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Inaugural Lecture

Phenolics in African grains and their foods – a tale of their significance for health and food security

Date: 18 August 2021

Abstract

Over the past four to five decades, phenolic compounds have emerged and gained prominence as important food constituents with an ever-increasing research focus and interest. Awareness of their antioxidant properties has driven research interest in their ability to promote health, particularly in relation to their potential to offer protection against diet-related non-communicable diseases. Apart from their potential health-promoting properties, phenolic compounds have effects on nutritional, functional and sensory properties of foods. In this inaugural lecture, we will map out the story of the emergence of phenolic compounds in foods as important health-promoting constituents and highlight our unique contribution to this odyssey. Over the years, our major contribution has been to draw attention to the health-promoting properties of underutilised, climate-smart African grains (sorghum, millets, cowpeas, Bambara groundnuts), primarily as a result of their content of phenolic compounds. In much of sub-Saharan Africa, rapid urbanisation accompanied by poor dietary choices, contribute to the growing incidence of diet-related non-communicable diseases. We will discuss how our research showcases the role that African grains can play in arresting this worrying trend. By taking the looming crisis of the adverse effect of climate change on food security and the growing epidemic of chronic non-communicable diseases into consideration, we will aver that these underutilised grains will play a pivotal role in combating food insecurity in Africa, combat the scourge of diet-related non-communicable diseases and contribute to the push towards realisation of some of the sustainable development goals.

Introduction

Professor Tawana Kupe, Vice-Chancellor of the University of Pretoria, Professor Barend Erasmus, Dean of the Faculty of Natural and Agricultural Sciences, University of Pretoria, Professor Elna Buys, Head of the Department of Consumer and Food Sciences, University of Pretoria, colleagues, family and friends, good evening.

I am extremely grateful for this opportunity to present this inaugural lecture. I am also grateful to you for your interest and taking the time to listen to this lecture. It is on a topic that is very dear to me and has occupied my research endeavours for close to two decades now. As you can see, the topic of the lecture is "Phenolics in African grains and their foods – a tale of their significance for health and food security." I intend to speak to you about these compounds known as "phenolics" and their significance for health promotion. More importantly, I would like you to take home a keen awareness of what we are referring to here as "African grains" and their importance for health and food security.

What are phenolic compounds?

Perhaps a logical place to begin is to get an understanding of what phenolic compounds are. Phenolic compounds are a large class of plant secondary metabolites that show great diversity in terms of amount and type. In other words, there are many of them and there are many different types of them. Where our "African grains" of interest are concerned, we conveniently divide phenolic compounds into three main classes in order of increasing molecular weight – phenolic acids, flavonoids and condensed tannins. Strictly speaking, because they are simply polymeric forms of flavonoids, condensed tannins are sometimes simply classified as flavonoids. However, due to the fact that they exert some important nutritional and sensory effects, it helps to study condensed tannins as a class on their own.

Why are phenolic compounds important?

The answer is simple – phenolic compounds are important because they exert potential health-promoting effects particularly in regard to diet-related non-communicable diseases.

The quote “Let food be thy medicine and medicine be thy food” is attributed to Hippocrates, the ancient Greek physician regarded as the “Father of medicine” and for whom the Hippocratic oath is named. For us, what this quote brings to the fore is the thinking that food should be viewed as not only providing nutritional benefits but also health benefits. Therefore, the link between food and health has become of great interest and we believe that phenolic compounds play a significant role in this regard.

Brief historical context of phenolics and health

In order to better understand the evolution and metamorphosis of the field of dietary phenolics and health, a brief historical perspective would be useful.

The compound phenol itself is said to have been discovered in 1834. For this brief historical view, we shall begin from the 1940’s.

1940’s to 1960’s

This period featured some early papers reporting on antioxidant properties of phenolic compounds in oils. An example is a paper in the journal “Oil and Soap” by Golumbic and Mattil which reported on the antioxidant properties of gallic acid in vegetable oils and animal fats in 1942.

