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Aldol Condensation: A Stereoselective Approach to Tetrahydrophenanthrene Derivatives and 3-Oxa-bicyclo[3.3.1]nonan-6-ones

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SYNTHETIC COMMUNICATIONS, 21(1), 31-42 (1991)

ALDOL CONDENSATION: A STEREOSELECTIVE APPROACH TO TETRAHYDROPHENANTHRENE DERIVATIVES AND 3-OXA-BICYCLO[3.3.1]NONAN-6-ONES

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ABSTRACT: *Aldol condensation of the lithium enolate of **2** with m-methoxyphenylacetaldehyde afforded **3a** and **3b** with good erythro stereoselectivity (5:95). Acid catalyzed cyclization of **3a** gave the tetrahydrophenanthrene **5** while **3b** yielded the 3-oxobicyclononanones **6**. A mechanism is discussed to account for the derived products and a detailed ^1H NMR structural analysis of the [3.3.1] bicyclic systems is utilized to indirectly characterize the threo and erythro alcohols **3a** and **3b**.*

Substituted tetrahydrophenanthrene-2-carboxylic acid derivatives[1] have been useful in veterinary medicine for the treatment of underdeveloped females, for caponization in the poultry industry, for the fattening of cattle, and as anti-fertility agents. Recently we reported[2] that the 1,4-addition process (**1**→**2**) and subsequent trapping of the resulting enolate with formaldehyde gas occurs with a high degree of stereo-selectivity. As indicated in Scheme I this methodology might be extended to a facile two-step entry to highly functionalized tetrahydrophenanthrene-2-carboxaldehydes and related

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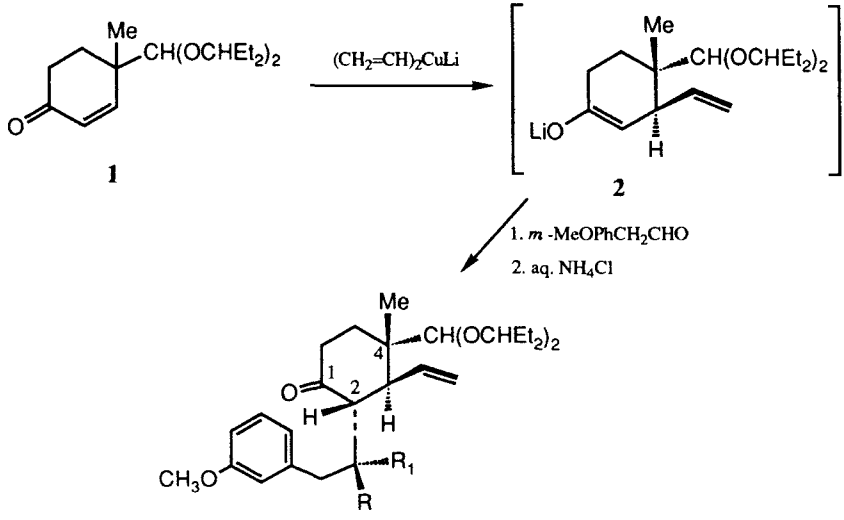
Scheme I



3a: R=H, R_1=OH, threo

3b: R=OH, R_1=H, erythro

steroid[3,4] intermediates *via* an acid catalyzed cyclization of precursor alcohols **3**.

Reaction of enone 1 with lithium divinyl cuprate (Scheme I) at -55°C and subsequent trapping of the regiospecifically generated enolate with *m*-methoxyphenylacetaldehyde[5] afforded a 5:95 mixture of diastereomeric alcohols **3a** and **3b**, respectively, as determined by ^{1}H NMR analysis. Interestingly, addition of $ZnCl_2$[6] prior to trapping with the aldehyde gave a 60:40 ratio of the respective alcohols **3a** and **3b**. Based on steric considerations it is reasonable to assume that the 1,3-aldol condensation in the above cases should occur trans to the C-4 methyl and the C-3 vinyl in enolate **2** to afford an equatorially disposed group at C-2 in **3**. That this postulation is correct was proven by the following NMR studies. Irradiation [500 MHz, ^{1}H NMR] of the C-4 methyl group in **3a**

