New Terpenoids from Basidiomycetes *Russula lepida*

by **Tan Jian-Wen**, **Dong Ze-Jun**, and **Liu Ji-Kai***

Kunming Institute of Botany, The Chinese Academy of Sciences, Kunming 650204, P. R. China
(Fax: +86-871-51 50 227; e-mail: jkliu@mail.kib.ac.cn)

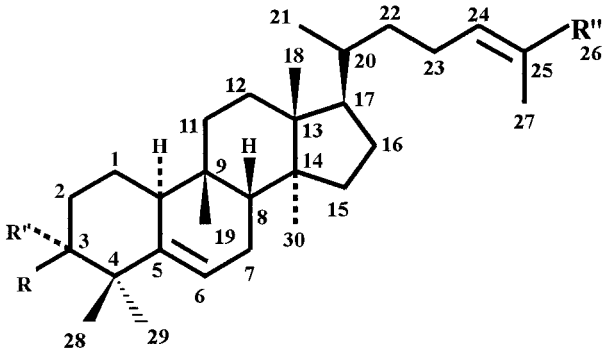
Three new triterpenoids and two new aristolane sesquiterpenoids, namely (24*E*)-3β-hydroxycucurbita-5,24-diene-26-oic acid (**1**), (24*E*)-3,4-secocucurbita-4,24-diene-3,26-dioic acid (**4**), (24*E*)-3,4-secocucurbita-4,24-diene-3,26,29-trioic acid (**5**), rulepidadiol (**6**), and rulepidatriol (**7**), were isolated from the fruiting bodies of Basidiomycetes *Russula lepida*. Their structures were established by spectral methods. Acids **4**, and **5** are the first examples of naturally occurring seco-ring-A cucurbitane triterpenoids. Alcohols **6** and **7**, belonging to the aristolane-type sesquiterpenoids, are of a type rather rare in nature, especially among fungal species.

Introduction. – The Russulaceae family is one of the largest in the subdivision Basidiomycotina in *Witthaker*'s 'Kingdom of Fungi' and comprises hundreds of species [1]. While secondary metabolites occurring in the fruiting bodies of European *Lactarius* species have been well investigated, the *Russula* mushrooms have received less attention, notwithstanding the larger number of existing species [2]. *Russula lepida* FR. has been used as a food and medicinal agent in China. The extract of its fruiting bodies showed antitumor activity [3]. As one part of our study on the bioactive metabolites of the higher fungi in Yunnan Province, which is one of the areas with the richest fungi sources in the world, the chemical constituents of *R. lepida* collected at the Ailao Mountain in Yunnan Province were investigated. This report describes the structure elucidation of three new triterpenes, (24*E*)-3β-hydroxycucurbita-5,24-diene-26-oic acid (**1**), (24*E*)-3,4-secocucurbita-4,24-diene-3,26-dioic acid (**4**), and (24*E*)-3,4-*seco*-cucurbita-4,24-diene-3,26,29-trioic acid (**5**), two new aristolane sesquiterpenes, rulepidadiol (**6**) and rulepidatriol (**7**), from the EtOH and $CHCl_3$/MeOH 1:1 extract of the fruiting bodies of *R. lepida.*

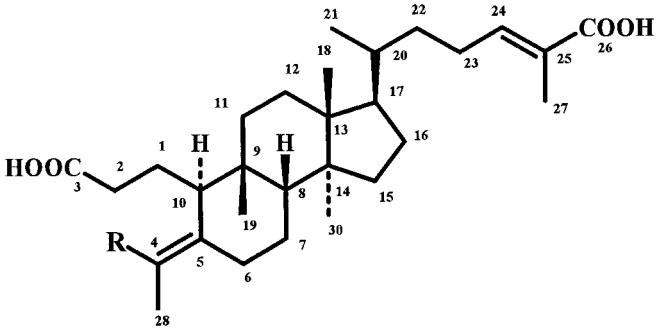
Results and Discussion. – The $CHCl_3$ fraction of the EtOH and $CHCl_3$/MeOH 1:1 extract from the fruiting bodies of *R. lepida* was subjected to repeated chromatography to afford (24*E*)-3β-hydroxycucurbita-5,24-diene-26-oic acid (**1**), (24*E*)-3,4-secocucurbita-4,24-diene-3,26-dioic acid (**4**), (24*E*)-3,4-secocucurbita-4,24-diene-3,26,29-trioic acid (**5**), rulepidadiol (**6**), and rulepidatriol (**7**).

