

THE GUM EXUDATES FROM *BRACHYSTEGIA* AND *JULBERNARDIA* SPECIES*

D. M. W. ANDERSON, P. C. BELL, M. C. L. GILL and C. W. YACOMENI

Chemistry Department, The University, Edinburgh EH9 3JJ, U.K.

(Received 22 February 1984)

Key Word Index—*Brachystegia*; *Julbernardia*; Caesalpinaceae, gum exudates; amino acids

Abstract—Analytical data are presented for the water-soluble gum exudates from *Brachystegia glaucescens*, *B. spiciformis*, and *Julbernardia globiflora*. They are acidic polysaccharides containing glucuronic acid, 4-O-methylglucuronic acid and galacturonic acid, together with galactose, minor amounts of arabinose, and relatively high proportions of rhamnose. The exudate from *B. glaucescens* is of particular interest in having high molecular weight, high intrinsic viscosity, and a high methoxyl content. The nitrogen content of all three gums is low, but amino acid analysis shows that proteinaceous components are involved, as in the gum exudates from other genera.

INTRODUCTION

Analytical data are available for the chemical composition of the gum exudates from many species of several genera within the Order Leguminales, particularly for the Mimosaceae. Attention has not been given in this respect to genera within the Caesalpinaceae, however, which is the source of several important industrial seed polysaccharides such as tara gum (*Caesalpinia spinosa*), locust bean (carob) gum (*Ceratonia siliqua*), and tamarind gum (*Tamarindus indica*). Although the heartwood of *Julbernardia globiflora* has been studied [2], little attention has been given to secondary metabolic products from *Julbernardia* and *Brachystegia* species, although they have been described as the sources of gums and resins by Greenway [3] and by Allen and Allen [4]. Data are now presented for the water-soluble gum exudates from *Brachystegia glaucescens*, *B. spiciformis* and *Julbernardia globiflora*.

RESULTS AND DISCUSSION

The analytical data obtained for the polysaccharide components are shown in Table 1; the amino acid compositions of the proteinaceous components are shown in Table 2. All three polysaccharides have features in common, such as low nitrogen contents; positive specific rotations; low arabinose and relatively high rhamnose contents; and a high acidity, with glucuronic acid, 4-O-methylglucuronic acid, and galacturonic acid all present. The presence of all three uronic acids is not unusual in exudates from genera within the Anacardiaceae, e.g. *Lannea* [5] and the Combretaceae [6], but genera within the Mimosaceae (*Acacia*, *Albizia*, *Prosopis*) customarily contain only glucuronic and 4-O-methylglucuronic acids. The ash contents of purified specimens of gum from the *Brachystegia* species are unusually high and, as aqueous solutions of these gums

are not strongly acidic (pH 5.5), it is clear that the majority of the carboxyl groups of the uronic acids in the gum molecules are present as salts and not in the free acid form. Comparison must be made with the *Acacia* gums, which have a strong buffering capacity because the gum molecules exist as the half-neutralized salts of the gum acid, i.e. approx 50% of the carboxyl groups are in the free acid form, 50% exist in the salt form. Gum arabic (*Acacia senegal* (L.) Willd.) thus typically has a uronic acid content of ca 15%, an ash content of ca 3% and aqueous solutions give pH 4.6. The gum from *Julbernardia globiflora*, with an ash content of 7%, has a higher proportion of free carboxyl groups than the *Brachystegia* spp. and hence its solutions are more acidic.

Brachystegia glaucescens gum is of interest in respect of its high MW, high intrinsic viscosity, and comparatively high methoxyl and rhamnose contents, which suggest that this gum could serve as an efficient emulsifier for oil/water systems. The comparatively low arabinose contents of the three gums studied are not unusual features in some gum exudates, e.g. from *Acacia falcata* and *A. calamifolia* [7], *A. implexa* and *A. cyclops* [1, 8].

The three exudates studied are undoubtedly water-soluble polysaccharides, although the amino acid compositions reported in Table 2 show that the minor amount of nitrogen found is associated with proteinaceous components, as has been established for the gum exudates from several genera [1, 9]. The two *Brachystegia* exudates show considerable similarities in their amino acid compositions, apart from the very high hydroxyproline content of *B. spiciformis* gum. In contrast, the three major amino acids (alanine, glutamic acid, serine) of *Julbernardia globiflora* gum are quite different from those for the *Brachystegia* spp.

Together with the specimens of gums from *B. glaucescens* and *B. spiciformis*, a dark red material collected from a tree suspected to be a cross between *B. glaucescens* and *B. spiciformis* was also examined and found to be a water-insoluble resin or kino, not a water-soluble gum exudate. Allen and Allen [4] observed that differentiation between *Brachystegia* spp. is at best fraught with difficulty; that

*Part 69 in the series "Studies of Uronic Acid Materials". For part 68, see ref [1].

Table 1. Analytical data for gum exudates from *Brachystegia glaucescens*, *B. spiciformis* and *Julbernardia globiflora*

	<i>Brachystegia glaucescens</i>	<i>Brachystegia spiciformis</i>	<i>Julbernardia globiflora</i>
Loss on drying, 105°C, %	11.1	13.3	14.7
Total ash, 550°C, %*	11.7	10.2	7.0
Nitrogen, %*	0.14	0.13	0.11
Hence protein (N × 6.25), %*	0.9	0.8	0.7
Methoxyl, %†	1.39	0.69	0.59
Sp. rotation, degrees†	+49	+88	+65
Intrinsic viscosity, ml/g†	46.9	19.8	15.3
Molecular weight, $\bar{M}_w \times 10^5$ †	32	0.42	7.4
Neut. equiv. (electrodialysis)†	475	468	520
Hence uronic anhydride, %‡	37	38	34
Sugar composition after hydrolysis			
4-O-Methylglucuronic acid§	8.5	4	3.5
Glucuronic acid	11.5	14	14
Galacturonic acid	17	20	16.5
Galactose	42	44	37
Arabinose	8	4	9
Rhamnose	13	14	20

* Corrected for moisture content.

