Pergamon 0031-9422(95)00561-7 Phytochemistry, Vol. 41, No. 2, pp. 661–662, 1996

0031-9422/96 $15.00 + 0.00

FLAVONOIDS FROM *ESCHSCHOLTZIA CALIFORNICA*

L. JAIN, M. TRIPATHI, V. B. PANDEY* and G. RÜCKER†

Department of Medicinal Chemistry, Institute of Medical Sciences, Banaras Hindu University, Varanasi-221 005, India; †Pharmazeutisches Institut der Universität Bonn, Kreuzbergweg 26, D-53115 Bonn, Germany

(*Received* 22 *May* 1995)

Key Word Index—*Eschscholtzia californica*; Papaveraceae; 2′-methoxyformononetin; 7-methoxy-2′,4′-dihydroxyisoflavone; quercitrin.

Abstract—Two new isoflavones, together with quercitrin have been isolated from whole plants of *Eschscholtzia californica*. The structures of the new isoflavones were determined as 2′-methoxyformononetin and 7-methoxy-2′,4′-dihydroxyisoflavone by spectroscopic methods.

INTRODUCTION

Eschscholtzia californica has been introduced into India as an annual herb [1]. A number of isoquinoline alkaloids [2–8] and the flavonoid, rutin [9], have earlier been reported from this species. We report herein the isolation of two new isoflavones and quercitrin from whole plants of *E. californica*.

RESULTS AND DISCUSSION

Chromatographic resolution of the ethyl acetate fraction furnished flavonoids A–C. Compound A(**1**), $C_{17}H_{14}O_5$ ($[M]^+$ *m/z* 298) showed in its IR spectrum bands for hydroxyl (3200–3400 cm^1), methoxyl (2820 cm^{-1}) and carbonyl (1630 cm^{-1}) groups. UV absorption maxima, together with the chemical shift at δ8.08 (1H, *s*) in its ^{1}H NMR spectrum indicated it to be an isoflavone. The ^{1}H NMR exhibited the presence of two *ortho*- and four *meta*- coupled protons similar to that of 2′-hydroxydaidzein (**2**) [10], together with two methoxyl and one hydroxyl groups. The H R mass spectrum showed a $[M]^+$ peak at *m/z* 298 and an intense peak at *m/z* 267 (ion a), characteristic of methoxyl or hydroxyl groups at the 2′-position [11]. Peaks at *m/z* 162 and 137 were due to RDA cleavage peaks of methoxyl groups in ring B of the molecule. The UV showed a bathochromic shift of 10 nm with NaOAc supported a hydroxyl group at the C-7 position.

Comparison of the ^{13}C NMR of compound A(**1**) with formononetin (**3**) [12] showed that the signal attributable to C-2′ of formononetin was shifted downfield from δ130.0 to 158.1 in A, and the signals of C-1′, C-3′ and C-5′ were shifted to higher fields by 9.9, 15.0 and 9.1 ppm. [13]. The above data thus supported the positions of methoxyl groups at C-2′ and C-4′ positions in **1**. The structure of compound A is 7-hydroxy-2′, 4′-methoxy isoflavone (**1**), which is 2′-methoxyformononetin.

Compound B (**4**), $C_{16}H_{12}O_5$ ($[M]^+$ *m/z* 284) showed spectral data comparable to those of compound A (**1**).

The M_r of compound B is 14 less than that of compound A indicating that it bears only one methoxyl group; this was substantiated by the ^{1}H NMR signal at 63.90 (3H, *s*). The fragment ion peaks formed by RDA cleavage appeared at *m/z* 151 and 134, the corresponding peaks of compound A appearing at *m/z* 137 and 162, respectively. This indicated that the lone methoxyl group is in ring A. The structure was thus deduced as 7-methoxy-2′,4′-dihydroxy isoflavone (**4**).

The structures of compound A and B were further proved by methylation experiments. Both A and B on methylation furnished the identical compound **5** (co-TLC, superimposable IR). Both are new flavanoids.

Compound C, $C_{21}H_{20}O_{11}$ ($[M]^+$ *m/z* 448) was identified as quercitrin [14] by a study of the spectral data, hydrolysis and direct comparison with an authentic sample (mmp, co-TLC and superimposable IR).

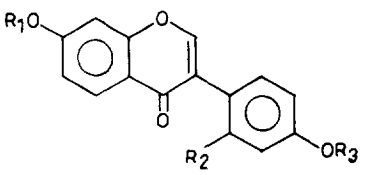
EXPERIMENTAL

E. californica Cham. was collected from Banaras Hindu University campus and identified by the Dept of Botany, Banaras Hindu University. A voucher specimen is kept in the department.

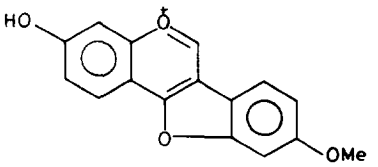
Plants were dried, powdered and extracted with MeOH in a Soxhlet extractor. Alkaloids and non-alkaloids were separated by usual methods. The non-alkaloidal fr. was chromatographed on a silica gel column. The benzene–EtOAc (1:1), (1:2) and EtOAc eluates furnished compounds A,B and C, respectively.

2′-Methoxy formononetin (**1**). Recrystallized from MeOH, yellow granules, mp 195–97°. IR ν_{max}^{KBr} (cm^{-1}): 3200–3400, 2820, 1630, 1610, 1590, 1570. UV λ_{max}^{MeOH} nm

*Author to whom correspondence should be addressed.



