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PRESENCE OF ATRANORIN IN PHYSCIA SOREDIOSA

Short report

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ABSTRACT

In this short report we inform over the presence of the depside named atranorin in the lichen *Physcia sorediosa* (Physciaceae) by means of isolation techniques and structural characterization by using NMR techniques. The lichen was collected at the UMSA campus Cota Cota in La Paz. To the best of our knowledge this is the first characterization of this depside in the lichen *Physcia sorediosa*.

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RESUMEN

***Spanish title**: Presencia de atranorina en Physcia sorediosa.* Reportamos la presencia del depsido denominado atranorina en el liquen *Physcia sorediosa* (Physciaceae) mediante su aislamiento y caracterización por RMN, el liquen fue colectado en el campus Universitario de Cota-Cota, UMSA, La Paz Bolivia.

INTRODUCTION

Lichens are vegetal organisms generated by the symbiosis of algae and mushrooms [1]. They synthesize secondary metabolites as depsides, terpenoids, acids, quinones, chromones, xanthones and anthraquinones [2]. In our study of the lichen *Physcia sorediosa*, collected in the main campus of UMSA in La Paz (3600 m.a.s.l.), we have isolated the depside atranorin **1**, see Figure 1. The structure was assigned by analysis of the ^{1}H NMR and ^{13}C NMR data of compound **1** (Fig. 2 and 3, Table 1) in comparison with those published in the literature for atranorin [3].

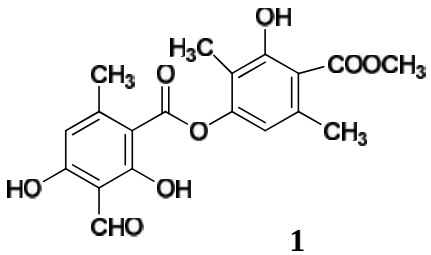

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***Figure 1.** The depside atranorin **1**, characterized in the lichen Physcia sorediosa*

RESULTS AND DISCUSION

Atranorin (**1**, IUPAC name: (3-hydroxy-4-methoxycarbonyl-2,5-dimethylphenyl)3-formyl-2,4-dihydroxy-6-methylbenzoate) was obtained as white crystals. The 1D NMR spectra are shown in Figure 2 and 3. There is a report of Carvalho et al. [3] in which the unambiguous assignment of the ^{1}H and ^{13}C NMR spectra was established. The elucidation work done by Carvalho et al. [3] included the use of 2D NMR techniques, namely, COSY, NOESY, HMQC and HMBC. We have also established all necessary homo and heteronuclear correlations through 2D NMR techniques; results are coinciding with the results published by Carvalho et al. [3]. Table 1 shows the comparison of chemical shift values of atranorin (**1**[a]) isolated from *Physcia sorediosa* with those of atranorin (**1**[b]) isolated from *Ouratea floribunda* [3]. These data permitted to identify the compound isolated from *Physcia sorediosa* and reported here, as atranorin (**1**). These values were also correlated with spectrometric additional bibliographic information in order to corroborate the identity of **1** [4-6]. To the best of our knowledge this is the first characterization of atranorin in the lichen *Physcia sorediosa.*

