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# Contamination of Grape Seed Oil with Mineral Oil Paraffins

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The contamination of 11 commercial grape seed oils with paraffins of mineral oil origin was analyzed by online-coupled HPLC−HPLC−GC−FID and ranged from 43 to 247 mg $kg^{-1}$. The analysis of the marc and seeds indicated that the contamination is primarily from the peels. Since superficial extraction of the seeds with hexane removed most of the mineral paraffins, the contamination of the seeds is largely on the surface, perhaps transferred from the peels during storage of the marc. Mechanical purification of the seeds combined with washing with hexane reduced the contamination of the oil by a factor of about 10. The refining process removed 30% of the mineral paraffins, primarily the more volatile components. Oil obtained from the seeds of fresh grapes, including grapes not having undergone any phytochemical treatment, contained clearly less mineral paraffins (up to 14 mg $kg^{-1}$), and the peels were less contaminated, suggesting an environmental background contamination. To this an additional contamination might be added by a treatment of the grapes used for wine making.

**KEYWORDS: Grape seed oil; contamination by mineral paraffins; online LC−GC**

## INTRODUCTION

**Food Contaminated by Mineral Paraffins.** Foods are often contaminated with paraffins of mineral oil origin (mineral paraffins). Jute and sisal fibers used for manufacturing bags were treated with batching oils consisting of brown mineral oil fractions containing 20−25% aromatic hydrocarbons to improve their processing properties (*1, 2*). Foods transported and stored in these bags, such as hazelnuts, cocoa beans (chocolate), linseeds, and rice, were typically contaminated with mineral paraffins at 10−100 mg $kg^{-1}$. Also (mostly alkylated) aromatics were transferred to the foods (*3, 4*). Other food packaging materials may release paraffin waxes and oils at concentrations reaching several hundred milligrams per kilogram (*5*−*8*). Printing inks applied to cardboard boxes often contained paraffin oils as a solvent, migrating into the packed foods at 10−100 mg $kg^{-1}$ (*9*). In the early 1990s, lubricating oils and release agents used in the food industry often consisted of white paraffin oils; concentrations, e.g., in bread and bakery products, frequently exceeded 1000 mg $kg^{-1}$ (*10, 11*).

Used edible oils and fats (e.g., frying oils) from restaurants and public waste collection sites were admixed to animal feeds. Sometimes motor oil and other technical products were erroneously added and in this way ended up in animal feeds, resulting in contaminated meat and eggs (*12*). Animal feeds often also contain paraffin oil as a binder for minor components such as minerals and vitamins in powder form. Fish commonly contains mineral oil paraffins and aromatics on the order of 50−1000 mg $kg^{-1}$ referring to the fat (*2*), the sources of which have not been identified.

Broad contamination of plant material with mineral oil components occurs from the atmosphere (*13*). It consists of soot from vehicles, heating systems, and industry, with lubricating oil from diesel engines being a dominant component. The branched hydrocarbons degrade slowly and accumulate in the soil.

The evidence that the paraffins are of mineral origin is discussed in ref *14*. The presence of hopanes, triterpenoid hydrocarbons formed under geological conditions, was an important element.

So far, the investigation of the sources was the only way to obtain information about the material accompanying the mineral paraffins analyzed. Raw mineral oil fractions contain highly alkylated aromatics, whereas the white oils most commonly used in food contact are virtually free of these. Soot also contains nonalkylated polyaromatic compounds from combustion, whereas lubricating oils include additives, such as viscosity modifiers and antioxidants.

**Exposure to Mineral Paraffins.** On the basis of food consumption data and estimated concentrations in the food items, Heimbach et al. (*15*) calculated the mean human daily dietary

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exposure to mineral hydrocarbons in the United States as 0.875 mg $kg^{-1}$ body weight (bw). Tennant (*16*) estimated the mean and 97.5 percentile exposure in Europe as 0.39 and 0.91 mg $kg^{-1}$ bw, respectively, for adults and as 0.75 and 1.77 mg $kg^{-1}$ bw, respectively, for children. Surveillance data of the Official Food Control Authority of Zurich might have agreed with this assessment for the early 1990s, but since the major uses were stopped or have never been authorized in Europe (such as application to grain and rice for dedusting), exposure in Europe is probably substantially lower.

