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Identification, quantification and distribution regularities of phenolics from six parts of Angolan plants by UPLC-ESI-TSQ-MS/MS with chemometrics analysis

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ABSTRACT

Two roots (*Heinsia crinite*, *Dorstenia convexa*), two seeds (*Piper guineense*, *Monodora myristica*) and pods of *Xylopia aethiopica* are extremely popular in Angola as traditional medicine and culinary applications. This study purpose is to obtain a comprehensive phenolic compound characterization of these plants by UPLC-ESI-TSQ-MS/MS due to that few information is known about their composition. Some different types of flavonoids were investigated to get distinctive ions to recognize some phenolics from which standards are not available, including bound complex acids and containing glucosides. As a result, a total of 134 phenolic compounds were identified, of which protocatechuic, p-coumaric acid, quercetin and rutin in all plants. In addition, luteolin, kaempferol, isorhamnetin, apigenin and quercitrin were also found as major flavonoids, but most of them were in the form of flavonoid glycosides. Some chemometrics analysis of quantitative phenolics revealed great variability in the phenolic composition about these plant parts. According to hierarchical clustered heatmap, roots contained more phenolic acids, seeds more poly-methylated flavonoids, pods more isorhamnetin and catechin analogs. Furthermore, principal components and orthogonal partial least squares-discriminant analysis confirmed the prevalence of vanillin, kaempferol, luteolin, quercetin and isorhamnetin in these plants. Correlation coefficient analysis demonstrated that phenolic acid type showed significant positive correlation with DPPH and FRAP, while quercetin and luteolin flavonoids played an important role in TEAC, indicating they are main antioxidant compounds. To conclude, these data will help optimize the use of these resources and enhance their commercialization potential.

1. Introduction

The domestic medicinal plant market in Africa is of substantial economic importance, among the report of the World Health Organization that 80 % of all Africans were used to choosing traditional medicines (Kloos, 2024). The Angolan plants *Xylopia aethiopica* (*X. aethiopica*), *Heinsia crinita* (*H. crinita*), *Monodora myristica* (*M. myristica*), *Dorstenia convexa* (*D. convexa*) and *Piper guineense* (*P. guineense*) are generally adopted for ritual purposes, women's health, and to treat malaria and its symptoms (Chipaca-Domingos et al., 2023). In addition, these plants have many other usages like spice for cooking as well as preservative for inhibiting corruption of foods (Catarino et al., 2019). However, few information is known about the active compounds that cause these activities to combat this illness, although some of them are included in the top-selling plant in some African regions. Until now, regarding these plants, special volatile aromatic properties have been widely noticed (Bakarnga-Via et al., 2014), while their compositions are not clear. In addition, the bioactivity data of *in vitro* assays mainly characterized alkaloids and terpenoids, while few available information was phenolics compounds.

There are some references that describe some phenolic compounds in these plants, including *M. myristica* and *P. guineense* seeds (Adefegha &

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Oboh, 2012; Moukette et al., 2015; Oyewale et al., 2020), *X. aethiopica* (Akolade et al., 2019; Okpoghono et al., 2023; Ribeiro et al., 2021; Tenyang et al., 2024) and *H. crinite* (Boumba et al., 2022), respectively, but there is no information about *D. convexa* phenolic profile. While literature shows some data about the phenolic profiles of these plants, only some simple phenolic acids were identified as well as common flavonoids. Polyphenols are a group of polyhydroxylated compounds widely found in spices and herbal plants, of which phenolic acids and flavonoids account for about 90 %. Studies conducted in recent years have shown that these plants contain abundant phenolics, which are also associated with their pharmacologically active functions (Irondi et al., 2022; Macedo et al., 2020). For this reason, the first objective of this work is to obtain an accurate and wide phenolic compound characterization of these plants, since it is well known that phenolics are the main constituent and other families like alkaloids, etc, are in minor composition.

Liquid chromatography combined with mass spectrometry (LC–MS) is considered as one of the most important techniques of the last decade of 20th century for analytical support in many stages of pharmacognosy development. On the current, LC-MS technology is widely used to analyze polyphenols in plants, which usually requires comparison of standards for accurate identification of phenolic compounds. However, the fact that polyphenols of these plants are very complex due to the presence of esters, glycosides, acylated glycosides, etc., and often these standards are not available (Zhu et al., 2023). In addition, polyphenols have a large number of positional isomers due to the differences in hydroxyl linkage positions, which brings great challenges to identify some unknown phenolics. Based on the above issues, secondary mass spectrometry (MS/MS) analysis is an important tool for the structural analysis of phenolic compositions, which can obtain fragment ions of compounds to be tested at specific collision energies (Farag et al., 2020). Furthermore, the cleavage patterns of some different types of flavonoids were explored to find the characteristic product ions from fragments, which can be used to identify flavonoids with glucosides. By comparing with the distinctive ions of some common phenolics, it is feasible to realize the identification of some lack of standards and complex phenolics, combining with the MS bank and PubChem databases.

In recent years, the rapid and efficient extraction of desired and useful information from LC-MS data by chemo-discriminative classification statistics has become a hot topic in current research. In addition, chemometric analysis play an important role in the comparative analysis of differences in phytochemical composition (Sun et al., 2024). In analyzing phenolic compounds from the results of LC-MC, HCA, PCA and OPLC-DA are often combined to recognize the differences and relationships in the components between several plants. Therefore, with the help of some chemometrics methods, while differentially analyzing phenolic compounds in six groups of Angolan plants, an attempt was made to discover and excavate structurally novel and biologically active composition.

2. Materials and methods

2.1. Samples and reagents

The five species of Angolan plants are originally from the northern region, especially from Uíge city. They were harvested by herbalists in 2023, pre-selected and dried at room temperature before being packed and shipped from Angola to the laboratory in Vigo (Spain). The samples comprised three different plant parts: roots (*H. crinita* and *D. convexa*), seeds (*P. guineense* and *M. myristica*) and pods of *X. aethiopica* at two states (whole and broken). These samples were ground into sealed plastic bags, and stored at room temperature away from light until further use.

2.2. Carbohydrate determination

The weight of 0.5 g each dried sample was added to 5 mL of 72 % H_2SO_4 (w/w), and then heated at 30 °C water bath maintaining for 1 h with periodic agitation. After the polysaccharides were hydrolyzed into oligomers, the solution was further diluted to the concentration of 4 % H_2SO_4 (w/w), and placed in an autoclave at 121 °C for an additional 1 h to break these oligomers into monomers. Each sample was filtered to remove insoluble acid residues, and the solution was collected to evaluate using high-performance liquid chromatography (HPLC). These monosaccharide standards were used to prepare mixed standard solutions at concentrations of 0.3125～20 mg/L. The monosaccharide composition as well as the concentration was calculated by comparison with the standard curve.

2.3. Extraction of polyphenols

There was a previous literature method of (Ringgit et al., 2024) to refer to extract phenolics from Angolan plants with some modifications. The weight of 1 g each sample was added into a 50 mL tube containing 5 mL of methanol, and sonicated in water at 50 °C for 20 min. After the samples were macerated overnight in a refrigerator at 4 °C, they were centrifuged at 7500 rpm for 5 min, and the supernatant was collected. Then, 5 mL of acetone was added to the solid fraction to centrifugate at 7500 rpm for 5 min, and this procedure was repeated 2 times. All the supernatants were collected together, and the solution was dried by rotary evaporation at 40 °C, then the extracted phenolics were re-solubilized with 5 mL of methanol and were stored at −20 °C. Since solutions precipitate solids at low temperatures, they were filtered through 0.22 μm before the analysis of sample.

2.4. Determination of polyphenol contents

2.4.1. Total phenolic contents (TPC)

The 400 mg/L gallic acid standard solution was diluted in half with 70 % methanol (v/v) for 6 times to obtain the concentrations of 200～6.25 mg/L. The volume of 25 μL sample or standard solution was pipetted into a 96-well plate, then added 100 μL of Folin-Ciocalteu reagent (6/24, v/v) to each plate well and shake slightly to room temperature for 4 min. The reaction was then continued by adding 75 μL of 7.5 % (w/v) Na_2CO_3 for 90 min away from light. The absorbance values were read at 750 nm by a microplate reader (Bio-Tek, Winooski, VT, USA). A standard curve for gallic acid was drawn, and TPC was calculated from this curve.

2.4.2. Total flavonoid contents (TFC)

The 400 mg/L rutin standard solution was diluted in half with methanol solvent (v/v) for 6 times to obtain the concentrations of 200 ～6.25 mg/L. The volume of 250 μL sample solution (diluted to 20 times) or standard solution was pipetted into a 96-well plate, and then added 15 μL of 5 % $NaNO_3$ solution into each well, which was placed in the dark at 20 °C; After reaction of 5 min, 15 μL of 10 % $AlCl_3$ solution was added to continue the reaction for 5 min; Finally, 100 μL of 1 mol/L NaOH solution and 120 μL of ultrapure water was added consecutively. The absorbance values were read at 510 nm by a microplate reader. A standard curve for rutin was drawn, and total flavonoid content was calculated from this curve.

2.5. Identification of phenolic compounds

The separation of phenolic compounds in sample was performed on an Eclipse Plus C18 RRHD column (2.1*50 mm, 1.8 μm) via UPLC-ESI-TSQ-MS/MS (ThermoFisher, USA). In order to obtain the best separation results, the separation parameters such as reagent type of the mobile phase, elution gradient and flow rate were optimized. The following optimized conditions were finally obtained: 0.1 % formic acid water (A)

and chromatographic grade acetonitrile (B), and the elution gradient: 0–3 min, 3–15 %B; 3–10 min, 15–50 %B; 10–17 min, 50 %B; 17–22 min, 50–70 %B; 22–27 min, 70-5 %B; 27–30 min, 5 %B. The mass spectrometry data were obtained by ionizing the eluent separated in the chromatographic system by an electrospray ionization source (ESI) in negative ion mode. Parameters such as MRM product ions, collision energy, fragmentation voltage, residence time and collision chamber accelerating voltage were also optimized and operated as follows: 2.5 kV ion spray voltage, scanning range m/z 50-1000 at a rate of 1000 Da/s.

2.6. Quantification of phenolic compounds

Each phenolic standard was accurately weighed and dissolved in methanol solution to make a master standard solution with a concentration of 1 mg/mL. At the same time, the standard solutions were diluted to a series of concentrations, 1000 ~ 31.25 ng/mL for plotting the standard curve. Finally, the amount of each phenolics was calculated by comparing it to a standard curve.

2.7. Chemometrics discrimination of Angolan plants by multivariate analysis

Differential comparative analysis of six Angolan plants on phenolic compounds from LC-MS data was achieved by chemically discriminative categorical statistical by referring to (Sun et al., 2024). These data were subjected to cluster analysis (hierarchical clustered heatmap, HCA) as well as principal component analysis (PCA) using Origin 2024 software, where HCA selected some key as well as mutual phenolics, while PCA included all phenolic compounds (these compounds were numbered, as shown in Table 1). In addition, these data were subjected to orthogonal partial least squares discriminate analysis (OPLS-DA) using SIMCA software, which has the advantage of weakening the intra-group differences, making the separation of samples between groups better and maximizing the highlighting of inter-group differences.

2.8. Correlation coefficient analysis between phenolics compounds and antioxidant capacity

So far, most analyses of antioxidant activity in plants have focused on assessing some common values such as DPPH, TERC and FRAP. However, they have a very complex composition, so it is not clear which group of components is significantly correlated with of antioxidant activity. The phenolic compounds were categorized according to their type, among their contents was accrued accordingly to one category. Therefore, the assessment model was constructed to analyze the correlation between the phenolic types and antioxidant activity in these plants by Origin 2024 (Serio et al., 2024).

