

Disidratazione di Zuccheri Pentosi in Fase Gassosa: Uno Studio Teorico



SAPIENZA
UNIVERSITÀ DI ROMA

**Facoltà di Farmacia e Medicina
Corso di Laurea in Farmacia
Tesi Sperimentale in Chimica Farmaceutica
a.a. 2015/2016**

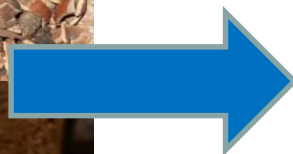
**Laureando: Lorenzo Antonini
Matricola: 1159665**

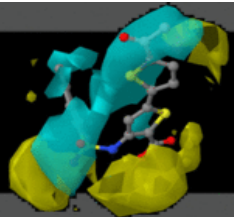
**Relatore: Prof. Rino Ragno
Correlatore: Prof. Federico Pepi**



Introduzione

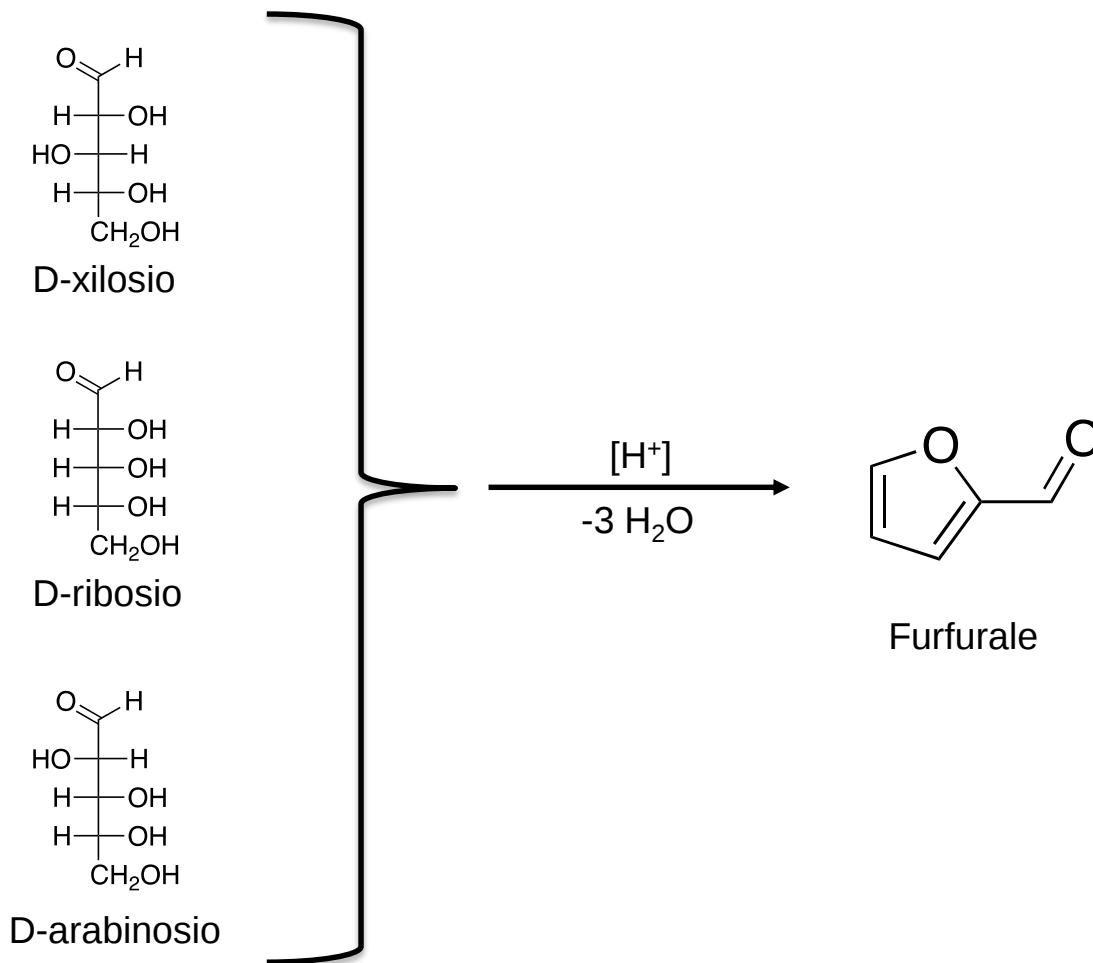
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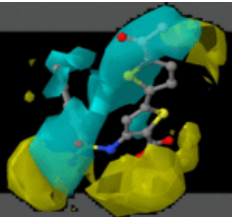




Introduzione

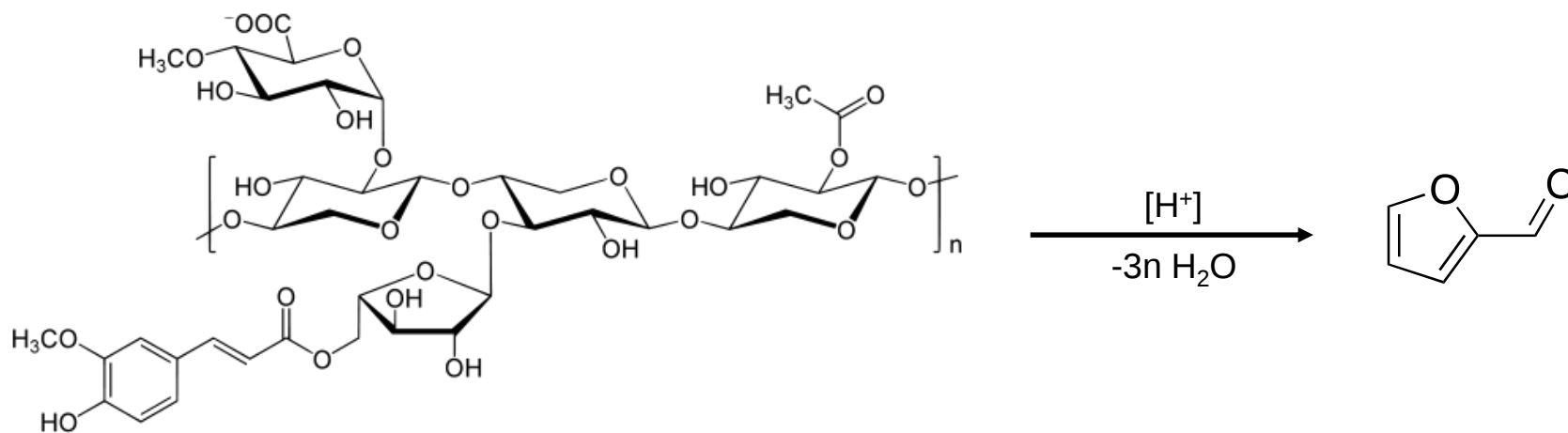
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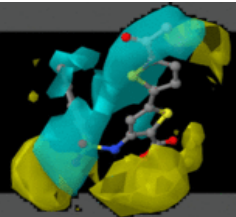


Introduzione

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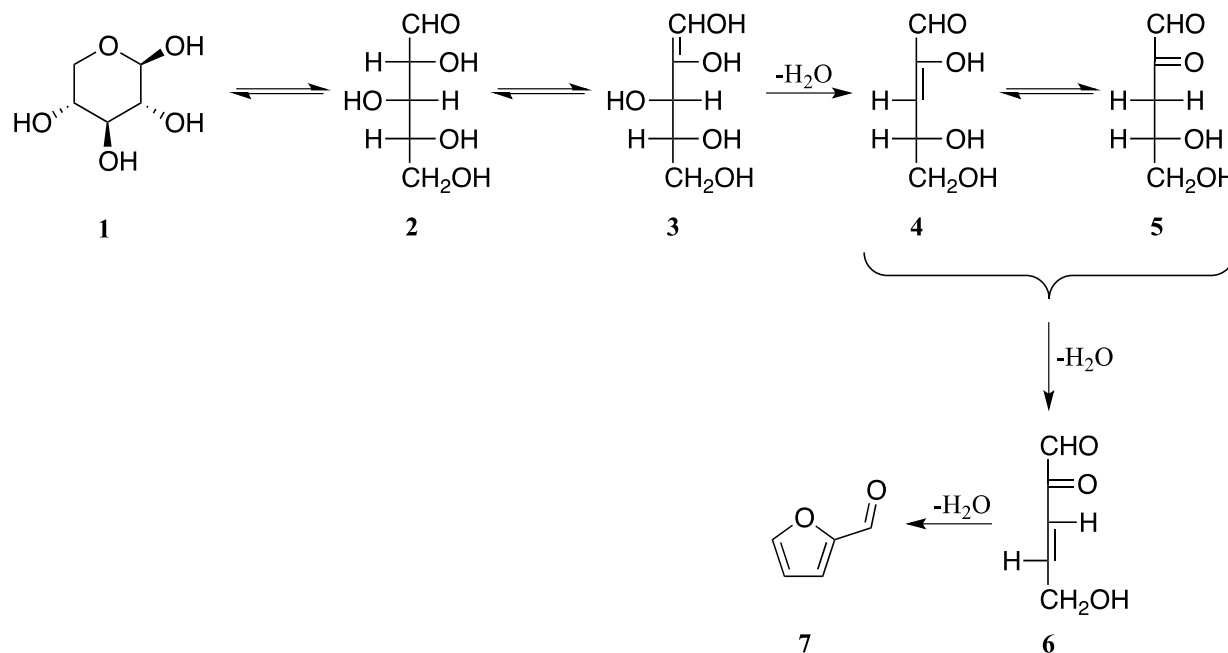


Xilano

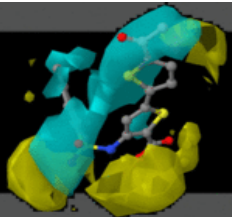


Contestualizzazione

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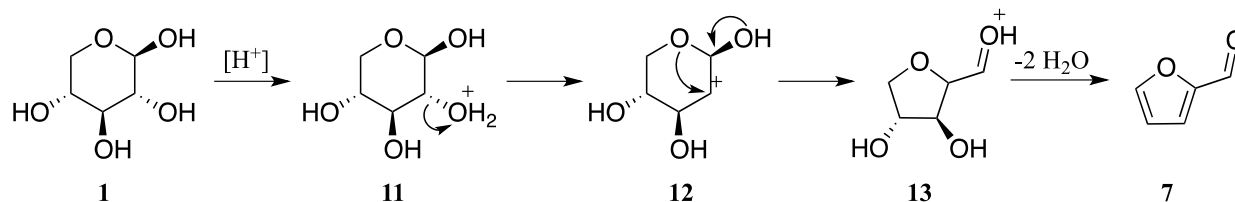
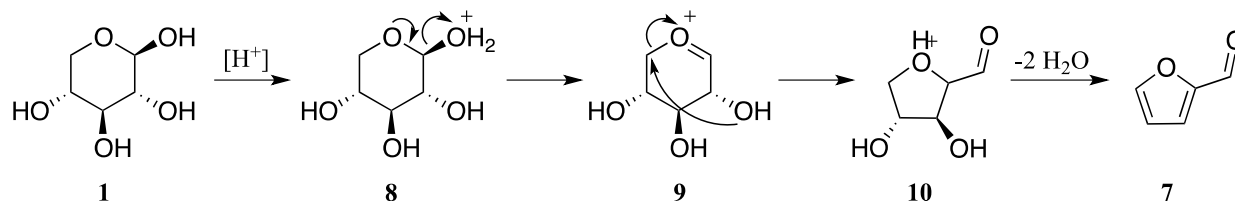


Harris, D. W.; Feather, M. S. *Carbohydr. Res.* 1973, 30, 359.

