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Composition of Lipid Classes in the Morphologically Different Parts of the Olive Fruit, cv. *Coratina (Olea europaea* Linn.) *

G. Bianchi and G. Vlahov **

This paper reports on the distribution of "minor components" of olive oil in the four parts of olive fruit. The minor components are the nonglyceridic classes of compounds comprising vegetable oils. It was found that the classes and amounts of minor components varied to a great extent in the lipid fractions from skin, pulp, wood shell and seed. For 100 g of olives the weights of material comprising the minor components extracted by chloroform-ethanol (95:5) were the following: 103 mg in the skin, 200 mg in the pulp, 30 mg in the wood shells and 80 mg in the seeds. When the minor components were chromatographed by column chromatography or on thin-layer plates, the following classes of compounds were separated: alkanes, alkyl esters, methyl phenyl esters, steryl esters, aldehydes, alcohols, sterols, cyclic triterpenoids and very long chain free fatty acids.

Lipidzusammensetzung in morphologisch unterschiedlichen Geweben der Olivenfrucht, cv. *Coratina (Olea europaea* Linn.)

Dieser Beitrag behandelt die Verteilung von Bestandteilen des Olivenöls, die in verschiedenen Gewebeteilen in geringen Konzentrationen vorkommen. Bei diesen Bestandteilen handelt es sich um die nicht Glycerin-haltigen Verbindungsklassen des Pflanzenöls. Die qualitative und quantitative Zusammensetzung dieser Bestandteile ist sehr unterschiedlich in den Lipidfraktionen, die aus der Schale, dem Fruchtfleisch, der Samenschale und dem Samen extrahiert wurden. Aus 100 g Oliven wurden Chloroform-Ethanol-Extrakte (95:5) hergestellt. Die in geringen Konzentrationen vorkommenden Substanzen wiesen folgende Anteile auf: 103 mg in der Schale, 200 mg im Fruchtfleisch, 30 mg in der Samenschale und 80 mg im Samen. Die Komponenten wurden mit Hilfe der Säulen- oder Dünnschichtchromatographie aufgetrennt. Folgende Substanzen konnten nachgewiesen werden: Alkane, Alkylester, Methylphenylester, Sterylester, Aldehyde, Alkohole, Sterine, cyclische Triterpenoide und sehr langkettige freie Fettsäuren.

Introduction

The olive fruit is a drupe schematically constituted by the skin (epicarp), the pulp (mesocarp) and the stone (endocarp) that includes the seed. The main components that make up almost the 98–99 % of the whole olive oil are substances of glyceridic nature concentrated in the pulp and in the seed. The remaining nonacylglycerol lipid fraction consists of a mixture of classes of compounds including alkanes, squalene, esters, fatty alcohols, tetracyclic (sterols) and pentacyclic triterpenes (acids, alcohols and esters) and free fatty acids. The free fatty acid proportions are in the narrow range 1–3 % for olive oils obtained simply by pressing the fruit, whereas their percentage may reach values as high as 10–15 % for solvent extracted oil ("sansa" olive oil). The minor classes of compounds, their concentration proportions and relative percentages are determinant elements for the characterization and the commercial grading of olive oil[1]. Besides, it has been pointed out that some of these minor components represent the factors that determine the stability of this commodity[2] and that they are also relevant for a salutistic point of view[2-4].

The natural concentration in an oil of these components may vary to a great extent and mainly in relation to the genetic asset of the cultivar, the ripeness of the drupes and to the extraction technique adopted and to a lesser degree by the soil and the climate[2].

Despite the great deal of information available on olive oil composition, only a limited number of studies on the minor components present in the morphologically different parts of the olive fruit are available in the literature. Parenthetically, even the composition of triacylglycerols present in the seed of olive pits is scarcely documented[5].

A variety of procedures have been applied to the analysis of olive oil components for its characterization and a great deal of data tabulated and discussed[6-13].

In the cited studies, the compositional analyses were carried out after saponification of the lipid samples, purification and recovery of the unsaponifiable substance by TLC and final analysis after derivatization of the various classes of substances by GLC.

