Dinorditerpene, Diterpenes, Alkaloids, and Coumarins from *Clausena dunniana*

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The new dinorditerpene 14,15-dinorclerod-3-ene-2,13-dione (**2**), the eight new clerodane diterpenes **4**, **5**, **7**–**10**, **13**, and **14**, and the new furoquinoline alkaloid **15**, besides thirty known compounds, were isolated from the aerial part of *Clausena dunniana* collected in Xishuangbanna, the south of China. The structures were elucidated by spectroscopic analysis including 1D- and 2D-NMR.

1. Introduction. – *Clausena dunniana* LÉVL. (Rutaceae) is a shrub widely distributed in the south of China [1]. In continuation of our investigations on the phytochemicals of the genus *Clausena* [2–5], 40 compounds including a dinorditerpene, clerodane diterpenes, labdane diterpenes, phytane diterpenes, carbazole alkaloids, a furoquinoline, triterpenes, coumarins, flavonoids, and aromatics were isolated from the aerial parts of *C. dunniana*. Their structures were elucidated, which allowed the identification of ten new compounds (see *Fig. 1*) including the new dinorditerpene 14,15-dinorclerod-3-ene-2,13-dione[1]) (**2**), the eight new clerodane diterpenes 2β-(acetyloxy)clerod-3-en-15-oic acid (**4**), 2β-(formyloxy)clerod-3-en-15-oic acid (**5**), 4α,18-dihydroxyclerodan-15-oic acid (**7**), 4β-hydroxyclerodan-15-oic acid (**8**), 3α,4α-dihydroxyclerodan-15-oic acid (**9**), 3β-hydroxy-clerod-4(18)-en-15-oic acid (**10**), ethyl clerod-4(18)-en-15-oate (**13**), ethyl clerod-3-en-15-oate (**14**), and the new furoquinoline alkaloid (2*S*)-1-[(6,7-dimethoxyfuro[2,3-*b*]quinolin-4-yl)oxy]-3-methylbutane-2,3-diol (**15**), besides 30 known compounds including 2-oxoclerod-3-en-15-oic acid (**1**) [6], 2α-methoxyclerod-3-en-15-oic acid (**3**) [7], 4α-hydroxyclerodan-15-oic acid (**6**) [7], clerod-4(18)-en-15-oic acid (**11**) [8], clerod-3-en-15-oic acid (**12**) [9], 8β-hydroxylabden-15-oic acid [10], (13*E*)-8β-hydroxylabd-13-en-15-oic acid [11], phyt-2-en-1-ol [12], *trans*-palmitoylphytol [12], kokusaginine [13], skimmianine [13], 3-hydroxy-9*H*-carbazole-3-carboxaldehyde [14], clausenamide [15], gult-5-en-3β-ol [16], tarolupenol [17], tarolupenyl acetate [17], haplociliatic acid [18], isoscopoletin, marmesin, and myricitrin [19], 5-hydroxy-3,4′,7-trimethoxyflavone, 3,5-dihydroxy-4′,7-dimethoxyflavone, 4′,5-dihydroxy-3,7-dimethoxyflavone, ombuin, paeonol, triacontan-1-ol, stearic acid, hexatriacontanoic acid, and β-sitosterol.

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[1]) The systematic name corresponding to the parent name clerodane is (1*R*,2*S*,4a*R*,5*S*,8a*R*)-decahydro-1,2,4a,5-tetramethyl-1-[(3*R*)-3-methylpentyl]naphthalene, according to *Chem. Abstr*. We use the name clerodane for the corresponding enantiomer; see *Exper. Part* for systematic names.

