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Counlarins, limonoids and an alkaloid from *Clausena excavata*

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Abstract

In addition to a known alkaloid, some limonoids and coumarins, the new coumarins excavatins A–M have been isolated from *Clausena excavata*. Their structures have been assigned by NMR and CD investigations. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: *Clausena excavata*; Rutaceae; Coumarins; Excavatins A–M

1. Introduction

Clausena excavata (Rutaceae) is a 1.5 m high bush growing wild and cultivated (Do Tat Loi, 1991) from India and South China through Southeast Asia (Perry, 1980). The plant is used as a remedy to treat paralysis, ulcerated nose, colic, stomach trouble, fever and headache. It is insecticide, tonic and vermifuge (Perry, 1980). The constituents of *Clausena excavata* have been frequently studied. The plant contains above all carbazole alkaloids (e.g. Ito et al., 1997), coumarins (e.g. Shiow-Chyn Huang, Pei-Lin Wu, & Tian-Shung Wu, 1997) and limonoids (e.g. Tian Shung Wu, Shiow Chyn Huang, & Jeng Shiow Lai, 1993). In the present study we isolated the carbazole alkaloid clauszoline-M (Ito et al., 1997) (yield 0.020%), the coumarins anisocoumarin H (Ngadjui, Ayafor, & Sondengam, 1989a) (yield 0.0051%), 5-geranyloxy-7-hydroxycoumarin (Ito, Ohta, Hugh, Tan, & Furukawa, 1996) (yield 0.0016%),7-[(*E*)-7′-hydroxy-3′,7′-dimethyl-octa-2′,5′dienyloxy]coumarin (Quader, El-Turbi, Armstrong, Gray, & Waterman, 1992) (yield 0.0007%), (5′*R*)-7-[4-(2,5-dihydro-3-methyl-2-oxo-5-furanyl)-2,3-epoxy 3-methylbutyloxylcoumarin (**11**, in this study called excavatin K, in Bohlmann and Clausen (1970) no configuration at C-5′ and specific rotation given) (yield 0.31%), the limonoids clausenarin (Ngadjui, Ayafor, & Sondengam, 1989b) (yield 0.012%), clausenolide (Ngadjui et al., 1989b) (yield 0.0026%), 1-*O*-methylclausenolide (Tian Shung Wu et al., 1993) (yield 0.0082%) and the new coumarins excavatins A (**1**) (yield 0.0018%), B (**2**) (yield 0.0019%), C (**3**) (yield 0.0007%), D (**4**) (yield 0.50%), E (**5**) (yield 0.077%), F (**6**) (yield ca 0.0002%), G (**7**) (yield 0.0049%), H (**8**) (yield ca. 0.0001%), 1 (**9**) (yield 0.0059%), J (**10**) (yield 0.0029%), L (**12**) (yield 0.028%) and M (**13**) (yield 0.0052%).

2. Results and discussion

The elemental compositions of the excavatins A–M (**1**–**13**) were established by high-resolution mass spectrometry (Section 3, for **1** only the [M–H2O]+ peak observed). Their structures were elucidated by detailed by NMR investigations (Tables 1 and 2) including

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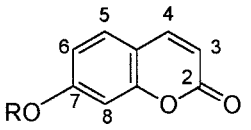

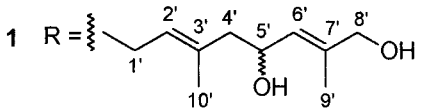

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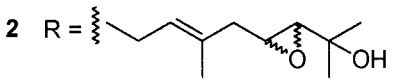

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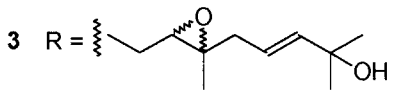

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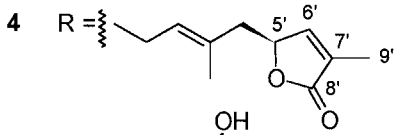

