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Potential Pharmaceutical Uses of Algal Residues of the European Third Generation Biofuels Sector

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ABSTRACT

The international gas crisis, the scarcity of oil and climatic upheavals has accelerated the development of alternative energy sources in Europe, such as algal biomass. This paper mainly aims to assess the potential uses of algal residues from the production of 3rd generation biofuels in the European pharmaceutical industry. It highlighted the antiviral activity and the antioxidant power of residual algal biomass from the production of 3rd generation biofuels in Europe. A residual algal biomass which also seems to carry molecules of interest in the pharmaceutical field since it could in the future constitute the basic component in the production of drugs on a large scale in Europe.

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INTRODUCTION

Algae form a very diverse group of non-flowering plants that live mainly in aquatic environments and have biochemical characteristics with high added values for a large number of applications in several fields, including those that interest us in our present study, namely the production of third-generation biofuels (Algofuels) in Europe as well as the production of molecules for the European pharmaceutical industry.

Creating bridges between these two areas can allow complementarity between the European energy sector (biofuels) and that of pharmaceuticals. Indeed, algal residues from the European biofuels sector, which a priori pose a problem because of their nuisance and their cost as waste, can be a source of wealth if they are valued for their pharmaceutical value.

Therefore, the question to which our study attempts to provide some answers is the following:

What are the potential pharmaceutical uses of algae residues from the production of third-generation biofuels in Europe?

To answer this question, several sub-questions have been posed to help lift the veil on biofuels, to shed light on the systems through which algae are produced in Europe and the therapeutic added value that the residues of these can provide after their use in the production of third-generation biofuels in Europe:

What are biofuels?

How is algal biomass produced in Europe for the needs of third-generation biofuels?

What is the evolution of the European biofuels market?

What added value pharmaceuticals can the residues of microalgae and giant algae produced in Europe provide after their use in the production of third-generation biofuels?

Also, the study aims to:

- Lifting the veil on biofuels and their different generations;

- Provide an overview of the evolution of the European biofuels sector,

- Highlight the two algal biomass production systems in Europe;

- Draw up a table of the potential pharmaceutical uses of the residual biomass of the main microalgae and giant algae produced in Europe for the needs of third generation biofuels.

General information on biofuels

Below we present the basic concepts relating to biofuels.

Definition

The expression biofuel refers to fuels obtained from organic matter (biomass). They are therefore fuels assimilated to a source of renewable energy [1], as opposed to other fuels derived from fossil resources, in particular oil.

Generations

There are three generations of biofuels; the one that interests us in this study is the third, called algofuels.

First generation biofuels

They are mainly of two types:

Ethanol

Any raw material of agricultural origin that can be converted into sugar, such as cellulose or starch, can be used to produce ethanol. The latter is therefore produced from sugar or starch from different sugar crops, the main ones being sugar cane (mainly for the ethanol produced in Brazil), corn (mainly for the ethanol produced in the USA) and sugar beet (mainly for ethanol produced in Europe).

The use of ethanol considerably reduces emissions of sulphur oxide known to be very carcinogenic [2].

Biodiesel

Biodiesel is produced from different fatty acid agricultural raw materials, mainly soybean oil, rapeseed oil but also palm oil and various other vegetable oils. It can also be produced from animal fats.

Unlike ethanol which is used as an alternative to gasoline, biodiesel is used as a replacement for diesel. And just like ethanol, biodiesel can be used neat or blended with diesel.

Second generation biofuels

Unlike first-generation biofuels, which are mainly produced from the edible parts of agricultural raw materials (sugar cane, beets, corn, wheat, barley, etc.), second-generation biofuels are derived from ligno-cellulose, which that is to say of the secondary walls of the plants with the richest biomass in the emerged zones. In simpler terms, second-generation biofuels come from agricultural and forestry waste, and therefore from the inedible parts of agricultural raw materials, among other things.

It is important to mention that another source of ligno-cellulosic biomass exists alongside agricultural and forestry waste, these are dedicated crops such as annual plants, perennial fodder plants and herbaceous plants.

Third generation biofuels

Also called "algofuels", these biofuels are obtained after the conversion of algal biomass into oil which is then refined to give algofuels (mainly biodiesel).

