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REVIEW

UV SPECTRAL DIFFERENTIATION OF 5-HYDROXY- AND 5-HYDROXY-3-METHOXYFLAVONES WITH MONO-(4′;), DI-(3′,4′) or TRI-(3′,4′,5′)-SUBSTITUTED B RINGS

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Key Word Index—Flavones; 3-methoxyflavones; UV spectral properties; structural analysis.

Abstract—The spectra of 151 flavonoids were measured in methanol alone and with added aluminium chloride and hydrochloric acid. A bathochromic shift in the presence of aluminium chloride separated flavonoids with a 3′,4′-*o*-dihydroxy system. The different flavonoids may be divided into two classes according to the shape of band I (single or double peak) in the presence of aluminium chloride + hydrochloric acid. Flavones and 3-methoxyflavones may be differentiated through their different UV spectral properties. In addition, it is possible to define the positions of substituents on the A (6; 8 and 6,8)- and B (4′; 3′,4′; 3′,4′,5′)-rings in most cases.

INTRODUCTION

Useful information on the structure of flavonoids can be gained by comparison of their UV spectra in methanol and in the presence of a number of spectral shift reagents [1,2]. However, these spectral data have never been examined in order to distinguish, among those compounds with a free 5-hydroxyl, substances which either have or lack 3-methoxysubstitution [3]. ^{1}H NMR spectroscopy has often been used to provide unequivocal distinction between these two classes of compounds[2,4] though it has the disadvantage of requiring mg quantities for analysis. In most cases, this method can be replaced by examining the UV spectra in methanol or methanol + aluminium chloride + hydrochloric acid as shown from the results reported here for more than 140 flavonoids (Table 1). These compounds may be easily identified by their purple fluorescence in UV light and by their spectra in methanol since the majority exhibit an *A* maximum in the long UV range (band I), above 326 nm, and generally the ratio of the *A* of band I–band II is greater than 0.7. Furthermore, this study provides information on the number and position of substituents that may be present on the A- and B-rings which renders it useful in those cases when only minute amounts of flavonoids are available for analysis.

RESULTS

The presence (or absence) of a 3′,4′-*o*-dihydroxy system in flavonoids can normally be deduced from examination of their UV spectrum in methanol, before and after addition of sodium acetate ± boric acid [5] or aluminium chloride ± hydrochloric acid. In the latter case [1,2,6], the formation of complexes (Scheme 1) in the presence of aluminium chloride is stable or labile to pH.

Although Harborne [7] suggested the use of aluminium chloride for the detection of *o*-dihydroxy groupings as early as 1954 his method was not sufficiently developed at that time [1]. Now that much more data are available, it is clear that the shape and position of band I in the methanol + aluminium chloride spectrum will reveal the presence of a 3′,4′-dihydroxy grouping in flavones and 3-methoxyflavones; the compounds possess such a system when there is a single peak between 420 and 454 nm or, if the λ_{max} of band Ia is above 449 nm, when this spectrum presents two bands, Ib and Ia (Fig. 1). The further addition of hydrochloric acid is also very revealing. Whilst Mabry *et al.* [1] indicated that, "the $AlCl_3$–HCl spectrum of 5-hydroxyflavones typically consists of four major absorption peaks, band Ia, Ib, IIa, IIb" (Fig. 2), I have found that in some cases band Ia may be completely absent. So far the flavonoids may be divided into two classes: the compounds of class I exhibit a single band (Ib) in contrast to the flavonoids of class II where Ib and Ia are present (Fig. 1).

Furthermore, from the data furnished by the spectra run in methanol and after addition of both neutral and acidic aluminium chloride, it is possible to define the type of substitution at position 3 of the flavonoid skeleton. The various flavones and 3-methoxyflavones can then be subdivided into 20 groups according to the number and position of substituents on ring A and the heterocyclic ring (Tables 2 and 3; Fig. 3).

FLAVONOIDS OF CLASS I

Only the compounds of this class (groups 1–4) exhibit a single peak for band I both in neutral and acidic aluminium chloride solution. The λ_{max} is always below 381 nm in aluminium chloride + hydrochloric acid. They

Table 1. UV spectral properties of 5,7-dioxygenated flavones and related 3-methoxy-derivatives

Substitution pattern				λ_{max}^{MeOH} nm		$\lambda_{max}^{MeOH+AlCl_3}$ / $\lambda_{max}^{MeOH+AlCl_3+HCl}$					$\Delta\lambda$ band I		
OH	OMe	Me	Trivial name	Band II	Band I						$AlCl_3$	$AlCl_3+HCl$	Origins
Group 1													
5,7,4′	6	—	Hispidulin	275 (0.65)	336 (1.00)	262s (0.35)	282i (0.55)	294s (0.60)	303 (0.64)	362 (1.00)	26		Herz* Tallahassee
						260s (0.31)		287i (0.65)	303 (0.74)	356 (1.00)		20	
5,7	6,4′	—	Pectolinarigenin	276 (0.78)	330 (1.00)	263s (0.41)		280i (0.66)	303 (0.77)	352 (1.00)	22		Chadenson* Lyon
						262s (0.42)		293s (0.85)	301 (0.86)	350 (1.00)		20	
5,4′	6,7	—	Cirsimaritrin	277 (0.73)	331 (1.00)	264s (0.39)	280i (0.65)	296s (0.76)	303 (0.77)	356 (1.00)	25		Wallace* Cullowhee
						263s (0.40)		295s (0.85)	303 (0.86)	353 (1.00)		22	
5	6,7,4′	—	Salvigenin	276 (0.81)	329 (1.00)	264s (0.50)		293s (0.74)	301 (0.79)	356 (1.00)	27		Lyon
						262s (0.54)		291i (0.82)	301 (0.87)	348 (1.00)		19	
5,7,3′	6,4′	—	Desmethoxy-centaureidin	244s (0.71)	254s (0.70) 274 (0.70) 342 (1.00)	262 (0.66)	284 (0.70)	298i (0.69)		370 (1.00)	28		Chadenson* Lyon
						260 (0.66)	286 (0.77)	296i (0.76)		364 (1.00)		22	
5,7,4′	6,3′	—	Jaceosidin	245s (0.71)	275 (0.67) 344 (1.00)	261 (0.68)	284 (0.68)	298i (0.62)		370 (1.00)	26		Horie* Tokushima
						258 (0.69)	286 (0.73)	298i (0.69)		366 (1.00)		22	
5,4′	6,7,3′	—	Cirsilineol	240s (0.72)	254s (0.63) 276 (0.67) 344 (1.00)	260 (0.62)	284 (0.69)	292i (0.61)		374 (1.00)	30		Lyon
						260 (0.62)	286 (0.69)	294i		368 (1.00)		24	
5,7	6,3′,4′	—	Eupatilin	243	277 340	258	282			366	26		Wagner [32] Liu [33]
						256	288			361		21	
5,3′	6,7,4′	—	Eupatorin	244 (0.70)	252s (0.68) 276 (0.70) 342 (1.00)	262 (0.72)	287 (0.81)	297i (0.78)		370 (1.00)	28		Wollenweber* Darmstadt
						261 (0.63)	284 (0.74)	292 (0.75)		363 (1.00)		21	

5	6,7,3′,4′	—		240 (0.80)	252s (0.69)	276 (0.72)	340 (1.00)		260 (0.65) 258 (0.66)	287 (0.72) 290 (0.76)	297i (0.67)		370 (1.00) 362 (1.00)		30	22	Rodriguez* Madrid		
5,7,3′	6,4′,5′	—				274 (0.90)	332 (1.00)			284 (0.70) 289 (0.80)	298s (0.60)		358 (1.00) 353 (1.00)		26	21	Liu [33]		
5,7,4′	6,3′,5′	—		242s (0.80)		275 (0.66)	350 (1.00)		258s (0.62) 258s (0.67)	282 (0.67) 283 (0.72)		310s (0.57) 308s (0.67)	382 (1.00) 372 (1.00)		26	22	Herz* Tallahassee		
5,4′	6,7,3′,5′	—		240s (0.96)		274 (0.61)	348 (1.00)		256s (0.62) 256s (0.64)	283 (0.62) 286 (0.64)		310s (0.37) 308 (0.44)	386 (1.00) 374 (1.00)		38	26	Lyon		
5,7,3′,4′	6	—	Nepetin		257 (0.90)	272 (0.90)	348 (1.00)		262 (0.78)	274 (0.78) 280 (0.82)	298 (0.63)	306s (0.39)	338 (0.23) 367 (1.00)	428 (1.00)	80	19	Lyon		
5,3′,4′	6,7	—	Cirsiliol	243 (0.80)	256 (0.79)	274 (0.79)	346 (1.00)		275 (0.70) 262s (0.80)	302s (0.63) 286 (0.85)	297i (0.84)	338 (0.52)	372 (1.00)	428 (1.00)	82	26	Morita* Toyama		
5,7,3′,4′	6,5′	—				273	352			272	280 280	304s 300s	356s 372	432	80	20	Liu [33]		
Group 2																			
5,6,7,4′	3	—				281	340					302 297	375 367		35	27	Ulubelen [11]		
5,6,4′	3,7	—				281	341					297 297	377 368		36	27	Ulubelen [11]		
5,6,7,4′	3,3′	—		240s (0.74)	257s (0.66)	280 (0.69)	349 (1.00)	244s (0.81)	260s (0.58) 262 (0.63)	278s (0.50)	302 (0.66) 296 (0.70)	312i (0.61)	396 (1.00) 376 (1.00)		47	27	Wagner* Munich		
5,6,4′	3,7,3′	—	Chrysosplenol C		256s (0.67)	281 (0.74)	352 (1.00)	243s (0.66) 242s (0.71)	266 (0.60) 263 (0.63)		296 (0.69) 296 (0.73)		382 (1.00) 378 (1.00)		30	26	Lyon		
5,6,3′	3,7,4′,5′	—	Apuleitrin	240s (0.77)		281 (0.85)	339 (1.00)	246s (0.75) 242s (0.75)	262s (0.56) 260s (0.58)		299 (0.80) 296 (0.81)		371 (1.00) 365 (1.00)		32	26	Braz Filho* Rio de Janeiro		

Table 1. (*continued*)

Substitution pattern				λ_{max}^{MeOH} nm			$\lambda_{max}^{MeOH+AlCl_3}$ / $\lambda_{max}^{MeOH+AlCl_3+HCl}$					$\Delta\lambda$ band I		
OH	OMe	Me	Trivial name	Band II		Band I						$AlCl_3$	$AlCl_3+HCl$	Origins
5,6,7,3′,4′	3	—		258	270s	350		274	305s		426	76		Ulubelen [11]
							262	276s		381			31	
5,6,3′,4′	3,7	—		259	279	348		281	300s	344	436	88		
				(0.84)	(0.82)	(1.00)		(0.83)	(0.65)	(0.52)	(1.00)			Lyon
							267		295	379			31	
							(0.85)		(0.86)	(1.00)				
Group 3														
5,6,7,4′					284	336	262	292i	304	375		39		
			Scutellarein		(0.84)	(1.00)	(0.12)	(0.64)	(0.86)	(1.00)				Lyon
							262s	292i	302	364			28	
							(0.16)	(0.68)	(0.84)	(1.00)				
5,6,7	4′	—			286	335		276s	302	380		45		Harborne*
					(0.86)	(1.00)		(0.50)	(1.00)	(0.90)				Reading
							262s	292i	302	358			23	
							(0.28)	(0.86)	(0.94)	(1.00)				
5,6,4′	7	—	Sorbifolin		285	335	266s	292i	303	367		32		Nogradi*
					(0.83)	(1.00)	(0.26)	(0.66)	(0.78)	(1.00)				Budapest
							266s	290i	302	362			27	
							(0.29)	(0.69)	(0.82)	(1.00)				
5,6	7,4′	—	Ladanein		286	331	265s	292i	303	362		31		Nair*
					(0.89)	(1.00)	(0.29)	(0.73)	(0.86)	(1.00)				Pondicherry
							264s	292i	302	358			27	
							(0.32)	(0.78)	(0.89)	(1.00)				
5,6,7,3′	4′	—		242s	284	342	255s	296	315s	380		38		Greger†
				(0.80)	(0.78)	(1.00)	(0.49)	(0.64)	(0.57)	(1.00)				Vienne
							257s	294		365			23	
							(0.71)	(0.69)		(1.00)				
5,6,7,4′	3′	—	Nodifloretin		276	344	262s		302	390		46		Ulubelen [11]
					(0.90)	(1.00)			(1.00)	(1.00)				
							255s	290		370			26	
								(1.00)		(1.00)				
5,6,3′	7,4′	—		246s	284	341	261	297		373		32		Martino*
				(0.69)	(0.75)	(1.00)	(0.59)	(0.77)		(1.00)				Buenos Aires
							259	296		367			26	
							(0.61)	(0.81)		(1.00)				

5,6,7,3',4'	—	—		248s (0.82)		283 (0.77)		346 (1.00)	248s (0.99)	270 (0.78)		302 (0.63)			420 (1.00)	74			Lyon
										258 (0.76)	296 (0.76)			372 (1.00)			26		
5,6,3',4'	7	—	Pedalitin		256s (0.69)	284 (0.65)		345 (1.00)	246s (0.56)	274 (0.55)		302 (0.61)	343s (0.32)		425 (1.00)	80			Martino* Buenos Aires
										260 (0.47)	296 (0.70)			372 (1.00)			27		
Group 4																			
5,6,4'	7,8,3'	—	Thymonin		250s (0.53)	292 (0.80)		343 (1.00)	241s (0.71)	261 (.50)		306 (0.69)	316 (0.64)	380 (1.00)		37			Van den Brouck† Anvers†
									240s (0.66)	259s (0.47)		305 (0.64)	316 (0.58)	369 (1.00)			26		
Group 5																			
5,7,4'	—	8				274 (1.00)	300s (0.77)	328 (0.87)	262s (0.60)	282 (0.96)	296i (0.83)	310 (1.00)	346 (1.00)	392 (0.56)		64			Chopin* Lyon
									260s (0.55)	282 (0.92)		307 (1.00)	342 (0.95)	392 (0.35)			64		
Group 6																			
5,4'	7	6				274 (0.85)		332 (1.00)		263s (0.48)	288 (0.84)	301 (0.87)	351 (1.00)	390s (0.45)		58			Wollenweber† Darmstadt
									—			—	—	—					
5	7,4'	6				270 (0.88)		328 (1.00)	262s (0.60)	279 (0.82)	292s (0.83)	302 (0.87)	346 (1.00)	388s (0.69)		60			Chadenson* Lyon
									262s (0.61)	278 (0.85)	292s (0.86)	301 (0.91)	342 (1.00)	387s (0.64)			59		
Group 7																			
5,7,4'	—	—	Apigenin			267 (0.92)	296s (0.68)	336 (1.00)			276 (0.81)	301 (0.78)	348 (1.00)	384 (0.85)		48			Mabry [1]
											276 (0.88)	299 (0.85)	340 (1.00)	381 (0.83)			45		
5,7	4'	—	Acacetin			269 (0.98)	303s (0.84)	327 (1.00)	259s (0.52)	277 (0.85)	292s (0.78)	302 (0.87)	344 (1.00)	382 (0.71)		55			Mabry [1]
									260s (0.63)	279 (0.92)	294s (0.90)	300 (0.93)	338 (1.00)	379 (0.64)			52		
5,4'	7	—	Genkwanin			269 (0.86)		336 (1.00)		277 (0.87)	294s (0.60)	303 (0.69)	348 (1.00)	384 (0.85)		48			Lyon
										276 (0.89)	294s (0.74)	301 (0.79)	343 (1.00)	382 (0.75)			46		

Table 1. (*continued*)

Substitution pattern				λ_{max}^{MeOH} nm					$\lambda_{max}^{MeOH+AlCl_3}$ / $\lambda_{max}^{MeOH+AlCl_3+HCl}$							$\Delta\lambda$ band I		
OH	OMe	Me	Trivial name	Band II		Band I										$AlCl_3$	$AlCl_3+HCl$	Origins
5	7,4′	—			270 (0.93)	298s (0.70)	329 (1.00)	262s (0.53)	280 (0.89)	294s (0.77)	303 (0.83)	344 (1.00)	382 (0.64)			53		Lyon
								264s (0.54)	278 (0.85)	294s (0.71)	304 (0.80)	342 (1.00)	384 (0.69)				55	
5,7,3′	4′	—	Diosmetin	240s (0.70)	252 (0.78)	267 (0.80)	291s (0.49)	344 (1.00)	267 (0.87)	273 (0.83)	296 (0.60)	362 (0.95)	390 (1.00)			46		Mabry [1]
									264s (0.84)	276 (0.85)	295 (0.66)	351 (1.00)	383 (0.92)				39	
5,7,4′	3′	—	Chrysoeriol	241 (0.85)	249s (0.82)	269 (0.81)		347 (1.00)	262 (0.85)	274 (0.85)	296 (0.53)	366s (0.91)	390 (1.00)			43		Mabry [1]
									259 (0.95)	276 (0.96)	294 (0.67)	353 (1.00)	386 (0.94)				39	
5,7	3′,4′	—		240 (0.92)	248s (0.87)	269 (0.87)	291s (0.58)	340 (1.00)	261 (0.91)	276 (0.92)	295 (0.59)	359 (1.00)	387 (0.97)			47		Mabry [1]
									259 (0.77)	279 (0.90)	293s (0.69)	348 (1.00)	381s (0.72)				41	
5,3′	7,4′	—	Pilloin	244 (0.84)	252 (0.92)	268 (0.84)	293s (0.62)	344 (1.00)	266 (0.96)	275 (1.00)	296 (0.70)	360 (0.93)	386 (0.93)			41		Lyon
									262 (0.96)	276 (1.00)	296s (0.76)	355 (0.96)	384 (0.88)				39	
5,7,4′	3′,5′	—	Tricin	244s (0.87)		268 (0.69)	298s (0.49)	350 (1.00)	256s (0.75)	277 (0.82)	307 (0.82)	365s (0.90)	393 (1.00)			43		Lyon
									257 (0.79)	278 (0.90)	306 (0.54)	362 (1.00)	390 (0.98)				40	
5,7	3′,4′,5′	—			270 (0.95)	310s (0.90)	331 (1.00)	253s (0.66)	278 (0.97)	300 (0.76)	348 (1.00)	385s (0.72)				54		Mabry [1]
										280 (1.00)	298s (0.75)	340 (0.96)	382s (0.47)				51	
5,7,3′,4′	—	—	Luteolin	242s (0.76)	253 (0.86)	267 (0.77)	291s (0.54)	348 (1.00)		272 (0.81)	300s (0.32)	330s (0.21)		423 (1.00)		75		Lyon
									264s (0.95)	276 (1.00)	296s (0.66)	358 (1.00)	385 (0.98)				37	
5,7,3′,4′,5′	—	—	Tricetin		260 (0.81)	269 (0.80)	302s (0.50)	354 (1.00)		272 (0.75)	310 (0.30)			424 (1.00)		70		Lyon
										277 (0.94)	306 (0.52)	364s (0.89)	393 (1.00)				39	