The procedure of hydrolyzing the lipid samples with aqueous potassium or sodium hydroxyde, however, caused possibly loss of components in different proportion and did not allow to evaluate the classes of compounds originally present in different forms. Thus, for example, the described approach could not permit to distinguish between neither free and esterified triterpenoids nor long chain alcohols and their ester derivatives.

This piece of research was planned with the aim of describing the composition of the individual lipid classes present supposibly in varying proportions in the different morphological parts of the drupe.

In particular, the present investigation reports the results of the analysis of minor lipid constituents of olives of cv. *Coratina*. A major aim of this piece of research was to prove what part or proportion of the so called minor components of olive oil derives from the four parts of the drupe, skin, pulp, wood shell and seed.

Materials and Methods

Olive fruits cv. *Coratina* were collected in the Institute olive groves in 1991. The fruits (100 g), sound and healthy, were dipped into cold chloroform for about 60 seconds to obtain the surface lipid fraction.

Stones were removed manually from the drupes. Seeds were obtained by careful crashing the stones with a hammer. The flesh was triturated to homogeneity for 3 minutes in an Ultraturrax at medium speed.

Some neutral alumina and anhydrous sodium sulphate was added to the homogenate to absorb the moisture

* This paper is part 3 of a series; for part 2 see: *G. Bianchi, G. Vlahov, C. Anglani* and *C. Murelli*, Phytochemistry **32**, 49 [1993].

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content. The sample so obtained was treated with 50 ml of chloroform/ethanol (95:5), rehomogenized and transferred into a Soxhlet apparatus for a protracted thorough extraction of the lipid substances (300 ml $CHCl_3/C_2H_5OH$ 95:5).

The separated wood shells and seeds from the same olive batch were ground in an Ultraturrax for 5 minutes, as described above for the olive pulp. The powdered samples needed not to be dried and were extracted in a Soxhlet apparatus with chloroform/ethanol (95:5, 100 ml for each sample).

The extracts were dried over anhydrous sodium sulphate. The solutions were filtered and the solvent removed under reduced pressure in a rotary film evaporator to leave the crude extracts.

The extracted lipid fractions from the four parts of the olive drupe were separated into the component classes of compounds by silica gel column chromatography (CC). Elution was carried out with cyclohexane (A), chloroform plus 1 % EtOH (B), chloroform – 1 % ethanol – 1 % acetic acid (C). Eluent (A) gave alkanes, squalene, long chain aliphatic esters, methyl phenyl esters, aldehydes, sterylesters, (B) eluted triacylglycerols, (C) with increasing percentage of ethanol (1–2 %) eluted alcohols and aliphatic and alicyclic (triterpene) acids, in that order.

Thin layer chromatography (TLC)

(I) Analytical TLC was used to identify the lipid classes by comparison with authentic samples with various solvent systems (carbon tetrachloride, cyclohexane, chloroform, chloroform with varying proportion of ethanol in the range 1–3 %, chloroform-ethanol-acetic acid). All the lipid classes were visualized with a 3 % solution of CrO_3 in H_2SO_4 (1:1). The presence of sterols and other cyclic triterpenes was confirmed by the Liebermann-Burchard test and carbazole spray of TLC development. The analytical TLC plates were 20 × 20 cm coated with 0.25 mm layer of silica gel (G).

(II) Preparative thin-layer chromatography (Preparative TLC). A concentrated chloroform solution of lipid material (about 30–50 mg/plate) was applied uniformerly along a line on 20 × 20 cm home made plates coated with 1 mm layer of silica gel (G) and developed with the solvent systems used for analytical TLC.

After developing, a strip 1.5 cm wide from the edge of the plate, was sprayed with the CrO_3-H_2SO_4 solution for marking the separate zones. Each zone was carefully scraped from the plate and thoroughly extracted with the appropriate solvent.

Some fractions from CC needed to be purified by repeated preparative TLC before GLC and GC-MS analyses.

