

REVIEW ARTICLE

CHEMOTAXONOMIC ASPECTS OF THE CHEMISTRY OF *ACACIA* GUM EXUDATES

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Abstract—The results of chemical studies of the gum exudates from thirty *Acacia* species are reviewed, and their taxonomic significance is discussed with respect to Bentham's divisions of the genus.

INTRODUCTION

CHEMICAL analysis offers one of the possible approaches to taxonomy; unfortunately, the chemical data available at present are often limited or sporadic.¹ Nevertheless, chemotaxonomists anticipate the time when useful chemical data will be available more frequently. This will require not only much more analytical chemistry, but also the compilation, based on botanical classifications, of the data that have already been obtained. In this connexion, a plea¹ for greater consideration from chemists has been made by the taxonomist. The knowledge gained from the application of chemistry should not only stimulate the chemist to further effort—it should also be presented in a way that is helpful to the taxonomist.²

As a result, interest in chemotaxonomy is growing quickly. Useful correlations have already been obtained in a number of plant groups, e.g. see Refs. 3–10. Generally the most useful substances for chemical taxonomy belong to the so-called secondary products¹¹ such as tannins, essential oils, alkaloids, glycosides, and gum exudates. In trees they are often associated with dead tissues such as heart-wood and external bark.

Although Maiden¹² suggested in 1889 that chemical studies of gum exudates might confirm

¹ V. H. HEYWOOD, *Comparative Phytochemistry* (edited by T. SWAIN), p. 17, Academic Press, London and New York (1966).

² T. SWAIN, *Chemical Plant Taxonomy* (edited by T. SWAIN), p. 8, Academic Press, London and New York (1963).

³ A. R. PENFOLD and J. L. WILLIS, *The Eucalypts in Botany, Cultivation, Chemistry, and Utilisation*. Leonard Hill Books, London (1961).

⁴ W. E. HILLIS, *Phytochem.* **6**, 845 (1967).

⁵ J. BORGES DEL CASTILLO, C. J. W. BROOKS, R. C. CAMBIE, G. EGLINTON, R. J. HAMILTON and P. PELLITT, *Phytochem.* **6**, 391 (1967).

⁶ N. T. MIROV, *J. Forestry* **27**, 176 (1929).

⁷ H. ERDTMAN, *Biochemistry of Wood* (edited by K. KRATZL and G. BILLEK), Pergamon Press, London (1959).

⁸ J. W. CLARK-LEWIS and I. DAINIS, *Australian J. Chem.* **20**, 2191 (1967).

⁹ M. HASEGAWA, *J. Japan Forest Soc.* **40**, 111 (1958).

¹⁰ E. C. BATE-SMITH, *Chemical Plant Taxonomy* (edited by T. SWAIN), p. 127, Academic Press, London and New York (1963).

¹¹ H. ERDTMAN, *Chemical Plant Taxonomy* (edited by T. SWAIN), p. 94, Academic Press, London and New York (1963).

¹² J. H. MAIDEN, *Proc. Linn. Soc. (New South Wales)* **4**, 605, 1277 (1889); **6**, 389 (1891).

botanical classifications, little effort has been given to this approach to date. There appear to be two reasons for this: very few chemists are active in the field of gum chemistry and, secondly, the collection of botanically interesting and authenticated specimens of gum has frequently, in the writers' experience, proved to be very difficult to arrange. Just as the taxonomist appeals¹ for greater assistance from chemists, gum chemists require greater co-operation from botanists and silviculturalists.

The genus *Acacia* is very large, and it still provides many complex botanical problems of nomenclature and classification. Indeed, the number of species in the genus is not known with certainty; Black¹³ has estimated the number at 500, Brenan¹⁴ and Ewart¹⁵ propose 750–800, and Hutchinson¹⁶ suggests 900 (see foot-note to Table 1). Plant gums are the most complex of the polysaccharide group of natural products; their study presents^{17, 18} the most formidable problems in carbohydrate chemistry. This is reflected in the fact that the gums from only seven *Acacia* species had been studied (two of these in very minor detail) by the end of 1955, and thirteen species (including five in minor detail) by the end of 1963. Progress has been more rapid since then; chemical data for the gum exudates from thirty *Acacia* species are now available, although six of these have not yet been studied in detail.

Although authoritative reviews of the progress of gum chemistry have been published periodically,^{19, 20} almost all of these (cf. Ref. 21) have been written from the chemical point of view; none has been devoted solely to the genus *Acacia*. The present review of the chemistry of *Acacia* gum exudates has been compiled largely for the chemotaxonomists' information, and an effort has been made to meet the challenge expressed by Heywood,¹ who has complained that the "special shorthand and abbreviations of chemistry" constitute a new hazard for taxonomists. Explanations have therefore been given in the text whenever abbreviations have been necessary to achieve economy of space (e.g. in Tables).

DISCUSSION

Gum exudates identified with the following specific names in *Acacia* have been studied chemically: *A. adansonii* Guill. et Perr.;²² *A. arabica* Willd.;^{22–25} *A. campylacantha* Hochst.;^{22, 24–26} *A. catechu* Benth.;^{27, 28} *A. cyanophylla* Lindl.;^{29, 30} *A. dealbata* Link;^{22, 24, 25}

¹³ J. M. BLACK, *Flora of South Australia* (2nd Ed.), Government Printer, Adelaide (1948–1957).

