THE PRESENCE OF GERANYLGERANIOL IN Bixa Orellana Linn.

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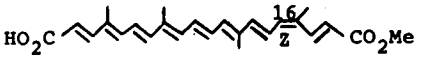
Abstract: The diterpene, geranylgeraniol, is present in the Bixa orellana's seeds, together with bixin and other carotenoid diacids which are responsable for the coloring action of these seeds. This diterpene is being reported for the first time in this genus and probably is reponsible for some unusual properties associated with the crude dye extracted from this plant.

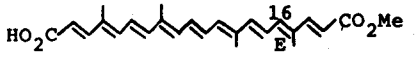
Introduction

Bixa orellana Linn is a well known and studied plant of the Bixaceae family which is widespread in all tropical America. Its seeds produce a natural dye used by the Amazon Indians to paint their bodies and is now also being used for coloring food, cosmetics and other products.

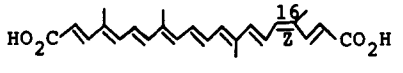
Bixin, the monomethyl ester of 4,8,13, 17, tetramethyleicosa-2,4,6,8,10,12,14,16,18 -nonenadioc acid (I), the major dye constituent of the Bixa orellana's seeds, occurs in the plant in the 16-cis form, and is easily transformed to the more stable trans form , known as isobixin (II). The free diacid is also present in the dye and is known as norbixin (III). (1)



BIXIN (I)



ISOBIXIN (II)



NOR-BIXIN (III)

The search for safe natural dyes, as a substitute for synthetic coloring products in the food ans cosmetic industries, has stimulated the development of several commercial coloring products based on this carotenoid mixture, directly extracted from Bixa orellana's seeds.

Its use as a histological dye was also recently porposed (2) and its specific property in being fixed, by lipophilic cells, prompted us to examine in more detail the chemical composition of the coloring material present in the external parts of the seeds.

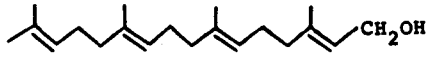
Result and Discussion

The ease of fixation by lipophilic cells of the dye mixture from Bixa orellana's seeds could not be explained easily in view of the relatively polar structure of the dicarboxilic acids, which are responsible for the coloring action. As a matter of fact the carboxylic acid salts are very soluble in water and can be used to give colorful red and yellow solutions to aqueous medium. It is also known that the dye has a "greasy" aspect when directly expressed from the seeds by hand, generating the special property, use by the Indians, which makes it suitable for body painting.This property makes the Bixin's dye very similar to lipstick, which is a combination of dyes and Cocoa butter.

These observations probably indicate the presence of another substance in the mixture which can work as a"vehicle"for the carotenoid acids and explain their unusual properties.

In fact, extraction of the external parts of the Bixa orellana's seeds, without allowing the extraction of the triglicerides present in the internal part, followed by partition of the dark red extract by silica gel chromatography, allowed the isolation of several colored fractions all related to the carotenoid diacids, and an oily fraction eluted in hexane:chloroform (8:2) and present in approximately 0,1% yielf of the total mixture. This oil was purified by preparative TLC, analised by 60 MHZ PMR, IR and MS and

identified as geranylgeraniol (IV) a well known diterpene occuring in several species (3-5).The presence of this diterpene alcohol which as far as we know is being reported for the first time in this species is probably responsible for the unexpected properties shown by the mixture of diacids used as dye.



GERANYLGERANIOL (IV)

Experimental

Bixa orellana's seeds (500g) were extracted with toluene in a Sohxlett apparatus giving 17.1g of a crude extract. Silica gel chromatography using solventes of increasing polarity gave 55 fractions. Fraction 21 was dissolved in ethyl ether and extracted with NaOH 5% (5x30ml) giving organic and aqueous layers. The ether layer was washed with water (2x30ml), dried with anhydrous sodium sulphate giving,after solvent evaporation,800mg of a viscous oil. This oil was chromatographed again on a preparative silica gel plate, eluted with chloroform:acetone (98:2) giving a pure material PMR (CDCl3) 60MHz: 5.30 (m, 1H), 5.05 (m,3H), 4.05 (d.2H), 2.0 (m,12H) , 1.65 (s,6H), 1.57 (s,9H). IR (film)(cm-1) : 3400, 2960, 2860, 1650, 1450, 1385, 1050. MS (m/z) (%): M+ 290(5), 275(8), 259(3), 257(5), 189(20), 177(18), 161(36), 159(14), 149(22) , 147(21), 137(48), 136(73), 135(47), 121(71) , 107(58), 93(84), 81(96), 69(100). Acetylation of this alcohol using pyridine/acetic anhydride gave a monoacetate which has spectral data identical to geranylgeraniol acetate (5).

Acknowledgements:

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POLIACETILENOS DE SIPHOCAMPYLUS HUMILIS WIMM. (LOBELIACEAE)

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Abstract: POLYACETYLENES FROM SIPHOCAMPYLUS HUMILIS WIMM. (LOBELIACEAE).
Analysis of ethereal extracts from brazilian species of Siphocampylus humilis Wimm., gave the tetra-4E,12E-diene-8,10-diyne-1,6,7-triol, its aldehyde derivative, and the tetradeca-4E,8E,12E-triene-10-yne-1,6,7-triol, all previously isolated from others Siphocampylus and Lobelia species.

Recentemente registramos a ocorrência de poliacetilenos contendo 14 átomos de carbono, em 6 espécies de Lobelia e 4 espécies de Siphocampylus[1].

Estamos comunicando agora, o isolamento dos poliacetilenos 1 - 3, de Siphocampylus humilis Wimm. (Lobeliaceae), espécie posteriormente coletada nos arredores de Campos de Jordão (SP), em julho de 1987. A planta é nativa do Brasil[2], de pequeno porte (ca 20 cm) e rara ocorrência.

Estes 3 poliacetilenos foram previamente encontrados em espécies de Lobelia e Siphocampylus, sendo que 1 foi originalmente iso-