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POLYPHENOL RESEARCH

Polyphenols in beer: the role of xanthohumol and isoxanthohumoL

Rosa M. Lamuela

University of Barcelona

Beer and Health

THE 7TH EUROPEAN

BEER AND HEALTH SYMPOSIUM

Index

- What are polyphenols
- Polyphenols and health outcomes
- Polyphenols from beer
- Health effects of prenylflavonoids from beer

PubMed

POLYPHENOL RESEARCH

In 1991, key word: polyphenols

Only 23 papers about:

- Antioxidant effects *in vitro*
- Presence in food
- Antitumoral properties

On September 26 2014, Key word: polyphenols

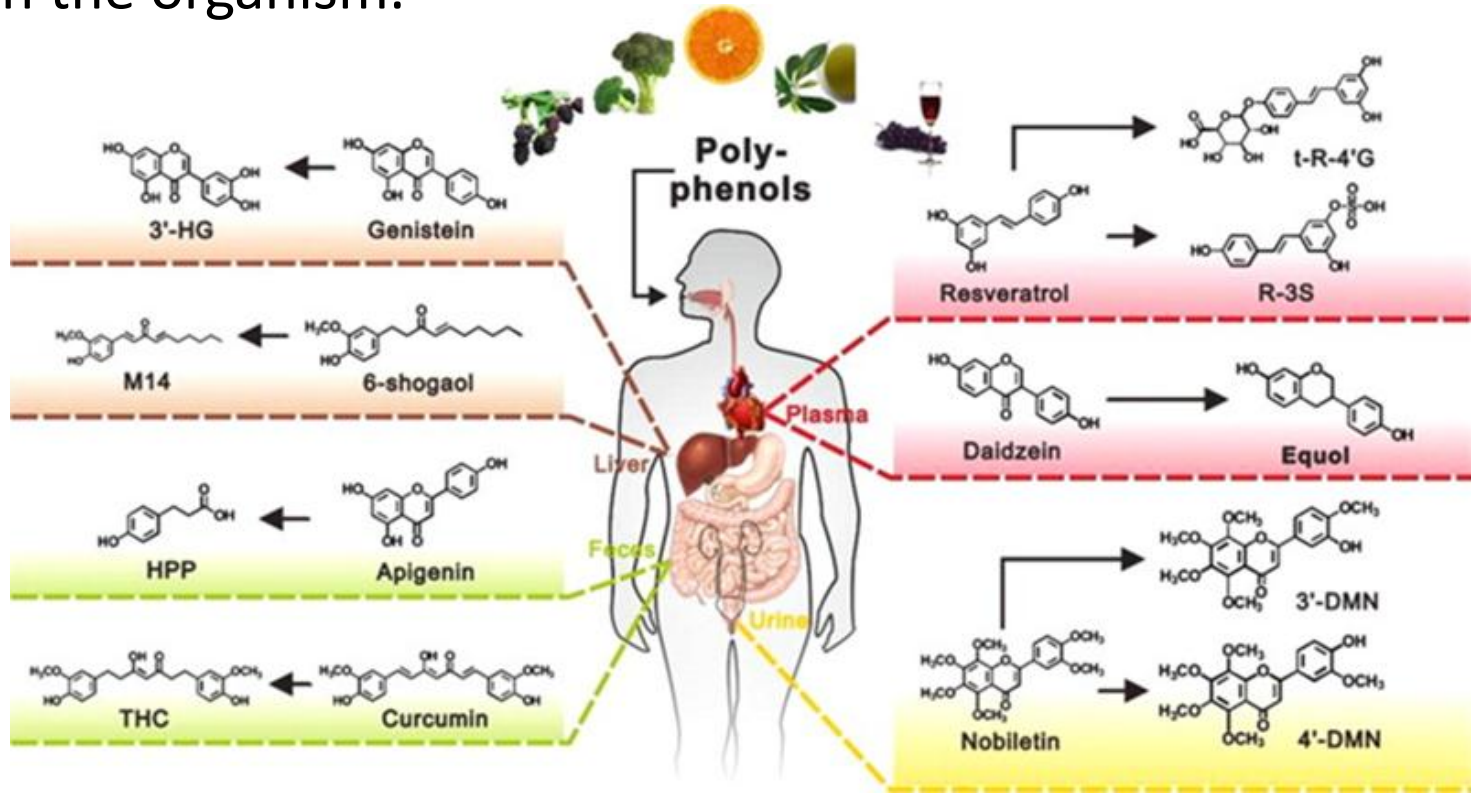
1318 papers in 12 months

- Apoptosis
- Arthritis
- Inflammation
- Effect on testosterone
- Antibactericide
- Cosmoceutical
- ...

Polyphenols

POLYPHENOL RESEARCH

Nowaday,s they are not considered **nutrients** however they are bioactive compounds, since they perform important physiological functions in the organism.



Chiou, Y.-S. *et al. 2014*

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- What are polyphenols
- Polyphenols and health outcomes
- Polyphenols from beer
- Health effects of prenylflavonoids from beer
- Isoxanthohumol reliable biomarker of beer consumption

Polyphenols and Cardiovascular Health

7447

55-80 years

Free of CVD but at high risk

FFQ 1 → FFQ 2 → FFQ n → CUMULATIVE polyphenol intake

Phenol-Explorer
Database on polyphenol content in foods

502 polyphenols in 452 foods

Polyphenol Intake and Cardiovascular

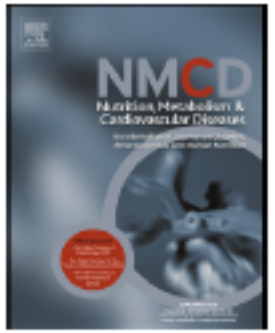
POLYPHENOL RESEARCH

Nutrition, Metabolism & Cardiovascular Diseases (2014) xx, 1–9

Available online at www.sciencedirect.com

Nutrition, Metabolism & Cardiovascular Diseases

journal homepage: www.elsevier.com/locate/nmcd



Inverse association between habitual polyphenol intake and incidence of cardiovascular events in the PREDIMED study

A. Tresserra-Rimbau [a,b], E.B. Rimm [c,d], A. Medina-Remón [a,b], M.A. Martínez-González [b,e], R. de la Torre [b,f], D. Corella [b,g], J. Salas-Salvadó [b,h], E. Gómez-Gracia [b,i], J. Lapetra [b,j], F. Arós [b,k], M. Fiol [b,l], E. Ros [b,m], L. Serra-Majem [b,n], X. Pintó [b,o], G.T. Saez [b,p], J. Basora [b,q], J.V. Sorlí [b,r], J.A. Martínez [b,s], E. Vinyoles [b,t], V. Ruiz-Gutiérrez [b,u], R. Estruch [b,v], R.M. Lamuela-Raventós [a,b,*] on behalf of the PREDIMED Study Investigators

POLYPHENOLS AND CARDIOVASCULAR HEALTH

Table 2 Association between quintiles of cumulative polyphenol intake (total and main groups) and incident CVD in the PREDIMED study.

	Q1	Q2	Q3	Q4	Q5	*P* for trend
Total polyphenols (mg/d)	562	701	800	917	1170	
No. of CVD cases	66	49	58	49	51	
No. of person years	5312	6668	6905	6629	5554	
Age and sex adjusted	1.00	0.60 (0.38–0.95)[a]	0.62 (0.39–0.97)	0.58 (0.36–0.91)	0.58 (0.36–0.93)	0.04
Model 2[b]	1.00	0.57 (0.36–0.92)	0.60 (0.38–0.95)	0.54 (0.34–0.87)	0.51 (0.30–0.84)	0.02
Model 3[c]	1.00	0.60 (0.38–0.97)	0.67 (0.42–1.07)	0.59 (0.37–0.96)	0.54 (0.33–0.91)	0.04
No. of person years	5341	6541	6640	6491	6055	
Age and sex	1.00	0.64 (0.40–1.04)	0.81 (0.52–1.27)	0.65 (0.42–1.02)	0.66 (0.42–1.04)	0.22
Model 2	1.00	0.94 (0.46–1.95)	1.17 (0.55–2.47)	0.96 (0.46–2.00)	0.69 (0.31–1.56)	0.19
Lignans (mg/d)	0.44	0.57	0.67	0.77	0.94	
No. of cases	69	57	53	44	50	
No. of person years	4625	6122	6899	6892	6530	
Age and sex	1.00	0.61 (0.40–0.95)	0.55 (0.36–0.86)	0.57 (0.35–0.91)	0.51 (0.31–0.84)	0.004
Model 2	1.00	0.65 (0.41–1.01)	0.55 (0.35–0.87)	0.61 (0.37–0.99)	0.50 (0.29–0.85)	0.007
Model 3	1.00	0.64 (0.41–0.99)	0.54 (0.34–0.85)	0.60 (0.36–0.97)	0.51 (0.30–0.86)	0.007
Age and sex	1.00	1.00 (0.65–1.55)	0.88 (0.55–1.39)	0.75 (0.46–1.21)	0.67 (0.40–1.11)	0.06
Model 2	1.00	0.97 (0.62–1.53)	0.86 (0.53–1.37)	0.70 (0.43–1.15)	0.63 (0.38–1.05)	0.02
Model 3	1.00	1.08 (0.69–1.71)	0.94 (0.58–1.53)	0.84 (0.51–1.38)	0.74 (0.43–1.26)	0.14

