Two New Triterpene Lactones from the Stems of *Kadsura polysperma*

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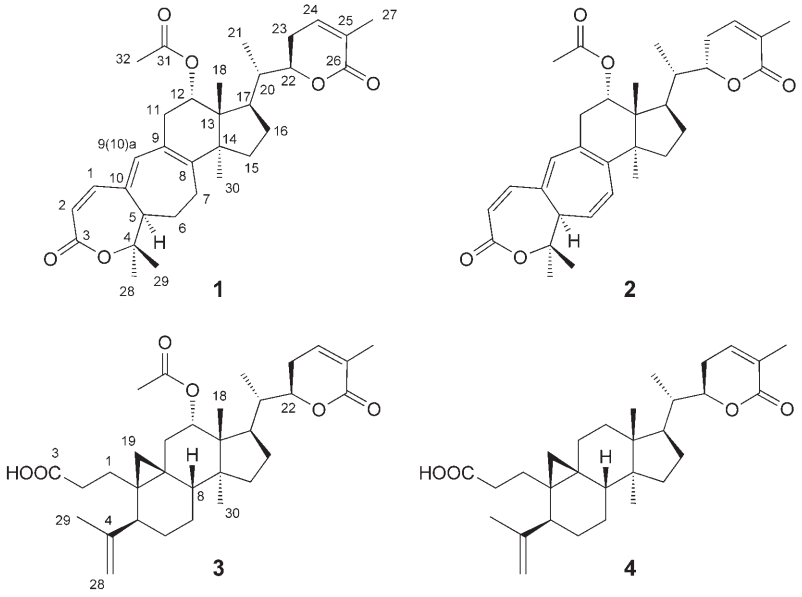
Two new triterpene lactones, polysperlactones A (**2**) and B (**3**), were isolated from the stems of *Kadsura polysperma*, together with the known compounds heteroclitalactone D (**1**) and schisanlactone E (**4**). Their structures were elucidated by spectroscopic methods, including 2D-NMR and HR-MS techniques. The configuration of **1** was confirmed by X-ray analysis. Compounds **2** and **3** are members of a rare class of 3,4-secolanostane metabolites with ring-expanded or cyclized structures, respectively.

Introduction. – The stems or roots of *Kadsura* plants (Schisandraceae) are commonly used in China as folk medicines. For example, the stems of *K. interior* and *K. heteroclita* are used in traditional Chinese medicine (TCM) to produce '*fufang-jixueteng-gao*' for the treatment of blood deficiency, numb hands and feet, painful aching of the joints, and irregular menstruation [1]. In our previous studies, some biologically active lignans and triterpenoids with novel structures were isolated from *Kadsura* medicinal plants [2–6], including three novel triterpene lactones from *K. lancilimba*, of which lancilactone C was identified as an anti-HIV principle [2]. An alcoholic extract of the stems of *K. polysperma*, a species indigenous to South China, was found to exhibit an inhibitory effect on the lipid peroxidation induced by Fe^{2+}/vitamine C [7].

So far, no detailed study on the constituents of *Kadsura polysperma* has been reported. A phytochemical investigation on the stems of this species was, thus, carried out, which led to the isolation of the known compound heteroclitalactone D (**1**), the novel triterpenoidal lactones polysperlactone A (**2**) and polysperlactone B (**3**), as well as the known compound schisanlactone E (**4**). This paper reports the isolation and structure elucidation of the new compounds.

Results and Discussion. – Repeated column chromatography of the Et_2O-soluble EtOH extract of the stems of *K. polysperma* yielded compounds **1**–**4**. Compound **1**, obtained as colorless needles, had the molecular formula $C_{32}H_{42}O_6$, as determined by HR-ESI-MS (*m*/*z* 545.2874 ($[M+Na]^+$)). The ^{1}H- and ^{13}C-NMR data of **1** (*Tables 1* and *2*, resp.) indicated a highly oxidized triterpene lactone, two extra C-atoms probably being assignable to an AcO group. The EI-MS fragment at *m*/*z* 111 suggested the presence of a six-membered α,β-unsaturated lactone moiety [2]. The ^{1}H-NMR spectrum (*Table 1*) showed special signals at δ(H) 6.68, 5.83 (2*d*, J = 12.1 Hz each) due to the olefinic H-atoms at C(1) and C(2), which suggested the presence of a seven-



membered lactone ring [8]. In the HMBC spectrum, the signal at δ(H) 6.17 (*s*) correlated with the C-atoms at δ(C) 151.0 (C(8)), 143.4 (C(1)), 140.4 (C(10)), 49.2 (C(5)), and 35.1 (C(11)), revealing that this H-atom corresponded to H–C(9(10)a). Thus, **1** had no cyclopropane ring in the structure.