3. Results and discussion

3.1. Carbohydrate profile

Since phenolics in Angolan plants have been found that they combine with glycosides, resolving complex compounds is facilitated by understanding the composition of saccharides, among that results are summarized in Fig. 1-A and Fig. 1-B. Comparing plant parts, the highest amounts were found in roots (434.84 mg/g *D. convexa* and 327.45 mg/g *H. crinita*), followed by seeds (297.80 mg/g *P. guinense* and 235.18 mg/g M. *myristica*) and pods (195.84 mg/g and 186.75 mg/g for whole and broken pods of *X. aethiopica*, respectively). From roots, it is important to highlight that *D. convexa* showed the highest content of Glc among all samples, with 400.46 mg/g, and other significant levels of Xyl (73.44 mg/g) were found in *H. crinita*, much higher than that found in *D. convexa* (10.13 mg/g). Other notable monosaccharides in *H. crinita* and *D. convexa* included Ara, with levels of 27.23 and 10.08 mg/g, respectively. In case of the seeds, Glu was the highest saccharide amount in *P. guinense* (267.54 mg/g) and *M. myristica* (174.67 mg/g) and Xyl was higher in *M. myristica* (39.17 mg/g) than *P. guineense* (6.81 mg/g). Comparing whole and broken pods of *X. aethiopica*, the broken pods exhibited the highest concentrations of R5P (15.90 mg/g) and Rha (15.89 mg/g) among all samples. In addition, the two pods also showed significant amounts of Ara (22.42 and 22.34 mg/g) and Xyl (28.92 and 28.91 mg/g) with no significant difference ($p > 0.05$), while Rha was higher in the broken pods (15.75 mg/g). The content of Glu in both whole and broken pods was lower compared to other samples, with levels of 114.44 mg/g and 101.88 mg/g, respectively. For other four monosaccharides (Fru, Suc, Mal and Sor) were very less in all samples.

3.2. Polyphenol contents

The TPC and TFC of these plants have been determined, and results are shown in Fig. 1-C. Comparing TPC quantities, whole pods of *X. aethiopica* exhibited the highest value (105.96 mg GAE/g), followed by the root of *D. convexa* (71.97 mg GAE/g), while the lowest value was for *P. guineense* seeds (31.60 mg GAE/g). It has been found that the contents of TPC for different plants and parts were significantly distinct. For example, the whole pods of *X. aethiopica* had higher TPC content (105.96 mg GAE/g) than that found in the roots from both *H. crinite* (66.36 mg GAE/g) and *D. convexa* (71.97 mg GAE/g) varieties, as well as seeds from *P. guineense* (31.60 mg GAE/g) and *M. myristica* (42.88 mg GAE/g). This is consistent with the findings of most previous studies about phenolic distribution in different plant parts, where the content order was pods, roots and seeds, respectively (Avanza et al., 2021; Mueed et al., 2023). For both states of *X. aethiopica* pods, the whole one had higher content, indicating the need to keep them intact during harvesting as well as preservation.

Regarding TFC, the highest content was for seeds of *P. guineense* (26.44 mg Rutin/g), followed by the broken pods of *X. aethiopica* (25.14 mg Rutin/g). While the lowest TFC was for roots of *D. convexa* (7.59 mg Rutin/g). For these results, it can be observed that the TFC of six samples were not fully positive correlation with their corresponding TPC. For instance, the pods of *X. aethiopica* possessed relatively high both TFC (105.96 mg GAE/g) as well as TPC (23.64 Rutin/g) comparing other samples. While two seeds (*P. guineense* and *M. myristica*) had high TFC, and two roots had low TFC (*H. crinite* and *D. convexa*). This is in agreement with some previous reports that the order of flavonoid content in different parts of plant was seeds, pods and roots (Sun et al., 2017). However, it also depends on plant species, comparing these five species, the *H. crinita* of Rubiaceae, *D. convexa* of Moraceae, *X. aethiopica* and *M. myristica* of *Senecio* family, as well as *P. guineense* of Piperaceae, among that as the *M. myristica* has a higher TPC than *P. guineense*, while the TFC is the opposite (Orji Victoria, Joseph, Mohammed Sani, & Ozor Josephat, 2023). Until now, there is little research on these plants, especially regarding phenolics, thus these data could provide reference for subsequent researchers.

3.3. Polyphenol profile

By performing a full scan of these plants, a primary mass spectrogram was obtained as they were shown in Fig. 2. In order to apply above mentioned methodology to analyze polyphenols in Angolan plants, chromatographic retention and cleavage characteristics were obtained by multi-collision energy analysis of phenolic acids and flavonoids standards. Based on the chemical substructure and cleavage patterns of MS/MS, and comparing some databases, the phenolic compounds were identified and deduced out in these plants.

3.3.1. Identification of phenolic acids

Phenolic acid compounds can be categorized into hydroxybenzoyl (vanillic acid, syringic, etc.) and hydroxycinnamoyl (caffeic acid, ferulic acid, etc.) based on the difference in the basic structural skeleton of C6-C1 and C6-C3. As shown in Table 1, by comparing the product ion and

Table 1
Characterization and quantification of the phenolic compounds from six Angolan plant samples by UPLC-ESI-TSQ-MS/MS.

MS	RT	MS/MS	Compound	Number	Content (μg/g)					
					H. crinita	D. convexa	P. quineense	M. myristica	X. aethiopiea W	X. aethiopiea B
Phenolic acid (PA)										
137.08	5.94	137, 93, 65	Salicylic acid*	PA1	10.03 ± 0.59	0.14 ± 0.52	—	0.27 ± 0.26	–	–
151.13	5.23	151, 108, 136	Vanillin*	PA2	3.59 ± 0.16	–	0.71 ± 0.05	1.28 ± 0.08	3.33 ± 0.11	0.57 ± 0.07
153.14	3.64	153, 108, 81	Protocatechuic acid*	PA3	4.95 ± 0.99	1.45 ± 0.06	2.75 ± 0.70	1.19 ± 0.23	32.37 ± 3.44	7.29 ± 0.37
163.13	0.49	163, 119, 93	P-coumaric acid*	PA4	1.35 ± 0.27	1.50 ± 0.27	1.30 ± 0.19	1.62 ± 0.31	2.73 ± 0.29	0.88 ± 0.07
165.09	0.49	165, 121, 77	Phthalic acid*	PA5	–	0.12 ± 0.04	0.73 ± 0.17	0.09 ± 0.02	2.95 ± 0.29	0.89 ± 0.45
179.09	0.49	179, 135, 107	Caffeic acid*	PA6	–	0.09 ± 0.05	1.38 ± 0.27	1.33 ± 0.23	–	–
191.05	0.54	191, 155	Quinic acid*	PA7	0.11 ± 0.13	–	0.97 ± 0.13	–	0.05 ± 0.01	3.69 ±0 .051
192.84	0.51	193, 178, 134	Ferulic acid*	PA8	–	–	0.78 ± 0.11	–	–	–
197.10	2.29	197, 182, 123	Syringic acid*	PA9	7.99 ± 1.69	–	–	–	–	–
337.10	7.60	337, 191, 173, 163	4-p-Coumaroylquinic acid**	PA10	1.87 ± 0.42	–	–	–	–	–
341.09	2.97	341, 191, 173	4-O-vaniloylquinic acid**	PA11	1.15 ± 0.23	–		–	–	–
353.12	2.34	295, 191, 173	Chlorogenic Acid*	PA12	1.35 ± 0.19	–		–	–	–
367.32	22.64	193, 191, 173	4-O-Feruloylquinic acid **	PA13	1.33 ± 0.29	–	–	–	–	–
371.13	3.24	197, 191, 157	Syringoylquinic acid**	PA14	1.39 ± 0.22	–	–	–	–	–
515.2	6.13	353, 281, 269, 225, 191, 179, 173, 161	Isochlorogenic acid A**	PA15	1.48 ± 0.30	–	–	–	–	–
533.19	5.59	263, 251, 197, 191, 173, 161, 155, 153	4-O-Caffeoyl-3-O-syringoylquinic acid**	PA16	6.94 ± 0.31	–	–	–	–	–
647.42	21.64	370, 359, 343, 326, 319, 305,	Trigalloyl quinic acid**	PA17	–	–	–	–	–	6.23 ± 0.45

(*continued on next page*)

Table 1 (*continued*)

MS	RT	MS/MS	Compound	Number	Content (μg/g)					
					H. crinita	D. convexa	P. quineense	M. myristica	X. aethiopiea W	X. aethiopiea B
		288, 205								
Flavonoids (F)										
249.18	12.84	234, 220, 193	3′,6-Dimethylflavone***	F1	–	–	7.33 ± 1.09	–	–	–
269.22	8.79	269, 199, 172, 153	Apigenin*	A1	–	2.79 ± 0.48	–	–	–	3.09 ± 0.50
285.19	8.33	285, 261, 253, 204, 185, 179, 164, 154	Kaempferol*	K1	1.53 ± 0.26	3.49 ± 0.47	–	0.13 ± 0.01	0.18 ± 0.07	4.05 ± 0.50
285.12	7.31	285, 199, 133	Luteolin*	L1	–	50.89 ± 4.94	1.56 ± 0.63	–	0.28 ± 0.08	3.46 ± 0.18
289.09	4.07	271, 247, 231, 187, 179, 165	Catechin*	C1	–	–	–	–	1.10 ± 0.20	–
297.26	19.75	282, 254, 226, 221, 211, 209, 194, 182	3′,7-Dimethoxy-3-hydroxyflavone***	F2	–	–	27.38 ± .0.57	6.44 ± 0.97	–	–
299.18	22.85	265, 234, 209, 151	Kaempferide*	F3	–	–	1.09 ± 0.20	–	–	–
301.12	7.42	301, 285, 255, 243, 230, 216, 211, 178	Quercetin*	Q1	1.32 ± 0.18	0.06 ± 0.03	1.21 ± 0.25	0.19 ± 0.04	4.72 ± 1.01	0.78 ± 0.06
305.23	9.55	285, 208, 187, 156	(−)-Epigallo catechin*	E1	–	–	–	–	1.43 ± 0.18	–
311.23	12.24	253, 239, 210, 207, 197, 195, 183, 156	4′,5,7-Trimethoxyflavone*	F4	4.67 ± 0.55	–	2.49 ± 0.31	19.22 ± 0.96	–	–
313.29	11.57	235, 218, 212, 208, 194, 185, 161, 159	3,7-Dihydroxy-3′,4′-dimethoxyflavone	F5	–	–	14.50 ± 0.69	0.59 ± 0.16	–	–
315.23	12.90	315, 283, 272, 267, 257,	Isorhamnetin*	I1	–	0.27 ± 0.04	14.31 ± 0.92	0.24 ± 0.04	10.35 ± 1.23	28.41 ± 1.78

(*continued on next page*)

Table 1 (*continued*)

MS	RT	MS/MS	Compound	Number	Content (μg/g)					
					H. crinita	D. convexa	P. quineense	M. myristica	X. aethiopiea W	X. aethiopiea B
		225, 213, 183								
317.23	11.09	316, 283, 231, 197, 186	Myricetin*	M1	–	–	–	–	0.06 ± 0.01	–
321.15	8.17	275, 273, 221, 215, 211, 187, 185, 181	Taxifolin hydrate**	T1	–	–	–	–	–	10.21 ± 1.00
327.3	8.03	327, 297, 267, 195, 185, 183, 167	3-Hydroxy-3′,4′,5′-trimethoxyflavone*	F6	5.62 ± 0.56	–	7.34 ± 0.76	–	–	–
329.25	8.50	315, 289, 277, 245, 242, 213, 201, 171	Tricin*	F7	3.87 ± 0.72	–	2.86 ± 0.27	1.63 ± 0.29	–	–
331.21	11.74	285, 272, 263, 224, 175, 163, 162	Taxifolin 7,3′-dimethyl ether**	T2	–	–	1.41 ± 0.17	0.44 ± 0.07	0.29 ± 0.08	5.30 ± 1.02
339.24	11.57	260, 253, 239, 225, 197, 195, 193, 183	Prenyl apigenin**	A2	2.4 ± 0.56	–	2.83 ± 0.42	6.64 ± 1.15	0.20 ± 0.02	2.64 ± 0.56
341.13	8.42	286, 263, 234, 224, 209, 185, 178, 175	3′,4′,5,7-Tetramethoxyflavone***	F8	–	–	3.74 ± 0.46	–	–	–
353.09	11.47	314, 307, 279, 255, 236, 201, 183, 173	8-Isopentenyl-kaempferol **	K2	–	1.53 ± 0.12		–	0.37 ± 0.11	–
357.17	7.52	357, 237	3′,4′,5,7-Tetramethylquercetin**	F9	–	–	2.05 ± 0.18	–	–	–
359.24	17.78	317, 267, 236, 203, 171, 161, 156, 153	Myricetin 3,7,3′-trimethyl ether**	M2	–	–	–	–	8.36 ± 1.09	26.35 ± 1.84