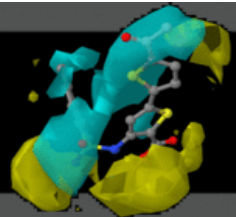


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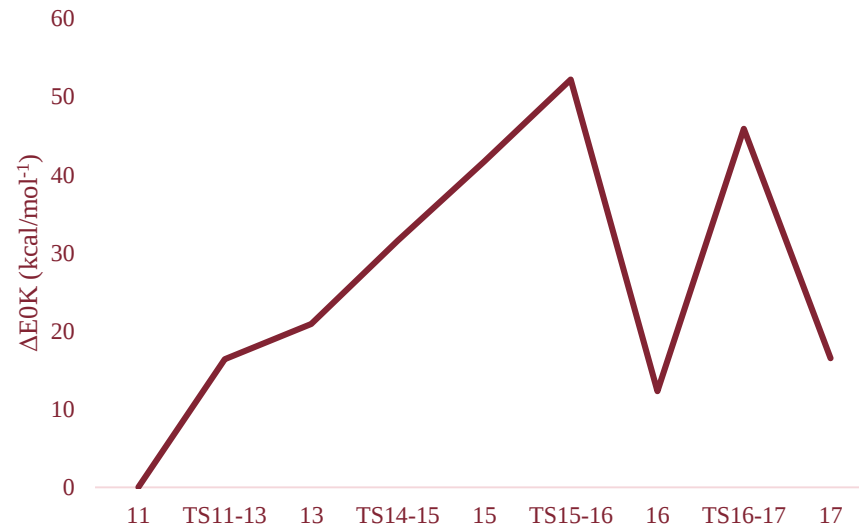
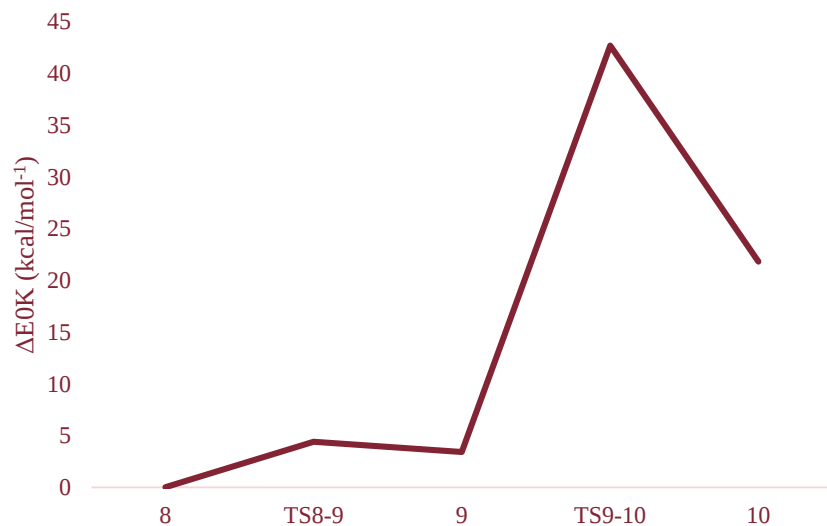
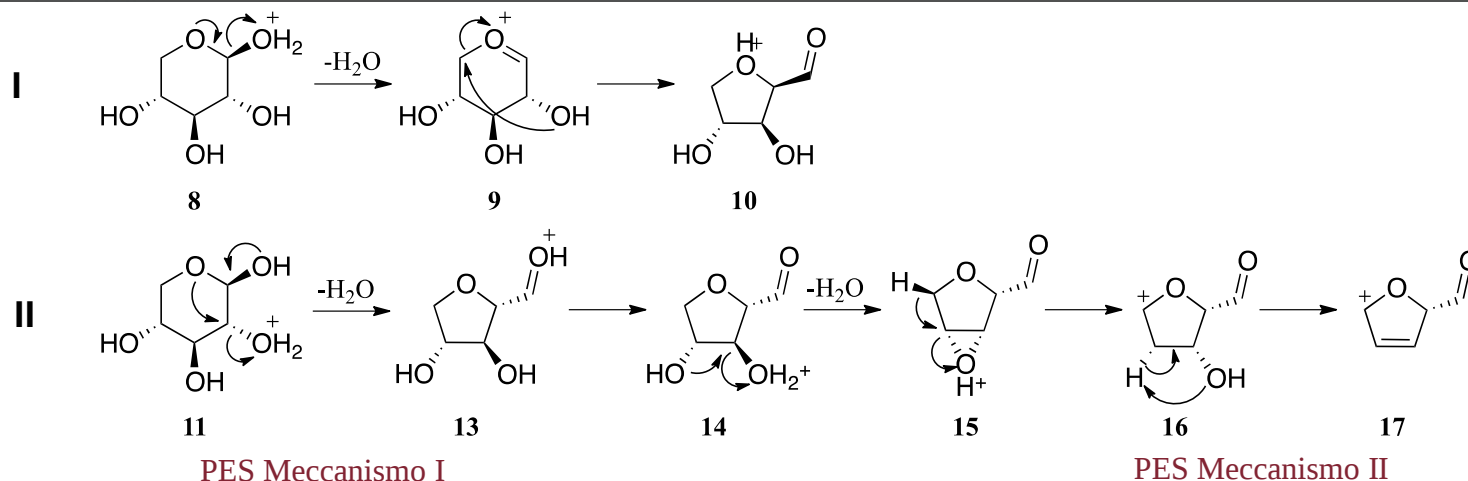


Antal Jr., M.J., Lee Somboon, T., Mok, W.S., Richards, G.N.: *Carbohydr. Res* 217, 71–85 (1991).

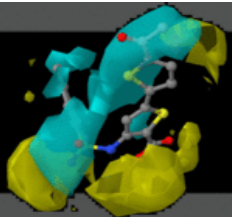


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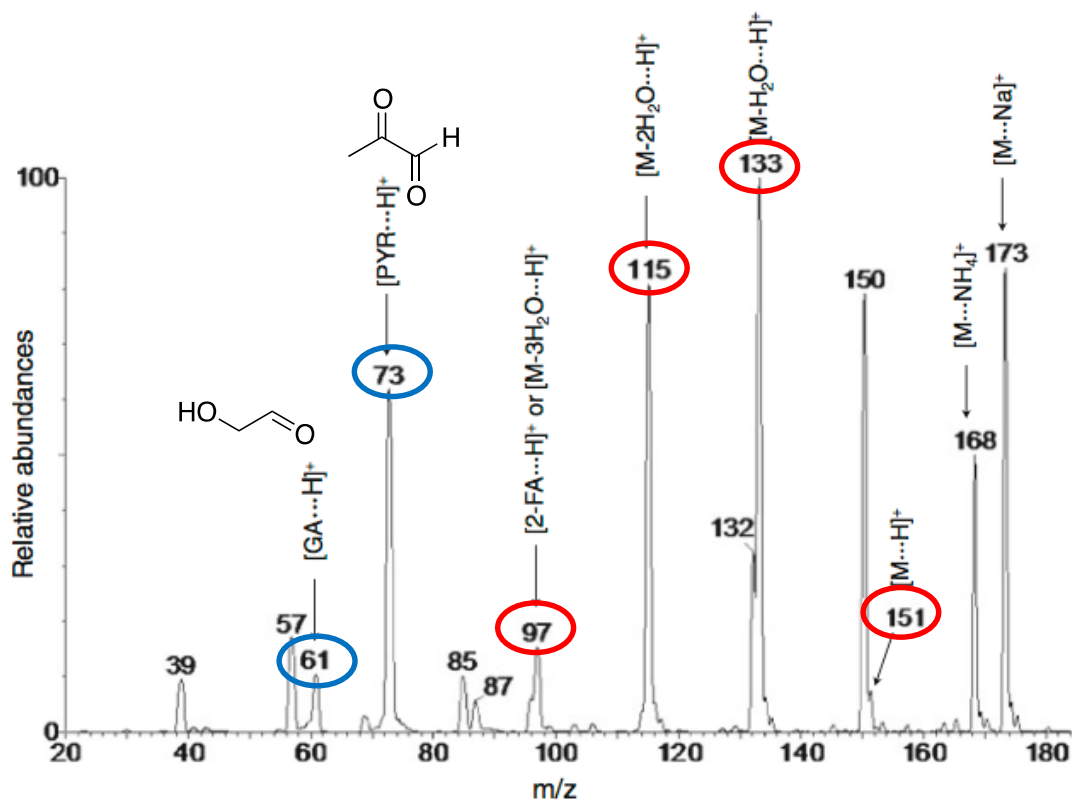
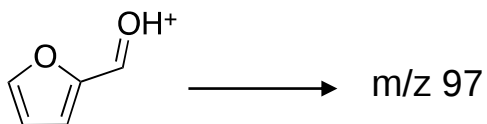
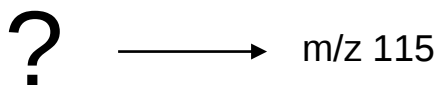
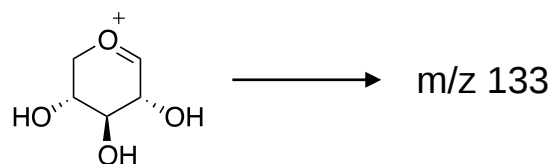
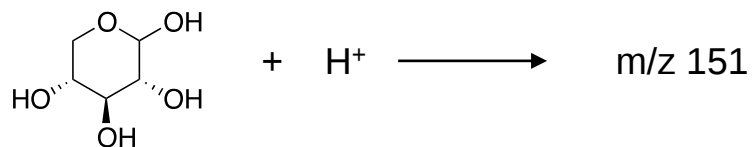