Acetyl derivatives

Free long chain aliphatic alcohols and triterpene alcohols were converted to acetates by allowing 5–10 mg samples of compounds to stand in acetic anhydride (1 ml) and pyridine (1 ml) in a flask for 24 h at room temperature. The crude residue obtained was mixed with water and then extracted with diethylether. The ether extract was washed with water and dried over anhydrous Na_2SO_4. The solution was filtered and the solvent evaporated off in the rotary evaporator to give the acetylated product. In the case of mixtures of classes of compounds, they were separated by preparative TLC.

Trimethylsilyl derivatives

Aliphatic and alicyclic compounds were converted to trimethylsilyl ethers with a silylation reagent made up of pyridine, hexamethyldisilazane (HMDS) and trimethylchlorosilane (TMCS) (in the ratio 2:1:1). The derivatized compounds were kept in *iso*-octane for GC and GC-MS analyses.

Gas liquid chromatography (GLC)

GLC was performed with a C. ERBA Mega Series instrument on a OV 1 fused-silica glass capillary column (25 m × 0.32 mm i. d., 0.1–0.15 μm film thickness). Injection was "on column" mode. Authentic samples of each class of compounds were used as standard. Flame ionization was used for detector.

Gas liquid chromatography-mass spectrometry (GC-MS)

A Hewlett-Packard Model 5890A capillary GC, equipped with a HP 5970 B mass selective detector was used for identification of the compounds by comparison of their mass spectra with reference spectra. The capillary column used was directly introduced into the ion source operating in the electron impact mode (EI). The chromatographic conditions were as follows: injector 250 °C, interface 280 °C, column oven programs as most appropriate. He was the carrier gas with a head pressure of 2.5–3.5 psi, 25 cm sec^{-1} linear velocity. The mass detector was optimized with the disk software under auto-tune condition with perfluorotributylamine calibration.

Mass spectra were acquired over 40–800 mass unit range at 1 scan sec^{-1} with ionizing electron energy 70 eV, electron current 0.3 mA, ion source 200 °C; the vacuum was 10^{-5} Torr. The samples were dissolved in suitable solvents and injected (1 μl) in a splitless mode.

High performance liquid chromatography (HPLC)

HPLC analyses were carried out on a LICHROSORB RP-18, 5 μm, 25 cm × 4.5 mm i. d. column (Merck) using MeCN-Me_2CO (1:1) as mobile phase at a flow rate of 0.7 ml min^{-1}. Samples were injected in a minimum volume of Me_2CO: compounds were detected by refractive index (RI). Authentic samples of each class of compounds were used as standard. Quantitation was based directly on area %. Shoulders were included with the main peaks.

Results and Discussion

The amount and weight of material extracted by chloroform-ethanol from skin, pulp, wood shell and seed of olive fruit are shown in Table 1. The composition of the lipid fractions as separate classes of compounds is also shown in Table 1.

Comparison of the data reveals spectacular differences among the four samples. For 100 g of olives, the amounts of minor components by weight in the skin, the pulp, the wood shell of the kernel and the seed were 103, 200, 30 and 80 mg, respectively. In percentage surface lipids contained the greatest proportion of the so called minor components of olive oil including the very long chain fatty acids.

Surface lipids comprised almost the whole of alkanes, wax esters, alkyl aryl esters, aldehydes, alcohols and triterpenoids. As expected, the major triacylglycerol proportions were found in the pulp and in the seeds. Our method of analysis did not allow to isolate and quantify neither the

Table 1

Weight and composition (%) of $CHCl_3$-EtOH extractable material of the epicarp, mesocarp, wood shell and seed

	Epicarp	Mesocarp	Wood Shell	Seed
Weight of $CHCl_3$-EtOH extractable lipids in mg 100 g^{-1} fruits	110	23000	210	600
Weight (mg 100 g^{-1} of fruits) of minor components and percentages in brackets	103 (93)	200 (0.9)	30 (14)	80 (13)
Olive fruit lipid classes and percentages				
Alkanes	8	tr	1.7	tr
Squalene	–	0.1	–	tr
Alkyl esters	2	tr	–	0.3
Methyl phenyl esters	2	–	–	–
Steryl esters	–	tr	1.1	2
Aldehydes	2	–	–	–
Triacylglycerols	3	92	78	80
Alcohols	10	tr	0.1	0.2
Free sterols	1	tr	tr	tr
Pentacyclic triterpenic alcohols with a cyclopropane ring	–	0.1	–	0.1
Pentacyclic triterpenic alcohols	6	tr	1.5	0.4
Triterpene acids	63	0.2	0.6	4
Free fatty acids	1	5	7	8
Unidentified*	2	2.6	10	5

