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Gum Arabic: Past, Present and Future

TIMOTHY C. BALDWIN*

Abstract

Plant gum exudates have been of importance in world trade for several thousand years and still have a wide variety of practical applications particularly in the food industry, in which they are commonly used as food additives. These exudates are the result of the wound response to injury in the plant species from which they are harvested. This process (gummosis) and the molecular structure and composition of these exudates are of immense interest and the study of which, form the basis of numerous basic and applied research projects throughout the globe. The objective of the current monograph is to provide a broad overview of the research data pertaining to one of the most agronomically significant of these plant gum exudates, namely gum arabic, and to highlight possible avenues for future research.

Key words : Gum arabic, *Acacia senegal*, Plant gum exudate.

Introduction

Gum exudates from *Acacia* species commonly known as gum arabic or gum acacia were harvested from the Gulf of Aden and exported to Egypt as early as the seventeenth century B.C. (Whistler and BeMiller, 1993) and are still of major commercial value today. The ancient Egyptians refered to gum arabic in their inscriptions as 'kami' which was used primarily as an adhesive for mineral pigments in paints and for the flaxen wrappings used to embalm mummies (Whistler and BeMiller, 1993). Through trade with Arab nations the gum gradually found its way into European commerce and acquired the name 'gum arabic' from its place of origin/port of export.

The *Acacia* species from which gum arabic is harvested, are endemic to the Sahelian region of Africa and to date approximately 1200 *Acacia* species have been identified (Ross, 1979). The commercial grades of gum exudates obtained from these species vary considerably in quality (Islam

* University of Cambridge, Department of Biochemistry, Building O, Downing Site, Cambridge CB2 1QW, United Kingdom.

et al., 1997). Currently, the principal source of gum arabic is the Kordofan province of Sudan which produces over 90% of the world's supply (Joseleau and Ullmann, 1990) with a production figure of 40,000 tons being achieved in 1996 (Islam *et al.*, 1997). Nigeria is the second largest producer, followed by Chad, Mali and Senegal. Although the best quality gum is traditionally associated with Sudan, in recent years indigenous gum from Chad has been produced of comparable quality.

In the "gum trade", the gum obtained from *Acacia senegal* (L.) Willdenow has the greatest commercial value and is recognised as the best in quality. Primarily because of this, over the past fifty or so years, most research concerned with *Acacia* plant gum exudates has focused on the gum obtained from this species. As a consequence of which gum arabic is currently defined by the FAO/WHO Joint Expert Committee on Food Additives (JECFA), as "a dried exudation obtained from the stems and branches of *A. senegal* (L.) Willdenow or closely related species of *Acacia* (family Leguminosae)" (FAO, 1995).

Biosynthesis of Gum Arabic (Gummosis)

Gum formation (gummosis) occurs within the cambial zone of the branches and stems of *Acacia* species and is promoted when trees of this genus are subjected to stress conditions such as heat, drought, insect attack or systematic wounding. Unfortunately, few rigorous investigations of this process have been performed. The most thorough investigation to date of gummosis in *Acacia* species was that presented by Joseleau and Ullmann (1990). These authors noted that an extremely high molecular weight polysaccharide, with a sugar composition very similar to that previously observed for gum arabic was present in a zone between the inner bark and the cambium. They speculated that this polysaccharide was the 'precursor' for the gum arabic exudate. These studies also indicated that gum production in *A. senegal* requires a certain maturation of the tree. This is in agreement with the observation in the 'trade' that only trees over five years of age are able to yield an 'economically significant' quantity of gum.

Industrial Applications

The best commercial grades of gum are defined as being "clean" *i.e.* they are highly water-soluble and give colourless or pale yellow aqueous solutions. The gum arabic exported from Sudan is currently marketed in various grades. *Hand Picked Selected* is the highest grade and contains the cleanest and largest gum nodules, with the lightest colour and therefore commands the highest price. *Cleaned and Sifted* is the material which remains after the Hand Picked Selected and the Siftings have been removed. *Cleaned* is the standard grade used throughout the world, where the colour varies from light to dark amber and the gum contains various amounts of siftings, but has had dust removed. *Siftings* are the residue formed by sorting the above choicer grades. *Dust*, the lowest grade is collected upon completion of

the cleaning process, and comprises very fine particles of gum, admixed with sand and dirt (Islam *et al.*, 1997).

