3.80 (3H, *s*, OMe), 3.85 (3H, *s*, OMe) 6.42 (1H, *d*, $J = 2$ Hz, H-6), 6.71 (1H, *d*, $J = 2$ Hz, H-8), 6.89 (2H, *d*, $J = 9$ Hz, H-3', H-5'), 7.90 (2H, *d*, $J = 9$ Hz, H-2', H-6').

Acknowledgements—We are indebted to Dr. H. C. Hsieh, President of Kaohsiung Medical College and Professor S. T. Lu, Kaohsiung Medical College, for their encouragement; Associate Professor T. Okuyama, Meiji College of Pharmacy, for ^{13}C NMR measurement, and Messrs M. Morikoshi and H. Hori, Faculty of Pharmaceutical Sciences, Toyama Medical and Pharmaceutical University, for mass spectral measurement and elemental analysis, respectively.

REFERENCES

1. Tang-Shui Liu. (1962) *Illustrations of Native and Introduced Ligneous Plants of Taiwan*, p. 832. National Taiwan University, Taipei.
2. Mabry, T. J., Markham, K. R. and Thomas M. B. (1970) *The Systematic Identification of Flavonoids*, p. 269. Springer, New York.
3. Budzikiewicz, H., Djerassi, C. and Williams, D. H. (1964) *Structure Elucidation of Natural Products by Mass Spectrometry*, Vol. II, p. 209. Holden-Day, San Francisco.
4. Matsuura, S. and Iinuma, M. (1978) *Chem. Pharm. Bull.* **26**, 1936.
5. Morita, N. Arisawa, M., Nagase, M., Hsu, H.-Y. and Chen, Y.-P. (1977) *Yakugaku Zasshi* **97**, 649.
6. Wenkert, E. and Gottlieb, H. E. (1977) *Phytochemistry* **16**, 1813.
7. Ternai, B. and Markham, K. R. (1976) *Tetrahedron* **32**, 545.
8. Markham, K. R., Ternai, B., Stanley, R., Geeger, H. and Mabry, T. J. (1978) *Tetrahedron* **34**, 1389.

Phytochemistry, Vol. 21, No. 6, pp. 1468–1470, 1982.
Printed in Great Britain.

0031-9422/82/061468-03$03.00/0

PRENYLATED FLAVONOIDS FROM *TEPHROSIA PURPUREA* SEEDS*

BHARATI SINHA, A. A. NATU and D. D. NANAVATI

National Chemical Laboratory, Pune 411 008, India

(*Revised received* 13 *October* 1981)

Key Word Index—*Tephrosia purpurea*; Leguminosae; purpuritenin; purpureamethide; pongamol; karanjin; lanceolatin B; prenylated flavonoids; methylated chalcone.

Abstract—Two new prenylated flavonoids, purpuritenin and purpureamethide, have been characterized from the seeds of *Tephrosia purpurea* together with the known compounds pongamol, karanjin and lanceolatin B.

Tephrosia Pers. (Galegeae, Lotoideae, Leguminosae) is a large tropical and sub-tropical genus of some 300 species[1]. Earlier phytochemical screening [2] of a number of species have revealed the presence of rotenoids, isoflavones, flavanones, chalcones, flavonols and flavones. Within the group of flavones, 5, 7-oxygenated and 7-oxygenated compounds which are characterized by the presence of a C-8 prenyl unit are well known. In many cases, these prenylated flavones have undergone further substitution and cyclization leading to complex molecules. *T. purpurea* Pers. occurs throughout the Indian subcontinent. This species has been reported to contain a number of rotenoids [3] besides pongamol [4], isolonchocarpin[5], karanjin, lanceolatin B, kanjone and sitosterol[6]. Recent reports[7] indicating insecticidal and repellent properties of the seed extract of this plant prompted us to undertake a study of the active principle from this species. We now report the occurrence of five flavonoids; pongamol (**1**), karanjin (**2**), lanceolatin B (**3**) and two new compounds purpuritenin (**4**) and purpureamethide (**5**) (Fig. 1) from the seeds of *T. purpurea*.

Pongamol (**1**) was identified by complete spectral analysis (UV, IR, ^1H NMR, MS) and comparison with an authentic sample. Karanjin (**2**) and lanceolatin B (**3**) were also characterized by spectral data and comparison with authentic samples.