(*continued on next page*)

Table 1 (*continued*)

MS	RT	MS/MS	Compound	Number	Content (μg/g)					
					H. crinita	D. convexa	P. quineense	M. myristica	X. aethiopiea W	X. aethiopiea B
369.23	9.30	350, 197, 182	8-prenylquercetin**	Q2	–	1.19 ± 0.14	–	–	–	–
373.23	19.82	347, 265, 228, 195, 190, 176, 163	Casticin***	F10	0.39 ± 0.14	–	–	–	–	7.32 ± 0.77
385.23	10.76	370, 317, 281, 161	Quercetin pivaloyl ester**	Q3	–	–	–	–	2.20 ± 0.29	–
387.09	10.63	313, 252, 224, 212, 196, 169	Apigenin derivative**	A3	–	–	1.23 ± 0.11	–	–	–
393.25	3.81	274, 194, 183, 166, 156	Tetra-hydroxyethyl-quercetin**	Q4	–	–	–	3.16 ± 0.60	–	–
395.24	3.05	246, 196, 194, 183, 180, 168, 167, 155	Apigenin triacetate**	A4	–	–	2.78 ± 0.46	2.87 ± 0.37	–	–
413.15	5.94	252, 202, 151	Quercetin 3,3′-dimethyl ether 4'-(2-methylbutyrate) **	Q5	–	1.86 ± 0.26	–	–	–	–
415.09	14.02	252, 224, 209, 201, 195, 186, 167, 159	Apigenin 7-rhamnoside**	A5	1.12 ± 0.22	–	4.38 ± 0.46	–	–	–
417.16	7.83	329, 308, 305, 262, 255, 186, 183, 154	Kaempferol-3-O-alpha-L-arabinoside**	K3	–	–	–	–	1.57 ± 0.32	6.27 ± 0.70
433.12	6.90	300, 281, 273, 255, 243, 229, 201, 179	Quercetin 3-O-beta-D-xylopyranoside**	Q6	–	37.27 ± 1.44	–	–	–	6.98 ± 0.62
433.14	5.99	269, 241, 225, 212, 201, 197, 179, 163	Apigenin 7-O-glucoside**	A6	–	–	–	–	1.78 ± 0.22	–
433.17	3.75	314, 208, 185, 183, 175	Luteolin-6-xyloside**	L2	–	–	5.30 ± 0.45	–	–	–

(*continued on next page*)

Table 1 (*continued*)

MS	RT	MS/MS	Compound	Number	Content (μg/g)					
					H. crinita	D. convexa	P. quineense	M. myristica	X. aethiopiea W	X. aethiopiea B
435.26	10.54	255, 244, 229, 211, 197, 182, 170, 154	Taxifolin 3-O-beta-D-xylopyranoside**	T3	–	–	–	–	–	3.37 ± 0.47
447.2	6.74	355, 300, 273, 255, 243, 211, 179, 163	Quercitrin*	F11	6.98 ± 0.87	1.70 ± 0.21	2.6 ± 0.36	–	1.26 ± 0.18	
449.15	5.64	301, 285, 273, 255, 244, 229, 211, 201	Astilbin**	Q7	–	–	–	–	1.45 ± 0.25	8.72 ± 0.59
451.23	12.44	267, 241, 239, 211, 197, 189, 182, 174	Luteolin 7-O-glucuronide**	L3	–	1.80 ± 0.22	–	–	–	–
453.23	14.70	267, 243, 239, 225, 189, 175, 173, 164	Luteolin peracetate**	L4	–	1.25 ± 0.10	–	–	–	–
459.24	4.89	315, 281, 277, 245, 202, 197, 183, 179	Apigenin 7-O-methylglucuronide**	A7	–	–	2.87 ± 0.56	2.14 ± 0.28	–	46.35 ± 1.84
463.29	5.29	297, 283, 271, 255, 239, 223, 215, 211	Quercetin 3-glucoside**	Q8	–	1.86 ± 0.30	3.09 ± 0.45	–	1.46 ± 0.15	–
469.18	4.58	283, 251, 249, 245, 224, 205, 189, 161	Quercetin, 3,3′,4′,7-Tetraacetate**	Q10	–	2.31 ± 0.11	4.44 ± 0.60	1.35 ± 0.31	–	–
475.28	6.18	388, 315, 255, 214, 194, 183, 159	Isorhamnetin 5-glucoside**	I2	–	–	2.96 ± 0.27	1.43 ± 0.33	–	3.65 ± 0.38
477.19	3.56	364, 292,	Quercetin-3-O-glucuronide**	Q11	9.56 ± 0.73	–	–	–	–	–

(*continued on next page*)

Table 1 (*continued*)

MS	RT	MS/MS	Compound	Number	Content (μg/g)					
					H. crinita	D. convexa	P. quineense	M. myristica	X. aethiopiea W	X. aethiopiea B
		245, 231, 201, 183, 168, 153								
477.19	2.32	315, 285, 271, 255, 243, 227, 199, 169	Isorhamnetin-3-O-glucoside**	I3	–	–	–	–	1.13 ± 0.09	–
483.32	20.55	315, 291, 289, 271, 228, 221, 212, 200	Digalloyl hexoside***	F12	–	–	–	–	–	3.95 ± 0.34
487.39	10.65	319, 267, 253, 241, 213, 211, 201, 186	6″-O-Acetylglycitin***	F13	1.57 ± 0.17	8.37 ± 1.02	–	–	–	–
489.33	22.84	329, 309, 295, 213, 191, 179, 173, 161	Kaempferol-3-O-β-D-6″-acetylglucoside**	K4	22.71 ± 1.69	–	–	1.20 ± 0.19	–	–
489.34	22.84	281, 255, 243, 229, 227, 211, 201, 163	Quercetin 3-O-acetyl-rhamnoside**	Q12	–	104.67 ± 5.85	–	–	–	–
491.16	4.62	309, 279, 182, 175, 159, 153	6-Methoxy-luteolin-7-O-glucuronide**	L5	–	–	1.84 ± 0.31	–	–	–
493.15	7.25	336, 333, 241, 211, 201, 199, 188, 175	Quercetin glucuronate**	Q13	–	1.31 ± 0.19	–	–	–	–
499.3	11.17	434, 340, 296, 256, 246, 231, 193	Apigenin 7-(6″-crotonylglucoside) **	A8	–	2.08 ± 0.18	–	–	–	–
501.35	11.19	269, 253, 244, 225, 201, 196,	Apigenin 7-(2″-acetyl-6″-methylglucuronide) **	A9	–	–	–	–	–	5.41 ± 0.53

(*continued on next page*)

Table 1 (*continued*)

MS	RT	MS/MS	Compound	Number	Content (μg/g)					
					H. crinita	D. convexa	P. quineense	M. myristica	X. aethiopiea W	X. aethiopiea B
503.31	11.90	173, 151 267, 251, 245, 225, 213, 201, 197, 169	Apigenin 7-(2″-glucosyllactate) **	A10	–	13.68 ± 1.06	–	–	–	5.43 ± 0.53
505.27	22.09	283, 271, 257, 255, 245, 239, 229, 227	Quercetin 3-(6-O-acetyl-beta-glucoside) **	Q14	–	15.64 ± 1.09	–	–	–	–
509.27	4.43	367, 319, 313, 303, 231, 191, 176	Quercetin chalcone**	Q15	–	–	–	–	0.14 ± 0.03	–
513.33	10.98	339, 323, 287, 285, 269, 247, 244, 185	Luteolin derivative**	L6	–	–	–	–	–	9.07 ± 0.45
515.33	12.25	421, 393, 364, 325, 315, 313, 309, 285	Kaempferol 3-(2″,4″-diacetylrhamnoside) **	K5	–	–	–	–	1.05 ± 0.03	–
517.24	7.74	315, 285, 272, 255, 242, 229, 201, 184	Isorhamnetin 5-glucoside**	I4	–	–	–	0.39 ± 0.07	–	3.14 ± 0.37
519.22	10.00	281, 255, 229, 227, 231, 212, 201, 193	Quercetin 5,7,3′,4′-tetramethyl ether 3-galactoside**	Q16	–	2.26 ± 0.31	–	–	–	–
521.27	22.65	283, 257, 255, 245, 227, 201, 193, 163	Iridin*	F14	2.76 ± 0.30	52.59 ± 2.21	–	–	–	–
531.32	21.68	375, 297, 292, 281, 255, 224, 214, 168	Malonylglycitin***	F15	–	–	–	0.48 ± 0.12	–	5.16 ± 0.65

(*continued on next page*)

Table 1 (*continued*)

MS	RT	MS/MS	Compound	Number	Content (μg/g)					
					H. crinita	D. convexa	P. quineense	M. myristica	X. aethiopiea W	X. aethiopiea B
537.23	4.50	301, 293, 281, 279, 265, 255, 243, 239	Amentoflavone*	F16	2.91 ± 0.39	3.02 ± 0.61	3.34 ± 0.40	–	–	–
549.3	13.89	317, 308, 275, 245, 209, 195, 193, 159	Myricetin 3-(4″-malonylrhamnoside) **	M3	–	–	–	0.89 ± 0.12	–	–
549.37	10.31	357, 353, 306, 273, 259, 255, 213, 167	Quercetin-3-(6″-malonyl)-Glucoside**	Q17	–	–	–	–	–	6.68 ± 0.58
551.39	21.74	285, 257, 243, 239, 229, 211, 199, 175	Luteolin 7-(6″-p-benzoyglucoside) **	L7	2.36 ± 0.23	1.59 ± 0.25	–	–	–	–
553.34	13.30	299, 283, 279, 257, 243, 237, 201, 177	Cudranian 1**	K6	–	1.51 ± 0.16	–	–	–	–
557.32	22.80	293, 279, 269, 255, 243, 229, 219, 201	Kaempferol-3-O-(2,3,4-tri-O-acetyl-alpha-L-rhamnopyranoside) **	K7	–	13.28 ± 1.35	–	–	–	–
559.31	5.90	294, 255, 243, 237, 227, 217, 197, 171	Quercetin 3-o-beta-D-(6″-o-malonyl)-glucoside**	Q18	–	–	–	–	–	3.60 ± 0.59
563.2	4.64	293, 281, 251, 232, 211, 191, 175, 173	Kaempferol 3-alpha-L-arabinofuranoside-7-rhamnoside**	K8	–	1.55 ± 0.38	–	–	–	
575.39	14.25	315, 255, 240, 239, 225, 213, 197, 166	Chamaemeloside**	A11	–	–	1.47 ± 0.20	–	–	4.89 ± 0.33

(*continued on next page*)

Table 1 (*continued*)

MS	RT	MS/MS	Compound	Number	Content (μg/g)					
					H. crinita	D. convexa	P. quineense	M. myristica	X. aethiopiea W	X. aethiopiea B
577.21	5.82	300, 283, 269, 255, 239, 211, 199, 163	Kaempferitrin**	K9	–	–	4.07 ± 0.57	–	1.20 ± 0.14	–
583.21	7.01	301, 255, 227, 211, 201	Quercetin 3-(6″-p-hydroxybenzoylgalactoside) **	Q19	–	–	–	2.24 ± 0.42	–	–
589.26	22.8	305, 291, 263, 255, 225, 218, 203, 193	Quercetin 3-(2″,3″,4″-triacetylgalactoside) **	Q20	–	3.62 ± 0.84	–	–	–	–
593.37	10.31	315, 308, 293, 274, 255, 239, 227, 212	Isorhamnetin 3-alpha-L-arabinopyranosyl-(1->2)-rhamnoside**	I5	–	–	3.60 ± 0.50	–	–	5.36 ± 0.55
593.83	16.97	267, 252, 222, 209, 203, 194, 185, 183	Luteolin 5-O-rutinoside**	L8	–	–	–	0.75 ± 0.11	–	–
595.25	6.80	295, 285, 269, 254, 223, 212, 203, 187	Quercetin-3-O-arabinoglucoside**	Q21	1.58 ± 0.36	–	–	–	1.37 ± 0.14	–
607.27	6.98	293, 279, 267, 256, 249, 238, 237, 223	Kaempferide 3-O-neohesperidoside**	K10	–	–	–	–	2.34 ± 0.32	–
609.37	6.02	301, 283, 271, 255, 228, 201, 190, 178	Rutin*	F17	0.28 ± 0.23	0.36 ± 0.06	7.31 ± 1.58	0.37 ± 0.24	1.43 ± 0.23	11.71 ± 3.25
615.23	9.44	317, 307, 293, 277, 253, 243, 223, 187	Quercetin 3-O-(6″-galloyl)-beta-D-galactopyranoside**	Q22	–	1.57 ± 0.03	–	–		–
623.26	9.26	314, 306, 301, 299,	Isorhamnetin 3-galactoside-7-rhamnoside**	I6	–	–	1.24 ± 0.12	–	1.16 ± 0.24	–

