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COUMARINS FROM *CLAUSENA ANISATA*

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Key Word Index—*Clausena anisata*; Rutaceae; substituted coumarins; anisocoumarins A, B, C and D.

Abstract—The structures of four new coumarins from the combined stem bark and roots of *Clausena anisata*, anisocoumarins A, B, C and D, have been deduced on the basis of their spectral data and confirmed in some cases by partial synthesis from known compounds.

INTRODUCTION

Clausena anisata (Will) Hook. f. ex Benth. is a small tree which grows in the savanna regions of West Africa [1]. It is widely used as an insect-repellant [1]. Various parts of the plant are used in traditional medicine. A decoction of the leaves is given as a stomachic and laxative after childbirth and is also used for many gastrointestinal disorders. The roots and leaves are boiled to make a mouth wash to relieve toothache and other mouth infections [1, 2]. A root decoction is taken to control convulsions in children and as a tonic by pregnant women (Elwude, J. A., personal communication). *Clausena anisata* is known to contain a number of volatile constituents [3], substituted coumarins [4–6] and carbazole alkaloids [5, 7, 8]. As part of our continuing studies on Cameroonian plants of medicinal interest, we have examined the petrol and chloroform extracts of the combined stem bark and roots of this plant. The present paper reports on the isolation and structural elucidation of the substituted coumarins from these plant parts. Imperatorin [9], xanthoxyletin [9] and the toxic convulsant agent heliettin (**7**) [2, 10, 11] were obtained. It has been reported [9] that imperatorin and xanthoxyletin are antifeedants against the Africa army worm (*Spodoptera exempta* larvae). Gravelliferone methyl ether (**1**) [12], a probable precursor of the furocoumarin, was also isolated along with four new coumarins, anisocoumarins A(**2**), B(**5**), C(**8**) and D(**9**).

RESULTS AND DISCUSSION

The petrol and chloroform extracts of the finely powdered combined stem bark and roots of *C. anisata*, upon repeated column chromatographs, preparative TLC and crystallizations, afforded a mixture of sterols, ten substituted coumarins, six alkaloids and six limonoids. By means of spectroscopic data, published information or comparison with authentic specimens, six of these coumarins were identified as the already known imperatorin [9], xanthoxyletin [9], gravelliferone methyl ether (**1**) [12], heliettin (**7**), [10], 3-(1,1-dimethylallyl)xanthyletin [13] and swietenocoumarin I (**4**) [14]. Four new coumarins, tentatively named anisocoumarins A–D, were also fully characterized.

Anisocoumarin A(**2**) was obtained as a yellow oil which analysed for $C_{17}H_{18}O_4$ (M^+ *m/z* 286). Its UV spectrum (see experimental) was consistent with a coumarin oxygenated at C-7 [15]. The ^1H NMR spectrum of **2** (Table 1) showed two tertiary methyl groups at δ1.45 (6H) and a series of ABX signals at δ5.02, 5.08 and 6.15 (J_{AX} = 18 Hz, J_{BX} = 10 Hz, J_{AB} = 1 Hz) reminiscent of the presence of an 1,1-dimethylallyl group [12]. Three aromatic protons appeared as singlets at δ_H 7.50, 7.22 and 6.80; the values of their chemical shifts indicated that they were H-4, H-5 and H-8 respectively [13]. Furthermore, the spectrum showed signals for one methoxy group at δ_H 3.87 and one formylmethyl group at δ_H 3.80 (2H, *br s*) and 9.67 (1H, *br s*). The presence of this latter group was confirmed by the formation of a dinitrophenylhydrazone derivative and the appearance of a base peak in the EIMS at *m/z* 29. The above data suggested that anisocoumarin A was 3-(1,1-dimethylallyl)-6-formylmethyl-7-methoxycoumarin) (**2**) which is also in accord with biogenetic considerations. Structure **2** has been confirmed by partial synthesis. Oxidative cleavage of swietenocoumarin I(**4**) with sodium periodate in dioxan gave **2**. Reduction of **2** with sodium borohydride in methanol gave the corresponding alcohol **3**.