The optically active compound **1** was obtained as colorless crystals. Its IR spectrum revealed the presence of an OH group (3507 cm^{-1}), a COOH function (3400–3200, 1687 cm^{-1}), and a C=C bond (1642 cm^{-1}). The mass spectrum exhibited the molecular ion peak at *m*/*z* 456 and characteristic fragment ions at *m*/*z* 304 (**a**), 152 (**b**) and 134 (**b** – H_2O) due to *retro-Diels-Alder* cleavage.

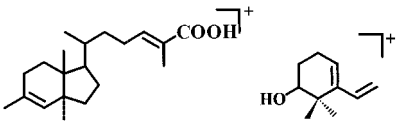
The ^1H- and ^{13}C-NMR (*Tables 1* and *2*), MS, and IR data and literature precedents suggested that **1** is a triterpenoid based on the cucurbitane skeleton [4–6] with the molecular formula $C_{30}H_{48}O_3$. Compound **1** and 10α-cucurbita-5,24-dien-3-ol (**3**) were



1 R=OH, R'=H, R"=COOH
2 R=H, R'=OH, R"=COOH
3 R=OH, R'=H, R"=CH_3



4 **R=CH_3**
5 **R=COOH**



a m/z 304 b m/z 152

found to have the same ring A and B moiety by comparing their NMR data. The NMR data of C(12) to C(28) of **1** were consistent with those of rosacea acid B (**2**) [6], indicating that these two compounds have the same ring C and D and side-chain moiety. The configuration at the C(24)=C(25) bond of **1** was established by a NOESY experiment (no NOE between Me(27) and H–C(24)), and HMQC and HMBC experiments confirmed the proposed structure **1**.

Table 1. *^{1}H-NMR Data for* **1**–**5**. δ in ppm, J in Hz.

	1[a])	**2**[a])	**3**[a])	**4**[a])	**5**[b])
CH_2(1)	1.56	1.56	1.55	1.53	1.54
CH_2(2)	1.68, 1.89	1.69, 1.89	1.70, 1.96	1.25, 1.88	1.11, 1.88
H–C(3)	3.49 (br. *s*)	3.23 (*dd*, J = 11.4, 4.3)	3.68 (br. *t*, J = 2.6)		
H–C(6) or CH_2(6)	5.59 (br. *d*, J = 5.2)	5.60 (*d*, J = 6.0)	5.59 (br. *d*, J = 6.0)	1.54	1.73
CH_2(7)	1.81, 2.37	1.81, 2.34	1.81, 2.39	2.40	2.69
H–C(8)	1.78	1.81	1.78	1.88	1.91
H–C(10)	2.28	2.32	2.28	2.40	2.77
CH_2(11)	1.42, 1.69	1.42, 1.72	1.40, 1.70	2.15, 2.25	2.15, 2.25
CH_2(12)	1.52, 2.26	1.51, 1.84	1.51, 1.77	1.52	1.60
CH_2(15)	1.50, 1.68	1.16, 1.22	1.20, 1.20	1.48, 1.68	1.48, 1.68
CH_2(16)	1.25	1.89, 2.10	1.30, 1.83	1.52	1.76
H–C(17)	1.52	1.51	1.55	1.52	1.53
Me(18)	0.85	0.85	0.85	0.82	0.89
Me(19)	0.92	0.86	0.92	1.15	1.21
H–C(20)	1.46	1.46	1.42	1.42	1.45
Me(21)	0.93 (*d*, J = 6.2)	0.93 (*d*, J = 6.1)	0.90 (*d*, J = 7.0)	0.92 (*d*, J = 6.0)	0.94 (*d*, J = 5.9)
CH_2(22)	1.12, 1.48	1.12, 1.44	1.07, 1.42	1.08, 1.51	1.10, 1.51
CH_2(23)	2.13, 2.22	2.14, 2.23	1.80, 2.04	2.05, 2.24	1.85, 2.14
H–C(24)	6.89 (br. *t*, J = 7.4)	6.89 (*td*, J = 7.4, 1.4)	5.09 (*t*, J = 7.0)	6.81 (br. *t*, J = 7.4)	7.20 (br. *t*, J = 7.4)
Me(26)			1.68		
Me(27)	1.85	2.11	1.60	1.84	2.22
Me(28)	1.02	0.93	1.02	1.55	2.12
Me(29)	1.14	1.13	1.13	1.62	
Me(30)	0.81	0.81	0.80	0.63	0.78

