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AN ANALYTICAL STUDY* OF GUM EXUDATES FROM SOME SPECIES OF THE GENUS *LANNEA* A. RICH.

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Abstract—The composition and properties of the gum exudates from *Lannea coromandelica* (syn. *L. grandis*), *L. schimperi*, and two specimens of the gum from *L. humilis* have been studied. The analytical results suggest that inter- and intra-species differences in *Lannea* are unlikely to be large, and the evidence obtained indicates that a considerable amount of the work published on this genus earlier must be regarded as incomplete or inaccurate.

INTRODUCTION

TO DATE, the gum from only one species of the genus *Lannea* A. Rich. (Sapindales; Anacardiaceae) has been studied. This species, properly described botanically as *L. coromandelica* (Houtt.) Merrill, is, however, unique in gum chemistry because of the extent to which it has been studied under different synonyms, and also because of the extent of the contradictions in chemistry that have arisen as a result. The gum has been studied under the native vernacular names Modal,[2] Shemat,[2] Jeol,[3,4] and also under the botanical synonyms *Odina wodier*,[4–8] *L. grandis*,[9–11] *L. grandis* Super,[12,13] *L. grandis* Engler,[13–17] and *L. coromandelica*.[18] There are also other botanical synonyms for this species, e.g. *Dialium coromandelica*, *Calesium grande*, and *Haberlia grandis*, but mercifully chemistry appears to have been spared their use.

The chemical results quoted in several of these publications are mutually contradictory.

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[2] V. M. PARIKH, T. R. INGLE and B. V. BHIDE, *J. Ind. Chem. Soc.* **33**, 119 (1956).
[3] A. K. BHATTACHARYYA and A. K. MUKHERJEE, *Bull. Chem. Soc. Japan* **37**, 1425 (1964).
[4] A. K. BHATTACHARYYA and C. V. N. RAO, *Can. J. Chem.* **42**, 107 (1964).
[5] S. N. MUKHERJEE and G. BANERJEE, *J. Ind. Chem. Soc.* **25**, 59 (1948).
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[12] S. N. MUKHERJEE, *J. Ind. Chem. Soc.* **25**, 333 (1948).
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[15] S. N. MUKHERJEE, *J. Ind. Chem. Soc.* **30**, 201 (1953).
[16] S. N. MUKHERJEE and S. K. SINHA, *J. Ind. Chem. Soc.* **30**, 647 (1953).
[17] S. N. MUKHERJEE, *J. Ind. Chem. Soc.* **30**, 851 (1953).
[18] R. RAMACHANDRAN and B. C. JOSHI, *Phytochem.* **7**, 2057 (1968).

The gum has been most recently described[18] as a *neutral* polysaccharide; all previous investigators found it to be acidic. So far the presence of only one aldobiouronic acid has been reported, but even this involves controversy, since the aldobiouronic acid has been stated to contain galacturonic acid[8] and, in contrast, 4-*O*-methyl glucuronic acid.[2] The specific rotation of the gum has been quoted as +29°,[5] −44°,[4] and +45°;[18] the equivalent weight as 1245,[2] 1150,[4] and 1361;[10] the methoxyl content as 2·38%,[2] 0·51%,[4] and zero.[18] The ratio of galactose to arabinose has been found to be 1·3/1;[5] 3/1;[4] 4/1;[18] and 5/1:[2] the gum has also been reported[8] to contain more arabinose than galactose.

Clearly such an unparalleled set of contradictions required analytical investigation. Since all of the work cited above is of Indian origin, specimens of gum from *L. coromandelica* and from other *Lannea* spp. were sought from other locations in an effort to establish whether the genus *Lannea* is indeed unprecedented in its variability, a result which would be surprising on botanical grounds. This paper presents the results that have been obtained for a Ceylonese specimen of *L. coromandelica* gum, a Nigerian specimen of *L. schimperi* gum, and two Sudanese specimens of *L. humilis* gum.

