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# Extraction and Purification Processes of Sinapic Acid Derivatives from Rapeseed and Mustard Seed By-Products

Valentin Reungoat <sup>a,b</sup>, Florent Allais <sup>a</sup>, H  l  ne Ducatel<sup>b</sup>, and Irina Ioannou <sup>a</sup>

<sup>a</sup>URD Agro-Biotechnologies Industrielles (ABI), CEBB, AgroParisTech, Pomacle 51110, France; <sup>b</sup>Extractis, Dury 80480, France

**ABSTRACT:** By-products obtained through the industrial processing of rapeseed and mustard seeds are exploited as feed or methanization. However they contain high added value phenolic compounds, such as sinapic acid and its derivatives, that could be recovered by extraction and purification processes. This review presents the state of the art on such recovery processes. It covers conventional extraction by solvent and emergent extraction processes, namely solvent extraction assisted by ultrasound, microwaves, pressure, electro-technologies or enzymes. Concerning the purification processes, liquid-liquid extraction, adsorption and membrane filtration processes are commonly implemented. This article summarizes the most promising methods and technologies for developing sustainable processes for the recovery of sinapic acid derivatives from rapeseed and mustard seed by-products.

## Introduction

Sinapic acid derivatives (SADs) belong to a specific group of highly valuable naturally occurring molecules, the phenolic compounds (PCs). Although SADs are very common in vegetables, high quantities are found in mustard plants concentrated in *Brassicaceae* oilseed crops.[1] Among these, the most produced worldwide in 2019 were rapeseed (70.5 Mt) and mustard (654 kt).[2,3] Their processing generates large amounts of by-products usually exploited as feed, fertilizer [4] or in methanization.[5] However, it could be valorized with a higher economic profitability on specific markets such as pharmaceuticals or nutraceuticals. Indeed, these by-products contain high added value components such as proteins, glucosinolates or phenolic compounds.[6–8] Therefore, the use of these food by-products is increasingly attracting the attention of economists, politicians and researchers as it can represent a resource for a bio-based economy to reduce dependence on fossil-based products.[9,10] In this context, the recovery of SADs from rapeseed and mustard seed waste seems relevant. On one hand, recovering highly valuable compounds from by-products would increase the economical profitability of the culture (Figure 1), and on the other hand, the animal feed nutritional content of the left-over would be greatly improved upon addition of more phenolic compounds reducing the amount needed to feed animals.[11]

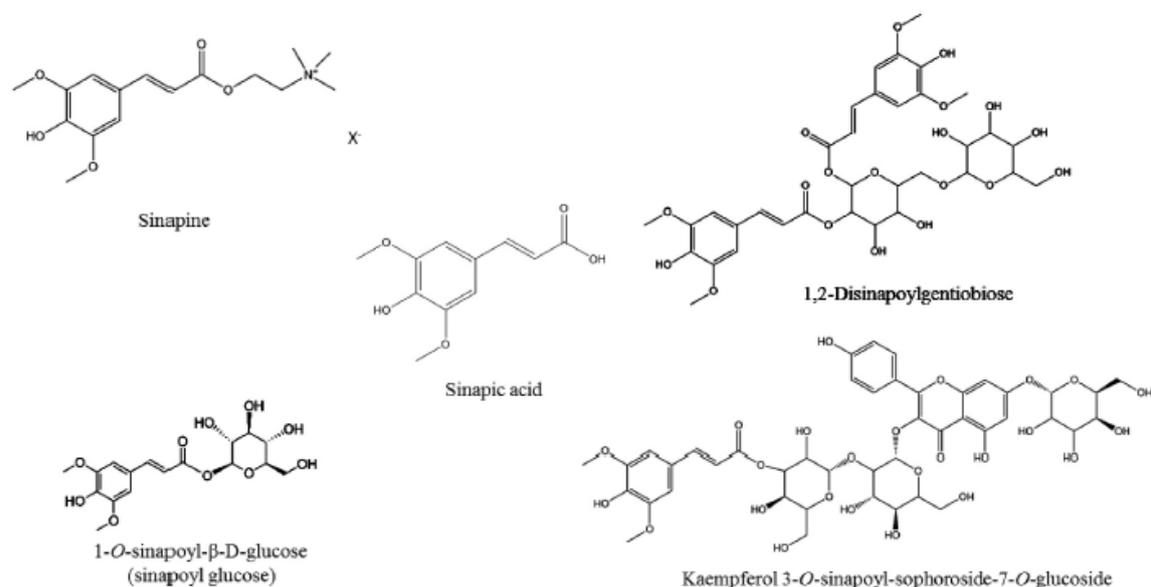
SADs are phenolic compounds with potent antioxidant and health properties.[1] Sinapic acid is the most studied SAD, indeed, it is particularly interesting as it can be used as a platform start-up for the synthesis of various molecules such as anti-UV agents (e.g., sinapoyl malate and analogues),[12–15] non-endocrine disruptive antiradical additives (e.g., syringaresinol),[16] bisphenol A substitutes for polymer/resin synthesis, [17] anticancer agents (e.g., canolol),[18,19] or substrates for pre-polymers (e.g., norbornene dihydrosinapate) .[20] Sinapic acid is currently obtained either by chemical synthesis,[21–23] or by the implementation of extraction/hydrolysis processes from rapeseed by-products.[24–26]

The first interest in recovering SADs from rapeseed and mustard seeds started in 1897.[27] The challenges with the extraction process of specific SADs are to optimize the extraction process without degrading them. SADs are sensitive to environmental conditions and degrade under high temperatures, oxygen, and pH.[28–30] They are also in low content (1% to 4% w/w) compared to the other constituents of the seeds of mustard and rapeseed that are proteins, sugars, phytates,

glucosinolates and other PCs.[31,32] A selective SAD extraction is therefore essential. Extraction processes using solvents have relatively low selectivity and result in low mass fraction of the extract dry matter (2% to 4% w/w).[33] Thus, a better purification process must be implemented to concentrate the selected SAD in order to obtain levels of purity adequate for the markets, with keeping costs sustainable.

Two last century reviews detailed the nature and extraction processes of specific PCs (phenolic acids and tannins) of rapeseed.[7,32] They covered their location in seeds, their different types, contents and interactions with proteins. The characteristics of SADs in rapeseed [6] and mustard [34] have also been detailed. More recently, two reviews presented some aspects of the extraction and purification processes of SADs from the *Brassica* genus.[35,36] In the present work, an in-depth review of the literature is provided for the recovery of SADs from rapeseed and mustard seeds. It is intended to help scientists to get key information to select the most relevant process fitting their applications.

Up to date, more than 100 articles dealt with the extraction/ removal of PCs from rapeseed and mustard seeds. Among these studies, conventional solvent extraction (CSE) is the most commonly used process. Intensification methods, either physical (ultrasound, microwave, electrical, pressure) or biotechnological accelerators (enzymatic), have also been studied to improve the contents of PC or certain SADs (sinapine, sinapic acid, sinapoyl glucose). The first part of this review presents the diversity of by-products from rapeseed and mustard seeds focusing on their SADs of interest. Next, the strengths and weaknesses of the different extraction and purification technologies will be discussed, and propositions and descriptions of the most promising process sequences will be given.



**Figure 1.** Chemical structures of sinapic acid and its main derivatives in rapeseed and mustard seeds.

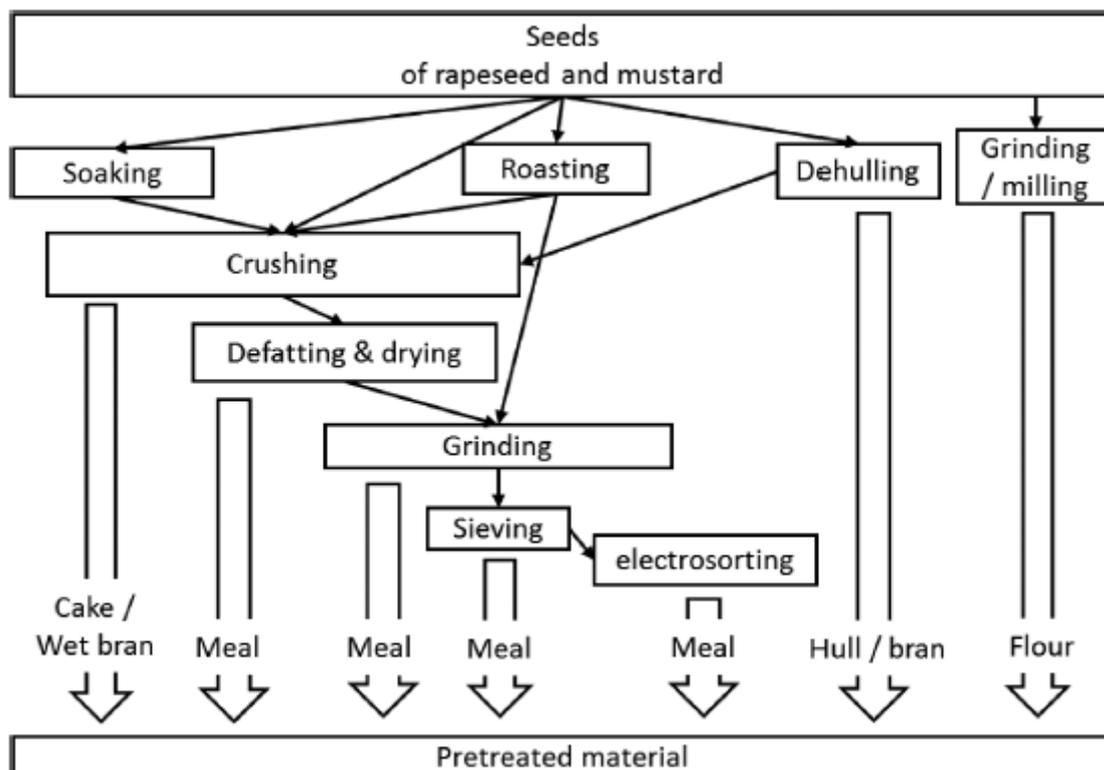
## CHARACTERIZATION OF BY-PRODUCTS

The most widely used *Brassicaceae* species in industry are rapeseed "*Brassica napus*" and brown/oriental mustard "*Brassica juncea*".[2,37] The production of white mustard "*Sinapis alba*" is also significant as it is the main form of mustard produced in North America.[38,39] Consequently, it is extensively studied in the literature regarding its characterization (composition, bioactivities) and transformation (pressing, extraction). The recovery of SADs from those *Brassicaceae* seeds has also been widely discussed. The term canola is often used in the literature to refer to cultivars of the

Brassica genus (*Brassica napus*, *Sinapis alba* or *Brassica juncea*) with low contents of erucic acid and glucosinolate, the “00 varieties” .[40,41] All relevant studies dealing with *B. napus*, *B. juncea* and *S. alba* are tentatively included in this review, regardless of their cultivar.

