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SESQUITERPENE XYLOSIDES FROM *IPHIONA SCABRA*

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Key Word Index —*Iphiona scabra*; Compositae; sesquiterpene xylosides; eudesmane derivatives; secoeudesmane derivative; new carbon skeletons.

Abstract—The aerial parts of *Iphiona scabra* afforded a complex mixture of sesquiterpene xylopyranosides. Separation of the peracetylated derivatives gave 10 compounds, seven eudesmane derivatives, a secoeudesmane and two sesquiterpene glycosides with new skeletons, named iphionane and isoiphionane. The biogenesis of these compounds is discussed.

INTRODUCTION

The North Eastern African genus *Iphiona* (Compositae, tribe Inuleae) is placed in the subtribe Inulinae, in the *Inula* group with genera which are characterized by species with mostly ligulate female florets, styles with rounded or obtuse arms and sweeping hairs in the upper part. The spine tips of the pollen grains are distinctly set off from their bases and the bacular thickenings mostly have a dome-like arrangement [1]. The chemistry of these genera is not very uniform though most species contain sesquiterpene lactones [2]. Nothing is known on the chemistry of *Iphiona*. We therefore studied one species collected on the Sinai peninsula. The results are discussed in this paper.

RESULTS AND DISCUSSION

The polar fractions of the aerial parts contained in addition to sitosterol-β-*O*-glucoside a complex mixture which could not be separated. The ^{1}H NMR spectrum indicated that most likely a mixture of 2-*O*-acetates of xylopyranosides were present. We therefore acetylated the mixture. The peracetylated compounds were separated by TLC followed by HPLC. Finally the acetates **1Ac**–**10Ac** were obtained; two of them, **3** and **5**, were an inseparable mixture.

The ^{1}H NMR spectrum of **1Ac** (Table 1) clearly indicated that a xylopyranoside triacetate was present. The signal of the sugar moiety was nearly identical with those of other 1β-xylopyranoside triacetates [3]. The remaining signals showed that most likely an eudesm-4(15)-ene derivative was present as several signals were nearly identical with those of isoalantolactone. The chemical shifts of the remaining methyl singlets indicated that the sugar moiety was at C-11. From the coupling of H-5, which could be assigned by spin decoupling, the presence of a *trans*-decalin derivative was deduced. The ^{1}H NMR spectrum of the mixture of **3Ac** and **5Ac** (Table 1) was close to that of **1Ac**. However, the signals of the exomethylene protons were replaced by those of olefinic methyls. Furthermore a broadened singlet at $\delta = 5.28$ indicated the presence of a Δ^3 double bond isomer of **1Ac**, i.e. **5Ac**. In the spectrum of the second compound in the mixture the downfield shift of H-6 ($\delta = 2.62$ *br d*) showed that most likely also a Δ^4 isomer was present, i.e. **3Ac**. Accordingly, the ^{1}H NMR signals of **3Ac** and **5Ac** were in part similar to those of the corresponding alantolactone isomers.

