

## Glucosinolates and Fatty Acid, Sterol, and Tocopherol Composition of Seed Oils from *Capparis spinosa* Var. *spinosa* and *Capparis ovata* Desf. Var. *canescens* (Coss.) Heywood

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Seed oils of 11 samples of *Capparis ovata* and *Capparis spinosa* from different locations in Turkey were characterized with regard to the composition of fatty acids, tocopherols, and sterols as well as the content of glucosinolates. The oil content of the seeds ranged from 27.3 to 37.6 g/100 g (*C. spinosa*) and from 14.6 to 38.0 g/100 g (*C. ovata*). The dominating fatty acid of both species was linoleic acid, which accounted for 26.9–55.3% in *C. ovata* seed oils and for 24.6–50.5% in *C. spinosa* seed oils. Oleic acid and its isomer, vaccenic acid, were both found in the seed oils in concentrations between 10 and 30%, respectively. The seed oils of both species were rich in tocopherols with the following composition:  $\gamma$ -tocopherol, 124.3–1944.9 mg/100 g;  $\delta$ -tocopherol, 2.7–269.5 mg/100 g; and  $\alpha$ -tocopherol, 0.6–13.8 mg/100 g. The concentration of total sterols ranged from 4875.5 to 12189.1 mg/kg (*C. ovata*) and from 4961.8 to 10009.1 mg/kg (*C. spinosa*), respectively. In addition to sitosterol, which amounted to ~60% of the total amount of sterols, campesterol and stigmasterol accounted for 16 and 10% of the total sterols, respectively. The seed oils showed remarkably high contents of  $\Delta^5$ -avenasterol (between 138.8 and 599.4 mg/kg). The total content of glucosinolates of *C. ovata* and *C. spinosa* samples was determined as 34.5–84.6  $\mu\text{mol/g}$  for *C. ovata* and 42.6–88.9  $\mu\text{mol/g}$  for *C. spinosa*, respectively, on a dry weight basis, with >95% as glucocapperin.

**KEYWORDS:** *Capparis ovata*; *Capparis spinosa*; fatty acid composition; glucosinolates; seed oil; sterols; tocopherols

### INTRODUCTION

Capers in the flora of Turkey, belonging to the family Capparaceae, are represented by the two species *Capparis spinosa* var. *spinosa* and *Capparis ovata* Desf. var. *canescens* (Coss.) Heywood (1). Some members of this family have medicinal and aromatic properties, whereas the fruits and the roots of the plants are indicated to help not only in gout but also as a diuretic, constipant, astringent, and tonic. The fresh aerial parts, including the fruits, can be stored in vinegar or brine for 3 months and used as a pickle (2–5). Even though the fruits and young shoots of capers are less abundant than their flower buds, the fruits are especially popular for consumption. Fruits with small, soft seeds are preferred for the production of pickles (6).

Interest in new sources of edible oils has recently grown. Plant seeds are important sources of oils for nutritional, industrial, and pharmaceutical applications. Lipids are important for the development of cells as structural components and

functional compounds and for storage of energy. However, no oil from any single source has been found to be suitable for all purposes, because oils from different sources generally differ in their composition. This necessitates the search for new sources of novel oils. The study of oilseeds for their minor constituents is useful in order that both the oil and its minor constituents be used effectively (7).

Recently, a great deal of attention has been given to *Capparis* spp. buds, fruits, young shoots, and seed oil. There is little information on the characteristic properties of the plant, the composition of raw and fermented buds, and the effect of brine and packing on the quality of capers (6, 8–12). Also, only a few studies on the fatty acid composition and other characteristics of seed oils from *C. spinosa* and *C. ovata* seed oils are available (13, 14). Gupta and Chakrabarty (13) determined that seeds contained ~30% oil, with oleic, palmitic, and linoleic acid as the main fatty acids. Akgül and Özcan (14) reported for caper seeds growing in Turkey that oleic and linoleic acids were the major unsaturated fatty acids, whereas palmitic acid was the predominant saturated one.

Glucosinolates are secondary plant metabolites that are of toxicological and pharmacological interest. They have been found in at least 11 plant families but most often are associated

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**Table 1.** Location of Harvest of 11 Samples Each of *C. ovata* and *C. spinosa* and Their Oil Content

sample	location of harvest	oil content (g/100 g)
<i>C. ovata</i> 1	Konya (Selcuklu)	35.3
<i>C. ovata</i> 2	Zonguldak (Karabük)	19.0
<i>C. ovata</i> 3	Karaman (Alacati)	24.9
<i>C. ovata</i> 4	Amasya (Karaköprü)	14.6
<i>C. ovata</i> 5	Konya (Kampus)	35.2
<i>C. ovata</i> 6	Tokat	35.3
<i>C. ovata</i> 7	Konya (Tatlicak)	38.0
<i>C. ovata</i> 8	Urfa	32.8
<i>C. ovata</i> 9	Ankara (Gölbasi)	18.8
<i>C. ovata</i> 10	Malatya	26.6
<i>C. ovata</i> 11	Karaman	30.2
<b>mean</b>		<b>28.3</b>
<b>SD</b>		<b>8.0</b>
<i>C. spinosa</i> 1	Mersin (Hirmanli-Silifke)	37.6
<i>C. spinosa</i> 2	Mersin (Silifke)	28.0
<i>C. spinosa</i> 3	Mersin (Burunköy-Mut)	35.6
<i>C. spinosa</i> 4	Mersin (Zeyne-Gülner)	27.3
<i>C. spinosa</i> 5	Adana (Kadirli)	28.0
<i>C. spinosa</i> 6	Burdur	30.0
<i>C. spinosa</i> 7	Mersin (Büyükeceli-Gülner)	34.1
<i>C. spinosa</i> 8	Mersin (Palantepe-Mut)	36.0
<i>C. spinosa</i> 9	Mersin (Delikkaya-Gülner)	35.4
<i>C. spinosa</i> 10	Mugla (Fethiye)	33.4
<i>C. spinosa</i> 11	Hatay	28.7
<b>mean</b>		<b>32.2</b>
<b>SD</b>		<b>3.8</b>

