Carbohydrate Polymers 2 (1982) 19–24

GUM EXUDATES FROM THE GENUS *GREVILLEA* (PROTEACEAE)†

D. M. W. ANDERSON & G. LEON DE PINTO‡

Department of Chemistry, University of Edinburgh, Edinburgh EH9 3JJ, UK

(Received: 8 June, 1981)

ABSTRACT

Analytical data are presented for gum specimens from Grevillea agrifolia, G. candelabroides, G. robusta, G. striata, *and* G. wickhamii *(two specimens), and brief botanical details of this large, complex genus are given. The gum exudates, which are of high molecular weight, show good solubility and give solutions that are much more viscous than any of the* Acacia *exudates studied so far; they may therefore be of industrial interest.*

INTRODUCTION

It is now widely acknowledged that urgent attention must be given to the increased use of solar energy, the utilisation of arid and under-developed regions, and the promotion of renewable annual crop resources. Recent publications have focused attention on these problems (US National Academy of Sciences, 1979, 1980); gum-bearing trees have an important part to play in their solution. The genus *Grevillea* has not been studied extensively so far; it is known to grow rapidly and to have several important properties (US National Academy of Sciences, 1980) and one of its more common and widely distributed species, *G. robusta*, is known to yield a gum exudate (Anderson & Harris, 1952; Stephen & van der Bijl, 1975). This paper presents data which show that the gum exudates from several other *Grevillea* species are unusually viscous and have properties that may be of interest for future industrial applications.

BOTANICAL SYSTEMATICS

The Proteaceae comprise evergreen trees, shrubs, undershrubs and, rarely, perennial herbs. Robert Brown (1811) was the first to divide this interesting family, on the basis

† Part of a series of studies of uronic acid materials (see also Anderson & Pinto (1980)).
‡ Present address: Chemistry Department, University of Zulia, Maracaibo, Venezuela.

Carbohydrate Polymers 0144-8617/82/0002-0019/$02.75

of the fruit characteristics, into two sub-families; Nucamentaceae (fruits indehiscent) with four tribes, and Folliculares (fruits dehiscent) with three tribes. Engler (1894) changed these names into Persoonioideae and Grevilleoideae respectively, but his use of the name Persoonioideae was subsequently altered to Proteoideae in accordance with the international rules of botanical nomenclature, because *Protea* (136 species) is the largest genus of this sub-family; the name Grevilleoideae has been retained as *Grevillea* (235 species) is its largest genus.

Bentham (1870) and Engler (1894) accepted Brown's seven tribes but Engler (1894) added another taxonomic criterion for distinguishing the sub-families, viz. the occurrence of flowers singly in bract axils in the Proteoideae and in pairs in the axils of common bracts in the Grevilleoideae. This classification of the Proteaceae was revised and expanded by Venkata Rao (1971) and by Johnson & Briggs (1975); as a result, 75 genera were recognised in place of 62 and additional sub-families, tribes, and sub-tribes were proposed. The essential features, with regard to the genus *Grevillea*, of the current classification by Johnson & Briggs (1975) are given in Fig. 1.

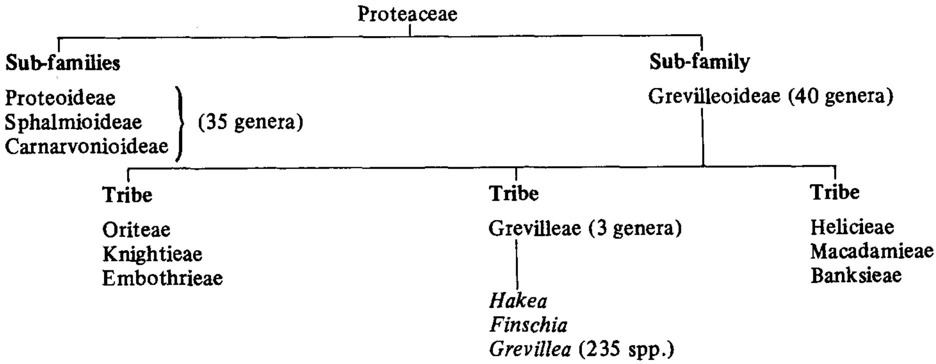

Fig. 1. The family Proteaceae (order Proteales).

The Proteaceae are distributed widely in Africa, Madagascar, Australasia, the Western Pacific and East Asia, and Central and South America. *Grevillea* species (particularly *G. robusta*, the silk oak) are decorative species that have been extensively introduced throughout the world, including temperate regions.

Chemical analysis offers one of the possible approaches to systematic taxonomy, the most useful materials being the secondary products such as tannins, essential oils, alkaloids, glycosides, resins and water-soluble gum exudates. Unfortunately the data available for *Grevillea* are much less extensive than those available for other important genera, such as *Acacia.* At present the data for *Grevillea* appears to be restricted to that for one gum exudate (Anderson & Harris, 1952; Stephen & van der Bijl, 1975), data for the phenolic components of some South African genera (van Oudtshoorn, 1963), and data for the fatty acids of the seed oils in 26 species spanning 10 of the present tribes (Vickery, 1971); such studies tend to give broad support for the current classification.