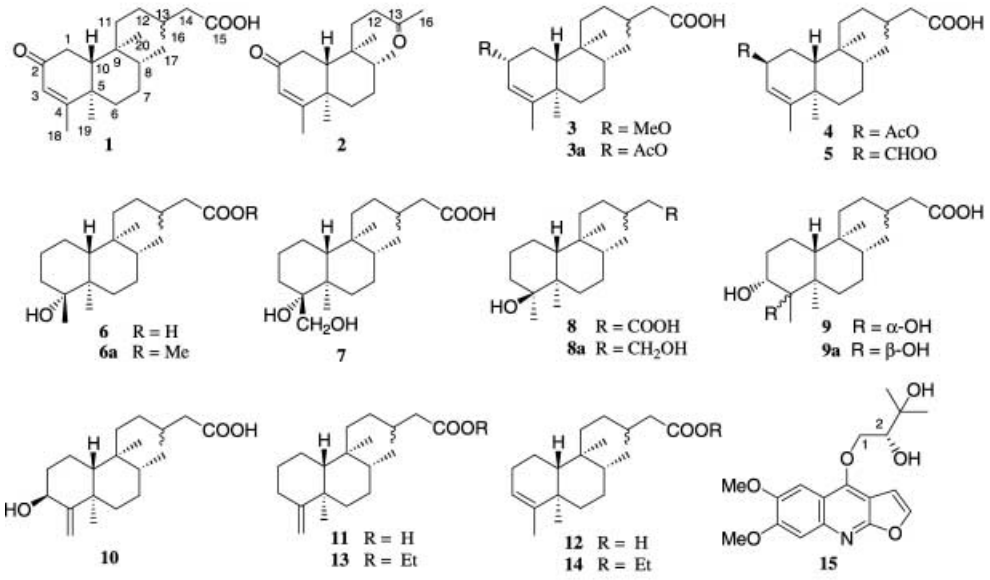

Fig. 1. *The structures of compounds* **1**–**15**

2. Results and Discussion. – The AcOEt extract of the aerial parts of *C. dunniana*, upon column chromatography, afforded the ten new compounds **2**, **4**, **5**, **7**–**10**, and **13**–**15**, besides 30 known ones.

Compound **2** has the molecular formula $C_{18}H_{28}O_2$ based on the high-resolution EI-MS (*m*/*z* 276.2114 (M^+; calc. 276.2089)). The spectroscopic data establish the structure of **2** as being 14,15-dinorclerod-3-ene-2,13-dione.

The ^{13}C-NMR spectra and DEPT (*Table*) of **2** show 18 resonances for five quaternary, three CH, five CH_2, and five Me C-atoms. Two C=O groups are evident from the ^{13}C-NMR signals at δ(C) 208.1 (*s*) and 199.8 (*s*). The signals at δ(C) 46.2 (*d*), 36.3 (*d*), 39.9 (*s*), and 38.4 (*s*) suggest that **2** has a clerodane-type skeleton [7]. In the HMBC experiment, the ^{1}H,^{13}C long-range correlations between the proton at δ(H) 5.73 (connected with the C-atom at δ(C) 125.6 (*d*)) and δ(C) 18.8 (*q*, C(18)), 35.0 (C(1)), and 39.9 (*s*, C(5)), and between δ(H) 2.35 and 2.29 (connected with the C-atom at δ(C) 35.0 (*t*)) and δ(C) 39.9 (*s*, C(5)), 46.2 (*d*, C(10)), and 199.8 (*s*, C(2)) reveal the presence of an α,β-unsaturated ketone moiety. The ^{1}H- and ^{13}C-NMR spectra show that **2** is partially similar to **1**, and has the same AB/*trans* junction as suggested by the characteristic chemical shift of C(19) (δ(C) 18.3(*q*)) [6] [20–21]. Based on the ^{1}H,^{13}C long-range correlations between δ(H) 2.26 and 2.21 (corresponding C-atom at δ(C) 37.1 (*t*)) and δ(C) 30.0 (*q*), 30.9 (*t*, C(11)), and 208.1 (*s*), and between δ(H) 2.13 (corresponding C-atom at δ(C) 30.0 (*q*)) and δ(C) 37.1 (*t*) and 208.1 (*s*), it is clear that the side chain at C(11) is an acetonyl group $MeCOCH_2$.

The ^{1}H- and ^{13}C-NMR spectra of **4** indicate the presence of a clerodane structure with an AcO group and a C=C bond, *i.e.*, of 2β-(acetyloxy)clerod-3-en-15-oic acid.

The ^{13}C-NMR spectra of **4** show the same AB/*trans* junction [6] [20–21] as compounds **1**–**3**. The ^{13}C-NMR signals at δ(C) 38.9 (*s*, C(5)), 18.2 (*q*, C(19)), 36.5 (*d*, C(8)), 15.9 (*q*, C(17)), 38.4 (*s*, C(9)), 18.5 (*q*, C(20)), 30.8 (*d*, C(13)), and 19.8 (*q*, C(16)) suggest the 3,4-position for the C=C bond. Comparison of the ^{1}H- and ^{13}C-NMR

Table. *^{13}C-NMR Data of Clerodane Diterpenes* **1**–**14** *in $CDCl_3$*. Trivial numbering.

