AgriWasteValue

To transform agricultural by-products
and residues into bioactive compounds

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EN SAVOIR PLUS

VALORISATION OF RESIDUES FROM THE AGROFORESTRY SECTOR FOR CHEMICAL APPLICATION

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VALORISATION OF RESIDUES FROM THE AGROFORESTRY SECTOR FOR CHEMICAL APPLICATION

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AN IN-DEPTH FOCUS: A BY-PRODUCT FOR PLANT PROTECTION APPLICATIONS

Limitations of the application of chemicals using residues from pruning fruit trees

It is a well-known fact that large numbers of chemical products currently used in plant protection products have harmful effects on the environment. Finding a less toxic alternative is therefore a high priority in European agricultural policy. Within the chemical sector, companies developing plant protection products are continuously on the look out for biobased alternatives to meet the demand for more environmentally friendly products. In fact, within the Farm to Fork (F2F) strategy implemented by the European Commission, two key targets for the reduction of pesticides have been agreed. This means that by 2030 there has to be:

- A 50% reduction in the overall use and risk of chemical pesticides, and
- A 50% reduction in the use of the most hazardous pesticides.

Industries in the plant protection sector and, more specifically, in the chemical sector, need to be regularly able to access large quantities of raw material throughout the year to ensure they can meet the demand.

The AgriWasteValue project examined the potential of different chemical applications, and has identified some restrictions concerning the use of raw materials. In terms of the use of pruning residues from fruit trees as a raw material, two main challenges were identified:

- To obtain sufficient quantities of raw material from one area (homogeneous)
- To have regular access to raw material. Residues from fruit trees are only harvested once a year from November to March.

Due to those limitations, the pruning residues collected from fruit trees prevent them from being a perfect residue to be used in the application of chemicals.

The following case study examines an alternative type of agroforestry by-product and presents some realistic, extremely promising alternatives.

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An alternative to plant protection products: a by-product of the forestry industry: bark

For many years, bark has been a by-product of the forestry industry and seems to be reasonably suitable as a raw material to produce botanical plant protection products. The advantages of it are that:

- It is available in large and regular quantities
- It is available at relatively low prices, and
- It has a high potential to enable the forestry industry to transform a low value by-product into high added-value products.

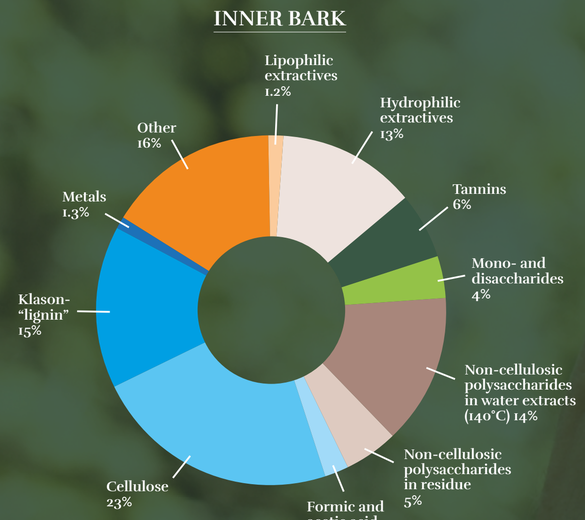
Moreover, bark, as a by-product, has a positive environmental profile in respect of environmental impact and is a renewable resource.

In terms of its composition, tree bark provides a wide variety of compounds including two particularly interesting families: terpenoids and polyphenols.

The full potential of the first, terpenoid molecules, has not yet been attained although they are known to have anti-fungal, anti-microbial, anti-viral and anti-parasitic properties. Polyphenols, the second family, are already known for their antioxidant fungicidal properties and tannins are one of the best-known categories of them.

Figure 1 illustrates the average composition of spruce bark by separating the inner and outer bark (Krogell et al. 2012).

According to Krogell et al. 2012, the inner and outer bark contain 28% and 15% of extractives respectively. These extractives are mainly hydrophilic and lipophilic with non-cellulosic polysaccharides in water extracts. Terpens and polyphenols are part of those extractives.



