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FIVE TRICYCLIC SESQUITERPENES FROM *CALLILEPIS SALICIFOLIA**

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Key Word Index—*Callilepis salicifolia*; *C. laureola*; Compositae; Inuleae; sesquiterpenes; isocomene derivatives; silphinene derivative; thymol derivatives; acetylenic sulfone; phellandrene endoperoxide; pinoresinol diisovalerate.

Abstract—The roots of *Callilepis salicifolia* afforded in addition to known compounds four derivatives of isocomene, one dihydroxysilphinene isovalerate, two thymol and one northymol ester, an acetylenic sulfone and the diisovalerate of pinoresinol, while the aerial parts of *C. laureola* gave the endoperoxide of phellandrene. The structures were elucidated by spectroscopic methods and a few chemical transformations.

INTRODUCTION

Callilepis is a small South African genus placed in the subtribe Athrixiinae (tribe Inuleae, Compositae) [1]. Its relationship to the other genera of this somewhat diverse subtribe is not very clear. Earlier it has been placed in the Buphthalminae. So far only one species, *C. laureola*, was investigated chemically, but no characteristic compounds had been isolated [2, 3]. We now have studied the constituents of a further species, *C. salicifolia* Oliver. In addition to known compounds five new sesquiterpenes all being tricyclic, two thymol derivatives, a diester of pinoresinol and a sulfone derived from a so far unknown phenyl diyne were isolated. The aerial parts of *C. laureola* gave the endoperoxide of phellandrene and several known compounds.

RESULTS AND DISCUSSION

The roots of *Callilepis salicifolia* Oliver afforded traces of tridecapentaynene, isocomene (**7**) [4, 5], its precursor **6** [6], stigmasterol, lupeol and as the main compound the aldehyde **1** [2]. Furthermore, several new compounds were present, thymol derivatives **3–5**, the sesquiterpenes **8–12**, sulfone **14** and pinoresinol diisovalerate **15**. The structure of the latter clearly followed from the spectral data. The ^{1}H NMR data (Experimental) were close to those of sesamine. However, the signals of two OMe groups were replaced by those of isovalerate residues. The relative positions of the oxygen functions were deduced from the chemical shifts of the aromatic protons. The fragmentation pattern in the mass spectrum of **15** also supported the structure. After elimination of the ester groups as isopropyl ketene the remaining fragment showed a very similar fragmentation as pinoresinol.

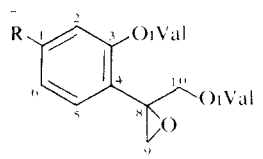
The sulfone **14** showed UV maximum at 282 nm and from the IR spectrum the presence of an acetylenic bond could be deduced. In the ^{1}H NMR spectrum (Experimental) the downfield multiplets between 7.5 and 7.3 ppm were similar to those of other phenylacetylene derivatives, while the methyl singlet at 3.09 ppm was that of a methyl sulfone. A downfield triplet was coupled with doublet quartet, which itself was coupled with a methyl triplet, as could be shown by spin decoupling. The stereochemistry of the double bond followed from the chemical shift of the signal of the olefinic proton, which would be more downfield in a sulfone of *cis*-configuration. **14** obviously was formed by addition of methylmercaptan to the hitherto unknown phenylhexa-1,3-diyne followed by oxidation of the thioether. The structures of **3–5** could be deduced from the ^{1}H NMR data (Table 1), which were

Table 1. ^{1}H NMR spectral data of compounds **2–5** (400 MHz, $CDCl_3$, TMS as int. standard)

