A NEW FLAVANONE FROM *ACHYROCLINE FLACCIDA*[1]

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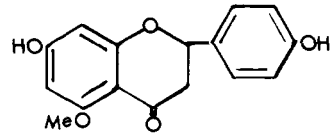
Continuing our search for flavonoid compounds in plants used in folk medicine, we examined the Argentine plant *Achyrocline flaccida* (Weinm) D.C., a shrub that grows in the North of Argentina and South of Brazil (its common name is "marcela hembra", "marcela macho" "falso yatei caá"). Its popular use is described as antispasmodic and febrifugue (1), stimulant and emenagogue (2), and as having tonic, excitant, antihelmintic and antispasmodic properties (3). In a previous paper we reported the isolation and identification of galangin, galangin 3-methyl ether, quercetin 3-methyl ether and two esters of calleryanin (3,4-dihydroxy-benzyl alcohol 4-glucoside) with caffeic acid and protocatechuic acid from *Achyrocline satureioides* (4). In the present paper we describe the isolation and determination of the structure of a flavanone, 7,4' dihydroxy 5-methoxy flavanone (**1**), and the corresponding chalcone from the aerial parts of *A. flaccida*. This is the first report of the isolation of the flavanone from a natural source.

This flavanone, though a 5-methoxy flavanone, has shown a behaviour similar to a 5-deoxy flavanone due to the facility with which its C-ring opens to give the corresponding chalcone in the presence of diluted alkali (5).



The chalcone had been obtained previously from various Compositae (6,7,8,9,10). It is well known that under certain conditions, an interconversion occurs between the chalcones and their corresponding flavanones.

To confirm that both compounds are really present as such in the plant itself, a methanolic extract was made at a low temperature over a 24-hour period with the aid of a magnetic stirrer and examined by tlc for the presence of the flavanone and chalcone. Both compounds were detected. In addition, a methanolic solution of the chalcone left for 10 days at room temperature did not show even trace quantities of its corresponding flavanone by tlc.

EXPERIMENTAL

MATERIAL.—*Achyrocline flaccida* (Wein **1**) D.C. (Compositae) was collected in Colonia Benitez, Chaco Province, and identified by Dr. A. Schultz (INTA). Voucher specimens are deposited in the University Herbarium (Museo de Botánica, Facultad de Farmacia y Bioquímica, Universidad de Buenos Aires).

EXTRACTION.—Air-dried ground aerial parts of *A. flaccida* (1.6 kg) were extracted successively with hexane, benzene, methylene chloride, acetone and methanol at room temperature. The extracts were taken to dryness. The acetone extract was dissolved in hot water and partitioned with methylene chloride and ethyl ether. The methylene chloride extract was evaporated to dryness and passed through a column packed with polyamid powder. The water eluates gave a precipitate identified as 7,4' dihydroxy 5 methoxy flavanone by uv, ms and ^{1}H nmr. The methanol-water eluate (7–3) from the polyamide column was passed through a Polyclar column for separation; the chloroform-methanol eluates (9–11) yielded a yellow compound identified as 4,2',4' trihydroxy 6' methoxy chalcone.

[1]Part 13 in the series Flavonoids from Argentine Medicinal Plants, for part 12 see reference 4.

7,4' DIHYDROXY 5 METHOXY FLAVANONE.—Pale yellow amorphous powder, mp 247.7–248.5°; uv color (366) deep purple; uv/NH_3, no change; pc in T.B.A. and 15% HOAc, Rfs: 0.82 and 0.55 respectively; uv (MeOH) (11) max 284,319 sh; λ max (addition NaOMe) 246, 321 nm; λ max (addition $AlCl_3$) 283, 318, 361 nm; λ max (addition $AlCl_3$/ClH) 281, 318, 361 nm; λ max (addition NaOAc) 250 sh, 280 sh, 320; λ max (addition NaOAc/BO_3H_3) 280, 320; ^{1}H-nmr (DMSO-d6) (δ); 2.90 (2 H, m, H-3), 3.75 (3 H, s, O-Me), 5.32 (1 H, c, H-2), 6.02 (2 H, d, H-6 and H-8); 6.80 (2 H, d, H-5' and H-3'); 7.30 (2 H, d, H-6' and H-2'); 9.50 (1 H, s, OH) and 10.48 (1 H, s, OH); ms: *m/z* (%) 286 (M^+, 56) 272 (6), 193 (20), 179 (13), 168 (100), 137 (33), 124 (27), 120 (45), 107 (10), 94 (13), 91 (25), 89 (9).

4,2',4' TRIHYDROXY 6' METHOXY CHALCONE.—Fine pale yellow powder, mp 240–241° with a change of color at 164°; uv (366 nm) greenish purple, uv/NH_3 orange; uv (MeOH) λ max: 250 sh, 304 sh, 364; λ max (addition NaOMe) 266 sh, 320 sh, 350 sh, 426; λ max (addition $AlCl_3$) 252 sh, 327 sh, 342 sh, 407; λ max (addition $AlCl_3$/HCl) 250 sh, 310 sh, 325 sh, 342 sh, 400; λ max (addition NaOAc) 270 sh, 310 sh, 332 sh, 391; λ max (addition NaOAc/BO_3H_3) 272 sh, 336 sh, 350 sh, 425.

TRANSFORMATION OF 7,4' DIHYDROXY 5 METHOXY FLAVANONE IN 4,2',4' TRIHYDROXY 6' METHOXY CHALCONE.—7,4' Dihydroxy 5 methoxy flavanone (10 mg) was dissolved in warm 10% NaOH and then acidified with 2 N HCl and extracted with ethyl ether (6). 4,2',4' Trihydroxy 6' methoxy chalcone was obtained from the organic layer. The identity of this compound was confirmed by tlc in three different systems and by uv spectra. These data were exactly the same as observed for 4,2',4', trihydroxy 6' methoxy chalcone previously isolated.

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