### Pretreatments

The seeds of rapeseed and mustard are usually processed to get the oil or the seed kernel for the food and energy markets .[7,42] By-products can represent as much as 60% (w/w) of the seed weight .[43,44] For rapeseed, the most common transformation is the total extraction of oil, rapeseed meal being the by-product. Concerning the mustard, the production of condiment is the main transformation of mustard seeds in Europe, whereas it is vegetable oil in Asia, [43,45] the respectively generated by-products are bran and meal. Their composition varies depending on the plant variety, growing conditions and processing methods. The seeds can undergo several pretreatments which include soaking, [33] de-hulling, [46] roasting, [47] crushing, [48] defatting, [31] grinding, sieving, [49] and electrosorting .[50] Figure 2 presents the different names that the by-products can take in function of the pretreatment step.



**Figure 2.** Overview of pretreatment processes of rapeseed and mustard seeds.

The few studies on the defatting step have shown that SADs are poorly extracted in the lipid phase .[34,51,52] However, the impact of defatting on the recovery of SADs does not seem to have been studied. In contrast, drying has been shown to reduce the PC content and increase that of the sinapine SAD in a mustard by-product .[53] The effects of pretreatments on the evolution of the SAD content are not well known. Thus, the pretreatments applied to the by-products will be a source of variability which makes it difficult to compare the different results of the studies on rapeseed and mustard.

## Sinapic Acid Derivative Contents

SADs are the main PCs [54,55] among other PC metabolites such as phenolic acids, [32,56–58] flavonoids [56,57,59–61] and condensed tannins [32,62] in the seeds of mustard and rapeseed as well as in their by-products. [63] The SADs found in the seeds of rapeseed and mustard are mainly derivatives of sinapic acid with ester linkages. Therefore, the main individual PC quantified in this study are the SADs: sinapine, sinapoyl glucose, and sinapic acid, named specific SADs. They are individually quantified by HPLC and GC chromatographic techniques, when only a global spectrophotometric measurement is used in the Folin-Ciocalteu method. These specific SADs will be referred as “PC – SADs” in this review. Table 1 summarizes the contents of PC-SADs and specific SADs found in the literature according to the by-product studied.

Table 1 shows that pure hull and bran contain low amounts of SADs. [67,68] Indeed, the SADs are located in the seed cotyledon much more than in the hull. [46] Data on this are scarce and could be more investigated. Likewise, there is little data on the distribution of sinapoyl glucose in the literature due to the price of the analytical standard. The contents in PCs, sinapine and sinapic acid can be considered equivalent for all the by-products of processed seeds (flour, cake and meal) (Table 1). The huge content variability can be explained by (i) the use of different operating conditions during the transformation, (ii) different cultivars, and (iii) variable growth conditions of the seeds, as well as (iv) the analytical methods. [69]

Among the SADs, sinapine - the choline ester of sinapic acid - is the predominant form. It accounts for 62% to 94% (w/w) in *B. napus*, [54] 90% to 94% (w/w) in *B. juncea* [46,54] and *B. alba*. [58,70] This result was expected because sinapine accumulates in the seed during plant metabolism. [64] The sinapine content varies from 5 to 35 mg/g of dry matter (DM) in the processed seeds of rapeseed and mustard (Table 1). Compared to the measured content of PCs, it appears clearly that sinapine is the main component. The sinapic acid in its free form is rather low in processed seeds (0.1 to 5 mg/g DM). [71] Other SADs have also been quantified in a lower extend such as disinsapoylgentiobioside (0.05–1.5 mg/g), sinapoyl malate (0.15–1.1 mg/g), di-sinapoyl glucose (0.15–0.75 mg/g), quercetin-sinapoyl di-hexosepentose (0.22–0.52 mg/g) in the case of *B. napus* [47,63]; and kaempferol 3-sinapoylsophorotrioside-7-glucoside (0.01–0.25 mg/g) [56] in the case of *B. juncea*. There are other minor kaempferol, glycoside and PC derivatives of sinapic acid. [50,63] The given quantification remains approximate as it is based on the calibration of sinapic acid. It should be confirmed with appropriate standards. All of these SADs are sinapic acid equivalent (SAE) as they can release sinapic acid upon hydrolysis.

Despite their higher content in *Brassicaceae*, the SADs remains minor seed components (0.5–3.5% w/w on the dry matter) compared to proteins (18% - 48% DM), [7,72] sugars (15% DM), [73] lipids (29% - 40% DM), [7,74] glucosinolates (0% - 4% DM), [11,75] phytic acid (1% - 4% DM), [62] and lignin (0.4% - 10% DM). [76,77] As a consequence, the development of selective extraction and purification processes is essential for the recovery of SADs.

**Table 1.** Characterization of the main SADs in rapeseed (*B. napus*) and mustard (*B. juncea*, *B. nigra*, and *S. alba*) seeds and their by-products.

Material for extraction	Compounds measured	Rapeseed		Mustard	
		Contents	Ref.	Contents	Ref.
Flour	Phenolics	32 ± 4 μmol(sinapine equivalent)/g dry seed [12.4–19.4] mg (SAE)/g flour [7–64.67–83] μmol/g flour	[54,64,65]	8 mg (GAE)/g seeds [11.5–42.3] mg (SAE)/g flour	[31,66]
	Sinapine	[6.0–34.4] mg/g flour	[47,64,67,68,86,87]	27 ± 11 μmol/g dry seed 5.8 ± 1.9 μmol/g fresh seeds [7.8–26.3] mg/g flour	[31,64,88,89]
	Sinapoyl glucose	[0.1–0.55] mg/g dry flour [0.05–1.40] mg/g dry flour	[47]	[0.15–0.48] mg/g flour	[31]
Cake	Phenolics	[9.0–20.1] mg (SAE)/g dry cake	[48,54,89,90]		
	Sinapine	[8.5–16] mg/g dry cake	[90,91]		
Meal	Sinapic acid	0.50 ± 0.00 mg/g dry cake	[90]		
	Phenolics	64.2 ± 1.2 μmol (SAE)/g dry meal [5.7–20.1] mg (SAE)/g dry meal Fraction in meal: 1.5% - 2.7% (w/w)	[46,54,69,90,92–100]	[1.0–40.0] mg (SAE)/g meal	[31,46,54,95,97,98,101]
	Sinapine	[31.0–45.0] μmol (SAE)/g dry meal [7.5–34] mg/g dry meal Fraction in meal: 1.7% ± 0.1% (w/w) Fraction of the phenolics: 79% (w/w)	[11,25,26,31,46,68,69,90,91,94,97,98,102–104]	10.0–22.2 mg/g meal Fraction of the phenolics: 90% (w/w)	[31,54,97,98,105]
	Sinapoyl glucose	8.7 ± 0.8 mg/g dry meal	[46,97,98]	0.49–0.67 mg/g	[46,54]
	Sinapic acid	[2.2–3.8] μmol (SAE)/g dry meal [0.2–5.4] mg/g dry meal	[25,26,31,46,90,94,97,98,103]	[0.15–0.4] mg/g meal	[31,46,54,58,71]
Hull	Phenolics			6.24 ± 0.40 mg (SAE)/g	[46]
	Sinapine	[0.68–6.0] mg/g dry hull	[67,68]	4.74 ± 0.28 mg/g	[46]
	Sinapoyl glucose			0.41 ± 0.02 mg/g	[46]
	Sinapic acid			0.90 ± 0.01 mg/g	[46]

GAE: gallic acid equivalent; SAE sinapinic acid equivalent.

## CONVENTIONAL SOLVENT EXTRACTION

Conventional solvent extraction is the most widely used process for the identification and quantification of individual PC in plant material due to its ease of implementation. It consists of the immersion of the grinded starting material into a solvent and then recovering the extract once equilibrium has been reached. The main factors influencing the extraction process are the nature of the solvent, the extraction temperature, the duration of the extraction, and the solvent to matter ratio. [78] The different extraction conditions implemented on rapeseed and mustard seeds for PC characterization are presented in Table 2.

The main measurement method is the Folin-Ciocalteu spectrophotometric method. However, interference is known to occur when using this method. Thus it is difficult to draw precise conclusions, only certain trends can be highlighted. [79] The important SADs are sinapine, sinapic acid and sinapoyl glucose measured by chromatographic methods related to their aforementioned abundance in the seeds. From Table 2, it appears that there is no universal extraction procedure. However, methanol, ethanol, and their combinations with water, are the most commonly used. Solvents with intermediate polarity have a high capacity to dissolve PCs. [78] The extraction temperature is either around 80°C for 10 to 30 min or at room temperature for up to 24 h. Extraction temperature and time appear to be interdependent factors. 2, 3 or 4 extraction cycles are often needed to extract and to quantify the maximum PC - SADs content of the material. The solvent to matter ratio is mainly between 10 to 30 mL/g of dry matter, most likely to limit solvent consumption and to avoid too viscous mixtures to handle. It is not possible to propose optimal operating conditions maximizing the PC contents since the variety of seeds and cultivation conditions impose to be versatile in extraction conditions. Thus, the Table 3 comparative and optimization studies shall provide useful information. The following sections describe the optimal conditions found focusing on the solvent.

### Methanol

Methanol is a proton donor polar bio-based and cheap solvent. It has a high capacity to dissolve SADs due to similar polarities. [78] Therefore, methanol has been the most popular solvent for SAD extraction from the seeds of mustard and rapeseed (Table 2). Optimization studies showed that at cold or room temperature, methanol has the lowest efficiency compared to other aqueous solvents: ethanol 70%-80% > acetone 70% > methanol 80% (v/v) (Table 3). The time to reach extraction equilibrium need to be increased sometimes (8 h or 16 h). [80–84] At hot or boiling temperature, the extraction yield is higher. However, 70% (v/v) aqueous acetone gives better yields than 80% (v/v) aqueous methanol. [83] Beside, extraction with 70% methanol has been shown to have similar performance than 70% ethanol. [85,109] Despite its common use, methanol remains a toxic solvent and is poorly ranked in the Glaxo SmithKline industrial sustainability solvent guide. [111] Therefore,

that explains why more and more authors prefer to use ethanol to extract SADs from the seeds of mustard or rapeseed. These trends show the strong influence of temperature on the solvent composition that gives the highest extraction yield. However, these results obtained for PC extraction must be confirmed with studies focused on specific SADs.

