Influence of the Substituent at C-7 on the Rate of Flavonol Decomposition in Basic Medium: Measurement by Uv Spectroscopy

ARTICLE *in* JOURNAL OF NATURAL PRODUCTS · JULY 1986

Impact Factor: 3.8 · DOI: 10.1021/np50046a029

3 AUTHORS, INCLUDING:

Óscar Barberá
University of Valencia
44 PUBLICATIONS **321** CITATIONS

Journal of Natural Products
Vol. 49, No. 4, pp. 702-703, Jul-Aug 1986

INFLUENCE OF THE SUBSTITUENT AT C-7 ON THE RATE OF FLAVONOL DECOMPOSITION IN BASIC MEDIUM: MEASUREMENT BY UV SPECTROSCOPY

OSCAR BARBERÁ, JUAN F. SANZ, and J. ALBERTO MARCO*

Departamento de Química Orgánica, Facultad de Químicas, Burjasot, Valencia, Spain

It has been established (1-4) that a decrease with time of the band I in the uv spectra of flavonols, after addition of NaOMe, is a good indication of the presence of 3,4′-diOH or 3,3′,4′-triOH substitution patterns. Thus, if the uv spectrum is rerun 5-10 min after addition of NaOMe, a distinctive decrease in the intensity of the band I at 410-460 nm should be observed, provided the above-mentioned structural features are present. In fact, practically all the examples commented on in the literature also bear a free hydroxyl at C-7. However, we have found that the flavonol, rhamnocitrin (7-*O*-methylkaempferol), is only slightly decomposed even 1 h after the addition of NaOMe (see Table 1 and Figure 1). In contrast, only ca. 25% of kaempferol survives after 1 h of basic treatment. Furthermore, rhamnocitrin decomposes more slowly than rutin (quercetin-3-rutinoside), which lacks the 3-OH group.

The same relative behavior can also be observed in other pairs of flavonols with and without a free OH at C-7. Rhamnetin, with the 3,5,3′,4′-tetraOH pattern, decomposes somewhat faster than isorhamnetin (3,5,7,4′-tetraOH) but clearly slower than quercetin (3,5,7,3′,4′-pentaOH), which decomposes almost instantaneously. Isorhamnetin is practically decomposed after 12 min of basic treatment, whereas rhamnazin (3,5,4′-triOH) undergoes less than 50% decomposition after 1 h in the same conditions.

Thus, the rate of alkaline decomposition of flavonols is influenced to an appreciable extent by the presence of a free OH group at C-7, a marked decrease of this rate being observed if this OH is methylated (or also probably glycosylated). On the other hand, a 3′-OMe

TABLE 1. Variation with Time of the Band I Absorbance of Flavonols after Treatment with NaOMe.

Compound	Time (min)	Band I after NaOMe addition λmax nm (absorbance)
Kaempferol (3,5,7,4′-OH)	0	421 (0.62)
	30	430 (0.37)
	60	442 (0.16)
Rhamnocitrin (3,5,4′-OH, 7-OMe)	0	433 (0.65)
	30	445 (0.61)
	60	448 (0.57)
Quercetin (3,5,7,3′,4′-OH)	0	Band disappears instantaneously
Rhamnetin (3,5,3′,4′-OH, 7-OMe)	0	446 (0.23)
	8	Band disappeared
Isorhamnetin (3,5,7,4′-OH, 3′-OMe)	0	436 (0.68)
	8	440 (0.19)
	12	Band disappeared
Rhamnazin (3,5,4′-OH, 3′,7-OMe)	0	443 (0.70)
	8	451 (0.66)
	60	462 (0.48)
Rutin (5,7,3′,4′-OH, 3-ORut)	0	416 (0.72)
	60	416 (0.58)