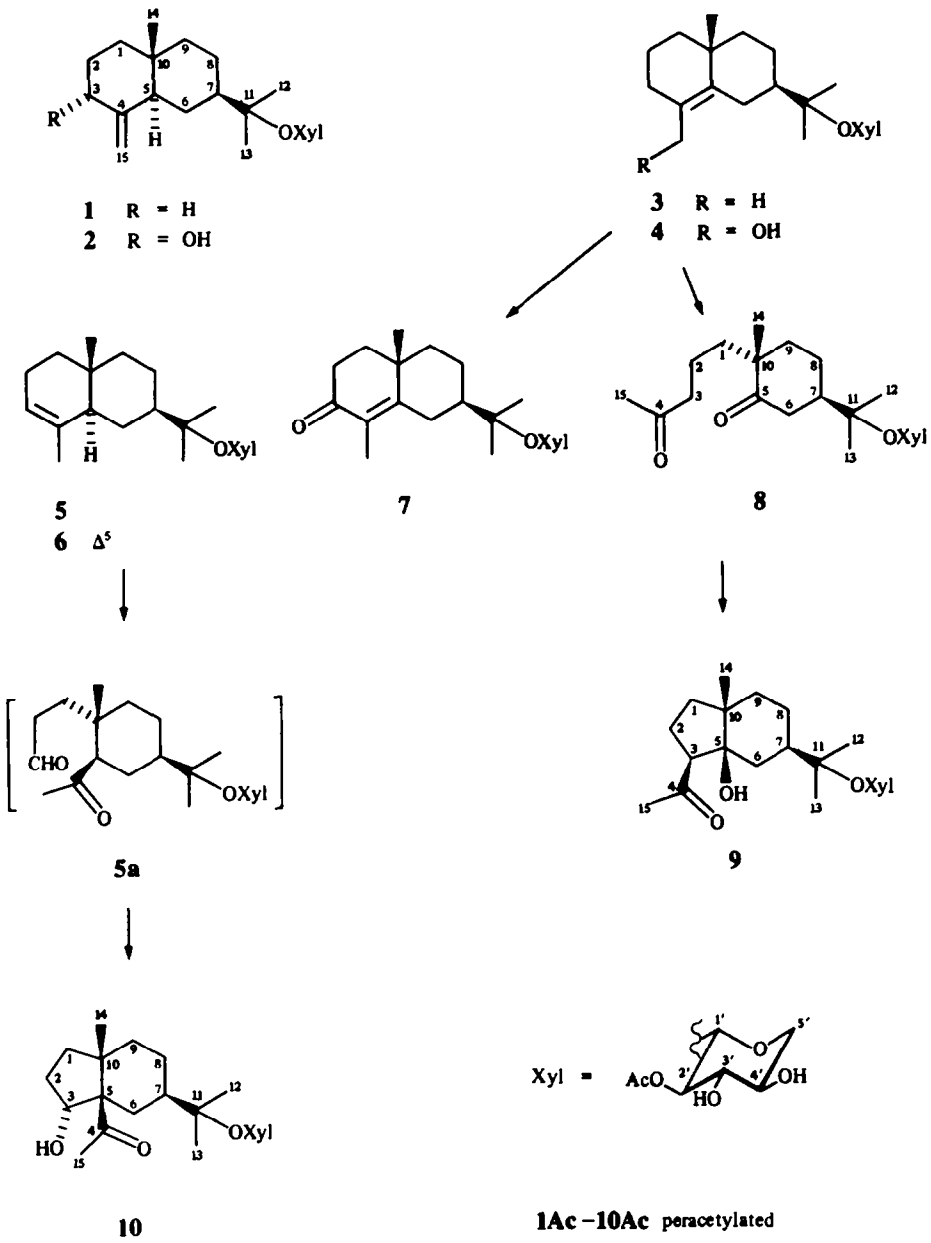
The ^{1}H NMR spectrum of **2Ac** (Table 1) was in part close to that of isotelekin and similar eudesmanes [4, 5]. Especially the couplings of H-3 were identical to isotelekin but clearly differed from those of the 3-epi-lactone. Accordingly, a 3α-acetoxy group was present.

The ^{1}H NMR spectrum of **4Ac** (Table 1) was close to that of **3Ac**. However, the olefinic methyl signal was replaced by a pair of doublets at $\delta = 4.57$ and 4.52. Together with an additional acetoxy methyl signal this indicated that the corresponding 15-acetoxy derivative of **3Ac** was present. The position of the acetoxy group followed from the chemical shifts of H-15 and from NOE difference spectroscopy. Clear effects were obtained between H-12 and H-13, H-6 and H-1′. The ^{13}C NMR data also agreed nicely with the structure (see Experimental).

The ^{1}H NMR spectrum of **6Ac** (Table 1) displayed two broadened singlets which only could be assigned to olefinic protons and was similar to that of dehydroalantolactone [5]. The chemical shifts of these protons and that of H-7 ($\delta = 2.40$) indicated the presence of a 3,5-diene. Accordingly, H-14 was shifted downfield. The ^{13}C NMR spectrum also supported the proposed structure (see Experimental).

The ^{1}H NMR spectrum of **7Ac** (Table 1) was in part close to that of 3-oxo-isoalantolactone [6] or carrissone [7]. All data therefore indicated the presence of the 3-oxo derivative of **3Ac**. This was further supported by the IR and MS spectra (see below).

The ^{1}H NMR spectrum of **8Ac** displayed a methyl singlet at $\delta = 2.12$ which could be assigned to a methyl ketone. The spectrum was in part close to that of secoeudesmanes [8, 9]. This was established by the ^{13}C NMR spectrum (see Experimental) which clearly indicated two keto groups. The chemical shifts showed that one was a cyclohexanone carbonyl group.



Accordingly, the presence of a secoeudesmane derivative was proposed. This was supported by the mass spectrum (see below). All data therefore agreed with the proposed structure.