**Table 2.** Conditions for conventional solvent extraction of sinapic acid derivatives from rapeseed (*B. napus*) and mustard (*B. juncea*, *B. nigra*, and *S. alba*) seeds and by-products.

Solvent nature (% v/v)	Starting material	Temp. (°C)	Duration (min)	S/M (mL/g)	Rapeseed		Mustard	
					Target compounds	Ref.	Target compounds	Ref.
MeOH 100%	Seeds, cake and meal	50–75	20–30	10–100	PC, Sin, SA	[25,64,90,94,99]	Sin	[64]
MeOH 100% + 1% HCl	Meal	25	2–1440	10	PC, Sin	[80,91]	Sin	[89]
MeOH 70% – 85%	Meal	75	10–15	20	PC, Sin, SA	[58,69,93]	Sin, SA	[58,105]
MeOH 70%	Flour, meal, hulls	4–20	20–120	10	PC, Sin, SG, SA	[47,68,100]		
MeOH 50% + 2% HCl or acetic acid	Meal, seeds	90	3 x 30	50	Sin, SA	[87,103]		
MeOH 15%	Seeds	80	20	11.5	Sin	[88]		
MeOH/Acetone/water (7:7:6) (v/v/v)	Meal	70	20	10	PC	[106,107]		
MeOH/Acetone/water (7:7:6) (v/v/v)	Meal	RT	6 time extracted	20	SA	[71]	SA	[71]
EtOH 95%	Meal	80	180	23 (Soxhlet)	Sin	[102]		
EtOH 70%	Cake, meal	80	30	17–20	PC	[48,92]		
EtOH 70%	Meal, cake	RT	60–120	10–25	Sin	[11]		
EtOH 50%	Cake	60	240	30			Sin	[30]
Water/NaOH, pH 12	Cake	75	120	10			Sin, SA	[52]
Water/NaOH, pH 11–12	Meal	RT	30 or 1080	8 or 18	PC, SA	[94,96,108]		[30]
Water	Meal	50–80	30	16.7–20	PC, Sin, AS	[26,92]	PC	[101]
Water	Dehulled or full seed flour	4 or RT	5 or 30	33			PC, Sin	[66,88]

MeOH: methanol, EtOH: ethanol, PC: phenolic compounds, Sin: sinapine, SG: sinapoyl glucose, SA: sinapic acid, SAD: sinapic acid derivatives, RT: room temperature, S/M: solvent to matter ratio.

**Table 3.** Optimization studies on conventional solvent extraction of SADs from rapeseed (*B. napus*) and mustard (*B. juncea* and *S. alba*) seeds and by-products.

Solvent (% v/v)	Starting material	Temp. (°C)	Duration (min)	S/M (mL/g)	Method (target compounds)	Optimal condition	Ref.
MeOH 70% or 100%	Rapeseed meal	50 or 75 or reflux	10 or 20	100	HPLC (PC, Sin, AS)	MeOH 70% (v/v) for 20 min under 75°C.	[109]
MeOH [70%-100%] or Acetone [70%-100%] or water or mixtures.	Rapeseed cake	25	120	10	FC (PC)	MeOH 100% (v/v) is found as effective as acetone 70%v and water.	[80]
MeOH [0%-100%] or acetone [0%–100%] or water or mixtures.	Mustard meal	25	20	40	FC (PC)	DOE optimization: acetone 50% (v/v) was more efficient than mixtures of MeOH.	[81]
MeOH 80% or acetone 70%	Rapeseed meal	21	30	5	FC (PC)	Acetone 70% is more efficient than MeOH 80% (v/v).	[82]
MeOH 70% or EtOH 70%	Mustard cake or meal	75	3 x 30	9	FC (Sin)	EtOH 70% (v/v) is as effective as methanol 70% at 75°C.	[85]
EtOH [30%-100%]		30 to 55	30 to 360	10 to 50		DOE optimization: EtOH 65% (v/v), 55°C, 4 h, 35 mL/g, matter not defatted.	
MeOH 70% or EtOH 70% or Water	Mustard dry cake	4	2 x 240	1.5	FC (PC)	EtOH 70% is more efficient than MeOH 70% (v/v) or water.	[84]
EtOH 70% or Water/NaOH	Mustard meal	50	60	18	FC (PC)	EtOH 70% (v/v) is 2.4 times more efficient than water extraction.	[110]
EtOH [0%-70%]/NaOH pH 12	Mustard cake	75	120	10	HPLC (SA, ES)	Under pH 12, EtOH 0% and 70% (v/v) yields the highest SA and ES content respectively.	[30]
EtOH 95% or water	Rapeseed meal	80	30	17	FC (PC)	EtOH 95% (v/v) is more efficient than water.	[92]
EtOH 0% to 85%	Rapeseed cake	20 to 70	3	5 to 20	FC (PC)	EtOH 35% (v/v), 65°C, 20 mL/g.	[63]
EtOH [45%-95%]	Mustard cake	45 to 75	40	10 to 30	HPLC (Sin)	DOE optimization: EtOH 70% (v/v), 75°C, 10 mL/g under 30 min.	[33]
EtOH 70%	Mustard cake	80	3 x 30 min or 24 h or 7 days	20	FC (PC)	EtOH 70% (v/v), 80°C for 3 cycles of 30 min.	[48]

FC: Folin Ciocalteu spectroscopic method, HPLC: High Pressure Liquid Chromatography, PC: Phenolic compounds, Sin: sinapine, AS: sinapic acid, ES: ethyl sinapate, S/M: solvent to matter ra

## Ethanol

Ethanol is also a proton donor polar solvent, excellent substitute to methanol due to its non-toxicity, similar polarity, easy access in high purity at low cost and with fully biodegradable property .[112] Optimization studies show that the highest PC and sinapine extraction yields are obtained from a 70% (v/v) hydro-ethanolic mixture [33,85] and temperature just below the ebullition point (75–80°C) .[48] Under these conditions, a kinetic study showed that an extraction time of 30 min is generally sufficient. However, some conflicting optimizations were found based on Folin-Ciocalteu spectrophotometric measurements that do not allow for the precise quantification of a given SAD.[63,85] Therefore, the selection of chromatographic methods is recommended when performing comparison and optimization studies.

The optimum sinapine amount found is 3.5% (w/w DM), representing a relatively low selectivity of the extraction process.[33] Indeed, the addition of water to the organic solvent decreases the solubility of sinapine in the extract. The use of pure ethanol can reach 4.2% to 7.1% w/w DM.[33,92] This is due to the relative low selectivity of ethanol and water for SADs over other components of plant material (proteins, sugars). Therefore, it seems difficult to expect higher purities using conventional solvent

extraction conditions which optimize the extraction yield of PC - SADs. Despite the advantages of ethanol, it has still a higher cost and flammability hazard compared to the greenest solvent: water.

### Water

Water is the most polar, cheap, safe, and eco-friendly solvent.[113] It attracts high attention as can be seen with the 2020 patent using water to purify canolol .[114] Although lower extraction yields are obtained with water compared to methanol, acetone or ethanol at uncontrolled or acid pH, [30,80,81,84,92,110] longer extraction durations (week) can increase the yields. Thus, an extraction time of 7 days at room temperature with water would lead to the highest PC content in extract than an increase of temperature or an organic solvent.[48] This phenomenon might be explained by a change in the structure of the raw material during maceration. However, those results on PC – SADs should be confirmed by studies focused on specific SADs.

Some authors modified the extraction conditions by increasing the pH with NaOH or Ca(OH)<sub>2</sub> (Table 2) (i) to improve protein extraction, (ii) to hydrolyze sinapine into sinapic acid, [26] (3) to prepare the extract for the purification process, [101] and (4) to remove SADs considered as antinutritional compounds .[93] However, at high pH SADs are easily oxidized into degradation products of sinapic acid: thomasidioic acid, then 6-hydroxy-5,7-dimethoxy-2-naphthoic acid and 2,6 dimethoxy-*p*-benzoquinone .[115] This degradation can be limited by low temperature as demonstrated by the interesting reported sinapic acid yields of 7.8 to 14 mg/g meal .[94,108] The other downsides of using alkaline solutions are the need for an acid neutralization step that increases the cost of the process) and a more difficult handling of the side streams.[116]

### Discussion on Conventional Solvent Extraction

By gathering information on conventional solvent extraction, some interesting conclusions can be drawn. It is clear that all operating factors (nature of the solvent, extraction temperature, liquid/solid ratio and the extraction duration) are related. It has been shown that when the temperature increases, the SAD content in extract also increased. Two reasons can explain this: (i) the solubility of the molecule increased, (ii) bonds are weakened between SADs and proteins or sugars. However, a too high increase of temperature could degrade the PCs.[117] Moreover, the increase of temperature is limited by the solvent boiling point. Temperatures above the solvent boiling point are possible but require sophisticated equipment compared to those commonly used in extraction. The pressurized liquid extraction is a technology that seems relevant to go beyond this limitation. This could be of particular interest to evaluate the competitiveness of water compared to organic solvents.

The combination of polar organic solvents with water appears to be effective in obtaining the highest PC - SAD yields. Indeed, water improves the extraction capacity of organic solvent mixtures as it can improve the swelling of the plant material .[79] Organic solvents, such as alcohols, have the advantage of leading to greater yield and selectivity of SADs compared to pure water .[118] Ethanol is preferable than methanol for reasons of toxicity and equivalent extraction efficiency. Therefore, the best CSE conditions for the recovery of SADs under the form of sinapine seems to be ethanol 70% (v/v), reflux (75–80°C), 10 mL/g DM, for 30 min or less. Extraction of sinapine is favored by acidic conditions whereas alkaline pH promotes the transesterification of sinapine into ethyl sinapate .[30]

The use of water as an extraction solvent would be limited to specific objectives. This is due to its lower efficiency or the longer extraction time required. Its application could be for the extraction of proteins, or due to constraints imposed by another process (purification or conversion of the SADs), or to comply with environmental regulations. The pH of the medium is an important factor for the recovery of specific SADs. At low pH, the main SAD recovered is sinapine, while at high pH, it may be sinapic acid or its degradation products .[29] Concerning the extraction time, some studies showed that the

extraction duration necessary to obtain the same PC - SAD extraction yield depends on the nature of the solvent .[48] Therefore, moving towards kinetics studies concerning their extraction would enhance the understanding of the links between the nature of the solvent and the extraction time. Further comparative and optimization studies focussing on solvents (ethanol, water), temperature and solvent to matter ratio are needed.

