

FA and Tocopherol Composition of Vietnamese Oilseeds

Bertrand Matthaus^{a,*}, Klaus Vosmann^a, Long Quoc Pham^b, and Kurt Aitzetmüller^a

^aInstitute for Lipid Research, Federal Center for Cereal, Potato and Lipid Research, D- 48147 Münster, Germany,

and ^bInstitute of Natural Products Chemistry, National Center of Natural Science and Technology, Hanoi, Vietnam

ABSTRACT: Seeds of 40 oilseed species from 23 different plant families (Brassicaceae, Cucurbitaceae, Fabaceae, Sapindaceae, Malvaceae, Gnetaceae, Clusiaceae, Bruseraceae, Ranunculaceae, Convolvulaceae, Amaranthaceae, Tiliaceae, Basellaceae, Solanaceae, Umbelliferae, Labiatae, Compositae, Theaceae, Euphorbiaceae, Caesalpiniaceae, Sapotaceae, Anacardiaceae, and Connaraceae) grown in Vietnam were analyzed for oilseed oil content, FA, and vitamin E. The seed oil content varied between 0.2 g/100 g for *Mangifera indica* and 75.7 g/100 g for *Calophyllum inophyllum*, whereas only nine seeds contained more than 40% oil. The tocopherol content ranged from 26 (*Sapindus mukorossi*) to 9361 mg/kg (*Litchi chinensis*). In nine seed oils unusual FA such as conjugated, cyclopropenoic, or epoxy FA were found.

Paper no. J10504 in *JAACS* 80, 1013–1020 (October 2003).

KEY WORDS: FA composition, oilseeds, tocopherols, tocotrienols.

The oleochemical industry is increasingly interested in custom-made and novel oils with specific FA compositions for applications in the oil and pharmaceutical industries (1). Such oils can be used for the synthesis of high-quality products without expensive purification of raw materials. In addition, oilseed breeders are searching for species to produce beneficial new genotypes (1). A recent example is rapeseed oil with 40 to 60% lauric acid, which normally contains little or none of this FA (2).

Plant seeds contain tocopherols and tocotrienols, which are used as natural antioxidants and vitamin E (3–5). In nature four different derivatives of tocopherols and tocotrienols (α -, β -, γ -, and δ) can be found, which differ in the methylation of the chroman ring. The antioxidant activity increases for tocopherols and tocotrienols in the order α to δ , whereas the biological activity is inversely proportional to the antioxidant activity (6,7). Plastochromanol-8 (P-8) is a related compound that is more effective against oxidation than α -tocopherol (8).

A large part of the genetic resources of the world is located in the southern hemisphere. These can be considered as potential sources of raw material for the development of future medicines and food, as well as renewable resources with interesting FA and associated enzyme systems. Unfortunately, very little information about this genetic potential is available and many species are disappearing. Therefore, identifying commercially valuable lipid-bearing plants is a timely issue.

Vietnam is very rich in plants, most of which have not been investigated with respect to their FA and tocopherol compositions. Some information about the FA composition of oilseeds is available in the Seed Oil Fatty Acid (SOFA) database (9), but to our knowledge this database contains only very limited data about seed oils from plants grown in Vietnam. Therefore, the aim of this work was to determine the FA and tocopherol compositions of native North Vietnamese seeds. Correlations between the content of PUFA and the tocopherol/tocotrienol composition were objects of special interest.

MATERIALS AND METHODS

Plant material. Seeds from 40 plant species grown in Vietnam were obtained from a typical Vietnamese market and used for the investigation (Table 1).

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

Isolation of oil from seeds. About 2 g of the seeds were ground in a ball mill and extracted with 70 mL petroleum ether in a Twisselmann apparatus for 6 h. The solvent was removed with 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.

Vitamin E. To determine vitamin E content (tocopherols, tocotrienols, and P-8) a solution of 250 mg oil in 25 mL heptane was used for 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 wavelengths for excitation 295 nm, for emission 330 nm) and a D-2500 integration system (10). Twenty microliters of sample was injected by a Merck 655-A40 autosampler onto a Diol phase HPLC column (25 cm \times 4.6 mm i.d.; Merck), which was used at a flow rate of 1.3 mL/min. The mobile phase used was heptane/*tert*-butyl methyl ether (99 + 1, vol/vol) (10). The results are given as mg vitamin E/100 g oil.

FA composition. GLC determination of FAME followed the ISO draft standard method ISO/FDIS 5509:1997 (11). In brief, about 10 mg of oil was dissolved in 1 mL of petroleum ether. Twenty-five microliters of a solution of 2 M sodium methanolate in methanol was added, and the closed vial was agitated vigorously for 1 min. About 20 μ L water was added, and after centrifugation at 4500 \times g the aqueous phase was removed by a Pasteur pipet. Then 20 μ L methyl orange in 0.1 N HCl was added as a pH indicator. The mixture was agitated carefully and

*To whom correspondence should be addressed at Federal Center for Cereal, Potato and Lipid Research, Institute for Lipid Research, P.O. Box 1705, D-48006 Münster, Germany. E-mail: matthaus@uni-muenster.de

TABLE 1
Systematic and Trivial Names of 40 Species of Vietnamese Plants Investigated

