*), West Africa (*S. setigera*) and Australia (*S. caudata*, syn. *Brachychiton diversifolium*), and by the gum from the botanically unrelated *Cochlospermum gossypium* (Bixineae)[24–26]. These gums occur naturally as partially acetylated polysaccharides and partial structures for the essentially similar parent polysaccharides are shown in *Figure 8*. Direct evidence for the presence of D-glucuronic acid residues as single unit side-chains follows from methylation studies and from the characterization of *O*-(β-D-glucopyranosyluronic acid)-(1→3)-*O*-(α-D-galactopyranosyluronic acid)-(1→2)-L-rhamnose as one of the products of partial acid hydrolysis.

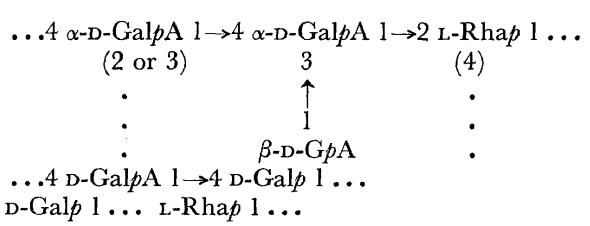


Figure 8. Partial structures for gums from *Sterculia* spp. and from *Cochlospermum gossypium*

The second sub-group of exudate gums of the galacturonorhamnan family is represented by those from the *Khaya* genus (Meliaceae)[2,27,28]. Like the *Sterculia* gums the *Khaya* gums occur naturally as partly acetylated polysaccharides, and the major polysaccharide components contain many of the same structural units, although they differ in detailed molecular architecture. The interior chains possess substantial blocks of contiguous D-galacturonic acid residues between which are interposed L-rhamnose residues. As in the *Sterculia* gums, the residues of D-glucuronic acid (as the 4-methyl ether) are present as end groups, but in the *Khaya* gums these units are joined to

D-galactose residues, which are probably linked in turn to L-rhamnose branching points (*Figure 9*).

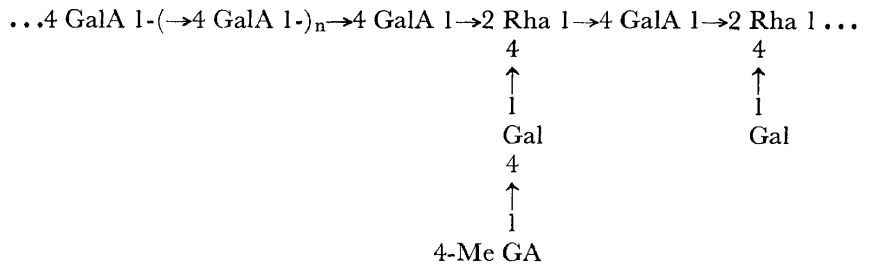


Figure 9. Major polysaccharide components of gums from *Khaya* spp.

Tragacanthic acid, the main polysaccharide component of gum tragacanth from *Astralgus gummifer* (Leguminosae), is the only known representative of the third sub-group. In this polysaccharide the main chains are composed mainly of 1→4′ linked α-D-galacturonic acid residues, although the recent isolation of small amounts of the aldobiouronic acid, 2-*O*-(α-D-galactopyranosyluronic acid)-L-rhamnose, as a partial hydrolysis product[29] suggests that the main chains may be interrupted occasionally by L-rhamnose residues. The short side-chains consist of either single β-D-xylopyranose or substituted 2-*O*-α-L-fucopyranosyl-D-xylopyranose or 2-*O*-β-D-galactopyranosyl-D-xylopyranose units. The key degradations leading to the assignment of the main structural features of the polysaccharide are shown in *Figure 10*[1]. It is noteworthy that L-fucopyranosidic, like L-rhamnopyranosidic, linkages are readily hydrolysed in aqueous solution, but are sufficiently stable to acetolysis to permit the isolation of 2-*O*-α-L-fucopyranosyl-D-xylose as one of the products. D-Glucuronic acid is only a trace constituent of tragacanthic acid and probably terminates some of the side-chains[29].