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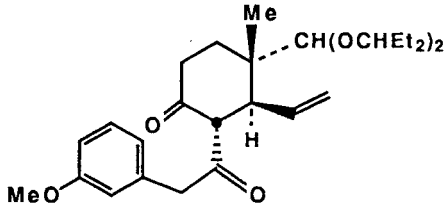
showed significant enhancements for the acetal, vinyl and C-2 methines. Likewise, irradiation of the C-4 methyl group in **3b** showed the same enhancements, indicating that the C-2 proton is axial in both alcohols. The possibility that **3a** and **3b** were



4

regioisomers, resulting from alkylation at both C-2 and C-6, was ruled out since each isomer afforded the same diketone **4** when subjected to Collins oxidation.

It might be anticipated that the stereochemical disposition of the alcohols depicted in **3** would be inconsequential during an acid catalyzed cyclization to afford the tetrahyrdophenanthrene nucleus. Contrary to this expectation it was found that two different modes of cyclization (Scheme II) are operative with alcohols **3a** and **3b**. Treatment of the faster moving threo alcohol **3a** with 10N HCl in MeOH (1:5) and subsequent hydrolysis of the resulting 50:50 mixture (**5** and the methyl acetal of **5**) with 10% HCl-THF afforded an 88% yield of carboxaldehyde **5**. When an identical acid catalyzed cyclization was carried out with the slower moving erythro alcohol **3b** a 55:45 ratio of the [3.3.1] bicyclic acetals **6a** and **6b** was obtained in 90% yield.

The determination of the erythro and threo stereochemistry in alcohols **3a** and **3b** is not straightforward. It is well documented that boron,[7] and zinc[6] enolates of cyclohexanone[8] favor enhanced threo selectivity and that the lithium enolate[9] is non-selective. The threo:erythro ratios in these cases can readily be determined from NMR coupling constants ($J_{threo} > J_{erythro}$)[6]. However in the case of the threo and erythro

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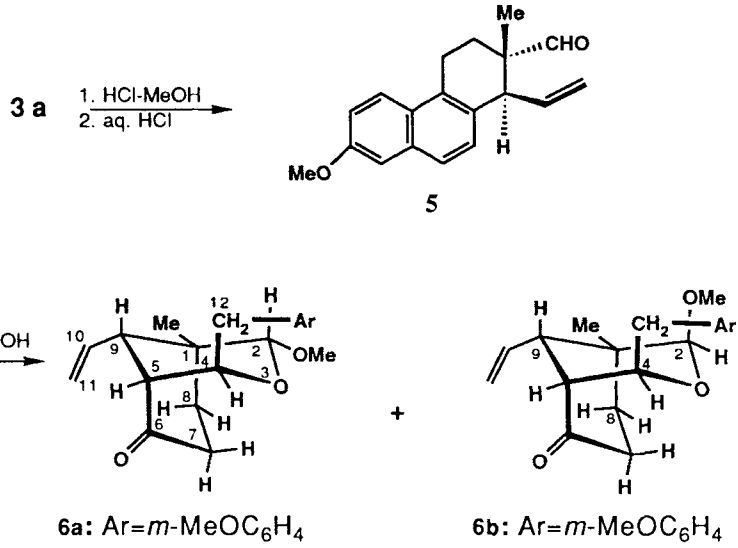
Scheme II



isomers **3a** and **3b** the presence of an additional substituent at C-3 precludes an estimation of the relative rotamer population of each alcohol. Thus application of the relevant J-values could not be confidently used to determine the diastereoselectivity. In this context, it was surmised that the best indirect way to ascertain the diastereoselectivity observed in the aldol condensations of enolate **2** was to determine the stereochemistry of the rigid[10] bicyclic acetals **6**, since each acetal must reflect the configuration of the carbinol carbon of alcohol **3b**.

Based on NOE (500 MHz ^{1}H NMR) studies it was shown that irradiation of the acetal methine proton in isomer **6a** showed an enhancement of both benzylic protons (δ3.29 and δ2.84) as well as the C-9 proton at δ2.7; thus confirming the (1,3,5) coaxial relationship between the benzylic substitutent at C-4 and protons at C-2 and C-9 in **6a**.