Studies reporting on tea catechins (e.g. their analysis using paper chromatography) were predominant during this period. When one considers that these catechins were being characterized using paper chromatography, in comparison with the current state-of-the-art analytical techniques such as liquid chromatography mass spectrometry, it gives one an indication of how far things have advanced in the field. The study of phenolics was by no means restricted to catechins in tea during this period. There were reported studies on anthocyanin pigments and tannins in cocoa; phenolics in brewing materials, glycoflavones in wheat and oat and proanthocyanidins in apple and grape

Interestingly, one of earliest reports on health-promoting properties of phenolics was an in vivo study of the influence of dietary flavonoids on frostbite in the rat in 1955 by Frederick Fuhrman in the American Journal of Physiology, and then in 1962 a study on anticariogenic activity of phenolic acids in oat hulls was reported by Vogel and co-workers in the Journal of Dental Research.

In the field of phenolic antioxidant research, structure-antioxidant activity relationships are important. This simply refers to the thesis that the antioxidant activity of a phenolic compound is related to its structure. In this regard, one of the earliest reports on structure-activity relationships of phenolics was by Miller and Quackenbush in 1957 in the Journal of the American Oil Chemists' Society. They showed that a free phenolic hydroxyl group and occurrence of electron-withdrawing substituents on the phenolic ring were important for antioxidant activity.

1970's and 1980's

The 1970's and 1980's featured more reports on phenolics in grains such as cashew, oats, rapeseed, sorghum and beans.

Talking about grains, sorghum is of particular interest to me as a lot of my research on phenolics has been on sorghum and sorghum-based foods. In this regard, one of the earliest reports about studies on phenolics in sorghum which caught my attention was one on the relationship between tannin content, enzyme inhibition, rat performance and characteristics of sorghum grain by Maxson, Rooney and Lewis in 1973. One of the co-authors, the late Professor Lloyd Rooney was known to me personally. He was a colossus of sorghum and millet science and all of us in the field have benefited tremendously from his trailblazing and pioneering work.

The early contributions of South African scientists to the study of polyphenols in sorghum is worth mentioning. An example of this is the published study on enzyme inhibition by polyphenols of sorghum grain and malt by Klaus Daiber of the CSIR in 1975.

A significant contribution to the study of phenolics in sorghum was made in 1978 by Gupta and Haslam who published an extensive chemical characterization of sorghum condensed tannins showing their polymeric nature with catechinic terminal and extension units.

As a demonstration of their health-promoting properties, a study on antimutagenic activity of green tea polyphenols was reported in 1989 by Wang and co-workers in the journal Mutation Research.

1990's and 2000's

This was followed by a similar study on antimutagenicity of polyphenol-rich fractions of sorghum grain in 1992 by Grimmer and co-workers of Wits University.

In general, the 1990's and 2000's was characterized by a general explosion of research reports on health-promoting properties of phenolic compounds, specifically in relation to diet-related non-communicable diseases.

Importantly, these studies highlighted structure-activity relationships. A review by Rice-Evans and co-workers on "Structure-antioxidant activity relationships of flavonoids and phenolic acids" which was published in Free Radical Biology and Medicine in 1996 was pivotal.

During this period, bioavailability of phenolics began to grow in importance as a research focus with a report on "Plasma and tissue levels of tea catechins in rats and mice during chronic consumption of green tea polyphenols" in 2000 in the journal Nutrition and Cancer by Kim and co-workers.

From this brief historical perspective, it is clear that by the 2000's, phenolic compounds in foods and their health-promoting properties had evolved and grown to become an area of intense research interest. It is at this time that I entered the timeline of the dietary phenolics and health story. When I joined the University of Pretoria as a full-time academic staff in March 2002, my mentors Professor John Taylor and the late Professor Amanda Minnaar stressed the importance of working towards "standing on my own" as a researcher. In simple terms, they advised that I needed to identify, establish and grow my own unique research area. My response to this was a decision to focus on the field of dietary phenolics and health.

Given my background in chemistry, the choice to focus on this research field was a very easy one as it offers the opportunity to engage in some exciting, interesting and stimulating chemistry. However, more importantly, my choice of this field of research is borne out of a strong conviction that it has the potential to impact positively on people's lives. Allow me to provide some context here.

