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Fitoterapia

Volume 119, June 2017, Pages 175-184



Chemotaxonomic and biosynthetic relationships between flavonolignans produced by *Silybum marianum* populations

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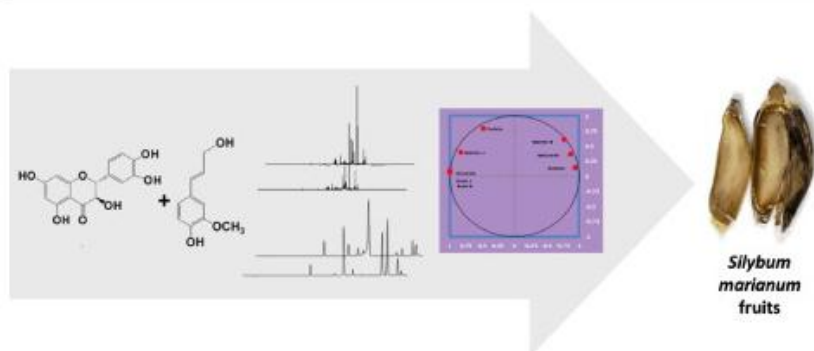
<https://doi.org/10.1016/j.fitote.2017.04.002>

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Abstract

Flavonolignans constitute an important class of plant secondary metabolites formed by oxidative coupling of one flavonoid and one phenylpropanoid moiety. The standardized flavonolignan-rich extract prepared from the fruits of *Silybum marianum* is known as silymarin and has long been used medicinally, prominently as an antihepatotoxic and as a chemopreventive agent. Principal component analysis of the variation in flavonolignan content in *S. marianum* samples collected from different locations in Egypt revealed biosynthetic relationships between the flavonolignans. Silybin A, silybin B, and silychristin are positively correlated as are silydianin, isosilychristin, and isosilybin B. The detection of silyamandin in the extracts of *S. marianum* correlates with isosilychristin and silydianin content. The positive correlation between silydianin, isosilychristin, and silyamandin was demonstrated using quantitative ¹H nuclear magnetic resonance spectroscopy (qHNMR). These correlations can be interpreted as evidence for the involvement of a flavonoid radical in the biosynthesis of the flavonolignans in *S. marianum*. The predominance of silybins A & B over isosilybin A & B in the silybin-rich samples is discussed in light of the relative stabilities of their respective radical flavonoid biosynthetic intermediates.

Graphical abstract



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Keywords

Silybum marianum; Flavonolignans; Biosynthesis; Principal component analysis; qHNMR