	R_1	R_2	R_3
1	H	OMe	Me
2	H	OH	H
3	H	H	Me
4	Me	OH	H
5	Me	OMe	Me



m/z 267 (ion a)

(log ε): 241 (4.58), 248 (4.65), 285 (4.10), 313 sh (3.90); $\lambda_{max}^{MeOH+NaOAC}$ nm: 260, 314. 300 MHz ^{1}H NMR (DMSO-d_6): δ3.78 (3H, *s*,-OMe); 3.69 (3H, *s*,-OMe), 8.08 (1H, *s*, C-2-H), 7.92 (1H, *d*, *J* = 8.8 Hz, C–5–H), 6.85 (1H, *d*, *J* = 2.2 Hz, C–8–H), 6.92 (1H, *dd*, *J* = 8.8, 2.2 Hz, C–6–H), 7.13 (1H, *d*, *J* = 8.8 Hz C–6′–H), 6.62 (1H, *d*, *J* = 2.2 Hz, C–3′–H), 6.55 (1H, *dd*, *J* = 8.8, 2.2 Hz, C-5′-H). ^{13}C NMR (DMSO-d_6): δ153.5 (C-2), 121.3 (C-3), 174.1 (C-4), 116.4 (C-4a), 126.9 (C-5), 114.8 (C-6), 162.1 (C-7), 101.9 (C-8), 157.2 (C-8a), 113.3 (C-1′), 158.1 (C-2′), 98.5 (C-3′), 160.4 (C-4′), 104.4 (C-5′), 131.8 (C-6′), 55.1 (–OCH_3), 55.4 (–OCH_3). HRMS (rel. int.): *m/z* 298.0864 ($C_{17}H_{14}O_5$), 297 (12), 267.0608 (24), 162.0669 (14), 161.0596 (30), 152.0823 (36), 151.0765 (97), 137.0232 (100).

7-Methoxy-2′,4′-dihydroxy isoflavone (**4**). Recrystallized from MeOH, yellowish granules, mp 213.15°. IR ν_{max}^{KBr} (cm^{-1}): 3350–3600, 2800, 1630, 1610, 1550; UV λ_{max}^{MeOH} nm (log ε): 247 (4.8), 262 (4.5), 289 (4.0), 313 (3.5); $\lambda_{max}^{MeOH+NaOMe}$ nm: 248, 268, 310, 338. 300 MHz ^{1}H NMR (DMSO-d_6): δ3.90 (3H, *s*, – OMe), 8.19 (1H, *s*, C–2–H), 7.95 (1H, *d*, *J* = 8.6 Hz, C-5-H), 7.14 (1H, *d*, *J* = 2.2 Hz, C–8–H), 7.07 (1H, *dd*, *J* = 8.6 Hz, 2.2 Hz, C–6–H), 6.95 (1H, *d*, *J* = 8.6 Hz, C–6′–H), 6.36 (1H, *d*, *J* = 2.2 Hz, C–3′–H), 6.27 (1H, *dd*, *J* = 8.6 Hz, 2.2Hz, C-5′-H), 9.2 (1H, *br*,-OH), 9.3 (1H, *br*, -OH). ^{13}C NMR (DMSO-d_6): δ154.2 (C-2), 121.8 (C-3), 174.8 (C-4), 117.3 (C-4a), 126.6 (C-5), 114.3 (C-6), 163.3 (C-7), 102.7 (C-8), 156.0 (C-8a), 109.7 (C-1′), 157.1 (C-2′), 100.3 (C-3′), 158.1 (C-4′), 106.1 (C-5′), 131.7 (C-6′), 55.9 (OMe). HRMS (rel. int.): *m/z* 284.0684 ($[M]^+$, $C_{16}H_{12}O_5$) (41); 267.0661 (17); 151.0393 (100), 134.0372(13).

Methylation of (**1**) *and* (**4**). Methylation with $(Me)_2SO_4$ and K_2CO_3 by refluxing under anhydrous conditions with dry Me_2CO gave methylated compounds identical to compound **5** (co-TLC and superimposable IR).

REFERENCES

1. *The Wealth of India, Raw Materials* (1952) Vol III p. 202 CSIR, New Delhi.
2. Listy, C. (1955) *Coll. Czech. Chem. Commun* **20**, 27
3. Gertig, H. (1964) *Acta, Polon, Pharm*, **21**, 127.
4. Manske, R. H. F. and Shin, K. H. (1965) *Can J. Chem.* **43**, 2180.
5. Gertig, H. (1965) *Acta. Polon. Pharm.* **22**, 367.
6. Gertig, H. (1965) *Acta. Polon. Pharm.* **22**, 443.
7. Slavik, J. and Dolejs, L. (1973) *Coll. Czech. Chem. Commun.* **38**, 3514.
8. Urzua, A. and Mendoza L. (1986). *J. Nat. Prod.* **49**, 922.
9. Sando, C. E. and Bartlett, H. H. (1920) *J. Biol. Chem.* **41**, 495.
10. Woodward, M. D. (1980) *Phytochemistry* **19**, 921.
11. Harborne, J. B. and Mabry, T. J. (1982) *The Flavonoids; Advances in Research*, p. 563. Chapman and Hall, London.
12. Kinjo, J., Furusawa, J., Baba, J., Takeshita, T., Yamasaki, M. and Nohara, T. (1987). *Chem. Pharm. Bull.* **35**, 4846.
13. Yahara, S., Ogata, T., Saijo, R., Konishi, R., Yamahara, J., Miyahara, K. and Nohara, T. (1989) *Chem. Pharm. Bull.* **37**, 979.
14. Pandey, V. B., Singh, J. P., Khosa, R. L. and Shah, A. H. (1985) *J. Chem. Soc. Pakistan* **7**, 33.