Supporting Information

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Activity Guided Fractionation of *Arum italicum* Miller Tubers and the LC/MS-MS Profiles

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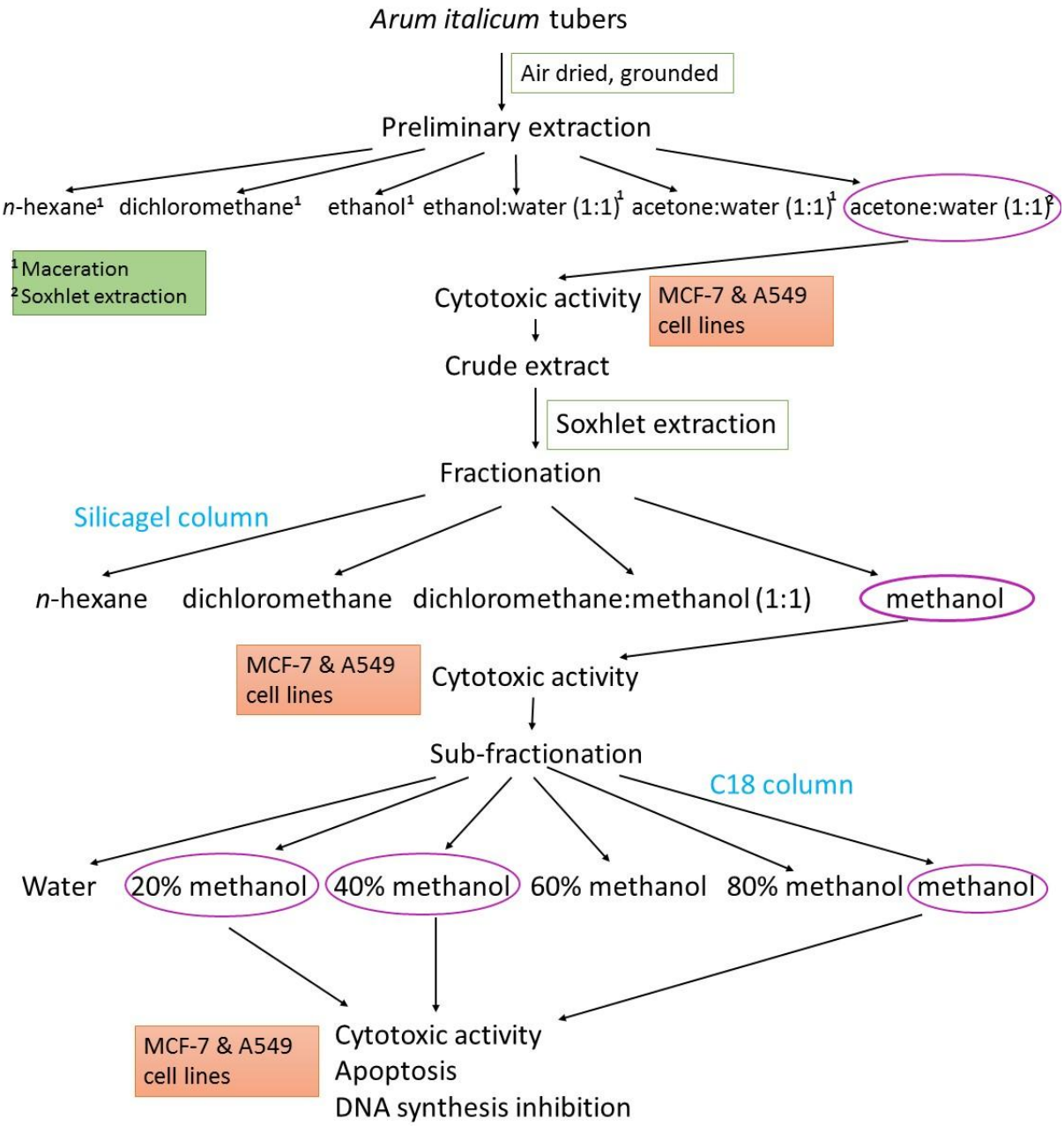

