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LETTER TO THE EDITOR

Changes in Tocopherols, Tocotrienols, and Fatty Acid Contents in Grape Seed Oils during Oxidation

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Grape seeds are waste products of the wine and grape juice industry. However, grape seeds have recently been utilized for the production of seed oil. Grape seed oil (GSO) is generating increased interest as a functional food product since it has been shown to contain high levels of vitamin E, unsaturated fatty acids, and phytosterols.

This study was undertaken to determine the changes in the contents of tocopherols, tocotrienols, and fatty acids in grape seed oils during oxidation. Three different GSOs, soybean oil, and olive oil were stored at 25 or 60 °C for up to 120 days. The peroxide values (PV) and conjugated diene values (CD) of the oils were measured during the storage period to determine the degrees of oxidation of the oil samples. Simultaneously, the contents of tocopherols, tocotrienols, and fatty acids in the samples were monitored for up to 120 days.

The oxidative stabilities of soybean oil, olive oil, and three GSOs stored at 25 or 60 °C for 120 and 55 days, respectively, were monitored by determining their PVs and CDs. The PVs of soybean oil and each of the GSOs stored at 25 °C increased gradually after 60 days, whereas the PV of olive oil stored at 25 °C remained constant throughout the storage period (Fig. 1). Significant increases in the PVs of each of the oil samples except olive oil occurred within 5–10 days at 60 °C. The PV of olive oil stored at 60 °C did not change for 30 days, but increased significantly thereafter. With the exception of olive oil stored at 25 °C, the PVs of all of the oil samples increased during storage. The changes in the CDs and PVs of all of the oil samples showed similar trends for all types of oil and both storage temperatures (data for CDs not shown). The PVs and CDs indicated that olive oil had the highest oxidative stability of all of the oil samples. This result may be due to the fatty acid composition of olive oil, which contains higher amounts of oleic acid than soybean oil or GSO. Kamal-Eldin [1] reported that oxidative stability of oils depends mainly on their degree of unsaturation. Naz et al. [2] reported that olive oil is more stable than corn or soybean oils. The three GSOs are mainly composed of linoleic acid (67.15–69.58%), whereas olive oil is composed mostly of oleic acid (81.24%). The observed ranges of linoleic acid and oleic acid in GSO and olive oil are 61–76% [3, 4] and 72–75% [5], respectively. The fatty acid compositions of all of the oil samples remained unchanged for 120 days at 25 °C. At 60 °C, the oxidation index [18:2/(16:0 + 18:0 + 20:0)] decreased from 5–7 to 2–3 during longer storage periods. Soybean oil contained 908 mg of total vitamin E per kg oil, the greatest initial amount of total vitamin E among the samples. Olive oil contained only 134 mg of total vitamin E per kg oil. No tocotrienols were detected in the soybean or olive oil samples, but tocotrienols were the main vitamin E constituents in the GSOs. According to data compiled by Eitenmiller and Lee [6], palm oil, rice bran, and GSO contain high levels of tocotrienols. Table 1 shows the tocopherol and tocotrienol contents of oil samples stored at 25 °C for 120 days. The contents of α- and δ-tocopherols in soybean oil were reduced by 54 and 22 mg kg^{-1}, respectively, whereas those of γ-tocopherols were decreased by about 200 mg kg^{-1}. The amounts of α- and γ-tocopherols in olive oil stored at 25 °C for 120 days did not change. With the

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Table 1 Vitamin E contents of soybean oil, olive oil, and grape seed oils stored at 25 °C for 120 days (mg kg^{-1})

Sample	Days	α-Tocopherol	γ-Tocopherol	δ-Tocopherol	α-Tocotrienol	γ-Tocotrienol	Total
Soybean oil	0	63	651	194	–	–	908
	5	55	626	195	–	–	876
	20	57	637	200	–	–	894
	40	51	594	182	–	–	827
	60	43	578	189	–	–	810
	80	37	596	188	–	–	821
	100	12	435	164	–	–	611
	120	9	451	172	–	–	632
Olive oil	0	120	14	–	–	–	134
	5	102	16	–	–	–	118
	20	118	20	–	–	–	138
	40	994	13	–	–	–	113
	60	101	15	–	–	–	116
	80	109	19	–	–	–	128
	100	100	14	–	–	–	114
	120	102	15	–	–	–	117
Grape seed oil A	0	187	27	–	216	318	748
	5	156	24	–	195	266	641
	20	169	26	–	211	303	709
	40	161	23	–	184	271	639
	60	160	26	–	191	296	673
	80	166	26	–	193	331	716
	100	127	24	–	143	288	582
	120	131	26	–	150	271	578
Grape seed oil B	0	237	36	3	152	250	678
	5	204	31	4	133	211	583
	20	219	37	5	150	272	683
	40	198	28	3	128	215	572
	60	212	31	3	137	257	640
	80	204	33	4	131	265	637
	100	153	33	4	96	217	503
	120	148	27	2	99	210	486
Grape seed oil C	0	151	28	2	156	291	628
	5	146	30	3	150	274	603
	20	151	26	2	154	296	629
	40	146	26	1	141	265	579
	60	139	31	3	142	314	629
	80	124	27	1	127	283	562
	100	93	27	1	89	248	458
	120	91	26	2	95	259	473