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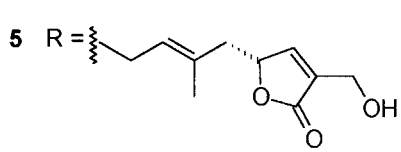

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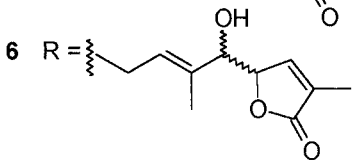

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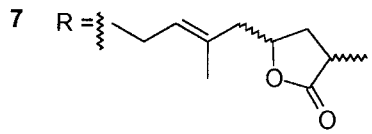

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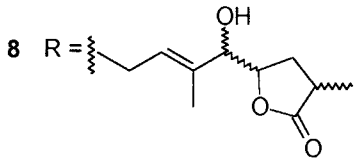

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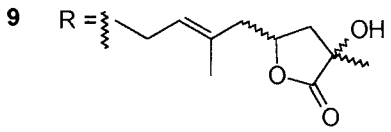

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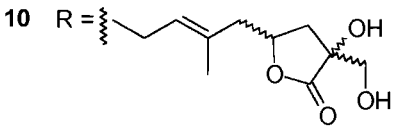

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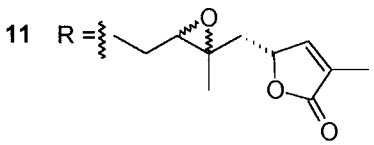

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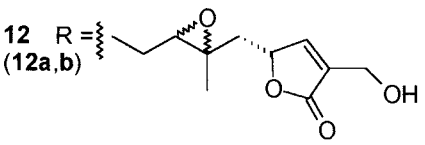

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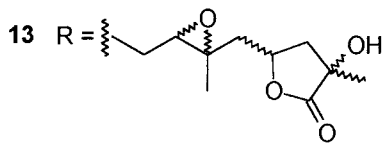

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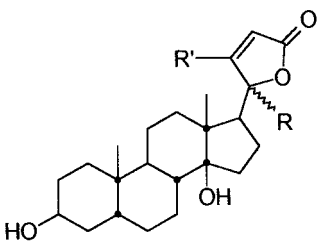

14 R = α-H, R' = H
15 R = α-H, R' = Me
16 R = β-H, R' = H

APT, ^{1}H–^{1}H DQF COSY, gradient selected HSQC, gradientselected HMBC and NOESY measurements. The compounds **1**–**13** showed similar ^{1}H and ^{13}C chemical shifts and proton coupling patterns for the coumarin moieties (Tables 1 and 2). In each case (except **2** and **10**, for which no HMBC spectra were recorded), a long-range correlation between H-1′A/B and C-7 of the coumarin skeleton was observed, indicating the side chain attached to C-7. The structures of the different side chains were elucidated by combined use of homo- and heteronuclear 2D NMR experiments, whereby the most useful information was

Table 1
^{1}H NMR data of the coumarins [499.8 MHz, δ values, J (Hz) in parentheses]

