Published in Chimia 47, 230-232, 1993
which should be used for any reference to this work

A Novel Synthesis of *rac*-5-(Hydroxymethyl)-1-(Tetrahydro-2'-oxofur-3'-yl)-1*H*-pyrrole-2-carboxaldehyde

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Abstract. A novel six-step synthesis of *rac*-5-(hydroxymethyl)-1-(tetrahydro-2'-oxo-fur-3'-yl)-1*H*-pyrrole-2-carboxaldehyde (*rac*-**1**) starting from 2-methylfuran has been developed. The key step is the formation of *rac*-2-methyl-1-(tetrahydro-2'-oxofur-3'-yl)-1*H*-pyrrole (*rac*-**7**) according to the *Clauson-Kaas* procedure. Subsequent *Vilsmeier* formylation, oxidation with lead tetraacetate, and enzymatic hydrolysis led to *rac*-**1**.

Introduction

Compared to the tetrapyrroles the number of identified monopyrrolic natural products has been astonishingly small. Their structures vary widely, but most are stabilized by the presence of aromatic rings or acyl groups. The monopyrrolic natural products fulfil a large variety of functions: pheromones and trail-marking secretions isolated from animals [1], micro-organisms produced pyrrolic antibiotics [2] and finally alkaloids and plant hormones containing a pyrrole ring detected in plants [3].

Recently, *Lynn et al.* [1] reported the isolation and structure determination of 5-(hydroxymethyl)-1-[(*R*)-tetrahydro-2'-oxofur-3'-yl)-1*H*-pyrrole-2-carboxaldehyde ((*R*)-**1**). Its structure as well as its function is unusual. The authors showed that (*R*)-**1**, which was isolated from 10-d old seedlings of *Pisum sativum* (garden peas) is an antagonist of trigonelline, a plant hormone which promotes G_2 cellular arrest [5][6]. The trigonelline-induced G_2 arrest can be inhibited by administering concentrations greater than $5 \cdot 10^{-7}$ M of (*R*)-**1** [4]. In the first successful synthesis a symmetrically substituted α,α'-diisobutylidene pyrrole **2** was used as the key intermediate (*Scheme 1*). The isobutylidene side chains were oxidized with O_3 to the corresponding diformylpyrrole, which was reduced to the unsymmetrically substituted α-formyl-α'-hydroxymethylpyrrole **1**. Using the enantiomerically pure α-aminobutyrolactones both (+)- and (–)-**1** were obtained and *Lynn et al.* could show that the synthetical (+)-**1** was identical with the natural product. The selective monoreduction was not straightforward. In a previous attempt *Lynn et al.* had tried to synthesise **1** starting from the α,α'-dimethylpyrrole **3** (*Scheme 1*). The oxidation of the two Me groups to one CHO and one CH_2OH group unfortunately was not achieved.

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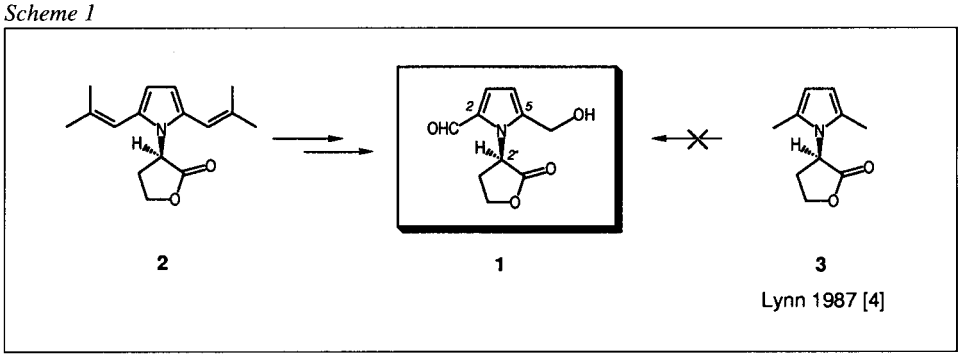
Results

