Bioactive Compounds Present in Oilseeds

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Oilseeds are a great source of affordable and potent bioactive compounds (e.g., carotenes, flavonoids, PUFAs, organosulphur compounds, phytosterols, and polyphenols) generally used in the pharmaceutical (anti-microbial toxins, adjuvants for cancer therapy, cholesterol-lowering therapeutics), agricultural (animal welfare) and cosmetic (oil-based creams) industries. However, oilseeds also contain certain molecules called anti-nutrients, which are toxic compounds synthesized by plants as a defense mechanism. Controlling these compound's amounts, namely glucosinolates and phytic acid, is essential to maximize beneficial effects over toxicity.

Keywords: oilseeds; health benefits; micronutrients; bioactive compounds

1. Glucosinolates

Glucosinolates are secondary metabolites of sulfur-rich anionic plants. Their structure comprises of a moiety of β -D glucose bound to sulphatated thiohydroximate. About 100 different glucosinolates were discovered from 16 families of plants, namely Bataceae, Bretschneideraceae, Phytolaccaceae, Resedaceae, Moringaceae, Tovariaceae, Tropaeolaceae, Limnanthaceae, Gyrotemonaceae, Euphorbiaceae, Cruciferae (syn. Brassicaceae), Pentadiplandraceae, Pittosporaceae, Capparaceae, Caricaceae, and Salvadoraceae.

Glucosinolates are present predominantly in Brassicaceae vegetables, which include mustard, rapeseed, broccoli, cauliflower, cabbage, and brussels sprouts, among others. Earlier reports revealed biocidal, anti-oxidant, bioherbicidal and antineoplastic properties of glucosinolates and derived by-products present in Brassicaceae vegetables. They express tolerance/resistance to pests and diseases and gathered in the organs leading to tolerance/resistance at a relevant development stage. It has been proven that glucosinolates and their derivatives have beneficial effects on human health by minimizing the danger of some cancers. Epidemiological research has linked consumption of Brassicaceae vegetables with a decrease in cancer incidence (including stomach, rectum, lung and colon cancers). Dietary glucosinolates were found to block the emergence of exogenous or endogenous carcinogens to avoid the activation of carcinogenesis. These healthy properties are mainly attributed to their hydrolytic products derived from the metabolism: isothiocyanates. In contrast, glucosinolates produce a toxic effect when ingested by livestock, in particular, pigs seem to be more affected by dietary glucosinolates than ruminants, rabbits, poultries, or fish. Glucosinolates' toxicity includes enlarged thyroid and reduced thyroid hormone levels; liver, kidney and growth abnormalities; reduced reproduction rate, and even mortality.

2. Phenolic Compounds

Phenolic compounds are other secondary metabolites of plants whose original function is mostly defensive. Although they can be found in all plant parts, phenolic composition is really variable between them and between plants, both, quantitatively and quantitatively. Phenolic compounds comprise a broad group of molecules, that can be classified into five major categories: phenolic acids (hydroxycinnamic acids and hydroxybenzioic acids); stilbenes; quinones; flavonoids (anthocyanins and anthocyanidins, flavonols, flavones and isoflavones); and tannins and lignans. In food matrixes, they are usually related to the organoleptic properties (color and taste), although they also perform preservative functions, and have beneficial effects for human health. These beneficial properties are mainly attributed to their remarkable antioxidant capacity, which participates in the prevention of different illnesses linked to oxidative stress such as premature aging, neurodegenerative and cardiovascular diseases and several cancers. Phenolic compounds not only have antioxidant effects, but also have strong antithrombotic, antimicrobial, antidiabetic, and antiatherogenic effects. Besides, due to their scavenging activity, phenolic compounds play a crucial role in the stabilization of edible oils, protecting them against off-flavors development and enlarging their shelf life.

Total phenolic compounds (TPC) and total flavonoids are commonly determined by spectrophotometric techniques. TPC content is given as gallic acid equivalents (GAE), while total flavonoids are usually given as (+)-catechin equivalents.

When analyzing single phenolic compounds, chromatographic methods are employed, such as HPLC-DAD/MS or LC-ESI-MS systems.

Oilseeds' phenolic composition varies along with the species and, as mentioned above, depends on the extractive and refining techniques employed. Generally speaking, peanut contains proanthocyanidins and flavonoids as major constituents, and phenolic acids and stilbenoids as minor components. High quantities of these compounds are found in peanut skin, so avoiding pealing peanuts is beneficial for human health. TPC in peanuts (82.64–92.12 mg GAE/g of seeds) is associated with favorable memory functions and inversely linked with stress response (cortisol, anxiety, and depression levels. Soybeans are known to be rich in isoflavones and phenolic acids, with a TPC ranging from 5 to 25 mg GAE/g. Certain phenolic compounds present in soybeans and flaxseed (e.g., hydroxytyrosol) show the peculiarity of forming complexes with proteins contained in these matrixes, facilitating their isolation. In sesame seeds, TPC values are 146.25 mg GAE/g; and major phenolic compounds are phenolic acids (ferulic acid, gallic acid, protocatechuic acid and hydroxybenzoic acid), flavonols (quercetin) and certain lignans such as sesamin. TPC in sunflower seed values are 22.29–33.09 mg GAE/g of seeds, mainly being phenolic acids, flavonoids and lignans. In rapeseeds, the TPC is around 18 mg GAE/g, and the main constituents are sinapic acid derivatives and canolol. Cottonseeds and safflower seeds show TPCs of 0.16 mg GAE/g (mainly, phenolic acids and isoflavones), and 16 mg GAE/g (mainly, rutin and quercetin), respectively.

