300–301°.

Acid hydrolysis of aervanone. Compound **1** remained unaffected on heating with 1 N HCl at 100° for 2 hr.

Ferric chloride oxidative hydrolysis. Compound **1** (3 g) and ferric chloride (2.5 g) in water (25 ml) were refluxed for 6–8 hr [11]. The mixture was cooled, adjusted the pH to 8.0 with an aq. solution of NaOH and a ppt. was removed by centrifugation. The ppt. (ii) thus obtained was recrystallized from EtOH, mp 105–106° (1.4 g) and was identified as 7,8,4′-trihydroxyflavanone [17, 18] (mp lit. [18] 104–105°), M^+ 272: (Found: C, 66.0; H, 4.5. $C_{15}H_{12}O_5$ required: C, 66.18; H, 4.41%). NMR(CCl_4^1): δ 7.3 (H-2′), 7.2 (H-6′), 6.8 (H-3′), 6.7 (H-5′), 6.3 (H-6), 7.6 (H-5). It formed a triacetate with Py–Ac_2O, mp 166–167° (lit. [18] 165–166°). The supernatant was adjusted to pH 7.0 with aq. HCl, and was extracted with pentyl alcohol several times. The pale yellow aq. solution was passed successively through Amberlite resin IR-120 (H) and IR-4B (OH) until all ferrous and chloride ions were removed. The neutral solution was concd and subjected to PC in phenol (90%)–H_2O (89:11) when the presence of D-galactose (R_f 0.44) and D-lyxose (R_f 0.05) was confirmed by comparing the two with authentic specimens.

Acknowledgements—The authors are grateful to Prof. M. Mikolajczyk, Polish Academy of Sciences, Poland, for the mass spectra and to CSIR (India) for the award of a Junior Research Fellowship to R. B.

REFERENCES

1. Gupta, R. K., Gaur, Y. D., Malhotra, S. P. and Dutta, B. K. (1966) *J. Agric. Trop. Bot. Appl.* **XIII,** 250.
2. Venkatesh, M. V. and Singh, B. (1973) *Indian J. Entomol.* **35,** 32.
3. Simpson, T. H. and Beton, J. L. (1954) *J. Chem. Soc.* 4065.
4. Jurd, L. (1962) *The Chemistry of Flavonoids* (Geismann, T. A., ed.). Pergamon Press, London.
5. Jurd, L. and Horowitz, R. M. (1957) *J. Org. Chem.* **22,** 1618.
6. Jurd, L. and Geismann, T. A. (1956) *J. Org. Chem.* **21,** 1395.
7. Swain, T. (1954) *Chem. Ind.* 1480.
8. Murti, V. V. S., Rajgopalan, S. and Row, L. R. (1951) *Proc. Ind. Acad. Sci. Sect. A* **34,** 319.
9. Eade, R. A., Salasoo, I. and Simes, J. J. H. (1966) *Aust. J. Chem.* **19,** 1717.
10. Evans, W. H., McGookin, A., Jurd, L., Robertson, A. and Williamson, W. R. N. (1957) *J. Chem. Soc.* 3510.
11. Koeppen, B. H. and Roux, D. G. (1965) *Biochem. J.* **97,** 444.
12. Prox, A. (1968) *Tetrahedron* **24,** 3697.
13. Pelter, A., Stainton, P. and Barber, M. (1965) *J. Heterocycl. Chem.* **2,** 262.
14. Mabry, T. J. and Markham, K. R. (1975) *The Flavonoids* (Harborne, J. B., Mabry, T. J. and Mabry, H., eds.) Chapman & Hall, London.
15. Gentili, B. and Horowitz, R. M. (1968) *J. Org. Chem.* **33,** 1571.
16. Hay, J. E. and Haynes, L. J. (1956) *J. Chem. Soc.* 3141.
17. Clarke-Lewis, J. W. and Porter, L. J. (1972) *Aust. J. Chem.* **25,** 1943.
18. Drewes, J. E. and Roux, D. G. (1966) *Biochem. J.* **98,** 493.
19. Dave, K. G., Telang, S. A. and Venkataraman, K. (1960) *J. Sci. Ind. Res.* **19b,** 470.

