METABOLITES OF CAROTENOIDs AS ALLELOCHEMICALS. STRUCTURE
REVISIÓN DE ANNUIONONES A, B AND E

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INTRODUCTION

Many apocarotenoids, compounds with fewer than 40 carbon atoms, but with carotenoid-like structures, are found in plant essential oils and they are often related with flavour of plants, and others are essentially nonvolatile. Synthesis of these compounds appears to occur mainly by catabolism of carotenoids.1

Otherwise, hexylideneallene moiety can be found in certain carotenoids as neoxanthin, mimulaxanthin, furoxanthin, peridinin or paracentrene. This functionalization is maintained in some apocarotenoids as grasshopper ketone, which has been proposed as precursor of the important flavour damascenone.2 Its direct progenitors are not completely clarified. One of them, the β-D-glucopyranoside of the allenic triol (1) has been isolated from the leaves of Premna subscandens3 and as its pentaacetate from the leaves of Lycium halimifolium4.

RESULTS AND DISCUSSION

Fresh leaves of H. annuus cv. Stella and SH-222 were extracted with water at room temperature for 24 h. This aqueous extracts were re-extracted with methylene chloride and ethyl acetate. The different fractions obtained were fractionated and assayed. The polar bioactive fractions yielded compounds 1-8 (Figure 1). The spectroscopic data of 2-7 were identical to those previously reported.5 This is the first time that compound 1 has been isolated as aglycone natural product. 8 is also described for the first time.

On the other hand, we isolated annuionones A (2) and E (3) from H. annuus.6 Since it was possible to isolate more amounts of both compounds a more comprehensive spectroscopical study could be realized. We have reinvestigated the 13C NMR spectrum assignment of 2 and 3 by 1H-13C gHSQC, gHMBC and 2D-INADEQUATE spectroscopy, in addition to one dimensional 1D-1H NMR spectrum, decoupled 13C NMR spectrum, and COSY were performed. These studies suggested the revision of the previously reported structures for these compounds.

Figure 1. Bisnorsesquiterpenoids isolated from Helianthus annuus
All compounds were bioassayed (Figure 2) and a structure-activity relationship study has been performed.

![Figure 2. Bioactivities of compounds 1-7 in wheat coleoptile bioassay](image)

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