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Mass spectrometric elucidation of polyphenol constituents in *Vernonia amygdalina* Del.

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V*ernonia amygdalina* Del. (VA), family Asteraceae is a well-known shrub in tropical countries because of its nutritive and medicinal properties. The antioxidant and anticancer therapeutic effects of VA were related to polyphenol content. For this purpose, mass spectrometric investigation was conducted aiming at characterizing the polyphenol composition of *Vernonia amygdalina*. Previous publications on the polyphenol constituents in VA raise some questions on the component composition caused by inadequacy of the data. It seems necessary to prove the presence of luteolin 7-O-glucosides and the aglycone luteolin. Monocaffeoyl-, dicaffeoyl- and tricaffeoylquinic acids, as well as, feruloyldicaffeoylquinic acid were also reported. In this study the polyphenols were extracted using methanol in an ultrasound bath for 40 min at room temperature (25°C). The extract was evaporated to dryness, resolved in water and divided into chloroform fraction and ethyl acetate fraction. The compounds in both the fractions were characterized by HPLC-PDA. Structural elucidation was performed on Orbitrap UHPLC mass spectrometer. Two flavone aglycones luteolin and apigenin were identified in the chloroform fraction. In the ethyl acetate fraction six flavone glycosides luteolin 7-O-glucoside, luteolin 7-O-glucuronide, luteolin 4'-O-glucoside, apigenin 7-O-rutinoside, apigenin 7-O-glucoside and apigenin 7-O-glucuronide were found, as well as mono and

dicaffeoylquinic acids and feruloylquinic acid-O-glycoside. The caffeoylquinic acids (chlorogenic 1,5-3,5 and 4,5-dicaffeoylquinic acids), luteolin 7-O-glucoside, luteolin 7-O-glucuronide and luteolin are the main compounds composing the polyphenol complex of VA. The largest percentage of them was due to 1,5 and 3,5 dicaffeoylquinic acids. Furthermore, the presence of luteolin 4'-O-glucoside, apigenin 7-O-rutinoside and feruloylquinic acid-O-glycoside as minor constituents in *Vernonia amygdalina* is reported for the first time.

t _R	Name	[M-H] ⁻	MS ² /MS ³
3.74	neo-Chlorogenic acid	353	191, 179, 163, 135
5.78	Chlorogenic acid	353	191, 179
6.95	4-Caffeoylquinic acid	353	191
10.96	Lut-7-O-glucuronide	463	269, 191, 175, 151, 133, 107
11.09	Lut-7-O-glucoside	447	269, 175, 151, 133, 107
11.51	1,4-di-CQA	525	353, 191, 179, 173, 161, 135
11.79	3,4-di-CQA	525	353, 191, 179, 173, 161, 135
11.94	1,5-di-CQA	525	353, 191, 179, 163, 135
11.97	Apig-7-O-rutinoside	577	269, 151, 117
12.33	Apig-7-O-glucoside	431	431, 269, 151, 107
12.45	Apig-7-O-glucuronide	445	269, 175, 151, 149, 117
12.64	3,5-di-CQA	525	353, 191, 179, 163, 135
13.11	Lut-4'-O-glucoside	447	447, 269, 151, 133, 107
14.01	4,5-di-CQA	525	353, 191, 179, 173, 161, 135
14.89	FQA-glucoside	529	529, 367, 179, 163, 135, 133
15.60	Lut	269	269, 217, 199, 175, 151, 133, 121, 107
17.55	Apig	269	269, 151, 149, 117, 107

Table 1. Polyphenol constituents in *V. amygdalina* Del. Legend: Lut-Luteolin, Apig-Apigenin, di-CQA-Dicaffeoylquinic acid, FQA-Feruloylquinic acid

Pharmacognosy and Medicinal Plants

Recent Publications

1. Imafidon C, Akomolafe R, Sanusi A, Ogundipe O, Olukiran O and Ayowole O (2015) Polyphenol-rich extract of *Vernonia amygdalina* (del.) leaves ameliorated cadmium-induced alterations in feeding pattern and urine volume of male Wistar rats. *Journal of Intercultural Ethnopharmacology* 4(4):284–292.
2. Johnson C E, Lin L, Harnly J M, Oladeinde F O, Kinyua A M, Michelin R and Bronner Y (2011) Identification of the phenolic components of *Vernonia amygdalina* and *Russelia equisetiformis*. *Journal of Natural Products* 4:57–64.
3. Ong K W, Hsu A, Song L, Huang D and Tan B K H (2011) Polyphenols-rich *Vernonia amygdalina* shows anti-diabetic effects in streptozotocin-induced diabetic rats. *Journal of Ethnopharmacology* 133(2):598–607.
4. Ola S S, Catia G, Marzia I, Francesco F V,

Afolabi A A and Nadia M (2009) HPLC/DAD/MS characterisation and analysis of flavonoids and cinnamyl derivatives in four Nigerian green-leafy vegetables. *Food Chemistry* 115(4):1568-1574.

5. Igile G O, Oleszek W, Jurzysta M, Burda S, Fafunso M and Fasanmade A A (1994) Flavonoids from *Vernonia amygdalina* and their antioxidant activities. [Erratum to document cited in CA121:251243]. *Journal of Agricultural and Food Chemistry* 42(11):2445–2448.

Biography

Soleya Dagnon has her expertise in evaluation and chromatography profiling of polyphenols in plants. Her analytical and chromatography evaluation model based on deep cognition of chemical and spectral properties of compounds and their chromatographic behavior creates confidence in the information needed for improving the knowledge. She has built this model after many years of experience in chromatography, method evaluation and teaching both in research and education institutions. At the Plovdiv University, she is teaching Modern Chromatographic Methods and Chromatographic Methods in Pharmaceutical Analysis.