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Phytochemistry, Vol 28, No 10, pp 2871–2872, 1989
Printed in Great Britain

0031–9422/89 $3.00+0.00

FLAVONOIDS FROM *SALVIA TEXANA*

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(*Received* 3 *January* 1989)

Key Word Index—*Salvia texana*, Labiatae, flavones, flavanone, spectroscopy; circular dichroism

Abstract—From a methanolic root extract of *Salvia texana*, 5-hydroxy-7,4′-dimethoxyflavone and (+)-2(*S*)-5-hydroxy-7-methoxyflavanone were isolated and characterized by spectroscopy. The absolute configuration of the latter compound was established by CD readings

In the course of our study of secondary metabolites with biological activity from the medicinal flora of Latin America, various new aromatic diterpenes have been isolated from the roots of *Salvia texana* [1, 2] and 5-hydroxy-7,4′-dimethoxyflavone (**1**) and (+)2(*S*)-5-hydroxy-7-methoxyflavanone (**2**) from the same source have now been identified.

Compound **1** was isolated as a yellow crystalline solid with the molecular formula $C_{17}H_{14}O_5$ (HRMS). In its IR spectrum bands for phenol (3650 cm^{-1}), a conjugated carbonyl (1650 cm^{-1}) and ether (1250 and 1030 cm^{-1}) were observed. The UV spectrum and the ^{1}H NMR in pyridine-d_6 confirmed that **1** is a flavone with a free phenol group and two methoxyl groups. A one-proton singlet at δ13.60 exchangeable with D_2O and assigned to the phenolic proton bridged to the carbonyl suggested that the free phenol group was at C-5. A fragment at *m/z* 122 (hydroxyanisol ion) in the MS spectrum [3] together with two broad one-proton singlets at δ6.62 and 6.70 in ^{1}H NMR for *meta* H-6 and H-8, placed one of the methoxyl groups at C-7. Fragments at *m/z* 132 and 135 in the MS and two doublets of two protons each at δ7.12 and 7.96, respectively, sited the other methoxyl group on C-4′. These data and the ^{13}C NMR (Table 1) confirmed the structure of **1** as 5-hydroxy-7,4′-dimethoxyflavone. The physical and ^{1}H NMR data coincided with those of di-*O*-methylapigenin isolated from *Sideritis gomerae* Bolle [4].

Table 1. ^{13}C NMR data of **1** ($CDCl_3$) (50 MHz)

C		C	
2	162.4	10	105.2
3	104.5	1′	123.8
4	182.5	2′	128.1
5	157.4	3′	114.6
6	98.1	4′	162.5
7	165.6	5′	114.6
8	92.7	6′	128.1
9	162.0	7-OMe	55.5*
		4′-OMe	55.7*

*Interchangeable values.

Compound **2** proved to be a new flavanone the structure and absolute configuration of which were established from the following: the MS spectrum showed the molecular ion at *m/z* 270, $C_{16}H_{14}O_4$ (HRMS); the IR spectrum had bands for phenol (3650 cm^{-1}), conjugated carbonyl (1630 cm^{-1}) and ether (1040 cm^{-1}). In the ^{1}H NMR spectrum, a single methyl group was seen as a singlet at δ3.81. A one-proton singlet at δ11.5, interchangeable with D_2O, sited the free phenol group at C-5 with a bridge to the carbonyl. A broad two-proton singlet at δ6.07 attributable to *meta* H-6 and H-8, together with a fragment at *m/z* 193 in MS (generated by the loss of the B-ring), placed the methoxyl group on C-7. A five-proton multiplet at δ7.44 confirmed the non-substitution of the B-ring. The most characterized feature of the ^{1}H NMR was the absence of the typical flavone H-3 proton and the presence of an ABX system The X part appeared as a double doublet for a proton centred at δ5 42 attributable to H-2 and the AB portion, as two double doublets of one proton each centred at δ3 09 and 2.81 attributable to H-3 (*trans*) and H-3 (*cis*), respectively All these data were in agreement with the structure of a 5-hydroxy-7-methoxyflavanone for this product. The melting point and ^{1}H NMR of **2** coincided with those given in the literature for pinostrobin[5] but measurement of the optical activity gave $[\alpha]_D = +5'$, which is the same value as that reported for pinostrobin [6] except that is was (+) rather than (−). The CD spectrum of **2** exhibited the positive Cotton effect of the $n \rightarrow \pi$ transition of 329 nm and the negative Cotton effect of the $\pi \rightarrow \pi^*$ transition at 289 nm This agreed with a 2*S* configuration [7] with the 2-aryl group substituted equatorially to the heterocyclic ring With few exceptions, natural flavanones are laevorotatory [8] The small amount of pinostrobin available after HPLC purification did not permit a more precise measurment of the optical activity