† Corrected for moisture and protein content.

‡ If all acidity arises from uronic acids.

§ If all methoxyl groups located in this acid.

Table 2. The amino acid composition (residues per 1000 residues) of the proteinaceous components of the gums from *Brachystegia glaucescens*, *B. spiciformis* and *Julbernardia globiflora*

	<i>Brachystegia glaucescens</i>	<i>Brachystegia spiciformis</i>	<i>Julbernardia globiflora</i>
% nitrogen	0.14	0.13	0.11
Alanine	66	68	94
Arginine	17	3	28
Aspartic acid	92	78	66
Cystine	1	—	1
Glutamic acid	91	63	91
Glycine	61	36	63
Histidine	35	27	33
Hydroxyproline	70	195	38
Isoleucine	38	14	56
Leucine	60	20	83
Lysine	117	145	54
Methionine	8	—	12
Phenylalanine	25	6	41
Proline	119	140	74
Serine	60	60	88
Threonine	47	42	73
Tyrosine	38	47	30
Valine	59	57	78

Brachystegia gum is dark, of poor quality and low solubility; and that the bark yields high amounts of tannin. The fact that *Brachystegia* spp. can also yield water-soluble gum polysaccharides is therefore of interest, particularly because genera within the Caesalpiniaceae are

recorded [3] as being sources of copal and dammar type resins, e.g. from *Cassia*, *Copaifera*, *Daniella*, *Detarium*, *Dialium*, *Hymenaea* and *Trachylobium* spp. Greenway [3] also states that *B. spiciformis* gives a deep red gum, but that other genera within Caesalpiniaceae, e.g. *Erythrophleum* and *Delonix*, give water-soluble gum exudates of the gum arabic type. It is clear therefore that exudates from Caesalpiniaceae may be tannin-rich kinos, copal or dammar type resins, or water-soluble gum polysaccharides. The Mimosaceae yield either tannin-rich kinos (e.g. *Acacia mearnsii* and *A. decurrens*, which, however, may also yield water-soluble gum exudates), essentially tannin-free gum exudates (e.g. *A. senegal*, *A. laeta*), or gum exudates containing detectable amounts of tannins (*A. dealbata*). Studies of the factors and differing stimuli that lead to a tree of a certain species being able to yield either a tannin-rich kino or a water-soluble acidic polysaccharide—substances of completely different compound classes—would be of interest from the point of view of gaining insight into the mechanism of their biosynthesis.

EXPERIMENTAL

Origin of gum specimens. The gum exudates studied were collected by Mr. Trevor Gordon at Audley End Farm, Darwendale, Lomagundi District, Zimbabwe, in April 1971, and were sent for analysis by Mr. T. R. Müller, Curator, Botanic Garden, Salisbury. The voucher numbers are as follows: *B. glaucescens* Burt & Hutch, Gordon 180, SRGH; *B. glaucescens* × *B. spiciformis*, natural fertile hybrid (source of the dark red resin/kino), Gordon 181, SRGH; *J. globiflora* (Benth.) Troup. (syn. *Isobertinia globiflora* Hutch., ex Greenway, syn. *Berlinia emuni* Taub.), Gordon 182, SRGH. The gum specimen from *B. spiciformis* Benth. (syn. *B. randii* Bak.f.) was also collected

by Mr. Gordon (no voucher) and sent by Mr. Müller in April 1972 after exchanges of correspondence regarding the great differences between the water-soluble gums and the dark red insoluble resin/kino.

Immediately upon receipt, the water-soluble specimens were dissolved in water, filtered (muslin, then paper) to remove bark and other botanical debris, dialysed against tap water (48 hr) followed by distilled water (24 hr), and recovered by freeze-drying. The purified specimens were kept in a cool place in dark, air-tight jars during their extended examination during the period 1972–1978. Publication of the data obtained has been delayed because of the need to devote all attention to urgent toxicological studies of gum exudates [e.g. 10].

Analytical methods. The standard analytical methods for polysaccharides [7], uronic acids [5, 6] and amino acid components [1] have been described.

Acknowledgements—We thank Mr Gordon and Mr. Müller for the collection of specimens and for extensive correspondence

REFERENCES

1. Anderson, D. M. W., Gill, M. C. L., McNab, C. G. A. and Pinto, G. (1984) *Phytochemistry* **23**, 1923.
2. Pelter, A., Amenichi, P. I., Warren, R. and Harper, S. (1969) *J. Chem. Soc. C* 2572.
3. Greenway, P. J. (1941) *E. Afr. Agric. J.* 241.
4. Allen, O. N. and Allen, E. K. (1981) *The Leguminosae*. Macmillan, London.
5. Anderson, D. M. W. and Hendrie, A. (1970) *Phytochemistry* **9**, 1585.
6. Anderson, D. M. W. and Bell, P. C. (1977) *Carbohydr. Res.* **57**, 215.
7. Anderson, D. M. W., Bell, P. C. and McNab, C. G. A. (1972) *Phytochemistry* **11**, 1751.
8. Churms, S. C., Merrifield, E. H. and Stephen, A. M. (1981) *S. Afr. J. Chem.* **34**, 68.
9. Anderson, D. M. W., Hendrie, A. and Munro, A. C. (1972) *Phytochemistry* **11**, 733.
10. Eastwood, M. A., Brydon, W. G. and Anderson, D. M. W. (1984) *Toxicol. Letters* **21**, 73.