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Secondary metabolites in sorghum and its characteristics

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Abstract

Humans can use specific secondary metabolites as antioxidants or medicinal raw materials. Each plant has different secondary metabolites and a unique structure. Similarly, secondary metabolites were found in sorghum (*Sorghum bicolor* L. Moench). This paper aims to describe the types, characteristics, and benefits of secondary metabolites found in sorghum plants. The results of phytochemical screening showed that sorghum contains several secondary metabolites, namely alkaloids, flavonoids, tannins, polyphenols, saponins, steroids, and terpenoids. Epidemiological studies show that consuming plants rich in polyphenolic compounds reduces the rate of heart disease, cancer, gastrointestinal tract, neurological disease, liver disease, atherosclerosis, and obesity. Flavonoids are one of the phenol groups. Phenolic compounds have potential antioxidant activity and some of them be more effective than vitamins C, E, and carotenoids. Antioxidants are believed to have a role in reducing oxidative stress which plays a role in the development of chronic degenerative diseases including heart disease, cancer, and premature aging. Alkaloids are a group of compounds containing aromatic nitrogen. Alkaloids in the health sector are used as anti-tumor, antipyretic (fever-reducing), anti-pain (analgesic), stimulating the nervous system, raising and lowering blood pressure, and fighting microbial infections.

Keywords: secondary metabolites; sorghum; characteristics; benefits.

Practical Application: Hopefully it will be useful information for human health.

1 Introduction

One of the food ingredients that have the potential to be developed in Indonesia is sorghum. As a cereal commodity that contains complex carbohydrates and a source of dietary fiber, sorghum has the potential to be developed as a functional food ingredient. Sorghum also has the potential to be developed as a gluten-free food that is suitable for consumption by people with chronic enteropathic disorders defined as celiac disease or gluten intolerance (Benkadri et al., 2018; Pestorić et al., 2017; Shahzad et al., 2021).

The dietary fiber component contained in sorghum is β -glucan. This component is known to have health benefits such as prebiotics, and the prevention of diabetes and colon cancer (Niba & Hoffman, 2003). According to Brown & Gordon (2001) β -glucanhas the same antitumor and antimicrobial stimulatory capabilities as dietary fiber. According to Khan et al. (2021), β -glucan is a soluble fiber and has been shown to reduce blood glucose and cholesterol levels, also supported by research by Rehman et al. (2021) that besides that it can also lose weight.

Sorghum contains phytochemical components such as tannins, phenolic acids, anthocyanins, phytosterols, and polycosanols, which significantly affect health (Awika & Rooney, 2004). Several studies have reported that the bioactive components contained in sorghum function as antioxidants, and antimicrobials and can lower blood cholesterol levels. Hexane extract from sorghum seed flour given to experimental rats can inhibit the activity of the enzyme HMG-CoA reductase in rat liver and can reduce the risk of cardiovascular disease (Cho et al., 2000). Increased antioxidant activity of DPPH and antimicrobial methanol extract from sorghum seed flour was reported by Kil et al. (2009). These functional components include metabolites. Especially antioxidants in foodstuffs make consumer attractiveness especially related to positive aspects for food health and safety, thus influencing consumer choices for food. As the results of research by Mitterer-Daltoe, et al. (2021), showed the potential of natural antioxidants in foodstuffs which attracted the food industry to develop due to the high public interest in consuming antioxidant-rich foods.

About 400,000 plant species are sources of hundreds of thousands of metabolites whose structure, function, and use have only been partially explored (Willis, 2017). It appears that plants exhibit much greater metabolic diversity than other organisms, with the plant kingdom generally being stated to contain between 200000 and one million metabolites, with a single species estimated to contain more than 5000 metabolites (Dixon & Strack, 2003; Rai et al., 2017; Fang et al., 2019; Fernie et al., 2004). Plants have a great capacity to synthesize several secondary metabolites which make up the majority of their metabolome (Alseekh & Fernie, 2018). This compound is an organism as an effective means of defense against biotic and abiotic stresses from plants (Wang et al., 2019). However, the composition, characteristics, quality, and amount (quantity) of secondary metabolites in plants are strongly influenced by

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genetic, environmental and cultivation factors (Ade et al., 2012; Hussain et al., 2022).

This paper aims to describe the types, characteristics, and benefits of secondary metabolites found in sorghum plants.

2 Characteristics and formation of metabolic compounds

An organism needs to transform and convert organic compounds into food to sustain life, develop and reproduce. Organic compounds are used as basic materials to build tissues and produce energy in the form of ATP. Organic compounds are processed in the body of organisms through complex chemical reactions with the help of enzymes. Each organism has a different ability to transform organic compounds. Plants can synthesize organic compounds from inorganic compounds through the process of photosynthesis (Dalimunthe & Rachmawan, 2017). Plants obtain organic compounds from food intake. The process of processing organic compounds in the organism's body is called a metabolic process, while the stages and pathways involved are called metabolic pathways (Dewick, 2009).

According to Anurag et al. (2015) that there are two types of metabolism, namely primary and secondary. Primary metabolism occurs in all organisms with almost the same processes and pathways, while secondary metabolism has pathways and products that are specific and unique to each organism. Primary metabolism is directly involved in growth, whereas secondary metabolism is generally not involved in growth activity. Primary metabolism modifies and synthesizes carbohydrates, fats, proteins, and nucleic acids, while secondary metabolism produces secondary metabolites of relatively small size, generally with a molecular weight of less than 3000 Da (Dewick, 2009).