The algae biomass is obtained after an algae culture which is carried out in two different ways as we will see later. This culture only needs water (preferably waste because of the presence of microorganisms on which the algae feed), sun for photosynthesis and CO2 which the algae also feed on, hence the need to build the Algofuel production facilities near major cities, industrial centers or polluting factories as shown in (Figure 1) [3].

Given the high oil content of algae, the potential for obtaining fuel is extremely large and far surpasses the yield of other feedstocks used in the production of first and second generation biofuels while using less surface area such as shown in (Table 1)

It is noted that the use of microalgae for the production of biofuels allows for a much better oil yield and higher productivity in biodiesel while occupying a smaller surface.

European biofuels market

In this part we will first present some elements of the projections of the European biofuels market, then we will highlight the paradigm shift towards biofuels generated by the RED II Directive, and finally we will explain why 3rd generation biofuels can represent a future key market within the EU, particularly in the field of aviation.

Elements of European biofuels market projections

Since 2010, support for biofuels within the European Union has been governed by the Biofuels Directive 2009 on renewable energies (RED), which sets at 10% the minimum proportion that renewable energies renewables will have to represent in the final energy consumption in transport to 2020 horizon. In June 2018, it was agreed to raise this target to 14%; national caps for biofuels from food and feed crops are set at 1 percentage point above 2020 levels and cannot exceed 7%. The new framework, adopted under Directive 2018/2001 (RED II) of December 11, 2018, will be in place by 2030. Under RED II, biodiesel produced from palm oil is among the biofuels with a high risk of indirect land use change (ILUC), which should reduce its consumption.

The IEA baseline scenario projects a decrease in the shares of diesel and gasoline in the total energy consumption of the sector transport. Diesel fuels fell sharply; ethanol consumption should increase (+0.1 billion liters), while that of biodiesel should decline in absolute value (-1.7 billion liters). This decrease will mainly affect palm oil-based biodiesel, given the sustainability concerns that palm oil production raises in the EU. Biodiesel from other vegetable oils will also suffer, but to a lesser extent, while the production of biodiesel from waste oils is unlikely to change much. There is therefore every reason to think that in 2029, even if the European Union still occupies first place in the world ranking of biodiesel producing regions, it will only represent 28% of world production, against 34 % currently. Total EU biofuel consumption is projected to fall by 0.7% per year by 2029, but the share of advanced biofuels is expected to rise to 24%, down from 17% today (Figure 3).

Capsizing of the EU position towards biofuels

In the early 2000s, the European Union set itself the objective of promoting the use of biofuels, with three main arguments:

1. Reducing GHG emissions in the transport sector.
2. Improving the security of energy supply in the EU.
3. Support for European agricultural production.

The use of biofuels was encouraged by the RED directive (Renewable Energy Directive) relating to the promotion of the use of energy produced from renewable sources adopted in 2009. Critics nevertheless began to be heard against this promotion of biofuels and their role in several global crises:

1. Soaring food prices, especially in 2006-2008 and 2011, which caused "hunger riots" in countries like Mexico.
2. Increased deforestation, particularly in Indonesia, Malaysia and Brazil through the so-called "indirect land use change" (ILUC) mechanism.

RED II Directive, a paradigm shift for biofuels

Critics against the RED I directive have prompted the European authorities to change course, in particular with regard to first-generation biofuels, which resulted in the adoption in December 2018 of a new directive called RED II (2018/2001/EC), which replaces that of 2009 and establishes the European legislative framework now in force concerning biofuels.

3rd generation biofuels: Future key market within the EU

Faced with competition from the electrification of individual vehicles and the European bet on hydrogen in the heavy goods vehicle segment, the market for 3rd generation biofuels could develop in other modes of transport that can hardly be decarbonized, such as aviation.

The future "ReFuelEU Aviation" regulation announced by the Commission could remove certain obstacles to the development of 3rd generation biofuels in air transport. Similarly, several European countries including Germany, France, Spain and the Nordic countries support the implementation of obligations to incorporate 3rd generation biofuels into aircraft fuels.

Some operators are explicitly betting on the take-off of demand for 3rd generation biofuels in the aviation sector, such as Total, which recently decided to convert its "Grandpuits" refinery for this purpose.

But several obstacles could prevent a breakthrough of 3rd generation biofuels on the jet fuel market. On the one hand, it is not certain that the investments necessary for the production of 3rd generation biofuels for aviation will be profitable given the narrowness of the market. On the other hand, the incorporation of 3rd generation biofuels for aviation would greatly increase the costs of the sector given that the majority of fuels for aircraft are today largely zero-rated.

