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STRUCTURE OF MUCROFLAVONE B

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A new flavonoid, mucroflavone B, is isolated from the terrestrial part of Tanacetopsis mucronata *(Regel. et Schmalh.) S. Kovalevsk. IR, mass, UV, and PMR spectra and a comparison with those of similar compounds provide a basis for proposing the structure 5,6,4′-trihydroxy-7,8,3′-trimethoxyflavone for mucroflavone B.*

We continued our study of the plant *Tanacetopsis mucronata* [1-5] by isolating a new flavonoid with mp 103°C of composition $C_{18}H_{16}O_8$ and naming it mucroflavone B.

The IR spectrum of mucroflavone B contains absorption bands characteristic of carbonyl (1655 cm^{-1}) and an aromatic ring (1550-1600 cm^{-1}). The mass spectrum gives a peak for the molecular ion with *m/z* (%) 360 (M^+, 21.57) and peaks for ions characteristic of flavones of similar structure: 359 (M^+ - 1, 100), 358 (M^+ - 2, 27.0), 346 (12.94), 345 (M^+ - CH_3, 53.0), 342 (M^+ - H_2O, 11.18), 332 (M^+ - CO, 1.0), 330 (M^+ - $2CH_3$, 2.35), 315 (M^+ - $3CH_3$, 2.74), 312 (M^+ - $2CH_3$, - H_2O, 0.8), 212 (A_1^+, $C_9H_8O_6$, 0.5), 168 ($C_8H_8O_4$, 2.0), 151 ($C_8H_7O_3$, 11.2), 149 (22.55), 148 ($C_9H_8O_2$, B_1^+, 2.4), 142 (22.8), etc. (see Experimental).

Mass spectra indicate that ring *A* has two hydroxyls and two methoxy groups, i.e., this ring is tetrasubstituted [6]. Ring *B* has one methoxy and one hydroxyl, i.e., it is disubstituted [7].

The PMR spectrum recorded in C_5D_5N contains signals for H-3 at 6.81 ppm; aromatic protons at 7.24 (d, J = 9 Hz, H-5′), 7.86 (dd, J = 9 and 2.5 Hz, H-6′), and 7.84 ppm (d, J = 2.5 Hz, H-2′); hydroxyls at 12.7 ppm (1H, s, 5-OH), and methoxy groups at 3.75 and 3.90 ppm ($2CH_3$).

Considering the mass spectra, i.e., knowing *a priori* that ring *B* has one hydroxyl and one methoxy group, and the nature of the splitting of the PMR signals for the aromatic protons, it can be hypothesized that mucroflavone B has a 3′,4′-substituted ring *B*. The similarity of the resonances for H-2′ and H-6′ and the upfield chemical shift of H-5′ relative to H-2′ and H-6′ indicate that the hydroxyl is located on C-4′ and the methoxy group on C-3′ [8-11]. The chemical shift of the hydroxyl proton (12.7 ppm) is consistent with a hydroxyl on C-5 [12]. Then, three positions are possible for the second hydroxyl: C-6 (5,6-*o*-dihydroxy), C-7 (5,7-dihydroxy), and C-8 (5,8-*p*-dihydroxy). The last possibility is eliminated owing to the lack of a positive reaction for *p*-dihydroxyls [13].

The UV spectrum (MeOH, λ_{max}) exhibits maxima at 252 (band II) and 342 nm (band I). The UV spectrum recorded in MeOH with added NaOMe shows a bathochromic shift by 64 nm for band I (Table 1). This is characteristic of 4′-OH flavonoids [13-15].

A bathochromic shift by 30-55 nm for band I is usually observed in the UV spectrum taken with added $AlCl_3$. The shift may be less with added $AlCl_3$ + HCl than with $AlCl_3$ if *ortho* dihydroxyls are present, i.e., 20-25 nm [16]. In our instance, the bathochromic shift is 13 nm in the spectrum with added $AlCl_3$ and 21 nm with added $AlCl_3$ + HCl. Such a small bathochromic shift of band I is observed in the UV spectrum with added $AlCl_3$+HCl and in the presence 5-hydroxyl if C-6 has an oxidized substituent [17].

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TABLE 1. UV Spectra of Mucroflavone B with Added Shift Reagents

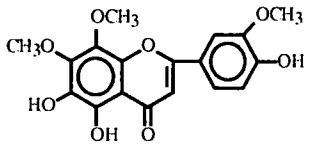
λ_{max}, nm					
MeOH	+NaOAc	+NaOAc +H_3BO_3	+$AlCl_3$	+$AlCl_3$ +HCl	+MeONa
252	254	254	254	254	251
342		349	355	363	335 406

First line is absorption band II; second, I.

The UV spectra of the compound with 5,7-dihydroxyls that were obtained with added $AlCl_3$ and $AlCl_3$ + HCl differ from the spectra of mucroflavone B. This suggests 5,6-dihydroxyls [14, 17]. A bathochromic shift by 5-20 nm is usually observed for band II in the UV spectrum with added NaOAc if a 7-hydroxyl is present. In our instance, the shift is only 2 nm. If a 4′-hydroxyl is present, the bathochromic shift of band I with added NaOAc should be similar or even greater than that in the spectrum with added NaOMe, which is also not observed. The data presented above prove that C-7 has no hydroxyl [11].