[a] HR (95% CI).
[b] Additionally adjusted for smoking, BMI, alcohol, physical activity, family history of CVD, aspirin use, antihypertensive drugs, cardiovascular drugs, diabetes status, and total energy intake.
[c] Additionally adjusted for intake of protein, saturated fatty acids, polyunsaturated fatty acids, monounsaturated fatty acids, and cholesterol.

FLAVONOIDS AND CARDIOVASCULAR HEALTH

Table 3 The relationship between CVD and cumulative flavonoids subclasses intake (in quintiles) in participants from the PREDIMED study.

Flavonoids	Q1	Q2	Q3	Q4	Q5	*P* for trend
Anthocyanins (mg/d)	11.8	23.6	32.8	45.7	74.6	
No. of cases	69	57	52	43	52	
No. of person years	5375	6347	6589	6963	5795	
Age and sex	1.00	0.95 (0.65–1.40)[a]	0.62 (0.41–0.94)	0.52 (0.34–0.80)	0.60 (0.39–0.90)	0.004
Model 2[b]	1.00	1.15 (0.74–1.79)	0.82 (0.51–1.33)	0.65 (0.39–1.09)	0.62 (0.36–1.06)	0.03
Model 3[c]	1.00	1.18 (0.76–1.84)	0.85 (0.52–1.38)	0.67 (0.40–1.11)	0.67 (0.39–1.13)	0.05
Dihydrochalcones (mg/d)	0.8	1.8	2.6	3.5	5.8	
No. of cases	47	59	55	57	55	
No. of person years	5036	6268	7563	5524	6677	
Age and sex	1.00	1.11 (0.73–1.67)	0.92 (0.60–1.40)	0.96 (0.62–1.48)	0.62 (0.39–0.99)	0.02
Model 2	1.00	1.25 (0.78–1.99)	0.90 (0.55–1.46)	0.92 (0.56–1.52)	0.61 (0.35–1.05)	0.02
Model 3	1.00	1.24 (0.78–1.99)	0.92 (0.56–1.50)	0.95 (0.57–1.57)	0.63 (0.36–1.08)	0.03
Model 2	1.00	0.65 (0.41–1.02)	0.70 (0.44–1.09)	0.57 (0.36–0.91)	0.36 (0.20–0.63)	0.0004
Model 3	1.00	0.70 (0.44–1.10)	0.77 (0.49–1.21)	0.66 (0.41–1.05)	0.40 (0.23–0.72)	0.003
Flavanones (mg/d)	28	78	113	157	247	
No. of cases	50	51	49	55	68	
Flavanols (mg/d)	90	129	158	192	263	
No. of cases	69	51	59	59	35	
No. of person years	4841	6409	7058	6860	5900	
Age and sex	1.00	0.64 (0.43–0.94)	0.65 (0.44–0.95)	0.55 (0.37–0.82)	0.33 (0.21–0.53)	<0.0001
Model 2	1.00	0.65 (0.41–1.02)	0.70 (0.44–1.09)	0.57 (0.36–0.91)	0.36 (0.20–0.63)	0.0004
Model 3	1.00	0.70 (0.44–1.10)	0.77 (0.49–1.21)	0.66 (0.41–1.05)	0.40 (0.23–0.72)	0.003
Model 3	1.00	0.94 (0.56–1.56)	1.37 (0.83–2.27)	1.30 (0.79–2.12)	1.07 (0.64–1.80)	0.72
Flavonols (mg/d)	56	74	88	101	124	
No. of cases	69	57	55	40	52	
No. of person years	5608	6961	6668	6179	5652	
Age and sex	1.00	0.85 (0.58–1.25)	0.63 (0.42–0.95)	0.44 (0.28–0.70)	0.56 (0.35–0.88)	0.002
Model 2	1.00	0.79 (0.51–1.22)	0.69 (0.44–1.09)	0.48 (0.28–0.80)	0.58 (0.34–0.98)	0.02
Model 3	1.00	0.84 (0.54–1.31)	0.74 (0.46–1.17)	0.53 (0.31–0.90)	0.69 (0.40–1.19)	0.08

[a] HR (95% CI).
[b] Model 2 – age, sex, smoking, BMI, alcohol, energy, physical activity, family history of CVD, aspirin use, antihypertensive drugs, cardiovascular drugs, and diabetes status.
[c] Model 3 - model 2 plus intake of proteins, saturated fatty acids, polyunsaturated fatty acids, monounsaturated fatty acids, and cholesterol.

Beer

PHENOLIC ACIDS AND CARDIOVASCULAR HEALTH

Table 4 The relationship between CVD and cumulative phenolic acids subclasses intake (in quintiles) in participants from the PREDIMED study.

Phenolic acids	Q1	Q2	Q3	Q4	Q5	*P* for trend
Hydroxybenzoic acids (mg/d)	6.9	12.9	17.8	24.1	36.1	
No. of cases	69	62	47	55	40	
No. of person years	5398	6603	6734	6853	5480	
Age and sex	1.00	0.80 (0.54–1.17)[a]	0.60 (0.40–0.90)	0.54 (0.36–0.82)	0.46 (0.29–0.71)	0.0003
Model 2[b]	1.00	0.82 (0.52–1.29)	0.65 (0.40–1.06)	0.59 (0.36–0.97)	0.37 (0.20–0.66)	0.0006
Model 3[c]	1.00	0.91 (0.57–1.43)	0.74 (0.46–1.22)	0.73 (0.44–1.21)	0.47 (0.26–0.86)	0.02
Hydroxycinnamic acids (mg/d)	138	207	252	316	422	
No. of cases	61	50	42	59	61	
No. of person years	5632	6486	6869	6914	5167	
Age and sex	1.00	0.80 (0.53–1.20)	0.55 (0.35–0.87)	0.92 (0.62–1.36)	1.08 (0.72–1.63)	0.40
Model 2	1.00	0.81 (0.51–1.29)	0.57 (0.34–0.96)	0.91 (0.58–1.42)	0.99 (0.62–1.58)	0.71
Model 3	1.00	0.79 (0.49–1.25)	0.58 (0.35–0.97)	0.86 (0.55–1.36)	0.93 (0.58–1.49)	0.93
Other phenolic acids (mg/d)	0.1	2.5	4.6	8.6	17.9	
No. of cases	58	66	47	62	40	
No. of person years	5100	5225	6571	7787	5385	
Age and sex	1.00	1.11 (0.75–1.64)	0.69 (0.45–1.08)	0.79 (0.52–1.21)	0.73 (0.46–1.14)	0.10
Model 2	1.00	1.31 (0.83–2.09)	0.75 (0.44–1.28)	0.88 (0.54–1.42)	0.74 (0.45–1.24)	0.11
Model 3	1.00	1.39 (0.87–2.22)	0.82 (0.48–1.39)	0.92 (0.57–1.51)	0.82 (0.49–1.39)	0.19

[a] HR (95% CI).
[b] Model 2 – age, sex, smoking, BMI, alcohol, energy, physical activity, family history of CVD, aspirin use, antihypertensive drugs, cardiovascular drugs, and diabetes status.
[c] Model 3 - model 2 plus intake of proteins, saturated fatty acids, polyunsaturated fatty acids, monounsaturated fatty acids, and cholesterol.

