A PRELIMINARY INVESTIGATION OF FLAVANOLIGNANS OF SILYBUM MARIANUM (L.) GEARTN FRUITS GROWING IN EGYPT

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ABSTRACT

The flavanolignans of the fruits were isolated by column chromatography and identified by TLC and HPLC in addition to m.p., ms, uv and optical rotation measurements. A comparative study by TLC and HPLC of the flavanolignans from the purple-flowered and the white-flowered plants of Silybum marianum was performed. The major flavanolignans of the white flowered plants were identified as silybin, silychristin, silydianin and taxipholin. The major flavanolignans of purple-flowered plants were found to be silybin, silichristin and taxipholin.

INTRODUCTION

The fruits of Silybum-marianum (L.) Geartn, exert remarkable antihepatotoxic activities1. Silymarin, the major constituent of the fruits, consists of the isomers silybin, silydianin and silychristin2,3. Silychristin inhibits damage induced by Amanita phalloids, pyrrolizidine alkaloids and some rare metals (e.g. praseodymin). These flavanolignans appear in several popular products currently marketed in Europe and U.S.A. A German drug, Legalon, contains just silymarin, while the American Health Food Supplement, Arista Herb's liver cleanser, has the entire Silybum marianum (L.) Geartn fruits, combined with powdered beets, dandelion, golden-seal roots and black-radish seeds3.

The genus Silybum of the family Asteraceae (Compositae) includes two species, S. marianum (L.) Geartn and S. eburneum (Coss). Two varieties of S. marianum were also known, purple-flowered and white-flowered, both may have a large population, depending on the region of growth. The white-flowered and purple-flowered plants growing in Hungary and other localities of Europe was found to contain flavanolignans which differ qualitatively4,5. On the other hand, the Egyptian authors do not agree with this statement7. The varieties growing in Egypt were studied, the macromorphology of the capitula of both plants were found to be without any significant differences other than colours7. The full grown ripe fruits of the less common white-flowered variety were subjected to a study of the flavonoid contents. A preliminary TLC examination of the purified ethyl acetate extract using polyamide and cellulose sheets revealed the presence of seven flavonoid spots. The purple-flowered plants, however, were found to contain flavonoids from which five could be characterised (m.p., chem. reactions, cochromatography, UV, IR) as silybin, silydianin, silychristin, taxifolin and quercetin7. Accordingly, the white-flowered and purple-flowered plants were considered to be similar, concerning their flavonoidal contents7.

The aim of this work is the confirmation of this statement and comparison of the two varieties of
Silybum marianum (L.), regarding the flavanolignan contents of the fruits using HPLC methods.

RESULTS AND DISCUSSION

The pure mixture of flavanolignans of the purple-flowered and white-flowered plants were separated using the known patented procedure. The yield of flavanolignans separated from the fruits for the purple-flowered plants was (3.5%) and for the white-flowered plants 94%, mixtures were composed of 70-75% of the flavanolignans. The separation of the pure crystalline flavanolignans from the mixtures was achieved by separation on column chromatography on polyamide and silica gel. The separated flavanolignans were identified as taxipholin, silybin, silydianin and silychristin on the basis of physicochemical properties in comparison with those given in the literature.

The composition of the flavanolignans of the fruits of the purple-flowered and white-flowered varieties was found to be qualitatively similar, but different in their quantitative composition. Thus, the major flavanolignans of the fruits of purple-flowered variety were silychristin followed by silybin; silydianin and taxipholin were minor components. It seems that silychristin and silybin are formed in that variety at the expense of the two minor flavanolignans. The fruits of the white variety, on the other hand, contained silychristin and taxipholin as the two major flavanolignans, while silybin and silydianin were still present in respectable amounts (Fig. 1 and Table 1). It is interesting that the unknown components present in the flavanolignans mixture appear to be the same from HPLC data. Further work needed to isolate and identify such compounds from the flavanolignan mixture of both varieties of S. marianum L. Geartn.
Spectroscopic analysis:

**Silybin:**
C₂₅H₂₂O₁₀ (482.45, M⁺ 482), m.p. 166-168°C, (1% MeOH), UV-Spectrum: λ<sub>max</sub> 288, 330 nm; λ<sub>max</sub> + KOH 255, (320), 355 nm; (α)<sub>25</sub> + 11°.

**Silydianin:**
C₂₅H₂₂O₁₀ (482.45, M⁺ 482), m.p. 173-180°C, (1% MeOH), UV-Spectrum: λ<sub>max</sub> 292, 328, λ<sub>max</sub> + KOH 245, 330 nm, (α)<sub>25</sub> + 180°.

**Silychristin:**
C₂₅H₂₂O₁₀ (482.45, M⁺ 482), m.p. 174-176°C (corrected), (1% MeOH), UV-Spectrum: λ<sub>max</sub> 288, 325, λ<sub>max</sub> + KOH 250, (320), 330 nm, (α)<sub>25</sub> + 81°.

**Taxipholin:**
C₁₅H₁₂O₇ (304.26, M⁺ 304), m.p. 235-237°C (corrected), (1% MeOH), UV-Spectrum: λ<sub>max</sub> 288, 331, λ<sub>max</sub> + KOH 255, (288), 325 nm, (α)<sub>25</sub> + 63°.

<table>
<thead>
<tr>
<th>Flavanolignans</th>
<th>Purple-flowered variety</th>
<th>White-flowered variety</th>
</tr>
</thead>
<tbody>
<tr>
<td>Taxipholin</td>
<td>4.92</td>
<td>20.55</td>
</tr>
<tr>
<td>Silychristin</td>
<td>39.61</td>
<td>28.25</td>
</tr>
<tr>
<td>Silydianin</td>
<td>10.23</td>
<td>24.58</td>
</tr>
<tr>
<td>Unknown</td>
<td>24.47</td>
<td>13.34</td>
</tr>
<tr>
<td>Silybin</td>
<td>20.76</td>
<td>13.26</td>
</tr>
</tbody>
</table>

* Area was determined by triangulation method.
** These were identified according to retention times compared with authentic compounds.

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Fig. 1: HPLC chromatogram of flavanolignans of fruits of *S. marianum* purple-flowered variety (A) and fruits of *S. marianum* white-flowered variety (B).
REFERENCES


3-J. Heinerman; Milk Thistle Seed as an effective drug therapy for liver diseases, 29th Annual meeting of the American Soc. of Pharmacognosy, July 19-22, Univ. of Rhode Island, Kingston, Ri. 1987.


دراسة متكاملة للمواد الفلافلوجينائية في ثمار
نبات سيليا باي ماريانثور - لينيه - قارنون النضوج يتم إنتاجه في مصر
ل. درانيك، د. دجانكو، م. جريسوبر، م. لينين و أ. الشامي.
معهد الاتحاد السوفيتي لباحث كيمياء العقاقير وتكنولوجيا الأدوية- خاركوف جمهورية أوكرانيا.
قسم العقاقير - كلية الصيدلة - جامعة طنطا - مصر

تم فصل المواد الفلافلوجينائية من ثمار النبات وتم التعرف عليها بواسطة كروماتوجرافيا الضغط العالي
ويعتبر دورة الانصهار عالياً، الكثافة والحيوية الضوئية وقد وجد أن ثمار النبات ذو الازهار البيضاء والقرمزية
متشابهة نوعياً ومختلفة كمية في محتواها من المواد الفلافلوجينائية وذلك بعد فصل هذه المواد على عمود
الكروماتوجلافيا.

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