EXPERIMENTAL

^{1}H and ^{13}C NMR 200 MHz, pyridine or $CDCl_3$ as solvent and TMS as int standard IR $CHCl_3$ Dry CC was carried out on silica gel 0 05–0 2 mm HPLC was carried out on a μPorasil 3 9 mm × 15 cm using *n*-hexane–EtOAc (4 1) as solvent The concentration of the CD sample (MeOH) was determined from the UV spectrum using the ε value of 19 000^7.

Voucher plant specimens were lodged with the Herbarium of the Department of Botany, Instituto Tecnológico y de Estudios Superiores de Monterrey, Mexico

The finely-cut roots of *Salvia texana* Torr (3 kg) were extracted with cold MeOH (5 l) Filtration and evapn of the solvent *in vacuo* gave a reddish-brown extract (48 g) which was chromatographed on Sephadex using a mixture of *n*-hexane–$CHCl_3$–MeOH (1 1 2) as solvent 500 ml fractions were collected Only fractions 40–58 were studied After repeated chromatography on silica gel using mixtures of *n*-hexane–EtOAc as solvent, the following compounds were isolated

5-Hydroxy-7,4'-dimethoxyflavone (**1**). (7 mg), mp 164°, (*n*-hexane–EtOAc), $[M]^+$ at *m/z* 298 0837 (Calc for $C_{17}H_{14}O_5$, 298 0833), UV λ_{max} (EtOH nm 325, 292, 260, IR ν_{max} cm^{-1} 3650, 2980, 2920, 2900, 2800, 1650, 1600, 1570, 1500, 1490, 1450, 1430, 1410, 1400, 1360, 1340, 1300, 1290, 1250, 1230, 1180, 1170, 1145, 1100, 1090, 1030, 1020, 940, 900 and 830, ^{1}H NMR (pyridine-d_6) δ 3 74, 3 76 (each 3H, *s*, 2 × OMe), 6 62 (1H, *br s*, H-6), 6 70 (1H, *br s*, H-8), 6 96 (1H, s, H-3), 7 11, 7 96 (each 2H, *d*, $J = 8$ 7 Hz, 3', 5' and 2', 6'), 13 6 (1H, *br s*, OH), MS, *m/z* (rel int %) 298 $[M]^+$ (100), 283 (1), 269 (28), 256 (3), 255 (14), 240 (2), 227 (2), 212 (93), 166 (11), 135 (10), 132 (16), 122 (1), 95 (18), 69 (22)

(+)-2-(S)-*5-Hydroxy-7-methoxyflavanone* (**2**) 2 5 mg, $[\alpha]_D^{25} = +5°$, (*c* 0 05), $[M]^+$ at *m/z* 270 0894 (Calc for $C_{16}H_{14}O_4$, 270 0896), UV λ_{max} (EtOH) nm 325 (sh), 287, 226 (sh), CD (MeOH) λ_{ext} nm 329 ($\theta = +1690$), 289 ($\theta = -4820$), IR ν_{max} cm^{-1} 3650, 2990, 2980, 2880, 1630, 1560, 1485, 1450, 1430, 1360, 1285, 1175, 1140, 1075, 1040 and 815, ^{1}H NMR ($CDCl_3$) δ 2 81 (1H, *dd*, $J = 17$ 1, 3 4 Hz, H-3 *cis*), 3 09 (1H, *dd*, $J = 17$ 1, 12 8 Hz, H-3 *trans*), 3 81 (3H, *s*, –OMe), 5 92 (1H, *dd*, $J = 12$ 8, 3 4 Hz, H-2), 6.07 (2H, *br s*, H-6 and H-8), 7 46 (5H, *m*, H-2', 3', 4', 5', 6'), 12 02 (1H, *br s*, OH), MS, *m/z* (rel int %) 270 $[M]^+$ (81), 269 (47), 252 (6), 242 (4), 227 (5), 193 (100), 181 (2), 166 (70), 138 (69), 118 (1), 115 (7), 95 (98)

Acknowledgements—This investigation was subsidized by CAICYT Project No 0694-84 and PB84–1184 Z E A is indebted to the AIETI for a research grant

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