(1.00) of each spectrum given in parentheses: MeOH 254 sh, 290 (1.00), 340 (1.00); +NaOMe: 294 sh, 326 (1.00); $+AlCl_3$: 261 (0.63), 303 (0.83), 324 sh, 372 (1.00); $+AlCl_3+HCl$: 256 (0.70), 302 (0.84), 322 sh, 363 (1.00); +NaOAc: 290 (1.00), 330 (0.94); $+NaOAc+H_3BO_3$: 289 (1.00), 336 (0.73). MS m/z (rel. int.): 374 $[M]^+$ (90) (found: 374.1002; calc. for $C_{19}H_{18}O_7$: 374.1005), 373 $[M-1]^+$ (14), 359 $[M-Me]^+$ (100), 197 $[A-15]^+$ (38) (found: 197.0086; calc. for $C_8H_5O_6$: 197.0085). ^1H NMR (350 MHz, DMSO-d_6): δ7.69 (1H, *dd*, J = 8.4 and 2 Hz, H-6′), 7.58 (1H, *d*, J = 2 Hz, H-2′), 7.18 (1H, *d*, J = 8 Hz, H-5′), 6.98 (1H, *s*, H-3), 3.97 (3H, *s*, OMe), 3.94 (3H, *s*, OMe), 3.89 (3H, *s*, OMe), 3.87 (3H, *s*, OMe). R_f 0.50 on Polyamide DC6 (Merck), C_6H_6–petrol (bp 100–140°) –MeOH–MeCOEt (5:5:1:1) and 0.22 on cellulose in 30% HOAc.

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STRUCTURAL REVISION OF THE FLAVONE MAJORANIN FROM *MAJORANA HORTENSIS*

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Key Word Index—*Majorana hortensis*; Labiatae; majoranin; thymonin; 5,6,4′-trihydroxy-7,8,3′-trimethoxyflavone.

Abstract—Majoranin isolated from *Majorana hortensis* and characterized earlier as 5,7,4′-trihydroxy-6,8,3′-trimethoxyflavone was found to be different from sudachitin of the same structure. Its true structure has been established as 5,6,4′-trihydroxy-7,8,3′-trimethoxyflavone (thymonin) by spectral data and direct comparison.

INTRODUCTION

A trihydroxytrimethoxyflavone, majoranin, was isolated from the leaves of *Majorana hortensis* and assigned the structure 5,7,4′-trihydroxy-6,8,3′-trimethoxyflavone by Subramanian *et al.* [1]. Owing to the earlier occurrence of a flavone, sudachitin, with the same structure [2], Wollenweber [3] cited majoranin as a synonym. However, there exist subtle differences in the physical constants and UV spectra of the two compounds. This necessitated a re-examination of the structure of majoranin. Thus, since the precise differentiation of the positions of hydroxyl and methoxyl groups in flavonoid compounds can be accomplished by UV measurements [4], a re-examination of the structure of majoranin was undertaken and the results

Table 1. UV spectral properties (λ_{max}, nm) of the flavones

	Sudachitin					Majoranin					Thymonin				
MeOH	256 sh	281 (0.80)		344 (1.00)		254 sh		290 (0.86)		343 (1.00)	256 sh		290 (0.83)		342 (1.00)
$AlCl_3$	262 (0.61)	290 (0.73)	303 i	372 (1.00)	412 sh (0.41)	242 sh	262 (0.66)	302 (0.70)	322 i	378 (1.00)	244 sh	262 (0.72)	302 (0.91)	318 i	380 (1.00)
$AlCl_3 + HCl$	260 (0.64)	292 (0.77)	302 i	366 (1.00)	412 sh (0.41)	240 sh	258 (0.77)	300 (0.72)	320 i	370 (1.00)	244 sh	261 (0.87)	302 (0.94)		372 (1.00)
NaOMe	260 sh	284 (0.93)		340 sh	412 (1.00)		266 (0.46)	302 i	324 i	404 (1.00)		270 (0.80)	308 (0.79)	324 sh	407 (1.00)
NaOAc		282 (1.00)	322 (0.52)		404 (0.73)		266 (0.91)	282 sh	330 sh	400 (1.00)		260 (0.93)	284 sh	328 sh	400 (1.00)

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

led to the establishment of its structure as 5,6,4'-trihydroxy-7,8,3'-trimethoxyflavone.