We envisaged a synthesis of the target molecule (*R*)-**1** from an unsymmetrically substituted pyrrole. Using the *Paal-Knorr* condensation [7][8] we hoped to obtain either directly the natural product or a precursor of it. Condensation of α-aminobutyrolactone with an adequately substituted 1,4-diketone or a synthetic equivalent thereof would directly lead to the pyrrole **1**. The equivalent of the 1,4-diketone was thought to be obtainable from the appropriately α,α'-substituted furan *via* bromination followed by reduction according to *Clauson-Kaas* [9[10]. Unfortunately, our attempts to oxidize the corresponding furan rings with bromine in methanol were unsuccessful and untractable mixtures were obtained.

The synthetic plan was, therefore, modified (*Scheme 2*). A monosubstituted furan was used as starting material, with the second substituent to be introduced at a later stage in the synthesis. From 2-methylfuran the desired equivalent of the 1,4-ketoaldehyde was obtained in two steps. The yield of the bromination was improved when Br_2 was introduced into the well stirred MeOH solution containing 2-methylfuran *via* a *Teflon* tube dipped into the reaction mixture. Large quantities of side products were otherwise obtained, which made the isolation and purification of the product difficult. Reduction of the diastereoisomeric mixture **4** of two pairs of enantiomers under H_2 with *Raney*-Ni as catalyst [11] proceeded in good yield. Distillation of the raw material afforded a diastereoisomeric mixture **5** of two pairs of enantiomers and the acetal **6** of the ketoaldehyde in yields of 45 and 37%, respectively. Treatment of this mixture with α-aminobutyrolactone in AcOH and NaOAc as base [10] gave the alkyl pyrrole *rac*-**7** in 96% yield, which was used without purification in the next step. Due to its instability the purification was only carried out on analytical samples.

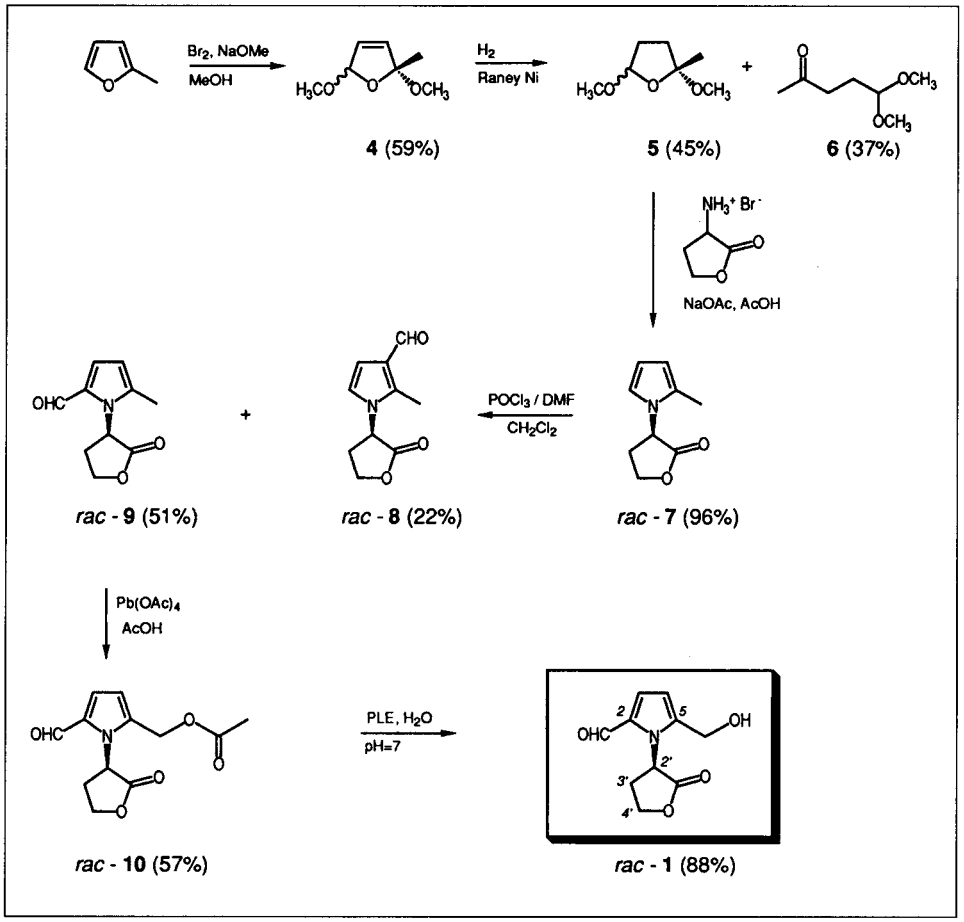
The *Vilsmeier-Haack* formylation [12] of *rac*-**7** gave two regioisomers which were separated by flash chromatography. The ^{1}H-NMR shifts allowed a tentative assignment. Additional NOE measurements confirmed that in the major isomer *rac*-**9** the CHO group had been introduced at the α-position (*Fig.*). For the side product the NOE between the Me and the newly introduced CHO group proved that the 3-formyl-2-methylpyrrole *rac*-**8** had been obtained. The major product *rac*-**9** was treated with an excess of lead tetraacetate in refluxing AcOH [13] to give the