DISCUSSION

Consideration of the analytical results shown in Tables 1 and 2 indicates that the gum exudates from these four *Lannea* spp. have very similar analytical parameters. A characteristic of the genus is the high ratio of galactose to arabinose. Indeed, our value of 6/1 for *L. coromandelica* gum is higher than any of the wide range of values published by earlier Indian investigators; a similarly high ratio also occurs in *L. humilis* and *L. schimperi*. Clearly, the work[8] in which more arabinose than galactose was reported must be discounted. Further, the strong similarity found between the two samples of *L. humilis* gum indicates that neither the inter- nor intra-species differences in *Lannea* are likely to be great, and this is in agreement with the known botanical characters of this genus. With such complex natural products as plant gums, both inter- and intra-species differences in properties and composition must be expected to occur; recent work has shown that for some genera, e.g. *Prunus*[19] and *Combretum*[20] (which botanically are best described as systems of complexes), the variations can be much larger than for others, e.g. *Acacia*,[21] *Araucaria*.[22] Nevertheless, the variations implied for *Lannea* spp. by the lack of agreement between the results presented in the earlier papers cited in this communication are barely credible botanically or chemically; the most likely explanation is that they have arisen either through faulty chemical analysis, faulty botanical identification of the species, or through working with mixtures or commercial gum samples.

There is no doubt whatsoever that *Lannea* gum exudates are acidic polysaccharides that exist—as is customary—in the natural state as complex, nearly neutralized salts of the polysaccharide gum acid. It is unfortunate that the recent work of Ramachandran and Joshi[18] suggests that the purified polysaccharide is neutral, with a structure containing only galactose and arabinose; this is so greatly in error that there is no alternative to discounting that work.

The other major attempt[4] to establish a structure for the gum polysaccharide must also be regarded with caution. It is based on several doubts and inaccuracies. The arabinose content appears to be high; a strongly negative optical rotation (−44°) was reported;

[19] I. C. M. DEA, forthcoming publication.
[20] C. E. SPEED, M.Sc. Thesis, Edinburgh University, 1969.
[21] For a review, see D. M. W. ANDERSON and I. C. M. DEA, *Phytochem.* **8**, 167 (1969).
[22] D. M. W. ANDERSON and A. C. MUNRO, *Carbohyd. Res.*, **11**, 43 (1969).

rhamnose was not detected; nitrogen was not found; the methoxyl content was deliberately ignored; and only galacturonic acid was stated to be involved. Our examination has indicated that the uronic acid system is complex, with galacturonic, glucuronic, and 4-*O*-methyl-glucuronic acids all present. Since Bhattacharyya and Rao's structure has been used[9–11] in attempted interpretations of physico-chemical measurements, it is important that a structural model that reflects all the known facts should be available. A structural study of the gums from *Lannea* spp. is therefore in progress.

TABLE 1. ANALYSES OF PURIFIED GUM SAMPLES

	L. coromandelica	*L. humilis* A	*L. humilis* B	*L. schimperi*
Moisture, %	11·8	10·6	12·9	7·2
Ash, %	3·5	2·5	2·6	4·2
Nitrogen, %*	0·22	0·28	0·29	0·27
Protein (%N × 6·25)	1·38	1·75	1·81	1·69
Methoxyl, %†	1·6	0·4	0·4	0·9
Uronic anhydride (decarboxyln.)†	17	13	14	17
$[\alpha]_D$†	+27°	+36°	+43°	+30°
Limiting flow-time number, $cm^3\ g^{-1}$*†	11·7	9·6	8·7	14·4
$\bar{M}_w$‡*	$2{\cdot}57 \times 10^5$	$3{\cdot}10 \times 10^5$	$2{\cdot}57 \times 10^5$	$2{\cdot}41 \times 10^5$
Sugar composition† §				
galactose, %	69·5	72·5	71	69·5
arabinose, %	11	13	12	10
rhamnose, %	2·5	3	5	3·5
uronic acid, % ‖	17	11·5	12	17

* Corrected for moisture and ash.
† Corrected for moisture, ash, and protein.
‡ In M-NaCl.
‖ Average of decarboxylation value and value calculated from equivalent wt.
§ Sugars calculated as anhydro forms.