C	**1**[a])	**2**[b])	**3**[b])	**3a**	**4**	**5**	**6**[a])	**7**	**8**	**8a**	**9**	**9**[a])	**10**[b])	**11**	**12**	**13**[c])	**14**[c])
C(1)	35.8	35.0	23.1	24.7	22.1	25.0	24.3	26.4	22.3	22.3	20.2	16.4	20.7	21.8	24.9	21.8	25.0
C(2)	203.1	199.8	74.6	72.3	74.5	69.1	22.3	21.1	21.3	21.2	31.1	30.5	37.4	28.7	33.1	28.7	33.1
C(3)	125.8	125.6	120.1	120.3	120.1	117.6	37.8	33.0	35.8	35.7	77.0	76.3	70.0	33.2	120.4	34.4	120.4
C(4)	176.4	172.1	150.0	149.6	149.9	153.0	76.8	87.1	76.0	75.5	77.4	76.9	162.4	160.7	144.4	160.5	144.4
C(5)	41.3	39.9	38.8	38.6	38.9	38.5	43.3	40.2	38.8	41.6	42.6	41.3	40.5	40.1	38.2	40.1	38.4
C(6)	36.7	35.7	36.2	36.4	36.9	36.2	33.2	31.8	31.9	31.8	33.6	32.5	37.4	37.4	37.2	37.4	37.3
C(7)	28.0	26.9	27.5	27.3	27.4	27.2	28.4	27.2	27.4	27.3	27.9	26.6	27.5	27.6	26.9	27.6	26.7
C(8)	37.2	36.3	36.1	35.9	36.5	36.2	37.9	36.3	36.4	36.2	37.1	36.1	36.8	36.7	36.4	36.6	36.3
C(9)	39.7	38.4	38.4	38.3	38.4	38.2	39.8	38.8	38.8	38.9	39.7	38.5	39.4	39.2	38.5	39.2	38.8
C(10)	47.2	46.2	41.3	45.1	41.3	41.3	44.3	41.4	40.9	40.4	41.8	40.9	48.6	48.7	46.6	48.7	46.4
C(11)	36.0	30.9	35.7	35.2	36.2	34.9	36.7	35.8	35.8	35.6	37.1	35.8	35.5	35.3	35.2	35.4	35.4
C(12)	30.1	37.1	29.1	29.3	29.3	28.7	30.5	29.3	29.7	29.8	30.7	29.7	29.5	29.4	29.6	29.6	29.6
C(13)	32.2	208.1	31.2	30.9	30.8	30.8	32.2	30.9	30.9	30.2	32.3	31.0	31.0	30.8	30.8	31.0	31.0
C(14)	42.6	–	41.3	41.4	41.4	41.4	42.6	41.4	41.5	39.9	42.8	42.1	41.6	41.4	41.5	41.9	41.9
C(15)	176.8	–	178.1	173.4	178.1	177.4	177.0	178.1	178.6	61.3	177.2	177.1	178.6	179.1	179.5	173.7	173.2
C(16)	20.2	30.0	20.0	19.9	19.8	19.9	20.2	19.8	20.0	20.0	20.0	19.9	20.0	19.8	19.8	19.8	19.8
C(17)	16.1	15.7	15.8	15.9	15.9	15.7	16.4	16.0	16.1	16.1	16.2	15.9	16.0	16.0	15.9	15.9	15.7
C(18)	19.1	18.8	17.9	17.7	17.9	18.0	23.4	70.1	24.4	24.4	21.2	21.3	99.5	102.5	18.4	102.4	18.5
C(19)	18.6	18.3	18.3	19.7	18.2	18.5	15.4	24.4	17.8	17.7	17.8	17.3	21.5	20.9	20.9	20.8	20.8
C(20)	18.4	17.7	18.6	18.4	18.5	18.3	18.8	18.4	18.6	18.6	18.8	18.4	18.3	18.2	18.2	18.8	18.1
MeO			56.2	51.3													
*Me*CO				21.3	21.7												
Me*C*O				170.7	171.2	161.0											

[a]) ^{13}C-NMR Spectra were measured in CD_3OD. [b]) Assignments by 2D NMR (HMQC, HMBC, ^{1}H,^{1}H COSY) experiments; all other assignments by comparison. [c]) Other ^{13}C-NMR data of **13** and **14**: 60.0 (*t*) and 13.6 (*q*).

spectra of **4** with those of **3a**, whose configuration has been established unambiguously by a partial synthesis, reveals that **4** is 2-epimer of **3a** [7].

Compound **5** has the molecular formula $C_{21}H_{34}O_4$, based on the HR-EI-MS (*m*/*z* 350.2461 (M^+; calc. 350.2457). The ^{13}C-NMR data are similar to those of **4**, except for the presence of a formyl instead of an acetyl group (**5**: δ(C) 161.0 (*s*) and δ(H) 8.07 (*s*)). Hence, **5** is 2β-(formyloxy)clerod-3-en-15-oic acid. It is possibly an artifact produced from **4** and formic acid by transesterification on workup (usually 0.2% of elution when such an acid is isolated by column chromatography over silica gel).

