273°, 264–266°), UV: (MeOH) λ_{max} (log ε) 253 (4,23), 272 (4, 17), 346 (4, 30). IR: (KBr) Hydroxyl 3410 cm^{-1}, Carbonyl 1662 cm^{-1}. NMR: (DMSO-d_6) δ = 3,74 (3H, *s*, C_6-OMe), 6,56 (1H, *s*, C_3-H), 6,67 (1H, *s*, C_8-H), 6,90 (1H, *d*, $C_{5'}$-H), 7,40 (2H, *m*, $C_{2',6'}$-H), 13,04 (1H, *s*, C_5-OH). MS: *m/e* 316,0580 (100%)(M^+) [ber. für $C_{16}H_{12}O_7$: 316,0582] 302 (8), 301 (50), 299 (4), 298 (25), 297 (2), 287, (2,5), 274 (2,5), 273 (28), 270 (4), 167 (6), 153 (2), 139 (13), 137 (3,5), 135 (10). 10 mg F_3 wurde in Me_2CO mit Dimethylsulphat methyliert. Weisse Kristalle aus MeOH–H_2O (4 mg). Schmp. 173–174° (Lit. [4] 175–176°). MS: *m/e* 372, 1207 (100%) (M^+) [ber. für $C_{20}H_{20}O_7$ (5,6,7,3',4'-Pentamethoxyflavon): 372, 1208] 342 (1,5), 341 (5,5), 326 (1), 314 (1), 313 (1,5), 195 (1,5), 179 (2), 168 (6). F_4 (5,7,4'-Trihydroxy-6-methoxyflavon, Dinatin), hellgelbe Nadeln aus MeOH (102 mg). Schmp. 290–293° (Lit. [6] 291–292°). F_5(5,7-Dihydroxy-6,4'-dimethoxyflavon, Pectolinarigenin), dunkelgelbe Nadeln aus MeOH (42 mg). Schmp. 216–217° (Lit. [7] 217°). UV: (MeOH) λ_{max} (log ε) 276 (4,33), 331 (4,39). IR: (KBr) Hydroxyl 3400 cm^{-1}, Carbonyl 1650 cm^{-1}. NMR: (DMSO-d_6) δ = 3,77 (3H, *s*, C-OMe) 3,86 (3H, *s*, C-OMe), 6,63 (1H, *s*, C_3-H), 6,86 (1H, *s*, C_8-H), 7,12 (2H, *d*, $C_{3',5'}$-H), 8,03 (2H, *d*, $C_{2',6'}$-H), 13,00 (1H, *s*, C_5-OH). MS: *m/e* 314, 0789 (100%)(M^+) [ber. für $C_{17}H_{14}O_6$: 314,0790] 300 (9), 299 (56), 297 (4), 296 (32), 272 (2,5), 271 (25), 167 (5,5), 157 (1,5), 153 (1,5), 139 (5), 135 (3,5), 133 (13), 132 (3).

Anerkennungen—Wir danken Herrn Prof. Dr. R. H. Thomson für die Aufnahme der 100 MHz NMR- und hochaufgelöste MS-Spektren. Ebenso danken wir den Herrn Professoren Dr. S. M. Kupchan und Dr. K. Fukui für die Überlassung von 6-Methoxyluteolin.

LITERATUR

1. Imre, S. und Öztunc, A. (1976) *Z. Naturforsch.* **31c**, 403.
2. Imre, S., Tulus, R. und Sengün, I. (1973) *Phytochemistry* **12**, 2317.
3. Geissman, T. A. (1962) *The Chemistry of Flavonoid Compounds.* MacMillan, New York.
4. Kupchan, S. M., Sigel, C. W., Hemingway, R. J., Knox, J. R. und Udayamurthy, M. S. (1969) *Tetrahedron* **25**, 1603.
5. Fukui, K., Nakayama, M. und Horie, T. (1969) *Experientia* **25**, 355.
6. Herz, W. und Sumi, Y. (1964) *J. Org. Chem.* **29**, 3438.
7. Farkas, L. Nogradi, M., Sudarsanam, V. und Herz, W. (1966) *J. Org. Chem.* **31**, 3228.

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5,4'-DIHYDROXY-6,7,8,3'-TETRAMETHOXYFLAVONE FROM *SIDERITIS MUGRONENSIS*

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Key Word Index—*Sideritis mugronensis*; Labiatae; flavones.

