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Alkylresorcinols and fatty acids in primitive wheat populations of Italian and Black sea region countries origin

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ABSTRACT

Alkylresorcinols, fatty acid content, and antioxidant activity were analysed in *Triticum monococcum, T. dicoccum, T. timopheevi*, *T. palaeo-colchicum* and *T. macha* accessions from Turkey, Georgia, Armenia, Bulgaria and Italy, also including modern durum wheat (*T. durum*) and bread wheat (*T. aestivum*) varieties as controls, grown in a common environment. Total alkylresorcinol content ranged between 478.3 and 1153.9 mg kg^{-1} dm, with the highest contents detected in *T. aestivum*, *T. macha* and some *T. monococcum* accessions. All alkylresorcinol homologues effectively contributed at genotype discrimination. Hexaploid wheats showed higher A19 (23.3–27.5%) and lower A23 (14.0–15.9%) and A25 (4.3–8.1%) relative contents, with respect to other species. C18:2 (50.4–62.3%), C18:1 (14.5–25.8%) and C16 (13.3–16.7%) were the most abundant fatty acid compounds in all accessions. PUFA/MUFA, C18:1/C16 and C18:1/C18:2 ratios significantly differed among genotypes, with special respect to *T. monococcum*, *T. aestivum* and *T. macha*. Significant differences were also observed for protein and total phenolic content, and antioxidant activity. The data indicate that some genotypes could represent interesting sources of specific compounds, with a potential use either as promising material for the selection of improved varieties or raw materials to manufacture foods with naturally enhanced content of health promoting compounds.

1. Introduction

The term "primitive wheats" is currently used to indicate *Triticum* species, populations or local varieties neglected by modern breeding or selection programs, retaining therefore traits not suitable to modern growing systems, such as individual variability, low harvest index and, in some cases, hulled kernels.

Primitive wheats survived as relict crops in marginal areas for the production of both traditional human food or animal feed, generally declining, often facing the risk of extinction. However, consumers' interest for these species raised in recent years, as a reaction to standardised industrial products, and a developing identification of primitive wheats with environmental friendly crops or putative health beneficial products. As a consequence, some species and old varieties have been recovered as interesting niche products.

Among hulled species, einkorn (*Triticum monococcum* L. subsp. *monococcum*) and emmer wheat (*T. turgidum* L. subsp. *dicoccum* (Schrank ex Shubler) Thell) are traditional crops in several south European and Black sea area countries. Other minor species, such as *T. timopheevi* (Zhuk). Zhuk, *T. turgidum L. subsp. palaeocolchicum* (Menabde) Á. Löve & D. Löve and *T. aestivum* L. *subsp. macha* (Dekapr. & Menabde) McKey are still grown in the Caucasian area.

Available literature does not seem to support the widespread common belief that primitive wheats are richer sources of bioactive compounds than modern cultivars (Giambanelli et al., 2013; Shewry and Hey, 2015). Previous studies were mainly focused at evaluating tocol, carotenoid, sterol and phenolic contents of *Triticum* species (Abdel-Aal and Rabalski, 2008; Hidalgo et al., 2006; Pelillo et al., 2003; Serpen et al., 2008). Einkorn and durum wheat cultivars has been characterised by their higher carotenoid content, mainly represented by lutein (Giambanelli et al., 2013; Lachman et al., 2013; Serpen et al., 2008).

Tocopherols and tocotrienols are differently distributed in the caryopses, with α- and β-tocotrienol prevailing in the endosperm and α- and β-tocopherol in the germ (Hidalgo and Brandolini, 2008).

Relative phytosterol amount is species dependent, and is likely associated to ploidy level (Giambanelli et al., 2013; Iafelice et al., 2009).

Phenolic compounds are present as free and bound fractions, the latter generally being the most abundant. Emmer wheat has been recognised as a richer source of phenolics than einkorn wheat (Serpen et al., 2008), whereas hexaploid species were reported as higher phenolic sources by Giambanelli et al., 2013. Among phenolics lignans are

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of increasing interest for their potential anticarcinogenic activity; high contents of this class of phytochemicals were detected in wheat bran (Smeds et al., 2007). Dinelli et al. (2007) highlighted a higher lignan content, and peculiar composition in old wheat cultivars, in comparison to modern varieties.

