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Production of natural antioxidants from vegetable oil deodorizer distillates: Effect of catalytic hydrogenation

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ABSTRACT

Natural tocopherols are one of the main types of antioxidants found in living creatures, but they also have other critical biological functions. The biopotency of natural (+)-α-tocopherol (RRR) is 36% higher than that of the synthetic racemic mixture and 300% higher than the SRR stereoisomer. Vegetable oil deodorizer distillates (DD) are an excellent source of natural tocopherols. Catalytic hydrogenation of DD preconcentrates has been suggested as a feasible route for recovery of tocopherols in high yield. However, it is important to know whether the hydrogenation operation, as applied to these tocopherol-rich mixtures, is capable of preserving the chiral (RRR) character, which is critical to its biopotency.

Fortified (i.e., (+)-α-tocopherol enriched) sunflower oil and methyl stearate, as well as sunflower oil DD, were fully hydrogenated using commercial Ni and Pd catalysts (120–180 °C; 20–60 psig). Products were analyzed by chiral HPLC. Results show that the desired chiral configuration (RRR) is fully retained. Thus, the hydrogenation route can be safely considered as a valid alternative for increasing the efficiency of tocopherol recovery processes from DDs while preserving their natural characteristics.

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1. Introduction

Eight different molecules with vitamin E activity can be found in living creatures. These molecules belong to two ‘families’, whose generic names are *tocols* and *tocotrienols*. Each family member is designated as the α-, β-, γ- or δ-congener, depending upon the number and position of the methyl groups attached to the chromane ring (Fig. 1). The lateral chain of the molecule (phytyl) is completely saturated in tocols, and it has three double bonds (or *unsaturations*) in tocotrienols. Tocols are commonly known as tocopherols, even though the latter is the generic name that groups both families. Tocols have three chiral centers (C-2, C-4′ and C-8′) in their structure, while tocotrienols have a chiral center at C-2 and two additional positions that give rise to geometric isomers at C-3′ and C-7′. Eight diastereoisomers are possible for each of the eight tocopherols, but only the RRR isomers of the tocols and the R-*cis,cis* isomers of tocotrienols are found in nature.

It is generally accepted that α-tocopherol, the most abundant of these compounds, has a greater ability for hydrogen donation than the γ-homolog, but the latter has been shown to be a better antioxidant in pure lipid-phase systems, especially at high concentration (Huang et al., 1994). Yet, each of the family members is considered to have a high antioxidant activity. Likewise, the antioxidant activity of the different stereoisomers of each tocopherol is about the same: the all-*rac* mixture of α-tocopherols has the same effect as the pure, natural 2R, 4′R, 8′R-α-tocopherol (Hudson, 1990).

One of the most important aspects related to the biology of these compounds – and one not yet fully understood – is that they possess other physiological functions in addition to their antioxidant activities. Different members of the family are involved in such diverse functions as the hepatic cholesterol synthesis (Khor et al., 1995), defense against nitrogen radicals (Cooney et al., 1993) and regulation of blood pressure (Wechter et al., 1996). Moreover, the biological activity was found to be highly dependent on the configuration of the homolog.

Vitamin E has long been identified as a key factor in preventing gestation miscarriages, and this physiological function is still customarily used to measure the biopotency of each of the vitamin E homologs *via* the fetal resorption test in pregnant rats. By means of this test, it was demonstrated that the naturally found α-tocopherol stereoisomer (2R, 4′R, 8′R) is approximately 36% more active than the synthetic, all-*rac* α-tocopherol. The stereoisomer with an inverted configuration at the two-position (2S, 4′R, 8′R) is threefold less active than the natural α-tocopherol (Burton et al., 1985; Acuff et al., 1998). The epimeric configuration at the two-position is apparently dominant in determining of biological activity (Kiyose et al., 1997; Kreimeyer and Schmidt, 1998).

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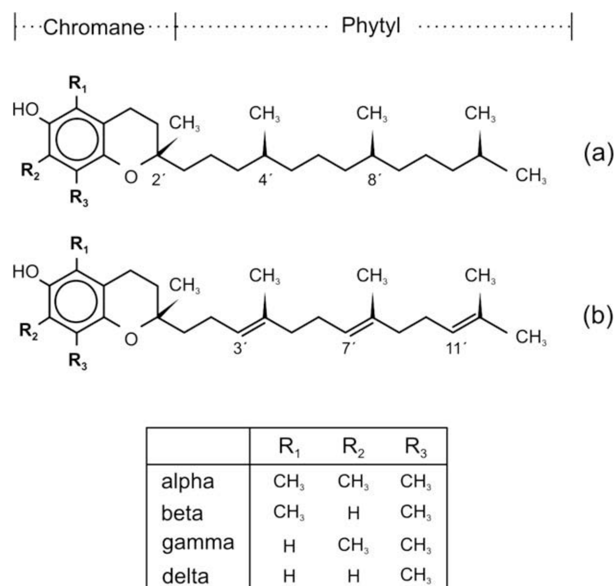

	R_1	R_2	R_3
alpha	CH_3	CH_3	CH_3
beta	CH_3	H	CH_3
gamma	H	CH_3	CH_3
delta	H	H	CH_3

Fig. 1. Schematic view of: (a) natural RRR tocol (tocopherol) and (b) R, *cis*,*cis* tocotrienol isomers.

Vegetable oils (VO) are the main source of tocopherols in the human diet. However, their concentration of vitamin E can be adversely affected by process and/or storage conditions. Under good manufacturing practices, the total content of tocopherols in VO is only reduced by 30–40% during refining (i.e., degumming, neutralizing, bleaching and deodorizing). Alkaline chemical refining eliminates 10–20% of the tocopherols originally present in the crude oil, presumably by sorption onto the soaps that are generated in the neutralization step (O'Brien, 1998).

