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Characterization of some glycoside iridoids by mass spectrometry

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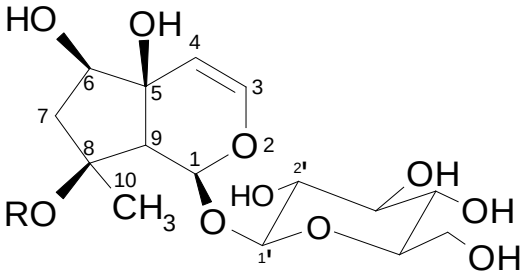
Abstract

The compounds extracted from medicinal plants started to be investigated due to their use in the treatments of different diseases. The studies of three iridoid compounds: harpagide, 8-O-acethyl harpagide and harpagoside, by quadruple mass spectrometry suggested the general mechanism of their fragmentation under electronic bombardment at 70 eV. The base peak obtained for all compound fragmentations, it was those corresponding of substituent from C_8, after the loose of glucose ion.

Introduction

Plants have formed basis of sophisticated traditional medicine systems [1]. The glycoside iridoids are known to be present only in the Dicotyledon Angiosperms within the superorders Cornanae, Ericanae, Gentiananae, Lamianae and Loasanae. Plants extracts from Stachys sieboldii Miq. containing glycosides iridoids were used as therapeutical products [2] with multiple actions [3, 4]: vasoconstrictor, antiinflammatory activity and the induction of immune response in the human body.

Around half of the drugs currently in clinical use are of natural product origin [5]. The renaissance of natural products as drug candidates is supported on the synergy of the compounds presented in the extracts and the pharmacological activities of the vegetable extracts. In this work we continued the study [6] about the characterization by mass spectrometry of harpagide, 8-O-acethyl harpagide and harpagoside, three glycoside iridoids which correspond to the general formula:



I: R = H - harpagide;
II: R = CH_3-CO- 8-O-acethyl harpagide;
III: R= cynnamoil – harpagoside

Scheme 1

It is necessary to mention the very pertinent studies of Bentley and coworkers[7] concerning cyclopentane monoterpenes of the iridoid group which not includes the presented compounds.

Materials and methods

The studied iridoids were: harpagide (purity >99%), harpagoside (purity >95%), both products of PhytoLab GmbH&Co.K.G and 8-O-acethyl harpagide, which was extracted and purified in the Laboratory of Chemical Department of Technical University of Lyngby, Denmark.

For the mass spectrometry study it was used a quadruple mass spectrometer QMD 1000 Carlo Erba Instruments.

The solutions obtained from 10µg of the substance in 200 µl ethyl alcohol were introduced in the vials and then in the mass spectrometer QMD 1000.

Working conditions:

- ionization energies 20eV and 70eV;
- detector voltage 350V;
- source temperature 160^0C.

The temperature program used for obtaining the steam of compounds was the following: during 2min. the temperature was maintained at 60^0C, then the temperature was increased at 500^0C, using a temperature gradient 50^0C/min.

Results

The sensibility of mass spectrometer at 20 eV was lower than the sensibility at 70 eV, but the spectra obtained at 20 eV were considered for better understanding of the complex spectra at 70 eV, which are showed in the figures 1-3.