Figure 1. The Scheme of Biological Activity Guided Fractionation

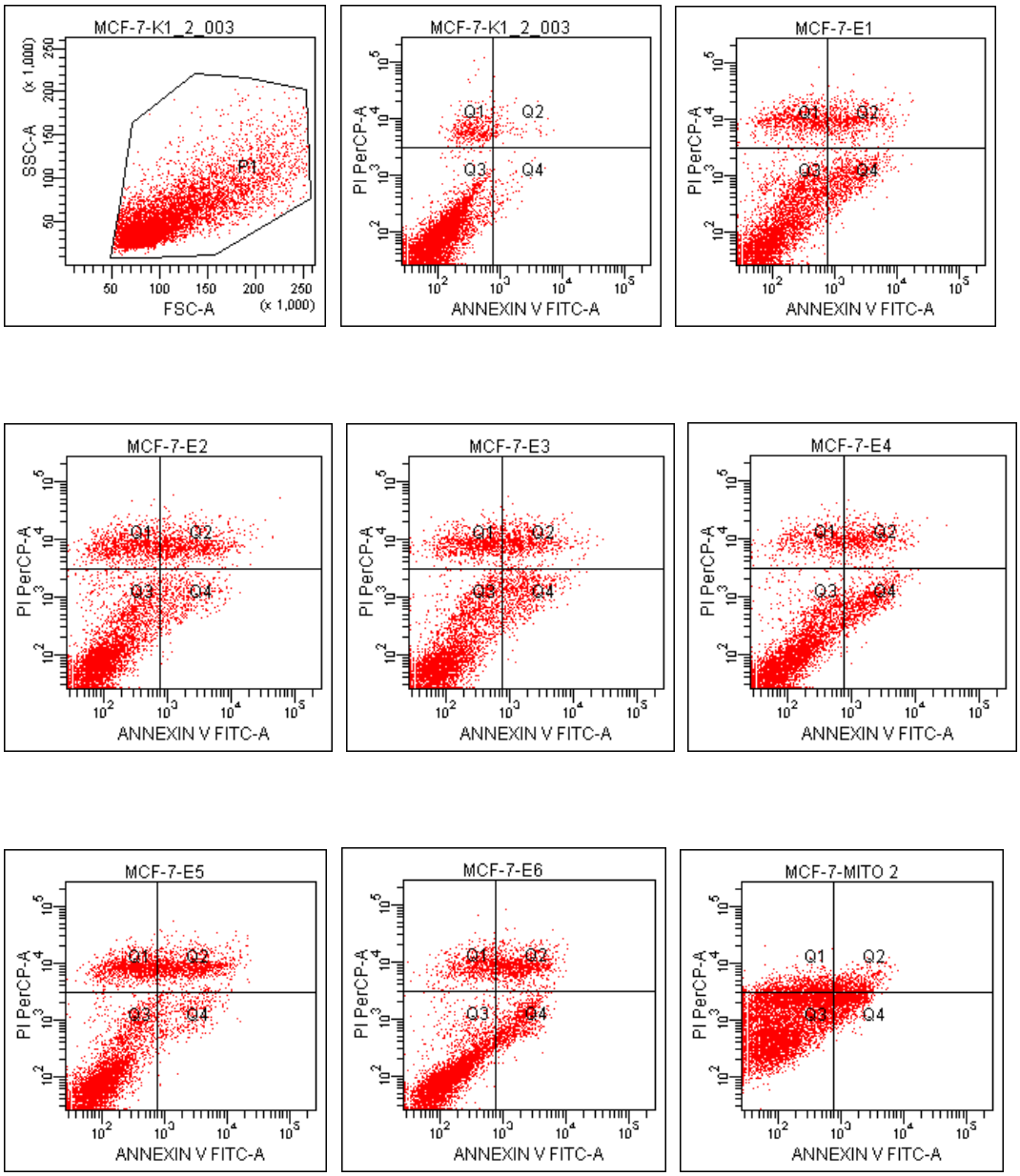

Figure 2. Typical quadrant analysis of Annexin V-FITC/propidium iodide flow cytometry of MCF-7 cells treated with subfractions and mitoxantrone

Control (a). MCF-7 cells were cultured for 24 hours in medium with IC_{50} value of each sample. At least 10.000 cells were analyzed per sample, and quadrant analysis was performed. The proportion (%) of cell number is shown in each quadrant. Q1, necrotic cells; Q2, late apoptotic cells; Q3, viable cells; Q4, early apoptotic cells. E1, water subfraction; E2, methanol:water (2:8, *v/v*) subfraction; E3, methanol:water (4:6, *v/v*) subfraction; E4, methanol:water (6:4, *v/v*) subfraction; E5, methanol:water (8:2, *v/v*) subfraction; E6, methanol subfraction; Mito, Mitoxantrone.