(*continued on next page*)

Table 1 (*continued*)

MS	RT	MS/MS	Compound	Number	Content (μg/g)					
					H. crinita	D. convexa	P. quineense	M. myristica	X. aethiopiea W	X. aethiopiea B
		278, 255, 227, 202								
625.56	12.06	283, 269, 267, 257, 241, 213, 211, 162	3-Gentiobiosyl-kaempferol**	K11	–	–	–	–	1.27 ± 0.16	–
626.88	9.80	303, 271, 256, 221, 205, 191, 187, 153	Quercetin derivative**	Q23	3.07 ± 0.60	–	–	–	–	–
631.47	22.55	314, 283, 263, 250, 242, 224, 189, 165	Isorhamnetin 3-(6″-galloylglucoside) **	I7	–	–	2.88 ± 0.48	0.66 ± 0.10	–	–
635.21	8.84	601, 593, 425, 356, 308, 306, 266, 197	Quercetin 3-(4″-acetylrhamnoside) 7-rhamnoside**	Q24	2.82 ± 0.72	–	–	–	–	–
639.31	7.47	315, 306, 300, 283, 254, 246, 216, 202	Isorhamnetin-3,7-di-O-glucoside**	I8	–	–	–	–	0.18 ± 0.06	–
641.23	17.12	317, 308, 297, 281, 241, 217, 204, 191	3-Rhamnosyl-Glucosyl Quercetin**	Q25	0.39 ± 0.14	0.18 ± 0.04	–	–	–	–
649.48	16.50	316, 293, 279, 245, 217, 202, 198, 167	6″-Malonylapiin**	A12	0.43 ± 0.14	–	–	–	1.07 ± 0.06	–
653.42	13.44	315, 305, 286, 257, 249, 228, 215, 201	Isorhamnetin 3-O-(6″-O-feruloyl)-glucoside**	I9	–	–	–	–	15.53 ± 1.94	58.41 ± 1.78
661.14	9.77	286, 257, 241, 202, 191,	Kaempferol 3-(2″,3″-diacetyl-4″-p-coumaroylrhamnoside) **	K12	3.71 ± 0.83	–	–	–	–	–

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Table 1 (*continued*)

MS	RT	MS/MS	Compound	Number	Content (μg/g)					
					H. crinita	D. convexa	P. quineense	M. myristica	X. aethiopiea W	X. aethiopiea B
		187, 185, 153								
663.41	21.31	531, 365, 322, 320, 243, 204, 190, 182	Rutin trihydrate**	F18	–	–	–	–	1.29 ± 0.24	–
665.47	12.65	317, 315, 283, 270, 252, 242, 215, 212	Isorhamnetin 3-rhamnosyl-(1->6)-(2″-acetylglucoside) **	I10	–	–	–	2.79 ± 0.60	1.19 ± 0.15	10.13 ± 0.94
675.37	11.44	300, 271, 266, 219, 214, 180, 178	Kaempferol derivative**	K13	–	–	2.25 ± 0.29	–	–	–
681.24	6.71	284, 267, 241, 209, 188, 179, 173, 161	Kaempferol 3-(2″-hydroxypropionylglucoside)-4′-glucoside**	K14	8.53 ± 0.85	–	–	–	–	–
687.35	5.93	329, 317, 301, 296, 239, 207, 176, 165	Quercetin derivative**	Q26	–	–	–	–	1.39 ± 0.09	–
693.3	5.67	647, 609, 442, 440, 356, 227, 207	Luteolin 7-O-[6‴-O-acetyl]-allosyl-(1 → 2)-[6″-O-acetyl]-glucoside**	L9	–	–	–	–	–	3.73 ± 0.46
695.17	7.80	377, 319, 269, 221, 191, 182, 175, 173	Quercetin 3-(6″-malonylglucoside)-7-rhamnoside**	Q27	1.59 ± 0.42	–	–	–	–	–
721.43	7.83	607, 349, 315, 305, 281, 266, 215, 169	Kaempferol & 2-Phenylethanol-O-(6-O-galloyl)-B-D-glucopyranoside**	K15	–	–	–	–	–	4.24 ± 0.66
725.22	6.15	418, 273, 239, 221, 219, 200, 191, 179	Kaempferol 3-lathyroside-7-rhamnoside**	K16	2.69 ± 0.82	–	–	–	–	–

(*continued on next page*)

Table 1 (*continued*)

MS	RT	MS/MS	Compound	Number	Content (μg/g)					
					H. crinita	D. convexa	P. quineense	M. myristica	X. aethiopiea W	X. aethiopiea B
740.55	5.93	349, 333, 312, 309, 291, 273, 206, 153	Quercetin-3-O-(2′′-O-arabinosyl) rutinoside**	Q28	–	–	1.59 ± 0.37	–	–	–
741.61	19.05	359, 317, 315, 305, 253, 227, 211, 194	Quercetin 3-O-xylosyl-rutinoside**	Q29	2.33 ± 1.18	–	–	–	9.82 ± 1.26	4.36 ± 0.72
749.31	9.44	635, 607, 288, 253, 243, 211, 191, 165	Quercetin derivative**	Q30	2.67 ± 0.73	–	–	–	–	–
844.37	9.44	776, 435, 427, 329, 315, 301, 204, 201	Isorhamnetin 3-(6’’-(E)-sinapoylsophoroside) **	I10	–	–	–	–	1.23 ± 0.13	–
865.22	4.64	381, 309, 305, 297, 255, 245, 227, 203	Procyanidin C1***	F19	–	–	–	–	1.35 ± 0.16	–
949.72	6.37	921, 873, 576, 496, 356, 329, 327, 292	Quercetin 3-(6‴-caffeylsophorotrioside) **	Q31	0.93 ± 0.46	–	2.82 ± 0.41	–	–	–
Other phenolic compounds (PO)										
265.15	13.48	264, 165	2-Hydroxyethylhexylsalicylate***	PO1	–	–	17.3 ± 1.08	–	–	–
293.24	18.97	275, 193	(6)-Gingerol***	PO2	1.82 ± 0.34	–	–	–	–	–
293.26	18.31	237, 221, 218, 211, 205, 189, 174, 164	Mono (2-ethyl-5-hydroxyhexyl) terephthalate***	PO3	–	–	1.04 ± 0.12	5.92 ± 0.86	–	–
295.26	16.57	295, 257, 195, 171	6-Ethoxy-3(4′-hydroxyphenyl)-4-methylcoumarin***	PO4	3.01 ± 0.56	–		0.93 ± 0.23	–	–
323.21	8.39	293, 206	Glabranine***	PO5	–	–	–	–	1.47 ± 0.21	–
325.26	21.14	197, 195, 183, 156	Trans-Fertaric acid***	PO6	2.12 ± 0.40	–	–	–	–	–

(*continued on next page*)

Table 1 (*continued*)

MS	RT	MS/MS	Compound	Number	Content (μg/g)					
					H. crinita	D. convexa	P. quineense	M. myristica	X. aethiopiea W	X. aethiopiea B
375.23	9.58	341, 315, 303, 287, 271, 237, 225, 192	Isomarticin***	PO7	–	–	–	–	1.43 ± 0.33	4.72 ± 0.54
409.17	8.66	285, 273, 262, 256, 248, 236, 197, 177	Mangostin***	PO8	–	2.28 ± 0.24	–	2.61 ± 0.39	–	–
421.17	18.21	301, 285, 274, 262, 251, 238, 217, 201	Mangiferin***	PO9	–	16.45 ± 1.43	–	–	–	–
581.27	4.69	313, 299, 287, 253, 213, 187, 173, 151	Eriodictyol-O-hexose-O-pentose***	PO10	12.21 ± 1.07	–	–	–	–	–
633.39	9.79	317, 308, 300, 273, 255, 243, 205, 179	Corilagin***	PO11	–	–	–	–	–	12.32 ± 1.33
709.33	19.77	295, 279, 271, 267, 241, 229, 201, 165	Chrysoeriol O-glucosylglucoside malonylated***	PO12	–	2.12 ± 0.51	–	–	–	–

Note: *, **, *** indicated that the quantification of these phenolic compounds was obtained by three different ways: 1) the corresponded standard (*), 2) some of the flavonoid glycosides by comparison with their flavonoid unit standard (**), as well as 3) some by comparison with quercetin standard (***).

retention time with the standards, it was confirmed the presence of salicylic acid (*m/z* 137), vanillin (*m/z* 151), protocatechuic acid (*m/z* 153), p-coumaric acid (*m/z* 163), phthalic acid (*m/z* 165), caffeic acid (*m/z* 179), quinic acid (*m/z* 191), ferulic acid (*m/z* 193) and syringic acid (*m/z* 197) in the Angolan plants. Among them, protocatechuic acid and p-coumaric acid were found in all plants, while the presence of other phenolic acids variably changed with plants. For example, vanillin and phthalic acid were not detected in the *D. convexa* and *H. crinita*, respectively. However, syringic acid and ferulic acid were detected only in the *H. crinita* and *P. guineense*, respectively. In addition, salicylic acid was found in the *H. crinita*, *M. myristica* and *D. convexa*, caffeic acid was found in the *P. guineense*, *M. myristica* and *D. convexa*, and quinic acid was found in the *H. crinita*, *P. guineense* and *X. aethiopica*. For bound phenolic acids linking with other acids and sugars, hydroxybenzoyl/hydroxycinnamoyl quinic acids and their glycosylated derivatives have complex structures due to differences in the esterification position and the number of acylation groups. In these Angolan plants, bound phenolic acids were detected only in the *H. crinita*, including 4-O-syringoylquinic acid (*m/z* 371) and 4-O-vaniloylquinic acid (*m/z* 341) in hydroxybenzoyl quinic acids, and 4-p-coumaroylquinic acid (*m/z* 337), chlorogenic acid (*m/z* 353) and 4-O-feruloylquinic acid (*m/z* 367) in hydroxycinnamoyl quinic acids (Liu et al., 2021), except the trigalloyl quinic acid of broken *X. aethiopica* pods. As shown in Fig. 3, the mass spectral cleavage pathways of these binding acids were made by a number of standards and comparative databases. As shown in Fig. 3-A, the 4-O-syringoylquinic acid whose major fragment ions in the secondary mass spectra included parent ion *m/z* 371 and product ions *m/z* 197, 191, 182, 173, 153. In the case of 4-O-vaniloylquinic acid, the major fragment ions included the parent ion *m/z* 341 and product ions *m/z* 191, 173, 167, 152, 123, 108. In the *H. crinita*, the *m/z* 197 and 191 were obtained from the parent ion *m/z* 371, as well as *m/z* 191 and 167 from the parent ion *m/z* 341, thus identifying them as 4-O-syringoylquinic acid as well as 4-O-vaniloylquinic acid, respectively. As shown in Fig. 3-B, for hydroxycinnamoyl quinic acids, the major fragment ions in the chlorogenic acid were parent ion *m/z* 353 and product ions *m/z* 191, 179, 173, 135, 117, 107, and for 4-O-feruloylquinic acid, parent ion