Primary metabolites play a role in the process of photosynthesis and respiration, while secondary metabolites play a more important role in plant defense functions (Anurag et al., 2015). Secondary metabolites are produced at certain growth rates or conditions. This group of compounds is produced in limited quantities, not continuously and only for specific purposes. The existence of the ability of plants to carry out photosynthesis causes the secondary metabolite products produced by plants to be very different from the secondary metabolites produced by other organisms.

Secondary metabolites in plants have several functions, including as attractants (attracting other organisms), defense against pathogens, protection and adaptation to environmental stress, protection against ultraviolet rays, as growth regulators and to compete with other plants allelopathy. Secondary metabolites are thought to be wastes or products of plant detoxification (Dewick, 2009; Kabera et al., 2014). Secondary metabolites are unique, have a variety of chemical structures, and are potential candidates for natural drugs and pesticides (Cavoski et al., 2011). Secondary metabolites have specific properties because they are produced in limited quantities and with different structures. The diversity of chemical structures of secondary metabolites is very abundant, many of which have very complex compositions. The uses of secondary metabolites include medicinal ingredients, agricultural chemicals, food additives and cosmetic ingredients. Some examples of secondary metabolites that have been commercially and widely known are penicillin, morphine, shikonin (anti-bacterial), ginsenoida (vitality enhancer), vinblastine vincristine (leukemia drug) and ajmalicin (anti-hypertensive) (Dewick, 2009; Mariska, 2013).

Primary metabolites are compounds produced by plants that are essential in the process of cell metabolism and the whole process of synthesis and overhaul of substances carried out by organisms for their survival. The characteristics of primary metabolites are that they are evenly distributed in each organism, have a universal function, are a source of energy, a source of enzymes, hereditary carriers, structural materials, the difference in chemical structure is small, and physiological activity is related to the chemical structure (Almatsier, 2009).

Secondary metabolites are a group of compounds contained in the body of microorganisms, flora and fauna that are formed through secondary metabolic processes synthesized from many primary metabolite compounds. The characteristics of secondary metabolites are unevenly distributed in each organism, have ecological functions, attract insects, protect themselves, compete tools, as hormones, the difference in chemical structure depends on the development of organic chemistry and the relationship between structure and activity, physiological activity is related to chemical structure and relationships. Among the structures, most of the secondary metabolites are lipid derivatives. Secondary metabolites include terpenoids, steroids, coumarins, flavonoids, and alkaloids. As one of a large group of secondary metabolites, many of its compounds have medicinal properties (De Luca & St-Pierre, 2000). Table 1 shows the differences between primary and secondary metabolites.

Secondary metabolites are mainly used by plants as defenses that protect themselves from predators that threaten plant life. The defense system possessed by a plant, among others, is a mechanical system or uses chemical substances. These chemicals which are one of the defenses of plants are called secondary metabolites. Secondary metabolites are the products of metabolism released by plants. In addition to plant defense, these secondary metabolites can be used for human purposes as medicine, dyes, fragrances, and cooking spices.

Secondary metabolites are compounds that are not essential for the growth of these organisms and are found in unique forms. Each organism usually produces secondary metabolites that differ from one species to another. It is even possible that one type of secondary metabolite compound is only found in

Table 1. Differences between primary and secondary metabolites.

Primary metabolites	Secondary metabolites
Same for all organisms	Depends on the species
Example:	Example:
 Natural polymer 	• Terpenoids
• Polysaccharides	• Steroids
• Protein	• Flavonoids
• Fat	 Polyketides
Nucleic acids	Alkaloids

one species in a kingdom. This compound is also not always produced, but only when needed or in certain phases. The function of secondary metabolites is to defend themselves from unfavorable environmental conditions, for example, to overcome pests and diseases, attract pollinators, and as signaling molecules. Basically, these secondary metabolites are used by organisms to interact with their environment.

Secondary metabolites are classified into three main groups, namely:

1. Terpenoids

Terpenoid compounds mostly contain carbon and hydrogen and are synthesized through the mevalonic acid metabolic pathway. Examples are monoterpenes, sesquiterpenes, diterpenes, triterpenes, and terpene polymers.

2. Phenolic

Phenolic compounds are composed of simple sugars and have benzene, hydrogen, and oxygen rings in their chemical structure. Examples are phenolic acids, coumarins, lignins, flavonoids, and tannins.

3. Compounds containing nitrogen. Examples are tanpa tanda alkaloids and glucosinolates.

Most plants that produce secondary metabolites use these compounds to defend themselves and compete with other living things around them. Plants can produce secondary metabolites (such as quinones, flavonoids, tannins, and others) that make other plants unable to grow around them. This is known as allelopathy. Various secondary metabolites have been used as drugs or models to make new drugs, for example, aspirin is made based on salicylic acid which is naturally found in certain plants. Another benefit of secondary metabolites is as a pesticide and insecticide, for example, rotenone and rotenoid. Several other secondary metabolites that have been used in producing soaps, perfumes, herbal oils, dyes, chewing gum, and natural plastics are resins, anthocyanins, tannins, saponins, and volatile oils. Table 2 shows some examples of secondary metabolites.