These various grades of gum have a wide variety of applications. In the food industry for example, the top grades are used to inhibit sugar crystallization in confectionary products, in the microencapsulation of flavour oils for use in dried food mixes such as soups, cakes etc and in the manufacture of soft drinks (McNamee *et al.*, 1998). Gum arabic is also used to clarify wine, as an adhesive (Anderson, 1978) and to encapsulate pharmaceuticals (Joseleau and Ullmann, 1990). In the brewing industry the gum is responsible for the so-called "lace-curtain effect" which develops on the sides of beer glasses. As mentioned above, inferior grades of gum are darker in colour and are less readily water-soluble. These lower grades of gum are used in non-food related industries such as printing and textiles, and in the production of explosives (Anderson, 1978).

Molecular Structure and Composition

From the extensive studies of the chemical and physicochemical properties of gum arabic over the past fifty years, it has been shown that the gum harvested from *A. senegal* consists primarily of polysaccharides, with galactopyranose (Gal*p*) and arabinofuranose (Ara*f*) being the major monosaccharides present. Gum arabic also contains a small proportion of protein (Anderson and Stoddart, 1966). Akiyama and his colleagues (Akiyama *et al.*, 1984) have suggested that gum arabic can be considered as "a kind of arabinogalactan-protein" (AGP). Vandevelde and Fenyo (1985) and Randall and colleaques (1988) have subsequently proposed that the gum consists of at least three "fractions". These fractions were termed an AGP fraction (10.4% of the total gum) with molecular mass 1.45×10^6 containing 11.8% protein, an arabinogalactan (AG) fraction (88.4% of the total) with molecular mass 2.79×10^5 containing 0.35% protein and a glycoprotein (GP) fraction (ca. 1% of the total) with molecular mass 2.5×10^5 containing 47.3% protein. All these fractions were shown to share similar branched structures composed of a β(1-3) linked Gal backbone with branches of β(1-6) linked Gal containing arabinose (Ara), rhamnose (Rha), uronic acids and their derivatives (Randall *et al.*, 1988)

Subsequently, Qi and his colleagues isolated two major fractions from gum exudates of *A. senegal* namely a gum arabic glycoprotein (GAGP) of high molecular weight containing ca. 90% carbohydrate (mainly Ara and Gal), and a gum arabic polysaccharide (GAP). This GAP was shown to be a glucorhamnoarabinogalactan with a low molecular weight and which contained little or no protein. These workers also observed that while the GAGP polypeptide backbone closely resembled that of extensins, the polysaccharide moiety was similar to that of the AGPs (Qi *et al.*, 1991).

Fractionation of gum arabic by size exclusion chromatography has further demonstrated the polydisperse nature of *A. senegal* gum components with respect to their molecular mass and chemical composition (Osman *et al.*, 1993a, b). This confirmed the heteropolymolecular nature of the gum

originally proposed by Anderson and Stoddart (1966).

It is also of interest to note, in relation to the physical structure of the molecular constituents of gum arabic, that Qi and his colleagues used electron microscopy techniques in order to image the native GAGP molecule. This technique revealed this molecule to consist of an extended 'twisted hairy rope' like structure, similar to that previously observed for extensin monomers (Heckman *et al.*, 1986). This data was of particular interest since it had previously been proposed, based upon biophysical data, that AGPs and similar molecules present in gum exudates would display a more ovoid/spherical 'wattle-blossom' type of structure (Fincher *et al.*, 1983). More recently, such ovoid structures have indeed been imaged by electron microscopy in studies of a secreted AGP isolated from carrot suspension culture media (Baldwin *et al.*, 1993). Therefore, since gum arabic has been shown to contain a large number of as yet uncharacterized protein moieties (Osman *et al.*, 1993b) it is quite feasible that it may contain both such structures and perhaps others besides! Unfortunately, the resolution of this intriguing question will have to await future more rigorous biochemical and structural studies as will be discussed later.

Serotaxonomic Studies

Whilst most studies of gum arabic and related *Acacia* gum exudates (and seed proteins) have focused purely upon the chemical, physicochemical and structural properties of these substances, a number of chemo/serotaxonomic investigations have also been reported.