The second new coumarin (**5**), $C_{14}H_{14}O_4$, exhibited in the IR spectrum, a hydroxyl group and an α,β-unsaturated lactone at 3460 and 1720 cm^{-1}, respectively. Its ^1H NMR (Table 1) spectrum contained a broad singlet at δ 7.35 which disappeared on deuteriation (OH). The aromatic region of the spectrum was well-resolved and showed four doublets of one proton each at δ_H 7.75 (J = 10 Hz), 7.70 (J = 2 Hz), 6.82 (J = 2 Hz) and 6.35 (J = 10 Hz) corresponding respectively to H-4, H-6, H-8 and H-3 [13]. The presence of 3,3-dimethylallyl group was indicated by the presence of two vinylic methyl singlets at δ_H 1.72 and 1.76 and one olefinic triplet at δ_H 5.65 (1H) which was coupled to a two-proton doublet (J = 8 Hz) at δ 5.0.

The presence of the prenyloxy group was further confirmed by the EIMS which showed a strong [$M-C_5H_8$]$^+$ peak. From the above spectral data and

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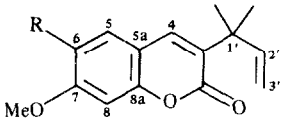
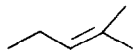
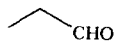
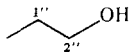
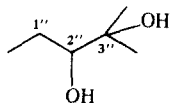
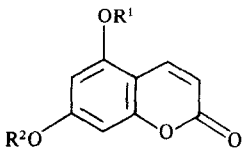


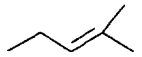
1 R = 

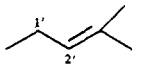
2 R = 

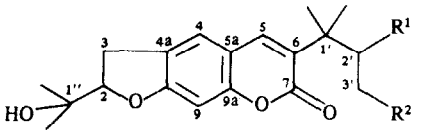
3 R = 

4 R = 



5 R^1 = H, R^2 = 

6 R^2 = H, R^1 = 



7 $R^1 = R^2$ = H $\Delta^{2',3'}$
8 $R^1 + R^2$ = O
9 $R^1 = R^2$ = OH
10 $R^1 = R^2$ = OAc

comparison with the isomer **6** previously obtained by Murray [16] during his synthesis of naturally occurring coumarins, structure **5**, 5-hydroxy-7-(3,3-dimethylallyloxy)coumarin was assigned to anisocoumarin B.

Compounds **8** and **9** showed in the EIMS the same base peak at *m/z* 287 corresponding to the loss of C_2H_3O and $C_2H_5O_2$, respectively, from the molecular ion. The UV spectrum of **9** (see Experimental) was characteristic of a linear furocoumarin and remained unchanged on addition of alkali [17]. The ^{1}H NMR spectra (Table 2) suggested a close relationship to heliettin (**7**) [10]. In addition, the ^{1}H NMR spectrum of anisocoumarin C (**8**) (Table 2) presented a monosubstituted epoxide {δ_H 3.30 (1H, *br m*), 2.90 (1H, *dd*, J = 3, 5 Hz) and 2.78 (1H, *dd*, J = 4, 5 Hz)} whereas that of anisocoumarin D(**9**) (Table 2) exhibited a monosubstituted ethyleneglycol moiety at δ_H 4.19 (1H, *br dt*, J = 7.7, 5.4 Hz), 3.32 (1H, *dd*, J = 11.4, 7.7 Hz), 3.20 (1H, *br d*, J = 11.4 Hz), 4.57 (1H, *br d*, J = 4 Hz), 4.28 (1H, *br t*, J = 5.4 Hz). The last two signals disappeared on deuteriation. Anisocoumarin D (**9**) easily gave a diacetate (**10**). The two substituents (monosubstituted epoxide and ethyleneglycol) both attached to a tertiary carbon, can only be situated at C-1′. Based on the above facts, structures **8** and **9** were proposed for anisocoumarins C and D, respectively. The strucure **9** was fully supported by (i) the ^{13}C NMR spectrum which exhibited peaks for 19 carbons atoms (Table 3 and, (ii) its partial synthesis from racemic heliettin (**7**) by oxidation with *m*-chloroperbenzoic acid. In the course of this conversion the racemic form of the epoxide (**8**) was also obtained.

