

## Research Note

Is plastoquinone<sub>10-ox</sub> an antioxidant marker of red wines?

ANNA GVOZDĀKOVÁ, J. KUCHARSKÁ, P. DURĀŠIN and E. MINÁRIK

**S u m m a r y :** Antioxidant activities of 20 different types of Slovak wines were examined. For the first time evidence of plastoquinone<sub>10-ox</sub> (PQ<sub>10-ox</sub>) in red wines was documented. Twice higher levels of  $\alpha$ -tocopherol (vitamin E) were determined in red wine varieties in comparison to white wine varieties. Enzymatic activities of superoxidodismutase (SOD) in all red wine varieties were higher compared to white wines; in some white wines they were not detectable.

The beneficial effects of antioxidants are discussed, especially the role of coenzyme Q<sub>10</sub> (analogue of plant PQ<sub>10-ox</sub>), vitamin E and SOD in preventing cardiovascular diseases. It is supposed that PQ<sub>10-ox</sub> could be an antioxidant marker of red wines. To prove the protective effect of a moderate consumption of red wine in human cardiology further studies are required.

**K e y w o r d s :** wine, plastoquinone<sub>10-ox</sub>, vitamin E, superoxidodismutase, human health.

**Introduction:** Moderate daily wine consumption especially of red wine lowers the arteriosclerosis (disease of arteries) development and coronary heart disease (CHD) mortality (KLATSKY *et al.* 1990). The protective effect of wine has been attributed both to the content of several naturally occurring compounds like "fungicides", tannins, anthocyanins, phenolic flavonoids and to the low alcohol content (TROUP and HUTTON 1994, DEMROW *et al.* 1995). However, high doses of alcohol increase the risk of CHD (FRIEDMAN and KIMBALL 1986) and initiate the development of alcohol cardiomyopathy (GVOZDĀK *et al.* 1973).

In view of the occurrence of antioxidants in wines the aim of this study was to determine plasto-quinone<sub>10-ox</sub> (PQ<sub>10-ox</sub>),  $\alpha$ -tocopherol and superoxide-dismutase (SOD) in some Slovak varietal wines.

Plastoquinone is the plant form of coenzyme Q in eucaryotic cells and it has an important function in the process of photosynthesis of green plants. The mechanism of ATP synthesis in chloroplast during photosynthesis is similar to oxidative phosphorylation in animal cells - it is driven by a protonmotive force and CoQ participates in this process.

**Materials and methods:** S a m p l e s : 20 different varietal wines from the Slovakian vintage 1994 (Table).

**A n a l y t i c a l t e c h n i q u e :** Plastoquinone<sub>10-ox</sub> and  $\alpha$ -tocopherol were determined simultaneously by a modified HPLC method (LKB Sweden) according to TANAKA *et al.* (1982) and LANG *et al.* (1986) with a spectrophotometric detection at 275 nm. Elution was per-

formed with the mobile phase consisting of methanol-acetonitrile - ethanol (6:2:2) at a flow rate of 0.65 ml/min.

**S a m p l e p r e p a r a t i o n :** 1.0 ml of sample was vortexed for 5 min with the extraction mixture hexane-ethanol (5:2), the hexane layer was evaporated under a gentle stream of N<sub>2</sub> and residues were dissolved in 96 % ethanol. 20  $\mu$ l of the extract was injected into a Separon SGX C18, 7  $\mu$ M (150 x 3 mm) column. External standards of ubi-quinone<sub>10</sub> (CoQ<sub>10</sub>) and  $\alpha$ -tocopherol (Sigma) were used. SOD activity was determined spectrophotometrically according to FLOHE and ÖTTING (1984).

T a b l e

Samples of Slovakian wines, vintage 1994

Sample No.	Variety	Wine type
1	Limberger	red
2	St. Laurent-Limberger	red
3	St. Laurent	red
4	Limberger	red
5	Limberger	red
6	Cabernet Sauvignon	rosé
7	Müller-Thurgau	white
8	Müller-Thurgau	white
9	Riesling	white
10	Müller-Thurgau	white
11	Green Veltiner	white
12	Welsh Riesling	white
13	Müller-Thurgau	white
14	Pinot blanc	white
15	Riesling	white
16	Muscat Ottonel	white
17	Riesling	white
18	Riesling	white
19	Riesling	white
20	Riesling	white

**Results:** Plastoquinone<sub>10-ox</sub> was detectable only in samples of red wines in concentrations of 23.0 - 29.0  $\mu$ g/l, but not in white and rosé wines (Figure, a).

The concentration of  $\alpha$ -tocopherol varied from 132 to 788  $\mu$ g/l, in Welsh Riesling  $\alpha$ -tocopherol was not detectable. The average concentrations in red wines were 589  $\mu$ g/l, in white wines 385  $\mu$ g/l and in the rosé wine 448  $\mu$ g/l (Figure, b).