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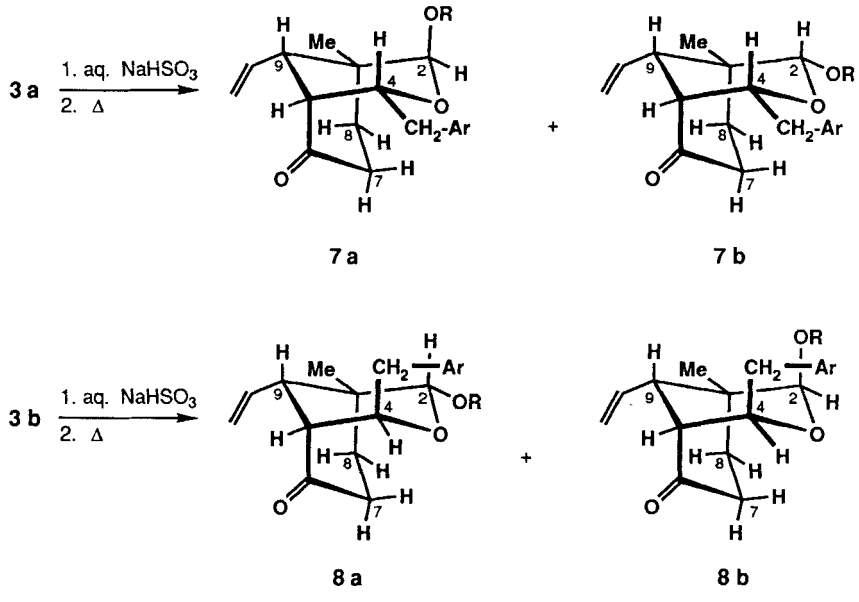
Scheme III



R = $CHEt_2$, Ar = *m*-$CH_3OC_6H_4$

Irradiation of the acetal methine in **6b** showed a NOE enhancement of the C-8 equatorial proton (endo:endo orientation of the C-8e and C-2 protons) which is indicative of an equatorial acetal methine. Due to the similar chemical shifts of the benzylic protons and the C-9 proton in **6b**, an NOE experiment could not be performed, leaving the stereochemistry at C-4 and C-9 unproven.

Fortunately it was found that after treating alcohols **3a** or **3b**, respectively, with saturated $NaHSO_3$, cyclization to all four isomeric acetals were obtained upon heating.[11] Thus reaction of **3a** (Scheme III) gave a 45:55 ratio of **7a** and **7b** (~100%) and subsequent chromatography afforded pure **7a** (41%) and pure **7b** (38%). Treatment of **3b** gave approximately a 50:50 ratio of **8a** and **8b** (~100%) which was chromatographed to afford pure **8a** (45%) and pure **8b** (30%).

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Table I. Isomeric [3.3.1] Bicyclic Acetals' Chemical Shift Assignments

Isomers	Δδ	C_4-H(δ)	C_9-H(δ)	C_{8c}-H(δ)
7 a		4.30	2.90	1.78
	0.46			
7 b		3.84	2.33	2.23
8 a		4.17	2.76	~2.2 dd
	0.19			
8 b		3.98	3.22	~1.8 dd

With all four bicyclic acetals in hand it was now possible to carry out an NMR study to determine the configuration at C-4 in acetals **7** and **8** thus providing indirectly the diastereoselectivity observed in the aldol condensation reaction. Conceptually the C-7 and C-8 protons in acetals **7** and **8** could serve as a valuable probe in verifying the proposed stereochemical assignments. Toward these ends it was observed that the axial proton at C-8 appeared as a ddd at ~δ1.6 and that the deshielded C-7 axial proton (ddd) appeared at ~δ2.8 in all four isomers. Using the chemical shift values of the indicated axial protons, the assignments of the remaining protons[12] in each isomer could readily be deduced from the corresponding COSY spectrum.