In Africa, reference is made to the "triple burden of malnutrition". Micronutrient malnutrition and macronutrient malnutrition are well-known in Africa. A third form of malnutrition, namely "Overnutrition" has emerged in Africa in recent years. Rapid urbanisation, rising incomes and the quest for convenience has led to poor dietary choices and produced a nutrition transition. This, coupled with relatively low levels of physical activity has driven the occurrence of obesity, metabolic syndrome and in general, diet-related non-communicable diseases. Taking South Africa as an example, data from the World Health Organisation indicates that there has been a steady increase in the proportion of deaths due to non-communicable diseases over the years – 29% in 2011, 43% in 2014 and 51% in 2018.

With this background in mind, the thesis on which my research area is based is that dietary phenolics can play a role in modulating physiological processes brought on by overnutrition and by so doing, potentially offer protection against the occurrence of and mortality from diet-related non-communicable diseases. As important sources of these phenolic compounds, African grains can play a significant role.

Why African grains?

About just over a week ago, the Intergovernmental Panel on Climate Change (IPCC) presented its Sixth Assessment Report on climate change. Unfortunately, it was not good news. The UN Secretary-General, Mr Antonio Guterres described the report as "code red for humanity". In terms of agricultural productivity, most of Africa will be negatively affected by climate change.

In this climate change era, crops that will be important food sources for Africa should be drought-tolerant and have generally low water footprint. In addition, they should be nutritious and health-promoting. We propose that African cereal and legume grains are perfect candidates.

Cereals such as sorghum and the millets and legumes such as cowpea, Bambara groundnut and marama (or morama) bean have been the focus of our research. Most of them are believed to have African origins and are also relatively drought tolerant and have a wide variety of food uses.

Utilisation of African cereal and legumes

The utilisation of African cereal and legume grains may be broadly classified into three main levels:

Utilisation level 1

This level involves the use of simple, traditional processing methods which may be loosely described as "low level" technology such as cooking, boiling, fermentation, malting, roasting etc. These are used to produce mainly traditional foods at the household level.

Utilisation level 2

This level involves the use of modern "high level" technology processing methods such as extrusion, micronisation, microwave processing etc. An example would be their use to produce ready-to-eat foods that may be targeted towards the urbanised consumer.

Utilisation level 3

This level involves waste reutilisation. This is where by-products from primary processing of cereal and legume grains are reutilised e.g. using bran and seed coats as sources of bioactive phenolic antioxidants for various food applications.

I will now share some of the research we have done to show the health-promoting properties of phenolics in African cereal and legume grains at these three levels of utilisation.

Utilisation level 1

Health-promoting properties of sorghum-cowpea composite porridge (Dr Franklin Apea-Bah; PhD)

Cereals and legumes are combined in composite foods to achieve enhanced protein quality. Cereals are generally deficient in the essential amino acid lysine but contain adequate amounts of sulphur-containing amino acids. On the other hand, legumes tend to contain relatively low levels of sulphur-containing amino acids but are rich sources of lysine. Therefore, the cereal-legume composite food would contain a better complement of essential amino acids for enhanced protein quality.

In Franklin Apea-Bah's work, we saw an opportunity to combine sorghum and cowpea in a composite porridge to achieve enhanced phenolic profile and health-promoting properties. This is because, characterisation of the flavonoid components of the two grains using LCMS showed that while they both contained flavan-3-ols and flavanones, sorghum contained flavones which were absent in cowpea which in turn contained flavonols which were absent in sorghum.

Furthermore, we hypothesised that the composite porridge would have enhanced antioxidant properties if structure-antioxidant activity relationships are considered. Some structural features of flavonoids that are important for antioxidant activity are: a 3'4' catechol group on the B ring, a 4-

oxo functional group adjacent to and in conjugation with a C2-C3 double bond in the C ring and Oh groups on C5 and C7 of the A ring. The presence of the four groups of flavonoids in the sorghum-cowpea composite brings together the best assembly of all these required structural features for enhanced antioxidant activity of the composite porridge.

Additive effects of radical scavenging properties were observed in the composite flours and the composite porridges showed good ability to protect erythrocyte membranes from oxidation.

Health-promoting properties of cooked cowpeas (Dr Alice Nderitu and Dr Twambo Hachibamba; PhD)

Dr Alice Nderitu and Dr Twambo Hachibamba conducted their doctoral research on phenolics and health-promoting properties of cowpeas. This was part of a USAID Dry Grains and Pulses Collaborative Research Support Program project on "Increasing utilisation of cowpeas to promote health and food security in Africa" where we collaborated with Texas A & M University, University of Zambia and Egerton University in Kenya.