3 Formation of secondary metabolites

The basic ingredients of secondary metabolites are derived from primary metabolism and are broadly divided into four, namely acetyl coenzyme A, shikimic acid, mevalonic acid and methylerythritol phosphate (Dewick, 2009; Kabera et al., 2014). Based on these basic ingredients, there are the acetate malonate pathway, shikimate pathway, mevalonate pathway and methylerythritol phosphate pathway. Various types of secondary metabolites are synthesized from one or a combination of these basic constituents.

1. Malonic acetate pathway

According to Dewick (2009), the acetate malonate pathway is formed from the basic ingredient of acetyl coenzyme A, which is composed of two carbon atoms. Acetyl coenzyme A reacts by condensation to form larger units with multiples of the number of carbon atoms, called poly-beta keto or polyketides (Figure 1). Secondary metabolites included in this pathway are fatty acids (lauric, myristic, palmitic, stearic, oleic, linoleic, linolenic), polyacetylene, prostaglandins, macrolides, and aromatic compounds (anthraquinones and tetracyclines). Plants that produce this compound include jatropha, oil palm, coconut, corn, peanut, olive, sunflower, soybean, sesame, cotton, cocoa, and avocado (Mariska, 2013).

2. Shikimat path

The shikimate metabolic pathway is only found in microorganisms and plants (Herrmann & Weaver, 1999). The

Class	Examples of Compounds	Examples of Sources	Effects and Uses
a. COMPOUNDS CONTAININ	G NITROGEN		
Alkaloids	Nicotine, cocaine, theobromine	Tobacco, chocolate	Affects neurotransmission and inhibits enzyme activity
b. TERPENOIDS			
Monoterpene	Mentol, linalool	Mint plants and many other herbs	Affects neurotransmission, inhibits ion transport, anesthetics
Diterpena	Gossypol	Cotton	Inhibits phosphorylation, toxic
Triterpenes, cardiac (heart) glycosides	Digitogenin	Digitalis (Foxglove digitalis sp.)	Cardiac muscle stimulation, affects ion transport
Sterols	Spinasterol	Spinach	Affects the work of animal hormones
c. PHENOLIK			
Phenolic acid	Cafeat, Chlorogenat	All plant	Causes oxidative damage the appearance of brown color in fruit and wine.
Tannins	Gallotanin, condensed tannins	Oaks, nuts	Binds to proteins, enzymes, inhibits digestion, antioxidants.
Lignin	Lignin	All land plants	Structure, fiber

Table 2. Some examples of secondary metabolites.

main intermediate of this pathway is shikimic acid, a compound that was first isolated from the plant Illicium sp. The shikimate pathway is an alternative pathway for the formation of aromatic compounds, especially the aromatic amino acids L-phenylalanine, L-tyrosine and L-tryptophan (Figure 2). L-phenylalanine and L-tyrosine are the building blocks of the phenylpropane group compounds and aromatic polyketides (including flavonoids). Together with L-tryptophan, these two amino acids are also the building blocks of a group of alkaloid compounds (Gleason & Chollet, 2012).

3. Mevalonate and methylerythritol phosphate pathway

According to Dewick (2009), the mevalonate and methylerythritol phosphate (non-mevalonate) pathways are pathways for forming

groups of terpenoid and steroid compounds. The mevalonate pathway occurs in the cytosol and mitochondria, while the methylerythritol phosphate pathway occurs in the plastids. In the mevalonate pathway, the initial precursor is acetyl Co-A, whereas, in the methylerythritol phosphate pathway, the initial precursors are pyruvate and glyceraldehyde-3-phosphate (Nes & Zhou, 2001). Both pathways will form isopentenyl pyrophosphate (IPP) and dimethylallyl pyrophosphate (DMAPP) which are universal precursors for the formation of a five-carbon chain, C5. Terpenoids are the largest group of all metabolites (Bohlmann & Keeling, 2008). Terpenoids are composed of a series of isoprene units (five-carbon chains) linked via head-to-tail bonds. Terpenoids are classified into hemiterpenes (C5), monoterpenes (C10), sesquiterpenes (C15), diterpenes (C20), sesterterpenes (C25), triterpenes (C30), and tetraterpenes (C40).

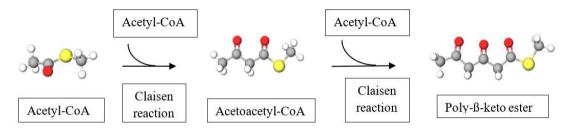


Figure 1. Melonate acetate formation pathway (modification). Source: Dewick (2009).

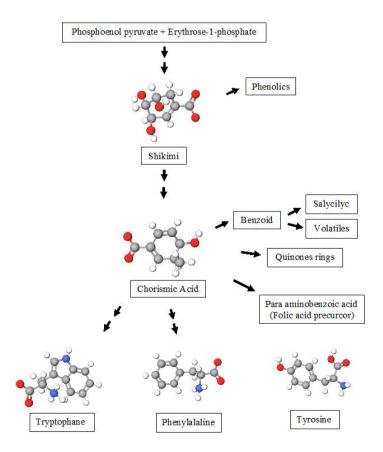


Figure 2. Pathway of shikimic acid formation from erythrose (modification). Source: Gleason and Chollet, 2012.