The HR-EI-MS establishes the formula $C_{20}H_{36}O_4$ for **7**. The ^{13}C-NMR spectra and DEPT show the similarity between **7**, **6** (*Table*), and **6a** [7], revealing that the signal at δ(C) 87.1 (*s*) has to be attributed to C(4), and the signal at δ(C) 70.1 (*t*) to C(18). These assignments are further supported by the *γ-gauche* effect observed between OH–C(18) and C(3) and C(5), and the *β-gauche* effect to C(4). Thus, **7** is 4α,18-dihydroxyclerodan-15-oic acid.

The ^{13}C-NMR spectra and DEPT of **8** show that it is an epimer of **6** [7] at C(4). The relative β-configuration of OH–C(4) is determined by comparing the ^{13}C-NMR data of C(3), C(5), C(10), C(18), and C(19) (*Table*) with those of **6**, **6a**, and **8a** [7]. Thus, **8** is β-hydroxyclerodan-15-oic acid.

The ^{1}H- and ^{13}C-NMR spectra of **9** show a clerodane-type skeleton with AB/*trans* junction [6][20–21]. The ^{13}C-NMR spectra (*Table*) of **9** are similar to those of methyl 3α,4β-dihydroxyclerodan-15-oate (**9a**) [7], except for the signal of C(4) (δ 76.9 (*s*) in $CDCl_3$), suggesting the α-configuration of OH–C(4). This is also supported by the upfield shift of the signals of C(1), C(5), and C(19) (see *Table*) due to the *γ-gauche* effect of OH–C(3) as compared to the corresponding signals of **6** and **6a** having an α-positioned OH–C(4). Thus, **9** must be 3α,4α-dihydroxyclerodan-15-oic acid.

The HR-EI-MS gave the formula $C_{20}H_{34}O_3$ for **10** (*m/z* 322.2507 (M^+; calc. 322.2508)). Further data suggest that the structure of **10** is that of 3β-hydroxyclerod-4(18)-en-15-oic acid.

The ^{13}C-NMR spectra and DEPT (*Table*) of **10** show 20 signals for four Me, eight CH_2 including an olefinic one, four CH, and four quaternary C-atoms, revealing the presence of a clerodane diterpene. However, comparison with the ^{13}C-NMR data of **1** suggest Me–C(4) is missing and replaced by a CH_2=C(4) group (δ(C) 99.5 (*t*), δ(H) 4.70 and 4.90, δ(C) 162.4(C(4)). This is confirmed by the ^{1}H,^{13}C long-range correlations (HMBC experiment) between δ(H) 1.02 (Me(19)) and δ(C) 162.4 (*s*, C(4)), 48.6 (*d*, C(10)), 40.5 (*s*, C(5)), and 37.4 (*t*, C(6)). The OH-substituted CH at δ(C) 70.0 is determined to be C(3) based on the *γ-gauche* effect of the OH group to C(1) (δ 20.7). The ^{1}H,^{13}C long-range correlations between δ(H) 4.90 and 4.70 (2 H–C(18)) and δ(C) 70.0 (*d*), 40.5 (*s*, C(5)), and 162.4 (*s*, C(4)) further support the assignment of δ(C) 70.0. The NOE between δ(H) 4.32 (H–C(3)) and 1.02 (Me(19)) indicates the α-configuration of H–C(3).

The 4-methylidene diterpene **11** was not obtained in pure form but was accompanied by a small amount of its 3,4-unsaturated isomer **12**, even after repeated column chromatography.

The signals for an exocyclic C=C bond of **11** at δ(C) 102.4 (*t*) and 160.5 (*s*) (*Table*) are assigned to C(18) and C(4) [8]. The presence of other C-resonances at 144.4 (*s*), 120.4 (*d*), 46.4 (*d*), and 39.1 (*s*) suggest that the minor component is the 3,4-unsaturated isomer **12** of **11** [9].

Compounds **13** and **14** are also 4,18-unsaturated and 3,4-unsaturated isomers, similar to **11** and **12**. The ^{13}C-NMR carbonyl signal (C(15)) of **13** and **14** is upfield-shifted to *ca.* δ 173 (*s*), suggesting they are esters of **11** and **12**, respectively. Their structures are confirmed by further ^{13}C-NMR and EI-MS data.

