SHORT COMMUNICATIONS

ULTRAVIOLET VISIBLE SPECTROSCOPY OF CERTAIN RARE FLAVONOIDS

A. G. RAMACHANDRAN NAIR, S. MOHANDOSS and BERNARD VOIRIN*
Department of Chemistry, Pondicherry University, JIPMER Campus, Pondicherry 605 006, India.
**Laboratoire de Phytochimie, U.E.R. des Sciences de la Nature, 69623 Villeurbanne, France.*

UV-VISIBLE absorption spectroscopy is probably the single most useful technique for flavonoid structure analysis and used for the determination of flavonoid type and the oxygenation pattern. Also, unsubstituted hydroxyl groups on the flavonoid skeleton are located using selective shift reagents. The small quantity of the sample (or its eluate from PC or TLC) required and the availability of data on various types of flavonoids for comparative interpretations renders this technique superior over others. Different aspects of this technique have been reviewed earlier[1-6]. Voirin[6] while analysing the UV-visible spectra of 151 flavonoid compounds in MeOH and in presence of $AlCl_3$/HCl developed a reliable empirical method for determining the finer structural details including differentiation of closely-related flavonoids. Based on this observations, suggested re-determination of the spectral data for Nodifloretin[7] as the data reported earlier were found untenable.

There has been considerable variation in the interpretation of 5,6,7-trioxygenated flavones with one or both the 6/7–OH blocked by alkylation/glycosylation. Nair and Kotiyal[8] found that the absence of bathochromic shift in band II of the NaOAc spectrum (compared to MeOH spectrum) is not indicative of free 7–OH in the case of 6,7-dioxygenated flavonoids with 6–O–substituent. Later Voirin *et al*[7] revised the structure of Majoranin by a judicious comparison of the UV spectra with those of two very closely related compounds and substantiated a method of detection of free 7–OH in 6-oxygenated flavonoids. Following this approach, Nair *et al*[10] revised the structure of triumboidin and observed that 6–O–glycosylation (especially of a 5,6,7-trioxygenated type) could be differentiated by a discernible shoulder around 385 nm in the $AlCl_3$ and $AlCl_3$/HCl spectra though the observation needed further support from the analysis of different compounds. The differentiation of 7-hydroxy flavone from 7–O–substituted flavone by observing the presence or the absence of an additional band (band III) between 305 and 350 nm in the NaOMe spectrum and the comparative value of the λ_{max} of band I in NaOAc and NaOMe was suggested[11]. In the light of these recent developments and as a part of the continuing study of new and rare flavonoid compounds, we have studied the UV spectra of three rare 6–O–glycosylated flavones and two rare aglycones and the results are presented here. A very rare and novel iso-prenylated flavone, cycloartocarpin (isolated from *Artocarpus hirsutus*) whose structure was established by chemical and spectral methods was subjected to UV analysis in MeOH and in the presence of five diagnostic reagents. The UV data reported (table 1) for this flavone are quite characteristic of this compound and distinctly different from its regioisomer revealing the usefulness of the technique in surveying similar flavonoids.

Voirin[6] observed that nodifloretin (5,6,7,4′-tetra hydroxy-3′-methoxy flavone) was one of the two flavones among 33 examined whose reported UV data differed from a general rule (exhibiting λ_{max} higher than 279 nm in band II); the other being 3–O–methyl quercetagetin. Nodifloretin was isolated from *Lippia nodiflora*[12] and subjected to a rigorous UV analysis. The UV data obtained (table 1) confirm Voirin's observation that the data reported by Ulubelen *et al*[7] were in error. In the case of Triumboidin[10], a 6–O–glycoside of 5,6,7-trioxygenated flavone, a distinct shoulder was observed around 385 nm in $AlCl_3$ and $AlCl_3$/HCl spectra. This shoulder was absent in 6–O–methylated flavones indicating its utility in the detection of 6–O–glycosylation. However, data on simple 6–O–glycosylated flavones with other OH groups free, were not studied to test the general applicability of this characteristic. Hence the UV data have now been recorded (table 1) for 6-O-glucosyl-5,7-dihydroxy flavone[13] (baicalein-6-O-glucoside), its 4′-hydroxy derivative[14] (scutellarein-6-O-glucoside) and its 3′, 4′-dihydroxy derivative[8] (luteolin 6-O-glucoside).