Deodorizing is the process step that contributes the most to loss of tocopherol. The amount of vitamin E that is lost depends upon the severity of the process with respect to temperature, contact time and steam flow rate. Under drastic conditions, up to 30–60% reduction can occur (O'Brien, 1998). Nevertheless, this vitamin is not actually *lost* but, rather, it is retained in (and becomes part of) the deodorizer distillate (DD). Therefore, DDs constitute an excellent source, or feedstock, for the recovery of natural tocopherols.

These deodorizer distillates, also commonly known as 'deodorizer scum' among practitioners, are obtained as by-products from refining edible or industrial vegetable oils (e.g., sunflower, rapeseed, soybean, corn, sunflower, palm or linseed) and contain tocopherols in a wide percentage range, from 1 to 20 wt.%. However, DDs also contain fatty acids (30–60 wt.%), sterols and sterol esters (10–30 wt.%), hydrocarbons (10–30 wt.%, mainly squalene), glycerides (10–20 wt.%, mainly mono- and diglycerides), as well as several other minor substances (Moreira and Baltanás, 2001a,b).

Thus, to obtain tocopherol concentrate from these DDs (most desirably as a solution in a triglyceride vehicle), all of the accompanying substances must be eliminated from the oily solution. Few literature references address methods for the recovery of tocopherols and/or sterols from DDs, but numerous such reports can be found in the patent literature. Generally, all such methods involve separation of the saponifiable matter (free fatty acids, mono-, di-, and tri-glycerides) from the unsaponifiable fraction (tocopherols, sterols, high molecular weight alcohols, hydrocarbons, etc.), thus enriching a stream with the latter. Next, the separation and purification of tocopherols, sterols and other components from one another are addressed by means of different physical and/or chemical methods (Moreira and Baltanás, 2001a,b).

Among these separation methods, the hydrogenation of DD preconcentrates using metal catalysts such as palladium, platinum, rhodium, ruthenium or nickel, both in supported or bulk forms, was suggested in a now-expired patent (Takagi et al., 1984). According to the original proposal, the hydrogenation can be carried out between 150 and 250 °C, under hydrogen pressures in the 1–25 kg/cm^2 range. The process stage is ended when the iodine number is about 45 or 50. The final extraction of tocopherols is then achieved *via* fractional crystallization. The authors reported tocopherol yields of up to 70%. During hydrogenation, unsaturated hydrocarbons (e.g., squalene), as well as the unsaturated fatty acid chains undergo progressive saturation of their double bonds, which both increases their melting points and decreases their solubility in the solvent employed in the fractional crystallization. At the same time, tocotrienols – via saturation of the lateral phytyl chain – become part of the tocopherol 'pool', which remains in the non-crystallized mass.

Vegetable oil hydrogenation has not been identified as one of the VO processing steps where quantitative losses of tocopherols can occur, owing to the absence of oxygen and the reducing environment under which it is conducted (Hui, 1996). However, the stereochemistry of the tocopherols can potentially be altered on the catalyst surface (Pagani, 2003).

As stated above, even though all biological functions of tocopherols are not completely known or understood, enough evidence has been accumulated so as to ensure that the non-natural stereoisomers of the family do not harbor the same biopotency. In this regard, it is important to establish the effects that catalytic hydrogenation might have on tocopherols. Indeed, even though the reaction might be considered unobjectionable as far as quantitative losses of tocopherols are concerned, it is important to know whether '*qualitative losses*' may be present due to deleterious stereochemical alterations. If so, hydrogenation would not constitute an optimal or desirable alternative for the recovery of natural tocopherols from deodorizer distillates. This topic is the main focus of this work.

2. Methods

2.1. Strategy

Accomplishing our intended objectives calls for the hydrogenation of DDs under identical or similar conditions as those found in industrial practice. Yet, the particular characteristics of deodorizer distillates prevents the direct achievement of these goals because DDs, as it was previously noticed, are extremely complex mixtures of many different substances. Thus, as 'universal' guard columns are not yet available, some of them may damage the sensitive chiral HPLC columns that are needed (see below) to discriminate between the different tocopherol isomers.

Therefore, to overcome this problem (and streamline the study) we employed 'tocopherol-enriched mixtures' as a first step, using refined vegetable oils and/or methyl stearate as representative oily vehicles. This approach was considered applicable because our intention was to assess the possible impact of the hydrogenation process on the stereochemistry of the tocopherols whenever their concentration in the reaction mixture is high (i.e., when the likelihood for the heterogeneous catalyst to isomerize them is maximal). In the final stages of this work, and under 'conventional' experimental conditions, we performed hydrogenation runs using a true, preconcentrated DD.

2.2. Reagents

Commercial refined sunflower oil was purchased from a local vendor. Methyl stearate was obtained *via* transesterification of

commercial, high purity tristearin (Sigma–Aldrich Corp., St. Louis, MO) with methyl alcohol (ACS grade).

Sunflower oil deodorizer distillate was provided by Aceitera General Deheza S.A. (Gral. Deheza, Argentina). The free fatty acids and triacylglycerides of this DD were transformed into fatty acid ethyl esters, using 37 wt.% HCl as homogeneous catalyst (6/1 M ratio of ethanol/triglycerides; 2 wt.% HCl/triglycerides; 78–80 °C and 12 h, with stirring). These reaction conditions ensured that chemical equilibrium was reached. Afterwards, the whole mass was evaporated under vacuum. Two overhead fractions were removed: HCl, ethanol and water in a first cut ($T \leqslant 80$ °C; 25 mmHg), followed by the odorous compounds and fatty acid ethyl esters in the second fraction ($T \leqslant 200$ °C; 1 mmHg). The product left in the bottom, a 'tocopherol-enriched deodorizer distillate', was semi-solid at ambient temperature. Its main characteristics, together with the most relevant compositional data of this sunflower oil DD, are detailed in Table 1.