[a]) In $CDCl_3$, [b]) In C_5D_5N.

Table 2. *^{13}C-NMR (DEPT) Data for* **1**–**5**. δ in ppm.

	1[a])	**2**[a])	**3**[a])	**4**[a])	**5**[b])		**1**[a])	**2**[a])	**3**[a])	**4**[a])	**5**[b])
C(1)	21.1	20.1	21.1	22.3	23.4	C(16)	27.9	27.9	30.5	27.6	27.2
C(2)	28.9	30.5	28.9	28.4	28.0	C(17)	50.4	50.6	50.4	50.8	51.2
C(3)	76.7	77.4	76.6	177.2	176.2	C(18)	15.4	15.4	15.4	15.4	15.6
C(4)	41.4	42.0	41.4	122.9	124.6	C(19)	28.0	28.0	28.0	30.5	30.8
C(5)	141.2	143.8	141.2	133.5	149.1	C(20)	35.9	35.8	35.9	35.9	36.3
C(6)	121.4	119.1	121.4	36.6	37.1	C(21)	18.6	18.0	18.6	18.4	18.8
C(7)	24.4	24.4	24.3	22.3	25.0	C(22)	34.9	34.8	36.4	34.2	35.6
C(8)	43.7	43.6	43.6	43.7	44.3	C(23)	25.8	25.9	24.8	25.6	26.0
C(9)	34.5	34.7	34.4	37.2	38.1	C(24)	145.6	145.6	125.2	144.2	142.6
C(10)	37.9	35.9	37.8	42.7	43.6	C(25)	126.7	126.5	130.9	128.9	128.9
C(11)	32.3	32.3	32.3	32.6	33.4	C(26)	172.9	172.6	25.7	170.8	170.6
C(12)	34.9	34.9	34.7	34.9	34.5	C(27)	11.9	12.0	17.6	12.0	12.8
C(13)	46.4	46.4	46.2	45.9	46.1	C(28)	25.4	24.4	25.4	22.3	17.7
C(14)	49.2	49.2	49.1	49.0	49.4	C(29)	27.2	20.0	27.2	20.1	173.0
C(15)	30.5	31.0	30.4	30.1	30.5	C(30)	17.8	18.5	17.8	17.2	17.2

[a]) In $CDCl_3$. [b]) In C_5D_5N.

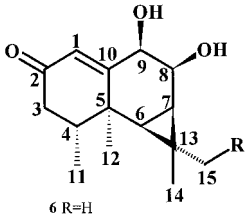
The signals in the ^{1}H-NMR spectrum of **1** at δ 6.89, 5.59, and 3.49 were assigned to two trisubstituted olefinic protons and an oxymethine group, respectively. Thirty signals in the ^{13}C-NMR (DEPT) spectrum of **1** were recognized (7 C, 7 CH, 9 CH_2, 7 CH_3), establishing the presence of a COOH, an oxymethine, two olefinic methines, and two olefinic quaternary C-atoms.