Therefore, the only hope of stimulating the production of 3rd generation biofuels would be to recover the algae residues that emanate from this production in various fields such as cosmetics, food, plastics or more particularly what interests us in our present study, the pharmaceutical field.

European algal biomass production systems

There are two main ways to grow seaweed in Europe:

Open system

Commonly referred to as "Raceway", these are large open pools that are easy to build, use, maintain, and clean (Figure 4). Their cost of construction and operation is low, and are also energy efficient unlike the closed system, which is why this system is currently the only one used for industrial production despite its many drawbacks, except start with daily and seasonal variations in light intensity and temperature, water evaporation and contamination of algae by bacteria, which makes this system difficult to control.

Closed system

Better known as a "photobioreactor", the latter is made from materials that are transparent for lighting, usually glass (Figure 5). This system makes it possible to control the various algae culture parameters (evaporation, temperature, CO2, O2, pH) to allow optimal production. Also, this system makes it possible to overcome the problems of the open system, particularly with regard to contamination by bacteria and parasites.

Potential pharmaceutical uses of residues of European microalgae

Hundreds of thousands of species of microalgae are distributed over the surface of the globe. The best known strains used in the pharmaceutical field and which we will discuss in this part are: Chlorella vulgaris and Spirulina spp.

Microbicides (fight against HSV)

Carraguard, a mixture of carrageenans similar to those in Irish moss, is currently being tested in various studies and appears to be an effective means of prevention against genital herpes which is a sexually transmitted infection caused by the herpes simplex virus (HSV).

Antiviral agents (anti-HIV)

The antiviral activity of extracts from a number of seaweeds has been proven by tests carried out in test tubes or similar devices (in vitro tests) or in animals, although few tests have been carried out in humans.

The Population Council, an international non-profit, non-governmental organization that conducts, among other things, research in biomedicine to build research capacity in developing countries, has carried out large-scale tests that have reached the stage where at here. These tests involved 6,000 women over four years and involved the vaginal use of a gel containing carrageenan. These tests have demonstrated the antiviral activity of microalgae in the fight against HIV. Another Australian company has also carried out several clinical trials in the USA and Australia, also revealed that extracts from microalgae had activity against HIV.

It has also been found that the antiviral substances contained in seaweed are very large molecules. The idea that they could be absorbed by eating this seaweed has led to tests to measure the rate of HIV infection in communities where it is consumed. These tests revealed that this rate of infection in these communities was very much lower than elsewhere. This result has in turn led to a number of smaller-scale trials on people with HIV who consume seaweed, in this case, Undaria powder. These tests in turn revealed a 25% drop in the viral load of these people. These studies concluded that these seaweeds are a very effective source of antiviral agents.

Antioxidants

For many living beings, molecular oxygen is vital and whose elimination in vivo leads to the formation of a certain number of toxic derivatives (active forms of oxygen and free radicals) that the cell eliminates in different ways. Photosynthesis allows microalgae to produce molecular oxygen, which makes us say that they have a highly developed antioxidant system.

By antioxidant, we are talking about an agent that prevents or slows down oxidation by neutralizing free radicals, the excess of which is responsible for cell damage, particularly on DNA, and can promote the emergence of diseases. Therefore, any substance capable of significantly reducing oxidizable substrates is considered an antioxidant [4].

The antioxidant power of foods is measured by the ORAC index (Oxygen Radical Absorbance Capacity). This index is very high for microalgae which gives them a great ability to reduce oxidizable substrates and great potential in the pharmaceutical industry which produces them to be sold as a food supplement in tablets, powders or capsules, chlorella are also in form of liquor, chocolate, cereals, cheese, crackers or sweets, Ditto for spirulina, of which three quarters of the biomass are used to produce food supplements in capsules, tablets, powders, micro-granules, twigs and sequins.

