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DITERPENOIDS FROM *RABDOSIA COETSOIDES*

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Key Word Index—*Rabdosia coetsoides*, Labiatae; *ent*-kaurene, diterpene, coetsoidin A–G

Abstract—Seven new *ent*-kaurene diterpenoids, coetsoidin A–G, were isolated from the air-dried leaves of *Rabdosia coetsoides*. Their structures were established by spectroscopic evidence and some chemical transformations.

INTRODUCTION

Rabdosia coetsoides C. Y. Wu is distributed mainly over south-western Yunnan. As a continuation of our studies on the biological active principles of *Rabdosia* plants, we have isolated seven new diterpenoids, namely coetsoidin A(**1**), B(**2**), C(**3**), D(**4**), E(**5**), F(**6**) and G(**7**) together with two known constituents ursolic acid and its glucoside from the leaves of this plant. The present paper describes the structural elucidation of these new compounds.

RESULTS AND DISCUSSION

An ethereal extract of *Rabdosia coetsoides* dried leaves was fractionated by column chromatography on silica gel. Further purifications of coetsoidin A(**1**)–G(**7**) were achieved either by recrystallization, conventional open-column chromatography or preparative TLC (silica gel).

Coetsoidin A(**1**), $C_{20}H_{28}O_5$ (M^+ at *m/z* 348), colourless needles, mp 230–232°; $[\alpha]_D^{21}$ −150.1° (MeOH; *c* 0.543), showed the presence of two methyl groups, six methylene groups, five methine groups, three quaternary carbons, two olefinic carbons, an acetal carbon, and a ketonic carbon in the ^{13}C NMR spectrum (Table 1). It had a five-membered ring with a ketone conjugated with an *exo*-methylene group judging from the following spectral data. λ_{max}^{EtOH} 231 nm (log 3.89); ν_{max}^{KBr} 1712 and 1642 cm^{-1}; ^1H NMR δ 5.37 and 6.30 (each 1H, *br s*), ^{13}C NMR δ 116.3 (*t*), 148.4 (*s*) (*exo*-methylene) and 206.2 (*s*) (ketone). Its IR spectrum showed the characteristic absorption of hydroxy groups at 3430 and 3380 cm^{-1}. Consideration of these facts with the structures of the diterpenoids isolated so far from the genus *Rabdosia* led to the assignment of an *ent*-15-oxo-16-kaurene skeleton to coetsoidin A(**1**) [1]. In fact, its dihydro-derivative (**10**) showed a negative ORD effect in methanol [2]. The locations of three hydroxy groups at the 3β,7α and 14β-positions, respectively, were deduced as follows. Acetylation of **1** gave a diacetate (**8**), in the ^1H NMR spectrum of which, a signal was observed at δ 6.03 (*br s*) and it suffered an abnormal downfield shift compared with the signal due to a proton attached to an acetoxy group bearing carbon, indicating that the signal was assigned to 14α-H [3]. Treatment of **1** with dry acetone in the presence of dry cupric sulphate gave an acetonide (**11**). Thus, a hydroxy group should be at C-7α with a *cis*-relationship to 14β-OH. Upon acetylation in the presence of boron trifluoride etherate, compound **1** afforded a tetraacetate (**9**) which indicated the presence of a hemiacetal ring. From this reaction and the spectral data of **1** (Tables 1 and 2), it was deduced that the tertiary hydroxy group was at the 3β-position in accordance with the following evidence. An acetal carbon at δ 97.7 (*s*), the upfield shift of C-18 (26.6, *q*) in the ^{13}C NMR due to the γ-effect of the 3β-OH, and the lowfield shifts of C-2 (29.1, *t*) and C-4 (39.6, *s*) [4]. The signal appeared as an ABdd type at δ 4.55 and 3.94 (2H, $J = 2$, 10 Hz) were assigned to 20-H_2, which was firmly supported by the *W*-coupling of 20-H_2 with 5β-H and 9β-H, respectively [5]. Accordingly, the structure of coetsoidin A(**1**) can be represented as *ent*-3α,7β,14α-trihydroxy-3β,20-epoxy-kaur-16-en-15-one.

