Determination and transformation of valuable phenolic compounds from their new and rich sources: galls of *Fraxinus angustifolia* and *Fraxinus ornus*

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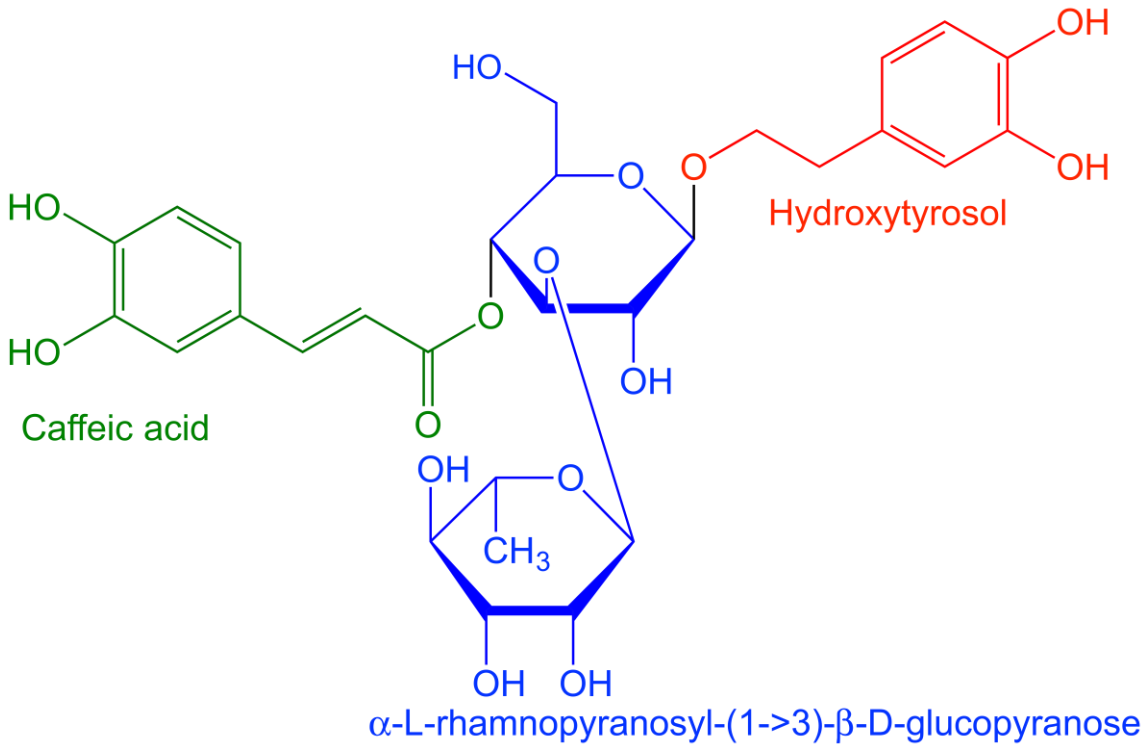
Acteoside

- Water-soluble phenylethanoid glycoside
- Chemotaxonomic characteristic for order of Lamiales
- Remarkable biological properties



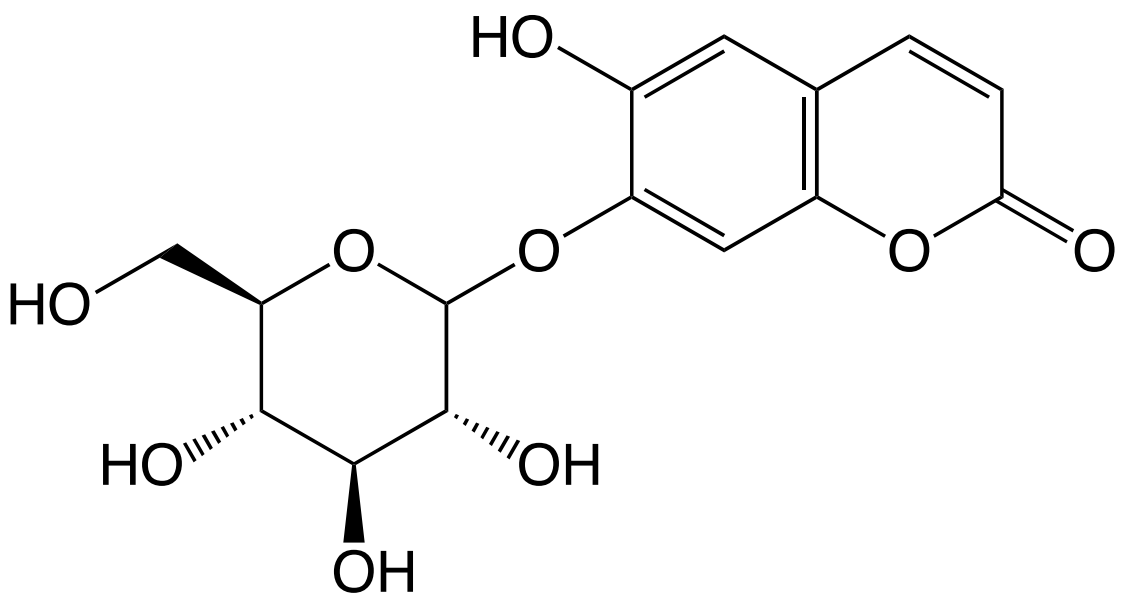
Order	Family	Acteoside	Desrhamnosyl-acteoside	Isoacteoside	Desrhamnosyl-isoacteoside	References
Lamiales	Acanthaceae	x		x		Ashour 2012; Mmatli et al. 2007
	Buddlejaceae	x				Pendota et al. 2014; Tai et al. 2011; Filho et al. 2012
	Bignoniaceae	x		x		Kanchanapoom et al. 2002; Pereira et al. 2014; Sofidiya et al. 2014
	Byblidaceae	x	x	x	x	Schlauer et al. 2004
	Calceolariaceae	x				Muñoz et al. 2013; Cespedes et al. 2013
	Gesneriaceae	x				Jensen 2000; Gutiérrez-Rebolledo et al. 2016
	Lamiaceae	x		x		Venditti et al. 2016; Delazar et al. 2004; Kabouche et al. 2005; Nishimura et al. 1991
	Lentibulariaceae	x				Damtoft et al. 1994; Grevenstuk et al. 2009
	Martyniaceae	x				Scogin 1992
	Oleaceae	x		x		Ayouni et al. 2016; Quirantes-Piné et al. 2013; Kostova & Iossifova 2007
	Orobanchaceae	x		x		Tóth et al. 2014; Mari et al. 2017; Huang et al. 2013
	Paulowniaceae	x		x		Si et al. 2013
	Pedaliaceae	x		x		Burger et al. 1987; Grąbkowska et al. 2016
	Phrymaceae	x				Su et al. 1999; Keefover-Ring et al. 2014
	Plantaginaceae	x		x		Gonçalves&Romano 2016; Navarrete et al. 2016; Wan et al. 2016; Jensen et al. 2005
	Scrophulariaceae	x		x		Zhou et al. 2016; Xiang et al. 2016; Lémus et al. 2015; Mihailović et al. 2016
	Stilbaceae	x				Jensen et al. 2005; Scogin 1992
	Tetrachondraceae	x				Scogin&Romo-Contreras 1992; Jensen 2000
	Verbenaceae	x	x	x		Ghisalberti, 2000; Liu et al. 2016; Cheng et al. 2015; Maquiaveli et al. 2016; Encalada et al. 2015; Oyourou et al. 2013; Billia et al. 2008
Asterales	Asteraceae	x				Jiménez & Riguera 1994
	Campanulaceae	x				van Heerden et al. 2002
Cucurbitales	Cucurbitaceae	x				Jiménez & Riguera 1994
Magnoliales	Magnoliaceae	x				Tsuruga et al. 1991; Porter et al. 2015
Icacinales	Icacinaceae	x				Rasonaivo et al. 1990

