

SHORT COMMUNICATION

ALUMINIUM COMPLEXES OF FLAVANONES AND DIHYDROFLAVONOLS*

L. J. PORTER and K. R. MARKHAM

Chemistry Division, Department of Scientific and Industrial Research, Petone, New Zealand

(Received 7 October 1971)

Abstract—Flavanones and dihydroflavonols containing *orthodihydroxyl* groups in the A-ring and 5-deoxy dihydroflavonols (through the 3-hydroxy-4-oxo-system) are shown to form acid-labile complexes with AlCl_3 in MeOH. These complexes are detectable in the UV spectrum, alone, or in the presence of one another. Their stability relative to other Al(III) complexes with flavonoids is: 3-hydroxyl (flavonol) > 5-hydroxyl (flavone) > 5-hydroxyl (flavanone) > *ortho*-dihydroxyl groups > 3-hydroxyl (dihydroflavonol).

INTRODUCTION

STRUCTURALLY significant, AlCl_3 -induced bathochromic shifts in the UV spectra of flavanones and dihydroflavonols in methanol have received little attention by comparison with those of flavones and flavonols. For example, it has been established that the presence of 5-hydroxyl groups, 3-hydroxyl, 3,5-dihydroxyl and *ortho*-dihydroxyl groups in either the A- or B-rings of flavones and flavonols can be detected by measuring and comparing shifts observed in the UV spectrum on the addition of AlCl_3 and AlCl_3/HCl .^{1,2} The most recently reported work on the diagnostic use of these reagents for structural investigations of flavanones and dihydroflavonols claims that 5-hydroxyl groups, and possibly also *ortho*-dihydroxyl groups in the A-ring, can be detected by using AlCl_3 and AlCl_3/HCl .¹ The data presented below establishes that for flavanones and dihydroflavonols: (1) A-ring *ortho*-dihydroxyl groups may be detected; and (2) 3-hydroxyl groups in the 5-deoxy flavonoid series may also be identified.

RESULTS AND DISCUSSION

Table 1 summarizes values for the position of the band of maximum intensity in the UV spectrum of selected flavanones and dihydroflavonols, and the bathochromic shifts produced by the presence of AlCl_3 and AlCl_3/HCl . From this data the following conclusions may be derived.

(1) 5-hydroxy-flavanones and dihydroflavonols form acid-stable complexes with Al(III) involving the 4-oxo-5-hydroxy-chelate ring system which result in a 20–22 nm bathochromic shift of the principal absorption band. This shift is probably associated with the formation of a 1:1 complex.⁵

(2) Dihydroflavonols lacking a 5-hydroxyl group form acid-labile complexes through the 4-oxo-3-hydroxyl system (analogous to flavonols) leading to a 31–38 nm bathochromic

* Part III in the series "Aluminium Complexes of Hydroflavones in Absolute Methanol". For Part II see L. J. PORTER and K. R. MARKHAM, *J. Chem. Soc. C*, 1309 (1970).

¹ T. J. MABRY, K. R. MARKHAM and M. B. THOMAS, *The Systematic Identification of Flavonoids*, Springer-Verlag, New York (1970), and references therein.

² L. J. PORTER and K. R. MARKHAM, *Phytochem.* 9, 1363 (1970).

TABLE 1. THE EFFECT OF AlCl_3 AND AlCl_3/HCl ON THE UV SPECTRA* OF FLAVANONES AND DIHYDROFLAVONOLS

	$\lambda_{\text{max}}(\text{nm})$ for band of maximum intensity		
	MeOH	$\text{AlCl}_3(\text{shift}\dagger)$	$\text{AlCl}_3/\text{HCl}(\text{shift}\dagger)$
Flavanones			
5,7,4'-Trihydroxy-	289	312(23)	311(22)
5,7,3',4'-Tetrahydroxy-	289	310(21)	309(20)
5,6,7-Trihydroxy-	295	328(33)	317(22)
7,8,3',4'-Tetrahydroxy-	288	314(26)	288(—)
Dihydroflavonols‡			
7,4'-Dihydroxy-	276	309(33)	276(—)
7,3',4'-Trihydroxy-	277	308(31)	278(—)
7,3',4',5'-Tetrahydroxy-	275	307(32)	275(—)
7,8,3',4'-Tetrahydroxy-	290	352(62)	290(—)
5,7,4'-Trihydroxy-	291	316(25)	312(21)
5,7,3',4'-Tetrahydroxy-	290	312(22)	312(22)
7,8,4'-Trimethoxy-	280	318(38)	280(—)
7,8,3',4'-Tetramethoxy-	282	317(35)	281(—)

* UV spectra were measured in pure MeOH on a Beckman DK2A spectrophotometer. Shift reagents were made up as described in Ref. 1.

† The shift in both cases refers to the difference between the position of the principal absorption band in MeOH and that in AlCl_3 or AlCl_3/HCl .

‡ The authors wish to thank Professor J. W. Clark-Lewis for samples of 7,8,4'-trimethoxy- and 7,8,3',4'-tetramethoxy-dihydroflavonol, and Dr. E. J. McGary for a sample of 7,8,3',4'-tetrahydroxy-dihydroflavonol.

shift. The complex, however, is weak. It is unstable to acid and it does not form in 0.1 M NaOAc, presumably since the 4-oxo-3-hydroxyl system is too weak a ligand to compete with acetate ions for $\text{Al}(\text{III})$. These features are probably due to the very weak acidic properties of the aliphatic 3-hydroxyl group. The instability of this complex in NaOAc enables a distinction to be made between the spectral shift observed for a 3-hydroxyl group and that observed for an *ortho*-dihydroxyl group. Earlier work^{3,4} has shown that the complex formed between $\text{Al}(\text{III})$ and the *ortho*-dihydroxyl group is stable in 0.1 M NaOAc.

(3) The 5-hydroxyl group is preferentially complexed in 5-hydroxy-dihydroflavonols.

(4) The presence of *ortho*-dihydroxyl groups in the A-ring of flavanones and dihydroflavonols may also be detected by the AlCl_3 -induced bathochromic shift of the principal absorption band in the absence of acid. The shift observed varies between 11 and 29 nm depending upon the position of the *ortho*-dihydroxyl group and is additive to the shifts produced by 3- or 5-hydroxylation in the same molecule. However the complex due to an *ortho*-dihydroxyl group in the A-ring may be distinguished from that due to a 5-hydroxyl group by its acid instability and from that due to a 3-hydroxyl group by its stability to 0.1 M NaOAc.

(5) From the conclusions derived here and in our earlier work,^{3,5} the order of stability of $\text{Al}(\text{III})$ complexes with the various chelating sites on flavonoids is: 3-hydroxyl (flavonol) > 5-hydroxyl (flavone) > 5-hydroxyl (flavanone) > *ortho*-dihydroxyl groups > 3-hydroxyl (dihydroflavonol).

³ L. J. PORTER and K. R. MARKHAM, *J. Chem. Soc. C*, 1309 (1970).

⁴ L. JURD and T. A. GEISSMAN, *J. Org. Chem.* **21**, 1395 (1956).

⁵ L. J. PORTER and K. R. MARKHAM, *J. Chem. Soc. C*, 344 (1970).

Key Word Index—Flavanones; flavanonols; UV spectra; aluminium chloride shifts.