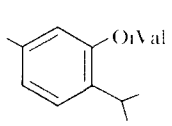
	2	**3**	**4**	**5**
H-1	—	7.35 *ddd*	—	7.98 *dd*
H-2	7.06 *d*	7.06 *dd*	6.78 *d*	6.84 *d*
H-5	7.44 *d*	7.48 *dd*	7.19 *d*	7.09 *d*
H-6	7.19 *dd*	7.23 *ddd*	7.01 *br d*	—
H-7	4.65 *br s*	—	2.30 *br s*	2.32 *br s*
H-8	—	—	2.97 *qq*	2.98 *qq*
H-9	3.02 *d*	3.04 *d*	1.17 *d*	1.18 *d*
H-9′	2.77 *d*	2.81 *d*		
H-10	4.57 *d*	4.61 *d*	1.17 *d*	1.18 *d*
H-10′	4.20 *d*	4.22 *d*		
PhOCOR	2.50 *dd*	2.50 *dd*	2.44 *d*	2.45 *d*
	2.45 *dd*	2.46 *dd*	2.23 *tqq*	2.23 *tqq*
	2.22 *ddqq*	2.23 *ddqq*	1.06 *d*	1.05 *d*
	1.07 *d*	1.06 *d*		
	1.065 *d*	1.05 *d*		
OCOR	2.14 *d*	2.15		
	2.00 *tqq*	2.03 *tqq*		
	0.90 *d*	0.87 *d*		

J(Hz): 2,6 = 1.8; 5,6 = 8; 9,9′ = 5; 10,10′ = 12; compound **3**: 1,5 = 2,6 = 1.5; 1,2 = 1,6 = 5,6 = 8; compound **5**: 1,2 = 8; 1,5 = 1.5; ROiVal: $2'_1,2'_2$ = 15; 2′,3′ = 3′,4′ = 3′,5′ = 7; OiVal: 2′,3′ = 3′,4′ = 3′,5′ = 7.

* Part 384 in the series 'Naturally Occurring Terpene Derivatives'. For Part 383 see Bohlmann, F. and Otto, W. (1981) *Justus Liebigs Ann. Chem.* (in press).



1 R = CHO
2 R = CH_2OH
3 R = H



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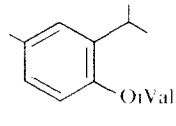

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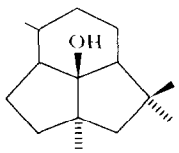

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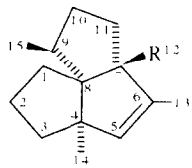
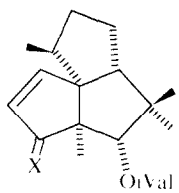
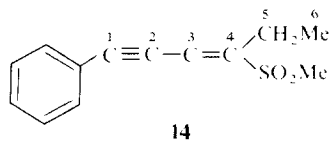


7 R = Me
8 R = CH_2OH
9 R = CH_2OIVal
10 R = CHO
11 R = CO_2Me



12 X = βOH, H
13 X = O



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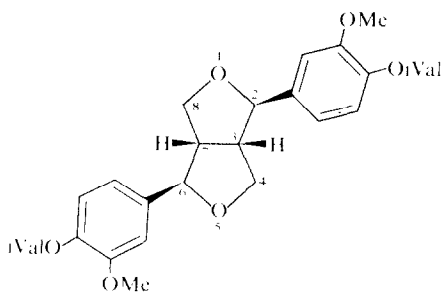

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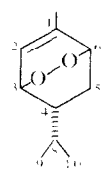

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close to those of known thymol derivatives. **3** was a northymol derivative, probably formed via **1** by further oxidation and decarboxylation. The sesquiterpenes **9** and **11** could not be separated completely from **10**. Only after sodium boranate reduction small amounts of **8** could be removed from **9** and **11**. As the reduction of **10** afforded **8** and **9**, **11** could also be transformed to **8** by addition of $LiAlH_4$, all compounds had the same carbon skeleton. As the ^1H NMR data of **8** (Table 2) were similar to those of **7**, the presence of derivatives of isocomene were most likely. The position of the hydroxy group could be deduced from the $Eu(fod)_3$-induced shifts. As the signal of the olefinic methyl was shifted much more than that of the olefinic proton, the CH_2OH group had to be placed at C-7 and not at C-4. In the mass spectrum of **8**–**11** as expected loss of the functional group led to the base peak *m/z* 189, which replaced the base peak *m/z* 162 typical for isocomene formed by loss of C_3H_6. The corresponding elimination in the spectrum of **8** led to a small fragment at *m/z* 178, while *m/z* 189 by loss of C_2H_4 led to *m/z* 161 as a further prominent peak. **12** still contained **1**, but reduction with sodium boranate afforded **2** and **12**, which easily could be separated. MnO_2 oxidation of **12** gave the conjugated ketone **13**. All signals in the ^1H NMR spectra of **12** and **13** (Table 3) could be assigned by spin decoupling indicating that **12** was a 3-hydroxy-5-*iso*-valeryloxysilphinene. The parent hydrocarbosilphinene [7] consequently showed a very similar ^1H NMR spectrum. Irradiation of the broadened double doublet at 5.14, which disappeared after oxidation, and therefore must be that of the proton under the hydroxyl, collapsed the olefinic double doublets, while further decouplings starting with the double doublet at 1.85 ppm led to the sequence