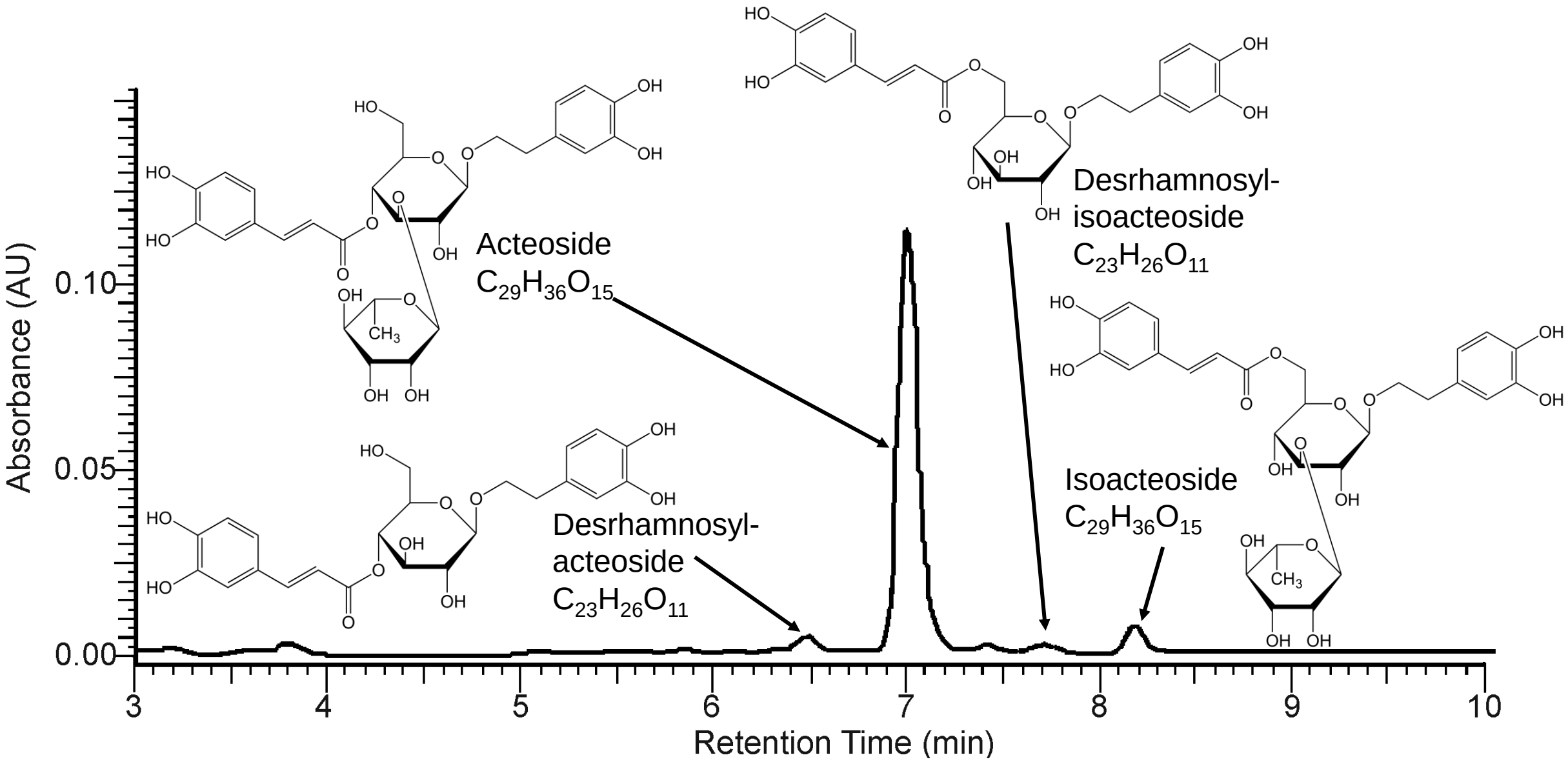
Pharmacological properties

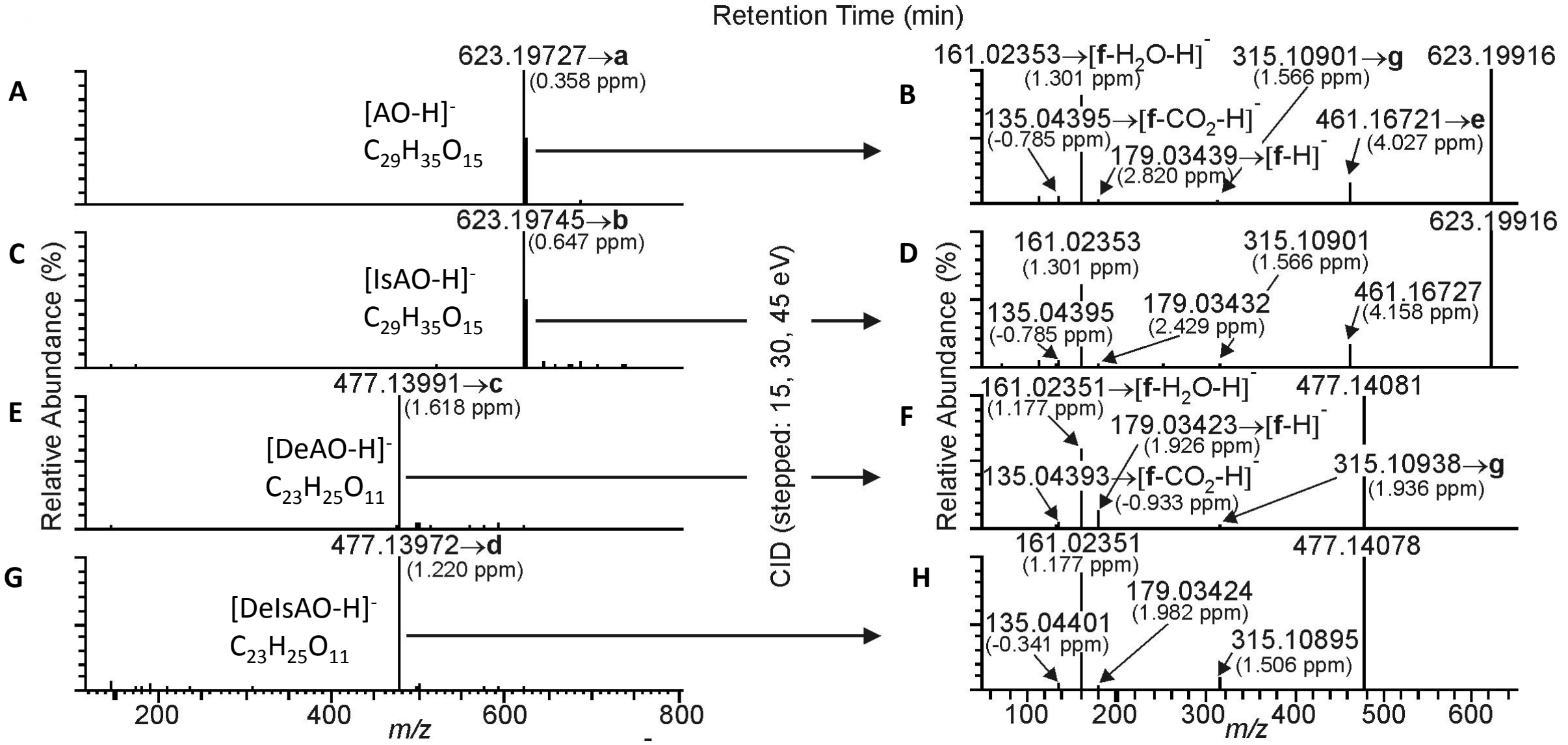
Effect	Acteoside	Isoacteoside	References
Antifungal	x		Funari et al. 2012; Oyourou et al. 2012
Anti-H1N1, Nrf2-activation	x		Ji et al. 2015
Antileishmanial	x	x	Maquiaveli et al. 2016
Antiinflammatory	x		Lee et al. 2006
Antioxidant	x	x	D'Imperio et al. 2014
Cytotoxic, anti-metastatic, anti-tumor	x	x	Sanchez et al. 2013; Pettit et al. 1990; Ohno et al. 2002; Inoue et al. 1998
