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SYNTHETIC STUDIES IN THE ALKALOID FIELD—VII†

STEREOCHEMISTRY OF 1,2,3,4,6,7,12,12b-OCTAHYDROINDOLO [2,3-*a*]QUINOLIZINE DERIVATIVES PREPARED BY ALKALINE DECARBOALKOXYLATIVE CYCLIZATION OR ACID-INDUCED CYCLIZATION OF APPROPRIATE TETRAHYDROPYRIDINES

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Abstract—The C(12b)–C(1)–C(2) stereochemical relationship in several racemic 1,2,3,4,6,7,12,12b-octahydroindolo [2,3-*a*]quinolizine derivatives has been determined by ^{13}C NMR spectral analysis. The proper shift assignment was confirmed by recording the spectra of selectively deuterated derivatives. The C(12b)–C(1)–C(2) stereochemical relationship in indolo[2,3-*a*]quinolizines obtained either by alkaline decarboalkoxylative cyclization or by acid-induced cyclization of partially hydrogenated 1-[2-(3-indolyl)ethyl]-3-methoxycarbonylpyridine derivatives is discussed. The ambiguity existing in the preparation of *dl*-18,19-dihydroantirhine **2** by analogous decarboalkoxylative cyclization is considered.

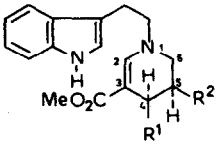
The uniform formation of C(12b)H–C(2)H *trans* compounds in the alkaline decarboalkoxylative cyclization of appropriate 1-[2-(3-indolyl)ethyl]-3-methoxycarbonyl-1,4,5,6-tetrahydropyridines **1** has been claimed,[1,2] but the recent ambiguity in the preparation of *dl*-18,19-dihydroantirhine **2** by an analogous method[2,3] has clearly revealed the need of further investigation. Moreover, the stereochemistry of compounds of the 1,2,3,4,6,7,12,12b - octahydro - 1 - methoxycarbonylindolo[2,3 - *a*]quinolizine type **3a, b**, prepared by acid-induced cyclization of appropriate 1 - [2 - (3 - indolyl)ethyl] - 3 - methoxycarbonyl - 1,4,5,6 - tetrahydropyridines **1**, lacks rigorous proof. We have now examined both reactions in more detail, using 1,4,5,6-tetrahydropyridines **1a** and **1b** as model compounds, and in the present report we describe the results obtained.

In connection with our studies concerning the preparation of indole alkaloid models of the vallesiachotamine **4** type by selective alkaline decarboalkoxylative cyclization of partially hydrogenated 1-[2-(3-indolyl) ethyl]-3,5-dimethoxycarbonyl-4-methylpyridine **1c**, we found that the 1,4,5,6,-tetrahydropyridine derivative **1c** yields only one of the four possible diastereoisomers for which the stereostructure **5c** (C(12b)H–C(2)H *trans* configuration) was assigned.[4,5] However, as the stereostructure **5c** appears to be a consequence of the C(4)H–C(5)H *cis* relationship in the intermediate 1,4,5,6-tetrahydropyridine **1c**, it cannot be used by way of analogy to resolve the ambiguity existing in the preparation of *dl*-18,19-dihydroantirhine **2**.

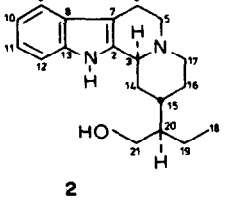
RESULTS

Palladium-catalyzed partial hydrogenation of the recently described[6,7] 1-[2-(3-indolyl)ethyl]-3-methoxycarbonyl pyridinium bromides **6a** and **6b** afforded 1,4,5,6-tetrahydropyridines **1a**[6] and **1b**, respectively, in good

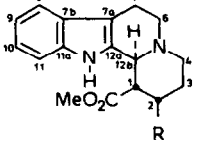
†VI: M. Lounasmaa and M. Puhakka, *Acta Chem. Scand.* **B32**, 77 (1978).