A **Carbohydrate profile (unit: mg/g)**

	Roots		Seeds		Pods	
	Heinsia crinita	*Dorstenia convexa*	*Piper guineense*	*Monodora myristica*	*Xylopia aethiopiea* whole	*Xylopia aethiopiea* broken
R5P	7.47±0.10	7.53±0.96	6.12±00.12	7.90±0.12	15.90±0.46	15.89±0.14
Rha	4.73±1.00	2.64±0.25	2.97±0.32	1.73±0.29	11.81±0.83	15.75±0.66
Ara	27.23±1.61	10.08±0.32	10.20±0.19	8.09±0.27	22.42±0.78	22.34±0.58
Glc	212.74±14.11	400.46±2.16	267.54±9.21	174.67±4.82	114.44±7.27	101.88±4.86
Xyl	73.44±4.40	10.13±0.10	6.81±0.34	39.17±0.75	28.92±0.93	28.91±0.90
Fru	0.59±0.01	2.04±0.17	1.08±0.18	0.84±0.10	0.41±0.01	0.22±0.04
Suc	0.42±0.07	0.86±0.15	1.62±0.13	1.58±0.03	0.86±0.04	0.60±0.02
Mal	0.11±0.02	0.20±0.03	0.16±0.03	0.08±0.01	0.07±0.01	0.08±0.01
Sor	0.73±0.07	0.91±0.85	1.30±0.22	1.13±0.08	1.01±0.13	1.05±0.11

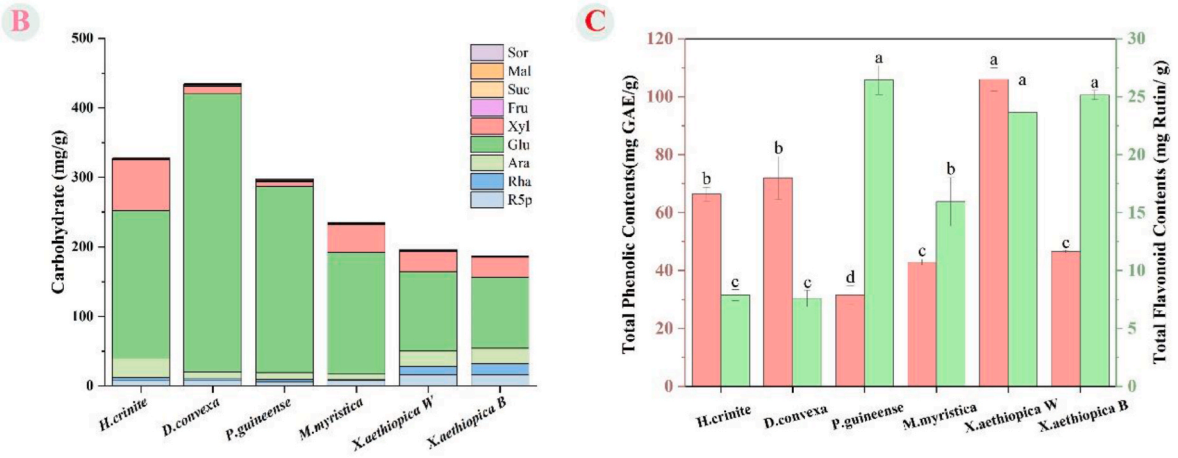


Fig. 1. A and B collect the profile of the main carbohydrate in these Angolan plants from *Heinsia crinita*, *Dorstenia convexa*, *Piper guineense*, *Monodora myristica* and *Xylopia aethiopiea*; These monosaccharides include ribose-5-phosphate (R5P), rhamnose (Rha), arabinose (Ara), glucose (Glc), xylose (Xyl), fructose (Fru), sucrose (Suc), Sorbitol (Sor) and maltose (Mal). C represents the total polyphenol and total flavonoid contents in the six plant samples.

m/z 367 and product ions *m/z* 193, 191, 173, 149, 134, and for 4-p-coumaroylquinic acid, parent ion *m/z* 337 and product ions *m/z* 191, 173, 163, 119, 93. Similarly, in the *H. crinita*, product ions *m/z* 191 and 173 were obtained from parent ion *m/z* 353, product ions *m/z* 193, 191, 173 from parent ion *m/z* 367, and product ions *m/z* 191, 173, 163 from parent ion *m/z* 337. Therefore, the parent ions *m/z* 353, 367 and 337 were inferred to be chlorogenic acid, feruloylquinic acid and 4-p-coumaroylquinic acid, respectively. Depending on the number of acylating groups, hydroxybenzoyl and hydroxycinnamoyl quinic acids can be classified as mono-, di-, tri-, or tetra-substituted compounds. As shown in Fig. 3-C, two-substituent binding acids were found, including two identical substituents (isochlorogenic acid A) and two different substituents (4-O-caffeoyl-3-O-syringoylquinic acid) in the *H. crinita*. In addition, the major fragment ions of isochlorogenic acid A were parent ion *m/z* 515 and product ions *m/z* 353, 335, 191, 173, 135, whereas 4-O-caffeoyl-3-O-syrinoylquinic acid were parent ion *m/z* 533 and product ions *m/z* 371, 353, 197, 191, 179. In the *H. crinita*, product ions *m/z* 353, 281, 269, 225, 191, 179, 173, 161 were obtained from parent ion *m/z* 515, and product ions *m/z* 263, 251, 197, 191, 173, 161, 155, 153 obtained from parent ion *m/z* 533. Thus, it can be inferred that parent ions *m/z* 515 and 533 were isochlorogenic acid A and 4-O-caffeoyl-3-O-syringoylquinic acid, respectively.

3.3.2. *Identification of flavonoids*

It is well known that the basic skeleton of flavonoids is C6-C3-C6, which can be classified into flavonols, flavones, flavanones, flavan-3-ols, isoflavonoids, chalcones, and so on, according to the differences in the ring-forming, oxidizing, and substituting modes of the C3 part. Flavonoid glycosides are often combined with different sugars, mono- and di-glycosides are common types in plants, and occasionally tri-glycosides, and even some of them are acylated by p-coumaroyl, malonyl and other groups. Theoretically, there are many possibilities for flavonoid to glycosylate, among that glycosides mainly exist as 3- or 7-position O-glycosides, but the 5, 3′ and 4′ positions are sometimes glycosylated (Alseekh et al., 2020). Based on the core structure of flavonoids (C6-C3-C6), the main cleavage pathway of some representative standards was shown in Fig. 4, in which the carbon-carbon bond of C-ring underwent the Retro Diels-Alder reaction to produce fragment ions A- (A-ring) and corresponding B- (B-ring). According to these fragment ions, the group composition and number contained in the A- and B- rings can be determined to identify flavonoid glycosides by figuring out these substituents (Yuan et al., 2020). In addition, flavonoids are prone to lose H2O (18), CO (28), CO2 (44), etc., which facilitates further de-inference to the flavonoid glycoside compounds in the plant. It had been found that a number of flavonoids are widely present in these plants (Evuen et al., 2022; Yin et al., 2019), including quercetin (*m/z* 301), luteolin (*m/z* 285), kaempferol (*m/z* 285), apigenin (*m/z* 269), taxifolin (*m/z* 303), myricetin (*m/z* 317), isorhamnetin (*m/z* 315) and catechin (*m/z* 289). These flavonoid compounds can be easily identified by comparing standards. However, for their corresponding

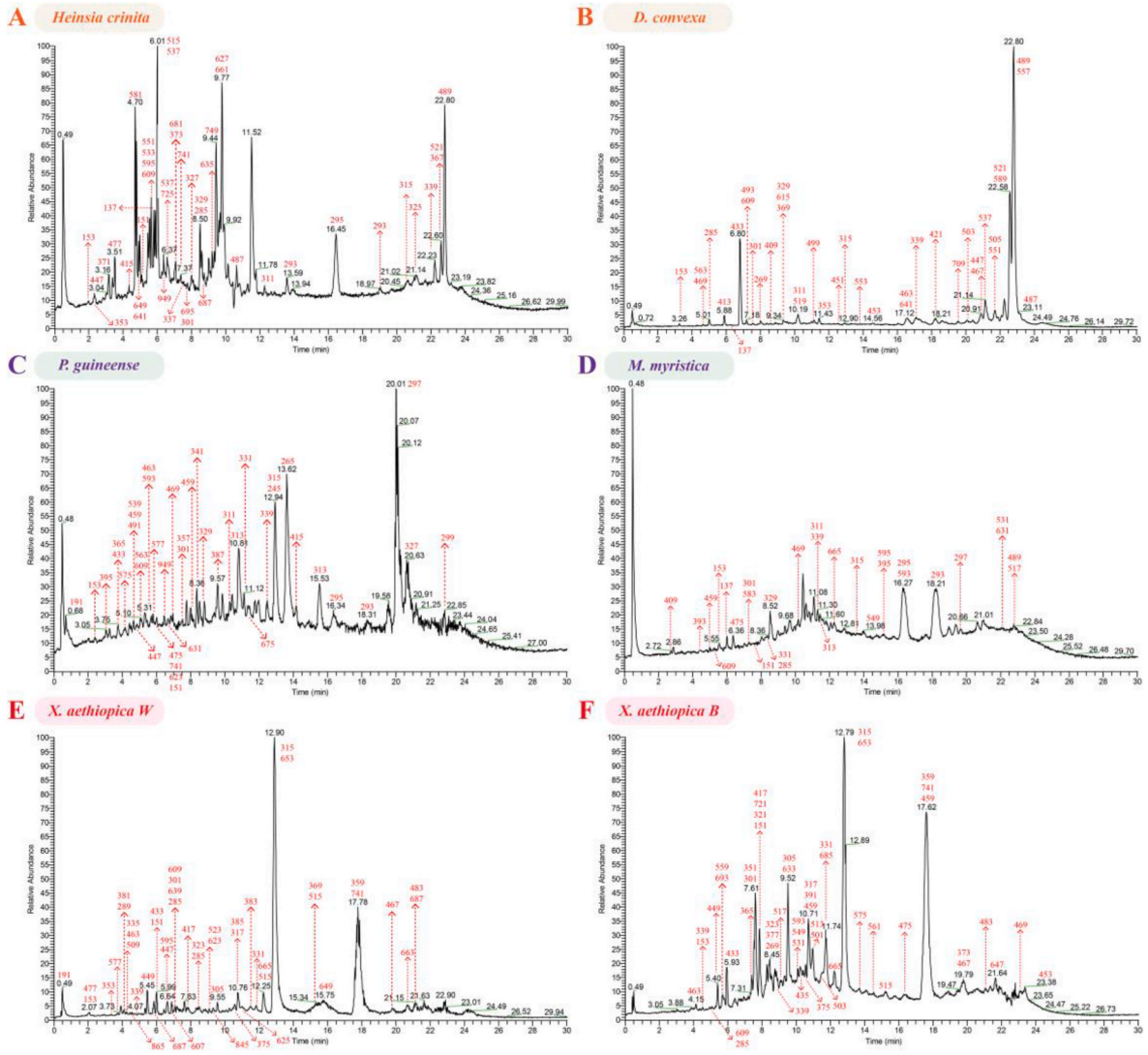


Fig. 2. Primary full-scan mass spectrometry chromatograms of six plants by LC-MS. Elution procedure: 0–3 min, 3–15 %B; 3–10 min, 15–50 %B; 10–17 min, 50 %B; 17–22 min, 50–70 %B; 22–27 min, 70-5 %B; 27–30 min, 5 %B. Fluid phase: 0.1 % miliq-water of formic acid (A), acetonitrile (B).

flavonoid glycosides, it is necessary to compare with the mass spectrometry cleavage pathways of these common flavonoids in order to identify some unknown compounds. From the fragment ions of some common standards in Table 2, the mass spectral cleavage paths of these different types of flavonoids were depicted as Figure-4. Although these flavonoids have some identical fragment ions, they also product various distinctive ions to distinguish. For the identification of flavonoid glycosides, they readily shed sugar fragment and produce the characteristic fragment ions. Therefore, some complex flavonoids containing glycosides readily be identified in these plants by comparing distinctive product ions from each flavonoid, as well as in conjunction with the composition of the monosaccharides. Furthermore, the database is particularly important in this identification process, because it is necessary to accurately match the identified compounds, especially some unknown or complex flavonoid glycosides.