The PC – SADs are often globally measured by the Folin- Ciocalteu spectrophotometry method that do not discriminate SADs, it is recommended to use HPLC or GC chromatographic methods with pure standards to quantify specific SADs. The process selectivity, its impact of the solvent nature on the next steps, the costs and environmental impacts on an industrial scale should all be considered. Furthermore, optimization studies should use the response surface methodology rather than the one-factor-at-a-time generally preferred .[118] Among the entire PC - SAD extraction processes, conventional solvent extraction have been the most used. However, some intensification technologies are effective in improving the extraction yields of PC from plant biomass.

### INTENSIFICATION OF EXTRACTION PROCESSES

The number of studies focusing on the specific intensification of SAD extraction from the seed of rapeseed and mustard is low in comparison with those using the conventional solvent extraction. This part presents the main results obtained by the implementation of intensification processes using ultrasound, microwave, electro-technologies, pressurized liquid, and enzymatic hydrolysis.

#### Ultrasound Assisted Extraction

Extraction intensified by ultrasound corresponds to a solvent extraction associated with a cavitation phenomenon due to ultrasound. This phenomenon, generated by acoustic waves, leads to destruction of cell matter and thus makes the target molecules more accessible to the solvent. Internal stirring is created in the matter and leads to the improvement of the diffusion phenomena of the molecules into the solvent. It is the most widely applied intensification technology for SAD extraction from rapeseed and mustard.

The parameters used to describe the intensification by ultrasound are the ultrasonic intensity ( $W/m^2$ ) or density ( $W/m^3$ ), and frequency (kHz). Other parameters such as extraction temperature, reactor design, solvent nature, solvent to matter ratio (mL/g), and particle size or structure characterize the extraction process .[119,120] Another important parameter is the type of the device generating ultrasounds, bath or probe. In the optimization studies presented in Table 4, the operating conditions studied are alcohol concentration, extraction time, temperature, ultrasonic intensity ( $W/cm^2$ ), and power density ( $W/cm^3$ ) .[119] Unfortunately, relevant information such as the type of equipment used, frequency or ultrasound power, is too rarely specified. Thus, a comparison study is difficult.

It is hypothesized that the application of ultrasound increases the SAD extraction yield, as it has been shown with other biomasses.[124] Thus, very few studies compare the results obtained using ultrasound to what was obtained by solvent extraction. In the twenty studied literature, two objectives were identified: (i) to characterize the contents of PC, whether total or individual sinapine, sinapic acid and sinapoyl glucose, [31,46,53] and (ii) to maximize the content of PC - SADs in the extract.[48,63,106] Several solvents were evaluated under ultrasonic bath for SAD extraction: aqueous methanol, ethanol, acetone, isopropanol, and water. However, due to the measurement method or the lack of experimental details, the listed results are for information only. Conflicting results were found on optimal composition of aqueous methanol for PC– SAD or sinapine extraction: methanol 70% (v/v) in ultrasonic bath) [54,95,121] or methanol 50% (v/v) using an ultrasonic probe.[65] Further studies are needed to clearly set the optimum of the hydro-methanolic composition.

**Table 4.** Optimization of ultrasound assisted extraction of SADs from rapeseed (*B. napus*) and mustard (*B. juncea* and *S. alba*) seeds and by-products.

Solvents (% v/v)	Starting material	Ultrasound conditions	Temp. (°C)	Duration	S/M (mL/g)	Method (target compounds)	Results	Ref.
MeOH 0% or 50% or 100%	Rapeseed Flour	40 kHz, 0.011 W/cm <sup>3</sup>	25	15 to 30 min in bath or without US (control)	5	FC (SAE)	MeOH 50% (v/v) at 25°C and 30 min under US was best.	[85]
MeOH 70% or EtOH 96%	Rapeseed Meal		RT	1 x 12 h + 2 x 45 min under US	10	FC (PC)	MeOH 70% was better than ethanol 96% (v/v).	[95]
MeOH 70% or EtOH 70% or Isopropanol 70%	Rapeseed Meal			3 x 1 min under US	9	HPLC (Sin, SG, SA)	MeOH 70% was better than EtOH 70% or isopropanol 70% (v/v)	[54]
MeOH or Acetone or Water or Ethyl acetate 70%	Mustard Meal		RT	16 h + 2 x 45 min under US	13.3	FC (PC) HPLC (Sin)	Water was best for PC. Yet, MeOH 70% was best for sinapine.	[121]
Acetone/MeOH/Water (7:7:6) (v/v/v)	Rapeseed Flour	bath (Elma): 200 W	40 to 70 or RT	20 to 35 min or 30 min (control)	5 to 20 or 10 (control)	FC (PC)	70°C, 20 min under US, 10 mL/g gave top PC, 20% higher than control but decreasing after 30 min US.	[106]
MeOH, acetone, ethyl acetate 70% or water	Rapeseed Meal		RT	16 h + 2 x 45 min under US	13.3	HPLC (Sin)	MeOH 70% was best for sinapine.	[121]
Water	Rapeseed Cylinder shaped stems	probe: 24 kHz, 0.33, 0.67 W/cm <sup>3</sup> , 0 to 400 W	20 to 85	5 to 60 min under US	8	FC (PC)	50 min under US 0.67 W/cm <sup>3</sup> with a 5 mm sample length of 0.5 cm 85°C. PC content 29% higher compared to water	[122]
EtOH 0 to 95%	Mustard cake	probe: 0.5 W/cm <sup>3</sup> , 60 W, 20 kHz	20 to 75	10 to 60 min	10 to 60	FC (PC) HPLC (Sin, SA)	EtOH 70%, 75°C, 40 mL/gDM, 30 min were optimal. SAD content 10 mg/g meal, purity 4.5% (w/w), PC content higher with US than with hot ethanol. Sinapine extraction yield higher at 75°C than 20°C.	[48]
EtOH 50%	Rapeseed meal	probe: 25 kHz, 200, 400, 600 W	RT	5 to 60 min under US	15 to 35	FC (PC)	30 min, 400 W, 30 mL/g and 5 L/min nitrogen. PC content 10%; 29% higher than conv solvent extraction EtOH 50% v/v, 6 h.	[123]
EtOH 45%	Rapeseed cake	probe (VC 750) 20 kHz, 73 W/cm <sup>2</sup>	25, 45, 65	1 to 15 min	10	FC (PC)	3 min, 45°C without US to get highest PC content. US did not improve the PC content.	[63]

RT: room temperature, MeOH: methanol, EtOH: ethanol, US: ultrasounds, FC: Folin Ciocalteu spectroscopic method, HPLC: High Pressure Liquid Chromatography, PC: Phenolic compounds, Sin: sinapine, SA: sinapic acid, SG: sinapoyl glucose, S/M: solvent to matter ratio, US: ultrasound

Several authors favored aqueous ethanol due to its lower toxicity. Ethanol 70% (v/v) was found to be the optimal condition for PC-SAD extraction with 0.5 W/cm<sup>3</sup> ultrasonic power, 75°C, 30 min, and 30 mL/g DM.[48] These ultrasound conditions improved the PC-SAD extraction yield by 13% [48] or 19% [123] compared to classical solvent extraction with the same solvent and condition. Optimizing extraction is effective for all sample constituents so the relative purity is not improved. The ultrasound extraction improves yield but has little or negative influence on purity.

Improvements in ultrasonic assisted extraction (UAE) used inert conditions flowing nitrogen to avoid SAD oxidation.[123] It helped to increase the PC-SAD content by 13%. The use of a hot air pretreatment also improved the PC-SAD content by 38%.[53] However, conflicting results on the optimal extraction conditions were also found .[63,83] Therefore, these results must be strengthened performing comparative studies using precise measurement methods. SAD degradation remains moderate under gentle 0.5 W/cm<sup>3</sup> for 60 min at 20°C [48] or 4 W/cm<sup>3</sup> for 30 min at 25°C [106] ultrasound treatments. Indeed, a weak degradation (1% for sinapic acid and 5% for sinapine) was noted in a mustard extract .[48] No degradation of PC – SADs was observed up to 60 min under 20 W/cm<sup>3</sup> ultrasonic power density .[123] Further insights on the mechanism of SAD degradation under ultrasound would be of interest to better control the application of UAE.

**Recommendations:** UAE is a promising technological process. For best results, the extraction time should be limited to 30 min with no more than 13 W/cm<sup>3</sup> as it was shown that the maximum PC-SAD yield was around this ultrasonic power density .[123] 30 min is faster than most conventional solvent extractions. The solvent temperature should be as high as possible to maximize SAD yield. A probe should be preferred to a bath because the probe delivers the ultrasound energy to the heart of the extraction medium enhancing SAD extraction yields .[120] Nitrogen flow and hot air pretreatment are useful. However, these pretreatments increase the total cost of the extraction process. Obviously, the ultrasonic power density used should always be mentioned in W/cm<sup>3</sup> for reproducible results.

#### Microwave Assisted Extraction

SAD microwave assisted extraction (MAE) with rapeseed dates from the 2010s. This electromagnetic technology is known to improve the extraction efficiency, probably due to a synergic effect of mass and heat transfer .[125] The variables characterizing the MAE efficiency are: water content of the sample, solvent/material ratio, extraction temperature, and duration. The parameter used to describe

the intensity of the microwaves can be the power in W or the specific power density in W per g of sample. The latter is recommended because it is more precise and provides more information as to microwave treatment .[126] The application of MAE on rapeseed and mustard seeds is presented in Table 5.