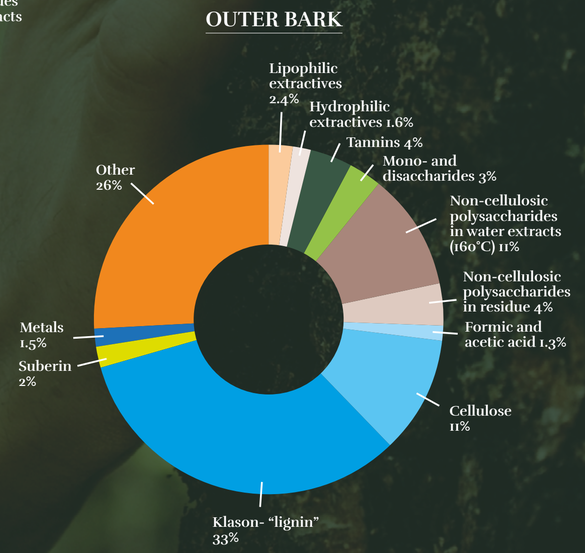


Figure1: Overall composition of spruce inner and outer bark (%) | Krogell et al. 2012

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The potential of spruce bark extracts as plant protection product

This section presents compelling evidence for the potential of spruce bark extracts as an alternative plant protection product. The bark from spruce trees has been studied in detail for its potential value and was found to be promising in terms of industrial application. Moreover, this particular bark is fairly widely transformed for use in the North-West Europe region.

Example one: Spruce bark extracts on important strawberry pathogens

Strawberry plants are known to be susceptible to various pests and diseases, including those of fungal origin with worldwide significance. Those types of disease significantly reduce yield and the quality of fruit which, in turn, results in consequential losses for the strawberry growing industry. In an attempt to provide a solution to this problem, Minova et al. explored the potential of spruce (*Picea abies*) bark ethanol extracts on pathogenous fungi causing disease in strawberries (Minova et al. 2015).

Fungal diseases are generally controlled by cultural methods or using systemic fungicides with chemical molecules. The use of chemicals to stem the problem is not a viable option in the long term because fungi are able to develop resistant strains leading to pathogen adaptation. Moreover, with long-term, use fungicidal residues accumulate in the environment which is why it is imperative that an environmentally friendly alternative is found.

The study of Minova et al. from 2015 focused on spruce bark as an alternative to protect strawberry plants as spruce is one of a number of trees that produce a wide variety of compounds (terpenoids and phenolics) with anti-fungal properties. In fact, phenolic compounds are the main anti-fungal agents in spruce extract.

Different doses of the spruce bark extracted using ethanol were tested against four common strawberry phytopathogenic fungi and the results are presented in the table below.

PHYTOPATOGENIC FUNGUS SPECIES	OBSERVATION OF THE FUNCIGIDE ACTIVITY OF THE BARK EXTRACT AGAINST THE DIFFERENT FUNGUS SPECIES
Botrytis cinerea	A higher dose of spruce bark extract (20 g/l) caused mycelial growth inhibition at 100%. The results did not differ from conventional fungicide (Signum®).
Colletotrichum acutatum	
Phytophthora cactorum	
Mycosphaerella fragariae	Spruce bark extract at a dose of 20 g/l was more effective against mycelial growth of *M.fragariae* than the conventional fungicide tested (Signum®).

Mycelial growth of all investigated fungi was inhibited by spruce bark extracts at the various doses tested, with the exception of *Phytophthora cactorum* where the extract stimulated the growth of fungi at a dose of 0.1 g/l.

Spores are a major vehicle for the dissemination of fungal diseases and, for this reason, the impact of spruce bark extract on sporulation was studied. The results demonstrated that spruce bark extract reduced sporulation of *B.cinerea, C. acutatum* and *P. cactorum* although at different doses of extract. At the lowest dose, no sporulation reduction was observed, although sporulation was inhibited with higher doses.

These results suggest that spruce bark extract could potentially be used as an alternative to conventional plant protection products.

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Example two: Application of spruce debarking waste water on wood-decaying fungi

INTRODUCTION

Hedenström et al. studied the potential of debarking waste water from a Norwegian spruce (*Picea abies*) as an inhibitor to the growth of nine species of wood-decaying fungi (Hedenström et al. 2016).

Large quantities of waste water are produced from the mill process of pulp and paper production. This waste water contains both toxic and non-toxic wood substances and research has been carried out to find ways of using the water or recovering substances from it.