Stilbene derivatives, such as resveratrol, exert significant anti-inflammatory activity by inhibition of lipopolysaccharide induced nitric oxide (NO) production. Stilbenoids are also reported to show cytotoxicity in vitro and in vivo in mouse macrophages and on human leukemia HL-60 cells; and neuroprotective effects. Phenolic acids, such as sinapic acid, achieve scavenging and antiproliferative activities by reducing oxidative stress damage, which decreases ROS, proinflammatory cytokines (interleukin-6) and tumor necrosis factor-α (TNF-α) production. Flavonoids are great antioxidant agents and, although their antitumoral properties are not remarkable, they also produce anti-inflammatory effects by diminishing pro-inflammatory factors such as COX-2 expression, prostaglandin E2 and NO levels. Proanthocyanins affect the lipidic metabolism, reducing FAs levels in rats, and playing an important role in hyperlipidemia, diabetes and obesity disorders. L'igname are derived from two molecules of p-hydroxyphenylpropane, and usually act as monomers in the formation of lignins. Flaxseeds' content of lignans is remarkable, with secoisolariciresinol diglucoside being the most abundant. This phytochemical is a potent antioxidant, and behaves as precursor of phytoestrogens. Besides, sesame seeds contain two significant groups of lignans: (1) oil-soluble lignans (sesamolino, sesamolinol, sesamin, pinoresinol, and sesaminol) and (2) glycosylated water-soluble lignin (pinoresinol triglucoside, pinoresinol monoglucoside, sesaminol triglucoside, and sesaminol monoglucoside). Consumption of lignans is associated with anticarcinogenic and hypolipidemic activities, also reducing atherosclerosis and CVDs' incidence. They also display immunomodulatory functions, neuroprotective function, antihypertensive activity, and prevent hypoxia and brain damage.

Summarizing, phenolic compounds present in oilseeds represent great candidates for industrial applications, as their use is doubly advantageous: it improves oxidative stability and preservation in the commercial product, and exerts numerous beneficial and prophylactic effects in human health.

3. Phytic Acid

Phytic acid (inositol hexaphosphate (IP6)) is a bioactive phytochemical broadly distributed in plant foods (e.g., cereals, soybeans, rapeseeds, legumes, and enriched fiber foods). This compound is considered an anti-nutrient because when dissociated by ruminants' digestive enzyme phytase, phytic acid (or its salt form, phytate) gives raise to inositol and phosphorus, two toxic molecules. However, for humans and non-ruminant animals phytates are not digestible, but can limit the bioavailability of nutrients such as minerals, proteins and starch. Nevertheless, phytic acid possesses beneficial properties. Phytic acid shows antioxidant capacity by chelating iron ions, reducing site-specific DNA damage, and preventing tumor growth by suppressing the formation of the highly reactive OH• and other ROS. In animal studies phytic acid has been shown to inhibit neoplastic growth and metastasis in multiple types of cancer. Phytates also show hypocholesterolemic capacity. The main oilseeds containing phytic acid are sunflower seed and rapeseed, with 1.52%, and sesame seed with 1.44–5.36%.

Analytical techniques to determine phytic acid in food matrixes include refractive index detection, gas chromatography (GC), and coupled plasma atomic emission spectrometry, although the most accurate is HPLC-UV. Recent research has studied the elimination of this component from oilseeds using phytase, soaking, germination, fermentation, cooking, extrusion, dehulling, ultrasound waves, and high energy electromagnetic radiations.

4. Tocopherols

Tocopherols are oil-soluble antioxidant compounds present in numerous natural matrixes, such as oilseeds. They are a vitamin E complex component that shows four homologs: α (5,7,8-trimethyltocol), β (5,8-dimethyltocol), γ (7,8-dimethyltocol), and δ (8-methyltocol). Tocopherols act as biological free radical scavengers and may prevent infections, apart from its key nutritional properties. The relative antioxidant activities in order of the homologs in vivo are $\alpha > \beta > \gamma > \delta$, whereas a reversed order ($\delta > \gamma \approx \beta > \alpha$) is observed when analyzed in oily systems in vitro. In vegetable oils, γ -tocopherol is the most abundant, and can prevent lipidic oxidation by scavenging lipid hydroperoxide radicals (LOO*). In comparison, α -tocopherol is essential for the diet and health effects of humans. Tocopherols constitute antitumor, antioxidant and hypocholesterolemic agents, diminishing the risk of heart diseases and some cancers. Thus, tocopherols are valuable nutraceuticals that offer health effects to consumers, while protecting oils from oxidative deterioration and rancidity. However, the extraction procedure can compromise the amount of tocopherols. Although each tocopherol shows different sensibility to degradation, in general terms, mild thermal treatments favor their release, while excessive intensity or temperature (over 180 °C) leads to decomposition.