The EI-MS peak at *m*/*z* 464 ($[M-58]^+$) suggested the presence of an AcO group in **1**, which was confirmed by the ^{1}H-NMR signal at δ(H) 2.08 (*s*, Me), along with the corresponding ^{13}C-NMR signals at δ(C) 169.9 and 21.4. By comparison of the ^{1}H- and ^{13}C-NMR spectra, the circular-dichroism (CD) and optical-rotation (ORD) data with those reported in the literature [9], as well as by single-crystal X-ray-diffraction analysis (*Fig. 1*), compound **1** was identified as heteroclitalactone D, which corresponds to '(12*S*,22*R*)-12-acetoxy-9(10)a-homo-19-nor-3,4-secolanosta-1,8,9(10)a,24-tetraene-3,4-lactone-26,22-lactone'[1]), and has been previously isolated from *K. heteroclita* [9]. The typical feature of its skeleton are two unsaturated seven-membered lactone rings, linked through three conjugated C=C bonds. Only a few triterpene derivatives with this type of carbon skeleton have been reported so far [2][9][10].

Polysperlactone A (**2**), obtained as colorless needles, was assigned the molecular formula $C_{32}H_{40}O_6$ on the basis of HR-ESI-MS (*m*/*z* 521.2899 ($[M+H]^+$)). The ^{1}H-NMR spectrum of **2** (*Table 1*) showed signals for one Me *doublet* at δ(H) 0.94 and six Me *singlet*s at δ(H) 0.87, 1.07, 1.51, 1.61, 1.93, and 2.06, respectively. The ^{13}C-NMR (DEPT) data (*Table 2*) indicated 16 low-field signals, corresponding to three C=O groups at δ(C) 169.9, 166.6, and 166.3, ten olefinic C-atoms at δ(C) 149.5, 141.3, 139.0, 134.7, 131.0, 128.5, 127.5, 124.6, 123.5, and 119.2, and three oxygenated C-atoms at δ(C) 80.0, 78.7, and 73.8, respectively, together with seven Me, four CH_2, and three CH

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

Table 1. *^{1}H-NMR Data of* **1**–**3**. At 400 MHz, 27°, in $CDCl_3$; δ in ppm, J in Hz. Arbitrary atom numbering.