The main objective was to determine the effect of cooking and simulated in vitro gastrointestinal digestion on cowpea phenolics and their health-promoting properties. Various phenolic acids and flavonoids (from the flavan-3-ol, flavonone and flavonol classes) were identified in the cowpeas. Extracts from the uncooked and cooked cowpeas as well as enzyme digests of the cooked cowpeas showed ability to reduce gene expression for the inflammatory biomarker tumour necrosis factor alpha (TNF-α), an indication of their potential anti-inflammatory effects. Cooked cowpeas and their enzyme digests showed significant protection of plasmid DNA against oxidative damage. Raw and cooked cowpeas showed significant induction of the activity of the phase II enzyme quinone reductase.

Soured finger millet gruels (Mr John Lubaale; MSc)

Soured cereal foods are consumed extensively in many African communities. In general, souring can be achieved using spontaneous fermentation (as practised in many African households) or by using specific lactic acid bacteria starter cultures (as practised for the manufacture of soured products such as mageu). Exogenous acidification to achieve souring is also widely practised at home level where fruit acids and juice from citrus fruits may be used to sour cereal foods in lieu of the longer and more cumbersome spontaneous fermentation route.

For his MSc, John Lubaale studied the effect of these three methods of souring on phenolics and antioxidant properties of finger millet gruels. Souring by the use of Lactobacillus plantarum starter culture, or using a back slopped inoculum or by exogenous acidification with lactic acid enhanced extractability of flavonoid compounds.

Utilisation level 2

Tannin sorghum instant porridge prepared using extrusion cooking (Dr Martin Adarkwah-Yiadom; PhD)

Some sorghums contain tannins and these are classified into two main groups: Type II and Type III tannin sorghums. The difference lies mainly in the mode of deposition of the tannins. The condensed tannins offer an agronomic advantage as they protect the tannin sorghums from being eaten by birds in the field. However, condensed tannin sorghums have relatively limited utilisation compared to condensed tannin-free sorghums. This is because the condensed tannins have adverse sensory effects (bitterness and astringency) and adverse nutritional effects (by reducing protein and starch digestibility and inhibiting digestive enzymes).

In tannin-type sorghums, the condensed tannins are located in the outermost layers of the grain – mainly the testa and the pericarp. Therefore, decortication is a simple method by which condensed tannins can be removed or reduced. Working under the supervision of myself, Professor John Taylor and Professor Riette de Kock, my MSc student Andile Mdluli showed that condensed tannin sorghum could be decorticated to a particular extraction rate such that it begins to resemble a non-tannin sorghum in terms of its sensory properties.

For Martin’s doctoral research, we decided to use a different approach. Instant cereal-based porridges usually produced using extrusion technology are consumed extensively by urban dwellers. We decided to work on an instant porridge prepared by extrusion cooking of whole grain tannin sorghum. We were interested in three main questions:

- Can extrusion cooking be used to break down proanthocyanidins in tannin sorghums?

- Will Type II and Type III tannin sorghums show differences in the susceptibility of their proanthocyanidins to breakdown?
- How bioaccessibile will the proanthocyanidin species from Type II and Type III tannin sorghums be?

For the two tannin sorghum types, extrusion cooking reduced the proportion of oligomers and increased the proportion of mainly dimers. While the bioaccessible fraction of the Type II tannin sorghum instant porridge contained only monomeric and dimeric proanthocyanidin species, that of the Type III tannin sorghum contained monomeric through hexameric proanthocyanidin species. This is a clear indication of differences in extractability of proanthocyanidins in the two tannin sorghum types. Proanthocyanidins in Type II tannin sorghums are deposited in vesicles which are in turn attached to the cell walls of the testa. On the other hand, proanthocyanidins in Type III tannin sorghums are deposited freely along the cell walls of the testa. In order to release and break down proanthocyanidins in Type II tannin sorghums, the processing method used (extrusion cooking in this instance) needs to break down the vesicles before the proanthocyanidins can be released, which is not the case for Type III tannin sorghums. Therefore, this makes proanthocyanidins from Type III tannin sorghums more extractable and potentially more bioaccessible than from Type II tannin sorghums. In agreement with the observations from the bioaccessibility studies, porridges and digests from the Type III tannin sorghums showed greater protection of Caco-2 cells against oxidative damage compared to Type II tannin sorghums.