As can be observed in Table 1, quercetin and rutin were identified in all plants, among most of them comprise luteolin, kaempferol, isorhamnetin and apigenin, while myricetin were identified only in the *X. aethiopica*. Besides, a number of flavonoids with polyhydroxy and methylated substituents were also identified, such as 3′,4′,5,7-tetramethoxyflavone (*m/z* 341), tricin (*m/z* 329), 3-hydroxy-3′,4′,5′-trimethoxyflavone (*m/z* 327), 3,7-dihydroxy-3′,4′-dimethoxyflavone (*m/z* 313), 4′,5,7-trimethoxyflavone (*m/z* 311) and 3′,7-dimethoxy-3-hydroxyflavone (*m/z* 297). In fact, flavonoids were mainly present in these plants in the form of glycosides, where the glycosidic portion was as detected at the above of 3.1 section, such as Mal, Suc, Fru, Xyl, Glc, Ara, Rha and R5P. However, the flavonoid glycoside composition of these plants varied considerably, with only a few of them being identical. For the flavonoid glycosides, they were all mainly dominated by quercetin glycosides, which was consistent with the result that all plants contained quercetin. In addition, for methylated flavonoids of quercetin, isorhamnetin glycoside analogs were widely found in Angolan plants, especially for *P. guineense* and *M. myristica*. There were some other flavonoid glycosides where their flavonoid units were mainly luteolin, kaempferol, and apigenin, taxifolin and myricetin, which bound to different monosaccharides. A number of acylated flavonoid glycosides (acetylated, malonylated, caffeoylated, feruloylated and p-coumaroylated) were also found in these plants, suggesting that this was a widespread phenomenon. Furthermore, poly-glycoside-substituted flavonoids were also identified in these Angolan plants, in which their flavonoid units were mainly isorhamnetin and kaempferol, such as kaempferol 3-(2″-hydroxypropionylglucoside)-4′-glucoside (*m/z* 681) in the *H. crinita*, isorhamnetin-3,7-di-O-glucoside (*m/z* 639) in the *X. aethiopica* (Tenyang et al., 2024), isorhamnetin 3-galactoside-7-rhamnoside (*m/z* 623) in the *P. guineense*, isorhamnetin 3-O-a-L-arabinopyranoside 7-O-a-L -rhamnopyranoside (*m/z* 593) in the *X. aethiopica*, and

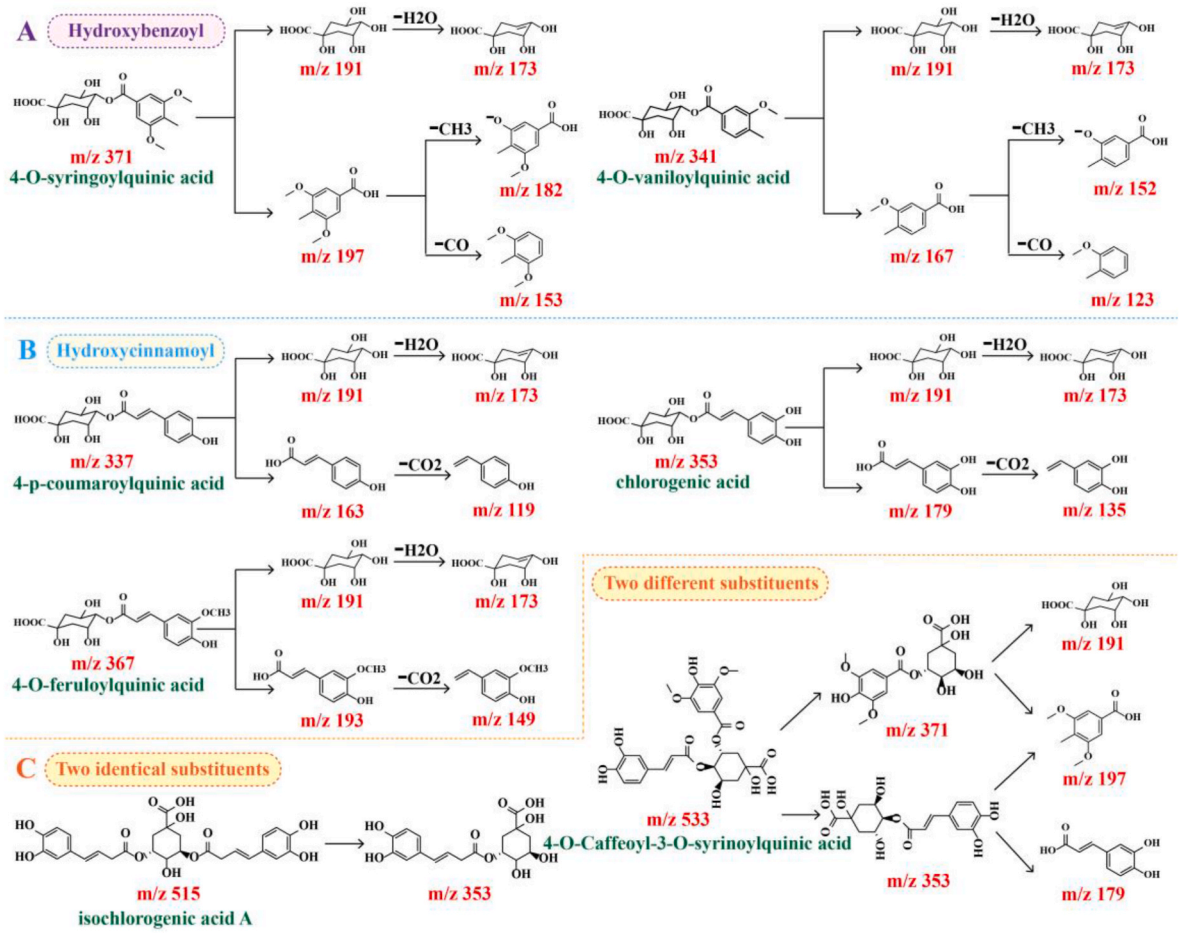


Fig. 3. Mass spectrometric cleavage pathways for identifying phenolic acids of *Heinsia crinite*.

kaempferol 3-alpha-L-arabinofuranoside-7-rhamnoside (*m/z* 563) in the *D. convexa*, but it was not found in the *M. myristica*. There was rarely literature in the current research on the identification of flavonoid glycosides from these Angolan plants. However, the biological activity of these plants is largely correlated with their flavonoid glycosides, which also can significantly enhance their pharmacological activity. Therefore, there is a great need to characterize these flavonoid glycosides, which is favorable to explore the active substances present in these plants.

3.3.3. Other phenolic compounds

In addition to the phenolics identified above, a number of other phenolics were present in Angolan plants, such as (6)-gingerol (*m/z* 293), 6-ethoxy-3(4′-hydroxyphenyl)-4-methylcoumarin (*m/z* 295) in the *H. crinita*, glabranine (*m/z* 323) and isomarticin (*m/z* 375) in the *X. aethiopica,* 2-hydroxyethylhexylsalicylate (*m/z* 265), mono (2-ethyl-5-hydroxyhexyl) terephthalate (*m/z* 293) and 2-O-sinapoylmalate (*m/z* 339) in the *P. guineense,* mangostin (*m/z* 409) in the *M. myristica*, and mangiferin (*m/z* 421) in the *D. convexa*. These phenolic compounds only present in particular plant and their amounts are minor. However, these phenolic compounds may have special biological activities, which were more extraordinary than those of phenolic acids and flavonoids. Therefore, the identification of some uncommon phenolics is of great significance, and some potential active substances can be explored to apply in different fields.

3.4. Phenolic compounds quantification

In order to indicate the content of these phenolic compounds, they were quantified by employing their standards as well as referring some similar analogue according to the above identification results. As can be observed in Table 1, the *H. crinita* and *X. aethiopica* had relatively high content of phenolic acid, while other three plants had very low content. Among the major phenolic acids in the *H. crinita* were salicylic acid (10.03 ± 0.59 μg/g) and syringic acid (7.99 ± 1.69 μg/g) and 4-O-caffeoyl-3-O-syringoylquinic acid (6.94 ± 0.31 μg/g). For *X. aethiopica*, both its whole and broken pods were enriched with protocatechuic acid, which was 32.37 ± 3.44 and 7.29 ± 0.37 μg/g respectively, suggesting that the entire shape had a higher content. As far as flavonoids were concerned, the content of some simple ones was very low, with luteolin (50.89 ± 4.94 μg/g) being found only in high levels in the *D. convexa*. These plants had a relatively high content of flavonoid glycosides, among which the top three in the *H. crinita* were kaempferol-3-O-β-D-6″-acetylglucoside (22.71 ± 1.69 μg/g), eriodictyol-O-hexose-O-pentose (12.21 ± 1.07 μg/g), and quercetin-3-O-glucuronide (9.56 ± 0.73 μg/g). For the whole pods of *X. aethiopica*, flavonoid glycosides were mainly dominated by isorhamnetin unit, including isorhamnetin 3-O-(6″-O-feruloyl)-glucoside (15.53 ± 1.94 μg/g), isorhamnetin (10.35 ± 1.23 μg/g) and quercetin 3-(2G-xylosylrutinoside) (9.82 ± 1.26 μg/g). However, for the broken pods of *X. aethiopica*, although its major flavonoid glycoside was also isorhamnetin, isorhamnetin 3-O-(6″-O-feruloyl)-glucoside (58.41 ± 1.78 μg/g) and isorhamnetin (28.41 ± 1.78 μg/g), there were many differences between the two, such as apigenin 7-O-methylglucuronide (46.35 ± 1.84 μg/g). In addition, the *D. convexa* had abundant flavonoid glycosides that mainly dominated by quercetin, including quercetin 3-O-acetyl-rhamnoside (104.67 ± 5.85 μg/g), iridin (52.59 ± 2.21 μg/g) and quercetin 3-O-beta-D- xylopyranoside (37.27 ± 1.44 μg/g). Unlike the above Angolan plants, the major flavonoids of *P. guineense* and *M. myristica* were some methylated

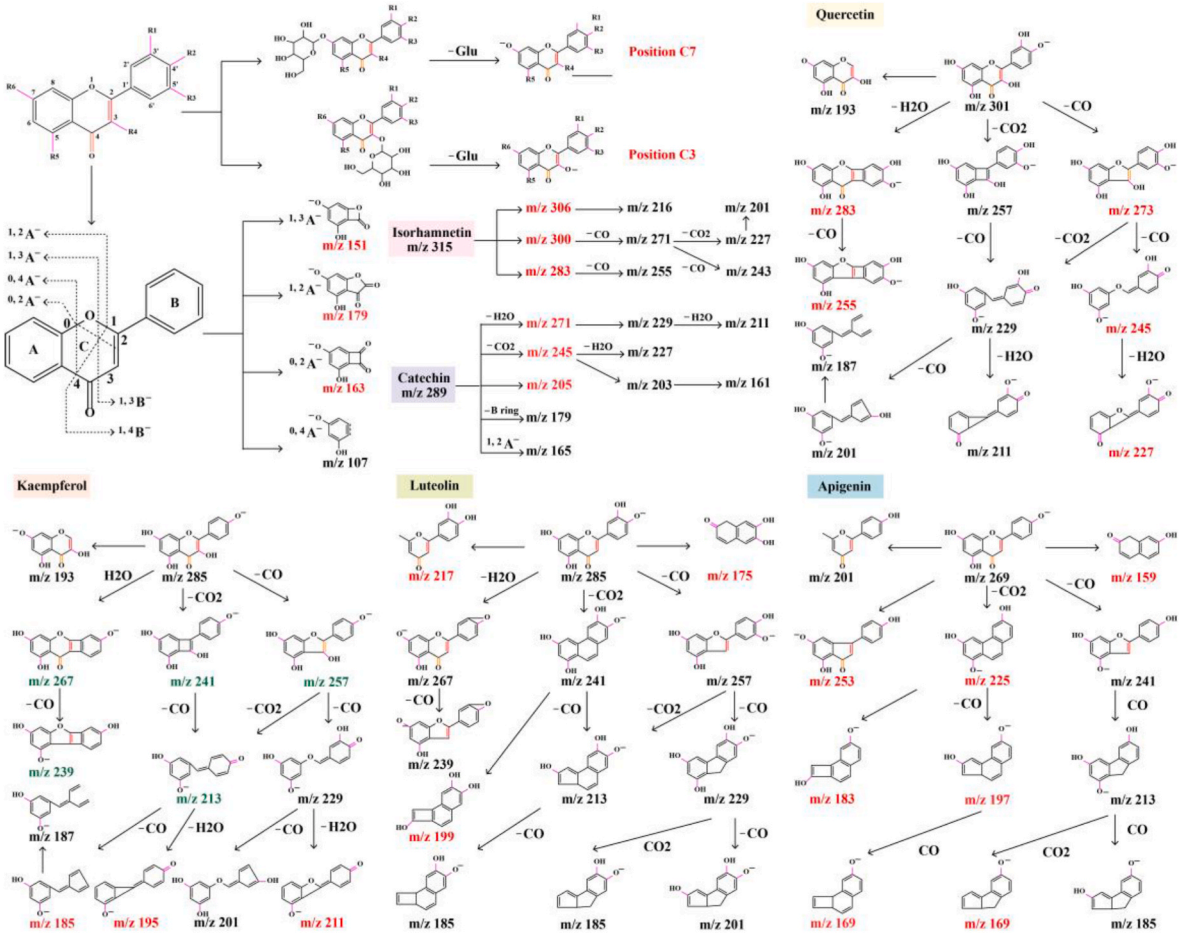


Fig. 4. Mass spectral cleavage paths of these different types of flavonoids to identify some complex flavonoids containing glycosides of six plant samples. There are luteolin and apigenin (flavones), kaempferol, quercetin and isorhamnetin (flavonols), catechin (flavan-3-ols).