No.	Botanical name	Family	Trivial names
1	<i>Raphanus sativus</i> L.	Brassicaceae	White radish or turnip
2	<i>Brassica campestris</i> L.	Brassicaceae	Cabbage
3	<i>Brassica</i> sp.	Brassicaceae	Cabbage
4	<i>Brassica juncea</i>	Brassicaceae	Cabbage, Chinese mustard
5	<i>Brassica chinensis</i> L.	Brassicaceae	Cabbage
6	<i>Brassica oleracea</i> L.	Brassicaceae	Head cabbage
7	<i>Luffa cylindrica</i> (Roem)	Cucurbitaceae	Rag gourd, vegetable sponge
8	<i>Momordica charantia</i> L.	Cucurbitaceae	Bitter gourd, balsam pear
9	<i>Cucurbita pepo</i> L.	Cucurbitaceae	Courgette
10	<i>Momordica cochinchinensis</i> Spreng.	Cucurbitaceae	Muricia
11	<i>Cucumis sativus</i> L.	Cucurbitaceae	Cucumber
12	<i>Delavaya toxocarpa</i> Franch.	Sapindaceae	
13	<i>Dimocarpus longan</i> Lour.	Sapindaceae	Longan
14	<i>Litchi chinensis</i> Sonn.	Sapindaceae	Litchi
15	<i>Nephelium lappaceum</i> L.	Sapindaceae	
16	<i>Sapindus mukorossi</i> Gaertn.	Sapindaceae	Chinese soapberry
17	<i>Aesculus sinensis</i> Hort.	Hippocastanaceae	
18	<i>Calophyllum inophyllum</i> L.	Clusiaceae	Laurel wood
19	<i>Canarium tramdenum</i>	Bruseraceae	
20	<i>Hibiscus sabdariffa</i> L.	Malvaceae	Red sorrel
21	<i>Gnetum</i> sp. L.	Gnetaceae	
22	<i>Camellia oleifera</i> Abel	Theaceae	
23	<i>Aleurites montana</i> E.H. Wilson	Euphorbiaceae	
24	<i>Erythrophleum fordii</i> Oliver	Caesalpinaceae	
25	<i>Ipomoea aquatica</i> Forssk.	Convolvulaceae	Watercress, water morning glory
26	<i>Amaranthus mangostanus</i> Blanco	Amaranthaceae	Amaranth (eggplant)
27	<i>Corchorus olitorius</i> L.	Tiliaceae	Jute
28	<i>Basella rubra</i> Salisb.	Basellaceae	Ceylon spinach
29	<i>Solanum melongena</i> L.	Solanaceae	Aubergine (eggplant)
30	<i>Canavalia ensiformis</i> D.C.	Fabaceae	Common bean, bush bean
31	<i>Anethum graveolens</i> L.	Umbelliferae	
32	<i>Coriandrum sativum</i> L.	Umbelliferae	Coriander
33	<i>Schizonepeta tenuifolia</i> Briq.	Labiatae	
34	<i>Ocimum basilicum</i> L.	Labiatae	Basil, basilic
35	<i>Perilla frutescens</i> Britton	Labiatae	
36	<i>Chrysanthemum coronarium</i> L.	Compositae	Crown daisy, chop suey green
37	<i>Achras sapota</i> L.	Sapotaceae	Sacoché, saboché, sapotillier
38	<i>Delphinium ajacis</i> L.	Ranunculaceae	Larkspur
39	<i>Mangifera indica</i> L.	Anacardiaceae	Mango, mangoier
40	<i>Connarus paniculatus</i> Roxb.	Connaraceae	

the aqueous phase was removed with a Pasteur pipet. About 20 mg of sodium hydrogen sulfate monohydrate (extra pure) was added. The closed vial was agitated again and then centrifuged at $4500 \times g$ for 1 min. The clear supernatant solution was transferred to another vial for chromatographic analysis. The results are reported as percent FA of the oil. The GLC conditions were as follows: capillary column: CP-Sil 88, 100 m length, 0.25 mm i.d., film thickness 0.2 μm ; temperature program: from 155°C heated to 220°C (1.5°C/min), 10 min isotherm, injector 250°C, detector 250°C; carrier gas: 36 cm/s hydrogen, split 1:50; detector gas: 30 mL/min hydrogen, 300 mL/min air and 30 mL/min nitrogen, manual injection, volume 0.9 μL .

Preparation of FA derivatives. Whenever possible, easily prepared dimethyldisulfide (DMDS) adducts were used for the identification of unknown FA. In other cases, when this method was not recommended, other derivatives were prepared that showed more indicative (13) mass spectra.

The DMDS adducts were prepared as described by Francis

(12). The procedure described by Yu *et al.* (13) for the preparation of dimethyloxazoline (DMOX) derivatives of FA was modified as follows and has been described earlier (14): 15 mg of 2-amino-2-methylpropanol was added to 5 mg of the FA mixture in a two-necked flask equipped with a gas inlet, a reflux condenser, and a magnetic bar. The mixture was heated at 190°C under nitrogen for 1.5–2 h. The cooled mixture was triturated with 1 N KOH and extracted three times with hexane (10 mL). The extract was washed with water, dried over anhydrous sodium sulfate, and evaporated to dryness in a rotary evaporator.

For a clear identification of cyclopropenoic FA, the ether rearrangement products of these FA were prepared as described earlier by Ahmad *et al.* (15) and Eisele *et al.* (16). The silylated hydroxy-methoxy derivatives of the epoxy acids were prepared as described by Kleimann and Spencer (17).

Capillary GC-MS of the different derivatives. For a complete description of the FA composition of the different seed oils, unknown FA were identified by GC-MS analysis of the

different derivatives in the electron ionization mode (70 eV) on a Hewlett-Packard instrument Model 5890 Series II/5989 A, equipped with a 0.25- μm ZB-1 fused-silica capillary column (30 m \times 0.25 i.d.; Phenomenex, Torrance, CA). The carrier gas was helium at a flow rate of 1.0 mL/min.

The column temperature for the DMOX derivatives was initially held at 170°C for 5 min, then programmed from 170 to 250°C at 2°C/min. In the case of the DMDS adducts, the column temperature was initially held at 100°C for 2 min, then programmed from 100 to 280°C at 10°C/min. For the methyl ether rearrangement products as well as for the silylated hydroxy-methoxy derivatives, the column temperature was initially held at 140°C for 5 min, then programmed from 140 to 260°C at 4°C/min.

In all cases, the final temperature was held for 5 min. Other operating conditions were a split/splitless injector (split 1:20, temperature 280°C), an interface temperature of 280°C, and an ion source temperature of 200°C.

Statistical analysis. Student's *t*-test was used to evaluate the statistical significance of independent variables and interactions with two-tailed *t*-tests at $P = 0.01$ and 0.05 , respectively. Data were evaluated using the Statgraphics computer program (Rockville, MD).

