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THE SESQUITERPENOID FROM *Polyalthia cheliensis* Hu

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Abstract — From the dried leaves of *Polyalthia cheliensis* Hu, three sesquiterpenoids were isolated. Their structures of the new sesquterpene, 3″,3‴-bispolycerasoidol (**1**) was elucidated by spectroscopic and chemical methods.

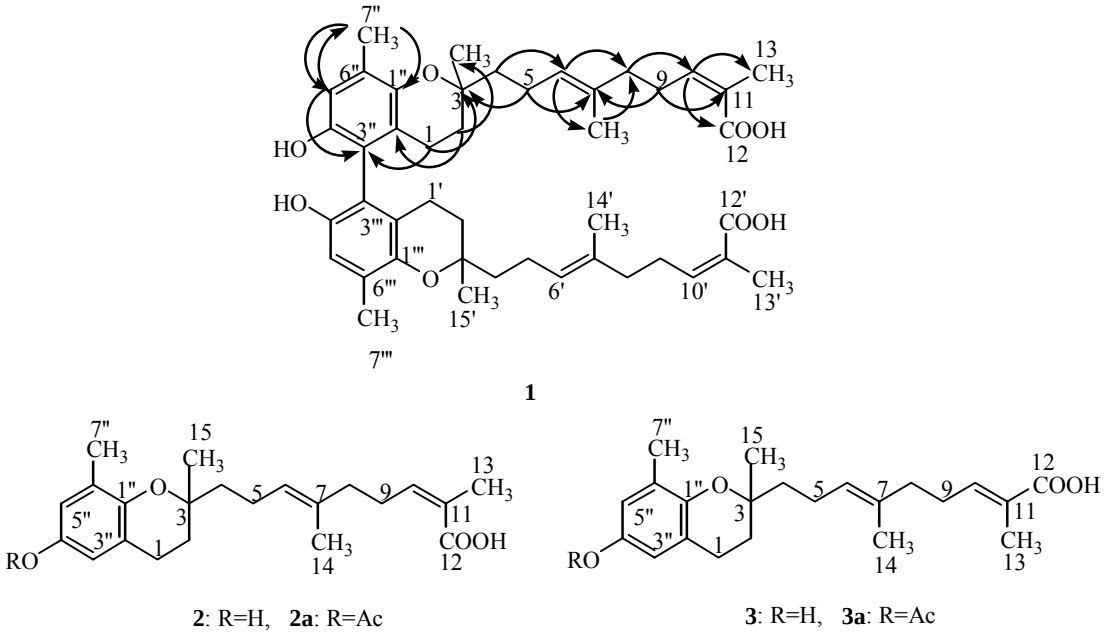

Figure 1 The structures of compounds (**1**~**3**) and selected HMBC of (**1**) (H→C)

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The genus plants *Polyalthia*, being rich in diterpenoids and alkaloids[1-7] which possess marked bioactivities such as leishmanicidal activity,[8] cytotoxic activity against human tumor,[2, 9] have been attracting an attention. *Polyalthia cheliensis* Hu is a bush mainly distributed in Xishuangbanna, Yunnan Province of China.[10] Our previous paper[7] reported the isolations of four clerodane diterpenes from the stem bark of this plants. Recent study on the chemical constituents of its dried leaves resulted in the isolation of a new benzosesquiterpenoid dimer, 3″,3‴-bispolycerasoidol (**1**) and another new *ent*-eudesmame-type sesquiterpenoid compound, *ent*-junenol, and two known benzosesquiterpenoids polycerasoidol (**2**)[11] and isopolycerasoidol (**3**).[12]