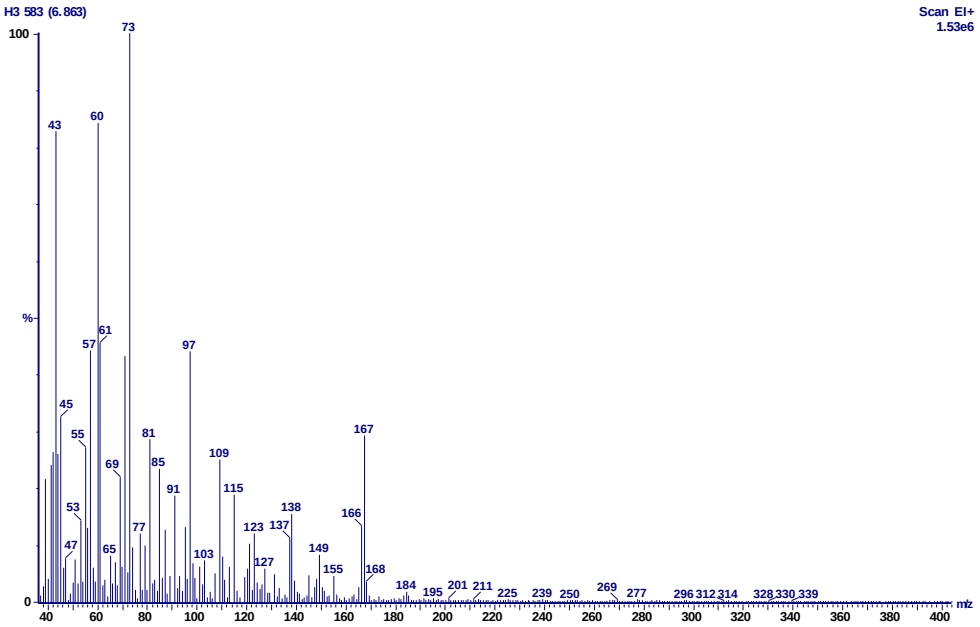


Figure 1. Mass spectrum of harpagide at 70 eV.