^{1}H	**1**[a]	**2**[a]	**3**[a]	**4**[a]	**5**[b]	**6**[a]	**7**[a]	**8**[a]	**9**[a]	**10**[c]	**11**[a]	**12a**[a]	**12b**[a]	**13**[a]
3	6.25 d (9.5)	6.26 d (9.5)	6.27 d (9.5)	6.25 d (9.5)	6.26 d (9.5)	6.26 d (9.5)	6.26 d (9.5)	6.26 d (9.5)	6.26 d (9.5)	6.23 d (9.5)	6.28 d (9.5)	6.27 d (9.5)	6.27 d (9.5)	6.27 d (9.5)
4	7.64 (9.5)	7.64 d (9.5)	7.65 d (9.5)	7.65 d (9.5)	7.96 d (9.5)	7.65 d (9.5)	7.65 d (9.5)	7.65 d (9.5)	7.64 d (9.5.)	7.87 d (9.5)	7.65 d (9.5)	7.66 d (9.5)	7.66 d (9.5)	7.64 d (9.5)
5	7.37 d (8.6)	7.37 d (8.6)	7.39 d (8.6)	7.38 d (8.6)	7.60 d (8.6)	7.38 d (8.6)	7.38 d (8.6)	7.38 (8.6)	7.38 d (8.5)	7.52 d (8.6)	7.40 d (8.6)	7.40 d (8.6)	7.40 d (8.6)	7.39 d (8.6)
6	6.84 d (8.6, 2.1)	6.85 dd (8.6, 1.9)	6.89 dd (8.6, 2,4)	6.84 dd (8.6, 2.4)	6.94 dd (8.6, 2.4)	6.85 dd (8.6, 2,5)	6.85 dd (8.6, 2,3)	6.85 dd (8.6, 2.4)	6.85 dd (8.5, 1.9)	6.92 dd (8.6, 2,4)	6.90 dd (8.6, 2,4)	6.90 dd (8.6, 2,4)	6.90 dd (8.6, 2.4)	6.90 dd (8.6, 2,4)
8	6.81 d (2.1)	6.82 d (1.9)	6.85 d (2.4)	6.80 d (2.4)	6.98 d (2.4)	6.80 d (2.5)	6.81 d (2.3)	6.79 d (2.5)	6.81 d (1.9)	6.89 d (2.4)	6.28 d (2.4)	6.86 d (2.4)	6.86 d (2.4)	6.86 d (2.4)
1′	4.62 d (6.4)	4.63 d (6.5)	4.26 dd (10.9, 4.0) 4.10 dd (10.9, 6.3)	4.63 d (12.6, 6.4) 4.62 dd (12.6, 6.4)	4.68 d (6.5)	4.59 m	4.62 d (6.2)	4.67 m	4.62 d (6.2)	4.69 d (6.4)	4.34 dd (11.1, 3.7) 4.09 dd (11.1, 6.4)	4.34 dd (11.1, 3.8) 4.09 dd (11.1, 6.4)	4.30 dd (11.0, 4.0) 4.13 dd (11.0, 6.2)	4.34 dd (11.2, 3.7) 4.08 dd (11.2, 6.3)