with members of the plant family Brassicaceae. Many garden vegetables belong to this family, and their characteristic odors and flavors are primarily due to glucosinolate hydrolysis products. Many plants of this family are used in agriculture and nutrition, for example, rapeseed, wintercress, false flax, crambe, Brussels sprouts, radish, cabbage, broccoli, or cauliflower (15, 16). Glucosinolates also can be found in members of the family Capparaceae. Some data on specific aspects of the qualitative composition of flavonoids and the occurrence of elemental sulfur as well as the glucosinolate composition of young shoots and flower buds of capers (*Capparis* spp.) have been published (12, 17–24), but up to now no detailed study on the composition of fatty acids, tocopherols, and sterols, the oil content, and the content and distribution of glucosinolates in seeds of caper berries is available.

The aim of this study was to determine the oil content as well as the fatty acid, tocopherol, and sterol composition of seed oils from caper berries collected from two different species of *Capparis* grown wild in different regions in Turkey. Glucosinolates are a characteristic feature of caper berries. Therefore, in addition to the fat-soluble components, also the total content of glucosinolates as a chemotaxonomic feature of this plants was determined.

## MATERIALS AND METHODS

**Plant Material.** Caper berries (fruits) of *Capparis spinosa* var. *spinosa* (*C. spinosa*) and *Capparis ovata* Desf. var. *canescens* (Coss.) Heywood (*C. ovata*) were picked from wild plants at different locations in Turkey in August 2002 (Table 1). Seeds of mature fruits from *Capparis* spp. were used in this investigation. Fruits were crushed in a blender, skin and pulp were removed, and seeds were obtained, washed with water, air-dried without direct sunlight, and stored in glass jars until analysis at 4 °C.

**Reagents.** Petroleum ether (40–60 °C) was of analytical grade (>98%) (Merck, Darmstadt, Germany). Heptane and *tert*-butyl methyl ether were of HPLC grade (Merck).

**Oil Content.** The oil content was determined according to ISO method 659:1998 (25). About 2 g of the seeds was ground in a ball mill and extracted with petroleum ether in a Twisselmann apparatus for 6 h. The solvent was removed by a rotary evaporator at 40 °C and 25 Torr. The oil was dried by a stream of nitrogen and stored at –20 °C until use.

**Fatty Acid Composition.** The fatty acid composition was determined following the ISO standard ISO 5509:2000 (26). In brief, one drop of the oil was dissolved in 1 mL of *n*-heptane, 50 µL of a solution of sodium methanolate (2 mol L<sup>-1</sup>) was added, and the closed tube was agitated vigorously for 1 min at room temperature. After the addition of 100 µL of water, the tube was centrifuged at 4500g for 10 min, and the lower aqueous phase was removed. Then 50 µL of HCl (1 mol with methyl orange) was added, the solution was briefly mixed, and the lower aqueous phase was discarded. Twenty milligrams of sodium hydrogen sulfate monohydrate (Merck) was added, and after centrifugation at 4500g for 10 min, the top *n*-heptane phase was transferred to a vial and injected in a Hewlett-Packard 5890 gas chromatograph with a 100 m × 0.25 mm i.d., 0.2 µm, capillary column, CP-Sil 88 (Varian Deutschland GmbH, Darmstadt, Germany). The temperature program was as follows: 155 °C, heated to 220 °C at 1.5 °C/min; 10 min isotherm at injector, 250 °C; detector, 250 °C; carrier gas, 36 cm/s hydrogen; split ratio, 1:50; detector gas, 30 mL/min hydrogen, 300 mL/min air, and 30 mL/min nitrogen; manual injection volume, <1 µL. The peak areas were computed by the integration software, and percentages of fatty acid methyl esters (FAME) were obtained as weight percent by direct internal normalization.

**Tocopherols.** For determination of tocopherols a solution of 250 mg of oil in 25 mL of *n*-heptane was directly used for the HPLC. The HPLC analysis was conducted using a Merck-Hitachi low-pressure gradient system, fitted with an L-6000 pump, a Merck-Hitachi F-1000 fluorescence spectrophotometer (detector wavelength for excitation of 295 nm and for emission of 330 nm), and a D-2500 integration system. Twenty microliters of the samples was injected by a Merck 655-A40 autosampler onto a 25 cm × 4.6 mm i.d. Diol phase column used with a flow rate of 1.3 mL/min. The mobile phase used was *n*-heptane/*tert*-butyl methyl ether (99+1, v/v) (27). A standard consisting of barley oil and linseed oil, containing the four tocopherol isomers, was used as external standard for the preparation of standard curves for each component. On the basis of these curves the chromanol isomers were calculated.