Tocopherols are usually detected and quantified by chromatographic methods: GC, LC or HPLC.

5. Phytosterols

Phytosterols are plant-based compounds, present in many oilseeds. Phytosterols (sterols and stanols) are triterpenes of plants with disease preventive functions, particularly in cancers. They also elicit anti-inflammatory, antioxidant, anti-tumoral, and antibacterial properties. Phytosterol-derived foods influence cholesterol absorption, increase its excretion, and decrease its gut absorption, which results in lower blood cholesterol levels. Sesame seeds show the highest phytosterols content (400–413 mg/100 g). β -sitosterol, when compared with other phytosterols, was more thoroughly researched for its physiological effect and advantageous impact on human beings. β -Sitosterol reduces the levels of cholesterol, increases immunity, and displays anti-inflammatory effects.

Chromatographic techniques such as GC, LC, HPLC or even high temperature gas chromatography-mass spectrometry (HTGC-MS) are the most used methods for determining phytosterols, although spectrometries can also be performed with this purpose, as NIRS.

6. Dietary Fiber-Rich Foods

Flaxseed has been grown for fiber and also for food supplements for its possible health effects and medicinal uses such as the prevention of cancer, heart related disease, obesity etc. Flaxseeds have been recently introduced with other food additives or nutraceuticals to increase the food nutritional quality. Recent studies on rich-fiber functional foods and nutrients have led to a growing interest in flaxseed consumption, because of its higher content in omega-3FAs, fiber, phytoestrogens, and flavonoids among many involved in minimizing the effects of colorectal cancer (CRC). Flaxseed fiber greatly increased the fecal excretion of fat by 50%. reducing low-density lipoprotein (LDL) activity.

7. Fatty Acids

Higher amounts of PUFAs enhance the oil quality for human intake. Flaxseeds contains 19.55 g omega-3 fatty acids per serving i.e., 85 g. Dietary PUFAs exert anti-thrombotic, anti-inflammatory, hypolipidemic, anti-arrhythmic, and vasodilatory activities (oxylipins), and improve immunity. In addition, the higher levels of linoleic acid decrease the systemic cholesterol levels, and play a crucial role in the prevention of atherosclerosis.

GC, UPLC-Q-Exactive Orbitrap mass spectrometry-based lipidomic method or HPLC-MS can be used to quantify these compounds.

The protective effect of high-oleic acid peanut oil and extra-virgin olive oil can be observed in rats with diet-induced metabolic syndrome by regulating branched-chain amino acids metabolism.

Alpha-Linolenic Acid (ALA) is an important omega-3 PUFA, which is necessary in the diet of humans. The daily intake of omega-3 PUFAs, such eicosapentaenoic acid (EPA) and docosahexaenoic acid (DHA), present in fish oils, is related with a lower risk of stroke. and colon cancer by changing the function and structure of membrane, raising the anti-inflammatory metabolites production and reducing cellular oxidative stress, out of other possible mechanisms. Epidemiological studies reported the importance of daily consumption of ALA-derived flaxseed oil to reduce CRC (and many other cancer types) growth development. Inflammatory and oxidative stress markers were decreased by ALA in a model of inflammatory

bowel disease. Reactive oxygen species (ROS) play a pathogenic role in hypertension. Interestingly, two studies evaluating the impact of enriched edible flaxseed oil in ALA have demonstrated a substantial reduction in Systolic Blood Pressure (SBP). A substantial inverse association between blood pressure and dietary ALA was observed throughout the INTERMAP study of a wide epidemiological trial of 4680 women and men. In pre-hypertensive patients, 12 weeks of regular intake of 14 g of oil enhanced by 2.6 g ALA caused a reduction of 10 mm Hg and 3 mm Hg in diastolic blood pressure (DBP) and systolic blood pressure (SBP), respectively. Flaxseed oil minimized DBP, SBP, and mean arterial blood pressure (MAP) by 10 mm Hg, 8 mm Hg, and 8 mm Hg, respectively, in patients with dyslipidemia who have ingested 15 mL flax oil including 8 g ALA/day in a meal, for 12 weeks. A 4-week intake of ground flaxseeds decreased plasmatic pro-inflammatory oxylipins in the elderly.

8. Phytoestrogens

Great attention has been given to dietary phytoestrogens for their impact on human health. A number of other studies revealed the beneficial impact of phytoestrogens on human health, including on osteoporosis, cancers, menopausal symptoms, CVDs, obesity, T2D, antiproliferative, and male infertility. A study reported that clinical symptoms of menopause can be decreased by consuming dietary phytoestrogens.

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