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SHORT COMMUNICATION

ANALYSIS OF SIX *ACACIA* GUM EXUDATES OF THE SERIES PHYLLODINEAE*

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Abstract—Gum specimens from *Acacia calamifolia*, *A. difformis*, *A. falcata*, *A. mabellae*, *A. retinodes*, and *A. rubida* have been analysed; the first named belongs to Bentham's Series 1, subseries 4C (*Calamiformes Uninerves*) and the others are in Bentham's Series 1, subseries 6F (*Uninerves Racemosae*). This group of gum exudates, of which *A. rubida* is the most divergent, is characterized by a low rhamnose content (<2%), low acidity, low intrinsic viscosity, and a high galactose/arabinose ratio, which, for *A. calamifolia* and *A. falcata*, is higher than for any other species studied so far. Although these gum species have good solubility, their solutions are of low viscosity and are dark in colour; they are unlikely to be of commercial importance. In the light of the chemical data now available for *Acacia* gum exudates, *A. cyanophylla* appears to be a highly anomalous species within the Phyllodineae.

INTRODUCTION

ALTHOUGH Bentham[2] placed 277 Australian species in his Series 1 (Phyllodineae) of the genus *Acacia*, Tindale[3] now believes the correct number to be 625. Apart from some studies of the distribution of amino acids in the seeds[4] and of the flavonoid content[5] of heartwoods and barks, relatively few species of this Series have been studied chemically in any respect so far. In particular, there have been studies of the gum exudates from only 6 of the Phyllodineae, viz. *A. cyanophylla*,[6,7] *A. harpophylla*,[8] *A. microbotrya*,[8] *A. penninervis*,[8] *A. podalyriifolia*,[7] and *A. pycnantha*,[9–11] all of which were placed by Bentham[2] in Series 1, sub-series 6F (Uninerves Racemosae) with the exception of *A. harpophylla* (Series 1, sub-series 7F, Plurinerves Nervosae).

This paper presents data for gum exudates from a further 6 species of the Phyllodineae. Of these, five are placed in Bentham's Series 1, Sub-series 6F (*Acacia difformis*, *A. falcata*, *A. mabellae*, *A. retinodes*, and *A. rubida*) and one species, *A. calamifolia*, is placed in Series 1, sub-series 4C (Calamiformes Uninerves).

RESULTS AND DISCUSSION

The analytical data obtained for the six species are shown in Table 1. Although there are a few divergences, such as the specific rotation of *A. rubida* (−25°), the relatively high

* Part XLI in the series "Studies of Uronic Acid Materials". For Part XL see ref. 1.

[1] D. M. W. ANDERSON and A. HENDRIE, *Carbohyd. Res.*, in press.
[2] G. BENTHAM, *Trans. Linn. Soc.* (*London*) **30**, 444 (1875).
[3] M. D. TINDALE, private communication.
[4] A. S. SENEVIRATNE and L. FOWDEN, *Phytochemistry*, **7**, 1039 (1968).
[5] M. D. TINDALE and D. G. ROUX, *Phytochem.* **8**, 1713 (1969).
[6] A. J. CHARLSON, J. R. NUNN and A. M. STEPHEN, *J. Chem. Soc.* 269 (1955).
[7] M. KAPLAN and A. M. STEPHEN, *Tetrahedron* 193 (1967).
[8] A. T. PROSZYNSKI, A. J. MICHELL and C. M. STEWART, C.S.I.R.O. (Australia) Division of Forest Products, Technological Paper No. 38 (1965).
[9] E. L. HIRST and A. S. PERLIN, *J. Chem. Soc.* 2622 (1954).
[10] G. O. ASPINALL, E. L. HIRST and A. NICOLSON, *J. Chem. Soc.* 1697 (1959).
[11] D. M. W. ANDERSON and G. M. CREE, *Carbohyd. Res.* **6**, 214 (1968).

MW (730 000) and uronic anhydride content (10%) of *A. retinodes*, the N content and intrinsic viscosity of *A. rubida* and *A. retinodes*, and the galactose–arabinose ratio (2:1) of *A. rubida*, the analytical parameters for the gum exudates from these species are remarkably similar, particularly when it is appreciated that the specimens studied were collected in such widely differing geographical locations as Australia, Scotland and Uruguay. There is evidence in the literature[12] that the exudates from *Acacia* species may vary with geography and, to obtain further evidence on this point, we have also examined gum specimens from two other species of the Phyllodineae, *A. pycnantha* and *A. cyanophylla*. The composition and properties of an African specimen (supplied by the Botanical Research Institute, Pretoria) and of a Western Australian specimen (supplied the Curator, Perth Botanic Gardens) of *A. cyanophylla* gum did not differ significantly from the values published[6] for a South African sample. A similar conclusion was reached when analytical data for two specimens of *A. pycnantha* gum from New South Wales (supplied by Mr. R. D. Croll) were compared with the values given in the literature[9] for a South Australian sample.