Each method was carried out in triplicate for each species. The mean values are given in the tables without the SD, because this value would represent only the deviation in the method and not the variation in the appropriate species.

RESULTS AND DISCUSSION

Seeds from 40 plants belonging to 23 different families were analyzed with respect to oil content, FA, tocopherols, and tocotrienol composition. The FA content of six species had not been previously reported (i.e., *Delavaya toxocarpa*, *Aesculus sinensis*, *Canarium tramdenum*, *Erythrophleum fordii*, *Amaranthus mangostanus*, *Schizonepeta tenuifolia*), and for most of the samples no prior information about the vitamin E composition was available (9).

Oil content. Seed oil contents varied between 0.2 g/100 g for *Mangifera indica* and 75.7 g/100 g for *Calophyllum inophyllum* (Table 2). The oil content of most seeds was lower than that of seeds commonly used in commercial oil production, which contain between 20% (soybean) and more than 40% (rapeseed) oil. Only nine seeds contained more than 40% oil, whereas eight seeds contained less than 10% oil. Seeds of *C. inophyllum* (75.7 g/100 g), *C. tramdenum* (64.2 g/100 g), *Momordica cochinchinensis* (52.7 g/100 g), and *Cucurbita pepo* (48.8 g/100 g) had the most potential with respect to oil content. Regarding the economic aspects of oilseed production, a high oil content is important for the utilization of seeds.

FA composition. The seed oil FA compositions are summarized in Table 3. Most seeds contained FA commonly present in seed oils in different proportions, such as the saturated FA palmitic acid or stearic acid and the unsaturated FA oleic, linoleic, or linolenic acid. However, nine seed oils also contained unusual FA such as conjugated FA, cyclopropenoic FA,

or epoxy FA, and in the seeds of *A. mangostanus* squalene was found.

In addition to the normally occurring saturated FA, the seeds of *Nephelium lappaceum* contained remarkable amounts of arachidic acid (20:0) (33.2 g/100 g). This high amount of arachidic acid in *N. lappaceum* is typical for members of the genus *Nephelium*. Some other species of this genus, such as *N. maingayi* (37.2 g/100 g) or *N. daedaleum* (34.0 g/100 g) are described in the literature (18) as also having such high amounts of arachidic acid.

In the seed oil of *M. charantia*, a polyunsaturated conjugated FA (9*c*,11*t*,13*t*-octadecatrienoic acid) was found in the amount of 60.6 g/100 g. This conjugated FA was identified by the preparation of the DMOX derivative. The molecular ion at *m/z* 331 indicated the presence of three double bonds. Their position was easily recognized by applying an empirical rule for double bond location (19). The mass intervals of 12 *m/z*, instead of the regular 14 *m/z*, occurred between *m/z* 196 (C_9) and 208 (C_{10}), *m/z* 222 (C_{11}) and 234 (C_{12}), *m/z* 248 (C_{13}) and 260 (C_{14}), indicating three double bonds at the $\Delta 9$ -, $\Delta 11$ -, and $\Delta 13$ -positions of the FA. Takagi (20) described α -eleostearic acid (9*c*,11*t*,13*t*-octadecatrienoic acid) as a major isomer in *M. charantia*.

Similar amounts of this FA were also found in the seed oils of *M. cochinchinensis* (58.6 g/100 g), from the same family Cuburbitaceae, and for *Aleurites montana* (73.0 g/100 g), from the family Euphorbiaceae. Members of these two families contained the highest amounts of this FA, although other plant families, such as Chrysobalanaceae or Rosaceae, are also known to contain 9*c*,11*t*,13*t*-octadecatrienoic acid (9).

The structures of malvalic and sterculic acid were confirmed by GC-MS of their ether rearrangement products, but the expected ketone derivatives were not observed (21). The mass spectra of the ether rearrangement products are well known (16). They had base peaks at *m/z* 85 and intense peaks at *m/z* 55, 71, 81, and 95. Besides the molecular ions at *m/z* 326 and 340, respectively, characteristic fragments of the parent minus 32 mass, which indicate the loss of methanol from the molecular ion, were present in the spectra. These FA were found in the seed oils of *Hibiscus sabdariffa* and *Gnetum* sp. in the amounts of 0.5 g/100 g (sterculic acid) and 1.2 g/100 g (malvalic acid) in *H. sabdariffa* and 8.7 g/100 g (sterculic acid) and 32.0 g/100 g (malvalic acid) in *Gnetum* sp. Additionally, in both seed oils dihydrosterculic acid, a cyclopropanoic acid, was found (2.0 and 2.7 g/100 g, respectively). The same cyclopropanoic acid could also be detected in the seed oils of *Dimocarpus longan* and *Litchi chinensis*, both of which belong to the family Sapindaceae. In other members of this family investigated in this work, no dihydrosterculic acid was found.

Cyclopropenoic acids are characteristically found in plants of the order Malvales. From a nutritional point of view, these FA are important because they can inhibit various enzyme systems involved in FA biosynthesis, particularly in FA desaturation. Therefore, these FA may be toxic to higher animals and humans, and perhaps even (co-)carcinogenic (22–24). In plants these FA presumably have an effect as a chemical defense of

TABLE 2
Oil Content and Vitamin E Composition of Seeds from 40 Plant Species of Vietnam^a