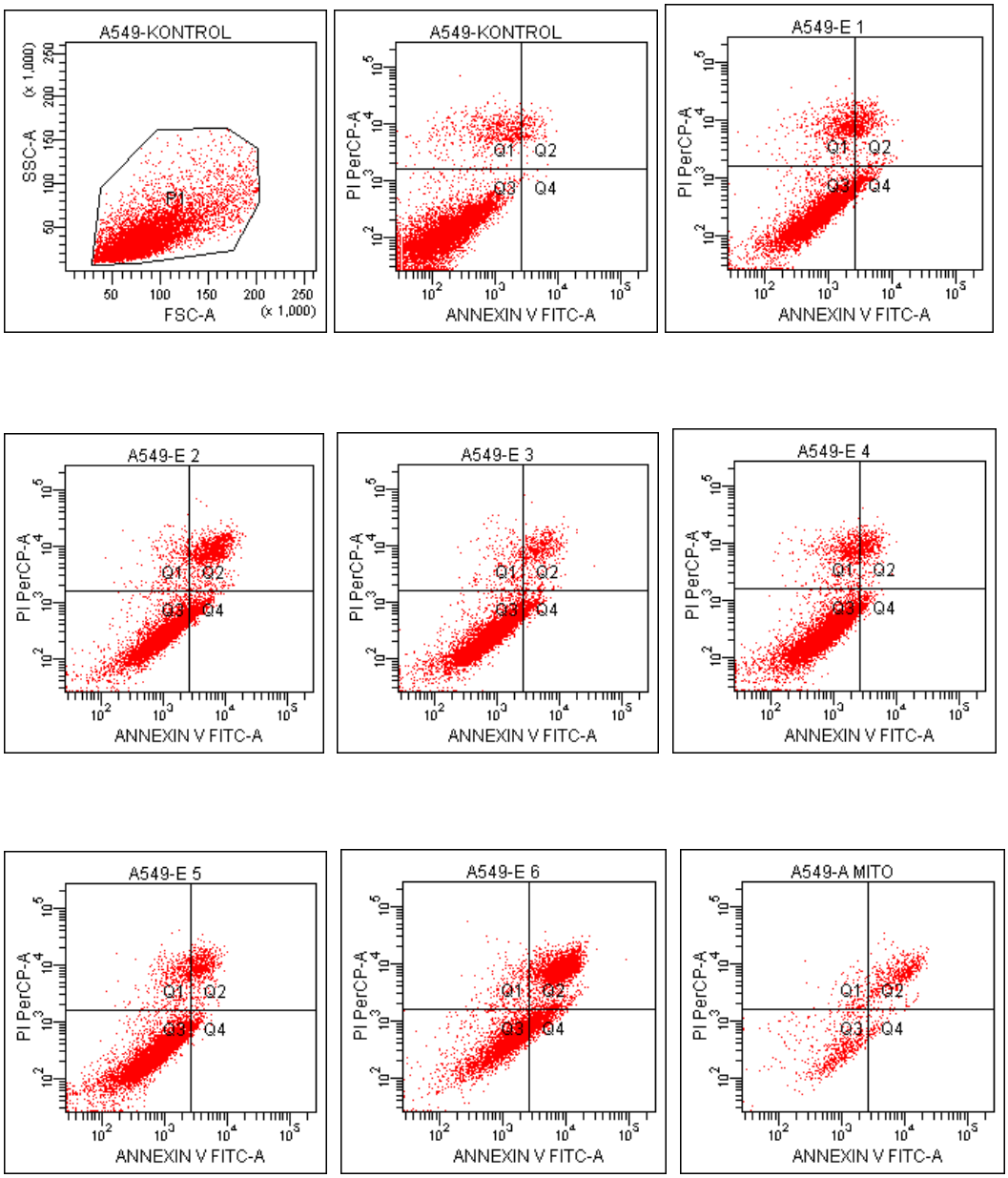

Figure 3. Typical quadrant analysis of Annexin V-FITC/propidium iodide flow cytometry of A549 cells treated with subfractions and mitoxantrone

Control (a). A549 cells were cultured for 24 hours in medium with IC_{50} value of each sample. At least 10.000 cells were analyzed per sample, and quadrant analysis was performed. The proportion (%) of cell number is shown in each quadrant. Q1, necrotic cells; Q2, late apoptotic cells; Q3, viable cells; Q4, early apoptotic cells. E1, water subfraction; E2, methanol:water (2:8, *v/v*) subfraction; E3, methanol:water (4:6, *v/v*) subfraction; E4, methanol:water (6:4, *v/v*) subfraction; E5, methanol:water (8:2, *v/v*) subfraction; E6, methanol subfraction; Mito, Mitoxantrone.

LC/MS-MS results

Compounds with their structures determined are classified according their compound main structures and given in Table 1.

Adenine (Vitamin B4). The compound with 135 molecular weight showed base peak at *m/z* 134 $[M-H]^-$ and deprotonated molecule appeared loss of 27 amu $[M-H-HCN]^-$. According to published data by [1, 2], this compound was identified as adenine which is a purine-derivative base of great significance for biochemistry of every organism as it forms DNA and RNA nucleotides. It often expresses cytokinin-like activity in plant development [3].

A benzoic acid derivative. This compound completely was not identified. It presented a molecular ion $[M-H]^-$ at *m/z* 187, yielded to *m/z* 125 $[M-H-44-18]^-$, *m/z* 169 $[M-H-18]^-$, *m/z* 143 $[M-H-44]^-$. In the literature, 1,3,5-trihydroxybenzene (floroglucinol) has a molecular ion $[M-H]^-$ at *m/z* 125 in negative ionization mode [4]. Also, *m/z* 169 and m/z 125 fragment ions may be associated with gallic acid [5]. For this, this compound may be identified as a benzoic acid derivative.

A hydroxybenzoic acid derivative. When spectrum of compound was determined, the molecular ion appeared $[M-H]^-$ at *m/z* 137. It was construed with a hydroxybenzoic acid derivative such as *p*-hydroxybenzoic acid, salicylic acid [6].

Dicaffeoyl-spermidine. This compound had a molecular ion $[M-H]^-$ at *m/z* 468 with the base peak at *m/z* 135, other fragments *m/z* 332 $[M-H-136]^-$, *m/z* 306 $[M-H-162]^-$, *m/z* 289, 261, 161. The polar extracts of *Phalaris canariensis* L. and *Triticum aestivum* L. have the same molecular ion and the fragment patterns, but the compound was not identified [6, 7]. Singh *et al*. [9] published that the compound was identified as N,N'-dicaffeoyl spermidine with a molecular ion $[M-H]^-$ at *m/z* 468 and other fragment ions *m/z* 307, 290, 233, 161. In a recent study, the fragment ions *m/z* 332, 306, 289 belonged to N,N-dicaffeoyl spermidine and these fragments were characteristic for the compound. These recent findings are matched with our results. Therefore, the compound was identified as N,N-dicaffeoyl spermidine [10, 11].

