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SESQUITERPENE LACTONES AND OTHER CONSTITUENTS FROM *PEGOLETTIA* SPECIES

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Key Word Index—*Pegolettia oxydonta*, *P. retrofracta*, *P. senegalensis*; Compositae; sesquiterpene lactones; eudesman-12,6β-olide; eudesman-12, 8α-olide; glycosides; linalool β-D-pyranosides; α-eudesmol-β-D-glucopyranosides.

Abstract—The aerial parts of *P. oxydonta* gave two new sesquiterpene lactones, one being a 12,6β-olide with a 10α-methyl group and the other a 12,8α-olide. Furthermore six new glucopyranosides were isolated. Two further species gave only known lactones but again with a 12,6β-olide moiety. Therefore these lactones may be of chemotaxonomic importance.

INTRODUCTION

The small subtropical, mainly African genus *Pegolettia* (tribe Inuleae) is placed in the first group of the subtribe Inulinae *sensu amplo* [1]. So far only one species has been studied chemically. It gave different types of 6,7-*cis*-lactones which may be characteristic [2]. Some of them are also present in *Calostephane* [3]. However, all other genera of the subtribe do not contain these relatively rare lactones. We now have studied two further species and again *P. senegalensis* from a different locality. The results are presented in this paper.

RESULTS AND DISCUSSION

The aerial parts of *P. oxydonta* DC afforded γ-humulene, thymol, the derivatives **10a** [4], **10b** [4] and **10c** [5], the himachalene derivative **11** [6], the sesquiterpene lactones tomentosin (**12**) [7], **1**, **2** [2] and **3** as well as the glucopyranosides **4**–**9**.

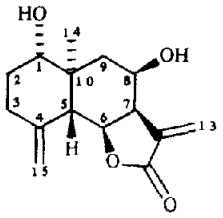
The ^{1}H NMR spectrum of **1** (Table 1) was in part very similar to that of **2** [2]. In particular the splittings of the signals of H-5–H-13 were nearly identical indicating that again a steiractinolide with a *cis*-6,7-lactone moiety was present. The presence of the $\Delta^{4(15)}$ isomer followed from the replacement of the olefinic methyl signal by those of exomethylene protons (δ5.01 and 4.86 *br s*).

The ^{1}H NMR spectrum of **3** (Table 1) indicated that a sesquiterpene lactone with an acetate and a 4-hydroxy tiglate group was present. The remaining ^{1}H NMR data differed markedly from those of **1** and **2**. Spin decoupling showed that an eudesman-12,8-olide with a Δ^3 double bond and oxygen functions at C-1, and C-9 was present. The observed couplings of H-8 differed from those of isoalantolactone and related 7,8-lactones, and from those of the corresponding steiractinolides. Therefore the stereochemistry most likely differed from that of both types. The observed NOE's allowed the assignment of the configuration at all centres. Clear effects were obtained between H-1, H-9 (6%), H-2α (10%) and H-5 (10%), between H-5, H-1 (10%), H-7 (6%) and H-9 (7%), between H-14, H-8 (12%) and H-6β (4%) as well as between H-9, H-1 (6%), H-5 (6%) and H-7 (8%). A small effect between H-1 and the acetate methyl (2%) indicated that most likely a 1β-acetoxy derivative was present. This was established by an INEPT experiment. H-1 gave an effect only with the acetate carbonyl (δ170.1) and H-9 only with the second ester carbonyl (δ166.0). The chemical shift of the latter required the proposed assignment of the carbonyl carbons. Thus the lactone **3** belongs to the rare *trans*-7,8-eudesmanolides. A 9-desacyloxy derivative has been reported from an *Inula* species [8]. The ^{13}C NMR spectrum (see Experimental) also supported the structure.

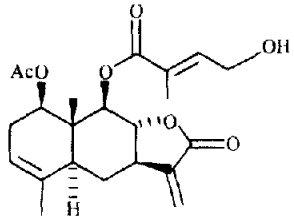
The ^{1}H NMR spectrum of **4** (Table 2) showed that a glycoside of linalool was present. Accordingly, the signals of the terpene part were nearly identical with those of linalool. A doublet at δ4.51 and broadened signals between δ3.2 and 3.8 indicated the presence of a glycoside. A double doublet at δ4.77 obviously was due to a proton under the acetoxy group. Spin decoupling showed that the latter was at C-2′. Acetylation gave a tetraacetate (**4Ac**) the ^{1}H NMR spectrum (Table 2) of which allowed a clear assignment of all signals. The couplings of the protons of the sugar moiety indicated the presence of a β-glucopyranoside.