M. R. Nimlos, X. Qian, M. Davis, M. E. Himmel, and D. K. Johnson, *J. Phys. Chem. A*, 2006, **110**, 11824.

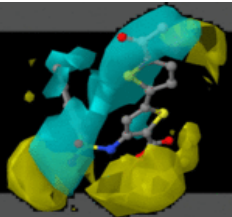


Disidratazione Xilosio

by www.RCMD.it



A. Ricci, S. Piccolella, F. Pepi, S. Garzoli and P. Giacomello, *J. Am. Soc. Mass Spectrom.*, 2013, **24**, 1082.

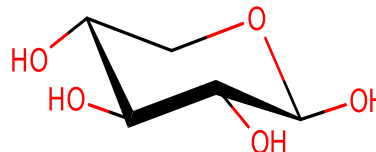


Scopo del Lavoro

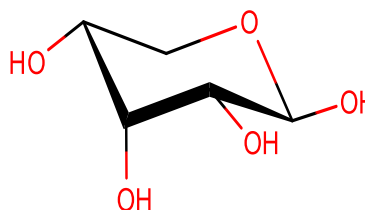
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Con questa tesi di laurea si propone il meccanismo di disidratazione in fase gassosa di tre zuccheri pentosi:

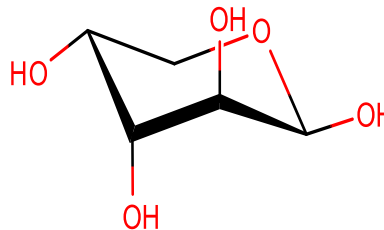
- D-xilosio

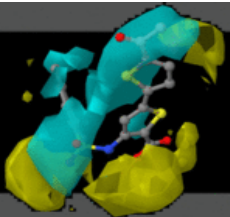


- D-ribosio



- D-arabinosio





Il calcolo Teorico

by www.RCMD.it

Ricerca delle Conformazioni

- MMFF94

$$E_{MMFF94} = \sum_i^{\text{legami}} k_i (r_i - r_{i,e})^2 + \sum_i^{\text{angoli}} k_i (\theta_i - \theta_{i,e})^2 + \sum_i^{\text{diedri}} r_i [1 \pm \cos(n_i \phi_i)] + \sum_i^{\text{atomi}} \sum_{j>1}^{\text{atomi}} \left(-\frac{A_i A_j}{r_{ij}^6} + \frac{B_1 B_2}{r_{ij}^{12}} + \frac{q_i q_j}{r_{ij}} \right)$$

Ottimizzazione delle Geometrie

- DFT M11/6-311++G(2d,2p)

$$E_{XC}^{M11} = \left(\frac{x}{100} \right) E_X^{HF} + \left(1 - \frac{x}{100} \right) (E_X^{LR-HF} + E_X^{SR-M11}) + E_C^{M11}$$

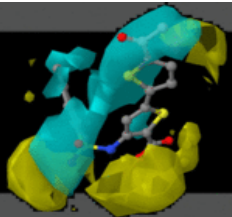
Calcolo delle Frequenze

- DFT M11/6-311++G(2d,2p)

Single Point Energy

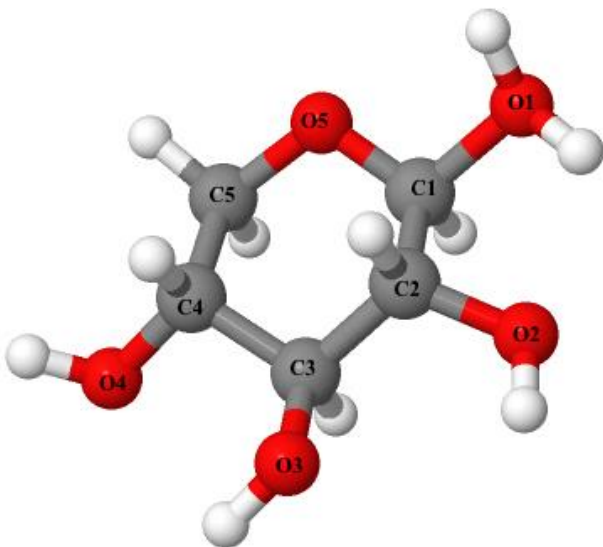
- CCSD(T)/cc-pVTZ

$$\langle \Psi^* | \hat{H}_e^T | \Psi_0 \rangle = E \langle \Psi^* | e^{\hat{T}} | \Psi_0 \rangle$$

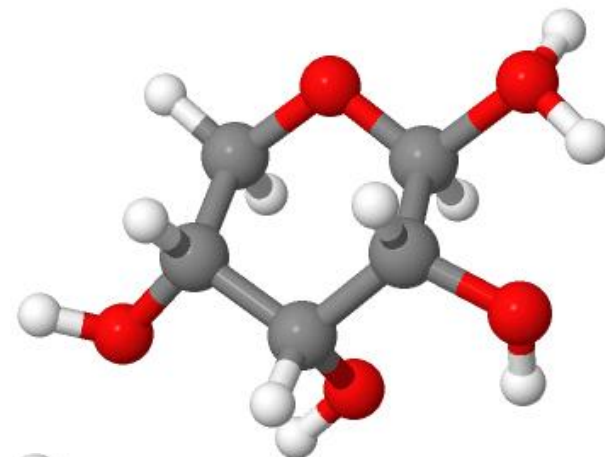


Le Prima Protonazione

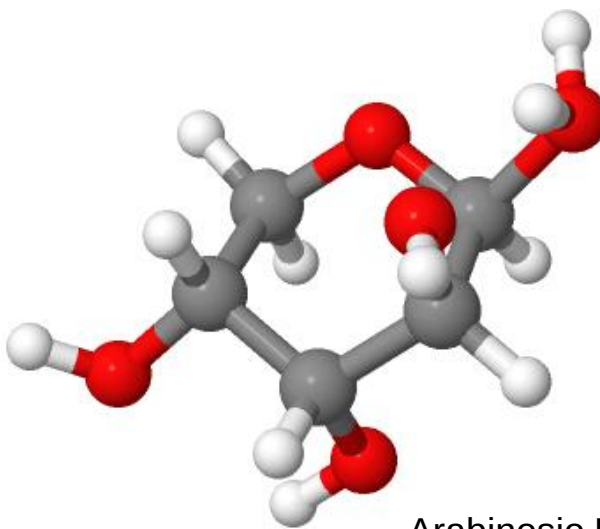
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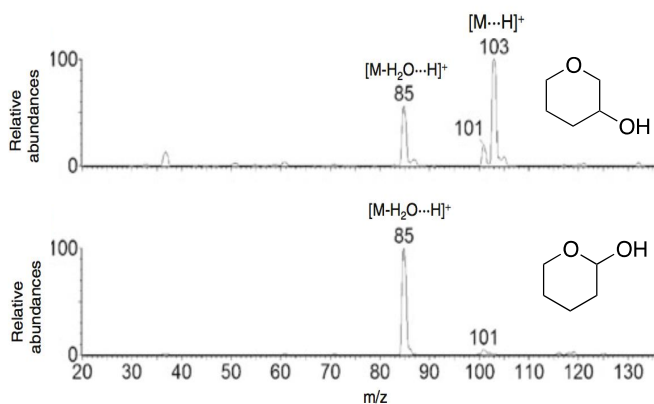
Xilosio protonato

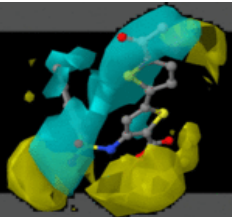


Ribosio protonato



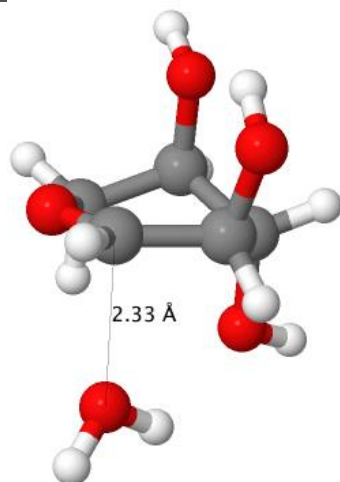
Arabinosio Protonato



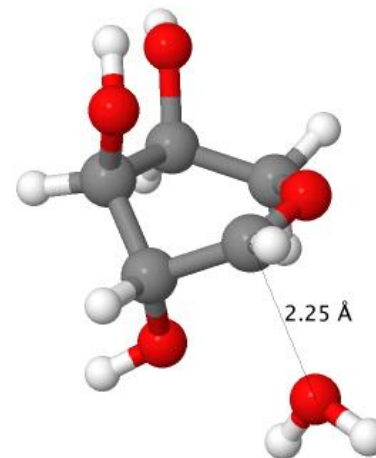


Le Prime Disidratazioni

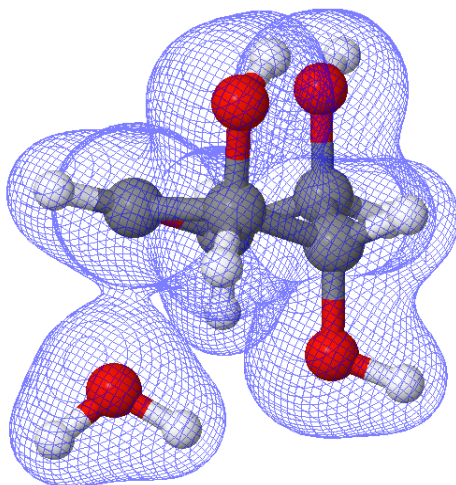
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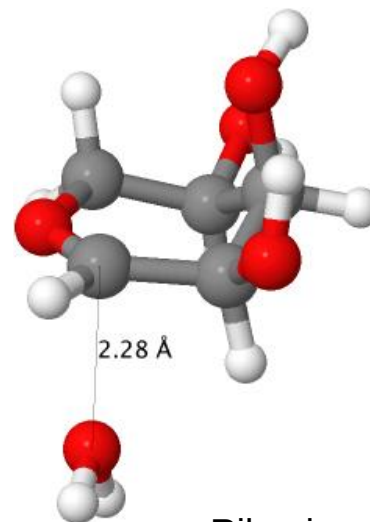
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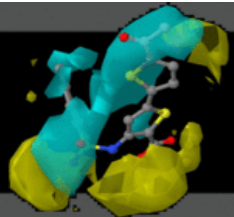
Arabinosio



Superficie Elettronica della
1^a Disidratazione dello Xilosio

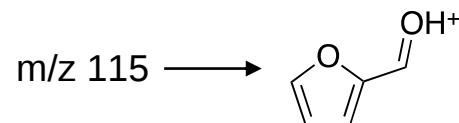
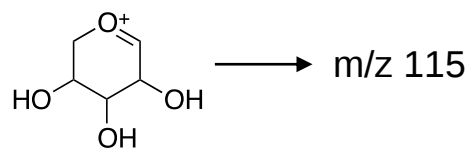
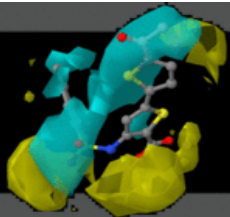


