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SHORT REPORTS

A NITROPROPANOYL-GLUCOPYRANOSIDE FROM *INDIGOFERA SUFFRUTICOSA*

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Key Word Index– *Indigofera suffruticosa*, Leguminosae, aliphatic nitrocompounds, structural determination

Abstract—An investigation of root and stem of *Indigofera suffruticosa* has led to the isolation of a new nitropropanoyl-glucopyranoside [2,3,4,6-tetra(3-nitropropanoyl) α-D-glucopyranose]. Its structure was determined by spectroscopic methods as well as GC analysis of the corresponding alditol acetate.

INTRODUCTION

Glucose esters of 3-nitropropanoic acid (NPA) were described as toxic constituents of plants of genera *Indigofera* (Leguminosae [1–3]; *Coronilla* (Leguminosae) [5, 6], *Corynocarpus* (Corynocarpaceae) [7, 8], *Hiptage* (Malpighiaceae) [9]; *Heteropteris* [10] *Astragalus* (Leguminosae) [11] There are mono-, di-, tri- and tetrasubstituted esters of NPA

D-(+)-Pinitol, β-sitosterol and louisfieserone have been isolated from petrol extracts of the whole plant of *Indigofera suffruticosa* [1, 2] This report describes the characterization of a new nitropropanoyl-α-glucopyranose from the same plant.

RESULTS AND DISCUSSION

Indigofera suffruticosa roots and stem were extracted with ethyl acetate. The major compound eluted from silica gel adsorption chromatography was 2,3,4,6-tetra(3-nitropropanoyl)-α-D-glucopyranose **1**, which structure was assigned primarily on the basis of NMR spectral evidence.

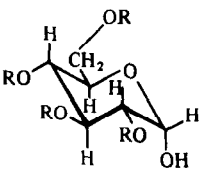
Triplets at δ3.08 and 4.80 correspond to the acyl and the nitromethylene protons of the NPA substituents, respectively. Comparison of the integration of all protons with the integral from nitropropanoyl substituents established **1** to be tetrasubstituted. The ^{1}H NMR spectrum of **1** displayed a signal at δ5 40 which became a doublet after D_2O exchange. This signal is due to the anomeric proton, and this is an indication that C-1 is not esterified [6, 8] The small coupling constant ($J=4$ Hz) can be attributed to an equatorial proton [12] and hence the sugar moiety is considered to be an α-glucopyranose. Substitution at C-6 was confirmed by the low field position (δ4.25) of C-6 methylene proton signals By comparison of H-2, H-3 and H-4 chemical shifts with those reported by Moyer [6, 8] we could unambiguously establish the assignments for the remaining protons (H-2, δ4 92; H-3, δ5.66 and H-4, δ5.20).

Further experimental results support the structural determination The identity of the sugar moiety was confirmed by GC (10% NPGS on Chromosorb WHP), of the corresponding alditol acetate prepared after acid hydrolysis, and sodium borohydride reduction

EXPERIMENTAL

Plant collection and extraction Indigofera suffruticosa was collected near Campo Grande, state of Mato Grosso do Sul, South-Western Brazil A voucher specimen, No 1966, was deposited in the herbarium of the University of Mato Grosso do Sul. The plant material (1 8 kg) was dried, powdered, extracted with hexane, then EtOAc and subsequently with EtOH. The extracts were evapd under red. pres and the residue of EtOAc extract was placed on a silica gel column and eluted with hexane increasing percentages of EtOAc

2,3,4,6-Tetra(3-nitropropanoyl)-α-D-glucopyranose (**1**) crystallized from MeOH to give colourless crystals, mp (uncorr.) 139–141° IR λ_{max}^{KBr} cm^{-1} 1737, 1542, 1368, 1196, 870. ^{1}H NMR



1 R = $\overset{O}{\overset{\|}{C}}CH_2CH_2NO_2$

[100 MHz, $(CD_3)_2CO$)]. δ6.39 (1H, *d*, J = 4 Hz, disappeared on addition of D_2O), δ5.66 (1H, *t*, J = 10 Hz), δ5.40 (1H, *t*, J = 4 Hz, doublet after D_2O exchange), δ5.20 (1H, *t*, J = 10 Hz), δ4.92 (1H, *dd*, J = 10 and 4 Hz), δ4.80 (8H, *t*, J = 6 Hz), δ4.25 (2H, *br*, $W/2$ = 7 Hz), δ4.30 (1H, *dt*, J = 10 and 4 Hz), δ3.08 (8H, *t*, J = 6 Hz) [Anal. found: C, 37.19; H, 4.21; N, 9.59. $C_{18}H_{24}N_4O_{18}$ (584) requires C, 36.98; H, 4.28; N, 9.58]

