

## Radiolysis study on some flavonoids in *Ulmus davidiana var. japonica* with methanolic solvents

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### 1. Introduction

Gamma-irradiation process is used for food preservation [1-3]. Recently, this method has been studied for the chemical changes of constitutive compounds in foods. In Asia, *Ulmus davidiana var. japonica* (UD) has traditionally been used as a tea, a thickener in soups and as a cereal flour additive in bread-making. Also, the extracts from the stem and root bark of the UD have been used in traditional oriental medicine for the treatment of inflammatory diseases [4,5]. Recently, some polysaccharides and flavonoids from the UD have been found [1,6] (Fig. 1), it needs to develop knowledge of radiation-flavonoid interaction under various irradiation conditions. In this study, the radiolysis of major flavonoids in the UD was investigated in methanolic solvent.

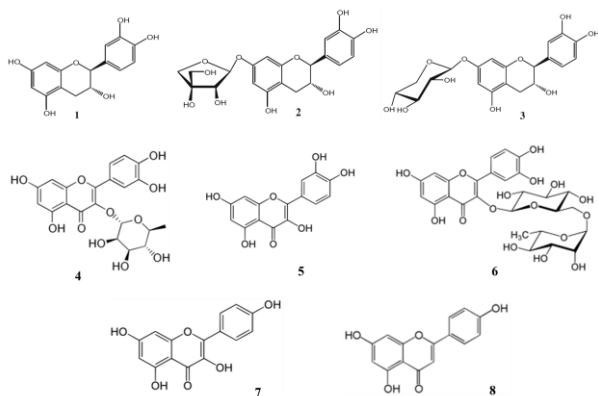


Fig. 1. Chemical structures of flavinols from UD; catechin (1), (-)-catechin-7-O- $\beta$ -D-apiofuranoside (2), (-)-catechin-7-O- $\beta$ -D-xylopyranoside (3), quercitrin (4), quercetin (5), rutin (6), kaempferol (7), apigenin (8).

### 2. Methods and Results

#### 2.1 General experimental procedures

The root bark of *Ulmus davidiana var. japonica* (UD) was purchased from Sinheung Science (Korea) and cut into pieces prior to use. All reagents and solvents for column chromatography were purchased from Aldrich (St. Louis, MO). Other commercially available reagents and solvent were used as received.

The radiation-induced chemical changes of major flavonoids in UD extracts were compared by ultra-performance liquid chromatography (UPLC) with slightly modifications of standard mobile phase condition (Table I). The UPLC analysis conditions are as follows;

- LC800, BM solution Co.
- Column: Inertsil ODS-3 (2.1 mm  $\times$  150 mm  $\times$  3  $\mu$ m)
- Detection wave length (Table II)

Table I: Standard mobile phase conditions

Mobile phase (Gradient system)	Gradient Time (min)	0.9% Acetic acid (%)	Acetonitrile (%)
	0	95	0
	3.5	65	100
Flow rate	1 mL/min		
Injection volume	10 $\mu$ L		

Table II: UV Detection condition

Flavonol	UV Wavelength (nm)
Quercitrin hydrate	256
Quercetin hydrate	375
Rutin hydrate	257
Kaempferol	366
Apigenin	334

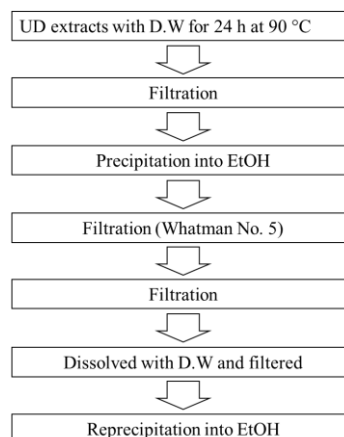


Fig. 2. Extraction process from root bark of UD.

Quercitrin hydrate (4), quercetin hydrate (5), rutin hydrate (6), kaempferol (7), and apigenin (8) were

identified by UPLC analysis by comparison with reported data [7]. The chemical structures and extraction process are shown in Fig. 1 and 2, respectively.

### 2.2 Radiation effects on flavonols in methanolic solvent

This radiolysis process was attributed to some reactive radical species generated indirect redox (oxidation-reduction) reactions in the solution [8]. The oxidative reactions can also occur on flavonoids by ionizing radiation [9]. In previous reports, the radiolysis of flavonols such as quercetin and kaempferol in solution produces reactions leading to a new series of polyphenols belonging to the depside group of molecules [10]. The UPLC analysis conditions and retention time of the flavonols are as follows (Table III) and the results were simply discussed.