The high-resolution FAB-MS (negative mode) of **4** showed an $[M-H]^+$ at 471 corresponding to the formula $C_{30}H_{47}O_4^+$. The EI-MS fragmentation pattern, IR, ^{1}H- and ^{13}C-NMR (*Tables 1* and *2*), HMQC, and NOESY data were consistent with the proposed structure **4**.

The EI-MS of **4** showed the characteristic fragmentation of the molecular ion of 3,4-secotriterpenoids with a prominent peak at *m*/*z* 399 (15%, $[M-CH_2CH_2CO_2H]^+$) [7], besides peaks at *m*/*z* 331 (loss of one side chain ($C_8H_{13}O_2$)) and 95 (100%, $C_7H_{11}^+$). The presence of two COOH groups was inferred from the IR ($\tilde{\nu}$(OH) 3400 and $\tilde{\nu}$(CO) 1697 cm^{-1}) and ^{13}C-NMR (δ 170.8(C(26)) and 177.2(C(3)) data. One olefinic proton was revealed in the ^{1}H-NMR spectrum at δ 6.81. Evidence for the two C=C bonds was provided by the presence of the ^{13}C-NMR signals δ 144.2(CH(24)), 133.5(C(5)), 128.9(C(25)), and 122.9(C(4)). In addition, signals representing seven Me groups were located at δ 0.63 (*s*, Me(30)), 0.82 (*s*, Me(18)), 0.92 (*d*, J = 6.0 Hz, Me(21)), 1.15 (*s*, Me(19)), 1.55 (*s*, Me(28)), 1.62 (*s*, Me(29)), and 1.84 (*s*, Me(27)). All these data suggested that **4** possesses a 3,4-secocucurbitane skeleton. This proposition was further supported by the diagnostic fragmentation ions at *m*/*z* 304 (**a**), corresponding to the loss of seco-ring A and ring B on cleavage of the C(7)–C(8) and C(9)–C(10) bonds, and *m*/*z* 163 ($C_{12}H_{19}$; 304-$C_8H_{13}O_2$), indicating the absence of Me–C(10) [8–10]. The *s* at δ 1.55 (Me(28) and 1.62 (Me(29)) appearing at relatively low field also suggested that the second double bond, an isopropylidene group, was located at C(4)=C(5).

Compound **5** showed in its ^{13}C-NMR spectrum (*Table 2*) three COOH, one olefinic CH, and three olefinic quaternary C-atoms, which were assigned to two C=C bonds. The molecular formula $C_{30}H_{46}O_6$ (HR-FAB-MS (neg.): 501.3220 ($[M-H]^+$) and the ^{13}C-NMR DEPT data (*Table 2*) suggested a tricyclic structure for **5**, which was confirmed by other MS and NMR data (*Tables 1* and *2*).

The EI-MS of **5** displayed characteristic peaks with the loss of the side chain at *m*/*z* 361 ($[M-C_8H_{13}O_2]^+$), 303 ($[M-C_8H_{13}O_2-C_2H_2O_2]^+$), and 289 ($[M-C_8H_{13}O_2-C_3H_4O_2]^+$), and prominent peaks at *m*/*z* 484 ($[M-H_2O]^+$), 440 ($[M-H_2O-CO_2]^+$), 425 ($[M-H_2O-CO_2-CH_3]^+$). In addition, no Me(29) signal was detected in the ^{1}H-NMR spectrum.



6 R=H
7 R=OH

Rulepidadiol (**6**) was obtained as a pale yellow oil. It showed IR absorptions at 1665 (conjugated unstrained C=O), 1649 (C=C), and 3415 cm^{-1} (br., OH). The presence of the conjugated keto group was further confirmed by a UV absorption maximum at 244 nm (log ε 4.05). MS, ^{1}H- and ^{13}C-NMR (*Table 3*), ^{1}H,^{1}H-COSY, HMBC, and NOESY data were consistent with the aristolene structure [11–14] **6**.