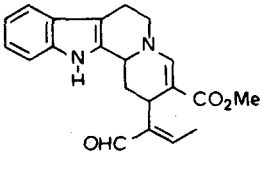
1a $R^1 = H$; $R^2 = H$
1b $R^1 = Me$; $R^2 = H$
1c $R^1 = Me$; $R^2 = MeO_2C$



2



3a R = H
3b R = Me



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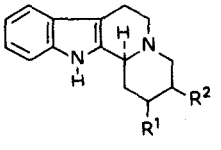
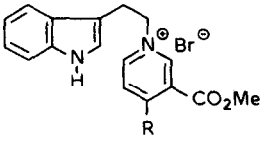


5a $R^1 = H$; $R^2 = H$
5b $R^1 = \beta$-Me ; $R^2 = H$
5c $R^1 = \alpha$-Me ; $R^2 = \alpha$-CO_2Me



6a R = H
6b R = Me

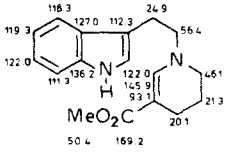
yield. Heating the 1,4,5,6-tetrahydropyridines **1a** and **1b** with aqueous alkali (alkaline decarboalkoxylative cyclization),[4] led to the indolo[2,3-*a*]quinolizines **5a** and **5b**, respectively. Noteworthily, in the case of tetrahydropyridine **1b** only one of the two possible diastereoisomers was found. When the tetrahydropyridines **1a** and **1b** were subjected in anhydrous methanol to acid-induced cyclization the indolo[2,3-*a*]quinolizines **3a**[6] and **3b** respectively, were obtained.

Several selectively deuterated analogues of compounds **1a**, **1b**, **3a**, **3b**, **5a** and **5b** were also needed. Palladium-catalyzed partial hydrogenation of the recently described[5] 4 - deuterio - 1 - [2 - (3 - indolyl)ethyl] - 3 - methoxycarbonyl - 1,4 - dihydropyridine (**10**-4-d_1 in Ref. 5) yielded 4 - deuterio - 1,4,5,6 - tetrahydropyridine **1a**-4-d_1, which was transformed by acid-induced cyclization to 2 - deuterio - 1,2,3,4,6,7,12,12b - octahydro - 1 - methoxycarbonylindolo[2,3-*a*]quinolizine **3a**-2-d_1. Palladium-catalyzed partial deuteration of **6a** and **6b** afforded 4,5,6 - trideuterio - 1 - [2 - (3 - indolyl)ethyl] - 3 - methoxycarbonyl - 1,4,5,6 - tetrahydropyridines **1a** - 4,5,6-d_3 and **1b** - 4,5,6 - d_3, respectively. Although some scrambling had taken place these compounds were useful for proper shift assignment in the ^{13}C NMR spectral analysis (*vide infra*) since scattering did not extend beyond the tetrahydropyridine ring (and the methyl group in the **1b** counterpart) (see Experimental). Alkaline decarboalkoxylative cyclization of **1a**-4-d_1 and **1b**-4,5,6-d_3 yielded the indolo[2,3-*a*]quinolizines **5a**-2-d_1 and **5b**-2,3,4-d_3, respectively, whereas the acid-induced cyclization of **1a**-4-d_1, **1a**-4,5,6-d_3, and **1b**-4,5,6-d_3 afforded the indolo[2,3 - *a*] - quinolizines **3a**-2-d_1, **3a**-2,3,4-d_3, and **3b**-2,3,4-d_3, respectively.

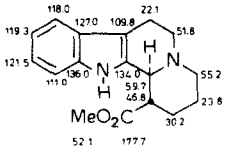
Compounds **3a,b** and **5a,b** can exist in three conformations,† which are in equilibrium by N(5) inversion and *cis*-decalin type ring inversion.[4,6] This means that one *trans*- and two *cis*-quinolizine C/D ring junctures have to be taken into consideration. The presence of the so-called Bohlmann bands[8–10] in the IR spectra of compounds **3a,b** and **5a,b** indicates that the *trans*-quinolizine C/D ring juncture dominates the conformational equilibrium between the three conformations. The preponderance of the *trans*-quinolizine C/D ring juncture is also supported by ^1H NMR spectroscopy. The absence of any signal downfield from δ 3.80 that could be assigned to the C(12b)H is generally considered to be characteristic of *trans*-quinolizine C/D ring juncture.[10–12] The C(12b)H signal of compound **3b** appears at δ 4.02 (*cf.* Experimental). Although this value is 0.22 ppm downfield from δ 3.80, it is considered, nevertheless, to support the predominance of the *trans*-quinolizine C/D ring juncture to the conformational equilibrium (*vide infra*). The magnitude of the coupling constant (10 Hz) for the interaction between the adjacent C(12b) and C(1) protons in the spectra of compounds **3a** and **3b** supports the *trans* diaxial relationship between these protons. As a consequence, the C(1) methoxycarbonyl group of compounds **3a** and **3b** is equatorial in the predominant conformation.

