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Phytochemistry, 1979, Vol. 18, pp 510–511. Pergamon Press Printed in England.

TWO NEW QUERCETIN SULPHATES FROM LEAVES OF *FLAVERIA BIDENTIS*

JOSÉ L. CABRERA and HÉCTOR R. JULIANI

Cátedra de Farmacognosia, Dpto. de Farmacia, Facultad de Ciencias Químicas, Universidad Nacional de Córdoba, Estafeta 32, 5000 Córdoba, Argentina

(*Revised received* 21 *September* 1978)

Key Word Index—*Flaveria bidentis* var. *angustifolia*; Compositae; quercetin 3,4′-disulphate and 3,7,4′-trisulphate.

In previous flavonoid studies of the genus *Flaveria*, three flavonol derivatives with a high degree of sulphation: isorhamnetin 3,7-disulphate; quercetin 3-acetyl-7,3′4′-trisulphate and quercetin 3,7,3′,4′-tetrasulphate were isolated [1–3]. The present work reports two new quercetin sulphate derivatives: 3,4′-disulphate (**I**) and 3,7,4′-trisulphate (**II**).

EXPERIMENTAL

Plant source. The leaves of *Flaveria bidentis* var. *angustifolia* O. Kuntze were collected in the neighbourhood of the Ciudad Universitaria (Córdoba, Rep. Argentina) during February and March, and identified by Prof. Ing. Agr. Armando T. Hunziker (Botanical Museum, National University of Córdoba).

Isolation. 350 g of leaves were dried, ground and extracted with (1) petrol, (2) CH_2Cl_2 and finally with EtOH–H_2O (1:1). The latter extract was concd and a crystalline ppt. (6 g) was obtained by the addition of EtOH. After recrystallization from H_2O, the solid was analysed electrophoretically and chromatographically on Whatman 3 MM paper using the conditions and solvent systems shown in Table 1. By this means four compounds were visualized under UV light, which were separated on a Sephadex G-10 column (23 × 2 cm, 200 mg each time) eluting with H_2O. Quercetin and isorhamnetin 3-sulphates were identified by standard procedures and co-chromatography with authentic samples.

Compound **I**. Chromatographic and electrophoretic data are given in Table 1, mp 285° (dec). Acid hydrolysis gave quercetin (mmp, co-PC and UV data) and sulphate (a white ppt. with $BaCl_2$). UV λ_{max} (nm) in EtOH–H_2O (1:1): 247 sh, 266 and 334; +NaOMe: 272, 371 with decrease in intensity; +NaOAc: 272 and 370; +$AlCl_3$ + HCl: 274,345 and 400. IR (KBr disc) ν_{max} cm^{-1}: 3350 (OH), 1640 (CO), 1250 and 1040 (SO). NMR (DMSO-d_6, 60 MHz): δ 5.9 (1H, *d*, $J_{6,8}$ = 2 Hz, C6); 6.1 (1H,*d*, $J_{8,6}$ = 2 Hz, C8); 7.05 (1H, *d*, $J_{5',6'}$ = 9 Hz, C5′) and 7.40 (2H, *br*, C2′, 6′). (Found: S, 11.27%. Cal. for $C_{15}H_8O_{13}S_2K_2$: S, 11.91%). The electrophoretic, spectral properties and dark colour (UV/+HN_3) suggest that this compound is a 3,4′ disubstituted quercetin derivative. Methylation followed by acid hydrolysis gave a product with the UV properties of quercetin 5,7,3′-tri-*O*-methyl ether. Partial hydrolysis gave four products, which were eluted and analysed for their UV and electrophoretic properties (Table 1). The first, R_f 0.00 was identified as quercetin, the second at R_f 0.11 as quercetin 4′-sulphate (λ_{max} in MeOH, nm: 251, 264 sh and 365; +NaOMe: 276, 407 with decrease in intensity; +NaOAc: 276 and 391; +$AlCl_3$ + HCl: 262 and 403), the third with R_f 0.37 as quercetin 3-sulphate and the last, R_f 0.82 was unchanged 3,4′-disulphate.

Table 1. Chromatographic and electrophoretic properties of the new flavonol sulphates, their partial hydrolysis products and other quercetin sulphates

Flavonol	R_f values (× 100) H_2O	BAW	15% HOAc	Electrophoretic mobility*
Isorhamnetin 3-sulphate	43	47	40	1.17
Quercetin 3-sulphate	37	39	35	1.00
Quercetin 4′-sulphate	11	51	17	0.39
Quercetin 3,4′-disulphate	82	20	79	4.80
Quercetin 3,7,4′-trisulphate	90	05	87	7.0
Quercetin 3-acetyl-7,3′,4′-trisulphate†	88	14	86	7.1
Quercetin 3,7,3′,4′-tetra-sulphate†	92	05	91	8.2

* Relative to quercetin 3-sulphate, run at pH 2.2 (formic acid–acetic acid) for 5 hr at 10 V/cm.

† Isolated from *Flaveria bidentis* [1, 2].

Compound **II**. Acid hydrolysis yielded quercetin and sulphate only. UV λ_{max} (nm) in EtOH–H_2O (1:1): 270 and 322; +NaOMe: 276, 369 with decrease in intensity; +NaOAc; 270 and 361; +$AlCl_3$ + HCl: 391, 342, 300 sh and 278. Partial hydrolysis gave 5 products, identified by UV data, chromatographic and electrophoretic properties as: (1) quercetin; (2) quercetin 4′-sulphate; (3) quercetin 3-sulphate; (4) compound **I** and (5) unchanged compound **II**. There was an insufficient amount of the compound for IR, NMR and MS studies, but the UV

data, partial hydrolysis products and its high mobility in aqueous solvents and on electrophoresis compared with other quercetin sulphates (Table 1), suggesting that it is quercetin 3,7,4,'-trisulphate.