From the aerial parts of *Sideritis mugronensis* Borja four previously known flavones have been isolated: 5-hydroxy-6,7,8,3',4'-pentamethoxyflavone (5-*O*-desmethylnobiletin) [1], 5-hydroxy-6,7,3',4'-tetramethoxyflavone [2, 3], 5,3'-dihydroxy-6,7,8,4'-tetramethoxyflavone (gardenin D) [4–6] and 5,4'-dihydroxy-6,7,3'-trimethoxyflavone (cirsilineol) [7, 8]. A new natural flavone, 5,4'-dihydroxy-6,7,8,3'-tetramethoxyflavone, previously known as synthetic product [9, 10], is also present.

EXPERIMENTAL

Mps are uncorrected.

Extraction of flavonoids. Air dried aerial parts of *S. mugronensis* (1 kg) were extracted with light petrol (bp 50–70°) for 90 hr in a Soxhlet. Column chromatography on SiO_2 of this extract (40 g) yielded by elution with $CHCl_3$–MeOH (33:1) a mixture of flavonoids (4 g). Repeated chromatography of this mixture on SiO_2 (preparative TLC) using C_6H_6–EtOAc (9:1) and (3:1) gave 5-*O*-desmethylnobiletin (1.5 g), 5-hydroxy-6,7,3',4'-tetramethoxyflavone (70 mg), gardenin D (120 mg), cirsilineol (400 mg) and 280 mg of the 5,4'-dihydroxy-6,7,8,3'-tetramethoxyflavone.

The previously known natural flavones were identified by mp, IR, NMR, UV and MS spectra and by physical and spectroscopic data of their acetyl and methyl derivatives.

5,4'-Dihydroxy-6,7,8,3'-tetramethoxyflavone. Mp 163.5–165° (lit. mp [10] 164–165°) (acetone–*n*-hexane). IR ν_{max}^{KBr} 3320, 3000, 2940, 2840, 1650, 1610, 1580, 1515, 1485, 1365, 1280, 1230, 1200, 1105, 1070, 1035, 1010, 960, 920, 845, 750, 690 cm^{-1}. UV λ_{max}^{MeOH} nm (log ε) 254 (4.16), 282 (4.19), 347 (4.35). λ_{max}^{NaOMe} 266 (4.27), 300 sh (4.00), 415 (4.52). $\lambda_{max}^{AlCl_3}$ 265 (4.17), 287 (4.24), 300 sh (4.19), 374 (4.40). $\lambda_{max}^{AlCl_3/HCl}$ 262 (4.16), 289 (4.23), 300 sh (4.21), 365 (4.39). NMR (100 MHz, $CDCl_3$) δ: 3.92, 3.94, 3.97, 4.08 (*s*, 3H each, 6-, 7-, 8-, 3'-OMe), 6.08 (*s*, 4'-OH), 6.54 (*s*, 3-H), 7.00 (*d*, *J* 8 Hz, 5'-H), 7,37 (*d*, *J* 2 Hz, 2'-H), 7.50 (*q*, *J* 8 Hz and 2 Hz, 6'-H) and 12.46 (*s*, 5-OH). MS (70 eV, direct inlet) *m/e* 374 (M^+). (Found: C, 61.13; H, 4.90. Calc. for $C_{19}H_{18}O_8$: C, 60.96; H, 4.85%). *Diacetate.* The flavonoid (60 mg) in Ac_2O (1 ml)/Py (0.5 ml) 24 hr at room temp. Mp 151–152° (acetone–*n*-hexane) (lit. [9] mp 149–150°) IR ν_{max}^{KBr} 3100, 3020, 2940, 2840, 1760, 1640, 1600, 1565, 1510, 1460, 1410, 1360, 1275, 1200, 1170, 1130, 1100, 1075, 1035, 1015, 1000, 965, 895, 875, 855, 760, 690 cm^{-1}. UV λ_{max}^{MeOH} nm (log ε) 235 (4.22), 268 (4.34), 316 (4.30). NMR (100 MHz, $CDCl_3$) δ: 2.31 (*s*, 3H, 4'-OAc), 2.45 (*s*, 3H, 5-OAc), 3.87, 3.89, 4.01, 4.07 (*s*, 3H each, 6-, 7-, 8-, 3'-OCH_3), 6.55 (*s*, 3-H), 7.12 (*d*, *J* 9 Hz, 5'-H), 7.43 (*d*, J 2 Hz, 2'-H) and 7.46 (*q*, *J* 9 and 2 Hz, 6'-H). MS (70 eV, direct inlet) *m/e* 458 (M^+). (Found: C, 60.43; H, 5.00. Calc. for $C_{23}H_{22}O_{10}$: C, 60.26; H, 4.84%). Identical in all respects to synthetic products [9, 10]. Total methylation yielded nobiletin mp 136–137°, IR, UV and NMR spectra identical with an authentic sample.