5,7,3',4'	5'	—	Selgin	250s (0.79)	268 (0.69)	300s (0.48)	350 (1.00)			270 (0.71) 275 (0.88)	310s (0.26) 303 (0.51)	344s (0.18) 363 (0.95)	386 (1.00)	430 (1.00)	80	36		Lyon
Group 8																		
5,7,4'	3,6	—			271 (0.84)		342 (1.00)	268s (0.62) 262s (0.63)	280 (0.79) 282 (0.86)	298s (0.63)	305s (0.62) 305s (0.68)	367 (1.00) 364 (1.00)	404s (0.78) 404s (0.67)		62	62		Lyon
5,7	3,6,4'	—	Santin		272 (0.92)		338 (1.00)	262s (0.53) 262 (0.53)	282 (0.75) 282 (0.80)	297s (0.67) 296s (0.73)	305s (0.65) 306s (0.67)	360 (1.00) 360 (1.00)	404s (0.54) 404s (0.51)		66	66		Lyon
5,4'	3,6,7	—	Penduletin		271 (0.92)		340 (1.00)	264s (0.58) 262s (0.58)	282 (0.71) 282 (0.78)		302s (0.57) 302s (0.63)	367 (1.00) 361 (1.00)	404s (0.65) 402s (0.55)		64	62		Wollenweber* Darmstadt
5	3,6,7,4'	—		255s	273		335	265s 263s	283 284		305s 305s	364 362	400s 400s			65 65		Southwick [35]
5,7,3'	3,6,4'	—	Centaureidin	258 (0.87)	269 (0.77)		346 (1.00)	267 (0.92) 264 (0.88)	279s (0.83) 280s (0.83)		300s (0.51) 300s (0.56)	375 (1.00) 364 (1.00)	406i (0.88) 400s (0.75)		60	54		Lyon
5,7,4'	3,6,3'	—	Jaceidin	254 (0.81)	270 (0.75)		350 (1.00)	267 (0.86) 264 (0.83)	279s (0.78) 280 (0.79)		302s (0.47) 301s (0.49)	380 (1.00) 372 (1.00)	408i (0.88) 408s (0.78)		58	58		Lyon
5,3'	3,6,7,4'	—	Casticin	257 (0.92)	270 (0.84)		348 (1.00)	267 (0.95) 266 (0.94)	280s (0.88) 282 (0.92)		298s (0.68) 300s (0.71)	380 (1.00) 370 (1.00)	406i (0.84) 406s (0.72)		58	58		Wagner* Munich
5,4'	3,6,7,3'	—	Chrysosplenetin	256 (0.86)	270 (0.77)		350 (1.00)	268 (0.85) 265 (0.81)	280s (0.85) 281 (0.86)		300s (0.58) 300s (0.52)	386 (1.00) 382 (1.00)	408i (0.87) 406s (0.80)		58	56		Lyon
5,7	3,6,3',4'	—	Bonanzin	255 (0.88)	272 (0.78)		348 (1.00)	265 (0.99) 260 (0.96)	280s (0.89) 281 (0.91)		302s (0.56) 302i (0.60)	376 (1.00) 364 (1.00)	408i (0.75) 406s (0.58)		60	58		Wollenweber* Darmstadt

Table 1. (*continued*)

Substitution pattern				λ_{max}^{MeOH} nm				$\lambda_{max}^{MeOH+AlCl_3}$ / $\lambda_{max}^{MeOH+AlCl_3+HCl}$								$\Delta\lambda$ band I		
OH	OMe	Me	Trivial name	Band II			Band I									$AlCl_3$	$AlCl_3+HCl$	Origins
5	3,6,7,3′,4′	—	Artemetin	256	271		346	266	280s		299s	377	408i			62		Wollenweber*
				(0.85)	(0.78)		(1.00)	(0.90)	(0.84)		(0.55)	(1.00)	(0.75)					Darmstadt
								263	283		300i	366	406s				60	
								(0.85)	(0.85)		(0.63)	(1.00)	(0.58)					
5,7,3′,5′	3,6,4′	—		254s	273		341	254s	278		311s	362	407s			66		
				(0.77)	(0.89)		(1.00)	(0.79)	(0.93)		(0.61)	(1.00)	(0.61)					Lyon
								259s	283		308s	360	406s				65	
								(0.75)	(0.96)		(0.61)	(1.00)	(0.53)					
5,7,3′	3,6,4′,5′	—		255s	272		338	254s	261s	282	309s	363	406s			68		
				(0.71)	(0.85)		(1.00)	(0.65)	(0.69)	(0.82)	(0.54)	(1.00)	(0.59)					Lyon
								255s		285	308s	357	406s				68	
								(0.71)		(0.97)	(0.69)	(1.00)	(0.51)					
5,7,4′	3,6,3′,5′	—		252	272		359	268	274s		312		400			41		Scott-Lewis [36]
								262	280		310	377	412s				53	
5,3′,5′	3,6,7,4′	—			274		339	258s	282		310	362	406s			67		Jefferies*
					(0.91)		(1.00)	(0.79)	(0.90)		(0.68)	(1.00)	(0.70)					Nedlands
								260s	281		308s	360	406s				67	
								(0.78)	(0.93)		(0.76)	(1.00)	(0.78)					
5,4′	3,6,7,3′,5′	—	Murrayanol	255	267	344i	360	263	275		310	360	420			60		Morita*
				(0.95)	(0.91)	(0.97)	(1.00)	(1.00)	(0.99)		(0.34)	(0.70)	(0.98)					Toyama
								263	275		310	367	420				60	
								(1.00)	(0.99)		(0.35)	(0.74)	(0.97)					
5,7,3′,4′	3,6	—	Axillarin	260	272s		354		278		306s	342s		440		86		
				(0.97)	(0.88)		(1.00)		(0.92)		(0.49)	(0.39)		(1.00)				Lyon
								269	282i		302s	372	410i				56	
								(0.98)	(0.93)		(0.71)	(1.00)	(0.84)					
5,3′,4′	3,6,7	—	Chrysosplenol D	259	273		354		274		306	342s		434		80		Bohm*
				(1.00)	(0.87)		(1.00)		(1.00)		(0.38)	(0.34)		(0.89)				Vancouver
								269	286i		300i	373	408i				54	
								(1.00)	(0.87)		(0.53)	(0.91)	(0.68)					
5,7,3′,4′	3,6,5′	—		255	268s	300s	357		275		316s			446		89		
				(0.80)	(0.75)	(0.56)	(1.00)		(0.93)		(0.41)			(1.00)				Lyon
								262i	275		310s	375	414i				57	
								(0.81)	(0.87)		(0.62)	(1.00)	(0.91)					

Group 9																			
5,7,4′	3	6				271 (1.00)		338 (0.96)	260s (0.84)	280 (0.96)	298s (0.84)	306s (0.84)	363 (1.00)	403s (0.76)		65		Lyon
									260s (0.72)	282 (0 96)		306s (0.82)	358 (1.00)	404s (0.65)			66	
5,7,3′,5′	3,4′	6				271 (1.00)	304s (0.76)	337 (0.94)	252s (0.76)	277 (1.00)		308s (0.73)	356 (0.99)	406s (0.64)		69		Lyon
									252s (0.78)	280 (1.00)		308s (0.73)	352 (1.00)	404s (0.69)			67	
5,7,3′,4′,5′	3	6	Alluaudiol		257 (0.91)	266i (0.82)	300s (0.48)	360 (1.00)		272 (1.00)		322 (0.42)	374i (0.63)		430 (0.96)	70		Lyon
									262s (0.87)	277 (0.90)		313 (0.62)	369 (1.00)	414s (0.60)			54	
Group 10																			
5,7,4′	3	6,8			254s (0.68)	275 (1.00)	300s (0.76)	332 (0.70)	264s (0.77)	284 (1.00)		310 (0.92)	360 (0.91)	416s (0.56)		84		Lyon
									260s (0.79)	284 (1.00)		308s (0.91)	356 (0.88)	414s (0.50)			82	
5,7,3′,5′	3,4′	6,8			258s (0.58)	279 (1.00)		334 (0.75)	258s (0.60)	281 (1.00)		311 (0.70)	352 (0.80)	438s (0.19)		104		Lyon
									258s (0.65)	284 (1.00)	291s (0.97)	312s (0.82)	356 (0.92)	430s (0.23)			96	
Group 11																			
5,7	3,6,8,4′	—	Araneosol		258s (0.52)	278 (1.00)		335 (0.88)	264s (0.56)	288 (0.87)		312 (0.80)	361 (1.00)	413s (0.38)		78		Herz* Tallahassee
									262s (0.57)	289 (0.96)		310 (0.92)	356 (1.00)	412s (0.32)			77	
5,4′	3,6,7,8	—	Calycopterin	233s		278		340	245s	288		310	368					Rodriguez [18]
5	3,6,7,8,4′	—				276		334		290		310	360					
									238s	286		310	357	415s		81		Gupta [37]
												307	355	415s			81	
5,7,4′	3,6,8,3′	—			257	277		353	265	286		306s	377	420s		67		Urbatsch [38]
									264	287			368	422s			69	
5	3,6,7,8,3′,4′	—			260 (0.95)	280 (1.00)		347 (1.00)	268 (0.81)	291 (0.87)		304i (0.72)	374 (1.00)	430s (0.55)		83		Tatum* Winter Haven
									269 (0.80)	294 (0.90)		304i (0.68)	370 (1.00)	424s (0.55)			77	
5,7,3′,5′	3,6,8,4′	—						336					360					Bohlmann [19]
													—					

Table 1. (*continued*)

Substitution pattern				λ_{max}^{MeOH} nm					$\lambda_{max}^{MeOH+AlCl_3}$ / $\lambda_{max}^{MeOH+AlCl_3+HCl}$					$\Delta\lambda$ band I		
OH	OMe	Me	Trivial name	Band II		Band I								$AlCl_3$	$AlCl_3+HCl$	Origins
5,3′,5′	3,6,7,8,4′	—		270		336			360							Bohlmann [19]
									—							
5,3′	3,6,7,8,4′,5′	—	Digicitrin	254s (0.70)	282 (1.00)	336 (0.80)		292 (0.91)	313s (0.79)	365 (1.00)	424s (0.51)			88		Nogradi* Budapest
								292 (0.94)	312s (0.87)	360 (1.00)	420s (0.52)				84	
5,7,3′,4′	3,6,8	—		260	274s	345		279	305s	365s		435		90		Martino†
							265	284	302s	365	416i				71	Buenos Aires
Group 12																
5,7,4′	6,8	—	Demethoxy-sudachitin		282 (0.90)	296i (0.87) 332 (1.00)	266 (0.46)	290s (0.71)	310 (0.92)	360 (1.00)	412i (0.36)			80		Nogradi* Budapest
							266s (0.44)	290s (0.77)	310 (0.98)	356 (1.00)	412s (0.27)				80	
5,4′	6,7,8	—	Xanthomicrol		281 (0.90)	294s (0.86) 332 (1.00)	267s (0.35)	288 (0.45)	311 (0.68)	361 (1.00)	407s (0.32)			75		Mabry [1]
							265s (0.31)	290 (0.55)	311 (0.72)	354 (1.00)	408s (0.25)				76	
5,7	6,8,4′	—	Nevadensin		284 (1.00)	329 (0.75)	265s (0.38)	290s (0.76)	310 (1.00)	356 (0.97)	413s (0.32)			84		Mabry [1]
							262s (0.37)	289s (0.75)	309 (1.00)	351 (0.93)	404s (0.25)				75	
5	6,7,8,4′	—	Gardenin B		282i (0.90)	293 (0.92) 328 (1.00)	263s (0.28)	287s (0.55)	311 (0.78)	354 (1.00)	411s (0.25)			73		Tatum* Winter Haven
							264s (0.29)	286 (0.62)	311 (0.89)	350 (1.00)	408s (0.23)				80	
5,7,3′	6,8,4′	—	Acerosin	254s (0.62)	281 (0.79)	344 (1.00)	263 (0.59)	284 (0.71)	304s (0.65)	368 (1.00)	412s (0.53)			68		Iinuma* Gifu
							261 (0.61)	292 (0.75)	304i (0.71)	363 (1.00)	414s (0.42)				70	
5,7,4′	6,8,3′	—	Sudachitin	256s (0.66)	281 (0.80)	344 (1.00)	262 (0.61)	290 (0.73)	303i (0.69)	372 (1.00)	412s (0.41)			68		Nogradi* Budapest
							260 (0.64)	292 (0.77)	302i (0.81)	366 (1.00)	412s (0.41)				68	

5,4′	6,7,8,3′	—		255 (0.76)	281 (0.81)		346 (1.00)	265s (0.62)	285 (0.72)	304s (0.60)	374 (1.00)	418s (0.48)		72			Rodriguez* Madrid
								264s (0.63)	288 (0.72)	304s (0.66)	366 (1.00)	418s (0.33)			72		
5,3′	6,7,8,4′	—	Gardenin D	255 (0.85)	283 (0.96)		344 (1.00)	265 (0.71)	290 (0.81)	304 (0.80)	370 (1.00)	420s (0.36)		76			Rodriguez* Madrid
								262 (0.63)	290 (0.82)	303 (0.83)	363 (1.00)	420s (0.32)			76		
5,7	6,8,3′,4′	—	Hymenoxin	255 (0.66)	282 (0.89)		339 (1.00)	260 (0.76)	290 (0.78)	302i (0.75)	362 (1.00)	415s (0.42)		76			Herz* Tallahassee
								260 (0.62)	293 (0.81)		361 (1.00)	412s (0.41)			73		
5	6,7,8,3′,4′	—	5-*O*-Desmethyl-nobiletin	254 (0.67)	284 (0.85)		342 (1.00)	264 (0.59)	293 (0.71)	302s (0.70)	362 (1.00)	420s?		78			Rodriguez* Madrid
								261 (0.61)	294s (0.74)	303 (0.75)	362 (1.00)	420s (0.31)			78		
5,3′,5′	6,7,8,4′	—	Gardenin E		285 (1.00)	296i (0.95)	332 (0.97)		291 (0.91)	313 (0.93)	358 (1.00)	420s (0.49)		88			Mabry* Austin
									294s (0.87)	313 (0.98)	352 (1.00)	420s (0.45)			88		
5	6,7,8,3′,4′,5′	—	Gardenin A		286 (1.00)	297i (0.94)	331 (1.00)	260s (0.50)	292 (0.70)	312 (0.79)	357 (1.00)	420s (0.28)		89			Wollenweber* Darmstadt
									290s (0.83)	312 (0.92)	356 (1.00)	420s (0.25)			89		
5,7,3′,4′	6,8	—		256s (0.74)	280 (0.85)		346 (1.00)		275		340		430	85			Chhabra [39]
								260		300	370				—		
5,3′,4′	6,7,8	—		258 (0.80)	280 (0.87)		349 (1.00)		279 (0.71)	306s (0.54)	342s (0.32)		438 (1.00)	89			Tomas* Murcie
								264s (0.68)	288 (0.81)	304s (0.77)	368 (1.00)	420i (0.51)			71		
Group 13																	
5,4′	7	6,8	Sideroxylin		280 (0.87)	294i (0.84)	328 (1.00)		283 (0.67)	310 (0.76)	350 (1.00)	410s (0.50)		82			Hillis* Melbourne
									284 (0.70)	309 (0.82)	348 (1.00)	406s (0.47)			78		
5	7,4′	6,8	Eucalyptin		282 (0.91)	292i (0.90)	326 (1.00)		284 (0.91)	312 (0.93)	342 (1.00)	410s (0.26)		84			Hillis* Melbourne
									286 (0.75)	309 (0.90)	342 (1.00)	408s (0.21)			82		

Table 1. (*continued*)

Substitution pattern				λ_{max}^{MeOH} nm				$\lambda_{max}^{MeOH+AlCl_3}$ / $\lambda_{max}^{MeOH+AlCl_3+HCl}$					$\Delta\lambda$ band I		
OH	OMe	Me	Trivial name	Band II		Band I							$AlCl_3$	$AlCl_3+HCl$	Origins
Group 14															
5,7,4′	3	—	Isokaempferide	269	298	322s	350	277		304	350	399	49		
				(1.00)	(0.68)	(0.71)	(0.82)	(1.00)		(0.70)	(0.74)	(0.67)			Lyon
								278		304	348	398		48	
								(1.00)		(0.69)	(0.75)	(0.64)			
5,7	3,4′	—	Ermanin	268	298s	320s	347	278	296s	304	350	400	53		
				(1.00)	(0.65)	(0.74)	(0.82)	(1.00)	(0.65)	(0.72)	(0.92)	(0.77)			Lyon
								278	297	304	345	399		52	
								(1.00)	(0.71)	(0.72)	(0.90)	(0.70)			
5,4′	3,7	—	Kumatakenin	268			350	276		302	352	398	48		Valesi [40]
								276		300	347	400		50	
5	3,7,4′	—		269	300s	324s	348	276	298s	304	348	399	51		
				(1.00)	(0.60)	(0.76)	(0.85)	(1.00)	(0.57)	(0.61)	(0.87)	(0.73)			Lyon
								277	296s	304	346	398		50	
								(1.00)	(0.61)	(0.63)	(0.85)	(0.67)			
5,7,4′	3,3′	—		256	268s	292s	356	267	275i	300s	364	404	48		
				(1.00)	(0.84)	(0.46)	(0.88)	(1.00)	(0.95)	(0.44)	(0.72)	(0.77)			Lyon
								264	276	298s	359	402		46	
								(1.00)	(0.98)	(0.50)	(0.75)	(0.74)			
5,7,3′	3,4′	—		253	266s	293s	353	268	278i	302	366	406	53		Nair*
				(1.00)	(0.87)	(0.53)	(0.91)	(1.00)	(0.95)	(0.59)	(0.69)	(0.77)			Pondicherry
								268	277s	300	360	402		49	
								(1.00)	(0.98)	(0.57)	(0.74)	(0.74)			
5,7	3,3′,4′	—		253	267	291s	353	266	276s	300.	362	402	49		Wagner*
				(1.00)	(0.88)	(0.50)	(0.94)	(1.00)	(0.96)	(0.47)	(0.75)	(0.81)			Munich
								265i	277	299s	355	401		48	
								(0.99)	(1.00)	(0.51)	(0.81)	(0.73)			
5,4′	3,7,3′	—	Pachypodol	254	262s		354	269	280	300	368	404	50		Gleye*
				(1.00)	(0.83)		(0.99)	(1.00)	(0.87)	(0.45)	(0.75)	(0.92)			Toulouse
								268	278	300	362	402		48	
								(1.00)	(0.94)	(0.48)	(0.74)	(0.79)			
5,3′	3,7,4′	—	Ayanin	256	265s	293s	353	270	275s	300	366	402	49		
				(1.00)	(0.81)	(0.40)	(0.86)	(1.00)	(0.90)	(0.45)	(0.68)	(0.79)			Lyon
								268	274s	298s	360	401		48	
								(1.00)	(0.96)	(0.43)	(0.64)	(0.70)			

5	3,7,3′,4′	—	Retusin	255 (1.00)	268 (0.84)	299s (0.46)		351 (0.88)	271 (1.00)	277s (0.95)	299s (0.44)	364 (0.72)	402 (0.77)		51		Lyon
									270 (1.00)	276 (0.98)	298s (0.50)	356 (0.75)	401 (0.74)			50	
5,7,3′,5′	3,4′	—			267 (1.00)	294s (0.49)		350 (0.74)		275 (1.00)	304 (0.48)	349 (0.64)	399 (0.57)		49		Lyon
										275 (1.00)	302 (0.45)	346 (0.66)	398 (0.50)			48	
5,7,5′	3,3′,4′	—		250s	264 (1.00)	304s		345 (0.83)		276 (1.00)	305 (0.15)	348 (0.66)	400 (0.50)		55		Ayanoglu [41]
										278 (1.00)	304 (0.26)	346 (0.43)	398 (0.55)			53	
5,3′,5′	3,7,4′	—			267 (1.00)	302s (0.65)		344 (0.83)		275 (1.00)	308 (0.52)	349 (0.69)	399 (0.65)		55		Jefferies* Nedlands
										276 (1.00)	306 (0.52)	344 (0.66)	398 (0.55)			54	
5,7	3,3′,4′,5′	—	(EtOH)		268 (1.00)	305s (0.69)		346 (0.92)		—	—	—	—				Lyon
									256s (0.57)	280 (1.00)	305s (0.66)	343 (0.83)	399 (0.57)			53	
5	3,7,3′,4′,5′	—	Combretol	252s (0.85)	266 (1.00)	300 (0.72)		346 (0.94)	252s (0.71)	276 (1.00)	306 (0.63)	355 (0.88)	399 (0.72)		53		Wollenweber* Darmstadt
									253s (0.66)	278 (1.00)	304 (0.62)	345 (0.79)	398 (0.60)			52	
5,7,3′,4′	3	—		256 (1.00)	268s (0.87)	292s (0.55)		359 (0.96)		277 (0.93)	303s (0.37)	339 (0.32)		440 (1.00)	81		Lyon
									268 (1.00)	277i (0.94)	303 (0.57)	360 (0.75)	402 (0.85)			43	
5,3′,4′	3,7	—		258 (1.00)	270s (0.77)	296s (0.37)		357 (0.90)		276 (1.00)	302s (0.28)	320s (0.20)		440 (0.96)	83		Lyon
									272 (1.00)	278i (0.96)	302s (0.36)	368 (0.60)	402 (0.76)			45	
5,7,3′,4′,5′	3	—		254 (0.94)	268i (0.88)	305s (0.67)		361 (1.00)		271 (1.00)	312 (0.28)			428 (1.00)	67		Lyon
										273 (1.00)	308 (0.43)	360 (0.70)	405 (0.84)			44	
Group 15																	
5,7,4′	8	—			274 (1.00)	300 (0.82)	324 (0.92)	350i (0.72)		282 (0.86)	310 (0.87)	349 (1.00)	398 (0.54)		48		Lyon
										282 (0.89)	309 (0.98)	344 (1.00)	397 (0.49)			47	

