

Antioxidative Activities of the Leave Extractives of *Platanus orientalis* L.

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Abstract : From the EtOAc soluble fractions of *Platanus orientalis* Linn leaves, (+)-catechin (1), (-)-epicatechin (2), (+)-gallocatechin (3), kaempferol (4), quercetin (5), kaempferol-3-*O*- α -L-rhamnopyranoside (6), quercetin-3-*O*- β -D-glucopyranoside (7) and tyrosol (8) were isolated. The structures of the isolated compounds were characterized by NMR and MS spectrometers. The antioxidative activities of the isolated compounds and fractions were evaluated by DPPH free radical scavenging method and the results indicated that compounds 1, 2, 3, 4, 5 and 7 and EtOAc soluble fraction exhibited greater activities than α -tocopherol and BHT, while compounds 6, 8 and other fractions showed low activity compared to the controls.

Key words : antioxidative activity, column chromatography, DPPH, flavonoid, *Platanus*

Introduction

P. orientalis (Platanaceae), one of the famous street and garden trees in Korea, is a very large, wide-spreading, and long-lived hardwood species native to Eurasia. Its leaves are alternately borne on the stem, deeply lobed and usually palmate or maple-like.

It usually has flaking bark, occasionally not flaking and becoming thick and rugged. Flowers and fruits are round and burr like, borne in clusters of between two and six on a stem. The timber, often called lacewood, is figured and valuable for indoor furniture (Lee, 1985).

The buds of *P. orientalis* are used in folk medicines as antiseptic and antimicrobial remedies of the urinary system (Mitrokotsa *et al.*, 1993). Although compounds such as flavonoid glycosides (Kaouadji, 1989), non-polar flavonoids (Kaouadji, 1986), as well as acetylated and non-acetylated kaempferol monoglycosides (Kaouadji, 1990) have been isolated from the buds of other *Platanus* species, to date, only a few kaempferol derivatives (Kostas *et al.*, 2000; Mitrokotsa *et al.*, 1993) have been separated from *P. orientalis* and the chemical constitution of this species has not been extensively studied.

As part of our continuing research for active com-

pounds from natural sources to develop medicines, functional supplementary foods and cosmetics, eight compounds (1~8) were isolated from its leaves. Antioxidative activities of all the isolated compounds and soluble fractions were evaluated here-in.

Materials and Methods

1. Plant material

Fresh *P. orientalis* leaves were collected in the campus forest, Kangwon National University in August 2001, air dried for two weeks and ground to fine particles to be extracted.

2. General

¹H and ¹³C-NMR were recorded at 400 and 100 MHz, respectively, using a Bruker Avance DPX spectrometer. EI-MS and Positive FAB-MS were obtained using a Micromass Autospec M363 spectrometer. CD₃OD and (CD₃)₂SO were used as NMR solvents.

TLC analysis were performed on 25 DC-Plastik-folien Cellulose F (Merk) plates and developed with *t*-BuOH-HOAc-H₂O (3:1:1, v/v/v, solvent A) and HOAc-H₂O (3:47, v/v, solvent B). Visualization was done by illuminating UV light at 254 and 365 nm and spraying vanillin-HCl-EtOH (60:0.15:6, w/v/v) followed by heating.

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3. Extraction and Isolation

Ground leaves (2 kg) were extracted three times with Me₂CO-H₂O (v/v, 7:3) at room temperature to give crude extractive. After filtration and concentration under the reduced pressure, the aqueous residue was sequentially fractionated with *n*-hexane, CH₂Cl₂ and EtOAc, then freeze dried.

A portion of EtOAc soluble fraction (10 g) was subjected to column chromatography on Sephadex LH-20, eluting with MeOH-H₂O (3:1, v/v) to give nine fractions and labeled PLE-1~9. When treated with MeOH, some crystalline material was precipitated in fraction PLE-7 to give quercetin (**5**) (38 mg). Fraction PLE-6 was rechromatographed on a Sephadex LH-20 column with MeOH-H₂O (1:1, 1:3, v/v) as eluting solvents to give kaempferol (**4**) (30 mg) and quercetin (**5**) (7 mg). Fraction PLE-4 was also reappplied on a column for further purification with MeOH-H₂O (1:1, 1:3, 1:5, v/v) and EtOH-Hexane (3:1, 2:1, v/v) as eluting solvents to forward (+)-catechin (**1**) (245 mg), (-)-epicatechin (**2**) (11 mg), (+)-gallocatechin (**3**) (20 mg), kaempferol-3-*O*- α -L-rhamnopyranoside (**6**) (55 mg) and quercetin-3-*O*- β -D-glucopyranoside (**7**) (35 mg). Fraction PLE-2 was further chromatographed using MeOH-H₂O (1:1, v/v) and EtOH-Hexane (3:1, v/v) as eluents to give tyrosol (**8**) (200 mg).