¹⁴ J. P. M. BRENNAN, Royal Botanic Gardens, Kew, private communications.

¹⁵ A. J. EWART, *Flora of Victoria*, Government Printer, Melbourne (1930).

¹⁶ J. HUTCHINSON, *The Genera of Flowering Plants*, Oxford University Press (1964).

¹⁷ E. L. HIRST, *Endeavour* **18** (1951).

¹⁸ E. L. HIRST, *Perspectives in Organic Chemistry* (edited by SIR A. TODD), p. 214, Interscience, London (1956).

¹⁹ J. K. N. JONES and F. SMITH, *Advances Carbohydr. Chem.* **4**, 243 (1949).

²⁰ E. L. HIRST and J. K. N. JONES, *Encyclopaedia of Plant Physiology* (edited by W. RUHLAND), p. 500, Springer-Verlag, Berlin (1958).

²¹ D. H. SHAW and A. M. STEPHEN, *South African Indust. Chem.* **19**, 146 (1965).

²² D. M. W. ANDERSON and G. M. CREE, *Carbohydr. Res.* **6**, 214 (1968).

²³ D. M. W. ANDERSON, SIR EDMUND HIRST and J. F. STODDART, *J. Chem. Soc. (C)*, 1476 (1967).

²⁴ D. M. W. ANDERSON and K. A. KARAMALLA, *J. Chem. Soc. (C)*, 762 (1966).

²⁵ D. M. W. ANDERSON, G. M. CREE, M. A. HERBICH, K. A. KARAMALLA and J. F. STODDART, *Talanta* **11**, 1559 (1964).

²⁶ A. C. MUNRO, *Edinburgh University*, forthcoming publication.

²⁷ R. K. HULYALKAR, T. R. INGLE and B. V. BHIDE, *J. Indian Chem. Soc.* **33**, 861 (1956).

²⁸ R. K. HULYALKAR, T. R. INGLE and B. V. BHIDE, *J. Indian Chem. Soc.* **36**, 31 (1959).

²⁹ M. KAPLAN and A. M. STEPHEN, *Tetrahedron* **193** (1967).

³⁰ A. J. CHARLSON, J. R. NUNN and A. M. STEPHEN, *J. Chem. Soc.* 269 (1955).

A. decurrens (J. Wendl.) Willd.;⁷⁴ *A. drepanolobium* Harms ex Sjöstedt;^{22, 24, 25, 31–34} *A. elata* A. Cunn. ex Benth.;²⁹ *A. farnesiana* (L.) Willd.;³⁵ *A. fistula* Schweinf.;^{22, 24, 25} *A. giraffae* Willd.;^{22, 25, 29} *A. harpophylla* F. Muell. ex Benth.;³⁶ *A. karroo* Hayne;^{22, 25, 37, 38} *A. laeta* R. Br. ex Benth.;^{22, 25, 39, 40} *A. leucophloea* (Roxb.) Willd.;⁴¹ *A. mearnsii* De Wild.;^{22, 25, 29, 42} *A. mellifera* (Vahl.) Benth.;^{22, 25} *A. microbotrya* Benth.;³⁶ *A. mollissima* Willd.;^{43, 44} *A. nilotica* (L.) Willd. ex Del.;^{22, 24, 25, 45} *A. nubica* Benth.;^{22, 24, 25, 46} *A. penninervis* Sieber ex DC.;³⁶ *A. podalyriifolia* A. Cunn. ex G. Don;²⁹ *A. pycnantha* Benth.;^{22, 47, 48} *A. senegal* (L.) Willd.;^{22, 49–67} *A. seyal* Del.;^{22, 25, 68, 69} *A. sieberana* DC.;³⁵ *A. sundra* Spreng.;^{70–73} and *A. tortilis* Hayne.^{22, 25}

Some of these gums (e.g. from *A. farnesiana*, *A. leucophloea*, and *A. sieberana*) have been studied only superficially. Some of the species listed above are now believed to be synonyms or subspecies, e.g. *A. fistula* Schweinf. is a synonym of *A. seyal* Del. var. *fistula* (Schweinf.)