Table 1. (*continued*)

Substitution pattern				λ_{max}^{MeOH} nm				$\lambda_{max}^{MeOH+AlCl_3}$ / $\lambda_{max}^{MeOH+AlCl_3+HCl}$						$\Delta\lambda$ band I		
OH	OMe	Me	Trivial name	Band II		Band I								$AlCl_3$	$AlCl_3+HCl$	Origins
5,7	8,4′	—	Cirsitakaogenin	275 (1.00)	299 (0.85)	322 (0.83)	358i (0.51)		284 (0.84)	310 (0.97)	346 (1.00)	398 (0.43)		40		
																Goudard [25]
									285 (0.88)	309 (1.00)	342 (0.94)	398 (0.40)			40	Lyon
5	7,8,4′	—		273 (1.00)	299 (0.86)	319 (0.88)	356i (0.51)	272i (0.71)	283 (0.83)	310 (0.93)	343 (1.00)	404 (0.37)		48		Iinuma*
																Gifu
								272s (0.79)	285 (0.96)	311 (1.00)	342 (0.98)	404 (0.35)			48	
5,7,4′	8,3′	—		253 (0.89)	273 (1.00)	294s (0.65)	337 (0.85)	262s (0.84)	282 (1.00)	304s (0.67)	362 (1.00)	401 (0.72)		64		
																Lyon
								262s (0.82)	284 (0.98)	304s (0.71)	356 (1.00)	400 (0.61)			63	
5,7	8,3′,4′	—			276 (1.00)		332 (0.79)		286		355					Krishnamurti [22]
									—		—					Chhabra [24]
5,4′	7,8,3′	—		255	270s		355		270		357	400		45		Le Quesne [28]
								265	275s		357	400			45	
5	7,8,3′,4′,	—		254 (0.88)	275 (1.00)	298i (0.66)	340 (0.95)	263s (0.80)	282 (0.98)	302 (0.72)	357 (1.00)	406 (0.62)		66		Streliski*
																Budapest
								262s (0.77)	283 (0.98)	302 (0.75)	353 (1.00)	406 (0.57)			66	
5,7,3′,5′	8,4′	—			275 (1.00)		327 (0.70)		285	310	350					Chhabra [23]
									285	305	345					
5,7	8,3′,4′,5′	—			278 (1.00)		323 (0.79)		289		351					Krishnamurti [22]
									—		—					
5,3′	7,8,4′,5′	—			265		345		277	305	347	400		55		Le Quesne [28]
									275	305	345	400			55	
5	7,8,3′,4′,5′	—			275		325		—		—					Chhabra [24]
									—		—					
5,7,3′,4′	8	—	Onopordin	258 (0.88)	274 (1.00)	296s (0.64)	349 (0.95)		277 (0.82)	306s (0.31)	336s (0.14)		433 (1.00)	84		Horie*
																Tokushima
								264s (0.82)	280 (1.00)	301 (0.71)	358 (0.98)	400 (0.66)			51	

5,7,3',4',5'	8					275		330	340		270 275		360		420	80			Chhabra [24]
Group 16			—																
5,7,4'	3,8	—	—	(EtOH)		274 (1.00)	305s (0.75)	327 (0.82)	359 (0.75)		—	—	—	—					Matsumoto† Hiroshima
											284 (1.00)	313 (0.86)	351 (0.95)	415 (0.65)				56	
5,4'	3,7,8	—				273 (1.00)	300s (0.58)	328 (0.68)	362 (0.65)		282 (1.00)	312 (0.64)	354 (0.90)	423 (0.56)		61			Nogradi* Budapest
											283 (1.00)	311 (0.69)	350 (0.89)	420 (0.52)				58	Budapest
5,7	3,8,4'	—				273 (1.00)	300s (0.64)	322 (0.65)	356s (0.55)		283 (1.00)	312 (0.76)	350 (0.84)	416 (0.49)		60			Mabry* Austin
											284 (1.00)	312 (0.77)	348 (0.83)	418 (0.47)				62	
5	3,7,8,4'	—		Flindulatin		273 (1.00)	300s (0.70)	322 (0.77)	361 (0.69)		284 (1.00)	313 (0.80)	350 (0.98)	422 (0.64)		61			Mabry* Austin
											283 (1.00)	312 (0.82)	346 (0.94)	422 (0.61)				61	
5,7,4'	3,8,3'	—			256 (0.93)	273 (1.00)		334i (0.75)	360 (0.86)	266s (0.90)	283 (1.00)	308 (0.64)	362 (0.84)	418 (0.67)		58			Mabry* Austin
										262i (0.86)	282 (1.00)	306 (0.55)	360 (0.86)	418 (0.65)				58	
5,4'	3,7,8,3'	—		Ternatin	256 (1.00)	273 (0.99)		332i (0.82)	366 (0.91)	272i (0.97)	282 (1.00)	306 (0.57)	366 (0.85)	424 (0.77)		58			Nogradi* Budapest
										268i (0.92)	282 (1.00)	306 (0.63)	361 (0.88)	422 (0.75)				56	
5,3'	3,7,8,4'	—			259 (1.00)	273 (0.93)		340i (0.64)	364 (0.73)	274i (0.97)	282 (1.00)	307 (0.51)	365 (0.70)	424 (0.61)		60			Nogradi* Budapest
										274s (0.97)	282 (1.00)	307 (0.53)	361 (0.69)	423 (0.51)				59	
5	3,7,8,3',4'	—			257	274			360	—	—	—	—	—					Tatum [42]
																		60	Sakakibara [10]
5,7,3'	3,8,4',5'	—				277 (1.00)	304i (0.72)	326 (0.74)	362s (0.67)		286 (1.00)	314 (0.71)	354 (0.82)	420 (0.59)		58			Jefferies* Nedlands
											286 (1.00)	313 (0.77)	350 (0.83)	420 (0.59)				58	
5,3',5'	3,7,8,4'	—				275 (1.00)	304s (0.62)	326 (0.65)	360 (0.64)		282 (1.00)	312 (0.57)	348 (0.70)	424 (0.49)		64			Mabry* Austin
											282 (1.00)	312 (0.59)	348 (0.70)	424 (0.47)				64	

Table 1. (*continued*)

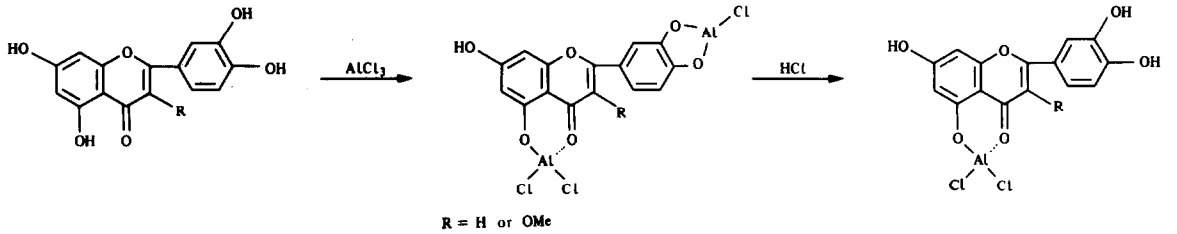
Substitution pattern				λ_{max}^{MeOH} nm					$\lambda_{max}^{MeOH+AlCl_3}$ / $\lambda_{max}^{MeOH+AlCl_3+HCl}$					$\Delta\lambda$ band I		
OH	OMe	Me	Trivial name	Band II			Band I								$AlCl_3$	$AlCl_3+HCl$	Origins
5,7	3,8,3′,4′,5′	—	Conyzatin	276	314	362	402		286 —	317 —	355 —	400 —	421 —				Tandon [30]
Group 16a																	
5,7,3′,4′	3,8	—		261 (1.00)	273 (0.99)	298s (0.60)	336i (0.73)	363 (0.84)		281 (1.00)	312s (0.39)	342s (0.35)		451 (0.92)	88		Jefferies* Nedlands
									272i (0.99)	282 (1.00)	306s (0.62)	361 (0.78)	418 (0.69)			55	
5,3′,4′	3,7,8	—		260 (1.00)	272s (0.94)	298s (0.44)	334i (0.65)	367 (0.81)		281 (1.00)	312s (0.33)	344s (0.24)		454 (0.98)	87		Jefferies* Nedlands
									273 (1.00)	282i (0.99)	306 (0.50)	362 (0.77)	422 (0.67)			55	
Group 17																	
5,7,8,4′	—	—	Isoscutellarein	280 (0.95)	305 (1.00)	330s (0.88)	364s (0.56)	250s (0.61)		299 (0.80)	326 (1.00)	360s (0.56)	432 (0.38)		68		Lyon
								262s (0.64)		286 (0.83)	316 (1.00)	347 (0.92)	404 (0.51)			40	
5,7,8	4′	—		281	302	328	360s	271	278	295	323	350					Porter† Petone
								272			313	388	400			40	
Group 17a																	
5,7,8,3′,4′	—	—	Hypolaetin	256 (0.82)	280 (1.00)	302s (0.82)		340 (0.93)	274s (0.90)	296 (1.00)	322s (0.75)	342s (0.67)	396 (0.95)		456 (0.72)	116	Lyon
									262 (0.77)	286 (0.90)	306 (0.80)	324s (0.77)	358 (1.00)	430s (0.58)		90	
Group 18																	
5,8,4′	7	—		280 (0.96)	306 (1.00)	330i (0.77)	366i (0.38)			285 (0.82)	321 (1.00)	351 (0.95)	424 (0.30)		58		Iinuma* Gifu
										285 (0.80)	320 (1.00)	348 (0.89)	424 (0.27)			58	
5,8,4′	7,3′	—		254	272	292s		342	266s	279	305	358	402		60		Whalen [43]
									266	279	304	356	401			59	

Group 19																		
5,7,3′,4′	3	8	260	272	299s	336i	362		280	308	340s		444	82			Lyon
			(1.00)	(0.99)	(0.43)	(0.66)	(0.80)		(1.00)	(0.25)	(0.16)		(0.94)				
								270i	280	302	360	413			51		
								(0.95)	(1.00)	(0.50)	(0.70)	(0.57)					
Group 20																		
5,8,4′	3,7	—		278	306	326	368s		284	320	356	438		70			Mabry* Austin
				(1.00)	(0.77)	(0.71)	(0.46)		(1.00)	(0.85)	(0.99)	(0.53)					
									284	320	354	436			68		
									(1.00)	(0.58)	(0.95)	(0.51)					
5,8,4′	3,7,3′	—	257	277	305	339	365s	274s	287	317	368	439		74			Sakakibara [10]
								272s	286	322	360	437			72		
5,8,3′,5′	3,7,4′	—		278	302	328s	372s		288	320	352	443		71			Whalen [43]
									288	320	352	438			66		
Group 20a																		
5,8,3′,4′	3,7	—	262	278	302s	343	378s	258s	284	318	400s		458	80			Wagner* Munich
			(0.92)	(1.00)	(0.68)	(0.81)	(0.61)	(0.54)	(1.00)	(0.48)	(0.52)		(0.83)				
								264i	285	314	362	438			60		
								(0.83)	(1.00)	(0.71)	(0.91)	(0.56)					

The relative A is presented for the λ_{max} for each compound using the highest peak as 100% (1.00) of each spectrum. s, Shoulder; i, inflection.

*Person the sample was furnished by.

†Xerox copy of UV spectrum.



Scheme 1. The types of complexes that aluminium chloride forms with 5-hydroxyflavones and 5-hydroxy-3-methoxyflavones with a 3',4'-*o*-dihydroxy system in the B-ring.

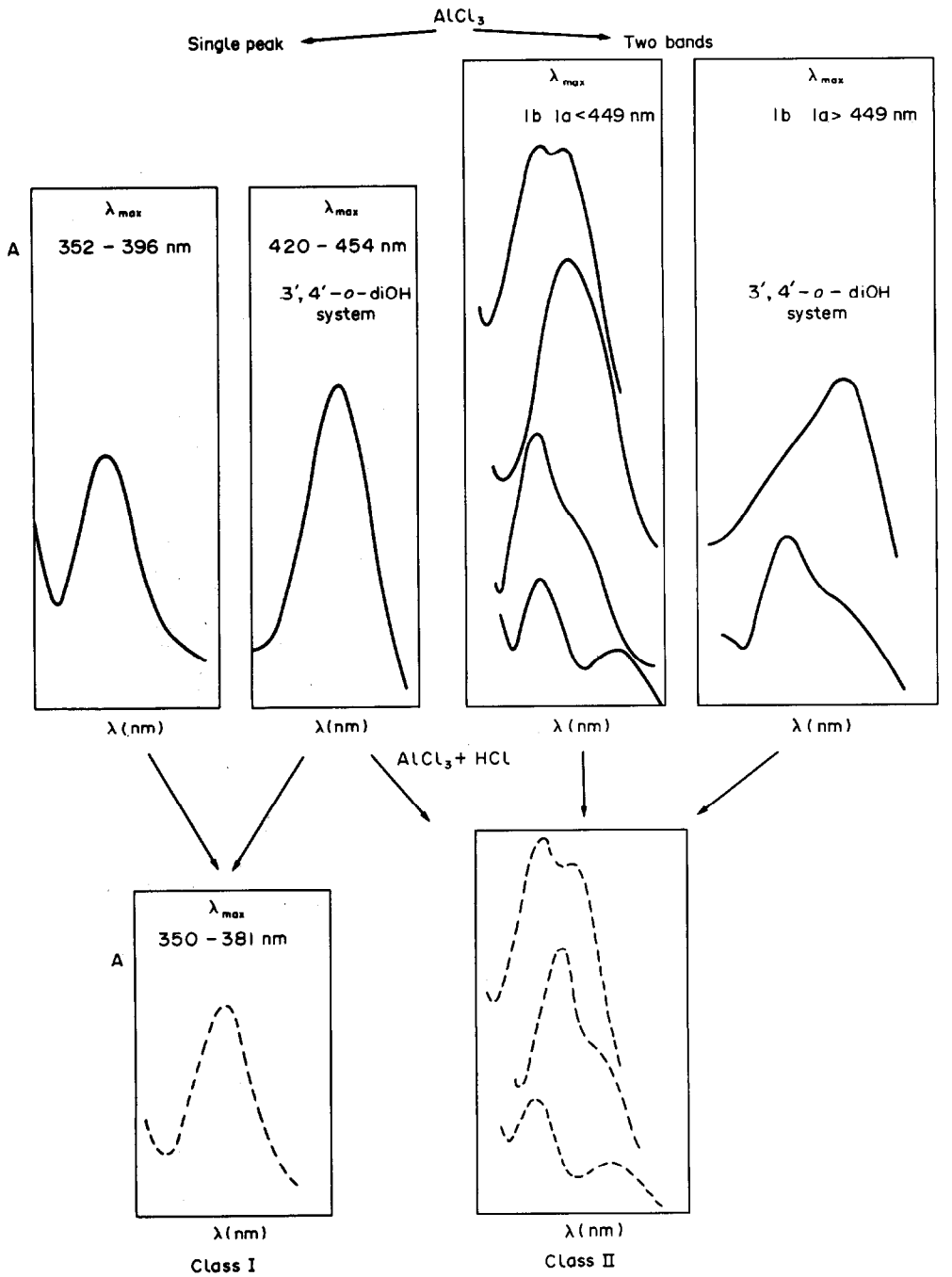


Fig. 1. Spectral modifications of band I of 5-hydroxyflavones and 5-hydroxy-3-methoxyflavones with 4'-, 3',4'- or 3',4',5'-substituted B-rings in the presence of aluminium chloride and aluminium chloride + hydrochloric acid.

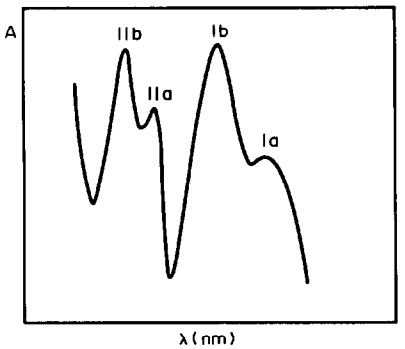


Fig. 2. 'Methanol + aluminium chloride + hydrochloric acid' typical spectrum of 5-hydroxyflavones.

always have 6-*O*-substitution. Nevertheless, from this class are excluded 3,6-dimethoxyflavones for which bands Ia and Ib are always present, the former appearing most often as a shoulder. This contrasts with the previous observations [8–10]. Moreover, for compounds of class I, the shift of band I on addition of aluminium chloride + hydrochloric acid varies from 19 to 31 nm which are slightly higher values than those indicated by Mears and Mabry [8].

From the position of band II in the methanol spectrum, most flavonoids of class I may be further divided into two categories: 6-methoxyflavones (group 1) which have a maximum below 279 nm, and 6-hydroxyflavonoids (groups 2–4) which exhibit a higher value (Tables 1–3). Among the 33 compounds examined of class I, only two compounds, which unfortunately were not available as reference samples, do not conform to this rule, namely 5,6,7,4′-tetrahydroxy-3′-methoxyflavone (nodifloretin) λ_{max} 276 nm [11] and 5,6,7,3′,4′-pentahydroxy-3-methoxyflavone, λ_{max} 258, 270sh nm [11]. Moreover, some data have to be corrected: Shen *et al.* [12] indicate for 5,6,4′-trihydroxy-3,7,3′-trimethoxyflavone (chrysosplenol C) a band at 433 nm in aluminium chloride; in fact this compound, which lacks a 3′,4′-*o*-dihydroxy system, lacks a shoulder at this value; Shen [13] indicated that quercetagetin 3,3′-dimethyl ether (5,6,7,4′-tetrahydroxy-3,3′-dimethoxyflavone), first isolated from *Parthenium tomentosum* [14, 15] was incorrectly assigned. He suggests that the compound isolated was the 3,7-dimethyl ether.

Finally, the compounds in groups 1–4 have an *A* ratio of band I–band II in methanol greater than 1, the 6-*O*-substitution producing a hypsochromic effect on band II.