MAE is used in two configurations: either with a solvent during the liquid/solid extraction, or dry roasting without solvent .[47,125] In both cases, MAE is considered as a pretreatment since a subsequent liquid/solid extraction is always needed .[90,127] The PC-SAD content increases with the microwave pretreatment intensity reaching a maximum above which degradation occurs .[47,51,107,127,128] PCs are degraded, for example sinapic acid is degraded in canolol by decarboxylation [19,90]). A 60% decrease of sinapine and sinapoyl glucose contents in extract occurred after roasting 5 min at 6 W/g and 115°C. The decrease reached 96% after 20 min at 240°C .[127] It is therefore critical to control power density and roasting time. Several optimal conditions have been listed for sinapine and sinapic acid production: 2–3 min under 4 W/g [51] or 16 W/g [128] or 6.25 min under 5 W/g with hydration pretreatment .[90] Additional treatments can be applied with MAE to improve the SAD extraction. Superheated steam to hydrate the sample for 18 h led to a 28% increase of the sinapine content .[90] Steam regulated the reaction temperature limiting SAD degradation.[127]

**Table 5.** Microwave assisted extraction of SADs from rapeseed (*B. napus*) and mustard (*B. juncea* and *S. alba*) seeds and by-products.

Starting material	Microwave pretreatment conditions				CSE conditions	Method (target compounds)	Results	Ref.
	Frequency, Power or power density	Temp (°C)	Duration (min)	Solvent and S/M (mL/g) or none				
Rapeseed cake	2.45 GHz 4 W/g	170	3 x 9	None	MeOH 70% RT 3 x 20 min 10 mL/g	HPLC (Sin, SG, SA, QSDG, SM, DSG, DDSG, canolol)	Decrease of the sinapine, sinapic acid and sinapoyl glucose contents by 11.3%, 14.4% and 59.1% respectively. Canolol was produced accordingly.	[47]
Mustard meal	300 W/g		20	Steam	MeOH 70% under US, 1 min, 9 mL/g	HPLC (Sin)	The microwaves did not influence the sinapine content.	[34]
Rapeseed meal	88 to 220 W/g		1, 3, 5	Water 4, 5, 6	MeOH/Acetone/Water (7:7:6) (v/v/v) 70°C 20 min US	FC (PC)	optimal conditions: 5 min, 127 W/g, 6 mL/g for highest PC.	[107]
Rapeseed meal	2.45 GHz 10,000 W 12 W/g/min	160	5.2 to 6.6	None or steam or hydration with water	Pure MeOH 75°C 20 min	FC (PC) HPLC (Sin, AS, canolol)	Decrease of the PC, Sin and AS contents by 4%, 24% and 6% by microwave. Increase of the Sin and SA contents by 28% and 91% by 18 h hydration and superheated steam.	[90]
Rapeseed meal	100 to 700 W 1,000 to 7,000 W/g		1 to 25	None	Diethyl ether/ethyl acetate 1:1, 3 x 5 mL	HPLC (SA, canolol)	Optimal condition 3 W/g with 58% SA conversion	[19]
Rapeseed seeds	2.45 GHz 4 W/g		0 to 8	None	MeOH 50% (v/v), RT, 20 min, 40 mL/g	HPLC (Sin, SA, canolol)	highest Sin, SA and canolol content after 3, 2 and 7 min respectively.	[51]
Rapeseed flour	6 W/g	120 to 200	5 to 20	None or steam	MeOH/Water 3 x 1 min under US 9 mL/g	HPLC (Sin, AS, SG, canolol)	SA content increased by 180% with 10 min microwave at 180°C. Slight increase for Sin and SG with 5 min microwave at 120°C. Extended time or temperature decreased all contents.	[127]
Rapeseed seeds, cake, meal	2.45 GHz 16 W/g		1 to 7	None	Pure MeOH 60°C 20 min 100 mL/g under US	HPLC (Sin, AS, canolol)	Optimum for sinapine content (mg/g): 800 W, 2 min for seeds (5.6), 3 min for cake (9.0), 4 min for meal (8.5), 2 to 4 min microwave. Canolol degrades afterward.	[128]
Rapeseed seeds	2.45 GHz 2.8 W/g	20 to 170	0 to 9	None	MeOH 70%, 75°C, 20 min	HPLC (canolol)	Optimum temperature 160°C with canolol formation after 7.5 min.	[129]

CSE: conventional solvent extraction; RT: room temperature, US: ultrasound, FC: Folin Ciocalteu's method, HPLC: High Pressure Liquid Chromatography, PC: Phenolic compounds, Sin: sinapine, AS: sinapic acid, SG: sinapoyl glucose, QSDG: quercetin sinapoyl di-glucose, SM: sinapoyl malate, DSG: disinapoyl gentiobioside, DDSG: disinapoyl glucoside, S/M: solvent to matter ratio.

**Recommendations:** Using MAE can generate high temperature depending on the power and roasting duration applied. Therefore, in order to recover intact SADs, only 2 to 3 min roasting time is recommended. Generally, the temperature should not exceed 120–140°C .[127,130,131] The specific power density should be applied accordingly.

### Electro-technology Assisted Extraction

Among the electro-technologies, pulsed electric field (PEF) and high voltage electric discharge (HVED) are promising technologies for PC recovery from oleaginous by-products, with lower energy consumption and potential higher yield and selectivity .[132,133] However, only three studies have dealt with the intensification of total PC extraction from rapeseed by electro-technologies. PEF and HVED used as biomass pretreatment are respectively based on electroporation and electric breakdown phenomena consecutive to an electrical pulse. The operating conditions that various authors optimized are: specific energy (kJ/kg) linked to energy cost, the electric field strength between the two electrodes (V/cm), the pulse duration ( $\mu$ s to ms), frequency (Hz), the treatment duration.

The use of electro-technologies was reported to give higher PC extraction yields compared to solvent extraction with water or ethanol 10% (v/v). Compared to solvent, PEF produce a 77% better yield with 5 kV/cm, 40 kJ/kg, at room temperature [134] or a good but not detailed yields with PEF 1.1 kV/cm, 182 kJ/kg, and room temperature, [107] or HVED at 80 kV/cm, 80 kJ/kg, and room temperature. The real advantages of the electro-technologies should be more clearly demonstrated. The SAD present in extract should be sinapine, but more evidence is required. These studies were conducted in water or with 10% ethanol and at room temperature. The interesting efficacy of these electro-technologies with low amounts of organic solvent is pointed out. The energy consumption is lower than that needed for solvent extraction. However, a too high treatment energy, passing 240 kJ/kg, is not recommended as it could result in the formation of radical species and decrease phenolic yield.[135] These conclusions should be reinforced regarding SAD specific measured by chromatography.

These electrotechnology studies are infancy with a lack of sufficient data to draw conclusions. Further optimization, modeling and comparative studies are required to demonstrate their potential for selective SAD extraction. Diffusion in the solvent after HVED treatment should also be studied.[135]

### Pressurized Liquid Extraction

Pressurized liquid extraction (PLE) is a green technology applied since the 2000s for the extraction of food nutraceuticals .[136] This technology works with solvents at high pressure and temperature above their boiling point but below their critical point. The known advantages compared to conventional solvent extraction are higher yields, faster extraction, and lower solvent consumption. The most important parameters for PLE technology in static modes are extraction temperature, duration and solvent to matter ratio .[137] The pressure to be applied will be to maintain the solvent in a saturated liquid form. It depends on the targeted temperature and the boiling point of the solvent.

PLE is attractive as it was found more efficient than classical solvent extraction increasing PC-SAD contents in extract .[49,92,138] Using water, 160°C, 6.9 MPa, 1 mL/min for 30 min, PLE extracted 3.4% w/w or 69% more SADs than conventional extraction with 95% ethanol or pure water at 80°C for 30 min. However, the extract purity was 46% lower than that obtained with conventional extractions with 95% ethanol .[92] This may be due to an increase in the dissolution of other compounds such as sugars starting to solve after 5 min at 200°C .[139] Further studies are needed to assess the impact of PLE on SAD purity in the extract. Concerning the particle size, the Folin-Ciocalteu method showed that thinner is better with a PC-SAD recovery improved by 51% when 0.5 mm particles were used compared to 1.0 mm ones .[49] However, this has to be confirmed with more precise analytical instruments. Another PLE advantage is that the extracts obtained can be separated in situ by paper or frit filtration.[34,92]

The optimal experimental conditions depend on the target SAD to recover. The optimal PC-SAD yield was obtained at 200°C with 60% methanol, static 20 min, and 93 mg/g meal [138] or at 180°C with 70% ethanol, 3 static 5 min .[49] The best sinapine production was obtained with pure methanol, 80 to 160°C, static 5 min, and 6–7 mL/g .[34,138] The best sinapic acid production were obtained with 60% to pure methanol, 160 to 200°C for static 5 min .[138]

**Recommendations:** Aqueous ethanol is increasingly used for the extraction of SADs from mustard and rapeseed seeds. So the PLE technology should also optimize ethanol uses. Pressures between 5 and 15 MPa have been studied and are sufficient to keep the solvent in a liquid state.[137] Knowledge of the thermostability of SADs is essential. All presented PLE studies were carried out on a small scale (1–15 g) in batch mode.[34,92] From an industrial point of view, scale up studies, techno-economic studies and environmental assessment on PLE processes should be carried out .[140] The use of a sequential process under two different temperatures makes it possible to be more selective for the molecules extracted. This would lead to a fractionation of the molecules of the extract.[137] Compared to PLE,

the technology of supercritical CO<sub>2</sub> extraction seems not recommended for polar SAD molecules. Polar co-solvents can be added to CO<sub>2</sub> not raising enough its solubilizing power for SADs.[141]

### Enzyme- Assisted Extraction

Enzyme-assisted extraction (EAE) consists in adding enzymes before or simultaneously with the liquid/solid extraction. Three distinct implementations are identified in the case of SAD extraction from rapeseed and mustard seeds: (i) destruction of the seed cell walls with cellulolytic enzymes, [73] (ii) SAD conversion into free sinapic acid with feruloyl/sinapoyl esterase, [94] (iii) oxidation or decarboxylation of the SADs to increase the antioxidant profile of the extract.[108,142] The critical parameters used to describe the intensification by enzymes are the enzymatic charge (mL of enzymatic solution/g of meal or U per g of meal with 1 U/g = 16.67 nkat/g of meal), the pH and the temperature.

