

## A DITHIOPHENE FROM *APHYLLOCLADUS DENTICULATUS*

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**Key Word Index**—*Aphyllocladus denticulatus*; *Urmenetea atacamensis*; Compositae; Mutisieae; dithiophene; triterpenes; flavonoid.

**Abstract**—A new dithiophene, aphyllocladine, lupeonone, lupeol and apigenin were isolated and identified from *Aphyllocladus denticulatus*. Lupeyl acetate and lupeol were isolated from *Urmenetea atacamensis*.

### INTRODUCTION

Gochnatiinae is the most fragmented and widely distributed subtribe of the tribe Mutisieae, with 21 genera in Central and Southern America and 15 in the Old World [1]. This subtribe is represented in Chile by eight species of which two have been studied earlier (*Gochnatia foliolosa* var. *fascicularis* [2] and var. *foliolosa*).

From the latter, for the first time in Mutisieae, a new germacranolide with a novel stereochemistry, a *trans*, *trans* germacra-1(10)4-dien-*cis*-6,12-olide [3, 4] was isolated.

### RESULTS AND DISCUSSION

Continuing our chemical investigation of Chilean Gochnatiinae we wish to report the isolation of a new dithiophene from *Aphyllocladus denticulatus* (Remy) Cabr. var. *denticulatus*. No dithiophene acetylene has been isolated so far from representatives of the subtribe Gochnatiinae, although some acetylenes have been found from *Pleiotaxis* [5], *Dicoma* [6], *Cnicothamnus* and *Gochnatia* [7] and *Onoseris* [8]. However dithiophene derivatives have been isolated from Mutisieae species (subtribe Mutisiinae) [9, 10].

Aphyllocladine, 1, has molecular formula  $C_{12}H_8OS_2$  as determined by high resolution MS. Further identification resulted from comparison of the  $^1H$  NMR spectrum with that of related dithiophenes [11] previously isolated from *Tagetes erectus* (Heliantheae). Lupeonone, lupeol and apigenin were also isolated and identified from *Aphyllocladus denticulatus* by spectroscopic methods.

As part of our chemical investigation of Chilean Gochnatiinae we also studied the aerial parts of *Urmenetea atacamensis* Phil. This plant only afforded known compounds, lupeyl acetate and lupeol.

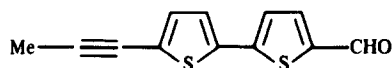
### EXPERIMENTAL

*A. denticulatus* var. *denticulatus* was collected in Quebrada Lanizalillo (near Cerrillos 35 km) in September 1985; a plant voucher specimen has been deposited at the Herbarium of the Departamento de Botánica Universidad de Concepción, Chile (CONC.)

The dried and ground aerial parts of *A. denticulatus* (1 kg) were extracted with MeOH, petrol,  $CH_2Cl_2$  and EtOAc. The petrol extract was purified by CC on silica gel to yield 1. MS (100 eV)  $m/z$  (rel. int.): 232.002  $[M]^+$  (30) calc. for  $C_{12}H_8OS_2$ : 232.002, 203  $[M-CHO]^+$  (21), 177  $[C_6H_5S_2]^+$  (14), 149  $[C_8H_5OS]^+$  (39), 121  $[C_7H_5S]^+$  (6), 77  $[C_2H_5OS]^+$  (6), 73,  $[C_2HOS]^+$  (8), 69 (6), 61  $[C_2H_5S]^+$  (45), 55 (8);  $^1H$  NMR (250 MHz,  $CDCl_3$ ), 9.85 (1H, s), 7.55 (1H, d,  $J = 4$  Hz), 7.2 (2H, dd,  $J = 10, 4$ ), 7.04 (1H, d,  $J = 4$  Hz), 2, 1 (3H, s).

The extract of the aerial parts of *Urmenetea atacamensis* (1.018 kg) collected near San Pedro de Atacama (Chile, September 1986) voucher deposited in the herbarium of the Universidad de Concepcion, Chile (CONC) afforded only known compounds lupeyl acetate and lupeol.