The ^{1}H NMR spectra of **5**–**7** (Table 2) were similar to that of **4**. However, additional signals indicated that we were dealing with the corresponding tiglate, isovalerate and 2-methylbutyrate respectively. The downfield shift of the H-6′ signals showed that the 6′-hydroxy group was esterified. The relative position of the ester groups was deduced from the fact that the shift of H-2′ was identical in the spectra of **4**–**7** while the shift of H-6′ differed in the expected way, i.e., the unsaturated ester group leading to a small downfield shift of the corresponding proton.

The ^{1}H NMR spectra of **8** and **9** and their acetates **8Ac** and **9Ac** (Table 3) showed that again β-glucopyranosides were present which were esterified also at C-6′ with tiglic or isovaleric acid. The remaining signals were very similar



1 $2\Delta^3$



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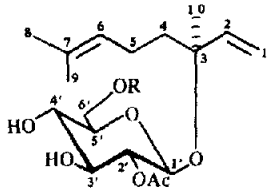
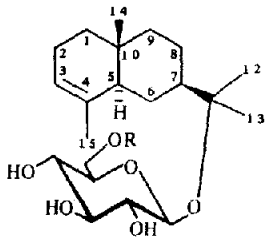


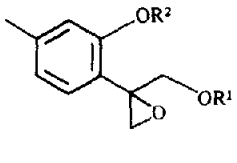
4 **5** **6** **7**

R H Tigl *i*Val MeBu



8 **9**

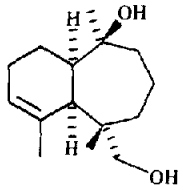
R Tigl *i*Val



10a **10b** **10c**

R^1 *i*Bu Tigl *i*Bu

R^2 Tigl *i*Bu *i*Bu



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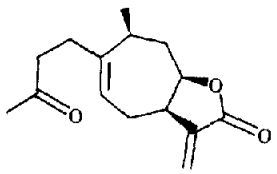

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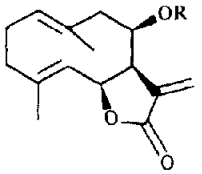

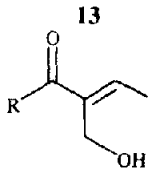

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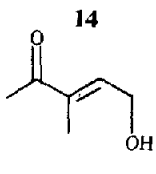

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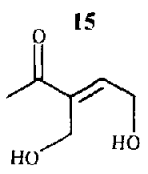

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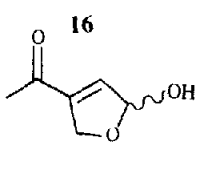

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to those of α-eudesmol. Accordingly, the corresponding β-glucopyranosides with ester groups at C-6′ were present. The ^{13}C NMR spectrum of **8Ac** (see Experimental) further supported the structure.

While in the mass spectra of **4**–**7** no molecular ions could be observed the eudesmol derivatives gave clear molecular ions. As in similar cases most fragments were due to the glycoside part. However, the terpene part was always represented by the corresponding hydrocarbon peak (*m/z* 136 and 204 respectively).

The aerial parts of *P. retrofracta* (Thunb.) Kiess gave in addition to widespread compounds (see Experimental) large amounts of the 6,7-*cis*-germacranolide **15** together with **13**, **14** and **16** which are also present in *P. senegalensis* [2].

A reinvestigation of the aerial parts of *P. senegalensis* Cass., collected from three different places in NE Namibia, gave no new compounds. However, if compared with the Transvaal collection [2] the variation of the lactones was less pronounced. Only 2,15,8-oxogermacra-1(10)*E*, 4*E*-(11)13-trien-12,6β-olide [2] and the $\Delta^{7(11)}$ isomer [2] were obtained but in much higher concentrations.