Coetsoidin B(**2**), $C_{20}H_{30}O_5$ (M^+ at *m/z* 350), colourless crystal, mp 147–149°; $[\alpha]_D^{21}$ −104.2° (MeOH; *c* 0.523). The ^1H NMR of **2**, comparing with that of kamebakaurin (**16**) [6], differs only in the A-ring and 20-H_2 signals: in the case of **2**, the upfield shift of C-18 (29.3, *q*) and the lowfield shifts of C-2 (25.7, *t*) and C-4 (42.4, *s*) required a hydroxy at the 3β-position [4] while in kamebakaurin (**16**) this effect was absent. The difference of the 20-H_2 signal between **2** and kamebakaurin (**16**) supported this assignment. Therefore, compound **2** was deduced as *ent*-3α,7β,14α,20-tetrahydroxykaur-16-en-15-one.

Coetsoidin C(**3**), $C_{21}H_{30}O_5$ ($[M+1]^+$ at *m/z* 363), mp 198–201°; $[\alpha]_D^{24}$ −35.5° (MeOH; *c* 0.507), differs from the known compound kamebacetal A(**15**) [6, 7] only by the signal of δ 3.72 (1H, *br s*) in **3** which replaced that at δ 3.23 in kamebacetal A(**15**) and the downfield shift of 18-Me (δ 1.15, 3H, *s*) and 19-Me (1.06, 3H, *s*) compared to that of kamebacetal A(**15**). Again a 3β-OH in **3** was required as followed from the effect of the hydroxy group [4]. The absolute configuration at C-20 was determined as *S* by the downfield shift of C-11 due to the δ-syn-axial effect between C-20-methoxy and C-11 [8]. Furthermore, the absolute configuration was established by NOE's between 20-H and 19-CH_3 (11%). Thus, coetsoidin C(**3**) was identified as *ent*-3α,14α-dihydroxy-20(*S*)-methoxy-7β,20-epoxy-kaur-16-en-15-one.

Coetsoidin D(**4**), $C_{21}H_{30}O_6$ ($[M+1]^+$ at *m/z* 379), mp 153–155°; $[\alpha]_D^{24}$ −27.3° (MeOH; *c* 0.513). The ^1H NMR spectrum of **4** was very similar to that of **3**. However, the presence of an extra signal at δ 4.41 (1H, *dd*, $J = 3.0$, 7.0 Hz, changed to *d* on adding D_2O, $J = 3.0$ Hz) in the ^1H NMR spectrum plus the difference in the ^{13}C NMR

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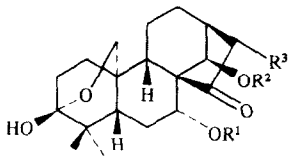

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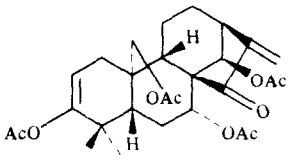
8 $R^1 = R^2 = Ac$, $R^3 =$ ( )

10 $R^1 = R^2 = H$, $R^3 = Me$

11 $R^1, R^2 =$ (CMe_2), $R^3 =$ ( )



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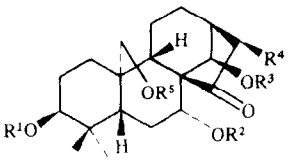
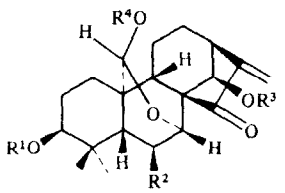


2 $R^1 = R^2 = R^3 = R^5 = H$, $R^4 =$ ( )

12 $R^1 = R^2 = R^3 = R^5 = Ac$, $R^4 =$ ( )

13 $R^1 = R^2 = R^3 = R^5 = H$, $R^4 = Me$

14 $R^1 = R^5 = H$, $R^2, R^3 =$ (CMe_2), $R^4 =$ ( )



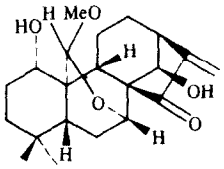
3 $R^1 = R^2 = R^3 = H$, $R^4 = Me$

4 $R^1 = R^3 = H$, $R^2 = OH$, $R^4 = Me$

5 $R^1 = R^2 = R^3 = H$, $R^4 = Et$

6 $R^1 = R^3 = R^4 = H$, $R^2 = OH$

17 $R^1 = R^3 = Ac$, $R^2 = H$, $R^4 = Me$



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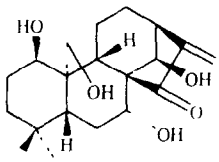

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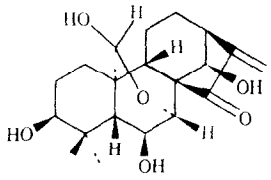