Scheme 1



acetoxy compound *rac*-**10**. The reaction did not go to completion and when forcing the reaction further was attempted, the formed product was destroyed. Careful optimization afforded a mixture consisting essentially of starting material and product, which could be separated with medium-pressure liquid chromatography. The pure crystalline product *rac*-**10** was obtained in 57% yield. The acetoxy compound was then hydrolyzed in 88% yield using pig liver esterase (PLE) [14][15]. Relatively large amounts of the enzyme had to be used to accelerate the hydrolysis, otherwise the product, which was not stable under the conditions of the reaction was transformed further and the yield dropped dramatically. The spectroscopic data of the synthetic pyrrole *rac*-**1** were identical in all respects except optical rotation with that of the natural product (+)-**1**.

Scheme 2



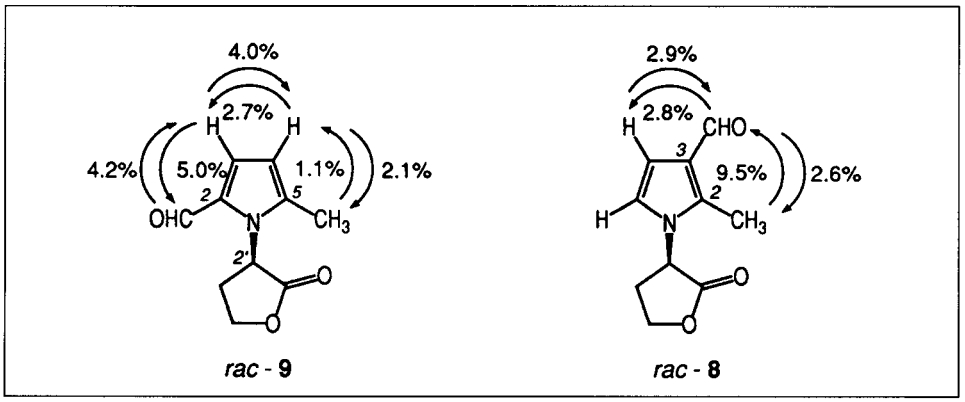


Figure. *NOE Experiments*

Discussion

The six-step synthesis affords the pyrrole *rac*-**1** in 11% overall yield from cheap and easily available starting materials. The key intermediate of the synthesis is the monosubstituted pyrrole *rac*-**7** from which *rac*-**1** could be obtained in three straightforward steps. In contrast to the literature report the α-formyl-α'-methylpyrrole *rac*-**9** could be acetoxylated at the methyl group. To separate the starting material from the product of the reaction medium-pressure liquid chromatography was necessary. This separation, unfortunately, could not be avoided. Even so, this novel synthetic approach is a considerable improvement over the reported procedure. This scheme also lends itself to the synthesis of the natural product (+)-**1** either using optically active α-aminobutyrolactone or trying to separate the racemic ester **10** with the help of an appropriate enzyme.