Alkylresorcinols are a specific class of phenolic compounds, mainly located in the bran part of the caryopses, in particular wheat and rye (Gunenc et al., 2013; Giambanelli et al., 2018), and have been indicated as potential markers of whole grain intake. These compounds have been studied for their antioxidant, antimicrobial and antifungal activities, and their effects on biological membranes due to their amphiphilic nature (Kozubek and Demel, 1981; Ross et al., 2004b). These phytochemicals are resorcinolic lipids including very simple homologues of the orcinol-type (1,3-dihydroxy-5-methylbenzene) phenols and a variety of homologues with a dual character, aromatic and acylic. They are synthesised by the addition of an alk(en)yl chain of different length (i.e., C15:0, C17:0, C19:0, C21:0, C23:0, C25:0) to position 5 of 1,3-dihydroxybenzene (Andersson et al., 2008). Their biosynthesis takes place in the cells, via the polyketide pathway, generating polyketomethylenic chains $-(CH_2\text{-}CO)_n$-. A similar pathway is observed for fatty acid biosynthesis, which linear chains are also built by the addition of C_2 units (Kozubek and Tyman, 1999). Fatty acids are indeed considered as alkylresorcinol biosynthetis precursors. Alkylresorcinols are likely synthesised by chain elongation, as reported by Fate and Lynn (1996), or by the attachment of preformed fatty acids to 1,3-dihydroxybenzene (Suzuki et al., 1997).

Several fatty acids have been identified in *Triticum* species. Hidalgo et al. (2009) isolated 14 fatty acids in *T. monococcum*, with linoleic (C18:2), oleic (C18:1) and palmitic (C16:0) acids being the most abundant.

Alkylresorcinol and fatty acid composition have been used to discriminate *Triticum* species. Armanino et al. (2002) used fatty acids to compare *T. durum* and *T. aestivum*, whereas Suchowilska et al. (2009) discriminated *T. monococcum*, *T. dicoccum* and *T. spelta* accessions. Other works further explored the variations of this class of compounds and the role played by the genetic factors in *Triticum* species (Bellato et al., 2013; Ciccoritti et al., 2013).

The BaSeFood project (Sustainable exploitation of bioactive components from the Black sea area traditional foods), was aimed at documenting and exploring the current uses and perspective potential health promoting traits of traditional local foods (D'Antuono, 2013). The project represented an excellent occasion to have access to otherwise neglected resources of local food species. Among these, primitive wheat genotypes were still grown in several countries of the area, from Italy to the Caucasus. In some cases *T. monococcum* or *T. dicoccum* still represented staples in local growing and food systems; in other contexts, these crops started to be re-considered, as specialist nice crops, as it happened in western countries since few decades ago.

In the perspective of the evaluation and potential valorisation of otherwise neglected plant material, this research was mainly aimed at the comparison of several primitive species, from different countries. Seed samples from Armenia, Bulgaria, Georgia, Italy and Turkey, with a prevalence of emmer and einkorn wheat, were collected on site, and planted in an experimental trial in Italy, in comparison with control modern bread, durum, einkorn and emmer wheat varieties. Harvested seeds were characterised for several analytical traits, among which alkylresorcinol, total phenolic, fatty acid, protein content, and antioxidant activity of the alkylresorcinol extracts represent the subject of this contribution.

2. Materials and methods

2.1. Chemicals

All chemicals and solvents were of analytical grade and were purchased from Sigma-Aldrich (St. Louis, MO, USA). Deionised water was obtained by an Elix 10 water purification system from Millipore (Bedford, MA, USA). Standards of methyl behenate, gallic acid, trolox, Folin-Ciocalteu reagent, 2,2-diphenyl-1-picrylhydrazyl (DPPH), 2,2′-azino-bis-(3-ethylbenzthiazoline-6-sulfonic acid) (ABTS) and sylilation reagents (pyridine, hexamethyldisilazane, trimethylchlorosylane) were from Sigma-Aldrich. Tablets for Kjeldahl analysis were bought from Kjeltabs ST, Thompson & Capper LTD (Cheshire, UK).