The waste water is rich in natural chemicals including: mono- and oligo saccacharides, hydroxystilbenes and their glucosides, catechin, polyphenols and resin acids. Some of these substances are used by the spruce tree for protection from different pests such as insects and fungi. This study explores the use of the water that is used during the debarking process.

OBJECTIVES AND METHODOLOGY

Diethyl ether extracts of the debarking water were obtained using solvent-solvent extraction of the debarking water (using pentane which was removed after extraction and then using diethyl ether). Five different fractions of the extracts were prepared with a malt agar solution to test fungicide activity using agar plates. The fractions are detailed in the result graph.

The extract was tested on the growth of nine fungal species of economic importance.

These fungi cause problems when they attack living trees in plantations, commercial timber and wood products. The nine fungi selected are presented in the table.

RESULTS

The diethyl ether extract from the debarking waste water, prepared at a fraction of 0.54 g/l, inhibited growth of all the fungi. The rate of inhabitation was different depending on the fungus species treated.

The table describes each fungus species, its potential damage and the results observed with the fraction considered the most active extract. *Antrodia xantha* fungus proved to be the most efficient inhibitor.

All other fractions showed very low inhibition effects for all nine fungi.

FUNGUS SPECIES	DESCRIPTION	DAMAGE CAUSED	FUNGICIDE ACTIVITY RESULTS WITH THE MOST ACTIVE EXTRACT
Antrodia sinuosa	Brown rot fungus	It attacks wood through ground contact in early decay stages and timber in buildings.	Showed no growth at all on seven of the nine plates and very limited growth on the last two plates.
Antrodia xantha	Brown rot fungus	It attacks wood through ground contact in early decay stages and timber in buildings.	No growth seen during the two weeks of observation.
Coniophora puteana	Brown rot fungus	It is frequently studied as it is one of the most economically important wood rot fungi in stored wood and construction, indoors and outdoors.	Grew a third of the control.
Fomitopsis pinicola	Brown rot fungus	It attacks dead-wood and wounds living trees.	Grew less than 10 % of the control.
Gloeophyllum sepiarium	Brown rot fungus	It prefers to attack fairly fresh, damaged, stored and construction wood.	No growth seen during the two weeks of observation.
Heterobasidion parviporum	White rot fungus	It attacks living and freshly killed spruce wood. It causes root rot, one of the most severe diseases in spruce.	The species which was least affected by the treatment.
Phlebiopsis gigantea	White rot fungus	It attacks and prefers fresh dead-wood.	Grew a third of the control.
Serpula himantioides	Brown rot fungus	It attacks plants and wood outdoors in dry and hot climates, for example, French wine districts.	Grew less than 10 % of the control.
Serpula lacrymans	Brown rot fungus	It causes serious destruction in wooden buildings in temperate and southern boreal regions.	Grew a third of the control.

Figure 2 shows the detailed results obtained.