A wide variety of compounds of a biochemical nature are also found in microalgae which make it possible, alone or in combination, to metabolize reactive oxygen species. We thus find:

- Carotenoids, in particular β-carotene with respect to the singular oxygen O2;

- Enzymes of the superoxide dismutase (SOD) family;

- Tocopherols (Vit E) with respect to the superoxide anion O2;

- Ascorbate (Vit C) with respect to the superoxide anion O2; - Enzymes of the catalase type, glu-

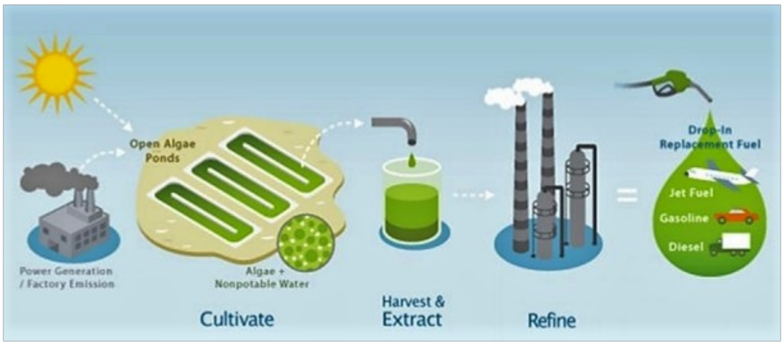

Figure 1: Algofuel production steps

Matière première	Teneur en huile (%pds)	Rendement en huile (L huile / ha. An)	Utilisation terrain (m² an/kg biodiesel)	Productivité en biodiesel (kg biodiesel/ha.an)
Mais	44	172	66	152
Chanvre	33	363	31	321
Soja	18	636	18	562
Jatropha	28	741	15	656
Caméline	42	915	12	809
Colza	41	974	12	862
Tournesol	40	1070	11	946
Ricine	48	1307	9	1156
Palme	36	5366	2	4747
Microalgues A	30	58 700	0,2	51 927
Microalgues B	50	97 800	0,1	86 515
Microalgues C	70	136 900	0,1	121 104

Figure 2: Oil content and yields between microalgae and other raw materials

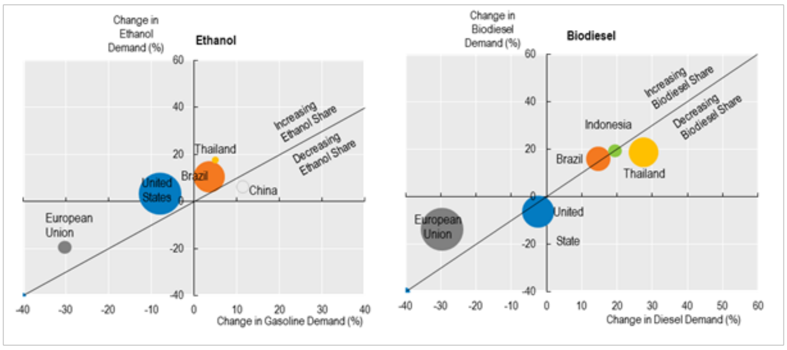

Figure 3: Evolution of the demand for biofuels in the major regions

Figure 4: Open system (Raceway)

Figure 5: Closed system (Photo bioreactor)

Figure 6: Algue Wakame

Composant	Unité	Teneur moyenne pour 100 g d'algue déshydratée
Energie	Kcal	211
Eau	g	10,8
Minéraux	g	18,9
Protéines	g	7,2
Glucides	g	18,5
Fibres alimentaires	g	41,8
Lipides	g	2,8
AG saturés	g	0,11
AG mono insaturés	g	0,19
Polyphénols	g	3,6
Sodium	mg	2.859
Magnésium	mg	836
Phosphore	mg	162
Potassium	mg	2.269
Calcium	mg	1652
Manganèse	mg	2,5
Fer	mg	21,8
Cuivre	mg	0,7
Zinc	mg	6,4
Iode	mg	68,2
Sélénium	µg	6,7
Bêta carotène	mg	4
Vitamine D	µg	1
Vitamine E	mg	14
Vitamine K	µg	1.017
Vitamine C	mg	94,8
Vitamine B1	mg	0,3
Vitamine B2	mg	1,0
Vitamine B3	mg	2,7
Vitamine B5	mg	0,02
Vitamine B6	mg	5,6
Vitamine B8	µg	18,4
Vitamine B9	µg	22,7
Vitamine B12	µg	2,1

Figure 7: Nutritional composition (Wakame)