Ergogenic	x		Zhu et al. 2016
Hepatoprotective	x		Lee et al. 2004; Xiong et al. 1998
Xanthine oxidase inhibition	x		Wan et al. 2016
Neuroprotective	x		Sheng et al. 2002; Koo et al. 2005
Photoprotective	x		Potapovich et al. 2013

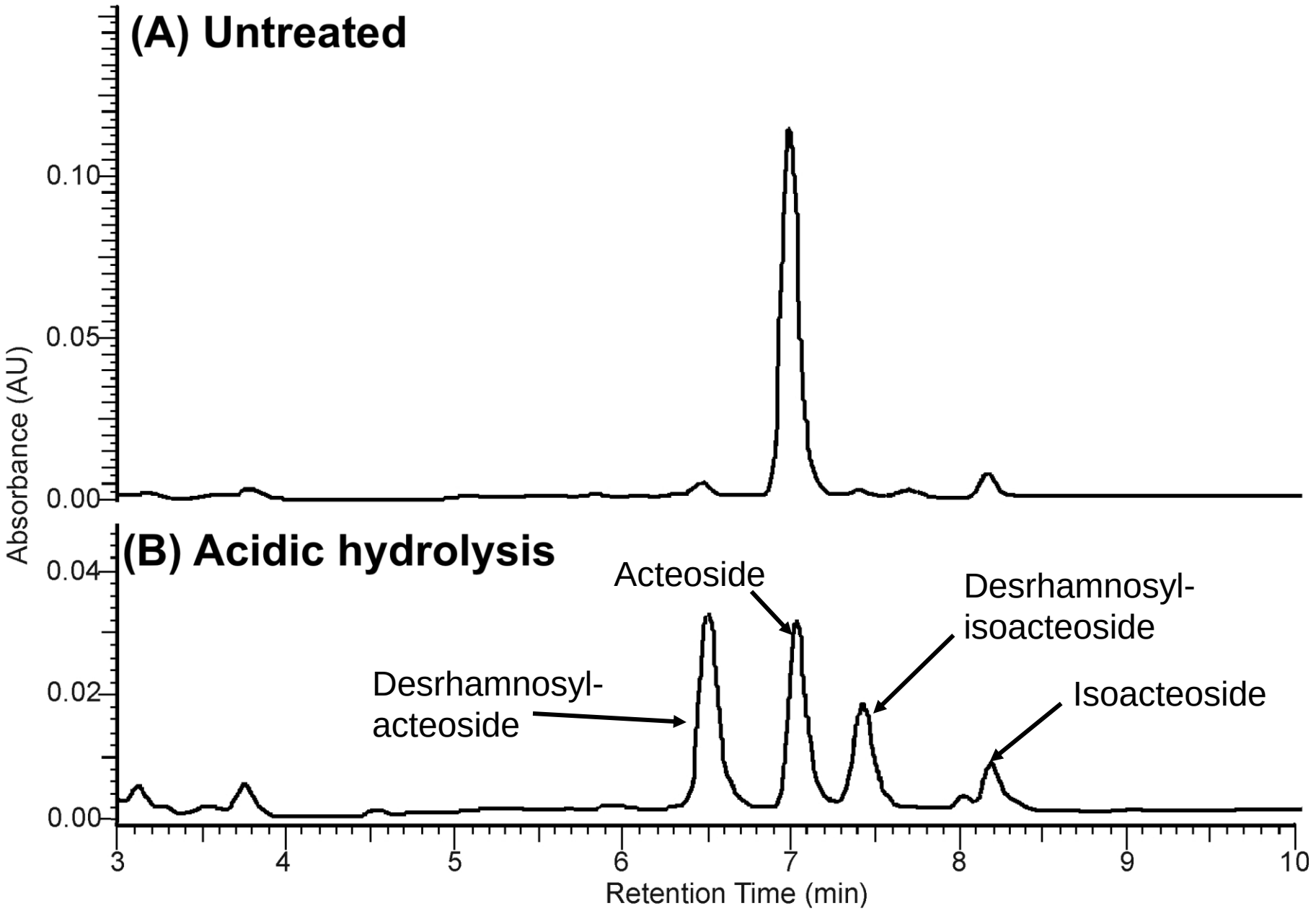
Cichoriin

- Coumarin glycoside type plant secondary metabolite
- Structural isomer of esculin
- Widely distributed in the plant kingdom (mainly Asteraceae; flowers and fruits of *F. ornus*)
- Pharmacologically promising compound