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spectrum of four signals ranging from 60 to 80 ppm which replaced two signals in the spectrum of **3**, indicated that **4** differs from **3** only by an extra hydroxy group This hydroxyl was assigned to the 6β-position on the basis of the following facts· its IR absorption for a ketone shifted to lower wave number (1700 cm^{-1}) and its UV data (237.5 nm) was in accord with hydrogen-bonding between the 6β-hydroxy group and the 15-keto of ring D [9] Thus, the structure of **4** was deduced to be *ent*-3α,6α,14α-trihydroxy-20(*S*)-methoxy-7β,20-epoxy-kaur-16-en-15-one

Coetsoidin E(**5**), $C_{22}H_{32}O_5$, mp 166–168°; $[\alpha]_D^{24}$ −36.8° (MeOH, *c* 0.502). Comparison the ^1H NMR and ^{13}C NMR spectra of **5** with those of **3** strongly suggested that the only difference between **5** and **3** was that the methoxy in **3** was replaced by an ethoxy in **5**. Consequently, the structure of **5** was determined to be *ent*-3α,14α-dihydroxy-20(*S*)-ethoxy-7β,20-epoxy-kaur-16-en-15-one

Coetsoidin F(**6**) and G(**7**) were isolated as a mixture which gave only one spot on TLC. The IR, UV and NMR spectra clearly showed the mixture to be composed of two very similar *ent*-kaurene diterpenoids in a 3:1 ratio as shown by the ^1H NMR and ^{13}C NMR spectra. The ^{13}C NMR data of **6** and **7** were almost the same except for the signal at δ20 0 and 17 9 assignable to C-11, respectively. It seemed most likely that **6** and **7** were epimeric at C-20 because in the case of **6** a clear δ-*syn*-axial effect between 20-OH and C-11 was present while in 7 this effect was absent [8] In conclusion, compounds **6** and **7** were

Table 1. ^{13}C NMR chemical shift of coetsoidin A(1)–G(7) in C_5D_5N

C	1	2	3	4	5	6	7
1	34.2 *t*	30.1 *t*	31.9 *t*	31.4 *t*	31.9 *t*	31.7 *t*	31.4 *t*
2	29.1 *t*	25.7 *t*	22.8 *t*	23.2 *t*	22.8 *t*	23.5 *t*	25.7 *t*
3	97.1 *s*	75.4 *d*	73.6 *d*	74.2 *d*	73.5 *d*	74.4 *d*	75.9 *d*
4	39.6 *s*	42.4 *s*	39.5 *s*	39.7 *s*	39.4 *s*	39.7 *s*	39.8 *s*
5	47.7 *d*	46.3 *d*	43.8 *d*	53.4 *d*	43.8 *d*	53.5 *d*	54.6 *d*
6	29.9 *t*	27.6 *t*	25.5 *t*	69.7 *d*	25.4 *t*	69.9 *d*	69.9 *d*
7	75.4 *d*	74.1 *d*	66.9 *d*	70.6 *d*	66.8 *d*	71.2 *d*	70.9 *d*
8	59.7 *s*	60.7 *s*	58.8 *s*	61.7 *s*	58.9 *s*	62.2 *s*	62.8 *s*
9	47.4 *d*	54.6 *d*	50.9 *d*	51.7 *d*	50.8 *d*	52.1 *d*	54.3 *d*
10	36.1 *s*	37.1 *s*	38.6 *s*	38.6 *s*	38.6 *s*	38.7 *s*	37.4 *s*
11	17.7 *t*	17.9 *t*	19.9 *t*	19.8 *t*	19.8 *t*	20.0 *t*	17.9 *t*
12	29.9 *t*	28.5 *t*	25.7 *t*	25.4 *t*	25.6 *t*	25.6 *t*	27.1 *t*
13	45.3 *d*	46.2 *d*	42.0 *d*	44.5 *d*	41.9 *d*	44.6 *d*	44.0 *d*
14	71.7 *d*	73.7 *d*	70.7 *d*	71.0 *d*	70.7 *d*	70.9 *d*	70.7 *d*
15	206.2 *s*	207.9 *s*	206.1 *s*	211.1 *s*	206.1 *s*	211.4 *s*	209.8 *s*
16	148.4 *s*	149.3 *s*	154.3 *s*	153.4 *s*	154.3 *s*	153.7 *s*	153.1 *s*
17	116.2 *t*	115.8 *t*	115.6 *t*	118.4 *t*	115.6 *t*	118.4 *t*	119.1 *t*
18	26.6 *q*	29.3 *q*	28.2 *q*	29.5 *q*	28.1 *q*	29.7 *q*	31.3 *q*
19	18.7 *q*	22.8 *q*	21.8 *q*	22.8 *q*	21.8 *q*	23.3 *q*	23.8 *q*
20	66.8 *t*	59.3 *t*	101.9 *d*	101.9 *d*	100.2 *d*	94.1 *d*	96.3 *d*
21			55.7 *q*	56.2 *q*	63.9 *t*		
22					15.6 *q*		