* Minor proportion of monoacylglycerols were identified; see materials and methods

Table 2

Homologue compositions of lipid classes from epicarp (E), mesocarp (M), wood shell (W) and seed (S) of olive fruits

No of	Alkanes				Acids				Alcohols				Aldehydes			
C atoms	E	M	W	S	E	M	W	S	E	M	W	S	E	M	W	S
16					12	17	12	16								
18:0					7	4	3	4								
18:1					14	76	82	67								
18:2					–	3	3	6								
22	–	–	5	–	21	–	tr	4	10	tr	21	29				
23	11	–	7	–	tr	–	–	tr	1	3	6	3				
24	–	–	11	–	15	tr	–	1	22	63	25	38				
25	33	–	17	20	tr	–	tr	1								
26	4	–	14	–	29	tr	tr	1	45	16	29	5				
27	30	–	13	20	–	–	tr	1								
28	3	–	9	–	2	–	tr	tr	21	17	15	9	2			
29	15	19	9	31	–	–	–	tr								
30	tr	–	8	–	–	–	tr	–	1	1	4	8	12			
31	2	44	3	21												
32	–	–	2	–	–	–	–	–	–	–	–	8	64			
33	1	37	2	8												
34	–	–	–	–	–	–	–	–	–	–	–	–	22			
35	1															

tocols (tocopherols and tocotrienols) nor the chlorophylls, nor phenolic substances.

Hydrocarbons

Relevant proportions of alkanes were found in epicarp (8 %) and in the woody part of the kernel (1.7 %) whilst they were obtained in trace amounts from the pulp and seeds. They were a mixture of $C_{22}-C_{35}$ homologues and their chain length distributions are presented in Table 2.

The composition pattern of alkanes from the epicarp was similar to that found in most surface lipids[14, 15], with the odd series dominating over the even homologues.

A striking feature of the chain length distribution of alkanes from wood shell was the presence of a large proportion of homologues with even numbered chains. The total amount of even chain components was 49 % compared to the 7 % in epicarp, and the almost total absence in pulp and seeds. The extremely low amount of hydrocarbons

isolated from the pulp and seeds permitted the identification of only the normal alkanes C_{25} through C_{33}.

In the same range, however, the chromatograms presented other minor peaks to whom the tentative structures of iso- and anteiso-alkanes have been previously attributed[16, 17]. Squalene was detected only in the pulp.

Aliphatic alcohols, aldehydes and acids

The quantitative and qualitative compositions of the biosynthetically linked alcohols, aldehydes and free fatty acids are shown in Tables 1 and 2. Alcohols comprised 0.1 – 0.2 % of the stone lipids, reached the 10 % in the skin and were practically absent in the pulp. Aldehydes were present only in surface lipids. Apart the epicarp, free fatty acids were present in relevant amount in each lipid sample.

Their occurrence in the reported proportions is typical of solvent extracted olive oil ("sansa"). It might be tentatively inferred that they arise from lipolysis by endogenous lipases during homogenization and fractionation. The aliphatic acids from the epicuticular wax comprised, beside the fatty acids ($C_{16}-C_{18}$), the very long chain fatty acids in the range $C_{22}-C_{28}$ (Table 2). The homologue compositions of alcohols shown in Table 2 reveal as major chains even homologues C_{22} through C_{28}. In pulp and seed the dominant chain was C_{24}, 63 % and 38 % respectively, followed by varying proportions of homologues in the range $C_{22}-C_{32}$.

The presence of aldehydes was found confined to only the skin. The homologue composition showed a bell shaped pattern with C_{32} major component.