Toxicological findings regarding mineral paraffins are summarized in ref *17*. In an opinion from 1989, the EU-Scientific Committee on Food (SCF) concluded that "there was no toxicological justification for the continued use of mineral hydrocarbons as food additives" (*18*). A temporary tolerable daily intake (TDI) of 0−0.005 mg $kg^{-1}$ bw was set for oleum-treated mineral hydrocarbons and of 0−0.05 mg $kg^{-1}$ bw for hydrogenated products. Resulting limits in foods would have been in the range of 0.3−3 mg $kg^{-1}$, but were not imposed by legislation. In 1995, the SCF considered higher exposure safe provided the paraffins have a sufficiently high molecular mass not to be absorbed to a relevant extent (*19*). For paraffin waxes, a group acceptable daily intake (ADI) of 0−20 mg $kg^{-1}$ bw was allocated to highly refined products characterized by a minimum viscosity, a maximum of 5% components with a boiling point below that of the *n*-alkane C25, and an average molecular mass of no less than 500 Da. A temporary group ADI of 0−4 mg $kg^{-1}$ bw was set for paraffin oils specified by a minimum viscosity, a maximum of 5% components below *n*-C25, and an average molecular mass of no less than 480 Da (*n*-C34, 478 Da). In 2001, the SCF set an ADI of 0−6 mg $kg^{-1}$ bw for hydrogenated poly-1-decene containing 1.5% components with less than 30 carbon atoms (*20*). In 2006, the European Food Safety Authority (EFSA) evaluated "waxes, paraffinic, refined, derived from petroleum based or synthetic hydrocarbon feedstocks", with an average molecular massof no less than 450 Da (about C32), a minimum viscosity, and a "content of hydrocarbons with carbon number less than 25, not more than 40% (w/w)". Owing to lack of toxicity data, a restriction of 0.05 mg $kg^{-1}$ food was recommended (*21*).

In the fat of human milk, the mean concentration of mineral paraffins was 95 mg $kg^{-1}$, influenced by extremely high values (reaching 1300 mg $kg^{-1}$) (*17*); the median was 26 mg $kg^{-1}$. Typical contents in the milk of the first days of breast feeding were around 50 mg $kg^{-1}$. In tissue fat collected from 144 Austrian volunteers with Caesarean sections, mineral paraffins at 15−360 mg $kg^{-1}$ fat were determined, with an average of 60.7 mg $kg^{-1}$ and a median of 52.5 mg $kg^{-1}$ (*22*). It was estimated that mineral paraffins in the human body widely amount to 1 g and reach 10 g in extreme cases. The composition of the mineral paraffins was almost identical for all individuals, primarily consisting of unresolved iso- and cycloalkanes, in gas chromatographic retention times ranging from that of *n*-C17 to that of *n*-C32 and centered at that of *n*-C23/C24. The milk samples of day 4 contained virtually the same mixture as the tissue fat at concentrations between 10 and 355 mg $kg^{-1}$ (average, 44.6 mg $kg^{-1}$; median, 30 mg $kg^{-1}$), the fats from the day 20 milks <5−285 mg $kg^{-1}$ (average, 21.7; median, 10 mg $kg^{-1}$).

**Grape Seed Oils.** A substantial proportion of the edible oils were found to be contaminated with more than 10 mg $kg^{-1}$ mineral paraffins (*11, 23*), with maximum concentrations of around 1000 mg $kg^{-1}$. For some oils the contamination could be traced back to paraffin oils used in the oil mill, but for the majority the source was not identified. Higher concentrations were reached in edible oils adulterated with mineral oil, such as in some Ukrainian sunflower oils (*24, 25*).

Frequently, high concentrations were found in olive pomace oil (*26*) and grape seed oils. According to an oil producer, it is difficult to obtain grape seed oils containing less than 50 mg $kg^{-1}$ mineral paraffins. Grape seeds are a byproduct of wine and grappa manufacturing. The oil obtained from them is said to have good nutritional and sensory characteristics (*27, 28*), even though there is no general agreement, e.g., when compared to olive oil (*29*).

In this paper we provide data on the amount and the composition of the mineral paraffins in grape seed oils. To investigate potential sources of the contamination, the various stages of the production chain were investigated. Fresh grapes were separated into skin and pulp as well as seeds, which were analyzed separately. Also the raw material industrially used for extracting oil was investigated.

