METABOLITES OF CAROTENOIDS AS ALLELOCHEMICALS. STRUCTURE REVISIÓN OF 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 paracentrone. 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 subscandens*[3] and as its pentaacetate from the leaves of *Lycium halimifolium*[4].

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 ^{13}C NMR spectrum assignment of **2** and **3** by ^{1}H-^{13}C gHSQC, gHMBC and 2D-INADEQUATE spectroscopy, in addition to one dimensional 1D-^{1}H NMR spectrum, decoupled ^{13}C NMR spectrum, and COSY were performed. These studies suggested the revision of the previously reported structures for these compounds.

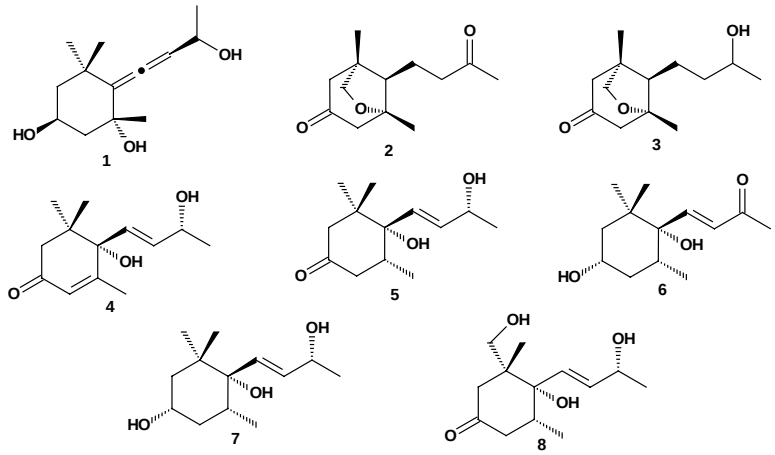

Figure 1. Bisnorsesquiterpenoids isolated from *Helianthus annuus*

All compounds were bioassayed (Figure 2) and a structure-activity relationship study has been performed.

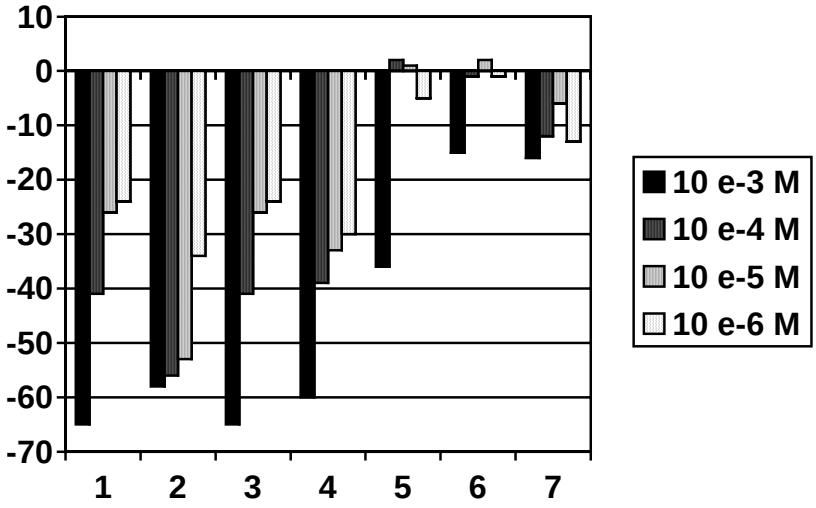

Figure 2. Bioactivities of compounds **1**-**7** in wheat coleoptile bioassay

ACKNOWLEDGMENTS

The research described in this abstract was performed as part of the project "FATEALLCHEM", "Fate and Toxicity of Allelochemicals (natural plant toxins) in Relation to Environment and Consumer". The project was carried out with financial support from the Commission of the European Communities under the Work programme Quality of Life, contract no. QLK5-CT-2001-01967.

REFERENCES

1. Parry A. D. and Horgan R. Carotenoids metabolism and the biosynthesis of abscisic acid. Phytochemistry, 1991, **30**: 815-821.
2. Ohlo G., Rautenstrauch V. and Schulte-Elte K. H. Model reactions for biosynthesis of compounds of damascone series and their synthetic application. Helv. Chim. Acta, 1973, **56**: 1503-1513; Skouroumounis, G. K. and Sefton, M. A. Acid-catalyzed hydrolysis of alcohols and their β-D-glucopyranosides J. Agric. Food Chem. 2000, **48(6)**: 2033-2039.
3. Sudo H., Ide T., Otsuka H., Hirata E., Takushi A., Shinzato T. and Takeda Y. Megastigmane, benzyl and phenethyl alcohol glycosides, and 4,4 '-dimethoxy-beta-truxinic acid catalpol diester from the leaves of Premna subscandens Merr. Chem. Pharm. Bull. 2000, **48(4)**: 542-546
4. Näf R., Velluz A. and Thommen W. Isolation of a glucosidic precursor of damascenone from Mycium halimifolium Mil. Tetrahedron Lett., 1990, **31 (45)**: 6521-6522.
5. González A. G., Guillermo J. A., Ravelo A. G., Jiménez I. A., Gupta M. P. 4,5-dihydroblumenol a, a new nor-isoprenoid from perrottetia-multiflora J. Nat. Prod. 1994, **57 (3)**: 400-402; Pauli, N., Sequin, U., Walter, A. Boscialin and boscialin 4'-*O*-glucoside, 2 new compounds isolated from the leaves of Boscia salicifolia Oliv Helv. Chim. Acta 1990, **73**: 578-582; Perez, C., Trujillo, J., Almonacid, L. N., Trujillo, J., Navarro, E., Alonso, S. J. Absolute structures of two new C-13-norisoprenoids from *Apollonias barbujana* J. Nat. Prod. 1996, **59**: 69-72
6. Macías F. A., Varela R. M., Torres A., Oliva R. M., Molinillo J. M. G. Bioactive norsesquiterpenes from Helianthus annuus with potencial allelopathic activity. Phytochemistry, 1998, **48**, 631-636; Macías F. A.; Torres A.; Galindo J. L. G.; Varela R. M.; Álvarez J. A.; Molinillo J. M. G. Bioactive terpenoids from sunflower leaves cv. Peredovick. Phytochemistry, 2002, **61**, 687-692.