The UV spectrum with added NaOAc + H_3BO_3 usually reveals the presence of *ortho* dihydroxyls. If *ortho* dihydroxyls are present in ring *B*, the bathochromic shift is 12-30 nm. Such groups in ring *A* give a much smaller shift [12]. The observed bathochromic shift of only 7 nm in mucroflavone B confirms that ring *A* contains *ortho* dihydroxyls.

Qualitative reaction with added $SrCl_2$ gave a positive test [13]. This also confirms the presence of 5,6-dihydroxyls. Thus, C-7 and C-8 have site for the methoxy groups. Unfortunately, placing a methoxy group on C-8 does not agree with the mass spectral data [6]. If it were present the [M^+ - 15] peak in the mass spectrum should be the base peak (100%) [18]. Perhaps this rule is not observed for tetrasubstituted flavonoids. Thus, we proposed the most probably structure 5,6,4′-trihydroxy-7,8,3′-trimethoxyflavone for mucroflavone B.



EXPERIMENTAL

IR spectra were recorded on a UR-20 (KBr) spectrophotometer; mass spectra, on an MX-1303 instrument; PMR spectra, on a Tesla BS-567A instrument at 100 MHz; UV spectra, on a Specord UV-Vis spectrophotometer. Chemical shifts are given on the δ-scale relative to HMDS at 0 ppm. TLC was performed on Silufol UV-254 plates, which were developed using vanillin (1%) in conc. H_2SO_4. Solvent systems were benzene—alcohol (4:1), ethylacetate—hexane (3:2), and $CHCl_3$—acetone (17:3).

Isolation of Mucroflavone B. Residues (10.047 g) were rechromatographed on KSK silica gel in a 1:30 ratio (resin:silica gel). Eluents were hexane (fraction 1), hexane—alcohol with constantly increasing polarity by adding alcohol (1:1) (fractions 2-20), and $CHCl_3$—alcohol (fractions 21-43). The volume of the eluted fractions was 30 ml. Recrystallization from fractions 13-18 produced a yellow finely crystalline substance with mp 103°C (acetone—hexane). R_f 0.74 (ethylacetate—hexane, 3:2), 0.31 (benzene-alcohol, 4:1), 0.30 ($CHCl_3$—acetone, 17:3).

IR spectrum (ν, cm^{-1}, KBr): 3520 (–OH), 2950 (CH_3, CH_2, CH), 1655 (C=O), 1550-1600 (aromatic group), 1510, 1480, 1440, 1360, 1295, 1250, 1210, 1180, 1140, 1100.

Mass spectrum, *m/z* (%): 360 (M^+, $C_{18}H_{16}O_8$, 21.57), 359 (M^+ - 1, 100), 358 (M^+ - 2, 27.0), 346 (12.94), 345 (M^+ - CH_3, 53.0), 343 (3.92), 342 (M^+ - H_2O, 11.18), 341 (6.47), 332 (M^+ - CO, 1.0), 331 (3.92), 330 (M^+ - $2CH_3$, 2.35), 328 (1), 327 (5.9), 318 (3.14), 317 (17.25), 316 (1.96), 315 (M^+ - $3CH_3$, 2.74), 314 (1.96), 313 (1.96), 312 (M^+ - $2CH_3$ - H_2O, 0.8), 311 (1), 302 (3.92), 300 (2.1), 299 (9.6), 287 (2.94), 284 (0.8), 282 (0.5), 274 (4.31), 270 (0.5), 267 (1.96), 264 (1), 256 (3.14), 252 (0.6), 251 (1.1), 246 (2.94), 242 (1.96), 241 (2.5), 240 (3.3), 239 (3.3), 237 (0.6), 234 (0.5), 229 (0.8), 228 (0.8), 219 (0.8), 217 (1), 216 (1.2), 213 (1), 212 (A_1^+, $C_9H_8O_6$, 0.5), 207 (1), 206 (1.2), 205 (1.5), 202 (1.4), 196 (1), 193 (5.3), 192 (22.8), 191 (1.2),

190 (1), 185 (1.9), 183 (1.9), 180 (5.5), 179 (2.35), 178 (5.8), 177 (23.14), 175 (2.74), 168 ($C_8H_8O_4$, 2.0), 167 (4.51), 166 (5.5), 165 (4.51), 164 (15), 163 (4.51), 161 (4), 154 (2.1), 153 (3.14), 152 (4.9), 151 ($C_8H_7O_3$, 11.2), 150 (3.92), 149 (22.55), 148 ($C_9H_8O_2$, B_1^+, 2.4), 142 (22.8), 137 (6.7), 135 (9.8), 129 (4.9), 125 (6.5), 123 (7.8), 121 (9.4), 120 (9), 119 (9.4), 111$^{\cdot}$(21.6), 110 (7.1), 109 (10.6), 108 (3.92), 105 (12.2), 99 (5.3), 98 (7.45), 97 (16.7), 96 (9.8), 95 (16.1), 91 (9.8), 85 (13.7), 84 (9.8), 83 (17), 82 (11.4), 81 (16), 80 (3.92), 79 (8), 77 (7.45), 73 (7), 71 (17.6), 70 (11.4), 69 (38), 68 (6.7), 67 (10.8), 60 (5), 58 (5.5), 57 (23.5), 56 (11.4), 55 (22.5), 46 (6), 45 (18.6), 44 (30), 42 (21.6), 41 (11.8), 40 (9.6).

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