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

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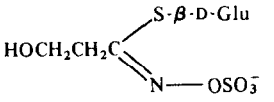
Key Word Index—*Capparis masaikai*, Capparidaceae, glucosinolate, oxazolidine-2-thione

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*.



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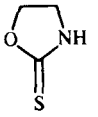

2

Against this background we have recently examined the seeds of *C. masaikai*, growing in Yunnan, for glucosinolates. We report here the results of this study.

RESULTS

Seeds of *C. masaikai* were collected in Yunnan and identified by Professor Wu Cheng-yin A specimen was deposited in the Herbarium of the Kunming Institute of Botany. The seeds were ground and defatted with 60–80 hexane to yield a meal. Preliminary HPLC [10] and subsequent MS [11] of an aqueous extract of the defatted product indicated the presence of a single glucosinolate having a M_r of 363 [negative-ion FAB mass spectrum, *m/z* 362, negative-ion FAB mass spectrum of the desulphated product, *m/z* 282]. Extraction of the defatted meal with 70% methanol, followed by alumina column chromatography and successive passage through G-10 Sephadex [12] and C-18 silica flash chromatography [13] columns afforded a colourless solid which was finally purified by recrystallization from aqueous alcohol.

Trimethylsilylation of this product under standard conditions gave a hexa-silylated product, indicating that one hydroxyl grouping was present in the side chain. Treatment with thioglucoside glucohydrolase (myrosinase) produced glucose. The ^{1}H NMR spectrum was similar to those of other aliphatic glucosinolates [14] and showed two triplets at δ3 10 and 4.10 characteristic of a 2-hydroxyethyl moiety. Decoupling the triplet at δ3.10 led to the collapse of the signal at δ4.10 to a singlet, whilst the remainder of the spectrum was unaffected. The ^{13}C NMR spectrum was similar to those of other glucosinolates [14] and confirmed the presence of glucose and the two-carbon side chain. The quaternary carbon C-7 (numbering as in ref. [14]) is particularly distinctive and typical of those in the glucosinolate molecule. On the basis of the above evidence the compound was shown to be 2-hydroxyethyl glucosinolate (**1**). When samples of the isolated product and the original defatted seed were treated with thioglucoside glucohydrolase, extraction of the products of the hydrolysis revealed the presence of oxazolidine-2-thione, identical in all respects with an authentic sample (**2**)

EXPERIMENTAL

TLC and HPTLC were carried out on silica plates using BuOH–HOAc–H_2O (4·1 2) as the mobile phase The glucosinolate was visualized with thymol–H_2SO_4 reagent HPLC of the desulphoglucosinolate was conducted as reported earlier [10], whilst a Zorbax ODS (4 6 mm × 25 cm) column was employed for the oxazolidine-2-thione, mobile phase 2 5 mmol H_2SO_4 containing MeOH (5%) NMR spectra were determined at 80 MHz and 400 MHz (^{1}H) and 100 MHz (^{13}C), the glucosinolate spectra being recorded in D_2O with MeOH as internal standard, those of oxazolidine-2-thione in deuteriomethanol or deuteriopyridine with TMS as internal standard FABMS were recorded at ambient and 6 kV, whilst EIMS were recorded at 70 eV

The ground seed was stirred with 60–80 hexane, air-dried and extracted with 70% MeOH as described elsewhere [13] The concd extract was applied to a column of acidic alumina, washed with H_2O and eluted with 5% K_2SO_4 After desalting, the product was dissolved in H_2O and applied to a column of G-10 Sephadex The column was eluted with H_2O, the fractions being monitored by TLC [R_f 0.15] Fractions containing the desired product were combined, dissolved in H_2O and applied to a column of C-18 silica and eluted under flash chromatographic conditions with 5% K_2SO_4 The product (**1**) was dried and recrystallised from eq. EtOH to provide colourless crystals, mp 145°, ^{1}H NMR (D_2O); δ5 19 (1H, *d*, *J* = 9 Hz), 4 10 (2H, *t*, *J* = 6 Hz), 3 92 (2H, *m*), 3 70 (4H, *m*), 3 10 (2H, *t*, *J* = 6 Hz) Irradiation at δ3 10 collapsed the triplet at δ4.10 to a singlet ^{13}C NMR (D_2O), δ35 9 (C-8), 59 4 (C-9), 61 5 (C-1), 69 9 (C-3), 72 7 (C-5), 77 8 (C-4), 80 8 (C-2), 82 6 (C-6), 162 1 (C-7)