2′	5.58 t (6.4)	5.60 t (6.5)	3.19 dd (6.3, 4.0)	5.62 ttq (6.4, 1.0, 1.4)	5.56 tq (6.5, 1.3)	5.89 tdq (6.5, 1.3)	558 m	5.92 tdq (6.2, 1.3, 1.3)	5.60 t (6.2)	5.62 tq (6.4, 1.3)	3.20 dd (6.4, 3.7)	3.21 dd (6.4, 3.8)	3.47 dd (6.2, 4.0)	3.21 dd (6.3, 3.7)
4′	2.34 dd (13.5, 8.6)	2.33 d (5.7)	2.38 ddd (14.1, 7.3, 1.1)	2.44 d (14.3, 6.0)	2.53 dd (14.3, 4.8)	4.28 br d (5.4)	2.50 dd (14.5, 7.6)	4.43 br d (4.0)	2.53 dd (14.2, 7.8)	2.53 dd (14.2, 7.6)	1.92 dd (14.3, 5.0)	1.97 dd (14.3, 5.0)	211 m	2.93 dd (14.4, 4.7)
	2.26 dd (13.5, 4.6)		2.32 ddd (14.1, 6.7, 1.2)	242 dd (14.3, 7.5)	2.27 dd (14.3, 8.4)		2.34 dd (14.5, 6.3)		2.37 dd (14.2, 5.3)	2.43 dd (14.2, 5.7)	1.85 dd (14.3, 8.8)	1.91 dd (14.3, 8.7)		1.90 dd (14.4, 8.6)
5′	4.60 m	3.14 td (5.7, 2.0)	5.63 ddd (15.6, 7.2, 6.7)	5.30 dddq (7.5, 6.0, 1.7, 1.9)	523 m	4.95 ddq (5.4, 1.6, 1.9)	4.70 m	4.50 ddd (10.0, 6.1, 4.0)	4.81 m	4.82 m	5.12 m	5.22 m	5.03 dddt (7.1, 5.4, 1.8, 1.8)	4.87 m
6′	5.48 d (8.4)	2.75 d (2.0)	5.75 dt (15.6, 1.2)	7.05 dq (1.6, 1.6)	7.42 dt (1.7, 1.7)	7.10 dq (1.6, 1.6)	2.17 ddd (12.9, 9.0, 4.8) 2.02 ddd (12.9, 7.6, 7.6)	2.25 ddd (15.2, 9.1, 6.1) 1.89 m	2.46 dd (13.6, 5.7) 1.82 dd (13.6, 9.3)	2.21 m	7.11 dq (1.6, 1.6)	7.38 dt (1.6, 1.6)	7.34 dt (1.8, 1.8)	2.53 dd (13.6, 5.7) 1.84 dd (13.6, 9.3)
7′	–	–	–	–	–	–	2.71 m	2.69 ddq (11.7, 9.1, 7.1)	–	–	–	–	–	–
8′	4.02 s	1.31 s	1.33 s	–	–	–	–	–	–	–	–	–	–	–
9′	1.73 s	1.24 s	1.33 s	1.92 dd (1.9, 1.6)	ca 4.11 m	1.94 dd (1.9, 1.6)	1.29 d (7.4)	1.28 d (7.1)	1.52 s	3.74 d (10.9) 3.50 d (10.9)	1.94 dd (2.0, 1.7)	4.46 dd (1.8, 1.8)	4.46 dd (1.8, 1.8)	1.52 s
10′	1.83 d	1.84 s	1.36 s	1.85 br s (1.3)	1.79 d (1.3)	1.87 d (1.3)	1.83 s	1.80 d (1.3)	1.83 s	1.85 d (1.3)	1.52 s	1.52 s	1.45 s	1.47

