Phytochemistry, Vol. 25, No. 3, pp. 767–768, 1986.
Printed in Great Britain.

0031–9422/86 $3.00 + 0.00

FALCIFORMIN, A FLAVANONE FROM PODS OF *TEPHROSIA FALCIFORMIS*

HAMID A. KHAN, INDRANI CHANDRASEKHARAN and A. GHANIM

Central Arid Zone Research Institute, Jodhpur, India

(*Revised received* 20 *August* 1985)

Key Word Index—*Tephrosia falciformis*; Leguminosae; pods; a new flavanone; falciformin; 7-hydroxy-8-(γ,γ-dimethylallyl)flavanone.

Abstract—Falciformin, a new flavanone with a 3-hydroxy-3-methyl-but-1-enyl side chain has been isolated from the pods of *Tephrosia falciformis* along with a known flavanone, 7-hydroxy-8-(γ,γ-dimethylallyl)flavanone.

INTRODUCTION

As part of our work on underexploited plants of west Rajasthan, we have examined the pods of *Tephrosia falciformis*. Recently we reported the isolation of triacontanol, pongamol, sitosterol, lanceolatin-B and lanceolatin-A [1]. We now wish to report the isolation and characterization of a new flavanone, falciformin along with a known flavanone, 7-hydroxy-8-(γ,γ-dimethylallyl)flavanone.

RESULTS AND DISCUSSION

Falciformin (1) was isolated as needles, $[M]^+$ at *m/z* 338, $C_{21}H_{22}O_4$, mp 108° (uncorr.). Both the UV and IR spectra were typical of a flavanone, the latter showing the presence of a hydroxyl group. The UV spectrum remained unchanged on addition of alkali indicating the absence of a phenolic hydroxyl group. High resolution ^{1}H NMR spectrum was characteristic of a flavanone nucleus [2, 3]. The C-2 proton, the X part, appeared as a double doublet at δ5.51 (1H, J_{AX} = 13, J_{BX} = 3.5 Hz) while the C-3 protons, the AB part, appeared at 3.02 and 2.9 (J_{AB} = 17, J_{AX} = 13, J_{BX} = 3.5 Hz). The high value of *J* (13 Hz) for the coupling constant J_{AX} was indicative of an axial–axial coupling. Therefore, the C-2 hydrogen was axial and ring B was equatorial [4].

In the aromatic region, a multiplet at δ7.47 (5H) and the two *ortho* coupled doublets at 7.92 and 6.7 (J = 9 Hz) showed lack of substitution in ring B and at the 5 and 6 positions respectively. The presence of a methoxyl group was also evident by a singlet at δ3.96 (3H). The remaining nine protons form part of the unusual 3-hydroxy-3-methyl-but-1-enyl side chain. The two singlets at δ1.38 (6H) and 1.52 (1H, replaceable with D_2O) were assigned to gem-dimethyl and hydroxyl groups respectively. The most unusual feature of the ^{1}H NMR spectrum was the appearance of olefinic protons as a singlet at δ6.86 (2H) which disappeared on addition of bromine. The appearance of the singlet even at 400 MHz showed that it is a case of accidental equivalence [5]. The IR absorption band at 970 cm^{-1} is, however, evidence that the configuration about the C=C double bond is *trans*. The relative positions of the methoxyl group and the side chain at C-7 and C-8 respectively were determined by benzene induced solvent shift which resulted in the upfield shift of the methoxy proton signal (0.23 ppm) [6]. Hence, the new flavanone, falciformin, is 7-methoxy-8-(3-hydroxy-3-methyl-but-1-enyl)flavanone.

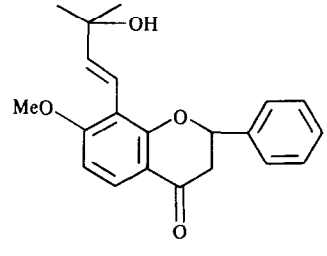
The second flavanone, mp 139–140° (lit. 144–145°) was identified as 7-hydroxy-8-(γ,γ-dimethylallyl)flavanone by comparing ^{1}H NMR and mass spectral data [7].

EXPERIMENTAL

Extraction and isolation. Air dried pods of *Tephrosia falciformis* were extracted with petrol and Me_2CO. The petrol extract was concd and chromatographed repeatedly on a column of silica gel. Falciformin was obtained as needles from C_6H_6. The Me_2CO extract afforded 7-hydroxy-8-(γ,γ-dimethylallyl)flavanone.

Falciformin (1). Recrystallized from EtOAc–petrol; mp 108°; UV λ_{max}^{MeOH} nm (log ε): 260 (4.11), 290 (3.81); IR ν_{max}^{Nujol} cm^{-1}: 3460, 1650, 970; ^{1}H NMR (100 MHz and 400 MHz, $CDCl_3$, TMS as int. standard): see text; MS *m/z* (rel. int.): 338 $[M]^+$ (4.12), 321 (21.9), 320 (51.6), 305 (9.57), 279 (5.6), 267 (8.58), 219 (16.4), 216 (27.4), 215 (6.1), 202 (14.2), 201 (100), 188 (25), 177 (22), 175 (30), 173 (27), 157 (15), 145 (25), 131 (22), 117 (15), 115 (20), 104 (12.5), 103 (17), 91 (17), 77 (20).