A special feature of the *C. anisata* coumarins is the incorporation of prenyl units either as the 3,3-dimethylallyl or the 1,1-dimethylallyl groups in oxidized or non-oxidized forms. These coumarins also present a complex structural diversity only comparable in the Rutales with those of *Chloroxylon swietenia* [14, 18, 19].

EXPERIMENTAL

General. Mps: uncorr; NMR: 25°, $CDCl_3$ unless otherwise mentioned. 90 or 200.13 MHz for ^{1}H (shifts relative to $CDCl_3$ at δ_H 7.25) and 25.2 or 50.32 MHz for ^{13}C (shifts relative to $CDCl_3$ at δ_H 77.0 ppm). EIMS: 70 eV, direct insert.

Isolation procedures and characterization. The combined stem bark and roots of *Clausena anisata* were collected, from Oku *ca* 180 km from Bamenda North West Province of Cameroon, by Mr Benoît Mpom of the National Herbarium, Yaounde, where voucher specimens have been deposited. The combined sun-dried stem bark and roots (8 kg) were extracted with petrol (40–60°) (13 l) and $CHCl_3$ (12 l) in a Soxhlet extractor. Removal of the solvents gave two dark green residues (70 g and 50 g respectively). The crude extracts (40 g each; different by TLC) were chromatographed separately over silica gel (Merck Kieselgel 60, 400 g) columns. Elution was started with petrol and continued stepwise through petrol–EtOAc mixtures, EtOAc, and EtOAc–MeOH mixtures. Fractions were combined on the basis of ^{1}H NMR or TLC. From the chromatographic separation above and in some cases with the aid of successive prep. TLC, a total of 10 coumarins, 6 alkaloids and 6 limonoids were obtained pure along with a mixture of sterols. The natures of the alkaloids and limonoids are described elsewhere [20]. The following coumarins were characterized: imperatorin (30 mg), xanthoxyletin (2.5 g), gravelliferone methyl ether (**1**) (65 mg), anisocoumarin A (**2**) (100 mg), swietenocoumarin I (**4**) (140 mg), anisocoumarin B (**5**) (18 mg), heliettin (**7**) (2.2 g), anisocoumarin C (**8**) (15 mg), anisocoumarin D (**9**) (30 mg) and 3-(1,1-dimethylallyl) xanthyletin (80 mg). Known compounds were identified by direct comparison (mp UV IR, ^{1}H NMR) with authentic samples and will therefore not be described here except **4** which was not completely characterized in a previous report [14].

Anisocoumarin A (**2**). Yellow oil, IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 1710 (very broad), 1620, 1570, 1490, 1460, 1435, 1360, 1195, 1130, 990, 830; UV λ_{max}^{EtOH} nm (log ε): 327 (4.11), 298 (3.93), 255 (3.80), 246 sh (3.84), 224 (4.13); ^{1}H and ^{13}C NMR: see Tables 1 and 4, respectively; EIMS *m/z* (rel. int.): 286 $[M]^+$ (43), 271 $[M-Me]^+$ (42), 257 $[M-CHO]^+$ (51), 243 $[271-CO]^+$ (31), 31 $[CH_2{=}O{-}H]^+$ (91), 29 $[CHO]^+$ (100). (Found: C, 71.30, H, 6.32; $[M]^+$ 286.3124; $C_{17}H_{18}O_4$ requires C, 71.31; H, 6.34% $[M]^+$ 286.3107).