It was observed that the relative differences in δ values (Δδ) for the C-4 proton in **7a** and **7b** (Table I) is large (0.46) as compared to 0.19 in **8a** and **8b**. This difference is consistent with the deshielding of the C-4 proton in **7a** by the axial pentoxy group at C-2. Likewise the observed deshielding of the C-9 proton in **7a** coupled with the observed shielding of the C-8 equatorial proton and the noted $J_{2a\text{-}8a}$ "W" coupling (J=1Hz) in **7b** is consistent with the stereochemical assignments depicted in **7a** and **7b**.

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The ^1H NMR spectra of **8a** showed $J_{2a\text{-}8a}$ coupling (J=1 Hz) which is indicative of an equatorially disposed C-2 pentoxy group. The observed deshielding of the C-8 equatorial proton in **8a** relative to that in **8b** is also consistent with an endo:endo relationship of the C-2 pentoxy and the C-8e proton. These results and the observed deshielding of the C-9 proton in **8b** is consistent with the stereochemistry depicted in **8a** and **8b**.

It might be postulated that the marked difference observed in the acid catalyzed cyclizations of **3a** and **3b** is a direct consequence of the disposition of the benzylic group in

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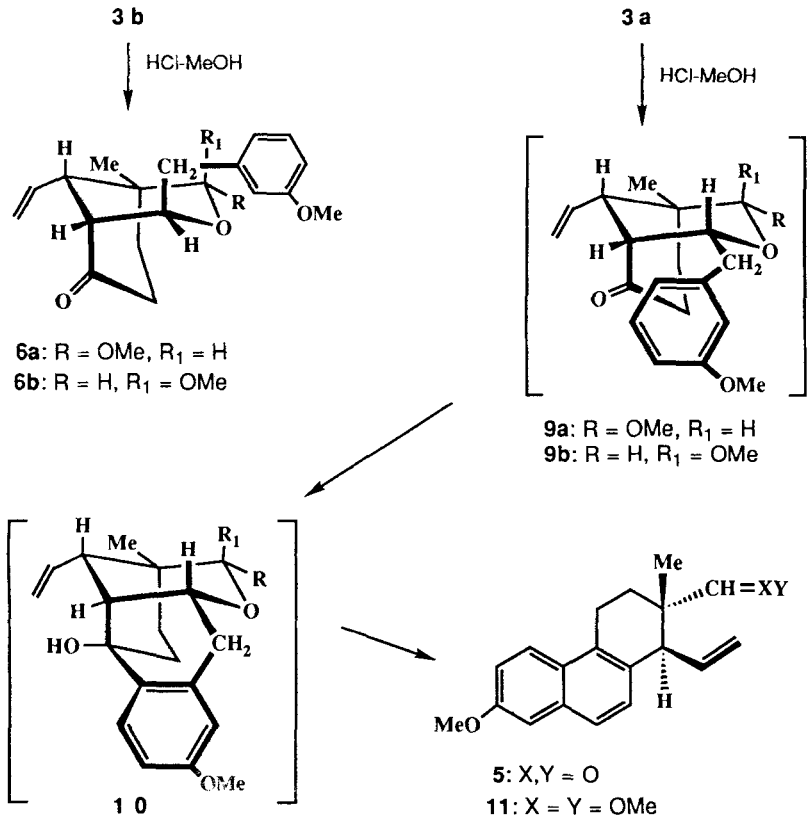
Scheme IV



acetals **6** and **9** as shown in Scheme IV. In support of this hypothesis it was demonstrated that cyclization of a 50:50 mixture of acetals **7a** and **7b** with 10N HCl-MeOH (identical to that used with **3a**) afforded cleanly a 60:40 ratio of aldehyde **5** and the corresponding acetal **11**. An identical cyclization of a 60:40 mixture of acetals **8a** and **8b** afforded approximately a 40:60 mixture of the methyl acetals **6a** and **6b** and two minor products. The latter products were presumably the hemi-acetals of **6a** and **6b** but were not characterized. Based on these findings it can be argued that the distinct selectivity observed in the acid catalyzed cyclizations of **3a** and **3b** is a function of the spacial orientation of the benzylic substituent relative to the carbonyl group in the initially formed bicyclic acetals. That is, in the case of the intermediate acetals **9** the benzylic and carbonyl groups are predisposed to give the transient intermediate **10** which after dehydration yields **5** and **11**, respectively. Since the axially disposed benzylic function can not approach the plane of the carbonyl component in acetals **6** for further cyclization, these acetals are isolated directly from the acid catalyzed cyclization of **3b**[13,14].