**Sterols.** The sterol composition of the oils was determined following ISO/FIDS 12228:1999 (E) (28). In brief, 250 mg of oil was saponified with a solution of ethanolic potassium hydroxide by boiling under reflux. The unsaponifiable matter was isolated by solid-phase extraction on an aluminum oxide column (Merck) on which fatty acid anions were retained and sterols passed through. The sterols fraction from the unsaponifiable matter was separated by thin-layer chromatography (Merck) and re-extracted from the TLC material, and afterward the composition of the sterol fraction was determined by GLC using betulin as internal standard. The compounds were separated on a 50 m × 0.32 mm i.d., 0.25 µm SE 54 CB column (Macherey-Nagel, Düren, Germany). Further parameters were as follows: hydrogen as carrier gas; split ratio, 1:20; injection and detection temperatures adjusted to 320 °C; temperature program, from 245 to 260 °C at 5 °C/min.

**Desulfoglucosinolates.** Desulfoglucosinolates were determined according to a modified method described by Fiebig and Jörden (29). In brief, 200 mg of the sample material was extracted twice with 70% (v/v) hot methanol at 75 °C for 10 min by ultrasonic treatment after addition of the internal standard glucotropaeolin (5 and 20 mmol, respectively). The moisture content of the seeds was 9%. This content was taken into account for the calculation of the individual glucosinolates. Then 2 mL of the crude extract was added onto a SAX 500 mg strong anion exchange column (Merck) for solid-phase extraction, which was conditioned with 2 mL of 70% methanol. Unwanted compounds were washed from the column with 2 mL of bidistilled water, and then the pH value of the column was adjusted by use of 1 mL of sodium acetate buffer (pH 4). Afterward, the glucosinolates on the column were treated with the enzyme sulfatase (1 mL of a solution of 10 mg of sulfatase/25 mL of water) overnight, which leads to the formation of desulfoglucosinolates. The neutral desulfoglucosinolates were eluted from the column using 1 mL of bidistilled water, whereas

**Table 2.** Fatty Acid Composition (Percent) of Seed Oils from *C. ovata* and *C. spinosa*

sample	myristic acid 14:0	palmitic acid 16:0	palmitoleic acid 16:1Δ9	stearic acid 18:0	oleic acid 18:1Δ9	cis-vaccenic acid 18:1Δ11	linoleic acid 18:2Δ9,12	linolenic acid 18:3eΔ9,12,15	eicosanoic acid 20:0	eicosenoic acid 20:1Δ11	behenic acid 22:0	lignoceric acid 24:0
<i>C. ovata</i> 1	0.35	13.14	3.80	3.49	31.84	17.27	26.92	0.60	0.71	0.21	0.76	0.07
<i>C. ovata</i> 2	0.29	8.85	2.25	2.74	20.58	15.27	46.04	1.22	0.60	0.28	0.64	0.16
<i>C. ovata</i> 3	0.12	6.72	1.98	2.32	23.14	15.23	46.70	0.95	0.59	0.33	0.76	0.17
<i>C. ovata</i> 4	0.15	6.08	2.29	2.42	18.89	18.84	46.85	1.26	0.69	0.31	0.87	0.18
<i>C. ovata</i> 5	0.17	7.17	1.63	2.19	20.41	13.34	51.37	0.83	0.51	0.31	0.61	0.14
<i>C. ovata</i> 6	0.29	8.74	1.45	2.39	24.70	10.67	48.51	0.92	0.45	0.35	0.60	0.11
<i>C. ovata</i> 7	0.22	9.82	1.62	2.14	22.18	12.17	49.28	1.13	0.43		0.48	
<i>C. ovata</i> 8	0.16	6.36	2.03	2.25	23.75	17.83	44.25	0.73	0.52	0.29	0.59	0.11
<i>C. ovata</i> 9	0.17	4.96	1.24	2.48	19.52	14.39	53.20	1.52	0.70		0.80	
<i>C. ovata</i> 10	0.17	6.09	1.96	2.13	22.33	17.10	46.84	1.05	0.53	0.30	0.60	0.12
<i>C. ovata</i> 11	0.14	6.50	1.16	2.44	19.84	10.92	55.28	1.12	0.55	0.32	0.57	0.12
<b>mean</b>	<b>0.20</b>	<b>7.68</b>	<b>1.95</b>	<b>2.45</b>	<b>22.47</b>	<b>14.82</b>	<b>46.84</b>	<b>1.03</b>	<b>0.57</b>	<b>0.30</b>	<b>0.66</b>	<b>0.13</b>
<b>SD</b>	<b>0.08</b>	<b>2.32</b>	<b>0.72</b>	<b>0.39</b>	<b>3.62</b>	<b>2.80</b>	<b>7.38</b>	<b>0.26</b>	<b>0.10</b>	<b>0.04</b>	<b>0.12</b>	<b>0.03</b>
<i>C. spinosa</i> 1	0.25	11.63	5.18	2.59	27.87	20.47	28.55	0.51	0.69	0.21	0.93	0.08
<i>C. spinosa</i> 2	0.58	13.99	4.90	3.75	26.10	19.81	27.04	1.07	0.73	0.15	0.72	0.08
<i>C. spinosa</i> 3	0.28	12.11	4.06	3.31	29.79	19.04	28.17	0.47	0.76	0.21	0.83	0.08
<i>C. spinosa</i> 4	0.40	12.63	4.92	3.34	21.21	21.19	32.65	0.73	0.69	0.17	0.71	0.08
<i>C. spinosa</i> 5	0.19	11.50	7.40	2.51	14.94	28.30	30.60	0.78	0.75	0.14	1.07	0.12
<i>C. spinosa</i> 6	0.13	5.42	1.32	2.49	23.12	14.29	50.45	0.65	0.59	0.33	0.64	0.13
<i>C. spinosa</i> 7	1.14	14.35	3.51	4.59	31.55	14.84	25.68	1.76	0.67	0.14	0.61	0.06
<i>C. spinosa</i> 8	0.32	12.77	4.01	3.44	30.61	18.21	27.29	0.70	0.73	0.22	0.76	0.08
<i>C. spinosa</i> 9	1.20	14.22	3.94	4.00	30.60	16.30	26.06	1.21	0.68	0.14	0.66	0.06
<i>C. spinosa</i> 10	0.11	6.35	2.23	2.18	22.72	18.80	44.58	0.76	0.54	0.28	0.64	0.12
<i>C. spinosa</i> 11	1.26	13.60	2.81	4.11	37.29	12.21	24.55	2.03	0.60	0.17	0.54	0.05
<b>mean</b>	<b>0.53</b>	<b>11.69</b>	<b>4.03</b>	<b>3.30</b>	<b>26.89</b>	<b>18.50</b>	<b>31.42</b>	<b>0.97</b>	<b>0.68</b>	<b>0.20</b>	<b>0.74</b>	<b>0.09</b>
<b>SD</b>	<b>0.43</b>	<b>2.90</b>	<b>1.56</b>	<b>0.74</b>	<b>5.83</b>	<b>4.10</b>	<b>7.99</b>	<b>0.49</b>	<b>0.07</b>	<b>0.06</b>	<b>0.15</b>	<b>0.02</b>