[a] $CDCl_3$.
[b] DMSO-d_6.
[c] CD_3OD.

Table 2
^{13}C NMR data of the coumarins (125.7 MHz, δ values)

^{13}C	**1**[a]	**2**[a]	**3**[a]	**4**[a]	**5**[b]	**6**[a]	**7**[a]	**8**[a]	**9**[a]	**10**[c]	**11**[a]	**12a**[a]	**12b**[a]	**13**[a]
2	161.3	161.2	161.3	161.2	160.3	161.1	161.2	161.1	161.3	163.4[d]	161.0	161.2	161.2	161.1
3	113.0	113.1[d]	113.4	113.01[d]	112.5	113.2	113.0	113.2	113.0[d]	113.3	113.4	113.3	113.3	113.4
4	143.5	143.4	143.3	143.4	144.4	143.3	143.4	143.3	143.5	145.7	143.3	143.5	143.5	143.3
4a	112.5	112.5	112.9	112.5	112.4	112.7	112.5	112.6	112.5	114.0	113.0	112.9	112.9	113.0
5	128.8	128.7	128.8	128.8	129.4	128.8	128.8	128.8	128.8	130.4	128.9	128.9	128.9	128.9
6	113.2	113.0[d]	112.8	112.95[d]	112.9	113.0	113.0	113.0	113.1[d]	114.4	112.8	113.0	113.0	112.9
7	162.0	161.9	161.6	161.8	161.6	161.6	161.8	161.7	161.8	163.7[d]	161.5	161.5	161.5	161.5
8	101.5	101.5	101.7	101.5	101.4	101.6	101.6	101.5	101.6	102.5	101.8	101.7	101.7	101.8
8a	155.8	155.8	155.7	155.8	155.4	155.8	155.8	155.8	155.7	15.70	155.7	155.7	155.7	155.7
1′	65.2	65.1	67.6	65.0	65.0	64.8	65.0	64.8	65.0	66.3	67.2	67.1	67.2	67.2
2′	122.1	121.0	59.3	122.9	122.4	122.9	122.4	122.0	122.4	123.7	61.2	61.2	59.0	60.9
3′	138.5	138.2	60.3	136.2	136.4	138.2	137.0	137.4	136.7	138.2	58.2	58.1	58.0	58.2
4′	47.5	41.5	40.8	43.1	42.3	75.7	44.9	74.4	44.8	45.9	42.7	42.3	40.3	44.3
5′	65.9	54.1	120.7	79.3	79.8	81.4	76.3	78.3	76.2	77.7	77.9	78.9	78.1	74.9
6′	127.1	64.6	142.1	148.1	150.0	145.6	35.0	30.0	42.7	39.0	148.4	149.1	149.1	43.1
7′	137.9	67.7	70.7	130.2	133.8	131.6	33.7	34.4	73.5	77.6	130.1	133.9	134.0	73.5
8′	67.7	27.6	29.8	173.8	171.8	173.7	179.7	179.1	177.6	178.7	173.7	172.1	172.1	177.2
9′	14.0	25.0	29.8	10.5	55.3	10.8	15.7	15.1	23.9	64.6	10.6	56.8	56.8	24.0
10′	17.0	17.3	17.2	17.3	16.8	13.7	17.2	14.0	17.1	17.2	17.0	17.0	18.5	17.0

[a] $CDCl_3$.
[b] DMSO-d_6.
[c] CD_3OD.
[d] May be exchanged.

extracted from the ^1H, ^1H COSY and ^1H, ^{13}C long-range correlation (HMBC) spectra. For all side-chain methyl groups (except **2** and **10**, for which no HMBC spectra were recorded) all possible HMBC correlations based on ^1H, ^{13}C couplings over two or three bonds were observed (H_3-9′ → C-6′, C-7′, C-8′; H_3-10′ → C-2′, C-3′, C-4′; for **3** also H_3-8 → C-6′, C-7′, C-9′). Open side chains (**1**–**3**) and those with a five-membered lactone ring (**4**–**13**) were easily distinguishable by the ^{13}C chemical shift of C-8′, which was at relatively high field in the first case and between δ 180 and δ 170 in the latter. All compounds with a C-2′-C-3′ double bond (**1**, **2**, **4**–**10**) showed NOESY cross peaks between H-1′A/B and H_3-10′ on the one hand and between H-2′ and H-4′A/B (H-4′ for **8**) on the other. Thus, all those coumarins have an E-configurated double bond C-2′-C-3′. The E-configuration of the double bond C-6′– C-7′ in **1** was proved by the NOE correlations H-5′/H_3-9′ and H-6′/H_2-8′. For **3** a vicinal coupling constant H-5′/H-6′ of 15.6 Hz was found indicating the *trans*-relationship of these two olefinic protons. As a result of the detailed NMR investigations all ^1H and ^{13}C NMR signals of **1**–**13** could be assigned unequivocally (with the only exception of C-2/C-7 in **10** and C-3/C-6 in **2**, **4** and **9**) (Tables 1 and 2). As indicated in the NMR spectrum excavatin L (**12**) consisted of two epoxy diastereomers **12a** and **12b** in a 3:1 ratio. In the NOESY spectrum, only the major component **12a** showed a cross peak between H-2′ and Me-10′. This suggested *cis* arrangement of both functions whereas **12b** exhibited the corresponding *trans* arrangement. The absolute configurations at C-5′ of the excavatins D (**4**), E (**5**), K (**11**) and L (**12**) were assigned by comparison of their circular dichroism with that of the steroids **14**–**16** (Ripperger, Lindig, & Snatzke, 1998) (Table 3). Because of their similarity the use of the different solvents should have no major influence on the values of the circular dichroism. Compounds **5** and **12** were measured as the acetates to avoid problems arising by hydroxy-double bond hydrogen bridges. The enantiomer of excavatin D (**4**) was already described in the literature (Bohlmann & Clausen, 1970). Because also all efforts to get suitable crystals for X-ray analysis failed, some stereochemical problems remained open in the present study.