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11. It was further noted that washing with $NaHSO_3$ was necessary to affect cyclization. Presumably a catalytic amount of acid is required for this process.
12. It was also observed that the respective equatorial protons at C-7 and C-8 could be identified as dd's, since the absence of e,e coupling was clearly demonstrated in the COSY spectra.
13. The ^1H NMR data for the compounds in this work are: **3a** ^1H NMR ($CDCl_3$) δ 7.20 (m, 1 H , m-Ar H), 6.73 (m, 3 H, o- and p-Ar H's), 5.30-5.54 (m, 1 H, -C<u>H</u>=CH_2), 5.03-5.24 (m,

2 H, -CH=C$\underline{H}_2$), 4.39 [s, 1 H, C$\underline{H}$(OR)$_2$], 3.83-3.97 (m, 1 H, C$\underline{H}$OH), 3.78 (s, 3 H, OCH$_3$), 3.30-3.53 (m, 2 H, C$\underline{H}$Et$_2$), 3.05-3.19 (overlapping C_3-H and ArC$\underline{H}_a$H$_b$, 2 H), 3.05 (d, 1 H, O$\underline{H}$, J = 11 Hz), 2.85 (dd, 1 H, Ar-CH$_a\underline{H}_b$, J_{vic} = 7 and J_{gem} = 13 Hz), 2.08-2.50 (overlapping C_{2a}-H, C_{5a}-H, C_{6a}-H and C_{6e}-H, 4 H), 1.79-1.91 (m, 1 H, C_{5e}-H), 1.30-1.68 [m, 8 H, CH-(C$\underline{H}_2$-CH$_3$)$_2$], 1.0 (s, 3 H, CH$_3$), 0.78-0.91 [m, 12 H, CH-(CH$_2$-C$\underline{H}_3$)$_2$]; **3b** ^{1}H NMR ($CDCl_3$) δ 7.22 (m, 1 H , m-Ar H), 6.81 (m, 3 H, o- and p-Ar H's), 5.57-5.78 (m, 1 H, -C$\underline{H}$=CH$_2$), 5.10-5.32 (m, 2 H, -CH=C$\underline{H}_2$), 4.49 [s, 1 H, C$\underline{H}$(OR)$_2$], 3.80 (s, 3 H, OCH$_3$), 3.75-3.90 (m, 1 H, C$\underline{H}$OH), 3.53 (d, 1 H, O$\underline{H}$, J = 11 Hz), 3.35-3.60 (m, 2 H, C$\underline{H}$Et$_2$), 2.68-2.97 (overlapping C_2-H, C_3-H and