RESULTS AND DISCUSSION

The compound is, in agreement with the data presented by earlier workers [1], a trihydroxytrimethoxyflavone with a free 5-hydroxyl group in the fully oxygenated A-ring and a B-ring with 4'-hydroxyl and 3'-methoxyl groups. The UV spectral data (Table 1; MeOH: λ_{max}, band II; and MeOH + $AlCl_3$ + HCl: band I, one peak, 350–381 nm) clearly indicate that the remaining hydroxyl group is located at C-6 [4] and not at C-7 as previously assigned [1]. The absence of any shift of band II in the NaOAc spectrum also supported this finding, though caution has to be exercised in drawing this conclusion in the case of flavonoids substituted at C-6 and/or C-8 [5]. The absence of band III in the NaOH spectrum further supports the absence of a 7-hydroxyl group (presence of 7-methoxyl) though there are exceptions [6]. The mass spectrum of the compound exhibited the parent ion at m/z 360 (78%) with the base peak at m/z 345, in agreement with the mass spectral pattern suggested for 5-hydroxy-7,8-dimethoxyflavones [7]. Thus, majoranin has been established as 5,6,4'-trihydroxy-7,8,3'-trimethoxyflavone or thymonin, a flavone recently isolated from *Thymus vulgaris* [8]. Comparison of the spectral data (UV, ^{1}H NMR and MS) of majoranin with those of thymonin [8] revealed the two flavones to be identical. Finally, direct comparison including co-chromatography with authentic thymonin and sudachitin confirmed the identity of majoranin with thymonin and its non-identity with sudachitin.

The name 'majoranin' appears to have priority over 'thymonin' as the flavone was first isolated from *Majorana hortensis* [1] in a crystalline form (mp 225–226°; triacetyl derivative, mp 186–187°) even though the credit for correct characterization goes to Van den Broucke *et al.* [8]. It is interesting that majoranin (thymonin) has been obtained in both cases from the Labiatae, which are known for synthesizing unusual flavonoids [9, 10].

EXPERIMENTAL

For isolation and purification of majoranin, see ref. [1]. UV spectral data for sudachitin, majoranin and thymonin are given in Table 1. ^{1}H NMR spectra were recorded at 350 MHz in DMSO-d_6; chemical shifts in δ values with respect to internal TMS. Majoranin: δ3.89, 3.93, 3.96 (3H each, *s*, OMe), 6.90 (1H, *s*, 3-H), 6.96 (1H, *d*, J = 9.0 Hz, 5'-H), 7.57 (2H, unresolved *m*, irradiation at 6.96 produces *s* at 7.50, 2'- and 6'-H). Thymonin [8]: δ3.88, 3.92, 3.94 (3H each, *s*, OMe), 6.92 (2H, *m*, 3-H and 5'-H), 7.52 (2H, *m*, 2'-H and 6'-H).

EIMS were recorded at 70 eV; intensities are indicated as % within parentheses. Majoranin: m/z 360 $[M]^+$ (78) (high resolution: 360.0843; calc. for $C_{18}H_{16}O_8$: 360.0845), 359 (5), 345 (100), 197 (27), 169 (10), 151 (7), 148 (5). Thymonin [8]: m/z 360 $[M]^+$ (68) (high resolution: 360.0815), 359 (5), 345 (100), 197 (20), 169 (6), 151 (5), 148 (2).

PC was done on Whatman No. 1 using 15% HOAc (A) and *t*-BAW (3:1:1) (B) solvents; TLC on cellulose using 30% HOAc (C) and on polyamide using C_6H_6–petrol (bp 100–140°)–MeCOEt–MeOH (5:5:1:1) (D). R_fs in the order majoranin, thymonin and sudachitin were: 10, 10, 6 (A); 91, 91, 93 (B); 24, 24, 29 (C) and 23, 23, 17 (D).

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