Polyphenol Intake and Mortality Risk

POLYPHENOL RESEARCH

Tresserra-Rimbau *et al. BMC Medicine* 2014, 12:77
http://www.biomedcentral.com/1741-7015/12/77

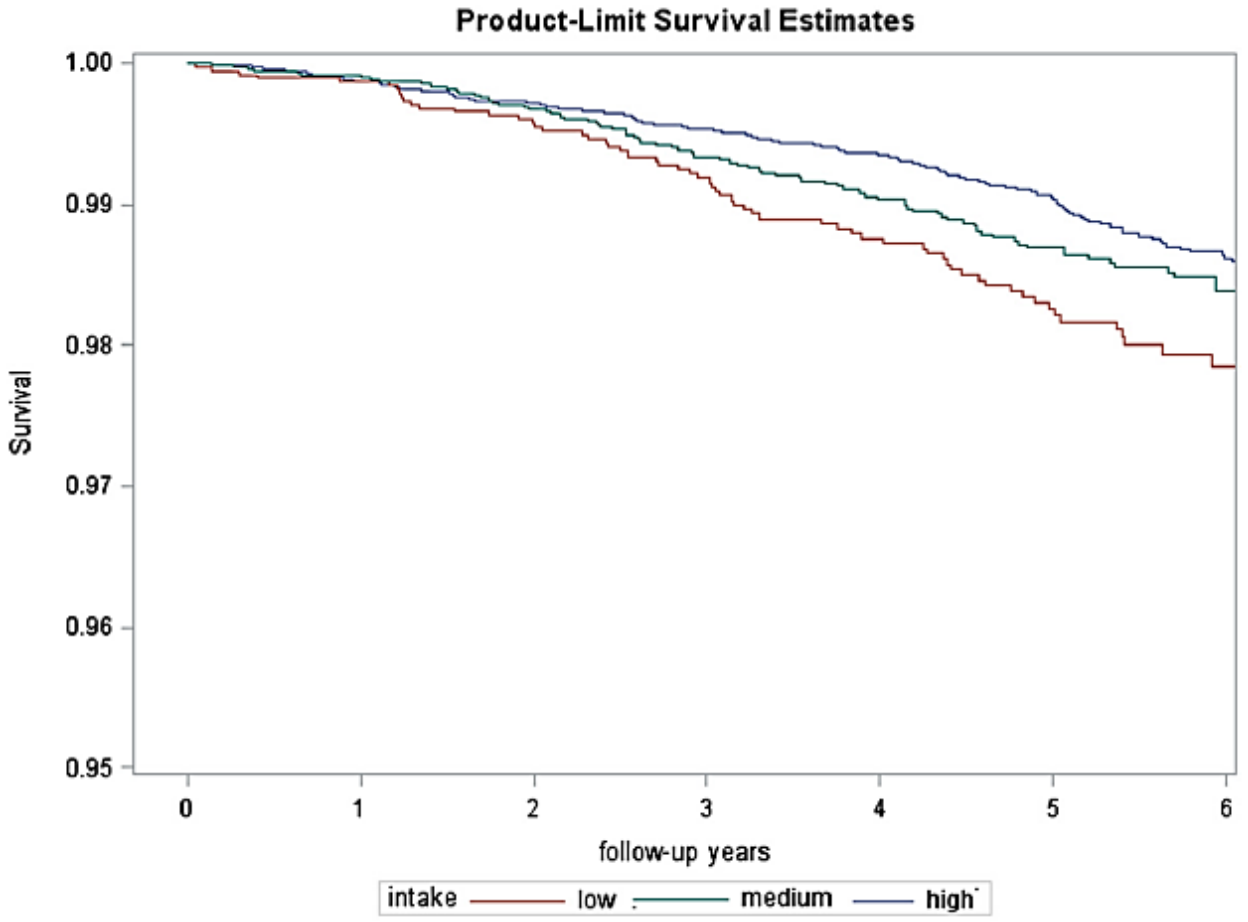
RESEARCH ARTICLE Open Access

Polyphenol intake and mortality risk: a re-analysis of the PREDIMED trial

Anna Tresserra-Rimbau[1,2], Eric B Rimm[3], Alexander Medina-Remón[2,17], Miguel A Martínez-González[2,4], M Carmen López-Sabater[1,2], María I Covas[2,5], Dolores Corella[2,6], Jordi Salas-Salvadó[2,7], Enrique Gómez-Gracia[2,8], José Lapetra[2,9], Fernando Arós[2,10], Miquel Fiol[2,11], Emili Ros[2,12], Lluis Serra-Majem[2,13], Xavier Pintó[2,14], Miguel A Muñoz[2,15], Alfredo Gea[2,4], Valentina Ruiz-Gutiérrez[2,16], Ramón Estruch[2,17], Rosa M Lamuela-Raventós[1,2*] and on behalf of the PREDIMED Study Investigators

Polyphenol Intake and Mortality Risk

POLYPHENOL RESEARCH



Beer and Health

Polyphenol Intake and Mortality Risk

POLYPHENOL RESEARCH

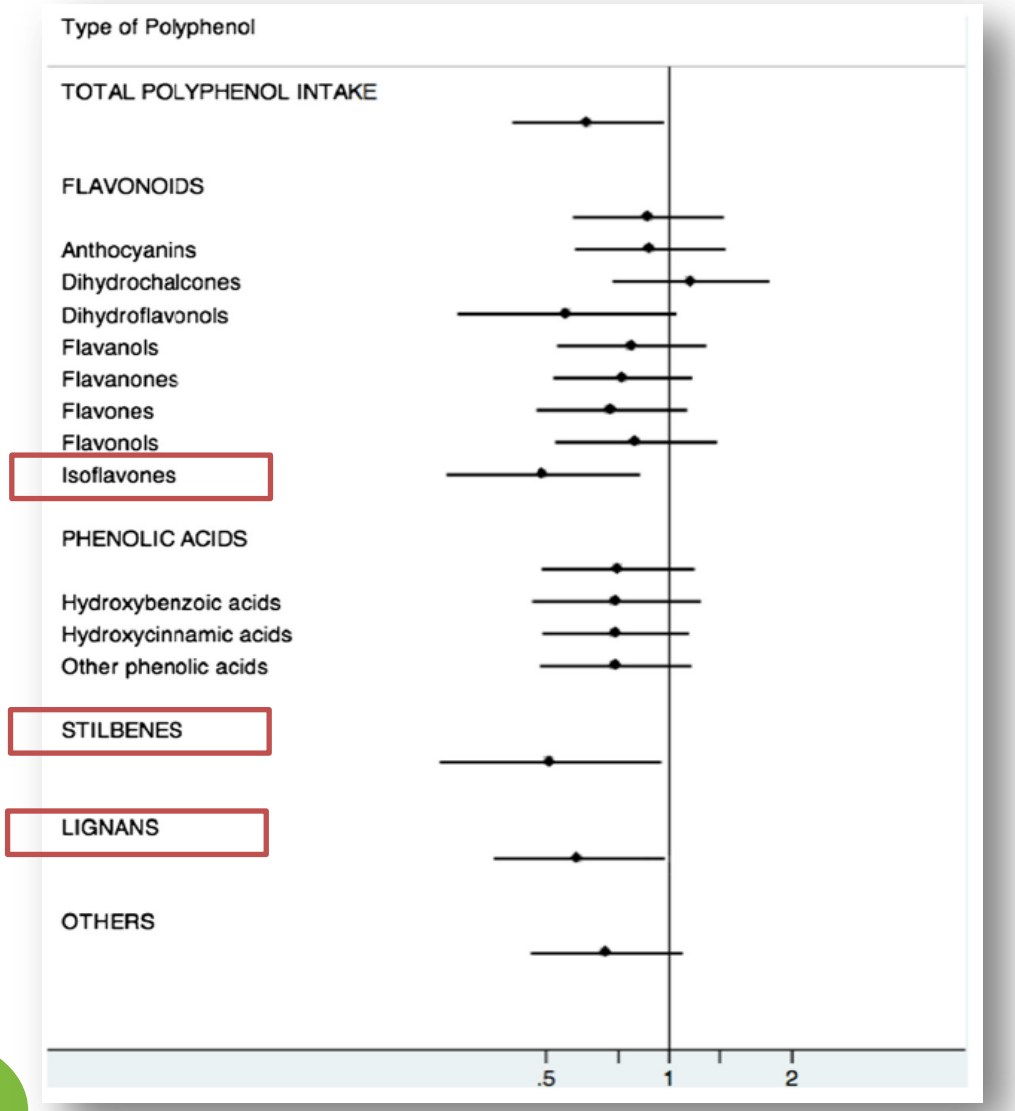
Table 2 Cox proportional hazard ratios for total mortality according to quintiles of cumulative total polyphenol intake