The overall picture of the chemistry of the genus *Pegolettia* indicates that sesquiterpene lactones with a 12,6β-olide moiety are typical while the presence of glucopyranosides in one species may indicate relationships to *Iphiona* which is taxonomically close and also contains sesquiterpene glycosides [9]. Thymol derivatives are reported from several genera of the first group of the subtribe Inulinae but of course also from other tribes. Several of these genera contain eudesmanolides but not with a *cis*-lactone ring. So far the only exception is *Calostephane*, a South African genus also placed in the same subtribe, where these *cis*-lactones are typical [10,

Table 1. ^{1}H NMR spectral data of compounds **1** and **3** ($CDCl_3$, 400 MHz, δ-values)

H	1	3
1	3.48 *dd*	5.04 *dd*
2β	1.83 *m*	2.58 *br d*
2α	1.54 *dq*	1.90 *br dd*
3	2.35 *ddd* 2.08 *m*	5.35 *br s*
5	2.01 *m*	2.44 *brd*
6α	4.83 *dd*	2.27 *dt*
6β		1.48 *q*
7	3.52 *dddd*	2.64 *ddddd*
8	4.34 *dt*	4.09 *dd*
9	2.03 *dd*(α) 1.70 *ddd*(β)	5.37 *d*
13	6.35 *d*	6.14 *d*
13'	6.13 *d*	5.51 *d*
14	0.77 *s*	1.18 *s*
15	5.01 *br s* 4.86 *br s*	1.71 *br s*
3'	—	6.92 *tq*
4'	—	4.39 *brdd*
5'	—	1.87 *dt*
OAc	—	1.83 *s*
OH	—	1.66 *t*

J[Hz] Compound **1**: 1,2α = 11; 1,2β = 4; 2α,2β = 13; 2α,3β = 12; 2α,3α = 4.5; 5,6 = 10; 6,7 = 7.5; 7,8 = 5; 7,13 = 3; 8,9α = 4; 8,9β = 9; 9α,9β = 13. Compound **3**: 1,2α = 7; 1,2β = 10; 2α,2β = 20; 5,6α = 6α,7 = 3; 5,6β = 6α,6β = 6β,7 = 12; 7,8 = 12; 7,13 = 3.3; 7,13' = 2.7; 8,9 = 10; 3',4' = 4', OH = 5.5; 3',5' = 4',5' = 1.

11]. The himachalene diol **11**, has so far been isolated only from a *Blumea* species [6], a genus which is placed in the third group of the Inulinae [1].

EXPERIMENTAL

The plants were collected during March 1988 in Namibia (vouchers are deposited in the SWA-Herbarium at Windhoek) and the air-dried material was extracted with Et_2O–MeOH–petrol (1 : 1 : 1). The extracts were worked-up and sepd as reported previously [12]. The extract of the aerial parts (450 g) of *P. oxydonta* (voucher 88/120) was first separated by CC into four crude fractions. The first one gave 10 mg γ-humulene and the second one 50 mg thymol. TLC of the third fraction afforded 600 mg **10a**, 300 mg **10b** and 100 mg **10c**. The last fraction was separated by medium pressure chromatography (MPC) (silica gel, ϕ 30–60 μ Et_2O/petrol 1 : 1–Et_2O/MeOH, 9 : 1, 85 fractions ea. 20 ml). Fractions 7–10 gave by TLC (Et_2O–petrol, 3 : 1) two fractions. The first one gave by HPLC (MeOH–H_2O, 17 : 3, always RP 18, *ca* 100 bar, flow rate 3 ml/min) 5 mg **12** (R_t 1.0 min) and 8 mg **11** (R_t 2.4 min). The second fraction afforded by HPLC (s.a.) 15 mg **5** (R_t 3.3 min), 10 mg **6** (R_t 3.9 min) and 6 mg **7** (R_t 5.0 min). Fractions 11–12 contained a complex mixture of esterified glucosides of linalool, its ^{1}H NMR spectrum indicated that mainly **4**–**7** were present. From fractions 23–28 300 mg crystalline **3** were obtained. The mother liquor was separated by TLC (Et_2O) and further by HPLC (MeOH–H_2O), 17 : 3, RP 8). In addition to 100 mg **3**, 500 mg crude **8** and 100 mg crude **9** were obtained which were purified as their acetates (Ac_2O, DMAP, $CHCl_3$, 24 hr, 20°) by HPLC (s.a.) affording **8Ac** (R_t 25 min) and **9Ac** (R_t 29 min). TLC of fractions 31–36 (Et_2O–MeOH, 30 : 1) gave 200 mg **2**, 10 mg **4** and a fraction which gave after HPLC (MeOH–H_2O, 9 : 11) 2 mg **1** (R_t 6.3 min) and 10 mg **2**.