(1) Compound 1

R_f: 0.55 (solvent A) and 0.36 (solvent B). EI-MS : Calculated for C₁₅H₁₄O₆, 290, Found *m/z* [M]⁺, 290.

¹H-NMR (400 MHz, δ , CD₃OD) : 2.51 (1H, *dd*, *J*=8.0 Hz and *J*=16.0 Hz, H-4ax), 2.82 (1H, *dd*, *J*=5.6 Hz and *J*=16.0 Hz, H-4eq), 4.01 (1H, *m*, H-3), 4.57 (1H, *d*, *J*=7.8 Hz, H-2), 5.86 (1H, *d*, *J*=2.1 Hz, H-6), 5.94 (1H, *d*, *J*=2.1 Hz, H-8), 6.71 (1H, *dd*, *J*=2.0 Hz and *J*=8.0 Hz, H-6'), 6.77 (1H, *d*, *J*=8.0 Hz, H-5'), 6.84 (1H, *d*, *J*=2.0 Hz, H-2').

¹³C-NMR (100 MHz, δ , CD₃OD) : 28.54 (C-4), 68.84 (C-3), 82.86 (C-2), 95.51 (C-8), 96.33 (C-6), 100.84 (C-10), 115.26 (C-2'), 116.11 (C-5'), 120.07 (C-6'), 132.23 (C-1'), 146.22 (C-3'), 146.24 (C-4'), 156.91 (C-9), 157.61 (C-5), 157.83 (C-7).

(2) Compound 2

R_f: 0.44 (solvent A) and 0.36 (solvent B). EI-MS : Calculated for C₁₅H₁₄O₆, 290, Found *m/z* [M]⁺, 290.

¹H-NMR (400 MHz, δ , CD₃OD) : 2.72 (1H, *dd*, *J*=2.7 Hz and *J*=16.4 Hz, H-4ax), 2.85 (1H, *dd*, *J*=4.8 Hz and *J*=16.4 Hz, H-4eq), 4.15 (1H, *brs*, H-3), 4.81 (1H, *s*, H-2), 5.91 (1H, *d*, *J*=2.1 Hz, H-6), 5.92 (1H, *d*, *J*=2.1 Hz, H-8), 6.75 (2H, *m*, H-5', 6'), 6.93 (1H, *d*, *J*=2.0 Hz, H-2').

¹³C-NMR (100 MHz, δ , CD₃OD) : 29.32 (C-4), 67.54 (C-3), 79.94 (C-2), 95.95 (C-8), 96.43 (C-6), 100.14 (C-

10), 115.37 (C-2'), 115.94 (C-5'), 119.45 (C-6'), 132.35 (C-1'), 145.85 (C-3'), 145.99 (C-4'), 157.42 (C-9), 157.73 (C-5), 159.0 (C-7).

(3) Compound 3

R_f: 0.42 (solvent A) and 0.41 (solvent B). FAB-MS : Calculated for C₁₅H₁₄O₇, 306, Found *m/z* [M+H]⁺, 307.

¹H-NMR (400 MHz, δ , CD₃OD) : 2.51 (1H, *dd*, *J*=8.0 Hz and *J*=16.1 Hz, H-4ax), 2.80 (1H, *dd*, *J*=5.4 Hz and *J*=16.1 Hz, H-4eq), 3.96 (1H, *m*, H-3), 4.52 (1H, *d*, *J*=7.4 Hz, H-2), 5.89 (1H, *d*, *J*=2.1 Hz, H-6), 5.94 (1H, *d*, *J*=2.1 Hz, H-8), 6.42 (2H, *s*, H-2',6').

