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^{13}C-NMR Studies of Some Heterocyclically Substituted Chromones

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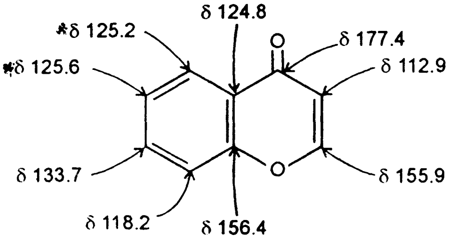
Synthesis of some heterocyclic substituted chromones was undertaken and results were reported depicting the structural elucidation based upon IR, PMR. Results of ^{13}C-NMR spectral studies of few heterocyclic substituted chromones constitute the subject matter of the present communication.

Key Words: ^{13}C-NMR spectra, 3-[2-(4-Morpholinyl)-thiazol-4-yl]-6-chloro-2-methylchromone, 6-(2-N-Substituted aminothiazol-4-yl)-2,3-dimethylchromone, 3-(2-Aminothiazol-4-yl)-2-methylchromone.

INTRODUCTION

In continuation of our efforts to synthesize heterocyclically substituted chromones and their structural elucidation[1–5], ^{13}C-NMR spectra of few heterocyclically substituted chromones were scanned which provided additional support to their structures. ^{13}C-NMR spectra of few (2-N-substituted aminothiazol-4-yl)-2-methylchromones are being discussed in this paper. Assignments of chemical shifts to the carbon atoms are done keeping in view analogies with the literature and effect of substituents. ^{13}C-NMR data for unsubstituted chromone[6–9] is given in Fig. 1. Still *et al.*[10] reported ^{13}C-NMR of 2-methyl-4-phenylthiazole. ^{13}C-NMR of 2-amino-4-phenylthiazole was published by Faure *et al.*[11] and δ-values are shown in Fig. 2.



*Assignments can be reversed

Fig. 1

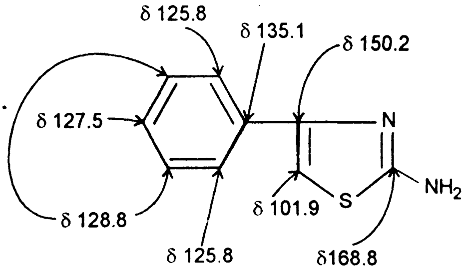


Fig. 2

EXPERIMENTAL

All the compounds were synthesized by reported methods[1-5]. Compounds were purified by re-crystallization from suitable solvent. Purity of the compounds was checked on silica gel coated TLC plates. ^{13}C-NMR spectra were recorded at 100 MHz on the Jeol FX-100 instrument and chemical shifts are expressed in δ.

RESULTS AND DISCUSSION

^{13}C-NMR spectrum of 3-[2-(4-morpholinyl)thiazol-4-yl]-6-chloro-2-methylchromone

^{13}C-NMR of 3-[2-(4-morpholinyl)thiazol-4-yl]-6-chloro-2-methylchromone (1), a representative compound of the series, scanned in $CDCl_3$, exhibited signals due to resonances of all the 17 carbon atoms appearing in the form of 15 signals (Fig. 3). Resonances due to all these carbons were assigned tentatively on the basis of analogy with the ^{13}C resonances of chromones and flavones[6-9], aminothiazoles[10, 11] and aminoethers having skeleton similar to morpholine[12] and taking into consideration intensities of the signals. The most downfield signal at δ177.4 can be safely assigned to C_4 of chromone since similar carbon in almost all the chromones appear in this region. The most up-field signal at δ20.44 is due to C_2 —CH_3. Similarly resonances appearing at δ 119.70, 124.11, 124.55, 125.35, 126.87, 133.23, 146.21 and 147.64 ppm were assigned to C_8, C_3, C_{4a}, C_5, C_7, C_2 and C_{8a} of chromone, respectively. Large downfield shift of C_3 is probably due to the presence of thiazole ring at this position.

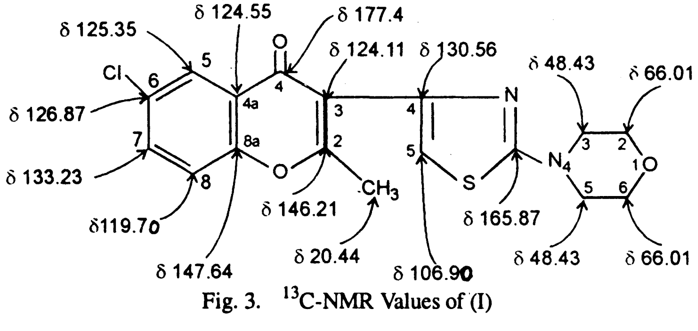


Fig. 3. ^{13}C-NMR Values of (I)

The remaining three carbon resonances at δ 106.90, 130.56 and 165.87 may be assigned to C_5, C_4 and C_2 of thiazole moiety, respectively.

