

TWO FLAVONOIDS FROM *Iboza riparia* AND THE UNAMBIGUOUS ASSIGNMENTS OF THE ^1H AND ^{13}C NMR SIGNALS OF THEIR METHOXYLE GROUPS

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Abstract : two rare flavonoids, salvigenin and cirsimaritin, were isolated from the leaves of *Iboza riparia*. Assignment of the ^1H NMR spectra came from NOE experiments, and unequivocal attributions of all non-quaternary carbon signals is demonstrated from the ^1H - ^{13}C shift-correlated 2D-NMR spectrum of salvigenin.

In recent years, attention has been focused on the isolation of new metabolites from the Labiate *Iboza riparia* NE Brown^{1,2}, a shrub used in folk medicine as a stomach aid. Examination of an acetone extract of the leaves now furnished two rare flavonoids which were identified spectroscopically as 5-hydroxy-6,7,4'-trimethoxyflavone **1** (salvigenin)³⁻⁵ and 5,4'-dihydroxy-6,7-dimethoxyflavone **2** (cirsimaritin)⁵⁻⁷. We wish to report the unambiguous assignment of their ^1H and ^{13}C NMR spectra by a combination of NOE measurements and ^1H - ^{13}C shift-correlated 2D-NMR spectroscopy. This constitutes the first report of flavonoids from the genus *Iboza*.

^1H NMR spectra.

NOE experiments allowed complete assignments of the ^1H NMR signals of **1** and **2** (Table 1). Thus in flavone **1** attribution of positions C-7 and C-4' for the methoxyls resonating at δ 3.96 and 3.89 respectively came from their interaction with the protons at C-8 (δ 6.53) and C-3'/C-5' (δ 7.00). The third MeO group corresponding to the signal at δ 3.92 did not interact with any H, confirming its location at C-6. Finally, the remaining signal at δ 6.56 was attributed to H-3, a finding which rectifies previously reported data³. Similarly, the NOE experiments observed for flavone **2** allowed to allocate the signal at δ 4.03 to the C-7 MeO group which interacts with the proton at C-8 (δ 7.02). The remaining MeO group and the proton

resonating at δ 6.95 did not interact with any other protons and were thus identified as the C-6 methoxyl and the H-3 respectively.

^{13}C NMR spectra.

The ^{13}C NMR spectrum of flavone **1** has been reported earlier⁹ but the MeO groups were not rigorously assigned. Indeed, from considerations on steric hindrance, it has been claimed¹⁰ that, in a 6,7-dimethoxyflavone, the O-methyl at C-7 should appear more shielded than the one at C-6. This is now being demonstrated from the ^1H - ^{13}C shift-correlated 2D-NMR spectrum of **1** (Fig. 1) which brought unequivocal attribution of all non-quaternary carbon signals. Thus carbons resonating at δ 55.43, 56.20 and 60.70 were found to bear the methoxyls whose signals appear at δ 3.89, 3.96 and 3.92 respectively and were consequently identified as the C-4', C-7 and C-6 MeO groups. Similarly, the remaining cross-peaks of the 2D-NMR spectrum furnished clear attributions of C-3, C-8, C-2'/C-6' and C-3'/C-5'. The corresponding signals of **2** were attributed by analogy with **1**. Final conclusions are consigned in Table 2¹¹.

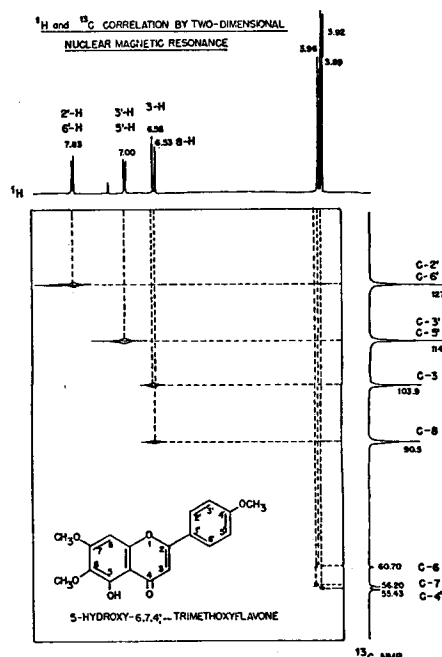


Figure 1 : ^1H - ^{13}C 2D-NMR of **1**

Table 1 : ^1H NMR data (360 MHz) of 1 and 2

H	<u>1</u>	<u>2</u>
3	6.56 s	6.95 s
8	6.53 s	7.02 s
2'/6'	7.83 d ^{9.25}	8.07 d ⁸
3'/5'	7.00 d ^{9.25}	7.04 d ⁸
6-OCH ₃	3.92 s	3.85 s
7-OCH ₃	3.96 s	4.03 s
4'-OCH ₃	3.89 s	-

Recorded on Brücker WH-360 apparatus.

1 was dissolved in CDCl₃ and 2 in DMSO-d₆ spectra were recorded at room temperature

Table 2 : ^{13}C NMR data (90.5 MHz) of 1 & 2

C	<u>1</u> ^{9,*}	<u>1</u>	<u>2</u>
2	163.1	163.88 s	164.13 s
3	102.9	103.92 d	102.74 d
4	181.5	182.51 s	182.21 s
5	152.0	153.07 s	152.65 s
6	132.0	132.56 s	132.04 s
7	158.1	158.63 s	158.64 s
8	91.0	90.49 d	91.57 d
9	151.7	152.95 s	152.14 s
10	104.9	106.00 s	105.15 s
1'	122.5	123.39 s	121.21 s
2'/6'	127.5	127.83 d	128.48 d
3'/5'	114.0	114.40 d	116.01 d
4'	161.9	162.55 s	161.31 s
6-OCH ₃	59.4	60.70 q	60.04 q
7-OCH ₃	55.9	56.20 q	56.45 q
4'-OCH ₃	55.0	55.43 q	-

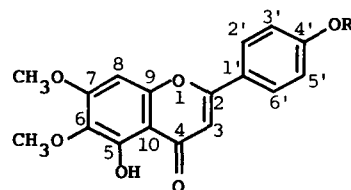
Recorded on a Brücker WH-360 apparatus.

* recorded in DMSO-d₆ at 25.1 MHz (100°C)

1 was dissolved in CDCl₃ and 2 in DMSO-d₆ spectra were recorded at room temperature

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1 R = Me

2 R = H

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- This is part VI of the series "Chemistry of Brazilian Labiatae"; for part V, see reference 1. Correspondance should be addressed to R. Zelnik.