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ANOMALOUS $AlCl_3$ INDUCED U.V. SHIFT OF C-ALKYLATED POLYPHENOLS

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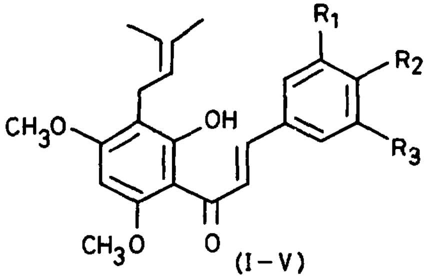
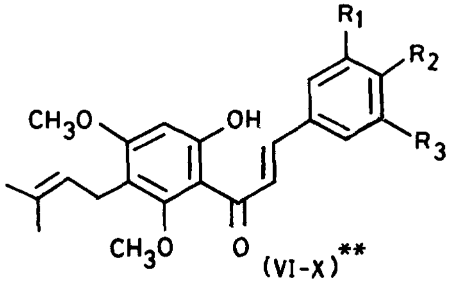
Our study has shown that there is no $AlCl_3$ induced shift in the U.V. spectra of C-alkylated polyphenols when a prenyl group is present ortho to the chelated hydroxyl group.

Flavonoids containing a chelated -OH group show a bathochromic AlCl$_3$ induced shift (20-60 nm) in the U.V. spectra[1]. An anomalous behaviour was observed by us while elucidating the structure of ovalichalcone[2] (I) and ovalichalcone-A[3] (II) isolated from <u>Milletia ovalifolia</u> seeds. These chalcones did not show the $AlCl_3$ induced shift for the chelated hydroxyl group. We have examined the U.V. spectra of a number of prenylated analogues of ovalichalcone and ovalichalcone-A with C-prenyl substituent at C-3' and C-5' positions (III-X). It was noticed that when a prenyl group is present ortho to a chelated hydroxyl group there is no $AlCl_3$ induced shift in the U.V. spectra.



(I-V)



(VI-X)**

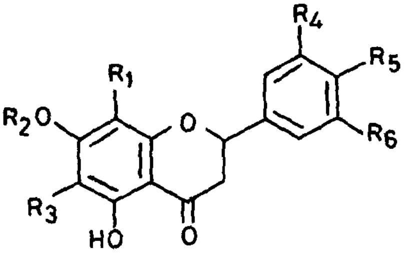
I, VI; $R_1 = R_2 = R_3 = H$

II, VII; $R_1 = R_2 = -O-CH_2-O-$, $R_3 = H$

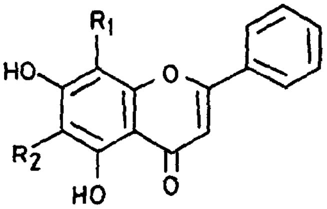
III, VIII; $R_1 = R_3 = H$, $R_2 = OCH_3$

IV, IX; $R_1 = R_2 = OCH_3$, $R_3 = H$

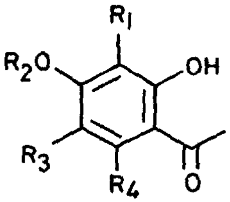
V, X; $R_1 = R_2 = R_3 = OCH_3$



XI-XVII



XVIII-XIX



a-j

XI $R_2=R_3=R_4=R_5=R_6=H$, $R_1=$ **

XII $R_1=R_2=R_4=R_5=R_6=H$, $R_3=$

XIII $R_1=R_4=R_5=R_6=H$, $R_2=CH_3$, $R_3=$

XIV $R_3=H$, $R_2=CH_3$, $R_4=R_5=R_6=OCH_3$, $R_1=$ **

XV $R_1=H$, $R_2=CH_3$; $R_4=R_5=R_6=OCH_3$; $R_3=$

XVI $R_2=R_3=H$, $R_4=R_5=R_6=OCH_3$, $R_1=$ **

XVII $R_1=R_2=H$, $R_4=R_5=R_6=OCH_3$, $R_3=$

XVIII $R_2=H$, $R_1=$ **

XIX $R_1=H$, $R_2=$

(a) $R_2=R_3=R_4=H$, $R_1=$

(b) $R_2=R_4=H$, $R_1=R_3=$

(c) $R_1=R_2=R_4=H$, $R_3=$ **

(d) $R_3=H$, $R_2=CH_3$, $R_4=OCH_3$, $R_1=$

(e) $R_2=R_3=H$, $R_4=OCH_3$, $R_1=$

(f) $R_1=H$, $R_2=CH_3$, $R_4=OCH_3$, $R_3=$ **

(g) $R_1=R_2=H$, $R_4=OCH_3$, $R_3=$ **

(h) $R_2=R_3=R_4=H$, $R_1=$Allyl

(i) $R_3=R_4=H$, $R_1=CH_3$, $R_2=H$

(j) $R_2=R_3=R_4=H$, $R_1=-CH_2C_6H_5$

** shows bathochromic $AlCl_3$ induced shift.

Further study of a number of C-prenyl, C-allyl, C-methyl, C-benzyl acetophenones[4] and prenylated flavones, flavanones and chalcones has confirmed that compounds having a hydrocarbon substituent adjacent to the chelated hydroxyl does not show any $AlCl_3$ induced shift. The structures of all compounds mentioned have been confirmed by independent published evidence. This anomalous behaviour could be due to steric factors. The above observation has been found to be of significance in the structure elucidation of natural and synthetic products.

References

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