Table III: UPLC analysis condition and  $R_t$  for flavonols

Flavonoid	Mobile phase	Retention time ( $R_t$ )
Quercitrin hydrate	MeOH : D.W = 50:50	3.7
Quercetin hydrate	MeOH : D.W = 50:50	3.8
Rutin hydrate	MeOH : D.W = 50:50	3.2
Kaempferol	MeOH : D.W = 70:30	2.9
Apigenin	MeOH : D.W = 70:30	3.0

The radiolysis of the flavonols in the methanolic solvent extracted from commercial UD was simply quantified and analyzed through UPLC analysis (Table IV). The quercitrin, quercetin, and apigenin were stable under  $\gamma$ -irradiation with absorbed dose up to 50 kGy. However, the rutin and kaempferol were decomposed at 25 kGy and decreased by 14.3 and 26.6 %, respectively. The changes in the rutin and kaempferol were generated by the reactive species such as methenium ( $\text{CH}_3^+$ ), carbon radicals ( $\text{CH}_3\cdot$ ) and hydroxyl radicals ( $\text{HO}\cdot$ ) formed during the radiolysis of the methanolic solvent.

Table IV: Area changes for irradiated flavonoids

Flavonoid	0 kGy	25 kGy
Quercitrin hydrate	-	-
Quercetin hydrate	-	-
Rutin hydrate	2,682,180	383,392 (▼14.3 %)
Kaempferol	957,503	254,706 (▼26.6 %)
Apigenin	-	-

### 3. Conclusions

In this study, the radiation effect on some flavonoids from the UD in methanolic solvent were preliminarily examined and discussed. The radiation degradation of materials in solution could be due to indirect redox

(oxidation-reduction) reactions [11]. Generally, in the majority of the UD extracts, the detectable radiolytic decomposition was not found at 25 kGy, commercially sterilization dose, except the rutin and kaempferol. These results can contribute to the considering of the irradiation dose for uses of the UD as additives in food processing. Also, if the further study it may provide that the UPLC method is available for the quantitative analysis of some flavonoids obtained from the UD by means of further study.

### REFERENCES

- [1] M. J. Jung, S. -I. Heo, M. -H. Wang, HPLC analysis and antioxidant activity of *Ulmus davidiana* and some flavonoids, *Food Chemistry*, Vol.120, p.313, 2010.
- [2] S. C. Verde, M. J. Trigo, M. B. Sousa, A. Ferreira, A. C. Ramos, I. Nunes, C. Junqueira, R. Melo, P. M. Santos, M. L. Botelho, Effects of gamma radiation on raspberries: safety and quality issues. *J Toxicol Environ Health A*. Vol.76, p.291, 2013.
- [3] M. N. C. Harder, V. Arthur, P. B. Arthur, Irradiation of Foods: Processing Technology and Effects on Nutrients: Effect of Ionizing Radiation on Food Components. *Encyclopedia of Food and Health*, p.476, 2016.
- [4] U. -D. Lee, S. -J. Suh, K. -S. Kim, D. -S. Kim, U. -H. Jin, I. -S. Lee, U. -H. Yoon, C. -H. Kim, Immunomodulatory activity of *Ulmus davidiana* Planch (*Ulmaceae*) water and ethanolic extracts on bone cells: Stimulation of proliferation, alkaline phosphatase activity and type I collagen synthesis. *Environmental Toxicology and Pharmacology*, Vol.23, p.154, 2007.
- [5] M. S, Zheng Y. K. Lee, Y. Li, K. Hwangbo, C. S. Lee, J. R. Kim, S. K. Lee, H. W. Chang, J. K. Son. Inhibition of DNA topoisomerases I and II and cytotoxicity of compounds from *Ulmus davidiana* var. *japonica*. *Arch Pharm Res*. Vol.33, p.1307, 2010.
- [6] S. Y. Eom, C. B. Chung, Y. S. Kim, J. H. Kim, K. S. Kim, Y. H. Kim, S. H. Park, Y. I. Hwang, K. H. Kim, Cosmeceutical properties of polysaccharides from the root bark of *Ulmus davidiana* var. *japonica*, *J Cosmet Sci*. Vol.57, p.355, 2006.
- [7] M. J. Jung, S. -I. Heo, M. -H. Wang, Free radical scavenging and total phenolic contents from methanolic extracts of *Ulmus davidiana*. *Food Chemistry*, Vol.108, p.482, 2008.
- [8] O. I. Aruoma, Assessment of potential prooxidant and antioxidant actions. *Journal of the American Oil Chemists' Society*, Vol.73, p.1617, 1996.
- [9] G. G. Balavonine, Y. V. Genleti, Peroxynitrite scavenging by different antioxidants, Part I: Convenient assay. *Nitric Oxide*, Vol.3, p.40, 1999.
- [10] A. Braca, G. Fico, I. Morelli, F. D. Simone, F. Tome, N. D. Tommasi, Antioxidant and free radical scavenging activity of flavonol glycosides from different *Aconitum* species. *Journal of Ethnopharmacology*, Vol.86, p.63, 2003.
- [11] J. S. Beckman, T. W. Beckman, J. Chen, P. A. Marshall, B. A. Freeman.. Apparent hydroxyl radical production by peroxynitrite: Implications for endothelial injury from nitric oxide and superoxide. *Proceedings of the National Academy of Sciences of the United States of America*, Vol.87, p.1620, 1990.