Long chain aliphatic esters and methyl phenyl esters

While long chain alkyl esters have been known for long time as common minor components of olive oil, methyl phenyl esters have been reported as olive lipids only recently[14]. This study has shown that alkyl esters are present in traces in the pulp, in low proportions in seeds and in relatively more consistent amount on the surface of olive fruit. Methyl phenyl esters were found only on the skin of the olives.

The chain length distribution of alkyl esters is presented in Table 3 where a comparison is apparent among the homologues from epicarp, mesocarp and seed. A common feature was that all the homologous esters were made up of straight chain alcohols and acids with an even number of carbon atoms[14]. The ester fraction from pulp resulted composed of the only two chains C_{36} and C_{38}. The latter were first reported by *Grob, Lanfranchi* and *Mariani* and were tentatively assigned the structure of esters of diterpene alcohols[19]. In the seeds the group of esters comprised the chains in the range $C_{40}-C_{48}$. The esters present in the epicarp lipids defined a two bell shaped curve, the first centered at the C_{40} chain, the second at the C_{52} homologue. The composition of methyl phenyl esters confirmed our previous report[14]. The long chain aliphatic acids esterified with benzyl alcohol were C_{26}, C_{28} and C_{30}.

Triterpenoids

(I) The free triterpene alcohol fractions were analysed both as acetyl derivatives and as trimethylsilyl derivatives.

Measurable amounts of cycloartenol and methylenecycloartanol were found both in the pulp and in the seeds (0.1 % each). In the pulp cycloartenol was twice methylenecycloartanol (Tables 1 and 4).

Monohydroxy pentacyclic triterpene amyrins were detected in all fruit parts but they could be isolated in measurable amount from all lipid fractions but pulp. The concentration of α-amyrin was in most cases higher than that of the isomer β-amyrin.

Table 3
Homologue compositions of alkyl and methyl phenyl esters from epicarp (E), mesocarp (M), wood shell (W) and seed (S) of olive fruits

No. of C atoms	E	M	W	S
Alkyl esters				
36	tr	57	–	–
38	3	43	–	–
40	17	–	–	16
42	15	–	–	29
44	3	–	–	28
46	1	–	–	18
48	2	–	–	9
50	8	–	–	–
52	23	–	–	–
54	18	–	–	–
56	8	–	–	
Methyl phenyl esters (acyl moiety)				
26	38	–	–	–
28	48	–	–	–
30	14	–	–	–

Table 4
Composition % of triterpenes from epicarp (E), mesocarp (M), wood shell (W) and seed (S) of olive fruits

Components	E	M	W	S
Cycloartenol	–	22	–	tr
24-Methylenecycloartanol	–	11	–	2
Oleanolic acid	44	8	29	90
Maslinic acid	47	59	–	–
α-Amyrin	–	tr	71	7
β-Amyrin	1	tr	–	1
Erythrodiol	4	tr	tr	tr
Uvaol	4	tr	tr	tr

Dihydroxy pentacyclic triterpenes erythrodiol and uvaol were found mainly in the lipid layer covering the fruit.

As regards triterpenic acids, oleanolic was found distributed in all parts of the drupe, whilst maslinic was concentrated in epicarp and mesocarp.

The identification of individual triterpene components was performed either by GLC co-chromatography with standard of GC-MS or by comparison of their relative retention times with literature data[18].

(II) Free sterols were found in measurable quantity only in the lipid fraction from the skin of the olive fruit.

The composition of the free sterol sample was found similar to that previously reported for the olive surface lipids[14]. *Fedeli, Grob* and coworkers[19, 20] report on a gas-chromatographic method that allowed them the detection of free campesterol, stigmasterol, β-sitosterol and Δ-5-avenasterol in several types of olive oils of certified origin. However, the morphological origin of the free sterols was not specified in the cited papers.