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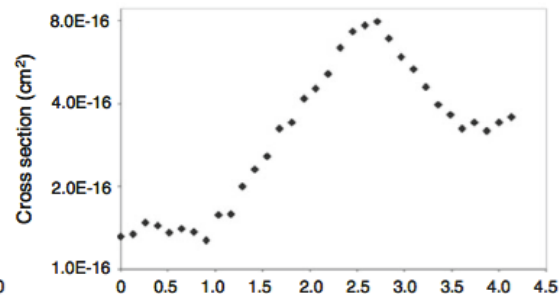
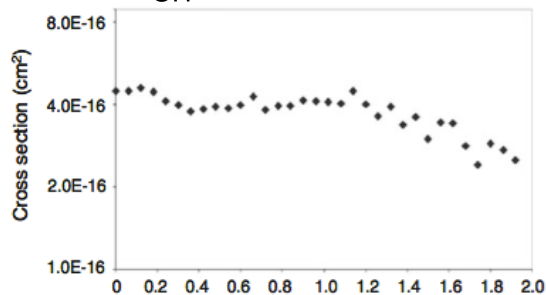


Car-Parrinello

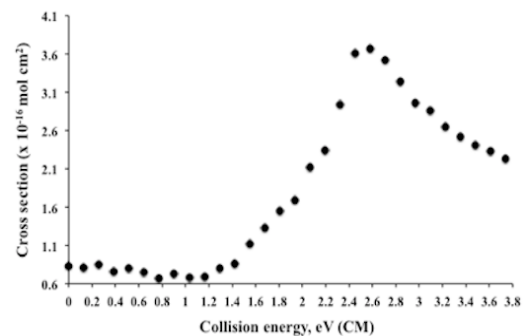
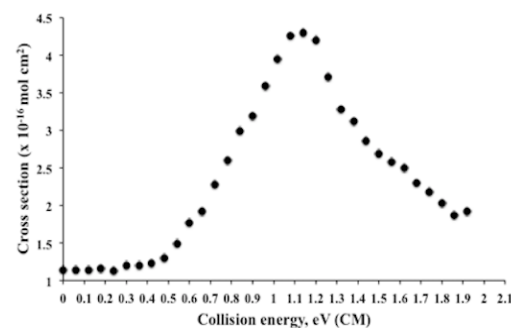
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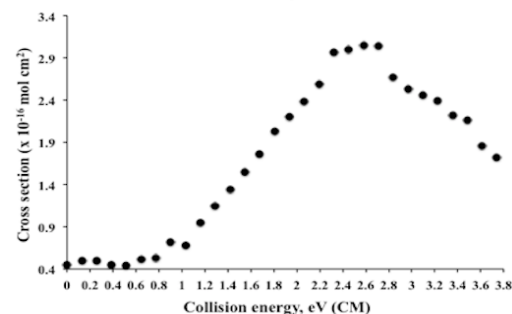
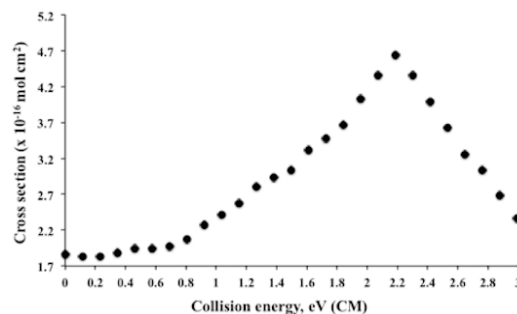
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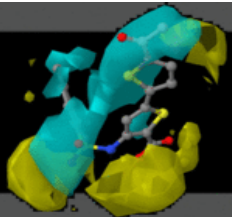


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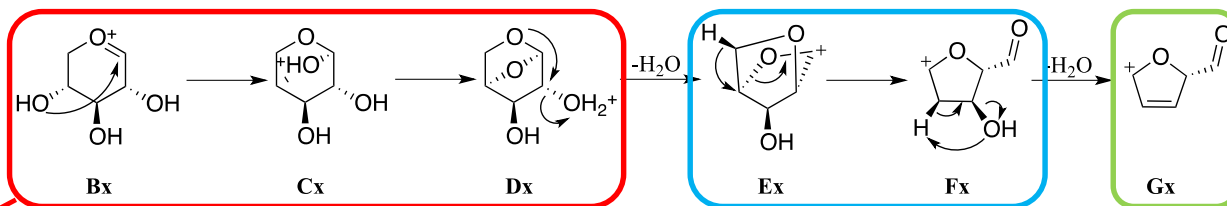
Arabinosio





Schema disidratazione Xilosio

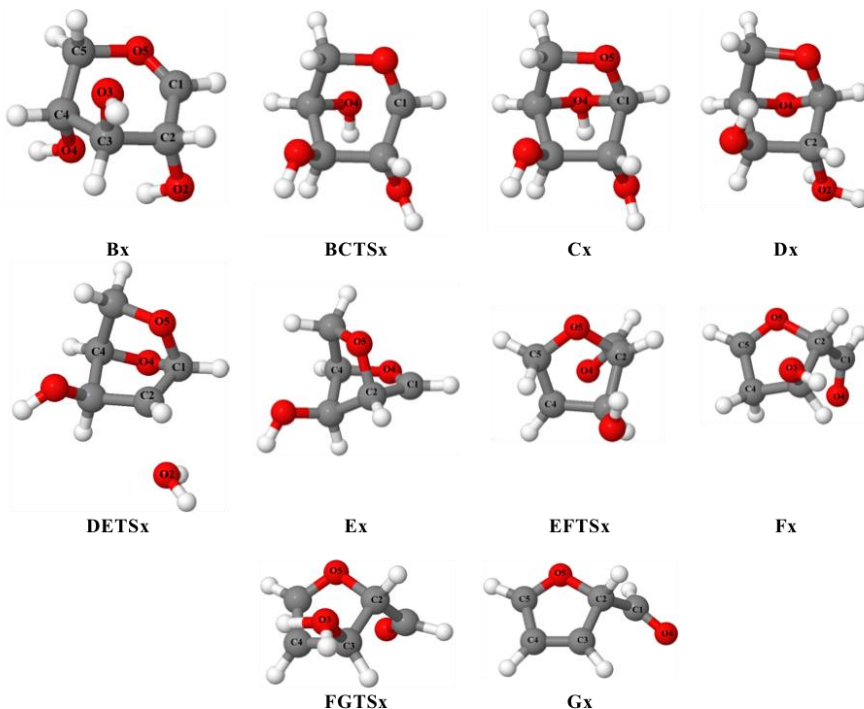
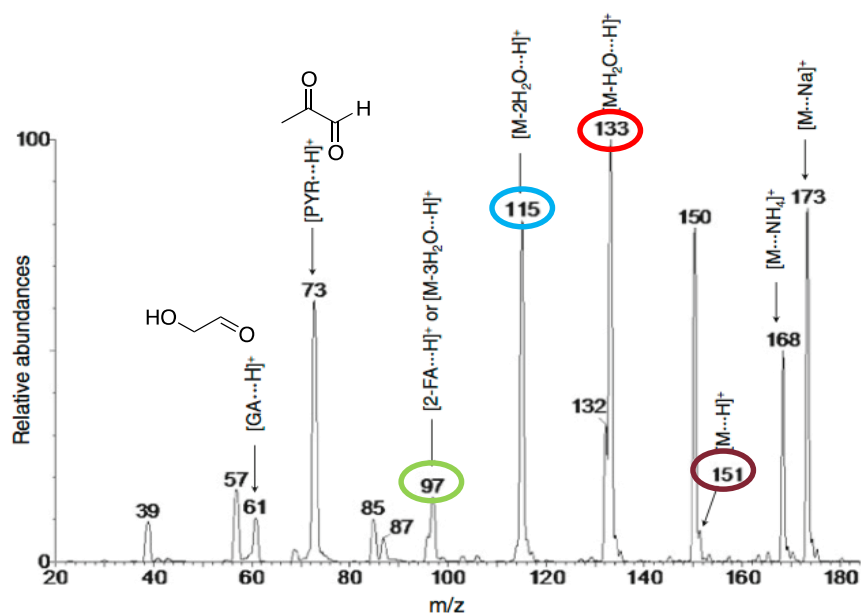
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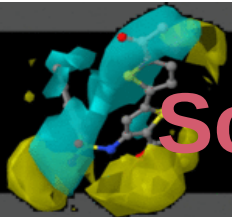