The C(12b)–C(1)–C(2) stereochemical relationships proposed for **3a,b** and **5a,b** were determined or confirmed by ^{13}C NMR spectral analysis. The fully proton-decoupled spectra of **3a**, **3b**, **5a**, and **5b** together with those of the hydropyridine derivatives **1a** and **1b**, taken in $CDCl_3$, showed the chemical shifts depicted on the formulas. The proper shift assignment was confirmed by recording single-frequency, off-resonance decoupled (sford) spectra and the spectra of selectively deuterated derivatives (Table 1), and by comparison with the earlier shift assignment.[5,7,13–15] The assignment of the chemical shifts of **5a** is based on previous investigations.[5,13,14] The correctness of the signal assignment for C(2) and C(3) was confirmed by the spectrum of **5a**-2-d_1.

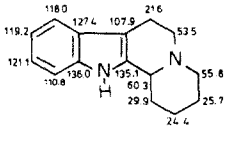
†Ring C is assumed to be in the half chair conformation and only the chair forms of ring D are considered.



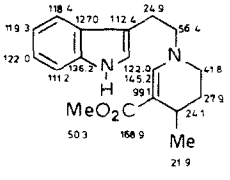
1a



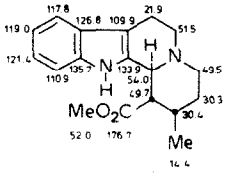
3a



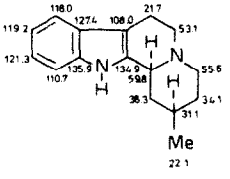
5a



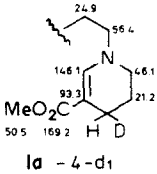
1b



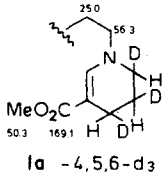
3b



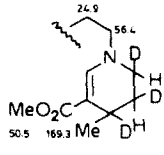
5b



1a - 4 - d_1



1a - 4,5,6 - d_3



1b - 4,5,6 - d_3

Table 1. ^{13}C Chemical shifts of deuterated indolo-[2,3-*a*]quinolizines[a]

	3a-2-d_1	3a-2,3,4-d_3	3b-2,3,4-d_3	5a-2-d_1	5b-2,3,4-d_3
C(1)	46.6	46.6	49.6	29.8	38.2
C(2)					
C(3)	23.6			25.5	
C(4)	55.1			55.7	
C(6)	51.6	51.6	51.4	53.5	53.1
C(7)	22.0	22.0	22.0	21.5	21.7
C(7a)	109.7	109.7	109.9	107.8	108.0
C(7b)	126.8	126.8	126.8	127.4	127.4
C(8)	118.0	118.0	117.9	118.0	118.0
C(9)	119.2	119.2	119.0	119.3	119.3
C(10)	121.5	121.5	121.4	121.2	121.2
C(11)	111.0	111.0	110.9	110.7	110.7
C(11a)	135.9	135.9	135.7	135.9	135.9
C(12a)	133.9	133.9	134.0	134.9	134.9
C(12b)	59.5	59.5	54.0	60.2	59.8
–Me			14.4		22.1
–OMe	52.1	52.2	52.0		
C=O	177.6	177.7	176.8		

[a]All the spectra were recorded in $CDCl_3$ solution. The δ values are in parts per million downfield from Me_4Si.

Table 2. Comparison of the observed and calculated ^{13}C chemical shifts for C(2), C(1), C(3), C(12b) and C(4) in compounds **3a**, **3b**, **5a** and **5b**.

