Neoclerodane Diterpenes from *Amoora stellato-squamosa*

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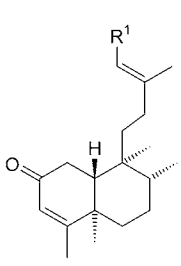
From the twigs of *Amoora stellato-squamosa*, five new neoclerodane diterpenes have been isolated and characterized, methyl (13*E*)-2-oxoneocleroda-3,13-dien-15-oate (= methyl (2*E*)-3-methyl-5-[(1*S*,2*R*,4a*R*,8a*R*)-1,2,3,4,4a,7,8,8a-octahydro-1,2,4a,5-tetramethyl-7-oxo-naphthalen-1-yl]pent-2-enoate; **1**), (13*E*)-2-oxoneocleroda-3,13-dien-15-ol (=(4a*R*,7*R*,8*S*,8a*R*)-1,2,4a,5,6,7,8,8a-octahydro-8-[(*E*)-5-hydroxy-3-methylpent-3-enyl]-4,4a,7,8-tetramethylnaphthalen-2(1*H*)-one; **2**), (3*α*,4*β*,13*E*)-neoclerod-13-ene-3,4,15-triol (=(1*R*,2*R*,4a*R*,5*S*,6*R*,8a*R*)-decahydro-5-[(*E*)-5-hydroxy-3-methylpent-3-enyl]-1,5,6,8a-tetramethylnaphthalene-1,2-diol; **3**), (3*α*,4*β*,13*E*)-4-ethoxyneoclerod-13-ene-3,15-diol (=(1*R*,2*R*,4a*R*,5*S*,6*R*,8a*R*)-1-ethoxydecahydro-5-[(*E*)-5-hydroxy-3-methylpent-3-enyl]-1,5,6,8a-tetramethylnaphthalen-2-ol; **4**), and (3*α*,4*β*,14*RS*)-neoclerod-13(16)-ene-3,4,14,15-tetrol (=(1*R*,2*R*,4a*R*,5*S*,6*R*,8a*R*)-decahydro-5-[3-(1,2-dihydroxyethyl)but-3-enyl]-1,5,6,8a-tetramethylnaphthalene-1,2-diol; **5**), together with two known compounds, (13*E*)-neocleroda-3,13-diene-15,18-diol (**6**) and (13*S*)-2-oxoneocleroda-3,14-dien-13-ol (**7**).

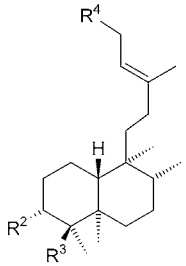
Introduction. – Our continuing investigation on the family Meliaceae has resulted in the isolation of a variety of novel tetranortriterpenoids [1]. So far, tetranortriterpenoids or protolimonoids, considered as chemotaxonomic markers and insect antifeedant active compositions of Meliaceae, have not been obtained from *Amoora yunnanensis* (H. L. LI) C. Y. WU [2]. The genus *Amoora*, mainly distributed in India and Malaysia, comprises *ca.* 25–30 species, of which six have been found in the Yunnan province, China [3]. The taxonomic position of this genus has given rise to some dispute [4][5], thus, we investigated another *Amoora* species, namely *A. stellato-squamosa* (C. Y. WU) et H. LI, in the hope of finally corroborating the taxonomy of this genus.

A. stellato-squamosa is a bush growing in Xishuangbanna and Xichou County in the Yunnan province, China [3]. This paper describes the isolation and structural elucidation of the new neoclerodane-type diterpenes **1**–**5**, which have been isolated, together with the known compounds **6** [6] and **7** [7], from the twigs of this plant. This is, as far as we know, the first report of clerodane-diterpene constituents from the genus *Amoora* [2][8]. The structures of the new compounds were determined by spectroscopic analysis, especially NMR.

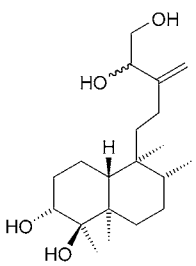
Results and Discussion. – The AcOEt-soluble fraction of the EtOH extract of the twigs of *A. stellato-squamosa* was repeatedly chromatographed on silica gel and *RP-18* gel to afford the compounds **1**–**7**, which were shown to belong to the neoclerodane-type diterpenoids. Generally, neoclerodanes possess a basic C_{20} skeleton of type **A**, including a C_6 'side chain' (either aliphatic or alicyclic) and a trimethylated *trans*-



1 R^1 = COOMe
2 R^1 = $HOCH_2$



3 R^2 = R^3 = OH, R^4 = OH
8 R^2 = AcO, R^3 = OH, R^4 = AcO
4 R^2= OH, R^3 = EtO, R^4 = OH



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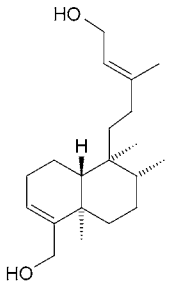