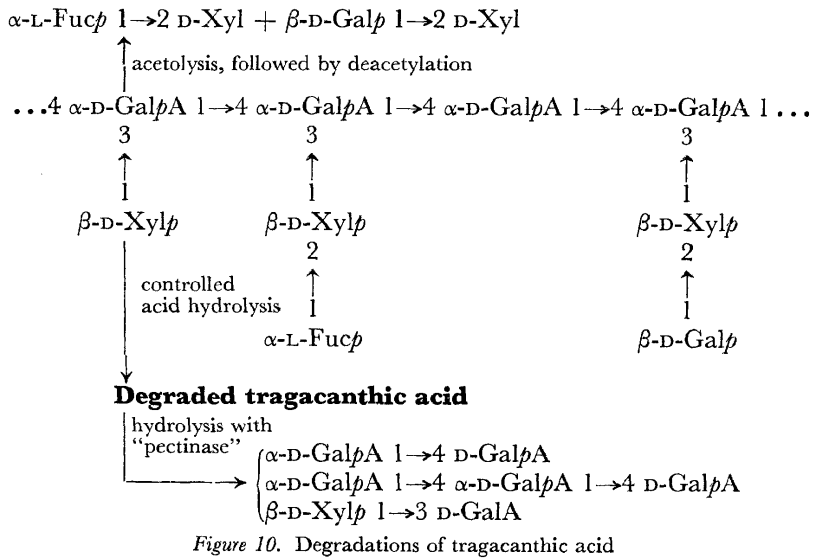


Figure 10. Degradations of tragacanthic acid

The structural relationship of tragacanthic acid to the pectins is immediately apparent in the interior galacturonan chains. Gums of the other two sub-groups, however, are related to pectins not only in containing similarly linked blocks of D-galacturonic acid residues but also in that these blocks are interposed by L-rhamnose residues. Galacturonans, as strictly homopolysaccharides, are now recognized to be of relatively infrequent occurrence, and several pectins, *e.g.*, those from lemon peel[30], lucerne (alfalfa)[31] and the bark of Amabilis fir[32] give rise on partial hydrolysis to 2-*O*-(α-D-galactopyranosyluronic acid)-L-rhamnose and higher oligosaccharides composed of these sugars. It now appears probable that the galacturonan chains in most pectins are interrupted at intervals by L-rhamnose residues. Recent investigations on the pectin-like acidic polysaccharides from soybean cotyledon meal[33] and soybean hulls[34] have provided most striking examples of polysaccharides in which different areas of the galacturonorhamnan chains may contain (a) blocks of galacturonic acid residues, (b) sequences of at least two rhamnose residues, and (c) alternating galacturonic acid and rhamnose units. The acidic oligosaccharides isolated from the soybean polysaccharides by partial hydrolysis or by acetolysis and the types of sequence from which they must arise are shown in *Figure 11.*

—GalA→GalA→GalA→GalA→Rha→GalA→Rha→GalA→GalA→Rha→
→Rha—

partial acid hydrolysis and/or acetolysis

↓

α-D-Gal*p*A 1→4 D-Gal*p*A
α-D-Gal*p*A 1→2 L-Rha
α-D-Gal*p*A 1→4 α-D-Gal*p*A 1→4 D-Gal*p*A
α-D-Gal*p*A 1→4 α-D-Gal*p*A 1→2 L-Rha
α-D-Gal*p*A 1→2 L-Rha*p* 1→2 L-Rha
α-D-Gal*p*A 1→2 L-Rha*p* 1→4 α-D-Gal*p*A 1→2 L-Rha
α-D-Gal*p*A 1→4 α-D-Gal*p*A 1→2 L-Rha*p* 1→2 L-Rha

Figure 11. Fragmentation of the interior chains of soybean polysaccharides

The structural relationship between the soybean polysaccharides and the galacturonan-galacturonorhamnan group of exudate gum is not, however, limited to the interior portions of the molecular structure. The outer chains include the same single β-D-xylopyranose units linked 1→3′ to D-galacturonic acid, and 2-*O*-α-L-fucopyranosyl-D-xylopyranose and 2-*O*-β-D-galactopyranosyl-D-xylopyranose units as tragacanthic acid. To complicate the structural picture yet further the soybean polysaccharides contain linear chains of β-D-galactopyranose residues linked 1→4′ as in the pectic galactan from *Lupinus albus* seeds[35]. These chains, however, are integral parts of an acidic polysaccharide rather than of a contaminating neutral galactan since stepwise degradation furnishes acidic oligosaccharides (not yet fully characterized) in which these chains are linked either directly or through xylose or rhamnose residues to a single galacturonic acid reducing unit. Fragmentations of the side-chains in the soybean cotyledon polysaccharide are summarized in *Figure 12.*

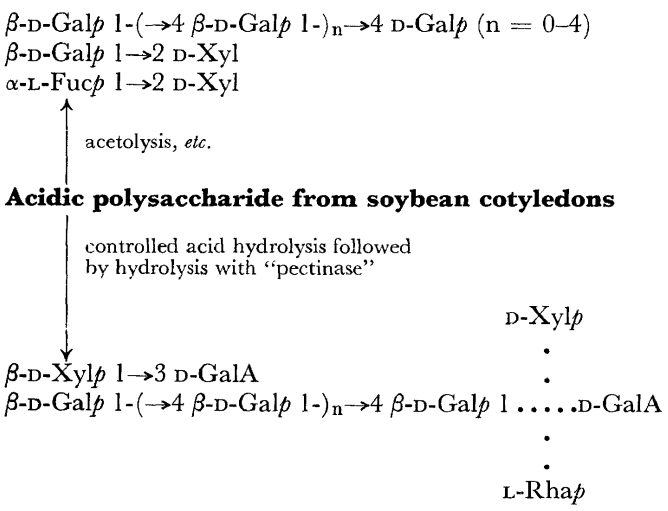


Figure 12. Fragmentations of the side-chains of soybean cotyledon polysaccharide

In terms of their basal chains as galacturonorhamnans in which the proportions of galacturonic acid to rhamnose residues vary from *ca.* 3:1 in the *Sterculia* and *Khaya* gums to possibly 100:1 in tragacanthic acid, the three sub-groups comprise a broad spectrum of chemically related polysaccharides. The structural inter-relationships with each other and with the pectins are summarized in *Figure 13.*