all non-glucosinolate anions remained on the exchange column. The solution obtained was used for the HPLC.

The HPLC analysis was conducted using a Merck-Hitachi low-pressure gradient system, fitted with an L-7100 pump, a Merck-Hitachi L-4250 UV-vis detector set at 229 nm, and a Knauer ChromGate for Windows integration system. Forty microliters of the desulfoglucosinolate-containing eluates were injected by an AS-4000 autosampler onto a 250 × 4 mm, 5 μm LiChrospher 100 RP-18e column (Merck) used with a flow rate of 1 mL/min. The mobile phase used consisted of water (A) versus acetonitrile (B) for a total running time of 43 min, and the gradient changed as follows: from 100% A to 95% A in 2.5 min, to 80% A in 18 min, isocratic for 5 min, and then back to 100% A in 1.5 min. The column was equilibrated at 100% A for 16 min.

For the correct identification of most of the peaks in the chromatogram a reference standard (BCR RM367) was run with the samples. Additionally, glucocapparin was identified by the preparation of the standard substance. The calculation of each glucosinolate identified in the samples was done by evaluation of the chromatograms obtained by UV detection at 229 nm as described in the EC standard method (30). The moisture of the plant material was determined gravimetrically, and the results were taken into account for the calculation of the glucosinolates. The content of each glucosinolate was calculated and expressed in micromoles per gram of plant material. Statistical parameters, such as precision, repeatability, and reproducibility, for the calculation of each glucosinolate were given in the EC standard method.

## RESULTS AND DISCUSSION

**Oil Content.** The oil contents of seeds of caper berries are given in **Table 1**. Whereas the oil content of samples from *C. spinosa* showed only a small variation from 27.3 g/100 g on a dry weight basis (dw%) (*C. spinosa* 4) to 37.6 g/100 g (*C. spinosa* 1), with a mean value of 32.1 g/100 g, the range of samples from *C. ovata* was much more pronounced, from 14.6 g/100 g (*C. ovata* 4) to 38.0 g/100 g (*C. ovata* 7), with a mean value of 28.3 g/100 g. Nevertheless, for *C. ovata* most seeds had oil contents >30 g/100 g, and only in seeds of samples *C. ovata* 2, *C. ovata* 4, and *C. ovata* 9 was the oil content <20 g/100 g. The oil contents of seeds from *C. spinosa* found in

this work are in agreement with previous findings that reported an oil content of 35.2 g/100 g (14), whereas oil contents of *C. ovata* are reported generally a little lower than the oil contents of seeds from *C. spinosa*. Gupta and Chakrabarty (13) had established that seeds of different caper species grown in India contained 30 g/100 g oil. Seeds of *C. ovata* at 6.7% moisture content had a yield of ~36.7 g/100 g oil by solvent extraction (14).

**Fatty Acid Composition.** The fatty acid composition of seed oil triacylglycerides varies widely among different plant species, and often the occurrence of unusual fatty acids is characteristic for particular plant families (31, 32). On the other hand, most seeds contain fatty acids commonly present in seed oils, such as saturated fatty acids such as palmitic or stearic acid and unsaturated fatty acids such as oleic, linoleic, or linolenic acid in different proportions. These fatty acids occur in all living tissues of plants and have therefore only a minor chemotaxonomic value (33). Nevertheless the fatty acid composition of seed oils is an interesting point with regard to the further use of the seeds or the oil.