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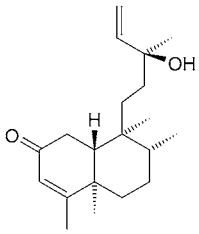

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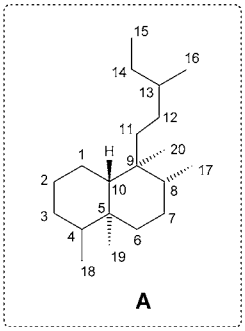

A

decalin (=decahydronaphthalene) moiety, with the Me(17) and Me(20) groups always being α-oriented at C(8) and C(9), respectively [9].

Compound **1**, obtained as colorless needles, was determined to have the molecular formula $C_{21}H_{32}O_3$ based on HR-EI-MS (*m/z* 332.2364 (M^+; calc. 332.2351)), corresponding to six degrees of unsaturation. The IR spectrum showed absorption bands at 1712, 1230, and 1154 cm^{-1} (α,β-unsaturated ester) and 1665 cm^{-1} (α,β-unsaturated ketone). By means of ^{1}H- and ^{13}C-NMR spectra (*Tables 1* and *2*, resp.), by HMQC, HMBC, and ROESY experiments, as well as by comparison with literature data (NMR data of **7** [7]), compound **1** was established as methyl (13*E*)-2-oxoneocleroda-3,13-dien-15-oate[1]).

The ^{13}C-NMR (DEPT) spectrum of **1** (*Table 2*) indicated the presence of six Me (δ_C 15.7, 17.8, 18.3, 19.0, 19.1, 50.8), five CH_2 (δ_C 26.8, 34.0, 34.9, 35.5, 35.5), and four CH groups (δ_C 36.0, 45.6, 115.1, 125.5), together with six quaternary C-atoms (δ_C 38.7, 39.8, 160.4, 167.1, 172.4, 200.0). The ^{1}H-NMR spectrum showed the signals for two trisubstituted C=C bonds at δ_H 5.69 (br. *s*, 1 H) and 5.62 (br. *s*, 1 H), one MeO group at δ_H 3.64 (*s*, 3 H), and a CH_2 group ((δ_H 2.36 (*dd*, J = 17.6, 13.6 Hz, 1 H) and 2.27 (*dd*, J = 17.6, 4.4 Hz, 1 H)) next to a C=O group (*Table 1*). These spectral data were quite similar to those of (13*S*)-2-oxoneocleroda-3,14-dien-13-ol (**7**) [7], except for the resonances attributable to the side chain. Hence, compound **1** was expected to contain a neoclerodane skeleton, with a $\Delta^{3,4}$ C=C bond and a C=O group at C(2)[2]). This was confirmed by the diagnostic

[1]) For systematic names, see the *Exper. Part*.

[2]) The semi-systematic atom numbering of the basic skeleton **A** (see chemical representation) differs from systematic atom numbers (see systematic names in the *Exper. Part*).

Table 1. *^{1}H-NMR Data of Compounds* **1**–**6**. Solvents: $CDCl_3$ for **1**, **2**, **4**, and **6**; CD_3OD for **3** and **5**. Chemical shifts δ in ppm, coupling constants J in Hz.

