

## THE COMPOSITION OF ACACIA GUM EXUDATES FROM SPECIES OF THE SUBSERIES JULIFLORAE\*

D. M. W. ANDERSON and M. C. L. GILL

Department of Chemistry, The University, Edinburgh EH9 3JJ, Scotland

(Received 14 May 1974)

**Key Word Index**—*Acacia* spp.; Leguminosae; gum exudates; polysaccharides; chemotaxonomy.

**Abstract**—An analytical study has been made of gum specimens from *Acacia auriculiformis* (two specimens), *A. holosericea*, *A. mangium*, *A. leptostachya* and *A. pubifolia*, which belong to subseries Juliflorae of the Series Phyllodineae. These gums appear to be more proteinaceous, more acidic and more viscous, with higher methoxyl contents and higher molecular weights but with lower proportions of rhamnose and arabinose, than the majority of *Acacia* gums studied so far.

### INTRODUCTION

Although Bentham [2] placed 277 Australian species in his Series I (Phyllodineae) of the genus *Acacia*, Tindale [3] now considers the correct number to be at least 570. This large number of species is still best subdivided, according to the divisions proposed by Bentham [2], Taubert [4] and Maiden and Betche [5] into eight subseries viz. Alatae; Continuae; Pungentes; Calamiformes; Brunioideae; Uninerves; Plurinerves; and Juliflorae [6].

Relatively few species of the Series Phyllodineae have been examined chemically so far, although there have been studies of the distribution of amino acids [7] in some seeds (including one species in the Juliflorae), and of the flavonoid content of some heartwoods [8,9] (including 15 species in the Juliflorae). To date, the gum exudates from only 13 species [10] in the entire Series Phyllodineae have been studied; of these, one is in Bentham's subseries 4C, eleven species are in subseries 6F, and one in subseries 7F. This paper presents the first data available for species in subseries 8 (Juliflorae), which contains 151 species and is the second largest subseries in the Phyllodineae.

Botanically, the Juliflorae is considered [3] to be a most complex group of Phyllodinous wattles, which occur in both tropical and more temperate regions of Australia, Malaysia and the East Indies.

### RESULTS AND DISCUSSION

The analytical data obtained for the five species studied (seven specimens) are shown in Table 1. Although generalizations cannot be drawn for the characteristic properties of gums from the Juliflorae (151 species) in terms of the few species studied here, it is clear that it is quite distinct from the other subseries of phyllodinous *Acacias* studied so far.

The gums studied are of high MW. Both the phyllodinous and bipinnate *Acacias* studied previously [10,11] have been of much lower MW than the African species studied (for some typical values see ref. 12), but the values for *Acacia holosericea* ( $3.8 \times 10^6$ ) and *A. mangium* ( $3.2 \times 10^6$ ) exceed considerably the highest value (*A. adansonii*, *A. arabica*,  $2.3 \times 10^6$ ) reported previously. In agreement with earlier reports [11]; the use of 1% aq. sodium borohydride [13] does not appear to cause any extensive degradation during the dissolution process; indeed, the previously established tendency [11] for borohydride-solubilized material to

\* Part 47 in the Series "Studies of Uronic Acid Materials". For Part 46 see ref. 1.

Table 1. Analytical data for purified gum polysaccharides from *Acacia* species of the subseries *Juliflorae*

	<i>A. auriculiformis</i>			<i>A. holosericea</i>	<i>A. mangium</i>	<i>A. leptostachya</i>	<i>A. pubifolia</i>
	A	B	C				
Moisture (%)	13.3	8.4	12.0	9.0	16.2	16.1	13.4
Ash (%)*	4.8	4.5	5.3	5.1	5.4	5.8	3.4
Nitrogen (%)*	1.14	1.12	0.92	0.28	0.98	0.66	1.66
Hence protein (%) ( $N \times 6.25$ )*	7.12	7.0	5.75	1.75	6.12	4.12	10.4
Methoxyl (%)†	1.71	1.90	1.68	0.47	1.49	2.24	1.20
$[\alpha]_D$ in water (degrees)†	+18.6	+15.6	+15.8	+2.9	+36.4	+58	-58
Intrinsic viscosity $[\eta]$ ( $\text{ml g}^{-1}$ )*	22.0	22.6	25.0	19.0	27.7	16.7	25.6
Molecular weight ( $\text{MW} \times 10^6$ )	1.9	2.3	3.0	3.8	3.2	1.35	2.44
Equivalent weight†	590	620	635	1010	545	475	680
Hence uronic anhydride (%)‡	29.7	28.4	27.7	17.3	32.2	37.0	25.9
Sugar composition after hydrolysis							
4-O-Methylglucuronic acid§	10.2	11.4	10.1	2.8	9.0	13.4	7.2
Glucuronic acid	19.5	17.0	17.6	14.5	23.2	23.6	18.7
Galactose	58	58	59	56	56	54	46
Arabinose	9	10	8	20	10	7	25
Rhamnose	3	4	5	6	2	2	3