The ^{1}H NMR spectrum of **9Ac** (Table 1) also showed a methyl singlet at $\delta = 2.19$ which was most likely due to a methyl ketone. This was supported by the ^{13}C NMR spectrum (see Experimental). The stereochemistry followed from the couplings of H-3 and model inspection. Furthermore the proposed configurations at C-3 and C-5 agreed with the preferred stereochemistry as the hydroxy ketone most likely is formed biogenetically by aldol-condensation of **8**.

The ^{1}H NMR spectrum of **10Ac** (Table 1) also displayed a methyl singlet which indicated the presence of a methyl ketone. Furthermore a double doublet at $\delta = 5.49$ indicated the presence of a secondary acetoxy group. The ^{13}C NMR spectrum (see Experimental) clearly showed that a rearranged system was present. Especially the lowfield singlet at $\delta = 63.4$ required a neighbouring keto group. NOE difference spectroscopy allowed the assignment of the stereochemistry and supported the proposed structure. Thus clear effects were observed between H-14 and H-15 as well as between H-15, H-14 and H-3.

The mass spectra of **1Ac–10Ac** always showed a clear peak at *m/z* 259, the oxonium ion being formed by loss of the sesquiterpene moiety. The following fragments formed by loss of acetic acid or ketene are *m/z* 199, 157, 139 and 97. Molecular ions only can be observed in a few cases. Thus **1Ac** showed *m/z* 480.272 (0.2%) corresponding to $C_{26}H_{40}O_8$, but the base peak (*m/z* 204) was due to the sesquiterpene moiety ($C_{15}H_{24}$). Compounds **2Ac** and **4Ac** showed a fragment *m/z* 478.257, which corresponds to M-HOAc, and at *m/z* 263 and 262. The latter are

Table 1. ^{1}H NMR spectral data of **1Ac–10Ac** (400 MHz, $CDCl_3$, TMS as internal standard)

H	1Ac	2Ac	3Ac	4Ac	5Ac	6Ac*	7Ac	8Ac	9Ac	10Ac
2					2.00 *m*	2.0 *m*	α 2.36 *ddd* β 2.49 *ddd*			
3	2.1–1.9 *m*	5.32 *br t*			5.28 *br s*	5.49 *br*	—	2.40 *m*†	3.81 *br t*	5.49 *dd*
5	2.28 *br d*	2.18 *br d*		—	1.72 *br d*	- -	—	—	—	—
6				2.64 *br d*		5.55 *br s*	α 2.86 *br dt*	2.42 *dd*		
6′			2.62 *br d*				β 1.87 *br dd*	2.31 *br d*		
12	1.19 *s*	1.19 *s*	1.18 *s*	1.18 *s*	1.18 *s*	1.20 *s*	1.24 *s*	1.19 *s*	1.19 *s*	1.19 *s*
13	1.15 *s*	1.15 *s*	1.15 *s*	1.13 *s*	1.14 *s*	1.09 *s*	1.17 *s*	1.15 *s*	1.11 *s*	1.14 *s*
14	0.67 *s*	0.67 *s*	0.98 *s*	1.02 *s*	0.73 *s*	0.92 *s*	1.17 *s*	1.09 *s*	0.97 *s*	0.93 *s*
15	4.70 *br s*	5.05 *br s*	1.57 *br s*	4.57 *d*	1.58 *br s*	1.75 *s*	1.75 *s*	2.12 *s*	2.19 *s*	2.18 *s*
15′	4.41 *br s*	4.67 *br s*		4.52 *d*						
1′	4.67 *d*	4.66 *d*	4.66 *d*	4.62 *d*	4.66 *d*	4.69 *d*	4.63 *d*	4.62 *d*	4.65 *d*	4.63 *d*
2′	4.89 *dd*	4.88 *dd*	4.87 *dd*	4.89 *dd*	4.87 *dd*	4.93 *dd*	4.91 *ddd*	4.91 *dd*	4.85 *dd*	4.89 *dd*
3′	5.17 *t*	5.17 *t*	5.16 *t*	5.16 *t*	5.16 *t*	5.17 *t*	5.18 *t*	5.15 *t*	5.16 *t*	5.19 *t*
4′	4.94 *ddd*	4.93 *ddd*	4.95 *ddd*	4.94 *ddd*	4.95 *ddd*	4.95 *ddd*	4.95 *ddd*	4.91 *ddd*	4.92 *ddd*	4.95 *ddd*
$5'_1$	4.09 *dd*	4.08 *dd*	4.08 *dd*	4.08 *dd*	4.08 *dd*	4.08 *dd*	4.06 *dd*	4.06 *dd*	4.06 *dd*	4.07 *dd*
$5'_2$	3.31 *dd*	3.30 *dd*	3.30 *dd*	3.29 *dd*	3.30 *dd*	3.30 *dd*	3.29 *dd*	3.28 *dd*	3.30 *dd*	3.29 *dd*
OAc	2.03 *s*	2.03 *s*	2.02 *s*	2.03 *s*		2.03 *s* (6H)	2.01 *s*	2.01 *s* (6H)	2.03 *s* (6H)	2.03 *s*
	2.02 *s* (6H)	2.02 *s*	2.03 *s*	2.00 *s* (9H)		2.01 *s*	2.02 s	2.02 s	2.02 s	2.02 s
		2.01 *s* (6H)					2.03 *s*			2.01 *s*
										2.04 *s*

