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AROMATIC SOLVENT-INDUCED SHIFTS OF SOME DIHYDROPYRANOCHALCONES - A MODEL STUDY TO DIFFERENTIATE ANGULAR AND LINEAR DIHYDROPYRANOISOFLAVONES

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Abstract : The aromatic solvent-induced shifts of dihydropyranochalcones I-XII have been studied with C_6D_6 and $CDCl_3$. The difference in the shifts can serve to distinguish between angular and linear dihydropyranoisoflavones.

Studies involving aromatic solvent-induced shifts (ASIS) have found use in solving many structural problems[1] and are largely based on the empirical carbonyl plane rule[2,3]. However, there is no report on the application of this technique to chalcones.

o-Hydroxydihydropyranochalcones I-XII can be considered to be made up of four rings A,B,B' and C as against the actual dihydropyrano ring (A), the phenyl ring fused to dihydropyrano ring (B) and the phenyl ring of the cinnamoyl side chain (C). As a result of chelation between the H-atom of phenolic -OH and the O-atom of carbonyl function, a six-membered ring B' can be invoked. The carbonyl plane rule states that all the protons lying in the front of the plane should show negative shift (shift $\Delta = \delta_{CDCl_3} - \delta_{C_6D_6}$) and those behind the plane should have a positive shift.

Application of the carbonyl rule to chalcones I-VIII should essentially indicate that the gem-dimethyl, $C_{3''}$- and $C_{4''}$-protons show positive shift and that the phenolic proton and $C_{3'}$-H show negative shift. These expectations were experimentally realized, which conversely prove the applicability of the carbonyl plane rule to such compounds. However, it was observed that the $C_{4''}$-protons of chalcones IX-XII showed negative shift contrary to chalcones I-VIII. The observation is attributed to the fact that the $C_{4''}$-benzylic protons in chalcones IX-XII lie in front of the carbonyl plane whereas in chalcones I-VIII the same lie behind the plane.

The shift values (Δ) for $C_{4''}$-benzylic protons of chalcones I-IV is of the order of 0.36 to 0.44 δ , while it is only 0.1 to 0.16 δ in chalcones V-VIII. This is attributable to the fact that with change in the position of the pendent cinnamoyl side chain there is a shift in the carbonyl plane itself, thus resulting in $C_{4''}$-benzylic protons lying closer to the plane. Also, as a result of this shift in the carbonyl plane the $C_{3'}$-H of chalcones I-IV have higher negative shift as compared with chalcones V-VIII.

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Table 1*

Aromatic Solvent-induced shift (Δ) values

S.No.	Compound[6]	Gem-dimethyl (ppm)	$C_{3''}$-CH_2 (ppm)	$C_{4''}$-CH_2 (ppm)	$C_{2'}$-OH (ppm)	$C_{3'}$-H (ppm)
1	I	0.30	0.50	0.42	- 0.92	- 0.50
2	II	0.26	0.46	0.36	- 0.84	- 0.48
3	III	0.26	0.46	0.38	- 0.88	- 0.60
4	IV	0.30	0.50	0.44	- 0.94	- 0.60
5	V	0.34	0.46	0.16	- 0.92	- 0.12
6	VI	0.32	0.44	0.12	- 0.88	- 0.14
7	VII	0.34	0.46	0.16	- 0.88	- 0.14
8	VIII	0.32	0.42	0.10	- 0.96	- 0.18
9	IX	0.24	0.38	- 0.12	- 0.94	-
10	X	0.22	0.40	- 0.10	- 0.94	-
11	XI	0.22	0.38	- 0.10	- 0.92	-
12	XII	0.26	0.42	- 0.10	- 0.90	-

*The PMR data for these compounds are available in ref.6

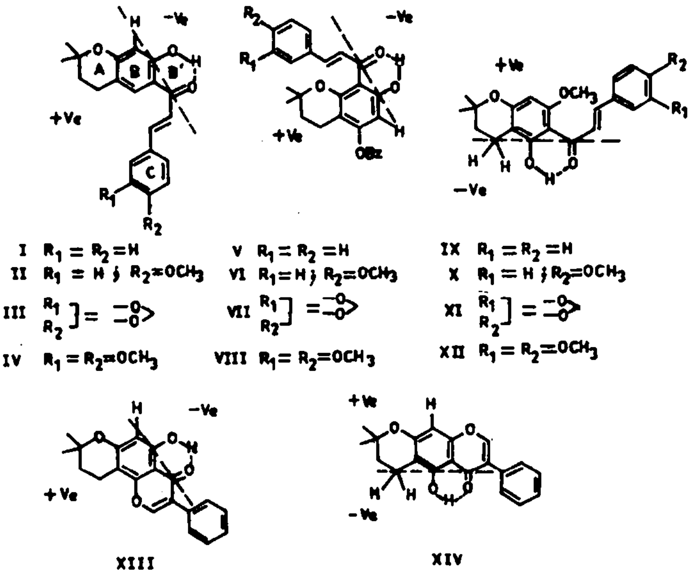

FIG.1

The scope of this method is profound in that, it could be exploited in differentiating isomeric angular and linear dihydropyranoisoflavones (XIII and XIV) which are the synthetic precursors for naturally occurring pyranoisoflavones in our studies[4,5]. The present work apart from being a model study to differentiate isomeric isoflavones, whose benzylic protons are expected to show negative and positive shifts respectively (Fig. 1), obviates the need to use elaborate lanthanide shift reagent and ^{13}C-NMR studies. Table 1 gives the nature and extent of solvent shifts for various protons belonging to different compounds. ^{1}H NMR spectra were taken with Varian XL-100 spectrometer at ordinary probe temperature. Sample concentrations were about 5% (w/v) or less. Accuracies of chemical shifts (Δ) are within ± 0.01.

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