Different B-ring substituted 6-methoxyflavones (group 1) may be distinguished by their bands, IIa and IIb in aluminium chloride (neutral or acidic): 4′-substituted compounds exhibit a main peak at *ca* 303 nm and

Table 2. UV spectral properties of flavonoids of class I

Solvent	Position of band I max	3′,4′-*o*-Dihydroxy system
MeOH + $AlCl_3$	Peak 350–396 nm or	–
	peak > 415 nm	+
MeOH + $AlCl_3$ + HCl	Peak 350–381 nm	

	Position of band II max in MeOH			
		> 279 nm		
Substitution at C No.	< 279 nm	< 283 nm	284–286 nm	292 nm
3	H	OMe	H	H
6	OMe	OH	OH	OH
8	H	H	H	OMe
Group	1	2	3	4
Figs.	5–8	9–11	12 and 13	—

Table 3. Spectral characteristics [positions of band II maxima (nm)] which distinguish between flavones of groups 1–4

		Groups			
Solvent		1	2	3	4
MeOH		< 279	279–281	283–286	292
$AlCl_3$ + HCl (B-ring substitution)	4′	301–303	297	302	—
	3′,4′	280–290	295–296	290–297	305
	3′,4′,5′	280–289	296	—	—
Spectral shift in band I after adding $AlCl_3$ + HCl		19–26	26–31	23–28	26

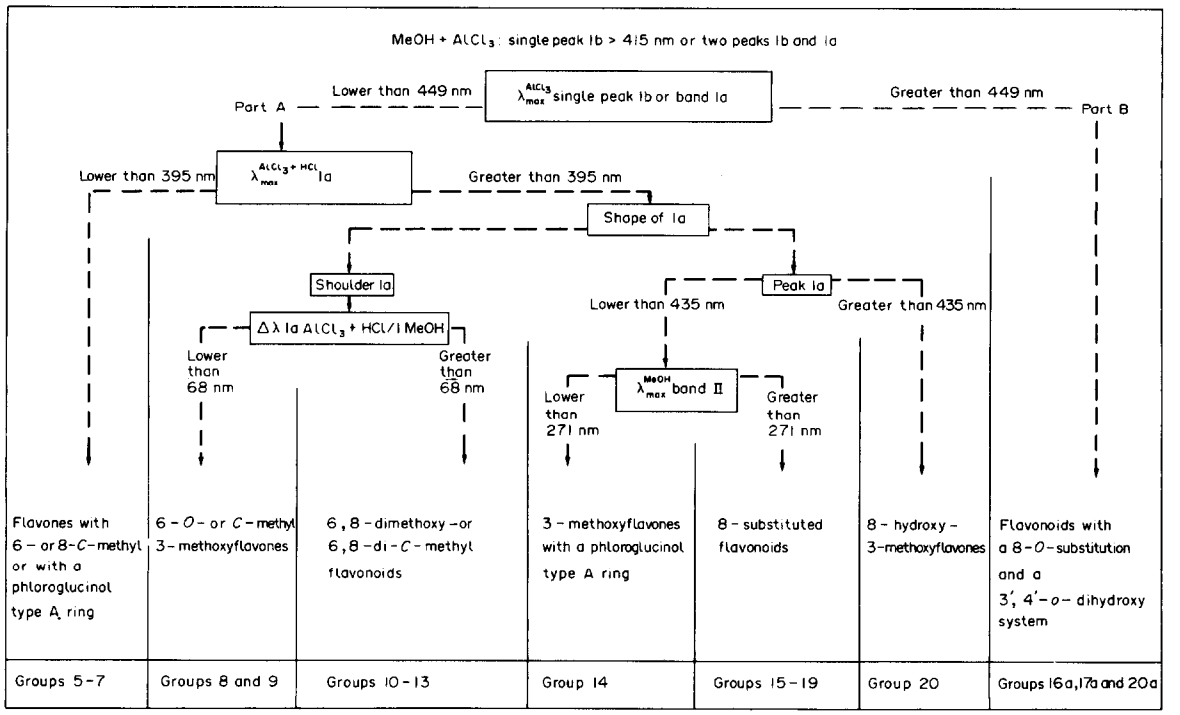


Fig. 3. UV spectral properties which distinguish between flavones of class II.

inflections (or shoulders, for distinction see Fig. 4) at *ca* 262 and 291 nm, respectively (Fig. 5) in the two solutions; 3',4'-disubstituted compounds have a double peak at *ca* 260 and 280–290 nm as well as an inflection at 292–298 nm either in neutral solution (compounds without *o*-dihydroxy system, Fig. 6) or in acidic solution for *o*-dihydroxy derivatives (Fig. 8); in neutral aluminium chloride for the latter, a main peak appears at *ca* 275 nm and a shoulder at 302–306 nm; all the 3',4',5'-trisubstituted derivatives examined present in acidic aluminium chloride a shoulder at *ca* 257 nm, a peak at 280–289 nm and a band at 300–310 nm (Fig. 7).

Similarly, the distinction between 6-hydroxy-3-methoxyflavones (group 2), 6-hydroxyflavones (group 3) and 6-hydroxy-8-methoxyflavones (group 4) is based on the position of the band II maxima in methanol, i.e. below 283 nm (Figs. 9–11) for group 2 compounds and above

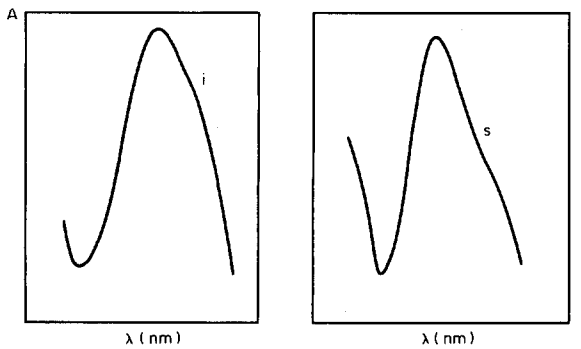


Fig. 4. Distinction between inflection (i) concave curve, and shoulder (s) convex curve.

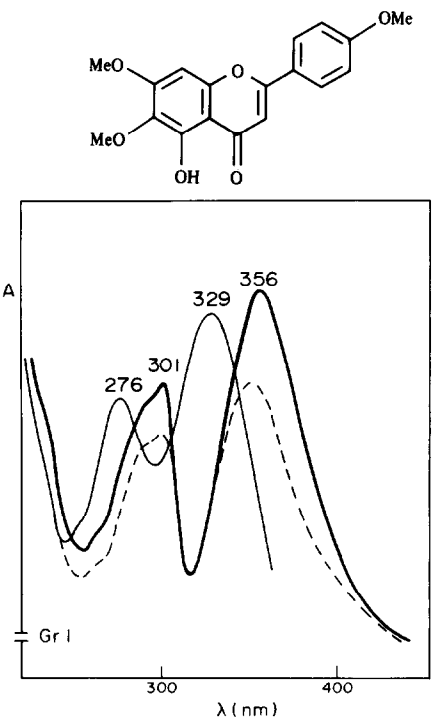


Fig. 5.

283 nm for group 3 and 4 compounds (Figs. 12 and 13; Table 2). Sakakibara and Mabry [9] have noted a spectral shift in band I after addition of aluminium chloride + hydrochloric acid of *ca* 25–30 nm for 6-hydroxy com-

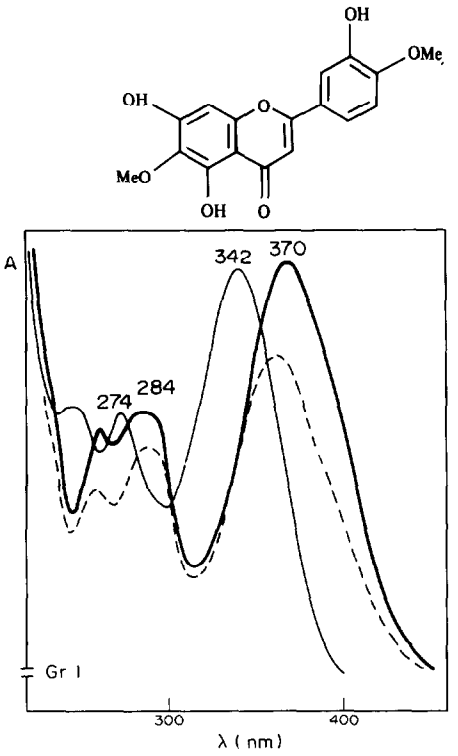


Fig. 6.

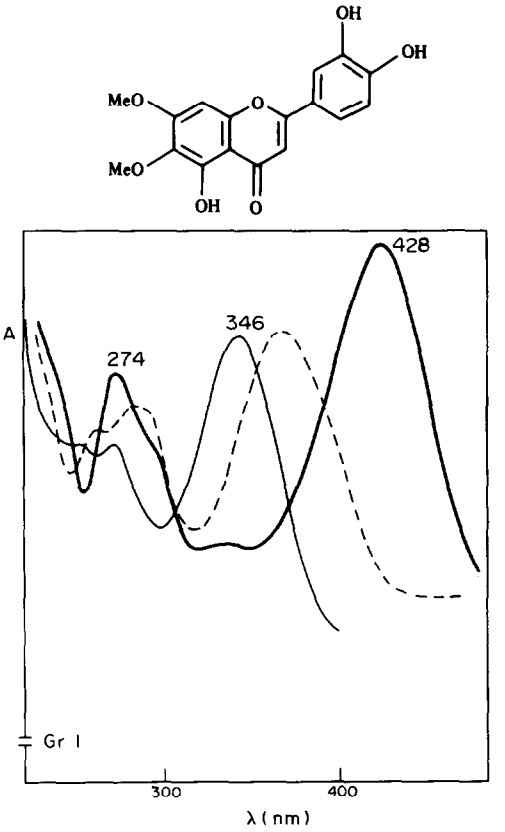


Fig. 8.

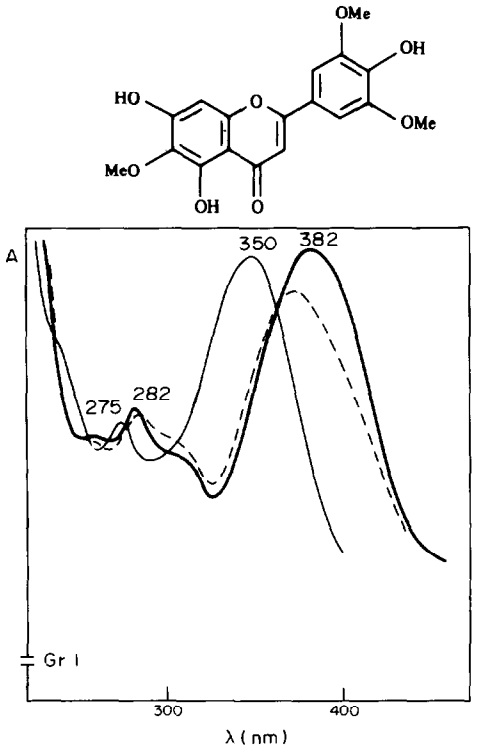


Fig. 7.

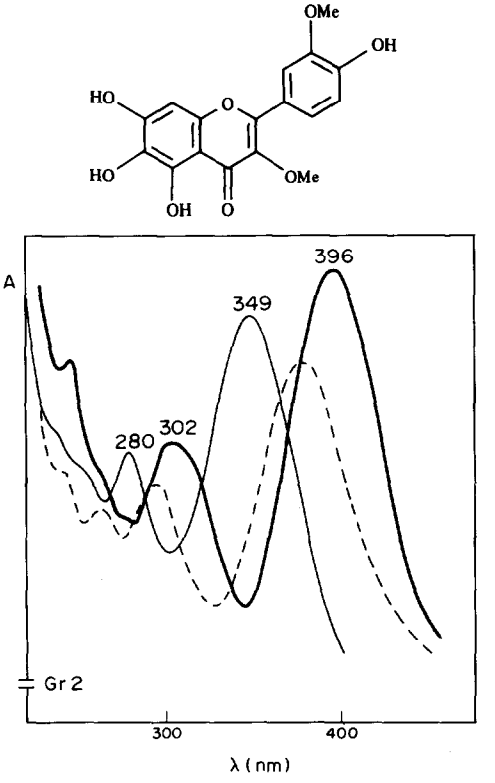


Fig. 9.

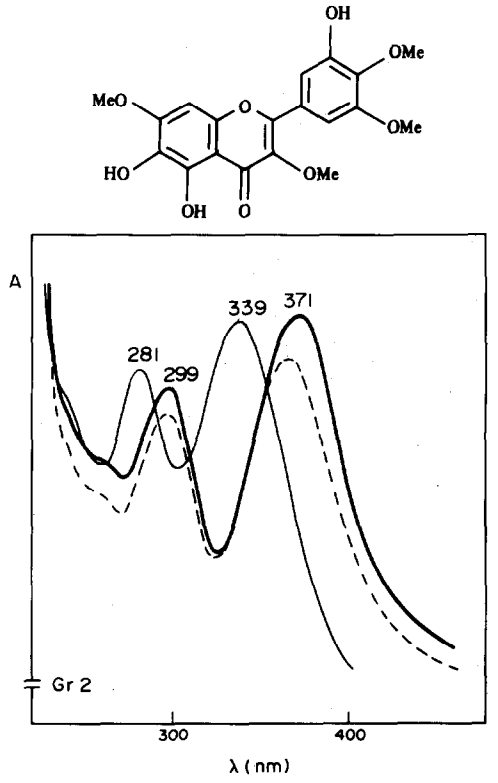


Fig. 10.

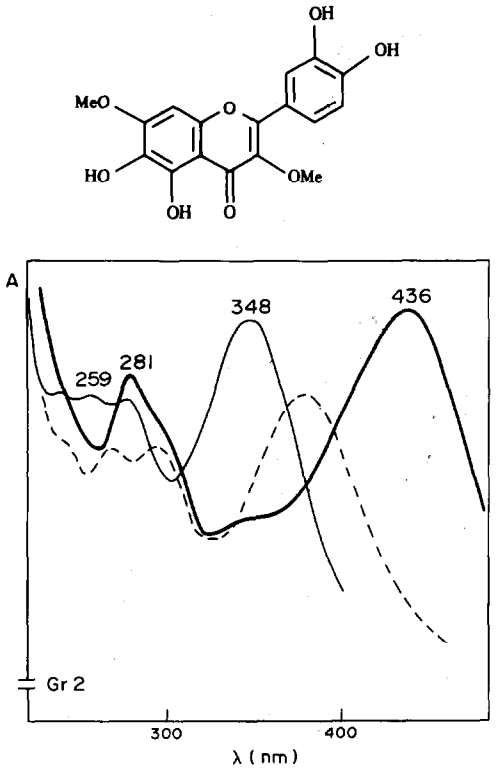


Fig. 11.

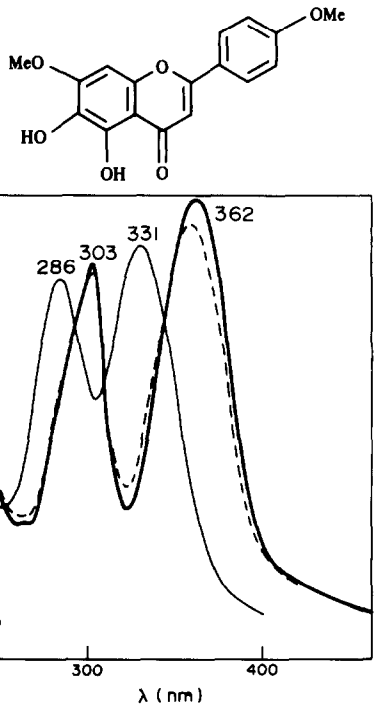


Fig. 12.

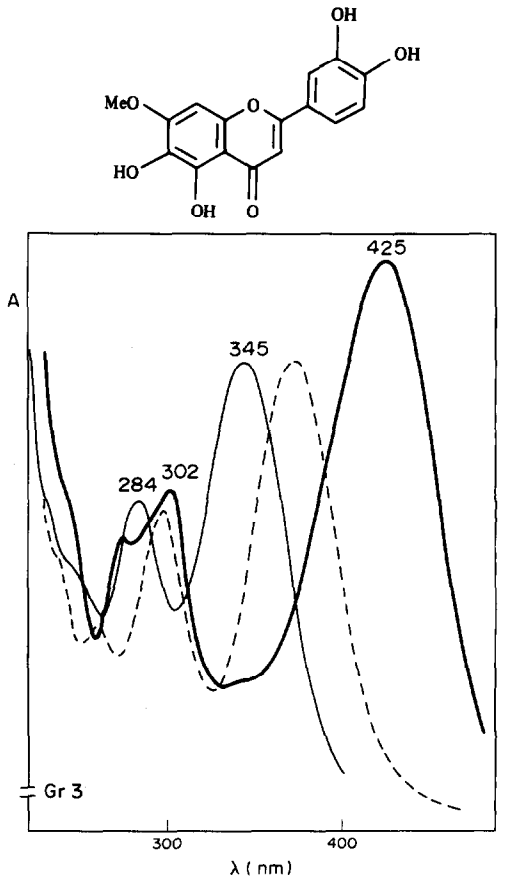


Fig. 13.

pounds and 16–23 nm for 6-methoxy derivatives. However, these data do not always distinguish between 6-hydroxy and 6-methoxy substitution (Table 3).

Among the 6-hydroxyflavones (group 3), only the 4′- and 3′,4′-substituted derivatives are presently known; the 4′-derivatives exhibit, in neutral or acidic aluminium chloride, a characteristic peak at *ca* 303 nm (Fig. 12), as with the related compounds of group 1, but its shape is sharper; in acidic solution, spectra of 3′,4′-di-*O*-substituted derivatives have a main peak at 290–297 nm and a secondary band at *ca* 260 nm (Fig. 13).

Except for 4′-monosubstituted flavones, all the 6-hydroxy derivatives exhibit, in aluminium chloride + hydrochloric acid a main peak (IIa) at 290–297 nm (Figs. 9, 10 and 13); there is one exception, namely 5,6,7,3′,4′-pentahydroxy-3-methoxyflavone [11]. For the only known 6-hydroxy-8-methoxyflavone (thymonin) [16], the main peak appears at 305 nm. Moreover, for 3′,4′,5′-trisubstituted derivatives of groups 1 and 2, we observe that 4′-*O*-methylation induces a hypsochromic shift in band I in methanol of *ca* 17–24 nm, which is a useful means of detecting such a substituent. A combination of these spectral characteristics thus provides a method for distinguishing the flavonoids of these four groups (Table 3).

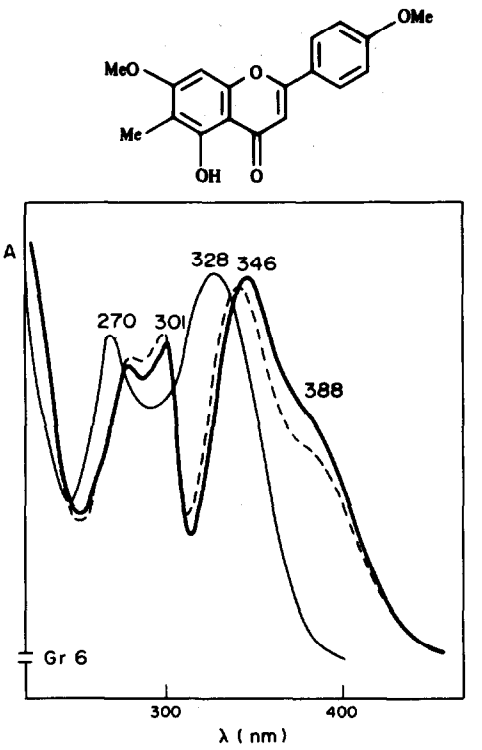


Fig. 14.

FLAVONOIDS OF CLASS II

The addition of aluminium chloride produces either two or one peak and an inflection (Ib and Ia), or there is one peak with a maximum between 420 and 454 nm; in this latter case, or if Ia is higher than 449 nm, the methanol + aluminium chloride spectrum permits the direct detection of the 3′,4′-*o*-dihydroxy system. All the spectra of compounds of this class, after addition of hydrochloric acid, exhibit two peaks, Ia and Ib (Fig. 1).

Based on the value of $\lambda_{max}^{AlCl_3}$ (lower or higher than 449 nm), flavonoids may be divided into two groups, A and B. Within group A, with a maximum below 449 nm, according to the $\lambda_{max}^{AlCl_3+HCl}$ of band Ia (lower or greater than 395 nm), the compounds may be further subdivided into two categories (Fig. 3). Thus, a value lower than 395 nm characterizes a flavone substituted by a *C*-methyl either at C-8 (group 5) or C-6 (group 6), or a flavone with a phloroglucinol-type A ring (group 7). These latter compounds exhibit a weak shift of band Ia in methanol + aluminium chloride + hydrochloric acid/methanol (36–55 nm), in contrast to the 6- or 8-*C*-methylflavones (*ca* 60 nm). Nevertheless, since the number of known 6- or 8-*C*-methylflavones is at present limited to those which are also substituted in the 4′-position, these characteristics should be used with prudence.