Purpuritenin (**4**) was analysed for $C_{19}H_{16}O_3$ ([M]$^+$ 292), $[\alpha]_D^{CHCl_3} \pm 0°$. The structure was assigned on the basis of spectral data. ^1H NMR of **2** was very similar to ovalitenin A isolated from *Milletia ovalifolia*[8] except for an additional aromatic methyl group in the former compound. Alkaline hydrolysis of **4** gave *p*-toluidic acid, mp 182–183°, thus confirming *para*-substitution in ring A with a methyl at C-4 and the structure of purpuritenin as 4-methyl-2'-methoxy-(3',4',2'',3'')furano-chalcone. Prenylated flavonoids [2] are very well known in the literature but to our knowledge, this is a rare example of a methylated

*NCL Communication No. 2823.

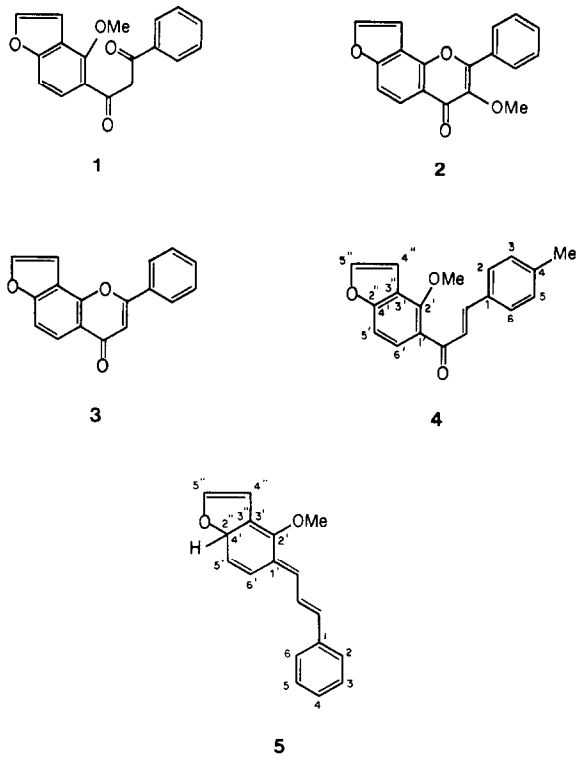


Fig. 1. Flavonoids isolated from seeds of *Tephrosia purpurea*.

chalcone, which may perhaps be a secondary fungal metabolite of the seeds.

Purpureamethide (**5**) analysed for $C_{18}H_{16}O_2$ ([M]$^+$ 264), $[\alpha]_D^{CHCl_3} \pm 0°$. Absence of Me-4 in the 1H NMR and a ketone band in the IR spectrum along with an appearance of a new olefinic proton as compared to **4** led us to structure **5**, 1'-cinnamylidene-2'-methoxy-(3',4',2'',3'')furanocyclohexa-2,5-diene. Absorption at higher wavelength (374 nm) also suggested extended conjugation. This structure was supported by the presence of a peak at *m/z* 185 representing the loss of ring A only and hence confirming the absence of any substitution in ring A. Quinone methides occur in nature both as fungal metabolites, and as wood pigments [9]. Purpureamethide is probably related to the cinnamyl phenols which co-occur with the neoflavonoids in the closely related genera *Dalbergia* and *Machaerium* [10].

EXPERIMENTAL

Mps are uncorr. UV spectra were run in MeCN and IR spectra in nujol. ^{1}H NMR spectra were run at 90 MHz in $CDCl_3$ using TMS as int. standard (^{1}H NMR of **4** was run at 60 MHz in CCl_4). MS were obtained at 70 eV. Petrol refers to the bp 60–80° fraction. For TLC, solvent system (C_6H_6–EtOAc, 1.7:0.3) was used. Seeds of *Tephrosia purpurea* were collected from plants growing in Kerala (South India).

Extraction of T. purpurea *seeds.* Ground seeds (2.305 kg) were defatted with petrol and extracted in a Soxhlet with EtOH to yield a brown gummy residue (58 g), of which 10 g were chromatographed over Si gel (Gr. II, 600 g) using C_6H_6–EtOAc with increasing amounts of EtOAc. Fraction (C_6H_6–EtOAc, 19:1) was dissolved in MeOH to yield **1**, 150 mg, mp 130–131° (MeOH).