m/z 133

m/z 115

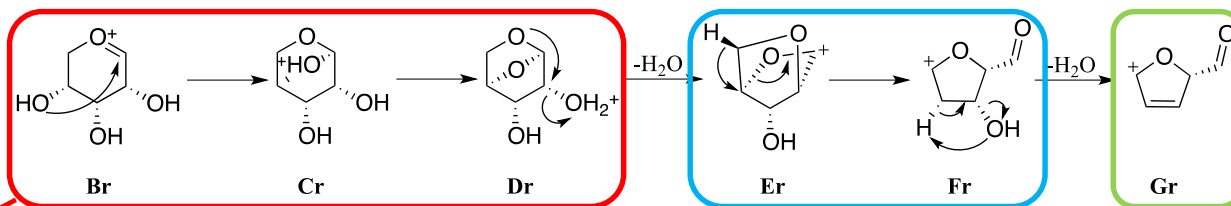
m/z 97





Schema disidratazione Ribosio

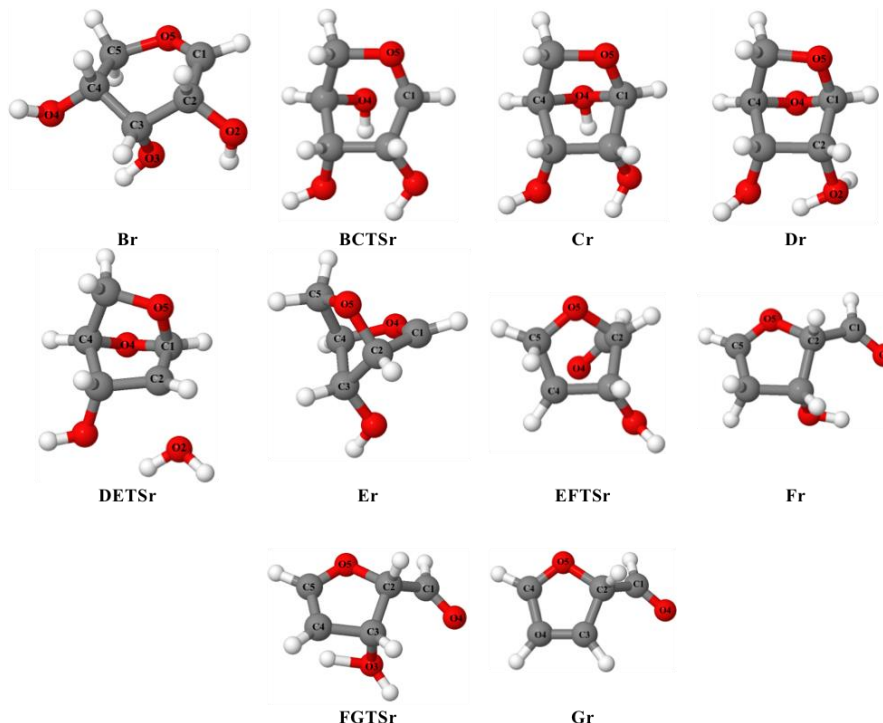
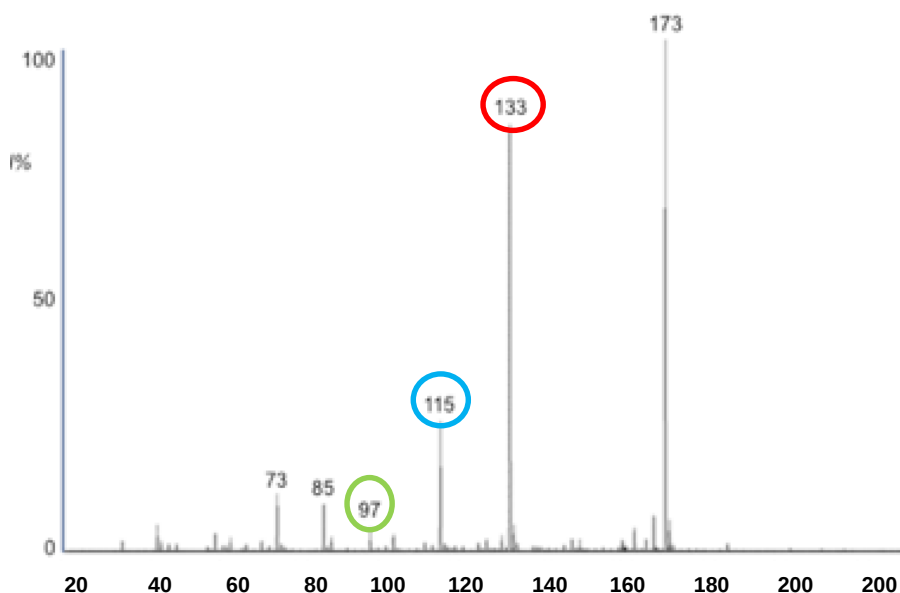
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m/z 133

m/z 115

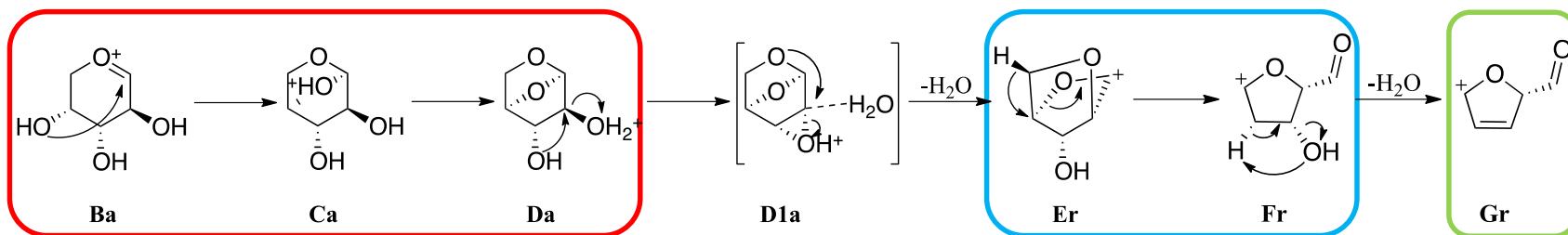
m/z 97





Schema disidratazione Arabinosio

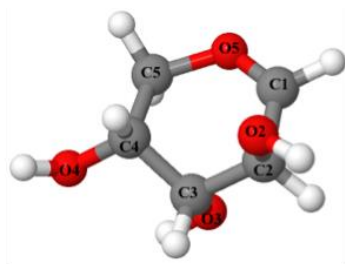
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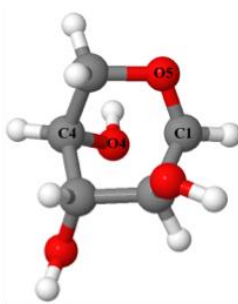
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m/z 97



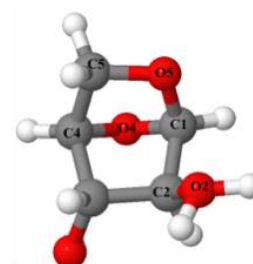
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BCTSa



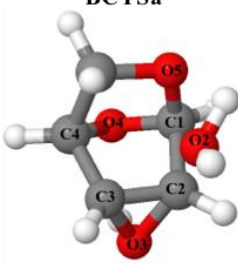
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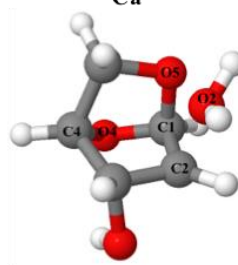
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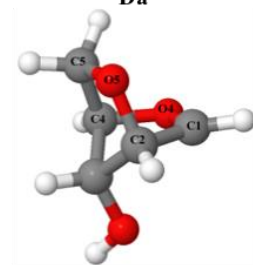
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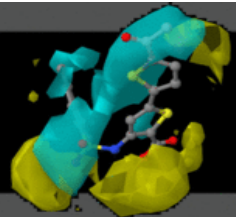
D1a



D1ErTSa

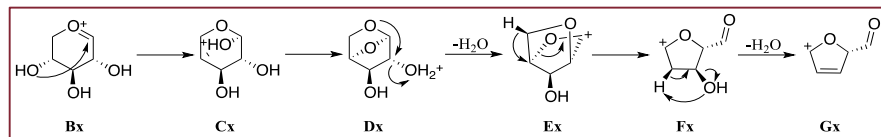


Er

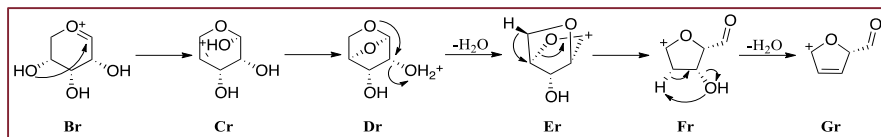


PES Xilosio/Ribosio

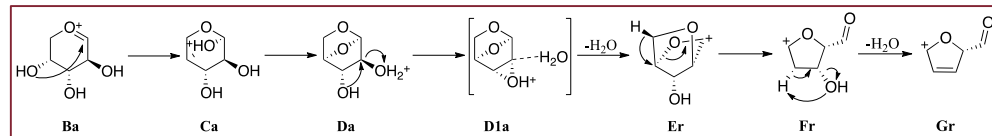
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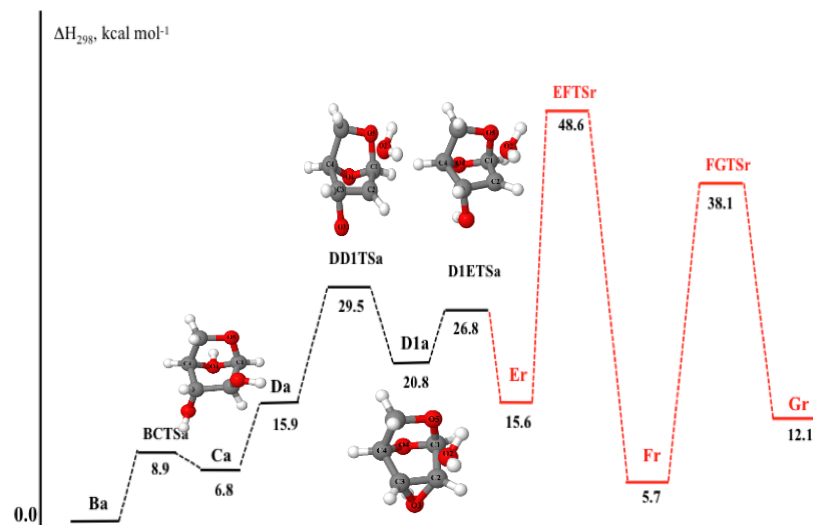
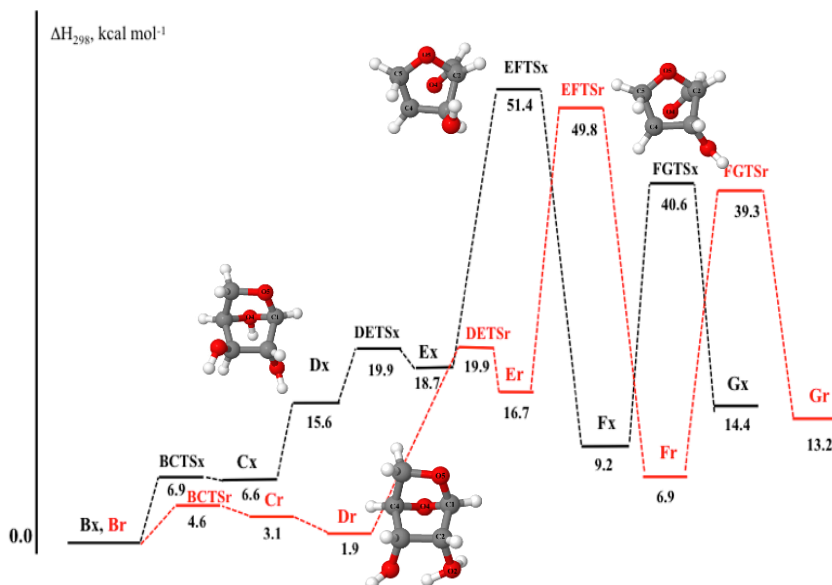
Xilosio

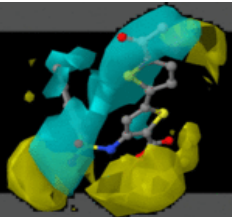


Ribosio



Arabinosio

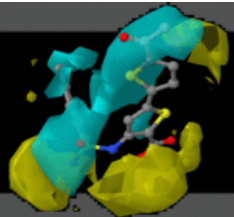




Conclusioni

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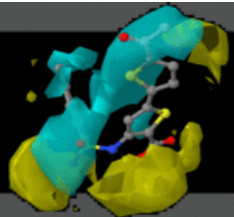
- Teoricamente si conferma che Xilosio, Ribosio e Arabinosio perdono facilmente la prima molecola d'acqua dal carbonio anomero.
- Il trend della perdita della seconda molecola di acqua è:
xilosio < ribosio < arabinosio
Come osservato sperimentalmente e confermato dal calcolo.
- Le terze disidratazioni hanno energie di attivazione simili.
- Il meccanismo di conversione dei tre pentosi a furfurale segue un meccanismo comune, caratterizzato da intermedi e stati di transizione comuni.
- Sulla base dei risultati sperimentali e teorici è possibile proporre un nuovo meccanismo per la disidratazione di xilosio, ribosio e arabinosio in fase gassosa



Prospettive Future

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- Estendere il lavoro ad un altro pentoso, il lixosio.
- Estendere il lavoro ad altri zuccheri esosi.