The method applied for determining mineral paraffins corresponded to that previously used (*13, 23*), conceived on the basis that no response factors can be determined for unknown mixtures of hydrocarbons and that, therefore, flame ionization detection (FID) must be used to enable the application of equal response for all hydrocarbons. Gas chromatography (GC) is adequate as it enables distinguishing between mineral paraffins and natural paraffins of plant origin (largely odd-numbered *n*-alkanes). Since FID is not selective and the mixtures of paraffins form broad humps of unresolved material, selectivity must be from the preseparation, which is achieved by two stages of high-performance liquid chromatography (HPLC). HPLC is coupled online with GC not only to automate the analysis, but also to rule out contamination of the samples and to achieve sufficient sensitivity by a complete transfer of the HPLC fraction containing the paraffins.

## MATERIALS AND METHODS

**Samples.** The refined grape seed oils O1−11 and the fresh grapes G1−4 were from the market in Zurich and the refined oils (O12−14) from Italian grape seed oil. Grapes without phytochemical treatment (bioG) were grown in a populated area near Zurich by one of the authors. Samples of grape marcs M1 and M2 and the industrial seeds IS1−3, obtained from an Italian wine producer, were from the harvests of the years 2004, 2005, and 2006. M3 was a grape marc from a small Italian home production. The industrial seeds IST, ISU, ISL, ISS, ISP, and ISA were from Tuscany, Umbria, Lazio, Sicily, Puglia, and Abruzzo, Italy, respectively.

To 5 g of dried grape seeds was added 15 mL of hexane. The mixture was homogenized (Polytron, Kinematica, Luzern, Switzerland) for 2 min and centrifuged. The extraction was repeated with 10 mL of hexane, homogenizing for 1 min. The extracts were allowed to dry, and the resulting oil was diluted to 50 mg $mL^{-1}$ in hexane for analysis. Peels and grape marc extracts were extracted in the same way and analyzed as hexane solutions of 250 mg $mL^{-1}$. The same procedure was applied to blank samples. Great care was taken to avoid grease on laboratory ware, hand creams, and other paraffin-containing products which could have contaminated the samples.

**Washing Experiment.** To 2 g of seeds ISP, manually purified from residues of peels and stems, was added 5 mL of hexane, and the resulting mixture was stirred for the time and at the temperature shown. Then the oil was extracted from the seeds as described above.

**NPLC−NPLC−GC−FID Analysis.** Samples were analyzed on an instrument for automated online HPLC−GC−FID from Thermo Scientific (Milano, Italy), consisting of a TriPlus autosampler, a Phoenix 40 dual syringe pump with 3 switching valves, and a Trace gas chromatograph equipped with on-column injector and a switching valve for the regulation of the transfer. On the first normal-phase HPLC (NPLC) column, 25 cm × 2 mm i.d., packed with Spherisorb Si 5 $\mu$m

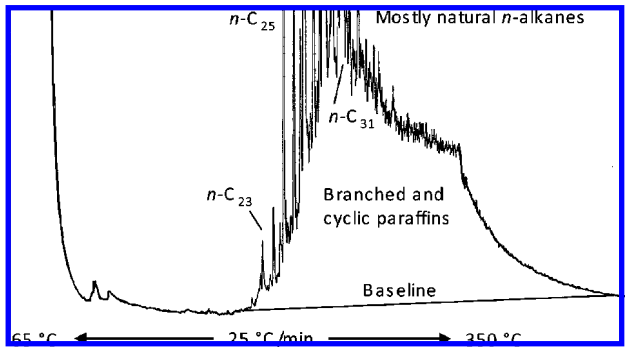


**Figure 1.** Typical NPLC−NPLC−GC−FID chromatogram of a grape seed oil contaminated by 70 mg $kg^{-1}$ mineral paraffins.