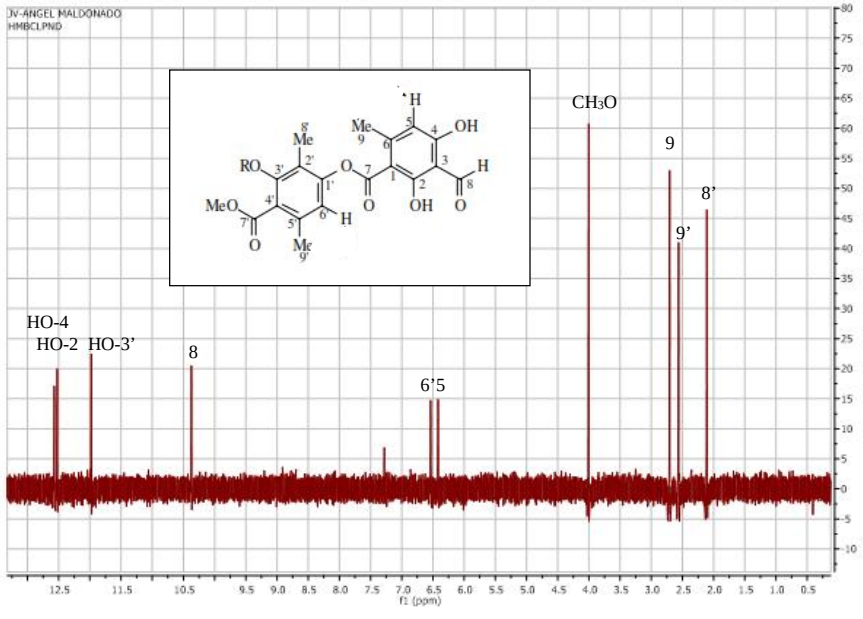


Figure 2. *^{1}H NMR spectrum of **1**, 300 MHz, $CDCl_3$, ¢ from TMS. Molecular drawing with numbering system extracted from Carvalho et al. [3], authorization pending from JBCS¥.*

Peak-picking	**1**[a]
Atom	$\delta^{1}H$
1	-
2	-
3	-
4	-
5	6.39 *s*
6	-
7	-
8	10.37 *s*
9	2.71 *s*
1'	-
2'	-
3'	-
4'	-
5'	-
6'	6.54 *s*
7'	-
8'	2.11 *s*
9'	2.56 *s*
CH_3O	4.00 *s*
HO-2	12.52 *s*
HO-4	12.57 *s*
HO-3'	11.95 *s*

EXPERIMENTAL

General

The NMR spectra were run in a Bruker DRX300, (300 MHz ^{1}H, 75 MHz ^{13}C) equipment at the Department of Chemistry of UMSA.

Vegetal material

Physcia sorediosa was collected at the main Campus of Major San Andres University (UMSA) at 3600 m.a.s.l. (La Paz, Bolivia) in December 2005, the material was identified in the National Herbarium of Bolivia (LPB).

Extraction and isolation

The plant material was selected, cleaned, dried and milled, it weighed 10.1 g. 10.1 g of dried material was extracted with acetone during 48 h. at room temperature. The filtrate was concentrated at reduced pressure and once dried it was crystalized in ethanol-dichloromethane (1:1) to afford a white crystalline solid or compound **1** (0.6 g, 5.94%).

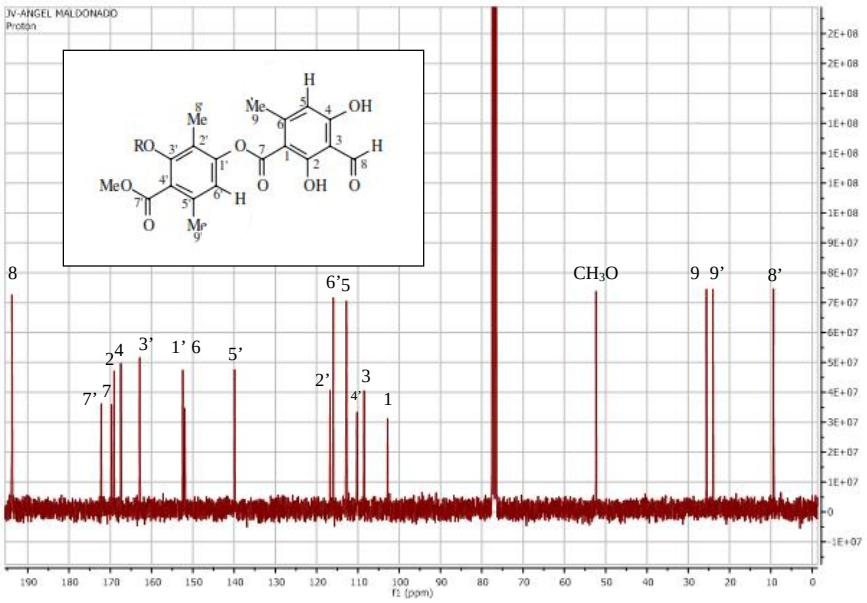


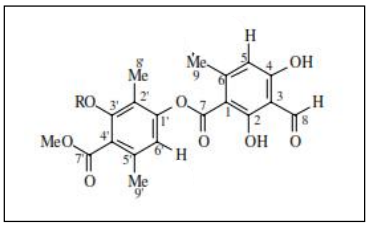
Figure 3. *^{13}C NMR spectrum of **1**, 75 MHz, $CDCl_3$, ¢ from TMS. Molecular drawing with numbering system extracted from Carvalho et al. [3], authorization pending from JBCS¥.*