High purity, standard grade (+)-α-, (+)-γ- and (+)-δ-tocopherol, obtained from natural sources, and synthetic (±)-α-tocopherol, β-sitosterol, stigmasterol, squalane and squalene were from Sigma–Aldrich Corp. Other chemicals were ACS grade.

The commercial metal catalysts used were nickel based: Nysosel 325 and 222 (Engelhard Corp., Iselin, NJ) and Pricat 9920 (Johnson-Matthey Inc., London, UK), with different catalytic selectivity properties, and palladium 11694 (Alfa Aesar/JM, Ward Hill, MA). Their main features are indicated in Table 2.

2.3. Reactor

A pressurizable, stainless steel stirred tank Parr minireactor (100 cm^3) was used to perform the experiments. The unit was furnished with a variable speed four-blade impeller, heating mantle, internal refrigerating coil, thermocouple well, inlet/outlet gas lines for purging, processing and/or evacuation, and liquid sampling provisions.

The reactor was also equipped with a 'cup and cap' device (Grau et al., 1987). It consists of two cylinders mounted along the stirrer axle: the *cup* (which contains the catalyst) is loose, while the *cap* (which prevents spilling of the catalyst) is fixed and rotates with the axle. A helicoidal channel on the latter allows the inertial, downward displacement of the cup (by means of a driving pin) when stirring is stopped momentarily. A short, horizontal groove, carved just at the upper end of the helicoidal channel, allows the cup to remain suspended on top of the reactor, 'immersed' in the gas phase, for catalyst activation and/or sample pre-treatment (e.g., drying under vacuum) under operational conditions (e.g., temperature or pressure) other than the reaction conditions, if needed. Hence, complete absence of induction times can always be achieved (Grau et al., 1987).

The working temperature was kept within ±0.2 °C using a Pt100 platinum thermoresistor linked to a Love 1600 process controller. A Matheson 8100 mass flow transducer/controller, interfaced to a registering device, was used to monitor and record hydrogen consumption along each run.

2.4. Operating variables and operating conditions

The performance of each of the above mentioned commercial catalysts was studied at three different levels of temperature (120, 140 and 180 °C) and hydrogen pressure (20, 40 and 60 psig). Levels of catalyst loading (0.03 wt.%, Ni or Pd) and stirring rate in the reactor (1000 rpm) were kept constant throughout the program to standardize operating conditions. The preactivation of the catalysts was accomplished by exposing them in situ (i.e., in the upper part of the reactor) to pure H_2 for 3 h at 140 °C and 40 psig.

About 50 cm^3 of liquid reactants were hydrogenated in each experiment for at least 60 min. At the end of this period, hydrogen consumption was almost negligible and the products obtained were solid at room temperature. Samples of the hydrogenated materials were taken immediately afterwards, and they were filtered (above 80 °C) through cellulose acetate membranes (0.2 μm). The samples were then stored at 4 °C in dark vials and under nitrogen atmosphere for further chromatographic analyses.

2.5. HPLC and chiral HPLC analyses

A Shimadzu Series 10 HPLC chromatograph (Shimadzu Corp. Tokyo, Japan), comprising two LC-10AS pumps, a CTO-10A column oven, an UV/vis SPD-10A detector, a CBM-10 communication module and the CLASS-LC10 software were used.

Tocopherols were quantified following AOCS's Official Method, Ce 8-89, (AOCS, 1997), using a Silica A/10 250 × 4.6 mm column (Perkin–Elmer Anal. Instr., Shelton, CT). Analytical conditions: UV/vis detector (292 nm); mobile phase: hexane/*i*-propanol 97.5/2.5 v/v, flow rate: 1 mL/min; oven temp.: 30 °C; injection vol.: 10 μL. Quantitative determination of sterols was also performed by HPLC (Holen, 1985) using a Spherisorb 5 μm 250 × 4.6 mm column (Waters Corp., Milford, MA). Analytical conditions: UV/vis detector (206 nm); mobile phase: methanol/water 99/1 v/v, 1 mL/min; oven temp.: 30 °C; injection vol.: 10 μL.

The analysis of tocopherol stereoisomers was done using a slightly modified version of the technique of Kiyose et al. (1999). This method requires two chiral stainless steel chromatographic columns (250 mm long, 4.6 mm I.D.) operating in series: Chiralcel OD-H 5 μm (Chiral Technologies Inc., West Chester, PA) and Sumichiral OA4100 5 m (Phenomenex, Torrance, CA), which allows separation of the α-tocopherol stereoisomers into two well-re-

Table 1
Compositional data of the sunflower oil deodorizer distillate.

	DD 'as received'	Purified DD[a]	Analytical method
Saponification number	165.1	82.5	AOCS Cd 3b-76
Total fatty acids	86.9%	43.4%	(As glyceryl trioleate)
Acid value	108.2	2.0	AOCS Cd 3d-63
Free fatty acids	54.3%	1.0%	(As oleic acid)
Tocopherols	6.0%	9.9%	AOCS Ce 8–89
Sterols	5.1%	9.3%	AOCS Ch 6–91
Squalene		3.5%	–
Iodine value	136.8	31.9	AOCS Tg 1a-64

[a] See text for details.

Table 2
Physical properties of the commercial catalysts used in this work.

Catalyst type	NYSOSEL 325	NYSOSEL 222	PRICAT 9920	Alfa AESAR 11694
Ni (wt.%)	22	22	46	N.A.
Pd (wt.%)	N.A.	N.A.	N.A.	5
Support	Silica	Silica	Silica	Carbon
Support (wt.%)	4	4	9	95
Protection agent	Saturated vegetable oil	Saturated vegetable oil	Saturated vegetable oil	N.A.
Protection agent (wt.%)	74	74	45	–

solved peaks: one corresponding to the four 2R epimers and another one for the remaining four 2S epimers. Analytical conditions: UV/vis detector (268 nm); mobile phase: hexane/isopropanol 97/3 v/v, 0.3 mL/min; oven temp.: 30 °C; injection vol.: 100 μL; dilution (in hexane): 1/30 w/v.