Botanical name	Oil content [% of seed material]	α T *11.2 min	α T ₃ *13.8 min	β T *17.9 min	γ T *19.6 min	β T ₃ *22.7 min	P-8 *23.5 min	γ T ₃ *25.3 min	δ T *27.9 min	δ T ₃ *35.9 min	TTC
											(mg/kg oil)
<i>Raphanus sativus</i>	45.2				516		20	3	21		560
<i>Brassica campestris</i>	33.1	114	5		445		56		8		627
<i>Brassica</i> sp.	34.2	91	2		363		19		7		483
<i>Brassica juncea</i>	34.8	122	2		310		46		5		485
<i>Brassica chinensis</i>	40.1	140	1		415		34		11		602
<i>Brassica oleracea</i>	38.0	130	2	1	240		64		8		446
<i>Luffa cylindrica</i>	19.5	9		3	320				2		334
<i>Momordica charantia</i>	25.4	398		1	492			30			921
<i>Cucurbita pepo</i>	48.8	12			285	9		5	4		315
<i>Momordica cochinchinensis</i>	52.7	176		3	93				2		274
<i>Cucumis sativus</i>	33.2	4	73	4	75		16		913		1086
<i>Delavaya toxocarpa</i>	38.6	2	29		1	2					34
<i>Dimocarpus longan</i>	4.9	139	2	2	92				3		238
<i>Litchi chinensis</i>	1.4	345	925	64	105			127	121	7675	9361
<i>Nephelium lappaceum</i>	29.7	7	7		4			4	4		26
<i>Sapindus mukorossi</i>	31.8	66			208			31	26		331
<i>Aesculus sinensis</i>	18.3	195	97		88		69	626		336	1411
<i>Calophyllum inophyllum</i>	75.7	58	49	36	42			57		94	337
<i>Canarium tramdenum</i>	64.2	51		45	68				939		1104
<i>Hibiscus sabdariffa</i>	16.9	135		38	159		36		40		407
<i>Gnetum</i> sp.	3.2	23	29		11			17			81
<i>Camellia oleifera</i>	42.6	107									107
<i>Aleurites montana</i>	25.1	255			1206			34	44		1539
<i>Erythrophleum fordii</i>	12.5	599	45	45	159		167		32		1048
<i>Ipomoea aquatica</i>	8.9	63			680			35	36		813
<i>Amaranthus mangostanus</i>	5.4	94			580		36				710
<i>Corchorus olitorius</i>	12.7	397		38	1237		109		32		1812
<i>Basella rubra</i>	23.2	138			290		32		29		488
<i>Solanum melongena</i>	21.7	56		35	372		34		39		535
<i>Canavalia ensiformis</i>	1.0	58		34	186		52	29	608	33	1000
<i>Anethum graveolens</i>	18.2	96	102		29		45	69	30	29	401
<i>Coriandrum sativum</i>	19.7	46	96		31			231		41	445
<i>Schizonepeta tenuifolia</i>	29.7	64			546		33		37		681
<i>Ocimum basilicum</i>	19.7	52			828				47		928
<i>Perilla frutescens</i>	25.4	57		37	538				40		672
<i>Chrysanthemum coronarium</i>	17.4	929		49	31			35	31	28	1104
<i>Achras sapota</i>	7.1	57			40		32				128
<i>Delphinium ajacis</i>	44.1	120	566	78	83	153					1000
<i>Mangifera indica</i>	2	103	179								283
<i>Conarus paniculatus</i>	40.2	355		65	61		76				557

^aT = tocopherol; T₃ = tocotrienol; P-8 = plastochromanol-8; TTC = total amount of vitamin E compounds. *Retention times of the vitamin E components as given in the HPLC chromatogram.

plant roots against fungi (25). Andrianaivo-Rafehivola *et al.* (23) observed that a part of the cyclopropenoic acids may be destroyed by higher temperatures, such as those used for frying or cooking processes. Because of the toxic effect of these FA, it is important to remove them during a refining process before using the oil in nutrition applications.

In the seed oils of *Chrysanthemum coronarium* and *H. sabdariffa*, small amounts of epoxy FA were determined. Structural determination of the epoxy FA was carried out by GC-MS of their silylated hydroxy-methoxy derivatives resulting from the reaction of the FA with MeOH/BF₃ with further trimethylsilylation of the -OH group (17,26). The two FA were identified as 12,13-epoxy-octadec-cis-9-enoic acid (vernolic acid) in *H. sabdariffa* (2.7 g/100 g) and 9,10-epoxy-octadec-cis-12-enoic acid (coronanic acid) in *C. coronarium* (1.5 g/100 g). In

both cases the spectra confirmed the location of the original oxirane ring between C-12 and C-13 (vernolic acid) and C-9 and C-10 (coronanic acid). The position of the double bond at C-9 in vernolic acid was indicated by a strong peak at *m/z* 217.

Based on the preparation of DMOX derivatives, the acetylenic FA was identified as crepenynic acid (octadeca-9-en-12-ynoic acid), as described by Christie (27). The mass interval of 24 *m/z* between *m/z* 236 (C₁₁) and 260 (C₁₃) indicated a Δ 12 triple bond, whereas the mass interval between *m/z* 196 (C₉) and 208 (C₁₀) determined the double bond at the Δ 9-position. In the seed oil of *C. coronarium*, this unusual FA was found in the amount of 2.7 g/100 g.

The presence of higher amounts of erucic acid in the seed oils of the plants investigated was limited to seeds belonging to the family Brassicaceae. In these seed oils the contents ranged