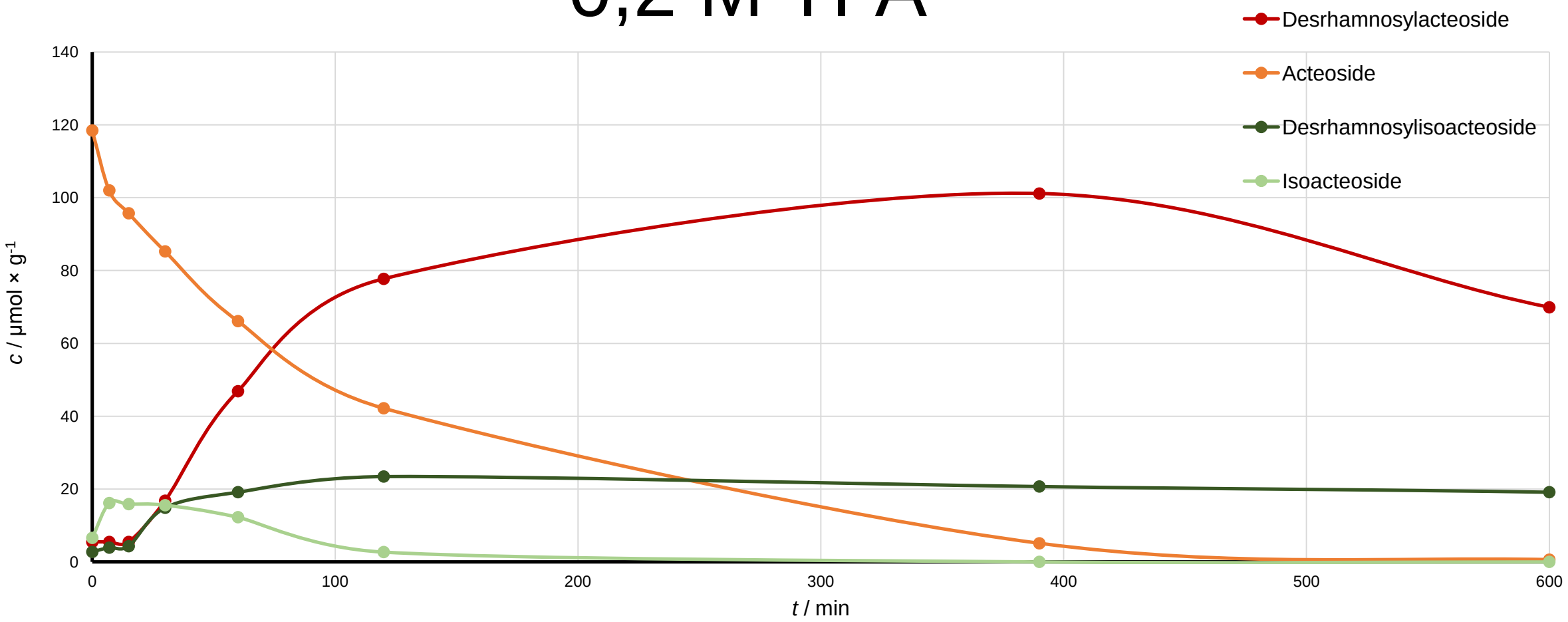



Absorbance (AU)
0.10
0.05
0.00
3
4
5
6
7
8
9
10
Retention Time (min)
Acteoside
C29H36O15
Desrhamnosyl-
isoacteoside
C23H26O11
Desrhamnosyl-
acteoside
C23H26O11
Isoacteoside
C29H36O15