The molecular formula of **15**, $C_{18}H_{21}NO_6$, is established by its HR-EI-MS (*m/z* 347.1377 (M^+, calc. 347.1369)). The UV spectra (244.5, 250.5, 308, 321, 334.5 nm) show the typical absorptions for a furoquinoline alkaloid [13]. Based on further spectroscopic data, **15** is identified as 1-[(6,7-dimethoxyfuro[2,3-*b*]quinolin-4-yl)oxy]-3-methylbutane-2,3-diol. The (*S*)-configuration at C(2) is deduced by comparison of the $[\alpha]_D$ value of **15** with that of (*S*)-porritoxinol (=6-[(2*S*)-2,3-dihydroxy-3-methylbutoxy]-4-methoxy-5-methylisobenzofuran-1(3*H*)-one [22] and (*S*)-peucedanol (=6-[(2*S*)-2,3-dihydroxy-3-methylbutyl]-7-hydroxy-2*H*-1-benzopyran-2-one) [23], which have a similar 2,3-dihydroxy-3-methylbutyl moiety and one stereogenic C-atom.

The ^{13}C-NMR spectra and DEPT of **15** show 18 signals for four Me (two MeO and two Me–C), one CH_2, five CH, and eight quaternary C-atoms. The ^{1}H-NMR spectra exhibit a pair of *AB* '*d*' (J = 2.6 Hz) at δ 7.79 and 7.40 corresponding to H–C(2′) and H–C(3′) of the furan ring, respectively [24]. Two 1-H *s* at δ 7.86 and 7.64 are assigned to the two isolated aromatic H–C(5′) and H–C(8′), respectively. In the HMBC experiment, the ^{1}H,^{13}C long-range correlations between δ(H) 7.86 (H–C(5′)) and δ(C) 114.2 (C(8′a)), 143.6 (C(4′a)), 148.6 (C(6′)), 153.5 (C(7′)), and 155.9 (C(4′)), between δ(H) 7.64 (H–C(8′)) and δ(C) 114.2 (C(8′a)), 143.6 (C(4′a)), 148.6

(C(6′)), and 153.5 (C(7′)), between δ(H) 3.83 (*s*, MeO) and δ(C) 153.5 (C(7′)), and between δ(H) 3.70 (*s*, MeO) and δ(C) 148.6 (C(6′)) reveal that one MeO (δ(H) 3.70, δ(C) 55.7) is linked to C(6′) and the other to C(7′) (δ(H) 3.83, δ(C) 55.7) (see *Fig. 2*). The ^{1}H,^{13}C long-range correlations between δ(H) 1.63 (*s*, 3 H) and δ(C) 28.0 (*q*), 71.8 (*s*), and 77.4 (*d*), between δ(H) 1.68 (*s*, 3 H) and δ(C) 25.7 (*q*), 71.8 (*s*), and 77.4 (*d*), and between δ(H) 4.51 (*dd*, *J* = 8.0, 2.7 Hz, 1 H) and δ(C) 25.7 (*q*), 28.0 (*q*), 71.8 (*s*), and 74.6 (*t*) suggest the presence of an $OCH_2CH(OH)C(OH)(Me)_2$ side chain. This side chain is linked to C(4′) *via* an O-atom as established by the ^{1}H,^{13}C long-range correlations between δ(H) 5.45 (*dd*, *J* = 9.8, 2.7 Hz, 1 H) and δ(C) 155.9 (*s*, C(4′)) and between δ(H) 5.11 (*dd*, *J* = 9.8, 8.0 Hz, 1 H) and δ(C) 155.9 (*s*, C(4′)).

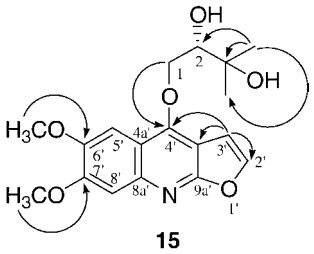

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Fig. 2. *Selected ^{1}H,^{13}C long-range correlations of furoquinoline alkaloid* **15**

Experimental Part

General. CC = Column chromatography. *UV-210A* spectrophotometer; λ_{max} in nm. IR Spectra: *Perkin-Elmer 577* spectrophotometer; $\tilde{\nu}$ in cm^{-1}. 1D NMR Spectra: *Bruker AM-400* spectrometer; δ in ppm, *J* in Hz. 2D NMR Spectra: *Bruker DRX-500* spectrometer. MS: *Autospec 3000* spectrometer at 70 eV; in *m*/*z* (rel. %).