Compound (**1**), a brown gum, $[\alpha]_D^{21}$ +16.5° (*c* 0.21, CH_3OH). High resolution FAB$^+$MS gave the (M^+ + 1) peak at *m/z* 715.4228 corresponding to the molecular formula $C_{44}H_{59}O_8$ (M + H, calcd 715.4209). EIMS showed the molecular ion peak at *m/z* 715 (M^+ + 1) and the fragments at 358 (M^+/2 + 1) and 311 (358 - 47) which revealed that compound (**1**) may be the dimer of the same monomer which bore a carboxyl group and whose molecular weight was 358. Besides, the peaks at *m/z* 697 (M^+ + 1 - 18) and 671(M^+ + 1 - 44) also revealed the presence of -OH and -COOH in the molecule of **1** (**Figure 2**). The ^{1}H- and ^{13}C-NMR spectra of **1** were very similar to those of polycerasoidol (**2**),[2] and the ^{13}C-NMR spectra of the former only showed 22 signals for four methyls, six methylenes, three methines and nine quaternary carbons, indicating that **1** was the dimer of polycerasoidol (**2**). Compairing with ^{13}C-NMR and ^{1}H-NMR signals of **1** and **2**, the ^{13}C-NMR signal at δ 114.1 (d) for the C-3″ of polycerasoidol was replaced by δ 121.8 (s) in **1**, and only one aromatic proton signal (δ 7.08) was observed in the ^{1}H-NMR spectra of **1**, revealing that the C-3″ and C-3‴ were combined. This linkage was further supported by 0.4 and 2.6 ppm of upfield shifts observed for C-2″ and C-4″, respectively (**Table 1**), and unambiguously as signed by the HMBC experiments, *i. e.* the ^{1}H-^{13}C long-range correlations between H-1/H-1′ (δ 2.79) and the quaternary carbon at δ 121.8 (C-3″/C-3‴), H-7″/H-7‴ (δ 2.32) and C-1″/C-1‴ (δ 145.9, s), and C-5″/C-5‴ (δ 117.1, d) (**Figure 1**). Thus, the structure of (**1**) was elucidated to be as shown.

The ^{1}H-, ^{13}C- NMR and EIMS spectra of **3** were very alike to those of **2**, except for H-9, H-10 and H-13, C-10, C-11 and C-13. In $CDCl_3$, the resonance position of H-9, H-10, H-13, C-10, C-11 and C-13 had a -0.51, +0.68, -0.23, -1.2, +0.9 and -7.9 ppm shift respectively. The same effects were also observed for their 4-″ acetoxyl derivatives (**3a**) and (**2a**) which were formed from the reactions of **3** and **2** with acetic anhydride in pyridine.[13] These spectra data indicated that **3** and **2** were the *cis-trans* isomer of the double bond C_{10}=C_{11} and consistent with those of ones in literature.[11-12]