	3a	Calc. for an eq. CH_3-group	Calc. for an ax. CH_3-group	3b	5a	Calc. for an ax. CH_3-group	Calc. for an eq. CH_3-group	5b
C(2)	30.2	35.8	31.3	30.4	24.4	25.5	30.0	31.1
C(1)	46.8	55.7	52.0	49.7	29.9	35.1	38.8	38.3
C(3)	23.8	32.7	29.0	30.3	25.7	30.9	34.6	34.1
C(12b)	59.7	59.7	54.3	54.0	60.3	54.9	60.3	59.8
C(4)	55.2	55.2	49.8	49.5	55.8	50.4	55.8	55.6

A comparison of the chemical shifts of C(1), C(2), C(12b) and C(3), as well as those of C(4) and C(7), in **5a** and **3a** gives clear evidence of the stereostructure of **3a** depicted in the formula. Since the chemical shift of C(7) reflects the contribution of different conformations to the conformational equilibrium (*vide supra*),[5] the value 22.1 ppm, found for C(7) in **3a**†, is in good agreement with the preponderance of the *trans*-quinolizine C/D ring juncture. As a consequence, it clearly supports the equatoriality of the C(1) methoxycarbonyl group in the preponderant conformation (*vide supra*).

With the chemical shifts found for **5a** and **3a** as a basis, the equatorial and axial Me group α-, β- and γ-parameters‡ were used to predict the chemical shifts of C(2), C(1), C(3), C(12b) and C(4) in **5b** and **3b**, respectively. A comparison of the observed and calculated chemical shifts (Table 2) fully confirms the stereochemical relationships proposed for **5b** and **3b**. As in the case of **3a**, the values 21.7 and 21.9 ppm found for C(7) in **5b** and **3b**, respectively, confirm the preponderance of the *trans*-quinolizine C/D ring juncture and supports the equatoriality of the C(1) methoxycarbonyl group of compound **3b** in the preponderant conformation (*vide supra*).

†The chemical shift found for C(7) in the C(1)-epimer of **3a** is 19.4 ppm.[16]

‡For an equatorial Me group, 5.6, 8.9 and 0.0 ppm, respectively. For an axial Me group, 1.1, 5.2 and −5.4 ppm, respectively.[17]

CONCLUSIONS

The alkaline decarboalkoxylative cyclization of 1 - [2 - (3 - indolyl) ethyl] - 3 - methoxycarbonyl - 4 - methyl - 1,4,5,6-tetrahydropyridine **1b** affords indolo[2,3 - *a*]quinolizine **5b**, which possesses the C(12b)H–C(2)H *cis* configuration. This clearly supports the recent claims[3] that the preparation of *dl*-18,19-dihydroantirhine **2** by analogous method yields the 15-*epi* compound as main product. The acid-induced cyclization of 1 - [2 - (3 - indolyl)ethyl] - 3 - methoxycarbonyl - 1,4,5,6 - tetrahydropyridines **1a** and **1b** yields indolo[2,3-*a*]quinolizines **3a** and **3b**, respectively, which possess the C(12b)H–C(1)H *trans* configuration, and, in the case of **3b**, also the C(12b)H–C(2)H *trans* configuration.

EXPERIMENTAL

The IR spectra were measured on a Perkin–Elmer 237 apparatus and the UV spectra on a Perkin–Elmer 137 UV apparatus. The ^1H NMR spectra were taken with a Jeol JNM-PMX-60 instrument and the ^{13}C NMR spectra with a Jeol JNM-FX-100 instrument operating at 25.20 MHz in the Fourier transform mode. TMS was used as internal standard. The mass spectra were recorded either on a Jeol JMS-D-100 Mass Spectrometer or on a Hitachi Perkin–Elmer RMU 6E Mass Spectrometer at 70 eV using direct sample insertion into the ion source, whose temp. was 100–120°. The elemental compositions when given for the molecular ions were confirmed by high-resolution mass measurements. The m.ps were determined in a Büchi capillary m.p. apparatus and are uncorrected.

4 - *Deuterio* - 1 - [2 - (3 - *indolyl*)*ethyl*] - 3 - *methoxycarbonyl* - 1,4,5,6-*tetrahydropyridine* **1a** - 4 - d_1. A mixture of 750 mg of 4 -

deuterio - 1 - [2 - (3 - indolyl)ethyl] - 3 - methoxycarbonyl - 1,4 - dihydropyridine (**10** - 4 - d_1 in Ref. 5), 300 mg of palladium-charcoal (10%) and 0.5 ml of triethylamine in 150 ml of abs. methanol was hydrogenated for 45 min at atmospheric pressure. After the normal work-up, the residue was purified by column chromatography (Al_2O_3; act. II–III) to yield 627 mg (83%) of **1a-4-d_1**. M.p. 105–106° (MeOH). MS M^+ at *m/e* 285. Other noteworthy peaks at *m/e* 155, 144, 130.