Anderson (1978) was the first to suggest that biochemical and biophysical data on *Acacia* gum exudates could be used to augment the classical botanical classification of *Acacia* based solely on external morphological features such as the 'classic' monograph of Bentham (1875). The first report to follow up on Anderson's suggestions was published by El Tinay *et al.,* (1979). In this study, seed proteins harvested from 22 species of *Acacia* collected from Northern, Central and Western Sudan were compared by serological methods in an attempt to classify Sudanese *Acacia* species. From the results of immunodiffusion and immuno-electrophoresis studies performed on these proteins, using polyclonal antisera raised against each sample, the seed proteins were divided into two main groups and six sub-groups. In general, the phytochemical groupings established agreed with the botanical classification for the main groups.

Subsequently, Brain reported a study using immunological techniques to investigate *Acacia* phylogeny, whereby the seed proteins of 37 species of *Acacia* were tested serologically by double diffusion and immuno-electrophoresis using rabbit antisera raised against whole seed contents of *A. karroo*, *A. ataxacantha* and *A. mearnsii* (Brain, 1987). Identity and absorption tests showed remarkable homogeneity in the Gummiferae series. In this study the seed proteins of *Acacias* from Africa and Australia were analysed, and were found to have virtually identical reactions with the antisera. In terms of the evolution and diversification of the Gummiferae

Acacias, it was remarkable that there was so little difference in the seed proteins of these species despite geographical separation for millions of years (Brian, 1987). However, the African Vulgares species studied were found to be serologically quite distinct from the various Gummiferae samples, which supports the view (Pedley, 1986) that the Gummiferae arose independently from the Vulgares, and therefore should not be included in the same genus.

In relation to these and more recent serological analyses, it is of interest to note that there is still some disagreement as to the source of gum arabic's immunogenicity. Some investigators have claimed that the precipitin - forming ability of gum arabic is due to protein associated with the gum (Akiyama *et al.*, 1984; Churms and Stephen, 1984; Connolly *et al.*, 1988). Other workers however, have ascribed these properties to carbohydrate residues present in the gum (Narita, 1985; Pazur and Kelly-Delacourt, 1985; Pazur *et al.*, 1991; Miskiel and Pazur, 1991). Bearing in mind the relatively low levels of protein present in gum arabic, and given the proven antigenicity of arabinogalactans and AGPs, both of which are abundant in samples of gum arabic (Anderson *et al.*, 1984; Knox *et al.*, 1992), it would therefore seem most probable that the carbohydrate moeities present in gum arabic comprise the dominant immunogens present**.** Indeed, Miskiel (1990) has determined two immunodeterminant groups present in gum arabic to be α-L-arabinofuranosyl-(1→4)-D-galactose and β-D-glucuronopyranosyl-(1→6)-D-galactose.

The first detailed description of the use of anti-gum arabic antibodies in an immunoassay was described by Pazur (1986). Since which time several similar reports have also been published (Pazur *et al.*, 1991; Miskiel and Pazur, 1991; Williams *et al.*, 1992; Menzies *et al*, 1992; Osman *et al.*, 1993a). Recently, a sensitive and specific ELISA for *A. senegal* gum has been reported which could differentiate this gum from other commonly used food hydrocolloids including other plant exudates such as gums ghatti, tragacanth and karaya (Williams *et al.*, 1992; Menzies *et al.*, 1992). Further studies of *Acacia* gums using this ELISA in combination with a range of chemical and physicochemical techniques indicated that the interaction with the anti-gum arabic antisera could be correlated with differences in the molecular composition of the gums. These studies suggested the usefulness of such an immunoassay in chemotaxonomic studies of *Acacia* (Osman *et al.*, 1993a). The only major drawback of this technique was that only a finite quantity of the polyclonal antisera was available. However, in the same year Osman and his colleagues also reported the use of a panel of anti-arabinogalactan/ arabinogalactan-protein (AG/AGP) monoclonal antibodies in conjunction with a range of chemical/physicochemical analyses to study the molecular composition of gum arabic (Osman *et al.*, 1993b). This and later studies (Osman *et al.*, 1995; Menzies *et al.*, 1996; Baldwin *et al.*, 1999) clearly demonstrated the utility of anti-plant cell wall monoclonal antibodies in analyses of the macromolecular composition of gum arabic and fractions derived from it, and also the ability of such antibodies to distinquish between gum exudates harvested from a wide variety of *Acacia* species. The ability

to distinquish quickly and cheaply between gums harvested from various species of *Acacia* via such immunological tests could be of immense benefit to quality control agencies in the food industry since consignments of gum arabic are in some cases 'doctored' with potentially dangerous 'non-food grade' gums.