Figure 8: Bladder Wrack

Composant	Unité	Teneur moyenne pour 100 g d'algue déshydratée
Energie	Kcal	194
Eau	g	11,6
Minéraux	g	19,4
Protéines	g	7,4
Glucides	g	15,7
Fibres alimentaires	g	44,6
lipides	g	1,3
AG saturés	g	0,35
AG mono insaturés	g	0,20
Polyphénols	g	5,6
Sodium	mg	4023
Magnésium	mg	885
Phosphore	mg	ND
Potassium	mg	3272
Calcium	mg	1167
Manganèse	mg	8,3
Fer	mg	14,7
Cuivre	mg	0,4
Zinc	mg	8,2
Iode	mg	40
Sélénium	µg	88,4
Bêta carotène	mg	ND
Vitamine D	µg	12
Vitamine E	mg	ND
Vitamine K	µg	12
Vitamine C	mg	ND
Vitamine B1	mg	ND
Vitamine B2	mg	ND
Vitamine B3	mg	1,7
Vitamine B5	mg	ND
Vitamine B6	mg	ND
Vitamine B8	µg	47,3
Vitamine B9	µg	ND
Vitamine B12	µg	ND

Figure 9: Nutritional composition (Bladder Wrack)

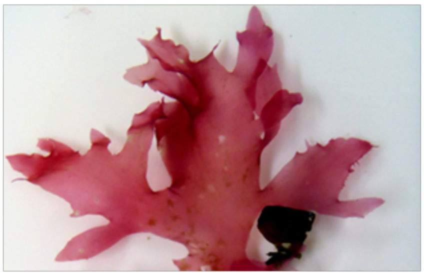

Figure 10: Porphyra umbilicalis

tathione peroxidase with respect to hydrogen peroxide H2O2. The interest in these antioxidants has been very significant for many years because of the demonstration of their role in a certain number of pathologies, whether acute such as septic shock, inflammation or reperfusion injury for example, or chronic conditions such as cataracts, cancer, osteoarthritis, atherosclerosis or even Parkinson's.

Potential pharmaceutical uses of residues of European giant algae

Like microalgae, there are a relatively high number of giant algae in the world. For our present study, we will present those that have the greatest potential in terms of creating added value for the pharmaceutical industry.

Wakame (Undaria pinnatifida)

Annual brown algae which grow mainly during the cold season in autumn and winter and can reach 2 meters in length Figure 8.

Nutritional composition

The nutritional composition of the giant Wakame seaweed (Undaria pinnatifida) is presented in (Fig-

Composant	Unité	Valeur moyenne pour 100 g d'algue séchée
Minéraux	g	13,6
Protéines	g	31,5
Fibres alimentaires	g	36,3
Sodium	mg	1.983
Magnésium	mg	486
Phosphore	mg	518
Potassium	mg	1.733
Calcium	mg	318
Manganèse	mg	3,9
Fer	mg	37,2
Cuivre	mg	1,1
Zinc	mg	4,5
Iode	mg	5,1
Sélénium	µg	51,2
Vitamine A	mg	4,65
Bêta-carotène	mg	5.265
Vitamine D	µg	0,6
Vitamine E	mg	2,9
Vitamine C	mg	57,3
Vitamine B1	mg	0,6
Vitamine B2	mg	1,9
Vitamine B3	mg	5,8
Vitamine B5	mg	0,25
Vitamine B6	mg	0,5
Vitamine B8	µg	7,0
Vitamine B9	µg	21,7
Vitamine B12	µg	38,8

Figure 11: Nutritional composition (Porphyra umbilicalis)

Table 1: RED II directive in the field of biofuels

View of the RED II directive in the field of biofuels
The RED II directive now requires that the share of renewable energies in the final consumption of transport reaches 14% in each State.
But it limits the share of biofuels in the sector's consumption through two measures put in place to respond to the problem linked to indirect land use change.
It forbids nothing. EU Member States are still able to import and consume conventional biofuels with a high risk. But they can now only count them towards the achievement of their renewable energy objectives up to the limits set in the directive.
Focus on the two main limits imposed on biofuels by the RED II directive
The contribution of biofuels produced from crops intended for human or animal consumption cannot exceed one percentage point more than in 2020, with a maximum of 7%, in order to mitigate the risks of indirect land use change.
The directive plans to limit biofuels produced from crops intended for human or animal consumption and presenting a high risk. From 2024, this contribution must even gradually decrease to reach 0% by 2030 at the latest.

ure 7).