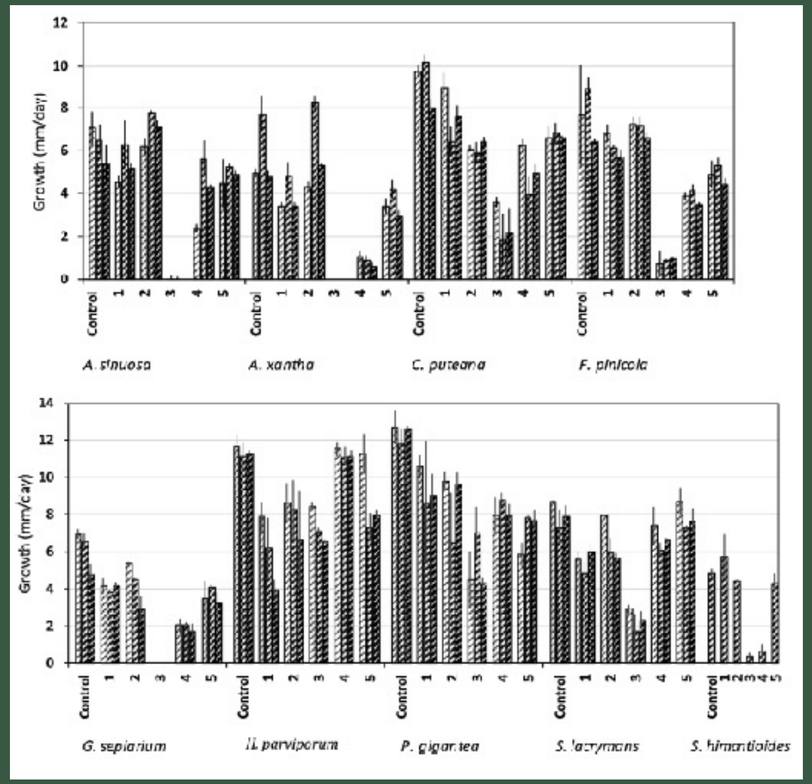

Figure 2: Observed mycelial growth rates in experiment 1, in which the fungi were treated with five fractions of diethyl ether soluble substances from debarking water, separated with MPLC. The concentrations correspond to 1.16 g of freeze-dried debarking water per agar plate (fraction 1: 0.973 g/l, fraction 2: 0.143 g/l, fraction 3: 0.54 g/l, fraction 4: 0.443 g/l, and fraction 5: 0.19 g/l). In cases where multiple bars with different fill patterns are shown for a given species and extract concentration, the individual bars represent the response of one of the tested strains of that species. Each bar (and the associated standard deviation) is based on three replications of treatment. *(Hedenström et al. 2016).*

The extract was purified to understand the specific molecules present in debarking waste water. The three major compounds found were hydroxylstilbenes resveratrol, piceatannol, and isorhapontigenin. These stilbenes and their mono- and diglucoside derivatives are abundant in natural resources including spruce trees and are well known to have anti-fungal, herbicidal, anti-microbial, and antioxidant activity.

After isolation of the three main molecules, the fungicidal activity of each one was tested separately against the nine fungi species.

When testing was carried out, at the same concentration as in the raw debarking water, the isolated compounds were not as active independently as the extract that contained them all. This might indicate that there is a synergistic effect, but needs further investigation to determine the most effective mixture of compounds. Mixtures of the substances are efficient, more general and easily obtained, making them more cost-effective.

To conclude, if an efficient extraction method can be designed and integrated into the pulp mill process, the spruce debarking water might be a valuable source of effective natural fungicides.

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Industrial application with wood extract

The potential use of some wood extracts as a plant protection product is already a reality. As of now, the company « *Silvateam* » produces and commercialises plant-based extracts rich in tannins (including wood extracts) for different applications. They already have a plant-extract solution used in the animal nutrition, food ingredients and leather tanning solution sectors.

In partnership with *IAZ Développement*, advanced research and product registration for plant protection products using wood extract from chestnut and larch has been carried out and some interesting fungicidal, bactericidal and nematicidal activities from these tannin rich wood extracts have been identified. These products are potential tools to improve crop protection strategies and are in the process of being approved by the European Union.

More information can be found at https://www.iazdeveloppement.fr/mentions-legales

Regional perspective to use bark from the forestry industry as a plant protection product (ppp)

The forestry industry is a relatively important sector in Europe, particularly in some regions including Sweden, Finland, Spain and France. The supply of raw materials presents a real challenge. It is crucial to maintain this sector on a regional/local level to ensure homogeneity regarding wood species in order to produce a high volume of similar by-products.

As a whole, the forestry industry generates a number of different types of by-products and there is a real need to price them correctly (bark market price 2022: 40 €/t on a wet basis (France)). To maintain profitability within the sector, a minimum revenue has to be guaranteed. Furthermore, all parts of the wood entering the forestry industry need to be bought and sold on at a correct value.

Some co-products (also called by-products) from wood processing, such as bark (and, to a lesser extent, knots), are known to be rich in several attractive extractable molecules.

These biobased molecules are also of interest to the high value-added cosmetics, pharmaceutical and nutraceutical sectors, **as well as to the development in greater volume of alternatives to current plant protection products, for which market expectations are very high**. However, bark is currently either not or hardly used, except as energy or as low-value horticultural mulch.

To develop homogenous bark extracts as potential alternatives to PPP, homogeneous wood species from one territory need to be located.

One concrete example of such a territory is the region of Wallonia in Belgium. In Wallonia, there are 71 sawmills and data are readily available. There are 20 hardwood sawmills, 33 softwood sawmills and 18 mixed sawmills (a hardwood sawmill is considered mixed if it processes at least 25% softwood and vice versa).

The following map (established in 2017) represents these sawmills according to their type and the volume of wood processed (Figure 3). It demonstrates that Wallonia is a compelling territory with a high concentration of sawmills which are in close proximity to each other.