4 Metabolite content in sorghum seeds and their benefits

Sorghum is a potential food source that contains primary and secondary metabolites. Types of primary metabolites found in sorghum seeds include carbohydrates, protein and fiber. In addition, sorghum contains phytochemicals including alkaloids, flavonoids, tannins, polyphenols, saponins, steroids and terpenoids (Agustina et al., 2021). Meanwhile, Awika & Rooney (2004) stated that sorghum contains phytochemical compounds including tannins, phenolic acids, anthocyanins, phytosterols and policosanols. These phytochemical compounds are referred to as secondary metabolites.

5 Alkaloids

Alkaloids are a group of organic compounds that are mostly found in nature. Alkaloids can be found in various parts of plants including seeds, leaves, twigs and bark. Almost all the alkaloids found in nature have certain physiological activities. Some are toxic but some are very useful as medicine (Ting et al., 2010; Lee et al., 2014). Quinine, morphine, and strychnine are well-known alkaloids and have physiological and psychological effects. All alkaloids contain at least one nitrogen atom which is usually basic. Alkaloids derived from several amino acids are distinguished into allylcyclic alkaloids derived from the amino acid ornithine and lysine, aromatic alkaloids derived from phenylalanine and thyroxine, and indole aromatic alkaloids derived from tryptophan.

Alkaloids are secondary metabolites that were originally defined as pharmacologically active compounds, consisting mainly of nitrogen (Croteau et al., 2000; Ziegler & Facchini, 2008). Alkaloids are synthesized from one of several common amino acids: lysine, tyrosine and tryptophan. More than 12,000 alkaloids, including more than 150 families, have been identified in plants, and about 20% of flowering plant species contain alkaloids. In plants, alkaloids are generally salts of organic acids such as acetic, malic, lactic, citric, oxalic, tartaric, tannic and other acids. Some weakly basic alkaloids (such as nicotine) occur freely in nature (Figure 3). Some alkaloids are also present as sugar glycosides such as glucose, rhamnose and galactose, such as solanum alkaloids (solanine), as amides (piperine) and as esters (atropine, cocaine) of organic acids (Ramawat et al., 2009).

The biological properties of various alkaloids have also led to their use as drugs, narcotics, stimulants, and poisons. Alkaloids are widely used in modern medicine such as morphine, quinine and codeine. Thus, alkaloids at low doses are pharmacologically useful but are toxic agents at high doses. Alkaloids can also be very effective poisons, such as strychnine, due to their various physiological effects. Therefore, this class of secondary metabolites is involved in the chemical defense mechanism of plants (Table 3).

Alkaloids are a group of nitrogenous base compounds that are mostly heterocyclic and are found in plants. Alkaloids are usually classified according to the common origin of the molecule (precursors), based on the metabolic pathway (metabolic pathway) used to form the molecule (Richard et al., 2013). Alkaloids are detoxifying, working to neutralize toxins in the body. Nitrogen atoms are distributed in a limited manner

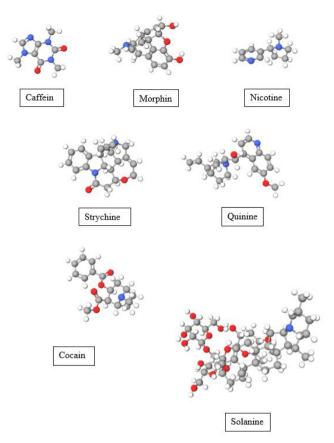


Figure 3. Alkaloid compounds (modification). Source: Richard et al. (2013).

in plants. The grouping of alkaloids is usually based on their constituent precursors. Most are formed from amino acids such as lysine, tyrosine, tryptophan, histidine and ornithine. For example, nicotine is formed from ornithine and nicotinic acid. The benzyl iso-quinone group of alkaloids, such as papaverine, berberine, tubocurarine, and morphine.

The core structure of the alkaloids is indole, grouped as indole alkaloids, such as, strychnine and quinine which taste bitter and are insect repellent compounds. The pyrrolizidine alkaloid group is an ester alkaloid in the Senecio genus, such as Senecio-nin. Another group of alkaloids derived from the amino acid lysine are the quinolizidines, which are often referred to as lupine alkaloids because they are abundant in the genus Lupinus. Polyhydroxy alkaloids have a stereochemistry similar to sugar, thus interfering with the work of the glucosidase enzyme. The polyhydroxy alkaloid group is also an insect repellent. Several types of alkaloids are derivatives of nicotinic acid, purines, anthranilic acid, poly-acetate and terpenes, which are grouped into purine alkaloids, such as caffeine.

The physical properties of alkaloids are usually colorless, and optically active, mostly in the form of crystals, for example, quinine and nicotine have a melting point of 100-300°C. Generally, have one N atoms although there are some that have more than one N atom as in Ergotamine which has 5 N atoms. These N atoms can be primary, secondary, or tertiary amines which are all basic (the degree of basicity depends on the molecular structure and

Compounds	Source	Effects and uses
Morphine	Papaver somniferum	Analgesic
Camptothecin	Camptotheca acuminata	Anticancer
Atropine	Hyoscyamus niger	Prevention of intestinal spams, antidote to other poisons
Vinblastine	Catharanthus roseus	Anticancer
Codeine	Papaver somniferum	Analgesic, antitusive
Caffeine	Coffea arabica	Stimulant, natural pesticides
Nicotine	Nicotiana tabacum	Stimulant, tranquillizer
Cocaine	Erythroxylon coca	Stimulant of the central nervous system, local anesthetic

Table 3. Example of alkaloids in plants.

functional group). Most of the alkaloids that have been isolated are insoluble crystalline solids with a certain melting point or range of decomposition. Few alkaloids are amorphous and some are like; nicotine and koniin are liquids. Some are complex, colored aromatic species (eg. berberine is yellow and betanin is red). In general, free base alkaloids are soluble only in organic solvents, although some pseudoalkaloids and proto-alkaloids are soluble in water. The salts of alkaloids and quaternary alkaloids are very soluble in water.