	1	**2**	**3**	**4**	**5**	**6**
CH_2(1)	2.36 (*dd*, $J = 17.6, 3.6$), 2.27 (*dd*, $J = 17.6, 4.4$)	2.29–2.37 (*m*)	1.29–1.35 (*m*), 1.60–1.67 (*m*)	1.43–1.50 (*m*), 1.21–1.30 (*m*)	1.54–1.58 (*m*), 1.28–1.31 (*m*)	1.85–1.93 (*m*)
CH_2(2)	–	–	1.99 (*tt*-like, $J = 13.7, 4.0$), 1.60–1.67 (*m*)	1.89 (*m*), 1.58 (*m*)	2.0 (*tt*, $J = 13.7, 4.0$), 1.57–1.64 (*m*)	1.98–2.04 (*m*)
H–C(3)	5.69 (br. *s*)	5.68 (*d*, $J = 1.2$)	3.46 (*t*, $J = 2.6$)	3.77 (*t*, $J = 2.7$)	3.47 (*t*, $J = 2.6$)	5.16 (br. *s*)
CH_2(6)	1.78 (*m*), 1.34 (*m*)	1.79 (*m*), 1.31–1.38 (*m*)	1.60–1.67 (*m*), 1.29–1.35 (*m*)	1.75 (*m*), 1.17 (*m*)	1.60–1.69 (*m*), 1.31–1.34 (*m*)	1.36–1.48 (*m*), 1.13 (*m*)
CH_2(7)	1.47 (*m*)	1.45 (*m*)	1.42–1.46 (*m*), 1.29–1.35 (*m*)	1.22–1.41 (*m*)	1.46–1.50 (*m*), 1.34–1.37 (*m*)	1.45–1.51 (*m*), 1.34–1.41 (*m*)
H–C(8)	1.49 (*m*)	1.48 (*m*)	1.49 (*m*)	1.38 (*m*)	1.47 (*m*)	1.41 (*m*)
H–C(10)	1.82 (*dd*, $J = 13.6, 4.3$)	1.85 (*m*)	1.82 (br. *d*, $J = 10.8$)	2.0 (*dd*, $J = 12.4, 2.2$)	1.83 (br. *d*, $J = 11.0$)	1.66 (*m*)
CH_2(11)	1.40–1.50 (*m*), 1.28–1.39 (*m*)	1.45–1.52 (*m*), 1.31–1.38 (*m*)	1.54 (*m*), 1.32–1.36 (*m*)	1.24–1.46 (*m*)	1.52 (*m*), 1.38–1.41 (*m*)	1.34–1.41 (*m*)
CH_2(12)	1.96 (*m*), 1.85 (*m*)	1.84 (*m*), 1.73 (*m*)	1.94 (*t*-like, $J = 8.0$)	1.80–1.88 (*m*)	1.88–1.95 (*m*)	1.95–2.0 (*m*)
H–C(14)	5.62 (br. *s*)	5.34 (*td*, $J = 6.8, 1.1$)	5.32 (*t*, $J = 6.8$)	5.39 (*td*, $J = 6.9, 1.1$)	4.08 (*tt*, $J = 7.4, 3.7$)	5.56 (*t*, $J = 6.9$)
CH_2(15)		4.09 (*d*, $J = 6.8$)	4.04 (*d*, $J = 6.8$)	4.11 (*d*, $J = 6.9$)	3.57 (*dd*, $J = 11.2, 3.9$), 3.44 (*ddd*, $J = 11.2, 7.4, 1.5$)	4.14 (*d*, $J = 6.9$)
Me(16)	2.11 (*d*, $J = 1.2$)	1.62 (*s*)	1.64 (*s*)	1.66 (*s*)	5.05 (br. *s*), 4.89 (br. *s*)	1.55 (*d*, $J = 1.2$)
Me(17)	0.81 (*d*, $J = 6.2$)	0.80 (*d*, $J = 6.8$)	0.77 (*d*, $J = 6.0$)	0.74 (*d*, $J = 6.3$)	0.79 (*d*, $J = 5.9$)	0.77 (*d*, $J = 6.9$)
Me(18)	1.85 (*d*, $J = 1.2$)	1.85 (*d*, $J = 1.1$)	1.16 (*s*)	1.13 (*s*)	1.18 (*s*)	4.11 (*s*)
Me(19)	1.08 (*s*)	1.08 (*s*)	1.09 (*s*)	1.06 (*s*)	1.11 (*s*)	0.96 (*s*)
Me(20)	0.79 (*s*)	0.77 (*s*)	0.72 (*s*)	0.68 (s)	0.75 (*s*)	0.69 (*s*)
Others	3.64 (*s*, MeO)			3.29, 3.35 (2*dq*, $J = 11.0$, 6.9, $MeCH_2$), 1.08 (*t*, $J = 6.9$, $MeCH_2$)		

Table 2. *^{13}C-NMR Data of Compounds* **1**–**6**[2]). Solvents: $CDCl_3$ for **1**, **2**, **4**, **6**, and **8**; CD_3OD for **3** and **5**. Chemical shifts δ in ppm.

	1	**2**	**3**	**8**	**4**	**5**	**6**
C(1)	34.9	35.0	17.7	16.7	16.2	17.64/17.69	18.2
C(2)	200.0	200.5	31.0	27.4	30.6	31.1	26.9
C(3)	125.5	125.4	77.0	76.9	71.9	77.0	120.5
C(4)	172.4	172.7	77.4	75.5	79.3	77.4	144.4
C(5)	39.8	39.8	42.6	41.4	42.3	42.6	38.6
C(6)	35.5	35.7	33.6	32.9	31.9	33.6	36.9
C(7)	26.8	26.8	27.9	26.6	26.8	27.9	27.4
C(8)	36.0	35.9	37.4	36.7	36.0	37.4	36.2
C(9)	38.7	38.6	39.7	38.6	38.5	39.8	38.1
C(10)	45.6	45.6	41.8	40.3	39.4	41.8	46.3
C(11)	35.5	35.5	38.5	36.0	37.2	38.97/38.92	36.7
C(12)	34.0	32.2	34.2	32.0	33.1	26.85/26.79	29.0
C(13)	160.4	139.7	140.9	143.1	141.3	151.8	144.7
C(14)	115.1	123.3	124.3	117.8	122.9	76.8	125.8
C(15)	167.1	59.3	59.5	61.4	59.5	66.6	58.3
C(16)	19.1	16.6	16.5	16.8	16.0	110.64/110.68	18.0
C(17)	15.7	15.7	16.4	15.9	16.4	16.5	16.0
C(18)	19.0	19.0	21.2	21.1	14.3	21.2	60.7
C(19)	18.3	18.3	17.9	16.8	17.5	17.9	19.9
C(20)	17.8	17.9	18.9	18.3	18.3	18.9	18.3
Others	50.8 (*q*, MeO)	–	–	170.1, 171.1 (2*s*, Me*C*=O); 21.0, 21.4 (2*q*, 2 *Me*C=O)	56.9 (*t*, Me*C*H_2); 16.3 (*q*, *Me*CH_2)		

