Cyanolipids from Sapindus saponaria L. Seed Oil.

Diego Rodríguez-Hernández (PQ)¹, Antonio J. Demuner (PQ)¹, Luiz C. A. Barbosa (PQ)^{1,2}, Ricardo M. Montanari (PQ)¹

¹Universidade Federal de Viçosa, Viçosa, Brazil; ²Universidade Federal de Minas Gerais, Belo Horizonte, Brazil;

Keywords: Cyanolipids, Sapindus saponaria, Sapindaceae, Fatty acids.

Abstract

The chemical composition of the oil extracted from seeds of Sapindus the saponaria L.. (Sapindaceae), was investigated. Cyanolipids constituted 5% of the total oil seeds, whereas triacylglycerols (TAG) accounted for 90%. The oil contains type III cyanolipids (**CL**) 1-cyano-2hydroxymethylprop-1-en-3-oldiesters. Structural investigation of the oil components was accomplished by chemical, chromatographic (TLC, CC, GC-MS), and spectroscopic (IR, NMR) analysis. GC-MS analysis showed that fatty acids were dominant in the CL components of the oil from S. saponaria L., with cis-11eicosenoic acid, cis-11-octadecenoic acid (vaccenic acid) and eicosanoic acid (arachidic acid) as the only esterified fatty acyl chains respectively.

Introduction

The composition of the seed oils of *Sapindus saponaria* commonly known as "Saboneteira" have been investigated.

The cyanolipids (**CL**), derived from amino acid metabolism^[1] are present, along with acylglycerols (AG) and triacilglicerols (**TAG**), in seed oils of plants belonging to the family Sapindaceae^[2]. Four types of **CL** structures (**Fig. 1**; I–IV), with fatty acids (FA) esterified to a mono- or a dihydroxynitrile moiety, have been reported as occurring in this plant Family.

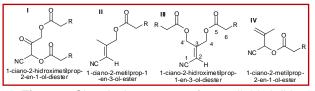


Figure 1. Chemical structures of cyanolipids I-IV.

Results and Discussion

Lipid extracts obtained from the seeds of *S. saponaria* was first investigated by TLC. Inspection of extract by TLC elution in hexane/Et₂O (9:1, v/v) showed the presence of three components suggested the presence of types of **CL** in the oil seed from this plant. Purification of the extracts from *S. saponaria* was accomplished by CC with hexane/Et₂O as eluent. In total, the main isolated constituents amounted to 90% (**TAG**), 5% **CL** III and 5% others. Purified components from plant extracts were further characterized by chromatographic and spectroscopic analyses.

IR spectra **CL** appear to be distinct for each structural type $I-IV^{[3-4]}$. This first attempt to identify the type of **CL** contained in our extracts was supported by the a narrow absorption band at 2224 cm⁻¹ attributed to a cyanogroup^[5] which is conjugated to a double bond, this are normally found in the spectra of acyl lipids and $2d^2$ *Bunife* Anual de Seciended Braziliar of Quipting Criere 5.5

are reported as diagnostic for type II and III CL (Fig. 1) [4].The ¹H-NMR and ¹³C-NMR spectral data and COSY correlations also facilitated the assignments of the relative signals. For example, signals at $\delta_{\rm C}$ 114.78, nitrile carbon, and the singlet at $\delta_{\rm H}$ 5.57, corresponding to the tertiary proton adjacent to the nitrile group, indicated that the isolated compounds were cyano derivatives. This was further supported by the signal at $\delta_{\rm C}$ 98.72, assignable to a vinylic carbon bearing the cyano function. The downfield shift of the two signals could be assigned, respectively, to the *cis*, H-4' ($\delta_{\rm H}$ 4.70) and *trans*, H-4 ($\delta_{\rm H}$ 4.88) methylene protons adjacent to the oxygen atoms of the dihydroxybutenyl cyanide moiety [4]. The assignment was made on the basis of chemical shifts (the nitrile group deshields the protons cis to it). The identification of this fraction of CL as 1-cyano-2-hydroxymethylprop-1-en-3-ol diesters was confirmed by the presence of two extra carbon signals at $\delta_{\rm C}$ 62.77 and $\delta_{\rm C}$ 61.71, which were assigned the two carbons C-4' and C-4 of the dihydroxybutenyl nitrile moiety, respectively.CL isolated from the seed oil of S. saponaria was also subjected to a transesterification before GC-MS analyses. FA esterified to the nitrile moiety of the CL were analyzed as their methyl ester derivatives by GC-MS. Identification of the constituents of CL oil fraction were identified by comparison with the data held in the Wiley 7.0 and NIST libraries, the CL, was represented by monounsaturated isomers with cis-11-octadecenoic (cis-vaccenic), cis-11-eicosenoic acids and saturated

Conclusion

eicosanoic acid (arachidic acid)

In the oil was isolated and indetified the **CL** tipe III, the **1-cyano-2-hydroxymethylprop-1-en-3-ol diesters**, in addition, were identified the FA bonded to **CL**. To our knowledge, this is the first detailed study reporting the composition of the oil lipid fractions from seeds of *S. saponaria*.

Aknowledgements

We are grateful to the following Brazilian agencies: CNPq, FAPEMIG, CAPES for financial support.

- ²Mikolajczak KL. Prog. Chem. Fats and other Lipids. 1977, 15, 91
- ³Mikolajczak KL, Smith CR. Jr, Tjarks LW. *Lipids*.**1970a**, 5, 672
- ⁴Mikolajczak KL, Smith CR. Jr, Tjarks LW. *Lipids*.**1970b**,5, 812
- ⁵ Barbosa, LCA, Espectroscopia no Infravermelho na caracterização de compostos orgânicos. Ed. UFV, 2007. 189 p.

39ª Reunião Anual da Sociedade Brasileira de Química: Criar e Empreender

¹Møller BL, Seigler DS..Biosynthesis of Cyanogenic Glycosides, Cyanolipids, and Related Compounds, in *Plant Amino Acids*. *Biochemistry and Biotechnology* (Singh, B.K., ed.), Marcel Dekker, New York, **1999**