flavonoids including 3′,7-dimethoxy-3-hydroxyflavone (27.38 ± .0.57 μg/g), 3,7-dihydroxy-3′,4′-dimethoxyflavone (14.50 ± 0.69 μg/g) and isorhamnetin (14.31 ± 0.92 μg/g) in the *P. guineense*, as well as 3′,4′-dimethoxy-3-hydroxy-6-methylflavone (19.22 ± 0.96 μg/g), prenyl apigenin (6.64 ± 1.15 μg/g) and 3′,7-dimethoxy-3-hydroxyflavone (6.44 ± 0.97 μg/g) in the *M. myristica*. By quantifying the phenolics content of these plants, which is important for the interpretation of their biological activities as well as for future isolation and purification studies (Fetse, Kofie, & Adosraku, 2016).

3.5. Chemometrics analysis

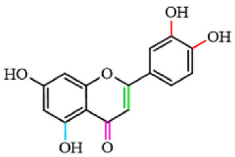
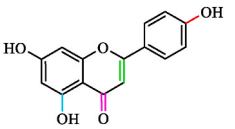
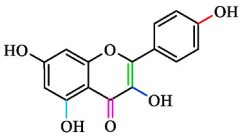
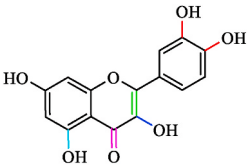
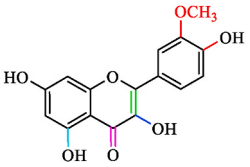
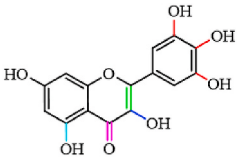
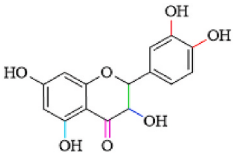
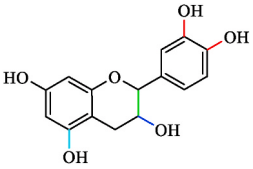
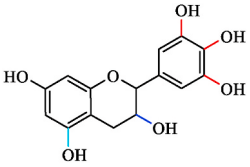
3.5.1. Hierarchical cluster analysis (HCA)

In order to make a comprehensive comparison of phenolic compounds from these Angolan plants, the main phenolics were analyzed by HCA and the results are shown in Fig. 5. The HCA can evaluate the difference of these phenolics as well as their contents between different plants by clustering them, as well as achieve the goal of identifying characteristic compounds (Ulewicz-Magulska & Wesolowski, 2023; Subbiah et al., 2021). Heat map can be more comprehensive and intuitive observation of the distribution and accumulation of phenolics in different plants. It was found that six samples are clearly different in color, where the red concentration in each column was their characteristic phenolic compounds. For *H. crinita*, its main differential compounds were centered on phenolic acids such as salicylic acid, syringic acid, chlorogenic acid, 4-O-caffeoyl-3-O-syringoylquinic acid, kaempferol 3-(2″-hydroxypropionylglucoside)-4′-glucoside and 4-p-coumaroylquinic acid (Boumba et al., 2022). For another root of *D. convexa*, its differential markers were focused on flavonoids, mainly including luteolin, mangiferin, kaempferol-3-O-(2,3,4-tri-O-acetyl-α-L-rhamnopyranoside), quercetin 3-O-acetyl-rhamnoside, quercetin 3-(6-O-acetyl-beta-glucoside) and iridin (Omisore et al., 2005). As for both seeds, the differential markers of *P. guineense* focused on polymethylated flavonoids including ferulic acid, 2-hydroxyethylhexylsalicylate, 3′,6-dimethylflavone, 3′,4′,5,7-tetramethoxyflavone, 3,7-dihydroxy-3′,4′-dimethoxyflavone, 3′,7-dimethoxy-3-hydroxyflavone, whereas the *M. myristica* had fewer differential markers, including prenyl apigenin, 4′,5,7- trimethoxyflavone, mono (2-ethyl-5-hydroxyhexyl) terephthalate, apigenin triacetate (Amadioha & Chidi, 2019; Irondi et al., 2023). For both states of *X. aethiopica* pods, the broken one had the most differential markers centered on taxifolin and isorhamnetin, mainly including taxifolin 7,3′-dimethyl ether, taxifolin hydrate, isorhamnetin 5-glucoside, isorhamnetin 3-rhamnosyl-(1->6)-(2″-acetylglucoside), isorhamnetin 3-O-(6″-O-feruloyl)-glucoside and isorhamnetin 3-alpha--L-arabinopyranosyl-(1->2)-rhamnoside, whereas the whole type possessed catechin analogs including mainly p-coumaric acid, 6″-malonylapiin, catechin, (−)-epigallo catechin, myricetin and protocatechuic acid (Okpoghono et al., 2023).To conclude, the roots contain more phenolic acids and the seeds have more poly-methylated flavonoids, as well as the pods include more isorhamnetin and catechin analogs.

3.5.2. Principal component analysis (PCA)

Since there were total 134 phenolic compounds from these plants, PCA was used to analyze all of them. As shown in Fig. 6-A, the PCA displayed 18 samples (each sample for triplicate), where the percentage of variance can be interpreted as the number of features of the original

Table 2
There are the fragment ions and distinctive product ions of some different types of flavonoids getting by LC-MS-TOF.

Type	Standard	structure	Fragment ions	Distinctive product ions
Flavones	Luteolin		285, 277, 267, 257, 243, 239, 229, 223, 217, 213, 201, 199, 189, 185, 175, 171, 167, 157, 151	217, 199, 175, 151
	Apigenin		269, 253, 251, 241, 225, 213, 209, 201, 197, 183, 179, 169, 159, 151	253, 225, 197, 183, 169, 159
Flavonols	Kaempferol		285, 267, 257, 253, 243, 239, 229, 219, 213, 211, 205, 201, 195, 187, 185, 171, 163, 159	211, 195, 187, 163
	Quercetin		301, 299, 283, 273, 255, 243, 227, 211, 201, 187, 179, 163	283, 273, 255, 227, 179
	Isorhamnetin		315, 306, 300, 283, 271, 255, 243, 227, 216, 201, 183, 163, 151	306, 300, 271
	Myricetin		317, 299, 289, 275, 271, 261, 255, 243, 233, 227, 219, 193, 179, 171, 165, 151	289, 275, 261, 233
Flavanonol	Taxifolin		303, 285, 275, 257, 243, 241, 231, 217, 213, 212, 201, 199, 189, 177, 175, 171, 153, 151	285, 275, 231
Flavan-3-ols	Catechin		289, 271, 247, 245, 243, 231, 227, 225, 221, 217, 211, 205, 203, 199, 191, 187, 185, 179, 175, 173, 167, 165, 161, 159, 157, 151	271, 245, 231, 205
	Epigallocatechin		305, 304, 277, 261, 219, 203, 198, 182, 179, 167, 165, 161	287, 261, 219

data implied by each principal component (André et al., 2020). Among them, the sum of cumulative variances from principal components 1–4 was 88.08 (>85 %), thus they can be selected as principal components, which the variance percentage of each constituent component explained the corresponding total variation. Principal component 1, the broken pod of *X. aethiopica*, explained 25.6 % of the total variation, while principal component 2 (the whole pod of *X. aethiopica*) was 22.2 %. There was a high degree of variability in the phenolics of each plant,

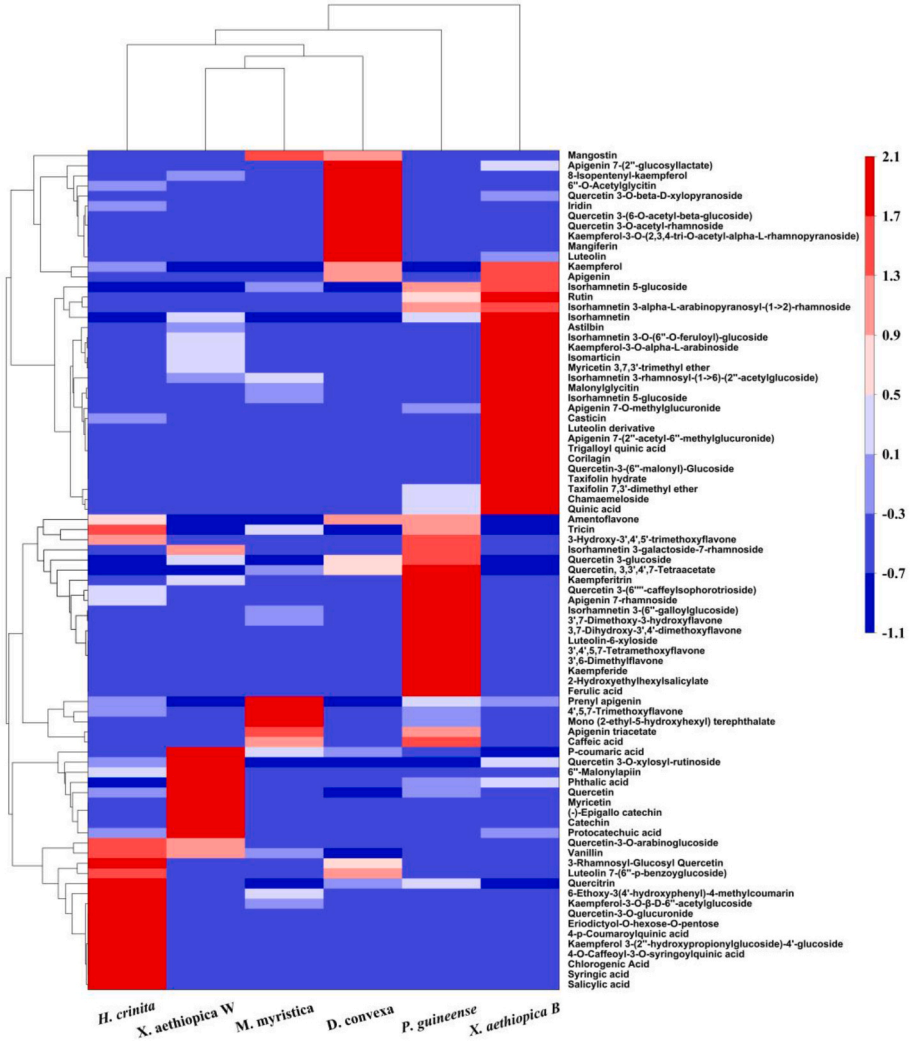


Fig. 5. Heat map obtained from hierarchical cluster analysis of phenolic compounds from six Angolan plant samples. Among that, the columns represent samples, the rows represent the 83 markers, and the cell colors represent the peak areas (i.e., the degree of relative abundance). The red color indicates that the compound is above the average for this sample group, in contrast that blue color indicates that the compound is below the average.

with the pods of *X. aethiopica* containing relatively the most information, and the variability when compared to other plants being relatively the least. Thus, PCA can be used to analyze the variability of phenolic compounds in multiple plant samples and even determine whose plant contain the most amount of phenolics that also present in other plant. In addition, the contribution of each variable on the principal components were shown in Fig. 6-B and C, where the longer lines corresponded to main phenolic compounds in each plant sample. These phenolic compounds were found to contribute more, including vanillin, kaempferol, luteolin, quercetin and isorhamnetin, which is consistent with their prevalence in several plants (Iftikhar et al., 2023; Qian et al., 2023). Thus, this allows for the identification of common phenolic compounds from multiple plant samples, *i.e.*, recognizing some of their similarities.