To provide more data for chemotaxonomic purposes and to stimulate interest in the future role that may be played by *Grevillea* in land development and re-afforestation schemes, a detailed analytical study has been made of the gum exudates from *Grevillea agrifolia*, *G. candelabroides*, *G. robusta*, *G. striata* and *G. wickhamii* (two specimens).

EXPERIMENTAL

Source of Materials

Gum from *Grevillea robusta* Cunn. ex R. Br. was obtained in 1972 from pruning wounds on a tree growing in the Temperate House, Royal Botanic Garden, Edinburgh.

Gum from *Grevillea candelabroides* C. A. Gardn. was collected on 11 June 1976 by Mr D. J. McGillivray at 29° 15′S, 115° 29′E, 9 km from Mingenew on the road to Three Springs, Western Australia.

Gum from *Grevillea striata* was collected by Mr J. R. Maconochie on 22 April 1975, at Alice Springs, Northern Territory, Australia.

Gum from *Grevillea wickhamii* (samples 1 & 2) was collected by Mr J. R. Maconochie at Napperby Station, Northern Territory, Australia, on 8 May 1975 and 21 June 1976, respectively.

Gum from *Grevillea agrifolia* A. Cunn. ex R. Br. was collected by Mr D. J. McGillivray on 23 June 1978 at 16° 08′S, 125° 30′E, at Gibb river crossing on the road to River Station, Western Australia.

On receipt, gum specimens were kept in lump form in tightly sealed jars in darkness. They were reduced to a fine powder immediately prior to analysis.

Purification of Gum Samples

All the gum samples dissolved readily in cold water except sample 2 from *G. wickhamii* which required mild treatment with sodium borohydride (Anderson *et al*., 1972) for two days to facilitate dissolution. The solutions were passed through Whatman No. 42 and No. 1 filter papers and dialysed against running tap water for two days (four days for the sample treated with borohydride); the gum was recovered by freeze-drying.

Analytical Methods

The standard analytical methods described by Anderson *et al.* (1972) were used with the exception that nitrogen contents were determined with a Perkin-Elmer Model 240 Autoanalyser.

Sugar Analyses

Chromatography was carried out on Whatman No. 1 and 3MM papers with the solvent systems described for neutral and acid sugars by Anderson & Munro (1969). The separations of both neutral and acidic sugars found to be necessary were achieved by the procedure described by Anderson *et al.* (1974). In addition, sugars were estimated by gas-liquid chromatography of their alditol acetates on a 3% ECNSS-M column at 190°C (Sawardeker *et al.*, 1965).

The *Grevillea* exudates were found to be much more resistant to acid hydrolysis than those of the *Acacia* genus. For complete hydrolysis of neutral sugars, samples (50 mg) were hydrolysed with 0·5 M sulphuric acid for 24 h on a boiling water-bath; for acidic sugars, treatment with 1 M sulphuric acid for 12 h was necessary. After hydrolysis, the solutions were cooled, neutralised ($BaCO_3$), deionised (Amberlite IR-120 resin, H^+ form) and concentrated to syrups on a rotary evaporator at reduced pressure at *c.* 30°C.

RESULTS

The analytical data obtained are shown in Table 1.

DISCUSSION

Of the *Grevillea* species studied, some reserve may be necessary in considering the data for *G. robusta* gum; the tree involved was growing in artificial conditions under glass in Scotland whereas the trees of the other species involved were growing under natural conditions in Northern and Western Australia. Nevertheless, the gum from a specimen of *Acacia falcata* growing under glass in Scotland (Anderson *et al.*, 1972) was not atypical when compared with the gum from closely related species growing in Australia.

Of the general analytical parameters, the nitrogen contents of these *Grevillea* spp. tend to be low; as the nitrogen content of a plant gum tends to reflect the protein content directly, *Grevillea* gums may be expected to show little allergenicity when evaluated in due course. This may be an important property in the future if assessment for allergenicity becomes a regulatory requirement for foodstuffs additives. The exceptionally high intrinsic viscosity of several of these *Grevillea* gums may be of industrial importance: of the water-soluble gum exudates, the more common *Acacia* spp. comprising commercial gum arabic have relatively low limiting viscosity numbers in the range 10–20. Previously, the most viscous water-soluble gum exudates were from the genera *Combretum* and *Terminalia* (Anderson, 1978), the highest value (312 ml g^{-1}) for the intrinsic viscosity being given by the gum exudate from *C. collinum.* The values for the gums from *Grevillea candelabroides*, *G. wickhamii*