The methylene carbon resonances of morpholine showed up as two signals at δ 48.43 and δ 66.01 which may be ascribed to C_3 and C_5 and C_2 and C_6, respectively.

^{13}C-NMR spectrun of 6-(2-N-methyl aminothiazol-4-yl)- 2,3-dimethylchromone

Among 6-(2-amino or N-substituted aminothiazol-4-yl)-2,3-dimethylchromones, a completely decoupled ^{13}C-NMR spectrum of 6-(2-N-methyl aminothiazol-4-yl)-2,3-dimethylchromone, **II** [a representative compound of the series] scanned in DMSO-d_6 showed 15 signals for 15 carbon. Chemical shift value assignment is based upon comparison with published values for chromones[5] and thiazoles[6, 7]. The ^{13}C-chemical shifts ranged from δ 9.0 to δ 175.8. The lowest field signal at δ175.8 can be safely assigned to C_4 of chromone, since the similar carbons of chromones appear in this region. Undoubtedly, the highest field signal at δ 9.0 is due to C_3—$\underline{C}H_3$ of chromone moiety. The aliphatic region of the spectrum was characterized by two more signals at δ 17.5 and δ 30.8, which may be due to C_2 —$\underline{C}H_3$ of chromone and C_2—NH$\underline{C}H_3$ of thiazole moieties, respectively. Signals at δ 115.4, 117.8, 121.2, 121.4, 130.0, 131.2, 154.0 and 161.2 may be assigned to C_3, C_8, C_5, C_{4a}, C_7, C_6, C_2 and C_{8a}, respectively. Downfield shift of C_6 of chromone is again due to the presence of thiazole ring on it. The remaining three signals at δ 100.8, 148.7 and 169.3 may have occurred due to the presence of C_5, C_4 and C_2 of thiazole moiety, respectively. These assignments are depicted in Fig. 4.

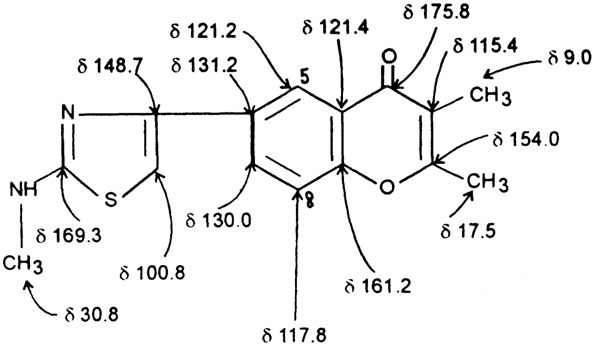


Fig. 4. ^{13}C-NMR Values of (II)

^{13}C-NMR spectrum of 3-(2-aminothiazol-4-yl)-2-methylchromone

Signals for all the thirteen magnetically non-equivalent carbons of 3-(2-aminothiazol-4-yl)-2-methylchromone, **III**, in its completely decoupled spectrum ($CDCl_3$) appeared between δ 19.2 to 177.9. As usual lowest field signal was due to C_4 of chromone ring. The most up-field signal at δ 19.2 was surely due to the presence of —CH_3 carbon present at C_2 of chromone. Resonances appearing at δ 117.0, 124.2, 124.7, 132.8, 134.5, 135.5, 154.5 and 166.4 are attributed to C_8, C_6, C_5, C_7, C_3, C_{4a},C_2 and C_{8a} of chromone moiety.

One outstanding feature of the ^{13}C-NMR of compound **III**, which deserves attention here is the large downfield shift of C_3 (δ 134.5) and C_{4a} (δ 135.5) resonances (C_3 appears at δ 112.9 in un-substituted flavones and C_{4a} at δ 124.8), respectively. The downfield shift of C_3 is ascribable to the presence of thiazole ring at this position, whereas that of C_{4a} is difficult to explain.

The remaining three carbon resonances at δ 174.3, 164.3 and 107.4 may be assigned to C_2, C_4 and C_5 of thiazole part of the molecule, respectively. The downfield shift of all these resonances is presumably due to the presence of chromone ring. These assignments are shown in Fig. 5.

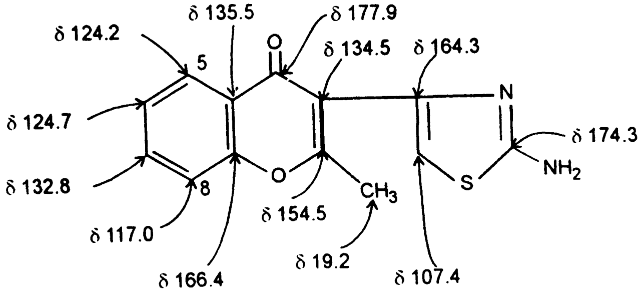


Fig. 5. ^{13}C-NMR Values of (III)

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