According to the results shown in **Table 2** the most predominant fatty acid of both seed oils of caper species was linoleic acid, which accounted for 26.9–55.3% in *C. ovata* seed oils, with a mean value of 45.9. and 24.6–50.5% in *C. spinosa* seed oils, with a mean value of 31.1%. The highest values for linoleic acid were found in samples *C. ovata* 11 and *C. spinosa* 6, collected from Karaman and Burdur provinces, respectively, with 55.3 and 50.5% of linoleic acid.

In addition to linoleic acid, seed oils of *C. spinosa* and *C. ovata* contained higher amounts of oleic acid. The range was between 18.9 and 31.8% for seed oils from *C. ovata*, with a mean value of 22.8%. The content of oleic acid in seed oils from *C. spinosa* varied more, from 14.9 to 37.3%, and the mean value was higher, 26.9%. Interesting is the high content of the isomer of oleic acid, *cis*-vaccenic acid, which ranged from 10.7% (*C. ovata* 6) to 18.8% (*C. ovata* 8), with mean values of

**Table 3.** Tocopherol, Tocotrienol, and Plastochromanol 8 Composition (Milligrams per 100 g) of Seed Oils from *C. ovata* and *C. spinosa*<sup>a</sup>

sample	$\alpha$ -T	$\alpha$ -T3	$\beta$ -T	$\gamma$ -T	P8	$\gamma$ -T3	$\delta$ -T	total amount
<i>C. ovata</i> 1	6.4	0.4	0.2	261.7	0.4	0.9	2.9	272.8
<i>C. ovata</i> 2	5.4	0.8	0.3	465.1	5.2	0.4	40.6	518.0
<i>C. ovata</i> 3	8.8	0.5	0.6	329.5	2.7	0.3	32.4	374.8
<i>C. ovata</i> 4	2.6	0.0	0.2	1944.9	2.7	1.3	124.3	2076.1
<i>C. ovata</i> 5	9.9	0.2	0.9	284.4	1.1	0.3	23.7	320.5
<i>C. ovata</i> 6	6.5	0.4	0.3	263.8	1.4	0.0	12.1	284.4
<i>C. ovata</i> 7	5.6	0.0	0.5	257.8	1.6	0.0	18.7	284.2
<i>C. ovata</i> 8	0.7	0.0	0.5	135.0	0.8	0.4	269.5	406.9
<i>C. ovata</i> 9	12.2	0.8	1.4	188.6	4.6	0.0	149.4	357.0
<i>C. ovata</i> 10	1.8	0.4	0.7	143.1	1.4	0.1	240.8	388.4
<i>C. ovata</i> 11	13.8	0.0	1.1	305.9	2.6	0.0	27.5	350.9
mean	6.7	0.3	0.6	416.4	0.0	2.2	0.3	85.6
SD	4.2	0.3	0.4	515.2	0.0	1.5	0.4	96.1
<i>C. spinosa</i> 1	3.4	0.0	0.1	278.4	0.4	0.5	4.3	287.0
<i>C. spinosa</i> 2	4.8	0.0	0.0	359.0	1.0	0.7	4.4	369.8
<i>C. spinosa</i> 3	7.6	0.0	0.2	288.7	0.3	0.7	4.2	301.6
<i>C. spinosa</i> 4	6.8	0.0	0.1	354.4	0.6	0.7	3.9	366.6
<i>C. spinosa</i> 5	3.6	0.0	0.0	1972.9	1.8	1.1	6.0	1985.4
<i>C. spinosa</i> 6	2.2	0.0	1.3	197.1	0.8	0.6	174.1	376.1
<i>C. spinosa</i> 7	4.1	0.0	0.0	296.1	1.3	0.2	4.7	306.4
<i>C. spinosa</i> 8	6.3	0.0	0.0	284.1	2.4	1.9	4.5	299.2
<i>C. spinosa</i> 9	4.9	0.0	0.1	254.2	0.8	0.3	7.2	267.6
<i>C. spinosa</i> 10	3.5	0.0	0.0	241.9	0.7	0.4	2.7	249.2
<i>C. spinosa</i> 11	0.6	0.0	0.5	124.3	1.1	0.5	269.2	396.2
mean	4.4	0.0	0.2	422.8	0.0	1.0	0.7	44.1
SD	2.0	0.0	0.4	494.2	0.0	0.6	0.4	86.1

<sup>a</sup> Abbreviations: T, tocopherol; T3, tocotrienol; P8, plastochromanol 8.

14.8% in seed oils of *C. ovata* and from 12.2% (*C. spinosa* 11) to 28.3% (*C. spinosa* 5), with a mean value of 18.5% in seed oils of *C. spinosa*. In commonly used edible oils this fatty acid can be found in amounts between 1 and 3% (34).

The seed oils of both species also contain appreciable amounts of saturated fatty acids, especially palmitic and stearic acids. Although levels of palmitic acid of *C. ovata* seed oils ranged between 5.0 and 13.1%, with a mean value of 7.7%, the amount of palmitic acid was a little higher in the oil of *C. spinosa* seeds. Here the range was between 5.4 and 14.4%, with a mean value of 11.7%. Stearic acid was found in lower amounts, but here also the amount found in seed oils of *C. ovata* was a little lower than that found in seed oils of *C. spinosa*.