■–CH(Me)CH_2CH_2CH(■)–■. As the only further downfield signal was a singlet, the isovaleryloxy group bearing carbon must have had two quaternary neighbouring carbons, thus leading to structure **12**. The stereochemistry at C-3 and C-5 followed from the $Eu(fod)_3$-induced shifts. Inspection of models showed that these shifts only could be explained if both oxygen

Table 2. ^{1}H NMR spectral data of compounds **8**–**11** (400 MHz, $CDCl_3$)

	8*	+Eu(fod)$_3$	**9***	**10***	**11***
H-5	5.08 *br s*	0.14	5.00 *br s*	5.22 *br s*	5.08 *br s*
H-9	2.01 *m*	0.10	2.02 *m*	2.06 *m*	2.02 *m*
H-12	3.68 *d*	0.53	4.10 *d* } 9.62 *s*		—
H-12′	3.64 *d*	0.50	4.03 *d* }		—
H-13	1.63 *d*	0.23	1.58 *d*	1.56 *d*	1.63 *d*
H-14	1.05 *s*	0.09	1.05 *s*	1.06 *s*	1.06 *s*
H-15	0.88 *d*	0.09	0.88 *d*	0.87 *d*	0.93 *d*
OR	—	—	2.18 *d*	—	3.68 *s*
			2.12 *tqq*		
			0.94 *d*		

* Signals not listed were broad overlapping multiplets.

J(Hz): 5,13 = 1.5; 12,12′ = 11.5; 9,15 = 7; iVal: 2′,3′ = 3′,4′ = 3′,5′ = 7.

Table 3. ^{1}H NMR spectral data of compounds **12** and **13** (400 MHz, $CDCl_3$, TMS as int. standard)

	12	+Eu(fod)$_3$	Δ	**13**
H-1	5.83 *dd*	6.06 *br d*	0.23	7.56 *d*
H-2	5.62 *dd*	6.01 *br d*	0.39	6.00 *d*
H-3	5.14 *br dd*	6.33 *br*	1.19	—
H-5	5.02 *s*	5.60 *s*	0.58	5.04 *s*
H-7	1.85 *dd*	2.06 *dd*	0.21	2.11 *dd*
H-9	1.98 *ddq*	2.23 *ddq*	0.25	2.19 *ddq*
H-10α	1.29 *m*	1.67 *m*	0.38	1.34 *dddd*
H-10β	1.83 *m*	1.95 *dddd*	0.12	1.94 *dddd*
H-11α	1.14 *dddd*	1.48 *dddd*	0.34	1.42 *dddd*
H-11β	1.65 *dddd*	1.78 *dddd*	0.13	1.78 *dddd*
H-12	1.00 *s*	1.67 *s*	0.67	1.16 *s*
H-13 }	0.89 *s*	1.12 *s*	0.23	0.91 *s*
H-14 }	0.89 *s*	1.09 *s*	0.20	0.82 *s*
H-15	0.88 *d*	1.05 *d*	0.17	0.92 *d*
OCOR	2.28 *d*	2.49 *d*	0.21	2.32 *dd*
	2.15 *tqq*	2.31 *tqq*	0.16	2.27 *dd*
	0.99 *d*	1.06 *d*	0.07	2.19 *ddqq*
				1.00 *d*
				0.99 *d*

J(Hz): 1,2 = 5.5; 1,3 = 1.5; 2,3 = 2; 7,11α = 12; 7,11β = 8; 9α,10α = 6; 9α,10β = 12; 9α,15 = 7; 10α,10β = 12; 10α,11α = 5; 10α,11β = 7; 10β,11α = 12; 10β,11β = 5; 11α,11β = 12; 2′,3′ = 3′,4′ = 3′,5′ = 7.

functions were α-orientated. The negative Cotton effect in the CD-spectrum of **13** would support the proposed absolute configuration, if the octant rule is valid in this case. If this is true, then the configuration of all compounds of this type can probably be correlated with that of **12**, since they are most likely all formed from caryophyllene through the corresponding cation of **6** [7]. The aerial parts contained germacrene D, α- and γ-humulene, α- and β-selinene, **1**, and **7**–**12**.