(III) The steryl ester fractions consisted of esters of sterols that have previously been identified in the nonsaponifiable fraction of olive oil according to standard procedures[21]. In fact, to our knowledge, all the studies concerning steryl esters have proceeded by hydrolysis of the intact molecules followed by separate analyses of the constituent sterol and acid moieties. Our efforts to identify the single component by gas chromatography – mass spectrometry (EI) failed. Molecular ions (M^+) were absent, as already reported in the literature[22]. However, in order to assign all compounds with a reasonable confidence, the reported GC elution order was applied[18]. Accordingly we found the following major steryl esters: campesterol (2–4 %), stigmasterol (1–2 %), clerosterol (1–2 %), β-sitosterol (75–80 %), Δ-5-avenasterol (5–11 %), others (1–16 %).

Triacylglycerols

They were obtained in pure form in the CC solvent B fractions. The molecular species were analysed by HPLC on the basis of their retention times. The latter were determined using authentic samples. Further attributions were reached by comparison with data available in the literature. The major molecular species of the pulp triacylglycerols were OOL+SLL (12.2 %), SOL+OOO (50.8 %) and POO (20 %), whilst the wood shell and seed oils were characterized by the same triacylglycerols species in 6.4 %, 16.8 %, 34.2 %, 48 % and 15.9 %, 27.9 %, yields respectively. The detailed compositions of the triacylglycerols are shown in Table 5.

Table 5

Composition % of triacylglycerols from epicarp (E), mesocarp (M), wood shell (W) and seed (S) of olive fruits

Components*	E	M	W	S
LLL	0.1	0.1	0.2	0.8
OLLn	0.1	0.1	0.1	0.1
OLL	2.0	1.1	0.7	6.3
PLL+OOLn	2.2	2.0	0.4	1.1
SLLn	0.1	0.4	0.2	0.1
OLL+SLL	8.0	12.2	6.4	16.8
POL	4.2	3.4	3.2	7.6
PLL	0.1	0.1	0.4	0.1
SOL+OOO	46.0	50.8	48.0	34.2
POO	25.0	20.0	27.9	15.9
PPO	2.0	2.2	3.9	1.7
PPP	7.1	1.0	4.0	0.1
SOO	1.0	4.9	3.3	3.4
PSO	2.0	1.3	1.1	0.7
SSO	0.1	0.4	0.2	0.1

* P = palmitic, St = stearic, O = oleic, L = linoleic, Ln = linolenic acid

Unidentified

Varying proportions of the chloroform-ethanol extracts from skin, pulp, wood shell and seed remained at the origin of the plate after the initial thin layer chromatography.

After acetylation and further preparative TLC the minor fractions obtained were analysed by GC-MS. The mass spectral analysis permitted the identification of only monoacylglycerols with the palmitoyl, oleoyl and stearoyl acid moieties at the 2*sn* position of glycerol.

Possible compounds making up the largest proportion of the unidentified fractions are triglyceride polymers, oxidized triglyceride monomers, diglycerides and lignans, the latter as regards the wood shells.

Conclusions

The results of the present study show significant quantitative and qualitative differences in the classes of compounds comprising the lipid fractions of the parts of the olive fruit. Inspection of the data of Table 1 reveals that more than 95 % of the classes of compounds comprising the lipid layer covering the olives is not of glyceridic nature but that such proportion decreases to 14–15 % in the wood shell and seed. Finally, as expected, the percentage of the minor components in the pulp is the lowest one, less than 1 %. Thus, being the yields of minor components, in 100 g of olives, 103 mg in the epicarp, 200 mg in the pulp, 30 mg in the woody part of the kernel and 80 mg in the seed, it follows that minor components are concentrated in the epicarp and in the seed.

From the observation of the data of Table 1 the most striking feature of the distribution of the lipid classes in the fractions studied is the consistent amount of free fatty acids found in all extracts but the lipids of epicarp. The fatty acids, in fact, isolated from these fractions exceeded largely the 0.5–2 % commonly found for cold pressed olive oil but are less than the amount commonly found in crude "sansa" oil.

A possible explanation of these findings, however, is that they originate from lipolysis occurring during homogenization and chromatographic separation.

Furthermore, consideration of the data obtained in this study, leads to the acknowledgment that not all the classes of compounds detected and identified, are found present in the mechanically extracted olive oil[1, 16].