The aerial parts of *P. retrofracta* (140 g) (voucher 86/62, collected *ca* 10 km S of Windhoek on the mountain Regenstein) gave by CC and TLC 40 mg taraxasterylacetate, 100 mg lupeyl acetate, 50 mg ledol, 100 mg **13**, 20 mg **14**, 800 mg **15** and 20 mg **16**.

The aerial parts of *P. senegalensis* (200 g) gave 100 mg **2**, 70 mg **15**, 850 mg 8-oxogermacra-1(10)*E*,4*E*-11(13)trien-12,6β-olide and 250 mg of its $\Delta^{7(11)}$ isomer together with some widespread compounds isolated previously [2]. Known compounds were identified by comparing the 400 MHz ^{1}H NMR spectra with those of authentic material.

1α,8β-Dihydroxy-5βH,10α-methyl-eudesma-4(15),11(13)-dien-12,6β-olide (**1**). Colourless gum, IR $\nu_{max}^{CHCl_3}$, cm^{-1}: 3600 (OH), 1770 (γ-lactone); MS: *m/z* (rel. int.): 264.136 [M]$^+$ (1.7) (calc. for $C_{15}H_{20}O_4$ 264.136), 246 [M − H_2O]$^+$ (8), 228 [246 − H_2O]$^+$ (62), 213 [228 − Me]$^+$ (34), 202 [246 − CO_2]$^+$ (100), 157 (36), 107 (52), 93 (70), 91 (79).

1β-Acetoxy-9β-[4-hydroxy tigloyloxy]-eudesma-3,11(13)-dien-12,8α-olide (**3**). Colourless crystals, mp 191°; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3600 (OH), 1780 (γ-lactone), 1720, 1655 (C=CCO_2R); MS: *m/z* (rel. int.): 404.184 [M]$^+$ (0.1) (calc. for $C_{22}H_{28}O_7$ 404.184), 386 [M − H_2O]$^+$ (0.2), 344 [M − HOAc]$^+$ (36), 228 [344 − RCO_2H]$^+$ (32), 213 [228 − Me]$^+$ (20), 119 (56), 99 [RCO]$^+$ (100), 81 [99 − H_2O]$^+$ (57), 71 [99 − CO]$^+$ (58); ^{13}C NMR ($CDCl_3$, C-1–C-15): δ77.7, 29.4, 120.3, 131.9, 47.1, 23.0, 46.4, 80.6, 76.2, 42.6, 138.0, 169.5, 118.3, 8.7, 21.3, OCOR (C-1'–C-5'): 166.0, 127.9, 141.6, 59.6, 12.6, OAc 170.1, 20.9 (assigned by 2D); $[\alpha]_D^{24°}$ −66 ($CHCl_3$; *c* 0.38); CD (MeCN): $\Delta\varepsilon_{271}$ + 0.1.

Linalool-β-D-glucopyranoside-2'O-acetate (**4**). Colourless oil, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1760 (OAc); acetylation (Ac_2O, DMAP, $CHCl_3$, 1 hr, 60°) afforded after TLC (Et_2O–petrol, 3 : 1) **4Ac**, colourless oil, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1760, 1230 (OAc); MS: *m/z* (rel. int.): 331 [M − Me_2C=$CHCH_2CH_2C$(Me)(CH=CH_2)O(*A*)]$^+$ (6), 271 [331 − HOAc]$^+$ (1), 229 [271 − ketene]$^+$ (2), 169 [229–HOAc]$^+$ (34), 136 [$C_{10}H_{16}$]$^+$ (22), 109 [169 − HOAc]$^+$ (35), 93 (100), 69 [Me_2C=$CHCH_2$]$^+$ (93); $[\alpha]_D^{24°}$ −7 ($CHCl_3$; *c* 0.65).

Linalool-β-D-glucopyranoside-2'O-acetate,6'O-tiglate (**5**). Colourless oil, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3480 (OH), 1755, 1260 (OAc), 1725, 1650 (C=CCO_2R); MS: *m/z* (rel. int.): 287 [M − A]$^+$ (10), 269 [287 − H_2O]$^+$ (5), 227 [287 − HOAc]$^+$ (3), 136 [$C_{10}H_{16}$]$^+$ (18), 93 (50), 83 [RCO]$^+$ (100), 69 [C_5H_9]$^+$ (56); $[\alpha]_D^{24°}$ −33 ($CHCl_3$; *c* 0.88).