A cleaning pre-treatment aimed at eliminating interferences was required. This treatment consists of a saponification with KOH in ethanol (70 °C, 30 min), with further extraction of the tocopherols with 1 wt.% NaCl and 10 wt.% ethyl acetate in hexane, stirring vigorously for 1 min and then centrifuging (5 min, 3000 rpm). The solvent of the upper layer, containing the tocopherols, is next evaporated at <50 °C and then the original volume is restored with hexane. As this cleaning pre-treatment does not allow quantitative analyses (see next section), the latter were done using the official AOCS method Ce 8-89 outlined above to confirm that, indeed, hydrogenation did not reduce the total content of tocopherols.

Identification of the 2R and 2S α-tocopherol isomers after the hydrogenation runs (if any) was done in the HPLC unit by comparing their retention times with those of the corresponding standards. To adequately match retention times, paired HPLC injections of said standards were routinely performed.

2.6. Other techniques

The usual AOCS official methods and recommended practices (AOCS, 1997) were used to evaluate the saponification number (Cd 3b-76), iodine value (Tg 1a-64), acid value (Cd 3d-63) and sterols/squalene (Ch 6-91) of the deodorizer distillate, sunflower oil and methyl stearate, whenever needed.

3. Results

3.1. Quantitative impact of catalytic hydrogenation on tocopherols content

A set of hydrogenation tests was carried out to assess the impact of process condition during catalytic hydrogenation, as described in the following paragraphs. Samples of the materials were taken at initial and final times. Each test lasted 2 h and was run in duplicate.

3.1.1. Impact of reaction temperature

Because tocopherols are sensitive to high temperature (although this sensitivity is mostly oxygen-related and should not be a concern whenever inert or reducing atmospheres are employed), a test was run to verify the integrity of the tocopherols using the maximum working temperature usually employed in the hydrogenation processes: 180 °C. The reactor was charged with methyl stearate and a small amount of α-tocopherol (0.06 wt.%) diluted in hexane, and then the reactor was pressurized with pure H_2 at 40 psig. No catalyst was added. Both the initial and final samples gave the same quantitative results, showing that the tocopherol content was preserved after 2 h in a hydrogen atmosphere at high temperature.

3.1.2. Impact of adsorption onto the catalyst's surface

Atoms on the catalyst surface have fewer nearest neighbors than those in the bulk metal; they are usually referred to as 'coordinatively unsaturated sites'. Thus, molecules from the fluid phase can interact with these free surface orbitals to give rise to strong (sometimes irreversible) chemisorptive bonds. Tests were run to evaluate this possibility: the reactor was loaded with the same methyl stearate and α-tocopherol (0.06 wt.%) mixture, but was pressurized with nitrogen (40 psig) to preclude eventual masking hydrogenation reactions. Nysosel 325 (0.03 wt.% Ni loading with respect to the liquid phase) was used. The reaction was run at 180 °C for 2 h. Again, the chromatographic results gave similar concentrations of tocopherols in the liquid phase before and after the experiment, showing that α-tocopherol (and, likewise, the other tocols) are not appreciably adsorbed by the metal catalysts under process conditions.

3.1.3. Impact of hydrogenation/hydrogenolysis reactions

The addition of hydrogen to a carbon–carbon double bond is one of the seemingly simplest catalytic reactions, despite the inherent complexity of the reacting system, in which concomitant isomerization (either positional or geometric) and/or possible competitive reactions (e.g., dehydrogenation, hydrogenolysis, cyclization, dehydrocyclization, etc.) can occur. Tocols are elaborate molecules and, therefore, may undergo some of these reactions. Thus, to verify molecular integrity, the methyl stearate/α-tocopherol (0.06 wt.%) mixture was put in contact with both types of metal catalysts: Ni (Nysosel 325) and Pd (AlphaAesar 11694) under a hydrogen atmosphere (40 psig) at 180 °C for 2 h. Once more, similar concentrations of α-tocopherol were found in every case, which allows us to conclude that no deleterious hydrogenation, dehydrogenation, hydrogenolysis, etc., reactions occur under habitual hydrogenation process conditions using these commercial supported metal catalysts.

3.2. Determination of the chiral isomers of α-tocopherol

Fig. 2 shows typical chiral HPLC chromatograms of the standards used, which correspond to the natural and synthetic α-tocopherols, respectively. As expected, the natural α-tocopherol ((+)-α-tocopherol) showed just a single peak (at 31.2 min), while the synthetic α-tocopherol ((±)-α-tocopherol) was separated into two symmetric, well-resolved peaks: the first one corresponds to the 2R epimers and the second (which elutes about 1 min later)

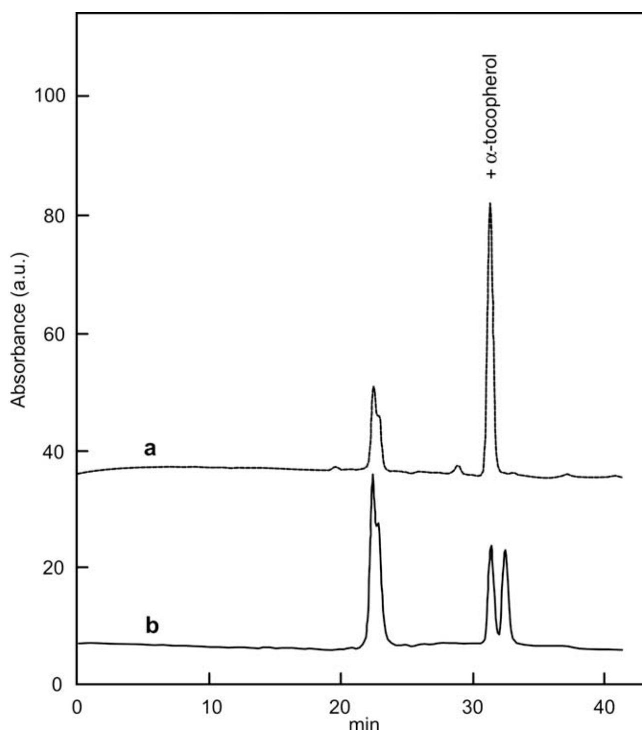

Fig. 2. Comparative chiral HPLC chromatograms of: (a) (+)-α-tocopherol (natural) and (b) (±)-α-tocopherol (synthetic) standards.