Atom	**1**	**2**	**3**
H–C(1)	6.68 (*d*, *J* = 12.1)	6.58 (*d*, *J* = 12.1)	
CH_2(1)			1.32–1.38 (*m*),
			2.07–2.15 (*m*)
H–C(2)	5.83 (*d*, *J* = 12.1)	5.82 (*d*, *J* = 12.5)	
CH_2(2)			2.24–2.31 (*m*),
			2.46–2.54 (*m*)
H–C(5)	2.44 (*t*, *J* = 11.2)	1.63 (*d*, *J* = 7.0)	2.40–2.46 (*m*)
CH_2(6)	1.50–1.57 (*m*),		1.04–1.15 (*m*),
	1.87–1.97 (*m*)		1.24–1.33 (*m*)
H–C(6)		5.83 (*t*, *J* = 8.2)	
CH_2(7)	2.24–2.32 (*m*),		0.98–1.06 (*m*),
	2.38–2.43 (*m*)		1.55–1.62 (*m*)
H–C(7)		6.19 (*d*, *J* = 9.8)	
H–C(8)			1.38–1.45 (*m*)
H–C(9(10)a)	6.17 (*s*)	6.12 (*s*)	
CH_2(11)	2.81 (*dd*, *J* = 19.6, 7.4),	3.22 (*dd*, *J* = 19.6, 7.8),	1.93–1.98 (*m*),
	2.14 (*d*, *J* = 19.9)	2.56 (*d*, *J* = 19.6)	1.98–2.04 (*m*)
H–C(12)	5.00 (*d*, *J* = 7.4)	5.00 (*d*, *J* = 7.4)	4.84 (*d*, *J* = 6.7)
CH_2(15)	1.42–1.48 (*m*),	1.52–1.57 (*m*),	1.34–1.43 (*m*),
	1.70–1.78 (*m*)	2.00–2.08 (*m*)	1.36–1.44 (*m*)
CH_2(16)	1.90–1.98 (*m*),	1.55–1.62 (*m*),	1.44–1.50 (*m*),
	2.06–2.14 (*m*)	1.97–2.04 (*m*)	1.80–1.88 (*m*)
H–C(17)	2.12–2.20 (*m*)	2.18–2.27 (*m*)	2.18–2.26 (*m*)
Me(18)	0.75 (*s*)	0.87 (*s*)	1.04 (*s*)
CH_2(19)			0.60, 0.69 (2*d*, *J* = 4.7)
H–C(20)	2.00–2.08 (*m*)	2.03–2.09 (*m*)	1.97–2.04 (*m*)
Me(21)	0.91 (*d*, *J* = 6.66)	0.94 (*d*, *J* = 6.7)	0.83 (*d*, *J* = 6.7)
H–C(22)	4.48 (*dt*, *J* = 13.3, 3.5)	4.51 (*dt*, *J* = 12.9, 3.5)	4.49 (*dt*, *J* = 12.9, 3.5)
CH_2(23)	2.06–2.14 (*m*),	2.08–2.17 (*m*),	2.18–2.14 (*m*),
	2.33–2.40 (*m*)	2.34–2.44 (*m*)	2.33–2.40 (*m*)
H–C(24)	6.61 (*d*, *J* = 6.3)	6.61 (*d*, *J* = 6.3)	6.62 (*d*, *J* = 6.3)
Me(27)	1.92 (*s*)	1.93 (*s*)	1.92 (*s*)
Me(28)	1.40 (*s*)	1.51 (*s*)	
CH_2(28)			4.81, 4.76 (2*s*)
Me(29)	1.53 (*s*)	1.61 (*s*)	1.68 (*s*)
Me(30)	1.25 (*s*)	1.07 (*s*)	1.01 (*s*)
Me(32)	2.08 (*s*)	2.06 (*s*)	2.03 (*s*)

groups, as well as two quaternary C-atoms in the high-field region. These data suggested that **2** was also a highly oxidized triterpene lactone closely related to **1**.

The EI-MS fragment at *m*/*z* 111 suggested the presence of a six-membered α,β-unsaturated lactone ring [2], which was assigned to the side chain of **2**. The signals at δ(H) 6.61 (*d*, *J* = 6.3 Hz) and 1.93 (*s*, 3 H) in the ^{1}H-NMR spectrum could be assigned to the olefinic H-atom and the Me group of the six-membered unsaturated lactone, respectively [11]. The cross-peaks between δ(H) 0.94 (Me(21)) and δ(C) 80.0 (C(22)), 39.0 (C(20)), and 39.2 (C(17)) in the HMBC spectrum (*Fig. 2*) indicated that this ring was connected to C(20).

Table 2. *^{13}C-NMR Data of* **1**–**3**. At 100 MHz, 27°, in $CDCl_3$; δ in ppm. Arbitrary atom numbering.