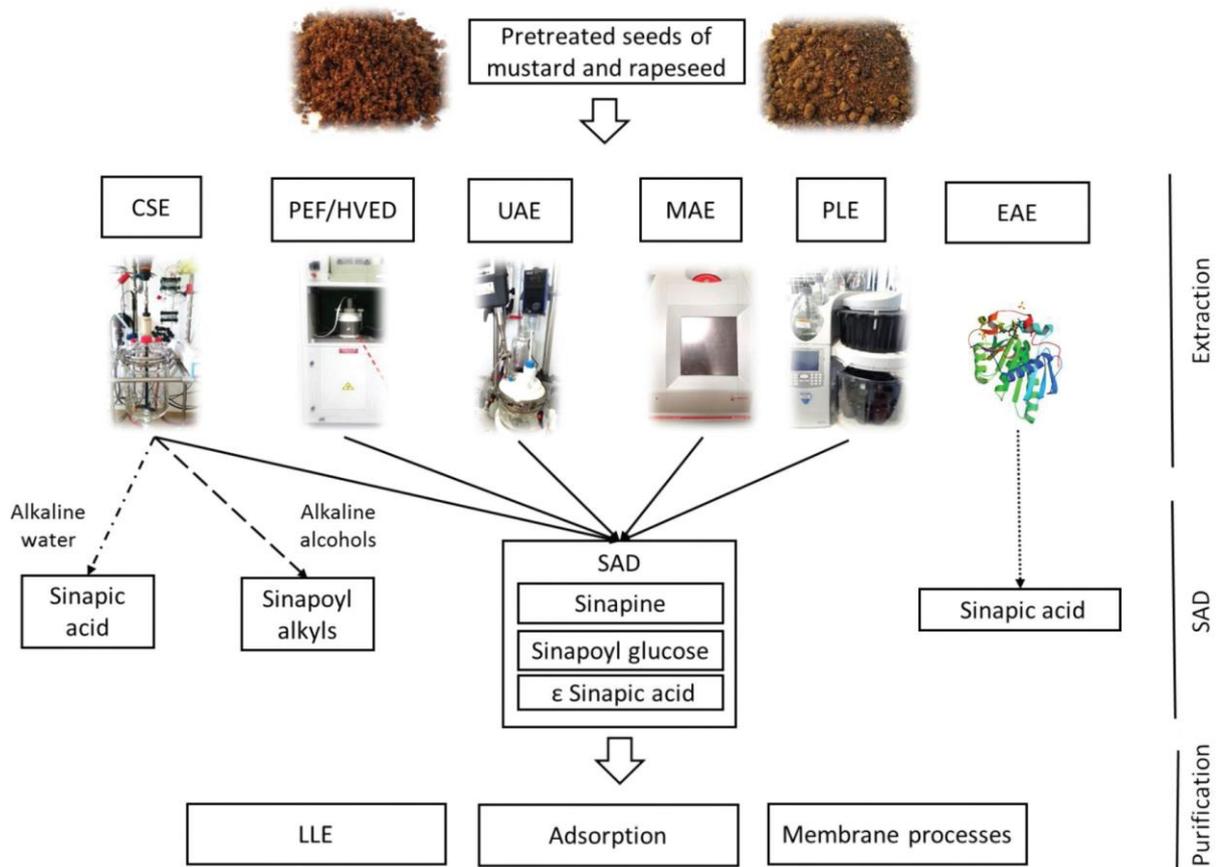
The first implementation consists of the deconstruction of the seed cell walls, which can be carried out using pure cellulase and hemicellulase such as endo-1,4- $\beta$ -xylanase [73] or commercial enzymatic cocktails .[143] A higher phenolic compound content in the extract has been reported after the use of such enzymes .[73] This might be explained by the release of SADs bound to cell walls by cellulolytic enzymes contained in the cocktail .[144,145] This hypothesis has already been verified on other biomasses such as quinoa seeds .[146] However, further studies are needed to reinforce the relevance of using such enzymes for SAD release considering the consequences on extract purity.

The second implementation is the conversion of SADs into sinapic acid. This can be carried out with two types of enzymatic formulations. The first one are pure feruloyl esterases (Fae) obtained from different microorganisms such as *Aspergillus niger* [25,94] or *Humicola insolens* .[19] It has been shown that some Fae allow total hydrolysis of sinapine and sinapoyl glucose [19] to sinapic acid but no other SADs such as kaempferol derivatives .[94] The second enzymatic formulation are the commercial cocktails containing cellulases, hemicellulases with relatively low amount of Fae .[26,143] These cocktails allow the simultaneous deconstruction of the cell wall and the production of sinapic acid. Multi-enzymatic cocktails are commercial product with low rate of purification. They are much more affordable than purified Fae. Both pure Fae and cocktails have the advantage to work under mild pH conditions (5.5 to 7.5) and temperatures (25 to 55°C) with a hydrolysis time of 4 h in water. Few optimization studies have been carried out. It was showed that a minimum of Fae dosage of 196 nkat/g or 11.8 U/ g of rapeseed meal was necessary to achieve a 76% hydrolysis yield of total SADs into sinapic acid in 3–4 h at 55°C).[25]

The third implementation of enzymes is their use to improve the antioxidant profile of the extract by the increase of the PC content. It can be obtained using horseradish peroxidase and tyrosinase, [142] feruloyl/sinapoyl decarboxylase [108] or *Neolentinus lepideus* .[25] However, the impact on specific SADs remains unknown.

**Recommendations:** Despite their assets, enzymes have some restrictions on the choice of solvent, temperature and pH of the extraction process. Many optimizations of SAD hydrolysis by Fae should be carried out focusing on pH, temperature and origin of Fae. Indeed, there is a variety of Fae from different microorganism sources to be compared as pure, in homemade cocktail or commercial cocktail formulation.[147] Besides, the mechanisms behind the Fae hydrolysis of SADs are still an area of research to deepen. However, when using enzymatic cocktails, there can be a release of other compounds from the biomass which can decrease the SAD purity in extract. Alkaline hydrolysis remains more efficient for the hydrolysis of SADs into sinapic acid.[26,94] However, for the sake of naturalness and sustainability of the entire process, the enzymatic pathway is preferred .[144] Comparative studies between EAE and the other extraction processes should be carried out to justify the economic interest of the implementation of enzymes.

Concluding this part, Figure 3 resumes the different extraction process implemented to obtain a variety of sinapic acid derivatives and related compounds. Despite the few information given, the extract purity is estimated to be below 10%. Purification processes are an absolute necessity.



**Figure 3.** Overview of fractioning processes for SAD recovery from rapeseed and mustard seeds. CSE: conventional solvent extraction; PEF: pulsed electric field; HVED: high voltage electric discharge; UAE: ultrasonic; MAE: microwave; EAE: enzymatic assisted extraction; PLE: pressurized; LLE: liquid/liquid extraction.

### PURIFICATION PROCESSES

Different purification processes were used to separate SADs from other extracted compounds. Three technologies were mainly utilized: liquid/liquid extraction, membrane processes, and adsorption. Some authors associated several of these processes to improve the purification step.

#### Liquid-Liquid Extraction

Liquid-liquid extraction (LLE) is based on a transfer of solutes from one liquid phase to another due to diffusion phenomena. The two liquids must be partially or completely immiscible. Thus, two layers are formed, one above the other according to their respective density.[148] The two key factors of this process are the partition coefficient of a selected compound ( $K_D$ ) and the selectivity factor over another compound ( $\alpha$ ). The main solvents utilized for LLE of PC-SADs are the aprotic solvents diethyl ether and ethyl acetate.[78] These solvents have a significant solubility in water ( $> 60$  g/L at  $20^\circ\text{C}$ ). This causes losses during LLE and makes the aqueous side stream polluted and more difficult to valorize. This might limit the development of LLE industrial processes.

LLE is preceded by pH 2 acidification of alkaline hydrolysates containing sinapic acid to increase the partition coefficients.[94,108] Thus, molecular protonated SADs migrate into the organic phase while

sugars and proteins remain in the aqueous phase .[149] The transfer between the hydrophilic and hydrophobic phases is simply carried out using a shake flask [149] or, more recently, by centrifugation/vortexing.[25,150] Although LLE is commonly used in the chemical industry, [151] pilot scale LLE has not been reported for SAD extraction from rapeseed and mustard seeds. Some improvements have been proposed for the LLE of SADs: (i) some authors have used a hexane defatting step to remove fatty acids before the purification step [58,108,152]; (ii) other authors added NaCl salt to increase the mass transfer of the targeted SAD by salting-out effect [25,150,153]; (iii) tetrahydrofuran was also reported as an intermediate solvent improving the extraction of phenolic acids, [152] (iv) a biphasic system coupling enzymatic decarboxylation and toluene extraction allowed to recover canolol with 90%+ purity and yield (3 mg/g meal) .[108] However, for environmental reasons, the use of hexane, tetrahydrofuran and toluene are not sustainable. Similarly, the addition of salts must be avoided at industrial scale since the end up waste waters become an environmental problem.[154] LLE will be improved working with liquid based membrane [155] or counter current chromatography.[156]

The use of LLE has been commonly used for the recovery of PC - SADs from extracts for analytical objectives.[71,93,108,157,158] Thus, this technology is implemented on a small scale only, certainly due to difficulties to design liquid-liquid extractors that have emulsion and phase dispersion issues .[151,155] Therefore, large-scale recovery of SADs by other purification processes, such as adsorption or membrane separation, is preferred.

### Membrane Filtration

Membrane processes can be used for the purification of extracts provided that the molecules to be separated have different molecular weights, shapes or electric charges.[159] Indeed, the choice of the membrane topography, hydrophobicity, molecular weight cut-off and charge will condition the separation of the constituents from the extract. The performance of the filtration process is evaluated in function of the permeate flux (J, L/m<sup>2</sup>/h), the retention factor (R) and the concentration factor (CF) of the solute .[159] Usually, PC are recovered from agri-food waste after microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), or a combination of filtration .[160] In the case of the treatment of extracts of rapeseed and mustard, membrane filtration was first applied in order to recover proteins and remove PC .[96,161] More recently, authors have been interested in the simultaneous recovery of both proteins and sinapic acid .[101,110] The studies using membrane processes are detailed in Table 6.

**Table 6.** Membrane processes for the recovery or removal of sinapic acid derivatives from rapeseed and mustard extracts.