Purpuritenin (**4**). The MeOH insoluble portion (345 mg) was triturated with a mixture of C_6H_6–EtOAc to give prisms (100 mg) of **4**, mp 134–135° (C_6H_6–MeOH), $[\alpha]_D^{CHCl_3} \pm 0°$. UV λ_{max}^{MeCN} nm (log ϵ): 210.5 (4.65), 287.4 (4.46) are characteristic of a furanoflavonoid chromophore [8]. IR ν_{max}^{nujol} cm^{-1}: 1587 (C=O of enolic ketone), 1053 (benzofuran) [11]. ^{1}H NMR (60 MHz, δ value, CCl_4): one aromatic Me-4 at 2.0 (*s*, 3H) and aromatic –OMe 4.0 (*s*, 3H, 2'-OMe), furan protons shown by peaks at 6.65 (1H, *d*, $J = 2$ Hz, H-4''), 7.29 (1H, *d*, $J = 2$ Hz, H-5''), aromatic protons and α,β protons appeared as follows: 6.83 (1H, *d*, $J = 9$ Hz, H-5'), 7.73 (1H, *d*, $J = 9$ Hz, H-6'), 7.08–7.26 (2H, *m*, H-2 and H-6), 7.5–7.66 (2H, *m*, H-3 and H-5), 7.5–7.66 (*br d*, 2H, α- and β-H). MS showed fragments at *m/z* (%) 292 (97), 277 (57.7), 265 (97.7), 176 (100), 77 (61.0).

Purpureamethide (**5**). The mother liquor from the crystallization of purpuritenin furnished red needles (180 mg) of **5**, mp 127–128° (C_6H_6–EtOAc), $[\alpha]_D^{CHCl_3} \pm 0°$. UV λ_{max}^{MeCN} nm (log ξ): 250 (4.80), 255 (4.57), 261 (4.41), 347 (4.79). IR ν_{max}^{nujol} cm^{-1}: 1600, 1065 (benzofuran), 1460, 1380, 1160, 980, 870, 760. ^{1}H NMR (90 MHz, δ value, $CDCl_3$), one aromatic –OMe at 4.14 (3H, *s*, 2'-OMe), furan protons appeared at 7.00 (1H, *dd*, $J = 2.25$ Hz, H-4''), 7.65 (1H, *d*, $J = 2.25$ Hz, H-5''), aromatic and α-, β- and γ-protons appeared as follows: 7.36 (1H, *d*, $J = 9$ Hz, H-5'), 8.03 (1H, *d*, $J = 9$ Hz, H-6'), 7.46–7.54 (3H, *m*, H-2, H-4 and H-6), 7.83–7.98 (2H, *m*, H-3 and H-5), 7.83–7.98 (1H, *d*, $J = 15$ Hz, α-H). 7.16 (1H, *dd*, $J = 15$ and 6 Hz, β-H), 7.65 (1H, *d*, $J = 6$ Hz, γ-H), 7.83–7.98 (1H, *m*, H-4'). MS showed fragments at *m/z* (%) 264 (100), 185 (20.89), 175 (38.37), 160 (31.39), 105 (32.56), 89 (20.89), 77 (31.39).

Karanjin (**2**) and *lanceolatin* B (**3**). Further elution with C_6H_6–EtOAc (17:3) yielded **2** mp 158–159° (MeOH) and **3** mp 135–136° ($Me_2CO + Et_2O$).

Acknowledgements—We are grateful to Professor S. K. Talapatra for authentic samples of **1** and **3**, to Mr. G. Samuel for measurement of 90 MHz ^{1}H NMR and M/S Orient Pharma (Pvt.) Ltd., Madras, for supplying the seeds of *T. purpurea*.

REFERENCES

1. The Wealth of India (Raw Materials) (1976), *A Dictionary of Indian Raw Materials and Industrial Products* Vol. 10, p. 153. Publications & Information Directorate, CSIR, New Delhi.
2. Waterman, P. G. and Khalid, S. A. (1980) *Phytochemistry* **19**, 909.
3. Sharma, R. and Khanna, P. (1975) *Indian J. Exp. Biol.* **13**, 84.
4. Rangaswami, S., Narayanaswamy, S. and Seshadri, T. R. (1954) *J. Chem. Soc.* 1871.
5. Naik Satyam, P. G. and Bringi, N. V. (1973) *Indian J. Chem.* **11**, 209.
6. Gupta, R. K. and Krishnamurti, M. (1976) *Phytochemistry* **15**, 832.
7. Saxena, B. N., Dubey, D. N. and Nair, A. L. (1974) *Def. Sci. J.* **24**, 43.

8. Islam, A., Gupta, R. K. and Krishnamurti, M. (1980) *Phytochemistry* **19**, 1558.
9. Ollis, W. D., Redman, B. T., Roberts, R. J. and Sutherland, I. O. (1968) *Chem. Commun.* **22**, 1392.
10. Jurd, L., Stevens, K. and Manners, G. (1972) *Tetrahedron Letters* 2149.
11. Sharma, P. and Parthasarathy, M. R. (1977) *Indian J. Chem.* **15B**, 866.