Position	**1**	**2**	**3**	Position	**1**	**2**	**3**
C(1)	143.4 (*d*)	141.3 (*d*)	28.6 (*t*)	C(17)	39.4 (*d*)	39.2 (*d*)	39.9 (*d*)
C(2)	118.2 (*d*)	119.2 (*d*)	31.0 (*t*)	C(18)	16.5 (*q*)	16.6 (*q*)	16.8 (*q*)
C(3)	167.0 (*s*)	166.6 (*s*)	178.4 (*s*)	C(19)			30.2 (*t*)
C(4)	80.3 (*s*)	78.7 (*s*)	148.8 (*s*)	C(20)	38.9 (*d*)	39.0 (*d*)	39.1 (*d*)
C(5)	49.2 (*d*)	51.5 (*d*)	45.9 (*d*)	C(21)	12.5 (*q*)	12.4 (*q*)	12.0 (*q*)
C(6)	26.2 (*t*)	123.5 (*d*)	25.3 (*t*)	C(22)	80.0 (*d*)	80.0 (*d*)	80.3 (*d*)
C(7)	39.4 (*t*)	124.6 (*d*)	28.0 (*t*)	C(23)	23.3 (*t*)	23.3 (*t*)	23.3 (*t*)
C(8)	151.0 (*s*)	149.5 (*s*)	48.8 (*d*)	C(24)	139.0 (*d*)	139.0 (*d*)	139.2 (*d*)
C(9)	126.8 (*s*)	131.0 (*s*)	26.5 (*s*)	C(25)	128.5 (*s*)	128.5 (*s*)	128.4 (*s*)
C(9(10)a)	142.0 (*d*)	134.7 (*d*)		C(26)	166.3 (*s*)	166.3 (*s*)	166.4 (*s*)
C(10)	140.4 (*s*)	127.5 (*s*)	20.6 (*s*)	C(27)	17.0 (*q*)	17.0 (*q*)	17.0 (*q*)
C(11)	35.1 (*t*)	37.3 (*t*)	36.0 (*t*)	C(28)	29.2 (*q*)	29.1 (*q*)	112.0 (*t*)
C(12)	73.8 (*d*)	73.8 (*d*)	75.4 (*d*)	C(29)	26.2 (*q*)	25.1 (*q*)	25.1 (*q*)
C(13)	51.4 (*s*)	47.7 (*s*)	48.6 (*s*)	C(30)	27.6 (*q*)	26.5 (*q*)	26.5 (*q*)
C(14)	48.0 (*s*)	51.1 (*s*)	48.5 (*s*)	C(31)	169.9 (*s*)	169.9 (*s*)	169.7 (*s*)
C(15)	31.9 (*t*)	31.8 (*t*)	36.5 (*t*)	C(32)	21.4 (*q*)	21.3 (*q*)	21.5 (*q*)
C(16)	27.8 (*t*)	26.1 (*t*)	27.0 (*t*)				

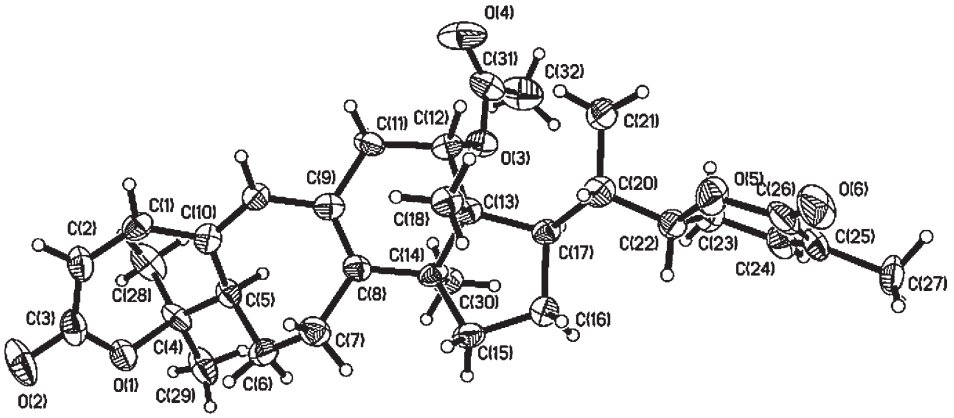


Fig. 1. *X-Ray crystal structure of* **1**

The ^{1}H-NMR spectrum of **2** further showed signals at δ(H) 6.58 (*d*, J = 12.1 Hz) and 5.82 (*d*, J = 12.5 Hz) due to the olefinic H-atoms at C(1) and C(2), suggesting the presence of a seven-membered lactone ring [8]. The HMBC correlations of δ(H) 6.58 (H–C(1)) with δ(C) 51.5 (C(5)), 127.5 (C(10)), and 166.6 (C(3)), of δ(H) 5.82 (H–C(2)) with δ(C) 127.5 (C(10)) and 166.6 (C(3)), and of both δ(H) 1.51 (Me(28)) and 1.61 (Me(29)) with δ(C) 78.7 (C(4)) confirmed the structure of a seven-membered lactone ring. In the HMBC spectrum of **2** (*Fig. 2*), the signal at δ(H) 6.12 (*s*, 1 H) correlated with those at δ(C) 149.5 (C(8)), 141.3 (C(1)), 127.5 (C(10)), 51.5 (C(5)), and 37.3 (C(11)), revealing that this olefinic H-atom was H–C(9(10)a). Thus, **2** was also devoid of a cyclopropane ring, just as **1**.