The aerial parts of *C. laureola* DC. afforded germacrene D, bicyclogermacrene, α-humulene, 4-hydroxygermacra-1(10),5-diene, sitosterol, lupeol, α-cadinol and the endoperoxide of phellandrene as clearly followed from the spectral data. From the ^{1}H NMR spectrum (see Experimental) the sequence of the ring protons could be deduced by spin decoupling, while the presence of an endoperoxide could be shown by the mass spectrum. However, only by chemical ionization a M + 1-ion could be detected. Elimination of H_2O_2 then led to the base peak.

So far the results on *Callilepis* do not show clear relationships to other genera in the Athrixiinae. However, the chemistry is very different from that of *Buphthalmum* and therefore its placement far away from the latter is surely correct. Highly oxygenated compounds seem to be characteristic for the genus, but further investigations are necessary to obtain a clearer picture of relationships.

EXPERIMENTAL

The air-dried plant material, collected in Transvaal, March 1981, was extracted with Et_2O–petrol (1:2) and the resulting extracts were separated first by CC (Si gel) and further by repeated TLC (Si gel). Known compounds were identified by comparing the IR and ^{1}H NMR spectra with those of authentic material.

Callilepis salicifolia (*voucher* 81/18, *deposited in the Herbarium of the National Botanic Research Institute, Pretoria*). The roots (900 g) afforded traces of tridecapentaynene, 5 mg lupeol, 5 mg stigmasterol, 150 mg **1**, 2 mg **3** (Et_2O–petrol, 1:3), 0.5 mg **4** (Et_2O–petrol, 1:10), 1.5 mg **5** (Et_2O–petrol, 1:10), 5 mg **6**, 60 mg **7**, 10 mg **8** (Et_2O–petrol, 1:3), 4 mg **9** (Et_2O–petrol, 1:10), 4 mg **10** (Et_2O–petrol, 1:10), 2 mg **11** (Et_2O–petrol, 1:10), 10 mg **12** containing 3 mg **1** (Et_2O–petrol, 1:1) (addition of $NaBH_4$ in MeOH and TLC afforded pure **12**), 2 mg **14** (Et_2O–petrol, 1:1) and 2 mg **15** (Et_2O–petrol, 1:1). The aerial parts (180 g) gave 3 mg germacrene D, 3 mg α- and 2 mg γ-humulene, 4 mg α- and 4 mg β-selinene, 80 mg **1**, 20 mg **7**, 20 mg **8**, 5 mg **9**, 5 mg **10**, 2 mg **11** and 5 mg **12**.

Callilepis laureola (*voucher* 81/127, *deposited in the Herbarium of the National Botanic Research Institute, Pretoria*). The aerial parts (70 g) afforded 3 mg germacrene D, 2 mg bicyclogermacrene, 2 mg α-humulene, 2 mg 4-hydroxygermacra-1(10),5-diene, 2 mg sitosterol, 4 mg lupeol, 5 mg cadinol T and 2 mg **16** (Et_2O–petrol, 1:20).

10-*Isovaleryloxy*-8,9-*epoxy* 7-*northymol isovalerate* (**3**). Colourless oil, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1760, 1740 (CO_2R); MS *m/z* (rel. int.): 232.110 $[M - RCO_2H]^+$ (0.5) ($C_{14}H_{16}O_3$), 85 $[C_4H_9CO]^+$ (70), 57 $[85 - CO]^+$ (100); CI (*iso*-butane): 335 $[M + 1]^+$ (100).

Thymol isovalerate (**4**). Colourless oil, not free from **5**, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1760 (PhOCOR); MS *m/z* (rel. int.): 234.162 $[M]^+$ (6) ($C_{15}H_{22}O_2$), 150 $[M - O{=}C{-}CHCHMe_2]^+$ (78), 135 $[150 - Me]^+$ (67), 85 $[C_4H_9CO]^+$ (20), 57 $[85 - CO]^+$ (100).