Phytochemistry, 1980, Vol. 19, pp. 1267–1268. © Pergamon Press Ltd. Printed in England. 0031-9422/80/0601-1267 $02.00/0

A NEW PRENYLATED FLAVANONE FROM *TEPHROSIA VILLOSA*

INDRANI JAYARAMAN, A. GHANIM and HAMID A. KHAN

Central Arid Zone Research Institute, Jodhpur, India

(*Received* 23 *July* 1979)

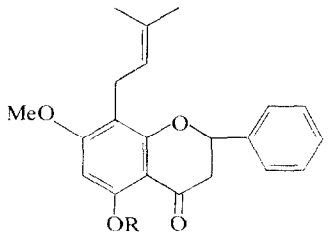
Key Word Index—*Tephrosia villosa*; Leguminosae; a new flavanone; 7-methylglabranin.

INTRODUCTION

Past work on pods of *Tephrosia villosa* has yielded four rotenoids—villosin, villosone, villol and villinol along with 6a, 12a-dehydrosumatrol (villosal) and 12a-hydroxysumatrol (villosinol) [1]. We now report the structure elucidation of a new flavanone from the roots of *Tephrosia villosa*.

RESULTS AND DISCUSSION

Elemental analysis and M^+ at *m/e* 338 led to the molecular formula $C_{21}H_{22}O_4$ of compound **1**. It gave a positive ferric chloride test, a colourless monoacetate **2** with Ac_2O–Py at room temperature and a monomethyl ether **3** with Me_2SO_4–K_2CO_3–Me_2CO indicating the presence of a phenolic hydroxyl group.



1 R = H
2 R = COMe
3 R = Me

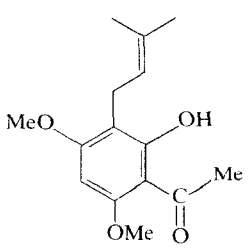
The ^{1}H NMR spectrum of **1** showed the presence of one methyoxyl and one hydroxyl group by singlets at δ 3.82 (3H) and 12.13 (1H, chelated, D_2O exchangeable), respectively, and also the presence of a C-γ, γ-dimethylallyl side chain by a triplet at 5.15 (1H), a doublet at 3.22 and a sharp singlet at 1.62 (6H) [2]. The aromatic region was defined by a sharp singlet at 7.4 (5H) indicating the unsubstituted nature of the B-ring and a singlet at 6.08 (1H) which could be assigned to either the C-6 or the C-8 proton.

The salient feature of the high resolution NMR spectrum of **1** was the ABX system, diagnostic for the C-2 and C-3 protons of a flavanone [3, 4]. The C-2 proton, the X part, appeared as a double doublet at δ 5.42 (1H, $J_{AX} = 12.7$, $J_{BX} = 3.3$ Hz), while the C-3 protons, the AB part, appeared at 3.05 and 2.86 ($J_{AB} = 17.5$, $J_{AX} = 12.7$, $J_{BX} = 3.3$ Hz).

The high value of J (12.7 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 [5].

The position of the hydroxyl group as shown in **1** followed from the low-field phenolic proton signal in the ^{1}H NMR spectrum which was also supported by a bathochromic shift of 20 nm in the UV spectrum on addition of a few drops of $AlCl_3$. Benzene-induced solvent shifts in the ^{1}H NMR spectrum of the methyl ether **3** resulted in the upfield shift of the methoxy proton signals (0.12 and 0.30 ppm) indicating that both methoxyl groups were *ortho* to an aromatic hydrogen [6]. The side chain must therefore be at C-8.

The nature of substitution in the A-ring was further confirmed by alkaline degradation of **3** in a nitrogen atmosphere which gave product **4**. Its mp (112–113°) and ^{1}H NMR data were in agreement with 2,4-dimethyl-5C-prenyl pholoracetophenone [7]. Glabranin (8-(γ,γ-dimethylallyl)-5,7-dihydroxyflavanone) has previously been isolated from *Glycyrrhiza glabra* [8]. Hence, the new flavanone is 7-methylglabranin.



4

EXPERIMENTAL

Mps are uncorr. UV spectra were recorded in MeOH and IR spectra in $CHCl_3$. ^{1}H NMR spectra were obtained in $CDCl_3$ using TMS as internal standard at 60 and 270 MHz.

Extraction and isolation. Dried roots of *Tephrosia villosa* were extracted with hot petrol. The combined petrol extracts were evapd to dryness and the extract was chromatographed over Si gel. It was eluted with petrol (60–80°). Fractions (100 ml each) were collected and fractions 10–15 were combined to yield compound **1**.