- ³¹ D. M. W. ANDERSON and I. C. M. DEA, *Carbohydr. Res.* **5**, 461 (1967).
- ³² D. M. W. ANDERSON and I. C. M. DEA, *Carbohydr. Res.* **7**, 109 (1968).
- ³³ D. M. W. ANDERSON and I. C. M. DEA, *Carbohydr. Res.* **7**, in press.
- ³⁴ D. M. W. ANDERSON and I. C. M. DEA, *Carbohydr. Res.* in press.
- ³⁵ L. ADRIAENS, *Mem. Inst. Royal Colonial Belge* **8**, 1(1939), see *Chem. Abs.* **37**, 4926 (1943).
- ³⁶ A. T. PROSZYNSKI, A. J. MICHELL and C. M. STEWART, C.S.I.R.O., Divn. of Forest Products, Australia. Technological paper No. 38 (1965).
- ³⁷ A. M. STEPHEN and D. C. VOGT, *Tetrahedron* **1473** (1967).
- ³⁸ A. J. CHARLSON, J. R. NUNN and A. M. STEPHEN, *J. Chem. Soc.* 1428 (1955).
- ³⁹ D. M. W. ANDERSON and R. N. SMITH, *Carbohydr. Res.* **4**, 55 (1967).
- ⁴⁰ D. M. W. ANDERSON, I. C. M. DEA and R. N. SMITH, *Carbohydr. Res.* **7**, in press.
- ⁴¹ V. K. KULSHRESTHA, *J. Polymer Sci.* **58**, 791 (1962).
- ⁴² J. J. CARLYLE, Ph.D. Thesis, Edinburgh Univ. (1966).
- ⁴³ A. M. STEPHEN, *J. Chem. Soc.* 646 (1951).
- ⁴⁴ R. YOUNG, Ph.D. Thesis, Edinburgh Univ. (1963).
- ⁴⁵ D. M. W. ANDERSON and K. A. KARAMALLA, *Carbohydr. Res.* **2**, 403 (1966).
- ⁴⁶ D. M. W. ANDERSON and G. M. CREE, *Carbohydr. Res.* **6**, 385 (1968).
- ⁴⁷ E. L. HIRST and A. S. PERLIN, *J. Chem. Soc.* 2622 (1954).
- ⁴⁸ G. O. ASPINALL, E. L. HIRST and A. NICOLSON, *J. Chem. Soc.* 1697 (1959).
- ⁴⁹ C. L. BUTLER and L. H. CRETCHER, *J. Am. Chem. Soc.* **51**, 1519 (1929).
- ⁵⁰ M. HEIDELBERGER and F. E. KENDALL, *J. Biol. Chem.* **84**, 639 (1929).
- ⁵¹ M. HEIDELBERGER, O. T. AVERY and W. K. GOEBEL, *J. Exptl. Med.* **29**, 847 (1929).
- ⁵² S. W. CHALLINOR, W. N. HAWORTH and E. L. HIRST, *J. Chem. Soc.* 258 (1931).
- ⁵³ R. D. HOTCHKISS and W. F. GOEBEL, *J. Am. Chem. Soc.* **58**, 858 (1936).
- ⁵⁴ R. D. HOTCHKISS and W. F. GOEBEL, *J. Biol. Chem.* **115**, 285 (1936).
- ⁵⁵ F. SMITH, *J. Chem. Soc.* 744 (1939); 1724 (1939); 1040 (1940).
- ⁵⁶ J. JACKSON and F. SMITH, *J. Chem. Soc.* 74 and 79 (1940).
- ⁵⁷ J. K. N. JONES, *J. Chem. Soc.* 1672 (1953).
- ⁵⁸ T. DILLON, D. F. O'CEALLACHAIN and P. S. O'COLLA, *Proc. R. Irish Acad.* **55B**, 331 (1953); **57B**, 31 (1954).
- ⁵⁹ P. ANDREWS and J. K. N. JONES, *J. Chem. Soc.* 583 (1955).
- ⁶⁰ F. SMITH and D. R. SPIESTERSBACH, *Abs. Am. Chem. Soc.* 15D (1955).
- ⁶¹ A. J. CHARLSON, P. A. GORIN and A. J. PERLIN, *Can. J. Chem.* **35**, 365 (1957).
- ⁶² G. O. ASPINALL, A. J. CHARLSON, E. L. HIRST and R. YOUNG, *J. Chem. Soc.* 1696 (1963).
- ⁶³ G. O. ASPINALL and R. YOUNG, *J. Chem. Soc.* 3005 (1965).
- ⁶⁴ D. M. W. ANDERSON and J. F. STODDART, *Carbohydr. Res.* **2**, 104 (1966).
- ⁶⁵ D. M. W. ANDERSON, SIR EDMUND HIRST and J. F. STODDART, *J. Chem. Soc. (c)*, 1959 (1966).
- ⁶⁶ D. M. W. ANDERSON, I. C. M. DEA, K. A. KARAMALLA and J. F. SMITH, *Carbohydr. Res.* **6**, 97 (1968).
- ⁶⁷ D. M. W. ANDERSON and I. C. M. DEA, *Carbohydr. Res.* **6**, 104 (1968).
- ⁶⁸ D. M. W. ANDERSON and M. A. HERBICH, *J. Chem. Soc.* 1 (1963).
- ⁶⁹ D. M. W. ANDERSON, I. C. M. DEA and SIR EDMUND HIRST, *Carbohydr. Res.*, in press.
- ⁷⁰ S. MUKHERJEE and A. N. SHRIVASTAVA, *J. Sci. Ind. Res. (India)* **16B**, 566 (1957).
- ⁷¹ S. MUKHERJEE and A. N. SHRIVASTAVA, *J. Am. Chem. Soc.* **80**, 2536 (1958).
- ⁷² S. MUKHERJEE and A. N. SHRIVASTAVA, *Proc. Ind. Acad. Sci.* **50A**, 374 (1959).
- ⁷³ A. N. SHRIVASTAVA, *Agra Univ. J. Res. (Sci.)* **11**, 237 (1962).
- ⁷⁴ B. A. LEWIS and F. SMITH, *J. Am. Chem. Soc.* **79**, 3929 (1957).