Isothymol isovalerate (**5**). Colourless oil, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1760 (PhOCOR); MS *m/z* (rel. int.): 234.162 $[M]^+$ (5) ($C_{15}H_{22}O_2$), 150 (70), 135 (72), 85 (30), 57 (100).

12-*Hydroxy-isocomene* (**8**). Colourless oil, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3650 (OH), 850 (CH=C$\diagdown\!\!\diagup$); MS *m/z* (rel. int.): 220.182 $[M]^+$ (4) ($C_{15}H_{24}O$), 202 $[M - H_2O]^+$ (0.5), 189 $[M - CH_2OH]^+$ (100), 178 $[M - C_3H_6]^+$ (7), 161 $[189 - C_2H_4]^+$ (22), 147 $[189 - C_3H_7]^+$ (18), 133 $[C_{10}H_{13}]^+$ (18), 119 $[C_9H_{11}]^+$ (30), 105 $[C_8H_9]^+$ (22), 91 $[C_7H_7]^+$ (17).

$$[\alpha]_{24}^{\lambda} = \frac{589 \quad 578 \quad 546 \quad 436\,\text{nm}}{-78 \quad -82 \quad -94 \quad -164} \quad (CHCl_3;\ c\ 0.6).$$

12-*Isovaleryloxyisocomene* (**9**). Colourless oil, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1740 (CO_2R), 850 (CH=C): MS *m/z* (rel. int.): 189.164

$[M - CH_2OCOR]^+$ (100) ($C_{14}H_{21}$), 85 $[C_4H_9CO]^+$ (30), 57 $[85 - CO]^+$ (85). To 2 mg **9** in 1 ml absolute Et_2O 5 mg $LiAlH_4$ was added at room temp. After 5 min, dil. H_2SO_4 was added. TLC afforded 1.5 mg **8**, identical with the natural compound.

Isocomen-12-al (**10**). Colourless oil, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 2720, 1720 (CHO), 850 (CH=C<); MS *m/z* (rel. int.): 218.167 $[M]^+$ ($C_{15}H_{22}O$), 189 $[M - CHO]^+$ (100), 161 $[189 - C_2H_4]^+$ (25), 147 (20), 133 (15), 119 (35), 105 (24), 91 (22). To 2 mg **10** in 1 ml MeOH 10 mg $NaBH_4$ were added. After addition of dil. H_2SO_4 usual work-up and TLC afforded 1.5 mg **8**, identical with the natural compound.

Methyl isocomen-12-oate (**11**). Colourless oil, not free from **9**, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1730 (CO_2R), 850 (CH=C); MS *m/z* (rel. int.): 248.178 $[M]^+$ (5) ($C_{16}H_{24}O_2$), 206 $[M - C_3H_2]^+$ (20), 189 $[M - CO_2Me]^+$ (100), 161 $[189 - C_2H_4]^+$ (30). 1 mg **11** was reduced as above with $LiAlH_4$ affording 0.7 mg **8**, identical with the natural compound.

3α-Hydroxy-5α-isovaleryloxysilphinene (**12**). Colourless oil, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1735 (CO_2R); MS *m/z* rel. int.): 320.235 $[M]^+$ (0.5) ($C_{20}H_{32}O_3$), 235 $[M - COR]^+$ (15), 218 $[M - RCO_2H]^+$ (41), 203 $[218 - Me]^+$ (20), 189 $[C_{14}H_{21}]^+$ (54), 175 $[C_{13}H_{19}]^+$ (35), 161 $[C_{12}H_{17}]^+$ (71), 147 $[C_{11}H_{15}]^+$ (38), 85 $[C_4H_9CO]^+$ (38), 57 $[85 - CO]^+$ (100).

$$[\alpha]_{24}^{\lambda} = \frac{589}{+14.5} \cdot \frac{578}{+15.2} \cdot \frac{546\,nm}{+17.3} \quad (CHCl_3;\ c\ 3.03).$$