(Grom, Rottenburg-Hailfingen, Germany), 100 $\mu$L of diluted oil or extract was injected and chromatographed using hexane at a flow rate of 300 $\mu$L $min^{-1}$. This hexane (Brenntag, Schweizerhall AG, Basel, Switzerland) was passed through activated aluminum oxide and redistilled. The bulk of the oil was retained and backflushed with redistilled methyl *tert*-butyl ether (MTBE; Brenntag, Schweizerhall AG) at 300 $\mu$L $min^{-1}$ starting 4 min after injection (10 min). From the hydrocarbons transferred to the second NPLC column (25 cm × 2 mm i.d., packed with Lichrospher Si 60 5 $\mu$m, Grom), the paraffins were isolated, using the same mobile phase. A fraction of 1 min width (300 $\mu$L), starting from breakthrough, was transferred to the GC instrument through the on-column interface by the retention gap technique (*30*), using a 7 m × 0.53 mm i.d. uncoated deactivated precolumn ahead of a solvent vapor outlet and a 5 m × 0.25 mm i.d. separation column coated in the laboratory with a 0.15 $\mu$m film of PS-255 (a dimethylpolysiloxane from Fluka, Buchs, Switzerland). Transfer and solvent evaporation occurred at an oven temperature of 65 °C (7 min) and was followed by a temperature program of 25 °C $min^{-1}$ to 350 °C (5 min). The carrier gas (hydrogen) was regulated at 50 kPa of inlet pressure. The solvent vapor exit was switched to a strong restriction 2 s before the end of solvent evaporation. The duration of solvent evaporation was determined by the flame method: the effluent from the vapor outlet was lit and the time up to the disappearance of the yellow flame measured by means of a stop watch. The concentration of the mineral paraffins was determined as described in ref *31*, using a pure paraffin oil (gift from a candy manufacturer) as the external standard added to a virtually clean vegetable oil at 100 mg $kg^{-1}$. The detection limit (LOD) and the quantification limit (LOQ) in the oils were around 3 and 8 mg $kg^{-1}$, respectively; in the peels and stems they were 0.3 and 1 mg $kg^{-1}$, respectively. All samples were analyzed at least in duplicate, and the reported values are averages. Measurement uncertainty was largely determined by the interpretation of the chromatogram and ranged from 15% to 30% (*30*).

## RESULTS AND DISCUSSION

**Figure 1** shows a typical NPLC−NPLC−GC−FID chromatogram of a refined grape seed oil containing 70 mg $kg^{-1}$ mineral paraffins. The mineral paraffins primarily consist of branched and cyclic components of a complexity forming a hump of unresolved compounds. This hump ranged from about *n*-C23 to beyond *n*-C50 at the end of the chromatogram (elution at 350 °C). Most of the signals on top of the hump represent natural *n*-paraffins in the range of C25−C33, with the odd-numbered species predominating the even-numbered species. They were not included in quantitation. A grape seed oil was analyzed at different stages of industrial raffination. There was no significant effect on the mineral paraffins during neutralization and bleaching, but deodoration (in which the temperature can reach 270 °C and which can take from 20 min to 5 h) completely removed the components up to the *n*-alkane C25 (largely components naturally occurring in the oil) as well as part of the paraffins up to approximately *n*-C30 (**Figure 2**). The

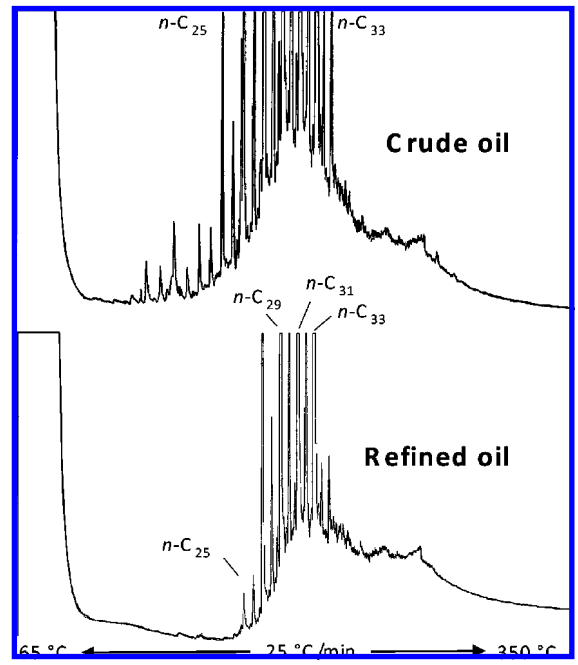


**Figure 2.** Paraffins in a crude and an industrially refined (deodorized) grape seed oil.

**Table 1.** Reduction of the Mineral Paraffins during Raffination: Concentrations before and after Deodorization

| | mineral paraffin concn (mg $kg^{-1}$) | |
|---|---|---|
| | crude | deodorized |
| O12 | 80 | 50 |
| O13 | 160 | 130 |

effect on the concentration of the mineral paraffins is shown in **Table 1**. **Figure 3** shows the concentrations of the mineral paraffins in 11 grape seed oils from the Swiss market (O1−11). They ranged from 43 to 247 mg $kg^{-1}$ and are clearly above those commonly encountered in vegetable oils (*23*). The fact that they are elevated for all samples indicates that the contamination is not incidental, but rather systematic. The contamination is considered serious, particularly since the nature of the contaminant is unknown: there are no grounds to assume that the paraffins entered as food-grade white oil.

