Phytochemistry, 1972, Vol 11, pp. 411 to 412 Pergamon Press Printed in England

SHORT COMMUNICATION

A PROCEDURE FOR THE UV DETECTION OF HYDROXYL AND METHOXYL GROUPS AT C_6 IN FLAVONES AND 3-*O*-SUBSTITUTED FLAVONOLS

JAMES A MEARS

The Academy of Natural Sciences, Philadelphia, Pa , U S A

and

TOM J. MABRY

The Cell Research Institute and The Department of Botany, University of Texas at Austin, Austin, Texas 78712, U S A

(*Received* 29 *March* 1971)

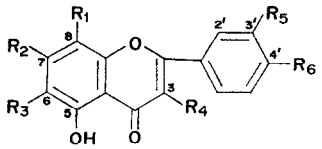
Abstract—The presence of hydroxyl or methoxyl groups at C_6 in flavones and 3-substituted flavonols is indicated when, in the UV spectral analysis in MeOH with added $AlCl_3$–HCl, a Band I bathochomic shift (relative to the MeOH spectrum) of about 20 nm is observed for the C_5-hydroxy-C_4-keto-$AlCl_3$ complex, the procedure distinguishes C_6 oxygenation from that at C_8 in these compounds

IT IS NOW well established[1–3] that much information with regard to the presence or absence of free 3′,4′-*o*-dihydroxyl groups and 3 and 5 hydroxyl groups in flavones and flavonols can be obtained by the examination of the UV spectra of the flavonoid in MeOH (but not in EtOH[4]), MeOH with anhydrous $AlCl_3$ and MeOH with $AlCl_3$–HCl Furthermore, some of the complexes formed between $AlCl_3$ and flavonoids have recently been characterized.[3,5] In addition, we[3,6] and at least one other worker[2] have noted that, with flavones and 3-substituted flavonols which contain a methoxyl or hydroxyl group at the 6 position, the magnitude of the shift of Band I (relative to the MeOH spectrum) resulting from the $AlCl_3$ complex (in the presence of HCl) with the 5-hydroxy-4-keto-system is only about 20 nm, otherwise, the shift is about 45 nm. After examining all the available data, it seemed worthwhile to emphasize here the reliability of this procedure for detecting hydroxyl and methoxyl substituents at C_6 in flavones as well as in 3-substituted flavonols. A few relevant data are presented in Table 1 Since anhydrous $AlCl_3$ in MeOH also complexes with 3′,4′-*o*-dihydroxyl groups and to a lesser extent with 3′-methoxy-4′-hydroxy, 4′-hydroxy-3′-methoxy and 3′,4′-dimethoxy systems,* the detection of C_6-oxygenated substituents in flavones and

* With *o*-3′,4′-dihydroxyl groups in flavones and flavonols, anhydrous $AlCl_3$ in MeOH produces a complex which shifts Band I bathochromically 30–40 nm relative to the MeOH spectrum, in addition, shifts of 10–15 nm may be observed for flavonoids with 3′-hydroxy-4′-methoxy, 3′-methoxy-4′-hydroxy and 3′,4′-dimethoxy groups (Shifts for these latter systems are not always observed probably because the complexes are extremely sensitive to traces of moisture and/or acid)

[1] K R MARKHAM and T J MABRY, *Phytochem* 7, 1197 (1968)
[2] L JURD, *Phytochem* 8, 445 (1969)
[3] T J MABRY, K R MARKHAM and M B THOMAS, *The Systematic Identification of Flavonoids*, Springer, New York-Heidelberg (1970)
[4] L J PORTER and K R MARKHAM, *Phytochem* 9, 1363 (1970)
[5] L J PORTER and K R MARKHAM, *J Chem Soc* C, 344, 1309 (1970)
[6] H ROSLER, A E STAR and T J MABRY, *Phytochem* 10, 450 (1970)

TABLE 1 BATHOCHROMIC SHIFT (nm) OF BAND I IN MeOH RELATIVE TO BAND Ia IN $AlCl_3$/HCl



Flavones and flavonols without a C_6 hydroxyl or methoxyl group

C_8 R_1	C_7 R_2	C_6 R_3	C_3 R_4	C_3 R_5	$C_{4'}$ R_6	Shift $\Delta\lambda$(nm)
H	OH	H	H	H	H	67
H	O-glc-O-glc*	H	H	OH	O-glc	50
H	OH	H	H	H	OCH_3	52
H	O-glc	H	H	H	OH	49
H	OH	H	H	OCH_3	OCH_3	42
H	OH	H	H	H	OH	44
H	OH	C-glc	H	H	OH	44
C-glc	OH	H	H	H	OH	47
C-glc	OH	C-glc	H	H	OH	48
H	OH	H	O-glc	OCH_3	OH	46
H	OH	H	O-rut	OCH_3	OH	44
H	OH	H	O-glc	OH	OH	43
H	OH	H	O-rut	OH	OH	43
H	O-glc-glc	H	OCH_3	OH	O-glc	50
OCH_3†	OCH_3	H	OCH_3	OCH_3	OH	56
OCH_3‡	OCH_3	H	OCH_3	OH	OCH_3	59
OCH_3‡	OCH_3	H	OCH_3	OH	OH	54

Flavones and flavonols with a hydroxyl or methoxyl group at C_6

H	OH	OH	H	H	H	23
OCH_3	OH	OCH_3	H	H	OCH_3	21
OCH_3	OCH_3	OCH_3	H	H	OH	22
H	OH	OCH_3	O-rut	OH	OH	19
H	OH	OCH_3	OCH_3	OCH_3	OH	17
H	O-glc	OCH_3	OCH_3	OH	OCH_3	17
H	OCH_3	OCH_3	OCH_3	OH	OCH_3	20

* O-glc = *O*-glucosyl, C-glc = *C*-glucosyl, O-rut = *O*-rutinosyl

† We thank Prof L H Briggs, The University of Auckland, for this sample

‡ We thank Prof P R Jefferies and Dr E L Ghisalbert, The University of Western Australia, for these samples

flavonols requires that the $AlCl_3$/HCl spectrum be compared with the one obtained in MeOH alone. It is noteworthy that flavonoids containing *C*-glucosyl groups at C_6 or oxygenated substituents at C_8 (but not at C_6) do not show the phenomenon

EXPERIMENTAL

All UV spectra were carried out by standard procedures[3] and many of the relevant spectra have been published elsewhere

Acknowledgements—This investigation was supported by the National Science Foundation (Grant GB-29576X), The National Institutes of Health (Grant HD-04488 and 5-TOI GM-00789) and the Robert A Welch Foundation (Grant F-130) We thank Lloyd Southwick for running some of the UV spectra

Key Word Index—UV spectra, determination of 6-substituted flavonoids, aluminium chloride spectral shifts