¹³C-NMR (100 MHz, δ , CD₃OD) : 28.16 (C-4), 68.80 (C-3), 82.92 (C-2), 95.55 (C-8), 96.31 (C-6), 100.76 (C-10), 107.24 (C-2',6'), 131.61 (C-1'), 134.07 (C-4'), 146.91 (C-3',5'), 156.89 (C-9), 157.67 (C-5), 157.90 (C-7).

(4) Compound 4

R_f: 0.72 (solvent A) and 0.00 (solvent B). EI-MS : Calculated for C₁₅H₁₀O₆, 286, Found *m/z* [M]⁺, 286.

¹H-NMR (400 MHz, δ , CD₃OD) : 6.28 (1H, *d*, *J*=1.9 Hz, H-6), 6.54 (1H, *d*, *J*=1.9 Hz, H-8), 7.03 (2H, *d*, *J*=8.8 Hz, H-3', 5'), 8.16 (2H, *d*, *J*=8.8 Hz, H-2', 6').

¹³C-NMR (100 MHz, δ , CD₃OD) : 94.51 (C-8), 99.18 (C-6), 104.17 (C-10), 116.35 (C-3',5'), 130.48 (C-2',6'), 136.96 (C-3), 147.03 (C-2), 157.79 (C-9), 160.17 (C-5), 162.33 (C-4'), 164.98 (C-7), 176.61 (C-4).

(5) Compound 5

R_f: 0.50 (solvent A) and 0.00 (solvent B). EI-MS : Calculated for C₁₅H₁₀O₇, 302, Found *m/z* [M]⁺, 302.

¹H-NMR (400 MHz, δ , (CD₃)₂SO) : 6.30 (1H, *d*, *J*=1.9 Hz, H-6), 6.55 (1H, *d*, *J*=1.9 Hz, H-8), 7.02 (1H, *d*, *J*=8.3 Hz, H-5'), 7.70 (1H, *dd*, *J*=8.3 Hz and *J*=2.1 Hz, H-6'), 7.80 (1H, *d*, *J*=2.1 Hz, H-2').

¹³C-NMR (100 MHz, δ , (CD₃)₂SO) : 94.94 (C-8), 99.55 (C-6), 104.36 (C-10), 116.11 (C-2'), 116.61 (C-5'), 121.89 (C-1'), 123.84 (C-6'), 137.04 (C-3), 146.26 (C-3'), 147.89 (C-2), 148.78 (C-4'), 158.03 (C-9), 162.04 (C-5), 165.49 (C-7), 177.03 (C-4).

(6) Compound 6

R_f: 0.79 (solvent A) and 0.42 (solvent B). FAB-MS : Calculated for C₂₁H₂₀O₁₀, 432, Found *m/z* [M+H]⁺, 433, [M+H-rhamnose]⁺ *m/z* 287.

¹H-NMR (400 MHz, δ , CD₃OD) : 0.92 (3H, *d*, *J*=5.8 Hz, H-6"), 3.32~4.25 (4H, *m*, H-2",3",4",5"), 5.39 (1H, *d*, *J*=1.6 Hz, H-1"), 6.19 (1H, *d*, *J*=2.0 Hz, H-6), 6.38 (1H, *d*, *J*=2.0 Hz, H-8), 6.95 (2H, *d*, *J*=8.8 Hz, H-3',5'), 7.77 (2H, *d*, *J*=8.8 Hz, H-2',6').

¹³C-NMR (100 MHz, δ , CD₃OD) : 18.08 (C-6"), 72.34 (C-5"), 72.45 (C-3"), 72.53 (C-2"), 73.60 (C-4"), 95.18 (C-8), 100.25 (C-6), 103.91 (C-1"), 106.34 (C-10),