	Quintiles of cumulative intake of total polyphenols, mg/d					
	Q1 (535)	Q2 (700)	Q3 (800)	Q4 (917)	Q5 (1170)	*P*-trend
No. of deaths	88	62	52	63	62	
No. of person-years	5,505	6,599	6,767	6,559	5,638	
Age- and sex-adjusted HR (95% CI)*	1.00	0.65 (0.44 to 0.95)	0.55 (0.37 to 0.82)	0.73 (0.50 to 1.06)	0.66 (0.44 to 0.98)	0.12
Multivariable-adjusted HR (95% CI)†	1.00	0.68 (0.46 to 1.01)	0.60 (0.39 to 0.90)	0.75 (0.51 to 1.12)	0.60 (0.39 to 0.91)	0.07
Additionally adjusted HR (95% CI)‡	1.00	0.71 (0.48 to 1.05)	0.62 (0.41 to 0.95)	0.79 (0.53 to 1.17)	0.63 (0.41 to 0.97)	0.12

HR, Hazard ratio; CI, Confidence interval.
*Analyses were stratified by sex, recruitment center and intervention group.
†The multivariable HR has been additionally adjusted for age (<60, 60 to 64.9, 65 to 69.9, 70 to 74.9, >/=75 years), smoking (never, past and current: cigarettes (<5, 5 to 19, >20 per day) or cigars and pipes (<3, 3 to 6, >6 per day)), BMI (<25, 25 to 29.9, or >/=30 Kg/m^2), baseline diabetes, alcohol (0, 0.1 to 14.9, 15 to 29.9, >/=30 g/day), total energy intake (continuous variable), physical activity (continuous variable), family history of CVD or cancer, aspirin use, antihypertensive drug use, use of cardiovascular medication, use of oral hypoglycaemic agents, insulin, other medication.
‡This model has been additionally adjusted for intake of protein, saturated fatty acids, polyunsaturated fatty acids, monounsaturated fatty acids and cholesterol (all as continuous variables).

Total polyphenol intake was significantly associated with a decrease (almost 40%) in all-cause mortality, after adjusting for all confounders.
The dose-response trend suggested an L-shaped relationship.

Polyphenol Intake and Mortality Risk



Hazard ratios (95% CI) of total mortality for the highest vs. lowest quintiles of polyphenol intake.

Isoflavones
HR 0.49; CI 0.28 to 0.84; P-trend=0.009

Stilbenes
HR 0.48; CI 0.25 to 0.91; P-trend=0.04

Lignans
HR 0.60; CI 0.37 to 0.95; P-trend=0.03

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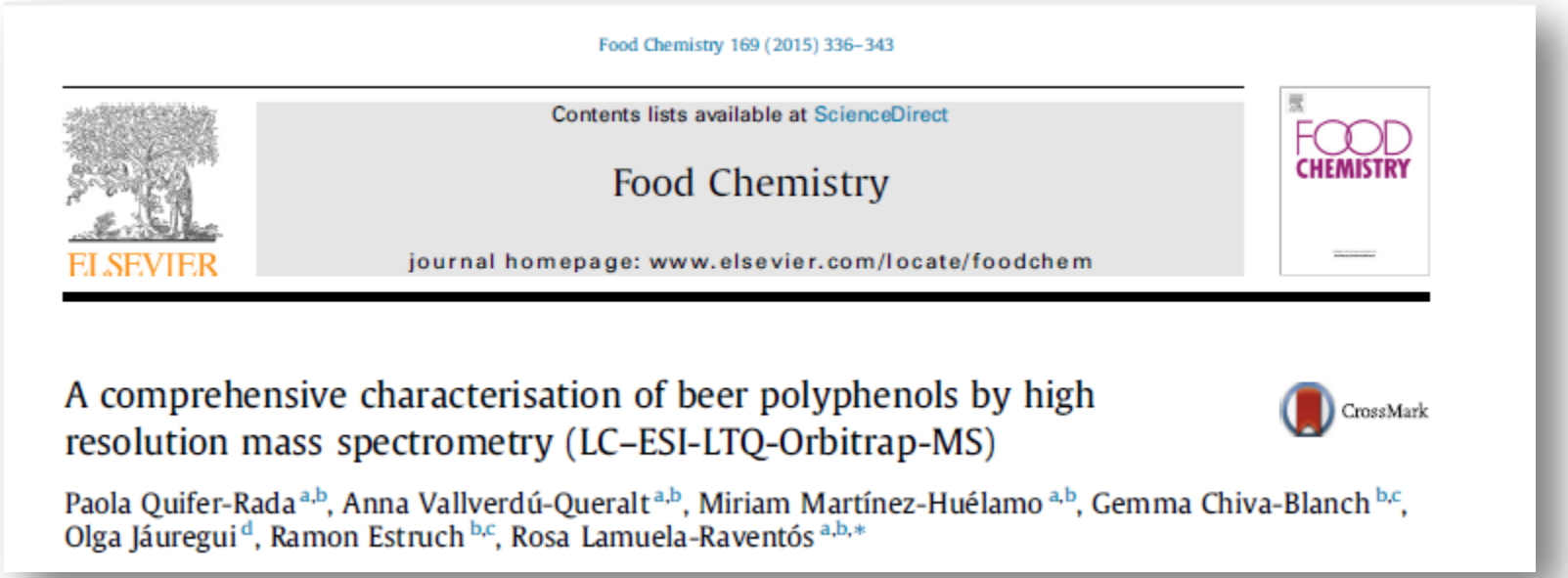
Beer Polyphenols by LC-LTQ-Orbitrap MS



Food Chemistry 169 (2015) 336–343

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Food Chemistry

journal homepage: www.elsevier.com/locate/foodchem

A comprehensive characterisation of beer polyphenols by high resolution mass spectrometry (LC–ESI-LTQ-Orbitrap-MS)

Paola Quifer-Rada [a,b], Anna Vallverdú-Queralt [a,b], Miriam Martínez-Huélamo [a,b], Gemma Chiva-Blanch [b,c], Olga Jáuregui [d], Ramon Estruch [b,c], Rosa Lamuela-Raventós [a,b,*]

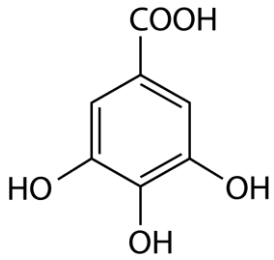
- We analyzed the beer polyphenolic profile by High Ressolution Mass Spectrometry (LC-LTQ-Orbitrap)
- 3 types of Beer: Marzen Bier, Pilsen and Lager.
- Full Scan Mode and Tandem MS/MS experiments with accurate mass measurements of the ions and the fragments
- **47 phenolic compounds were detected, 7 of them were reported for the first time**

Malt Polyphenols

70-80% of the beer polyphenols come from malt

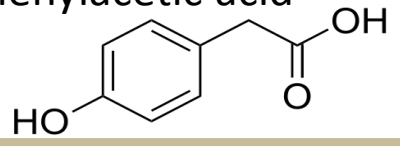
Hydroxybenzoic acids

Gallic acid
Protocatechuic acid-*O*-hexoside
Dihydroxybenzoic acid
Protocatechuic acid
Hydroxybenzoic acid
Vanillic acid