SOD activity varied from 47.0 to 65.0 IU SOD/ml in all red wines. In white wines the activity was 0 - 35.0 IU SOD/ml; no activity could be found in wine nos 10, 14, 20 and in the rosé wine (Figure, c).

**Discussion:** The cardioprotective effect of wine, especially of red wine, has been shown by several authors. DE WHALLEY *et al.* (1990) and STRUCK *et al.* (1994) found the antioxidative effect of phenolic substances in red wines. These substances reduce low density lipoprotein cholesterol oxidation in human plasma and by this mechanism act against the development of arteriosclerosis. The beneficial antiarteriosclerotic effect of a moderate daily consumption of red wine (400 ml daily during 2 weeks) by increasing high density lipoproteins in human plasma has

been proved by LAVY *et al.* (1994). FRANKEL *et al.* (1993) found a decrease of lipid peroxidation in human plasma by quercetin which occurs in red wine. Beneficial effects of red wine are described also by other authors (PATTICHIS *et al.* 1993). These effects may include an antioxidative activity.

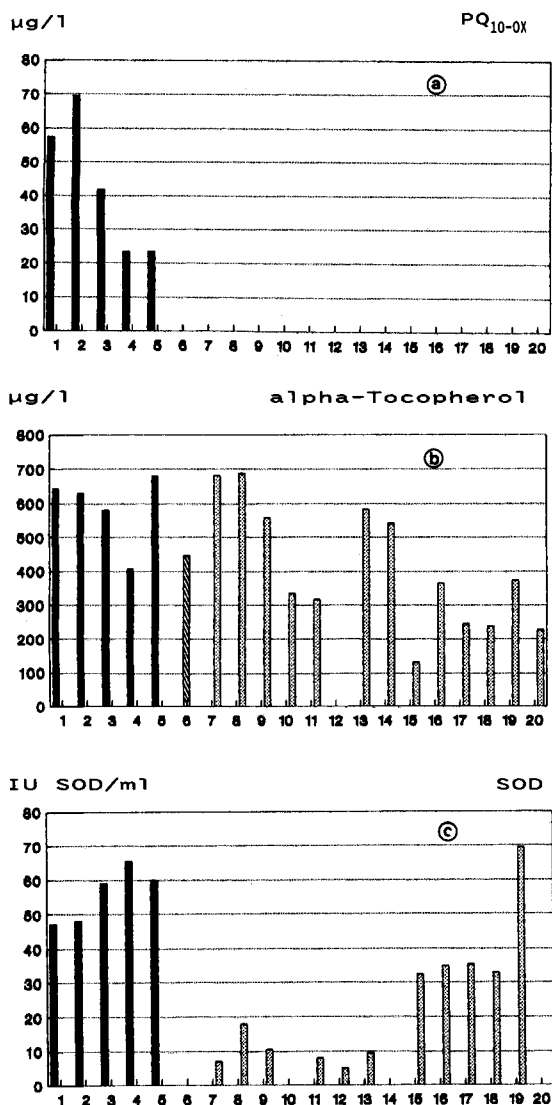


Figure: a) plastoquinone (PQ<sub>10-ox</sub>) content, b)  $\alpha$ -tocopherol content, c) superoxidodismutase (SOD) activity in Slovak varietal wines. Nos of wine samples see Table.

Antioxidative properties were also shown for other components in wines which have not been described yet. We have proved the presence of plastoquinone<sub>10-ox</sub>,  $\alpha$ -tocopherol and superoxidase activity. PQ<sub>10-ox</sub> was detected in all types of red wine while in white and rosé wines this compound did not occur. A lack of coenzyme Q, CoQ, an enzyme taking part in the phosphorylation process in human cells, was found being implicated in some myocardial diseases (FOLKERS 1993). Long-term administration of CoQ has a protective effect in myocardial ischemia (KUCHARSKÁ *et al.* 1994), improves mitochondrial bioenergetics of the heart muscle after administration for

3 months to adult rats (GVOZDÍJKOVÁ *et al.* 1991), and is important in the therapy of mitochondrial diseases (GVOZDÍJKOVÁ *et al.* 1994).

**Conclusion:** We suggest that plastoquinone<sub>10-ox</sub> could be the antioxidant marker of red wines. Regular, moderate red wine consumption can serve as an additional source of antioxidants ( $\alpha$ -tocopherol, PQ<sub>10</sub>) and antioxidative enzyme-superoxidodismutase. The beneficial effects of these compounds in red wines to prevent cardiovascular diseases require further studies.

This work was supported by a Grant of the Ministry of Education of the Slovak Republic, No. 1/1164/95.