10 mg **12** were stirred 1 hr in 3 ml Et_2O with 150 mg MnO_2. TLC afforded 7 mg **13**, colourless oil, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1740 (CO_2R), 1710 (C=CCO); MS *m/z* (rel. int.): 318.219 $[M]^+$ ($C_{20}H_{30}O_3$), 233 $[M - COR]^+$ (44), 217 $[M - OCOR]^+$ (10), 204 $[234 - CO]^+$ (25), 163 $[217 - C_4H_6]^+$ (100), 234 $[M - O{=}C{=}CHCHMe_2]^+$ (24), 85 $[C_4H_9CO]^+$ (24), 57 $[85 - CO]^+$ (57). CD (MeCN); $\Delta\varepsilon_{360} - 0.49$; $\Delta\varepsilon_{343} - 0.91$; $\Delta\varepsilon_{330} - 0.94$; $\Delta\varepsilon_{235} - 0.57$; $\Delta\varepsilon_{206} + 4.82$.

1-Phenyl-4-methylsulfonyl-hex-3-en-1-yne (**14**). Colourless gum, UV $\lambda_{max} = 282$ nm (Et_2O); IR $\nu_{max}^{CCl_4}$ cm^{-1}: 2240 (C≡C); MS *m/z* (rel. int.): 224.071 $[M]^+$ (13) ($C_{13}H_{14}O_2S$), 219 $[M - Me]^+$ (4), 155 $[M - SO_2Me]^+$ (100), 115 $[C_9H_7]^+$ (66), 77 $[C_6H_5]^+$ (63); CI (*iso*-butane): 235 $[M + 1]^+$ (100); ^{1}H NMR (400 MHz, $CDCl_3$): H-3 6.33 *t* ($J = 2.5$ Hz), H-5 2.52 *dq* ($J = 2.5$, 7.5 Hz), H-6 1.24 *t* ($J = 7.5$ Hz), SO_2Me 3.09 *s*; Ph 7.53–7.27 *m*.

Pinoresinol diisovalerate (**15**). Colourless gum, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1770 (PhOCOR), 1615 (aromate); MS *m/z* (rel. int.): 526.256 $[M]^+$ (0.1) ($C_{30}H_{38}O_8$), 442 $[M - O{=}C{=}CHCHMe_2]^+$ (7), 348 $[440 - O{=}C{=}CHCHMe_2]^+$ (50), 85 $[C_4H_9CO]^+$ (50), 57 $[85 - CO]^+$ (100); ^{1}H NMR (400 MHz, $CDCl_3$): H-2, 6 4.79 *d* ($J = 4$ Hz), H-3,7 3.09 *ddd* ($J = 6,5,3.5$ Hz), H-4,8 4.27 *dd* ($J = 9.5, 6$ Hz), H-4′,8′ 3.93 *dd* ($J = 9.5, 3.5$ Hz), H-2′, 6.97 *br s*, H-5′ 6.98 *d* ($J = 8.5$ Hz), H-6′ 6.87 *dd* ($J = 8.5, 1.5$ Hz), OiVal 2.44 *d*, 2.25 *tqq* ($J = 7, 7, 7$ Hz), 1.05 *d* (6 H, $J = 7$ Hz).

Phellandrene-3,6-endoperoxide (**16**). Colourless oil, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1445, 1380, 1350, 1125, 910; MS (CI, *iso*-butane) *m/z* (rel. int.): 169 $[M + 1]^+$ (24), 151 $[169 - H_2O]^+$ (20), 135 $[169 - H_2O_2]^+$ (100); ^{1}H NMR ($CDCl_3$, 400 MHz): 6.33 *ddq* (H-2), 4.57 *ddd* (H-3), 1.09 *dddd* (H-4), 1.82 *ddd* (H-5), 1.70 *ddd* (H-5′), 4.38 *dddd* (H-6), 1.93 *d* (H-7), 1.90 *dqq* (H-8), 0.98 *d* (H-9), 0.96 *d* (H-10) [*J*(Hz): 2,3 = 6; 2,6 = 2,7 = 2; 3,4 = 3,6 = 1.5; 4,5 = 4; 4,5′ = 10; 4,8 = 10; 5,5′ = 13.5; 5,6 = 4; 5′,6 = 2; 8,9 = 9,10 = 7]. $[\alpha]_D \sim -5$ ($c = 0.1$, $CHCl_3$).

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