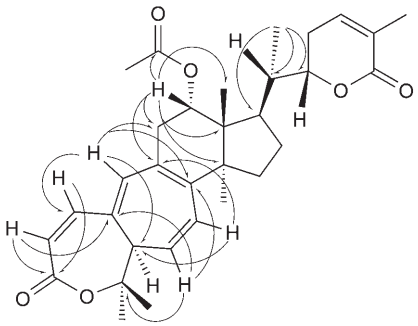


Fig. 2. *Key HMBC correlations of* **2**

The EI-MS peak at *m/z* 462 ($[M-58]^+$) suggested the presence of an AcO group in **2**, as confirmed by ^{1}H- and ^{13}C-NMR. The signal at δ(H) 5.00 (*d*, $J = 7.4$ Hz) in the ^{1}H-NMR spectrum was assigned to H–C(12), the position to which the AcO group was attached, as corroborated by HMBC correlations of δ(H) 5.00 (*d*, $J = 7.4$ Hz) with δ(C) 169.9 (C(31)), 131.0 (C(9)), 47.7 (C(13)), 51.1 (C(14)), 37.3 (C(11)), and 16.6 (C(18)).

Based on the above data, compound **2** was identified as a triterpenoid, with the same basic skeleton as **1**, but an additional C=C bond. Thus, the most-prominent differences in the ^{1}H-NMR spectra of **1** and **2** were the appearance of two olefinic resonances at δ(H) 6.19 (*d*, $J = 9.8$ Hz) and 5.83 (*t*, $J = 8.2$ Hz) in **2**. Correspondingly, the ^{13}C-NMR spectrum of **2** showed two additional olefinic C-atom signals in the low-field region, compared to **1**. In the HMBC spectrum (*Fig. 2*), the correlation of δ(H) 6.19 (*d*, $J = 9.8$ Hz) with δ(C) 131.0 (C(9)) and 51.5 (C(5)), and that of δ(H) 5.83 (*t*, $J = 8.2$ Hz) with δ(C) 149.5 (C(8)), 127.5 (C(10)), 78.7 (C(4)), and 51.5 (C(5)) indicated that the additional C=C bond was between C(6) and C(7).

The CD spectrum of **2** showed a negative *Cotton* effect at 248 nm, thus, C(22) was assigned the absolute (*S*)-configuration [11]. Me(18) showed ROESY cross-peaks with H–C(20) and Me(29), indicating that Me(18), H–C(20), and Me(29) are in *syn*- and β-positions. The correlations of Me(30)/H–C(17) and Me(28)/H–C(5) indicated that Me(30) and H–C(5) were α-configured. H–C(12) also showed ROESY cross-peaks with Me(18) and Me(21), confirming the α-configuration for the 12-AcO group. From these data, the structure of the new compound **2** was, thus, elucidated as '(12*S*,22*S*)-12-acetoxy-9(10)a-homo-19-nor-3,4-secolanosta-1,6,8,9(10)a,24-pentaene-3,4-lactone-26,22-lactone'[1]).

Polysperlactone B (**3**), obtained as colorless granules, had the molecular formula $C_{32}H_{46}O_6$, as revealed by HR-ESI-MS (*m/z* 549.3196 ($[M+Na]^+$)). The presence of an α,β-unsaturated lactone ring and an OH group was suggested by the IR absorption bands at 1731 and 3218 cm^{-1}. The ^{1}H-NMR spectrum (*Table 1*) showed signals for one Me *doublet* at δ(H) 0.83 and five Me *singlet*s δ(H) 1.01, 1.04, 1.68, 1.92, and 2.03. The ^{13}C-NMR (DEPT) data of **3** (*Table 2*) indicated 32 C-atoms and 45 C-bonded H-atoms. The ^{13}C-NMR spectrum showed three carboxylic C-atoms at δ(C) 178.4, 169.7, and 166.4, four olefinic resonances at δ(C) 148.8, 139.2, 128.4, and 112.0, and two oxygenated C-atoms at δ(C) 80.3 and 75.3, respectively. The high-field region showed six Me, nine CH_2, and four CH groups, together with four quaternary C-atoms. These

data suggested that **3** was a triterpene lactone, the two additional carbons being assigned to an AcO substituent.