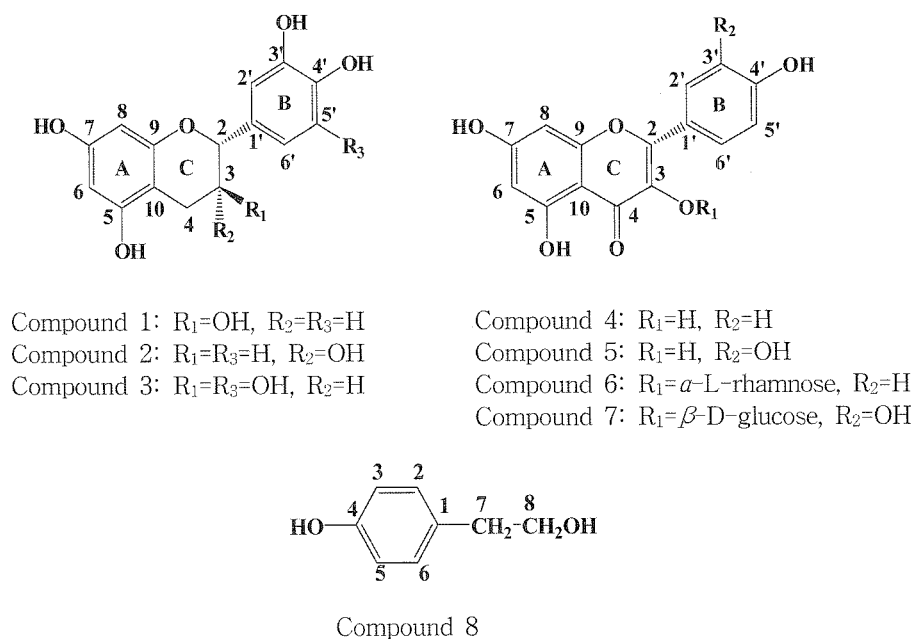


Figure 1. Isolated compounds from *P. orientalis* leaves.

116.93 (C-3',5'), 123.04 (C-1'), 132.33 (C-2',6'), 136.63 (C-3), 158.94 (C-2), 159.69 (C-9), 161.98 (C-4'), 163.61 (C-5), 166.26 (C-7), 180.61 (C-4).

(7) Compound 7

R_f: 0.62 (solvent A) and 0.16 (solvent B). FAB-MS : Calculated for C₂₁H₂₀O₁₂, 464, Found *m/z*, [M+H]⁺, 465, [M+H-glucose]⁺ *m/z* 303.

¹H-NMR (400 MHz, δ , CD₃OD) : 3.41~3.81 (5H, *m*, H-2", 3", 4", 5", 6"), 5.09 (1H, *d*, *J*=7.8 Hz, H-1"), 6.20 (1H, *d*, *J*=1.6 Hz, H-6), 6.40 (1H, *d*, *J*=1.6 Hz, H-8), 6.85 (1H, *d*, *J*=8.4 Hz, H-5'), 7.56 (1H, *dd*, *J*=8.4 Hz and 1.8 Hz, H-6'), 7.81 (1H, *d*, *J*=1.8 Hz, H-2').

¹³C-NMR (100 MHz, δ , CD₃OD) : 60.84 (C-6"), 68.92 (C-4"), 72.15 (C-2"), 73.97 (C-5"), 76.95 (C-3"), 93.95 (C-8), 99.07 (C-6), 104.33 (C-1"), 104.52 (C-10), 115.20 (C-2'), 116.85 (C-5'), 121.83 (C-1'), 122.04 (C-6'), 134.73 (C-3), 144.72 (C-3'), 148.86 (C-4'), 157.35 (C-2), 157.79 (C-9), 161.74 (C-5), 165.17 (C-7), 178.45 (C-4).

(8) Compound 8

R_f: 0.76 (solvent A) and 0.71 (solvent B). EI-MS : Calculated for C₈H₁₀O₂, 138, Found *m/z*, [M]⁺, 138.

¹H-NMR (400 MHz, δ , CD₃OD) : 2.72 (2H, *t*, *J*=7.2 Hz, H-7'), 3.65 (2H, *t*, *J*=7.2 Hz, H-8), 6.71 (2H, *d*, *J*=8.4 Hz, H-3',5'), 7.04 (2H, *d*, *J*=8.4 Hz, H-2',6').

¹³C-NMR (100 MHz, δ , CD₃OD) : 38.28 (C-8), 63.57 (C-7), 115.20 (C-2,6), 129.97 (C-3,5), 130.18 (C-1), 155.48 (C-4).