Financial support of this work by the *Swiss National Science Foundation,* and by *Ciba-Geigy Ltd.*, Basel, is gratefully acknowledged. We thank Prof. *Lynn*, University of Chicago, USA, for making the spectra of the natural product (+)-1 available to us. We are grateful to Prof. Dr. *T. Jenny,* Mr. *Ch. Fehr*, Mr. *F. Nydegger* (Fribourg), and Dr. *S. Claude*, Dr. *E. Defrancq,* and Mr. *H. Bursian* (Neuchâtel) for NMR and MS measurements.

Experimental Part

General. M.p. were determined on a *Kofler* hot stage melting point apparatus (*Thermovar, C. Reichert AG*, Vienna) and are uncorrected. Refractive indices were determined on a *C. Zeiss* (BRD) refractometer. IR Spectra were recorded on a *Perkin Elmer 683* or *Perkin Elmer FT-IR 170X* spectrophotometer. The wave numbers in cm^{-1} were characterised by *s* (strong), *m* (medium), *w* (weak), and br. (broad). NMR Spectra were recorded on a *Bruker AM 360* (^1H: 360 MHz, ^{13}C: 90 MHz) or a *Bruker AMX 400* (^1H: 400 MHz, ^{13}C: 100 MHz) spectrometer as dilute solns. in $CDCl_3$. Routine NMR spectra were measured on a *Varian Gemini 200.* Chemical shifts (δ) are reported in ppm relative to TMS as internal reference, coupling constants *J* in Hz. MS were measured on a *Vacuum Generator Micromass 7070E* instrument or a *Nermag R30-10* (70 eV); relative peak intensities are given in % of the base peak. Microanalyses were performed in the microanalytical laboratories of *Ciba-Geigy Ltd.*, Marly/Fribourg.

Diastereoisomeric Mixture of Two Pairs of Enantiomers of 2,5-Dihydro-2,5-dimethoxy-2-methylfuran (**4**). To a vigorously stirred methanolate soln. (26 g (1.13 mol) of Na in 250 ml of MeOH) at –5° 41 g (0.5 mol) of freshly distilled 2-methylfuran were added. A soln. of 25 ml (0.486 mol) of bromine in 250 ml of CH_3OH was then added dropwise *via* a *Teflon* tube dipped into the mixture during 20 min. After stirring for another 30 min, the white suspension was filtered and the cake was washed with benzene. The combined filtrates were reduced to 150 ml and filtered again. After evaporation of the solvent the product was distilled (b.p. 57°/20 Torr) to yield 40.86 g (58%) of **4** as a yellow liquid of n_d^{20} = 1.4268. The diastereoisomers were not separated. IR (film): 3087*w*, 2995*m*, 2940*m*, 2838*m*, 1375*s*, 1332*m*, 1237*m*, 1197*s*, 1170*s*, 1145*s*, 1104*s*, 1080*s*, 1052*s*, 1020*s*. ^1H-NMR (360 MHz, $CDCl_3$): 6.00/5.98 (*dd*, *J* = 5.6, 1.0/*J* = 6.0, 1.0, H–C(3) or H–C(4) for each diast.); 5.94/5.92 (*dd*, *J* = 5.6, 1.0/*J* = 6.0, 1.0, H–C(3) or H–C(4) for each diast.); 5.76/5.74 (s, H–C(5) for each diast.); 3.49/3.41 (*s*, CH_3O–C(2) or CH_3O–C(5) for each diast.); 3.18/3.11 (*s*, CH_3O–C(2) or CH_3O–C(5) for each diast.); 1.56/1.50 (*s*, CH_3–C(2) for each diast.). EI-MS: 143 (8, [*M* – H]$^+$), 129 (22, [*M* –

$CH_3]^+$), 113 (100, $[M-OCH_3]^+$), 99 (23, $[M-H-CO_2]^+$), 88 (6), 85 (18), 81 (27, $[M-OCH_3-HOCH_3]^+$), 75 (8), 71 (13), 59 (14), 53 (14), 43 (46).