TABLE 3
FA Composition (% of oil) of Seeds from 40 Plant Species of Vietnam^a

Botanical name	12:0	14:0	16:0	16:1n-7	18:0	18:1n-9	18:1n-11	18:2n-6	18:3n-3	18:3 conj	20:0	20:1n-9	22:0
<i>Raphanus sativus</i>	0.05	0.05	4.51	0.17	1.75	16.99	1.10	13.86	8.74		1.27	9.41	0.98
<i>Brassica campestris</i>	0.06	0.06	3.10	0.25	0.77	6.22	1.12	16.68	10.78		0.69	4.96	0.92
<i>Brassica</i> sp.	0.05	0.05	2.56	0.22	0.97	7.43	1.29	16.37	11.02		0.81	5.54	1.01
<i>Brassica juncea</i>	0.05	0.05	2.34	0.20	0.97	7.77	1.22	15.99	11.84		0.83	5.71	1.11
<i>Brassica chinensis</i>	0.03	0.03	1.99	0.16	1.22	18.13	1.02	11.66	7.13		0.91	7.24	1.19
<i>Brassica oleracea</i>	0.04	0.04	3.64	0.15	0.74	16.55	1.30	11.86	8.16		0.49	9.08	0.41
<i>Luffa cylindrica</i>	0.07	0.07	14.02	0.10	7.18	33.07	0.61	42.98	0.19		0.44	0.09	0.10
<i>Momordica charantia</i>	0.02	0.02	2.10	0.06	26.15	3.72	0.11	4.94	0.07	60.60	0.57	0.34	1.12
<i>Cucurbita pepo</i>	0.08	0.08	17.79	0.06	7.98	15.46	0.50	56.19	0.23		0.36	0.09	0.10
<i>Momordica cochinchinensis</i>	0.03	0.03	2.05	0.11	17.99	7.92	0.10	10.49	0.24	58.61	0.25	0.25	0.22
<i>Cucumis sativus</i>	0.07	0.07	13.65	0.11	10.41	18.01	0.61	54.32	0.37		0.37	0.07	0.06
<i>Delavaya toxocarpa</i>	0.01	0.01	4.20	0.05	2.12	39.10	0.54	2.72	0.62		9.65	37.49	0.78
<i>Dimocarpus longan</i>	0.26	0.26	12.15	0.18	8.04	36.87	0.66	8.40	2.65		4.27	1.90	2.74
<i>Litchi chinensis</i>	0.19	0.19	8.36	0.09	3.70	23.80	0.69	6.60	4.31		0.61	0.77	0.26
<i>Nephelium lappaceum</i>	0.02	0.02	4.12	0.34	5.16	36.22	1.18	2.99	0.20		33.24	8.24	3.92
<i>Sapindus mukorossi</i>	0.03	0.03	5.27	0.22	1.39	52.39	2.43	8.35	1.37		4.93	20.57	0.86
<i>Aesculus sinensis</i>	0.18	0.18	12.60	2.66	1.58	29.99	4.12	16.17	23.33		0.11	0.26	0.32
<i>Calophyllum inophyllum</i>	0.02	0.02	14.00	0.24	14.78	44.99	0.86	20.96	0.17		0.89	0.25	0.26
<i>Canarium tramdenum</i>	0.05	0.05	25.19	0.45	5.69	32.41	0.64	34.00	0.43		0.29	0.08	0.13
<i>Hibiscus sabdariffa</i>	0.15	0.15	17.17	0.47	2.77	27.38	1.01	42.49	0.28		0.39	0.03	0.33
<i>Gnetum</i> sp.	0.13	0.13	8.11	0.14	9.18	16.36	1.09	3.39	3.68		1.85	0.57	1.18
<i>Camellia oleifera</i>	0.05	0.05	10.63	0.11	3.48	77.89	1.09	5.03	0.17		0.07	0.30	0.43
<i>Aleurites montana</i>	0.03	0.03	2.54	0.02	2.41	8.02	0.36	10.25	0.03	73.00	0.16	1.01	0.09
<i>Erythrophloeum fordii</i>	0.03	0.03	11.18	5.07	6.44	20.60	14.30	37.00	0.23		1.39	0.13	0.34
<i>Ipomoea aquatica</i>	0.23	0.23	20.92	0.19	9.87	31.82	1.05	27.66	1.05		2.22	0.14	0.87
<i>Amaranthus mangostanus</i>	0.29	0.29	19.08	0.19	3.19	18.82	1.26	44.68	0.14		0.92	0.24	0.02
<i>Corchorus olitorius</i>	0.08	0.08	14.08	0.18	2.82	9.58	1.18	66.39	1.96		0.88	0.26	1.25
<i>Basella rubra</i>	0.11	0.11	18.51	0.81	6.43	47.44	4.27	15.82	0.28		1.46	0.27	0.63
<i>Solanum melongena</i>	0.12	0.12	9.49	0.22	3.22	14.53	1.00	68.95	1.49		0.23	0.08	0.12
<i>Canavalia ensiformis</i>	0.44	0.44	14.99	0.13	2.17	37.21	4.05	21.17	8.25		0.74	0.64	0.39
<i>Anethum graveolens</i>	0.07	0.07	3.64	0.21	0.87	7.79	0.82	5.51	0.34		0.12	0.03	0.01
<i>Coriandrum sativum</i>	0.05	0.05	2.91	0.19	0.51	14.26	0.82	14.23	0.20		0.07	0.31	0.06
<i>Schizonepeta tenuifolia</i>	0.05	0.05	9.11	0.12	1.65	7.43	1.48	29.18	42.45		0.21	0.19	0.06
<i>Ocimum basilicum</i>	0.03	0.03	7.33	0.12	2.60	11.41	0.78	24.89	54.58		0.16	0.11	0.04
<i>Perilla frutescens</i>	0.03	0.03	6.48	0.11	2.15	11.41	0.97	17.93	59.37		0.17	0.13	0.04
<i>Chrysanthemum coronarium</i>	0.07	0.07	9.40	0.11	2.25	3.91	0.51	77.75	0.14		0.49	0.11	0.24
<i>Achras sapota</i>	0.13	0.13	20.31	0.03	9.29	55.08	0.40	11.80	0.42		0.78	0.67	0.24
<i>Delphinium ajacis</i>	0.04	0.04	4.44	0.08	2.17	46.46	0.71	15.39	1.68		0.22	26.92	0.22
<i>Mangifera indica</i>	0.11	0.11	7.77	0.05	28.25	48.88	0.15	6.34	1.25		2.64	0.29	0.75
<i>Conarus paniculatus</i>	0.20	0.20	25.21	0.10	4.01	30.05	0.62	37.87	0.50		0.23	0.29	0.25

(Continued)

TABLE 3 (Continued)