Triacylglycerols, fatty acids, free aliphatic alcohols, pentacyclic triterpene acids were the lipid components present in every part of the olive, whilst alkanes and squalene, methyl phenyl esters, steryl esters, tetracyclic and pentacyclic mono and dihydroxy triterpene alcohols were not ubiquitous components of the olive fruit.

We believe that the presence – absence of some minor components in cold expressed olive oil is due to the extractive physical property of the natural organic "solvent" made up of several triacylglycerols. More precisely, the chemical structure and composition of triacylglycerols making up the liquid olive oil determine (I) its effectiveness as extractant of the other substances present in the whole olive drupe, (II) the distribution coefficient (defined as the ratio of the concentration of a substance in the extractant to that in the aqueous phase).

A third factor that should be taken into account when considering the chemical composition of olive oil of lower grade is that some substances present in the fruit may be soluble neither in water nor in the triacylglycerol mixture:

nevertheless they are extractable by other organic solvents such as hexane or petrol ether that are commonly used to obtaine "sansa" olive oil from pomace, and seed oils as well.

These considerations should make it plain that olive oil obtained by the simple physical procedures of milling and pressing the fruits followed by separation of the oil by decantation or centrifugation, should contain only the minor components extractable by triacylglycerols.

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Autosensitized Photooxidation of the Rose Hip (Wild Rose) Oil – Mechanism and Quantum Yield for Singlet Molecular Oxygen O_2 ($^1\Delta_g$) Generation

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The autosensitized photooxidation of the fatty acid components of rose hip (Wild Rose) oil was studied. Two important facts arise from the present investigation: a) Fatty acids of rose hip oil decompose upon visible light irradiation in the absence of external sensitizers by a mechanism that involves $O_2(^1\Delta_g)$. The pigments present in rose hip oil themselves efficiently sensitize the generation of $O_2(^1\Delta_g)$ with a quantum yield of 0.038 (upper limit). b) Visible irradiation also produces the degradation of the anthocyanines, native pigments which could behave as $O_2(^1\Delta_g)$ sensitizers in the oil. In this case a mechanism involving the production of superoxide ions by the pigment and further attack of the radicals on the phenol groups of the anthocyanine could account for the observed experimental evidences. These results should be carefully considered in a practical sense when rose hip oil is stored or employed under daylight conditions. Exposure to visible radiation may cause irreversible transformations in rose hip oil.

Selbstinduzierte Photooxidation des Wildrosenöles – Mechanismus und Quanten-Ausbeute für die Bildung des Singulett-Molekularsauerstoffes $O_2(^1\Delta_g)$

Die selbstinduzierte Photooxidation der im Wildrosenöl vorkommenden Fettsäuren wurde untersucht. Zwei wichtige Ergebnisse aus der vorliegenden Untersuchung sind: a) Fettsäuren des Wildrosenöles wurden unter Einwirkung des $O_2(^1\Delta_g)$ auch in Abwesenheit eines extern zugesetzten Sensibilisators zersetzt. Die im Öl vorhandenen Pigmente sind wirksam bei der Erzeugung von $O_2(^1\Delta_g)$ mit einer Quanten-Ausbeute von höchstens 0.038 b). Sichtbares Licht verursacht ebenfalls eine Zersetzung der Anthocyanine, natürlich vorkommender Pigmente, die sich als $O_2(^1\Delta_g)$-Sensibilisatoren im Öl verhalten. In diesem Fall ist die beobachtete Zersetzung von Pigmenten auf die Entstehung von Superoxid-Ionen durch das Pigment und auf den weiteren Angriff der gebildeten Radikale auf die phenolischen Gruppen der Anthocyanine zurückzuführen. In der Praxis sollten diese Ergebnisse z. B. bei der Lagerung und Verwendung des Wildrosenöles unter Tageslichtbedingungen kritisch berücksichtigt werden. Sichtbares Licht kann möglicherweise irreversible Veränderungen des Wildrosenöles verursachen.

Introduction

Rose Hip (RH) oil is susceptible to oxidation because it contains a large proportion of unsaturated fatty acids[1, 2]. In a recent study[2] we have investigated the kinetics of the dye-sensitized photooxidation of this oil in a process medi-

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