Diastereoisomeric Mixture of Two Pairs of Enantiomers of 2,5-Dimethoxy-2-methyltetrahydrofuran (**5**). A soln. of 38 g (0.26 mol) of **4** in 100 ml of MeOH was hydrogenated at 100 atm and r.t. in the presence of *Raney*-Ni (prepared from 2 g of *Raney*-Ni alloy (*Fluka, purum*)) [16] for 1 h. The catalyst was removed by filtration through *Celite* and the filtrate fractionally distilled to yield 17.21 g (44.7%) of **5** (b.p. 45–50°/15 Torr) of n_d^{20} = 1.4155 and 14.2 g (36.9%) of the acetal **6** of the 1,4-ketoaldehyde (b.p. 80–84°/15 Torr). **5**: IR (film): 2995*m*, 2982*m*, 2920*m*, 2840*m*, 1380*m*, 1355*m*, 1230*m*, 1104*s*, 1071*m*, 1037*m*. ^{1}H-NMR (360 MHz, $CDCl_3$): 5.03/5.02 (*d*, *J* = 5.4/*J* = 5.0, H–C(5) for each diast.); 3.41/3.33 (*s*, CH_3O–C(2) or CH_3O–C(5) for each diast.); 3.28/3.22 (*s*, CH_3O–C(2) or CH_3O–C(5) for each diast.); 2.20–1.66 (*m*, CH_2(3) and CH_2(4) for each diast.); 1.49/1.41(s, CH_3–C(2) for each diast.). EI-MS: 129 (7, $[M-OH]^+$), 115 (100, $[M-OCH_3]^+$), 99 (10, $[M-HOCH_3-CH_3]^+$), 88 (29), 83 (21, $[M-OCH_3-HOCH_3]^+$), 75 (56), 57 (22), 43 (84). *Acetal* **6**: IR (film): 2951*s*, 2918*m*, 1722*s*, 1440*m*, 1365*m*, 1196*m*, 1165*m*, 1130*s*, 1070br. *s*. ^{1}H-NMR (80 MHz, $CDCl_3$): 4.36 (*t*, *J* = 5.0, H–C(1)); 3.30 (*s*, 2 CH_3O–C(1)); 2.82 (*dt*, *J* = 7.0, 5.0, CH_2(2)); 2.50 (*t*, *J* = 7.0, CH_2(3)); 2.14 (*s*, CH_3(5)).

rac-*2-Methyl-1-(tetrahydro-2'-oxofur-3'-yl)-1H-pyrrole* (*rac*-**7**). A soln. of 4.34 g (23.8 mmol) of α-aminobutyrolactone hydrobromine (*Fluka, purum*), 3.2 g (22 mmol) of the mixture of **5** and **6** and 2 g of NaOAc (24 mmol) in 10 ml of AcOH was stirred at r.t. for 15 h. The light brown reaction mixture was then diluted with 50 ml of H_2O and made alkaline by cautiously adding 8 g of Na_2CO_3 and 8 g of $NaHCO_3$ while stirring. The aq. soln. was extracted with CH_2Cl_2. Drying and evaporation of the solvent afforded 3.49 g (96%) of *rac*-**7**. The purity determined by ^{1}H-NMR was more than 90% and the product was used without further purification. An anal. sample (1 g) of *rac*-**7** was further purified by distillation in a Kugelrohr (b.p. 150°/0.09 Torr) to give white needles (350 mg) of m.p. 55–57°. IR (KBr): 3110*w*, 3000*w*, 2980*w*, 2950*w*, 2870*w*, 1778*s*, 1494*m*, 1430*m*, 1379*m*, 1306*s*, 1223*m*, 1170*s*, 1151*s*, 1020*s*, 1007*m*. ^{1}H-NMR (360 MHz, $CDCl_3$): 6.55 (br. *s*, H–C(5)); 6.13 (*dd*, *J* = 3.2, 3.2, H–C(4)); 5.93 (*ddq*, *J* = 3.2, 0.8, 0.8, H–C(3)); 4.88 (*dd*, *J* = 11.1, 8.9, H–C(2')); 4.53 (*ddd*, *J* = 9.3, 9.0, 1.9, H–C(4')); 4.35 (*ddd*, *J* = 10.3, 9.3, 6.5, H–C(4')); 2.74 (*dddd*, *J* = 12.7, 8.9, 6.5, 1.9, H–C(3')); 2.52 (*dddd*, *J* = 12.7, 11.1, 10.3, 9.0, H–C(3')); 2.26 (*s*, CH_3–C(2)). ^{13}C-NMR (90 MHz, $CDCl_3$): 173.4 (*s*, C(1')); 128.9 (*s*, C(2)); 117.3 (*d*, C(5)); 108.5 (*d*, C(4)); 107.6 (*d*, C(3)); 65.2 (*t*, C(4')); 54.0 (*d*, C(2')); 30.2 (*t*, C(3')); 11.9 (*q*, C(2^1)). EI-MS: 165 (100, M^+), 120 (20, $[M-H-CO_2]^+$), 108 (23), 107 (25), 106 (28, $[M-CO_2-CH_3]^+$), 80 (93, [*M* – (tetrahydro-2-oxofur-3-yl)]$^+$), 66 (9), 53 (15), 39 (26).