ArC$\underline{H}_2$, 4 H), 2.13-2.55 (overlapping C_{5a}-H, C_{6a}-H and C_{6e}-H, 3 H), 1.2-1.8 [overlapping C_{5e}-H and CH-(C$\underline{H}_2$-CH$_3$)$_2$, 9 H], 1.10 (s, 3 H, CH$_3$), 0.80-1.0 [m, 12 H, CH-(CH$_2$-C$\underline{H}_3$)$_2$]; **5** ^{1}H NMR ($CDCl_3$) δ 9.55 (s, 1 H, CHO), 7.85 (d, 1 H, C_9-H, J_{9-10} = 10.4 Hz), 7.56 (d, 1 H, C_{10}-H , J_{9-10} = 10.4 Hz), 7.10-7.28 (m, 3 H), 5.76-5.96 (m, 1 H, C$\underline{H}$=CH$_2$), 5.08-5.16 (m, 2 H, CH=C$\underline{H}_2$), 3.91 (s, 3 H, OCH$_3$), 3.80 (d, 1 H, C$\underline{H}$-CH=CH$_2$, J = 10.4 Hz), 3.11-3.20 (m, 2 H), 2.12-2.29 (m, 1 H), 1.81-1.98 (m, 1 H), 1.11 (s, 3 H, CH$_3$); **6a** ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.21 (t, 1 H, m-Ar H), 6.77 (m, 3 H, o- and p-Ar H's), 5.74 (m, 1 H, C_{10}-H), 5.18 (m, 2 H, C_{11}-H's), 4.58 (d, 1 H, C_2-H, J_{2a-8a} = 0.9 Hz), 4.18 (ddd, 1 H, C_4-H, J_{4-5} = 0.9, J_{4-12} = 6.3 and $J_{4-12'}$ = 8.8 Hz), 3.78 (s, 3 H, Ar OCH$_3$), 3.40 (s, 3 H, C_2-OCH$_3$), 3.20 (dd, 1 H, ArCH$_{12}\underline{H}_{12'}$, $J_{4-12'}$ = 8.8 and $J_{12-12'}$ = 13.8 Hz), 2.92 (ddd, 1 H, C_{7a}-H, J_{7a-8e} = 9.1, J_{7a-8a} = 12.1, and J_{7a-7e} = 16.9 Hz), 2.84 (dd, 1 H, ArC$\underline{H}_{12}$H$_{12'}$, J_{4-12} = 6.3 and $J_{12-12'}$ = 13.8 Hz), 2.74 (br d, 1 H, C_9-H, J_{9-10} = 8.2 Hz), 2.40 (br s, 1 H, C_5-H), 2.30 (dd, 1 H, C_{7e}-H, J_{7e-8a} = 7.2 and J_{7a-7e} = 16.9 Hz), 2.12 (dd, 1 H, C_{8e}-H, J_{7a-8e} = 9.1 and J_{8a-8e} = 13.9 Hz), 1.51 (dddd, 1 H, C_{8a}-H, J_{2a-8a} = 1, J_{7e-8a} = 7.1, J_{7a-8a} = 12.1 and J_{8a-8e} = 13.8 Hz), 0.96 (s, 3 H, CH$_3$);