The MS of **6** exhibited M^+ at *m*/*z* 250 and characteristic fragment ions at *m*/*z* 232 ($[M-H_2O]^+$), 217 ($[M-H_2O-CH_3]^+$), and 152 (*retro-Diels-Alder* cleavage). The signals in the ^{1}H-NMR spectrum at δ 6.09, 4.39, and

Table 3. *^{1}H- and ^{13}C-NMR Data for Rulepidadiol* (**6**) *and Rulepidatriol* (**7**). δ in ppm, J in Hz. Terpene numbering.

	6[a])	**7**	**6**[a])	**7**	**6** (HMBC)[a])
H–C(1)	127.5	128.6	6.09 (*s*)	6.07 (*s*)	H–C(3), H–C(9)
C(2)	200.4	202.1			H–C(3), H–C(9)
CH_2(3)	41.9	42.9	2.23 (*m*)	2.38 (*m*)	H–C(1), Me(11)
H–C(4)	37.9	39.2	2.16 (*m*)	2.28 (*m*)	
C(5)	39.2	39.9			H–C(1), CH_2(3), H–C(4), H–C(9), Me(11), Me(12)
H–C(6)	32.8	30.4	0.98 (*m*)	1.28 (*m*)	H–C(8), Me(12), Me(14), Me(15)
H–C(7)	26.4	24.5	1.12 (*m*)	1.28 (*m*)	H–C(8), Me(14), Me(15)
H–C(8)	73.2	73.6	4.39 (*dd*, J = 7.2, 5.6)	4.40 (*dd*, J = 6.6, 6.2)	H–C(6)
H–C(9)	74.4	75.7	4.25 (*d*, J = 7.2)	4.20 (*d*, J = 6.6)	H–C(1), H–C(7)
C(10)	172.7	174.9			H–C(1), H–C(6), H–C(9), Me(12)
Me(11)	15.2	15.5	1.01 (*d*, J = 6.5)	1.10 (*d*, J = 6.5)	CH_2(3), H–C(4)
Me(12)	21.9	22.2	1.07 (*s*)	1.21 (*s*)	H–C(4)
C(13)	20.0	27.0			H–C(8), Me(14), Me(15)
Me(14)	17.3	13.5	1.09 (*s*)	1.22 (*s*)	H–C(6), H–C(7)
Me(15) or CH_2(15)	30.3	73.6	1.05 (*s*)	3.25, 3.20 (*AB*, J = 11)	H–C(6), H–C(7)

[a]) In $CDCl_3$. [b]) In CD_3OD.

4.25 were assigned to an olefinic H-atom of a trisubstituted C=C bond and to two oxymethine protons, respectively. Fifteen signals in the ^{13}C-NMR (DEPT) spectrum were recognized (4 C, 6 CH, 1 CH_2, 4 Me), among them a keto C-atom, two oxymethines, one olefinic CH, and one olefinic quaternary C-atom. The similarity of these data with those of aristolane [11–14] suggested for **6** an aristolane-derived sesquiterpenediol structure of the molecular formula $C_{15}H_{22}O_3$. ^{1}H,^{1}H COSY, and HMQC experiments confirmed the presence of two proton systems, one from CH_2(3) to Me(11), and another from CH(6) to CH(9). The connectivity of these two units was established by the cross-peaks between H–C(1) and H–C(9), and the weak correlation between H–C(1) and 2 H–C(3) that appeared in the ^{1}H,^{1}H COSY spectra and HMBC correlation (*Table 3*). Two- or three-bond couplings allowed us to establish the molecular structure of rulepidadiol as **6**. As to the configuration of the two OH groups at C(8) and C(9), that the coupling constant J(8,9) was moderate (7.2 Hz) indicated that H–C(9) and H–C(8) were not both either axial or equatorial ($J_{(9ax,\ 8ax)} \approx 14$ Hz, $J_{(9eq,\ 8eq)} \approx 2$ Hz) [14]. By studying models and considering the possible strong repulsion between OH–C(9) and one of the Me groups at the cyclopropane moiety or between OH–C(8) and Me(12) [13], which would probably force the molecule to assume another form with an equatorial OH, the most likely structure of rulepidadiol was ascribed to one in which both OH groups have the β configuration, as shown. This was confirmed by a NOESY experiment in which the important NOE correlations H–C(9) Me(12), H–C(8), and H–C(7) were observed.