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REFERENCES

1. Geissman, T. A. (1962) *Chemistry of the Flavonoids Compounds*. Pergamon Press, Oxford.
2. Morita, N. (1960) *Chem. Pharm. Bull. Japan* **8**, 59.
3. González, A. G. and Fraga, B. M., private communication.
4. Pinkas, J., Lavie, D. and Chorin, M. (1968) *Phytochemistry* **7**, 169.
5. Rama Rao, A. V., Venkataraman, K., Chakrabarti, P., Sanyal, A. K. and Bose, P. K. (1970) *Indian J. Chem.* **8**, 398.
6. Harborne, J. B., Mabry, T. J. and Mabry, H. (1975) *The Flavonoids*, p. 276. Chapman and Hall, London.
7. Segal, R., Cohen, D., Sokoloff, S. and Zaitschek, D. V. (1973) *Lloydia* **36**, 103.
8. Morita, N., Shimizu, M. and Arisawa, M. (1973) *Phytochemistry* **12**, 421.
9. Krishnamurti, M., Seshadri, T. R. and Sharma, N. D. (1970) *Indian J. Chem.* **8**, 575.
10. Wagner, H., Maurer, G., Hörhammer, L. and Farkas, L. (1971) *Chem. Ber.* **104**, 3357.

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4-EPIISOCOMMUNIC ACID AND AMENTOFLAVONE FROM *CALLITRIS RHOMBOIDEA*

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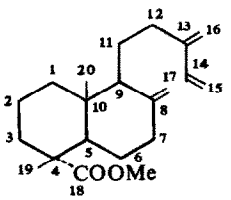
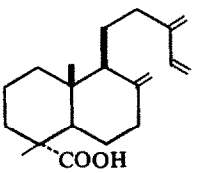
Key Word Index—*Callitris rhomboidea*; Cupressaceae; leaves; 4-epiisocommunic acid; amentoflavone.

The leaves of *Callitris rhomboidea* were previously examined for their essential oil content [1]. The present report deals with the isolation and characterization of a biflavonoid and a new diterpene acid. The residue from the combined petrol and benzene extracts showed one major acidic compound (TLC and colour tests) and the acid was partially extractable into aqueous sodium hydroxide. However, the isolation of the free acid was found to be difficult. Hence it was isolated as its methyl ester. Its MW, 316 (MS), is consistent with a molecular formula $C_{21}H_{32}O_2$ of a diterpene. The UV absorption spectrum of the compound showed the presence of a monosubstituted butadiene chromophore (224 nm). It readily formed an adduct with maleic anhydride. Its IR spectrum showed a terminal vinyl (990 cm^{-1}), an exocyclic methylene (890 cm^{-1}) and conjugation (1648 and 1595 cm^{-1}). The NMR spectrum indicated two tertiary methyls, six olefinic protons and a multiplet centered at δ 6.2, characteristic of the X-proton constituting an ABX system. In its MS, intense peaks at *m/e* 181 and 121 were observed. They were indicative of the bicyclic nature of the diterpene having an exocyclic methylene at C-8 [2]. A C_6H_9 side chain at C-9 was also indicated by the fragment at *m/e* 235 ($M^+ - 81$). With the help of these data, the structure of the methyl ester was formulated as **1**.

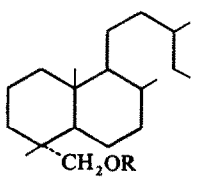


1

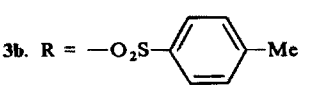
The equatorial nature of the ester group, indicated by a strong band at 1245 cm^{-1} in the IR spectrum [3], was confirmed by its easy saponification to the acid (**2**). The



2



3a. R = H



hexahydro compound obtained readily by hydrogenation of **1** over palladium, was reduced with LAH and the alcohol (**3**) showed the NMR signals expected for an equatorial —$C\underline{H}_2OH$ [4]. The alcohol was converted through its tosylate into the hydrocarbon (**4**), identical