* H-7 2.40 *br d*.

† Not first order.

J (Hz): 1′,2′ = 7.5; 2′,3′ = 3′,4′ = 9; 4′,$5'_1$ = 5; 4′,$5'_2$ = 9; $5'_1$,$5'_2$ = 12; compounds **1Ac**, **2Ac** and **5Ac**: 5,6 = 12; compounds **3Ac** and **4Ac**: 6,6′ = 13.5; compound **4Ac**: 15,15′ = 12; compound **7Ac**: 1,2 = 7; 1,2′ = 12; 1′,2 = 1′,2′ = 4; 2,2′ = 16; 6,6′ = 15; 6,7 = 11.5; 6′,7 = 6′,8 = 2; compound **8Ac**: 6,6′ = 14; 6,7 = 12; 6,7′ = 3; compound **9Ac**: 2,3 = 9; compound **10Ac**: 2,3 = 8; 2′,3′ = 3.5.

formed by loss of the sugar moiety. The corresponding peaks *m/z* 203 and 202 again are of high intensity. The spectrum of **6Ac** is close to those of **2Ac** and **4Ac** while that of **7Ac** gave a very weak molecular ion (*m/z* 494.251 corresponding to $C_{26}H_{38}O_9$) but intense fragments at *m/z* 219 and 218 formed by loss of the sugar moiety. Compound **8Ac** showed a relatively intense fragment at *m/z* 428, obviously formed by McLafferty fragmentation and loss of the C_5-unit at C-10. However, also *m/z* 237 is present, the result of elimination of the sugar moiety. The spectrum of **9Ac** only showed the fragments of the sugar part (*m/z* 259) and the sesquiterpene residue with loss of water. The spectrum of **10Ac** showed a clear fragment at *m/z* 511.254 corresponding to $C_{26}H_{39}O_{10}$ formed by loss of an acetyl group. The fragments due to loss of the sugar moiety (*m/z* 279) followed by loss of acetic acid and acetyl (*m/z* 219 and 176) were also present.

The carbon skeleton of **9** seems to be new. We have named it iphionane and the skeleton of **10** isoiphionane. There are two reports in the literature concerning sesquiterpenes related to **10**. The structure for faurinone was assigned as 10-epi-isoiphian-4-one [10] but later revised completely [11]. A further compound of this type may be cyperolone where no NMR data are available. However, it has been prepared by rearrangement [12].

EXPERIMENTAL

The air dried aerial parts (500 g, collected in March 1985 at Sinai near Saint Katherine, voucher deposited in the Herbarium of the University of Alexandria) were extracted with Et_2O–petrol, 1:1, at room temp. The defatted extract was first separated by CC (SiO_2, C_6H_6, C_6H_6–$CHCl_3$, $CHCl_3$ and $CHCl_3$–MeOH, 80 ml fractions). The polar fractions (2 g) were separated again by CC. The most polar fraction gave 10 mg *β*-sitosterol-*β*-D-glucoside (identical with an authentic sample). One tenth of the less polar CC fraction gave by PTLC (Et_2O–MeOH, 20:1) a mixture which was acetylated ($CHCl_3$, Ac_2O, DMAP, 2 hr, 70°) and separated by PTLC (Et_2O–petrol, 3:1) into fractions. HPLC (RP 8, MeOH–H_2O, 17:3, *ca* 100 bar) of the first band gave 12 mg **2Ac** (R_t 1.8 min), 35 mg **4Ac** (R_t 2.2 min), 10 mg **6Ac** (R_t 3.1 min), 3 mg **3Ac** and **5Ac** (R_t 3.8 min) and 1 mg **1A** (R_t 3.8 min). HPLC of the second band (MeOH–H_2O, 4:1) afforded 6 mg **9Ac** (R_t 1.7 min) and 7 mg **10Ac** (R_t 2.7 min). HPLC of the most polar part (MeOH–H_2O, 4:1) gave 15 mg **8Ac** (R_t 1.6 min) and 5 mg **7Ac** (R_t 2.1 min).