Future Prospects

As mentioned previously, the primary challenge that faces future basic scientific investigations in this field, concern the biosynthesis and macromolecular composition of the gum. Unfortunately, the 'traditional' sources of natural biopolymers such as gum arabic are subject to the vagaries of the weather, plant disease and local politics, all of which inevitably lead to variations in quality and supply problems. These problems would be greatly reduced, and the molecular synthesis and structure of the gum would become more ammenable to study, if it could be produced in large quantities using biotechnological methods such as plant cell culture. Using this technique the plant cells would be grown in large fermenters and the gum would be secreted into the liquid culture media, from which it would subsequently be extracted. Indeed such projects are already underway in a number of scientific institutions throughout the globe such as "The Cooperative Research Centre for Industrial Plant Biopolymers" based at the University of Melbourne, Australia.

Hopefully, these technologies once established will also be transferred to 'traditional' areas of gum production in developing countries, so that these countries do not suffer from a catastrophic loss of revenue once this technology becomes commonplace.

The eventual industrial scale production of gum arabic by such methods would thereby facilitate more rigorous studies of the molecular composition and biosynthesis of the gum. Once the molecular and biochemical basis of gummosis is better understood it may then be possible to genetically engineer the plant cells in such a way as to produce biopolymers with enhanced properties specific to their final end use. As yet this is still in the realms of "blue skies" research, but it is fascinating to speculate how this and other future technologies will further our understanding and knowledge of this unique and remarkably useful natural product.

References

Akiyama, K., S. Eda, and K. Kato, 1984, Gum arabic is a kind of arabinogalacatan - protein. *Agric. Biol. Chem*. 48: 235-237.

Anderson, D.M.W. and J.F. Stoddart, 1966, Studies on uronic acid materials. *Carbohydrate Research.* 2: 104-114.

Anderson, D.M.W., 1978, Chemotaxonomic aspects of the chemistry of Acacia gum exudates. *Kew Bulletin.* 32: 529-536.

Anderson, M.A., M.S. Sandrin, and A.E. Clarke, 1984, A high proportion of hybridomas raised to a plant extract secrete antibody to arabinose or galactose. *Plant Physiology*. 75: 1013 - 1016.

Baldwin, T.C., M. McCann, and K. Roberts, 1993, A novel hydroxyproline-deficient arabinogalactan protein secreted by suspension-cultured cells of *Daucus carota*. *Plant Physiology.* 103: 115-123.

Baldwin, T.C., P.E. Quah, and A.R. Menzies, 1999, A serotaxonomic study of *Acacia* gum exudates. *Phytochemistry.* 50: 599-606.

Bentham, G., 1875, Revision of the suborder Mimoseae. *The Transactions of the Linnean Society of London.* 30: 335- 668.

Brain, P., 1987, Immunology and phylogeny : a preliminary study of *Acacia . S. Afr. J . of Science*. 83: 422 - 427.

Churms, S.C. and A.M. Stephen, 1984, Structural studies of an arabinogalacatan protein from the gum exudate of *Acacia robusta*. *Carbohydrate Research*. 133: 105 - 123.

Connolly, S., J-C. Fenyo, and M.C. Vandevelde, 1988, Effect of a proteinase on the macromolecular distribution of *Acacia senegal* gum. *Carbohydrate polymers*. 8: 23 - 32.

El Tinay, A.H., K.A. Karamalla, H.M. El Amin, M.T.A. Shigida, and K.E.A. Ishag, 1979, Serotaxonomic studies on Sudan Acacias. *Journal of Experimental Botany.* 30: 607-615.

F.A.O., 1995, *Food and Nutrition Paper No 52*, Addendum 3 (Rome: FAO) 83.

Fincher, G.B., B.A. Stone, and A. Clarke, 1983, Arabinogalacatan-Proteins: Structure, Biosynthesis, and Function. *Ann. Rev. Plant Physiology*. 34: 47-70.

Heckman, J.W., B.T. Terhune, and D.T.A. Lamport, 1986, Characterisation of native and modified extensin monomers and oligomers by electron microscopy and gel filtration. *Plant Physiology*. 86: 848-856.

Islam, A.M., G.O. Phillips., A. Sljvo., M.J. Snowden, and P.A. Williams, 1997, A review of recent developments on the regulatory, structural and functional aspects of gum arabic. *Food Hydrocolloids.* 11: 493-505.

Joseleau, J-P, and G. Ullmann, 1990, Biochemical evidence for the site of formation of gum arabic in *Acacia senegal*. *Phytochemistry.* 29: 3401-3405.