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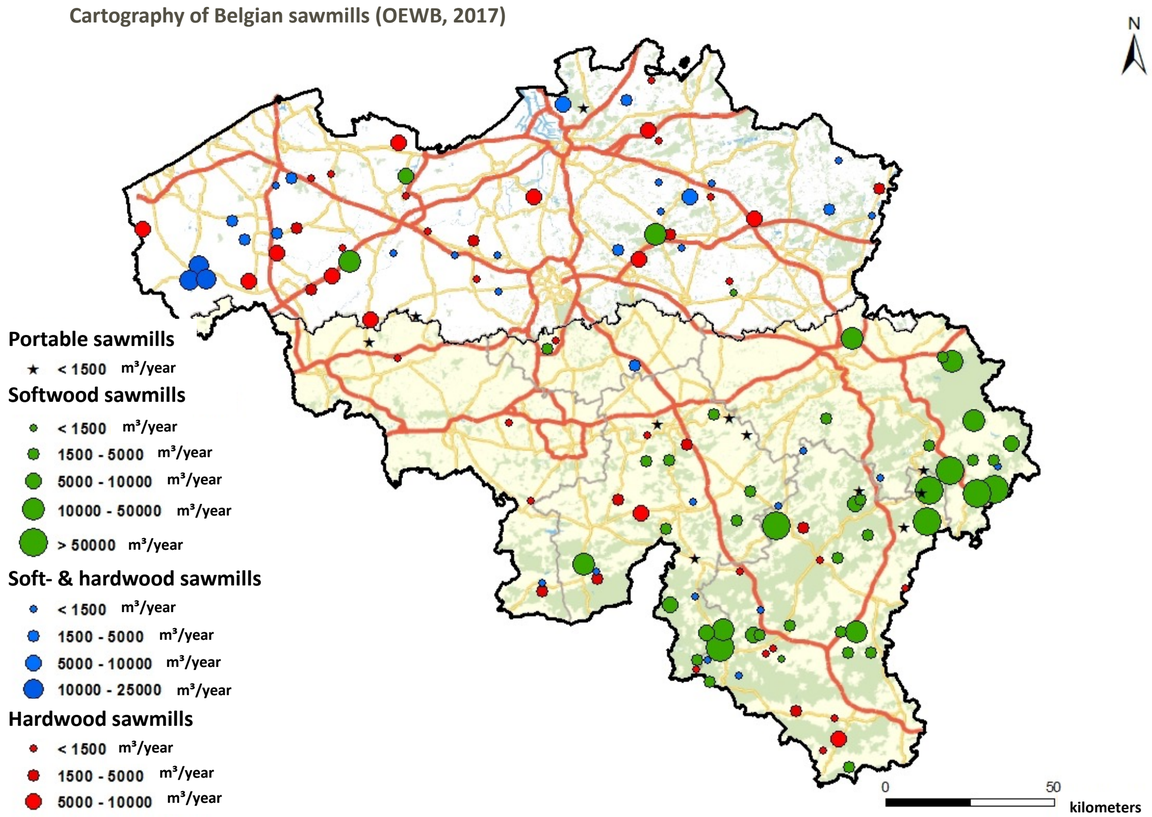

Figure 3: Mapping of the Belgian sawmills - OEWB, 2017

From this mapping, a survey done by "Hout Info Bois" and in accordance with average bark rates, it is possible to obtain a realistic estimation of volume of bark generated from the debarking process of logs in sawmills in Wallonia (Valbiom, P.-L. Bombeck, 2020). The table below summarises this information.

TREE SPECIES	THEORETICAL VOLUME OF BARK PRODUCED BY SAWMILLS (M³)	THEORETICAL VOLUME OF BARK PRODUCED BY OTHER WOOD INDUSTRIES (M³)	TOTAL THEORETICAL VOLUME (M³)	% OF TOTAL THEORETICAL VOLUME COVERED
Spruce	208.205	21.000	229.205	76,8 %
Douglas fir	38.457	6.000	44.457	14,9 %
Pine	5.810	3.000	8.810	3,0 %
Larch	7.612	-	7.612	2,5 %
Oak	6.465	-	6.465	2,2 %
Poplar	1.368	-	1.368	0,5 %
Beech	631	-	631	0,2 %
Other hardwoods	-	-	-	-
Total soft and hardwood	**268.548**	**30.000**	**298.548**	**100 %**

The following analysis helps us to define the most important species:

- Spruce representing 77% of the total bark in Wallonia
- Douglas representing 15% of the bark in Wallonia
- Oak representing 3% of the bark in Wallonia

These three species represent 95% of the total bark generated in Wallonia.