Reduction of **2** *with* $NaBH_4$. To a soln. of 2 (30 mg) in MeOH (5 ml) was added $NaBH_4$ (8 mg) and left at room temp. for 10 min. The reaction mixture was then diluted with H_2O (40 ml) and extracted with $CHCl_3$ (3 × 30 ml). The soln was dried (Na_2SO_4), evapd and purified by prep. TLC to give **3** (20 mg) as a colourless oil, IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3610 (OH), 1705, 1620, 1570, 1490, 1455, 1440, 1360, 1260, 1190, 1130, 1020, 980, 920, 830; ^{1}H and ^{13}C NMR: see Tables 1 and 4 respectively; EIMS *m/z* (rel. int.):

Table 1. ^{1}H NMR spectral data of coumarins **2**, **3**, **5** and **6*** recorded at 90 MHz

H	2	3	5	6
3	—	—	6.35 *d* (10)†	6.12 *d* (9.5)
4	7.50 *s*	7.53 *s*	7.75 *d* (10)	8.03 *d* (9.5)
5	7.22 *s*	7.28 *s*	—	
6	—	—	7.70 *d* (2)	6.61 *d* (2)
8	6.80 *s*	6.79 *s*	6.82 *d* (2)	6.35 *d* (2)
2′	6.15 *dd* (18, 10)	6.20 *dd* (18, 10)	—	
3′a	5.08 *dd* (10, 1)	5.10 *dd* (18.0, 1)	—	
3′b	5.02 *dd* (18, 1)	5.07 *dd* (10, 1)	—	
1″	3.80 *br s*	2.90 *br t* (8)	5.0 *d* (8)	4.55 *br d* (6.5)
2″	—	3.85 *br s*	5.65 *t* (8)	5.47 *br t* (6.5)
2″-OH	—	3.85 *br s*	—	
7-OH	—	—	—	8.5 *br s*
5-OH	—	—	7.35 *br s*	—
Me	1.45 *s*	1.48 *s*	1.72 *br s*	1.78 *s*
	1.45 *s*	1.48 *s*	1.76 *br s*	1.73 *s*
CHO	9.67 *br s*			
OMe	3.87 *s*	3.90 *s*		

* Data taken from ref. [16].
† Coupling constants (Hz) in parenthesis.

Table 2. ^{1}H NMR data for anisocoumarin C (**8**), anisocoumarin D (**9**), and its acetate (**10**).

H	8†	9*‡	10‡
2	4.72 *t* (9.0)§	4.66 *t* (8.6)	4.70 *t* (8.8)
3	3.20 *d* (9.0)	3.15 *d* (8.6)	3.18 *d* (8.8)
4	7.22 *s*	7.45 *s*	7.19 *s*
5	7.56 *s*	7.65 s	7.47 *s*
2′	3.30 *br m*	4.19 *br dt* (7.7, 5.4)	6.02 *dd* (8.0, 3.4)
3′-a	2.90 *dd* (3.0, 5.0)	3.32 *dd* (11.4, 7.7)	4.16 *dd* (11.8, 3.4)
3′-b	2.78 *dd* (4.0, 5.0)	3.20 *br d* (11.4)	4.00 *dd* (11.8, 8.0)
2′-OH	—	4.57 *d* (5.4)	—
3′-OH	—	4.28 *t* (5.4)	—
1″-OH	1.90 *br s*	4.67 *br s*	4.50 *br s*
Me	1.35 *s*	1.23 *s*	1.39 *s*
	1.31 *s*	1.20 *s*	1.34 *s*
	1.27 *s*	1.12 *s*	1.33 *s*
	1.21 *s*	1.12 *s*	1.20 *s*
OCO Me	—	—	2.00 *s*
	—	—	1.92 *s*
9	6.70 *s*	6.71 *s*	6.67 *s*

* In DMSO-d_6.
† 90 MHz.
‡ 200.13. MHz.
§ Coupling constants (Hz) in parentheses.

