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## SHORT REPORTS

# AMINO ACID COMPOSITION OF GUM EXUDATES FROM SOME AFRICAN *COMBRETUM*, *TERMINALIA* AND *ANOGEISSUS* SPECIES*

D. M. W. ANDERSON, J. F. HOWLETT† and C. G. A. MCNAB

Chemistry Department, The University, Edinburgh EH9 3JJ, U.K.; †Food Science Division, Ministry of Agriculture, Fisheries and Food, Horseferry Road, London SW1P 2AE, U.K.

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**Key Word Index** *Combretum*; *Terminalia*; *Anogeissus*; Combretaceae; gum exudates; amino acids.

**Abstract**—Amino acid compositions are presented for the proteinaceous components of the gum exudates from *Combretum glutinosum* (syn. *apiculatum*), *C. zeyheri*, *C. molle* (syn. *guenzii*), *C. psidioides* (syn. *grandifolium*), *C. obovatum*, *C. collinum* (syn. *binderanum*), *C. hartmannianum*, *C. fragrans* (syn. *ternifolium*); *Terminalia sericea* and *T. superba*; and for *Anogeissus schimperi*. The principal amino acids common to these species are aspartic acid, alanine and glycine, but there are considerable variations; glutamic acid, histidine, lysine, proline, serine, threonine and valine are also major components of some of the species studied. The Combretaceae are therefore similar to the Sterculiaceae in containing very low proportions of hydroxyproline, which is the major amino acid component of the gums studied so far from genera within the Mimosoideae.

## INTRODUCTION

Data for the amino acid compositions of the proteinaceous components of karaya (*Sterculia* spp.) [1], arabic (*Acacia senegal*) [2], guar (*Cyamopsis tetragonolobus*) [3], tragacanth (*Astragalus* spp.) [4] and mesquite (*Prosopis* spp.) [5] gums have been published recently. Gums arabic, tragacanth and mesquite are characterized by the presence of substantial quantities of hydroxyproline, of which only very small proportions are present in those of karaya and guar. Sequential Smith-degradations of *Acacia polyacantha* gum have shown [6] that the branched galactan core of this gum is associated with amino acids which were not taken into account in earlier structural studies [7, 8]. This paper presents the data obtained for the amino acid compositions of the gums from eight *Combretum* spp., two *Terminalia* spp. and for the gum from *Anogeissus schimperi*, the major source of commercial gum ghatti.

## RESULTS AND DISCUSSION

Table 1 shows the amino acid data for the gum exudates from *Combretum glutinosum*, *C. zeyheri*, *C. molle*, *C. psidioides*, *C. obovatum*, *C. collinum*, *C. hartmannianum* and *C. fragrans*. Table 2 shows the data obtained for gum specimens from *Terminalia sericea*, *T. superba* and from *Anogeissus schimperi*.

Although analytical data for the polysaccharide components of the gums from *Combretum hartmannianum* [9], *C. zeyheri*, *C. molle*, *C. psidioides*, *C. collinum* and *C. fragrans* [10, 11] have been published, the nitrogenous fractions associated with gums from this genus had not been studied previously. A similar situation existed with regard to the gums from *Terminalia* [12] and *Anogeissus* spp. [13]. Because of the taxonomic relationship between the genera *Combretum*, *Terminalia* and *Anogeissus* [10], it was of interest to ascertain whether there were similarities in the amino acid compositions of their gum exudates and whether these compositions differed from those reported recently for the gums from other genera [1–5].

The *Combretum* species studied are listed in Table 1 in order of increasing proportions of aspartic acid, the principal amino acid of all of the species studied other than *C. glutinosum*, for which the major amino acid component is valine. The *Combretum* gums studied also show diversities in respect of the relative proportions of their other major amino acids: *C. obovatum* and *C. fragrans* have alanine and glycine as their second and third most abundant amino acids but proline, glutamic acid, histidine, glycine and lysine are the second most abundant amino acids for *C. zeyheri*, *C. molle*, *C. psidioides*, *C. collinum* and *C. hartmannianum*, respectively. *Terminalia* and *Anogeissus* spp. also show (Table 2) considerable variability in terms of their three major amino acids, *viz.* lysine, serine, aspartic acid (*T. sericea*); aspartic acid, alanine, glycine (*T. superba*); glutamic acid, aspartic acid, alanine (*A. schimperi*).