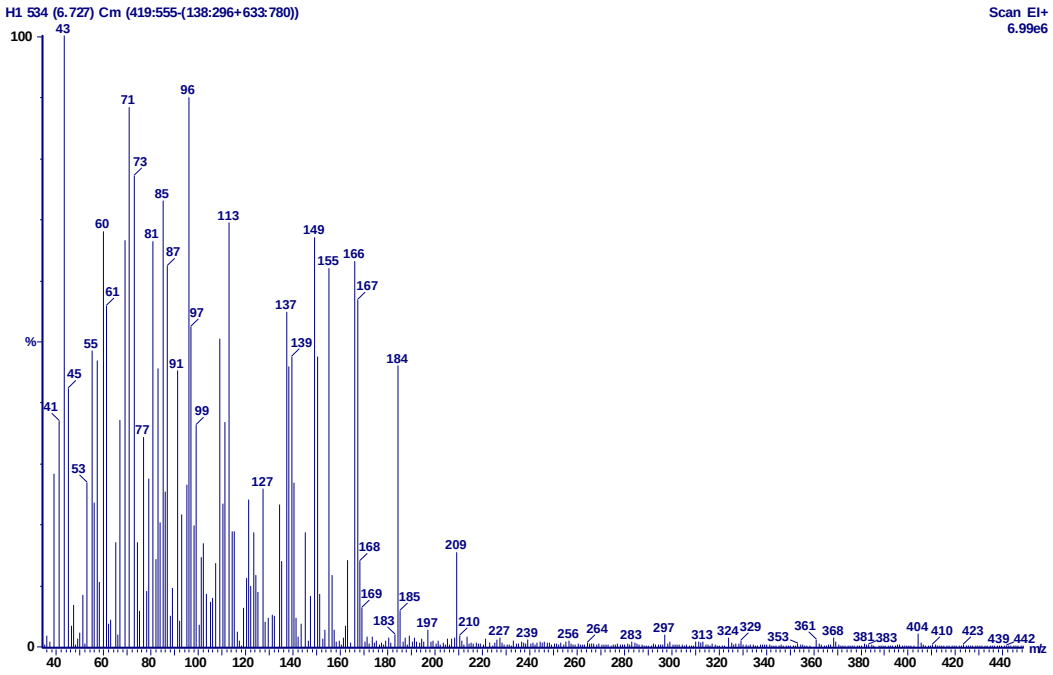


Figure 2. Mass spectrum of 8-O- acethylharpagide at 70 eV

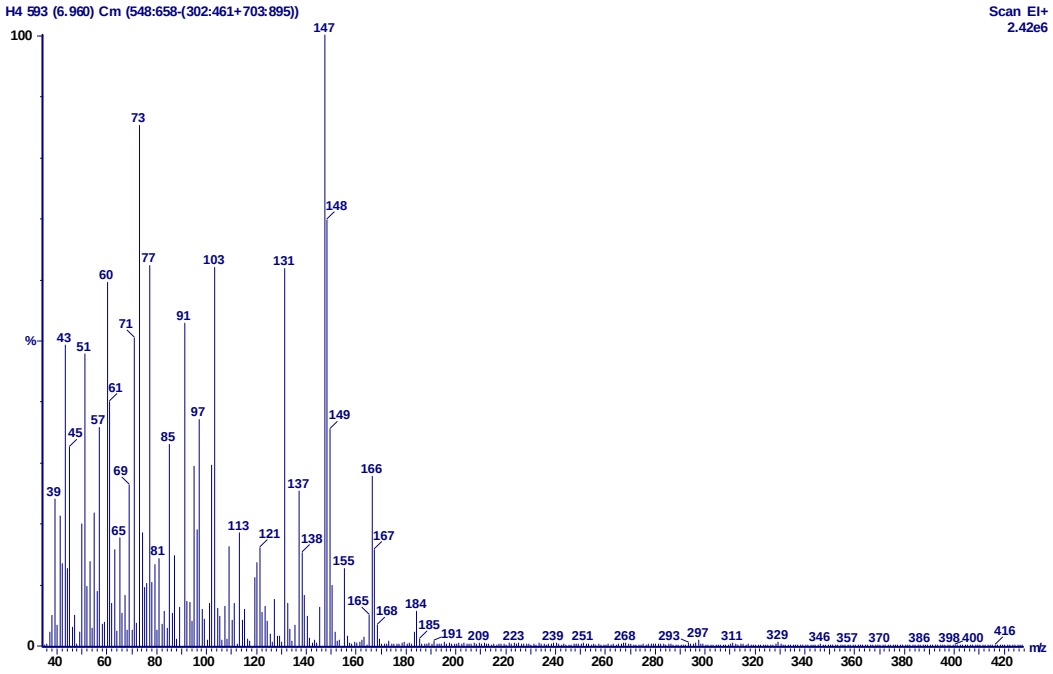


Figure 3. Mass spectrum of harpagoside at 70 eV

Take into consideration these spectra, it was observed the following ion compositions, presented in the tables 1-3.

Table 1. Ion Composition obtained at harpagide fragmentation (C15H24O10)

m/e	CH	m/e	CHO	m/e	CHO2	m/e	CHO3	m/e	CHO4
77	C6H5	71	C4H7O	71	C3H3O2	127	C6H7O3	184	C9H13O4
103	C8H7	81	C5H5O	73	C3H5O2	155	C8H11O3		
		97	C6H9O	85	C4H5O2	149	C8H5O3		
				109	C6H5O2	166	C9H10O3		
				137	C8H9O2	167	C9H11O3		
				138	C8H10O2				
				147	C9H7O2				
				148	C9H8O2				
				149	C9H9O2				

Table 2. Ion Composition obtained at 8-0-acethyl harpagide fragmentation (C17H26O11)

m/e	CH	m/e	CHO	m/e	CHO2	m/e	CHO3	m/e	CHO4
77	C6H5	43	C2H3O	71	C3H3O2	139	C7H7O3	184	C9H12O4
81	C8H9	69	C4H5O	96	C5H4O2	149	C8H5O3	197	C10H13O4
		71	C4H7O	99	C5H7O2	155	C8H11O3		
		81	C5H5O	110	C6H6O2	166	C9H10O3		
		85	C5H9O	111	C6H7O2	167	C9H11O3		
		95	C6H7O	127	C7H11O2	169	C9H13O3		
		96	C6H8O	137	C8H9O2				
		97	C6H9O						
		113	C7H13O						

Table 3. Ion Composition obtained at harpagoside fragmentation (C24H30O11)