Ringraziamenti

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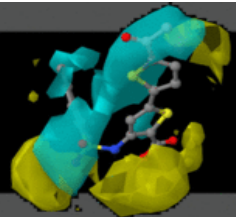
Si ringraziano sentitamente:

Il Prof. Ragno

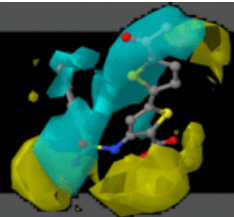
Il Prof. Pepi

La Dott.ssa Sabatino

Il Dott. Alexandros Patsilinakos

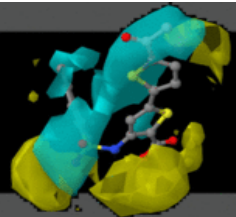


Grazie per l'attenzione.



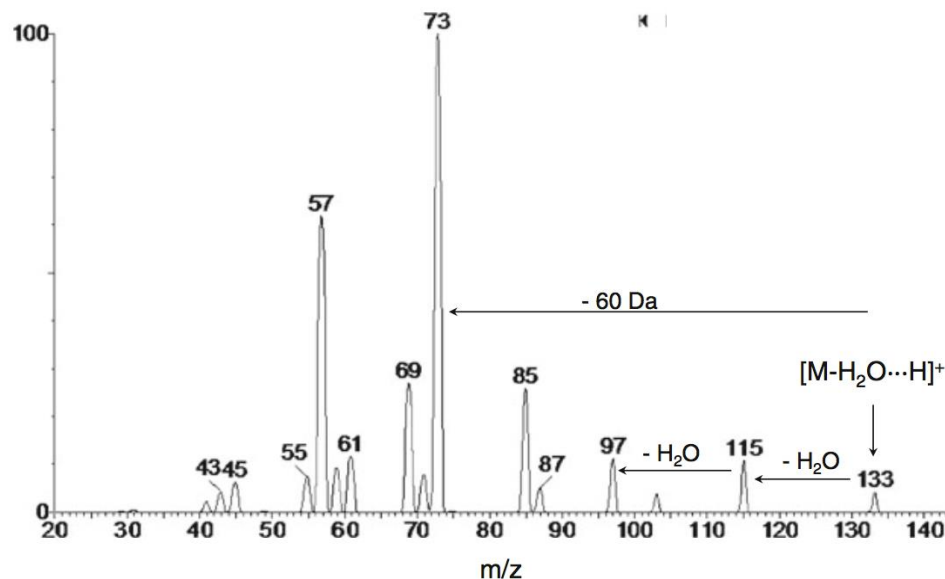
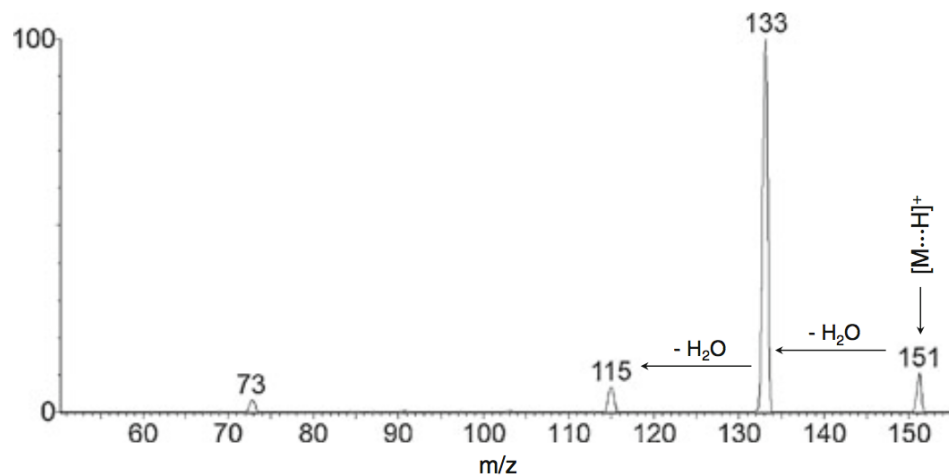
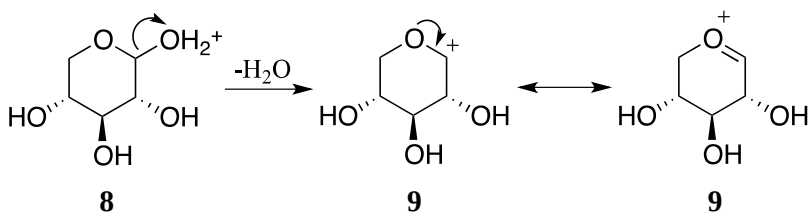
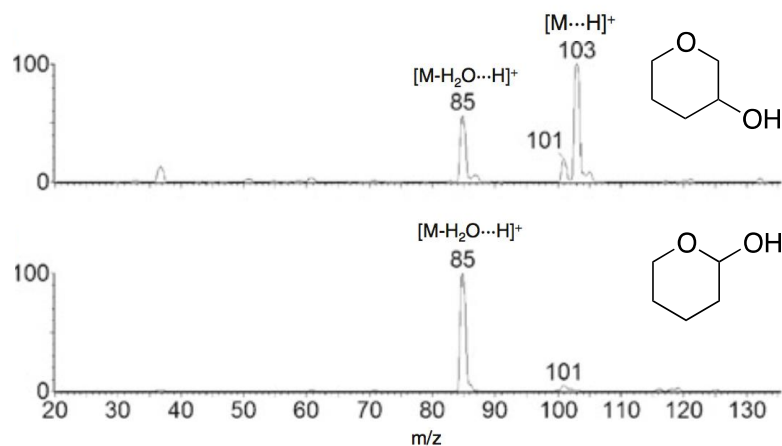
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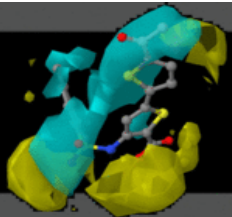
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Contestualizzazione

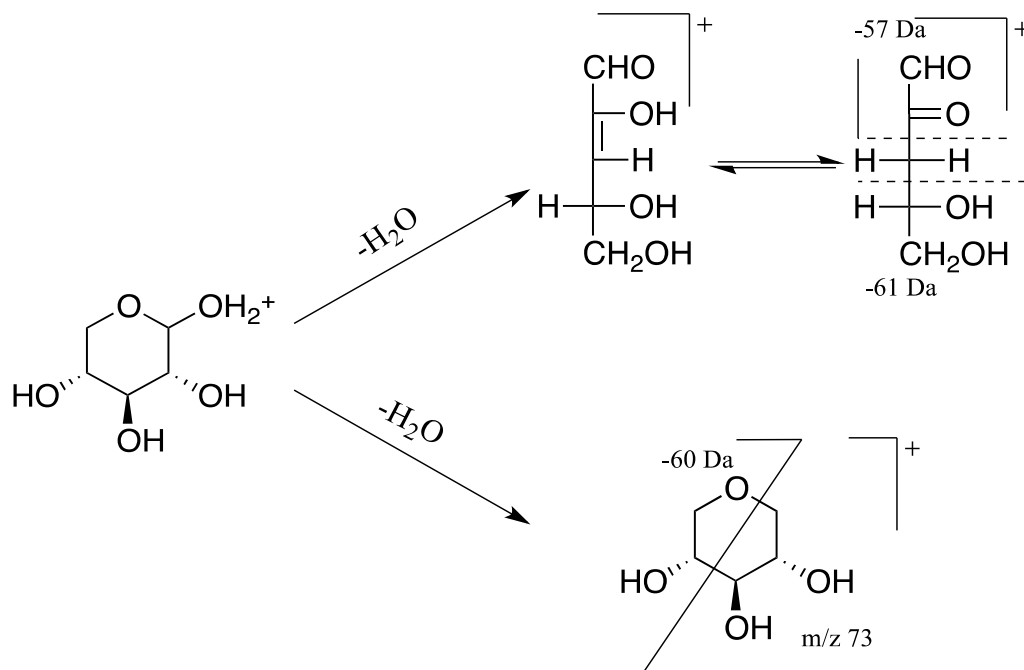
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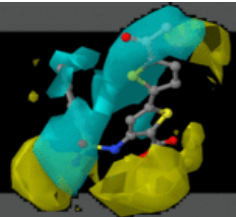




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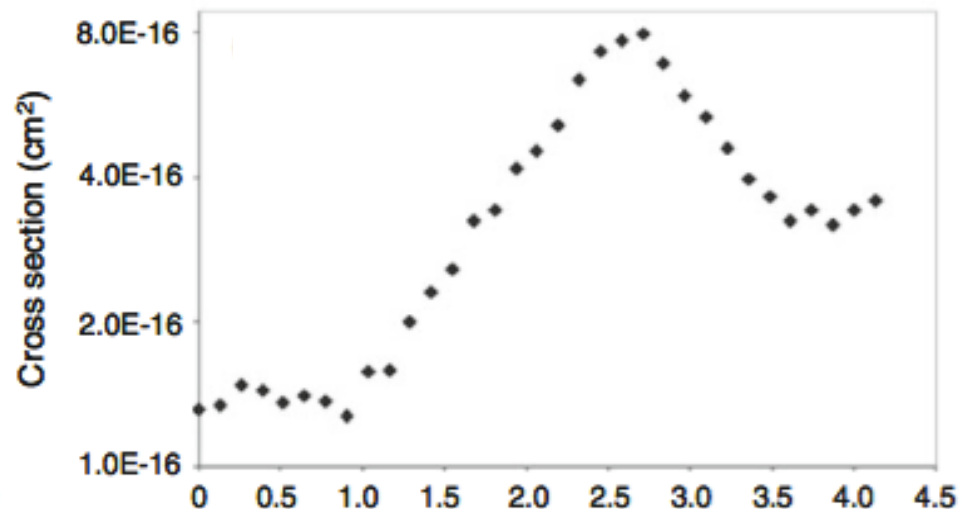
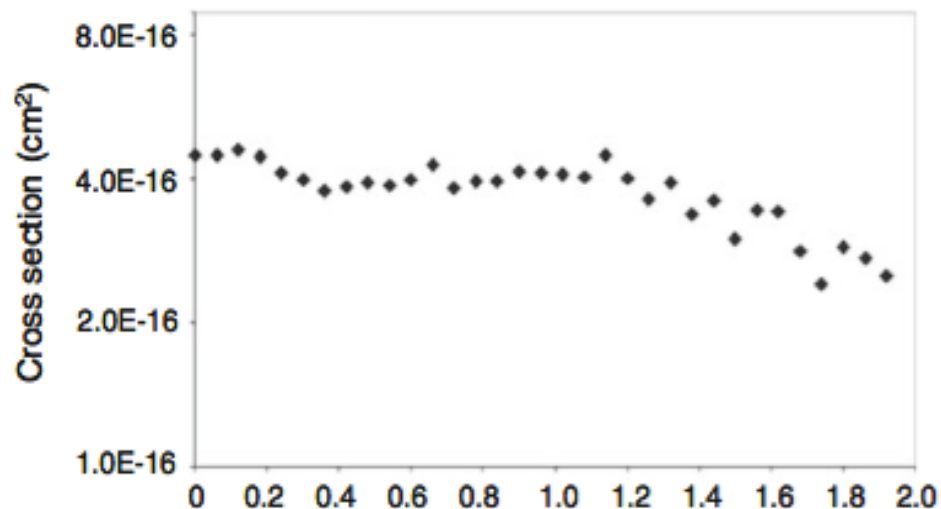
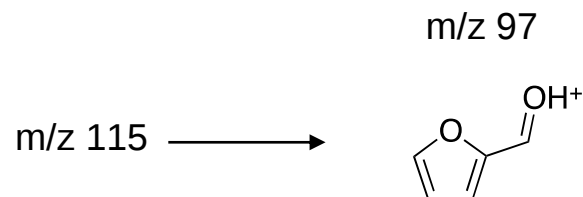
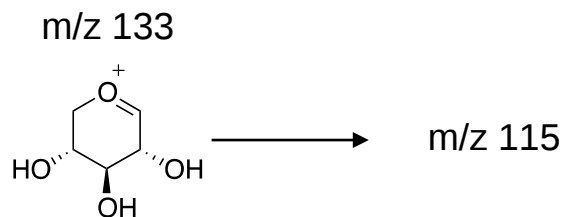
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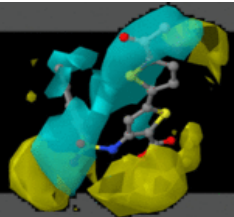