^{1}H-NMR signals for CH_2(1) and H–C(10), which appeared as *dd* (eq. H_β–C(1) at δ_H 2.27 (*dd*, J = 17.6, 4.4 Hz); ax. H_α–C(1) at 2.36 (*dd*, J = 17.6, 13.6 Hz); ax. H_β–C(10) at 1.82 (*dd*, J = 13.6, 4.3 Hz, 1 H)), confirming the relative configuration of this part of the molecule.

HMBC Experiments revealed long-range correlations between CH_2(1) (δ_H 2.36, 2.27 (2*dd*)) and C(2), C(5), and C(10) (δ_C 200.0, 39.8, 45.6, resp.); between H–C(3) (δ_H 5.69 (br. *s*)) and C(5) and C(1) (δ_C 39.8 and 34.9, resp.); between Me(18) (δ_H 1.85 (*d*, J = 1.2 Hz)) and C(3), C(4), and C(5) (δ_C 125.5, 172.4, and 39.8, resp.); between Me(17) (δ_H 0.81 (*d*, J = 6.2 Hz)) and C(7), C(8), and C(9) (δ_C 26.8, 36.0, and 38.7, resp.); as well as between Me(20) (δ_H 0.79 (*s*)) and C(10), C(8), and C(9) (δ_C 45.6, 36.0, and 37.8, resp.). In the ROESY spectrum, the Me(20) H-atoms (δ_H 0.79 (*s*)) showed NOE correlations with Me(19), Me(17), and H_α–C(1) (δ_H 1.08 (*s*), 0.81 (*d*), and 2.36 (*dd*), resp.), which suggested their *cis*-relationship.

The structure of the side chain was determined by IR, ^{1}H- and ^{13}C-NMR, in combination with HMQC, HMBC, and ROESY experiments. The IR data indicated the presence of an α,β-unsaturated ester group (1712, 1230, 1154 cm^{-1}), corresponding to the signals at δ_C 50.8 (MeO), 167.1 (C(15)), 115.1 (C(14)), and 160.4 (C(13)) in the ^{13}C-NMR spectrum, with the Me(16) group (δ_C 19.1) being located at C(13). These assignments were in accord with the HMBC spectrum, which showed the following long-range correlations: MeO (δ_H 3.46) to C(15) (δ_C 167.1); H–C(14) (δ_H 5.62) to C(16), C(15), C(13), and C(12) (δ_C 19.1, 167.1, 160.4, and 34.0, resp.); Me(16) (δ_H 2.11) to C(15), C(13), and C(12) (δ_C 167.1, 160.4, and 34.0, resp.). Therefore, it was deduced that the side chain was a 3-methylpent-2-enoate moiety. Thereby, the C=C bond had to be (*E*)-configured according to the chemical shift of the Me(16) group (δ_H 2.11) [10], and due to a NOE correlation between the H-atoms of Me(16) and those of the ester MeO group in the ROESY spectrum.

Compound **2**, obtained as a colorless oily solid, had the molecular formula $C_{20}H_{32}O_2$, as derived by HR-ESI-MS (*m/z* 305.2486 ($[M+1]^+$; calc. 305.2480)). By analysis of the ^{1}H- and ^{13}C-NMR spectral data of **2** and comparison with those of **1**, the structure of **2** was derived as (13*E*)-2-oxoneocleroda-3,13-dien-15-ol[1]).