228 $[M]^+$ (23), 273, $[M-Me]^+$ (27), 259 (16), 85 (87), 83 (100). Found C, 70.80; H, 6.97; $C_{17}H_{20}O_4$ requires C, 70.81; H, 6.99%.

Anisocoumarin B (**5**). Colourless granules mp 94–95°; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3460, 1720, 1620, 1580, 1495, 1400, 1335, 1300, 1290, 1170, 1140, 1090, 1030, 995, 925, UV λ_{max}^{EtOH} nm (log ε): 251 (3.80), 262 (3.84), 287 (4.10), 332 (4.12); $\lambda_{max}^{EtOH+2MNaOH}$ nm (log ε): 260 (3.79), 280 (3.82), 375 (4.20); ^{1}H NMR: see Table 1; EIMS *m/z* (rel. int.): 246 $[M]^+$ (5), 178 $[M-C_5H_8]^+$ (100), 177 (15), 70 (25), 69 $[C_5H_9]^+$ (71). (Found: C, 68.26; H, 5.70; $[M]^+$ 246.2528; $C_{14}H_{14}O_4$ requires C, 68.28; H, 5.73% $[M]^+$ 246.2513).

Anisocoumarin C (**8**). Colourless oil; $[\alpha]_D^{25}$ +15.5 $CHCl_3$; *c* 1.1); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3580, 1710, 1620, 1580, 1480, 1385, 1370, 1265, 1130, 1100, 1000, 960, 945, 860, 840; ^{1}H NMR: see Table 3; EIMS *m/z* (rel. int.): 330 $[M^+]$ (42), 320 (15), 288 (21), 287 $[M-C_2H_3O]^+$ (100), 271 $[M-C(Me)_2OH]^+$ (11), 269 (21), 85 (17), 83 (29), 59 $[(CH_3)_2COH]^+$ (58). (Found: C, 69.10; H, 6.68 $[M]^+$ 330.3749; $C_{19}H_{22}O_5$ requires C, 69.07; H, 6.71% $[M]^+$ 330.3714).

Anisocoumarin D (**9**). Colourless crystals mp 210–211° from MeOH; $[\alpha]_D^{25}$ +20.5 (MeOH; *c* 1.2): IR ν_{max}^{KBr} cm^{-1}: 3400–3430

Table 3. ^{13}C NMR (200.13 MHz) data of anisocoumarin D (**9**)* and its diacetate (**10**)

C	9†	10†
2	90.7	91.0
3	28.8	29.5
4	123.7	123.4
4a	125.0	124.9
5	139.2	139.3
5a	112.5	112.7
6	129.4	127.8
7	162.3	162.7
9	95.8	97.1
9a	153.8	154.7
1a	159.8	160.0
1′	41.4	40.7
2′	73.4	73.3
3′	62.8	63.5
1″	70.0	71.6
Me	25.9, 24.8	25.9, 24.2
	23.0, 21.7	23.5, 21.9
OCOMe		20.8, 20.7
		170.8, 169.9

*Recorded in DMSO-d_6.

†Multiplicities were assigned from DEPT spectra.

Table 4. ^{13}C NMR (25.2 MHz) data for anisocoumarin A (**2**) and its alcohol derivative (**3**)

C	2	3
2	160.0	160.1
3	132.5	131.7
4	137.4	137.8
5	129.6	124.1
5a	112.6	112.4
6	130.0	127.0
7	159.8	159.6
8	98.5	98.1
8a	154.8	153.9
1′	40.5	40.4
2′	145.6	145.5
3′	112.3	112.1
1″	33.9	33.3
2″	198.7	62.2
Me	26.2 (2)	26.1 (2)
OMe	56.1	55.9

Assignments are based on chemical shift rules, multiplicities in off-resonance decoupled spectra and comparison with published data on similar compounds [13, 21].