exceptions of γ- and δ-tocopherols, the levels of tocopherol and tocotrienol showed decreasing trends in all stored GSOs. Significant reductions in total vitamin E contents occurred in soybean oil and GSO stored at 25 °C between 80 and 100 days. The tocopherol and tocotrienol contents of oil samples stored at 60 °C for 50 days are shown in Table 2. Since rapid oxidation occurred at 60 °C, the amounts of tocopherol and tocotrienol in all of the oil samples decreased to undetectable levels after 20–25 days. With the exception of olive oil stored at 25 °C, the total vitamin E contents in all of the oil samples stored at 25 or 60 °C decreased during the storage period. While the above reductions were occurring in soybean oil, olive oil, and GSO, the PVs of the samples were simultaneously

Table 2 Vitamin E contents of soybean oil, olive oil, and grape seed oils stored at 60 °C for 50 days (mg kg^{-1})

Sample	Days	α-Tocopherol	γ-Tocopherol	δ-Tocopherol	α-Tocotrienol	γ-Tocotrienol	Total
Soybean oil	0	63	651	194	–	–	908
	5	29	616	201	–	–	846
	10	–	234	151	–	–	385
	15	–	–	70	–	–	70
	20	–	–	3	–	–	3
Olive oil	0	120	14	–	–	–	134
	5	112	17	–	–	–	129
	10	72	14	–	–	–	86
	15	3	4	–	–	–	7
	20	–	1	–	–	–	1
Grape seed oil A	0	187	27	–	216	318	748
	5	160	25	–	220	321	726
	10	–	6	–	–	56	62
Grape seed oil B	0	237	36	3	152	250	678
	5	212	39	4	153	258	666
	10	109	29	3	69	219	429
	15	–	3	3	–	21	27
Grape seed oil C	0	151	28	2	156	291	628
	5	141	30	4	158	303	636
	10	109	30	3	110	283	535
	15	–	–	1	–	5	6

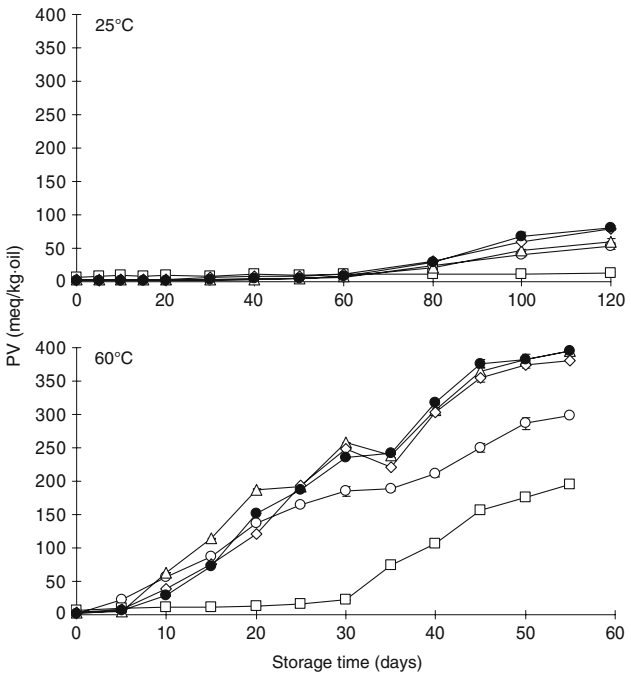

Fig. 1 Peroxide values (PV) of soybean oil (*open circles*), olive oil (*open squares*), grape seed oil A (*open triangles*), grape seed oil B (*open diamonds*), and grape seed oil C (*filled circles*) stored at 25 or 60 °C for up to 120 days

increasing (Fig. 1). These results suggest that vitamin E acts as an antioxidant in these oils, since oxidation actively progressed as the vitamin E contents of the oils decreased.

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