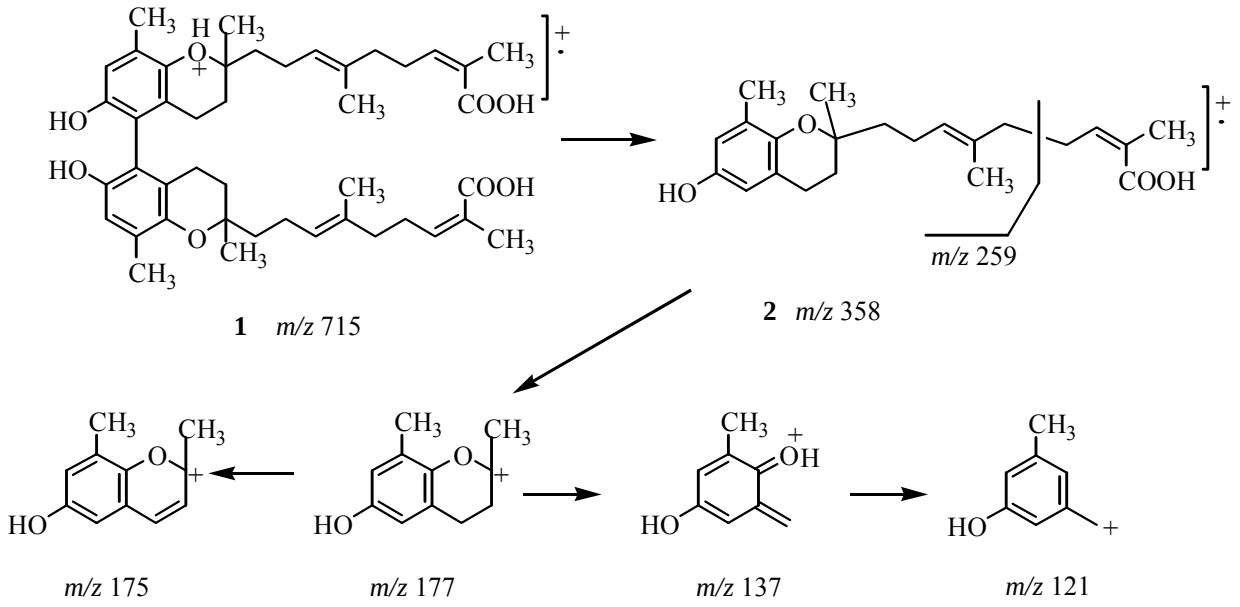

Figure 2 The selected EIMS fragments of **1**

Table 1 The NMR data for polycerasoidol (**2**) and (**1**)[a]

	Polycerasoidol (**2**)		(**1**)	
position	^{1}H	^{13}C	^{1}H	^{13}C
1 (1′)	2.69 (m, 6.5, 2H)	21.7t	2.79 (m, 7.8, 2H)	21.6t
2 (2′)	1.74 (dd, 6.5, 9.2), 1.60 (d, 7.3)	32.1t	1.74 (dd, 6.7, 10.2), 1.60 (d, 7.8)	31.8t
3 (3′)	/	75.6s	/	75.0s
4 (4′)	1.64 (t, 6.9, 2H)	39.9t	1.64 (t, 7.6, 2H)	39.5t
5 (5′)	2.22 (t, 6.9, 2H)	22.9t	2.39 (m, 7.6, 2H)	22.9t
6 (6′)	5.31 (t, 6.9)	125.6d	5.29 (t, 7.6)	124.6d
7 (7′)	/	135.1s	/	135.5s
8 (8′)	2.22 (t, 6.9, 2H)	40.3t	2.18 (t, 7.6, 2H)	40.3t
9 (9′)	2.92 (dd, 6.9, 7.1, 2H)	28.8t	2.92 (dd, 7.1, 7.6, 2H)	28.7t
10 (10′)	6.02 (t, 7.1)	141.9d	5.63 (t, 7.1)	132.7d
11 (11′)	/	129.3s	/	135.0s
12 (12′)	/	170.9s	/	173.2s
13 (13′)	2.11 (s, 3H)	21.7q	2.14 (s, 3H)	22.5q
14 (14′)	1.69 (s, 3H)	16.2q	1.63 (s, 3H)	16.1q
15 (15′)	1.28 (s, 3H)	24.4q	1.25 (s, 3H)	24.8q
1″ (1‴)	/	145.5s	/	145.9s
2″ (2‴)	/	121.9s	/	121.5s
3″ (3‴)	6.18 (s)	114.1d	/	121.8s
4″ (4‴)	/	151.5s	/	148.9s
5″ (5‴)	6.94 (s)	117.1d	7.08 (s)	117.1d
6″ (6‴)	/	127.2s	/	126.1s
7″ (7‴)	2.29 (s. 3H)	16.8q	2.32 (s, 3H)	16.5q

[a] ^{1}H-, ^{13}C- NMR and HMBC spectra were obtained at 500 MHz, 125 MHz and 500 MHz, and recorded in C_5D_5N at room temperature, respectiovely.

EXPERIMENTAL

General Experimental Procedures. MS were performed on an Autospec-3000 spectrometer under 70 eV. 1D NMR spectra were recorded on a Brucker AM-400 and a Brucker DRX-500 spectrometer. 2D NMR spectra were recorded on a Brucker DRX-500 spectrometer.