Similar results of the fatty acid composition were found by Akgül and Özcan (14), who reported the main fatty acids from seeds of *C. spinosa* and *C. ovata*, identified by gas chromatography as palmitic (13.2 and 11.3%), oleic (49.9 and 34.7%), and linoleic (25.2 and 24.5%) acid, respectively. Also, Gupta and Chakrabarty (13) described oleic acid (57%) as the main fatty acid of seed oils from capers, accompanied by lesser amounts of palmitic (21%) and linoleic acid (11%). Considering that in the literature the occurrence of vaccenic acid is not described, the predominant amount of oleic acid in the literature can be explained by the fact that the content given for oleic acid contained in addition to oleic acid also vaccenic acid. Thus, the amount of oleic found by Akgül and Özcan (14) is comparable to the sum of oleic acid and vaccenic acid found in this study.

**Tocopherols.** As a further important criterion for the assessment of seed oils, the content and the composition of tocopherols, tocotrienols, and plastochromanol 8 is presented in **Table 3**. There are certain differences in the tocopherol composition of the different seed oils, although it is obvious that  $\gamma$ - and  $\delta$ -tocopherols are the major vitamin E active

components in *C. ovata* and *C. spinosa* seed oils. The variation of the other tocopherols and tocotrienols was relatively small; these tocopherols seem to be independent of environmental influences resulting from different cultivation sites. Whereas in most seed oils the total amount of tocopherols ranged between 249.2 mg/kg (*C. spinosa* 10) and 518.0 mg/kg (*C. ovata* 2), *C. ovata* 4 (2076.1 mg/kg) and *C. spinosa* 5 (1985.4 mg/kg) were characterized by much higher amounts of tocopherols resulting from a remarkably high amount of  $\gamma$ -tocopherol. These high amounts of tocopherols could be interesting for the production of naturally occurring tocopherols for the stabilization of fats and oils against oxidative deterioration and for applications in dietary, pharmaceutical, or biomedical products (35).

Apart from these two samples the characteristic level of  $\gamma$ -tocopherol was relatively stable (124.3–465 mg/kg), in comparison to  $\delta$ -tocopherol, with a variation from 2.7 to 269.5 mg/kg. In most cases seed oils of *C. ovata* and *C. spinosa* comprise low amounts of  $\delta$ -tocopherol, but four samples of *C. ovata* and two samples of *C. spinosa* contained >100 mg/kg, with a maximum value of 269.5 mg of  $\delta$ -tocopherol/kg in *C. ovata* 8. The high contents of  $\delta$ -tocopherol occurring in these samples of caper berries are unusual in comparison to commonly used edible oils, which contain only very small amounts of this tocopherol. Apart from sample *C. ovata* 4, which was characterized by an extraordinarily high amount of  $\gamma$ -tocopherol, in all other samples this high amount of  $\delta$ -tocopherol came at the expense of a lower content of  $\gamma$ -tocopherol.

It is obvious that tocopherols were the predominant group of vitamin E active compounds in seed oils of *C. ovata* and *C. spinosa*. In the seed oils only  $\alpha$ - and  $\gamma$ -tocotrienols were found in very low concentrations, with <2.0 mg/kg for the sum of both tocotrienols and a mean value of 0.7 mg/kg. The content of plastochromanol 8 in the seed oils was also very small. The highest amount was found in *C. ovata* 2 (5.2 mg/kg), but the mean value of all samples was only 1.6 mg/kg. In seed oils of *C. ovata* slightly higher amounts (2.2 mg/kg) were found than in *C. spinosa* (1.0 mg/kg). The amount of tocopherols in seed oils of *C. ovata* and *C. spinosa* is comparable to that found in other commonly used seed oils such as sunflower oil or rapeseed oil (36).

**Sterols.** Sterols are probably the most important class of the minor components and comprise a major portion of the unsaponifiable matter of most vegetable oils (37). The content of phytosterols determined in *C. ovata* and *C. spinosa* seed oils is shown in **Table 4**. The concentration of total sterols ranged from 4875.5 (*C. ovata* 6) to 12189.1 mg/kg (*C. ovata* 9) in oils of *C. ovata* and from 4961.8 (*C. spinosa* 9) to 10009.1 mg/kg (*C. spinosa* 2) in oils of *C. spinosa*, respectively. In addition to sitosterol, which amounted to ~60% of the total amount of sterols, campesterol and stigmasterol were predominant, with about 16 and 10% of the total sterols, respectively. In seed oils of both species the same major sterols were found, even though the mean values of the total amounts were a little higher for seed oils from *C. ovata*. The reason is that these seeds contain higher amounts of campesterol and sitosterol, whereas the amounts of the other sterols were similar to those found in seed oils from *C. spinosa*.