Linalool-β-D-glucopyranoside-2'O-acetate,6'O-isovalerate (**6**). Colourless oil, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3500 (OH), 1745 (CO_2R); MS: *m/z* (rel. int.): 289 [M − A]$^+$ (5), 187 [289 − RCO_2H]$^+$ (3), 136 [$C_{10}H_{16}$]$^+$ (34), 93 (79), 69 [C_5H_9]$^+$ (100); $[\alpha]_D^{24°}$ −27 ($CHCl_3$; *c* 0.43).

Linalool-β-D-glucopyranoside-2'O-acetate-6'O-[2-methylbutyrate] (**7**). Colourless oil, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1745 (CO_2R); MS: *m/z* (rel. int.): 289 [M − A]$^+$ (3), 187 [289 − RCO_2H]$^+$ (6), 136 [$C_{10}H_{16}$]$^+$ (38), 93 (96), 69 [C_5H_9]$^+$ (100); $[\alpha]_D^{24°}$ −29 ($CHCl_3$; *c* 0.69).

α-Eudesmol-β-D-glucopyranoside-6'O-tiglate (**8**). Colourless oil, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3600 (OH), 1720 (C=CCO_2R); Acetylation (s.a.) gave **8Ac**, colourless oil, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1760 (OAc), 1715, 1650 (C=CCO_2R); MS: *m/z* (rel. int.): 592 [M]$^+$ (0.1), 371.134 [M − $C_{15}H_{25}O$]$^+$ (12) (calc. for $C_{27}H_{23}O_9$ 371.134), 204

Table 2. ^{1}H NMR spectral data of compounds **4**–**7** ($CDCl_3$, 400 MHz, δ-values)

H	**4**	**4Ac**	**5**	**6**	**7**
1*t*	5.18 *dd*	5.19 *dd*	5.18 *dd*	5.19 *dd*	5.19 *dd*
1*c*	5.23 *dd*	5.25 *dd*	5.22 *dd*	5.24 *dd*	5.24 *dd*
2	5.72 *dd*	5.72 *dd*	5.76 *dd*	5.76 *dd*	5.75 *dd*
4	1.60 *m*	1.60 *m*	1.59 *m*	1.58 *m*	1.60 *m*
4′	1.53 *m*	1.53 *m*	1.52 *m*	1.51 *m*	1.53 *m*
5	1.95 *m*	1.95 *m*	1.95 *m*	1.95 *m*	1.95 *m*
6	5.03 *br t*	5.02 *br t*	5.04 *br t*	5.04 *br t*	5.04 *br t*
8	1.65 *br s*	1.65 *br s*	1.65 *br s*	1.65 *br s*	1.66 *br s*
9	1.57 *br s*	1.56 *br s*	1.57 *br s*	1.57 *br s*	1.57 *br s*
10	1.31 *s*	1.33 *s*	1.33 *s*	1.33 *s*	1.33 *s*
1′	4.51 *d*	4.57 *d*	4.50 *d*	4.51 *d*	4.51 *d*
2′	4.77 *dd*	4.99 *dd*	4.77 *dd*	4.76 *dd*	4.76 *dd*
3′	3.54 *br t*	5.18 *t*	3.58 *br t*	3.58 *brt*	3.58 *br t*
4′	3.61 *br t*	5.02 *t*	3.39 *m*	3.41 *m*	3.41 *m*
5′	3.25 *dt*	3.63 *ddd*	3.42 *m*	3.38 *m*	3.38 *m*
6_1′	3.80 *br s*	4.19 *dd*	4.44 *dd*	4.38 *dd*	4.39 *dd*
6_2′		4.07 *dd*	4.35 *dd*	4.29 *dd*	4.29 *dd*
OCOR	—	—	6.93 *qq*	2.24 *d*	1.88 *ddq*
	—	—	1.81 *dq*	2.11 *tqq*	2.37 *dd*
	—		1.83 *dq*	0.97 *d*	2.16 *dd*
	—	—	—	—	1.55 *m*
	—	—	—	—	1.36 *m*
OAc	2.11 *s*	2.07 *s*	2.12 *s*	2.12 *s*	0.90 *t*
	—	2.03 *s*	—	—	0.94 *d*
		2.01 *s*			
	—	2.00 *s*			

J[Hz]: 1*t*,2 = 17; 1*c*,2 = 11; 5,6 = 7; 1′,2′ = 8; 2′,3′ = 3′,4 = 4′,5′ = 10; 5′,6_1′ = 4; 5′,6_2′ = 2; 6_1′,6_2′ = 12; *O*Tigl 3,4 = 7; 3,5 = 4,5 = 1; O*i*Val 2,3 = 3,4 = 3,5 = 7; OMeBu 2,3_1 = 6; 2,3_2 = 8; 2,5 = 3,4 = 7; 3_1,3_2 = 15.