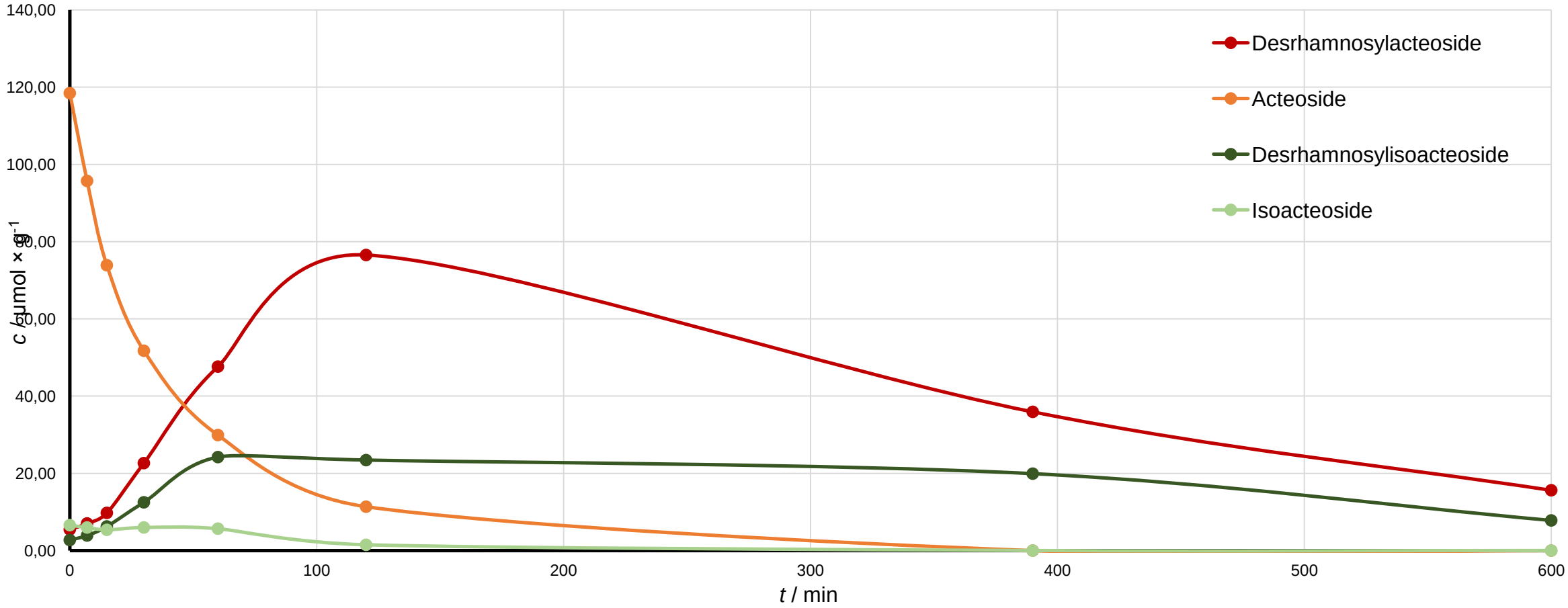

Retention Time (min)
A
623.19727→a
(0.358 ppm)
[AO-H]-
C29H35O15
B
161.02353→[f-H2O-H]-
(1.301 ppm)
315.10901→g
(1.566 ppm)
623.19916
135.04395→[f-CO2-H]-
(-0.785 ppm)
461.16721→e
(4.027 ppm)
179.03439→[f-H]-
(2.820 ppm)
C
623.19745→b
(0.647 ppm)
[IsAO-H]-
C29H35O15
D
623.19916
161.02353
(1.301 ppm)
315.10901
(1.566 ppm)
135.04395
(-0.785 ppm)
179.03432
(2.429 ppm)
461.16727
(4.158 ppm)
Relative Abundance (%)
CID (stepped: 15, 30, 45 eV)
E
477.13991→c
(1.618 ppm)
[DeAO-H]-
C23H25O11
F
161.02351→[f-H2O-H]-
(1.177 ppm)
477.14081
179.03423→[f-H]-
(1.926 ppm)
135.04393→[f-CO2-H]-
(-0.933 ppm)
315.10938→g
(1.936 ppm)
G
477.13972→d
(1.220 ppm)
[DeIsAO-H]-
C23H25O11
H
161.02351
(1.177 ppm)
477.14078
179.03424
(1.982 ppm)
135.04401
(-0.341 ppm)
315.10895
(1.506 ppm)
200
400
600
800
m/z
100
200
300
400
500
600
m/z


(A) Untreated
0.10
0.05
0.00
Absorbance (AU)
(B) Acidic hydrolysis
0.04
0.02
0.00
Acteoside
Desrhamnosyl-
isoacteoside
Desrhamnosyl-
acteoside
Isoacteoside
3
4
5
6
7
8
9
10
Retention Time (min)

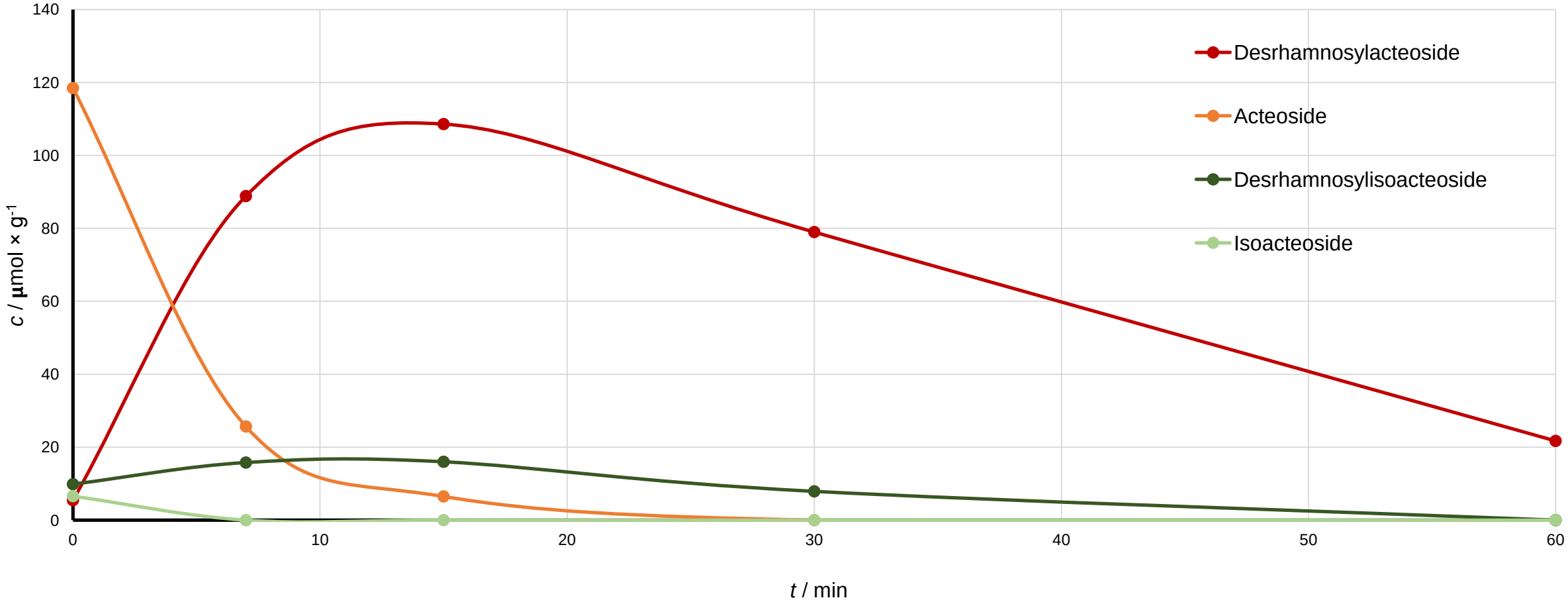
Acidic hydrolysis of acteoside
0,2 M TFA