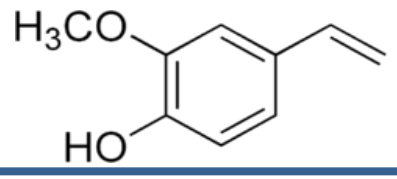
Hydroxyphenylacetic acids

Hydroxyphenylacetic acid



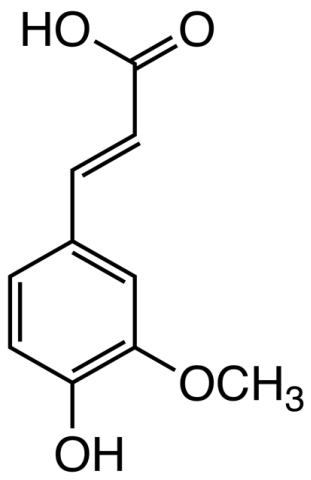
Alkylmethoxyphenols

4-vinylguaiacol



Hydroxycinnamic acids

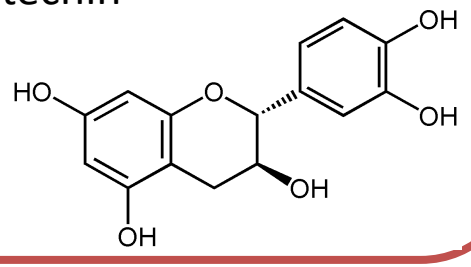
Caffeic acid *O*-hexoside
Caffeic acid
1-caffeoylquinic acid
3-caffeoylquinic acid
4-caffeoylquinic acid
5-caffeoylquinic acid
Coumaric acid *O*-hexoside
Feruoylquinic acid
Sinapic acid-*O*-hexoside
Sinapic acid
Ferulic acid



Malt Polyphenols

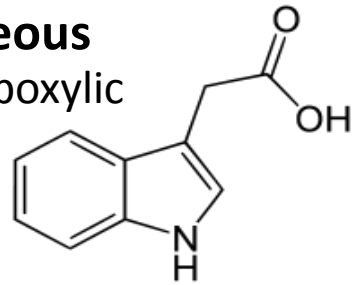
Flavanols

Catechin
Catechin-*O*-hexoside
Catechin-*O*-dihexoside
Epicatechin



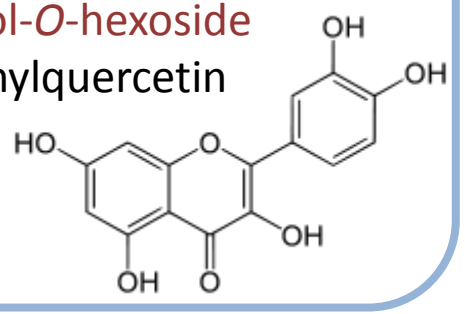
Miscellaneous

Indole-3-carboxylic acid



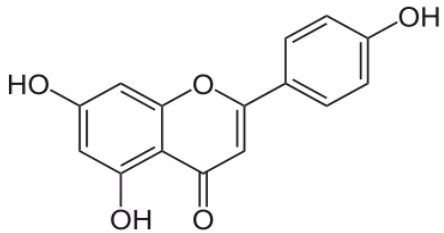
Flavonols

Quercetin-3-*O*-glucoside
Kaempferol-*O*-hexoside
3,7-dimethylquercetin



Flavones

Apigenin-*C*-hexoside-*O*-hexoside
Apigenin-*C*-hexoside-pentoside
Apigenin-*C*-hexoside

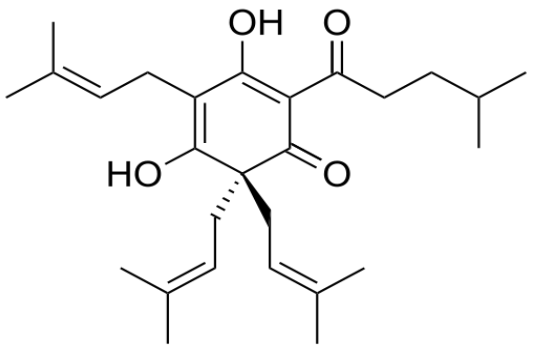


Hop Polyphenols

30-20% of the beer polyphenols come from hops

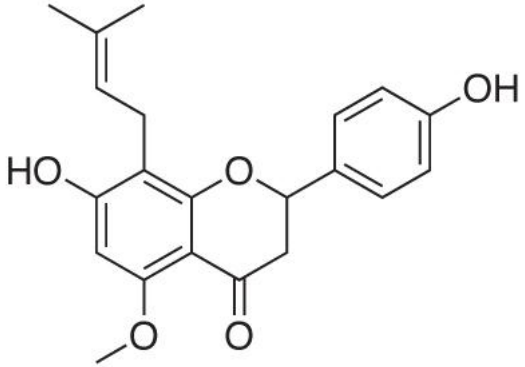
α-acids and β-acids

co-Humulone
ad-Humulone
n-Humulone
Iso-α-cohumulone
Iso-α-adhumulone
Iso-α-nhumulone
Lupulone



Prenylflavanoids

Isoxanthohumol
Xanthohumol
Desmethylxanthohumol
8-prenylnaringenin
6-prenylnaringenin