3. Experimental

Leaves of *Clausena excavata* Burm. f. were collected in the National Park Cuc Phuong, Ninh Binh, Vietnam in December 1995. The species was identified by Dr. Tran Dinh Dai, Hanoi. A voucher specimen [No. 750 (13.06.1996)] was deposited in the Herbarium of the Institute of Ecology and Natural Resources, National Centre for Natural Science and Technology, Hanoi. The plant material was dried at 45°C, ground (850 g) and extracted with 95% MeOH at room temp. MeOH was removed by destillation in vacuo and the aq. soln was extracted with *n*-hexane followed by

Table 3
Circular dichroism of γ-lactones

Compound	$\Delta\varepsilon_{max}$ (λ_{max}, nm)	Solvent	Refs.
4	+3.2 (216)	MeOH	-
5, acetate	−7.6 (210)	MeOH	–
10	−2.5 (219)	MeOH	–
11	−6.7 (208)	MeOH	–
12a, **b** acetate	−7.1 (208)	MeOH	–
14	+13.3 (209)	EtOH (96%)	(Ripperger et al., 1998)
15	+4.7 (217)	EtOH (96%)	(Ripperger et al., 1998)
16	−11.3 (210)	EtOH (96%)	(Ripperger et al., 1998)

EtOAc and *n*-BuOH. EtOAc and *n*-BuOH were evapd in vacuo. The residue of the EtOAc extract was chromatographed over silica gel with $CHCl_3$ with increasing amounts of MeOH (2–5%) and gave in the following order excavatin D (**4**), excavatin K (**11**), excavatin I (**9**), 7-geranyloxy-5-hydroxycoumarin, anisocoumarin H, excavatin M (**13**), excavatin C (**3**), excavatin E (**5**), a mixture of excavatins F (**6**) and H (**8**), clauszoline-M, excavatin B (**2**), 1-*O*-methylclausenolide, excavatin J (**10**), excavatin A (**1**), clausenolide, excavatin L (**12**) and clausenarin. The residue of the *n*-BuOH extract was chromatographed over silica gel with *n*-hexane–EtOAc (7:3) followed by EtOAc with increasing amounts of MeOH (10–15%) and gave excavatin G (**7**) and anisocoumarin H. The individual compounds were further purified as described below.

*3.1. Excavatin D, (5′S)-7-[(2E)-4-(2,5-dihydro-3-methyl-2-oxo-5-furanyl)-3-methylbut-2-enyloxy]coumarin (**4**)*

M.p. 124–125°C (from Me_2CO); lit. (Bohlmann & Clausen, 1970): 126°. $[\alpha]_D^{21}$ +34.0° ($CHCl_3$, *c* 2.00); lit. (Bohlmann & Clausen, 1970): $[\alpha]_{578}$ −26° (CH_2Cl_2). R_f 0.59 [silica gel, solvent system 1: $CHCl_3$–MeOH (19:1)]. EI-MS (70 eV) *m/z* (rel. int.): 326.1146 $[M]^+$ ($C_{19}H_{18}O_5$, calcd 326.1154) (7), 162.0325 ($C_9H_6O_3$, calcd 162.0316) (850), 97.0291 ($C_5H_5O_2$, calcd 97.0289) (100).