There is, however, one major feature in common to all the species listed in Tables 1 and 2; all have very low proportions of hydroxyproline, which is present in very high proportions in the leguminous gum exudates, e.g. from *Acacia* [2], *Astragalus* [4] and *Prosopis* [5] species.

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* Part 88 of the Series "Studies of Uronic Acid Materials". For Part 87, see ref. [6].

Table 1. Amino acid composition of the proteinaceous components (residues per 1000 residues) of the gum exudates from some *Combretum* species

| | *Combretum glutinosum* | *C. zeyheri* | *C. molle* | *C. psidioides* | *C. oboratum* | *C. collinum* | *C. hartmannianum* | *C. fragrans* |
|---|---|---|---|---|---|---|---|---|
| % N | 0.24 | 0.51 | 0.19 | 0.34 | 0.26 | 0.11 | 0.64 | 0.27 |
| Alanine | 99 | 92 | 100 | 97 | 107 | 83 | 71 | 110 |
| Arginine | 15 | 0 | 0 | 0 | 19 | 18 | 29 | 9 |
| Aspartic acid | 120 | 122 | 123 | 125 | 153 | 158 | 161 | 162 |
| Cystine | 0 | 0 | 0 | 3 | 6 | 8 | 35 | 3 |
| Glutamic acid | 66 | 80 | 106 | 78 | 71 | 89 | 63 | 60 |
| Glycine | 114 | 86 | 99 | 85 | 97 | 95 | 105 | 98 |
| Histidine | 40 | 75 | 85 | 98 | 20 | 35 | 29 | 35 |
| Hydroxyproline | 14 | 6 | 15 | 22 | 10 | 8 | 17 | 6 |
| Isoleucine | 45 | 41 | 45 | 41 | 44 | 34 | 44 | 52 |
| Leucine | 56 | 61 | 59 | 64 | 56 | 44 | 55 | 73 |
| Lysine | 44 | 36 | 34 | 54 | 48 | 75 | 106 | 35 |
| Methionine | 5 | 0 | 3 | 1 | 3 | 5 | 2 | 3 |
| Phenylalanine | 26 | 38 | 24 | 25 | 33 | 24 | 28 | 28 |
| Proline | 48 | 115 | 56 | 59 | 51 | 67 | 43 | 50 |
| Serine | 84 | 76 | 89 | 82 | 81 | 67 | 41 | 97 |
| Threonine | 70 | 76 | 70 | 70 | 85 | 74 | 70 | 68 |
| Tyrosine | 26 | 31 | 29 | 31 | 37 | 23 | 26 | 51 |
| Valine | 130 | 65 | 65 | 68 | 80 | 63 | 76 | 60 |

Table 2. Amino acid composition of the proteinaceous components (residues per 1000 residues) of the gum exudates from *Terminalia sericea*, *T. superba*, and *Anogeissus schimperi*

| | *Terminalia* | | *Anogeissus* |
|---|---|---|---|
| | *sericea* | *superba* | *schimperi* |
| % N | 0.46 | 0.18 | 0.20 |
| Alanine | 73 | 121 | 98 |
| Arginine | 22 | 47 | 10 |
| Aspartic acid | 98 | 127 | 104 |
| Cystine | 31 | 8 | 4 |
| Glutamic acid | 71 | 78 | 126 |
| Glycine | 88 | 106 | 96 |
| Histidine | 24 | 31 | 39 |
| Hydroxyproline | 8 | 19 | 4 |
| Isoleucine | 37 | 33 | 48 |
| Leucine | 65 | 49 | 70 |
| Lysine | 112 | 43 | 33 |
| Methionine | 9 | 6 | 3 |
| Phenylalanine | 13 | 26 | 29 |
| Proline | 50 | 61 | 65 |
| Serine | 101 | 81 | 83 |
| Threonine | 84 | 75 | 76 |
| Tyrosine | 32 | 20 | 42 |
| Valine | 83 | 69 | 69 |

Hydroxyproline is, however, a minor amino acid component of gum karaya (*Sterculia* spp.) [1] and of the seed galactomannan gum guar (*Cyamopsis* spp.) [3].

The variability in amino acid composition shown by these *Combretum*, *Terminalia* and *Anogeissus* species corresponds to the variability reported for their polysaccharide parameters [9–13]; the extent of the diversity in composition and complexity of the Combretaceae gums, which reflects the complexity of the genus *Combretum* itself, has already been the subject of detailed comment [11]. The Combretaceae gums are used extensively as adhesives and in a wide range of technological applications, but none of them has been subjected to toxicological evaluation of any kind and they are not permitted in foodstuffs.