Plant Material. The leaves of *Polyalthia cheliensis* Hu were collected in Xishuangbanna, Yunnan Province of China in the October 1997. The plant was identified by Mr. Hong Wang and the voucher specimen was deposited in the Xishuangbanna Garden of Tropical Plants, Chinese Academy of Sciences.

Extraction and Isolation — The powdered dried leaves (6 kg) of *P. cheliensis* Hu were extracted with 95% EtOH (25 L × 4) at rt for 100 h. The extract (200 g) was partitioned between water (700 mL) and petroleum ether, trichloromethane, ethyl acetate and *n*-butanol (600 mL × 3 each solvents). The trichloromethane fraction (40 g) was subjected to column chromatography over D-101 resin eluted with 30%, 50%, 70% and 90% acetone-water solution. The 70% fraction (15 g) was then subjected to flash column chromatography over silica gel H eluted with 2:1 (v/v) petroleum ether-EtOAc to afford Cl-1 (1 g) and Cl-2 (2g). By further column chromatography over reverse silica gel (RP-18) eluting with 6:4 (v/v) MeOH-H_2O, Cl-1 afforded **2** (6 mg) and Cl-2 afforded **1** (8 mg), **2** (100 mg) and the mixture of **2** and **3** (80 mg). The mixture of **2** and **3** was seperated with preparative thin layer chromatography over silica gel GF_{254} to give **2** (8 mg) and **3** (20 mg), respectively.

3″,3‴-Bispolycerasoidol (**1**), a brown gum, $[\alpha]_D^{21}$ +16.5° (*c* 0.21, CH_3OH). HRFAB$^+$MS *m/z* 715.4228 (calcd 715.4209 for M + H: $C_{44}H_{59}O_8$). FAB$^+$MS (*m*-nitrobenzyl alcohol) *m/z* (%): 715 (M^++H, 100), 533 (8), 329 (17), 176 (23), 85 (24). EIMS (70 eV) *m/z* (%): 715 (M^+ + 1, 36), 697 (M^+ -H_2O -H, 16), 671 (M^+ -HCO_2, 3), 614 (M^+ -$C_5H_9O_2$, 45), 358 (M^+ -$C_{22}H_{28}O_4$, 16), 311 (18), 257 (12), 175 (27), 161 (7), 137 (39), 121 (48), 107 (45), 93 (77), 81 (58), 67 (39), 55 (100). ^{1}H- and ^{13}C-NMR see **Table 1**.

Polycerasoidol-4″-acetate (**2a**), a yellowish oil. EIMS (70 eV) *m/z* (%): 400 (M^+, 100), 358 (91), 340 (11), 302 (10), 276 (12), 260 (12), 233 (8), 219 (76), 204 (23), 192 (44), 177 (94), 16 (30), 149 (29), 137 (96), 121 (64), 107 (51), 93 (57), 81(63), 69 (51), 55 (78). ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 2.71 (t, 2H, J=6.8 Hz, H-1), 1.78 (dd, 2H, J=6.9, 13.7 Hz, H-2), 1.72 (t, 2H, J=6.8 Hz, H-4), 2.04 (t, 2H, J=7.2 Hz, H-5), 5.12 (t, 1H, J=6.9 Hz, H-6), 2.08 (t, 2H, J=8.0 Hz, H-8), 2.56 (dd, 2H, J=7.4, 7.5 Hz, H-9), 6.01 (t, 1H, J=7.4 Hz, H-10), 1.88 (s, 3H, H-13), 1.54 (s, 3H, H-14), 1.25 (s, 3H, H-15), 6.59 (d, 1H, J=2.5 Hz, H-3″), 6.64 (d, 1H, J=2.5 Hz, H-5″), 2.23 (s, 3H, H-7″), 2.12 (s, 3H, Ac-). ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 22.4 (t, C-1), 31.2 (t, C-2), 75.9 (s, C-3), 39.8 (t, C-4), 22.2 (t, C-5), 125.1 (d, C-6), 134.3 (s, C-7), 39.0 (t,