The purified glucosinolate (5 mg) was incubated in citrate buffer (1 ml, pH 5 5) with myrosinase (5 mg) at 37° for 30 min The mixture was diluted to 20 ml with H_2O, passed through a Diaflo UF membrane PM5 and the effluent analysed by HPLC and TLC A single product was seen in both systems and shown to be chemically and chromatographically (R_t 7 68 min) identical to an authentic sample [15] of oxazolidine-2-thione (**2**).

Defatted seed meal was stirred in H_2O, filtered through gauze, concd to dryness and stirred with 75% MeOH The soln was decanted, passed through a column of Dowex 2 (Cl^- form) and the column eluted with distilled H_2O, monitoring at 254 nm The fractions showing such absorbance were combined then concd to afford colourless crystals. These were recrystallized from EtOH, mp 96 5–97°, *m/z* 103, 73, 60, 42, ^{1}H NMR (pyridine), δ11 2 (1H), 4 57 (2H, *t*, *J* = 8.5 Hz), 3 73 (2H, *t*, *J* = 8 6 Hz), ^{13}C NMR (CD_3OD), δ95 99, 69 5, 235, shown to be homogenous in the TLC and HPLC systems employed, and identical to authentic oxazolidine-2-thione [15] This was confirmed by X-ray analysis [16]

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N-ALKANES FROM CHILEAN EUPHORBIACEAE AND COMPOSITAE SPECIES

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Key Word Index Euphorbiaceae, Compositae, chemotaxonomy, *n*-alkanes

Abstract—The distribution pattern of *n*-alkanes in the 'refined hydrocarbon' fractions from four species of Compositae (*Lactuca serriola, Sonchus asper, Taraxacum officinale, Tessaria absinthioides*) and six species of Euphorbiaceae (*Adenopeltis serrata, Euphorbia copiapina, E lactiflua, Colliguaja dombeyana, C. odorifera, C salicifolia*) was studied Using well-established techniques, *n*-alkanes of the homologous series C_{19}-C_{33} were identified The major constituents were *n*-heptacosane (*n*-C_{27}) and *n*-nonacosane (*n*-C_{29}) Significant dominance of odd over even numbered chains and the absence of any significant quantity of branched alkanes was also found The two species of *Euphorbia* showed different distribution pattern of *n*-alkanes In two species of *Colliguaja* (*C salicifolia* and *C odorifera*), the major component was *n*-C_{27} with smaller amounts of *n*-C_{29}, but in *C dombeyana* the reverse occurred

INTRODUCTION

In recent years, there has been considerable interest in identifying and establishing new crops as renewable resources [1–5] Some of the studied plant species contain, on a dry basis, more than 5% of 'whole plant oil' (biocrude) either as the major component of a latex or distributed throughout major plant tissues

To assess the potential of the native flora, a screening programme was started and the suitability of some Chilean Euphorbiaceae and Compositae species as sources of hydrocarbon-like materials was evaluated In previous papers [6, 7] we reported that the main components of dichloromethane extracts from different plant species were *cis*-1,4-polyisoprene and waxes Analysis of the refined hydrocarbons from different species revealed almost exclusively the presence of *n*-alkanes Since *n*-alkane distributions have been utilized as taxonomic criteria [8–11], we have investigated the distribution of this type of compound in the refined hydrocarbons from the different plant species A report on the distribution of the high M_r components will be published elsewhere

RESULTS AND DISCUSSION

Refined hydrocarbons fractions, obtained from CH_2Cl_2 extracts of plant samples (leaves and stems), were analysed by IR, ^{1}H NMR, ^{13}C NMR, mass spectrometry and GC The results revealed the presence of *n*-alkane mixtures of chain lengths varying from *n*-nonadecane (*n*-C_{19}) to *n*-tritriacontane (*n*-C_{33}) All the spectral data obtained agreed with those reported in literature [11–13] The GC R_ts and mass spectra were compared with those of authentic standards The quantitative results are given in Table 1, they were obtained by measurement of peak