## EXPERIMENTAL

*Gum specimens.* Origins of the specimens from *Combretum hartmannianum* [9] and from *C. glutinosum*, *C. collinum* and *C. fragrans* [10] have been described. The gum from *C. molle* R. Br. was collected in August 1967 by Mr. G. E. Rweyemamu, Regional Forest Officer, at Tabora, Tanzania. The gums from *C. zeyheri* Sond., *C. psidioides* Welw. syn. *C. grandifolium* F. Hoffm., and *C. obovatum* F. Hoffm. were collected in September 1965 by Mr. J. H. Dick, Regional Forest Officer, at Isenegaza Public Lands, Tabora, Tanzania.

*Analytical methods.* N contents were determined by a semimicro Kjeldahl method and the methods used for the acidic hydrolysis (6 M HCl) of the proteinaceous components [1] and for the chromatographic sepn and identification of their constituent amino acids are described in refs. [1, 6].

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# *O*-ACETYLETHANOLAMINE, A NATURAL PRODUCT FROM THE LEGUMINOSAE

Alison R. Hayman and David O. Gray*

School of Biological Sciences, Queen Mary College, Mile End Road, London E1 4NS, U.K.

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**Key Word Index**—*Lens culinaris*; Leguminosae; lentil; isolation: amines; ethanolamine, *O*-acetyl; dansyl chloride.

**Abstract** - *O*-Acetylethanolamine, studied as its dns derivative throughout, was isolated from *Lens culinaris* and identified by spectroscopy/synthesis. Chromatographic evidence indicated its presence in 12 other legumes.

## INTRODUCTION

*N*-Acetylated derivatives of amines, like those of spermidine [1], putrescine [2], cadaverine [3], histamine [4], norepinephrine [5], serotonin [6], 5-methoxytryptamine [7] and tryptamine [8] are well known natural products, though, so far, only the latter has been found in a higher plant (*Prosopis nigra*). *O*-Acetylated amines are much rarer though acetylcholine occurs in *Viscum album* (mistletoe) [9], *Spinacea oleracea* [10], *Phaseolus vulgaris* [10], *Pisum sativum* [10], *Solanum nigrum* (black nightshade) [11] and *Ipomoea abutiloide* [12], as well as having an essential role in mammals.

Ethanolamine may well be a universal constituent of higher plants, probably due to its role in phospholipid metabolism, but its only known derivatives have been *N*-(γ-L-glutamyl)-ethanolamine, from the mushroom, *Agaricus bisporus* [13], and diethanolamine from a number of composite species [14]. We now add *O*-acetylethanolamine to this list of naturally occurring derivatives.

## RESULTS

Here, all amines were first reacted with 5-dimethylamino-naphthalene-1-sulphonyl chloride (dns chloride) to make them both easier to detect and to isolate. Dns-*O*-acetylethanolamine (dns-ethanol-2-amino-acetate) was first recognized as a fluorescent spot running slightly slower than dns methylamine in both solvents on standard 2D-TLC-chromatograms: $R_f$s were 0.46, 0.35, 0.68 and 0.45 in solvents A, B, C and D, respectively.

After isolation from *Lens culinaris* Medic cv continental seeds the compound gave the $^1$H NMR spectrum indicated in Table 1. Decoupling experiments revealed that the 4.96 ppm proton was coupled to the two protons at 3.20 ppm which were themselves coupled to the two protons at 3.98 ppm. These results suggested that the isolate was an ester of dns-ethanolamine. A mass spectrum produced a molecular ion with an $m/z$ of 336 indicating that the isolate was dns-*O*-acetylethanolamine. A synthetic dns standard co-chromatographed with the isolate in all four TLC solvents tested (A–D) and had an identical $^1$H NMR spectrum.

The *O*-acetylethanolamine isolated here might have been an artifact, produced when naturally occurring ethanolamine was evaporated in the aqueous acetic acid used to elute the amine fraction from an ion-exchange (CM52) column; this possibility was excluded first by eluting the CM52 with 0.5 M HCl in place of $CH_3 \cdot COOH$ (evaporating the eluate immediately to avoid the decomposition that otherwise occurs) and secondly by dansylating a concentrated extract directly: a spot having a green fluorescence and co-chromatographing with inter-

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*To whom correspondence should be addressed.