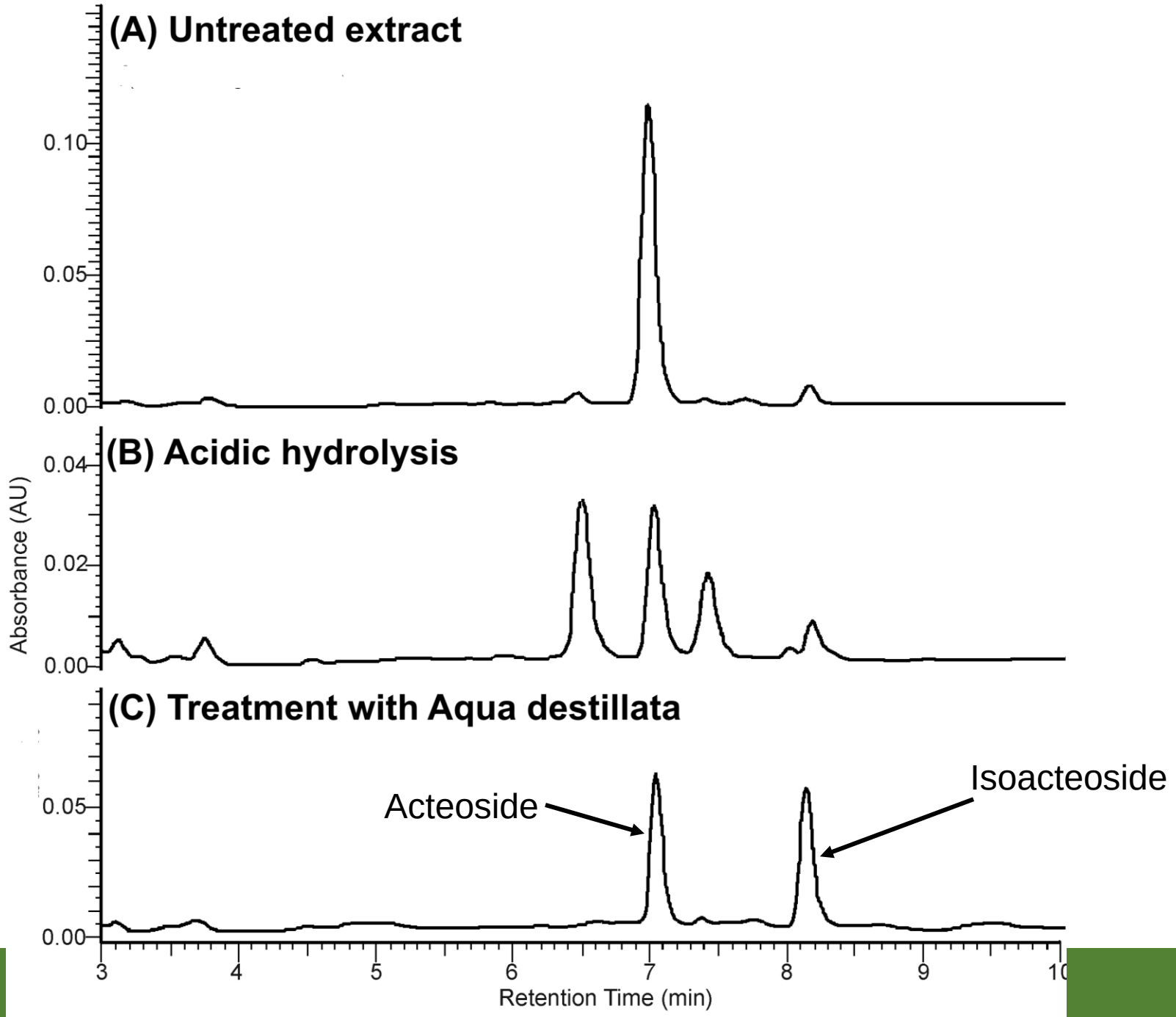


Acidic hydrolysis of acteoside
0,6 M TFA

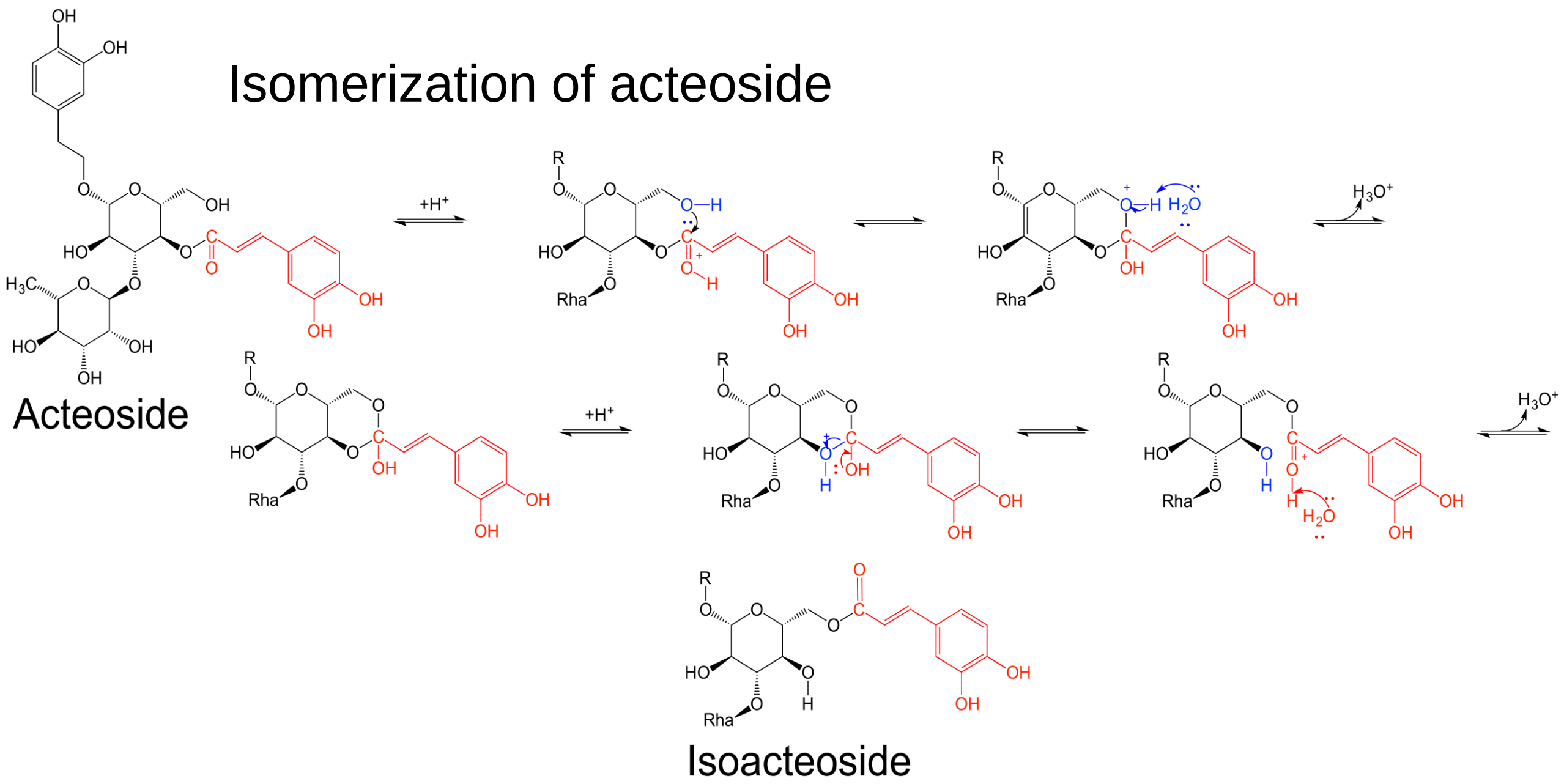


Acidic hydrolysis of acteoside
2 M TFA

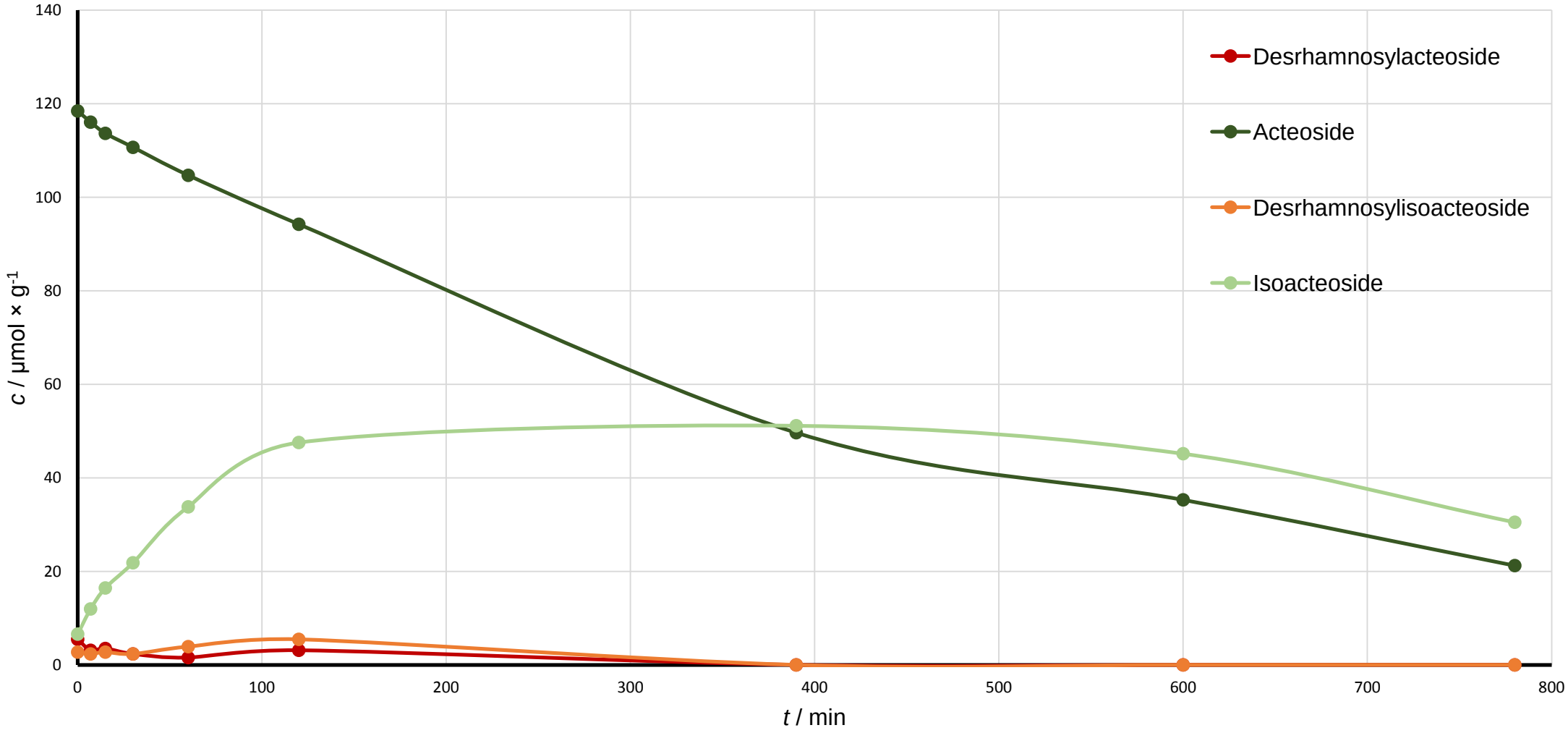


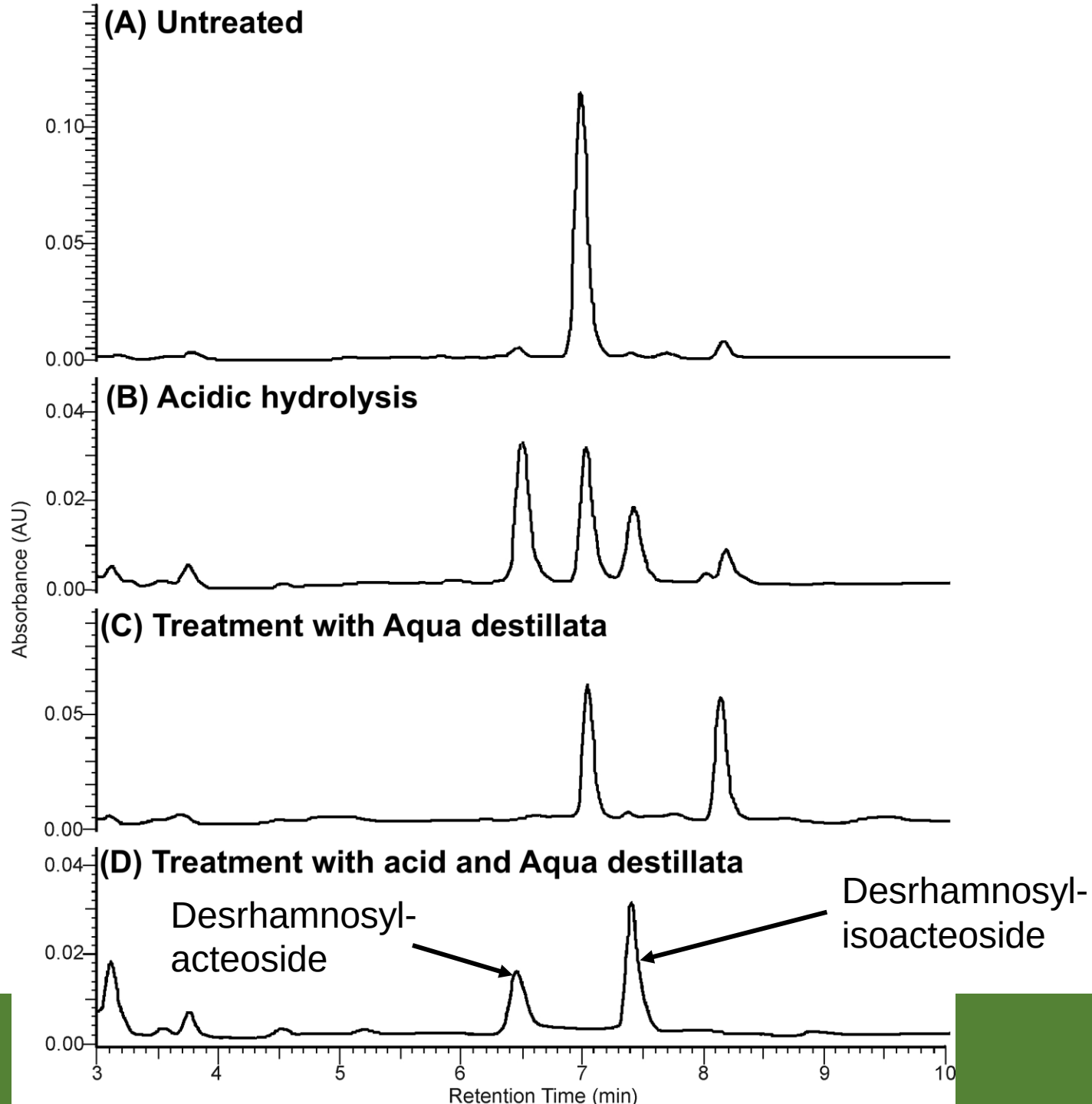

(A) Untreated extract
0.10
0.05
0.00
(B) Acidic hydrolysis
0.04
0.02
0.00
Absorbance (AU)
(C) Treatment with Aqua destillata
0.05
0.00
Acteoside
Isoacteoside
3
4
5
6
7
8
9
Retention Time (min)

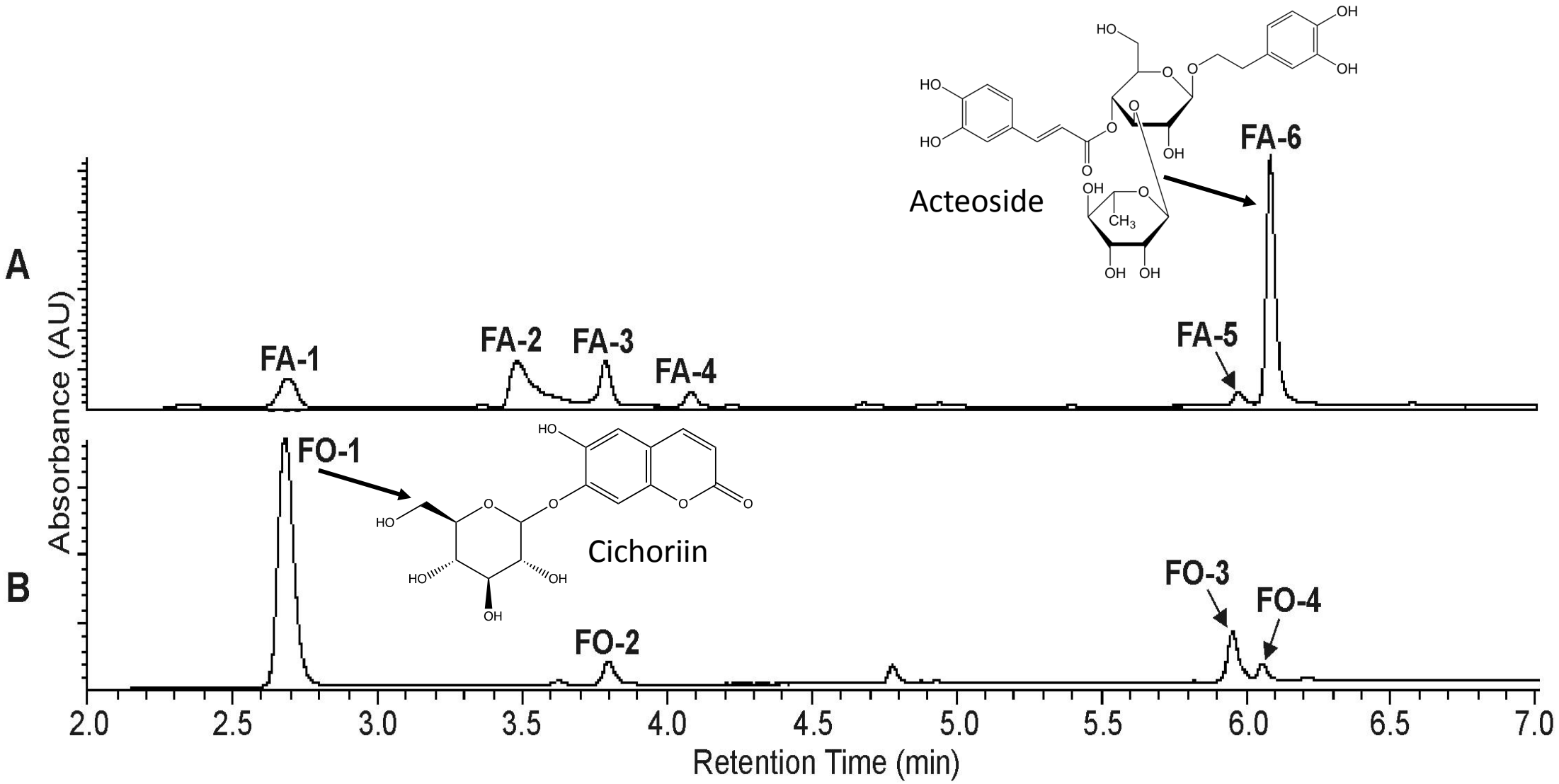
Isomerization of acteoside



