

Table 1. Flavonoid aglycones from *Flourensia* taxa

Compound	Trivial Name	Source*
1 5,7-Dihydroxyflavanone	Pinocembrin	<i>Flourensia ilicifolia</i> † <i>F. retinophylla</i> ‡
2 Kaempferol 3-methyl ether		<i>F. ilicifolia</i>
3 Galetin 6-methyl ether		<i>F. ilicifolia</i>
4 Galetin 3,6-dimethyl ether		<i>F. ilicifolia</i> <i>F. campestris</i> §
5 Kaempferol 3,7-dimethyl ether	Kumatakenin	<i>F. cernua</i> <i>F. retinophylla</i>
6 Quercetagenin 3,6-dimethyl ether	Axillarin	<i>F. ilicifolia</i>
7 Quercetagenin 3',3,6-trimethyl ether	Jaceidin	<i>F. ilicifolia</i>

* Voucher specimens are deposited in The University of Texas Herbarium Austin, Texas, U.S.A.

† Dillon & Bacon 629 (Mexico. Coahuila: near Parras); ‡ Dillon & Hartman 658 (Mexico. Coahuila: Sierra de Paila); § Dillon & Rodriguez 449 (Argentina. Cordoba: near Yocsino).

EtOAc (3:1) and later with CHCl_3 -MeOH-MeCOEt (12:3:1). UV-visible bands on the column were collected in fractions, and individual compounds were purified by TLC in appropriate solvents (CHCl_3 -Me₂CO, 9:1; C_6H_6 -MeOH, 9:1). All other taxa (Table 1) were worked up in a similar manner.

Acknowledgements—This research was supported at The University of Texas by the National Science (Grant DEB 76-09320), the Robert A. Welch (Grant F-130) and the Potts-Sibley Foundations.

REFERENCES

- Dillon, M. O. (1976) Ph.D. Dissertation, University of Texas at Austin.
- Dillon, M. O., Mabry, T. J., Besson, E., Bouillant, M. L. and Chopin, J. (1976) *Phytochemistry* 15, 1085.
- Mabry, T. J., Markham, K. R. and Thomas, M. B. (1970) *The Systematic Identification of Flavonoids*. Springer Verlag, Heidelberg.
- Rosler, H., Star, A. E. and Mabry, T. J. (1971) *Phytochemistry* 10, 450.
- Lebreton, P., Wollenweber, E., Southwick, L. and Mabry, T. J. (1971) *C.R. Acad. Sci. Ser. C* 272, 1529.
- Rodriguez, E., Carmen, N. J., Vander Velde, G., McReynolds, J. H., Mabry, T. J., Irwin, M. A. and Geissman, T. A. (1972) *Phytochemistry* 11, 3509.
- Valesi, A. G., Rodriguez, E., Vander Velde, G., and Mabry, T. J. (1972) *Phytochemistry* 11, 2821.
- Harborne, J. B., Mabry, T. J. and Mabry, H. (1975) *The Flavonoids*. Chapman & Hall, London.

Phytochemistry, 1977, Vol. 16, pp. 1319-1320. Pergamon Press. Printed in England.

FLAVONOIDS OF *REAUMURIA MUCRONATA* AND *THYMELAEA HIRSUTA*

MAHMOUD A. M. NAWWAR, MOHEB S. ISHAK, ALEI EL DIN A. EL SHERBIENY and SAYED A. MESHAAL
National Research Centre, El-Dokki, Cairo, Egypt

(Revised received 10 February 1977)

Key Word Index—*Reaumuria mucronata*; *Thymelaea hirsuta*; Tamaricaceae; Thymelaeaceae; kaempferol 3,7-disulphate; 6,8-C-glucosylapigenin.

The flavonoids of *Reaumuria mucronata* (Tamaricaceae) and *Thymelaea hirsuta* (Thymelaeaceae), two plants native to Egypt, have not been previously investigated. However a number of unusual flavonols derivatives have been identified in three *Tamarix* species. Thus tamarixetin (quercetin 4'-methyl ether) 3-sulphate has been isolated from *T. laxa* [1], rhamnetin 3'-glucuronide-3,5,4'-trisulphate, 7,4'-dimethylkaempferol 3-sulphate, quercetin 3-isomerulylglucuronide, rhamnocitrin 3-glucoside and 3-rhamnoside, isoquercitrin, tamarixin and taxifolin have been reported variously in the leaves,

flowers, galls and bark of *T. aphylla* and 7,4'-dimethylkaempferol 3-glucoside has been isolated from the leaves of *T. nilotica* [2-8]. Harborne [9] showed the presence of flavonoid sulphates in the leaves of five other *Tamarix* species: *T. africana*, *T. canariensis*, *T. gallica*, *T. hispida*, and *T. smyrnensis*.