DEMROW, H. S.; SLANE, P. R.; FOLTS, J. D.; 1995: Administration of wine and grape juice inhibits *in vivo* platelet activity and thrombosis in stenosed canine coronary arteries. *Circulation* **91**, 1182-1188.

DE WHALLEY, C. V.; RANKIN, S. M.; HOULT, J. R. S.; 1990: Flavonoids inhibit the oxidative modification of low density lipoproteins by macrophages. *Biochem. Pharmacol.* **39**, 1743-1750.

FLOHE, L.; ÖTTING, F.; 1984: Superoxidodismutase assays. In: PACKER, L. (Ed.): *Methods in Enzymology*, Vol. **105**. Oxygen Radicals in Biological Systems, 93-104. Academic Press, New York.

FOLKERS, K.; 1993: Heart failure is a dominant deficiency of coenzyme Q<sub>10</sub> and challenges for future clinical research on CoQ<sub>10</sub>. *Clin. Invest.* **71**, S51-S54.

FRANKEL, E. N.; KANNER, J.; GERMAN, J. B.; PARKS, E.; KINSELLA, J. E.; 1993: Inhibition of oxidation of human low-density lipoprotein by phenolic substances in red wine. *Lancet* **341**, 454-457.

FRIEDMAN, L. A.; KIMBALL, A. W.; 1986: Coronary heart disease mortality and alcohol consumption in Framingham. *Amer. J. Epidemiol.* **24**, 481-489.

GVOZDÍJKOVÁ, A.; BADA, V.; KRUTÝ, F.; NIEDERLAND, T. R.; GVOZDÍJKOVÁ, J.; 1973: Effect of ethanol on the metabolism of the myocardium and its relationship to development of alcoholic cardiomyopathy. *Cardiology* **58**, 290-297.

GVOZDÍJKOVÁ, A.; KUCHARSKÁ, J.; GVOZDÍJKOVÁ, J.; 1991: On the protective effect of coenzyme Q<sub>10</sub> in smoke cardiomyopathy. *J. Mol. Cell. Cardiol.* **23** (Suppl. 5), 72.

- - - - -; 1994: "Redox therapy" of mitochondrial diseases by means of coenzyme Q<sub>10</sub>. *Bratisl. Lek. Listy* **95**, 443-451.

- - - - -; HERICOVÁ, I.; KOPRENA, I.; GVOZDÍJKOVÁ, J.; 1993: On the beneficial longterm effect of CoQ<sub>10</sub> on the metabolic response of myocardial mitochondria. *J. Mol. Cell. Cardiol.* **24** (Suppl. 1), 108.

KLATSKY, A. L.; ARMSTRONG, M. A.; FRIEDMAN, G. D.; 1990: Risk of cardiovascular mortality in alcohol drinkers, ex-drinkers and non-drinkers. *Amer. J. Cardiol.* **66**, 1237-1242.

KUCHARSKÁ, J.; LILGOVÁ, M.; GVOZDÍJKOVÁ, A.; HERICOVÁ, I.; KOPRENA, I.; SNIRCOVÁ, M.; GVOZDÍJKOVÁ, J.; 1994: Role of coenzyme Q<sub>10</sub> in the protection of ischemic myocardium. In: HAUNSO, S.; KJELDSEN, K. (Eds.): *International Proceedings Division, XV. ISHR, European Section Meeting*, 639-642. Monduzzi Editore, Bologna, Italy.

LANG, J. K.; GOHL, K.; PACKER, L.; 1986: Simultaneous determination of tocopherols, ubiquinols and ubiquinones in blood, plasma, tissue homogenates and subcellular fractions. *Anal. Biochem.* **157**, 106-116.

LAVY, A.; TUHRMAN, B.; MARKEL, A.; DANKNER, G.; BEN-AMOTZ, A.; PRESSES, D.; AVIRAM, M.; 1994: Effect of dietary supplementation of red or white wine on human blood chemistry, hematology and coagulation: Favourable effect of red wine on plasma high-density lipoprotein. *Ann. Nutr. Metab.* **38**, 287-294.

PATTICHIS, K.; LOUCA, L. L.; JARMAN, J.; SANDLER, R. M.; GLOVER, V.; 1993: Phenolic substances in red wine and release of platelet 5-hydroxytryptamine. *Lancet* **341**, 1104.

STRUCK, M.; WATKINS, T.; TOMEO, A.; HALLEY, J.; BIERENBAUM, M.; 1994: Effect of red and white wine on serum lipids, platelet aggregation, oxidation products and antioxidants: A preliminary report. *Nutr. Res.* **14**, 1811-1819.

TROUP, G. J.; HUTTON, D. R.; 1994: Free radicals in red wine, but not in white? *Free Rad. Res.* **20**, 63-68.