Oliv.; *A. arabica* and *A. adansonii* are different subspecies¹⁴ of *A. nilotica* (L.) Willd. ex Del. True *A. mollissima* Willd. is a synonym of *A. pubescens* (Vent.) R. Br., but the name *A. mollissima* Willd. has been used in error by many authors⁴³ to refer to *A. mearnsii*. *A. decurrens*⁷⁴ is a distinct species. However *A. decurrens* var. *mollis* (and also var. *mollissima*) is not a variety of *A. decurrens* but a synonym of *A. mearnsii*.^{14, 75}

TABLE 1. THE GUM EXUDATES FROM *Acacia* SPECIES STUDIED TO DATE, CLASSIFIED ACCORDING TO BENTHAM'S INFRAGENERIC GROUPS OF THE GENUS *Acacia*

Species studied to date	
Series 1. PHYLLODINEAE (277)*	
Sub-series 1. Alatae (5)	—
2. Continuae (5)	—
3. Pungentes (35)	—
4. Calamiformes (18)	—
5. Brunioidae (8)	—
6. Uninerves (92)	<i>A. cyanophylla</i> , <i>A. penninervis</i> , <i>A. podalyriifolia</i> , <i>A. pycnantha</i> , <i>A. microbotrya</i>
7. Plurinerves (48)	<i>A. harpophylla</i>
8. Juliflorae (66)	—
Series 2. BOTRYOCEPHALAE (10)	<i>A. dealbata</i> , <i>A. decurrens</i> , <i>A. elata</i> , <i>A. mearnsii</i> , [<i>A. mollissima</i>]
Series 3. PULCHELLAE (8)	—
Series 4. GUMMIFERAE (60)	
Sub-series 1. Summibracteatae (13)	<i>A. giraffae</i> , <i>A. farnesiana</i> , <i>A. sieberana</i>
2. Medibracteatae (39)	<i>A. adansonii</i> , <i>A. arabica</i> , <i>A. drepanolobium</i> , <i>A. fistula</i> , <i>A. karroo</i> , <i>A. leucophloea</i> , <i>A. nilotica</i> , <i>A. nubica</i> , <i>A. seyal</i> , <i>A. tortilis</i>
3. Basibracteatae (8)	—
Series 5. VULGARES (75)	
Sub-series 1. Gerontogae spiciflorae (25)	<i>A. campylacantha</i> , <i>A. catechu</i> , <i>A. laeta</i> , <i>A. mellifera</i> , <i>A. senegal</i> , <i>A. sundra</i>
2. Americanae spiciflorae (19)	—
3. Americanae capitulatae (26)	—
4. Gerontogae capitulatae (5)	—
Series 6. FILICINAE (2)	—

* Figures in parentheses indicate the number of species assigned to series and sub-series by Bentham.⁷⁶

We are grateful to Dr. Mary Tindale, Royal Botanic Gardens, Sydney, N.S.W., for the information that at least 616 *Acacia* spp. are native to Australia. Dr. Tindale modifies Bentham's number of species as follows:

Phyllodineae, 570	Uninerves, 193
Alatae, 4	Plurinerves, 93
Continuae, 6	Juliflorae, 151;
Pungentes, 58	Botryocephalae, 32
Calamiformes, 47	Pulchellae, 14
Brunioidae, 18	

The genus *Acacia* has been divided into six Series and fifteen Sub-series by Bentham,⁷⁶ and into Sections and Sub-sections by Taubert.⁷⁷ Bentham's divisions, based upon habit,

⁷⁵ J. P. M. BRENAN and R. MELVILLE, *Kew Bulletin* 14, 37 (1960).

⁷⁶ G. BENTHAM, *Trans. Linn. Soc. (London)* 30, 444 (1875).

⁷⁷ P. TAUBERT, *Die Natürlichen Pflanzenfamilien*. (edited by A. ENGLER), p. 108, Engelmann, Leipzig (1894).

inflorescence and geographical distribution are: Series 1, PHYLLODINEAE; Series 2, BOTRYOCYPHALAE; Series 3, PULCHELLAE; Series 4, GUMMIFERAE; Series 5, VULGARES; Series 6, FILICINAE. Species from Series 1 are native to Australia, Hawaii and New Caledonia; species from Series 2 and 3 are native to Australia; species from Series 4 and 5 are found throughout tropical and semitropical parts of the world; and species from Series 6 are native to South America. The species whose gums have been studied chemically to date belong to Series 1,

TABLE 2. COMPARISON OF GUM EXUDATES FROM SPECIES IN SERIES 4 AND 5.

Properties	Series 4	Series 5
1. Sign of specific rotation	Positive	Negative
2. Ratio of rhamnose content to uronic acid content	Greater than unity	Unity
3. Aldobiouronic acids* yielded on acid hydrolysis	6- <i>O</i> -(β -D-GA)-D-Gal 6- <i>O</i> -(4-Me- β -D-GA)-D-Gal 4- <i>O</i> -(α -D-GA)-D-Gal 4- <i>O</i> -(4-Me- α -D-GA)-D-Gal	6- <i>O</i> -(β -D-GA)-D-Gal 6- <i>O</i> -(4-Me- β -D-GA)-D-Gal
4. Neutral disaccharides* obtained on mild acid hydrolysis	3- <i>O</i> - β -D-Galp-D-Gal 6- <i>O</i> - β -D-Galp-D-Gal 3- <i>O</i> - β -L-Araf-L-Ara 3- <i>O</i> - β -L-Arap-L-Ara	3- <i>O</i> - β -D-Galp-D-Gal 6- <i>O</i> - β -D-Galp-D-Gal 3- <i>O</i> - β -L-Araf-L-Ara 3- <i>O</i> - β -L-Arap-L-Ara 3- <i>O</i> - α -D-Galp-L-Ara
5. <i>O</i> -Methyl-L-arabinoses obtained from the methylated gums	2,3,5- and 2,3,4-tri-, 2,5-, 3,5- and 3,4-di- <i>O</i> -methyl-L-arabinose. [<i>A. nubica</i> gum gave no 3,4-di- <i>O</i> -methyl-L-arabinose]	2,3,5- and 2,3,4-tri- and 2,5-di- <i>O</i> -methyl-L-arabinose
6. Length of arabinose-containing side-chains	Some are at least 6 units long; none are terminated by galactose	Longest observed is 5 units long; some are terminated by galactose
7. Change in specific rotation of products on successive Smith degradations	Falls	Rises
8. Basis of molecular structure	Blocks of β 1,3-linked-D-galactoses interspersed by blocks of β 1,6-linked-D-galactoses in a branched galactan framework	Branched β 1,3-linked galactan framework
9. Approximate weight-average molecular weights.	$\bar{M}_w \geq 850,000$	$\bar{M}_w \leq 600,000$