Dicoumaroyl-spermidine. In the spectrum, the molecular ion $[M-H]^-$ at *m/z* 436 and the base peak at *m/z* 119. Other fragments were *m/z* 316, 273, 231, 174 and 145. This compound was thought as one of hydroxycinnamic acid-spermidine conjugates. The base peak was *m/z* 436 $[M-H]^-$ and other fragments were *m/z* 316 $[M-H-119]^-$, *m/z* 290 $[M-H-145]^-$, *m/z* 272 $[M-H-163]^-$, *m/z* 145 and *m/z* 119 amu. These findings noticed that the compound might be N,N-dicoumaroyl spermidine [12]. Bienz *et al*. [13] identified N^1,N^6-dicoumaroyl putrescine, N^1,N^5-dicoumaroyl spermidine, N^1,N^{10}-dicoumaroyl spermidine in *Arum maculatum* samples. Also, hydroxycinnamoyl acid amide derivatives are significant secondary metabolites in inflorescence of Araceae species [14].

Diferuloyl-spermidine. A molecular ion at *m/z* 496 $[M-H]^-$ and the base peak at *m/z* 134 were detected in the spectrum. Other fragment ions were *m/z* 346, 331/330, 261, 204, 175, 149. The fragments at *m/z* 175, 149, 134 supported the –feruloyl moiety at the structure.

When compared the published data and molecular weight, this compound was thought to be as a diferuloyl spermidine [11, 26].

Caffeoyl-coumaroyl spermidine. This compound showed a molecular ion $[M-H]^-$ at *m/z* 452 with the base peak at *m/z* 135, other fragments *m/z* 332, 316, 306, 289, 231, 119 amu. The fragments at *m/z* 332 $[M-H-120]^-$, *m/z* 316 $[M-H-136]^-$, *m/z* 306 $[M-H-146]^-$ were noticeable in the spectrum. The fragment at *m/z* 306 might be associated with deprotonated glutathione, the loss of 120 and 146 amu indicated rhamnoside moiety. These findings in an article by [8] were not identified successfully. But, in recently published two articles indicated that the compound might be N-caffeoyl-N'-coumaroyl spermidine [11, 12, 15].

Coumaroyl-feruloyl spermidine. This compound was identified as coumaroyl-feruloyl spermidine which gave a molecular ion at *m/z* 466 $[M-H]^-$ and the base peak *m/z* 134, other fragments *m/z* 346, 316, 273, 149, 135, 133. The fragments at *m/z* 161 and 119 supported the coumaroyl moiety and the fragments at *m/z* 175, 149 and 134 indicated the feruloyl moiety in the structure. Our spectrum findings agreed with the published data by [11, 12, 15].

Apigenin-6,8-C-pentoside-hexoside. A molecular ion at *m/z* 563 $[M-H]^-$ and the base peak *m/z* 353 were appeared in the spectrum. Other fragment ions were *m/z* 503, 473, 443, 425, 383, 323, 311 and 297 amu. The *m/z* 353 ion indicated that the structure had an aglycone as apigenin and di-C-glucoside. The fragments at *m/z* 503 $[M-H-60]^-$, *m/z* 473 $[M-H-90]^-$, *m/z* 443 $[M-H-120]^-$ supported the loss of sugar moiety from a carbon glucoside. The fragment at *m/z* 425 $[M-H-120-18]^-$ observed the loss of water molecule from the *m/z* 443 ion. The carbon glucosides of flavones are generally formed at 6th and 8th carbons [16]. Ibrahim *et al*. [17] evaluated these findings as apigenin-6-C-pentoside-8-C-hexoside. Because of the absence of the standard, the positions of both pentoside and hexoside were not stated. Therefore, this compound was named as apigenin-6,8-C-pentoside-hexoside.

Puerarin. In the spectrum, the molecular ion peak was detected at *m/z* 415 $[M-H]^-$ and the base peak was at *m/z* 295, other fragment ion was at *m/z* 325. The fragment at *m/z* 295 obtained by the neutral loss of 120 amu indicated that the structure was a carbon glucoside. The neutral losses of 120, 90 and 60 amu are characteristic for carbon glucosides. Based on the published data, the compound was identified as puerarin that is known as daidzein-8-C-glucoside. In the spectrum the fragment patterns at *m/z* 267 and 253 of puerarin was not seen [18].

A flavonoid derivative. The compound presented a molecular ion at *m/z* 329 $[M-H]^-$ and the fragment ions were *m/z* 211, 229, 311, 293, 183. When the spectrum compared with published data, this compound was identified as tricin (3',5'-O-dimethyltricetin) by [19]. Tricin is known to play significant role on biosynthesis of flavonolignan by conjugation with monolignols. Also, tricin stored at underground parts of plants transfers to soil to act as herbicidal [19-21]. Generally, methyl losses from polimethoxy flavones are characteristic and the fragment ions as $[M-H-15]^-$, $[M-H-30]^-$ and $[M-H-30-28]^-$ are commonly seen in the spectrum. But these characteristic fragments were not detected in our spectrum. Mincsovics *et al*. [22]remarked the compound as a flavonoid derivative with the molecular ion at *m/z* 329

$[M-H]^-$ and the fragments at *m/z* 229, 211,193, 183 and 171. Therefore, this compound was thought as a flavonoid derivative.