6- and 8-*C*-methyl-4′-substituted flavones may also be distinguished from their spectra in methanol band II, being more intense in the case of 8-*C*-methylflavones (ratio *A* band I–band II lower than 0.9). In the presence of aluminium chloride, band IIa of 8-*C*-methyl-4′-derivatives is located at *ca* 310 mn, while for a 6-*C*-methyl-4′-derivative this band appears at 301–302 nm as for 6-methoxy, 6-hydroxy- or phloroglucinol-type A ring-4′-substituted compounds (Figs. 14, 15 and 17b). Finally, band Ia of 6-*C*-methylflavones in aluminium chloride appears as a shoulder; by contrast, in 8-*C*-methylflavone, and in the majority of flavones with a phloroglucinol type A ring, this band appears as a peak.

In group 7, where all the compounds have a band

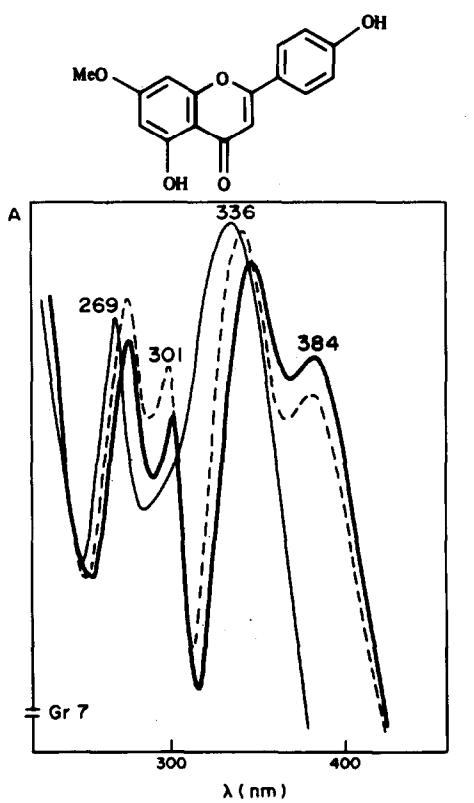


Fig. 15.

I–band II A ratio in methanol of greater than one, the disubstituted B-ring derivatives are characterized in aluminium chloride + hydrochloric acid by band IIa at 293–296 nm and a double band IIb at 259–264 and 276–279 nm of almost equal intensity (Figs. 16, 17a and 19). In mono- and trisubstituted B-ring derivatives, band IIa is always at a wavelength greater than 297 nm. In the aluminium chloride spectrum, the ratio, A band IIa $-A\lambda_{min}$ *ca* 320 nm/A band IIb $-A\lambda_{min}$ 320 nm is higher than 0.7 for the 4′-derivatives and lower than 0.45 for a 3′,4′,5′-trisubstituted compound (Figs. 15, 17b, c, 18 and 20). Finally, *O*-methylation at C-4′ of 3′,4′,5′-derivatives produces a hypsochromic shift in band I in methanol of 19–23 nm.

The second category of flavones which have a maximum in the presence of aluminium chloride + hydrochloric acid at wavelengths greater than 395 nm may be subdivided into two groups according to the shape (shoulder or peak) of band Ia. If Ia is a shoulder (or an inflection) all the compounds are 6-substituted; a shift of less than 68 nm in the position of Ia relative to that of band I in methanol is typical of 6-methoxy- or 6-*C*-methyl-3-methoxyflavones (groups 8 and 9), while a shift greater than 68 nm characterizes 6- and 8-dimethoxy- or di-*C*-methyl-substituted flavonoids (groups 10–13). When band Ia is a peak, its position either below or above 435 nm defines two ensembles, the first reunites groups 14–19, while the second is constituted by group 20. In the ensemble of groups 14–19, when band II in methanol (single peak or secondary band) is less than 271 nm, this is typical of 3-methoxyflavone with a phloroglucinol type A-ring (group 14); when band II is above 271 nm, this

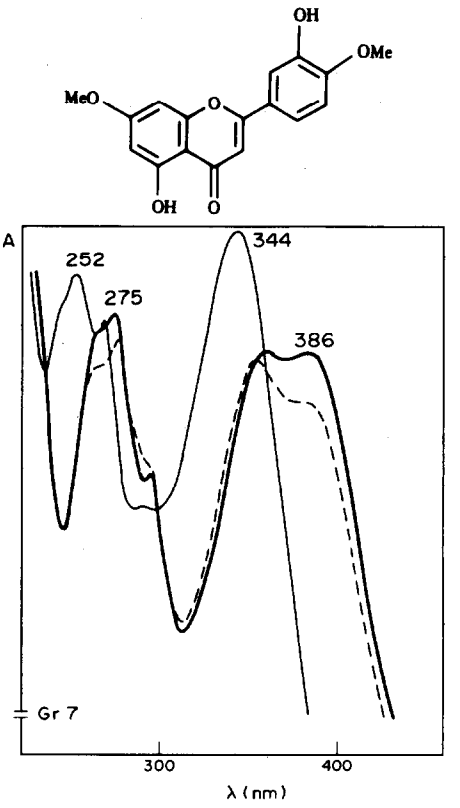


Fig. 16.

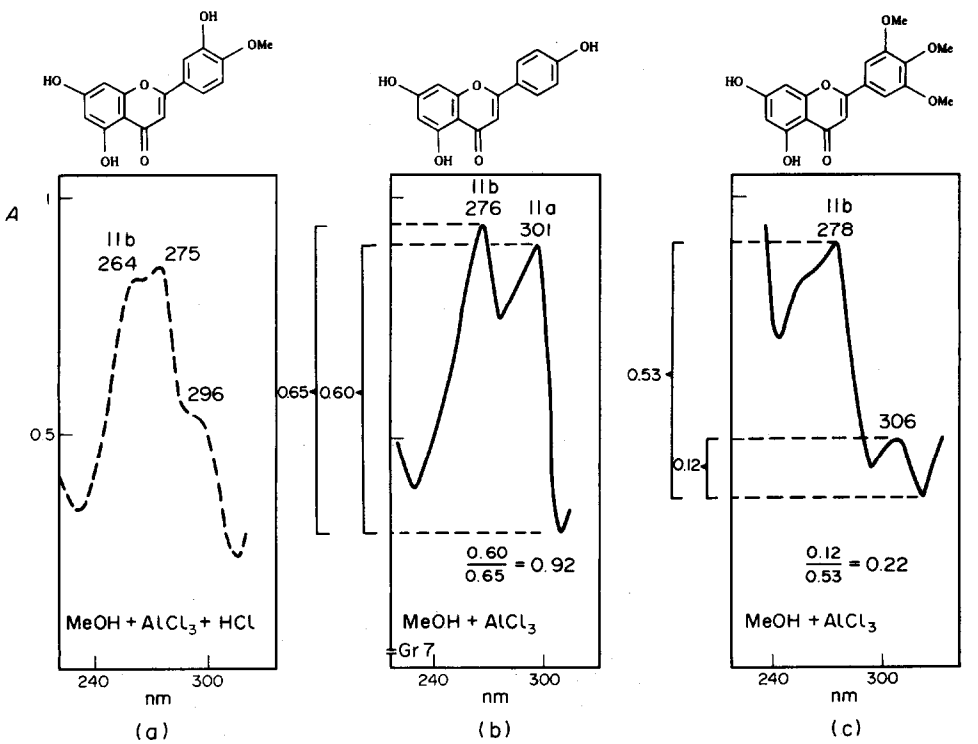


Fig. 17.

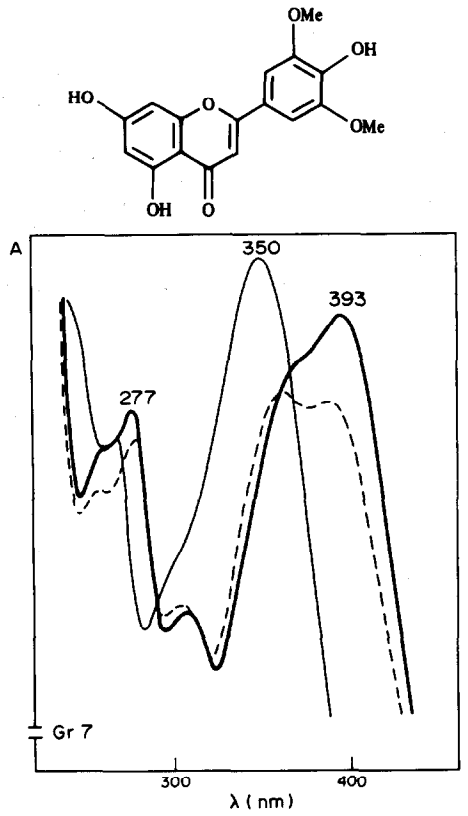


Fig. 18.

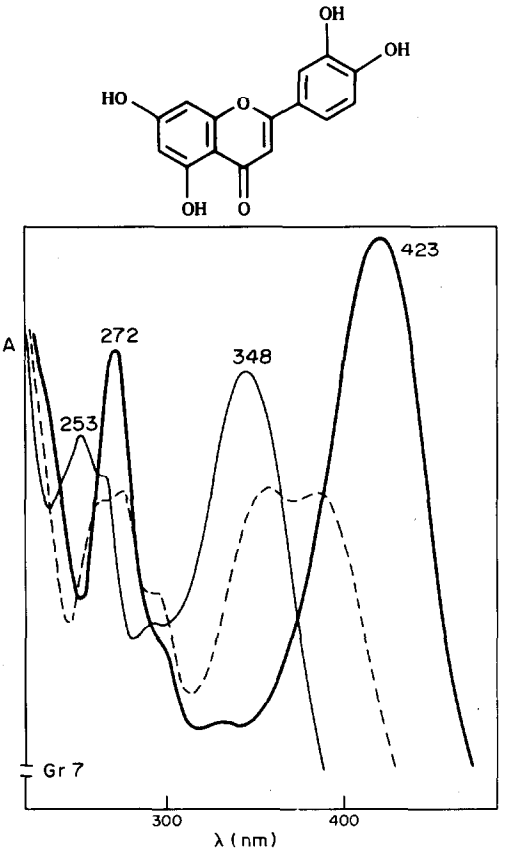


Fig. 19.

characterizes 8-substituted compounds (groups 15–19, Fig. 3).

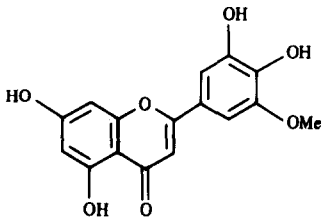
The spectra of 6-methoxy- or 6-*C*-methyl-3-methoxyflavones in the presence of aluminium chloride + hydrochloric acid exhibit band Ia which appears as a shoulder (or inflection) between 400 and 414 nm in 20 of 21 compounds examined. The one exception is 5,4'-dihydroxy-3,6,7,3',5'-pentamethoxyflavone [17] which has band Ia as a peak at 420 nm. However, we have observed that this band decreases as a function of time to become a shoulder. Moreover, this compound in methanol has an unusual band I, inflection at 344 nm and a peak at 360 nm.

Whenever band Ia is present, the magnitude of the shift for compounds of groups 8 and 9 is *ca* 60 nm (53–68 nm in our samples). This finding disagrees with the results of Mears and Mabry [8] and Sakakibara and Mabry [9, 10]. On the other hand, while 6-*C*-methyl-3-methoxyflavones exhibit the same magnitude of shift as 3,6-dimethoxy derivatives, such a value is not restricted to 6-*O*-substitution. These different UV data are, nevertheless, insufficient for distinguishing between 6-methoxy- or 6-*C*-methyl-substitution.

Within groups 8 and 9, 4'- and 3',4',5'-substituted compounds without an *o*-dihydroxy system in the B-ring have, in aluminium chloride + hydrochloric acid, a peak at 280–285 nm and a shoulder at longer wavelengths, 302–306 nm of high *A* for 4'-derivatives (Figs. 21 and 26), and 308–310 nm of lower *A* for 3',4',5'-derivatives (Figs. 23 and 27), with one exception, murrayanol. 4'-*O*-Methylation of trisubstituted compounds may also be detected by the hypsochromic shift of band I in methanol which amounts to *ca* 20 nm (Figs. 23 and 24).

The position of band II in aluminium chloride + hydrochloric acid appears to be a good means for distinguishing the nature of the 6-substituent among the homologous B-ring-substituted flavonoids: 4'-derivatives of groups 8 and 9 have a main peak at 282–284 nm while those of groups 1 and 3 (6-hydroxy- and 6-methoxyflavones) appear at *ca* 302 nm and those of group 2 (6-hydroxy-3-methoxyflavones) at 297 nm; 3',4'-derivatives of groups 8 and 9 present three bands at 260–269, 280–286 and 300–302 nm (Figs. 22 and 25) in contrast to the 6-hydroxy homologues (groups 2 and 3) which exhibit only two bands at 255–267 and 290–296 nm (Figs. 9, 11 and 13).

Among the flavonoids with a 6,8-dimethoxy- or di-*C*-methyl-substituted A-ring (groups 10–13), the bathochromic shift may be determined using band I in methanol as reference, although a very slight shoulder may be observed towards 350–370 nm with 4'-substituted 3-methoxyflavones (Fig. 28). Both the λ_{max} of band II and the shape of its aluminium chloride + hydrochloric acid spectrum are important for these compounds. Known derivatives with 3',4'-substitution have band IIa appearing at *ca* 304 nm (Figs. 30 and 35) while 4'- and 3',4',5'-derivatives have band IIa at 307–313 nm (Figs. 28, 29, 31, 32, 34 and 36); among these latter, 3-methoxyflavones (groups 10 and 11) and other flavones (groups 12 and 13) may be differentiated by the shape and the λ_{max}^{MeOH} of band II. The flavone derivatives have a main peak at 280–286 nm and an inflection at 294–298 nm (Figs. 32, 34 and 36), whereas the 3-methoxyflavones lack such an



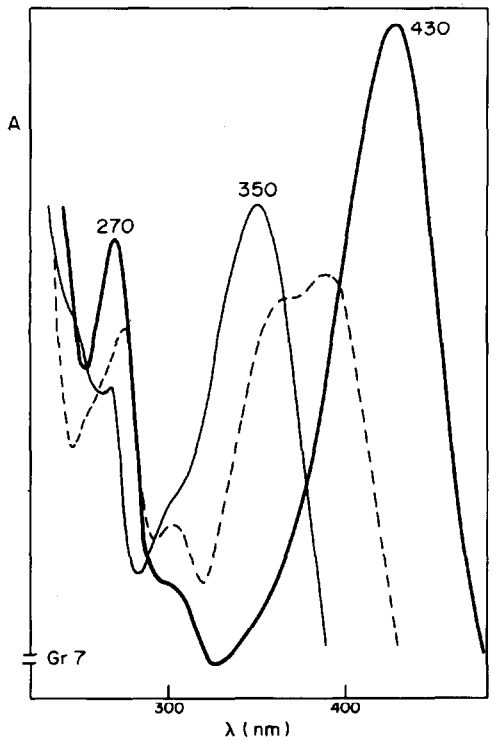
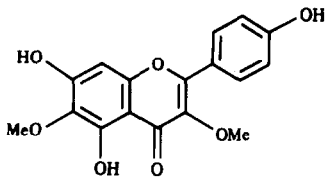


Fig. 20.



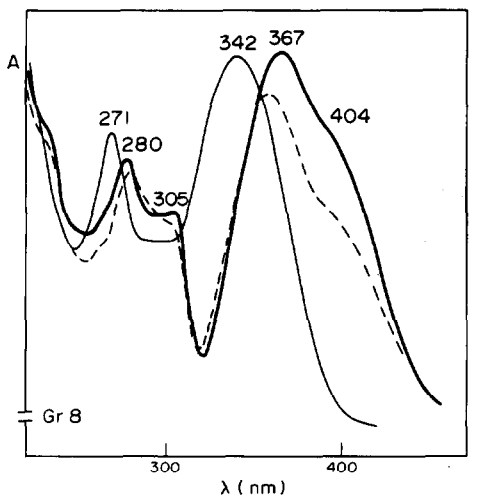
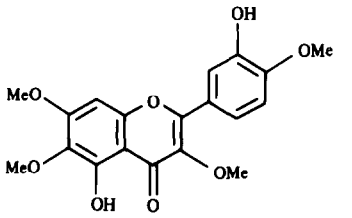


Fig. 21.



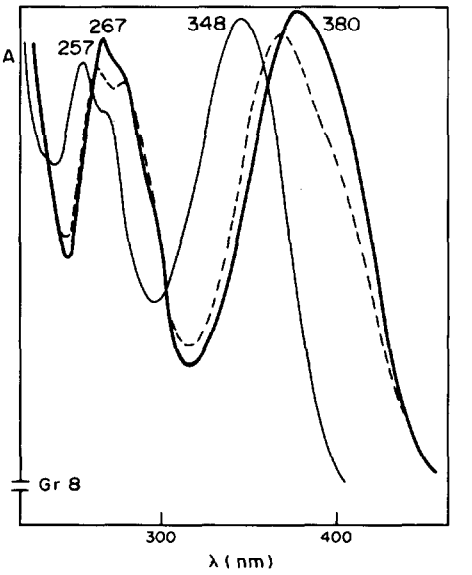
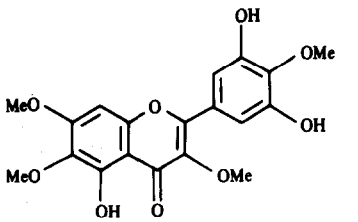


Fig. 22.



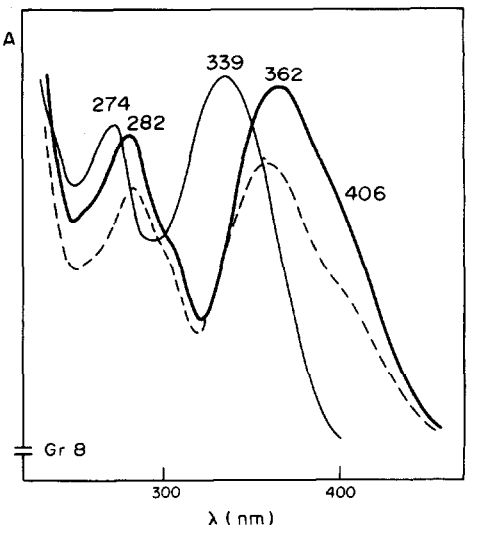


Fig. 23.

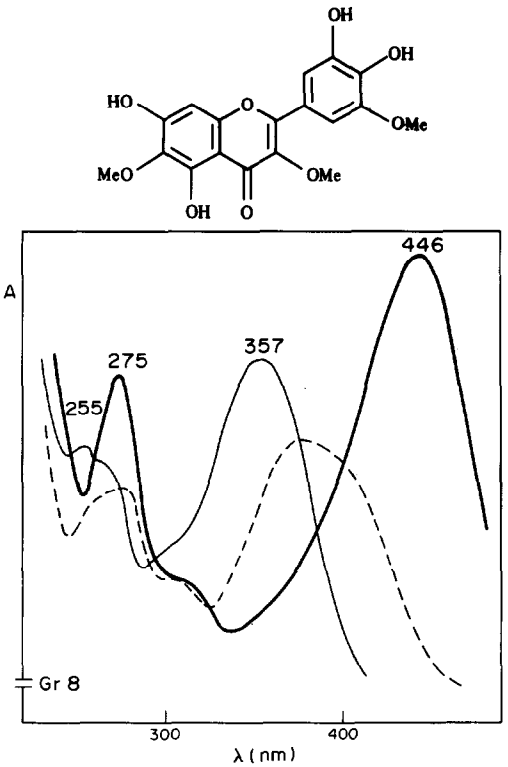


Fig. 24.