rac-*5-Methyl-1-(tetrahydro-2'-oxofur-3'-yl)-1H-pyrrole-2-carboxaldehyde* (*rac*-**9**). To a soln. of *Vilsmeier*'s reagent (prepared by dropwise addition of 10.2 g (67 mmol) of $POCl_3$ to 4.9 g (67 mmol) of DMF at 10–20° and subsequent stirring for 15 min at r.t.) [11] diluted with 19 ml of CH_2Cl_2 and chilled to 5° 10 g (61 mmol) of *rac*-**7** in 19 ml of CH_2Cl_2 were added dropwise at 5° during 1 h. The mixture was refluxed for 15 min, cooled to r.t., carefully hydrolyzed with an aq. NaOAc soln. (75 ml, 0.7M), refluxed for another 15 min and cooled to r.t. The separated org. phase was washed with Na_2CO_3, dried over $MgSO_4$ and evaporated. A 1:2 mixture of *rac*-**8** and *rac*-**9** was obtained. A flash chromatography on silica gel (*Merck* 60) (AcOEt) afforded 2.59 g (22%) of *rac*-**8** and 7.53 g (64%) of *rac*-**9**, which could be recrystallized in AcOEt to give 5.96 g (51%) of crystals of m.p. 113.5–114.5°. rac-*2-Methyl-1-(tetrahydro-2'-oxofur-3'-yl)-1H-pyrrole-3-carboxaldehyde* (*rac*-**8**): IR (KBr): 3120*w*, 3000-2910*w*, 2930*w*, 2850*w*, 2760*w*, 1780*s*, 1662*s*, 1443*m*, 1378*m*, 1181*s*, 1027*m*. ^{1}H-NMR (360 MHz, $CDCl_3$): 9.82 (*s*, CHO); 6.59 (*s*, H–C(4) and H–C(5)); 5.09 (*dd*, *J* = 11.5, 9.0, H–C(2')); 4.57–4.52 (*m*, H–C(4')); 4.39 (*m*, H–C(4')); 2.85–2.78 (*m*, H–C(3')); 2.60–2.49 (*m*, H–C(3')); 2.52 (*s*, CH_3–C(2)). ^{13}C-NMR (90 MHz, $CDCl_3$): 185.2 (*d*, CHO)); 172.4 (*s*, C(1')); 138.2 (*s*, C(2)); 122.7 (*s*, C(3)); 119.0 (*d*, C(5)); 109.5 (*d*, C(4)); 65.3 (*t*, C(4')); 53.9 (*d*, C(2')); 29.8 (*t*, C(3')); 10.0 (*q*, C(2^1)). *rac*-**9**: IR (KBr): 3010*w*, 2930*w*, 2870*w*, 2830*w*, 2750*w*, 1795*s*, 1787*s*, 1660*s*, 1499*s*, 1436*s*, 1381*m*, 1352*m*, 1326*m*, 1299*m*, 1182*s*, 1065*m*, 1045*m*, 1038*m*. ^{1}H-NMR (360 MHz, $CDCl_3$): 9.31 (*s*, CHO); 6.97 (*d*, *J* = 3.5, H–C(3)); 6.10 (*d*, *J* = 3.5, H–C(4)); 5.13–4.95 (br. *m*, H–C(2')); 4.70–4.60 (*m*, H–C(4')); 4.38 (*ddd*, *J* = 9.0, 9.0, 9.0, H–C(4')); 2.70–2.53 (*m*, CH_2(3')); 2.31 (*s*, CH_3–C(5)). ^{13}C-NMR (90 MHz, $CDCl_3$): 177.8 (*d*, CHO); 172.6 (*s*, C(1')); 141.1 (*s*, C(2)); 130.7 (*s*, C(5)); 126.4 (*d*, C(4)); 110.6 (*d*, C(3)); 65.4 (*t*, C(4')); 53.8 (*d*, C(2')); 28.2 (*t*, C(3')), 12.4 (*q*, C(5^1)). EI-MS: 193 (100, M^+), 176 (10, $[M-OH]^+$), 165 (23, $[M-CO]^+$), 134 (17, $[M-CH_3-CO_2]^+$), 120 (28, $[M-CHO-CO_2]^+$), 108 (77, [*M* – (tetrahydro-2-oxofur-3-yl)]$^+$), 93 (10, [*M* – (tetrahydro-2-oxofur-3-yl)–CH_3]$^+$), 80 (25, [*M* – (tetrahydro-2-oxofur-3-yl) – CO]$^+$), 73 (6), 65 (12), 53 (25), 39 (31).