Polyphenol Intake from one Drink

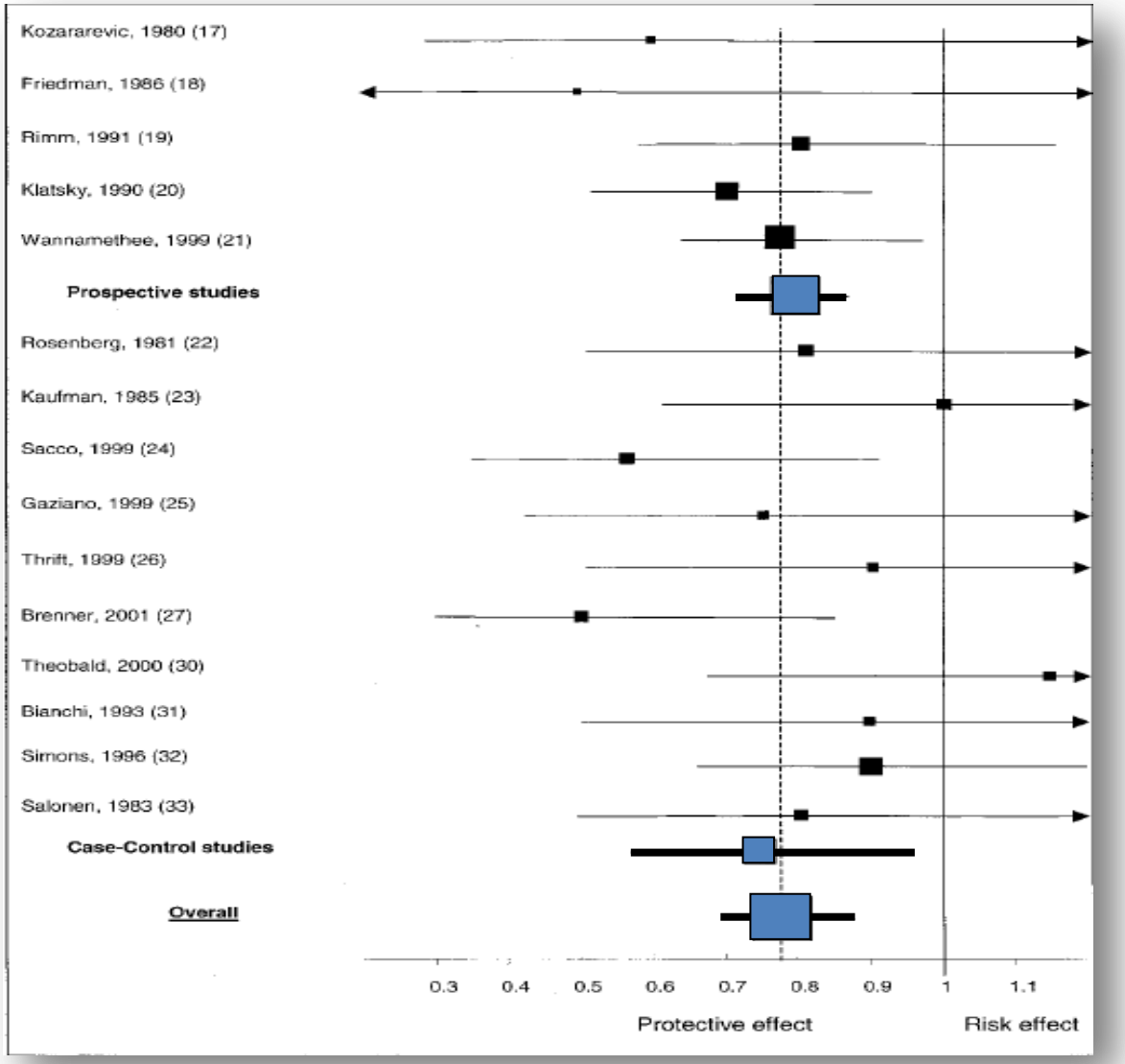
POLYPHENOL RESEARCH

330 mL

150 mL

150 mL

Beer and Wine: a Metanalisi



Reduction of cardiovascular risk

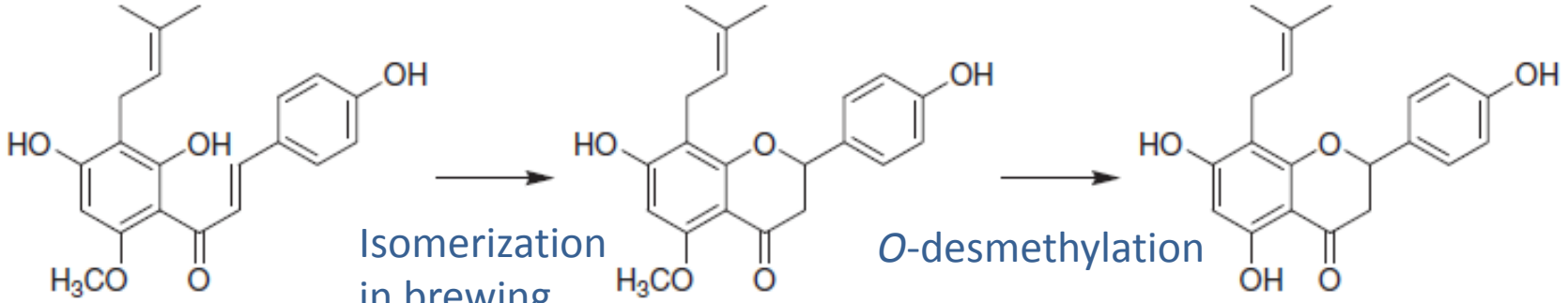
- Wine: –32%
- Beer: –22%

Circulation 2002

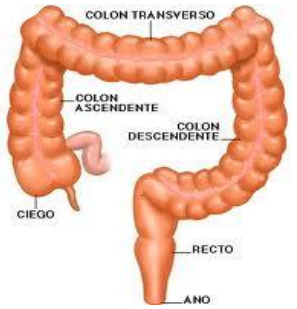
Index

- What are polyphenols
- Polyphenols and health outcomes
- Polyphenols from beer
- Health effects of prenylflavonoids from beer

Prenylflavanoids



Xanthohumol (XN) | Isoxanthohumol (IX) | 8-Prenylnaringenin (8-PN)



95% of the prenylflavanoids found in hops are xanthohumol, desmethylxanthohumol, and 3-geranylchalconenaringenina. (**Stevens et al, 1999**)

High content in isoxanthohumol (prenylflavanone) and low content in xanthohumol (**Stevens et al 1999)**

Isoxantohumol is converted to 8-prenylnaringenin by an *O*-desmethylation catalyzed by gut microbiota. (**Hanske L et al 2010, Possemiers S et al 2005)**

Biological Activity of Beer Prenylflavanoids

POLYPHENOL RESEARCH

8-prenylnaringenin

- Most potent phytostrogen known untill date. It showed similar binding characteristics to ERα and ERβ *in vitro*. The oestrogenic activity of 8-prenylnaringenin was greater than that of established phyto-oestrogens such as coumestrol, genistein and daidzein. **(Milligan et al. 2000)**
- Owing to this phytoestrogenic activity, 8PN has been proposed as a treatment for menopausal symptoms, such as hot flashes and osteoporosis

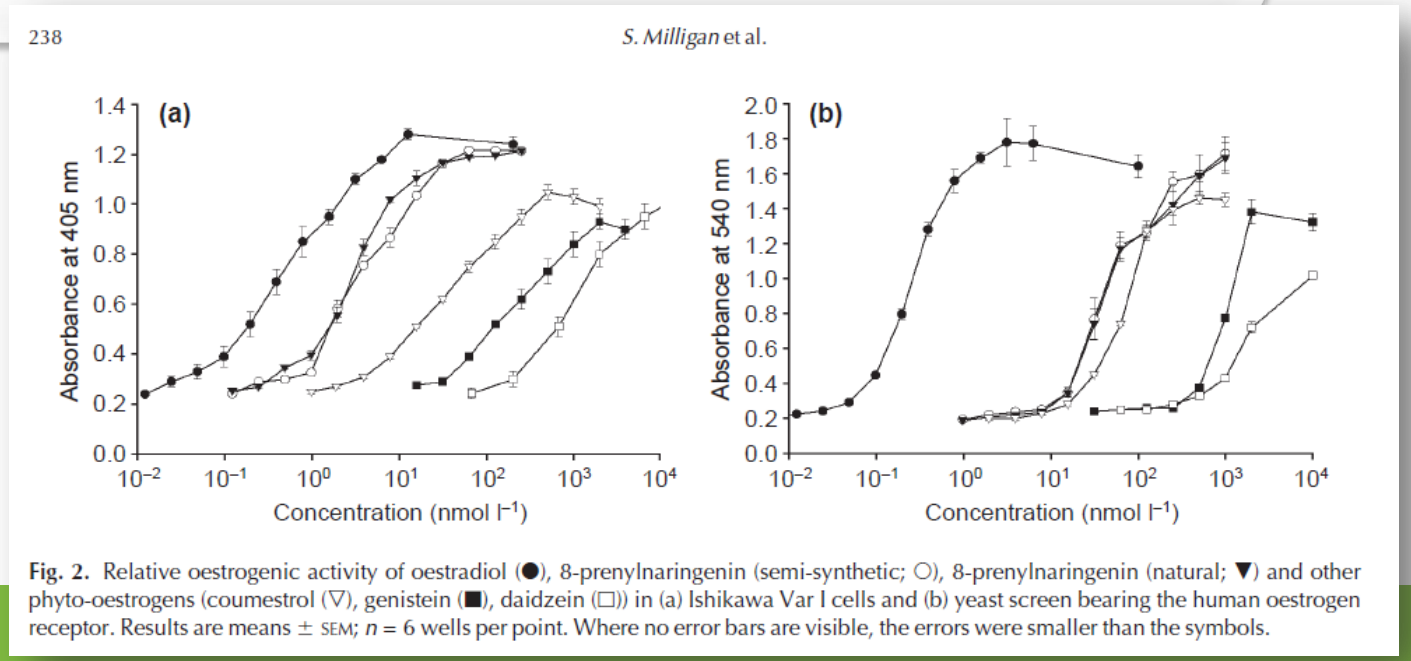


Fig. 2. Relative oestrogenic activity of oestradiol (●), 8-prenylnaringenin (semi-synthetic; ○), 8-prenylnaringenin (natural; ▼) and other phyto-oestrogens (coumestrol (▽), genistein (■), daidzein (□)) in (a) Ishikawa Var I cells and (b) yeast screen bearing the human oestrogen receptor. Results are means ± SEM; $n = 6$ wells per point. Where no error bars are visible, the errors were smaller than the symbols.

Biological Activity of Beer Prenylflavanoids

Xantohumol and Isoxanthohumol

- Xanthohumol and isoxanthohumol have shown weak or no estrogenic activity.
- IX is considered to be a source of 8-prenylnaringenin, becauseit is metabolized to 8-prenylnaringenin in the intestinal tract by gut microbiota.