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## REFERENCES

1. Cabrera, A. L. (1977) *The Biology and Chemistry of the Compositae* (Heywood, V. H., Harborne, J. B. and Turner, B. L., eds) pp. 1042, 1044. Academic Press, London.
2. Faini, F., Torres, R. and Castillo, M. (1984) *J. Nat. Prod.* **47**, 552.
3. Galvez, M. E., Hoeneisen, M., Silva, M. and Watson, W. H. (1986) *Bol. Soc. Chil. Quim.* **31**, 3.
4. Hoeneisen, M. and Becker, H. (1986) *J. Nat. Prod.* **49**, 360.
5. Bohlmann, F. and Zdero, C. (1982) *Phytochemistry* **21**, 1434.
6. Bohlmann, F. and Le Van, N. (1978) *Phytochemistry* **17**, 570.
7. Bohlmann, F. and Zdero, C. (1979) *Phytochemistry* **18**, 95.
8. Bohlmann, F., Zdero, C., King, R. and Robinson, H. (1980) *Phytochemistry* **19**, 689.
9. Bohlmann, F. and Zdero, C. (1977) *Phytochemistry* **16**, 239.
10. Bohlmann, F., Zdero, C. and Le Van, N. (1979) *Phytochemistry* **18**, 99.
11. Bohlmann, F., Grenz, M., Wotschokowsky, M. and Berger, E. (1967) *Chem. Ber.* **100**, 2518.

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## AZULENES, LABDANES AND A FUROCUMENE FROM *IXIOLAENA LEPTOLEPIS*

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**Key Word Index**—*Ixiolaena leptolepis*; Compositae; diterpenes; labdanes; sesquiterpenes; furocurcumene; azulenes.

**Abstract**—The extract of the aerial parts of *Ixiolaena leptolepis* yielded, in addition to widespread compounds, manool, and four new labdane derivatives, three azulenes and a furocurcumene derivative. The structures were elucidated by high field  $^1\text{H}$  NMR techniques.

### INTRODUCTION

The small Australian genus *Ixiolaena* (Compositae, tribe Inuleae) is placed in the subtribe Gnaphaliinae in the *Helichrysum* group [1]. But the exclusively dysploid numbers of this genus are unusual and some other characters approach the *Helipterum* group. As the chemistry of the large genus *Helichrysum* has been studied in detail it was interesting to investigate *Ixiolaena leptolepis* (DC) Benth. as so far only one species has been studied for fatty acids [2].

### RESULTS AND DISCUSSION

The aerial parts of *Ixiolaena leptolepis* afforded, in addition to tridecapentaynene, caryophyllen-1 $\beta$ ,10 $\alpha$ -epoxide and ferulic acid, a new type of bisabolene derivative, the furane **4**, the labdane derivatives (–)-manool and **5–9** as well as the azulenes **1** [3], **2** [4] and **3**.

The structure of **3** clearly followed from the spectroscopic data. The molecular formula ( $\text{C}_{14}\text{H}_{12}\text{O}_4$ ) and the  $^1\text{H}$  NMR spectrum indicated that a dicarbomethoxy derivative of a highly unsaturated norsesquiterpene was present, while the colour required a substituted azulene. Spin decoupling showed that the carbomethoxy groups must be placed at C-1 and C-4. Accordingly, the data were close to those of the corresponding aldehyde, only

some chemical shifts being slightly different. In the case of the aldehyde group at C-4 (**2**) the H-3 signal was shifted down field by 0.53 ppm. The absorption of visible light also differed by 6 nm.

The molecular formula of **4** ( $\text{C}_{15}\text{H}_{16}\text{O}_2$ ) indicated the presence of a highly unsaturated sesquiterpene. The  $^1\text{H}$  NMR spectrum showed an aldehyde singlet ( $\delta$  9.82) and a pair of broadened singlets ( $\delta$  6.28 and 7.91) which could be assigned to furane protons. A methyl singlet at  $\delta$  2.31, a pair of broadened two proton doublets at  $\delta$  7.06 and 7.09 and the remaining signals required a toluene derivative with a substituent in the *para*-position, and a  $\text{CH}(\text{Me})\text{CH}_2$  group. Thus all data agreed with the presence of a furocurcumene derivative. This was supported by spin decoupling which established the proposed assignments. Compound **4** has been named furoixiolal.

The  $^1\text{H}$  NMR spectra of **5–8** (Table 1) clearly showed that we were dealing with *ent*-labda-7,14-diene-13-ol derivatives. Spin decoupling allowed the assignment of the position of additional functions. In the spectrum of **5** a 2 $\beta$ -hydroxy group showed a signal at  $\delta$  3.85 with couplings indicating an equatorial hydroxy group. In the spectrum of **6** this signal was shifted to  $\delta$  5.04. Typical signals of a senecioate indicated the presence of the corresponding 2 $\beta$ -seneciyoxy-*ent*-labdane. The spectra of **5** and **6** further showed by the fact that the signals for H-14 and H-16 were doubled that pairs of 13-*epi* com-