corresponds to the 2S epimers. The area ratio between both peaks was close to one. It is worth mentioning that, in spite of minor changes in the absolute values of the retention times that were observed during the experimental program (especially whenever new stocks of the mobile phases were prepared) complete separation of the two groups of epimers was always achieved, and the differences in their retention times were always around 1.1 min.

When a small sample of sunflower oil diluted in hexane was injected into the HPLC unit equipped with the chiral columns, the (+)-α-tocopherol peak could be easily identified, but also present was a 'dirty' background that was considered to be a source of analytical confusion and/or poor resolution (Fig. 3a). Therefore, the aforementioned clean-up technique suggested by Kiyose et al. (1999) was adopted with excellent results (Fig. 3b). Indeed, use of this technique can lead to solvent losses in the various steps of sample preparation, and such losses may lead to artificially high tocopherol values. On the other hand, partial losses of tocopherols (by their occlusion into the soapy mass formed after the saponification step) are unavoidable but, nevertheless, no preferential extraction of the 2R vs. the 2S into the soap (that is, capable of altering the areas ratio of the two HPLC peaks) was envisioned. This was verified by spiking a sample of sunflower oil with synthetic (±)-α-tocopherol and subjecting said sample to the clean-up procedure. Two nearly identical, separated peaks were obtained. The technique is, to this extent, semi-quantitative, and it was judged to be sufficient for our structural discrimination purposes.

3.3. Structural (qualitative) effects of hydrogenation on the tocopherols

3.3.1. 'Fortified' sunflower oil and methyl stearate

To assess the viability of introducing a catalytic hydrogenation step into the process for recovering tocopherols from vegetable oil DDs, our first step was to hydrogenate refined sunflower oil 'fortified' with 10 wt.% (+)-α-tocopherol under the traditional processing range (120 and 180 °C, and 20 and 60 psig of pure hydrogen). Table 2 lists the full set of catalysts that were employed, including several of the widely used commercial types. This 'fortifying load' of (+)-α-tocopherol is about 100-fold higher than the natural tocopherol content of this oil, which is usually around 400–800 ppm. Duplicate runs under each process condition were made.

As an example, Fig. 4 shows the resulting chiral HPLC chromatogram obtained when Nysosel 225 was used at 120 °C and 60 psig. Similar results were found using the remaining catalysts throughout the entire set of process temperatures and hydrogen pressures.

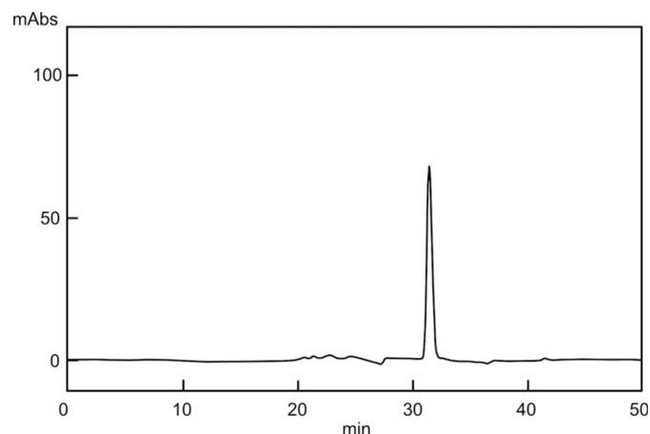

Fig. 4. Chromatograms of sunflower oil supplemented with 10 wt.% (+)-α-tocopherol and hydrogenated with Nysosel 225 nickel catalyst, at 120 °C, 60 psig. Process time = 60 min.

In addition, a mixture of methyl stearate and (+)-α-tocopherol (10 wt.%) was exposed to pure hydrogen with each of the catalysts (at 140 °C and 40 psig H_2) for 1 h. Because fully saturated fatty acids do not chemisorb onto the catalyst surface, highly concentrated (+)-α-tocopherol was made available to the catalysts under non-competitive conditions. Fig. 5 shows the resulting chiral HPLC chromatograms obtained when the complete set of Ni and Pd catalyst was used.

In both cases the chiral HPLC results indicated that only a single peak, corresponding to the 2R epimers of (+)-α-tocopherol, was present after the reaction. This implies that, under this broad range of test conditions, no racemization of (+)-α-tocopherol occurs during catalytic hydrogenation, even though the concentration of tocopherols in the reacting system was made deliberately high.