The ^{1}H- and ^{13}C-NMR spectra of **2** and **1** were similar, indicating that these two compounds had the same skeleton, except for their aliphatic side chains, as supported by HMBC and HMQC experiments. The signals at δ_C 123.3 (*d*) and 139.7 (*s*) indicated the presence of a trisubstituted C=C bond, attributed to C(14) and C(13). The high-field-shifted signal at δ_C 59.3 (*t*) was assigned to the oxygenated CH_2(15) group next to the side chain C=C bond. Accordingly, the side chain was identified as a 3-methylpent-2-en-1-ol moiety. This was confirmed by an HMBC experiment, in which long-range correlations were observed between H–C(15) at δ_H 4.09 (*d*, J = 6.8 Hz) and both C(14) and C(13); between H–C(14) at δ_H 5.34 (*td*, J = 6.8, 1.0 Hz) and C(12), Me(16), and C(15); as well as between the Me(16) H-atoms at δ_H 1.62 (*s*) and C(12), C(13), and C(14). The chemical shift of the Me(16) H-atoms (δ_H 1.62) indicated that the C(13)=C(14) bond was (*E*)-configured [10].

Compound **3**, obtained as a white powder, had the molecular formula $C_{20}H_{36}O_3$, as derived by HR-ESI-MS (*m/z* 347.2568 ($[M+Na]^+$; calc. 347.2562)). Its IR spectrum showed an OH absorption at 3416 cm^{-1}. According to its ^{1}H-NMR (*Table 1*) and ^{13}C-NMR (*Table 2*) spectra, assigned by means of HMQC and HMBC experiments, and by comparison of the spectral data with those of compound **2**, the structure of **3** was established as (3α,4β,13*E*)-neoclerod-13-ene-3,4,15-triol[1]).

The molecular formula of **3** suggested three degrees of unsaturation. The ^{1}H-NMR spectrum showed the typical signals of five clerodane-diterpene Me groups: a *d* at δ_H 0.77 (J = 6.0 Hz), and four *s* at δ_H 0.72, 1.09, 1.16, 1.64, resp. The signals at δ_H 5.32 (*t*, J = 6.8 Hz, H–C(14)), 4.04 (*d*, J = 6.8 Hz, H–C(15)), and a three-atom *s* at δ_H 1.64 (Me(16)) revealed the presence of the same side chain at C(9) as in **2**, as confirmed by ^{13}C-NMR (δ_C 140.3 C(13), 124.3 C(14), 59.5 C(15), 16.5 C(16)). The signals at δ_C 77.0 (*d*) and 77.4 (*s*) suggested two oxygenated C-atoms (HO–C(3) and HO–C(4), resp.), as supported by an HMBC experiment, which indicated the following long-range correlations: *a*) H_β–C(2) and H_α–C(2) at δ_H 1.60–1.65 (*m*) and 1.99 (*tt*-like), resp., with C(10) at δ_C 41.8 and C(3) at 77.0; *b*) H–C(3) at δ_H 3.46 (*t*) with C(1), C(5), and C(4) at δ_C 17.7, 42.6, and 77.4, resp.; and *c*) Me(18) at δ_H 1.16 (*s*) with C(3), C(4), C(5), resp. In the ^{1}H-NMR spectrum (*Table 1*), the *triplet* at δ_H 3.46 and its small coupling constant (J = 2.6 Hz) indicated an axially α-oriented HO–C(3) group.

We tried to determine the relative configuration of **3** by means of a ROESY experiment, but, except for NOEs between Me(16) and H–C(15), H–C(14) and H–C(12), Me(20) and Me(19), H–C(10) and H_β–C(2), as well as H–C(3) and Me(18), no useful information could be obtained. The Me(17), Me(18), Me(19), and Me(20) groups were assumed to be α-orientated on the basis of comparison with compounds **1**, **2**, and other 3,4-diol-type neoclerodanes [11][12]. Acetylation of **3** afforded the diacetate **8**. The ^{1}H-NMR spectrum (see *Exper. Part*) of the latter showed that H–C(3) was deshielded (shift change from δ_H 3.46 (**3**) to 4.74 (**8**; $\Delta\delta$ = 1.28), and the ^{13}C-NMR spectrum (*Table 2*) allowed the assignment of C(3) and C(4).

Compound **4**, obtained as a colorless, oily solid, had the molecular formula $C_{22}H_{40}O_3$, as derived by HR-ESI-MS (*m/z* 375.2882 ($[M+Na]^+$; calc. 375.2875)). From the ^{1}H- and ^{13}C-NMR spectra (*Tables 1* and *2*, resp.), HMQC, HMBC experiments, and by comparison of the spectral data with those of **3**, the structure of **4** was assigned as (3α,4β,13*E*)-4-ethoxyneoclerod-13-ene-3,15-diol[1])[3]).