The chemical nature of alkaloids is that they are generally basic, usually in combination as part of a cyclic system. Alkaloids can also form precipitates with solutions of phosphomolybdic acid, picric acid, and potassium mercury-oxide. It is basic depending on the presence of an electron pair on the nitrogen. If a functional group adjacent to the nitrogen loses electrons, for example an alkyl group, then the availability of electrons on the nitrogen increases and the compound is more basic. Triethylamine is more alkaline than diethyl-amine, and diethyl-amine compounds are more alkaline than ethylamine. On the other hand, if adjacent functional groups are electron-withdrawing (eg, carbonyl groups), the availability of electron pairs is reduced and the effect of the alkaloids can be neutral or even slightly acidic. For example a compound containing an amide group. The basicity of the alkaloids causes these compounds to decompose very easily, especially by heat and light in the presence of oxygen. The product of this reaction is often N-oxide. Decomposition of alkaloids during or after isolation can cause problems if stored for a long time. The formation of salts with organic (tartaric, citric) or inorganic (hydrochloric or sulfuric acids) compounds often prevents decomposition. Therefore, in the trade of alkaloids in the form of their salts.

Alkaloids can be classified into three groups, namely:

- 1. True alkaloids are compounds that have a heterocyclic nitrogen ring, are basic and are derived from amino acids.
- 2. Combined alkaloids are amino acid derivatives; the nitrogen atom is not in the form of a heterocyclic ring. The combined alkaloids are basic in nature, derived from the biosynthesis of the amino acids themselves. For example, mescalina.
- 3. Pseudo-alkaloids are plant bases that contain heterocyclic nitrogen, have activity and have no biosynthetic relationship with amino acids. Pseudo-alkaloids are derived from

terpenoid compounds derived from acetic acid and polyketonic acid. For example, caffeine is found in coffee.

6 Flavonoids

Flavonoids are the largest group of phenolic compounds found in nature, which are formed through the shikimate pathway. These flavonoids are a group of polyphenolic compounds in plants commonly found in vegetables, fruit, flowers, seeds, as well as honey and propolis (Ahmad et al., 2015]). This compound is a red, purple, and blue dye. And as a yellow dye found in plants. Flavonoids function to improve blood circulation throughout the body and prevent blockages in blood vessels, reduce cholesterol content and reduce fat accumulation in blood vessel walls, reduce the risk of coronary heart disease, contain anti-inflammatory (anti-inflammatory), function as antioxidants, help reduce pain if bleeding or swelling occurs Janicsák et al. (1999). The research results of Ho-Young Seon et al. (2021), showed a high significance that there was a correlation between the content of flavonoids and polyphenols with free radical and antioxidant activity.

Flavonoids are widely distributed in plant parts, roots, stems, leaves, and fruits. Based on the structure, flavonoid compounds are derivatives of the parent compound flavones, namely the name of a type of flavonoid with the largest number and easy to find. Most of the flavonoids found in plants are bound to sugar molecules as glycosides, and in mixed form, they are rarely found as single compounds. In addition, mixtures of flavonoids of different classes are often found. Flavonoids are polyphenolic compounds so they are slightly acidic and can be soluble in bases. In addition, it is a polyhydroxy compound (hydroxyl group), so it is polar so it can dissolve in polar solvents such as methanol, ethanol, acetone, water, butanol, dimethyl sulfoxide, dimethyl formamide.

The functions of flavonoids in plants include color pigments, pathological and cytological functions, and pharmacological activities. Flavonoids are thought to be derived from rutin (flavonol glycosides) which are used to strengthen the capillary structure, reduce the permeability and fragility of blood vessels. Janicsák et al. (1999), stated that flavonoids can be used as drugs because they have various bioactivities such as anti-inflammatory, anticancer, antifertility, antiviral, antidiabetic, antidepressant, diuretic, and others. Some of the structures of flavonoids are: (1) the molecular structure of backbone flavones (2-phenyl-1,4benzopyrone); (2) isoflavan structure; and (3) the structure of neoflavonoids.

Usually, one type of plant contains several kinds of flavonoids and almost every type has a distinctive flavonoid profile. The flavonoid framework is C6–C3–C6. The flavonoid core usually binds to sugar groups to form water-soluble glycosides. In plants, flavonoids are usually stored in cell vacuoles. In general, flavonoids are further grouped into smaller groups (sub groups), namely, flavones, for example, luteolin, flavanone, for example : naringenin, flavonol, for example: kaempferol, anthocyanin, and chalcone.

Phenolics are compounds that are commonly found in plants. Phenolics have an aromatic ring with one or more hydroxy groups (OH-) and other accompanying groups. These compounds are named after the name of the parent compound, phenol. Most phenolic compounds have more than one hydroxy group so they are called polyphenols. Phenols are usually grouped according to the number of carbon atoms in their constituent skeleton. The largest group of phenolic compounds are flavonoids, which are compounds that are generally found in all types of plants.

