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The effect of ripening on the polyphenol profile of commonly consumed varieties of date palm fruits

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Various lines of epidemiological evidence have indicated an inverse association between fruit and vegetable intake and chronic diseases such as cancer⁽¹⁾. With regard to colon cancer, polyphenols have been shown to interfere with cancer cell signalling, to induce apoptosis and inhibit the proliferation of cancer cells⁽²⁾ and to modify the microbiota in a beneficial way⁽³⁾. Date Palm Fruit (*Pheonix dactylifera*) is a rich source of polyphenols, although the precise polyphenol content is likely to be influenced by fruit ripening. The aim of the present study was to examine different cultivars of date fruits (Ajwa, Barni and Khalas), harvested at the main ripening stages (*kimri*, *khalal*, *Rutab*, *tamr*) for polyphenol content and profile using HPLC-diode array detection and LC-MS/MS. In all cultivars there was a significant reduction ($P < 0.001$) in the total polyphenol content (as assessed by the Folin–Ciocalteu method) during ripening [*kimri* > *khalal* > *rutab* > *tamr*]: Ajwa: $148.3 \pm 11 > 47.5 \pm 3.5 > 22 \pm 9.8 > 18.4 \pm 2.1$; Barni: $120 \pm 13.4 > 27 \pm 7.7 > 21 \pm 7.3 > 20 \pm 7.7$; Khalas: $94 \pm 6.3 > 30 \pm 4.2 > 19 \pm 9.8 > 19 \pm 5.6$ mg GAE/100 g of fresh weight. These data were supported by a similar reduction in the antioxidant activity (ferric-reducing antioxidant potential) attributable to each ripening stage: Ajwa: $829 \pm 10 > 347 \pm 12 > 169 \pm 7.8 > 126 \pm 11$; Barni: $774 \pm 12 > 322 \pm 16 > 227 \pm 11 > 142 \pm 11$; Khalas $568 \pm 10 > 202 \pm 10 > 144 \pm 10 > 114 \pm 4.5$ μmol FRAP values per 100 g of fresh weight. Indeed, the relationship between polyphenolic content and antioxidant activity showed a significant linear regression ($R^2 = 0.735$; $P < 0.001$).

Utilising both HPLC and LC/MS (ESI-), a range of individual polyphenols were identified and quantified including, phenolic acids (Gallic, protocatechuic, hydroxybenzoic, vanillic, isovanillic, syringic, caffeic, p-coumaric, ferulic, sinapic and isoferulic), flavonoid glycosides (rutin and glycosides of myricetin, quercetin, luteolin, apigenin, isorhamnetin, naringenin and kaempferol), proanthocyanidin and anthocyanin (petunidin glycosides). In agreement with the total polyphenol data, these polyphenols were present at higher amounts in the *kimri* and *khalal* stages compared with the later ripening stages *rutab* and *tamr*. With regards to cultivar differences, the *khalal* stage of the Ajwa cultivar contained 15.8 ± 16 mg/100 g of fresh weight that was significantly higher ($P < 0.001$) than that measured in the Barni and Khalas dates at the same degree of ripening, 2.5 ± 2.9 and 2.6 ± 2.8 mg/100 g of fresh weight, respectively. Our data also indicate for the first time that there is a relatively high amount of petunidin glycoside present in the *khalal* stage of the Ajwa variety but not in the other cultivars tested. Furthermore, all the cultivars tested were shown to contain naringenin glycosides. In conclusion, date fruit may contribute to the daily intake of polyphenols, in particular if the earlier ripening stages are consumed (as in the practice in the Middle East) and thus may contribute to biological effects in the large intestine.

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