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chemical shifts were determined from the ^{1}H COSY spectrum; **6b** ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.20 (t, 1 H, m-Ar H), 6.73 (m, 3 H, o- and p-Ar H's), 5.71 (m, 1 H, C_{10}-H), 5.17 (m, 2 H, C_{11}-H's), 4.45 (s, 1 H, C_2-H), 4.05 (dd, 1 H, C_4-H, $J_{4\text{-}12}$ = 8.8 and $J_{4\text{-}12'}$ = 6.4 Hz), 3.77 (s, 3 H, Ar $OC\underline{H}_3$), 3.46 (s, 3 H, C_2-OCH_3), 3.19-3.28 (two overlapping dd's, 2 H, $ArC\underline{H}_{12}\underline{H}_{12'}$, $J_{4\text{-}12'}$ = 6, $J_{4\text{-}12}$ = 9 and $J_{12\text{-}12'}$ = 14 Hz), 3.20 (br d, 1 H, C_9-H, $J_{9\text{-}10}$ = 9 Hz), 2.87 (ddd, 1 H, C_{7a}-H, $J_{7a\text{-}8e}$ = 8.9, $J_{7a\text{-}8a}$ = 12.5 and $J_{7a\text{-}7e}$ = 16.3 Hz), 2.39 (br s, 1 H, C_5-H), 2.33 (dd, 1 H, C_{7e}-H, $J_{7e\text{-}8a}$ = 6.9 and $J_{7a\text{-}7e}$ = 16.3 Hz), 1.82 (ddd, 1 H, C_{8a}-H, $J_{7e\text{-}8a}$ = 6.9 Hz, $J_{7a\text{-}8a}$ = 12.5 and $J_{8a\text{-}8e}$ = 14.0 Hz), 1.72 (br dd, 1 H, C_{8e}-H, $J_{7a\text{-}8e}$ = 9 and $J_{8a\text{-}8e}$ = 14 Hz), 0.95 (s, 3 H, CH_3); chemical shifts were determined from the ^{1}H COSY spectrum; **7a** ^{1}H NMR ($CDCl_3$) δ 7.20 (t, 1 H, m-Ar H), 6.80 (m, 3 H, o- and p-Ar H's), 5.70 (m, 1 H, C_{10}-H), 5.13 (m, 2 H, C_{11}-H's), 4.65 (s, 1 H, C_2-H), 4.30 (dt, 1 H, C_4-H, $J_{4\text{-}5}$ = 2 Hz and $J_{4\text{-}12}$ = 7), 3.80 (s, 3 H, OCH_3), 3.38 [p, 1 H, $C\underline{H}(Et)_2$, J = 5.8 Hz], 2.90 (br d, 1 H, C_9-H, $J_{9\text{-}10}$ = 7.7 Hz), ~2.82 (apparent ddd, 1 H, C_{7a}-H, $J_{7a\text{-}8e}$ = 9, $J_{7a\text{-}8a}$ = 12 and $J_{7a\text{-}7e}$ = 17 Hz), 2.60 (d, 2 H, $ArC\underline{H}_{12}\underline{H}_{12'}$, $J_{4\text{-}12}$ = 7.2 Hz), 2.43 (br s, 1 H, C_5-H), ~2.42 (br dd, 1 H, C_{7e}-H, $J_{7e\text{-}8a}$ = 7 Hz, $J_{7a\text{-}7e}$ = 16 Hz), 1.71-1.91 (overlapping C_{8e}-H and C_{8a}-H, 2 H), 1.32-1.55 [m, 4 H, ($C\underline{H}_2$-$CH_3)_2$], 0.90 (s, 3 H, C_1-CH_3), 0.84 (t, 3 H, CH_2-$C\underline{H}_3$, J = 7 Hz), 0.79 (t, 3 H, CH_2-$C\underline{H}_3$, J = 7 Hz) ; chemical shift were determined from the ^{1}H COSY spectrum; **7b** ^{1}H NMR ($CDCl_3$) δ 7.22 (t, 1 H, m-Ar H), 6.81 (m, 3 H, o- and p-Ar H), 5.72 (m, 1 H, C_{10}-H), 5.14 (m, 2 H, C_{11}-H's), 4.37 (d, 1 H, C_2-H, $J_{2a\text{-}8a}$ = 1.0 Hz), 3.85 (dt, 1 H, C_4-H, $J_{4\text{-}5}$ = 1.8 and $J_{4\text{-}12}$ = 6.8 Hz), 3.80 (s, 3 H, OCH_3), 3.47 [p, 1 H, $C\underline{H}(Et)_2$, J = 5.9 Hz], 2.90 (ddd, 1 H, C_{7a}-H, $J_{7a\text{-}8e}$ = 8.8 and $J_{7a\text{-}8a}$ = 12 Hz, $J_{7a\text{-}7e}$ = 17 Hz), 2.64 (d, 2 H, $ArC\underline{H}_{12}\underline{H}_{12'}$, $J_{4\text{-}12}$ = 6.8 Hz), 2.43 (br s, 1 H, C_5-H), 2.25-2.39 (overlapping C_{7e}-H and C_9-H, 2 H), 2.23 (dd, 1 H, C_{8e}-H, $J_{7a\text{-}8e}$ = 8.8 and $J_{8a\text{-}8e}$ = 14

