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^{13}C NMR ASSIGNMENTS OF SOME DIBENZYL-γ-BUTYROLACTONE LIGNANS

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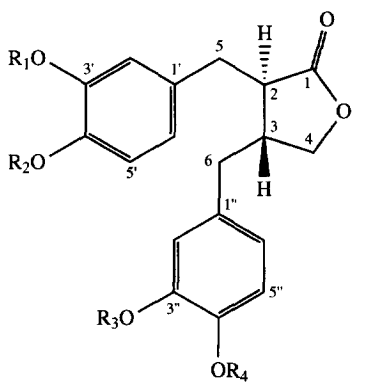
Key Word Index—*Bupleurum salicifolium*; Umbelliferae; 2D heteronuclear ^{1}H–^{13}C correlations; lignans; dibenzyl-γ-butyrolactone.

Abstract—^{1}H–^{13}C heteronuclear correlation and long-range correlation spectra with inverse detection, allowed the unequivocal assignment of ^{13}C spectra of some dibenzyl-γ-butyrolactones isolated from *Bupleurum salicifolium*.

INTRODUCTION

In the course of a phytochemical study of a plant species endemic to the Canary Islands, *Bupleurum salicifolium*, we isolated numerous metabolites derived from the shikimic acid pathway, most of them being lignans [1–8]. Lignans constitute a very interesting group of natural products because of their biological properties [9], such as nematostatic [10] and anti-HIV [11] activities. Most of the lignans isolated by us belong to the dibenzyl-γ-butyrolactone group and some of them, like buplerol (**1**) and guayarol (**2**) [4], were new to the literature. When we published the isolation of **1** and **2** and their structural elucidation, we made ^{13}C assignments of these lignans and their acetyl derivatives on the basis of chemical shift calculations and by comparison with values reported for other dibenzyl-γ-butyrolactone lignans [12]. Some assignments of aromatic carbons were ambiguous and we gave them as *interchangeable*.

From the leaves of *B. salicifolium* [8], we have recently isolated sizeable amounts of **1** and **2**. In this paper, we report the unequivocal assignments of ^{13}C NMR of both compounds. In addition, we report the assignments of bursehernin (**3**) and the dimethyl ether, matairesinol (**4**). Compounds **3** and **4** were also obtained as major secondary metabolites from the leaves of *B. salicifolium*; the literature was lacking ^{13}C NMR data.



1 $R_1 = R_2 = R_3 = Me$; $R_4 = H$
2 $R_1 = R_2 = Me$; $R_3 = R_4 = H$
3 $R_1 = R_2 = Me$; $R_3 = R_4 = -CH_2-$
4 $R_1 = R_2 = R_3 = R_4 = Me$

RESULTS AND DISCUSSION

The ^{1}H NMR assignments of **1**–**4** were made on the basis of COSY experiments and NOE effects [4]. In order to illustrate the protocol followed for assignation of the ^{13}C NMR to the lignans mentioned above, we discuss in detail compound **1**. The same methodology was used for the other lignans.

Direct analysis of the ^{13}C NMR proton noise-decoupled and DEPT spectra clearly showed that the signals at δ 178.8 and 71.2 corresponded to the carbonyl (C-1) and the lactonic methylene (C-4), respectively.

The direct ^{1}H–^{13}C correlation spectrum (HMQC) allowed us to assign the benzylic carbons C-5 and C-6 to the signals at δ 34.5 and 38.2, respectively. The following assignments were also deduced: C-2′, 112.4; C-5′, 111.1; C-6′, 121.3; C-2″, 111.1; C-5″, 114.5; and C-6″, 121.3, for the aromatic carbons.

The long-range ^{1}H–^{13}C correlation spectrum (HMBC) confirmed the results described above. However, it was mainly used to assign quaternary carbons,

Table 1. ^{13}C NMR (100 MHz) data ($CDCl_3$) for compounds **1–4**

C	1	2	3	4
1	178.8	179.5	178.4	178.6
2	46.5	46.6	46.3	46.4
3	41.1	40.9	40.9	41.0
4	71.2	71.6	71.0	71.1
5	34.5	34.6	34.5	34.4
6	38.2	37.9	38.1	38.1
1′	130.2	130.2	130.0	130.1
2′	112.4	112.6	112.1	112.3
3′	149.0	149.0	148.9	148.9
4′	147.9	147.9	147.8	147.9
5′	111.1	111.4	111.1	111.3
6′	121.3	121.6	121.4	121.3
1″	129.7	130.5	131.5	130.4
2″	111.1	115.7	108.6	111.8
3″	146.6	144.1	147.7	148.9
4″	144.4	142.6	146.2	147.8
5″	114.5	115.5	108.1	111.0
6″	121.3	120.8	121.2	120.5
OME	55.8	55.9	55.6	2 × 55.7
OME	55.9 × 2	55.9	55.6	2 × 55.7
OCH_2O	—	—	100.9	—
OAc	—	—	—	—

Values based on ^1H–^{13}C, HMBC and DEPT experiments. Chemical shifts given in δ.

whose assignments, by other methods, may be very difficult owing to multiple substitution of aromatic rings and, in some cases, to the presence of two equally substituted phenyl units showing very small differences in chemical shift. The three-bond coupling between H-5′ and the signals at δ 130.2 and 149.1 established the assignments of C-1′ and C-3′, respectively. The coupling between H-6′ and the signal at δ 147.9 established C-4′, determining all quaternary carbons of the aromatic ring on C-5. The assignments of C-1″, C-3″ and C-4″ were made in a similar way. These unequivocal chemical shift data can be used for compounds of the same series having different functional groups.

EXPERIMENTAL

NMR spectra were recorded in $CDCl_3$ solns with TMS as int. standard on Bruker AMX400 and WP200SY spectrometers equipped with aspect X32 and 3000 computers, respectively, using a 5-mm ^1H and ^{13}C dual probe. Automatic microprograms were used to obtain DEPT and 2D spectra. The H–H COSY experiments consisted of 512 × 1 K spectra with NS = 4, NE = 256 and were taken on a Bruker WP 200 SY. All other experiments were run on an AMX 400. The C–H COSY experiments had 512 × 1 K spectra with NS = 8 and NE = 256, the HMBC experiments 512 × 2 K spectra with NS = 32 and NE = 512. All 1D spectra were from 16 K data points and the resolutions of the ^1H and ^{13}C NMR were 0.25 and 1 Hz per point, respectively.

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