3.5.3. Orthogonal partial least squares discriminant analysis (OPLS-DA)

OPLS-DA is a "supervised" mode of discriminant analysis, which is better than PCA at distinguishing between groups of characteristic variables and determining their relationship (Oh et al., 2023). The relationship between these plants was modeled with the help of OPLS-DA, which allows better access to information about their differences among phenolic compounds (Li et al., 2024). For the score plot, the values in the horizontal and vertical coordinate direction showed the disparity between the groups and within the groups, respectively, where the percentage indicated the degree to which the component explained the dataset. As can be seen in Fig. 6-C, the *D. convexa* roots and broken *X. aethiopica* pods were relatively more different from other four groups. The degree of clustering of phenolic compounds can be observed from the bipot (combining the score plot and loading plot) in Fig. 6-D, where components next to each other indicated a high degree of similarity and can be clustered into one group. This is consistent with the previous results that those more scattered points correspond to phenolic compounds prevalent across these plants. Therefore, this allows for quick identification of phenolic compounds with high correlation from Angolan plants, as well as those that are not correlated. In addition, as shown in Fig. 6-E, a larger VIP value represented a greater contribution of phenolic compound to distinguish between these plants, where it is generally accepted that this value greater than 1 represents a significant difference. However, there were shortcomings in this model, just as R2X (0.388) and Q2X (0.29) represented the predictability (reliability) and interpretability (variability), respectively, which both values were not close to 1. As shown in Fig. 6-F, the results of permutation test to determine whether the model was "overfitting", were in which R2Y (0.147) and Q2Y (−0.793) also reflected the large differences among the six groups of plants. In conclusion, OPLS-DA is more suitable for the comparative separation of two groups of plants to find the different compounds.

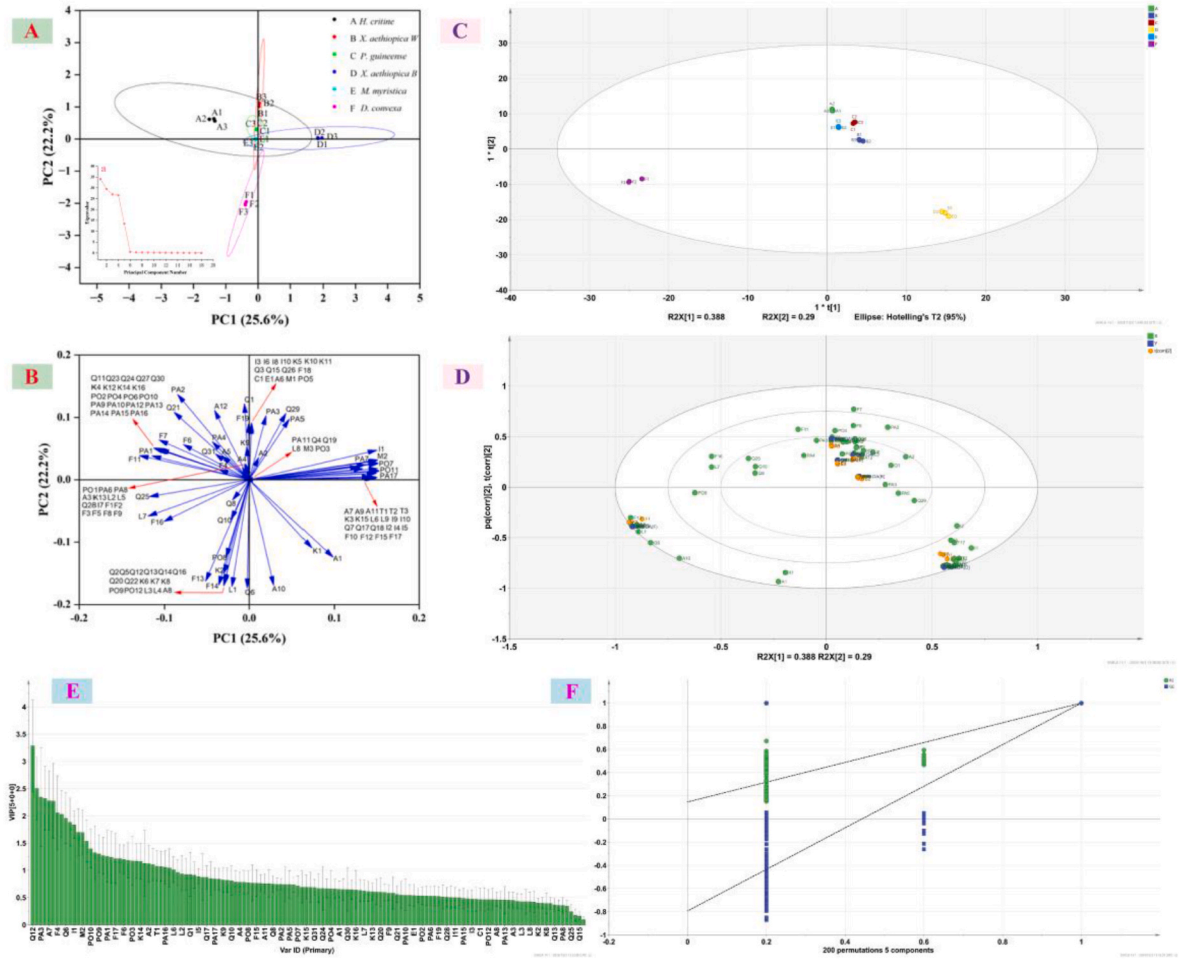


Fig. 6. A and B are the score and loading plots obtained from PCA analysis of phenolic compounds from the six Angolan plant samples, respectively, where a in figure A is a Scree plot. In general, a cumulative variance of 85 % or more can be considered that the resulting principal components contained most features of the original data. C and D are score plots and Biplot obtained from OPLC-DA analysis of phenolic compounds between six Angolan plant samples, respectively, while E and F are VIP values and permutation test plots, respectively. For the bipot (combining the score plot and loading plot), the loadings represented the correlation between the variable and principal component, so that the points in the first quadrant showed strong positive correlation, and the points in the fourth quadrant showed strong negative correlation.

3.6. Correlation plot between phenolics compounds and antioxidant capacity

As the results were shown in Fig. 7, with larger values indicating a higher association, the correlation coefficients of TPC with DPPH, TEAC and FRAP among these Angolan plants were 0.89, 0.82 and 0.92, respectively, showing significant positive relevance. The correlation coefficients of phenolic acid type (PA-M) with DPPH and FRAP were found to be 0.62 and 0.83, respectively, whereas quercetin type (QUE-M) and luteolin type (LUT-M) showed notable positive relevance with TEAC with values of 0.74 and 0.59, respectively. This is consistent with the composition as well as the content of phenolic compounds in these plants, reflecting the fact that quercetin types play a significant role in antioxidant activity (Yan et al., 2023; Zou et al., 2025). For other types of phenolic compounds, no remarkable differences were found, probably due to excessive variability in these plants. In conclusion, for some highly correlated plants as well as specific ingredients, this is a good way to find out the correlation between compounds and antioxidant activity, so that some crucial active phenolics can be identified by this analysis.

4. Conclusion

The presence of abundant phenolic compounds in these Angolan plants was confirmed by determining of TPC and TFC, which TPC results indicated that the whole pods of *X. aethiopica* exhibited the highest values (105.96 mg GAE/g), followed by the *D. convexa* roots (71.97 mg GAE/g), and the lowest levels of *P. guineense* seeds (31.60 mg GAE/g). It was also evident that TFC did not show positive correlation with TPC between six plant samples. The *P. guineense* seeds had the highest TFC, while two roots contained the lowest TFC, as well as the pods of *X. aethiopica* showed relatively higher TFC and TPC. Some complex phenolics lacking standards were identified, such as the binding acids (4-O-syringoylquinic acid, chlorogenic acid and isochlorogenic acid A) in the *H. crinita*, as well as a variety of flavonoid glycosides from all plants. The protocatechuic and p-coumaric acid, quercetin and rutin were found to be prevalent in all plants, while luteolin, kaempferol, isorhamnetin, apigenin and quercitrin were also their major flavonoids. It had been found that flavonoids were mainly present in the form of glycosides, where the glycosidic portion was detected, such as Mal, Suc, Fru, Xyl, Glc, Ara, Rha and R5P. Chemometrics analysis of quantitative phenolics by HCA, PCA and OPLC-DA revealed great variability in their composition between these Angolan plants, among the HCA results indicated that the roots contained more phenolic acids, the seeds included more poly-methylated flavonoids, and the pods comprised more isorhamnetin and catechin analogs. In addition, PCA and OPLC-DA confirmed the prevalence of vanillin, kaempferol, luteolin, quercetin and isorhamnetin in these plants, as well as identified a number of principal components and characteristic phenolics from them. Finally,

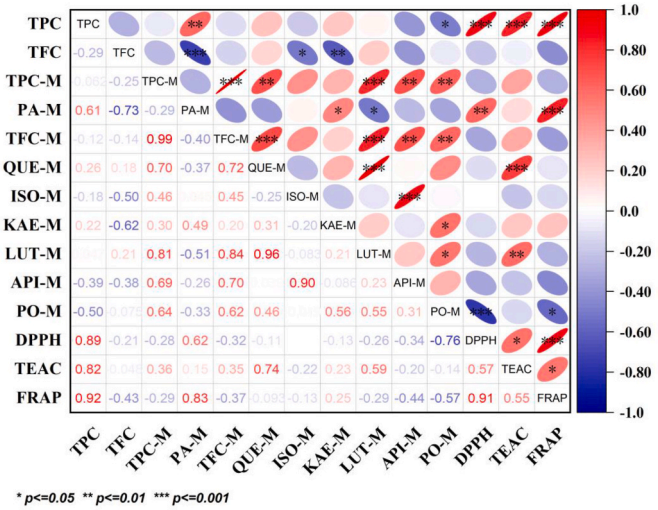


Fig. 7. Plot of correlation coefficients between the phenolic compounds and antioxidant activities of DPPH, TEAC and FRAP from six Angolan plant samples. Where TPC-M, PA-M, TFC-M, QUE-M, ISO-M, KAE-M, LUT-M and API-M are derived from the quantitative results of phenolic compounds as shown in Table 1, among that each of them represents the sum amounts of phenolic compounds of this type. DPPH, TEAC and FRAP were performed as another recently published work (Cameselle et al., 2025). The correlation coefficient reflected the direction and degree of change in the trend between these variables, with positive and negative values indicating a positive (red) and negative (blue) correlation, respectively.

correlation coefficient analysis demonstrated that phenolic acid type was mainly correlated with DPPH and FRAP, while quercetin and luteolin flavonoids showed significant positive relevance with TEAC, which reflects these phenolics play an important role in antioxidant activity. In conclude, these Angolan plants can be excavated to apply in food flavors, pharmaceuticals, cosmetics and other related fields.

CRediT authorship contribution statement

Pengren Zou: Writing – original draft, Methodology, Investigation, Formal analysis. **Carla Cameselle:** Writing – original draft, Methodology, Investigation. **Antía Torres:** Writing – original draft, Investigation. **Honória S. Chipaca-Domingos:** Investigation. **Paulina G. Gonçalves:** Investigation. **Hui Cao:** Writing – review & editing, Investigation. **Jesus Simal-Gandara:** Supervision, Resources, Investigation. **Paz Otero:** Writing – review & editing, Supervision, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Conceptualization.

Declaration of competing interest

Authors declare that there is no conflict of interest.

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Data availability

Data will be made available on request.

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