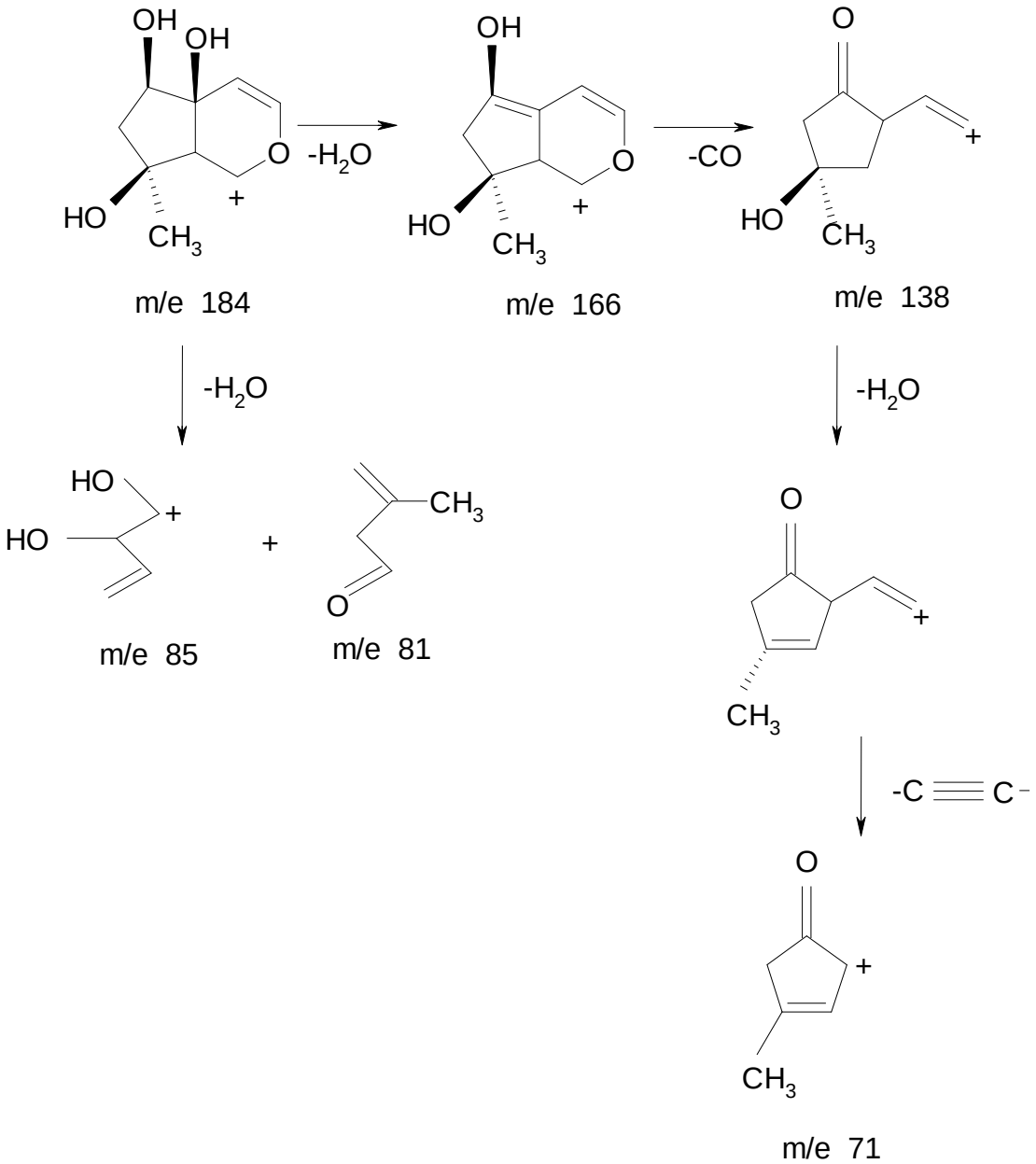
m/e	CH	m/e	CHO	m/e	CHO2	m/e	CHO3	m/e	CHO4
71	C5H11	71	C4H7O	43	C2H3O2	103	C4H7O3	155	C7H7O4
77	C6H5	81	C5H5O	71	C3H3O2	149	C8H5O3	184	C9H12O4
91	C7H7	97	C6H9O	73	C3H5O2	155	C8H11O3		
		121	C8H9O	85	C4H5O2	165	C9H9O3		
		131	C9H7O	137	C8H9O2	166	C9H10O3		
				147	C9H7O2	167	C9H11O3		
				148	C9H8O2				
				149	C9H9O2				

Discussions

From examination of 1-3 tables, the presence of the ion with m/e = 184 is very evident. This ion corresponds to the aglycon after the loose of glucose radical. The most intense peak with m/e=184 appeared in the spectrum of 8-O-acethyl harpagide. (see fig.2)

In the mass spectrum of harpagoside (fig.3), the base peak corresponds to cynnamoil radical (m/e = 147).

Based on the mass spectra (fig.1-3) and the rigorous analysis of the data contained in the tables 1-3, we proposed the following mechanism of harpagide fragmentation, in accord with some considerations from work of T.W. Bentley et all [6].



Schema 2. The mechanism of harpagide fragmentation

The similar mechanism was applied also in the case of 8-O-acethyl harpagide, with the following observations:

-the mass of corresponding aglicon radical is m/e = 227;

-the mass of acetyl radical was m/e 43;

-in the case of H_2O molecule elimination from substitutes positioned at C_5 and C_6, it was considered also the removal of acetyl radical, placed at C_8;

-during the process of division appeared the break of bonds C_3-O_2, C_5-C_9 and C_6-C_7, the acetyl radical can be eliminated from C_8.

Further considering the analog mechanism of fragmentation for harpagoside, it was proposed the following steps:

-the cinnamoyl radical with m/e=147 corresponded to base peak in the mass spectrum (see fig.3). This radical has been eliminated first and it did lead to appearance of the fragment with m/e=168. Although it was possible the loose of this one together with a H_2O molecule elimination

The molecular modeling calculations could complete these studies [8].

Conclusions

- The ratios of obtained peaks by fragmentation in the mass spectra were variable from compound to compound.
- All the mass spectra of studied glycoside iridoids contained as base peak those corresponding to the substitute from C_8.

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