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COUMARINS FROM *KIELMEYERA ARGENTEA*

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Key Word Index—*Kielmeyera argentea*; Guttiferae stems; 4-*n*-propylcoumarin; neoflavonoid.

Abstract—Two new prenylated 4-*n*-propylcoumarins, 7-hydroxy-8-(4-cinnamoyl-3-methyl-1-oxobutyl)-4-*n*-propyl-2′,2′-dimethyl 2H,6H-benzo[1,2-b:3,4-b′]-dipyran-2-one and 5-hydroxy-6-(4-cinnamoyl-3-methyl-1-oxobutyl)-4-*n*-propyl-2′,2′-dimethyl-2H,6H-benzo [1,2-b:3,4-b′]-dipyran-2-one, besides two known prenylated 4-phenylcoumarins, 7-hydroxy-8-(4-cinnamoyl-3-methyl-1-oxobutyl)-4-phenyl-2′,2′-dimethyl 2H,6H-benzo [1,2-b:3,4-b′]-dipyran-2-one and 5-hydroxy-6-(4-cinnamoyl-3-methyl-1-oxobutyl)-4-phenyl-2′,2′-dimethyl-2H,6H-benzo [1,2-b:3,4-b′]-dipyran-2-one, were isolated from the hexane extract of stems of *Kielmeyera argentea*. These compounds were identified by comparison with literature data, and their spectroscopic properties. © 1998 Elsevier Science Ltd. All rights reserved

INTRODUCTION

As part a developing investigation of the chemistry of the genus *Kielmeyera*, we have examined two species which occur in the sand dunes (restinga) on the coast of Bahia state, Brazil. Previous work on some *Kielmeyera* species, found in the cerrado (savanna) of the Central Brazilian plateau, described xanthones as the principal constituents [1–9]. From two restinga species, *K. reticulata* [10] and *K. argentea*, we isolated only prenylated 4-phenyl and 4-*n*-propylcoumarins; no xanthones were found.

RESULTS AND DISCUSSION

Four coumarins were isolated from the hexane extract of the stems of *K. argentea* by chromatographic methods. Their structures resembled those early in previously in the genus M*ammea* [11, 12, 13] and are distinguishable from them only by the oxidation and subsequent esterification of the 4″-OH in the acyl side-chain with cinnamic acid.

Compounds **1** and **2** have been previously isolated from *K. reticulata* [10] and were identified from spectroscopic data and by comparison with authentic samples.

The molecular formulae of the isomeric compounds **3** and **4**, $C_{31}H_{32}O_7$, were deduced by EI mass spectrometry, $[M]^+$ m/z 516 and by the count of 29 signals in the ^{13}C NMR, spectrum comprising two CH signals, δ 128.7 and δ 129.3 in **3** and δ 128.5 and δ 129.5 in **4**, twice the intensity of the others. The attached hydrogens were established by ^{1}H NMR, DEPT, and $^1H-^{13}C$ COSY (J = 140 Hz) experiments.

The ^{1}H NMR spectra of compounds **3** and **4** are very similar (Table 1). Both showed signals for the 2,2-dimethylchromene ring, a 3-H singlet, one hydroxyl hydrogen-bonded to a 4-cinnamoyl-3-methyl-1-oxobutyl side-chain and a 4-*n*-propyl group. The singlets at δ 6.01 and at δ 5.92, respectively, in compounds **3** and **4**, are a indication of the C-4 substitution in the coumarin ring. Both pairs of triplets at δ 2.89 and δ 1.04, and δ 2.90 and δ 1.0, respectively, in compounds **3** and **4**, suggested the presence of the *n*-propyl group at C-4, later confirmed by ^{13}C NMR.

The ^{13}C NMR spectra of the both compounds, **3** and **4** (Table 1) are also similar and confirmed the presence of the above groups and suggested that they are situated at different positions in a common 4-*n*-propylcoumarin nucleus. The unequivocal assignments of these groups were obtained by $^1H-^{13}C$ COSY long-range correlations. In **3**, the correlations (Table 2) of the signal at δ 6.01 (3-H) with the resonance δ 103.3 allowed the assignment of this signal to C-4a. Thus, the correlations of hydrogen at δ 14.38 (7-OH) with the resonances at δ 106.5 (C-6); δ 105.1 (C-8), and at δ 163.4 (C-7), allowed placement of the OH at C-7 and the 2,2-dimethylchromene ring at C-5 and C-6. Otherwise in compound **4**, the correlations

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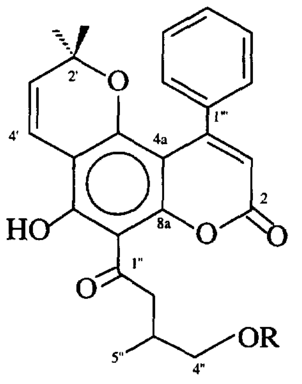

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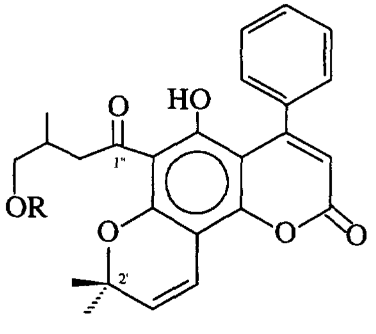