* See text for full chemical name of these acidic and neutral disaccharides.

2, 4, or 5, as shown in Table 1. *A. drepanolobium* does not appear in Bentham's classification; it was named in 1914 and placed in Series 4, GUMMIFERAE, Sub-series *Medibracteatae*, by Harms.⁷⁸ Gum exudates from ten *Acacia* species in Series 4 and from six species in Series 5 have been studied, and comparisons of the results indicate that these two groups of species are reasonably distinct (see Table 2). Gum exudates from species in Series 3 and 6 have not yet been studied.

⁷⁸ H. HARMS, *Bot. Jahrb.* 51, 361 (1914).

The gum exudates from six species in Series 5 all have negative specific rotations, and a unit molar ratio of rhamnose content to uronic acid content. On acid hydrolysis all yield two aldobiouronic acids, viz., 6-*O*-(β -D-glucopyranosyluronic acid)-D-galactose and 6-*O*-(4-*O*-methyl- β -D-glucopyranosyluronic acid)-D-galactose. The gum exudates from *A. campylacantha*,²⁶ *A. laeta*,⁴⁰ and *A. senegal*^{64, 65} have been the most systematically studied of the species in this Series. On partial acid hydrolysis they give five disaccharides, viz., 3-*O*- β -D-galactopyranosyl-D-galactose; 6-*O*- β -D-galactopyranosyl-D-galactose; 3-*O*- α -D-galactopyranosyl-L-arabinose; 3-*O*- β -L-arabinofuranosyl-L-arabinose; and 3-*O*- β -L-arabinopyranosyl-L-arabinose. Methylation of these gums, followed by methanolysis, yields 2,3,5- and 2,3,4-tri-, and 2,5-di-*O*-methyl-L-arabinose as the only *O*-methyl-L-arabinoses. On successive Smith degradations the specific rotation of the products rises and eventually becomes positive. Successive Smith degradations show that the molecular structures of these gums are based on a branched β 1,3-linked galactan, to which are attached short arabinose-containing side-chains (up to 5 units long in *A. laeta*⁴⁰ gum). Molecular-sieve chromatography suggests that these gums have similar number-average molecular weights. The weight-average molecular weights of *A. senegal* gum and *A. campylacantha* gum are 600,000⁶⁵ and 350,000²⁶ respectively.

The gum exudates of ten species in Series 4 have been studied. All have positive specific rotations, and do not have a unit molar ratio of rhamnose content to uronic acid content. On acid hydrolysis all yield four aldobiouronic acids, viz., 6-*O*-(β -D-glucopyranosyluronic acid)-D-galactose; 6-*O*-(4-*O*-methyl- β -D-glucopyranosyluronic acid)-D-galactose; 4-*O*-(α -D-glucopyranosyluronic acid)-D-galactose; and 4-*O*-(4-*O*-methyl- α -D-glucopyranosyluronic acid)-D-galactose. On methylation and methanolysis, the gums of *A. arabica*,²³ *A. drepanolobium*,^{33, 34} *A. nilotica*,⁷⁹ and *A. seyal*⁶⁹ yielded 2,3,5- and 2,3,4-tri-, and 2,5-, 3,5- and 3,4-di-*O*-methyl-L-arabinose. Methylation and methanolysis of the gums of *A. nubica*⁴⁶ and *A. giraffae*²⁹ yielded similar results, except that *A. nubica* gum did not yield 3,4-di-*O*-methyl-L-arabinose, and *A. giraffae* gum did not yield 2,3,4-tri- and 3,4-di-*O*-methyl-L-arabinose. Partial acid hydrolysis of the gums of *A. arabica*, *A. drepanolobium*, *A. nubica*, and *A. seyal* yielded 3-*O*- β -D-galactopyranosyl-D-galactose, 6-*O*- β -D-galactopyranosyl-D-galactose, 3-*O*- β -L-arabinofuranosyl-L-arabinose, and 3-*O*- β -L-arabinopyranosyl-L-arabinose. On successive Smith degradations of the gums from *A. arabica*, *A. drepanolobium*, and *A. seyal* the specific rotation of the products fell markedly; in contrast, the specific rotation of *A. nubica* gum fell slightly and remained highly positive. Successive Smith degradations show that molecules of the gums from *A. arabica*, *A. drepanolobium*, *A. nubica*, and *A. seyal* contain a number of periodate-resistant β 1,3-linked D-galactose residues, interspersed with periodate-vulnerable β 1,6-linked D-galactose residues in a branched galactan framework; some of the arabinose side-chains are at least 6 units long, and none of them are terminated by galactose. Light-scattering measurements have shown the weight-average molecular weights of *A. arabica*,²³ *A. seyal*,⁶⁹ *A. nubica*,⁸⁰ and *A. drepanolobium*³³ gums to be 23×10^5 , 8.5×10^5 , 8.6×10^5 , and 9.5×10^5 respectively.