\* 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.

be of higher MW than the corresponding water-soluble fraction is confirmed here (*A. auriculiformis* sample C).

In addition to high MW, the Juliflorae species studied give gum solutions of high intrinsic viscosity. The value given by *Acacia auriculiformis* equals the highest values reported previously (cf. *A. laeta* [14], *A. parramattensis* [11], and *A. tortilis* subsp. *heteracantha* [15]. *A. mangium*  $[\eta] = 27.7$   $\text{ml/g}$ ] must now be regarded as the most viscous of the *Acacia* gums studied so far.

The methoxyl contents reported here are also high. The value for *A. leptostachya* (2.24%) closely approaches the highest value reported [16] to date (*A. giraffae*, 2.40%) and with the exception of *A. holosericea*, the methoxyl contents of the other species studied here all exceed the values for *A. nilotica* [17] and *A. parramattensis* [11] which, previously, came second only to *A. giraffae*.

With the exception of *A. holosericea* and *A. leptostachya* gums the nitrogen contents of the Juliflorae species studied tend to be high, with *A. pubifolia* (1.66%) now exceeding the highest value reported [11] previously (*A. parramattensis*, 1.55%). Attention must also be drawn to the unusually high acidity of the Juliflorae species studied. With the exception of *A. holosericea*, the other species studied here have considerably higher uronic acid contents than *A. cyanophylla* (uronic

acid 24%), which, for nearly 20 years, has been the most acidic *Acacia* gum known [18].

Although the tendencies toward low rhamnose content and high galactose/arabinose ratios typical of the other subseries of phyllodinous wattles [10] are easily recognizable, it is already apparent that the botanical complexity of the Juliflorae is reflected in the wide ranges of values shown in their various analytical parameters for their gums.

## EXPERIMENTAL

*Origin of gum specimens.* Gum from *Acacia auriculiformis* A. Cunn. ex Benth. (Bentham No. 271) was collected by Mr. J. F. U. Zieck on 23 July 1973 from a bushy low-branched tree (about 4-yr-old, height 8 m, dbh 10 cm, with a smooth to cracked greyish bark, with flowers and fruit present) growing on black cracking clay soil of the Savannah belt in the office garden of the Forest Products Research Centre, Frangipanni Road, Port Moresby, Papua, New Guinea. Botanical voucher specimens from this tree have been kindly authenticated by Dr. M. D. Tindale as NSW 107339. This gum sample was soluble in cold water, and is shown as sample A in Table 1. A second sample of *A. auriculiformis* gum was collected on 7 May 1973 from the same location as sample A, but as a bulk sample from about 30 bushy low multiple-branched trees (age 3 yr, average height 8 m, dbh 10 cm) planted closely together to form a hedge. The exudation appeared to have formed on unhealthy trees that had probably been attacked by insects or some species of fungus. The water-soluble material from this second sample is shown as sample B in Table 1; the water-insoluble material present dissolved on the addition of a very small amount of  $\text{NaBH}_4$  [13] and gave sample C after dialysis, filtration, and freeze-drying. Gum from *Acacia holosericea* A. Cunn. ex G.

Don (Bentham No. 274) was collected by Mr. J. F. U. Zieck on 23 July 1973 from a crooked, low-forked tree (about 4-yr-old, height 8 m, dbh 11 cm, with a dark-coloured smooth to cracked bark, and flowers, young and mature fruit present) growing on black cracking clay soil of the Savannah belt in the office garden of the Forest Products Research Centre, Frangipanni Road, Port Moresby. Botanical voucher specimens from this tree have been authenticated by Dr. M. D. Tindale as NSW 107338. Gum from *Acacia mangium* Willd. (Bentham No. 275) was collected from a single tree at Ulu Kukut on 16 March 1971 by the Plantation Officer at Sandakan, Sabah, Malaysia. Gum from *A. leptostachya* Benth. (Bentham No. 256) was collected on 11 Aug 1969 from a shrub, 2 m high, growing on acidic volcanic outcrops 39 miles west of Chapter's Towers, Hughenden, Queensland, by Mr. W. R. Birch of the School of Biological Sciences, University College of Pimlico, Townsville, Queensland: botanical vouchers were authenticated by Mr. L. Pedley, Research Botanist at Brisbane Botanic Museum and Herbarium, as R.C. Correll E74. Gum from *Acacia pubifolia* Pedley was collected by Dr. M. Tindale on 5 Jan 1969 from a tree, 5 m high, with silvery foliage and black iron-bark, on a granite hillside at Wyberba, 4 miles south of Ballandean, S.E. Queensland: the reference voucher is NSW 102606.