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Hz), 1.41-1.60 [overlapping C_{8a}-H and $(C\underline{H}_2\text{-}CH_3)_2$, 5 H], 0.90 (s, 3 H, C_1-CH_3), 0.88 [overlapping t's, 6 H, $(CH_2\text{-}C\underline{H}_3)_2$] ; chemical shifts were determined from the ^{1}H COSY spectrum; **8a** ^{1}H NMR ($CDCl_3$) δ 7.22 (t, 1 H, m-Ar H), 6.78 (m, 3 H o- and p-Ar H's), 5.76 (m, 1 H, C_{10}-H), 5.20 (m, 2 H, C_{11}-H's), 4.73 (d, 1 H, C_2-H, $J_{2a\text{-}8a}$ = 1.0 Hz), 4.17 (ddd, 1 H, C_4-H, $J_{4\text{-}5}$ = 1.1, $J_{4\text{-}12}$ = 6.6 and $J_{4\text{-}12'}$ = 8.7 Hz), 3.79 (s, 3 H, OCH_3), 3.32 [p, 1 H, $C\underline{H}(Et)_2$, J = 5.8 Hz], ~3.17 (dd, 1 H, $ArCH_{12}\underline{H}_{12'}$, $J_{4\text{-}12'}$ = 8.7 and $J_{12\text{-}12'}$ =14.2 Hz), 2.97(ddd, 1 H, C_{7a}-H, $J_{7a\text{-}8e}$ = 9.0, $J_{7a\text{-}8a}$ = 12 and $J_{7a\text{-}7e}$ = 16 Hz), ~2.85 (dd, 1 H, $ArC\underline{H}_{12}H_{12'}$ $J_{4\text{-}12}$ = 6.6 and $J_{12\text{-}12'}$ =14.2 Hz), 2.76 (br d, 1 H, C_9-H, $J_{9\text{-}10}$= 8 Hz), 2.38 (br s, 1 H, C_5-H), 2.30 (dd, 1 H, C_{7e}-H, dd, $J_{7e\text{-}8a}$= 6.2 and $J_{7a\text{-}7e}$ = 16 Hz), 2.20 (dd, 1 H, C_{8e}-H, $J_{7a\text{-}8e}$ = 9 and $J_{8a\text{-}8e}$ =12 Hz], 1.35-1.54 [overlapping C_{8a}-H and $(C\underline{H}_2\text{-}CH_3)_2$, 5 H], 0.96 (s, 3 H, C_1-CH_3), 0.89 (t, 3 H, CH_2-$C\underline{H}_3$, J = 7 Hz), 0.78 (t, 3 H, CH_2-$C\underline{H}_3$, J = 7 Hz) ; chemical shifts were determined from the ^{1}H COSY spectrum; **8b** ^{1}H NMR ($CDCl_3$) δ 7.20 (t, 1 H, m-Ar H), 6.70 (m, 3 H o- and p-Ar H's), 5.73 (m, 1 H, C_{10}-H), 5.19 (m, 2 H, C_{11}-H's), 4.73 (s, 1 H, C_2-H), 3.98 (dd, 1 H, C_4-H, $J_{4\text{-}12}$ = 5.0 and $J_{4\text{-}12'}$ = 10 Hz), 3.77 (s, 3 H, OCH_3), 3.75 [m, 1 H, $C\underline{H}(Et)_2$], ~3.3 (dd, 1 H, $ArCH_{12}\underline{H}_{12'}$, $J_{4\text{-}12'}$ = 10.3 and $J_{12\text{-}12'}$ = 14 Hz), ~3.2 (dd, 1 H, $ArC\underline{H}_{12}H_{12'}$, $J_{4\text{-}12}$ = 5, and $J_{12\text{-}12'}$ = 14 Hz), 3.22 (d, 1 H, C_9-H, $J_{9\text{-}10}$ = 8 Hz), 2.84 (ddd, 1 H, C_{7a}-H, $J_{7a\text{-}8e}$ = 9.4 , $J_{7a\text{-}8a}$ = 11.9 and $J_{7a\text{-}7e}$ = 16.3 Hz), 2.37 (br s, 1 H, C_5-H), 2.26 (dd, 1 H, C_{7e}-H, $J_{7e\text{-}8a}$ = 6 and, $J_{7a\text{-}7e}$ = 16 Hz), 1.50-1.93 (overlapping C_{8a}-H, C_{8e}-H and $(C\underline{H}_2\text{-}CH_3)_2$, 6 H], 0.95 (s, 3 H, C_1-CH_3), 0.89 [t, 6 H, $(CH_2\text{-}C\underline{H}_3)_2$], J = 7 Hz] ; chemical shifts were determined from the ^{1}H COSY spectrum.

14. Satisfactory analytical and high-resolution mass spectral data were consistent with the proposed structures.

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