Rulepidatriol (**7**) showed in its ^{13}C-NMR spectrum (DEPT) four quaternary C-atoms, six CH, two CH_2 and three Me groups. Its MS exhibited M^+ at m/z 266, suggesting, combined with the ^{13}C-NMR (DEPT) data, the molecular formula $C_{15}H_{22}O_4$. From the similarities of the NMR spectra of **6** and **7** (*Table 3*), the structure of **6** could be deduced.

The signals in the ^{1}H-NMR spectrum of **6** at δ 6.07, 4.40 and 4.20, and 3.29 were assigned to an olefinic proton at a trisubstituted C=C bond, two oxymethine protons, and one oxymethylene proton, respectively. The deshielding of C(13) in the ^{13}C-NMR spectrum of **7** by *ca.* 7 ppm when compared with **6**, supported the bonding of the OH group at C(15) [14]. This was also confirmed by the ^{1}H- and ^{13}C-NMR spectra.

The intensely bitter tetracyclic triterpenes of the Cucurbitaceae are well-known to be toxic to a range of herbivores and to protect plant tissues from herbivory. In the

literature, there is extensive direct and indirect evidence concerning the biological importance of the nondegraded, rather apolar seco-A-triterpenes [15]. Early reports on biologically active, naturally occurring seco-A derivatives describe antibacterial lanostane-type fungal metabolites of eburicoic acid [16][17]. Synthetic compounds with a 3,4-seco-3-acid structure derived from steroids and tetracyclic triterpenes were also found to possess antibacterial activity [18–20]. In higher plants, the relatively apolar seco-A-triterpenoids occur in resins excreted in intercellular cavities, or are present in leaf or bark waxes at or near the plant's surface. Sometimes they constitute the main components of the resinous exudate that covers the galls produced by the insect. It has been suggested that the formation of defensive substances in galls is controlled by the gall-making insect and that the substances protect the gall makers from other herbivores and predators [21].

Aristolane sesquiterpenes are of a type rather rare in nature; they have been isolated both from terrestrial plants and marine organisms [22]. This is the second finding of members of these classes in a fungal species [2]. It is considered to be of evolutionary significance that the elaboration by *Russula lepida* of aristolane sesquiterpenes is antipodal to that usually found in higher plants, belonging, instead, to the enantiomeric series typical of several liverworts and Octocorallia [2].

Experimental Part

General. CC = column chromatography. M.p.: uncorrected. UV: λ_{max} (log ε). IR: KBr pellets; in cm^{-1}. ^1H- and ^{13}C-NMR: *Bruker AM-400* spectrometer; δ in ppm, J in Hz. MS: *VG Autospec-3000* spectrometer; *m/z* (rel. %).

Mushroom Material. The Basidiomycetes *Russula lepida* FR. was collected at the Ailao Mountain in Yunnan Province, China, in July 1998. The voucher specimen was deposited at the herbarium of Kunming Institute of Botany.

Extraction and Isolation. The fresh fruiting bodies of *R. lepida* (dry weight after extraction 475 g) were extracted twice with 95% EtOH, then $CHCl_3$/MeOH 1:1 and $CHCl_3$ at r.t. The residue obtained by evaporation was suspended in H_2O and extracted with $CHCl_3$ (4×) and BuOH (4×). The $CHCl_3$ extract (17 g) was fractionated by CC (silica gel (207 g, 200–300 mesh), $CHCl_3$/MeOH 99:1, 95:5, and 90:10) to afford several fractions. The fraction (2.5 g) from $CHCl_3$/MeOH 99:1 was purified by repeated CC and prep. TLC to give seven pure compounds including **1** (110 mg), **5** (13 mg), and **6** (50 mg). The $CHCl_3$/MeOH 90:10 fraction was purified by prep. TLC (petroleum ether/acetone 55:45): **4** (10 mg). The MeOH-soluble part (18 g) of the BuOH extract was purified by CC (silica gel, AcOEt/MeOH 95:5) and repeated prep. TLC ($CHCl_3$/MeOH 9:1, petroleum ether/acetone 6:4): **7** (33 mg).