So far the source of the contamination is unknown. The contaminant consists of a high boiling point mixture, clearly beyond bulk mineral oil products, such as diesel or heating oil. Often (**Figures 1** and **2**) it even exceeded the molecular mass typical for base oils used, e.g., for lubricating oils (*13*). However, the possibility should be taken into consideration that the material observed in the oil is merely the top end in the molecular mass range of a broader mixture from which the more volatile components evaporated or were removed during processing.

Grape seed oils are obtained at the end of a fairly long processing chain. After wine production, the residue primarily consisting of skins and seeds (grape marc) is commonly fermented another time to produce distillates (such as grappa). The residue of this process is dried, and the seeds are isolated for the extraction of the oil.

The investigation of the source of the contamination started with the fresh grapes. The seeds were separated from the fruit, and both parts were dried in an oven at 80 °C and extracted as described in the Materials and Methods. **Table 2** shows the amount of oil extracted (%, w/w) related to the dried seeds for

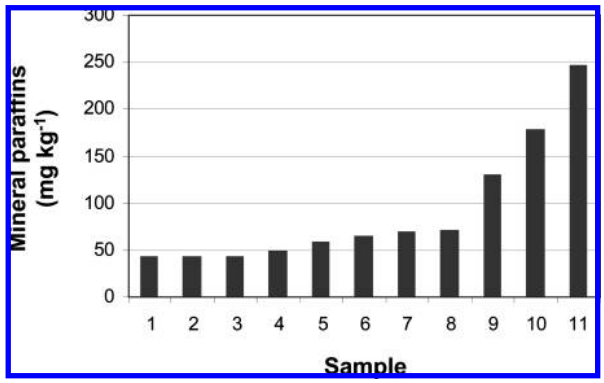


**Figure 3.** Concentrations of mineral paraffins in 11 samples of commercial grape seed oil.

**Table 2.** Mineral Paraffins in Fresh Grapes: Amount (%) of Oil Extracted from the Dried Seeds and Mineral Paraffin Concentrations (mg $kg^{-1}$) in the Extracted Oil, Peels, and Pulp

| | | mineral paraffin concn | | |
|---|---|---|---|---|
| | extracted oil amt | seeds | extracted oil | stems and peels |
| G1 | 15 | <1 | <8 | 2 |
| G2 | 15 | 2 | 14 | 2 |
| G3 | 16 | <1 | <8 | 2 |
| G4 | 13 | <1 | <8 | 6 |
| bioG | 10 | 1 | 10 | 7 |

four samples from the market (G1−4) and grapes grown by one of the authors without phytochemical treatments (Gbio). The concentrations of the mineral paraffins are given for the extracted oil as well as for the other part of the dried grapes (related to the dry weight). The results show detectable contamination of all oils, but in concentrations clearly below those of the commercial oils. The concentration in the peels (dry weight) tended to be higher than in the seeds (1 mg $kg^{-1}$ in the seeds versus 7 mg $kg^{-1}$ in the peels).

The bioG belonged to the more contaminated grapes. It was hypothesized that this contamination is from the environment and could be considered as a reference for an oil without direct contamination during growth and processing. In fact, a majority of vegetable oils were found to be contaminated at around this level (*23*). Since all commercial grape seed oils analyzed clearly exceeded this level, there must have been an additional source of contamination. The molecular mass distributions of the mineral paraffins in the oils from the fresh grapes did not significantly differ from those in the commercial grape seed oils, but considering the substantial variation between the samples, this is not conclusive for the nature or source of the contamination.

From two samples of grape marc obtained from industry (M1 and M2) and one from a small home production (M3), the seeds were isolated from the residues of the peels, pulp, and stems by the help of tweezers. The seeds amounted to 47−60% of the marc (**Table 3**). The oil extracted from the purified seeds amounted to 12−14%. The mineral paraffins were determined in the oils extracted from the marc and the purified seeds as well as in the residues. Concentrations were far higher than in the oils from the fresh grapes, with the difference being drastic for the two industrial marcs M1 and M2. M3 contained more mineral paraffins in the residues than the fresh grapes, but the concentration in the oil from the purified seeds was below the detection limit.