Table 2. H NMR chemical shift of coetsoidin A(1)–G(7) in C_5D_5N

H	1	2	3	4	5*	6	7
3α-H		3.68 *br s*	3.73 *br s*	3.70 *d*, 2	3.73 *br s*	3.82 *d*, 2.5	3.72 *d*, 2.5
6α-H				4.42 *dd*, 3.0, 7.0.		4.55 *dd*	4.55 *dd*
						3.4, 6.9	3.4, 6.9
7β-H	4.59 *dd*, 4.0, 12.0	5.07 *dd*, 6.0, 10.0	4.79 *dd*, 2.0, 4.0	4.77 *d*, 3.0	4.79 *dd*, 2.0, 3.0	4.91 *d*, 3.4	4.89 *d*, 3.4
13α-H	3.18 *m*, $W_{1/2}=7.0$	3.33 *m*, $W_{1/2}=7.0$	3.18 *d*, 10	3.20 *d*, 8.0	3.20 *d*, 10	3.16 *d*, 9.0	3.25 *d*,
							10.0
14α-H	4.71 *br s*	5.72 *br s*	5.15 *br s*	5.08 *br s*	5.23 *br s*	5.52 *br s*	5.52 *br s*
17-H_a	6.30 *br s*	6.33 *br s*	6.20 *br s*	6.18 *br s*	6.20 *br s*	6.17 *br s*	6.21 *br s*
17-H_b	5.37 *br s*	5.39 *br s*	5.41 *br s*	5.46 *br s*	5.51 *br s*	5.45 *br s*	5.46 *br s*
18-Me	1.33 *s*	1.20 *s*	1.15 *s*	1.57 *s*	1.16 *s*	1.63 *s*	1.63 *s*
19-Me	1.21 *s*	1.05 *s*	1.06 *s*	1.13 *s*	1.07 *s*	1.12 *s*	1.12 *s*
20-H_a	4.54 *dd*, 9.0, 2.0	4.34 *br s*	5.38 *s*	5.28 *s*	5.37 *s*	6.10 *s*	6.10 *s*
20-H_b	3.94 *dd*,	4.34 *br s*					
	9.0, 2.0						
21-Me			3.45 *s*	3.40 *s*			

5*: 20-OEt: 3.95 and 3.50 (each 1H, *dq*, $J^2=10.0$ Hz, $J^3=7.0$ Hz), 1.19 (3H, *t*, $J^3=7.0$ Hz).

suggested to be *ent*-3α,6α,14α,20(*S*)-tetrahydroxy-7β,20-epoxy-kaur-16-en-15-one and *ent*-3α,6α,14α,20(*R*)-tetrahydroxy-7β,20-epoxy-laur-16-en-15-one, respectively.

EXPERIMENTAL

Mps: uncorr. UV spectra were determined in EtOH. IR spectra were measured in KBr discs. MS were obtained by direct inlet at 70 eV. ^1H and ^{13}C NMR were recorded at 400, 90 and 100.6, 22.63 MHz using TMS as int standard; chemical shift values are reported in δ (ppm) units (C_5D_5N).

Plant material. Rabsodia coetsoides leaves were collected in Baoshan, Yunnan, China in July, 1987 and identified by Prof. H. W. Li of our institute where a voucher specimen has been deposited.