Table 5. ^1H NMR (220.13 MHz) data for swietenocoumarin I (**4**)*

H	δ ($CDCl_3$)
4	7.50 *s*
5	7.27 *s*
8	6.74 *s*
2′	6.13 *dd* (18.0, 10.1)†
H_a-3′	5.06 *dd* (10.1, 1.1)
H_b-3′	5.04 *dd* (18.0, 1.1)
H_a-1″	2.97 *dd* (13.8, 2.0)
H_b-1″	2.51 *dd* (13.8, 10.3)
2″	3.60 *ddd* (10.3, 3.7, 2.0)
2″-OH	2.35 *d* (3.7)
3″-OH	2.24 *s*
OMe	3.85 *s*
Me	1.44 *s*
	1.44 *s*
	1.28 *s*
	1.25 *s*

*Colourless needles mp 120–121° from Et_2O.

†Coupling constants (Hz) in parentheses.

(br band), 1715, 1625, 1575, 1485, 1390, 1270, 1150, 1080, 1040, 1000, 960, 865, 830, 785, 740; UV λ_{max}^{EtOH} nm (log ε): 337 (4.25), 302 (4.00), 290 sh (3.93), 262 (3.88), 251 (3.93), 228 (4.08); ^1H and ^{13}C NMR: see Tables 2 and 3 respectively; EIMS *m/z* (rel. int.): 348 $[M^+]$ (5), 288 (43), 287 $[M-C_2H_5O]^+$ (100), 269 $[M-(Me)_2COH]^+$ (20), 215 (15) 59 $[(Me)_2COH]^+$ (25). (Found: C, 65.48; H, 6.90; $[M]^+$ 348.3854; $C_{19}H_{24}O_6$ requires C, 65.51; H, 6.94%; $[M]^+$ 348.3810).

Acetylation of anisocoumarin D (**9**). Ac_2O–pyridine treatment of **9** overnight at room temp. gave **10** as a yellow oil; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3580, 1730 (br band), 1620, 1575, 1480, 1385, 1365, 1260, 1230, 1150, 1125, 1100, 1050, 1000, 975; UV λ_{max}^{EtOH} nm (log ε): 338 (4.43), 302 (4.21), 290 sh (4.16), 262 (4.13), 252 (4.16), 228 (4.28); ^1H and ^{13}C NMR: see Tables 2 and 3 respectively; EIMS *m/z* (rel. int.): 432 $[M^+]$ (2), 288 (8), 287 (35) 87 (12), 86 (24), 85 (67), 84 (36), 83 (100), 43 (32). (Found: C, 63.90; H, 6.50; $C_{23}H_{28}O_8$ requires C, 63.88; H, 6.53%).

Synthesis of ± anisocoumarin C (**8**) *and D* (**9**). A soln of heliettin (**7**) (0.3 g) and *m*-chloroperbenzoic acid (0.2 g) in dry $CHCl_3$ (40 ml) was stirred in an ice bath for 2 hr and allowed to stand at room temp. for 48 hr. The reaction mixture was washed with 5% aq. Na_2CO_3 soln., dried (Na_2SO_4) and the $CHCl_3$ evapd. The resulting residue (250 mg) showed one major product (TLC). Part (100 mg) of this residue was purified (flash CC, prep. TLC; petrol–EtOAc 3:2) to yield a colourless oil (35 mg) identical in all respects (IR, ^1H NMR MS) with natural **8**. The rest of the hielettin oxidation residue (150 mg) in H_2SO_4 (20%, 25 ml), was refluxed for 45 min after which it was cooled, diluted with H_2O (40 ml) and extracted with $CHCl_3$ (3 × 40 ml). The combined $CHCl_3$ extracts were washed (H_2O), dried and evapd to yield a gum (100 mg). Purification of this gum (flash CC; $CHCl_3$–MeOH, 19:1) yielded colourless crystals mp 209° identical in all respects (IR, ^1H NMR, UV, MS) with an authentic sample of **9**.

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