Compounds **1**–**3** all possess the same side-chain moiety, as indicated by similar ^{1}H- and ^{13}C-NMR data. The common EI-MS fragment at *m*/*z* 111 agrees with this conclusion. From the ^{1}H- and ^{13}C-NMR spectra of **3**, it became clear that a COO group (δ(C) 178.4) and an isopropenyl group [δ(H) 4.81 (*s*, 1 H), 4.76 (*s*, 1 H), 1.63 (*s*, 3 H)] were present, as confirmed by the corresponding ^{13}C-NMR signals at δ(C) 112.0 and 148.8. Thus, it was concluded that cleavage of ring *A* had furnished a carboxylic acid at one terminus and an isopropenyl group at the other [12]. In the ^{1}H-NMR spectrum, two mutually coupled *doublet*s at δ(H) 0.69 and 0.60 (J = 4.7 Hz) indicated the presence of a cyclopropane ring, whose position was revealed by the HMBC correlations (*Fig. 3*) of both δ(H) 0.69 and 0.60 (J = 4.7 Hz) with δ(C) 48.8 (C(8)), 45.9 (C(5)), 36.0 (C(11)), 28.6 (C(1)), 26.5 (C(9)), and 20.6 (C(10)).

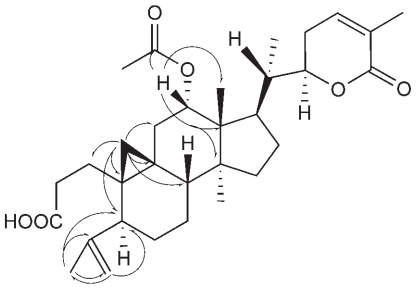


Fig. 3. *Key HMBC correlations of* **3**

Based on the above spectroscopic data, compound **3** had the same skeleton as schisanlactone E [10]. The ^{1}H-NMR signal at δ(H) 2.03 (*s*, 3 H), along with the corresponding ^{13}C-NMR signals at δ(C) 169.7 and 21.5, suggested the presence of an AcO group located in 12-position, based on HMBC correlations of δ(H) 4.84 with δ(C) 169.7 (C(31)), 48.6 (C(13)), 48.5 (C(14)), and 16.8 (Me(18)), in accord with a *doublet* at δ(H) 4.84 (J = 6.7 Hz) due to an oxygenated H-atom at C(12).

Compound **3** showed a positive *Cotton* effect at 257 nm, similar to that of schisanlactone E, indicating the absolute (*R*)-configuration at C(22) [11]. The correlations between Me(18)/H–C(20), Me(18)/Me(29), Me(30)/H–C(17), Me(28)/H–C(5), H–C(12)/Me(18), and H–C(12)/Me(21) in the ROESY spectrum indicated that the configurations at C(12) and C(20) were the same as those in **1** and **2**. Thus, the structure of **3** was assigned as '(12*S*,22*R*)-12-acetoxy-3-hydroxy-3-oxo-9,19-cyclo-3,4-secolanosta-4(28),24-dien-26,22-lactone'.

Compound **4** was identified as schisanlactone E (=(22*R*)-3-hydroxy-3-oxo-9,19-cyclo-3,4-secolanosta-4(28),24-dien-26,22-lactone) by comparison of its spectroscopic data with those reported previously [12].

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Experimental Part

General. Petroleum ether (PE) for chromatography was of b.p. 60–90°. Anal. TLC: silica gel F_{254} plates (0.15 mm; *Yantai*). Column chromatography (CC): silica gel (200–300 or 300–400 mesh; *Qingdao*). M.p.: *XT-4* micro-melting-point apparatus (*Tai-KE Instrument Co.*, Beijing); uncorrected. Optical rotations: *Jasco P-1020* spectropolarimeter. UV Spectra: *756 MC* spectrometer; in anh. MeOH; λ_{max} (log ε) in nm. CD Spectra: *Jasco J-715* spectropolarimeter; λ in nm ($\Delta\varepsilon$ in mdeg). IR Spectra: *Thermo-Nicolet Avatar 360-ESP* spectrophotometer, as KBr pellets; in cm^{-1}. ^1H- and ^{13}C-NMR Spectra: *Bruker DRX-400* apparatus, in $CDCl_3$ soln.; δ in ppm rel. to Me_4Si, J in Hz. EI-MS: *Hewlett-Packard 5989A* mass spectrometer. HR-ESI-MS: *Micromass Q-Tof* mass spectrometer; in m/z.

Plant Material. Stems of *Kadsura polysperma* were collected in Chongqing, P. R. China, in November 1992, and identified by *D. C.* A voucher specimen (Chen-NC921101) was deposited at the Herbarium of Materia Medica, Department of Pharmacognosy, School of Pharmacy, Fudan University, Shanghai, P. R. China.