3.3.2. Preconcentrated and purified deodorizer distillate

To further assess the feasibility of introducing a hydrogenation step to simplify and improve the isolation of highly concentrated natural tocopherols from deodorizer distillates, a sample of the preconcentrated sunflower oil DD was hydrogenated using both Ni and Pd-based catalysts. In these cases, even though no HPLC peak assignable to the 2S epimers of α-tocopherol was observed (data not shown) we judged the information to be inconclusive because the hydrogen consumption plots were too 'flat', especially when the nickel catalysts were used. These results indicated that

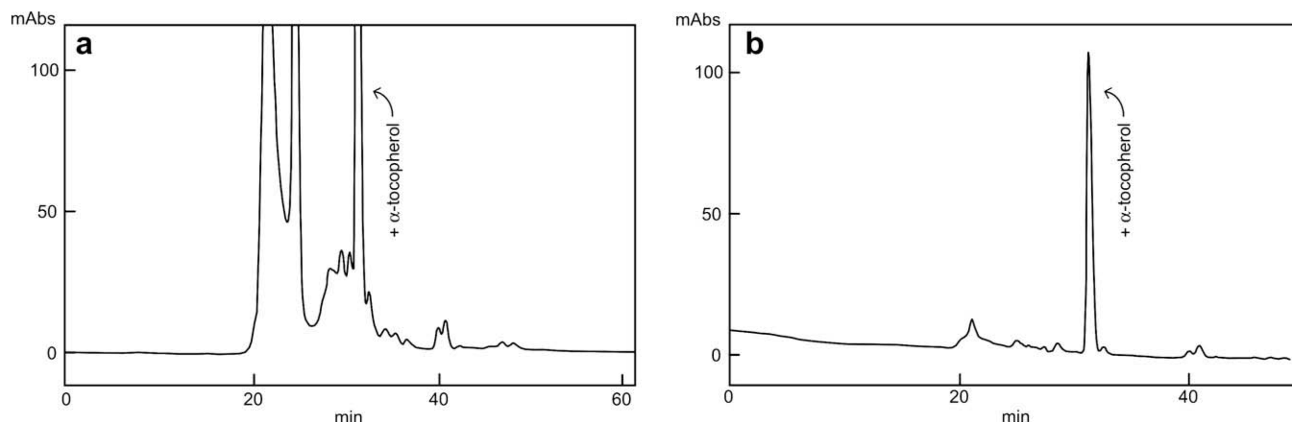

Fig. 3. Comparative chiral HPLC chromatograms of: (a) 'untreated' (i.e., just hexane-diluted) sunflower oil and (b) sunflower oil pretreated by following Kiyose et al.'s (1999) clean-up procedure.

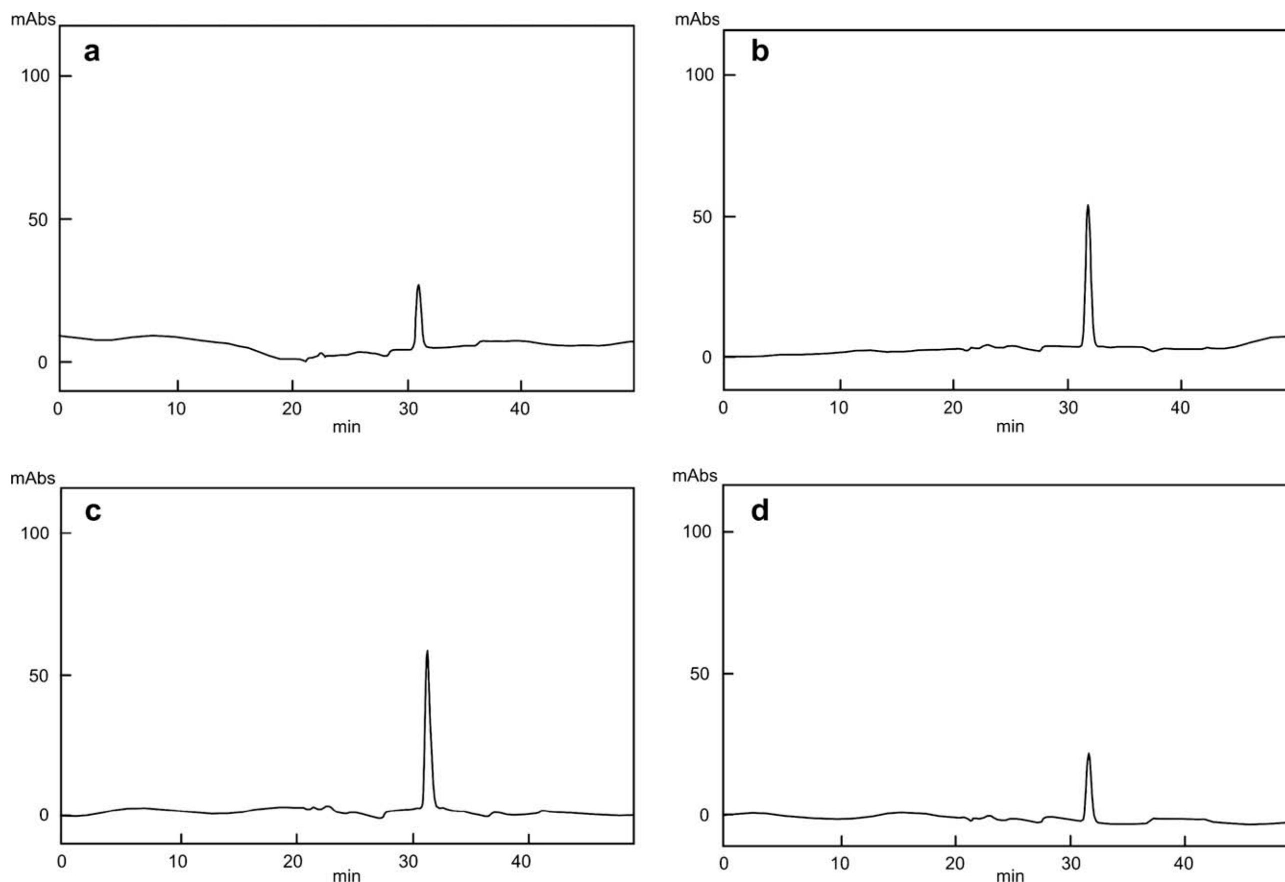

Fig. 5. Chromatograms of methyl stearate supplemented with 10 wt.% (+)-α-tocopherol and hydrogenated with the set of supported Ni and Pd catalysts, at 140 °C and 40 psig H_2: (a) Nysosel 325; (b) Nysosel 222; (c) Pricat 9920; (d) Alfa Aesar 11694. Process time = 60 min. *Note:* samples dilution was not standardized.

hardly any hydrogenation had occurred (most likely owing to catalyst poisoning, as discussed in the following paragraphs).