*(24*E*)-3β-Hydroxycucurbita-5,24-diene-26-oic Acid* (= *(3β,9β,10α,24*E*)-3-Hydroxy-9-methyl-19-norlanosta-5,24-dien-26-oic Acid*; **1**). Colorless crystals. M.p. 229.5–231.5° ($CHCl_3$). $[\alpha]_D^{20} = +37.7$ ($c = 0.35$, $CHCl_3$). IR: 3507, 3400–3200, 1687, 1642. ^1H- and ^{13}C-NMR: *Tables 1 and 2*. HR-FAB-MS (neg.): 455.3595 ($C_{30}H_{47}O_3^+$, $[M-H]^+$; calc. 455.3525). EI-MS: 456 (10), 438 (7), 314 (10), 304 (98), 289 (50), 192 (25), 163 (47), 152 (73), 134 (100), 119 (69), 107 (58), 95 (65).

*(24*E*)-3,4-Secocucurbita-4,24-diene-3,26-dioic Acid* (= *(9β,10α,24*E*)-9-Methyl-19-nor-3,4-secolanosta-4,24-diene-3,26-dioic Acid*; **4**). M.p. 174.5–176.5° ($CHCl_3$). $[\alpha]_D^{20} = +26.3$ ($c = 0.2$, $CHCl_3$). IR: 3400, 1697, 1278. ^1H- and ^{13}C-NMR: *Tables 1* and *2*. HR-FAB-MS (neg.): 471.3482 ($C_{30}H_{47}O_4^+$, $[M-H]^+$; calc. 471.3474). EI-MS: 472 (10), 457 (6), 429 (6), 399 (15%), 331 (37), 317 (45), 304 (75), 289 (20), 235 (25), 195 (45), 107 (66), 95 (100).

*(24*E*)-3,4-Secocucurbita-4,24-diene-3,26,29-trioic Acid* (= *9β,10α,4*E*,24*E*)-9-Methyl-19-nor-3,4-secolanosta-4,24-diene-3,26,29-trioic Acid*; **5**). Colorless crystals. M.p. 201.5–202.5° (MeOH). $[\alpha]_D^{20} = +64.0$ ($c = 0.3$, MeOH). IR: 3421 (br.), 1685, 1414, 1384, 1282, 932. ^1H- and ^{13}C-NMR: *Tables 1* and *2*. EI-MS: 502 (13), 484 (30), 440 (31), 425 (32), 361 (10), 303 (25), 289 (16), 249 (19), 235 (36), 181 (32), 105 (90), 95 (100).

Rulepidadiol (= *(1aα,2β,3β,7a,7aα,7bα)-1,1a,2,3,6,7,7a,7b-Octahydro-2,3-dihydroxy-1,1,7,7a-tetramethyl-5*H*-cyclopropa[a]naphthalen-5-one*; **6**). Pale yellow oil. $[\alpha]_D^{10} = +21.2$ ($c = 0.43$, $CHCl_3$). UV 244 (4.05). IR: 3415 (br.), 1665, 1649. ^1H- and ^{13}C-NMR: *Table 3*. EI-MS: 250 (10), 232 (8), 217 (12), 189 (15), 152 (50), 137 (35), 109 (55), 91 (80), 77 (70), 55 (100).

Rulepidatriol (=*(1α,1aα,2β,3β,7α,7aα,7bα)-1,1a,2,3,6,7,7a,7b-Octahydro-2,3-dihydroxy-1-(hydroxymethyl)-1,7,7a-trimethyl-5*H-*cyclopropa[*a*]naphthalen-5-one*; **7**). Colorless crystals. M.p. 229–231° (MeOH). $[\alpha]_D^{10} = +4.3$ ($c = 0.41$, MeOH). IR: 3421 (br.), 1653, 1423, 1360, 1287, 1044, 1017. ^{1}H- and ^{13}C-NMR: *Table 3*. EI-MS: 266 (48), 248 (10), 219 (35), 191 (20), 152 (100), 137 (30), 121 (42), 109 (65), 91 (75), 77 (60), 55 (83).