The situation concerning the gum exudates from species in Series 1 is not so clear. Of the six species studied, only the gums of *A. cyanophylla*,^{29, 30} *A. podalyriifolia*²⁹ and *A. pycnantha*^{47, 48} have been examined in detail, although none has been submitted to successive Smith degradations. Charlson, Nunn, and Stephen³⁰ realized that *A. cyanophylla* and *A. pycnantha* were closely related taxonomically, and expressed surprise that the sugar compositions of

⁷⁹ J. F. STODDART, personal communication.

⁸⁰ D. M. W. ANDERSON and S. RAHMAN, *Carbohydr. Res.* 4, 298 (1967).

these gums were so different; the uronic acid contents of *A. cyanophylla* and *A. pycnantha* gums are 20 and 5 per cent respectively. (In Series 4, Sub-series 2, the gums of *A. seyal*⁶⁹ and *A. nubica*⁴⁶ have similar molecular structures, although their uronic acid contents are 13 and 7 per cent respectively.) Joubert⁸¹ found a comparatively low molecular weight ($\bar{M}_w = 189,000$) for *A. cyanophylla* gum, and recent experiments⁸² have shown that *A. pycnantha* gum has an unusually low molecular weight ($\bar{M}_w = 60,000$) for an *Acacia* species.

Series 2 contains only ten species; the gums from five of these have been examined, although only two, *A. elata*²⁹ and *A. mearnsii*,^{29, 42} have been studied in any detail.

Although much more work on the gums from species in Series 1 and 2 is required, the present indication is that the gums from Series 1 (Phyllodineae) are quite varied. This is not surprising since many native Australian genera exhibit considerable taxonomic variation and endemism.⁸³ In this endemic Series, evolution during the long isolation of Australia may have resulted in wider intra-series divergences than in the pantropical groups.

In the past it has sometimes been assumed that all *Acacia* gums are very similar,⁸⁴ and some structural studies have been interpreted to support this; e.g. it has been claimed⁴² that the gum exudates of *A. pycnantha* (Series 1), *A. mearnsii* (Series 2) and *A. senegal* (Series 5) show distinct similarity to one another. All three gums have negative specific rotations, but the ratios of uronic acid content to rhamnose content for the gums of *A. pycnantha*, *A. mearnsii*, and *A. senegal* are 1:2.5, 1:1.3 and 1:1.0 respectively. On acid hydrolysis they all yield two aldobiouronic acids, viz., 6-*O*-(β -D-glucopyranosyluronic acid)-D-galactose and 6-*O*-(4-*O*-methyl- β -D-glucopyranosyluronic acid)-D-galactose. On partial acid hydrolysis *A. pycnantha* gum⁴⁸ yielded 3-*O*- β -L-arabinofuranosyl-L-arabinose as the only arabinose-containing disaccharide, while *A. mearnsii* gum⁴² yielded only 3-*O*- β -L-arabinopyranosyl-L-arabinose. Partial acid hydrolysis of *A. senegal* gum has yielded 3-*O*- α -D-galactopyranosyl-L-arabinose, 3-*O*- β -L-arabinofuranosyl-L-arabinose, and 3-*O*- β -L-arabinopyranosyl-L-arabinose. Methylation of *A. pycnantha* gum,⁴⁸ followed by methanolysis, yielded 2,3,5-tri-, and 2,5- and 3,5-di-*O*-methyl-L-arabinose as the only *O*-methyl-L-arabinoses, while methylation and methanolysis of *A. senegal* gum⁶⁵ yielded 2,3,5- and 2,3,4-tri-, and 2,5-di-*O*-methyl-L-arabinose. Methylation of *A. mearnsii* gum,⁴² followed by methanolysis, yielded 2,3,5- and 2,3,4-tri-, and 2,5- and 2,3-di-*O*-methyl-L-arabinose; 2,3-di-*O*-methyl-L-arabinose was present to approximately the same extent as 2,5-di-*O*-methyl-L-arabinose. The weight-average molecular weights of *A. senegal* gum,⁶⁵ *A. pycnantha* gum,⁸² and *A. mearnsii* gum⁸² are ca. 600,000, 60,000, and 460,000 respectively. Successive Smith degradations have shown⁶⁵ that *A. senegal* gum is based on a branched β 1,3-linked galactan. No analogous experiments have been performed on the gums from *A. pycnantha* and *A. mearnsii*.

A comparison of the gums of *A. pycnantha*, *A. mearnsii*, and *A. senegal* is listed in Table 3, and it can be seen that they have differing properties. It is, however, obvious that more of the gums from species of Series 1 and 2 must be studied in greater detail before conclusions can be reached regarding their relationship to the gums from other Series. Nevertheless, the limited data available indicate that it might be possible in the future—if chemical studies of *Acacia* gums are based on carefully selected species—to obtain chemical confirmation of the taxonomic divisions that have been proposed in *Acacia*.