To verify this hypothesis, the iodine value (IV) of the material resulting from the hydrogenation run executed using Pricat 9920 was determined; an IV = 56.4 was obtained. Since the preconcentrated DD had an initial IV = 31.9 (Table 1), this result was clearly incongruent and revealed that unidentified substances generated during the hydrogenation of the DD mixture – different from the conventional triacylglycerols – were interfering with the redox reaction that is customarily used by IUPAC or AOCS to establish the iodine value (namely, the Wijs method). Indeed, it is enough for these substances to possess a reduction potential capable of reducing iodine to falsify (i.e., enhance) any IV result. Likewise, conjugated double bonds cannot be quantified by the Wijs reagent.

As stated above, the virtual absence of hydrogenation was attributed to catalyst poisoning. Deodorizer distillates are extremely complex mixtures that contain many known deleterious substances. Possible candidates include free fatty acids (which were not completely eliminated during the DD purification, see Table 1), as well as aldehydes and degradation compounds from hydroperoxides (which are eliminated from vegetable oils during deodorization) in the deodorizer, together with residual traces of sulphur- and phosphorous-containing compounds (e.g., phospholipids).

To overcome this potential problem, an extra hydrogenation run was included by increasing by fivefold the amount of catalyst (in this case the highly selective Nysosel 325) and diluting the DD by half with methyl stearate. In addition, the deodorizer distillate was first neutralized with a saturated solution of sodium bicarbonate, and then was further washed with distilled water until neutrality was reached. The primary goal of this neutralizing treatment was to eliminate any residual free fatty acids from the DD, so as to suppress one of the possible causes of the low catalytic activity.

After this extra pre-treatment, the hydrogenation of the deodorizer distillate proceeded smoothly, and the hydrogen consumption was significant. As the chromatogram in Fig. 6 shows, again a single peak corresponding to the 2R epimers of (+)-α-tocopherol was present in the hydrogenated material, indicating explicitly that no undesirable isomerization had occurred in this case either.

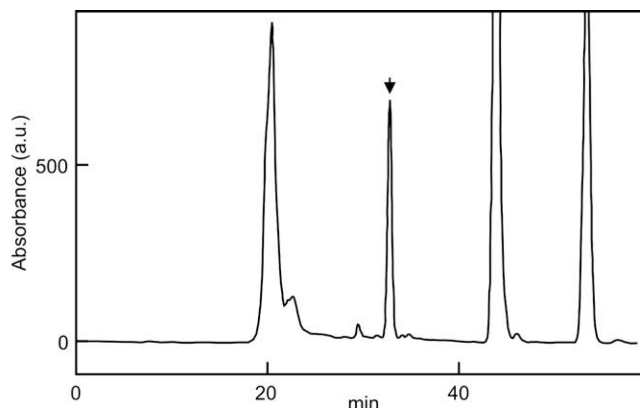

Fig. 6. Chromatogram of sunflower oil deodorizer distillate preconcentrated, purified (see text) and mixed (in equal parts) with methyl stearate, hydrogenated with Nysosel 325, at 140 °C and 40 psig H_2. Process time = 60 min. The arrow indicates the location of the natural RRR (+)-α-tocopherol signal.

4. Discussion

The underlying reasons that can help explain why no deleterious isomerization of the C-2 carbon of (+)-α-tocopherol was observed during hydrogenation of the DD can be explored by evaluating: (a) the probability of (chemi)sorption of the tocopherol molecules onto the surface of the catalysts; and, if chemisorption were feasible, (b) possible factors that would preclude the isomerization reaction from occurring.

4.1. (Chemi)sorption onto the catalyst surface

The adsorption of at least one of the reactants onto the catalyst surface is a prerequisite for any heterogeneous catalytic reaction to occur at a significant rate. Also, the bond energies must be high enough so as to ensure sufficient surface coverage, but not so high as limit the reaction progress (via excessive surface coverage with the reaction products).

No literature data related to the adsorption of tocopherols onto commercial (metallic) vegetable oil hydrogenation catalysts is available. However, an analysis of the bonding possibilities of the different functional groups of the tocopherol molecule to the catalytic surface can be attempted. The molecule has three centers through which it could potentially adsorb onto the catalyst: the cloud of π electrons of the aromatic ring, the two pairs of free electrons of the phenolic oxygen and the two pairs of free electrons of the ether oxygen (Fig. 1).

With regard to adsorption through the aromatic ring and/or the phenolic oxygen, numerous works about hydrogenation of benzene, toluene, xylenes, phenols or cresols using supported metal catalysts have been published (Orozco and Webb, 1983; González Velasco et al., 1995; Chen and Falconer, 1984; Shin and Keane, 1998). In the hydrogenation of phenol on Pd catalysts, the acid–base properties of the support have been shown to exert a decisive influence on both activity and selectivity of the reaction toward cyclohexanone. Neri et al. (1994) suggested that the adsorption of the molecule occurs onto the support areas that surround (i.e., that interface with) the metal crystallites. On acidic supports such as alumina, the adsorption is dissociative *via* the oxygen atom; the ring is coplanar with the surface and the interaction between both is strong. On basic (e.g., MgO) or neutral supports (such as carbon or the silica used in this work) the adsorption is similar, but the ring is not coplanar, which leads to a weaker interaction. In the hydrogenation of phenol on Ni/SiO_2 catalysts, a higher turnover frequency (TOF) was observed compared to that of benzene or other non-oxygenated compounds, and it was proposed that the interaction of the former reactant with the catalyst occurs through both the aromatic ring and the oxygen atom (Chen and Falconer, 1984). Other authors state, in the case of the adsorption through the oxygen atom, that the aromatic ring can be coplanar or perpendicular to the catalyst surface. Shin and Keane (1998) suggested that the interaction of phenol with the catalyst occurs *via* a phenoxy anion. This proposition was justified by comparison of the different hydrogenation rates of phenol and cresols: the higher the pK_a of the reactant was (phenol > *m*-cresol > *p*-cresol), the higher the hydrogenation rate became. The methyl substituents of the cresols are electron donors and, thus, they destabilize the phenoxy anion. In the case of (+)-α-tocopherol, there are three methyl substituents on the aromatic ring, but this molecule is extremely efficient at delocalizing charge, which suggests that the stability of the eventual ion would be important. Nevertheless, steric factors due to the adjacent heterocyclic ring would, most likely, prevent a good interaction with the catalyst surface.