Phytochemistry, Vol. 21, No. 6, pp. 1470–1471, 1982.
Printed in Great Britain.

0031-9422/82/061470-02$03.00/0

(−)-*N*-ETHYLCYTISINE, A LUPIN ALKALOID FROM THE FLOWERS OF *ECHINOSOPHORA KOREENSIS**

ISAMU MURAKOSHI, MASANAO WATANABE, JOJU HAGINIWA, SHIGERU OHMIYA† and HIROTAKA OTOMASU†

Faculty of Pharmaceutical Sciences, University of Chiba, Yayoi-cho 1-33, Chiba, 260, Japan; †Hoshi College of Pharmacy, Ebara 2-4-41, Shinagawa-ku, Tokyo, 142, Japan

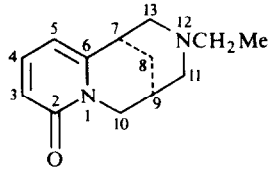
(*Received* 9 *September* 1981)

Key Word Index—*Echinosophora koreensis*; Leguminosae; lupin alkaloid; (−)-*N*-ethylcytisine; (−)-cytisine.

Abstract—A new lupin alkaloid, (−)-*N*-ethylcytisine, was isolated from the fresh flowers of *Echinosophora koreensis*. Its structure has been confirmed by spectroscopic data and by direct comparison with a synthetic sample prepared from (−)-cytisine and ethylbromide.

INTRODUCTION

As part of our chemical [1–9] and biochemical [11–13] studies on the lupin alkaloids in Japanese leguminous plants, we have recently isolated (−)-*N*-(3-oxobutyl)cytisine [4], (−)-cytisine, (−)-*N*-formylcytisine, (−)-*N*-methylcytisine, (−)-rhombifoline, (−)-baptifoline, (−)-anagyrine, (−)-lupanine and 5,6-dehydrolupanine from the fresh leaves, stems and roots of *Echinosophora koreensis* [10]. *E. koreensis* is a deciduous shrub, which is a native of Korea and closely related to the genus *Sophora* (Leguminosae). Further examination of the basic constituents in the fresh flowers has resulted in the isolation of a new lupin alkaloid, (−)-*N*-ethylcytisine (**1**); this paper deals with its structure determination.



1

*This work was presented at the 101st Annual Meeting of the Pharmaceutical Society of Japan at Kumamoto, 2 April 1981 (*Meeting Abstract* p. 518).

RESULTS AND DISCUSSION

From the freshly harvested flowers of *E. koreensis*, a new lupid alkaloid (**1**) was isolated in a yield of 0.001% of the fr. wt as colourless needles, mp 112°, $[\alpha]_D^{27}$ −216.7°; UV λ_{max}^{EtOH} nm (log ϵ): 235 (3.98), 310 (4.07).

The mass spectrum of 1 showed a $[M]^+$ at *m/z* 218 (28%) with predominant ions at *m/z* 160 (6) and 146 (7), characteristic of lupin alkaloids containing an α-pyridone ring [1, 2, 4, 6, 9]. The UV spectrum of **1** also suggested the presence of an α-pyridone moiety in the molecule [1, 2, 4, 6, 9]. The ^{1}H NMR spectrum ($CDCl_3$) of **1** clearly indicated the presence of aromatic protons at δ 5.97 (1 H, *dd*, J = 1.5 and 7 Hz), 6.43 (1 H, *dd*, J = 1.5 and 9 Hz) and 7.27 (1 H, *dd*, J = 7 and 9 Hz) attributable to the C-5, C-3 and C-4 positions, respectively, of an α-pyridone ring in a cytisine-type lupin alkaloid [1, 2, 4, 6, 9]. Other significant signals revealed in the NMR spectrum included an *N*-ethyl side chain at δ 0.91 (3 H, *t*, J = 7 Hz) and 2.32 (2 H, *q*, J = 7 Hz), and an equatorial H on C-11 and C-13 at δ 2.92 (2 H, *m*) very similar to those of (−)-*N*-methylcytisine and (−)-*N*-(3-oxobutyl)cytisine [4]. A base peak at *m/z* 72 in the mass spectrum of **1** was also indicative of the presence of an ethyl function at the *N*-12 position of the cytisine ring in contrast to the characteristic base peak of (−)-*N*-methylcytisine at *m/z* 58. From the above spectroscopic results, the new lupin alkaloid (**1**) was presumed to be (−)-*N*-ethylcytisine. Further confirmation of the identity of the new alkaloid as **1** was obtained by comparing the