Acknowledgements—The authors are indebted to Dra. Blanca B. de Deferrari (Fac. de Ciencias Exactas y Naturales, Univ. Nac. de Buenos Aires, Rep. Argentina) for the sulphur determination.

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Phytochemistry, 1979, Vol. 18, pp. 511–512 © Pergamon Press Ltd Printed in England. 0031-9422/79/0301-0511 $02.00/0

A NEW BENZOPHENANTHRIDINIC BASE FROM *FAGARA MAYU*

ESTRELLA M. ASSEM, ISABEL A. BENAGES and SEM M. ALBONICO
Facultad de Farmacia y Bioquimica, Junin 956, 1113 Buenos Aires, Argentina

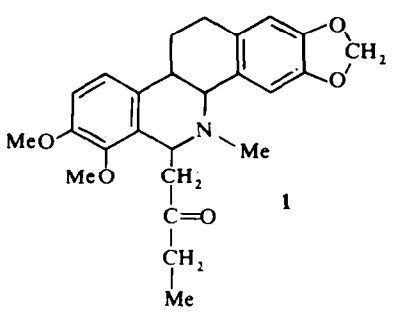
(*Received* 3 *July* 1978; *revised received* 19 *September* 1978)

Key Word Index—*Fagara mayu*; Rutaceae; alkaloid; 11-(2'-ketobutane)-dihydrochelerythrine; synthesis.

During an investigation of the chemical constituents of South American *Fagara* species [1], several bases were isolated from an extract of the bark of *F. mayu* (Bert. ex Hook. et Arn.) Engler [2]. From this extract a new base was isolated in low yield (0.001%).

The UV spectrum suggested that it belonged to the 1,2,8,9-tetrasubstituted benzophenanthridinic group [3]. The MS fragmentation was characteristic of 11-substituted benzophenanthridines with a parent peak [4] at *m/e* 348 (100%) (M^+-71). The PMR spectrum confirmed the presence of an 11-substituted dihydrochelerythrine and also established the nature of the substituent. The signal of the proton on C-11 is a quartet centred at δ 5.05 with $J_{AX} = 5$ Hz and $J_{BX} = 10$ Hz, showing that the substituent is a $-CH_2-$ [4], whose signals were overlapped with those corresponding to another $-CH_2-$ at δ 1.9–2.59. Furthermore, a C—Me signal at δ 0.99, together with the IR spectrum (ν_{max} 1700 cm^{-1}) suggested a 2-ketobutane as the substituent on C-11.

The proposed structure **1** was confirmed by comparison with a synthetic sample prepared by reaction between chelerythrine and 2-butanone in an alkaline medium.



1

A closely related base, 11-acetonyldihydrochelerythrine has been isolated from *Toddalia aculeata* [5] and *Zanthoxylum tsihanimposa* [4], a plant belonging to a genera connected with *Fagara* [6]. The possibility that 11-substituted dihydrochelerythrines are an isolation artifact was discussed by Manske *et al.* [7] and by Poisson *et al.* [4]. However, no 2-butanone was used during the isolation procedure in the present work.

EXPERIMENTAL

The sources of the plant material were as previously indicated [2].

Isolation of 11-(2'-*ketobutane*)-*dihydrochelerythrine* **1**. The alkaloid mixture contained in a MeOH extract of the bark was partially resolved by extraction from an aq. soln with $CHCl_3$ at different pHs. The fraction extracted at pH 10 (0.8 g) was transferred to Si gel (40 g). Elution of the column with $CHCl_3$–EtOAc (1:1) afforded 25 mg of **1** from EtOAc, mp 206–208.5°. (Found: C, 71.4; H, 6.15; N, 3.5. $C_{25}H_{25}NO_5$ requires: C, 71.6; H, 6.01; N, 3.37%). MS *m/e*: 419 (12), 349 (22), 348 (100), 333, 332 (17), 318 (12), 304, 290 (15), 276, 261, 247, 233, 218. PMR 60 MHz ($CDCl_3$, TMS int. stand.): δ 0.99 (3H, *t*, *J* = 8 Hz, C-Me), 1.90–2.59 (4H, *m*, $-CH_2-$), 2.63 (3H, *s*, N—Me), 3.9 (3H, *s*, O—Me), 3.93 (3H, *s*, O—Me), 5.05 (1H, *q*, $J_{AX} = 5$ Hz, $J_{BX} = 10$ Hz, C-11), 6 (2H, *s*, $-O-CH_2-O$), 6.92 (1H, *d*, *J* = 8.5 Hz, C-3) 7.09 (1H, *s*, C-7), 7.40 (1H, *d*, *J* = 9.8 Hz, C-6), 7.5 (1H, *s*, C-10), 7.58 (1H, *d*, *J* = 8.5 Hz, C-4), 7.75 (1H, *d*, *J* = 9.8 Hz, C-5). Insufficient material precluded optical rotation measurements.

Synthesis of **1**. Chelerythrine chloride (5 mg) in 2-butanone (1 ml) containing 1.4 M Na_2CO_3 (0.2 ml) was heated for 6 hr at 80°. After usual work-up, the product was crystallized from EtOAc, giving 3 mg of **1**, mp 206–208°, identical with the alkaloid isolated from *F. mayu*.

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