Table 3. ^{1}H NMR spectral data of compounds **8**, **8Ac**, **9** and **9Ac** ($CDCl_3$, 400 MHz, δ-values)

H	**8**	**8Ac**	**9**	**9Ac**
3	5.27 *br s*	5.27 *br s*	5.30 *br s*	5.29 *br s*
5	1.96 *m*	1.89 *br d*	1.95 *m*	1.95 *m*
6α	1.46 *br d*	1.42 *br d*	1.45 *br d*	1.44 *br d*
6β	0.93 *q*	0.88 *q*	0.97 *q*	0.89 *q*
7	1.78 *m*	1.80 *m*	1.80 *m*	1.80 *m*
12	1.22 *s*	1.29 *s*	1.24 *s*	1.21 *s*
13	1.19 *s*	1.23 *s*	1.21 *s*	1.14 *s*
14	1.57 *br s*	1.57 *br s*	1.59 *br s*	1.58 *br s*
15	0.75 *s*	0.73 *s*	0.76 *s*	0.75 *s*
1′	4.46 *d*	4.67 *d*	4.47 *d*	4.67 *d*
2′	3.35 *br t*	4.98 *dd*	3.35 *t*	4.99 *dd*
3′	3.57 *t*	5.21 *t*	3.58 *t*	5.22 *t*
4′	3.35 *t*	5.01 *t*	3.37 *t*	5.01 *t*
5′	3.48 *ddd*	3.72 *ddd*	3.45 *ddd*	3.68 *ddd*
6_1′	4.39 *dd*	4.24 *dd*	4.37 *dd*	4.18 *dd*
6_2′	4.32 *dd*	4.14 *dd*	4.30 *dd*	4.09 *dd*
OCOR	6.88 *qq*	6.88 *qq*	2.22 *d*	2.20 *d*
	1.78 *dq*	1.79 *dq*	2.08 *m*	2.08 *m*
	1.81 *dq*	1.81 *br s*	0.95 *d*	0.95 *d*
OAc	–	2.01 *s*		2.03 *s*
	–	2.00 *s*		2.02 *s*
	—	1.98 *s*	—	2.00 *s*

J[Hz]: 5,6β = 6α,6β = 6β,7 = 12; 1′,2′ = 8; 2′,3′ = 3′,4′ = 4′,5′ = 10; 5′,6_1′ = 2,5; 5′,6_2′ = 6.5; 6_1′,6_2′ = 12; (compounds **9** and **9Ac** 5′,6_1′ = 6.5; 5′,6_2′ = 2.5) *O*Tigl 3,4 = 7; 3,5 = 4,5 = 1; O*i*Val 2,3 = 3,4 = 3,5 = 7.

$[C_{15}H_{24}]^+$ (72), 161 (46), 83 $[RCO]^+$ (100); $[\alpha]_D^{24°} + 2$ ($CHCl_3$, *c* 2.85); ^{13}C NMR ($CDCl_3$, C-1–C-15): δ40.1, 23.7, 120.7, 135.3, 46.5, 22.3, 48.7, 22.9, 37.8, 32.2, 80.9, 25.0, 22.4, 14.4, 21.1; OCOR 167.5, 128.8, 138.1, 15.6, 12.9; OAc 170.4, 169.4, 169.0, 20.6, 2 × 20.7; C-1′–C-6′: 95.1, 73.1, 71.7, 69.1, 71.5, 62.7.

*α-Eudesmol-β-*D*-glucopyranoside-6′O-isovalerate* (**9**). Colourless oil which was purified as its acetate **9Ac**, colourless oil, IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1760 (OAc), 1735 (CO_2R); MS: *m/z* (rel. int.): 594 $[M]^+$ (0.1), 373.150 $[M-C_{15}H_{25}O]^+$ (7) (calc. for $C_{17}H_{25}O_9$ 373.150), 204 $[C_{15}H_{24}]^+$ (82), 161 (100), 85 $[RCO]^+$ (58).

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