4. DPPH free radical scavenging assay

The antioxidative activity was determined on the basis

of the scavenging activity of the stable 1,1-diphenyl-2-picrylhydrazyl (DPPH) free radical method firstly introduced by M. S. Blois (Blois, 1958) with slight modification. Samples of different concentrations (20~160 μ g/ml) were added to a solution of DPPH (1.5 \times 10⁻⁴ M, 1 ml) in 4 ml MeOH. After mixing gently and standing at room temperature for 30 min, the optical density was measured at 517 nm with a UV-visible Spectrophotometer (Libra S32, Biochrom LTD). The results were calculated by taking the mean of all triplicated values. IC₅₀ values were obtained through extrapolation from concentration of sample necessary to scavenge 50% of the DPPH free radicals. BHT and α -tocopherol were used as controls.

Results and Discussion

Three flavans, (+)-catechin (**1**), (-)-epicatechin (**2**) and (+)-gallocatechin (**3**), and the two flavonols, kaempferol (**4**) and quercetin (**5**), were all isolated as yellowish powders, which showed physical and spectral data virtually identical to those we had reported before (Si *et al.*, 2005; Kim *et al.*, 2002).

1. Isolated compounds

(1) Kaempferol-3-O- α -L-rhamnopyranoside

Compound **6** was obtained as a yellowish powder and gave a protonated molecular iron at *m/z* 433 [M+H]⁺ by positive FAB-MS, which was consistent with the molecular formula C₂₁H₂₀O₁₀. Fragment at *m/z* 287 was observed for aglycone. In the ¹H-NMR spectrum, two *meta* protons resonated (*J*=2.0 Hz) as doublets at δ 6.19 and δ

6.38, each integrated to one proton, ascribed to the H-6 and H-8 presenting the characteristic AX system in the 5,7-dihydroxyflavonol A-ring. Two doublets ($J=2.0$ Hz), each 2H, in the aromatic region at δ 6.95 and δ 7.77 suggested the presence of a para-substituted aromatic B-ring. The presence of a α -configuration rhamnose was evidenced by the anomeric proton resonating at δ 5.39 as doublet ($J=1.6$ Hz) and the methyl protons typically appeared at δ 0.92 (3H, d , $J=5.8$ Hz), together with four sugar protons between δ 3.32–4.25 (Mabry *et al.*, 1970; Andary *et al.*, 1982).

In ^{13}C -NMR spectrum, three oxygen-containing carbons appeared at 159.69, 163.61 and 166.26 ppm, C-8 and C-6 corresponded to 95.18 and 100.25 ppm, respectively, for the phloroglucinol A-ring. Two pairs of symmetrical carbons, C-3' or C-5' and C-2' or C-6', gave two strong singlets at 116.93 and 132.33 ppm, respectively, which corroborated the catechol B-ring of aglycone. As for the heterocyclic C-ring, generally, carbons of pure kaempferol give three signals at 147.03, 136.96 and 176.61 ppm for C-2, C-3 and C-4, respectively (See compound 4). However, substitution at C-3 causes a slight upfield shift by 0.3 ppm for C-3 as well as a large downfield shift by 12.9 and 4.0 ppm for C-2 and C-4 respectively, due to electronegativity from a substituent (Harbone and Mabry, 1982). The signal at 18.08 ppm was a characteristic methyl group of rhamnosyl C-6" and C-1" linked to kaempferol C-3 showed a signal at 103.91 ppm shifted downfield by 9.9 ppm compared to a free rhamnose (94 ppm) (Markham *et al.*, 1992). Four other rhamnosyl carbons typically resonated at 71.91–73.36 ppm.

Therefore, compound 6 was elucidated as kaempferol-3- O - α -L-rhamnopyranoside and the literature data supported the results (Kazuma *et al.*, 2002; Han *et al.*, 2001).

(2) Quercetin-3- O - β -D-glucopyranoside

Compound 7 was isolated as a whitish powder. The positive FAB-MS spectrum gave m/z 465 for $[\text{M}+\text{H}]^+$ ions indicating the molecular weight 464, well coincided with the molecular formula $\text{C}_{21}\text{H}_{20}\text{O}_{12}$. Fragment at m/z 303 for $[\text{M}+\text{H}-\text{glucose}]^+$ indicated the aglycone of quercetin. In the ^1H -NMR spectrum, the aglycone of compound 7 was similar with that of compound 6 except that the aromatic B-ring exhibited a set of ABX system protons, not of AA'BB' system, at δ 7.81 (d , $J=1.8$ Hz), δ 6.85 (d , $J=8.4$ Hz) and δ 7.56 (dd , $J=8.4$ Hz and 1.8 Hz) belonging to the aglycone H-2', H-5' and H-6', respectively. The doublet at δ 5.09 derived from anomeric proton of glucose moiety, and the coupling constant ($J=7.8$ Hz) was characteristic for a β -linked glucose (Kamerling *et al.*, 1972).