Acknowledgements—We thank Dr. F. Bohlmann for the ^{1}H NMR spectrum (400 MHz), Dr. P. P. Joshi for helpful discussions and Mr. V. Alphonse Amalraj for identification and collection of the plant material. We also thank Dr. K. A. Shankarnarayan, Director, Central Arid Zone Research Institute, Jodhpur for encouragement.



1

REFERENCES

1. Khan, H. A., Chandrasekharan, I. and Ghanim, A. (1984) *Annals of Arid Zone* **23**, 39.
2. Massicot, J. and Marthe, J. P. (1962) *Bull. Soc. Chim. Fr.* **10**, 1962.
3. Hansel, R., Ohlendrof, D. and Pelter, A. (1970) *Z. Naturforsch. Teil. B* **25**, 989.
4. Clark-Lewis, J. W. (1968) *Aust. J. Chem.* **21**, 2059.
5. Brown, R. F. C., Rae, I. D. and Sternhell, S. (1965) *Aust. J. Chem.* **18**, 61.
6. Wilson, R. G., Bowie, J. H. and Williams, O. H. (1968) *Tetrahedron* **24**, 1407.
7. Gupta, R. K. and Krishnamurti, M. (1976) *Phytochemistry* **15**, 832.

Phytochemistry, Vol. 25, No. 3, pp. 768–769, 1986.
Printed in Great Britain.

0031–9422/86 $3.00 + 0.00
Pergamon Press Ltd.

TRUE STRUCTURE OF TRIUMBOIDIN, A FLAVONE GLYCOSIDE FROM *TRIUMFETTA RHOMBOIDEA*

A. G. RAMACHANDRAN NAIR, T. R. SEETHARAMAN, BERNARD VOIRIN* and JEAN FAVRE-BONVIN*

Department of Chemistry, Jawaharlal Institute, Pondicherry-605006, India; *Laboratoire de Phytochimie, U.E.R. des Sciences de la Nature, 69623 Villeurbanne, France

(*Received* 20 *June* 1985)

Key Word Index—*Triumfetta rhomboidea*; Tiliaceae; triumboidin; structural revision; 5,4′-dihydroxy-6-*O*-β-D-xylopyranosyloxy-7-*O*-α-L-rhamnopyranosyloxyflavone; FAB-MS; ^{13}C NMR.

Abstract—The structure of triumboidin isolated from *Triumfetta rhomboidea* as scutellarein 7-*O*-L-arabinorhamnoside is inconsistent with the spectral data. Its true structure has been established as scutellarein 6-xyloside 7-rhamnoside. ^{1}H and ^{13}C NMR and FAB-MS data for scutellarein 7-*O*-α-L-rhamnoside have also been provided.

INTRODUCTION

The isolation of a new flavone glycoside, triumboidin from the leaves of *Triumfetta rhomboidea* was reported by Srinivasan and Subramanian [1] who characterized it as the 7-*O*-L-arabinosylrhamnoside of scutellarein and wrongly named it scutellarein-7-*O*-L-rhamnosylarabinoside based on products of hydrolysis and UV spectral data. However the λ_{max}^{MeOH} reported for triumboidin (238 sh, 277, 335 nm) was different from that of scutellarein (286, 335) [2], 7-*O*-methylscutellarein (285, 335) [2] and 7-*O*-rhamnosylscutellarein (238 sh, 286, 335) [1] and close to 6-*O*-methylscutellarein (275, 336) [2] and 6,7-di-*O*-methylscutellarein (277, 331) [2], indicating the involvement of the 6-hydroxyl in glycosylation. Also no evidence was provided for the presence of the disaccharide moiety. We therefore decided to reinvestigate its structure and the results are reported here.

RESULTS AND DISCUSSION

Triumboidin was reisolated from fresh leaves of *Triumfetta rhomboidea* and obtained as light yellow needles, mp 220–222°. It was indistinguishable from the sample [1] kindly provided by Srinivasan and Subramanian except in mp (198°). On treatment with 2 N HCl (MeOH medium, 100°, 2 hr) it yielded scutellarein, L-rhamnose and D-xylose in approximately 1:1:1 proportion. The identity of the sugars was established by co-chromatography with authentic markers using water saturated phenol and other developing solvents. H_2O_2 oxidation [3] of triumboidin gave only L-rhamnose and D-xylose, indicating it to be a diglycoside and not a bioside. On partial hydrolysis (2% H_2SO_4, 28°, 24 hr), triumboidin yielded a scutellarein monoside and D-xylose along with small quantities of scutellarein and L-rhamnose. The monoside was identical with the second glycoside [1] present in the plant and was fully characterized as 7-*O*-α-L-rhamnopyranosylscutellarein by enzyme hydrolysis, UV, ^{1}H and ^{13}C NMR and FAB-MS (see Experimental).

The methanol spectrum of triumboidin (275, 334 nm) in comparison with that of the aglycone, scutellarein (285, 335 nm) indicated [2] glycosylation at the 6-hydroxyl. The presence of 6-*O*-glycosylation was also supported by a discernible shoulder around 390 nm in the $AlCl_3$ as well as $AlCl_3$–HCl spectrum (this shoulder was absent in the monoside as well as 6-hydroxy- and 6-methoxyflavones). The absence of any shift of band II by NaOAc was indicative of the absence of free 7-hydroxyl, although this is a not very reliable indicator in 6-*O*-substituted flavones