Financial support was provided by grants from the *National Natural Science Foundation of China* (39969005) and *Natural Science Foundation of Yunnan Province* (98C086M, 98C008Z). We are grateful to Profs. *Liu Pei-Gui* and *Ji Dan-Gan* for their support in this project. This paper is dedicated to Profs. *Jia Zhong-Jian* and *Zuo Chun-Xu* on occasion of their 70th birthday.

REFERENCES

[1] R. H. Witthaker, *Science (Washington, D.C.)* **1969**, *163*, 150.
[2] G. Vidari, Z. Che, L. Garlaschelli, *Tetrahedron Lett*. **1998**, *39*, 6073.
[3] M. Yuan, P. Sun, 'Sichuan Mushrooms', 1st edn., Sichuan Academic Press, Sichuan, 1995, p. 375.
[4] C. B. Gamlath, A. A. L. Gunatilaka, E. O. Schlemper, *J. Chem. Soc., Chem. Commun*. **1988**, 249.
[5] W. D. Nes, R. Y. Wong, M. Benson, T. Akinisa, *J. Chem. Soc., Chem. Commun*. **1991**, 1272.
[6] H. Wang, G. Yang, S. Wu, G. Li, W. Xu, L. Meng, Z. Li, *Acta Pharmaceutica Sinica* **1994**, *29*, 39.
[7] T. Tai, A. Akahori, T. Shingu, *Phytochemistry* **1991**, *30*, 2796.
[8] T. Akihisa, H. Oinuma, K. Yasukawa, Y. Kasahara, Y. Kimura, S. Takase, S. Yamanouchi, M. Takido, K. Kumaki, T. Tamura, *Chem. Pharm. Bull*. **1996**, *44*, 1255.
[9] H. Greger, C. Zdero, F. Bohlmann, *Phytochemistry* **1983**, *22*, 2085.
[10] C. B. Gamlath, A. A. L. Gunatilaka, S. Subramaniam, *J. Chem. Soc., Perkin Trans. 1* **1989**, 2259.
[11] E. Piers, R. W. Britton, W. de Waal, *Can. J. Chem*. **1969**, *47*, 831.
[12] J. Krepinsky, G. Jommi, Z. Samek, F. Sorm, *Coll. Czech. Chem. Commun*. **1970**, *35*, 745.
[13] M. N. Do, K. L. Erikson, *J. Org. Chem*. **1983**, *48*, 4410.
[14] G. Ruecker, R. Mayer, E. Breitmaier, G. Will, A. Kirfel, M. Kordy, *Phytochemistry* **1984**, *23*, 1647.
[15] W. J. Baas, *Phytochemistry* **1985**, *24*, 1875.
[16] A. I. Laskin, P. Grabowich, C. de Lisle Meyers, J. Fried, *J. Med. Chem*. **1964**, *7*, 406.
[17] A. I. Laskin, J. Fried, *Chem. Abstr*. **1968**, 96005h.
[18] J. Fried, G. W. Krakower, D. Rosenthal, H. Basch, *J. Med. Chem*. **1965**, *8*, 279.
[19] J. Klinot, V. Summanova, A. Vystrcil, *Coll. Czech. Chem. Commun*. **1972**, *37*, 603.
[20] J. Klinot, E. Ulehlova, R. Straka, A. Vystrcil, *Coll. Czech. Chem. Commun*. **1973**, *38*, 2648.
[21] G. A. Rosenthal, D. H. Janzen, 'Herbivore, Their Interaction with Secondary Plant Metabolites', Academic Press, New York, 1979, p. 22.
[22] J. D. Connolly, R. A. Hill, 'Dictionary of Terpenoids', Chapman and Hall, London, Vol. I.

Received July 3, 2000