Botanical name	22:1n-9	22:2n-6	24:0	18:1n-12	9,10-cpa-19:0	9,10-cpe-19:1	8,9-cpe-18:1	12,13-O-18:1Δ9c	7,8-cpa-17:0	18:2Δ9c,12a	9,10-O-18:1Δ12c	Squalene
<i>Raphanus sativus</i>	35.69	0.35	0.87									
<i>Brassica campestris</i>	44.11	2.07	0.69									
<i>Brassica sp.</i>	43.34	1.62	0.64									
<i>Brassica juncea</i>	43.27	1.46	0.67									
<i>Brassica chinensis</i>	44.20	0.52	0.39									
<i>Brassica oleracea</i>	42.05	0.45	0.29									
<i>Luffa cylindrica</i>		0.11	0.09									
<i>Momordica charantia</i>												
<i>Cucurbita pepo</i>			0.54									
<i>Momordica cochinchinensis</i>		0.06	0.03									
<i>Cucumis sativus</i>		0.07	0.16									
<i>Delavaya toxocarpa</i>	0.91		0.16									
<i>Dimocarpus longan</i>			2.41		16.93							
<i>Litchi chinensis</i>					38.03				4.31			
<i>Nephelium lappaceum</i>	1.06	0.60	0.79									
<i>Sapindus mukorossi</i>	0.75		0.50									
<i>Aesculus sinensis</i>	0.35		0.16									
<i>Calophyllum inophyllum</i>	0.06		0.85									
<i>Canarium tramdenum</i>		0.04	0.09									
<i>Hibiscus sabdariffa</i>			0.19		2.05		1.33			2.70		
<i>Gnetum sp.</i>	0.39		0.44		2.70		32.25					
<i>Camellia oleifera</i>	0.03	0.32	0.17									
<i>Aleurites montana</i>	0.04	0.06	0.05									
<i>Erythrophleum fordii</i>			0.33									
<i>Ipomoea aquatica</i>		0.65	1.54									
<i>Amaranthus mangostanus</i>		0.11										
<i>Corchorus olitorius</i>	0.18	0.09	0.31									
<i>Basella rubra</i>			3.84									
<i>Solanum melongena</i>		0.03	0.15									
<i>Canavalia ensiformis</i>	0.28	.26	1.27									
<i>Anethum graveolens</i>	0.06		0.04	70.30								
<i>Coriandrum sativum</i>		0.06	0.07	78.76								
<i>Schizonepeta tenuifolia</i>	0.03	0.05										
<i>Ocimum basilicum</i>			0.05									
<i>Perilla frutescens</i>		0.04										
<i>Chrysanthemum coronarium</i>	0.03	0.09								2.67		1.51
<i>Achras sapota</i>		0.02	0.39									
<i>Delphinium ajacis</i>	0.05	0.12	0.24									
<i>Mangifera indica</i>	0.01		0.89									
<i>Conarus paniculatus</i>		0.22	0.14									

^a-cap- designates a cyclopropane ring; -cpe-designates a cyclopropene ring.

TABLE 4
Correlation Coefficients Between the Oil Content, FA, Tocopherols and Tocotrienols^a

	16:0	18:0	18:1	18:2	18:3	20:1	22:1	α T	β T	γ T	δ T	α T ₃	β T ₃	γ T ₃	δ T ₃	TTC
Oil content	-0.08	-0.03	-0.02	-0.03	0.07	0.27	0.30	-0.20	0.00	-0.12	0.16	-0.01	0.18	-0.18	-0.31*	-0.23
16:0		0.08	0.16	0.47 ⁺	-0.39*	-0.37*	-0.57 ⁺	0.00	0.25	-0.08	0.36*	-0.18	0.12	0.05	0.02	0.07
18:0			-0.02	-0.14	0.16	-0.25	-0.31*	0.04	-0.13	-0.17	0.02	0.05	-0.08	-0.15	0.08	-0.15
18:1				-0.36*	-0.47 ⁺	0.15	-0.51	-0.31*	-0.06	-0.52*	-0.02	0.29	0.15	0.23	0.00	-0.34*
18:2					-0.23	-0.32*	-0.12	0.36*	0.29	0.23	0.24	-0.18	-0.05	-0.11	-0.17	0.25
18:3						-0.16	-0.03	0.06	-0.17	0.51*	-0.10	-0.16	-0.08	0.01	-0.09	0.20
20:1							0.03	-0.20	0.00	-0.16	-0.14	0.37*	0.48*	-0.15	-0.11	-0.20
22:1								-0.15	-0.33*	0.17	-0.16	-0.25	-0.15	-0.22	-0.33*	-0.13
α T									0.45 ⁺	0.06	-0.16	0.01	-0.03	0.10	0.23	0.47*
β T										-0.15	0.13	0.48*	0.38*	0.06	0.62*	0.60*
γ T											-0.13	-0.27	-0.11	-0.19	-0.17	0.39*
δ T												-0.05	-0.06	-0.08	-0.07	0.22
α T ₃													0.86*	0.18	0.28	0.27
β T ₃														-0.07	-0.05	0.09
γ T ₃															0.40*	0.36*
δ T ₃																0.83*

^a α T = α -tocopherol; β T = β -tocopherol; γ T = γ -tocopherol; δ T = δ -tocopherol; α T₃ = α -tocotrienol; β T₃ = β -tocotrienol; γ T₃ = δ -tocopherol; δ T₃ = δ -tocotrienol; TTC = total amount of vitamin E compounds. ⁺ Significant at 0.05 probability level; *significant at 0.01 probability level.

from 35.7 g/100 g for *Raphanus sativus* to 44.2 g/100 g for *Brassica chinensis*. This FA is characteristic of members of this family, although some species contain no or only very low amounts of erucic acid (28,29). Because the presence of this FA in higher concentrations is confined to only very few families, erucic acid is described in the literature as a chemotaxonomic feature of members of this family (29).

Vitamin E. As further important criteria for the assessment of seed oils, the contents and composition of tocopherols, tocotrienols, and P-8 were determined; these data are presented in Table 2. The contents of vitamin E varied between 26 mg/kg for *N. lappaceum* and 9361 mg/kg for *L. chinensis*.