The ^{13}C-NMR spectrum of **4** showed 22 signals: six Me, eight CH_2, and four CH groups, and four quaternary C-atoms. Relative to the ^{1}H-NMR spectrum of **3**, additional resonances were observed at δ_H 3.35, 3.29 (2*dq*, J = 11.0, 6.9 Hz each, MeC*H*$_2$O) and 1.08 (*t*, J = 6.9 Hz, *Me*CH$_2$O), corresponding to an EtO group (δ_C 59.9 (*t*) and 16.3 (*q*)). This was confirmed by an HMBC experiment, which showed cross-peaks for the diastereotopic CH_2 resonances of the 4-EtO group with C(4) at δ_C 79.3 (*s*) and 16.3 (*q*, *Me*CH$_2$O); and of the corresponding Me resonance at δ_H 1.08 with the CH_2 group at δ_C 56.9 (*t*). The relative configuration of **4** was determined by comparison with **3** and on biogenetic grounds (co-occurrence of neoclerodane-type diterpenes in

[3]) The EtO group of **4**, most probably, is no artifact (despite EtOH being used for extraction): first: similar diterpenes have been found where no EtOH had been used during extraction and purification [13][14], and, second, subjecting **3** to the same isolation conditions (see *Exper. Part*) did not lead to **4**.

the same plant). Regarding the configuration at C(4): the signal at δ_H 2.0 (H–C(10)) was shifted to higher field relative to that of **3** (δ_H 1.82) due to shielding *Van der Waals* effects of the EtO group, which confirmed that the 4-EtO and 4-OH groups of **4** and **3**, resp., are *cis* to H_β–C(10), and, thus, β-configured.

Compound **5**, a white powder, had the molecular formula $C_{20}H_{36}O_4$ (HR-ESI-MS: *m/z* 363.2513 ($[M+Na]^+$; calc. 363.2511); EI-MS: *m/z* 340 (M^+)). However, not 20 but 24 C-atom signals were observed in the ^{13}C-NMR spectrum, four 'couples' of resonances, each of similar intensity, being very close together: δ_C 17.64 and 17.69, 26.79 and 26.85, 38.92 and 38.97, and 110.64 and 110.67 ppm (*Table 2*). Based on the similarities of the NMR spectra of **5** and **3**, we counted each 'couple' as one C-atom, and the structure of **5** was determined as (3α,4β,14*RS*)-neoclerod-13(16)-ene-3,4,14,15-tetrol[1]).

The ^{13}C-NMR spectral data of **5** (*Table 2*) were quite similar to those of **3**, except for the side-chain resonances. The ^{1}H-NMR spectrum (*Table 1*) showed the signals of a terminal vinyl group at δ_H 5.05 (br. *s*) and 4.89 (br. *s*), corresponding to C(13) at δ_C 151.8 (*s*) and C(16) at 110.6 (*t*), resp. The signals at δ_H 3.57 (*dd*, *J* = 11.2, 3.9 Hz, 1 H) and 3.44 (*ddd*, *J* = 11.2, 7.4, 1.5 Hz, 1 H) indicated an oxygenated CH_2 group (C(15)). The signals at δ_H 4.08 (*tt*, *J* = 7.4, 3.7 Hz, 1 H) established an OH group at a CH group (C(14)), as confirmed by HMBC long-range correlations between CH_2(16) (δ_H 5.05, 4.89 (2 br. *s*, 1 H each)) and C(12), C(15), C(14), C(13) (δ_C 26.8, 66.6, 76.8, 151.8, resp.); between H–C(14) (δ_H 4.08 (*tt*, 1 H)) and C(16), C(13), C(12), C(15) (δ_C 110.6, 151.8, 26.8, 66.6, resp.); and between CH_2(15) (δ_H 3.57 (*dd*, *J* = 11.2, 3.9 Hz, 1 H) and 3.45 (*ddd*, *J* = 11.2, 7.4, 1.5 Hz, 1 H)) and C(15), C(14), C(13).

The relative configuration of **5** was determined by spectral comparison with **3**. The absolute configuration of **5** was not determined, but the observed 'peak doubling' in the ^{13}C-NMR spectrum suggested that **5** was a *C*(14)-epimeric mixture (*ca.* 1:1).

Compound **6** was identified as (13*E*)-neocleroda-3,13-diene-15,18-diol – a reduced, oxygenated derivative of **1**. The compound has been described before [6], but its ^{1}H-NMR data were not given correctly. Our revised NMR data (*Tables 1* and *2*) were assigned by HMBC and HMQC experiments, and by comparison with those of similar compounds [15].

Experimental Part

General. Silica gel (200–300 mesh) for column chromatography (CC) and silica-gel GF_{254} for TLC were obtained from *Qingdao Marine Chemical Factory* (China). M.p.: *XRC-1* Apparatus; uncorrected. Optical ratios: *Horiba SEAP-300* polarimeter. UV Spectra: *UV-210A* spectrophotometer, λ_{max} in nm (log ε). IR Spectra: *Bio-Rad FTS-135* spectrophotometer, KBr pellets; in cm^{-1}. NMR Spectra: *Bruker AM-400* or *DRX-500* spectrometers; δ in ppm rel. to Me_4Si as internal standard, *J* in Hz. EI-MS: *VG Autospec-3000* spectrometer, at 70eV; in *m/z* (rel. int.).