Knox, J.P., 1992, Molecular probes for the plant cell surface. *Protoplasma.* 167: 1 - 9.

McNamee, B.F., E.D. O'Riordan, and M.C. O'Sullivan, 1998, Emulsification and microencapsulation properties of Gum Arabic. *J. Agricultural Food Chemistry.* 46: 4551-4555.

Menzies, A.R., M.E. Osman, G.O. Phillips, and P.A. Williams,1992, An enzyme linked immunosorbent assay (ELISA) for *Acacia senegal* gum exudate (gum arabic). In : *Gums and Stabilizers for the Food Industry.* 6: 507 - 512.

Menzies, A.R., M.E. Osman, A.A. Malik, and T.C. Baldwin, 1996, A comparision of the physicochemical and immunological properties of the plant gum exudates of *Acacia senegal* (gum arabic) and *Acacia seyal* (gum tahla). *Food additives and contaminants.* 13: 991-999.

Miskiel, F.J., (1990), PhD thesis. The Pennsylvania State University.

Miskiel, F.J. and J.H. Pazur, 1991, The preparation and characterisation of antibodies with specificity for the carbohydrate units of gum arabic and gum mesquite. *Carbohydrate Polymers.*16: 17 - 35.

Narita, K., 1985, Immunogenic specificity of gum arabic and genetic regulation of Lewis expression. *Jap. J. Med.* 39: 275 - 290.

Osman, M.E., P.A.Williams, A.R. Menzies, and G.O. Phillips, 1993a, Characterisation of commercial samples of gum arabic. *Journal of Agricultural and Food Chemistry.* 41: 71 - 77.

Osman, M.E., A.R. Menzies, P.A. Williams., G.O. Phillips, and T.C. Baldwin, 1993b, The molecular characterisation of the polysaccharide gum from *Acacia senegal*. *Carbohydrate Research.* 246: 303-318.

Osman, M.E., A.R. Menzies, B. Albo Martin, P.A. Williams, G.O. Phillips, and T.C. Baldwin, 1995, Characterisation of gum arabic fractions obtained by anion-exchange chromatography. *Phytochemistry*. 38 (2): 407 - 417.

Pazur, J.H. and S.A. Kelly – Delacourt, 1984, The identification of antigenic determinants by coupled inhibition agar diffusion method. *J. Immunol. Meth.* 75: 107- 116.

Pazur, J.H., S.A. Kelly-Delacourt, F.J. Miskiel, L. Burdett, and J.J. Docherty, 1986, The isolation of anti-gum antibodies by affinity chromatography. *J. Immunol. Meth.* 89: 19-25.

Pazur, J.H., F.J. Miskiel, T.F. Witham, and N. Marchetti, 1991, Affinity chromatography of two sets of isomeric antibodies having specificity for different oligosaccharide units of gum arabic. *Carbohydrate Research.* 214: 1 - 10.

Pedley, L., 1986, Derivation and dispersal of *Acacia* (Leguminosae) with particular reference to Australia, and *Racosperma*. *Bot. J. Linn. Soc.* 92: 219 - 254.

Qi, W., C. Fong, and D.T.A. Lamport, 1991, Gum arabic is a twisted hairy rope. *Plant Physiology*. 96: 848-855.

Randall, R.C., G.O. Phillips, and P.A. Williams, 1988, The role of the proteinaceous component on the emulsifying properties of gum arabic. *Food Hydrocolloids.* 2: 131-140.

Ross, J.H., 1979, A conspectus of the African *Acacia* species. *Mem. Bot. Surv. S. Afr.* 44: 5-9.

Stephen, A.M., 1987, Plant polysaccharides - how regular are they? *S.Afr. J. Chem.* 40: 89 - 99.

Vandewelde, M.C. and J.C. Fenyo, 1985, Macromolecular distribution of *Acacia senegal* gum arabic by size exclusion chromatography. *Carbohydrate Polymers* 5: 251-271.

Whistler, R.L. and J.N. BeMiller, 1993, *Industrial Gums*, 3rd Edition, Academic Press, San Diego, CA, USA.

Williams, P.A., A.R. Menzies, G.O. Phillips, and C.J. Smith, 1992, Specific identification and assessment of the emulsification properties of gum arabic by ELISA. In: *Food Safety and quality assurance : Applications of immunoassay systems*; Morgan MRA, Smith CJ, Williams Elsevier Science Publishers : Barking, Essex, UK p 385 - 392.