TABLE 2. ANALYSES OF ELECTRODIALYSED SAMPLES

	L. coromandelica	*L. humilis* A	*L. humilis* B	*L. schimperi*
Moisture, %	8·8	9·0	8·4	8·9
Ash, %	0·4	0·2	0·2	0·04
Equivalent wt.*	1060	1753	1774	1059
Hence uronic anhydride, %†	17	10	10	17

* Corrected for moisture and ash content.
† If all acidity arises from uronic acid groups.

Prior to this study, only two values of $\bar{M}_w$, as determined by light-scattering, had been reported for a *Lannea* gum. Bhattacharyya and Mukherjee reported[3] that the fully methylated gum had $\bar{M}_w = 1{\cdot}68 \times 10^5$, but more recently it was reported[9] that "the original acid polysaccharide derived from the plant exudate, *L. grandis*" had $\bar{M}_w = 17{\cdot}5 \times 10^6$. This is an unusually high value of $\bar{M}_w$ for an acidic gum exudate. Molecular-sieve chromatography[23] has indicated that *Lannea* exudates are not of particularly high molecular weight, and our

[23] D. M. W. ANDERSON, A. HENDRIE and A. C. MUNRO, *J. Chromatog.*, **44**, 178 (1969).

light-scattering values are in reasonable agreement with that of the earlier workers.[3] The value of 0·1695 for *dn/dc* reported recently[9] also appears to be unusually high for an acidic polysaccharide; allowing for this difference from our value (0·154), the difference between our value for $\bar{M}_w$ and that of Chaudhuri and Mukherjee[9] appears to involve a factor of almost exactly 10^2.

EXPERIMENTAL AND RESULTS

Origin of Specimens

The gum from *Lannea coromandelica* (Houtt.) Merrill was obtained in October 1967 from the Research Officer of the Conservator of Forests, Colombo 2, Ceylon. Gum from *L. schimperi* (Hochst. ex A. Rich) Engl. was collected at Shilca Research Station on 25 March 1969 by Mr. G. O. Magaji for Professor D. M. Ramsay, Department of Plant Science, Ahmadu Bello University, Zaria, Nigeria. Gum from *L. humilis* (Oliv.) Engl. was obtained from the Gum Research Officer to the Republic of the Sudan; sample A was collected near El Obeid in April 1969, and sample B from Layyuna Central Forest Reserve, Central Kordofan, in May 1969.

Analytical Methods

The standard analytical methods have been described in detail,[24] with the exception that the Hilger and Watts H1200 i.r. spectrometer was used in analyses involving i.r. vapour-phase measurements.

Weight-average molecular weights, $\bar{M}_w$, were obtained from light-scattering measurements made with a Sofica Model 42000 Photogonio Diffusometer using unpolarized green light (546 nm); the values quoted in Table 1 are the average of two values obtained at concentrations of approx 0·2% and 0·1% respectively in M-NaCl. These solutions were clarified by passage through Millipore filters of pore-sizes 0·45 and 0·22 μm. In the evaluation of $\bar{M}_w$, the value $dn/dc = 0{\cdot}154$ (found for the sample of *L. coromandelica* gum by Dr. I. C. M. Dea) was used for all samples.

Optical rotations were determined with a Perkin–Elmer electronic polarimeter, Model 141.

Purification of Samples

Each of the four gum samples dissolved readily in cold distilled water after several hours. The solutions were filtered, then dialysed for several days; the polysaccharide was recovered as the freeze-dried product. The recoveries, on a dry wt. basis, were in the range of 75–80% for all four species. The results of analyses made on these products are shown in Table 1.

A portion of each of the four gum samples was dissolved in distilled water and exhaustively electrodialysed to convert the gum polysaccharides to the free acid form. The acidic polysaccharides were recovered by freeze-drying, then analysed as shown in Table 2.

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[24] D. M. W. ANDERSON and J. F. STODDART, *Carbohyd. Res.* **2**, 104 (1966).