rac-*5-(Acetoxymethyl)-1-(tetrahydro-2'-oxofur-3'-yl)-1H-pyrrole-2-carboxaldehyde* (*rac*-**10**). To a refluxing soln. of 2.6 g (13.5 mmol) of *rac*-**9** in 25 ml of AcOH 7 g (17 mmol) of $Pb(OAc)_4$ were added in small portions (0.75 g every 5 min) and further 2 g more at the end. The mixture was refluxed for another 10 min and quenched with 50 ml of cold H_2O. Extraction with CH_2Cl_2, drying and evaporating afforded 3.53 g of the crude mixture which still contained some unreacted *rac*-**9**. It was purified by MPLC (silica gel, CH_2Cl_2/AcOEt 95:5) to give 1.93 g of *rac*-**10** (57%), which could be crystallized from $CHCl_3$/hexane. IR (KBr): 3110*w*, 3010*w*, 2970*w*, 2930*w*, 2850*w*, 1788*s*, 1741*s*, 1662*s*, 1495*m*, 1455*m*, 1384*m*, 1362*m*, 1346*m*, 1244*s*, 1230*s*, 1200*m*, 1176*s*, 1050*m*, 1024*s*. ^{1}H-NMR (360 MHz, $CDCl_3$): 9.39 (*s*, CHO); 6.97 (*d*, *J* = 4.0, H–C(3)); 6.34 (*d*, *J* = 4.0, H–C(4)); 5.20–5.05 (br. *m*, 1H, H–C(2')); 5.09 (br. *s*, CH_2–C(5^1)); 4.64–4.59 (*m*, H–C(4')); 4.35 (*ddd*, *J* = 9.0, 9.0, 9.0, H–C(4')); 2.63–2.55 (*m*, CH_2(3')); 2.00 (*s*, CH_3(5^4)). ^{13}C-NMR (90 MHz, $CDCl_3$): 179.2 (*d*, CHO); 172.1 (*s*, C(1')); 169.9 (*s*, CO(5^3)); 137.7 (*s*, C(5)); 131.9 (*s*, C(2)); 125.3 (*d*, C(3)); 112.8 (*d*, C(4)); 65.3 (*t*, C(4')); 56.7 (*t*, C(5^1)); 54.5 (*d*, C(2')); 28.5 (*t*, C(3')); 20.5 (*q*, C(5^4)). EI-MS: 251 (26, M^+), 209 (100, $[M-C_2H_2O]^+$), 192 (21, $[M-C_2H_2O-OH]^+$), 180 (21, $[M-C_2H_2O-CHO]^+$), 152 (50), 134 (16), 124 (22, $[M-C_2H_2O-$ (tetrahydro-2-oxofur-3-yl)]$^+$), 106 (13, $[M-C_2H_2O-$ (tetrahydro-2-oxofur-3-yl) – $H_2O]^+$), 86 (15), 65 (5.5), 55 (9) 43 (43, [acetyl]$^+$). Anal. calc. for $C_{12}H_{13}NO_5$: C 57.37, H 5.22, N 5.58; found: C 56.82, H 5.32, N 5.44.