Concentrations in the oil from the marc were many times higher than in that from the purified seeds, with those in the oils from the marc tending to be higher than in the commercial grape seed oils and those in the oil from the purified seeds tending to be lower. The analysis of the residues confirmed that most of the mineral paraffins originated from these.

**Table 3.** Mineral Paraffins in the Marc: Proportion (%) of Seeds in the Marc, Yield (%) of Oil Extracted from the Purified Seeds, and Mineral Paraffin Concentrations (mg $kg^{-1}$) in the Oil Extracted from the Marc and the Purified Seeds as Well as in the Residues from the Peels, Pulp, and Stems

| | proportion of seeds in the marc | extracted oil yield | mineral paraffin concn in the oil | | mineral paraffin concn in the residues |
|---|---|---|---|---|---|
| | | | marc | purified seeds | |
| M1 | 60 | 14 | 340 | 54 | 60 |
| M2 | 55 | 14 | 170 | 10 | 27 |
| M3 | 47 | 12 | 91 | <3 | 20 |

**Table 4.** Mineral Paraffins in Industrially Worked Grape Seed Samples (See the Materials and Methods): Proportion (%) of Residues from the Pulp and Peels, Amount (%) of Oil Extracted from the Purified Seeds, and Mineral Paraffin Concentrations (mg $kg^{-1}$) in the Oils from the Crude and the Purified Seeds as Well as in the Residues

| | proportion of residues | extracted oil amt | mineral paraffin concn in the oil | | mineral paraffin concn in the residues |
|---|---|---|---|---|---|
| | | | crude seeds | purified seeds | |
| IS4 | 1 | 14 | 24 | 22 | 22 |
| IS5 | 1 | 14 | 61 | 59 | 27 |
| IS6 | 1 | 14 | 25 | 24 | 18 |
| IST | 1 | 15 | 32 | 30 | 43 |
| ISU | 7 | 15 | 17 | 14 | 9 |
| ISL | | 17 | 8 | 8 | |
| ISS | 1 | 15 | 30 | 27 | 47 |
| ISP | 15 | 15 | 105 | 40 | 75 |
| ISA | 1 | 18 | 15 | 14 | 30 |
| ISK | 0 | 19 | 26 | 26 | |

For 10 samples of grape seeds obtained from the oil industry, the residues of the pulp and the peels were separated from the seeds and amounted to 1−15% of the raw material (second column in **Table 4**). Again the concentrations of mineral paraffins were determined in the oils extracted from the crude and the purified seeds as well as in the isolated residues. The results confirm a strong contamination of the residues of the pulp and the peels: the content of mineral paraffins was 3−14 times higher in the residues than in the respective seeds. The contamination of the oil was substantially higher when the raw material contained a substantial amount of residues.

**Figure 4** compares the contamination of the seeds with that of the residues from the pulp, peels, and stems of the same sample. First, it confirms that the contamination of the peels and stems is far higher than that of the seeds. Second, it shows that the composition of the paraffins varies between different marcs (compare also with **Figures 1** and **2**), but is the same for the peels and seeds from the same grapes.

To obtain information about the distribution of the mineral paraffins in the seeds, intact purified seeds ISP were superficially extracted with hexane before crushing and oil extraction. Without such pretreatment, the oil contained 40 mg $kg^{-1}$ mineral paraffins (**Table 4**). After immersion of the seeds in hexane for 1 h at ambient temperature, half of the contamination was removed (**Table 5**). Extraction at 50 °C for 1 h eliminated three-quarters of the mineral paraffins. The dried residue of the extract from 2 g of seeds amounted to 6 mg, which means that hardly any oil was extracted under these conditions and much of the mineral paraffins are in the surface layer, possibly transferred