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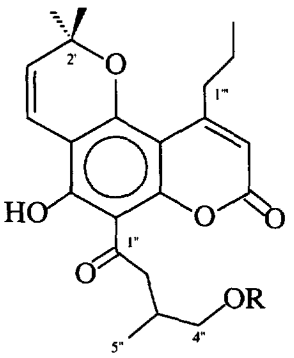

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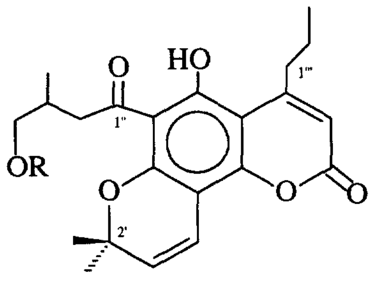

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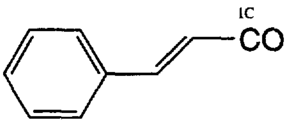

of the signal at δ 15.23 (5-OH) with δ 103.9 (C-4a), δ 107,9 (C-6), and δ 165.5 (C-5), and that of the signal at δ 5.92 (H-3) with δ 103.9 (C-4a) established the position of the OH at C-5 and the 2,2-dimethylchromene ring at C-7 and C-8. Finally, the larger bathochromic shift of the long wavelength band for **4** (356 to 396 nm) than for **3** (367 to 383 nm) after addition of alkali, which is characteristic of 6-acylcoumarins [11], was in agreement with the structures proposed.

EXPERIMENTAL

UV: MeOH and MeOH/NaOH. EIMS: probe at 70 eV. NMR: Gemini 300-Varian.

Plant material.

K. argentea Saad, was collected in the sand dunes of Parque Metropolitàno da Lagoa do Abaeté, Salvador, Bahia, Brazil, in August 1995. A voucher specimen, N° 026392, is deposited in the 'Alexandre Leal Costa' Herbarium, Instituto de Biologia, Universidade Federal da Bahia, Salvador, Brazil.

Extraction and isolation.

Dried stems were extracted with hexane. The extract (97 g) was concd under red. pres. and then submitted to a chromatography on a silica gel column using a hexane-EtOAc gradient. Some frs were rechromatographed by silica gel CC using a hexane-EtOAc gradient to give **1** (0056 g), **2** (0.581 g), **3** (0.034 g), and **4** (0.086 g).

Compound **1**: 7-hydroxy-8-(4-cinnamoyl-3-methyl-1-oxobutyl)-4-phenyl-2',2'-dimethyl-2H,6H-benzo[1,2-b:3,4-b']-dipyran-2-one. $C_{34}H_{30}O_7$. See ref. [10].

Compound **2**: 5-hydroxy-6-(4-cinnamoyl-3-methyl-1-oxobutyl)-4-phenyl-2',2'-dimethyl-2H,6H-benzo [1,2-b:3,4-b']-dipyran-2-one. $C_{34}H_{30}O_7$. See ref. [10].

Table 1. ^1H (300 MHz) and ^{13}C (75 MHz) NMR data for compounds **3** and **4** [$CDCl_3$, δ].

	3		**4**	
H/C	^1H	^{13}C	1H	^{13}C
2		159.5		160.4
3	6.01, 1H, *s*	111.2	5.92, 1H, *s*	111.0
4		158.9		158.1
4a		103.3		103.9
5		157.3		165.5
6		106.5		107.9
7		163.4		155.8
8		105.1		102.2
8a		157.8		159.8
2′		80.3		80.4
3′	5.54, 1H, *d*(10.1 Hz)	126.9	5.59, 1H, *d* (10.0 Hz)	126.9
4′	6.70, 1H, *d* (10.1 Hz)	116.4	6.83, 1H, *d* (10.0 Hz)	116.2
5′	1.51, 3H, *s*	28.8	1.55, 3H, *s*	28.7
6′	1.51, 3H, *s*	28.8	1.57, 3H, *s*	28.8
1″		205.6		206.5
2a″	3.27, 1H, *dd*(6.2, 16.2 Hz)	49.4	3.09, 1H, *dd*(7.2; 16.8 Hz)	49.3
2b″	3.38, 1H, *dd*(7.2, 16.2 Hz)		3.29, 1H, *dd*(6.5; 16.8 Hz)	
3″	2.67, 1H, *m*	30.7	2.70, 1H, *m*	30.1
4a″	4.16, 1H, *dd*(6.7, 10.8 Hz)	69.4	4.17, 1H, *dd*(6.4, 11.1 Hz)	69.3
4b″	4.23, 1H, *dd*(5.8, 10.8 Hz)		4.21, 1H, *dd*(5.5, 11.1 Hz)	
5″	1.14, 3H, *d*(6.9 Hz)	17.9	1.12, 3H, *d*(6.8 Hz)	17.9
1‴	2.89, 2H, *m*	39.5	2.90, 2H, *t*(7.6 Hz)	39.0
2‴		23.8		23.2
3‴	1.04, 3H, *t*(7.3 Hz)	14.5	1.00, 3H, *t*(7.3 Hz)	14.5
5-OH			15.23, 1H, *s*	
7-OH	14.38, 1H, *s*			
1C		167,3		167.3
2C	6.38, 1H, *d*(16.0 Hz)	118.6	6.37, 1H, *d*(16.0 Hz)	118.3
3C	7.63, 1H, *d* (16.0 Hz)	145.2	7.61, 1H, *d*(16.0 Hz)	145.5
4C		135.1		134.8
Phenyl	7.37, 3H, *m*	128.7(×2)	7.38, 3H, *m*	128.5(×2)
(cinnamoyl)	7.50, 2H, *m*	129.3(×2)	7.46, 2H, *m*	129.5(×2)
		130.7		130.9