Extraction and isolation. Dried and powdered leaves (2.2 kg) were extracted with Et_2O and the solvent evapd. The residue was dissolved in MeOH and decoloured by activated charcoal when the soln was concd to *ca* 1 l and the deposition formed during standing was removed. The MeOH soln was evapd and the residue (200 g) was subjected to CC (silica gel) eluting with $CHCl_3$ and increasing proportions of Me_2CO–$CHCl_3$. Fractions were monitored by TLC. All components were further

Table 3 Comparison of IR, MS, UV data of A(1)–G(7)

	IR ν_{max}^{KBr} cm^{-1}	MS (*m/z*)	UV λ_{max}^{EtOH} nm (log ε)
1	3430, 3380, 1712, 1642, 1154, 1103, 1085, 1044, 1014, 952	348 $[M]^+$, 330 $[M-H_2O]^+$, 312 $[M-2H_2O]^+$, 302, 284, 257, 215, 169, 153, 105, 91, 41 (base peak)	231 (log 3 89)
2	3410, 3320, 1718, 1642, 1080, 1060, 1025, 995, 975	350 $[M]^+$, 332 $[M-H_2O]^+$, 314 $[M-2H_2O]^+$, 296 $[M-3H_2O]^+$, 283, 213, 178, 165, 151, 133, 117, 105, 91, 79, 67, 57, 43 (base peak)	233(log 3 86)
3	3500, 3405, 1705, 1640, 1200, 1110, 1060, 1015, 1000, 928	363 $[M+1]^+$, 345, 331, 302, 284, 269, 241, 215, 169, 129, 117, 105, 91, 79, 69, 55, 43 (base peak)	231 5 (log 4 53)
4	3320, 1700, 1642, 1200, 1120, 1070, 1030, 940, 930, 710	379 $[M+1]^+$, 361, 329, 300, 282 (base peak), 267, 239, 169, 105, 91, 79, 67, 55, 43 (base peak)	237 5 (log 4 34)
5	3410, 1705, 1640, 1110, 1065, 1020, 965, 930	330 $[M-EtOH]^+$, 302, 284 (base peak), 269, 241, 223, 197, 185, 169, 136, 107, 69, 43	231 5 (log 4 54)
6/7	3500, 3380, 3240, 1688, 1630, 1095, 1064, 1026, 1000, 948, 920	364 $[M]^+$, 346 $[M-H_2O]^+$, 328, 300, 282, 267, 164, 105, 91, 85, 79, 67, 55, 41 (base peak)	235 (log 4 31)

purified by recrystallization and prep. TLC (silica gel) yielding in order of increasing polarities E(**5**) (80 mg), C(**3**) (150 mg), D(**4**) (50 mg), A(**1**) (5 g), B(**2**) (6 g), F(**6**) (15 g) and G(**7**) (5 g)

All the data of coetsoidin A(**1**)–G(**7**) are shown in Tables 1–3

Diacetate of coetsoidin A (**8**). A soln of **1** (50 mg) in a mixture of pyridine (1 ml) and Ac_2O (1 ml) was allowed to stand at room temp for 4 hr, then H_2O (5 ml) was added to the soln and the mixture extracted with $CHCl_3$. The crude product, after drying with Na_2SO_4 and evapn of the solvent, was purified by CC on silica gel to give **8** (40 mg) $C_{24}H_{32}O_7$, MS *m/z* 432 $[M]^+$, 414, 390, 372, 354, 344, 330, 312, 294, 269, 251, 169, 91, 43 (base peak) IR ν_{max}^{KBr} cm^{-1} 3350, 1733, 1723, 1645, 1250, 1233, 1170, 1097, 1073, 1063, 1041 ^{1}H NMR δ 6 24 and 5 40 (each 1H, *br s*, 17-H_2), 5 78 (1H, *br s*, 14α-H), 5 59 (1H, *dd*, J = 4, 12 Hz, 7β-H), 4 76 (1H, *dd*, J = 8 8, 2 3 Hz, 20-H_a), 4 00 (1H, *d*, J = 8 8 Hz, 20-H_b), 3 06 (1H, *m*, $W_{1/2}$ = 7 Hz, 13α-H), 2 10 and 1 93 (each 1H, *s*, 2 × OAc), 1.40 (3H, *s*, 18-Me), 1 16 (3H, *s*, 19-Me).