The ^{13}C -NMR spectrum confirmed that the glucose moiety was connected to C-3 of aglycone on the basis of chemical shifts of C-2, 3 and 4, which were in agreement with compound 6. The careful examination of the ^{13}C -NMR data and comparison of these results with the values previously reported in the literature (Agrawal, 1989; Kim *et al.*, 2004), compound 7 was identified as quercetin-3- O - β -D-glucopyranoside.

(3) Tyrosol

Compound 8 was also obtained as a yellowish powder and its EI-MS spectrum gave $[\text{M}]^+$ at m/z 138, suggesting its molecular formula as $\text{C}_8\text{H}_{10}\text{O}_2$. In the ^1H -NMR spectrum, an AA'BB' proton type constituted by two doublets ($J=8.5$ Hz) at δ 6.8 and 7.7 originated from H-3,5 and H-2,6 ascribe to a *para*-substituted aromatic ring. The triplet signal at δ 2.72 ($J=7.2$ Hz) was assignable to the α - CH_2 (H-7a,b), while another triplet at δ 3.65 ($J=7.2$ Hz) were ascribed to the β - CH_2 (H-8a,b) of the ethyl alcohol group.

In the ^{13}C -NMR spectrum, two sets of symmetrical carbons, C-2,6 and C-3,5 resonated at 115.20 and 129.87 ppm, respectively. Signals at 155.48 and 130.18 ppm were attributed to hydroxyl-bearing C-4 and quaternary C-1, respectively. The two methylene carbons C-7 and C-8 of ethyl alcohol group characteristically appeared at 63.57 and 38.28 ppm, respectively.

Consequently, from the foregoing spectral studies, the structure of compound 8 was established as tyrosol (*p*-hydroxyphenethyl alcohol), which is well coincided with the report (Kiyoshi and Yosuke, 1980).

Table 1. Antioxidative activities (IC_{50} values) of the isolated compounds and soluble fractions from *P. orientalis* leaves.

Samples		IC_{50} ($\mu\text{g}/\text{ml}$)
Controls	α -tocopherol	26
	BHT	30
Fractions	Crude	39
	Hexane soluble fraction	94
	CH_2Cl_2 soluble fraction	41
	EtOAc soluble fraction	24
	H_2O soluble fraction	31
Isolated compounds	(+)-Catechin	9
	(-)-Epicatechin	11
	(+)-Gallicocatechin	13
	Kaempferol	13
	Quercetin	9
	Kaempferol-3- O - α -L-rhamnopyranoside	114
Quercetin-3- O - β -D-glucopyranoside	25	
Tyrosol	42	

2. Antioxidative activity

Antioxidative activities of the soluble fractions and isolated compounds from *P. orientalis* leaves were tested by DPPH radical scavenging activity (Table 1). The results showed that EtOAc soluble fraction, (+)-catechin (1), (-)-epicatechin (2), (+)-galocatechin (3), kaempferol (4), quercetin (5) and quercetin-3-*O*- β -D-glucopyranoside (7) exhibited significantly potent antioxidative activities, while the remaining kaempferol-3-*O*- α -L-rhamnopyranoside (6), tyrosol (8) and other soluble fractions showed weak activity compared with BHT and α -tocopherol, which were used as controls.

Conclusion

Eight compounds were isolated by column chromatography using Sephadex LH-20 from the leaves of *P. orientalis* and elucidated as (+)-catechin (1), (-)-epicatechin (2), (+)-galocatechin (3), kaempferol (4), quercetin (5), kaempferol-3-*O*- α -L-rhamnopyranoside (6), quercetin-3-*O*- β -D-glucopyranoside (7) and tyrosol (8) by NMR and MS spectroscopy. DPPH radical scavenging activity indicated that EtOAc soluble fraction, compounds 1, 2, 3, 4, 5 and 7 showed strong antioxidative activities, while compounds 6 and 8 and other fractions were relatively less active compared with α -tocopherol and BHT.

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