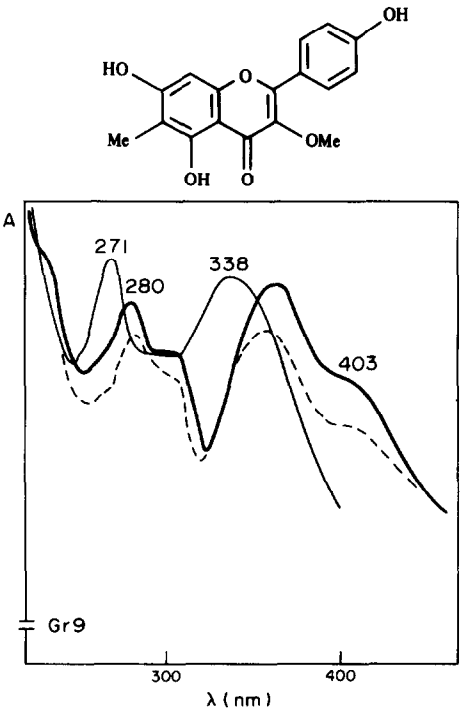


Fig. 26.

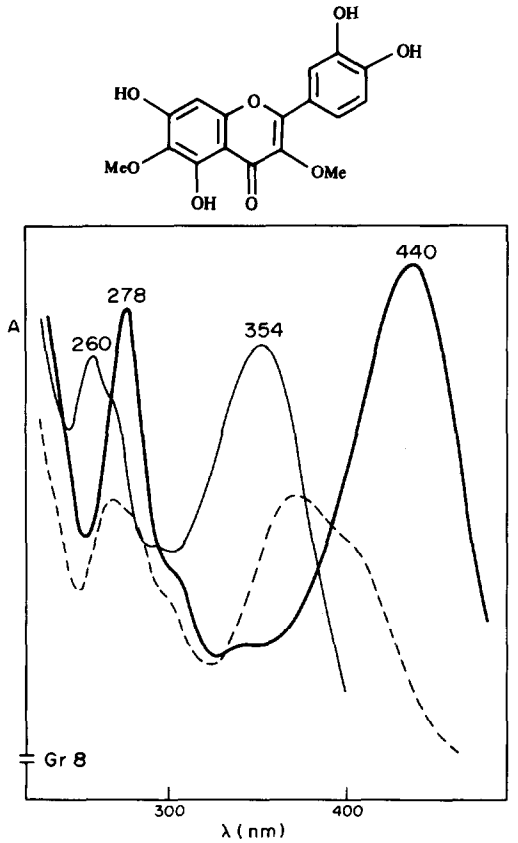


Fig. 25.

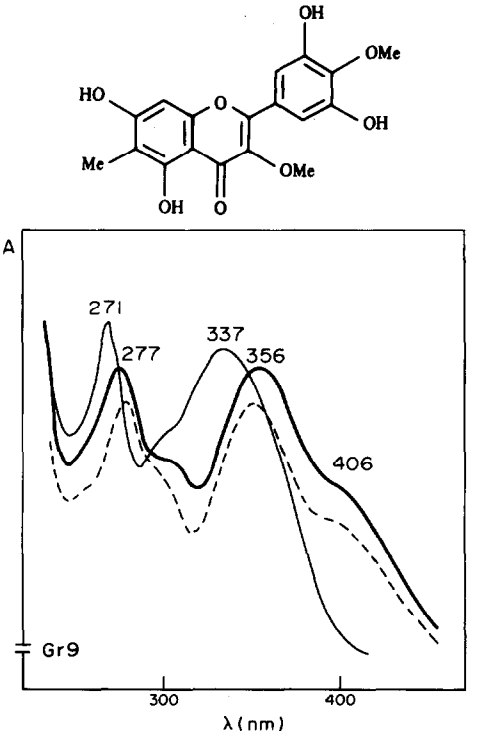


Fig. 27.

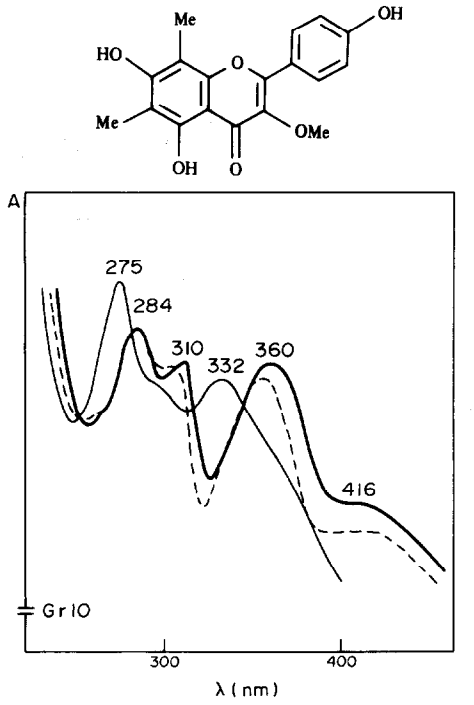


Fig. 28.

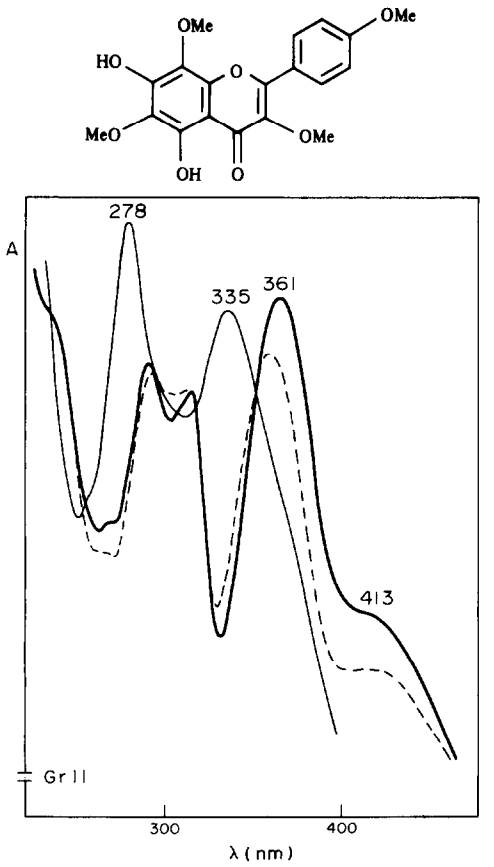


Fig. 29.

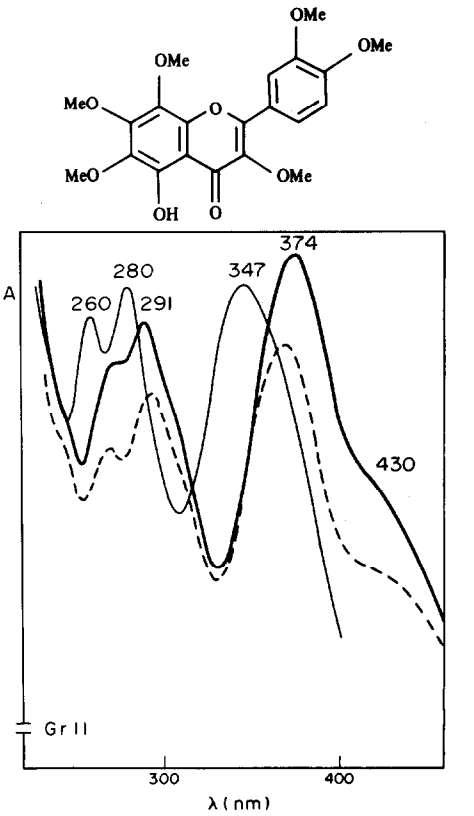


Fig. 30.

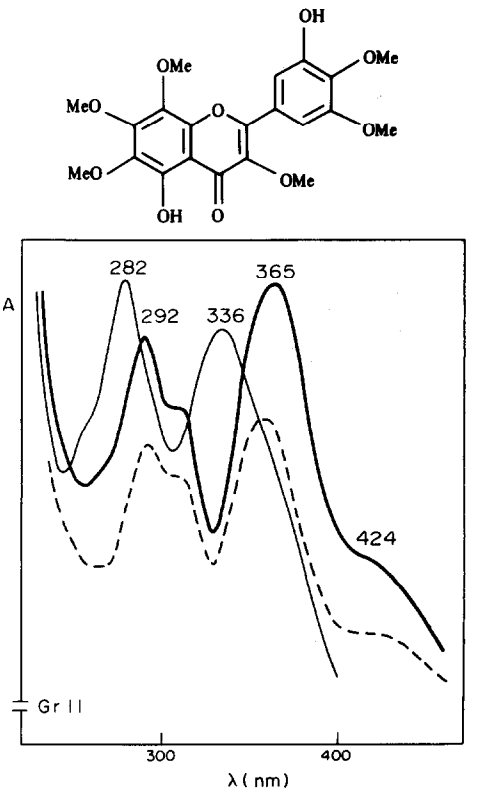


Fig. 31.

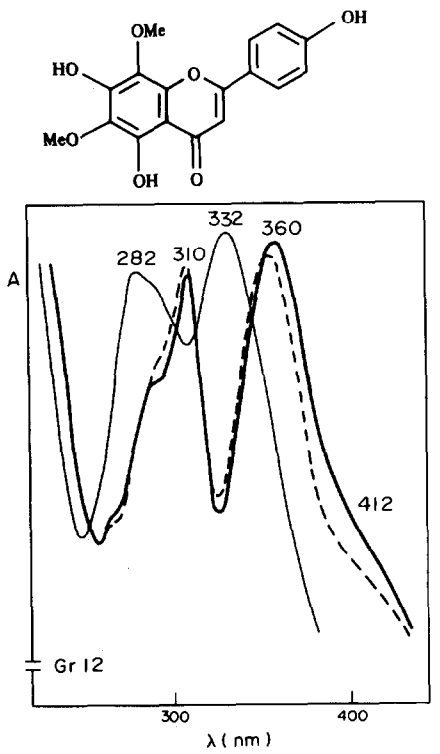


Fig. 32.

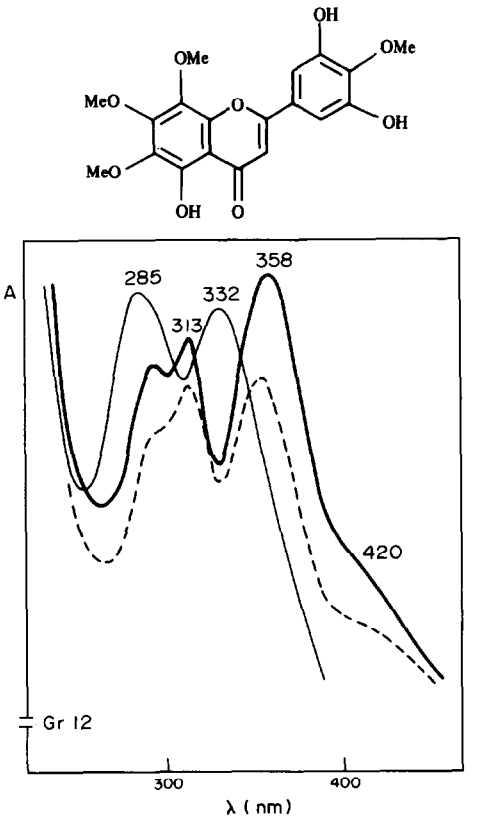


Fig. 34.

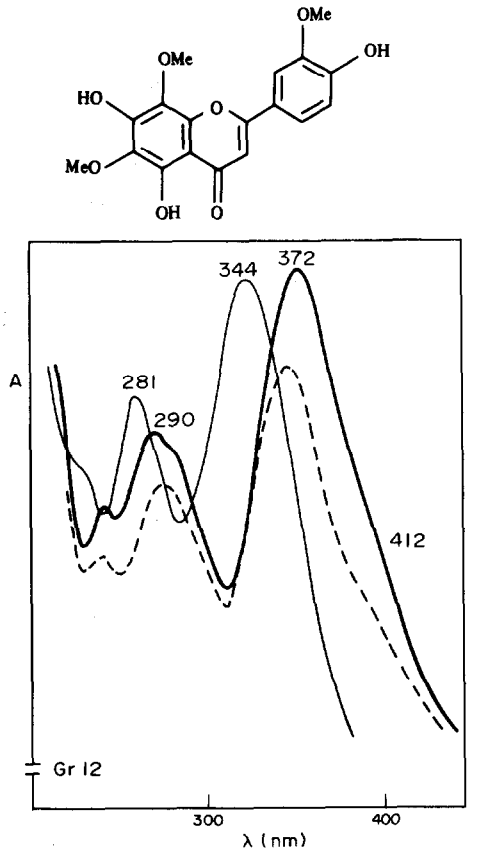


Fig. 33.

inflection (Figs. 28, 29 and 31). Moreover, the aluminium chloride + hydrochloric acid spectrum of 3-methoxyflavones exhibits a main peak IIb at 284–292 nm (Figs. 28, 29 and 31), whereas those of flavones exhibit their main peak IIa at 308–313 nm (Figs. 32, 34 and 36). Within the 3-methoxy derivatives of groups 10 and 11 and the flavones of groups 12 and 13 the UV data do not indicate the nature of 6,8-disubstitution (dimethoxy- or di-C-methyl) or the degree of substitution in the B-ring (4′ or 3′,4′,5′). Among the 3′,4′-derivatives, only the 6,8-dimethoxy substituted compounds are presently described, but differentiation between 3-methoxy- and other flavones cannot be made (groups 11 and 12).

The bibliographic data on flavonoids of group 11 are incomplete [18, 19]. Moreover, the λ_{max} of band I (352 nm), reported by Liu and Mabry [20], for 5,7-dihydroxy-3,6,8,4′-tetramethoxyflavone does not correspond to the value (335 nm) that we have measured (Fig. 29).

For flavonoids of group 14, the peak of band II in methanol of 3-methoxyflavones is always below 271 nm (single peak 264–269 nm, (Figs. 37 and 39) or double peak 250–258 and 262–270 nm (Figs. 38, 40 and 41)). Moreover, the $\lambda_{max}^{AlCl_3+HCl}$ of band Ia is 398–405 nm and the magnitude of the shift Ia/I in methanol is 43–54 nm. These three measurements together provide a means of identifying such compounds. A double band II in methanol characterizes all 3′,4′-derivatives as well as 3′,4′,5′-trisubstituted compounds with a 3′,4′-*o*-dihydroxy system (Figs. 38, 40 and 41, respectively). 4′- and 3′,4′,5′-Derivatives lacking a

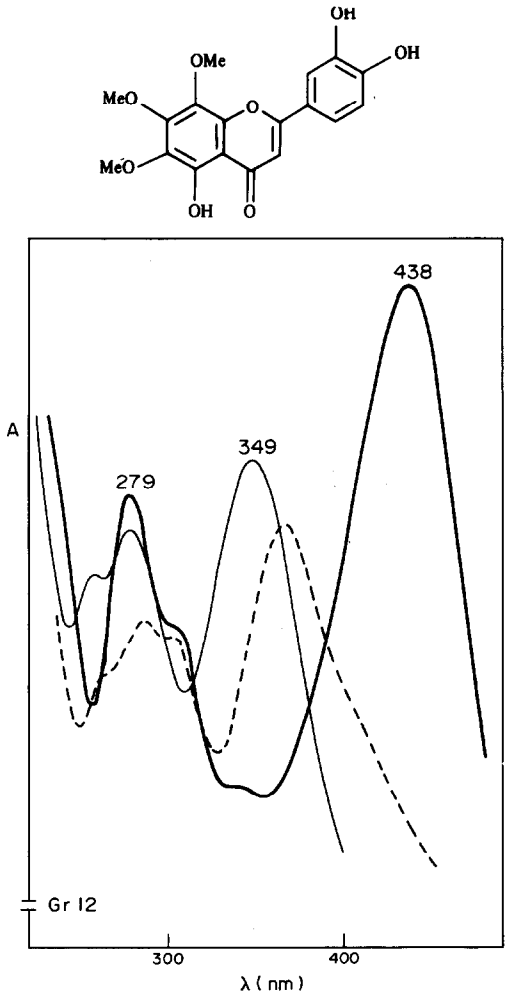


Fig. 35.

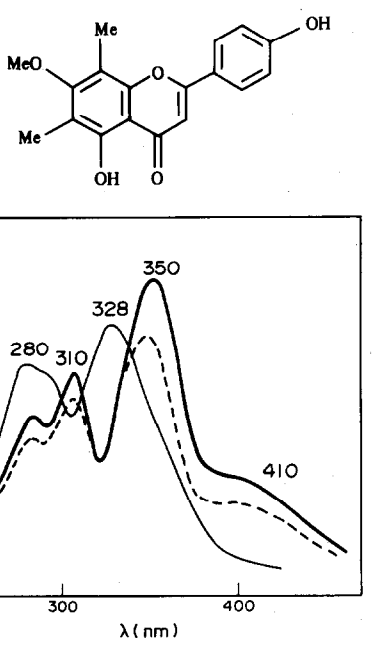


Fig. 36.

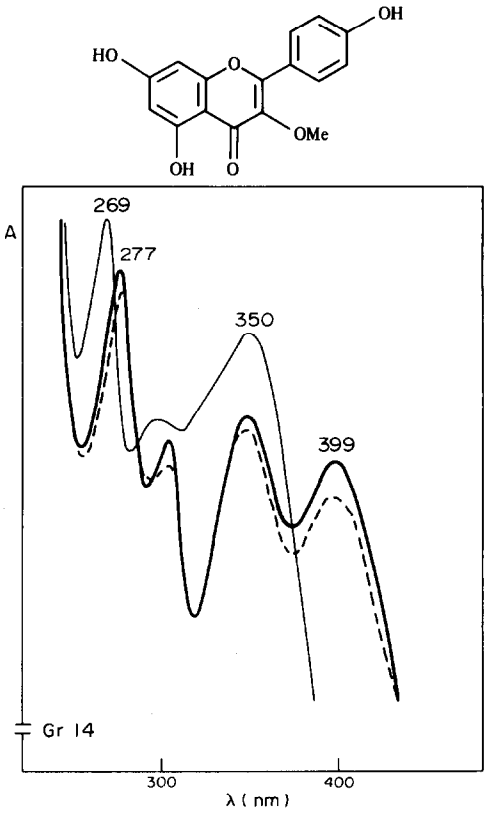


Fig. 37.

3′,4′-*o*-dihydroxy system have almost the same UV spectral characteristics (Figs. 37 and 39). However, the *A* of band IIa in aluminium chloride is more intense for the 4′-derivatives.

Among the flavonoids which possess substitution at C-8 (groups 15–20), it is possible to separate those with a 4′- or 3′,4′,5′-substituted B-ring from those with 3′,4′-di-substitution: in the methanol spectrum, a single peak at 273–281 nm characterizes the former (Figs. 42, 45, 47, 49 and 51), whereas two peaks at 253–262 and 272–280 nm are typical of the latter (Figs. 43, 44, 46, 50 and 52).

Among the 4′- and 3′,4′,5′-substituted flavones, a major peak in methanol at 273–278 nm (Figs. 42, 45 and 47) appears characteristic of 8-methoxy compounds (groups 15 and 16), whereas that at 305 nm (Figs. 49 and 51) indicates a free hydroxyl at C-8 (groups 17 and 18). Within 8-methoxy compounds, a maximum for band Ia in aluminium chloride + hydrochloric acid at 397–406 nm appears to be characteristic of flavones from group 15 (Figs. 42–44), whereas a maximum at 415–424 nm is typical of 3-methoxyflavones from group 16 (Figs. 45–48).