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REFERENCES

1. Dominguez, X. A., Martinez, C., Calero, A., Dominguez, Jr., X. A., Hinojosa, M., Samudio, A., Watson, W. H. and Zabel, U. (1978) *Planta Med.* **34**, 172.
2. Dominguez, X. A., Martinez, C., Calero, A., Dominguez Jr., X. A., Hinojosa, M., Zamudio, A., Zabel, V., Smith, W. B. and Watson, W. H. (1978) *Tetrahedron Letters* 429.
3. Garcez, W. S., Garcez, F. R. and Honda, N. K. (1985) *Ciência Cult.* (Suppl.) **37**, 312.
4. Finnegan, R. A. and Mueller, W. H. (1965) *J. Pharm. Sci.* **54**, 1136.
5. Majak, W. and Bose, R. J. (1976) *Phytochemistry* **15**, 415.
6. Moyer, B. G., Pfeffer, P. E., Moniot, J. L., Shamma, A. and Gustine, D. L. (1977) *Phytochemistry* **16**, 375.
7. Carter, C. L. (1950) *J. Sci. Food Agric.* **2**, 54.
8. Moyer, B. G., Pfeffer, P. E., Vallentine, K. M. and Gustine, D. (1978) *Phytochemistry* **18**, 111.
9. Finnegan, R. A. and Stephani, R. A. (1968) *J. Pharm. Sci.* **57**, 353.
10. Stermitz, F. R., Hnatyszyn, O., Bandoni, A. L., Rodina, R. V. D. and Coussio, J. D. (1975) *Phytochemistry* **14**, 1341.
11. Stermitz, F. R., Lowry, W. T., Norris, F. A., Buckeridge, F. A. and Williams, M. C. (1972) *Phytochemistry* **11**, 1117.
12. Hall, L. D. (1974) *Adv. Carbohyd. Chem. Biochem.* **29**, 11.

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2-HYDROXYETHYL GLUCOSINOLATE FROM *CAPPARIS MASAIKAI* OF CHINESE ORIGIN

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Key Word Index—*Capparis masaikai*, Capparidaceae, glucosinolate, oxazolidine-2-thione

Abstract—Detailed chemical, degradative and spectroscopic studies have led to the isolation and characterization of 2-hydroxyethyl glucosinolate from the seed of *Capparis masaikai*. This is the first report of this glucosinolate, which is the simplest member of the group of glucosinolates which spontaneously cyclize upon treatment with thioglucoside glucohydrolase (EC 3.2.3.1) [myrosinase], thereby yielding oxazolidine-2-thione.

INTRODUCTION

Plants of *Capparis masaikai* Lévl. (local name mabinlang) grow in the subtropical region of the Yunnan region of China. The seed meal is a traditional Chinese medicine, and the seeds are commonly chewed for their sweet taste, due to the presence of sweet proteins, mabinlins [1].

Sporadic, though detailed, investigations amongst other *Capparis* species have revealed the occurrence of a variety of glucosinolates. Thus three independent examinations of the dried leaves of *C. flexuosa* revealed the presence of benzyl [2], methyl and 5-oxoheptyl [3], butyl, 3-hydroxybutyl, 4-hydroxybutyl, but-3-enyl and 2-hydroxybut-3-enyl glucosinolates [4]. Possible reasons for these discrepancies have been advanced by Kjaer and Schuster [4], but these have not been examined in detail. Elsewhere, *C. angulata* and *C. ovata* have been shown to contain 4-oxoheptylglucosinolate [5, 6], whilst Ahmed *et al.* [6] have further reported prop-2-enyl, methyl, 3-methylsulphinylpropyl, 2-hydroxy-2-methylbutyl, 3-indolylmethyl and 1-methoxy-3-indolylymethyl glucosinolates in Egyptian varieties of *C. ovata*. Two other ketone-containing glucosinolates, possessing 5-oxoheptyl and 5-oxooctyl sidechains have also been identified in *C. salifolia* [7, 8], the former also being found in *C. ferruginea*. Perhaps most intriguing of all, Gaind *et al.* [9] have isolated and characterized a unique 4,5,6,7-tetrahydroxydecyl glucosinolate from the dried roots of *C. grandis*.