Urinary Isoxanthohumol as a Biomarker of Beer Consumption

The Journal of Nutrition
Nutritional Epidemiology

J. Nutr. 144: 484–488, 2014.

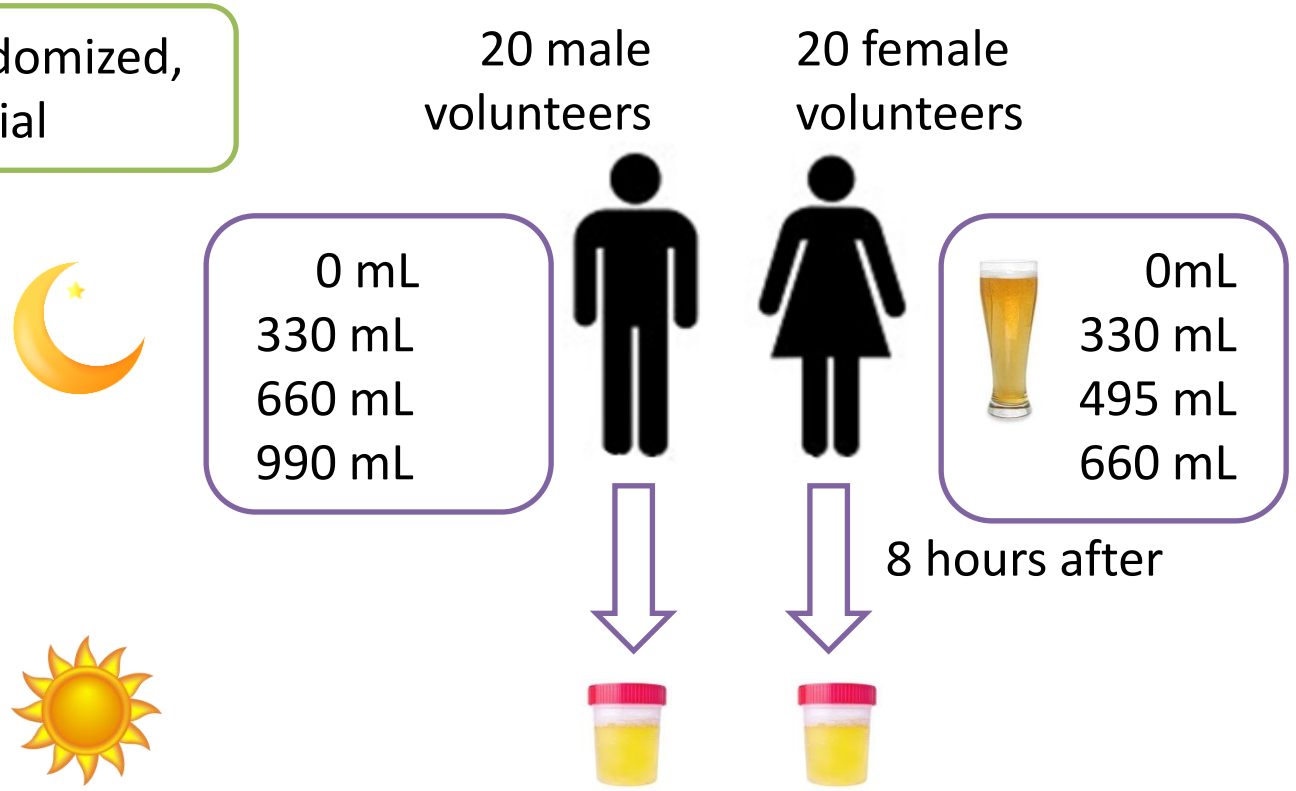
Urinary Isoxanthohumol Is a Specific and Accurate Biomarker of Beer Consumption[1–3]

Paola Quifer-Rada,[4,5] Miriam Martínez-Huélamo,[4,5] Gemma Chiva-Blanch,[5,6] Olga Jáuregui,[7] Ramon Estruch,[5,6] and Rosa M. Lamuela-Raventós[4,5]*

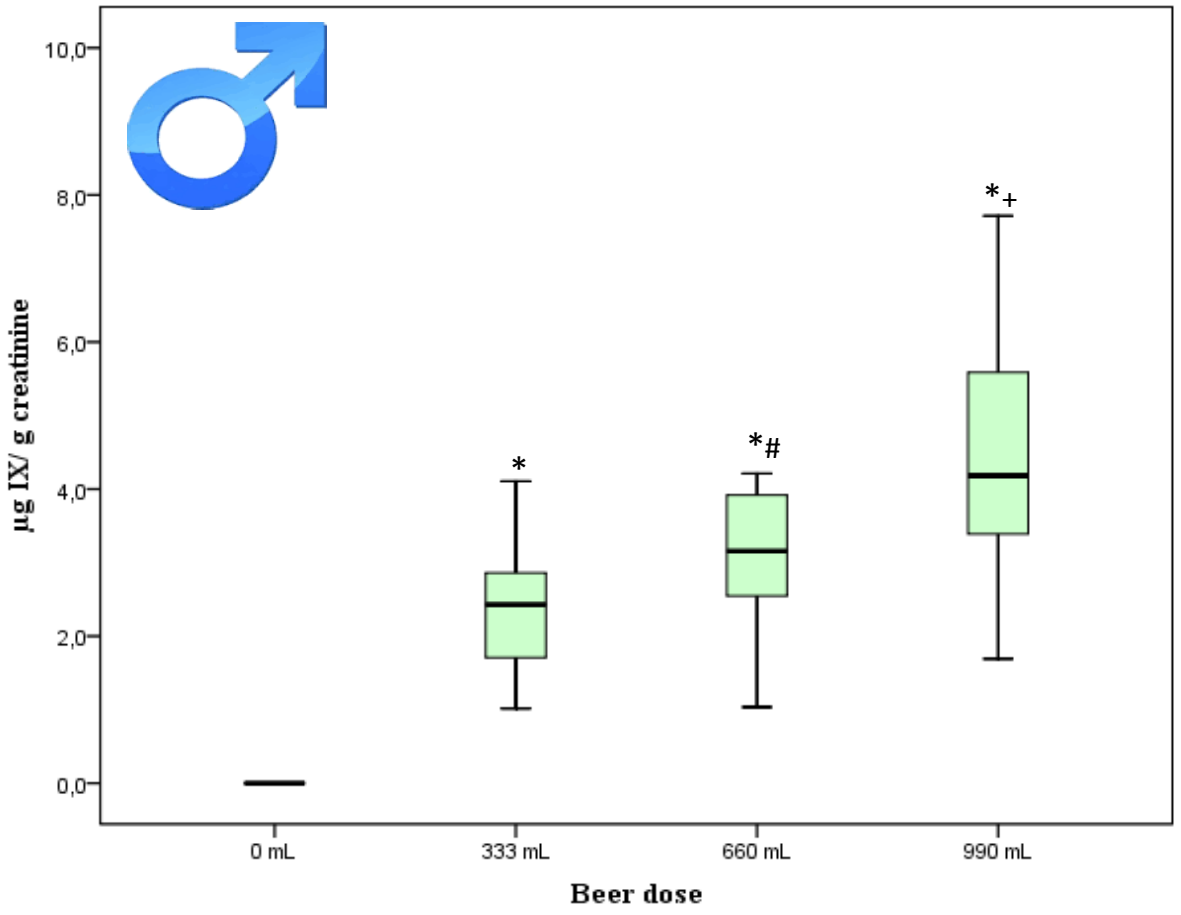
[4]Department of Nutrition and Food Science-XARTA-INSA, School of Pharmacy, University of Barcelona, Barcelona, Spain; [5]CIBER Physiopathology of Obesity and Nutrition, Institute of Health Carlos III, Madrid, Spain; and [6]Department of Internal Medicine, Hospital Clínic, Institute of Biomedical Investigation August Pi i Sunyer, and [7]Scientific and Technological Center, University of Barcelona, Barcelona, Spain