One of the main objects of this Review is to indicate which *Acacia* species should be

⁸¹ F. J. JOUBERT, *J. S. Afr. Chem. Inst.* **7**, 107 (1954).

⁸² D. M. W. ANDERSON and I. C. M. DEA, forthcoming publication.

⁸³ R. GOOD, *The Geography of Flowering Plants*, p. 243, Longmans, London (1965).

⁸⁴ S. U. LAKSHMI and T. N. PATTABIRAMAN, *Indian J. Biochem.* **4**, 181 (1967).

studied in the immediate future in order to achieve a more comprehensive survey of the genus. To date, gum chemists have usually been glad to undertake the study—solely for the challenge to chemical analysis involved—of any specimen that happened to be offered at random by one of the very few active gum collectors. This Review shows that it is now desirable to introduce a much more systematic approach to chemical studies of gum exudates. This is desirable both taxonomically and chemically; botanists must be prepared to offer greater initiative and collaboration in collecting taxonomically interesting specimens for investigation, because a reasonably complete chemical study of a gum sample takes, at best, about one year with the analytical methods and techniques available at present.

The contribution of gum chemistry to plant taxonomy is therefore only at the beginning of a more efficient and productive future if the necessary co-operation from expert collectors

TABLE 3. COMPARISON OF THE GUMS FROM *A. pycnantha* (SERIES 1), *A. mearnsii* (SERIES 2) AND *A. senegal* (SERIES 5)

Properties	<i>A. pycnantha</i>	<i>A. mearnsii</i>	<i>A. senegal</i>
1. Sign of specific rotation	Negative	Negative	Negative
2. Ratio of L-rhamnose content to uronic acid content	1:2.5	1:1.3	1:1.1
3. Aldobiouronic acids yielded	All three gums yielded 6-O-(β -D-glucopyranosyluronic acid)-D-galactose and its 4-O-methyl analogue		
4. Arabinose-containing* disaccharides obtained on mild acid hydrolysis	$\text{L-Araf} \xrightarrow{1\beta 3} \text{L-Ara}$	$\text{L-Arap} \xrightarrow{1\beta 3} \text{L-Ara}$	$\text{D-Galp} \xrightarrow{1\alpha 3} \text{L-Ara}$ $\text{L-Arap} \xrightarrow{1\beta 3} \text{L-Ara}$ $\text{L-Araf} \xrightarrow{1\beta 3} \text{L-Ara}$
5. O-Methyl-L-arabinoses obtained from methylated gums	2,3,5-tri- and 2,5- and 3,5-di-O-methyl-L-arabinose	2,3,5- and 2,3,4-tri-, and 2,5- and 2,3-di-O-methyl-L-arabinose	2,3,5- and 2,3,4-tri- and 2,5-di-O-methyl-L-arabinose
6. Approximate weight-average molecular weight	ca. 60,000	ca. 460,000	ca. 600,000

* See text for full chemical name of disaccharides.

can be achieved. Since individual chemical characters are frequently of limited importance, the whole range of characteristic products should, wherever possible, be taken into account when one group of plants is compared taxonomically with another.⁸⁵ Because the chemical study of a gum exudate takes longer than for other characteristic secondary products, it is important that the efforts of gum chemists should henceforth be applied to authenticated specimens from species carefully selected for their potential chemical or taxonomic interest. For example, species from Bentham's Series 3 and 6, from Sub-series other than Sub-series 6 of Series 1, and from Sub-series 2, 3, and 4 of Series 5 should be given a top priority.

It is unfortunate that many of the early phytochemical studies are now of very limited value. It has been pointed out^{20, 86, 87} that the importance of early work on the chemistry

⁸⁵ R. HEGNAUER, *Chemical Plant Taxonomy* (edited by T. SWAIN), p. 425, Academic Press, London and New York (1963).

⁸⁶ D. M. W. ANDERSON, G. M. CREE, J. J. MARSHALL and S. RAHMAN, *Carbohydr. Res.* **1**, 320 (1965).

⁸⁷ D. M. W. ANDERSON, G. M. CREE, J. J. MARSHALL and S. RAHMAN, *Carbohydr. Res.* **2**, 63 (1966).

of gum exudates is considerably diminished because commercial samples, now believed to have been mixtures, were used. The continued use⁸⁴ of trivial names such as "gum arabic" and other meaningless terms such as "gum acacia" is to be deplored.

In other studies, the correct identity of the species (and even the genus) involved has proved to be uncertain, and the doubts remain permanently because specimens were not preserved. For the future, it is most desirable that good voucher specimens, with details of the date and place of collection, should be deposited in an accessible herbarium.^{1,14} A resolution to this effect was passed¹⁴ at the International Botanic Congress, Edinburgh (1964). Details of the collection of the gum specimens used in the studies carried out by Anderson and his co-workers are given in the experimental part of each of the relevant Papers referred to in this Review; these details have also been summarized.²² Even information such as this is not available, however, for many of the gum specimens studied by other investigators to date.

