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Glucosinolates from Maca (*Lepidium meyenii*)

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1. Subject and Source

Maca (*Lepidium meyenii* Walp) is a food plant belonging to the Cruciferae family. It is very interesting because it has one of the highest frost tolerances of any cultivated plant and can be grown at high altitudes (3800–4800 m) (Bonnier, 1986). Maca dry tubers were bought from INIA (Instituto National de Investigation Agroindustrial de Huancayo, Peru); a sample has been deposited in the Herbarium Neapolitanum the Dipartimento di Biologia Vegetale Università degli Studi 'Federico II' of Naples (herbarium code NAP).

2. Previous work

Maca tubers present a nutritional profile better than other common edible tubers, such as potato (Dini et al., 1994). The fresh tuber is unusually high in minerals and contains a cocktail of compounds called 'phytochemicals' that protect against a wide range of pathologies (Gonzales et al., 2001; Zheng et al., 2000; Cicero et al., 2001).

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3. Present study

Two glucosinolates, benzylglucosinolate (glucotropaeolin) and *m*-methoxybenzylglucosinolate have been isolated, identified and determined quantitatively from methanol extract of maca tubers. Powder of tubers (113 g) was treated with diethylamine (2 ml), extracted in a Soxhlet apparatus with CH_2Cl_2, and subsequently with boiling MeOH (2×200 ml). The methanolic extract was partitioned between *n*-BuOH and H_2O. The *n*-BuOH extract was dried under vacuum (4.52 g), and chromatographed on a Sephadex LH-20 column (100×5 cm) with MeOH as the eluent. A total of 79 fractions (9 ml) were collected and checked by TLC [Si-gel plates in n-BuOH-HOAc-H_2O (60:15:25)]. Fractions 60–79 (1527 mg), containing the crude glucosinolates mixture were submitted to RP–HPLC using MeOH–H_2O (60:40), flow rate 3 ml/min, to yield pure benzylglucosinolate diethylammonium salt. The structures of isolated compounds were elucidated by chemical and spectroscopic methods, including HMQC, HMBC, COSY and FABMS (Table 1). The content of glucosinolates was determined by the procedure of VanEtten and Tookey(1979). The whole flour from the tubers (6.21 g) was extracted with boiling methanol for 15 min, and then with boiling methanol/water 70/30. The combined extracts under vacuum at < 50 °C were concentrated to 15 ml and were added to a glass column (100×9 mm i.d.) containing 0.8 g of resin (Ion Exchanger III. Strongly alkaline anion-exchanger Merck's Reagent). Phosphate buffer (3 ml, pH 7.6; 13.2 ml of $Na\ H_2PO_4 \cdot 2\ H_2O$ and 86.8 ml of $Na_2HPO_4 \cdot 12\ H_2O$) was added as eluent on the column after repeated washings with distilled water (10 ml). The resin–glucosinolate complex, dichloromethane (25 ml), and myrosinase [Sigma, thioglucosidase (E.C.3.2.3.1)] (10 mg; 24.4 units) were shaken in a plugged glass culture tube over night. The dichloromethane layer was submitted for GC–MS analysis. The ion chromatogram (total ion/time) showed two peaks, the first one was $> 99.5\%$ of the latter. Total glucose in maca powder was detected in the water solution by enzymatic Sigma Diagnostic Method, using Single Reagent System Glucose [HK] 10. The content of glucotropaeolin (practically the only component of the glucosinolate fraction) was estimated from glucose released by GC–MS.

4. Chemotaxonomic significance

Two glucosinolates, glucotropaeolin and its methoxyderivative (**1**, **2**) (Fahey et al., 2001), were found for the first time in a maca commercial sample, provided by a Peruvian producer. Their presence could be used as a chemotaxonomic marker for these species because this combination does not occur in other Brassicaceae family plants (Fahey et al., 2001).

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Table 1
Spectroscopic data of glucotropaeolin and *m*-methoxybenzylglucosinolate[a]

NMR data of benzylglucosinolate diethylammonium salt (500 MHz CD_3OD)						
Position	^1H	^{13}C	DEPT	^1H-^1H 2D COSY correlated H	^{13}C -^1H 2D HMQC correlated C	^{13}C-^1H 2D HMBC correlated C
1		137.4				
2,6	7.45	129.3	CH	3,5	129.3	
3,5	7.37 (d d; J = 8; 2 Hz)	129.9	CH	2,6	129.9	
4	7.29	128.2	CH		128.2	
7a	4.08 (d; J = 16.3 Hz)	39.6	CH_2	7b	39.6	C-8 (160.8)
7b	4.28 (d; J = 16.3 Hz)			7a		C-1 (137.4)
8		160.8				
		Glucose				
1’	4.82 (d; J = 7.7 Hz)	82.8	CH		82.8	
2’	3.25	74.2	CH		74.2	
3’		79.5	CH			
4’	3.30-3.55	71.1	CH			
5’		82.2	CH			
6’a	3.63 (d d; J = 12.5;5.5 Hz)	62.7	CH_2	6’b	62.7	
6’b	3.86 (d d; J = 12.5;5.5Hz)			6’a		
		Diethylamonium group				
1’’	3.02 (q; J = 7 Hz)	43.5	CH_2	2’’	43.5	
2’’	1.37 (t; J = 7 Hz)	11.6	CH_3	1’’	11.6	
NH_2	7.94			1’’		
		Mass Spectra				
Compound		FABMS				
Glucotropaeolin		$[M-H]^-$ *m/z* 408				
m-methoxybenzylglucosinolate		$[M-H]^-$ *m/z* 408				

[a] DEPT: Distortionless Enhancement by Polarization Transfer; GLS: Glucosinolate; HMQC: Heteronuclear Multiple Quantum Coherence ; HMBC; Heteronuclear Multiple Bond Correlation

di Ricerca Interdipartimentale di Analisi Strumentale' and FABMS spectra were performed at the 'Servizio di Spettrometria di Massa' of the University 'Federico II' Napoli. The assistance of the staffs of those facilities is gratefully appreciated.

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