A review of the literature shows that spruce bark has quite an interesting concentration of extracts (see figure 1) and confirms that there is a relatively high volume of bark that could be put to better use.

Valbiom (an association that promotes biomass resources in Wallonia and partner of the AgriWasteValue project) has recently launched a new project to look at the technical and economic feasibility of bark extract and to evaluate its potential as an alternative plant protection product. The project is called "ExtraForWal" and aims to characterise the extractives present in sawmill, paper mill and wood panel production by-products, more specifically in bark. The project will also evaluate the types and qualities of extracts that can be obtained from this "co-product" resource, and the most suitable extraction methods, confirming the technical and economic feasibility of developing a forestry extraction sector in Wallonia. In this context, some concrete tests are going to be done to study the pesticide activity of the bark extractives of certain species present in Wallonia: spruce (*Picea abies*), douglas fir (*Pseudotsuga menziesii*) and oak (*Quercus robur* and *Q. petrea*).

Through the promotion of co-products, the project will contribute to strengthening the local anchorage of the transformation of forest resources in Wallonia. In this way, ExtraForWal is contributing to consolidating the resilience and competitiveness of Walloon players in the wood sector, in particular sawmills in their core activity of material production. In a context of price pressure, an increased value of co-products can only improve their purchasing power for mobilising raw material upstream.

By adding an additional value-added loop to low-value wood components (such as bark), and without disrupting the current wood transformation processes used in the industry, ExtraForWal is promoting the development of a circular economy and aims to harmoniously integrate this new value-added process into the existing transformation/value-added chain. Moreover, in a context of uncertain evolution of the Walloon forest resource, extraction represents an innovative possibility to potentially increase the value of wood in a different way. However, this recovery method must be developed before it is too late to adapt to the evolution of the Walloon forest resource, a resource that our industries must be able to transform in coming decades.

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Some pointers for the development of botanical plant protection products

When the potential development of botanical plant protection products is evaluated, there are a number of elements to consider.

Before launching a product onto the market, the **regulatory requirements** required for product registration can be very restrictive. Indeed, the budget for the whole registration process and testing is considerable and can be time consuming.

Despite that, companies are searching for alternative PPP that are more environmentally friendly than the products that are currently available. As the preliminary results look very interesting, companies are ready to invest because there is an urgent need to fill this gap in the market.

Recommendations for making the process more simple:

- If extraction is necessary, choose a simple, tried and tested extraction method. If there is nothing innovative about the extraction process, product registration will be simpler.
- If possible, keep the extract raw rather than using purified molecules. Some studies have shown that there is a synergistic effect between molecules in a raw extract that can provide better results.
- To register the product, aim for the most “standardised” product possible. In the case of bark extract, be careful with seasonality and raw extract.

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AgriWasteValue project

The majority of natural actives used in cosmetic or nutraceutical formulations are currently imported to Europe, although a huge diversity of resources is present in North-West Europe. This means that a large amount of residues in covered areas, known for their arboriculture and viticulture sectors, are not being fully exploited for the sourcing of natural actives and are therefore going to waste.

The AgriWasteValue project aims to take agricultural residues from the European North-West regions and to transform them into bioactive compounds. These will be used, initially in key industrial sectors such as cosmetic and nutraceutical fields and then, in a second phase, in the energy, chemical and agricultural fields.

The agricultural residues and biomass that will be used for this project come principally from pruning vines and apple and pear trees.

The project is possible thanks to the financial support of the European Regional Development Fund (ERDF) and Wallonia.

Budget of the project :

- Global budget : 3.193.157,19€

- Fund ERDF : 1.744.580,84€

The AgriWasteValue project is a transnational cooperation that will open up new ways of recycling residues from the agricultural, viticulture and arboriculture sectors.

Contact

Do not hesitate to contact **Flora Mer (f.mer@valbiom.be)** or **Pierre-Louis Bombeck (Pl.Bombeck@valbiom.be)** if you are interested to know more about the case study or AgriWasteValue project.

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