Compound **1**. Obtained as flakes from petrol: TLC R_f 0.65 (C_6H_6–$CHCl_3$, 1:2), mp 123–125°; UV λ_{max}^{MeOH} nm (log ε): 240 sh (4.11), 292 (4.19), 343 (3.41); IR $\gamma_{max}^{CHCl_3}$ cm^{-1}: 1620 (C=O); ^{1}H NMR: δ 3.82 (3H, *s*, OMe-7), 12.13 (1H, *s*, OH-5), 5.42 (1H, *q*, J = 12.7, 3.3 Hz, C-2), 3.05 (2H *mc*, C-3), 5.15 (1H, *t*, J = 7.0 Hz) 3.22 (2H, *d*, J = 7.0 Hz), 1.62 (6H, *s*, γ,γ-dimethylallyl), 7.4 (5H, *s*, ArH) and 6.08 (1H, *s*, C-6).

Acetate **2**. $C_{23}H_{24}O_5$, mp 108–110°; UV λ_{max}^{MeOH} nm (log ε): 240 sh (4.24), 285 (4.23), 338 sh (3.36); ^{1}H NMR: δ 3.88 (3H, *s*, OMe-7), 2.40 (3H, *s*, COMe-5), 5.45 (1H, *q*, J = 12.7, 3.3 Hz, C-2), 2.9 (2H, *mc*, C-3), 5.18 (1H, *q*, J = 7.0 Hz), 3.35 (2H, *d*, J = 7.0 Hz), 1.65 (6H, *d*, J = 12.5 Hz, γ,γ-dimethylallyl), 7.4 (5H, *s*, ArH), 6.29 (1H, *s*, C-6).

Methyl ether **3**. $C_{22}H_{24}O_4$, mp 92–94°, UV λ_{max}^{MeOH} nm (log ε): 240 sh (4.21), 285 (4.20), 338 sh (3.40); ^{1}H NMR: δ 3.9 (3H, *s*, OMe-5), 3.85 (3H, *s*, OMe-7), 5.52 (1H, *q*, J = 12.7 3.3 Hz, C-2), 3.0 (2H, *mc*, C-3), 5.2 (1H, *t*, J = 7.0 Hz), 3.35 (2H, *d*, J = 7.0 Hz), 1.65 (6H, *s*, γ,γ-dimethylallyl), 2.27 (5H, *s*, Ar(H) and 6.1 (1H, *s*, C-6).

Alkaline degradation. 140 mg of **3** was refluxed with 50% KOH in MeOH for 6 hr in N_2 atmosphere. The product was chromatographed on Si gel and eluted with C_6H_6–petrol (1:3) to give cryst. acetophenone **4**.

Acetophenone (**4**). $C_{15}H_{20}O_4$, TLC R_f = 0.5 (C_6H_6), mp 112–113°; [Found: C, 68.6; H, 7.8. $C_{15}H_{20}O_4$ Calc.: C, 68.2; H, 7.6%]. UV λ_{max}^{MeOH} nm: 282; ^{1}H NMR: δ 3.79, (6H, *s*, OMe-2, OMe-4), 5.1 (1H, *t*, J = 12.7, 3.3 Hz), 3.18 (2H, *d*, J = 7.0 Hz), 1.65 (6H, *d*, J = 10 Hz, γ,γ-dimethylallyl), 2.82 (3H, *s*, COMe-1), 5.82 (1H, *s*, C-3).

Acknowledgements—We thank Drs. Aboo Shoeb and P. K. Mahanta for the ^{1}H NMR spectra and Dr. H. S. Mann, Director, Central Arid Zone Research Institute, Jodhpur, for encouragement.

REFERENCES

1. Krupadanum, G. L. D., Sarma, P. N., Srimannarayana, G. and Subba Rao, N. V. (1977) *Tetrahedron Letters* **24,** 2125.
2. Smalberger, T. M., Vleggar, R. and Weber, J. C. (1974) *Tetrahedron* **30,** 3927.
3. Massicot, J. and Marthe, J. P. (1962) *Bull. Soc. Chim. Fr.* **10,** 1962.
4. Hansel, R., Ohlendrof, D. and Pelter, A. (1970) *Z. Naturforsch. Teil B* **25,** 989.
5. Clark-Lewis, J. W. (1968) *Aust. J. Chem.* **21,** 2059.
6. Wilson, R. G., Bowie, J. H. and Williams, O. H. (1968) *Tetrahedron* **24,** 1407.
7. Jain, A. C. and Zutshi, M. K. (1972) *Tetrahedron* **28,** 5589.
8. Kattaev, N. Sh. and Nikonov, G. K. (1972). *Khim. Prir. Soedin.* **8,** 805.