There is virtually a complete correlation between taxonomy and the analytical data for the exudates from *A. calamifolia*, *A. difformis*, *A. falcata*, and *A. mabellae*. These species form a distinct group in terms of their exudate content. The galactose–arabinose ratio in *A. calamifolia* and *A. falcata* is greater than in any *Acacia* gum exudate studied so far.[13] It would be of interest to ascertain if these species differ significantly in structure-type from the model established by Stephen *et al.*[7,14,15] for the gum from *A. elata* (syn. *A. terminalis*), a member of the Botryocephalae that gives an exudate which appears to be essentially an arabinogalactan.

So far as we are aware, the only previous reference to *A. difformis* gum was published in 1897 by Baker,[16] who commented that it was one of the few Australia *Acacias* to exude a soluble form of gum. The brief chemical details quoted[16] dealt only with the solubility of the gum and dark colour of its solutions, and with the negative optical rotation (no value specified), low ash content, and formation of large amounts of mucic and oxalic acids on treatment with nitric acid. Baker concluded[16] that *A. difformis* gum would be of commercial value if obtainable in quantity, but he classified it "with the second-class wattle gums, of which that from *A. pycnantha* is a type". Our results are in agreement with these views.

Baker[16] stated that Australian *Acacias* often give optically inactive gum exudates, but this is in error, and must have arisen from a lack of sensitivity in the polarimeter available to him. Although the majority of Australian *Acacia* species studied[13] by us so far have specific rotations that fall in the range $-10°$ to $+10°$, several species of the Botryocephalae Series have strongly negative rotations, e.g. *A. deanei* ($-66°$), *A. parramattensis* ($-49°$), *A. parvipinnula* ($-54°$) and *A. trachyphloia* ($-57°$).

Only two [*A. pycnantha* (Bentham No. 131) and *A. cyanophylla* (Bentham No. 130)] of the species in the Phyllodineae Series examined previously by other authors were studied in sufficient detail to permit chemical comparison with the species at present under study. From a chemotaxonomic[17] point of view, it is becoming increasingly obvious that the most anomalous *Acacia* species studied so far are *A. pycnantha* and *A. cyanophylla*. No two species differ so widely in terms of their exudates, yet Bentham placed *A. pycnantha* next

[12] J. F. CAIUS and K. S. RADHA, *J. Bombay Nat. Hist. Soc.* **41**, 261 (1939).
[13] D. M. W. ANDERSON, P. C. BELL and C. G. A. MCNAB, *Carbohyd. Res.* **20**, 269 (1971).
[14] P. I. BEKKER, A. M. STEPHEN and G. R. WOOLARD, *Tetrahedron* **24**, 6967 (1968).
[15] P. I. BEKKER, S. C. CHURMS, A. M. STEPHEN and G. R. WOOLARD, *Tetrahedron* 25 (1969) 3359.
[16] R. T. BAKER, *Proc. Linn. Soc., N.S.W.* **22**, 153 (1897).
[17] D. M. W. ANDERSON and I. C. M. DEA, *Phytochem.* **8**, 167 (1969).

TABLE 1. ANALYTICAL DATA FOR PURIFIED GUM POLYSACCHARIDES FROM ACACIA SPECIES OF THE PHYLLODINEAE SERIES

	A. calamifolia	*A. difformis*	*A. falcata*	*A. mabellae*	*A. retinodes*	*A. rubida*
Recovery from crude gum (%)	82	93	92	70	81	88
Moisture (%)	12·9	10·2	9·8	11·5	11·4	12·6
Ash (%)*	2·0	1·5	1·8	1·7	2·1	2·0
Nitrogen (%)*	0·26	0·28	0·21	0·23	0·48	0·50
Hence protein (%) (N × 6·25)*	1·6	1·8	1·3	1·4	3·0	3·1
Methoxyl (%)†	0·87	0·64	0·49	0·41	0·41	0·25
$[\alpha]_D$, in water (degrees)†	+4	−5	+9	+4	+1	−25
$[\alpha]_D$, in 7M urea (degrees)†	+8	−6	+9	+6	+3	−18
Intrinsic viscosity [n] (ml g^{-1})*	5·8	6·2	5·1	5·8	9·5	9·7
Molecular weight (MW × 10^4)	24	4·7	7·9	12	73	32
Equivalent weight†	2430	3420	2290	2870	1770	3010
Hence uronic anhydride (%)†‡	7	5	8	6	10	6
Sugar composition† after hydrolysis						
4-*O*-Methylglucuronic acid§	5	3·5	3	2·5	2·5	1·5
Glucuronic acid	2	1·5	5	3·5	7·5	4·5
Galactose	84	75	85	76	76	63
Arabinose	8	19	7	17	12	30
Rhamnose	1	1	Trace	1	2	1