The seed oils of most of the plant seeds contained amounts of vitamin E characteristic of commonly used vegetable oils (100 to 1000 mg/kg). The seed oils of only *A. sinensis*, *A. montana*, *Corchorus olitorius*, and *L. chinensis* contained amounts of vitamin E (1411, 1539, 1812, and 9361 mg/kg, respectively) that could be of interest in the production of naturally occurring tocopherols and tocotrienols for the stabilization of fats and oils against oxidative deterioration or for application in dietary, pharmaceutical, or biomedical products (30).

Tocopherols were obviously the predominant group of vitamin E-active compounds in most of the seed oils. Nevertheless, some of the seed oils contained remarkable amounts of tocotrienols. In only six seed oils was α -tocopherol the predominant vitamin E component. In the seed oils of *C. coronarium* (929 mg α -tocopherol/kg oil) and *E. fordii* (599 mg/kg oil), the amount of α -tocopherol was comparable to that in commonly used edible oils containing high amounts of α -tocopherol, such as sunflower oil or wheat germ oil. Therefore, these seed oils could be of value for the production of vitamin E concentrates.

In nearly half of the seed oils, γ -tocopherol was the predominant tocopherol, whereas its part of total vitamin E varied from 53.4 to 95.9%. In two seed oils, no γ -tocopherol was found at all; α -tocopherol and α -tocotrienol, respectively, were predominant in these seed oils (*Camellia oleifera* and *Mangifera indica*). Only three seed oils (*C. trandenum*, *Cucumis sativus*,

and *Canavalia ensiformis*) contained appreciable amounts of δ -tocopherol (939, 913, and 608 mg/kg, respectively), which is described as having a low biological activity (6).

β -Tocopherol was found in the seed oils of only *L. chinensis*, *Delphinium ajacis*, and *Conarus paniculatus*, where the amounts ranged from 65 to 107 mg/kg.

In eight seed oils, instead of tocopherols the appropriate unsaturated derivatives, tocotrienols, were found as the predominant vitamin E group. In these seeds the content of tocotrienols varied from 57.2 to 82.0% of the total vitamin E content. The highest amount of one individual tocotrienol, δ -tocotrienol, was found in the seed oil of *L. chinensis* in an amount of 7675 mg/kg. In the other seeds α - and γ -tocotrienol were predominant.

Higher amounts of P-8 were detectable in the seed oils of only *E. fordii* (167 mg/kg) and *C. olitorius* (109 mg/kg).

Correlations. Correlation coefficients between oil content, FA, and vitamin E are given in Table 4. In the present investigation, the oil content was positively correlated with the content of erucic acid ($r = 0.30$) and negatively correlated with the content of δ -tocotrienol ($r = -0.31$). No further correlations were found between oil content and other characteristic features determined in this study.

A negative correlation ($r = 0.34$) was found between the total vitamin E content and the content of oleic acid. Other FA showed no correlation with the total vitamin E content.

Some correlations between different FA were obvious. Here especially, the negative correlation between the contents of oleic and erucic acids should be mentioned ($r = -0.51$). This high correlation was mainly characteristic of the members of the Brassicaceae family, which contained the highest amounts of erucic acid.

Goffman *et al.* (28) found a strong correlation between linolenic and erucic acid, which could not be confirmed in the present study when taking into account only the members of the Brassicaceae family. A negative correlation was also found between oleic acid on the one hand and linoleic and linolenic acids on the other. This result is in agreement with results published by Goffman *et al.* (28).

The strong positive correlation between the contents of linolenic acid and γ -tocopherol ($r = 0.51$) shows that plants with seeds containing high amounts of PUFA in the seed oil produce more of the more active antioxidants, i.e., γ -tocopherol, than other seeds. The content of oleic acid was negatively correlated with α -tocopherol, γ -tocopherol, and total vitamin E, which could be an indication that tocopherols are unnecessary to protect oils with a high content of oleic acid against oxidative deterioration.

In addition, a strong positive correlation was found between β -tocopherol and δ -tocotrienol ($r = 0.60$). One unexpected result was the correlation between δ -tocopherol and saturated palmitic acid ($r = 0.36$). Contrary to other studies carried out in corn germ oil (31), rapeseed (32), and *Ribes* species (33), which found a strong correlation between oil content and γ -tocopherol, in the present study this result could not be confirmed. A possible explanation could be that the studies cited investigated individual families in which this correlation was given, whereas the present study comprised 23 different families.

ACKNOWLEDGMENTS

The authors would like to thank Birgitta Bielefeld and Dr. Ludger Bruhl from the Institute of Lipid Research for their skillful assistance. In addition, the authors are grateful to the German Academic Exchange Service (DAAD) for their financial support, which enabled Dr. Pham Quoc Long to stay in Germany.