4,5,6 - *Trideuterio* - 1 - [2 - (3 - *indolyl)ethyl*] - 3 - *methoxycarbonyl* - 1,4,5,6 - *tetrahydropyridine* **1a** - 4,5,6 - d_3. Catalytic deuteration of a mixture of 1.25 g of **6a**, 375 mg of palladium-charcoal (10%), and 0.6 ml of triethylamine in 180 ml of abs. MeOH gave after 24 h reaction time 768 mg (77%) of **1a** - 4,5,6 - d_3. M.p. 104–106° (MeOH). MS M^+ at *m/e* 287. Other noteworthy peaks at *m/e* 157, 144, 130.

1 - [2 - (3 - *Indolyl)ethyl*] - 3 - *methoxycarbonyl* - 4 - *methyl* - 1,4,5,6 - *tetrahydropyridine* **1b**. A mixture of 1 g of **6b**, 300 mg of palladium–charcoal (10%) and 0.5 ml of triethylamine in 150 ml of abs. methanol was hydrogenated for 24 h at atmospheric pressure. After the normal work-up, the residue was purified by column chromatography (Al_2O_3; act. II–III) to yield 501 mg (63%) of **1b**. M.p. 137–138° (MeOH). IR (KBr): NH 3360 (s), C=O 1665 (s), C=C 1605 (s) cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.02 (3H, d, J 7 Hz, $-CH_3$), 3.64 (3 H, s, $-COOCH_3$) 6.90 (1 H, d, J 2 Hz, indolyl α -H), 7.30 (1 H, d, J 1 Hz, C–2–H), 8.42 (1 H, br s, NH). MS M^+ at *m/e* 298 corresponding to $C_{18}H_{22}N_2O_2$. Other noteworthy peaks at *m/e* 168, 144, 130.

4,5,6 - *Trideuterio* - 1 - [2 - (3 - *indolyl)ethyl*] - 3 - *methoxycarbonyl* - 4 - *methyl* - 1,4,5,6 - *tetrahydropyridine* **1b** - 4,5,6 - d_3. Catalytic deuteration of a mixture of 1.25 g of **6b**, 375 mg of palladium–charcoal (10%), and 0.6 ml of triethylamine in 180 ml of abs. MeOH gave after 24 h reaction time 824 mg (82%) of **1b** - 4,5,6 - d_3. M.p. 136–137° (MeOH). MS M^+ at *m/e* 301. Other noteworthy peaks at *m/e* 171, 144, 130†.

2 - *Deuterio* - 1,2,3,4,6,7,12,12*bα* - *octahydro* - 1*α* - *methoxycarbonylindolo*[2,3 - a]*quinolizine* **3a** - 2 - d_1. Cyclization of 237 mg of **1a** - 4 - d_1 yielded 208 mg (88%) of **3a** - 2 - d_1. M.p. 144–145° (MeOH); MS M^+ at *m/e* 285. Other noteworthy peaks at *m/e* 284, 254, 226, 197, 170, 169.

2,3,4 - *Trideuterio* - 1,2,3,4,6,7,12,12*bα* - *octahydro* - 1*α* - *methoxycarbonylindolo*[2,3 - a]*quinolizine* **3a** - 2,3,4 - d_3. Cyclization of 511 mg of **1a** - 4,5,6 - d_3 yielded 480 mg (94%) of **3a** - 2,3,4 - d_3. M.p. 144–145° (MeOH); MS M^+ at *m/e* 287. Other noteworthy peaks at *m/e* 286, 285, 199, 198, 170, 169.