Interesting is the remarkably high amount of  $\Delta^5$ -avenasterol in the oils of both species, which accounted for ~3–10% of the total amount of sterols, resulting in mean amounts of 416 mg/kg for *C. ovata* and 337 mg/kg for *C. spinosa*, respectively. In comparison, in rapeseed oil 250 mg of  $\Delta^5$ -avenasterol/kg, in sunflower oil 170 mg/kg, and in *Camelina sativa* oil 400 mg/kg were found in an unpublished investigation. The occurrence

**Table 4.** Sterol Composition (Milligrams per Kilogram) of Seed Oils from *C. ovata* and *C. spinosa*

sample	cholesterol	brassicasterol	24-methylene-cholesterol	campesterol	campestanol	stigmasterol	5,23-stigmastadienol*	sitosterol	sitostanol*	5-avenasterol*	5,24-stigmastadienol*	7-stigmasterol	7-avenasterol	total amount
<i>C. ovata</i> 1	19.0	14.4	88.8	769.9	23.0	658.7	52.6	3352.9	77.3	369.8	57.0	15.4	30.3	5529.0
<i>C. ovata</i> 2	24.9	20.9	0.0	1483.5	38.6	868.3	73.1	5316.1	168.8	385.0	76.9	0.0	12.5	8468.6
<i>C. ovata</i> 3	25.1	13.1	0.0	1832.3	34.7	659.9	72.7	6070.4	134.2	225.1	78.0	19.2	22.4	9187.2
<i>C. ovata</i> 4							not determined							
<i>C. ovata</i> 5	25.5	1.1	32.2	1038.1	23.5	489.0	58.2	4275.1	91.6	424.8	56.4	7.5	16.9	6540.0
<i>C. ovata</i> 6	16.7	15.7	33.7	645.5	15.6	521.5	46.0	2985.6	72.7	446.5	53.2	6.0	16.7	4875.5
<i>C. ovata</i> 7	16.6	7.9	36.1	863.0	22.3	465.8	55.1	3644.7	88.2	599.4	62.1	0.0	21.8	5883.0
<i>C. ovata</i> 8	21.0	0.0	0.0	1003.5	18.3	523.2	56.7	4030.3	50.1	341.2	56.7	9.5	24.0	6134.4
<i>C. ovata</i> 9	44.9	315.8	0.0	1932.2	59.3	1603.2	92.9	7410.6	150.7	425.9	69.7	16.8	32.3	12189.1
<i>C. ovata</i> 10	21.0	17.3	0.0	1410.1	28.9	668.2	60.2	4803.5	73.4	370.6	61.0	15.9	72.5	7602.6
<i>C. ovata</i> 11	20.8	13.8	25.4	1231.5	26.2	564.4	66.3	4988.8	91.9	577.6	73.1	11.1	21.9	7713.0
<b>mean</b>	<b>42.7</b>	<b>49.8</b>	<b>26.3</b>	<b>1338.0</b>	<b>26.4</b>	<b>763.7</b>	<b>66.0</b>	<b>4939.9</b>	<b>112.8</b>	<b>416.4</b>	<b>69.0</b>	<b>9.2</b>	<b>24.6</b>	<b>7888.0</b>
<b>SD</b>	<b>63.9</b>	<b>95.1</b>	<b>31.2</b>	<b>568.6</b>	<b>14.9</b>	<b>380.1</b>	<b>15.5</b>	<b>1522.7</b>	<b>56.1</b>	<b>104.0</b>	<b>17.6</b>	<b>7.2</b>	<b>18.1</b>	<b>2585.1</b>
<i>C. spinosa</i> 1	34.2	0.0	73.5	936.4	21.8	779.2	56.0	3825.6	77.0	407.1	58.8	12.9	23.5	6306.2
<i>C. spinosa</i> 2	25.2	0.0	81.3	1068.0	24.2	980.5	64.5	4264.5	79.7	331.6	60.4	17.3	27.2	7025.1
<i>C. spinosa</i> 3	13.4	13.0	45.0	648.5	14.9	690.0	47.6	3078.0	54.8	313.7	46.5	9.5	16.3	4991.1
<i>C. spinosa</i> 4	22.4	20.6	6.4	807.1	20.2	850.6	46.1	2999.9	92.0	138.8	44.8	15.8	18.3	5093.0
<i>C. spinosa</i> 5	23.7	34.0	0.0	1398.4	30.0	1170.0	72.1	4948.4	109.2	245.2	68.6	9.2	14.8	8123.5
<i>C. spinosa</i> 6	27.7	18.7	11.9	1225.3	31.4	789.9	57.6	4177.6	102.1	307.5	51.7	9.1	17.1	6827.7
<i>C. spinosa</i> 7	28.0	0.0	119.6	1000.5	22.6	645.7	51.9	3307.6	66.5	426.1	50.1	17.3	0.0	5736.0
<i>C. spinosa</i> 8	19.8	15.1	55.2	862.0	25.4	777.9	57.9	3659.0	82.3	329.9	53.0	14.9	24.7	5977.3
<i>C. spinosa</i> 9	19.9	15.0	161.5	814.3	19.9	623.1	43.4	2820.0	60.8	315.0	38.6	8.6	12.8	4961.8
<i>C. spinosa</i> 10	21.7	15.5	177.8	782.3	19.8	448.4	47.4	2963.1	64.3	444.8	38.7	0.0	22.5	5059.5
<i>C. spinosa</i> 11	27.0	15.5	133.5	1014.7	26.0	511.9	54.8	3863.7	75.4	442.4	57.5	11.0	27.1	6269.3
<b>mean</b>	<b>23.9</b>	<b>13.4</b>	<b>78.7</b>	<b>959.8</b>	<b>23.3</b>	<b>751.6</b>	<b>54.5</b>	<b>3627.9</b>	<b>78.6</b>	<b>336.6</b>	<b>51.7</b>	<b>11.4</b>	<b>18.6</b>	<b>6033.7</b>
<b>SD</b>	<b>5.5</b>	<b>10.3</b>	<b>62.4</b>	<b>215.0</b>	<b>4.8</b>	<b>205.2</b>	<b>8.6</b>	<b>666.4</b>	<b>17.1</b>	<b>92.3</b>	<b>9.3</b>	<b>5.1</b>	<b>7.9</b>	<b>1013.5</b>