β-Eudesmol-[α-xylopyranoside-triacetate] (**1Ac**). IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1760, 1230 (OAc); MS *m/z* (rel. int.): 480.272 $[M]^+$ (0.2) (calc. for $C_{26}H_{40}O_8$: 480.272), 259 $[A]^+$ (48), 205 $[C_{15}H_{25}]^+$ (59), 204 $[C_{15}H_{24}]^+$ (100), 199 $[A-HOAc]^+$ (37), 189 $[204-Me]^+$ (24), 161 $[204-C_3H_7]^+$ (30), 157 $[199-ketene]^+$ (71), 139 $[199-HOAc]^+$ (59), 97 $[157-HOAc]^+$ (61).

3α-Acetoxy-β-eudesmol-[α-xylopyranoside-triacetate] (**2Ac**). IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1760, 1230 (OAc); MS *m/z* (rel. int.): 478.257 $[M-HOAc]^+$ (0.2) (calc. for $C_{26}H_{38}O_8$: 478.257), 259 $[A]^+$ (64), 203 $[C_{15}H_{23}]^+$ (56), 202 $[C_{15}H_{22}]^+$ (50), 199 (50), 157 (100), 139 (84), 97 (86); $[\alpha]_D^{20°}$ −33 ($CHCl_3$; *c* 1.1).

α- and γ-Eudesmol-[α-xylopyranoside-triacetate] (**3Ac** *and* **5Ac**). IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1760, 1230 (OAc); MS *m/z* (rel. int.): 480.272 $[M]^+$ (0.2) (calc. for $C_{26}H_{40}O_8$: 480.272), 259 $[A]^+$ (52), 205 (62), 204 (100).

15-Acetoxy-γ-eudesmol-[α-xylopyranoside-triacetate] (**4Ac**). IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1760, 1230 (OAc); MS *m/z* (rel. int.): 478.257 $[M-HOAc]^+$ (0.8) (calc. for $C_{26}H_{38}O_8$: 478.257), 418 $[478-HOAc]^+$ (1.2), 358 $[418-HOAc]^+$ (0.7), 259 $[A]^+$ (70), 203 (100), 202 (86), 199 (42), 157 (97), 139 (86), 97 (87); ^{13}C NMR ($CDCl_3$, C-1–15): 41.7 *t*, 26.0 *t*, 29.3 *t*, 124.2 *s*, 142.5 *s*, 22.6 *t*, 49.3 *d*, 18.7 *t*, 39.7 *t*, 34.9 *s*, 79.9 *s*, 23.3 *q*, 24.7 *q*, 24.3 *q*, 64.6 *t*; C-1′–5′: 95.3 *d*, 71.4 *d*, 72.0 *d*, 69.1 *d*, 62.0 *t*; OAc: 171.2, 170.2, 169.7, 169.1 *s*, 21.0 *q*, 21.7 *q* (3 ×); $[\alpha]_D^{24°}$ −11 ($CHCl_3$; *c* 3.3).

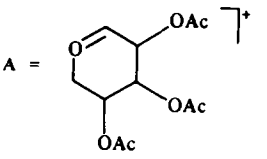
5,6-Dehydro-α-eudesmol-[α-xylopyranoside-triacetate] (**6Ac**). IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1760, 1230 (OAc); MS *m/z* (rel. int.): 478.257 $[M]^+$ (0.4) (calc. for $C_{26}H_{38}O_8$: 478.257), 259 (70), 203 (96), 199 (76), 161 (58), 157 (100), 139 (94), 97 (98); ^{13}C NMR ($CDCl_3$, C-1–15): 38.0 *t*, 20.2 *t*, 124.3 *d*, 131.5 *s*, 142.9 *s*, 120.4 *d*, 47.2 *d*, 20.6 *t*, 37.1 *t*, 32.2 *s*, 81.0 *s*, 22.8 *q*, 23.2 *q*, 24.4 *q*, 22.0 *q*; C-1′–5′: 95.3 *d*, 71.5 *d*, 72.2 *d*, 69.2 *d*, 62.0 *t*; OAc: 170.2, 169.8, 168.2 *s*, 20.7 *q* (2 ×), 20.6 q: $[\alpha]_D^{24°}$ −58 ($CHCl_3$; *c* 0.73).