Some types of flavones, flavanones and flavonols absorb light, giving flowers and other plant parts a light yellow or cream color. Meanwhile, the colorless species are insect repellents (eg catechins) or are toxic (eg rotenone). Flavonol glycosides, which are found in almost all types of plants, are also repellents for polyphagous insects, such as Schistocerca Americana.

Flavonoids have a basic carbon skeleton consisting of 15 carbon atoms. Two benzene rings (C6) are bonded to a propane chain (C3) to form a C6-C3-C6 arrangement. This arrangement can produce three types of structures, namely 1,3-diarylpropane or flavonoids, 1,2-diarylpropane or isoflavonoids, and 1,1-diarylpropane or neo-flavonoids (Dewick, 2009). Flavonoid compounds that are usually found in nature are flavones, flavonols and anthocyanidins. Isoflavonoid compounds are isoflavones, rotenoids and kumestan, while neoflavonoids include 4-arylkumarins and various dalbergoins.

Flavonols are the main polyketides and flavonoids in Arabidopsis thaliana (Veit & Pauli, 1999; Rohde et al., 2004). The most abundant flavonol from arabidopsis is the kaempferol glycoside (D'Auria & Gershenzon, 2005), but quercetin glycosides have also been described to accumulate after UV exposure (Veit & Pauli, 1999; Ryan et al., 2001). Although found mainly in shoots, flavonol glucosides can be induced in roots after exposure to light (Hemm et al., 2004), and are also found in roots (Narasimhan et al., 2003; D'Auria & Gershenzon, 2005). The corresponding flavonol aglycones, together with quercetin, have also been shown to play a developmental role by regulating polar auxin transport (Silva-Navas et al., 2016; Tohge et al., 2005). D'Auria & Gershenzon (2005) documented that only 13 flavonoids have been reported in Arabidopsis. This number was later extended to 24 and following various studies now approaches 170 (Tohge et al., 2005; Nakabayashi et al., 2009; Tohge et al., 2005).

7 Tannins

Tannins are polyphenolic compounds with molecular weights between 500 to 20000 daltons. In-plant cells, tannins

always bind to proteins so that they are substances that reduce the nutritional value of plant tissues for those who eat them. Tannin compounds are able to bind proteins so that protease enzymes are not able to degrade proteins (Kondo et al., 2014). Tannin compounds are components of very complex organic substances, consisting of phenolic compounds, and are difficult to separate and crystallize. Desmiaty et al. (2008), said that tannins can precipitate proteins from solution and combine with these proteins. Tannins protect proteins from enzyme and microbial degradation. Tannins are chemical compounds belonging to polyphenol compounds. Tannins contain a number of groups of strong functional bonds with protein molecules, resulting in large and complex cross-links, namely protein-tannin bonds (Deaville et al., 2010).

Apart from being anti-nutrition, tannins in certain (small) amounts function as biological antioxidants. Antioxidants in a chemical sense, are electron-donating compounds. Antioxidants work by donating one electron to compounds that are oxidants so that the activity of these oxidant compounds can be inhibited. Antioxidants stabilize free radicals by complementing the electron deficiency of free radicals and inhibit the chain reaction of free radical formation (Hagerman, 2002; Winarsi, 2007). Tannins are known to have several properties, namely as astringent, antidiarrhea, and anti-bacterial (Malangngi et al., 2012).

Natural tannin compounds dissolve in water and give water its color. The color of the tannin solution varies from light to dark red or brown because each tannin has a distinctive color depending on the source (Cheng et al., 2008). Tannins are classified into two groups based on the type of structure and activity towards hydrolytic compounds, namely condensed tannins and hydrolyzable tannins (Hagerman, 2002). The molecular weight of tannins is 500-3000 daltons (Da) (Naumann et al., 2013a). The chemical structures of hydrolyzed and condensed tannins are presented in Figure 4.

Hydrolyzed tannins bind to carbohydrates to form oxygen bridges, hydrolyzed by heating using sulfuric acid or hydrochloric acid, to produce gallic or ellagic acid. Gallo-tannin is an example of a hydrolyzed tannin (Figure 5). Gallo-tannin is a compound in the form of a combination of carbohydrates and gallic acid. Another example is ellagitannin (composed of Hexa-hydroxy-diphenyl acid). When tannins undergo hydrolysis, simple polyhydroxy phenols are formed, for example, pyrogallol, which is the result of the breakdown of gallic acid and catechol which is the result of the hydrolysis of proto-catechus acids. Hydrolyzed tannins are amorphous, hygroscopic, yellow-brown, soluble compounds in hot water, forming colloidal solutions instead of true solutions. The purer the tannin, the less soluble it is in water and the easier it is to obtain in the form of crystals. Condensed tannins are tannins on heating with hydrochloric acid to produce phlobaphene-es such as phloroglucinol. Condensed tannins consist mostly of flavonoid polymers (Figure 6). This type of tannin is known as pro-anthocyanidin which is a polymer of flavonoids linked through C8 to C4, for example, sorghum procyanidin is composed of catechins and epic-catechins (Naumann et al., 2013b).