Target	Starting extract	Filtration type	Membrane composition	MW cut-off	Temp. (°C)	Q feed, CF, DV	TMP (bar)	% Reject.	Recovery	Comments	Ref.
PC	Aqueous alkaline (pH 10) extract from mustard flour centrifuged and filtered. 600 mL	MF	Regenerated cellulose	0.1 µm pore size	RT					Microfiltration was not sufficient to remove the phenolic compounds from the proteins.	[161]
PC	Aqueous alkaline extract (pH 11) from mustard meal, centrifuged.	UF	CTA	5 kDa	50	DV = 3	4			90% of the PC of the alkaline extract were isolated in the permeate.	[110]
PC	Aqueous alkaline extract (pH 12) from rapeseed meal centrifuged and filtered. 1.5 L	UF		5 to 10 kDa	RT	DV = 5				The successive treatments of NaCl, SDS with diafiltration decreased the phenolic content by 70% ± 5% compared to the control.	[96,162]
PC, SA	UF permeate from mustard meal extract. 10 L. pH 3.5 or 9.8	NF	PE, PS, PA	150 to 300 Da	30–36	1.5 L/min CF = 4 DV = 4	17	87% (pH 3.5) 70% (pH 9.8)	77% (retentate pH 3.5)	Diafiltration increased by 10% PC in retentate. NF step increased SA content in UF permeate by 371%.	[101]
PC	Aqueous/buffer extract (pH 8) from rapeseed meal centrifuged. 100 L	NF		1 kDa	RT					88.5% discoloration of aqueous extract. No phenolic oxidation. EDTA and sodium bisulfite unbounded phenolics from proteins.	[163]

MF: microfiltration, NF: nanofiltration, MWCO: molecular weight cut-off, TMP: transmembranaire pressure, PE: polyester, PS: polysulfone, PA: polyamide, CTA: hydrophilic cellulose triacetate, CF: concentration factor of PC or SADs, DV: diavolume, Q feed: volumetric flow of the feed, SDS: sodium dodecyl sulfate, RT: room temperature.

Most studies dealing with membrane filtration aim to extract large proteins in mild, pH 8, [163] or strong (pH 10 to 12) alkaline conditions.[96] This allows the simultaneous hydrolysis of SADs that can also be degraded at high pHs .[164] Very few studies using filtration have been carried out starting

from an acid extract. This could be an interesting path to recover sinapine, which is positively charged. MF (cut off: 50 to 100 kDa) is generally used as a pretreatment step to recover macromolecules (proteins) before UF/NF steps. [160,161] UF (cut off: 1 to 10 kDa) is mainly used to recover proteins in the retentate, whereas SADs and other small components (sugars, salts) are found in the permeate. [96,110,163] NF (cut off: 0.15 to 1 kDa) is effective to recover sinapic acid under acidic condition (pH  $\leq$  4). Sinapic acid is recovered in the retentate due to its high rejection coefficient ( $R = 0.87$  [101] or  $0.68$  [165]). This phenomenon was explained by a NF membrane pore size shrinking due to low pH and, more problematic, a membrane fouling by aggregates. Indeed, in alkaline condition, the retention of sinapic acid is lower ( $R = 0.7$  [101] or  $0.5$  [165]). However, NF of a mild alkaline extract of rapeseed/mustard (pH = 8) was found not to retain the PC-SAD. This could be explained by the fact that the SADs were in sinapine form at this pH. [163]

An important challenge in the implementation of membrane methods for the filtration of SADs is to dissociate the phenol-protein complexes. [96] Indeed, at pH  $<3$  and pH  $> 12$ , a complexation phenomenon occurs between the SAD and the proteins which makes the separation of these compounds more difficult. [166,167] Since the weakening of the phenol-protein interaction occurs at pH 3.5, [168] several authors have chosen a pH range of between 3.5 and 6.5, for the precipitation of proteins before the membrane filtration step. [110,161,166,169] However, this process involves the conversion of SADs into sinapic acid with a risk of degradation during alkaline extraction [19,170] and acidification of the hydrolysate. Other authors carried out the aqueous extraction of protein under pH 3 to 5 [171] or 7 to 8 to limit the complexation phenomenon. [163,172] In that case, the SADs would be rather in the form of sinapine. From an environmental and economic point of view, the best SAD recovery pathway is the one limiting pH switches to reduce acid/base inputs. An alternative to pH switch is to add NaCl (0.05 to 0.75 M), SDS, EDTA or sodium bisulfite. These additions improve the separation of SADs from proteins and tannins. [96,163]

Diafiltration is another membrane process increasing SAD concentration and purity in the retentate. In the case of NF sinapic acid recovery, concentration factor and diavolume are around 4 to 5. [101,165,173] Diafiltration has a positive effect on purity. This could lead to a recovery of 68% to 77% of sinapic acid from a mustard extract under acidic pH. [101,165,173] Indeed, the alkaline condition was not suitable as it led to a 60% drop in SAD yield. [101] The scaling up of membrane processes is easier because the volume treated (0.6 to 100 L) in the studies is generally higher than what is treated by adsorption, liquid-liquid extraction or other purification processes. However, data on membrane process yield and SAD purity are scarce. The highest sinapic acid content obtained in retentate is 1.27 g/L. [165] Moreover, only one study calculated the purity which was only 4.5% (w/w) with a concentration factor of 4 and diavolume of 4. [101] An additional purification step (such as adsorption) seems needed.

*Recommendations:* There is a need for data on SAD purification by membrane processes. The differences in behavior of sinapine and sinapic acid require the use of more precise measurement methods, such as chromatography. Evaluation of the membrane filtration of organic solvents extracts has not been studied yet. This could be of interest for the recovery of sinapine [118] or alkyl sinapate. [30] Besides, a concentration of the SAD in the retentate can be obtained by water removal using reverse osmosis. [160]

### Adsorption Processes

The separation process based on adsorption phenomenon depends on the affinity of the molecule to be purified (adsorbate or ion) with the surface of a solid support (adsorbent or ion exchanger). Large scale adsorption process and ion exchange chromatography are similar purification processes. They are generally not differentiated in practical applications. [174] They follow the successive steps of

adsorption-washing-desorption-regeneration. Compared to membrane separation and liquid-liquid extraction, adsorption processes have high selectivity and extraction capacity for PC, with a relative ease of use and scaling.[175] The most important operating parameters for adsorption/desorption are the nature of the adsorbent and adsorbate, ionic strength, solvent used, and temperature .[175] Adsorption conditions applied for the removal/recovery of SADs from rapeseed/mustard extracts are presented in Table 7.

**Table 7.** Adsorption processes applied on rapeseed and mustard seed extracts for the recovery of sinapic acid derivatives.

Target compound	Starting solution	Resin commercial name and type	Resin parameters	Adsorption conditions	Elution conditions	q <sub>max</sub> (mg/g)	Recovery	Comments	Ref.
Ethylsinapate	rapeseed meal 80% ethanolic extract, filtrated, dried, dissolved in ethanol.	Cationic Amberlite XH 2071 H	5% (w/v) (adsorbent)	<b>Adsorption:</b> EtOH, 5% adsorbent (w/v), RT, 0.5 h <b>Transesterification:</b> EtOH, 80°C, 48 h.	None		Recovery: 98%	isolation of sinapine followed by transesterification. ethyl sinapate purity 64% (w/w).	[176]
SA	rapeseed meal aqueous extract pH 6 with SA, glucose, sinigrin hydrate and phytic acid	FPX66 resin with AKTA Avant systems	Total volume: 7.4 mL Porosity: 0.3, 22.5% (w/v) (adsorbent for 3 bed volumes)	Water, pH 6 or 8 1 mL/min 25°C, 3 h	EtOH 70% (v/v)	103 ± 12	Adsorption: 70% Desorption: 100%	higher SA adsorption capacity with FPX66, 3 bed volumes than Amberlite XAD16, 7, 4, 1180 N, 761, and Diaion HP 20 resins. No sugar, glucosinolate or phytic acid interferences.	[177]
SA and canolol	Aqueous/MOPS (pH 5) extract from rapeseed meal, filtrated and acidified. 8 L.	Amberlite XAD 16, XAD1180N, XAD2 and Sepabeads SP207	6.25% (w/v) (adsorbent)	Water, pH 4, 30°C, overnight	EtOH		Recovery: 91% (SA)	85%+ adsorption for all resins at pH 4. XAD2 allowed a high recovery of SA at pH 4 and canolol at pH 7 (97% compared to 31% for SA). SA concentration 25 g/L in EtOH.	[25,178] (patent)
SA	Aqueous pH 12 extract from rapeseed meal centrifuged. 10 mL.	Cationic β-zeolite (Clariant Group)	527 m <sup>2</sup> /g, 5% (w/v) adsorbent	Water, pH 5, 25°C, 1 h	EtOH 70% or MeOH 70% (v/v)	43.8	Recovery: 96.3%	Ethanol 70% to elute SA. SA recovery yield 77%; purity > 80% (w/w). SA binding rate on zeolite: 0.071 min <sup>-1</sup> .	[26,179] (patent)
SA and Sin	Aqueous extract from rapeseed meal centrifuged. 10 mL.	Zeolites SiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> (Süd-Chemie AG), Amberlite XAD7HP, XAD16, PVPP	0.5% (w/v) adsorbent	Water, pH 6, RT, 16 h, 0.1 g(SA or Sin)/L	EtOH 70% (v/v), 60°C, 3 h	Zeolites 48.5 to 85.3 (SA)	Zeolites Adsorption: 100% (SA) 100% (Sin) Desorption: 72.1% to 80.1% (SA) 0% (Sin)	Highest SA recovery with zeolites compared to the other resins.	[168]
SA and Sin	rapeseed meal methanolic extract filtrated, re-extracted, dried, dissolved in methanol. 8 mL	Sephadex LH-20 column	2 x 60 cm	MeOH	EtOH 95% (v/v)			Elution with EtOH was better than MeOH.	[180]

RT: room temperature, FC: Folin Ciocalteu's method, HPLC: High Pressure Liquid Chromatography, PC: Phenolic compounds, Sin: sinapine, AS: sinapic acid, q<sub>max</sub>: maximum adsorption capacity of the resin, EtOH: ethanol

The adsorption process uses the liquid extract obtained after filtration of the solid residue from the extraction.[25,26,180] It is carried out for an hour or more at room temperature, [25,177] starting from a solution of either water, [26] methanol [180] or ethanol .[176] Comparative studies on the influence of the starting solvent have to be done. The adsorption equilibrium of sinapic acid needs 1 h using a resin XAD16 at 5% (w/v) for solution concentration between 0.5 to 2 g/L.[26,177] The highest adsorption capacity of sinapic acid will be obtained under acidic condition (pH<6 .[177] Then, the best elution solvent for desorption is 70% ethanol better than methanol and water.[168,177,180] This step take 1 h at 60°C .[26] Next, regeneration of the adsorbent is usually conducted with acetic acid and fresh water [173] or isopropanol followed by drying [168] or 70% aqueous ethanol using 8 column volumes .[181] A re-equilibration step with 5 column volumes of buffer may be required.[181] A thermal treatment is not recommended as it can lead to small destruction or deformation of the zeolite [168] A slight decrease of the adsorption capacity can be observed beyond three adsorption/desorption cycles .[168] Further studies could assess other regeneration treatment .[175]