*3.2. Excavatin K, (5′R)-7-[4-(2,5-dihydro-3-methyl-2-oxo-5-furanoyl-2,3-epoxy 3-methylbutyloxy]coumarin (**11**)*

M.p. 112–116°C (from Me_2CO); lit. (Bohlmann & Clausen, 1970): 125°. $[\alpha]_D^{22}$ +12.0° ($CHCl_3$, *c* 2.00). R_f 0.49 (silica gel, solvent system 1). ^1H NMR identical with data of lit. (Bohlmann & Clausen, 1970). EI-MS (70 eV) *m/z* (rel. int.): 342.1102 $[M]^+$ ($C_{19}H_{18}O_6$, calcd 342.1104) (28), 162.0323 ($C_9H_6O_3$, calcd 162.0317) (15), 97.0283 ($C_5H_5O_2$, calcd 97.0289) (100).

*3.3. Excavatin I, 7-[(2E)-4-(2,3,4,5-tetrahydro-3-hydroxy-3-methyl-2-oxo-5-furanyl)-3-methylbut-2-enyloxy]coumarin (**9**)*

M.p. 148–150°C (from $CHCl_3$–MeOH). $[\alpha]_D^{29}$ +22.2° (MeOH, *c* 1.00). R_f 0.25 (silica gel, solvent system 1). EI-MS (70 eV) *m/z* (rel. int.): 344.1247 $[M]^+$ ($C_{19}H_{20}O_6$, calcd 344.1260) (2), 162 (100).

*3.4. Excavatin M, 7-[4-(2,3,4,5-tetrahydro-3-hydroxy-3-methyl-2-oxo-5-furanyl)-2,3-epoxy 3-methylbutyloxy]coumarin (**13**)*

The compound was purified by prep. TLC over silica gel with $CHCl_3$–MeOH (97:3). M.p. 173–175° (from $CHCl_3$). $[\alpha]_D^{25}$ +68.5° ($CHCl_3$, *c* 0.20). R_f 0.24 (silica gel, solvent system 1). EI-MS (70 eV) *m/z* (rel. int.): 360.1215 $[M]^+$ ($C_{19}H_{20}O_7$, calcd 360.1209) (62), 162.0307 ($C_9H_6O_3$, calcd 162.0317) (100).

*3.5. Excavatin C, 7-[(5E)-2,3-epoxy-7-hydroxy-3,7-dimethyloct-5-enyloxy]coumarin (**3**)*

The compound was purified by prep. TLC over silica gel with $CHCl_3$–MeOH (19:1). Oil. $[\alpha]_D^{25}$ +4.6° (MeOH, *c* 0.50). *Rf* 0.25 (silica gel, solvent system 1). EI-MS (70 eV) *m/z* (rel. int.): 330.1430 $[M]^+$ ($C_{19}H_{22}O_5$, calcd 330.1467) (15), 162.0303 ($C_9H_6O_3$, calcd 162.0317) (100).

*3.6. Excavatin E, (5′R)-7-[(2E)-4-(2,5-dihydro-3-hydroxymethyl-2-oxo-5-furanyl)-3-methylbut-2-enyloxy]coumarin (**5**)*

M.p 175–178°C (from Me_2CO–MeOH). $[\alpha]_D^{23}$ −2.7° (pyridine, *c* 1.00). R_f 0.23 (silica gel, solvent system 1). EI-MS (70 eV) *m/z* (rel. int.): 342.1101 $[M]^+$ ($C_{19}H_{18}O_6$, calcd 342.1103) (4), 162.0329 ($C_9H_6O_3$, calcd 162.0317) (100).