The presence of tannins is spread in almost all parts of the plant, such as in leaves, shoots, roots, stems, bark, seeds, fruits, and tissues. In the xylem and phloem tissues, as well as in the

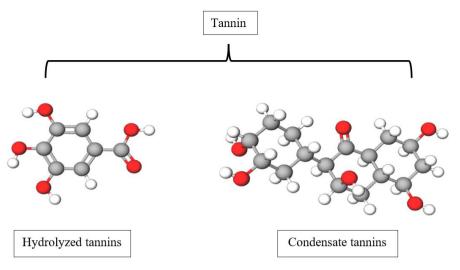


Figure 4. Simple chemical structure of hydrolyzed and condensate tannins

layer between the cortex and the epidermis. Tannins can help in the growth of these tissues. The distribution of tannins is found in all plant species and is usually found in gymnosperms and angiosperms. Tannins are located in vacuoles or parts of the plant surface (Figure 7). The part that acts as permanentstorage, will be active against predatory organisms. In addition, the temporary storage of tannins can affect the metabolism of living plant tissues, but only after the cells are damaged or dead, so that the tannins will be active to provide metabolic effects (Rooney & Awika, 2004).

To distinguish tannins from other secondary metabolites can be seen from the properties of the tannins themselves. The properties of tannins include physical, chemical, and metal chelating properties. Tannins have properties that can be dissolved in water or alcohol because tannins contain lots of phenols that have OH groups, and can bind heavy metals. In water, it forms a colloidal solution that reacts with acids and has a sour and astringent taste. In addition, it can precipitate gelatin solutions and alkaloid solutions, cannot crystallize, alkaline solutions are able to oxidize oxygen, and precipitate proteins from the solution. Then it combines with the protein, so it is not affected by proteolytic enzymes (Khanbabaee & van Ree, 2001; Oliveira et al., 2010).

Tannin compounds can reduce the bioavailability of protein and other nutrients from sorghum seeds, as well as reduce protein digestibility (Narsih et al., 2008; Spalinger et al., 2010), According to Gilani et al. (2005) that high levels of tannins in cereals cause reduced protein and amino acid digestibility by up to 23%. The protein digestibility value of sorghum seeds varies from 73.2 to 96.0% (Duodu et al., 2003), while according to Ratnavathi & Komala (2016), the digestibility value of sorghum seeds is 20.37-70.57%. Tannins in sorghum seeds have an antioxidant effect, so tanpa the processed products can be used as functional foods. But in addition to having antioxidant properties, tannins have an antinutritional effect. Although the nutritional content of sorghum (especially protein and carbohydrates) is high, its nutritional value has decreased and is relatively low due to the high content of tannins

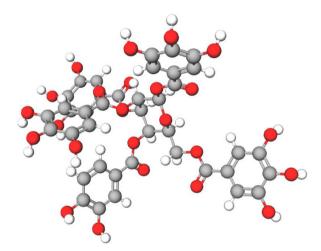


Figure 5. Hydrolyzed tannins (gallotannins) composed of gallic acid esters associated with sugar cores (modification) (Naumann et al., 2013a)

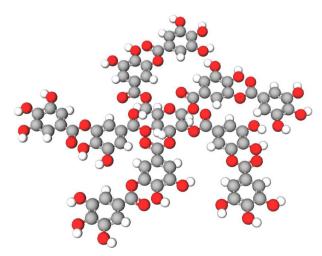


Figure 6. The basic structure of condensed tannins showing the stereochemistry, relationship between flavans and ß-ring hydroxylation (modification) (Naumann et al., 2013a).

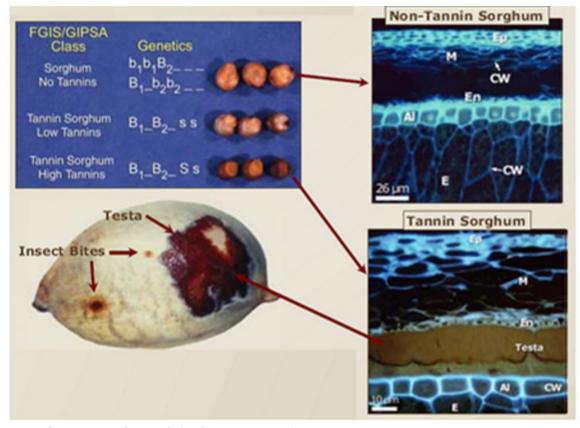


Figure 7. Position of tannins in sorghum seeds (Awika & Rooney, 2004).

as antinutrients. For nutritional needs, the safe tannin content in sorghum for consumption ranges from 1170 ppm (0.117%) in food, equivalent to about 60 mg/kg body weight (Food and Agriculture Organization, 1970). The content of tannins in sorghum seeds in each variety is different, the content of tannins in sorghum seeds is also influenced by the level of maturity of sorghum. The tannin content in some varieties of sorghum is 0 (white pericarp color) to 12.8% (red pericarp color) (Cheng et al., 2008).

8 Polyphenol

Polyphenols have a distinctive sign that has many phenol groups in their molecules. Polyphenols play a role in giving color to a plant such as the color of leaves in autumn. In several studies, it is stated that the polyphenol group has a role as an antioxidant that is good for health. Polyphenol antioxidants can reduce the risk of heart and blood vessel disease, cancer, and reduce the risk of Alzheimer's disease.

