

Title Zahdi dates skin as source of proanthocyanidin
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Abstract

The Date Palm (*Phoenix dactylifera* L. Areaceae) is recorded in ancient history extending over an area from the Indus Valley (now Pakistan) to Mesopotamia (now Iraq), the Nile Valley, Arabian Peninsula, Southern Persia, Eastern Mediterranean and North Africa. According to the F AOST AT 2009, the date's world production is around 7.4 million ton. With annual production of 2 million ton, dates are regarded as the major crop in the Gulf Cooperation Council (GCC) countries. Date palms are exquisitely adapted to desert climates and problem soils, providing returns where no other crop can. Date fruit is nutritious, high-energy food consumed fresh, dried and in various processed forms. Besides dietary fiber, vitamin A and minerals dates contain antioxidants. Accordingly, numerous publications had been carried out to determine the antioxidants capacity, the phenolic content etc. The present work investigates the location and structure of date's polyphenols. The sugar free, dewaxed by organic solvents (petroleum ether and diethyl ether) dates skin of Zahdi cultivar have been extracted by acetone: water (50:50) and (70:30) consecutively. The hygroscopic brown colored lyophilized extract gave the typical cyanidin chloride red color ($\lambda_{\max}^{\text{MeOH/HCl}} = 535 \text{ nm}$, PC R_f value = 0.49 in Forestal solvent) when treated with MeOH/HCl. Approximate molecular weight studies by ultracentrifuge disclosed a molecular weight ranging from 1558-4792 depending on the fractions of sephadex LH 20 column. The spectroscopic data (IR and ^{13}C -NMR spectra) indicate the occurrence of proanthocyanidine oligomer. To confirm these finding and to elucidate the monomers structures, the propose oligomers have been degraded through thiolysis with benzyl mercaptan in acidic medium. Thiolysis products have been identified by capillary GC/MS. Fragmentation pattern of the silylated thioether showed derivatives of (+)-epicatechin [(2*R*, 3*S*, 4*S*) - 4- β -Benzyl thioepicatechin as the main monomer. As terminal units of the oligomer appear (-)-catechin and (+)- epicatechin are found in 1: 1.5 ratio respectively. These results have been confirmed through the 2D-PC (2, 6-Dibromobenzoquinone-4-chlorimid acetone 0.5%w/v) of the thiolysis products, and the reduction of (+)-epicatechin thioether derivatives by raney nickel alloy. Accordingly, it can be concluded that the Zahdi date skin contains two types of procyanidin oligomer: Epicatechin (4 β \rightarrow 8)-(epicatechin)_n-(4 β \rightarrow 8) - epicatechin, and Epicatechin

- (4P → 8)-(epicatechin) n -(4P → 8) - catechin. These results reveal that the date peel is a potential source of antioxidants and should be considered in any further fruit processing, or preservation.