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OCCURRENCE OF HYSTERIN AND DIHYDROISOPARTHENIN IN *PARTHENIUM HYSTEROPHORUS*

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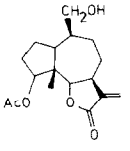
Key Word Index—*Parthenium hysterophorus*; Compositae; sesquiterpene lactones; hysterin; dihydroisoparthenin.

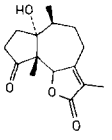
Abstract—Two sesquiterpene lactones, hysterin and dihydroisoparthenin, have been identified in *Parthenium hysterophorus* from Argentina and Jamaica by TLC and NMR.

INTRODUCTION

Parthenium hysterophorus L. (Compositae) is a common weed of the southern United States, Mexico, the Caribbean and parts of Central and South America. In the last hundred years this plant has been introduced into Africa, Asia and Australia[1] where in some areas it causes serious agricultural problems. In India it is also responsible for a high incidence of allergic contact dermatitis in humans[1]. The allergenic properties of *P. hysterophorus* have been attributed to sesquiterpene lactones[1] which also exhibit other biological activities[2, 3]. Most populations of *P. hysterophorus* contain parthenin or hymenin as the major sesquiterpene lactone[1, 4]. Other lactones found in smaller quantities in some populations are ambrosin[1], coronopilin[5], and tetraneurin-A[6]. Here we report the finding of two additional sesquiterpene lactones, hysterin (**1**) and dihydroisoparthenin (**2**), which have not been reported previously for *P. hysterophorus*.



1 (Hysterin)



2 (Dihydroisoparthenin)

RESULTS AND DISCUSSION

Hysterin (**1**) was isolated and identified (NMR, R_f, and colour reactions on TLC plates) in chloroform extracts of *P. hysterophorus* collected in the provinces of Salta, Tucuman, and La Rioja of Argentina and in material from Jamaica. This lactone was first isolated and its structure determined by Romo de Vivar *et al.*[7] from material presumed to be *P. hysterophorus* but which was later established to be *P. bipinnatifidum* [8, 9].

Dihydroisoparthenin (**2**) was detected by NMR and TLC (R_f and colour reactions) in one Argentinian sample from Cordoba Province. To our knowledge this is the first report of the natural occurrence of dihydroisoparthenin.

We identified hysterin and dihydroisoparthenin in some South American and Jamaican populations of *P. hysterophorus* only. These populations contain hymenin as the major sesquiterpene lactone[4]. But hysterin and dihydroisoparthenin were absent from all samples of *P. hysterophorus* containing parthenin as the major sesquiterpene lactone (populations from North America, Central America, Africa, India, Australia, and some areas of Jamaica)[4].

Hysterin possesses an α-methylene-γ-lactone moiety which is a potentially active site of many sesquiterpene lactones[2, 3]. Therefore, this compound might contribute to some of the biological activities of *P. hysterophorus*.

EXPERIMENTAL

Hysterin. Ground dried leaves (8 g) of *P. hysterophorus* collected in Argentina (Salta Province, Pampa Blanca, 24°30'S 64°30'W in 1979 by I. Dale) were extracted with $CHCl_3$ overnight. The extract was filtered, concd *in vacuo*, and chromatographed on a Si gel column packed and eluted with $CHCl_3$–Me_2CO (6:1). Earlier fractions contained hymenin identified by TLC[10] and by the NMR[11]. Later fractions gave a grey spot (R_f = 0.19) with the vanillin spray reagent[10] and ^{1}H NMR (80 MHz, $CDCl_3$ with TMS): δ6.20 (*d*, H-13b), 5.45 (*d*, H-13a), 4.50 (*d*, H-6), 3.85 (*s*, C-10-CH_2O), 2.08 (*s*, acetyl-Me), 0.80 (*s*, C-5-Me). The NMR values correspond to those reported for hysterin[11] and the colour and R_f on chromatograms were identical with those of an authentic sample.

Dihydroisoparthenin. A soln of 100 mg of parthenin in 10 ml of EtOH (95%) was hydrogenated at room temp. and atm pres. for 5 hr with 10 mg of 10% palladium on charcoal (Nutritional Biochemicals Corp.). Separation of dihydroiso-

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parthenin and tetrahydroparthenin was achieved by using TLC (Si gel) with the solvent system $CHCl_3$–Me_2CO (6:1). Dihydroisoparthenin ($R_f = 0.45$) gave a vivid orange spot with the vanillin reagent fading rapidly on cooling the plate giving a light yellow colour. ^1H NMR (80 MHz, $CDCl_3$ with TMS): δ5.42 (*br s*, H-6), 0.83 (*s*, C-5-Me), 1.12 (*d*, C-10-Me) corresponds to the reported NMR values of dihydroisoparthenin[12].

Identification of hysterin and dihydroisoparthenin in plant samples. Ground shoots (1 g) of samples of *P. hysterophorus* were extracted with 30 ml $CHCl_3$ overnight. Each filtered extract was completely evaporated *in vacuo* and taken for NMR analyses (80 MHz, $CDCl_3$ with TMS). The NMR spectra with the lower field peaks maximized were compared with the characteristic peaks of the NMR spectra of hysterin and dihydroisoparthenin. The crude $CHCl_3$ extracts were chromatographed by two-directional TLC[4] and sesquiterpene lactones identified using the vanillin spray reagent[10].

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DESANGELOYLSHAIRIDIN, A SESQUITERPENE LACTONE FROM *GUILLONEA SCABRA*

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Key Word Index—*Guillonea scabra*; Umbelliferae; new guaianolide; desangeloylshairidin.

Abstract—From the roots of *Guillonea scabra* a new sesquiterpene lactone has been isolated. Its structure has been established by spectroscopic means as desangeloylshairidin.

INTRODUCTION

In a previous communication [1] we reported guaiol, malaphilinin [2] and badkysin (**1**) [3] as the sesquiterpene constituents of the roots of *Guillonea scabra* (Cav.) Cosson (= *Laserpitium scabrum* Cav.). New study of the plant material and careful chromatography of the fractions containing badkysin (**1**), has now allowed the isolation of two other sesquiter-