Plant Material. The twigs of *A. stellato-squamosa* were collected in the Xishuangbanna County, Yunnan Province, P. R. China, in January 2002. The plants were identified by Prof. *Jing-Yun Cui*, Xishuangbanna Botanical Garden, Academia Sinica, China.

Extraction and Isolation. The air-dried twigs of *A. stellato-squamosa* (9.0 kg) were extracted with EtOH/H_2O 9:1 (3 × 25 l) at r.t. The extract was evaporated *in vacuo* to give a black-brown gum, which was suspended in H_2O and extracted with AcOEt. The AcOEt extract (110 g) was subjected to CC (SiO_2; $CHCl_3$/acetone 1:0 → 1:1) to afford nine fractions (*Fr. 1–9*), as judged by TLC. *Fr. 2* (50 g), *Fr. 3* (27 g), and *Fr. 4* (10 g) were repeatedly chromatographed on SiO_2 (petroleum ether/AcOEt 49:1 → 1:1, 10:1 → 1:1, and 9:1 → 1:1, resp.), affording **1** (40 mg) from *Fr. 2*; **2** (160 mg), **4** (13 mg), and **7** (28 mg) from *Fr. 3*; and **6** (220 mg) from *Fr. 4*. *Fr. 5* (4 g) was repeatedly chromatographed (1. SiO_2; petroleum ether/Me_2CO 7:3 → 1:1; 2. *RP-18* gel, MeOH/H_2O 1:1 → 1:0) to afford **3** (470 mg) and **5** (94 mg).

*Methyl (2*E*)-3-Methyl-5-[(1*S*,2*R*,4a*R*,8a*R*)-1,2,3,4,4a,7,8,8a-octahydro-1,2,4a,5-tetramethyl-7-oxonaphthalen-1-yl]pent-2-enoate* (**1**). Colorless crystals. M.p. 88–89. $[\alpha]_D^{19} = -38.69$ ($c = 0.17$, $CHCl_3$). UV ($CHCl_3$): 247

(2.73). IR: 2951, 2877, 1712, 1665, 1646, 1614, 1437, 1381, 1230, 1154, 1055, 924, 869. ^{1}H- and ^{13}C-NMR: see *Tables 1* and *2*, resp. EI-MS: 332 (16, M^+), 317 (5), 301 (21), 285 (32), 259 (24), 243 (19), 205 (56), 189 (22), 177 (16), 161 (27), 135 (66), 121 (68), 109 (100), 83 (30), 69 (14), 55 (13). HR-EI-MS: 332.2364 (M^+, $C_{21}H_{32}O_3^+$; calc. 332.2351).

*(4a*R,*7*R,*8*S,*8a*R*)-1,2,4a,5,6,7,8,8a-Octahydro-8-[(*E*)-5-hydroxy-3-methylpent-3-enyl]-4,4a,7,8-tetramethylnaphthalen-2(1*H*)-one* (**2**). Colorless, oily solid. $[\alpha]_D^{30} = -27.54$ ($c = 0.35$, $CHCl_3$). UV ($CHCl_3$): 246 (2.26). IR: 3432, 2929, 2874, 1669, 1438, 1382, 1327, 1284, 1080, 947, 849. ^{1}H- and ^{13}C-NMR: see *Tables 1* and *2*, resp. EI-MS: 304 (4, M^+), 289 (3), 276 (3), 271 (4), 259 (10), 243 (7), 205 (33), 189 (20), 175 (10), 161 (19), 149 (20), 135 (53), 121 (100), 109 (40), 95 (27), 81 (22), 69 (12), 55 (17). HR-ESI-MS: 305.2486 ($[M + H]^+$, $C_{20}H_{33}O_2^+$; calc. 305.2481).

*(1*R,*2*R,*4a*R,*5*S,*6*R,*8a*R*)-Decahydro-5-[(*E*)-5-hydroxy-3-methylpent-3-enyl]-1,5,6,8a-tetramethylnaphthalene-1,2-diol* (**3**). White powder. M.p. 98–99. $[\alpha]_D^{30} = -12.63$ ($c = 0.20$, $CHCl_3$). IR: 3416, 2941, 2875, 1667, 1637, 1454, 1382, 1324, 1308, 1093, 1053, 1014, 978, 917, 865. ^{1}H- and ^{13}C-NMR: see *Tables 1* and *2*, resp. EI-MS: 324 (1, M^+), 306 (6), 291 (2), 263 (18), 245 (7), 223 (71), 207 (90), 189 (100), 177 (37), 163 (57), 149 (43), 137 (55), 135 (54), 123 (54), 121 (49), 109 (63), 95 (94), 81 (46), 67 (30), 55 (34). HR-ESI-MS: 347.2568 ($[M+Na]^+$, $C_{20}H_{36}NaO_3^+$; calc. 347.2562).