The data showed that the appearance of a shoulder around 385 nm in $AlCl_3$ and $AlCl_3$/HCl spectra is a reliable indicator of 6–O–glycosylation. Our results further showed that UV absorption

Table 1 *UV-visible spectral data of flavonoids [$\lambda_{max.}$ (nm) intensity relation to most intense peak as 1]*

Compound	MeOH	NaOMe	NaOAc	NaOAc/H_3BO_3	$AlCl_3$	$AlCl_3$/HCl
Cycloartocarpin	259(0.74)	259(0.56)	260(0.84)	258(0.82)	272(0.59)	259(0.50)
	292(1.00)	299(1.00)	291(1.00)	292(1.0)	408(1.0)	293(1.00)
	368(0.86)	386(0.91)	381(0.83)	370(0.82)		379(0.53)
Nodifloretin	260 sh		280(1.00)	284(0.84)	301(0.57)	252 sh
	294(0.69)	321(0.40)	320(0.86)	351(1.00)	313(0.58)	295(0.77)
	345(1.00)	402(1.00)	360(0.98)		388(1.00)	368(1.00)
Baicalein-6-O-glucoside	270(1.00)	274(0.60)	272(1.00)	273(1.00)	254 sh	252 sh
	317(0.53)	324(0.39)	300(0.73)	358(0.87)	282(1.00)	282(1.00)
		374(1.00)	365(0.87)		334(0.59)	332(0.57)
					385 sh	385 sh
Scutellarein-6-O-glucoside	271(0.69)	274(0.58)	273(1.00)	272(1.00)	280 sh	300(0.71)
	334(1.00)	326(0.38)	300(0.65)	347(0.83)	302(0.65)	351(1.00)
		394(1.00)	369(0.80)		358(1.00)	386 sh
					386 sh	
Luteolin-6-O-glucoside	256(0.69)	266(0.69)	272(1.00)	262(0.92)	275(0.83)	268(0.71)
	270(0.68)	330 sh	330 sh	382(1.00)	300 sh	279(0.75)
	349(1.00)	404(1.00)	381(0.99)		385 sh	300 sh
					417(1.00)	366(1.00)
						385 sh

characteristic is a more reliable indicator of 6–O–glycosylation contrasted with the recent observation on the unreliability of the inference based on the absence of enzyme hydrolysability[14] of 6–O–glycosides.

The authors thank Prof. N. Nogradi, Technical University, Budapest, Hungary, for the sample of baicalein 6–O–glucoside.

5 March 1988

1. Jurd, L., In: *The chemistry of flavonoid compounds*, (ed.) T. A., Geissman, Pergamon Press, Oxford, 1962, p. 108.
2. Harborne, J. B., *Comparative biochemistry of the flavonoids*, Academic Press, London, 1967.
3. Mabry, T. J., Markham, K. R. and Thomas, M. B., *Systematic identification of flavonoids*, Springer-Verlag, New York, 1970.
4. Jay, M., Gonnet, J. F., Wollerweber, E. and Voirin, B., *Phytochemistry*, 1975, **14**, 1605.
5. Markham, K. R., *Techniques of flavonoid identification*, Academic Press, New York, 1982.
6. Voirin, B., *Phytochemistry*, 1983, **22**, 2017.
7. Ulubelen, A., Kerr, K. M. and Mabry, T. J., *Phytochemistry*, 1980, **19**, 1761.
8. Nair, A. G. R. and Kotiyal, J. P., *Indian J. Chem.*, 1979, **B18**, 188.
9. Voirin, B., Favre-Bonvin, J., Nair, A. G. R. and Indira, V., *Phytochemistry*, 1984, **23**, 2973.
10. Nair, A. G. R., Seetharaman, T. R., Voirin, B. and Favre-Bonvin, J., *Phytochemistry*, 1986, **25**, 768.
11. Bacon, J. D. and Mabry, T. J. *Rev. Latinoam Quim.*, 1976, **7**, 83.
12. Nair, A. G. R., Ramesh, P., Nagarajan, S. and Subramanian, S. S., *Indian J. Chem.*, 1973, **11**, 1316.
13. Mezey-Va'ndor, G., Farkas, L. and Nogradi, M., In: *Flavonoids and bioflavonoids*, (eds) L. Farkas *et al.*, Elsevier, Amsterdam, 1977, p. 187.
14. Nair, A. G. R., Mohandoss, S., Voirin B., Bayet, C. and Favre Bonvin, J., *J. Indian Chem. Soc.*, 1988, 65, 150.