Tetraacetate of coetsoidin A (**9**) Boron trifluoride etherate (1 ml) was added into a soln of **1** (40 mg) in pyridine at 0° temp Work-up in the usual way gave **9** (30 mg) $C_{28}H_{36}O_9$, IR ν_{max}^{KBr} cm^{-1} 1735, 1645, 1370, 1235, 1070, 1040. ^{1}H NMR ($CDCl_3$) δ 6 16 and 5 44 (each 1H, *br s*, 17-H_2), 5 93 (1H, *br s*, 14α-H), 5.31 (1H, *dd*, J = 3 5, 12 Hz, 7β-H), 5 18 (1H, *d*, J = 5 4 Hz, 2-H), 4 50 (2H, *br s*, 20-H_2), 3 09 (1H, *m*, 13α-H), 2 18, 2 15, 2 02 and 1 97 (each 3H, *s*, 4 × OAc), 1 09 (3H, *s*, 18-Me), 0 94 (3H, *s*, 19-Me) ^{13}C NMR ($CDCl_3$) δ35 2 (1-C), 110 6 (2-C), 152 1 (3-C), 40 6 (4-C), 50 7 (5-C), 25 3 (6-C), 75 7 (7-C), 60 7 (8-C), 53 9 (9-C), 37 6 (10-C), 17 9 (11-C), 31 5 (12-C), 44 3 (13-C), 74 1 (14-C), 203 6 (15-C), 146 0 (16-C), 117 6 (17-C), 28 1 (18-C), 19 9 (19-C), 63 5 (20-C), 20 9, 21.1, 21.1, 21.2 and 170 7, 170 4, 169 5, 169 2 (4 × OAc)

Dihydrocoetsoidin A (**10**) Compound **1** (50 mg) was dissolved in MeOH (1 ml) and a little Pd/C were added The mixture was stirred at room temp for 3 hr under H_2 atmosphere and treated in the usual way to give **10** $C_{20}H_{30}O_5$, ^{1}H NMR [$(CD_3)_2SO$] δ4.32 (1H, *br s*, 14α-H), 4 20 (1H, *dd*, J = 1 8, 8 4 Hz, 20-H_a), 3 62 (1H, *d*, J = 8 4 Hz, 20-H_b), 3 72 (1H, *dd*, J = 3 2, 11 6 Hz, 7β-H), 2 69 (1H, *quintet*, 7 0 Hz, 16α-H), 2 26 (1H, *m*, 13α-H), 0 93 (3H, *s*, 18-Me), 0 92 (3H, *s*, 19-Me) ^{13}C NMR [$(CD_3)_2SO$] δ34.1 (1-C), 29 1 (2-C), 97 0 (3-C), 39.6 (4-C), 48 3 (5-C), 30 0 (6-C), 75 4 (7-C), 59 0 (8-C), 41 9 (9-C), 35 9 (10-C), 17.3 (11-C), 24 1 (12-C), 42.7 (13-C), 72 1 (14-C), 220 0 (15-C), 47 5 (16-C), 8 8 (17-C), 26 5 (18-C), 18 7 (19-C), 66 7 (20-C). CD (MeOH) $\Delta\varepsilon_{304}$ −0 63

Tetraacetate of coetsoidin B (**12**) Compound **2** (50 mg) was treated in the same way as in the case of **1** to give **12** (40 mg) $C_{26}H_{38}O_9$, MS *m/z* 458 $[M-AcOH]^+$, 430, 416, 310, 296, 283, 43 (base peak) IR ν_{max}^{KBr} cm^{-1} 1735, 1645, 1368, 1245, 1235, 1071, 1055, 1049, 1025 ^{1}H NMR (C_5D_5N) δ6 26 and 5 49 (each 1H, *br s*, 17-H_2), 6 08 (1H, *br s*, 14α-H), 5 76 (1H, *dd*, J = 6, 10 Hz, 7β-H), 4 85 (1H, *m*, 3α-H), 5 05 (1H, *d*, J = 12 9 Hz, 20-H_a), 4.78 (1H, *d*, J = 12 9 Hz, 20-H_b), 3 20 (1H, *br s*, 13α-H), 2 20, 2 12, 2 00 and 1 88 (each 3H, *s*, 4 × OAc), 0 93 (6H, *s*, 18-Me and 19-Me) ^{13}C NMR (C_5D_5N) δ31 8 (1-C), 23 1 (2-C), 76 7 (3-C), 42 2 (4-C), 48 6 (5-C), 24 3 (6-C), 76 4 (7-C), 61 4 (8-C), 55 7 (9-C), 36 7 (10-C), 17 8 (11-C), 28 7 (12-C), 44 6 (13-C), 75 0 (14-C), 204 2 (15-C), 146.8 (16-C), 117 3 (17-C), 28 2 (18-C), 20 8 (19-C), 62 5 (20-C), 22 1, 21 3, 21 1, 14.2 and 170 7, 170 7, 170 1, 169 4 (4 × OAc)