Heywood¹ considers that the specimens studied should be collected in the wild, since hybridization frequently occur during cultivation in botanic gardens. Clearly, both the phytochemist and the taxonomist have their own criteria that must be satisfied,¹ but it may, on occasion, be impossible to satisfy both simultaneously e.g. when the quantity of a sample, important botanically, is insufficient for detailed chemical study.

For a proper discussion of plant taxonomy it is important to know how far intrinsic and extrinsic factors may influence⁸⁸ the production and chemical content of plants. All living systems are subject to genetic variation, and the differences between individuals of the same species may be considerable.¹¹ Absolute results are difficult to obtain, even when the same clone of a species is compared from one season to another. Several individual plants of a species, if possible grown under different conditions, should therefore be examined.¹¹ In the light of all these factors, a start has been made to study the effects of different soils, age of tree, and seasonal variation on the composition of samples of the gum from *A. senegal*.⁶⁶ Other studies have established the extent of the variation in composition and properties of the gum exuded by different trees of *A. seyal* Del.,⁶⁸ *A. nilotica* (L.) Willd. ex Del.,⁴⁵ and *A. laeta* R. Br. ex Benth.³⁹ It has also been possible to study the extent of the analytical variations between different gum nodules from a particular tree; this has been done for *A. senegal*⁶⁶ and for *A. laeta*.³⁹ There is no doubt that whilst gum exudates are characteristic of a gum-forming species, they are, in turn, much more characteristic of each individual tree of that species. It is therefore clear that chemical studies should be made on a single large nodule of gum; for species exuding small nodules, the total gum collected from one tree should preferably be used. In either case, several similar samples from other trees of the same species should be analysed to an extent sufficient to ascertain that the main study is being made on a specimen that is acceptably typical of the species.

Interesting atypical variants⁶⁶ of *A. senegal* gum have also been studied. These included gum exuded at holes made by wood-boring beetles; this gum was closely similar, after purification, to typical samples of natural exudate and of tapped gum. In contrast, a dark-coloured, sweet-tasting gum that exudes from the lower, main, stem of *A. senegal* trees differed in two respects⁶⁶ from the gum obtained by normal tapping of the upper branches: (a) few, if any, of its uronic carboxyl groups were in the free acid form, (b) its rhamnose content was less than 50 per cent of that present in typical forms of the gum.

In conclusion, the attention of gum chemists and taxonomists alike should be drawn to Erdtman's very useful comments¹¹ regarding the necessity for more careful and more

⁸⁸ H. FLÜCK, *Chemical Plant Taxonomy* (edited by T. SWAIN), p. 167, Academic Press, London and New York (1963).

extensive use of proper nomenclature. There are certainly many instances in the literature of gum chemistry where confusion has arisen through the incorrect latin binomial being used for a gum specimen, or through gum from the same species being studied under different names by different authors. Some chemists have been careless in these respects in the past. On the other hand, chemists are dependent on their botanical collectors in this respect. It is understandable that botanists may require to change the scientific names of plants¹¹ as knowledge increases, but it is desirable for such changes to be made more widely known or more easily traced—possibly through review articles of a type complementary to this chemical review. Certain botanical genera, e.g. *Albizia* (for which a short appendix on nomenclature has been published⁸⁷) and *Acacia*, contain many revisions that are not easily located, and there are therefore traps into which the unsuspecting chemist can fall. For example, Bentham⁷⁶ lists no fewer than nineteen synonyms for *Acacia pennata* Willd.; seventeen for *A. filicina* Willd.; sixteen for *A. longifolia* (Andr.) Willd.; fourteen for *A. macracantha* Humb. et Bonpl.; ten for *A. caesia* Willd.; and ten for *A. juniperina* Willd. Another source of confusion can be illustrated by reference to *A. giraffae* Willd., of which *A. giraffae* Burch. is synonymous; however, the name *A. giraffae* was used in error by Sieber for *A. seyal* Del., and by Hochstetter for *A. hockii* De Wild.¹⁴ The possible confusion over *A. decurrens*, *A. mollissima*, and *A. mearnsii* has already been mentioned.

It is possible that gum chemistry will be able to provide valuable evidence in confirming whether a particular taxon is a subspecies of, or merely synonymous with, another taxon. For example, the typical subspecies of *A. nilotica* (L.) Willd. ex Del. is now¹⁴ preferably named *A. nilotica* (L.) Willd. ex Del. subsp. *nilotica*; *A. adansonii* Guill. et Perr. is more correctly named *A. nilotica* subsp. *adansonii* (G. et P.) Brenan, and *A. arabica* is most probably *A. nilotica* subsp. *tomentosa* (Benth.) Brenan. Of these, subsp. *nilotica* is much more closely related¹⁴ to subsp. *tomentosa* than it is to subsp. *adansonii*. There are, in addition, three further subspecies⁸⁹ viz., subsp. *kraussiana* (Benth.) Brenan, subsp. *leiocarpa* Brenan, subsp. *indica* (Benth.) Brenan, and two new geographical races, hitherto unknown taxonomically, have apparently been found recently in West Pakistan¹⁴ by Dr. S. Ali. Specimens of subsp. *nilotica*⁴⁵ and subsp. *tomentosa*²³ have already been studied; subsp. *adansonii*²² and subsp. *indica* have become available for study recently, and it will therefore be of considerable interest to ascertain how closely these four subspecies correspond chemically.

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⁸⁹ J. P. M. BRENAN, *Kew Bulletin* 12, 84 (1957).