REFERENCES

- Murphy, D.J., The Future of New and Genetically Modified Oil Crops, in *Perspectives on New Crops and New Uses*, edited by J. Janick, ASHS Press, Alexandria, VA, 1999, pp. 216–219.
- Murphy, D.J., Engineering Oil Production in Rapeseed and Other Oil Crops, *TIBTECH* 14:206–213 (1996).
- Kamal-Eldin, A., S. Gorgen, J. Pettersson, and A.-M. Lampi, Normal-Phase High-Performance Liquid Chromatography of Tocopherols and Tocotrienols: Comparison of Different Chromatographic Columns, *J. Chromatogr.* 881:217–227 (2000).
- Beringer, H., and W.U. Dompert, Fatty Acid- and Tocopherol-Pattern in Oil Seeds, *Fette Seifen Anstrichm.* 78:228–231 (1976).
- Kamal-Eldin, A., and R. Andersson, A Multivariate Study of the Correlation Between Tocopherol Content and Fatty Acid Composition in Vegetable Oils, *J. Am. Oil Chem. Soc.* 74:375–380 (1997).
- Pongracz, G., H. Weiser, and D. Matzinger, Tocopherole—Antioxidantien der Natur, *Fat Sci. Technol.* 97:90–104 (1995).
- Papas, A.M., Oil-Soluble Antioxidants in Foods, *Toxicol. Ind. Health* 9:123–149 (1993).
- Olejnik, D., M. Gogolewski, and M. Nogala-Kalucka, Isolation and Some Properties of Plastochromanol-8, *Nahrung* 41:101–104 (1997).
- Bundesanstalt fur Getreide-, Kartoffel- und Fettforschung (BAGKF), Seed Oil Fatty Acids, www.bagkf.de/sofa (accessed February 2002).
- Balz, M., E. Schulte, and H.-P. Thier, Trennung von Tocopherolen und Tocotrienolen Durch HPLC, *Fat Sci. Technol.* 94:209–213 (1992).
- ISO, ISO/DIS 5509:1998—Animal and Vegetable Fats and Oils—Preparation of Methyl Esters of Fatty Acids, International Organization for Standardization, Geneva, Switzerland, 1998.
- Francis, G.W., Alkylthiolation for the Determination of Double-Bond Position in Unsaturated Fatty Acid Esters, *Chem. Phys. Lipids* 29:369–374 (1981).
- Yu, Q.T., B.N. Lin, J.Y. Zhang, and Z.H. Huang, Location of Double Bonds in FA of Fish Oil and Rat Testis Lipids. GC-MS of the Oxazoline Derivatives, *Lipids* 24:79–83 (1989).
- Tsevegsuren, N., K. Aitzetmuller, and K. Vosmann, Unusual FA in Compositae: γ -Linolenic Acid in *Saussurea* spp. Seed Oils, *J. High Resolut. Chromatogr.* 20:315–320 (1997).
- Ahmad, M.S., Jr., M.U. Ahmad, S.M. Osman, and J.A. Ballantine, *Eriolaena hookeriana* Seed Oil: A Rich Source of Malvalic Acid, *Chem. Phys. Lipids* 25:29–38 (1979).
- Eisele, T.A., L.M. Libbey, N.E. Pawlowski, J.E. Nixon, and R.O. Sinnhuber, Mass Spectrometry of the Silver Nitrate Derivatives of Cyclopropenoid Compounds, *Chem. Phys. Lipids* 12:316–326 (1974).
- Kleimann, R., and G.F. Spencer, Gas Chromatography–Mass Spectrometry of Methyl Esters of Unsaturated Oxygenated Fatty Acids, *J. Am. Oil Chem. Soc.* 50:31–38 (1973).
- Shukla, V.K.S., and U. Blicher-Mathiesen, Studies in Evaluation of Unconventional Oils from Southeast Asia, *Fat Sci. Technol.* 95:367–369 (1993).
- Zhang, J.Y., Q.T. Yu, B.N. Liu, and Z.H. Huang, Chemical Modification in Mass Spectrometry IV—2-Alkenyl-4,4-dimethylloxazolines as Derivatives for the Double Bond Location of Long-Chain Olefinic Acids, *Biomed. Environ. Mass Spectrom.* 15:33–44 (1988).
- Takagi, T., Occurrence of Mixtures of Geometrical Isomers of Conjugated Octadecatrienoic Acids in Some Seed Oils: Analysis by Open-Tubular Gas–Liquid Chromatography and High-Performance Liquid Chromatography, *Lipids* 16:546–551 (1981).
- Hosamani, K.M., Fatty Acids in Seed Oil from *Turnera ulmifolia*, *Phytochemistry* 34:1363–1365 (1993).
- Schuch, R., and F. Ahmad, Structure and Biological Significance of Triacylglycerols Containing Cyclopropene Acyl Moieties, *Fat Sci. Technol.* 89:338–339 (1987).
- Andrianaivo-Rafehivola, A.A., J.M. Cao, and E.M. Gaydou, Effects of Fresh and Heated Baobab Seed Oil Feeding on Growth, Food Consumption and Weight of Some Organs in Rats, *Rev. Fr. Corps Gras* 41:53–59 (1994).
- Cao, J., J.P. Blond, and J. Bezaud, Inhibition of FA Δ -6- and Δ -5-Desaturation by Cyclopropene Fatty Acids in Rat Liver Microsomes, *Biochim. Biophys. Acta* 1210:27–34 (1993).
- Schmid, K.M., and G.W. Patterson, Distribution of Cyclopropenoid Fatty Acids in Malvaceous Plant Parts, *Phytochemistry* 27:2831–2834 (1988).
- Spitzer, V., K. Aitzetmuller and K. Vosmann, The Seed Oil of *Bernardia pulchella* (Euphorbiaceae)—A Rich Source of Vernolic Acid, *J. Am. Oil Chem. Soc.* 73:1733–1735 (1996).
- Christie, W.W., Mass Spectrometry of Fatty Acids with Methylene-Interrupted Ene–yne Systems, *Chem. Phys. Lipids* 94:35–41 (1998).
- Goffman, F.D., W. Thies, and L. Velasco, Chemotaxonomic Value of Tocopherols in Brassicaceae, *Phytochemistry* 50:793–798 (1999).
- Kumar, P.R., and S. Tsunoda, Fatty Acid Spectrum of Mediterranean Wild Cruciferae, *J. Am. Oil Chem. Soc.* 55:320–323 (1978).
- Ivanov, S.A., and K. Aitzetmuller, Untersuchungen uber die Tocopherol- und Tocotrienol-Zusammensetzung der Samenole einiger Vertreter der Familie Apiaceae, *Fat Sci. Technol.* 97:24–29 (1995).
- Levy, R.D., Genetics of Vitamin E Content in Corn Grain, Ph.D. Thesis, University of Illinois, Urbana-Champaign, 1973.
- Goffman, F.D., and H.C. Becker, Genetic Variation of Tocopherol Content in a Germplasm Collection of *Brassica napus* L., *Euphytica* 125:189–196 (2002).
- Goffman, F.D., and S. Galletti, γ -Linolenic Acid and Tocopherol Contents in the Seed Oils of 47 Accessions from Several *Ribes* Species, *J. Agric. Food Chem.* 49:349–354 (2001).

[Received November 22, 2002; accepted July 8, 2003]