Dihydrocoetsoidin B (**13**) $C_{20}H_{32}O_5$, ^{1}H NMR (C_5D_5N) δ5 75 (1H, *br s*, 14α-H), 4 85 (1H, *dd*, J = 4.5, 12 Hz, 7β-H), 3 67 (1H, *m*, 3α-H), 4 38 and 4 32 (each 1H, AB*d*, 11 76, 20-H_2), 3 25 (1H, *quintet*, J = 7, 16α-H), 1 22 (3H, *d*, J = 7 Hz, 17β-Me), 1 18 (3H, *s*, 18-Me), 1 02 (3H, *s*, 19-Me) ^{13}C NMR (C_5D_5N) δ29 6 (1-C), 24 7 (2-C), 76 7 (3-C), 43 5 (4-C), 47 5 (5-C), 28 4 (6-C), 75 7 (7-C), 61 2 (8-C), 49 7 (9-C), 37 9 (10-C), 18 7 (11-C), 26 6 (12-C), 43 7 (13-C), 74 8 (14-C), 222 5 (15-C), 55 7 (16-C), 9 7 (17-C), 29 6 (18-C), 23 1 (19-C), 60 2 (20-C) CD (MeOH) $\Delta\varepsilon_{298}$ −0 67

Acetonide of coetsoidin B(**14**) Compound **2** (50 mg) was dissolved in 50 ml of dry Me_2CO The mixt was refluxed for 48 hr in the presence of dry cupric sulphate at 80°, and the mixture was filtered, concd, and purified on a silica gel column to give **14** (35 mg) $C_{23}H_{34}O_5$, ^{1}H NMR (C_5D_5N) δ6 29 and 5 35 (each 1H, *br s*, 17-H_2), 5 44 (1H, *br s*, 14α-H), 4 76 (1H, *dd*, J = 5 7, 12 5 Hz, 7β-H), 4 34 (1H, *d*, J = 11.7 Hz, 20-H_a), 4 17 (1H, *d*, J = 11 7 Hz, 20-H_b), 3 68 (1H, *m*, 3α-H), 3 16 (1H, *m*, 13α-H), 1 75 and 1 39 [each 3H, *s*, C(Me)$_2$], 1 21 (3H, *s*, 18-Me), 1 11 (3H, *s*, 19-Me) ^{13}C NMR (C_5D_5N) δ30 6 (1-C), 26 8 (2-C), 74 9 (3-C), 42 3 (4-C), 46.3 (5-C), 27.5 (6-C), 72 2 (7-C), 55 6 (8-C), 53 4 (9-C), 38 0 (10-C), 18 6 (11-C), 29 0 (12-C), 44 0 (13-C), 72 0 (14-C), 207 0 (15-C), 149 1 (16-C), 115 3 (17-C), 29 3 (18-C), 22 7 (19-C), 61 4 (20-C), 31 4 and 25 6 [C(Me)$_2$]

Diacetate of coetsoidin C(**17**) $C_{25}H_{34}O_7$, ^{1}H NMR (C_5D_5N) δ6.18 and 5 26 (each 1H, *br s*, 17-H_2), 6 15 (1H, *br s*, 14α-H), 5 37 [1H, *br s*, 20(*S*)-H], 4.92 (1H, *m*, 7β-H), 4 32 (1H, *m*, $W_{1/2}$ = 7 Hz, 3α-H), 3 46 (3H, *s*, 20-OMe), 3 13 (1H, *m*, 13α-H), 2 14 and 1 93 (each 3H, *s*, 2 × OAc), 1 01 (3H, *s*, 18-Me), 0 85 (3H, *s*, 19-Me)

^{13}C NMR (C_5D_5N): δ 31.5 (1-C), 22 5 (2-C), 76.2 (3-C), 39 2 (4-C), 43 2 (5-C), 24.8 (6-C), 69.2 (7-C), 56 6 (8-C), 50.7 (9-C), 37 5 (10-C), 19.5 (11-C), 24 8 (12-C), 41.0 (13-C), 75.1 (14-C), 204 3 (15-C), 152.0 (16-C), 116 8 (17-C), 27 1 (18-C), 21 0 (19-C), 101.1 (20-C), 55 5 (21-C), 23.2, 21 0 and 170 3, 170 2 (2 × OAc)

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