TABLE 1
Analytical Data for the Gums from *Grevillea* Species

	G. robusta	*G. cande-labroides*	*G. striata*	*G. wickhamii* (1)	*G. wickhamii* (2)	*G. agrifolia*
Moisture, %	11·0	15·5	7·8	12·4	6·8	11·4
Ash, %	5·8	3·3	1·4	2·6	3·4	2·9
Nitrogen, %[a]	0·20	0·04	0·24	0·07	nil	0·10
Hence protein, %[a]	1·3	0·25	1·5	0·43	–	0·62
Methoxyl, %[b]	0·68	1·0	0·50	0·77	0·23	0·08
Specific rotation,[b] degrees	−24	+10	−71	−36	−33	−33
Intrinsic viscosity,[a] ml/g	89	521	26	575	356	312
Molecular weight,[a] $\overline{Mw} \times 10^5$	88	8·6	8·8	23	36	27
Equivalent weight	1296	1030	1921	2000	3645	1957
Hence uronic acid, %[b, c]	13·6	17·0	9·0	8·8	4·8	9·0
Sugar composition[b] after hydrolysis:						
4-*O*-Methylglucuronic acid[d]	4·1	6·0	3·0	4·6	1·3	0·5
Glucuronic acid + galacturonic acid	9·5	11·0	6·0	4·2	3·5	8·5
Galactose	42	56	46	50	53	40
Mannose	4	2	trace	trace	trace	trace
Arabinose	36	16	29	27	23	32
Xylose	–	7	9	14	19	19
Rhamnose	4	trace	7·0	–	–	–

[a] Corrected for moisture content.
[b] Corrected for moisture, ash and protein content.
[c] If all acidity arises from uronic acids.
[d] If all methoxyl groups are located in this acid.

and *G. agrifolia* now exceed that value considerably, although the molecular weight of *C. collinum* ($11 \cdot 6 \times 10^6$) remains the highest yet recorded for a gum exudate. The methoxyl contents of the *Grevillea* gums, except for *G. agrifolia* gum, fall within the normal range for gum exudates (e.g. *Acacia* spp.) that act as good emulsifiers. The range of equivalent weights given by exhaustively electrodialysed samples of the *Grevillea* gums studied is also similar to that shown by the more common acacias (e.g. *A. senegal*, *A. seyal*), but the gums from *Grevillea* spp. have an advantage over those from *Acacia* spp. in being much more resistant to acid hydrolysis.

Thus the *Grevillea* species studied give extremely viscous water-soluble gums which have several other interesting properties relevant to industrial applications. Because of their widespread geographical distribution, tolerance to a wide range of climates, and other commercial/ecological properties (US National Academy of Sciences, 1980) to which must now be added their gum-producing potential, it seems that the properties of the gums from further *Grevillea* spp. should be studied. Consideration should also be given to other genera of the Proteaceae, studies of which have been sparse, with the exception of the work performed on the exudates from *Hakea acicularis* (Stephen, 1956) and *Brabeium stellatifolium* (Stephen & van der Bijl, 1974).

REFERENCES

Anderson, D. M. W. (1978). *Process Biochem.* **13** (7), 4.
Anderson, D. M. W. & Pinto, G. (1980). *Bot. J. Linn. Soc.*, **80**, 85.
Anderson, E. & Harris, L. (1952). *J. Am. Pharm. Soc.* **41**, 529.
Anderson, D. M. W. & Munro, A. C. (1969). *Carbohydr. Res.* **11**, 43.
Anderson, D. M. W., Bell, P. C. & McNab, C. G. A. (1972). *Phytochem.* **11**, 1751.
Anderson, D. M. W., Bell, P. C. & Millar, J. R. A. (1974). *Phytochem.* **13**, 2189.
Bentham, G. (1870). *Flora Australiensis (London)*, 5.
Brown, R. (1811). *Trans. Linn. Soc.* **10**, 167.
Engler, A. (1894). *Die Naturalichen Planzenfamilien*, 128.
Johnson, L. A. S. & Briggs, B. C. (1975). *J. Linn. Soc. Bot.* **70** (2), 83.
Oudtshoorn, R. van (1963). *Plant Biochem.* **11** (4), 399.
Sawardeker, J. S., Sloneker, J. H. & Jeanes, A. (1965). *Anal. Chem.* 37, 1603.
Stephen, A. M. (1956). *J. Chem. Soc.* 4487.
Stephen, A. M. & Bijl, P. van der (1974). *J. South African Chem. Inst.* 27 (2), 37.
Stephen, A. M. & Bijl, P. van der (1975). *J. South African Chem. Inst.* 28 (1), 43.
US National Academy of Sciences (1979). *Tropical Legumes*, Washington DC.
US National Academy of Sciences (1980). *Firewood Crops*, Washington DC.
Venkata Rao, C. (1971). *Botanical Monograph* No. 6, Council for Scientific & Industrial Research, New Delhi, India.
Vickery, J. R. (1971). *Phytochem.* **10** (1), 123.