Carisson-[α-xylopyranoside-triacetate] (**7Ac**). IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1765, 1235 (OAc), 1675, 1615 (C=CC=O); Ms *m/z* (rel. int.): 494.252 $[M]^+$ (0.1) (calc. for $C_{26}H_{38}O_4$: 494.252), 259 (45), 219 (81), 218 $[C_{15}H_{22}O]^+$ (100), 203 $[218-Me]^+$ (12), 199 (39), 175 $[218-C_3H_7]^+$ (20), 157 (86), 139 (78), 97 (86).

4,5-Dioxo-seco-γ-eudesmol-[α-xylopyranoside-triacetate] (**8Ac**). IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1760, 1250, 1225 (OAc), 1720, 1710 (C=O); MS *m/z* (rel. int.): 512.362 $[M]^+$ (0.1) (calc. for $C_{26}H_{40}O_{10}$: 512.362), 428 $[M-C_5H_8O$, McLafferty$]^+$ (8), 259 (80), 237 $[C_{15}H_{25}O_2]^+$ (44), 199 (51), 157 (100), 152 $[237-C_5H_9O]^+$ (28), 139 (86), 97 (82); ^{13}C NMR ($CDCl_3/C_6D_6$, C-1–15): 37.2 *t*, 21.3 *t*, 44.0 *t*, 215.0 *s*, 208.2 *s*, 39.2 *t*, 48.9 *d*, 18.1 *t*, 35.9 *t*, 47.0 *s*, 78.7 *s*, 23.1 *q*, 22.9 *q*, 24.4 *q*, 29.5 *q*; C-1′–5′: 95.3 *d*, 71.4 *d*, 71.9 *d*, 69.0 *d*, 61.7 *t*; OAc: 169.9, 169.4, 168.9 *s*, 20.5, 20.4, 20.3 *q*.

5β,11-Dihydroxy-iphionan-4-one-11-O-[α-xylopyranoside-triacetate] (**9Ac**). IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3470 (OH), 1760, 1230 (OAc), 1700 (C=O); MS *m/z* (rel. int.): 428.205 $[M-C_5H_8O]^+$ (1) (calc. for $C_{21}H_{32}O_9$: 428.205), 259 (18), 219 (17), 199 (10), 139 (100), 97 (30), 85 (48); ^{13}C NMR ($CDCl_3$, C-1–15): 37.6 *t*, 32.4 *t*, 54.6 *d*, 213.7 *s*, 82.7 *s*, 24.2 *t*, 45.7 *d*, 22.6 *t*, 36.4 *t*, 45.0 *s*, 79.9 *s*, 24.4 *q*, 22.7 *q*, 18.3 *q*, 31.5 *q*; C-1′–5′: 95.2 *d*, 71.4 *d*, 71.9 *d*, 69.1 *d*, 61.9 *t*; OAc: 170.2, 169.8, 169.3 *s*, 20.7 *s* (3 ×); $[\alpha]_D^{24°}$ −25 ($CHCl_3$; *c* 0.57).

3α-Acetoxy-11-hydroxy-iso-iphionan-4-one-[α-xylopyranoside-triacetate] (**10Ac**). IR $\nu_{max}^{CCl_4}$ cm^{-1}: 1760, 1250, 1230 (OAc), 1700 (C=O); MS *m/z* (rel. int.): 511.254 $[M-MeCO]^+$ (0.6) (calc. for $C_{26}H_{39}O_{10}$: 511.254), 279 $[C_{17}H_{27}O_3]^+$ (16), 259 (77), 219 $[279-HOAC]^+$ (96), 199 (45), 176 $[219-MeCO]^+$ (36), 157 (100), 139 (66), 97 (94); ^{13}C NMR ($CDCl_3$, C-1–15): 37.5 *t*, 31.1 *t*, 80.5 *d*, 213.2 *s*, 63.4 *s*, 21.4 *t*, 44.5 *d*, 26.1 *t*, 37.0 *t*, 43.7 *s*, 79.6 *s*, 24.7 *q*, 22.2 *q*, 23.2 *q*, 30.0 *q*; C-1′–5′: 95.5 *d*, 71.6 *d*, 72.1 *d*, 69.2 *d*, 62.1 *t*; OAc: 170.2 (2 ×), 169.8, 169.0 *s*, 20.7 *q* (4 ×) $[\alpha]_D^{24°}$ −24 ($CHCl_3$; *c* 0.63).



Scheme 1.

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