Plant Material. The aerial parts of *Clausena dunniana* were collected in Yishuangbanna, Yunnan Province, P.R. China, in April 1999. The plant was identified by Prof. *D. D. Tao* of the Kunming Institute of Botany. A voucher specimen (No. H98041703) of this plant was deposited at the Kunming Institute of Botany, Kunming, China.

Extraction and Isolation. The powdered aerial parts of *C. dunniana* (2.0 kg) were extracted with AcOEt (4 × 6 l) under reflux for 6 h each time. The extract (130 g) was separated into five fractions by CC (porous resin *D101*, 20 → 100% EtOH/H_2O): *Fr. 1–5*. *Fr. 1* mainly contained sugars. *Fr. 2* (5.50 g) was subjected to CC (silica gel, $CHCl_3$/MeOH 95 :5, 90 :10, 85 :15): **9** and **15**. *Fr. 3* (10.10 g) was subjected to repeated CC (silica gel), kokusaginine, skimmianine, and **10**. *Fr. 4* was subjected to repeated CC (silica gel): **1**–**8** and **10**. Compounds **11**–**14** were isolated from *Fr. 5*.

14,15-Dinorclerod-3-en-2,13-dione (=*(4a*R,*7*R,*8*S,*8a*R*)-4a,5,6,7,8,8a-Hexahydro-4,4a,7,8-tetramethyl-8-(3-oxobutyl)naphthalen-2(1*H*)-one*; **2**). Colorless oil. $[\alpha]_D^{17} = -20.0$ (*c* = 0.35, $CHCl_3$). ^{1}H-NMR (400 MHz, $CDCl_3$): 0.83 (*d*, *J* = 6.7, Me(17)); 0.84 (*s*, Me(20)); 1.12 (*s*, Me(19)); 1.39 (*m*, H–C(8)); 1.52 (*m*, 1 H–C(7)); 1.54 (*m*, 1 H–C(7)); 1.56 (*m*, 1 H–C(11)); 1.62 (*m*, 1 H–C(11)); 1.78 (*dd*, *J* = 14.0, 3.8, H–C(10)); 1.88 (*dt*, *J* = 16.6, 0.75, 2 H–C(6)); 1.89 (*s*, Me(18)); 2.13 (*s*, Me(16)); 2.21 (*m*, 1 H–C(12)); 2.26 (*m*, 1 H–C(12)); 2.29 (*m*, 1 H–C(1)); 2.35 (*dd*, *J* = 14.0, 9.0, 1 H–C(1)); 5.73 (br. *s*, H–C(3)). ^{13}C-NMR (100 MHz, $CDCl_3$): *Table.* EI-MS: 276 (24, M^+), 261 (47), 258 (55), 243 (47), 205 (49), 187 (20), 163 (19), 149 (36), 135 (66), 121 (100), 109 (71), 95 (50), 83 (51). HR-EI-MS 276.2114 ($C_{18}H_{28}O_2^+$; calc. 276.2089).

2β-(Acetyloxy)clerod-3-en-15-oic Acid (=*(βξ,1*S,*2*R,*4a*R,*7*S,*8a*R*)-7-(Acetyloxy)-1,2,3,4,4a,7,8,8a-octahydro-β,1,2,4a,5-pentamethylnaphthalene-1-pentanoic Acid*; **4**). Colorless oil. $[\alpha]_D^{17} = -6.25$ (*c* = 0.40, $CHCl_3$). ^{1}H-NMR (400 MHz, $CDCl_3$): 0.75 (*s*, Me(20)); 0.80 (*d*, *J* = 6.6, Me(17)); 0.98 (*d*, *J* = 7.0, Me(16)); 0.99 (*s*, Me(19)); 1.64 (*s*, Me(18)); 2.18 (*s*, AcO); 5.71 (br. *s*, 1 H–C(3)). ^{13}C-NMR (100 MHz, $CDCl_3$): *Table.* EI-MS: 364 (2, M^+), 350 (4), 334 (15), 209 (100), 189 (23), 163 (11), 149 (15), 135 (25), 123 (65), 112 (40), 98 (79), 83 (61). HR-EI-MS: 364.2619 ($C_{22}H_{36}O_4^+$; calc. 364.2614).