Peak-picking	**1**[a]
Atom	δ ^{13}C
1	102.8 *s*
2	169.1 *s*
3	108.5 *s*
4	167.5 *s*
5	112.8 *d*
6	152.4 *s*
7	169.7 *s*
8	193.0 *s*
9	25.6 *q*
1’	152.4 *s*
2’	116.8 *s*
3’	162.9 *s*
4’	110.2 *s*
5’	139.9 *s*
6’	116.0 *d*
7’	172.2 s
8’	9.4 *q*
9’	24.0 *q*
CH_3O	52.3 *q*

Table 1. *Comparison of ^{1}H and ^{13}C chemical shift values of atranorin from two different vegetal sources*

	Compound			
	1[a]	**1**[b]	**1**[a]	**1**[b]
Atom	δ^{1}H	δ ^{1}H	δ ^{13}C	δ ^{13}C
1	-	-	102.8 *s*	102.8 *s*
2	-	-	169.1 *s*	169.1 *s*
3	-	-	108.5 *s*	108.5 *s*
4	-	-	167.5 *s*	167.5 *s*
5	6.39 *s*	6.39 *s*	112.8 *d*	112.8 *d*
6	-	-	152.4 *s*	152.4 *s*
7	-	-	169.7 *s*	169.7 *s*
8	10.37 *s*	10.30 *s*	193.0 *s*	193.8 *s*
9	2.71 *s*	2.67 *s*	25.6 *q*	25.6 *q*
1’	-	-	152.4 *s*	152.0 *s*
2’	-	-	116.8 *s*	116.7 *s*
3’	-	-	162.9 *s*	162.8 *s*
4’	-	-	110.2 *s*	110.3 *s*
5’	-	-	139.9 *s*	139.9 *s*
6’	6.54 *s*	6.50 *s*	116.0 *d*	115.9 *d*
7’	-	-	172.2 s	172.2 s
8’	2.11 *s*	2.07 *s*	9.4 *q*	9.4 *q*
9’	2.56 *s*	2.53 *s*	24.0 *q*	24.0 *q*
CH_3O	4.00 *s*	3.97 *s*	52.3 *q*	52.3 *q*
HO-2	12.52 *s*	12.49 *s*		
HO-4	12.57 *s*	12.54 *s*		
HO-3’	11.95 *s*	11.94 *s*		

[a]*Physcia sorediosa*, (300 and 75 MHz, $CDCl_3$); [b]*Ouratea floribunda* [3], (400 and 100 MHz, $CDCl_3$)



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REFERENCES

1. Purvis, W. Lichens, Smithsonian Institution Press, **2000**, Washington D.C., USA.
2. Hale, M., The Biology of lichens, Spottiswoode Ballantyne Ltd. Press, 3rd ed., **1983**, London, U.K.
3. Carvalho, M.G., Carvalho, G.J.A., Braz-Filho, R. **2000**, Chemical constituents from *Ouratea floribunda*: complete ^{1}H and ^{13}C NMR assignments of atranorin and its new acetyl derivative. *J. Braz. Chem. Soc*., *11* (2), 143-147.
4. Vila, J.L., Mollinedo, P., Sterner, O. **2011**, Spectrometric studies of lichen depsides and depsidones, *Rev. Bol. Quim*., *28* (1), 28-34.
5. Sundholm, E.G., Huneck, S. **1980**, ^{13}C NMR spectra of lichen depsides, depsidones and depsones. 1. Compounds of the orcinol series, *Chemica Scripta*, *16*, 197-200.
6. Sundholm, E.G., Huneck, S. **1981**, ^{13}C NMR spectra of lichen depsides, depsidones and depsones. 2. Compounds of the β-orcinol series, *Chemica Scripta*, *18*, 233-236.

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