Vitexin/Isovitexin. The compound presented a molecular ion at *m/z* 431 $[M-H]^-$ and the base peak at *m/z* 311 $[M-H-120]^-$. Other fragment was *m/z* 341 $[M-H-90]^-$. Sakalem *et al*. [23] identified these findings as vitexin. If the base peak is comprised by a neutral loss of 120 amu, it is thought to be a carbon glucoside of apigenin. The mono carbon glucosides of apigenin present a characteristic ion at *m/z* 311. It was obvious that the compound was an apigenin-C-glucoside. In the same time, the molecular weight and the fragment patterns of vitexin (apigenin-8-C-glucoside) are similar to isovitexin (apigenin-6-C-glucoside). The fragments at *m/z* 269 and *m/z* 283 increased the possibility of vitexin. But, the standard compound is an essential to certain identification. Vitexin was identified in the seeds of *Arum dioscoridis*, vitexin and isovitexin were identified in the leaves of *A. palaestinum* by different researchers [23-25].

Ferulic acid. The compound with a molecular ion at *m/z* 193 $[M-H]^-$ and other fragments *m/z* 178, 149 and 134 was identified as ferulic acid. Ferulic acid was identified in the polar extract of *Arum italicum* tubers and *A. palaestinum* leaves. Also, it was found in some Araceae plants as *Pinella ternata* fresh rhizomes and *Acorus calamus* rhizomes [25-28].

Caffeic acid. A molecular ion at *m/z* 179 $[M-H]^-$ and the base peak observed by losing of carboxylic acid (44 amu) at *m/z* 135 $[M-H-44]^-$ were detected at the spectrum. The compound was identified as caffeic acid [29]. Caffeic acid was identified in the extracts of *Arum palaestinum* leaves [25, 30].

Caffeic acid hexoside. The compound presented a molecular ion at *m/z* 341 $[M-H]^-$ and the base peak at *m/z* 179 $[M-H-162]^-$. The fragments ions at *m/z* 179 [caffeic acid-H]$^-$, 161 [caffeic acid-H-H_2O]$^-$ and 135 [caffeic acid-H-CO_2]$^-$ were characteristic to caffeic acid. It is noticed that the loss of 162 amu shows caffeic acid hexoside [31-33]. Caffeic acid hexoside was identified in polar extracts of *Arum palaestinum* leaves [25].

A caffeic acid derivative. A molecular ion at *m/z* 357 $[M-H]^-$ and the ions at *m/z* 177 and 133 were detected in the spectrum. Not only the ion at *m/z* 133 was seen but also *m/z* 135 peak was appeared in the spectrum. The fragment at *m/z* 179 was next to the fragment at *m/z* 177. *m/z* 133 might be consisted of the loss of 44 amu from *m/z* 177 ion. This relation might be happened between *m/z* 179 and *m/z* 135. It is thought to be carboxyl moiety at phenolic structure. *m/z* 179 and *m/z* 135 fragment ions indicated that the compound contained caffeic acid. When noticed the molecular weight (MW 358), this compound is thought to be occurred by dimerization of caffeic acid [34]. This compound was not identified exactly, but it was identified as a caffeic acid derivative.

***p*-Coumaric acid**. This compound was identified as *p*-coumaric acid with the molecular ion at *m/z* 163 $[M-H]^-$ and the base peak at *m/z* 119 $[M-H-44]^-$. *p*-Coumaric acid was identified in the seeds of *Arum dioscoridis* [24].

A disaccharide derivative. The molecular ion at *m/z* 341 $[M-H]^-$ and the base peak at *m/z* 179 $[M-H-162]^-$ were detected. The base peak might be occurred by the neutral loss of hexose (-162 amu) such as glucose, galactose, fructose. The other fragments at *m/z* 143, 119 and 131 supported to losses of H_20 and $-CH_2O$ moieties from hexose. This compound was not UV detectable at 280 nm but this compound was well ionized at our system. Due to the spectrum data, this compound was identified as a disaccharide such as sucrose, maltose [13, 35]. Disaccharide derivatives were identified in *Arum maculatum* tubers and *A. palaestinum* leaves [25, 36].

Pinoresinol. The molecular ion at *m/z* 357 $[M-H]^-$ and other fragments at *m/z* 151, 136 and 342. In published data, this compound was fully matched with the spectrum of pinoresinol standard [37, 38]. Previous studies reported that lignans and glucoside forms were identified in *Arum italicum* tubers.

Hydroxypinoresinol. The compound presented a molecular ion at *m/z* 373 $[M-H]^-$ and a base peak at *m/z* 163. The other fragments were detected at *m/z* 343, 313, 298, 188, 175, 166, 147, 136, 108. The fragments at *m/z* 343 and 313 indicated that the loss of $–CH_2O$ moieties (30 amu) from the structure. Also, the fragment ions at *m/z* 298 and 285 were comprised by one -methyl and one -carbonyl moieties. These characteristic fragmentation patterns might be originated from hydroxypinoresinol [39, 40].