C-8), 28.1 (t, C-9), 145.6 (d, C-10), 126.2 (s, C-11), 173.1 (s, C-12), 20.1 (q, C-13), 15.7 (q, C-14), 24.3 (q, C-15), 142.7 (s, C-1″), 121.0 (s, C-2″), 119.1 (d, C-3″), 149.8 (s, C-4″), 121.2 (d, C-5″), 127.3 (s, C-6″), 16.0 (q, C-7″), 21.0 (q, Me of acetoxyl), 170.5 (s, C=O of acetoxyl).

Isopolycerasoidol (**3**), a brown oil. EIMS (70 eV) *m/z* (%): 358 (M^+, 100), 340 (14), 328 (7), 279 (10), 216 (13), 203 (12), 192 (20), 191 (18), 177 (80), 175 (61), 149 (40), 137 (93), 121 (38), 107 (40), 93 (54), 81 (65), 67 (63), 55 (70). ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 2.70 (t, 2H, J=6.8 Hz, H-1), 1.76 (dd, 2H, J=6.9, 13.7 Hz, H-2), 1.58~1.63 (m, 2H, H-4), 2.11 (t, 2H, J=7.6 Hz, H-5), 5.18 (t, 1H, J=6.8 Hz, H-6), 2.10 (t, 2H, J=7.5 Hz, H-8), 2.26 (dd, 2H, J=7.5, 7.1 Hz, H-9), 6.87 (t, 1H, J=7.1 Hz, H-10), 1.82 (s, 3H, H-13), 1.60 (s, 3H, H-14), 1.25 (s, 3H, H-15), 6.38 (d, 1H, J=2.4 Hz, H-3″), 6.47 (d, 1H, J=2.4 Hz, H-5″), 2.27 (s, 3H, H-7″). ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 22.2 (t, C-1), 31.2 (t, C-2), 76.2 (s, C-3), 39.8 (t, C-4), 22.4 (t, C-5), 125.3 (d, C-6), 133.6 (s, C-7), 37.9 (t, C-8), 27.6 (t, C-9), 144.5 (d, C-10), 127.1 (s, C-11), 173.0 (s, C-12), 12.3 (q, C-13), 15.5 (q, C-14), 23.6 (q, C-15), 145.6 (s, C-1″), 121.1 (s, C-2″), 113.0 (d, C-3″), 147.4 (s, C-4″), 115.4 (d, C-5″), 127.0 (s, C-6″), 16.0 (q, C-7″).

Isopolycerasoidol-4″-acetate (**3a**), a yellowish oil. EIMS (70 eV) *m/z* (%): 400 (M^+, 64), 358 (80), 340 (10),300 (4), 258 (8), 245 (7),219 (25), 203 (20), 192 (30), 191 (31),177 (66),175 (56), 161 (28), 149 (31), 137 (85), 121 (72), 107 (54), 93 (73),81 (68),67 (69),55 (100). ^{1}H-NMR (500 MHz, $CDCl_3$) δ: 2.73 (t, 2H, J=6.3 Hz, H-1), 1.75 (dd, 2H, J=6.7, 13.2 Hz, H-2), 1.56~1.68 (m, 2H, H-4), 2.12 (t, 2H, J=7.9 Hz, H-5), 5.17 (t, 1H, J=6.8 Hz, H-6), 2.09 (t, 2H, J=7.6 Hz, H-8), 2.29 (dd, 2H, J=7.5, 7.5 Hz, H-9), 6.87 (t, 1H, J=7.5 Hz, H-10), 1.83 (s, 3H, H-13), 1.61 (s, 3H, H-14), 1.27 (s, 3H, H-15), 6.61 (d, 1H, J=2.4 Hz, H-3″), 6.67 (d, 1H, J=2.4 Hz, H-5″), 2.25 (s, 3H, H-7″), 2.15 (s, 3H, Ac-). ^{13}C-NMR (125 MHz, $CDCl_3$) δ: 22.4 (t, C-1), 30.6 (t, C-2), 75.8 (s, C-3), 39.7 (t, C-4), 22.1 (t, C-5), 125.2 (d, C-6), 133.9 (s, C-7), 38.0 (t, C-8), 27.4 (t, C-9), 144.7 (d, C-10), 127.0 (s, C-11), 173.3 (s, C-12), 12.0 (q, C-13), 15.8 (q, C-14), 24.1 (q, C-15), 142.5 (s, C-1″), 121.1 (s, C-2″), 119.0 (d, C-3″), 149.7 (s, C-4″), 120.9 (d, C-5″), 127.3 (s, C-6″), 16.1 (q, C-7″), 21.1 (q, CH_3 of acetoxyl), 170.3 (s, C=O of acetoxyl).