Table 2. $^1H-^{13}C$ COSY ($J = 9.0$ Hz) for compounds **3** and **4**.

δ(H)	δ(C)
Compound 3	
5.54(3′)	106.5(6)
6.01(3)	103.3(4a); 159.5(2)
6.70(4′)	157.3(5)
14.38(7-OH)	105.1(8); 106.5(6); 163.4(7)
Compound 4	
5.59(3′)	102.2(8);
5.92(3)	103.9(4a); 160.4(2)
6.83(4′)	158.1(8a)
15.23(5-OH)	103.9(4a); 107.9(6); 165.5(5)

Compound 3: 7-hydroxy-8-(4-cinnamoyl-3-methyl-1-oxobutyl)-4-n-propyl-2′,2′-dimethyl-2H,6H-benzo [1,2-b:3,4-b′]-dipyran-2-one. $C_{31}H_{32}O_7$. Amorphous yellow-greenish solid. ^1H NMR (Table 1). ^{13}C NMR (Table 1). EIMS (probe) 70 eV *m/z* (rel. int): 516 $[M]^+$ (13), 501 (21), 387 (8), 369 (9) 368 (30), 367 (10), 355 (10), 354 (23), 353 (100), 325 (9), 313 (11), 311 (9), 297 (13), 269 (7), 269 (7), 149 (10), 148 (27), 147 (40), 131 (73), 103 (35), 102 (10), 91 (11), 77 (19). $[\alpha]^{24}_D - 11.05°$ ($CHCl_3$, 4.6 mg ml^{-1}).

Compound 4: 5-hydroxy-6-(4-cinnamoyl-3-methyl-1-oxobutyl)-4-n-propyl-2′,2′-dimethyl-2H,6H-benzo [1,2-b:3,4-b′]-dipyran-2-one. $C_{31}H_{32}O_7$. Amorphous yellow-greenish solid. ^1H NMR (Table 1). ^{13}C NMR (Table 1). EIMS (probe) 70 eV *m/z* (rel. int): 516 $[M]^+$ (3), 368 (12), 353 (43), 354 (10), 313 (10), 311 (11), 297 (18), 148 (25), 147 (35), 132 (10), 131 (100), 103 (41), 102 (11), 91 (12), 77 (20). $[\alpha]^{24}_D + 3,26°$ ($CHCl_3$, 4.9 mg ml^{-1}).

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REFERENCES

1. Gottlieb, O. R., Magalhães, M. T., Camey, M., Mesquita, A. A. L. and Corrêa, D. B., *Tetrahedron*, 1966, **22**, 1777.
2. Gottlieb, O. R., Magalhães, M. T., Pereira, M. O. S., Mesquita, A. A. L., Corrêa, D. B. and Oliveira, G. G., *Tetrahedron*, 1968, **24**, 1601.
3. Gottlieb, O. R., Mesquita, A. A. L., Da Silva, E. M. and Melo, M. T., *Phytochemistry*, 1969, **8**, 65.
4. Gottlieb, O. R. and Stefani, G. M., *Phytochemistry*, 1970, **9**, 453.
5. Corrêa, D. B., Silva, L. G. F., Gottlieb, O. R., Gonçalves, S. J., *Phytochemistry*, 1970, **9**, 447.
6. Gottlieb, O. R., Mesquita, A. A. L., de Oliveira, G. G. and de Melo, M. T., *Phytochemistry*, 1970, **0**(9), 2537.
7. Gottlieb, O. R. and Nagem, T. J., *Rev. Latinoam. Quim.*, 1977, **8**, 137.
8. Lopes, J. L. C., Lopes, J. N. C., Gilbert, B. and Bonini, S. E., *Phytochemistry*, 1977, **16**, 1101.
9. Nagem, T. J. and Silva, M. A., *Phytochemistry*, 1988, **27**, 2961.
10. Cruz, F. G., David, J. M., Guedes, M. L. S., Chávez, J. P., Moreira, L. M. *Phytochemistry*, 1998, **47**(7), 1363.
11. Crombie, L., Games, D. E. and McCromick, A., *J. Chem. Soc.*(*C*), 1967, **0**, 2545.
12. Carpenter, I., McGarry, E. J. and Scheinmann, F., *J. Chem. Soc.*(*C*), 1971, **0**, 3783.
13. Crichton, E. G., Waterman, *Phytochemistry*, 1978, **17**, 1783.