*3.7. Excavatin F and H, 7-[(2E)-4-(2,5-dihydro-3-methyl-2-oxo-5-furanyl)-4-hydroxy-3-methylbut-2-enyloxy]coumarin (**6**) and 7-[(2E)-4-(2,3,4,5-tetrahydro-3-methyl-2-oxo-5-furanyl)-4-hydroxy-3-methylbut-2-enyloxy]coumarin (**8**) (mixture)*

This mixture was isolated by prep. TLC over silica gel with $CHCl_3$–MeOH (19:1). R_f 0.27 (silica gel, solvent system 1). EI-MS (70 eV) *m/z* (rel. int.): 344.1280 $[M]^+$ ($C_{19}H_{20}O_6$, calcd 344.1260) (5), 342.1090 $[M]^+$ ($C_{19}H_{18}O_6$, calcd 342.1104), 162 (100).

*3.8. Excavatin B, 7-[(2E)-5,6-epoxy-7-hydroxy-3,7-dimethyloct-2-enyloxy]coumarin (**2**)*

The compound was purified by prep. TLC over

silica gel with EtOAc–*n*-hexane–MeOH (8:2:1). Amorphous. $[\alpha]_D^{25}$ +7.7° (MeOH, *c* 0.25). R_f 0.23 (silica gel, solvent system 1). EI-MS (70 eV) *m/z* (rel. int.): 330.1455 $[M]^+$ ($C_{19}H_{22}O_5$, calcd 330.1467) (20), 162.0319 ($C_9H_6O_3$, calcd 162.0317) (100).

3.9. Excavatin J, 7-[(2E)-4-(2,3,4,5-tetrahydro-3-hydroxy-3-hydroxymethyl-2-oxo-5-furanyl)-3-methylbut-2-enyloxy]coumarin (**10**)

The compound was purified by CC over silica gel with EtOAc–*n*-hexane–MeOH (8:2:1). M.p. 80–82°C (from $CHCl_3$–Me_2CO). $[\alpha]_D^{29}$ +22.1° (MeOH, *c* 0.40). R_f 0.64 [silica gel, solvent system 2: $CHCl_3$–MeOH (17:3)]. EI-MS (70 eV) *m/z* (rel. int.): 360.1182 $[M]^+$ ($C_{19}H_{20}O_7$, calcd 360.1209) (9), 162 (100).

3.10. Excavatin A, 7-[(2E,6E)-5,8-dihydroxy-3,7-dimethylocta-2,6-dienyloxy]coumarin (**1**)

Amorphous. $[\alpha]_D^{26}$ +2.9 (MeOH, *c* 0.50). R_f 0.62 (silica gel, solvent system 2). EI-MS (70 eV) *m/z* (rel. int.): 312.1383 $[M–H_2O]^+$ ($C_{19}H_{20}O_4$, calcd 312.1362) (1) 162 (100). ESI-MS: 353 $[M+Na]^+$.

3.11. Excavatin L, (5′R)-7-[4-(2,5dihydro-3-hydroxymethyl-2-oxo-5-furanyl)-2,3-epoxy 3-methylbutyloxy]coumarin (**12a,b**)

M.p. 123–125°C (from $CHCl_3$–MeOH). $[\alpha]_D^{30}$ +16.1° (CH_2Cl_2, *c* 2.00). R_f 0.17 (silica gel, solvent system 1). EI-MS (70 eV) *m/z* (rel. int.): 358.1094 $[M]^+$ ($C_{19}H_{18}O_7$, calcd 358.1052) (32), 162.0325 ($C_9H_6O_3$, calcd 162.0317) (100).

3.12. Excavatin G, 7-[(2E)-4-(2,3,4,5-tetrahydro-3-methyl-2-oxo-5-furanyl)-3-methylbut-2-enyloxy]coumarin (7)

The compound was purified by CC [silica gel, *n*-hexane–EtOAc (3:2). Amorphous. $[\alpha]_D^{30}$ +39.0° (CH_2Cl_2, *c* 1.00). R_f 0.53 (silica gel, solvent system 1). EI-MS (70 eV) *m/z* (rel. int.): 328.1300 $[M]^+$ ($C_{19}H_{20}O_5$, calcd 328.1311) (4), 162.0315 ($C_9H_6O_3$, calcd 162.0317) (100).

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