Lariciresinol glucoside. The compound had a molecular ion at *m/z* 521 $[M-H]^-$ and a base peak at *m/z* 329. Other fragments were *m/z* 359 and 299. When spectrum evaluated at first, this compound was thought to be isoiridin. Wang *et al*. [41] reported the fragments of isoiridin at *m/z* 521 $[M-H]^-$, *m/z* 359 $[M-H\text{-glucose}]^-$, *m/z* 344 $[M-H\text{-glucose-methyl}]^-$ and *m/z* 329 $[M-H\text{-glucose-methyl-methyl}]^-$. But, *m/z* 344 ion was not detected in our spectrum. Eyles *et al*. [37] published that the molecular ion at *m/z* 521 $[M-H]^-$ and the other ions *m/z* 329 $[M-H-162-CH_2O]^-$ and *m/z* 359 $[M-H-162]^-$ belonging to lariciresinol glucoside. The same findings by Huis *et al*. [42] were positively related with lariciresinol glucoside. So, the compound was identified as lariciresinol glucoside. In *Arum italicum* tubers, lariciresinol-4-O-β-glucopyranoside was identified by [26].

A furofuranolignan derivative. The compound showed the molecular ion at *m/z* 343 $[M-H]^-$ as the most intense ion. The other ions were *m/z* 325, 313, 297, 191, 177, 151 and 136. The fragments at *m/z* 325 and 313 might be occurred by the losses of water and methoxy/dimethyl groups. *m/z* 151 and 136 ions were noticeable in the spectrum. *m/z* 151 and 136 exhibit much higher intensities among fragmentation patterns of furafuranolignans. According to previous study by [43] obtained spectrum was similar to pinoresinol spectrum. This compound might be dimethyl derivative of pinoresinol with high possibility. But, the identification of the compound was not done completely. So, it was named as a furofuranolignan derivative.

Coniferyl alcohol. The molecular ion at *m/z* 179 $[M-H]^-$, the ions *m/z* 164 $[M-H-15]^-$, *m/z* 146 $[M-H-15-18]^-$ and *m/z* 135 were detected. This data was good related with coniferyl alcohol in a published article by [44]. Coniferyl alcohol glucoside was identified in *Arum italicum* tubers [26].

Coniferyl alcohol (8-5) ferulic acid. The compound presented a molecular ion at *m/z* 371 $[M-H]^-$ and the other fragments at *m/z* 353, 341, 309, 297, 277, 235, 206, 191 and 148. Due to the spectrum data and previous studies, this compound might be a (8-5) cross-bonded conjugation between coniferyl alcohol and ferulic acid. The fragment ions at *m/z* 353 $[M-H-18]^-$ and 341 $[M-H-30]^-$ might be occurred by loss of water and formaldehyde molecules from the conjugation [42, 45].

9-hydroperoxy-octadecenoic acid. The molecular ion at *m/z* 313 $[M-H]^-$ and the other fragments at *m/z* 295 $[M-H-18]^-$ and 251 $[M-H-18-44]^-$ were detected in the spectrum. The loss of water molecule and then loss of carboxyl moiety indicated that hydroperoxy-octadecenoic acid derivative. The ion at *m/z* 251 supported the identification of the compound as 9-hydroperoxy-octadecenoic acid [46].

9-oxo-octadecadienoic acid. The compound gave a molecular ion at *m/z* 293 $[M-H]^-$ and other fragments at *m/z* 249 $[M-CO_2-H]^-$, 236, 197 and 185. This data was similar to 9-oxo-octadecadienoic acid in which published by [47].

15,16-dihydroxy-9,12-octadecadienoic acid. The highest intensity was exhibited by *m/z* 311 $[M-H]^-$ ion was molecular ion and the second intense peak belonged to the *m/z* 223. Other fragments were *m/z* 293, 275, 255 and 183. In published data by [48], 15,16-dihydroxy-9,12-octadecadienoic acid had a molecular weight of 312 and it gave *m/z* 223 and 183 fragment patterns in negative ionization mode. Due to the high similarity between our finding and published spectrum, this compound was identified as 15,16-dihydroxy-9,12-octadecadienoic acid.

Hydroperoxy-octadecenoic acid isomer. The compound had a molecular ion at *m/z* 313 $[M-H]^-$ and a base peak at *m/z* 171. Two fragment ions at *m/z* 201 and 127 had as high intensity as the base peak. According to Oliw *et al*. [46], this compound was named as hydroperoxy-octadecenoic acid isomer.

Oxo-dihydroxy-octadecenoic acid isomer. The compound presented a molecular ion at *m/z* 327 $[M-H]^-$ and other fragments at *m/z* 309 $[M-H-18]^-$, 291 $[M-H-18-18]^-$, 239 $[M-H-88]^-$, 229, 211, 171, 163, 149 amu. Abu-Reidah *et al*. [25] did not identify a compound that had the same spectrum in *Arum palaestinum* leaves. But, Llorent-Martinez *et al*. [49] reported that oxo-dihydroxy-octadecenoic acid gave the fragment patterns at *m/z* 327, 291/292, 229, 211, 171, 209, 165 in negative ionization mode. Based on this published data, this compound might be identified as oxo-dihydroxy-octadecenoic acid isomer.

Trihydroxy-octadecadienoic acid. The fragment patterns were matched with 9,12,13-trihydroxy-octadecadienoic acid published in the article by [45]. The fragment ions at *m/z* 211, 201 and 199 seen in the spectrum may be related with the closely stated of hydroxyl groups. Also, the fragments at *m/z* 229 and *m/z* 171 indicate the positions of hydroxyl groups of fatty acids (that means at 12 and/or 13, 9 and/or 10th carbon). According our limited data, it was not easy to assigned the functional groups and double bonds [50]. Therefore, this compound was identified as trihydroxy-octadecadienoic acid. Some of polyunsaturated fatty acids were identified in *Arum palaestinum* leaves [25].