1,2,3,4,6,7,12,12*bα* - *Octahydro* - 1*α* - *methoxycarbonyl* - 2*α* *methylindolo*[2,3, - a]*quinolizine* **3b**. A solution of 1,4,5,6 - tetrahydropyridine derivative **1b** (171 mg) in anhydrous MeOH was saturated with dry HCl gas during a 2 h period. The solution was left standing for 20 h at room temp. and then poured slowly into a suspension of $NaHCO_3$ in dichloromethane. The inorganic salts were filtered off and the dried filtrate evaporated under vacuum. The residue was chromatographed on alumina (act. IV). Yield 161 mg (94%). M.p. 116–118° (MeOH). IR (KBr): NH 3450 (s), Bohlmann bands 2815 (m), 2765 (m), C=O 1715 (s), C=C 1625 (m) cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.02 (3 H, d, J 7 Hz, $-CH_3$), 3.76 (3 H, s, $-COOCH_3$), 4.02 (1 H, d, J 10 Hz, C–12b–H), 8.40 (1 H, br s, NH). MS M^+ at *m/e* 298 corresponding to $C_{18}H_{22}N_2O_2$. Other noteworthy peaks at *m/e* 297, 283, 197, 184, 170, 169, 156.

2,3,4 - *Trideuterio* - 1,2,3,4,6,7,12,12*bα* - *octahydro* - 1*α* - *methoxycarbonyl* - 2*α* - *methylindolo*[2,3 - a]*quinolizine* **3b** - 2,3,4 - d_3. Cyclization of 250 mg of **1b** - 4,5,6 - d_3 yielded 190 mg (72%) of **3b**-2,3,4-d_3. M.p. 117–118° (MeOH); MS M^+ at *m/e* 301. Other noteworthy peaks at *m/e* 300, 299, 286, 285, 199, 198, 185, 170, 169.‡

1,2,3,4,6,7,12,12*b* - *Octahydroindolo*[2,3 - a]*quinolizine* **5a**. Reaction between 150 mg of **1a** and 1.5 g of potassium hydroxide in 10 ml of MeOH and 5 ml of water yielded 60 mg (50%) of **5a**. M.p. 153–155° (MeOH) (lit.[1] 153–155°). MS M^+ at *m/e* 226 corresponding to $C_{15}H_{18}N_2$. Other noteworthy peaks at *m/e* 225, 197, 170, 169 (*cf.* Ref. 11).

2 - *Deuterio* - 1,2,3,4,6,7,12,12*b* - *octahydroindolo*[2,3 - a]*quinolizine* **5a** - 2 -d_1. Reaction between 300 mg of **1a** - 4 - d_1 and 2.5 g of potassium hydroxide in 15 ml of MeOH and 10 ml of water yielded 105 mg (44%) of **5a** - 2 - d_1. M.p. 150–152° (MeOH); MS M^+ at *m/e* 227. Other noteworthy peaks at *m/e* 226, 197, 170, 169.

1,2,3,4,6,7,12,12*bα* - *Octahydro* - 2*β* - *methylindolo*[2,3-a]*quinolizine* **5b**. Reaction between 190 mg of **1b** and 2.4 g of potassium hydroxide in 15 ml of MeOH and 10 ml of water yielded 37 mg (24%) of **5b**. M.p. 165–166° (MeOH); IR (KBr): NH 3390 (m), Bohlmann bands 2815 (s), 2760 (s), C=C 1625 (m) cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.00 (3 H, d, J 7 Hz, $-CH_3$), 7.90 (1 H, br s, NH). MS M^+ at *m/e* 240 corresponding to $C_{16}H_{20}N_2$. Other noteworthy peaks at *m/e* 239, 197, 184, 170, 169, 156.

2,3,4 - *Trideuterio* - 1,2,3,4,6,7,12,12*bα* - *octahydro* - 2*β* - *methylindolo*[2,3 - a]*quinolizine* **5b** - 2,3,4 - d_3. Reaction between 350 mg of **1b** - 4,5,6 - d_3 and 2.6 g of potassium hydroxide in 22 ml of MeOH and 10 ml of water yielded 53 mg (28%) of **5b** - 2,3,4 - d_3. M.p. 163–166° (MeOH); MS M^+ at *m/e* 243. Other noteworthy peaks at *m/e* 242, 241, 199, 198, 170, 169.‡

†The peaks at *m/e* 304, 303, 302, 174, 173 and 172 indicated that the introduction of 4, 5 and 6 deuterium atoms had taken place to some extent. These results combined with the results of the ^{13}C NMR measurements indicated that the introduction of the 1–3 supplementary deuterium atoms had taken place mainly into the methyl group.

‡Also in this case the MS indicated that the introduction of 1–3 "supplementary" deuterium atoms had taken place to some extent (*vide supra*).

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