Pharmaceutical added value

Thanks to the many molecules of this alga such as fucoidans which are polysaccharides, and polyphenols with among them phlorotannins, Wakame algae are used to produce drugs that would allow:

- Block the cell cycle of cancer cells;

- Absorb fat and lose weight;

- Reduce high blood pressure [5];

- Decrease the absorption of dietary lipids;

- Improve skin hydration and firmness;

- Improve physiological balance and cell regeneration;

- To lower their phosphate levels in the event of chronic renal failure;

- To increase the iodine content;

- Promote anticoagulant action [6].

Bladder Wrack

Also called kelp, bladder wrack is brown seaweed belonging to the Fucaceae family and which can reach 1m in length (Figure 10). It is the most sought-after seaweed in the world and the most consumed and is used in particular to make sushi.

Nutritional composition

The nutritional composition of the giant seaweed Bladder wrack is shown in (Figure 9).

Pharmaceutical added value

Thanks to molecules such as phlorotannins, fucoxanthin and fucoidans, Bladderwrack algae are used to produce drugs that would allow:

- To reduce symptoms in subjects with osteoarthritis;

- Increase the menstrual cycle in number of days and decrease the duration of menstruation in three pre-menopausal women;

- Increase in progesterone levels [7];

- To reduce thyroid disorders;

- To increase the iodine content;

- To reduce the insulin peak caused by the absorption of these carbohydrates;

- To inhibit the accumulation of lipids in adipocytes and thus decrease the absorption of glucose by adipocytes;

- To inhibit the aromatase enzyme, thus inducing effects anti-estrogenic, and thus inhibits the development of cell lines of estrogen-dependent cancer cells

- To lower the viability of pancreatic cancer cell lines by inhibiting their cell cycle;

- Stimulate hepatic protectors;

- Stimulate the immune system;

- To protect against oxidative damage and mitochondrial dysfunction of striated muscle cells.

Porphyra umbilicalis

Very common dark red algae, the erect part of which arises from a basal disc attached to the rock (Fig. 7.). It is made up of a reddish-brown blade whose ribbon-like lobe can lengthen and reach several tens of cm in length.

Nutritional composition

The nutritional composition of the giant seaweed Porphyra umbilicalis is presented in (Figure 11).

Pharmaceutical added value

These algae contain sulphated polysaccharides called porphyrins present in quantity which seem to be molecules of interest in the pharmaceutical field. They are the basic component for producing drugs that would allow:

- To provide cellular protection by inducing the synthesis of stress proteins during physical, physiological constraints or physiopathological attacks on the cells;

- Stimulate the synthesis of HSP (Heat Shock Protein) which are also called heat shock proteins, and which are secreted by most cells during exposure to high temperatures but also in stressful situations;

- Stimulate the activity of the immune system [8];

- An antioxidant action;

- An anti-inflammatory action;

- Reduce edema and ulcers;

- Prevent the death of cells subjected to UVA radiation by trapping free radicals and reducing inflammation;

- To reduce diabetes by raising the level of adiponectin, a hormone involved in the stimulation of glucose metabolism, and by reducing the activity of the intestinal enzyme disaccharidase [9];

- Promote the absorption of iron, copper, sodium, potassium, calcium, zinc and magnesium [10];

- To fight against tumors thanks to the anti-tumor properties;

- To reduce the rate of absorption of dioxins, therefore a detoxification activity [28].

CONCLUSION

In recent years, we have witnessed the proliferation of European research projects on alternative energies, including that of producing third-generation biofuels (algofuels) from the intensive cultivation of algae. This project therefore makes it possible to produce biofuels by refining the oil extracted from algal biomass, itself produced from CO2, sun and wastewater, all on land that is unsuitable for agriculture. This European production of biofuels from algal biomass generates algal residues that can be recycled in various fields, including pharmaceuticals. Indeed, this residual algal biomass has great potential in the pharmaceutical industry since it represents a very effective source of antiviral agents. It also has an ORAC (Oxygen Radical Absorbance Capacity) index considered to be very high, which gives it an enormous capacity to reduce oxidizable substrates. This capacity may enable it to play a leading role in the European production of several drugs intended for the treatment of a certain number of pathologies, such as cataracts, cancer, osteoarthritis, atherosclerosis or even Parkinson's.

Conflict of Interest

The authors declare that there is no conflict of interest.

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