The impact of the ether oxygen on the adsorptivity of the molecule was recently studied by Kacer et al. (2003). These authors compared the relative hydrogenation rate of allyl phenyl ether. allylbenzene on Pd/carbon and Pt/carbon catalysts, estimating the relative adsorption coefficient of both species. Their results showed that the first compound was about 2.5–3 times more reactive, which was explained in terms of the participation of the nonbonding pair of electrons of the oxygen atom on the link between the molecule and the metal surface. Regarding the (+)-α-tocopherol situation, one has to consider that not only is the aromatic ring much more substituted, but the phytyl group (located on the other side of the oxygen atom) is much bulkier than the group on the Kacer's model molecule, which therefore might imply that the steric factor could be affecting tocopherol proximity.

Admittedly, our reaction studies do not give an indication about whether or not (+)-α-tocopherol adsorption occurs with the catalysts. It is clear, though, that such an adsorption (if it occurs) cannot be considered irreversible (or 'catalyst poisoning'). The latter can be assured because the IV steadily decreased in all of the tocopherol-concentrated mixtures that were hydrogenated, rendering solid materials in every case.

4.2. Possible (precluded) reactions

For any isomerization reaction to occur at C-2 of (+)-α-tocopherol, the ether oxygen of the molecule must be involved. C-2 is a tertiary carbon with sp^3 hybridization, so epimerization of this chiral center is possible only if the bond to the ether oxygen were broken and then reformed with a different orientation. In the previous section we discussed the feasibility of adsorption *via* the phenolic ring because the cyclic part of the molecule is relatively planar (and has high electron density) and has a restricted conformation due to the sp^2 hybridization of the carbons in the ring. In other words, one should primarily explore whether, once the tocopherol molecule is adsorbed via the aromatic ring, the heterocyclic ether oxygen atom might become located next to the catalytic surface in a more favorable position for an eventual, surface-mediated reaction. An effect of this type was observed in the preferential hydrogenation of allyl phenyl ether vs. allyl alcohol (Kacer et al., 2003). During this competitive hydrogenation, it was found that, although the reaction rates are similar for both compounds, the first one was favored due to its higher relative adsorption, which was attributed only to the positioning and bonding to the catalysts induced by the aromatic ring.

The ether group can undergo hydrogenation on Ni/Al_2O_3 and Ni/SiO_2 catalysts as well. In temperature programmed reduction (TPR) studies on the hydrogenation of dimethyl ether, its conversion to methane was observed (Chen and Falconer, 1984), but this reaction only occurred above 200 °C. The rate-determining step was an inverse spillover of the oxygenated species (which adsorbs onto the support) towards the metal, where hydrogen is dissociatively chemisorbed. In fact, the reaction took place at the metal-support interface. However, considering the size of the (+)-α-tocopherol molecule, this situation seems unlikely in our case.

Lastly, another reaction that has some resemblance to our system is the hydroisomerization of oxirane and methyloxiranes. These are oxacycloalkanes with a three-membered ring (two carbons and one oxygen atom). During the reactions with hydrogen on Ni, Cu, Pd or Pt catalysts, these chemicals can undergo hydrogenolysis of the C–O bond to give primary alcohols (or secondary, in the case of methyloxiranes, depending upon the metal) or isomerization with ring opening to give aldehydes (or aldehydes and ketones in the case of methyloxiranes, again depending upon the catalyst being used) (Notheisz et al., 1986). These reactions can occur at lower hydrogen pressures and/or lower temperatures than the ones used in our work. In the case of (+)-α-tocopherol, the C–O bond with higher breakage probability is the C-2 carbon, since the dissociation energy is lower for alkyl ethers than for aryl ethers

(339 kJ/mol vs. 422 kJ/mol) (Furimsky, 2000). However, the rate-limiting step in the case of methyloxiranes is the rupture of the C–O bond. The energy needed to break a three-membered ring is much lower (owing to the structural tensions caused by the 60° bonding angle, whereas the sp^3 hybridization of the atoms in the cycle would rather prefer an angle closer to 109.5°) than the one needed to break a six-membered ring. Therefore, again it is hard to foresee any C–O bond breaking in the (+)-α-tocopherol molecule via any of these mechanisms.

5. Conclusions

During the selective catalytic hydrogenation of sunflower oil deodorizer distillates with supported nickel and palladium catalysts, no stereochemical modification at the C-2 carbon of (+)-α-tocopherol was observed. Therefore, hydrogenation of these materials to produce fully saturated fatty acids can be considered as a valid and safe alternative to improve the yield and/or separation of tocopherols during recovery from deodorizer distillates, while simultaneously preserving the natural characteristics of the tocopherols.

From an economic standpoint, further studies using a broader range of catalytic materials (and/or pre-treatment and process conditions) are still needed to overcome the severe poisoning problems found during the hydrogenation of the deodorizer distillate with conventional commercial Ni or Pd hydrogenation catalysts.

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