In the present study another new flavonol derivative, kaempferol 3,7-disulphate has been identified in leaves of *Reaumuria mucronata*. Chromatographic, electrophoretic and UV data for the new compound are given in Table 1. Acid hydrolysis with 2N HCl at 100° for

Table 1. Properties of kaempferol 3,7-disulphate and its intermediates

	H ₂ O	R _f (×100) 15% HOAc	BAW	Electrophoretic* mobility	MeOH	AlCl ₃ †	UV data λ _{max} (nm) in NaOAc‡	MeONa‡
Km 3,7-diSO ₄	78	76	6	11	270, 345	392	269	405
Intermediate I	10	28	70	2.8	268, 368	418	268	455
II	40	60	56	5.6	267, 343	394	270	(decomp.) 398
Isorh 3,7-diSO ₄ §	78	72	47	n.d.	253, 353	401	253	416
Kaempferol	0	n.d.	85	0	256, 368			

Key: Km = Kaempferol, Isorh = Isorhamnetin, n.d. = not determined

* Distance travelled in cm in acetate-formic buffer, pH 2 at 50V/cm in 90 min; † = Band II; ‡ = Band I; § From Cabrera and Juliani [10].

40 min gave only kaempferol and sulphate (confirmed by BaCl₂ ppt.). The absence of a NaOAc shift confirms that one sulphate ion is attached at the 7-position, while a positive AlCl₃ shift and the colour reactions of the glycoside (dark absorbing changing to yellow on fuming with NH₃) show that both the 5- and 4'-hydroxyls are unsubstituted. Two intermediates were detected on controlled acid hydrolysis, which both gave kaempferol and sulphates on further hydrolysis. The first (I) appeared yellow on UV and was identified from R_f, electrophoretic and UV data (Table 1) as kaempferol 7-sulphate. The second (II), which appeared dark absorbing in UV and changed to yellow on treatment with NH₃ vapour, was unstable and was tentatively identified from R_f, electrophoretic and UV data (Table 1) as kaempferol 3-sulphate. The presence of two sulphate ions in the original compound was confirmed by quantitative sulphur analysis (found: S, 11.1%; calc: S, 11.4%).

From the leaves of the second plant, *Thymelaea hirsuta*, a known compound, 6,8-di-*G*-β-D-glucopyranosylapigenin (vicenin-2) was isolated. Its structure was determined from chromatographic data, UV analysis and 40 min and 4 hr acid hydrolysis. Refluxing with a mixture of HI and phenol gave apigenin and *p*-hydroxybenzoic acid was identified as the product of alkali fusion. Professor J. Chopin of the University of Lyon, France, kindly confirmed the identity of the *G*-glucoside by MS of the permethyl ether and TLC comparison with authentic vicenin-2.

This represents the first report of a flavone *G*-glycoside

in the Thymelaeaceae. The discovery of kaempferol 3,7-disulphate in *Reaumuria mucronata*, on the other hand is not surprising since flavonoid sulphates are characteristic constituents of other members of the Tamaricaceae [4, 6, 7]. The related substance, isorhamnetin 3,7-disulphate has recently been reported for the first time in the flowers of *Flaveria bidentis* (Compositae) [10].

Acknowledgements—The authors thank Prof. Vivi Tackholm, Dept. of Botany, Cairo University for identifying the plant material, which was collected from the Mediterranean coastal plain at El-Sallum.

REFERENCES

1. Utkin, L. M. (1966) *Khim. Prir. Soedin.* 2, 162.
2. Ishak, M. S., El Sissi, H. I., Nawwar, M. A. M. and El Sherbieny, A. E. A. (1972) *Planta Med.* 21, 246.
3. Ishak, M. S., El Sissi, H. I., El Sherbieny, A. E. A. and Nawwar, M. A. M. (1972) *Planta Med.* 21, 374.
4. Saleh, N. A. M., El Sissi, H. I. and Nawwar, M. A. M. (1975) *Phytochemistry* 14, 312.
5. Nawwar, M. A. M., El Sherbieny, A. E. A. and El Ansari, M. A. (1975) *Experientia* 31, 1118.
6. El Ansari, M. A., Nawwar, M. A. M., El Sherbieny, A. E. A. and El Sissi, H. I. (1976) *Phytochemistry* 15, 231.
7. Nawwar, M. A. M. (1970) M.Sc. Thesis, Cairo University.
8. Nawwar, M. A. M. (1974) Ph.D. Thesis, Cairo University.
9. Harborne, J. B. (1975) *Phytochemistry* 14, 1331.
10. Cabrera, J. L. and Jugliani, H. R. (1977) *Phytochemistry* 16, 400.