proton). (Found: C, 64.2: H, 5.8; $C_{20}H_{20}O_7$ requires C, 64.51: H, 5.38%).

Alkali fission of A. (0.015 g) A was refluxed with 50% ethanolic KOH (7 ml) for 15 hr. 10 ml H_2O was added and C_2H_5OH removed. After treatment with Et_2O, the aq. reaction mixture was acidified and extracted with EtOAc. Removal of EtOAc left a gummy residue from which by preparative TLC (Si gel G, C_6H_6–Me_2CO; 9:2), 2,4-dimethoxybenzoic acid, mp 109–110° (lit. mp 108° [3]), (R_f 0.12), and mono-*O*-methylphloroglucinol (R_f 0.42) were obtained. The identity of the above samples was confirmed by comparison with authentic samples (CO-IR).

Compound B. This separated as yellowish–orange needles (0.075 g) from $CHCl_3$–petrol, mp 152–153°. λ_{max}^{MeOH} nm (log ε): 250(3.953), 381(4.522); + $AlCl_3$ + HCl: 255, 410 nm: + NaOAc: 250, 380 nm: + NaOMe: 300, 345 nm; ν_{max}^{KBr} cm^{-1}: 2970, 1625 (Found: C, 66.5; H, 6.0; $C_{19}H_{20}O_6$ requires C, 66.28: H, 5.81%). The acetate of B crystallized from $CHCl_3$–petrol as yellow plates, mp 116–117°; NMR ($CDCl_3$, δ): 2.24 (3H, *s*, —OCOMe), 3.92 (12H, *s*, 4 × —OMe), 6.53 (4H, *br. s*, C-3, C-5, C-3′ and C-5′ protons), 6.91 (1H, *d*, J = 17 Hz, C-α proton), 7.44 (1H, *d*, J = 8 Hz, C-6 proton) and 7.68 (1H, *d*, J = 17 Hz, C-β proton). (Found: C, 65.0; H, 6.0: $C_{21}H_{22}O_7$ requires C, 65.28: H, 5.7%).

Alkali fission of B. 0.01 g B was subjected to alkali fission by the procedure described earlier. By preparative TLC of the reaction mixture in the same solvent system, 2,4-dimethoxybenzoic acid and di-*O*-methylphloroglucinol (R_f 0.66, identified by comparison with an authentic sample) were obtained.

Compound C. This was obtained as orange plates (0.015 g) from EtOAc–C_6H_6, mp 157–159°: λ_{max}^{MeOH} nm (log ε): 250(3.902), 378(4.338): + $AlCl_3$ + HCl: 260, 400 nm: + NaOAc: 255, 395 nm: + NaOMe: 400 nm: ν_{max}^{KBr} cm^{-1}: 3300, 2965, 1615 (Found: C, 65.1: H, 5.7: $C_{18}H_{18}O_6$ requires C, 65.45; H, 5.45%).

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FLAVONOID AGLYCONES FROM *FLOURENSIA*

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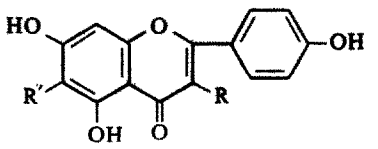
Key Word Index—*Flourensia*; Asteraceae; flavonoids; 5,7-dihydroxyflavanone; methyl ethers of galetin; kaempferol; quercetagetin.

INTRODUCTION

In the continuing biosystematic investigation of the genus *Flourensia* [1, 2] we report here seven flavonoid aglycones from three *Flourensia* taxa. *Flourensia ilicifolia* Blake elaborates a complex mixture of aglycones including: 5,7-dihydroxyflavanone (pinocembrin) (**1**) [3], kaempferol 3-methyl ether (**2**) [4], galetin (6-hydroxykaempferol) 6-methyl ether (**3**) [5], galetin 3,6-dimethyl ether (**4**) [4], quercetagetin 3,6-dimethyl ether (axillarin) (**5**) [6], and quercetagetin 3,6,3′-trimethyl ether (jaceidin) (**6**) [3]. *Flourensia retinophylla* Blake yielded **1** in addition to kaempferol 3,7-dimethyl ether (kumatakenin) (**7**) [7], a flavonol previously reported from *F. cernua* DC [2]. *Flourensia campestris* Griseb. also contains **4** (see Table 1). This is the first report of compounds **1**, **3** and **5** in the Asteraceae [8].

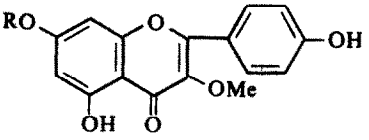
All compounds were isolated and identified by UV, NMR and co-chromatography (TLC) with authentic samples. Spectral values and color reactions for these compounds were identical with previously reported values.



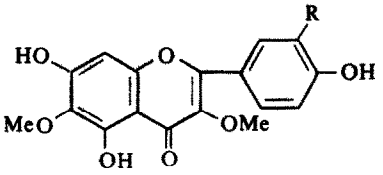
3 R = OH, R′ = OMe
4 R = R′ = OMe

EXPERIMENTAL

Two-dimensional chromatograms employed Whatman 3MM paper and were developed first in TBA (*t*-BuOH–HOAc–H_2O, 3:1:1) and then in 15% HOAc. The NMR spectra were recorded using TMS as an internal standard. Preparation of the TMS ethers and TLC co-chromatography were carried out by standard procedures [3, 8]. Air-dried and powdered leaves (69 g) of *Flourensia ilicifolia* were extracted exhaustively with $CHCl_3$. The combined extracts were taken to dryness *in vacuo*, yielding a dark green syrup (5.8 g). This syrup was chromatographed over polyamide (150 g packed in the first elution solvent); the column was initially developed with $CHCl_3$–



2 R = H
5 R = Me



6 R = OH
7 R = OMe

Table 1. Flavonoid aglycones from *Flourensia* taxa

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

* 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 ($CHCl_3$–Me_2CO, 9:1; C_6H_6–MeOH, 9:1). All other taxa (Table 1) were worked up in a similar manner.

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FLAVONOIDS OF *REAUMURIA MUCRONATA* AND *THYMELAEA HIRSUTA*

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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-isoferulylglucuronide, 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