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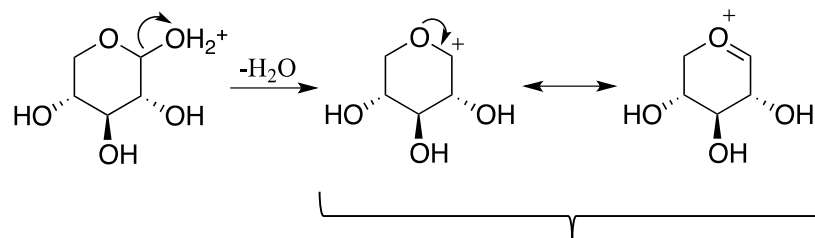
by www.RCMD.it





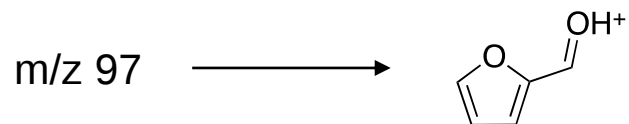
Il Punto di Partenza

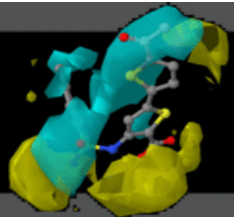
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m/z 133

1° disidratazione < 2° disidratazione < 3° disidratazione



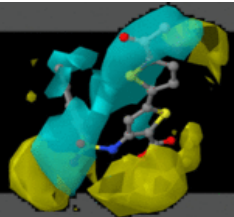


Tecniche Spettrometriche di massa:

- Trappola ionica
- Triplo Quadrupolo
- Spettri CAD e ERMS

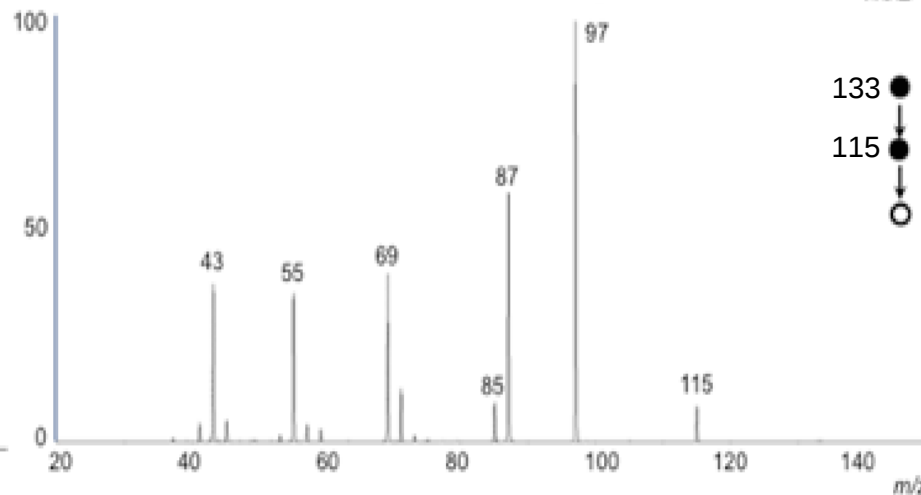
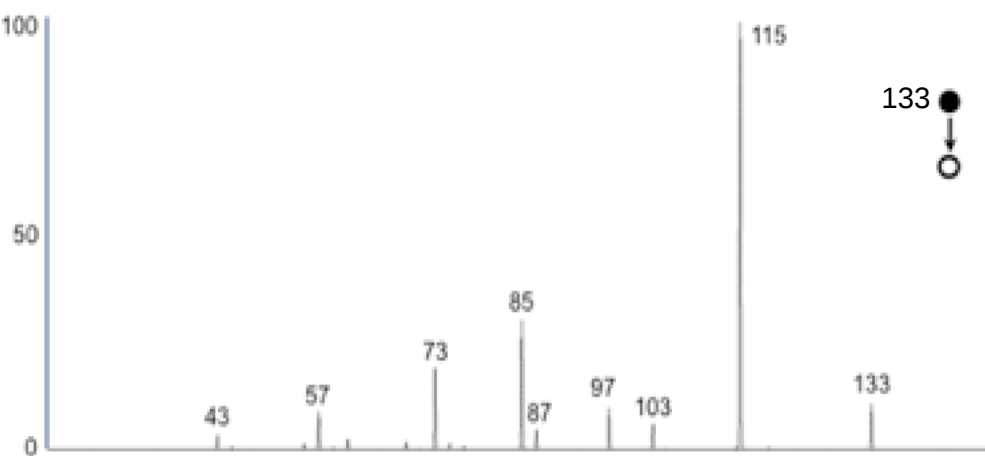
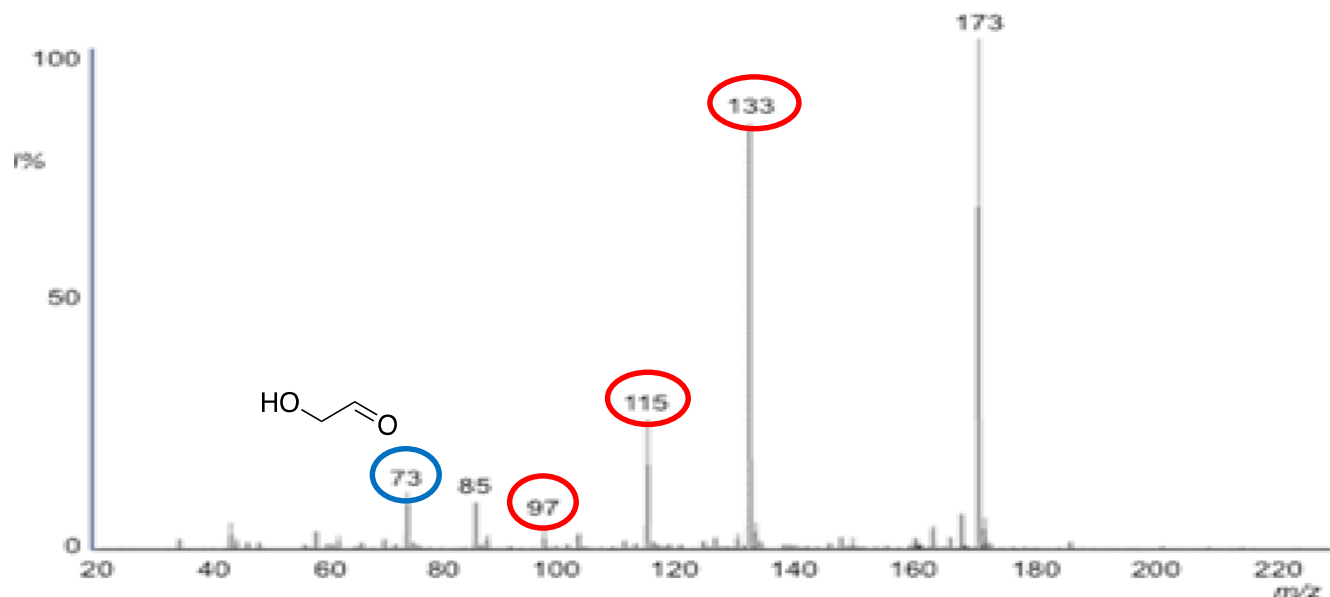
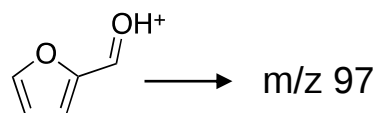
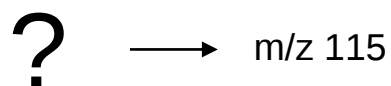
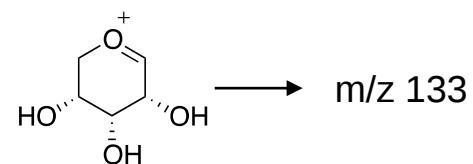
Metodi Computazionali

- Ricerca conformazionale sistematica MMFF94
- Ottimizzazione M11/6-311++G(2d,2p)
- Single Point Energy CCSD(T)/cc-pVTZ
- Simulazioni CPMD



Parte Sperimentale

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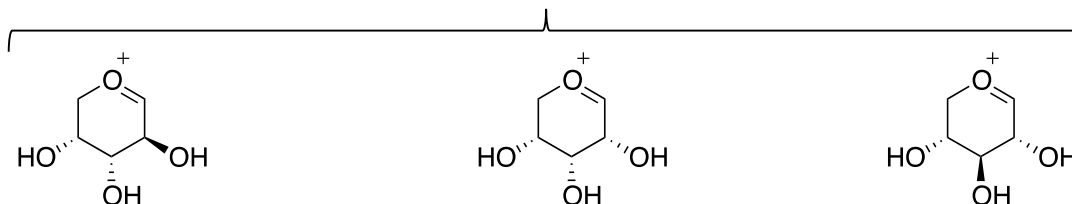