Isomerization of acteoside




(A) Untreated
0.10
0.05
0.00
(B) Acidic hydrolysis
0.04
0.02
0.00
Absorbance (AU)
(C) Treatment with Aqua destillata
0.05
0.00
(D) Treatment with acid and Aqua destillata
0.04
0.02
0.00
Desrhamnosyl-
acteoside
Desrhamnosyl-
isoacteoside
3
4
5
6
7
8
9
10
Retention Time (min)


A
B
Absorbance (AU)
FA-1
FA-2
FA-3
FA-4
FA-5
FA-6
Acteoside
FO-1
FO-2
FO-3
FO-4
Cichoriin
2.0
2.5
3.0
3.5
4.0
4.5
5.0
5.5
6.0
6.5
7.0
Retention Time (min)

Syllabus

- Identification of the flower galls of *F. angustifolia/F. excelsior* and *F. ornus* to be new and extremely rich sources for AO (175.5 mg/g) and cichoriin (200 mg/g), respectively.
- Confirmation of chemotaxonomic classification of *Fraxinus* species and the importance of acteoside and cichoriin as chemotaxonomic markers.
- Characterization of conversion into closely related compounds (for AO)
- Optimization of treatment resulting in highest amounts of acteoside derivatives leading to easy isolation of all four derivatives

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