2β-(Formyloxy)clerod-3-en-15-oic Acid (=*(βξ,1*S,*2*R,*4a*R,*7*S,*8a*R*)-7-(Formyloxy)-1,2,3,4,4a,7,8,8a-octahydro-β,1,2,4a,5-pentamethylnaphthalene-1-pentanoic Acid*; **5**). Colorless oil. $[\alpha]_D^{21} = -59.70$ (*c* = 0.067, $CHCl_3$). ^{1}H-NMR (500 MHz, $CDCl_3$): 0.72 (*s*, Me(20)); 0.80 (*d*, *J* = 6.4, Me(17)); 0.93 (*d*, *J* = 6.9, Me(16)); 0.94 (*s*, Me(19)); 1.66 (*s*, Me(18)); 8.07 (*s*, CHO). ^{13}C-NMR (125 MHz, $CDCl_3$): *Table.* EI-MS: 350 (4, M^+), 332 (15),

322 (5), 304 (44), 209 (63), 189 (43), 161 (30), 139 (87), 123 (71), 105 (72), 69 (92), 55 (100). HR-EI-MS: 350.2461 ($C_{21}H_{34}O_4^+$; calc. 350.2457).

4α,18-Dihydroxyclerodan-15-oic Acid (=*(βξ,1*S,*2*R,*4a*R,*5*R,*8a*R*)-Decahydro-5-hydroxy-5-(hydroxymethyl)-β,1,2,4a-tetramethylnaphthalene-1-pentanoic Acid*; **7**). Colorless oil. $[\alpha]_D^{21} = -23.33$ ($c = 0.30$, $CHCl_3$). ^{1}H-NMR (400 MHz, $CDCl_3$): 0.68 (*s*, Me(20)); 0.77 (*d*, *J* = 6.3, Me(17)); 0.97 (*d*, *J* = 6.9, Me(16)); 1.39 (*s*, Me(19)); 3.47 (*d*, *J* = 8.3, 1 H−C(18)); 3.90 (*d*, *J* = 8.3, 1 H−C(18)). ^{13}C-NMR (100 MHz, $CDCl_3$): *Table*. EI-MS: 340 (2, M^+), 322 (12, $[M - H_2O]^+$), 305 (22), 265 (36), 209 (62), 189 (37), 149 (55), 109 (60), 95 (71), 69 (87), 55 (100). HR-EI-MS: 340.2608 ($C_{22}H_{36}O_4^+$; calc. 340.2614).

4β-Hydroxyclerodan-15-oic Acid (=*(βξ,1*S,*2*R,*4a*R,*5*S,*8a*R*)-Decahydro-5-hydroxy-β,1,2,4a,5-pentamethylnaphthalene-1-pentanoic Acid*; **8**). Colorless oil. $[\alpha]_D^{16} = +13.06$ ($c = 1.80$, $CHCl_3$). ^{1}H-NMR (400 MHz, $CDCl_3$): 0.74 (*s*, Me(20)); 0.80 (*d*, *J* = 6.3, Me(17)); 0.95 (*d*, *J* = 7.0, Me(16)); 1.39 (*s*, Me(18)). ^{13}C-NMR: *Table*. EI-MS: 324 (26, M^+), 306 (13), 291 (16), 264 (8), 209 (78), 191 (92), 149 (29), 137 (43), 123 (61), 109 (68), 95 (76), 69 (100). HR-EI-MS: 324.2706 ($C_{20}H_{36}O_3^+$; calc. 324.2664).

3α,4α-Dihydroxyclerodan-15-oic Acid (=*(βξ,1*S,*2*R,*4a*R,*5ξ,6*R,*8a*R*)-Decahydro-5,6-dihydroxy-β,1,2,4a,5-pentamethylnaphthalene-1-pentanoic Acid*; **9**). Colorless oil. $[\alpha]_D^{19} = +9.32$ ($c = 0.32$, MeOH). ^{1}H-NMR (400 MHz, CD_3OD): 0.73 (*s*, Me(20)); 0.77 (*d*, *J* = 6.5, Me(17)); 0.95 (*d*, *J* = 7.0, Me(16)); 1.10 (*s*, Me(19)); 1.17 (*s*, Me(18)); 3.48 (1 br. *s*, H−C(3)). ^{13}C-NMR: *Table*. EI-MS: 340 (80, M^+), 322 (81), 279 (21), 276 (10), 225 (100), 207 (89), 189 (67), 163 (65), 137 (92), 123 (85), 109 (83), 95 (97), 69 (100). HR-EI-MS: 340.2619 ($C_{20}H_{36}O_4^+$; calc. 340.2614).