rac-*5-(Hydroxymethyl)-1-(tetrahydro-2'-oxofur-3'-yl)-1H-pyrrole-2-carboxaldehyde* (*rac*-**1**). A suspension of 300 mg (1.2 mmol) of *rac*-**10** and 1 ml of PLE suspension (*Aldrich*, 10 mg enzyme) in 20 ml of 0.1M phosphate buffer thermostated at 30° was allowed to react in a pH-stat at pH 7.0. 1.2 ml of 1M NaOH were consumed within 1 h. The mixture was thoroughly extracted with CH_2Cl_2 (10 x 50 ml). The org. layers were dried and evaporated to yield 220 mg of *rac*-**1** (88%). The product was crystallized from $CHCl_3$ as white cubic crystals of m.p. 120.5–121.5° for analysis. IR (KBr): 3471*s*, 3120*w*, 3000*w*, 2970*w*, 2915*w*, 2860*w*, 2840*w*, 2810*w*, 2740*w*, 1768*s*, 1665*s*, 1478*m*, 1453*s*, 1427*m*, 1390*m*, 1368*m*, 1350*m*, 1317*m*, 1293*m*, 1256*m*, 1220*m*, 1194*s*, 1182*s*, 1049*m*, 1025*s*, 1018*s*. ^{1}H-NMR (360 MHz, $CDCl_3$): 9.44 (*s*, CHO); 6.99 (*d*, *J* = 4.0, H–C(3)); 6.26 (*d*, *J* = 4.0, H–C(4)); 5.50–5.30 (br *m*, H–C(2')); 4.75–4.63 (*m*, CH_2(5^1) and H–C(4')); 4.40 (*ddd*, *J* = 9.0, 9.0, 9.0, H–C(4')); 2.77–2.65 (*m*, H–C(3')); 1.99 (br. *dd*, *J* = 5.8, 5.7, OH). ^{13}C-NMR (90 MHz, $CDCl_3$): 179.1 (*d*, CHO); 172.9 (*s*, C(1')); 144.5 (*s*, C(5)); 132.7 (*s*, C(2)); 125.8 (*d*, C(3)); 110.4 (*d*, C(4)); 65.7 (*t*, C(4')); 56.3 (*t*, C(5^1)); 55.0 (*d*, C(2')); 29.0 (*t*, C(3')). EI-MS: 209 (100, M^+), 191 (8, $[M-H_2O]^+$), 180 (50, $[M-CHO]^+$), 163 (18, $[M-CHO-OH]^+$), 152 (68), 146 (12), 134 (24), 124 (55, [*M* – (tetrahydro-2-oxofur-3-yl)]$^+$), 118 (16), 106 (30, [*M* – (tetrahydro-2-oxofur-3-yl) – $H_2O]^+$), 86 (26), 79 (20), 68 (15), 55 (19), 39 (53). Anal. calc. for $C_{10}H_{11}NO_4$: C 57.41, H 5.30, N 6.70; found: C 57.16, H 5.48, N 6.63.

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