Much of the spectral data reported for the 13 flavones which belong to group 15 are incomplete [21–24]. Moreover, the published data for 5,7-dihydroxy-8,4′-dimethoxyflavone are conflicting. Goudard [25] reported the following data. UV λ_{max}^{EtOH} nm (log ε): 275 (4.34), 298 (4.27), 322 (4.26); $\lambda_{max}^{EtOH+AlCl_3}$ nm: 285, 310, 358 (we have confirmed and extended these data, see Table 1), whereas Lin *et al.* [26] found λ_{max}^{MeOH} nm (log ε): 274 (4.12) and 332 (4.32) and $\lambda_{max}^{MeOH+AlCl_3}$ nm: 301 and 360 (shoulders at 264

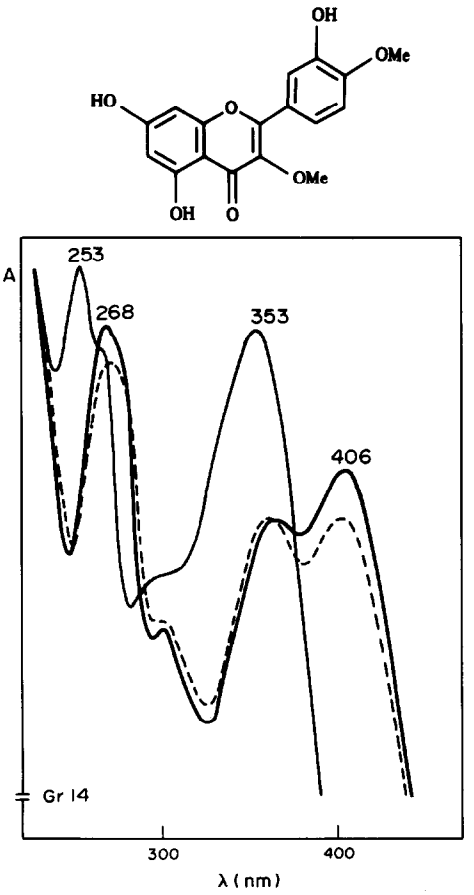


Fig. 38.

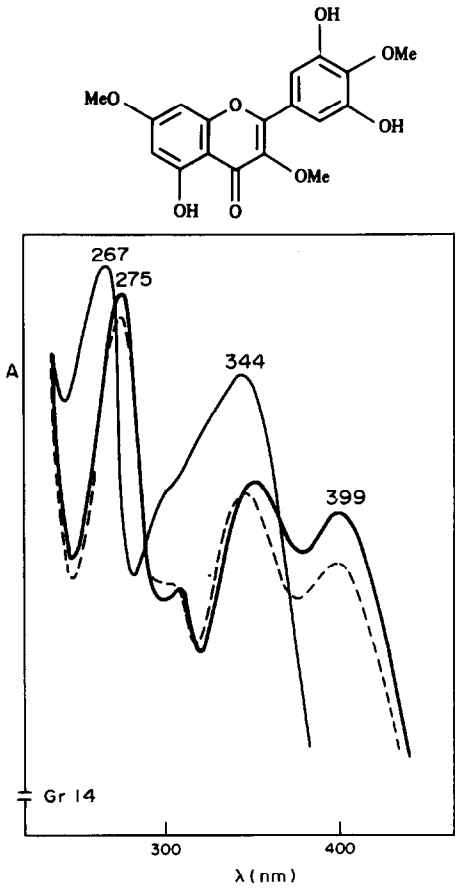


Fig. 39.

and 292). Since the ratio of band I–band II is greater than one in methanol and there is a peak at 301 nm in the aluminium chloride spectrum, the compound studied by Lin *et al.* appears to be a 6-methoxy-4′-substituted flavone (see group 1 above). On the other hand, the data presented by Goudard [25] fit in with those expected for an 8-methoxyflavone. Recently, Markham [27] has published the revised structure of cirsitakaogenin but he has not indicated the UV values.

In the same way, the data published by Le Quesne *et al.* [28] for 5,4′-dihydroxy-7,8,3′-trimethoxyflavone and 5,3′-dihydroxy-7,8,4′,5′-tetramethoxyflavone are also conflicting. The various spectra of these compounds do not present the expected values of 8-methoxyflavones, previously described both in methanol and in the presence of neutral or acidic aluminium chloride. Also, the relative abundance of $[M]^+$ and $[M-15]^+$ peaks in the mass spectrum indicated by Le Quesne *et al.* [28] are not typical of 5-hydroxy-7,8-dimethoxyflavones according to the rules defined by Goudard *et al.* [29].

The majority of compounds of group 16 exhibit four bands in methanol with major peaks at 273–278, 300–305 (sh), 322–328 and 356–362 nm (Figs. 46–48). Characteristically for 8-substituted flavones, the ratio of the A band at 356–362 nm to that at 273–276 nm is less than 0.75. The UV data do not distinguish between mono- and trisubstitution in the B-ring. Among the 3′,4′,5′-trisubstituted compounds of group 16, 5,7-dihydroxy-3,8,3′,4′,5′-pentamethoxyflavone (conyzatin) is remarkable in having a peak at 402 nm in the methanol spectrum [30].

There are no 3′,4′,5′-trisubstituted derivatives among the 8-*O*-substituted flavones of groups 17 and 18. The 4′-derivatives again have four major bands at 280–281, 302–306, 328–330 and 360–366 nm (Fig. 49). The peak at 302–306 nm appears a major band in compounds of group 17 (7,8-*o*-dihydroxy system, Fig. 49) and 18 (8-hydroxy-7-methoxy-derivatives, Fig. 51). There is a smaller shift in the presence of aluminium chloride + hydrochloric acid in band Ia for compounds of group 17 than for those of group 18.

Within groups 14–19, no compounds are known in groups 17 and 19 where the 3′,4′-dihydroxy system is masked by methylation; the 3′,4′-derivatives of groups 16a and 17a with a free 3′,4′-dihydroxy system have a long wavelength maximum in the presence of aluminium chloride above 449 nm (part B *pro parte*). Among the remaining 3′,4′-dihydroxy flavonoids, 8-substituted, 8-methoxy- or *C*-methyl-substituted-3-methoxyflavones [31] (groups 16 and 19) have a double band in methanol at 332–340 nm inflection and 360–366 nm (Fig. 46), while the related 8-methoxyflavones (group 15) lack this double band (Figs. 43 and 44). However, the UV spectral data do not permit the separation of 3′,4′-derivatives of groups 15

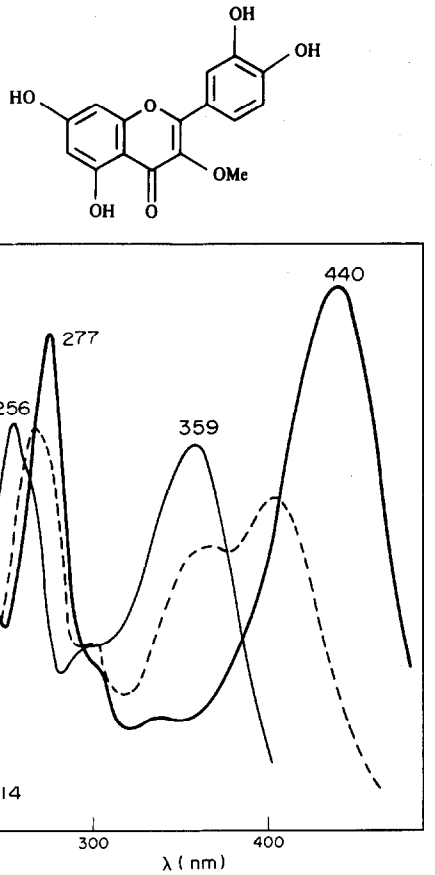


Fig. 40.

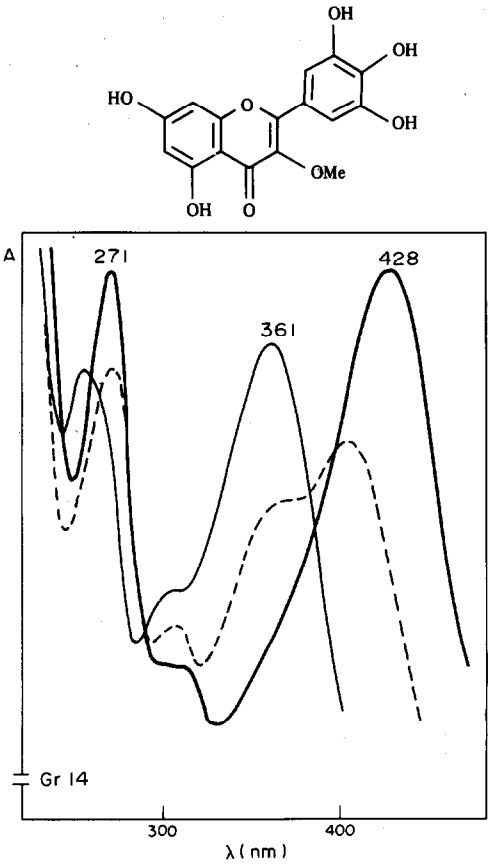


Fig. 41.

(8-methoxyflavones) and 18 (8-hydroxyflavones).

3-Methoxyflavones with 8-hydroxylation (group 20) have a peak in aluminium chloride + hydrochloric acid above 435 nm. All these derivatives have four bands in the methanol spectrum, the longest wavelength band at 365–378 nm appearing as a shoulder. In the case of 4′-and 3′,4′,5′-derivatives, there is a single peak in the methanol spectrum at 278 nm; for 3′,4′-derivatives, there are two bands, 257–262 and 277–278 nm. The former compounds are also distinguished by the presence of a band at 314–320 nm in the presence of aluminium chloride + hydrochloric acid.

If the spectral shift of band I in the presence of aluminium chloride is above 449 nm (part B), the compounds possess both 8-*O*-substitution and a 3′,4′-*o*-dihydroxy system. 7,8-*o*-Dihydroxyflavones (group 17a) have a shoulder in band Ia when hydrochloric acid is added (Fig. 50), whereas 8-hydroxy-3-methoxyflavones (group 20a) show a peak (Fig. 52). Moreover, there is a single band I peak in aluminium chloride for 5,7,3′,4′-tetrahydroxy-3,8-dimethoxyflavone (Fig. 48) and two peaks, Ia and Ib, for 8-hydroxy-derivatives, Ia being a peak if there is a 3-methoxy group (Fig. 52) and a shoulder if not (Fig. 50). Finally, the 3′,4′-derivatives of groups 20 and 20a have four bands in methanol as related homologues of groups 16 and 16a, the band of longest wavelength appearing as a shoulder in the former (Fig. 52) and as a peak in the latter (Figs. 46 and 48).

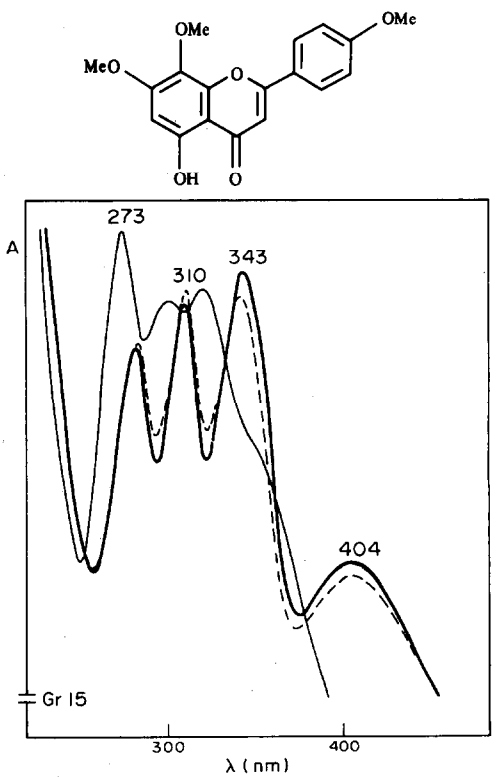


Fig. 42.

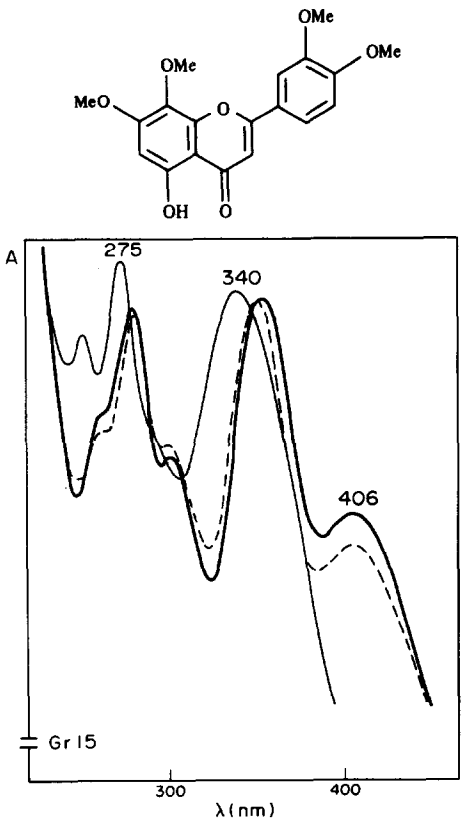


Fig. 43.

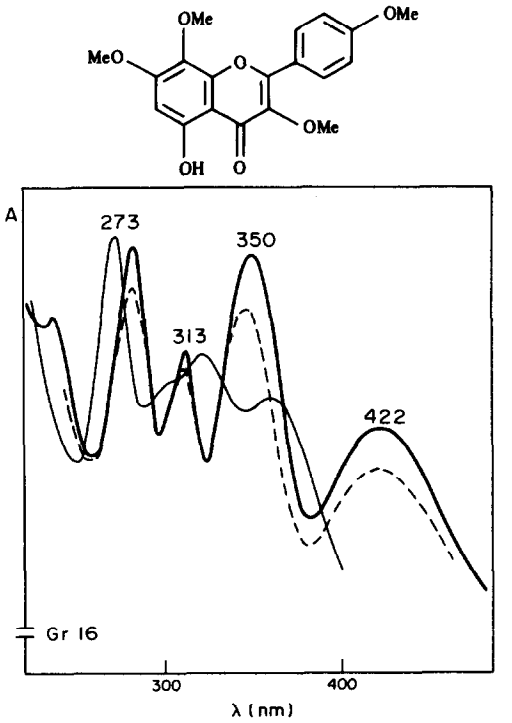
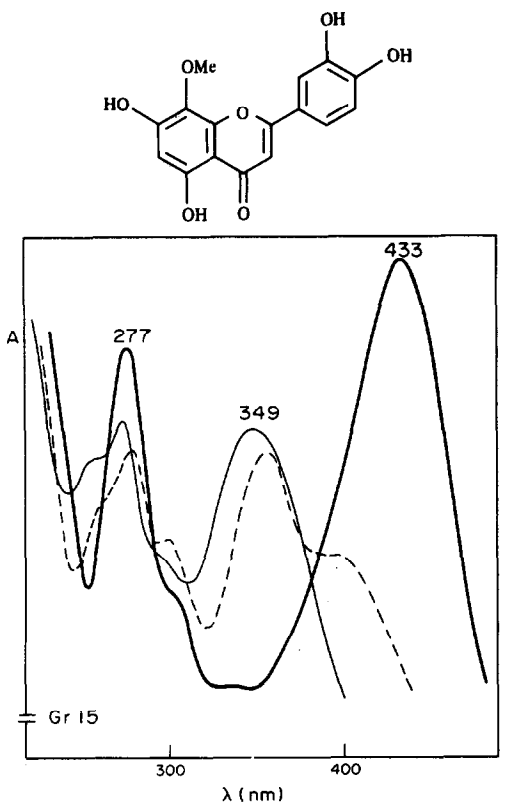


Fig. 45.



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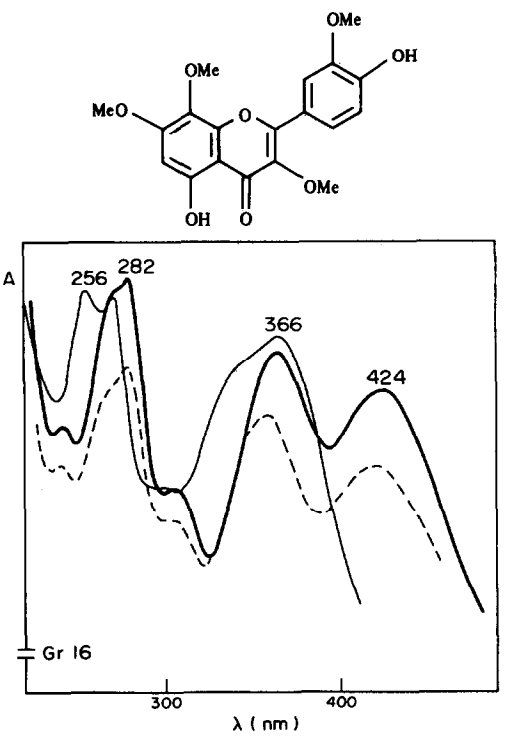

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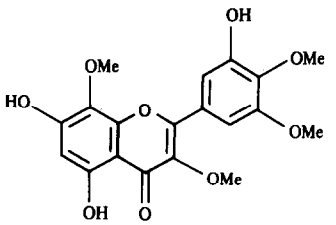


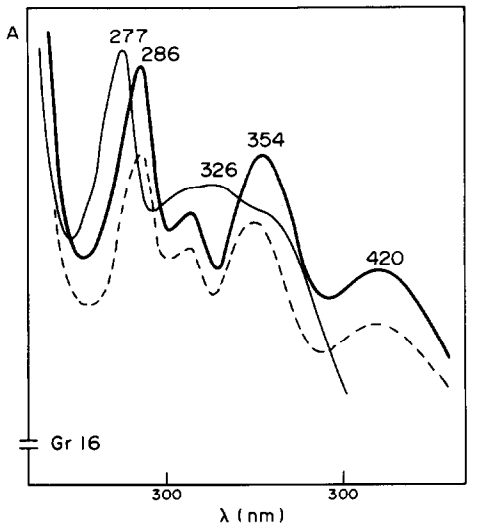
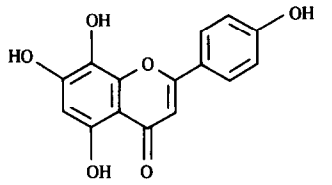


Fig. 47.



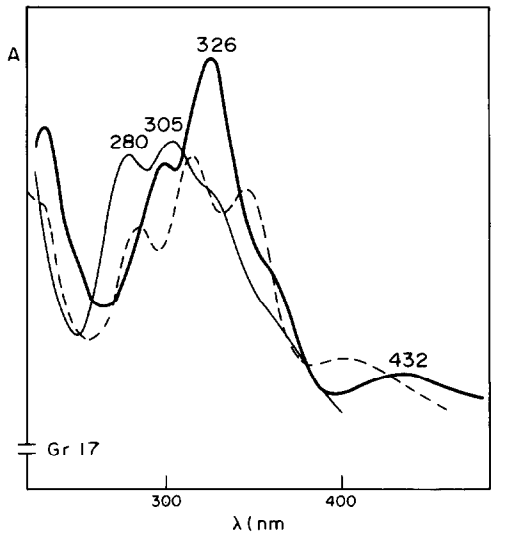
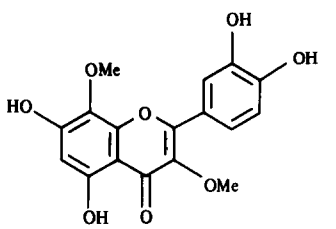


Fig. 49.



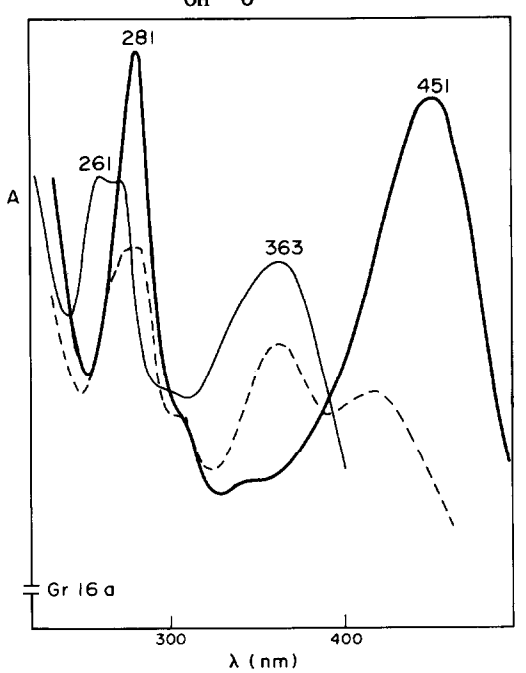
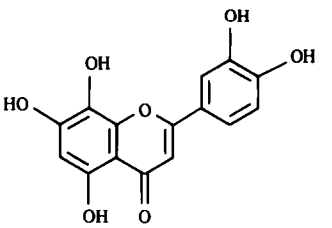


Fig. 48.