3β-Hydroxyclerod-4(18)-en-15-oic Acid (=*(βξ,1*S,*2*R,*4a*R,*6*S,*8a*R*)-Decahydro-6-hydroxy-β,1,2,4a-tetramethyl-5-methylenenaphthalene-1-pentanoic Acid*; **10**). Colorless oil. $[\alpha]_D^{16} = +33.83$ ($c = 1.50$, $CHCl_3$). ^{1}H-NMR (400 MHz, $CDCl_3$): 0.69 (*s*, Me(20)); 0.76 (*d*, *J* = 6.5, Me(17)); 0.92 (*d*, *J* = 6.8, Me(16)); 1.02 (*s*, Me(19)); 1.46 (*m*, 1 H−C(1)); 1.58 (*m*, 1 H−C(1)); 1.43 (*m*, 1 H−C(7)); 1.54 (*m*, 1 H−C(7)); 0.91 (*m*, 1 H−C(12)); 1.17 (*m*, 1 H−C(12)); 1.82 (*m*, H−C(13)); 1.18 (*m*, 1 H−C(11)); 1.32 (*m*, 1 H−C(11)); 1.40 (*m*, H−C(8)); 1.50 (*m*, 1 H−C(2)); 2.15 (*m*, 1 H−C(2)); 1.12 (*m*, 1 H−C(6)); 2.17 (*m*, 1 H−C(6)); 2.36 (*m*, 1 H−C(14)); 2.14 (*m*, 1 H−C(14)); 1.08 (*m*, H−C(10)); 4.32 (br. *s*, H−C(3)); 4.70 (br. *s*, 1 H−C(18)); 4.90 (br. *s*, 1 H−C(18)). ^{13}C-NMR (100 MHz, $CDCl_3$): *Table*. EI-MS: 322 (15, M^+), 304 (19), 289 (13), 237 (16), 207 (37), 189 (72), 161 (32), 137 (45), 123 (53), 109 (61), 95 (76), 55 (100). HR-EI-MS: 322.2507 ($C_{20}H_{34}O_3^+$; calc. 322.2508).

Ethyl Clerod-4(18)-en-15-oate (**13**) *and Ethyl Clerod-3-en-15-oate* (**14**). Colorless oil. ^{13}C-NMR: *Table*. EI-MS: 334 (41, M^+), 319 (33), 291 (45), 191 (98), 95 (100), 69 (88). HR-EI-MS: 334.2878 ($C_{22}H_{38}O_2^+$; calc. 334.2872).

*(2*S*)-1-[(6,7-Dimethoxyfuro[2,3-*b*]quinolin-4-yl)oxy]-3-methylbutane-2,3-diol* (**15**). $[\alpha]_D^{24} = -14.4$ ($c = 0.45$, MeOH). UV (MeOH): 210.5, 244.5, 250.5, 293, 308, 321, 334.5. IR (KBr): 3444, 3129, 2970, 1625, 1592, 1550, 1510, 1483, 1434, 1369, 1260, 1218, 1094, 1012, 852, 777. ^{1}H-NMR (400 MHz, C_5D_5N): 1.63 (*s*, Me(4)); 1.68 (*s*, Me−C(3)); 3.70 (*s*, MeO−C(6′)); 3.83 (*s*, MeO−C(7′)); 4.51 (*dd*, *J* = 8.0, 2.7, H−C(2)); 5.11 (*dd*, *J* = 9.8, 8.0, 1 H−C(1)); 5.45 (*dd*, *J* = 9.8, 2.7, 1 H−C(1)); 7.40 (*d*, *J* = 2.6, H−C(3′)); 7.64 (*s*, H−C(8′)); 7.79 (*d*, *J* = 2.6, H−C(2′)); 7.86 (*s*, H−C(5′)). ^{13}C-NMR (100 MHz, C_5D_5N): 25.7 (C(4)); 28.0 (C(5)); 55.7 (*Me*O−C(6′)); 55.7 (*Me*O−C(7′)); 71.8 (C(3)); 74.6 (C(1)); 77.4 (C(2)); 101.8 (C(5′)); 103.7 (C(3′a)); 105.8 (C(3′)); 107.6 (C(8′)); 114.2 (C(4′a)); 143.1 (C(2′)); 143.6 (C(8′a)); 148.6 (C(6′)); 153.5 (C(7′)); 155.9 (C(4′)); 163.8 (C(1′a)). EI-MS: 347 (85, M^+), 332 (11), 287 (11), 245 (100), 230 (41), 216 (10), 202 (22), 188 (13), 59 (59). HR-EI-MS: 347.1377 ($C_{18}H_{21}NO_6^+$; calc. 347.1369).

This work was financially supported by the grant from *The National Nature Science Foundation of China* (No. 39525025 and 30200350). All spectra were recorded by the analytical group of the Laboratory of Phytochemistry, Kunming Institute of Botany, Chinese Academy of Sciences, PR China.

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Received April 24, 2003