of  $\Delta^5$ -avenasterol in the seed oil is interesting because this compound is known to act as an antioxidant and as an antipolymerization agent in frying oils (38, 39). These authors point out that those sterols with an ethyldiene group in the side chain are most effective as antioxidants and suggested that a synergistic effect of the sterols with other antioxidants may occur.

Brassicasterol, a characteristic feature of seed oils from members of the family Brassicaceae, is very low in seed oils of *C. ovata* and *C. spinosa*, although both seeds contain glucosinolates, also characteristic for seeds belonging to the family Brassicaceae. In seed oils of *C. spinosa* only 13.4 mg of brassicasterol/kg and in *C. ovata* 42.0 mg/kg were found, whereas seed oils of *Brassica napus* contain >20 times as much of this sterol (36).

**Glucosinolates.** Another characteristic feature of caper berries is the content and composition of the glucosinolates. Members of this group of compounds occur primarily in members of the family Brassicaceae, but they are also typical for members of the family Capparaceae. These glucosinolates may contribute to the prevention of diseases, but they also act as insect attractants and repellants to protect the plants against insects (15).

The total glucosinolate contents of the seeds are shown in **Table 5**. Glucocapperin was the predominant glucosinolate in seeds of *C. ovata* and *C. spinosa*, which came to >95% of the total amount of glucosinolates. The total amount of glucosinolates ranged from 34.5 to 84.6  $\mu\text{mol/g}$  in seeds of *C. ovata* and from 42.6 to 88.9  $\mu\text{mol/g}$  in seeds of *C. spinosa* on a dry weight basis.

In comparison to shoots or buds of *C. spinosa* or *C. ovata* the total amount of glucosinolates was much higher in the seeds. Matthäus and Özcan (24) reported that 12 different glucosinolates were determined in the young shoots and buds of *C. spinosa* and *C. ovata*. The total content of glucosinolates ranged between 6.6  $\mu\text{mol/g}$  (large buds of *C. spinosa*) and 45.6  $\mu\text{mol/g}$  (young shoots of *C. ovata*). In comparison with other glucosi-

**Table 5.** Total Content of Glucosinolates of Seeds from *C. ovata* and *C. spinosa*

sample	total content of glucosinolates ( $\mu\text{mol/g}$ )
<i>C. ovata</i> 1	73.2
<i>C. ovata</i> 2	38.7
<i>C. ovata</i> 3	42.2
<i>C. ovata</i> 4	47.3
<i>C. ovata</i> 5	76.0
<i>C. ovata</i> 6	81.3
<i>C. ovata</i> 7	84.6
<i>C. ovata</i> 8	54.9
<i>C. ovata</i> 9	34.5
<i>C. ovata</i> 10	54.0
<i>C. ovata</i> 11	61.0
<b>mean</b>	<b>58.9</b>
<b>SD</b>	<b>17.7</b>
<i>C. spinosa</i> 1	42.6
<i>C. spinosa</i> 2	46.6
<i>C. spinosa</i> 3	75.3
<i>C. spinosa</i> 4	49.2
<i>C. spinosa</i> 5	51.2
<i>C. spinosa</i> 6	78.6
<i>C. spinosa</i> 7	56.7
<i>C. spinosa</i> 8	88.9
<i>C. spinosa</i> 9	62.4
<i>C. spinosa</i> 10	54.3
<b>mean</b>	<b>60.6</b>
<b>SD</b>	<b>15.4</b>

nolate-containing plants or seeds, the amounts found in seeds of the two different species of *Capparis* were comparable with results found in *B. carinata* (111  $\mu\text{mol/g}$ ), *C. sativa* (38  $\mu\text{mol/g}$ ), *L. fendleri* (70  $\mu\text{mol/g}$ ), and *L. sativum* (127  $\mu\text{mol/g}$ ) (15). In other oilseeds such as *Crambe abyssinica*, *Brassica napus* (rapeseed), or *Brassica nigra* (mustard), 115  $\mu\text{mol}$  of glucosinolates/g, 15  $\mu\text{mol/kg}$ , and 130  $\mu\text{mol/g}$ , respectively, were found (40).

With oil contents between 20 and nearly 40%, seeds of *C. ovata* and *C. spinosa* could be interesting sources for the production of vegetable oil. The results indicate that the oil contains linoleic acid as the major fatty acid accompanied by oleic acid and its isomer vaccenic acid. The content and composition of tocopherols are comparable to those of other sources such as rapeseed or sunflower oil. The relatively high content of  $\Delta^5$ -avenasterol is interesting, because it has been suggested as an antioxidant and as an antipolymerization agent in frying oils.

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