Extraction and Isolation. The stems (3.3 kg) of *K. polysperma* were air-dried, ground, and extracted exhaustively with 95% EtOH at r.t. The alcoholic extract was evaporated *in vacuo* to yield a semisolid (166 g), which was suspended in H_2O (500 ml) and extracted with Et_2O (7×). The etheral soln. was concentrated to yield 28 g of a residue, which was purified by CC (500 g SiO_2; PE/AcOEt gradient) to afford several fractions (Fr.). *Fr. 5* was subjected to repeated CC (SiO_2; $CHCl_3$/MeOH 20:1) to yield **4** (1.10 g). *Fr. 7* was subjected to repeated CC (SiO_2; PE/$CHCl_3$/acetone 4:4:1→4:4:2) to afford **1** (29 mg), **2** (5 mg), and **3** (92 mg).

Polysperlactone A (= *(3*R*,3a*R*,4*S*,11a*R*,13b*S*)-1,2,3,3a,4,5,9,11,11a,13b-Decahydro-3a,11,11,13b-tetramethyl-3-{(1*S*)-1-[(2*S*)-3,6-dihydro-5-methyl-6-oxo-2*H*-pyran-2-yl]ethyl}-9-oxoindeno[5′,4′:4,5]cyclohepta[1,2-c]oxepin-4-yl Acetate*; **2**). Colorless needles (PE/AcOEt). M.p. 290–294°. $[\alpha]_D^{24} = -77.0$ (c = 0.07, acetone). UV (MeOH): 209 (3.56), 327 (3.14). CD (c = 0.06, MeOH): 248 (−12). IR (KBr): 2966, 2868, 2243, 1689, 1596, 1429, 1377, 1362, 1290, 1267, 1197, 1126, 1029, 973, 724, 644, 589, 526. ^1H- and ^{13}C-NMR: see *Tables 1* and *2*, resp. EI-MS: 462 (13), 402 (100), 361 (13), 305 (10), 261 (15), 247 (13), 209 (23), 192 (11), 111 (11), 83 (18), 55 (25), 44 (60). HR-ESI-MS: 521.2899 ($[M + H]^+$, $C_{32}H_{41}O_6^+$; calc. 521.2903).

Polysperlactone B (= *3-[(1*R*,3a*S*,3b*S*,6*S*,6a*R*,7a*R*,9*S*,9a*R*)-9-Acetoxydecahydro-3a,9a-dimethyl-6-(1-methylethenyl)-1-{(1*S*)-1-[(2*R*)-3,6-dihydro-5-methyl-6-oxo-2*H*-pyran-2-yl]ethyl}-1*H*-cyclopenta[a]cyclopropa[e]naphthalen-6a(7*H*)-yl]propanoic Acid*; **3**). Colorless granules (PE/AcOEt). M.p. 148–150°. $[\alpha]_D^{24} = 82.9$ (c = 0.09, acetone). UV (MeOH): 208 (3.45). CD (c = 0.07, MeOH): 257 (+4). IR (KBr): 3218, 2949, 1731, 1457, 1391, 1377, 1358, 1274, 1246, 1163, 1142, 1121, 1031, 987. ^1H- and ^{13}C-NMR: see *Tables 1* and *2*, resp. EI-MS: 453 (4), 367 (5), 327 (8), 311 (5), 267 (4), 211 (6), 187 (6), 159 (11), 133 (15), 111 (21), 83 (25), 55 (35), 44 (100). HR-ESI-MS: 549.3196 ($[M + Na]^+$, $C_{32}H_{46}NaO_6^+$; calc. 549.3192).

Crystal Structure of Heteroclitalactone D (**1**)[2]). Diffraction data for **1** were collected on an *Enraf-Nonius CAD4* diffractometer, using MoK_α radiation (λ = 0.71073 Å) and the $\omega - 2\theta$ scan mode. The structure was solved with SHELXTL-97, and refined by means of full-matrix least-squares on F^2. Crystals of **1** (0.30 × 0.20 × 0.15 mm) were orthorhombic (space group $P\ 2_12_12$), with cell dimensions a = 11.9190(14), b = 33.080(6), c = 7.4390(14) Å, $\alpha = \beta = \gamma = 90.00°$, V = 2933.1(9) A^3; Z = 4, D_c = 1.184 Mg/m^3, $F(000)$ = 1182, T = 293(2) K.

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[2]) The crystallographic data of **1** have been deposited with the *Cambridge Crystallographic Data Centre* as supplementary publication number CCDC-273570. Copies of the data can be obtained, free of charge, at http://www.ccdc.cam.ac.uk/data_request/cif.

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