Trihydroxy-octadecadienoic acid isomer. This compound had the same molecular weight of trihydroxy-octadecadienoic acid and it gave very similar fragment patterns. But this compound had different retention time in the chromatogram. In the mass spectrum, the fragment at *m/z* 211 exhibited more intensity than *m/z* 229 ion and the fragment at *m/z* 183 exhibited more intensity than *m/z* 171 ion while compared with the data of trihydroxy-octadecadienoic acid. So, this compound was identified as trihydroxy-octadecadienoic acid isomer [50].

Trihidroxy-octadecenoic acid. The molecular ion at *m/z* 329 $[M-H]^-$ and the base peak at *m/z* 211 were detected in the spectrum. The other fragments were *m/z* 311, 293, 241, 229, 199, 183, 171, 155, 127. Our findings were well related with the data of trihidroxy-octadecenoic acid published by [49]. Aghofack-Nguemezi *et al*. [51] gave the fragment patterns as *m/z* 329, 311, 293, 229, 211, 193, 171, 125 and 99 for trihidroxy-octadecenoic acid. Due to the high similarity between these published data and our findings, this compound was identified as trihidroxy-octadecenoic acid. Abu-Reidah *et al*. [25] was identified trihydroxy-10-octadecenoic acid in the leaves of *Arum palaestinum*.

Trihidroxy-octadecenoic acid isomer 1. The compound had the same molecular weight (MW 330) and the spectrum was highly similar to trihydroxy-octadecenoic acid. But the retention time was different. Therefore, this compound was identified as trihydroxy-octadecenoic acid isomer 1.

Trihidroxy-octadecenoic acid isomer 2. This compound was identified as trihydroxy-octadecenoic acid isomer 2 because of the same molecular weight (MW 330) and the high similarity of spectrum of trihydroxy-octadecenoic acid isomer 1.

10-methoxydihydrofuscin. The deprotonated molecule *m/z* 307 $[M-H]^-$ gave the base peak at *m/z* 263 $[M-H-44]^-$ by the loss of carboxyl group. The fragment ion at *m/z* 233 $[M-H-44-30]^-$ was occurred by the loss of dimethyl from the molecule. This compound is named as 10-methoxydihydrofuscin and it was isolated from a soil fungus known as *Oidiodendron griseum* [52]. Our material, *Arum italicum* tubers, was collected from underground and the soil was removed with a brush. The cleaned tubers without removing cortex were sliced and dried. Therefore, this compound might be biosynthesized in the fungus.

Dihydrocapsiate. The compound presented a molecular ion at *m/z* 307 $[M-H]^-$ and a base peak at *m/z* 185. The other fragments were at *m/z* 235, 223, 209, 197, 289, 191 and 163. According to a published data, this compound was highly matched with dihydrocapsiate (vanillyl-8-methylnonanate) which was identified in *Arum palaestinum* leaves [25].

Glycerophosphoinositol. The deprotonated molecule was detected at *m/z* 333.The most abundant fragment (*m/z* = 153) corresponds to the loss of the inositol group from the molecule. The ion at *m/z* 241 was characteristic of the phosphoinositol moiety. So, this compound was identified as glycerophosphoinositol [53, 54].

***L*-Malic acid**. The molecular ion at *m/z* 133 $[M-H]^-$ and the fragment ion at *m/z* 115 $[M-H-18]^-$ by the loss of the water molecule were characteristics for *L*-malic acid. Malic acid was identified in *Arum palaestinum* leaves [25, 55].

A Methyl-4-chromanone derivative. The protonated molecule (*m/z* 161) gave fragment patterns at *m/z* 146 and 119. These fragments indicated the chromanone derivatives. Ravi *et al*. [56] isolated a strong cytotoxic compound named as 6-methyl-4-chromanone in the methanol extracts of *Aegle marmelos* Correa roots. The obtained mass spectrum was highly matched with this compound, but the position of methyl may be at 6-, 7-, or 8th carbon. Therefore, this compound was identified as a methyl-4-chromanone derivative.

Paxanthone. The compound gave a deprotonated molecule at *m/z* 339 $[M-H]^-$ and a base peak at *m/z* 324 $[M-H-15]^-$ by the loss of the methyl group. The other fragments were detected at m/z 307 $[M-H-32]^-$, *m/z* 292, 263, 251, 161 and 145 amu. Tusevski *et al*. [57] reported the spectrum data as *m/z* 339 (molecular ion), *m/z* 324 (base peak), *m/z* 307 amu for paxanthone. Because of the high similarity, this compound was identified as paxanthone.

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Table 1. Identified compounds in *Arum italicum* subfractions.