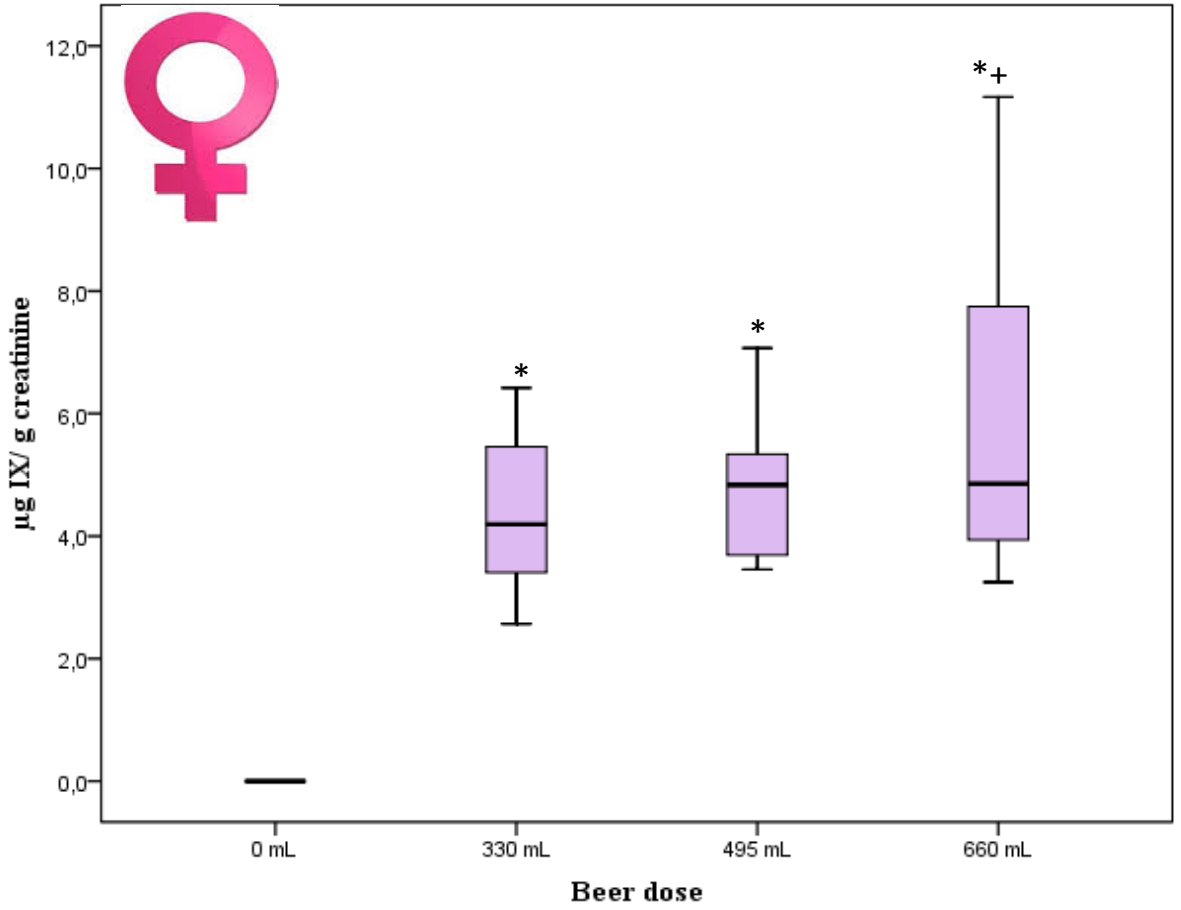
Urinary Isoxanthohumol as a Biomarker of Beer Consumption

Dose-response, randomized, cross-over clinical trial

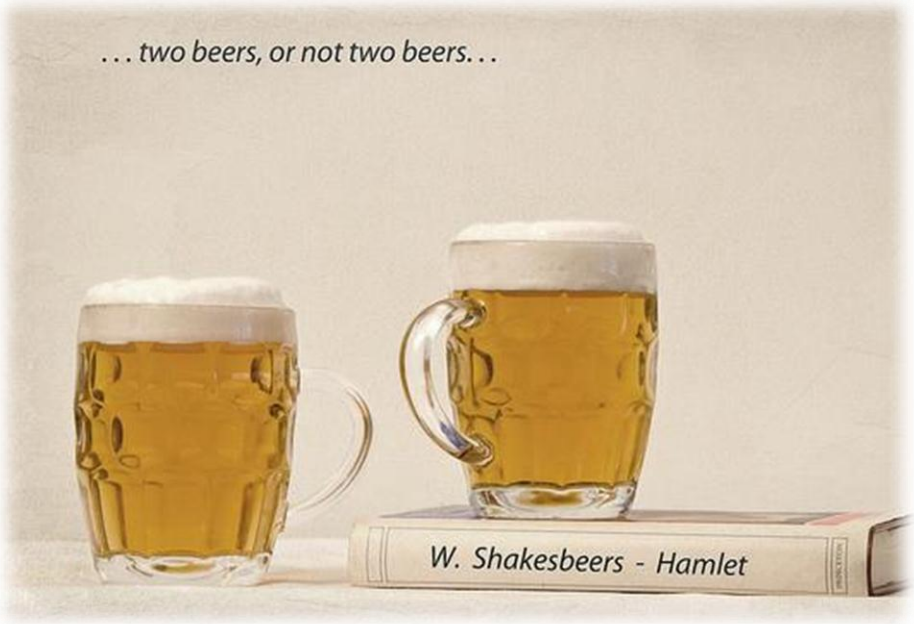


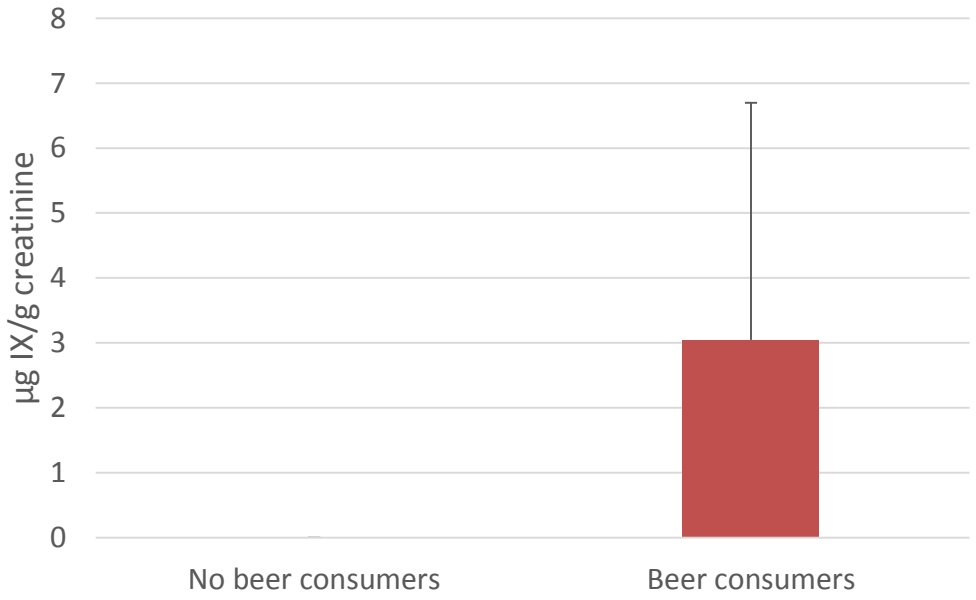
Urinary excretion of Isoxanthohumol in male (A) and female (B) volunteers 8 hours after the intake of different volums of beer





In Free Living Population in PREDIMED





IX is really a good boomarker that can be used in epidemilogical studies to evaluate beer health outcomes.

Conclusions

- Polyphenols consumption decrease all cause of mortality and CVD
- Beer has been shown to be a good source of polyphenols and it is one of the main food contributor to hydroxybenzoic acid intake in the European Prospective Investigation into Cancer and Nutrition cohort study.
- High intake of hydoxibenzoics decrease cardiovascular risk by 53% in the PREDIMED population
- IX is a good biomarker that may be used in epidemiological studies to evaluate beer health outcomes

We would like to thank:

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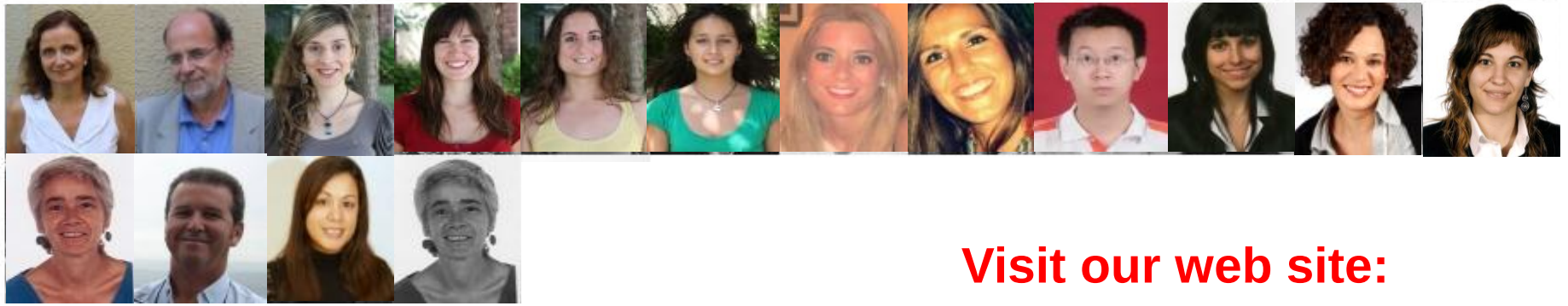

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Group director Rosa Mª Lamuela Raventós

Board Committee Ramón estruch Riba

Predoctoral researchers

Miriam Martínez Mariel Colman Gemma Sasot Naiara Orrego
Anna Tresserra Paola Quifer Guao Xiao Hui Ana Barrionuevo Anna Creus

Collaborators

Mónica Vázquez Montse Illán Xavier Torrado


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THANK YOU
lamuela@ub.edu