The most used adsorbents are the organic Amberlite resins and inorganic zeolites .[25,26,176] Zeolites seem to be more attractive than other adsorbents because of their mild regeneration conditions, their high adsorption capacity for sinapic acid and higher adsorption rate .[168] However, Amberlite resins have also interesting adsorption capacity above 85% for both sinapic acid and canolol .[25] For sinapic acid recovery, the most efficient adsorbent found were the resin Amberlite XAD2 (91% recovery) [25] and the β-zeolite (96% recovery) .[26] However, data about the target purity were poorly reported. For sinapic acid, using a zeolite, it was found above 80% (w/w).[26] The technology of adsorption seems to attract high interest as seen by the two recent patents filed.[178,179]

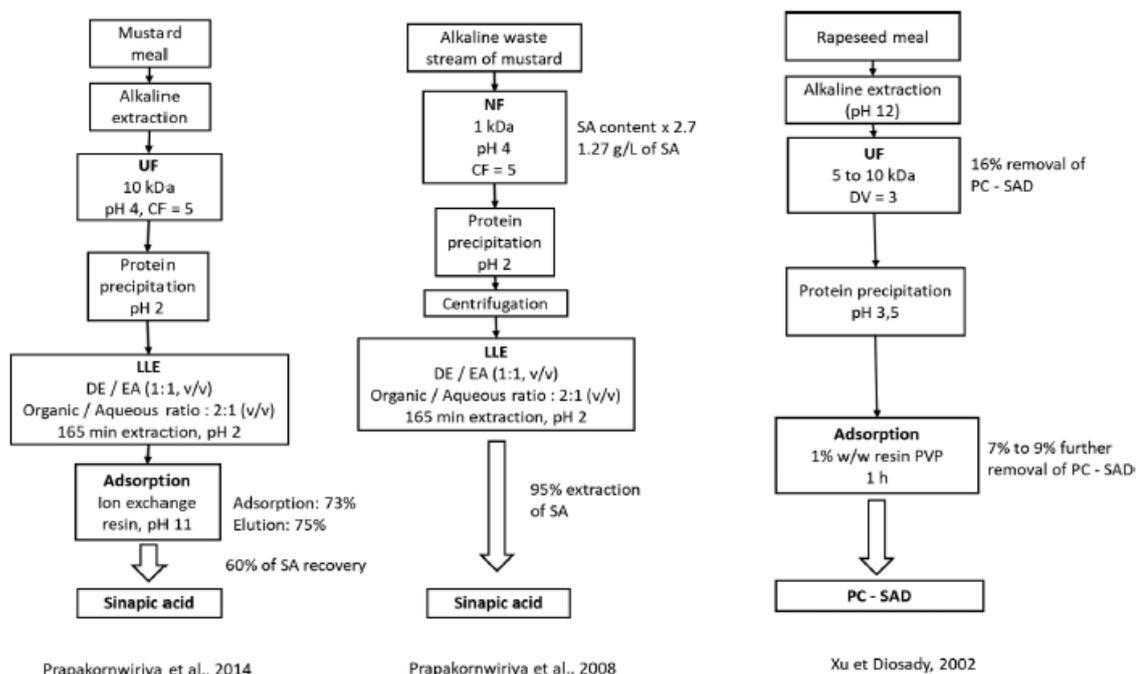
The selectivity of Amberlite resins for SADs contained in a complex mixture is higher than that for sugars, phytic acid and glucosinolates .[177] These unwanted compounds do not influence SAD adsorption capacity as proteins do, [163] another point needed studies. Good adsorption capacities of sinapine were obtained with zeolites (100%) and Amberlite resins (62%). However, sinapine desorption is difficult with 0% zeolite desorption and 0.9 to 5.1% desorption with resins.[168] This is due to a great affinity of sinapine for the adsorbent not broken by any elution solvent. The resin Sephadex LH-20 has to be used for sinapine purification. Unfortunately, the recovery efficiency was not properly assessed due to the use of imprecise analytical equipment.[105,109,182] Further studies could explore this path again.

Cationic resins can also be used for both SAD purification and their catalysis for transesterification. Ethyl sinapate is an example of compound produced from a rapeseed meal ethanolic extract using a cationic resin with a 98% recovery and 64% purity.[176] This opens interesting perspective for the production of a variety of esters. The adsorption processes described were mainly carried out in batch mode with less than 10 mL volumes to purify. However, larger scale is feasible (8 L) .[25] The implementation of continuous process is a relevant way to improve the efficiency and the productivity. This could be optimized using expanded/fluidized bed.[175] Continuous processes could be modeled using the SAD Langmuir isotherms .[181] A simulated semi-continuous adsorption treatment of a rapeseed meal extract was found more efficient than batch mode with a sinapic acid recovery yield above 97%, and a productivity of 10.3 g/L/h) .[181] Further pilot-scale studies are needed to confirm this encouraging results .[175]

**Recommendations:** According to the data available on SAD purification by adsorption processes, this technology seems efficient. High recovery rate can be obtained using green solvents (ethanol, water, isopropanol). However, further work should study the impact of the nature of the adsorbent and its regeneration due to potential irreversible adsorptions .[175] For industrial applications, the regeneration of the adsorbent is required for the economic viability of the process. To date adsorption processes rarely passed 80% w/w purity .[26] Therefore, a combination of purification technology must be considered.

#### Combination of Purification Processes

Extracts of mustard and rapeseed seeds consist of a complex mixture of oligomers, proteins, lipids, and low molecular weight compounds: monosaccharides, salts, secondary metabolites, SADs, condensed tannins, or glucosinolates. The chemical and physical similarity of these compounds prevents any one-step separation and purification. Therefore, the combination of different purification technologies appears imperative to achieve high SAD purities. Few combinations of purification technologies were reported in the literature (Figure 4).



**Figure 4.** Overview of the most complete processes for the recovery of SADs from rapeseed and mustard seeds. Y: yield, P: purity. PVP: Polyvinylpyrrolidone, CF: concentration factor, SA: sinapic acid, UF: ultrafiltration, NF: nanofiltration, LLE: liquid-liquid extraction.

The combination of purification technologies has been mainly investigated by the Diosady team who associated either UF followed by adsorption with resin [96] or UF/NF and liquid-liquid extraction, [165] followed by an adsorption process. [173] In the first study, [96] the objective was the removal of the phenolic acids to improve the purity of the targeted proteins. The removal of phenolic acids was improved by 16% with ultrafiltration and by 7% to 9% with the use of 1% (w/w) resin of polyvinylpyrrolidone. However, these data need to be deepened especially since a spectrophotometric measurement was used. This work appears of commercial interest with two patent filed. [162,183] In the second study, [165] the objective was the recovery of sinapic acid from a waste stream from processing of mustard. The use of nanofiltration (1 kDa) with CF 5 at pH 4 allowed to increase the content of sinapic acid in the retentate by 2.73 to 1.27 g/L. Afterwards, the use of two extraction stages with diethyl ether/ethyl acetate (1:1, v/v) at a solvent to aqueous phase ratio of 2:1 (v/v) at pH 2 for 165 min allowed to get a 95% extraction yield of the sinapic acid contained in the permeate. Although the obtained sinapic acid purity was not given, the authors advise to use further purification steps to increase its value. This was carried out with an ion exchange resin column. [173] In a third study, [173] the process first starts with a 10 kDa UF of an hydrolysate containing sinapic acid at pH 4 processed at a concentration factor of 5. It is followed by LLE with diethyl ether/ethyl acetate (1:1, v/v) for 165 min. After drying of the organic phase and redissolution in methanol, a concentration of 10 g/L of sinapic acid was reached. The use of LLE is supposed to facilitate the further purification by adsorption. Afterward, the use of an ion exchange resin column (Dowex 1x8, pH 11, 10 bed volume for column loading) allowed to recover 60% of the sinapic acid from the methanolic extract again not listing its purity. In conclusion, all the previously detailed purification technologies have been implemented in the form of combinations. However, the few data available were obtained with the non-precise Folin-Ciocalteu methods, which does not allow any significant conclusion to be drawn on the quantitative improvement in purity.

**Recommendations:** More data should be obtained on SAD yields and purity from precise chromatographic measurements in order to justify the increase in the cost of purification by the use

of several technologies. Emerging purification technologies that are derived from membrane processing and LLE deserve to be explored for SAD recovery. They are: countercurrent chromatography, [156] liquid-based membrane [155] or electro-membrane processes.[184] Preparative chromatography as the final purification step is highly efficient to recover high SAD purity. This technology is widely used at industrial scale due to its scalability, robustness and selectivity.[185] However, its sustainability is questionable due to the significant solvent consumption .[186] For this reason, studies should be carried out using the specific Environmental Assessment Tool .[187] Further studies should explore the techno-economic and environmental aspects of the presented purification technologies and integrated processes.

## CONCLUSION

This review detailed the extraction and purification processes to recover SADs from the seed by-products of rapeseed and mustard. Among the extraction processes, the main SADs extracted are under the form of sinapine and sinapoyl glucose. Intensification processes using pressurized liquid extraction, ultrasonic or microwave assisted extraction showed promising results to improve the yield of SADs compared to the conventional solvent extraction. Sinapic acid can also be obtained with enzymatic assisted extraction. Alkaline water can yield sinapic acid but its degradation into thomasidioic acid and 6-hydroxy-5,7-dimethoxy- 2-naphthoic acid. Canolol can also be generated with too long or too hot extractions. The presence of an alcohol can also produce sinapoyl alkyls. Further comparative studies based on a single raw material and using measurements based on chromatography are crucial in order to highlight the relevance of intensification processes.

Extracted SADs are in low concentration. Therefore, the cost of implementing purification and concentration steps is high (energy flow, solvents, several unit operations) and often not economically viable at industrial scale. Although the adsorption process appears interesting for selective SAD recovery, the regeneration of the sorbent and the final purity in the extract are still limiting aspects. Further development of innovative purification technologies and their integration may offer a new perspective for the production of bio-based SADs at industrial scale.

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## ORCID

Valentin Reungoat <http://orcid.org/0000-0003-2832-3760>

Florent Allais <http://orcid.org/0000-0003-4132-6210>

Irina Ioannou <http://orcid.org/0000-0002-1914-2717>

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