*(*E*)-5-[(1*S,*2*R,*4a*R,*5*R,*6*R,*8a*R*)-6-Acetoxydecahydro-5-hydroxy-1,2,4a,5-tetramethylnaphthalen-1-yl]-3-methylpent-2-enyl Acetate* (**8**). A soln. of **3** (50 mg) in anh. pyridine/Ac_2O (10 ml each) was left to stand at r.t. for 48 h. After usual work-up, the product was purified by prep. TLC (petroleum ether/acetone 2:1): 38 mg of **8**. Colorless, oily solid. ^{1}H-NMR (500 MHz, $CDCl_3$[4]): 4.74 (*d*, $J = 2.9$, H–C(3)); 1.79 (*dd*, $J = 12.4$, 2.1, H–C(10)); 4.57 (*d*, $J = 7.1$, CH_2(15)); 5.33 (*td*, $J = 7.1$, 0.8, H–C(14)); 2.05, 2.07, 1.70, 1.11, 1.08, 0.73 (6*s*, 6 Me); 0.79 (*d*, $J = 6.0$, Me(17)). ^{13}C-NMR: see *Table 2*. EI-MS: 348 (5, $[M - AcOH]^+$), 306 (3), 288 (5), 265 (77), 205 (81), 189 (100), 177 (16), 163 (17), 149 (29), 135 (32), 123 (80), 107 (57), 95 (41), 69 (40), 55 (45).

*(1*R,*2*R,*4a*R,*5*S,*6*R,*8a*R*)-1-Ethoxydecahydro-5-[(*E*)-5-hydroxy-3-methylpent-3-enyl]-1,5,6,8a-tetramethylnaphthalen-2-ol* (**4**). Colorless, oily solid. $[\alpha]_D^{25} = -22.04$ ($c = 0.43$, $CHCl_3$). IR: 3448, 2945, 2870, 1710, 1666, 1455, 1385, 1279, 1107, 1062, 1017, 978, 958, 941, 845. ^{1}H- and ^{13}C-NMR: see *Tables 1* and *2*, resp. EI-MS: 352 (3, M^+), 350 (14), 334 (92), 306 (6), 288 (6), 253 (51), 237 (39), 219 (7), 207 (62), 189 (61), 177 (12), 163 (28), 149 (53), 137 (81), 123 (73), 115 (100), 95 (82), 81 (69), 73 (70), 55 (61), 43 (51). HR-ESI-MS: 375.2882 ($[M+Na]^+$, $C_{22}H_{40}NaO_3^+$; calc. 375.2875).

*(1*R,*2*R,*4a*R,*5*S,*6*R,*8a*R*)-5-[3-(1,2-Dihydroxyethyl)but-3-enyl]decahydro-1,5,6,8a-tetramethylnaphthalene-1,2-diol* (**5**). White powder. M.p. 141–163°. $[\alpha]_D^{22} = -8.15$ ($c = 0.18$, MeOH). IR: 3424, 2943, 2873, 1633, 1452, 1384, 1092, 1051, 1018, 978, 901. ^{1}H- and ^{13}C-NMR: see *Tables 1* and *2*, resp. EI-MS: 340 (7, M^+), 322 (2), 310 (5), 261 (12), 243 (11), 225 (34), 207 (71), 189 (100), 177 (19), 163 (61), 149 (45), 137 (60), 123 (48), 109 (54), 95 (62), 81 (36), 69 (29), 55 (39). HR-ESI-MS: 363.2513 ($[M+Na]^+$, $C_{20}H_{36}NaO_4^+$; calc. 363.2511).

*(*E*)-3-Methyl-5-[(1*S,*2*R,*4a*R,*8a*R*)-1,2,3,4,4a,7,8,8a-octahydro-5-(hydroxymethyl)-1,2,4a-trimethylnaphthalen-1-yl]pent-2-en-1-ol* (**6**). Colorless, oily solid. $[\alpha]_D^{30} = -23.49$ ($c = 0.15$, $CHCl_3$). IR: 3406, 2935, 1721, 1654, 1452, 1382, 1284, 1173, 1075, 1001. ^{1}H- and ^{13}C-NMR: see *Tables 1* and *2*, resp. EI-MS ($C_{20}H_{34}O_2$): 288 (6, $[M - H_2O]^+$), 286 (10), 273 (4), 271 (9), 255 (11), 205 (9), 191 (44), 189 (100), 175 (23), 159 (21), 149 (22), 135 (39), 121 (66), 107 (62), 95 (85), 81 (43), 69 (20), 55 (23).

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