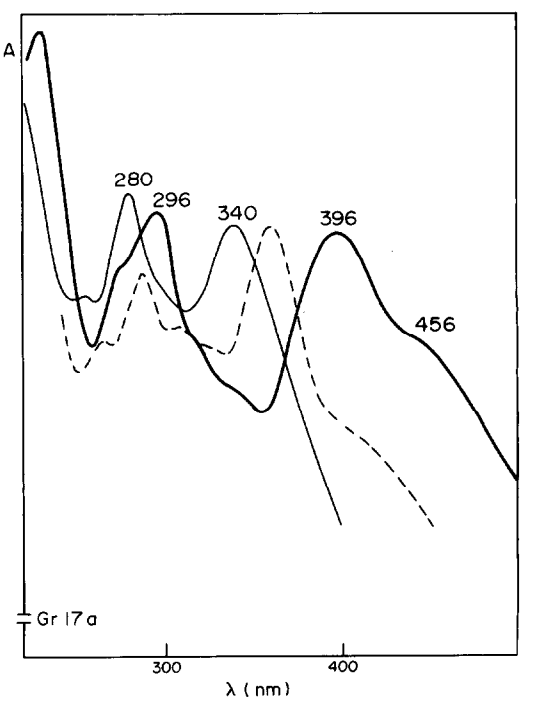


Fig. 50.

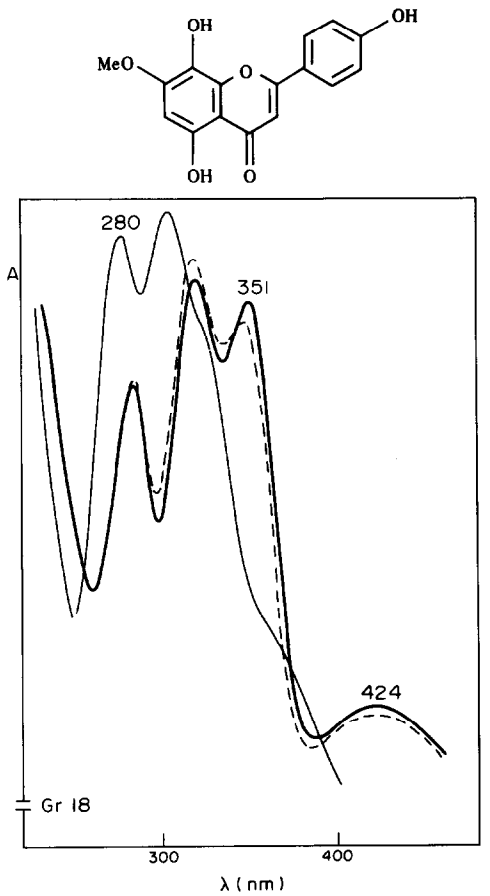


Fig. 51.

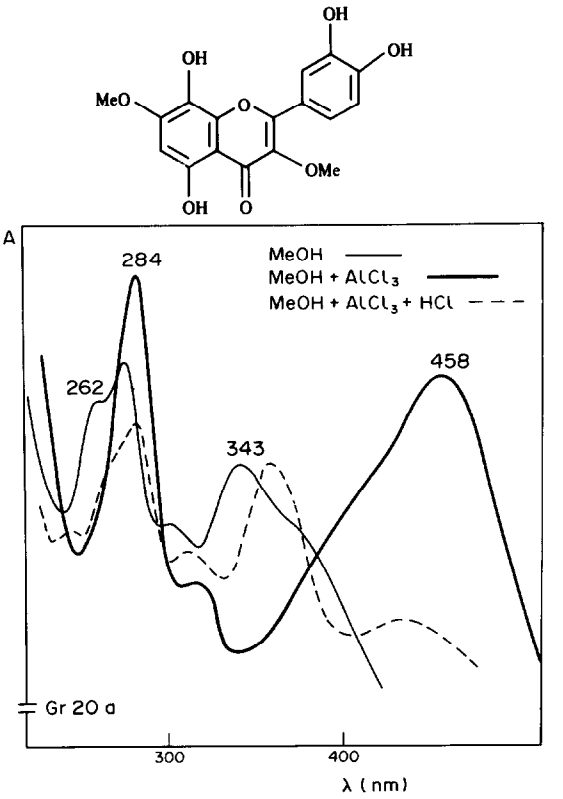


Fig. 52.

DISCUSSION

Comparisons between the spectrum in methanol of 5-hydroxy-7-*O*-substituted flavones and related 3-methoxyflavones which possess a phloroglucinol-type A-ring, the same degree of substitution on the B-ring and the same substituent at the C-4′ (hydroxyl or methoxyl) show that the position of the band I maximum of 5-hydroxy-7-*O*-substituted flavones is always lower than that of homologous 5-hydroxy-3-methoxyflavones (Table 4). A similar conclusion may be drawn from comparisons of the spectra of 5-hydroxyflavones and 5-hydroxy-3-methoxyflavones which present the same substitution on the A- and B-rings (Figs. 53 and 54).

The exchange of hydroxyl for methoxyl at C-4′ always produces a hypsochromic shift in band I, the shift being as much as 7–23 nm for 3′,4′,5′-substituted derivatives (Table 4).

6-Substitution and 6,8-disubstitution produce an important hypsochromic effect, except for 6-hydroxy-4′-methoxyflavones. 8-*O*-Substitution produces a split in band I, the supplementary band appearing at longer wavelengths for 4′-monosubstituted flavonoids. Moreover, such a substitution induces either a bathochromic shift (5-hydroxy-3-methoxyflavones, Fig. 53) or a hypsochromic shift (3′,4′- or 3′,4′,5′-substituted flavones, Fig. 54). The position of the band II maximum is also affected by the introduction of substituent(s) at position(s) 6 and/or 8. Hydroxylation at C-6 produces the most important bathochromic shift. Finally, the ratio of *A* band I–band II constitutes a criterion for distinguishing the

Table 4. Spectral properties of band I in methanol (nm) of 3-methoxyflavones and flavones with a phloroglucinol-type A-ring and the same substituents at C-4′

	Substitution of B-ring					
	4′		3′,4′		3′,4′,5′	
Type of compound	OH	OMe	OH-4′	OMe-4′	OH-4′	OMe-4′
3-Methoxyflavones	350	347–348	354–359	351–353	361	344–350
Flavones	336	327–329	347–348	340–344	350–354	331

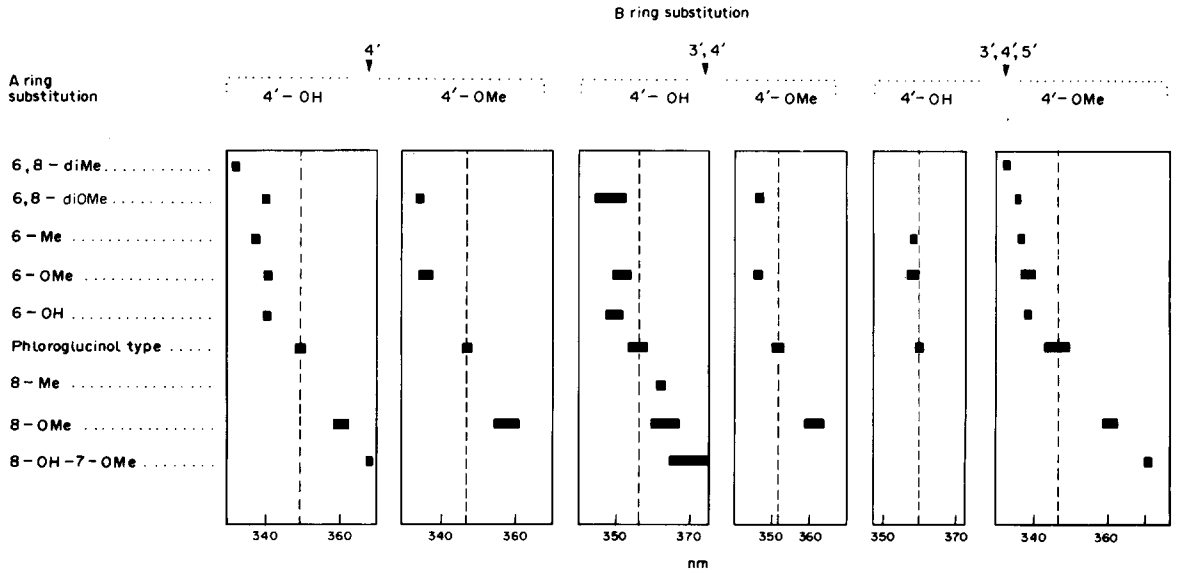


Fig. 53. Diagram illustrating the influence of A-ring substitutions on the position of band I in the methanol spectrum of 5-hydroxy-7-oxygenated-3-methoxyflavones.

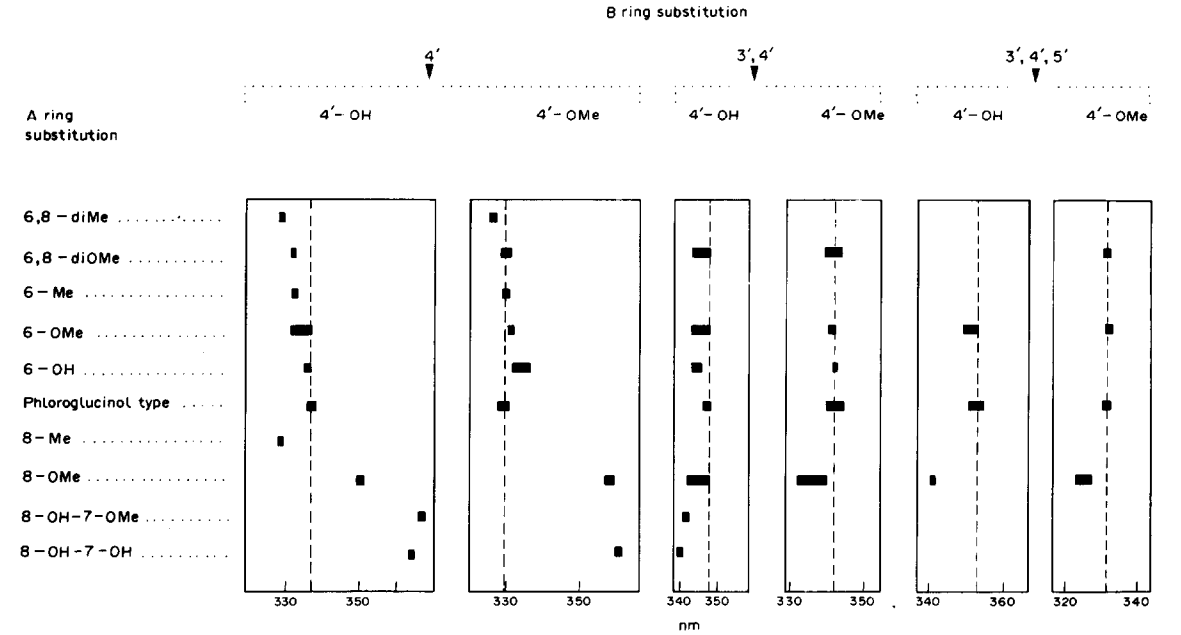


Fig. 54. Diagram illustraing the influence of A-ring substitutions on the position of band I in the methanol spectrum of 5-hydroxy-7-oxygenated flavones.

substituted position on the A-ring. So, 8-substitution particularly decreases this value, whereas 6-substitution increases it.

As shown from the results summarized in Fig. 55, the presence of a single band I or a double band Ib and Ia after addition of aluminium chloride + hydrochloric acid is primarily associated with the nature and the position of substituent(s) on the A-ring. When there is a band Ia, the presence (or absence) of a methoxyl at C-3 influences only its position. Moreover, as indicated by the spectra of Fig. 56, the shape and the position of band II in presence of acidic aluminium chloride is determined by the combined effects of three parameters: the number of substituent(s) on the B-ring, the number, nature and position of

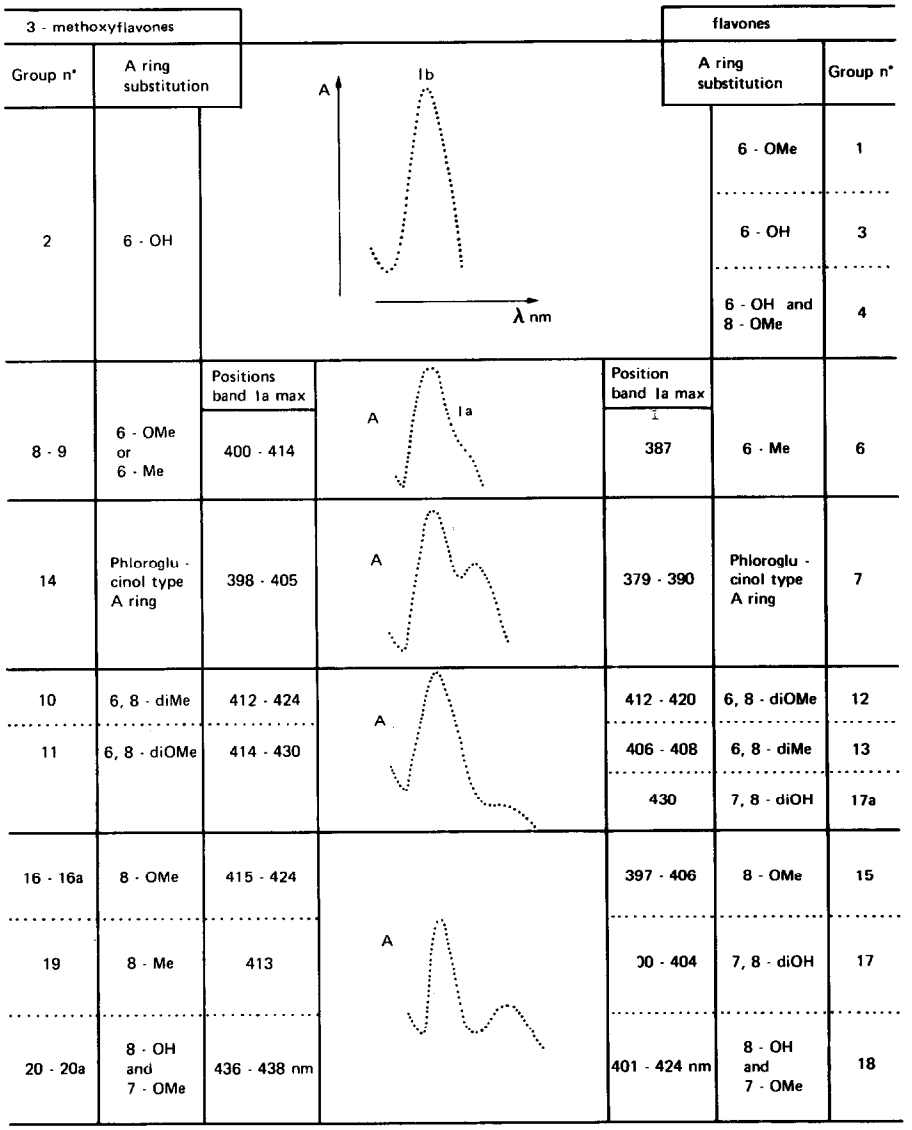


Fig. 55. Shapes and positions of band I of 5-hydroxy-7-oxygenated flavones and related 3-methoxyflavones with a 4'-, 3',4'- or 3',4',5'-substituted B-ring in the presence of methanol + aluminium chloride + hydrochloric acid.

substituent(s) on the A-ring and the presence or absence of a 3-methoxy substitution.

EXPERIMENTAL

The spectra have been recorded on a Jobin-Yvon Duospac 203 spectrophotometer. $AlCl_3$ soln used in all cases was freshly prepared (6% $AlCl_3$ in MeOH, addition of three drops to the soln of flavonoid). Two drops of conc. HCl were added to the neutral soln. The spectra were immediately measured after addition of reagents. In the majority of cases, the flavonoid samples were purified on an LH-20 Sephadex column.

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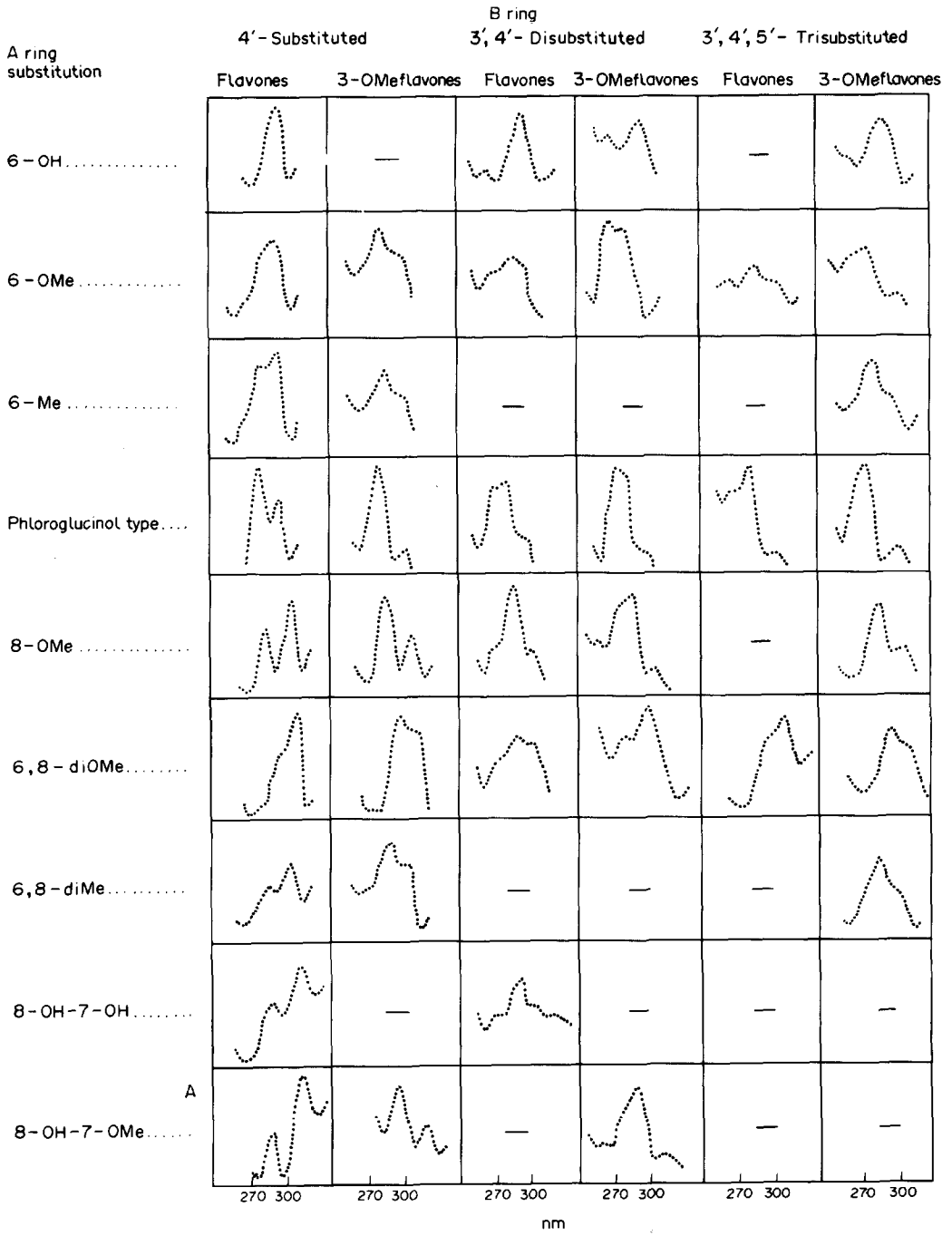

Fig. 56. Shapes and positions of band II of 5-hydroxy-7-oxygenated flavones and related 3-methoxyflavones in the presence of methanol + aluminium chloride + hydrochloric acid in function of substituents of the A- and B-rings.

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