9 Saponins

Saponins have a characteristic in the form of foam so that when reacted with water and shaken it will form a foam that can last a long time. Saponins are easily soluble in water and insoluble in ether. Saponins have a bitter taste and cause sneezing and irritation of the mucous membranes. Saponins are poisons that can destroy blood grains or hemolysis in the blood, and are toxic to cold-blooded animals. Saponins that are harsh or toxic are commonly referred to as sapotoxins. The chemical structure of saponins is a glycoside composed of glycons and aglycones. The glycon portion consists of sugar groups such as glucose, fructose, and other types of sugar. The aglycone part is sapogenin. This amphiphilic nature can make natural ingredients containing saponins function as surfactants. Surfactants are ingredients that are commonly used in soap preparations. A surfactant is a molecule that simultaneously has a hydrophilic group and a lipophilic group so that it can unite a mixture consisting of water and oil. Surfactant molecules have a polar part that likes water (hydrophilic) and a non-polar part that likes oil/fat (lipophilic). The polar part of the surfactant molecule can be positively, negatively or neutrally charged (Martin & Rhein, 2008).

If used properly saponins can be useful as a source of antibacterial and antiviral, boost the immune system, increase vitality, reduce blood sugar levels, and reduce blood clotting. According to Rachmawati (2008), saponin compounds have the ability to cure various types of diseases. Saponin is a glycoside, which is a mixture of simple carbohydrates with aglycones found in various plants. Saponins are distinguished based on their hydrolysis results into carbohydrates and sapogenins, while sapogenins consist of two groups, namely steroidal saponins and triterpenoid saponins (Kumar et al., 2009).

10 Steroids

Steroids are a class of secondary metabolites. These groups of compounds are known to have bioinsecticide (Sugita et al., 2000), antibacterial (Lalitha et al., 2010; Laksono et al., 2014), antifungal (Saraswathi et al., 2010) and antidiabetic activities (Hidayah et al., 2016). Steroids are important bioactive molecules with a basic framework of 17 C atoms composed of 4 ring combinations, 3 of which are cyclohexane and cyclopentane. Steroid compounds are needle-shaped crystals with characteristics containing OH groups, methyl groups, and unconjugated double bonds (Suryelita & Kurnia, 2017).

This steroid is a compound that is quite important in the medical field. More than 150 types of steroids have been registered as drugs (Suryelita & Kurnia, 2017). Steroids in the medical world are used as drugs and contraception, for example, androgens are steroid hormones that can stimulate male sexual organs, estrogens can stimulate female sexual organs, adrenocorticoids can prevent inflammation and rheumatism. Stigmasterol compounds can lower blood cholesterol, inhibit the absorption of intestinal cholesterol so that it can inhibit the development of colon cancer, and suppress liver cholesterol. Apart from these steroid compounds, there are many other compounds which are used in the medical world. Based on their chemical composition, steroids can be used as secondary metabolites which are used as aspirin in children. In addition, it is also used as a pesticide and insecticide, for example, rotenone and rotenoid (Jones et al., 2000).

11 Terpenoids

The terpenoid group of compounds can be separated from the plant source through steam distillation or extraction and is known an essential oil. Terpenoids are the largest group of secondary metabolites. Currently, nearly twenty thousand types of terpenoids have been identified. This group is derived from mevalonic acid or other similar precursors and has a great variety of structures. The structure of terpenoids is one isoprene unit (C5H8) or a combination of more than one isoprene unit, so the grouping is based on the number of isoprene units that make up. Examples of compounds and structures of the terpenoid group are presented in Figure 8 (Dewick, 2009).

Terpenoids found in nature are mostly components of essential oils. The group of essential oil compounds is considered to have a curative effect in alternative medicine (Kabera et al., 2014). Terpenoids are a group of compounds that give plants their taste, smell and colour. Terpenoids are usually found in the leaves and fruit of higher plants, for example in pine and citrus plants. The results of fractional distillation of essential oils consist of terpenoid group compounds containing 10 atoms or 15 carbon atoms. Other natural ingredients besides essential oils also contain terpenoids with 20, 30 and 40 carbon atoms. Terpenoid compounds that are very familiar in everyday life are natural rubber (cis 1,4 polyisoprene).

12 Closing

Secondary metabolites are metabolites that are not essential for the growth of organisms where the main function of the

organism is to defend itself from unfavorable environmental conditions. Most plants that produce secondary metabolites use these compounds to defend themselves. Various secondary metabolites have been used as drugs. Another benefit of secondary metabolites is as a pesticide and insecticide.

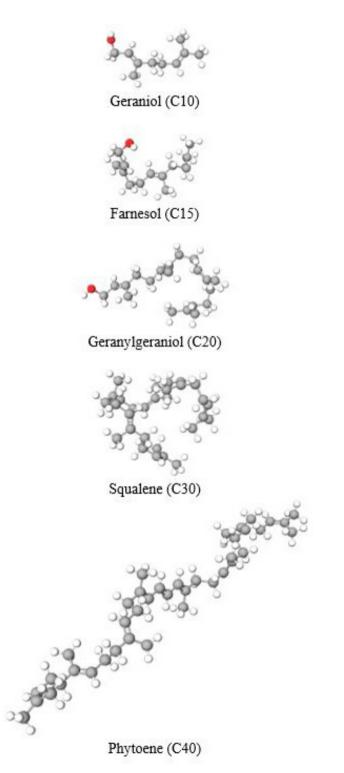


Figure 8. Examples of compounds and structures of the terpenoid group (modification). Source: Dewick (2009).

Sorghum is a potential food source that contains secondary metabolites. Types of secondary metabolites in sorghum include alkaloids, flavonoids, tannins, polyphenols, saponins, steroids, terpenoids, phenolic acids, anthocyanins, phytosterols and policosanols. These secondary metabolites are beneficial for health.

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