Table 1
List of the primitive wheats and control accessions included in the experiment.

tag	species	type	origin (location)
mG1	*Triticum monococcum*[1]	s, p	Georgia, Elkana collection[4]
mT2	*Triticum monococcum*[1]	s, p	Turkey (Ishangazı)
mT3	*Triticum monococcum*[1]	s, p	Turkey (Katalyazi Koyu)
mI4	*Triticum monococcum* cv. Monlis[1]	s, v	Italy, selected variety
eG1	*Triticum dicoccum*[2]	s, p	Georgia, Elkana collection[4]
eT2	*Triticum dicoccum* [2]	s, p	Turkey (Ishangazı)
eT3	*Triticum dicoccum* [2]	s, p	Turkey (Katalyazi Koyu)
eI4	*Triticum dicoccum* [2]	w, p	Italy (Leonessa)
eI5	*Triticum dicoccum* [2]	s, p	Italy (Leonessa)
eI6	*Triticum dicoccum* [2]	s, p	Italy (Monteleone di Spoleto)
eI7	*Triticum dicoccum* cv. Zefiro[2]	w, v	Italy, selected variety
eI8	*Triticum dicoccum* cv. Rosso rubino[2]	s, v	Italy, selected variety
eI9	*Triticum dicoccum*[2]	w, p	Italy (Garfagnana)
eA10	*Triticum dicoccum*[2]	s, p	Armenia (Fantan)
eA11	*Triticum dicoccum*[2]	s, p	Armenia (Fantan)
eA12	*Triticum dicoccum*[2]	s, p	Armenia (Vayotz Dzor)
eA13	*Triticum dicoccum*[2]	s, p	Armenia (Rubik)
eB14	*Triticum dicoccum*[2]	s, p	Bulgaria (Beden)
tG	*Triticum timopheevi* var. *rubiginosum* Eritz[2]	s, p	Georgia, Elkana collection[4]
pG	*Triticum palaeo-colchicum* Men[2]	w, p	Georgia, Elkana collection[4]
dG1	*Triticum durum* var. *leucurum* Al. Desf. [2]	w, p	Georgia, Elkana collection[4]
dG2	*Triticum durum* var. *leucurum* Al. Desf. [2]	w, p	Georgia, Elkana collection[4]
dG3	*Triticum durum* var. *apulicum* Koern[2]	s, p	Georgia, Elkana collection[4]
dC4	*Triticum durum* cv. Yelodur[2]	s, v	commercial variety
dC5	*Triticum durum* cv. Miradoux[2]	s, v	commercial variety
hG	*Triticum macha* Dek et Mer Makha[3]	s, p	Georgia, Elkana collection[4]
aC1	*Triticum aestivum* cv. Kalango[3]	w, v	commercial variety
aC2	*Triticum aestivum* cv. Nogal[3]	w, v	commercial variety

m: *T. monococcum*; e: *T. dicoccum*; t: *T. timopheevi*; p: *T. palaeo-colchicum*; d: *T. durum*; h: *T. macha*; a: *T. aestivum*.
G: Georgia; T: Turkey; I: Italy; A: Armenia; B: Bulgaria; C: Commercial.
s: spring variety; w: winter variety.
v: selected variety; p: local landrace.
[1] diploid; [2] tetraploid; [3] hexaploid;[4] all the subspecies attribution of the material from the Elkana collection is as received by suppliers.

2.2. Seed samples

The samples used in this study have been previously described in Giambanelli et al. (2013). Briefly a total of 23 *T. monococcum*, *T. dicoccum*, *T. palaeo-colchicum*, *T. timopheevi* and *T. macha* accessions from Armenia, Bulgaria, Georgia, Italy and Turkey were considered and compared, also including 4 commercial durum and bread wheat varieties (Table 1).

The seeds of local populations and landraces were obtained on place from local farmers, whereas the seeds of control bread, durum and recently selected emmer and einkorn wheat varieties were purchased in Italy.

The analytical samples were subsequently obtained from a field experiment planted in the experimental farm of the University of Bologna (Cadriano, Italy; 44° 33′ N, 11° 21′ E, 32 m a.s.l.). Sowing took place on two dates, to discriminate between winter and spring habit populations: late fall (15 December), and spring (18 March). A 3-replication split-plot experimental scheme, with sowing dates in the main plots and genotypes in the sub plots was adopted. Harvest was carried