Parte Sperimentale

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m/z 133

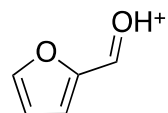
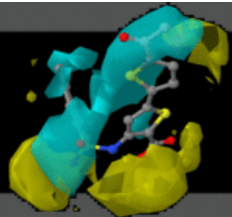


Frammento (m/z)	Arabinosio	Ribosio	Xilosio
115	2.9	3.4	2.5
97	2.1	4.1	3.4
87	1.6	2.1	1.3
85	6.5	8.3	8.0
73	50.8	29.5	40.0
71	1.1	4.0	1.7
69	5.3	9.3	7.6
61	5.3	4.6	4.0
59	3.7	4.6	1.6
57	11.8	15.1	26.2
55	4.8	9.5	0.8
45	2.1	1.8	1.7
43	1.6	2.8	0.8
41	0.5	0.9	0.4



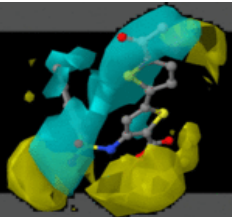
m/z 115

Frammento (m/z)	Arabinosio	Ribosio	Xilosio
97	7.7	7.8	13.7
87	9.3	4.3	6.4
85	20.9	13.5	23.7
73	0.7	0.6	1.1
71	4.2	8.7	3.3
69	18.5	15.5	26.6
59	1.5	2.0	1.7
57	12.1	14.5	10.7
55	20.3	27.4	7.0
43	2.4	3.1	1.9
41	2.4	2.6	3.9



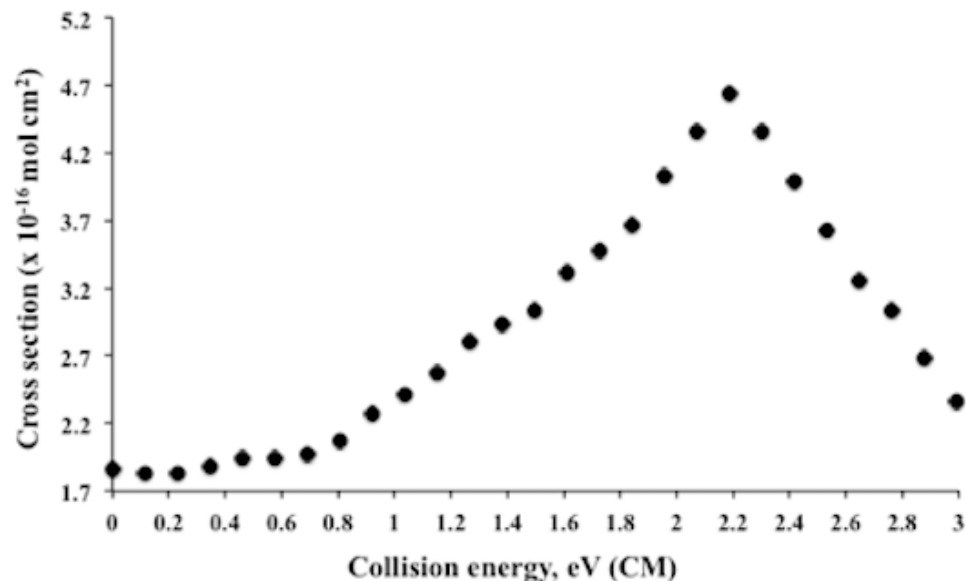
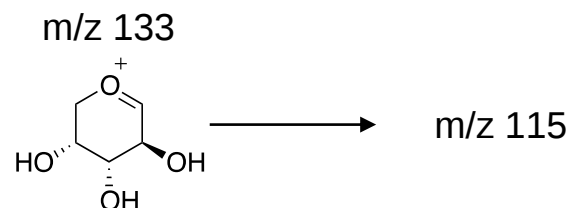
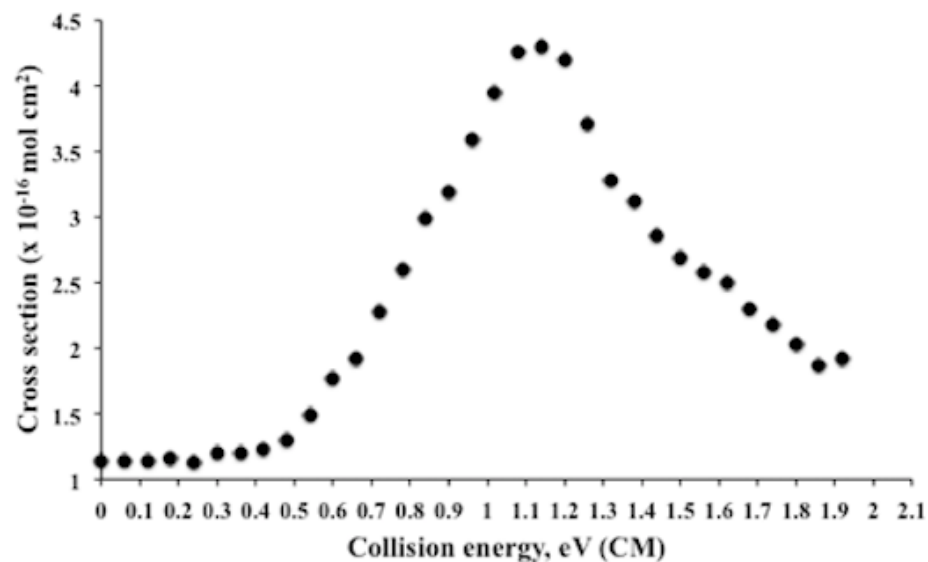
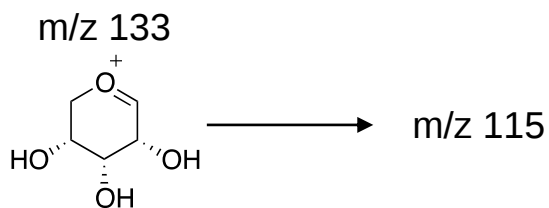
m/z 97

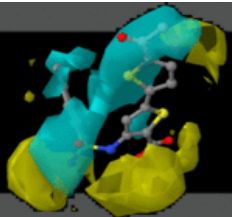
Frammento (m/z)	Arabinosio	Ribosio	Xilosio
71	3.2	5.3	2.1
69	51.4	50.8	52.5
55	2.2	1.6	1.2
43	5.1	4.8	3.1
41	38.1	37.5	40.1



2^a Disidratazione Rib e Ara

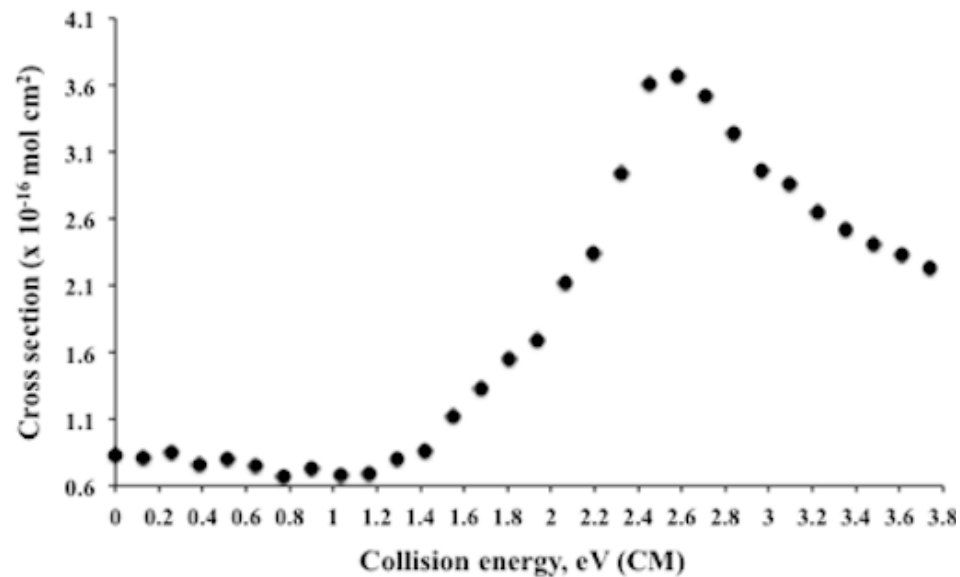
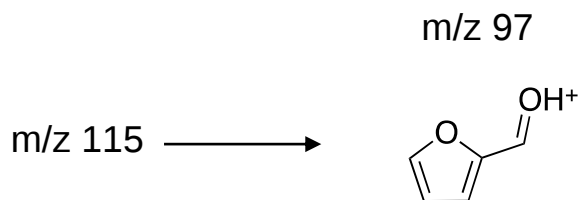
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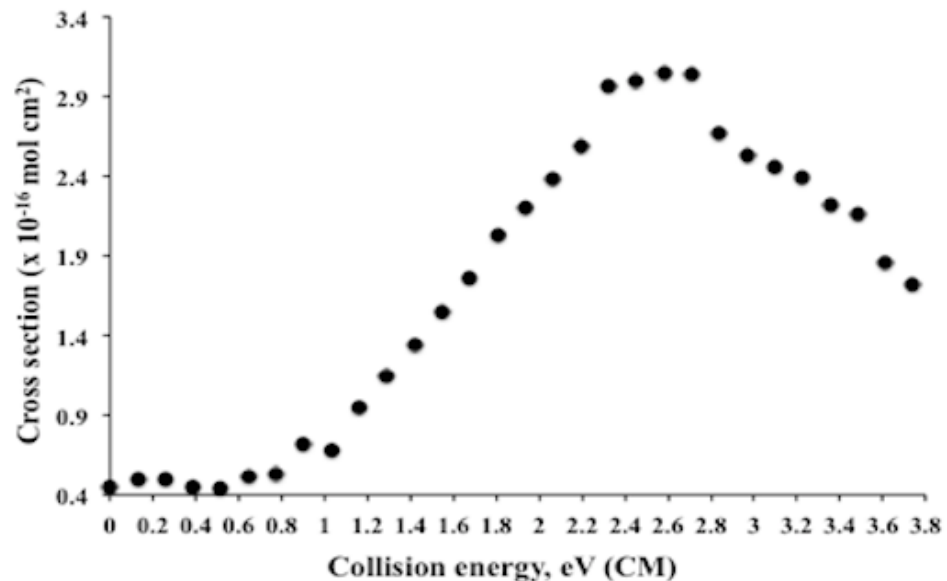
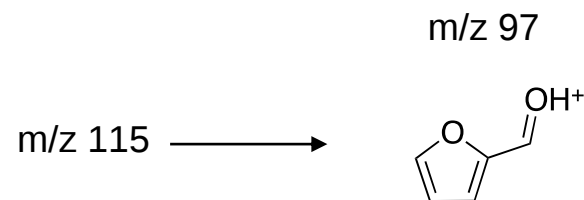


3^a Disidratazione Rib e Ara

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Ribosio



Arabinosio