The search for a complete structural basis for the classification of the highly branched polysaccharides from the exudate gums is still in its early stages. The three groups of polysaccharides to which I have directed attention may need to be extended or modified to accommodate the discovery of polysaccharides with further variations in detailed structure, and it is probable that entirely new structural groups of exudate gums will be recognized. There are indeed several well-known exudate gums, *e.g.,* the various *Prunus* gums[9], mesquite gum[9], and cholla gum[9,36], which have not been considered in this survey. Although much is known of certain aspects of the chemistry of these gums, the evidence in my opinion, is not yet sufficient to provide a clear indication of which sequences of sugar units comprise the basal chains of the polysaccharides and of which are attached as side-chains to these interior chains.

The exudate gums are end products of plant metabolism, but in two of the groups to which I have referred the structural relationships to other types of plant polysaccharides indicate that similar biosynthetic pathways are followed in their formation. It is indeed possible in some cases that in gum formation polysaccharides which are already present in the plant, *e.g.,* as cell-wall constituents, undergo the apposition of additional sugar residues to the outer chains to give the yet more complex polysaccharides which are exuded to protect the injured plant against desiccation in hot dry climates and against infection by micro-organisms. Speculation aside, it is clear that advances in knowledge of the nature of plant heteropolysaccharides will come from parallel studies on the exudate gums as end products and on the

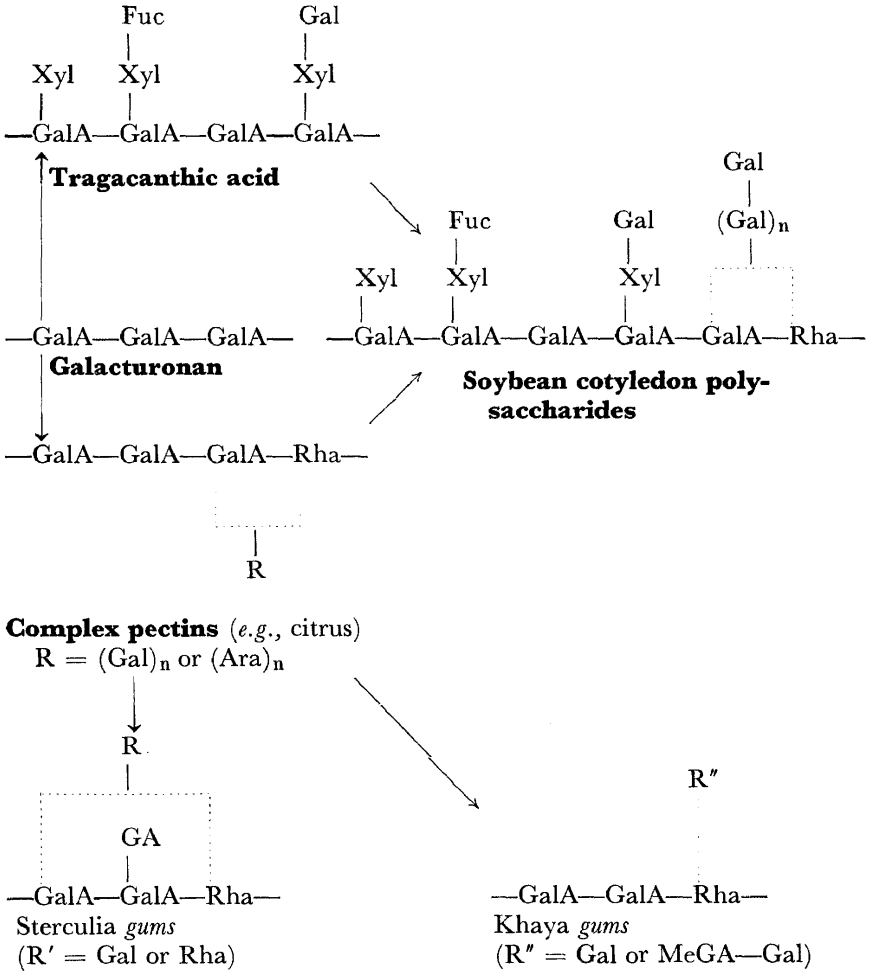


Figure 13. Structural inter-relationships between polysaccharides of the galacturonan-galacturonorhamnan group

various cell-wall polysaccharides which are involved in the normal metabolism of the plant.

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