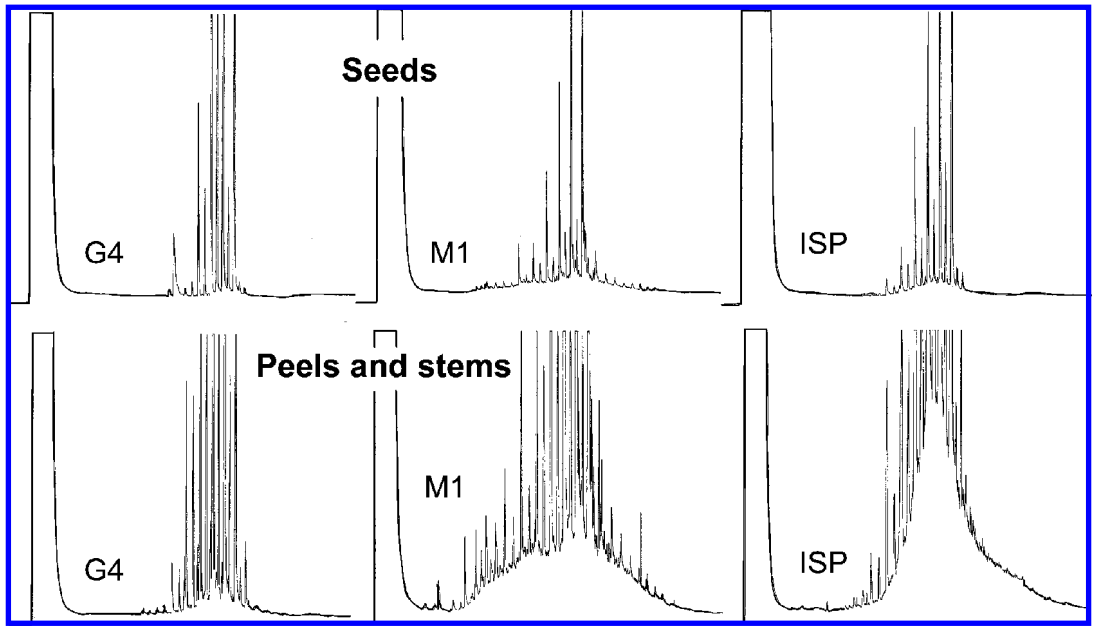


**Figure 4.** Chromatograms of extracts obtained from purified grape seeds (upper row) and the residues from the peels, pulp, and stems recovered from the same crude sample (lower row) (constant sensitivity).

**Table 5.** Mineral Paraffin Concentrations (mg $kg^{-1}$) in the Oils Obtained from Purified Seeds ISP after Superficial Extraction of the Intact Seeds with Hexane at Various Conditions

| treatment | mineral paraffin concn in the oil |
|---|---|
| none | 40 |
| 60 min, 25 °C | 20 |
| 5 min, 50 °C | 19 |
| 15 min, 50 °C | 14 |
| 60 min, 50 °C | 10 |

from the peels. This notwithstanding, there may also be mineral paraffins in the center of the seeds.

In conclusion, the data confirm that the contamination of the grape seed oils with mineral paraffins is more than occasional. The concentrations found (between 40 and 250 mg $kg^{-1}$) are considered high, and efforts should be taken to reduce them. A safety assessment is difficult as long as the composition of the contaminant is unknown. High exposure to mineral paraffins should be prevented in light of the accumulation in the human body (*22*), but the contaminant is unlikely to merely consist of saturated hydrocarbons. The source should be identified to assess the composition, but also to search for ways to avoid the contamination. The results provide hints about the origins of the contamination, but more work is needed to identify them.

There is an environmental background contamination which might reach 10 mg $kg^{-1}$ in the oil, as shown by oil from seeds of untreated fresh grapes (a level found in many edible oils).

Commercial grape seed oils are usually additionally contaminated by a so far unknown material leaving a residue of a composition similar to that of the environmental contamination.

This additional contamination is already present in the marc as it arrives at the oil mill.

As the concentration is far higher in the outer part of the fruit (principally the peels), the contamination is likely to originate from the surface of the fresh grape. This is supported by the composition of the mineral paraffins in the seeds corresponding to that in the peels.

Since high molecular mass paraffins are unlikely to be transported through the aqueous pulp, the seeds are probably contaminated by contact with the peels in the marc. This is confirmed by the seed contamination being largely superficial (washing experiment).

A substantial part of the mineral paraffins in the grape seed oils, particularly in the highly contaminated ones, is from the incomplete removal of the peels from the seeds.

The majority of the marcs used for wine production contained this additional contamination, but the grapes for direct consumption did not. This suggests that the source is a treatment commonly applied to grapes for wine making, but not to grapes for direct consumption.

The results also suggest a way for a strong reduction of the oil contamination without having identified/eliminated the source: Improved mechanical purification of the seeds substantially reduces the mineral paraffins in the oil, in particularly helping to avoid the high levels. Washing of the seeds with solvent (such as hexane) before the extraction process further reduces the contamination. In an example, the combination of the two measures reduced it from 110 to 10 mg $kg^{-1}$.

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