* 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.

to *A. cyanophylla* in his Series, and Tindale[3] has recently advised us that "*A. pycnantha* appears to be quite closely related morphologically to *A. cyanophylla*, although a noteworthy difference is that the flowerheads of the former have 50–100 flowers in each capitulum, whereas in the latter there are about 40". It is therefore surprising that the gum exudates of these species should differ so markedly. According to Hirst and Perlin,[9] *A. pycnantha* has $[\alpha]_D$ −8°, and glucuronic acid–galactose–arabinose–rhamnose = 1–5:65:27:1–2; for *A. cyanophylla*[6] the corresponding sugar ratios are 24:46:8:21, and $[\alpha]_D$ −20°. At the present time, the gum from *A. cyanophylla* has the highest contents of glucuronic acid and rhamnose recorded for the *Acacia* genus; we have verified that the values quoted in the literature for these species are substantially correct, and have investigated[18] their MWs [*A. pycnantha*, MW = 60 000; *A. cyanophylla*, MW = 470 000 (South African), 610 000 Western Australian)]. In the light of the analytical data now available for the Phyllodineae Series, there seems little doubt that *A. pycnantha* gum, which remains the least acidic of all *Acacia* spp. studied to date,[13] is much more typical of this Series of *Acacias* than *A. cyanophylla*.

Recently it was suggested[19] that comparisons of the specific rotations of polysaccharides in water and in 7 M urea solution provide a new parameter for the conformational analysis of polysaccharide chains. The optical rotation in water is considered to be the resultant of the contributions from the primary and tertiary structures; the latter exists in aqueous

[18] D. M. W. ANDERSON and I. C. M. DEA, *Carbohyd. Res.* **10**, 161 (1969).
[19] S. HIRANO, *Life Sci.* **10**, 151 (1971).

solution, but not in concentrated urea or guanidine solutions. The values obtained for the present species are shown in Table 1. Of these, only *A. rubida*, which contains much the highest proportion of arabinose, appears to have significant contributions from tertiary structure to its specific rotation in aqueous solution.

EXPERIMENTAL

Origins of gum specimens. Gum from *Acacia calamifolia* Sweet ex Lindl. (Bentham No. 57) was collected by Mr. R. D. Croll from a bush 10 ft high, 10 miles west of Rankin's Springs, New South Wales, on 24 January 1970. Gum from *A. difformis* R. T. Bak. was collected by Mr. Croll from a bush infested with beetle-borers at Rankin's Springs, New South Wales, on 23 January 1970. Reference vouchers for both these species have been verified and are lodged in the Herbarium, Royal Botanic Gardens, Kew. Gum samples from *A. falcata* Willd. (Bentham No. 123) were obtained on 15 September 1970 and 25 June 1971, from pruning wounds on a large specimen of this species growing in the tropical house, Royal Botanic Gardens, Edinburgh. Gum from *A. mabellae* Maiden was collected by Mr. J. Pickard at The Vines, 8 miles SSW of Sassafras, New South Wales, on 13 June 1970 (Voucher No. NSW 105156). The gum exudate from *A. retinodes* Schlechtd. (Bentham No. 126) was collected by Dr. P. Moyna at Montevideo, Uruguay, in May 1970. Gum from *A. rubida* A. Cunn. was collected by Mr. A. Rodd at Burbong, New South Wales, on 25 April 1968 (No. NSW 99697).

Preparation of samples for analysis. All of the specimens dissolved slowly in cold water. After dialysis against tap water for 24 hr and then against distilled water for 2 × 24 hr, the gum solutions were filtered through Whatman No. 42 then No. 1 papers, and freeze dried. The yields recovered are recorded in Table 1.

Analytical methods. The standard analytical methods have been described[21,22] in earlier parts of this Series, with the following exceptions. Equivalent weights were found by potentiometric titration (to pH 7) of weighed amounts of gum (50–100 mg) that had been exhaustively electrodialysed. In the calculation of MW from light-scattering data, the mean value of dn/dc (0·146), established[18] in a survey of *Acacia* species was used.

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[20] D. M. W. ANDERSON and A. C. MUNRO, *Carbohyd. Res.* **11**, 43 (1969).
[21] D. M. W. ANDERSON and A. HENDRIE, *Phytochem.* **9**, 1585 (1970).

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