Compound	Molecular weight	$[M-H]^-$	Fragments	Subfraction
Purin base				
Adenine	135 ($C_5H_5N_5$)	134	134*, 107	E1
Benzoic acid derivatives				
A hidroxybenzoic acid derivative	138	137	137*	E3
A benzoic acid derivative	188	187	125*, 169, 143	E2, E3
Hydroxycinnamic acid- Spermidine conjugates				
Dicaffeoyl spermidine	469 ($C_{25}H_{31}N_3O_6$)	468	135*, 332, 306, 289, 261, 161	E2, E3, E4
Dicoumaroyl spermidine	437 ($C_{25}H_{31}N_3O_4$)	436	436*, 316, 290, 272, 145, 135, 119	E1-E6
Diferuloyl spermidine	497 ($C_{27}H_{35}N_3O_6$)	496	134*, 480, 346, 330, 304, 204, 149	E2
Caffeoyl-coumaroyl spermidine	453 ($C_{25}H_{31}N_3O_5$)	452	135*, 332, 316, 306, 289, 273, 261, 161, 145, 119	E2
Coumaroyl-feruloyl spermidine	467 ($C_{26}H_{33}N_3O_5$)	466	134*, 346, 316, 273, 149, 133	E2
Flavone glucosides				
Apigenin-6,8-C-pentoside-hexoside	564 ($C_{26}H_{28}O_{14}$)	563	353*, 473, 443, 383, 323, 311, 297	E1-E4
Puerarin	416 ($C_{21}H_{20}O_9$)	415	295*, 325	E1

A flavonoid derivative	330	329	329*, 311, 293, 211, 229, 183	E3-E5
Vitexin/isovitexin	432 ($C_{21}H_{20}O_{10}$)	431	311*, 341	E3
Hydroxycinnamic acid derivatives				
Ferulic acid	194 ($C_{10}H_{10}O_4$)	193	134*, 178, 149, 121	E1-E4
Caffeic acid	180 ($C_9H_8O_4$)	179	135*, 107	E1, E2
Caffeic acid hexoside	342 ($C_{15}H_{18}O_9$)	341	179*, 135	E1
A caffeic acid derivative	358	357	357*, 177, 133	E4
p-Coumaric acid	164 ($C_9H_8O_3$)	163	119*	E1-E3
Carbohydrates				
A disaccharide derivative	342	341	179*, 161, 149, 143, 119, 113	E1, E2
Lignan and glucosides				
Pinoresinol	358 ($C_{20}H_{22}O_6$)	357	357*, 342, 151, 136	E3
Hydroxypinoresinol	374 ($C_{20}H_{22}O_7$)	373	163*, 343, 313, 298, 188, 175, 166, 147, 136, 108	E2-E4
Lariciresinol glucoside	522 ($C_{26}H_{34}O_{11}$)	329	329*, 359, 299	E1-E3
A furofuranolignan derivative	344	343	343*, 325, 313, 297, 191, 177, 151, 136	E2, E3
Monolignol/Dilignol derivatives				

Coniferyl alcohol	180 ($C_{10}H_{12}O_3$)	179	179*, 164, 146, 135	E3
Coniferyl alcohol (8-5) ferulic acid	372 ($C_{20}H_{20}O_7$)	371	371*, 353, 341, 309, 297, 191	E2
Oxylipins				
9-Hydroperoxy-octadecenoic acid	314 ($C_{18}H_{34}O_4$)	313	313*, 295, 251	E6
9-Oxo-octadecadienoic acid	294 ($C_{18}H_{30}O_3$)	293	293*, 249, 236, 197, 185	E6
15,16-Dihydroxy-9,12-octadecadienoic acid	312 ($C_{18}H_{32}O_4$)	311	311*, 293, 275, 255, 223, 183	E5, E6
Hydroperoxy-octadecenoic acid isomer	314 ($C_{18}H_{34}O_4$)	313	171*, 201, 127	E5
Oxo-dihydroxy-octadecenoic acid isomer	328 ($C_{18}H_{32}O_5$)	327	327*, 309, 291, 239, 229, 211, 171, 163, 149	E2, E4
Trihydroxy-octadecadienoic acid	328 ($C_{18}H_{32}O_5$)	327	327*, 309, 291, 273, 239, 229, 221, 211, 177, 171	E2-E5
Trihydroxy-octadecadienoic acid isomer	328 ($C_{18}H_{32}O_5$)	327	327*, 309, 291, 273, 239, 229, 221, 211, 183, 171	E2, E3
Trihydroxy-octadecenoic acid	330 ($C_{18}H_{34}O_5$)	329	211*, 311, 293, 241, 199, 183, 171, 155, 127	E4
Trihydroxy-octadecenoic acid isomer (1)	330 ($C_{18}H_{34}O_5$)	329	211*, 311, 293, 201, 171	E4, E5
Trihydroxy-	330	329	329*, 311, 293, 199,	E5

octadecenoic acid isomer (2)	($C_{18}H_{34}O_5$)		171	
Miscellaneous				
10-Methoxydihydrofuscine	308 ($C_{16}H_{20}O_6$)	307	263*, 233	E2-E4
Dihydrocapsiate	308 ($C_{18}H_{28}O_4$)	307	185*, 235, 223, 209, 197, 289, 191, 163	E3
Glycerophosphoinositol	334 ($C_9H_{19}O_{11}P$)	333	133*, 241, 171, 153	E5
L-Malic acid	134 ($C_4H_6O_5$)	133	133*, 115	E3
Methyl-4-chromanone	162 ($C_{10}H_{10}O_2$)	161	161*, 146, 119	E2-E4
Paxanthone	340 ($C_{19}H_{16}O_6$)	339	324*, 307, 292, 263, 251, 161, 145	E2