Utilisation level 3

Marama bean seed coats as sources of bioactive phenolics (Dr Jeremiah Shelembe; PhD)

The marama bean is an underutilised legume crop that is native to the Kalahari Desert. It is found growing wild in southern parts of Africa, mainly South Africa, Namibia and Botswana. The marama bean is usually dehulled, the cotyledons are consumed mainly as a roasted snack and the seed coats are discarded as waste. Part of Jeremiah Shelembe's doctoral research was to conduct an in-depth characterisation of proanthocyanidins in the seed coat of marama bean.

Aqueous extracts from marama bean seed coats contained extremely high levels of condensed tannins (as determined using the vanillin-HCl and Butanol-HCl methods) and significantly higher protein precipitation capacity compared to aqueous extracts from condensed tannin sorghum bran.

The aqueous extracts were separated into oligomer and polymer fractions and the constituent proanthocyanidins were subjected to thiolytic degradation using benzyl mercaptan as a nucleophilic agent. The benzyl mercaptan tags extension units of the proanthocyanidins and converts them to benzylthioether derivatives, while leaving the terminal units free and untagged. LCMS analysis subsequently enables identification of the extension units and terminal units.

The terminal units of proanthocyanidins from marama bean seed coats consisted of (epi)gallocatechin-3-*O*-gallate and (epi)catechin-3-*O*-gallate compared to just catechin in proanthocyanidin from tannin sorghum bran. The extension units from proanthocyanidins from marama bean seed coats consisted of (epi)gallocatechin, (epi)gallocatechin-3-*O*-gallate, (epi)catechin and (epi)catechin-3-*O*-gallate. In contrast, extension units in proanthocyanidins from condensed tannin sorghum bran consisted of (epi)catechin. From these results, a possible structure of a B-type proanthocyanidin in marama bean seed coat could be proposed. The structure of proanthocyanidins from marama bean seed coats was found to be unique compared to other legumes because of the high percentage of galloylated units. The marama bean proanthocyanidins also had higher mean degree of polymerisation compared to tannin sorghum proanthocyanidins.

The aqueous extracts from marama bean seed coats also showed protection against human red blood cell hemolysis and LDL oxidation.

What next and concluding remarks

Going forward, I will briefly mention three areas which we would like to focus on where African grains and their health-promoting properties are concerned.

1. We would like to expand our research into phenolics in African grains and their health-promoting properties to begin looking at in vivo work using animal models and human intervention studies. African grains and their foods are generally under-researched in this regard. This will provide insights into bioavailability of phenolics and their metabolites and how this impacts health-promoting properties.

2. African grains and their foods are intricate and complex systems which contain many other components apart from phenolic compounds. Therefore, phenolic compounds do not work in isolation. There is a need to adopt a more holistic approach and study how phenolic compounds work in concert with other bioactive components of the grain to promote health – in a fashion akin to the functioning of a music orchestra.

3. Our research should make a difference in the lives of consumers. The formation of strong transdisciplinary research consortia puts us in a strong position to achieve this and these are opportunities we will be looking out for. It is easy to see how research on health-promoting properties of African grains and their foods can have a positive impact on the health of the general population. However, there are opportunities to improve the livelihoods of consumers. Professor Bruce Hamaker, Distinguished Professor of Food Science at Purdue University is a strong advocate of the Hub-and-Spoke Food Innovation model. One can envisage such a model being implemented for an African grain-based food with proven health benefits in rural, urban and semi-urban communities. This would promote entrepreneurship, build capacity and empower important people groups such as women and the youth and promote health.

There is no doubt that African grains and their foods will play an ever-increasing role and be critical for health and well-being, especially in Africa. Their promotion and increased utilisation will put us firmly on a path towards helping to achieve the Sustainable Development Goals of No Poverty, Zero Hunger and Good Health and Well-being.

It is my hope that I have succeeded in raising awareness about African grains and foods and that at the very least, I have put a pebble in your shoe in this regard.

The odyssey continues.

My thanks go to my family, all the postgraduate students I have had the absolute pleasure and privilege of working with, my colleagues and all friends and loved ones.

THANK YOU