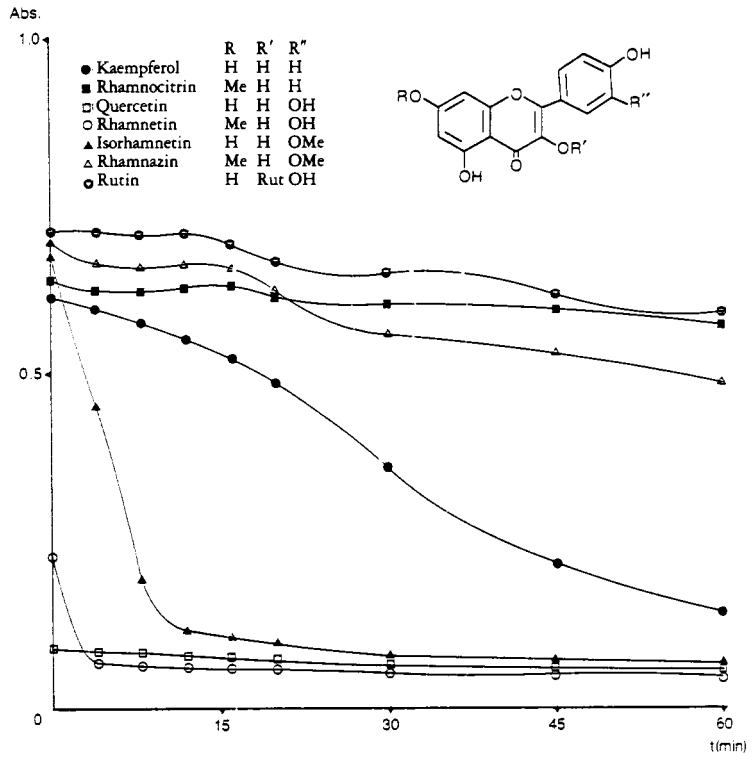

FIGURE 1. Variation with time of the band I absorbance of flavonols after treatment with NaOMe.

group also enhances the rate of decomposition, as evidenced by the pairs rhamnocitrin/rhamnazin and kaempferol/isorhamnetin (Table 1 and Figure 1). These facts may help in structural assignments of flavonol derivatives in some cases.

EXPERIMENTAL

REFERENCE COMPOUNDS.—The flavonols mentioned in Table 1 were isolated as glycosides from a plant source (5-7). Acid hydrolysis and careful purification by column chromatography (Polyamide and Sephadex LH-20) gave the corresponding aglycones. Their purity was checked by ms and nmr. Rutin was of commercial origin (Fluka).

SPECTROSCOPY.—The uv measurements were performed on a Beckman DU-8B spectrophotometer. Methanolic solutions of the flavonols were prepared and the absorbances of the band I were adjusted to 0.500 (before NaOMe addition). The absorbances after the addition of NaOMe are given in Table 1. As can be seen, not only the absorbance but also the position of the absorption maximum changes with time, a shift of 15-20 nm being usually observed.

LITERATURE CITED

1. T.J. Mabry, K.R. Markham, and M.B. Thomas, in: "The Systematic Identification of Flavonoids," Springer Verlag, New York, 1970, pp. 34-61.
2. K.R. Markham and T.J. Mabry, in: "The Flavonoids." Ed. by J.B. Harborne, T.J. Mabry, and H. Mabry, Academic Press, New York, 1975, pp. 45-77.
3. E. Wollenweber, in: "The Flavonoids: Advances in Research." Ed. by J.B. Harborne, and T.J. Mabry, Chapman & Hall, London, 1982, pp. 189-260.
4. K.R. Markham, "Techniques of Flavonoid Identification," Academic Press, London, 1982, pp. 36-49.
5. J.A. Marco, O. Barberá, J.F. Sanz, and J. Sánchez-Parareda, *Phytochemistry*, **24**, 2471 (1985).
6. J.A. Marco, O. Barberá, J.F. Sanz, and J. Sánchez-Parareda, *J. Nat. Prod.*, **49**, 151 (1986).
7. O. Barberá, J.F. Sanz, J. Sánchez-Parareda, and J.A. Marco, *Phytochemistry*, **25** (in press).

Received 24 December 1985