*Preparation of samples for analysis.* *Acacia auriculiformis* gum sample A and *A. holosericea* gum dissolved slowly in cold H<sub>2</sub>O to give clear, colorless solutions. After dialysis against tap H<sub>2</sub>O for 24 hr and then against distilled H<sub>2</sub>O for 2 × 24 hr, the gum solutions were filtered through Whatman No. 41, then No. 1, and finally No. 42 papers, and freeze-dried.

*Acacia auriculiformis* gum sample B contained some water-insoluble material; this dispersed on the addition of a small amount of NaBH<sub>4</sub>, and the material recovered after dialysis and freeze-drying is shown as sample C in Table 1. *Acacia mangium*, *A. leptostachya* and *A. pubifolia* gums required the addition of traces of dil. alkali and NaBH<sub>4</sub> [13] to effect complete dissolution; although these gums were partially soluble in cold water, the amounts of gum available were very small and it was decided not to examine the water-soluble and water-insoluble fractions separately. After recovery as the freeze-dried solid, *A. mangium* gum gave a clear, colorless solution; the solutions from *A. leptostachya* and *A. pubifolia* gums were respectively orange-yellow and pale yellow in colour.

*Analytical methods.* The standard analytical methods used have been described [10].

*Acknowledgements*—We gratefully acknowledge financial support from Rowntree-Mackintosh Ltd. (York) and Laing-National Ltd. (Manchester). We thank those mentioned above for collection and authentication of the various gum samples.

## REFERENCES

1. Anderson, D. M. W., Bell, P. C. and Millar, J. R. A. (1974) *Phytochemistry* **13**, 2189.
2. Bentham, G. (1875) *Trans. Linn. Soc. (London)* **30**, 444.
3. Tindale, M. D., Royal Botanic Gardens, Sydney, private communication.
4. Taubert, P. (1894) in *Die natürlichen Pflanzenfamilien* (Engler, A. and Prantl, K. eds.), Engelmann, Leipzig.
5. Maiden, J. H. and Betche, E. (1916) *A Census of New South Wales Plants*, p. 89. Government Printer, Sydney.
6. Anderson, D. M. W. and Dea, I. C. M. (1969) *Phytochemistry* **8**, 167.
7. Seneviratne, A. S. and Fowden, L. (1968) *Phytochemistry* **7**, 1039.
8. Tindale, M. D. and Roux, D. G. (1969) *Phytochemistry* **8**, 1713.
9. Tindale, M. D. and Roux, D. G. (1974) *Phytochemistry* **13**, 829.
10. Anderson, D. M. W., Bell, P. C. and McNab, C. G. A. (1972) *Phytochemistry* **11**, 1751.
11. Anderson, D. M. W., Bell, P. C. and McNab, C. G. A. (1971) *Carbohydr. Res.* **20**, 269.
12. Anderson, D. M. W. and Dea, I. C. M. (1969) *Carbohydr. Res.* **10**, 161.
13. Anderson, D. M. W., Bell, P. C. and King, H. A. R. (1972) *Carbohydr. Res.* **22**, 453.
14. Anderson, D. M. W., Dea, I. C. M. and Smith, R. N. (1968) *Carbohydr. Res.* **7**, 320.
15. Anderson, D. M. W. and Bell, P. C. (1974) *Phytochemistry* **13**, 875.
16. Anderson, D. M. W., Cree, G. M., Herbich, M. A., Karamalla, K. A. and Stoddart, J. F. (1964) *Talanta* **11**, 1559.
17. Anderson, D. M. W. and Karamalla, K. A. (1966) *Carbohydr. Res.* **2**, 403.
18. Charlson, A. J., Nunn, J. R. and Stephen, A. M. (1955) *J. Chem. Soc.* 269.