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Kunming, China.

REFERENCES AND NOTES

1. A. Kijjoa, Madalena M. M. Pinto, and W. Herz, *Planta Med*., 1989, **55**, 205.
2. G. X. Zhao, J. H. Jun, D. L. Smith, K. V. Wood, and J. L. Mclaughlin, *Planta Med*., 1991, **57**, 380.
3. Paulo M. M. Pinho and W. Herz, *Phytochemistry*, 1993, **34**, 457.
4. X. Ma, I. -S. Lee, H. B. Chai, K. Zaw, N. R. Farnsworth, D. D. Soejarto, G. A. Cordell, J. M. Pezzuto, and A. D. kinghorn, *Phytochemistry*, 1994, **37**, 1659.
5. M. Chakrabarey and A. C. Nath, *J. Nat. Prod.*, 1992, **55**, 256.
6. N. Hara, H. Asaki, Y. Fujimoto, Y. Gupta, A. K. Singh, and M. Sahai, *Phytochemistry*, 1995, **38**, 189.
7. X. J. Hao, X. S. Yang, Z. Zhang, and L. J. Shang, *Phytochemistry*, 1995, **39**, 447.
8. P. Richomme, M. C. Godet, F. Foussard, L. Toupet, T. Sevenet, and J. Bruneton, *Planta Med*., **1991**, 57, 552.
9. Y. C. Wu, C. Y. Duh, S. K. Wang, K. S. Chen, and S. S. Yang, *J. Nat. Prod.* , **1990**, 53, 1327.
10. Delectis Florae Reipublicae Popularis Sinicae Agendae Academiae Sinicae Edita, 'Flora Reipublaris Sinicae', Tomus **30**, Science Press, Beijing, 1979, pp. 83-85 (in Chinese).
11. M. C. Gonzalez, A. serrano, M. Carmen, Zafra-Polo, and D. Cortes, *J. Nat. Prod.*, 1995, **58**, 1278.
12. M. C. Gonzalez, M. A. Sentandreu, K. S. Rao, M. C. Zafra-Polo, and D. Cortes, *Phytochemistry*, 1996, **43**, 1361.
13. The acetylations of compounds (**2**) and (**3**): The solution of **2** (18 mg, 0.05 mmol) in 2 mL of pyridine was mixed with 2 mL of Ac_2O in 2 mL of pyridine at rt for overnight. 20 mL of water was added and the mixture was extracted by 100 mL of AcOEt which was then washed by water. The fraction of AcOEt was dried over anhydrous Na_2SO_4 and evaporated to dryness on vacuum. After being subjected to flash column chromatography over silica gel H eluted with 4:1 (v/v) petroleum ether-EtOAc to afford **2a** (17 mg, 85% yield). Compound (**3**) (18 mg, 0.05 mmol) was acetylated under the same conditions to afford **3a** (16 mg, 80% yield).