

CONFORMATION OF (5S)-4,6-DIDEOXYHEXONIC ACID LACTONES*

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The ¹H-NMR and CD spectra of the lactones of 4,6-dideoxy-L-ribo-hexonic acid (*I*), 4,6-dideoxy-L-xylo-hexonic acid (*II*), 4,6-dideoxy-L-arabino-hexonic acid (*III*) and 4,6-dideoxy-L-lyxo-hexonic acid (*IV*), and of their O-methyl and O-benzoyl derivatives have been measured. According to these measurements, the half-chair conformation ³H₄ prevails in lactones *I* and *II* whereas the boat ^{2,5}B in lactones *III* and *IV*. This state is not changed by the substitution of hydroxy groups on C₍₂₎ and C₍₃₎ atoms by methoxy or benzyloxy groups and it does not undergo any remarkable change in dependence on solvent polarity.

In previous papers²⁻⁵ we have described the synthesis of four diastereoisomeric lactones of 4,6-dideoxyhexonic acids of L-ribo (*I*), L-xylo (*II*), L-arabino (*III*) and L-lyxo (*IV*) configuration. In order to explain some differences in their behaviour (e.g. the different stability of their lactone ring in water solutions⁶), we needed to know the steric arrangement of these compounds.

With respect to the known fact⁷⁻⁹ that the four ring atoms forming the lactone group, i.e., C₍₂₎—CO—O—C₍₅₎, are located in one plane, two boat and two half-chair conformations can be expected for the steric arrangement of the six-membered lactone ring. For the preliminary assignments of the preferred conformations some "rules" dealing with the internal ring-strain¹⁰, with the position and size of substituents and with the way of attachment to another ring¹¹ were deduced on the basis of studies of various natural six-membered lactones. According to them, the role of the substitution in α- and δ-positions seems to be decisive in monocyclic lactones. In the case of the substitution of hydrogen atoms only, the boat conformation is preferred; this conformation changes into the half-chair one when the larger substituents in the critical positions evoke 1,4-interaction¹¹. It seems, however, that these "rules" do not hold fully; various lactones in half-chair conformation were described¹²⁻¹⁵

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in which no restriction for their preferred existence in boat conformation (in sense of the "rules" mentioned above) was observed. In addition to it, some cases have been described in the literature^{16,17} in which the location of the four ring atoms of lactone group in one plane is not supposed. The deviation of the C₍₅₎ atom from the plane formed by C₍₂₎, C₍₁₎ and ring oxygen has been proved by X-ray analyses of the δ -lactone of D-gluconic acid¹⁸ and of the γ -lactone of D-glucuronic acid¹⁹. The different results and opinions mentioned above evoke an increasing interest in this field.

The presented solution of conformation of the four diastereoisomeric lactones of 4,6-dideoxyhexonic acids *I–IV*, as well as of their O-methyl (*V–X*) and O-benzoyl (*XI–XVIII*) derivatives* could bring some new information on these problems. The methods of ¹H-NMR spectroscopy and circular dichroism spectroscopy have been independently used for this purpose.

EXPERIMENTAL

The preparation of the measured lactones *I–IV* is described in refs^{2–5} and of their O-methyl and O-benzoyl derivatives in ref.¹ The ¹H-NMR spectra were measured at 100 MHz on a Varian XL-100-15 instrument; the assignment of the signals was carried out on the basis of decoupling experiments. The indicated values of the chemical shifts (δ -scale, tetramethylsilane as internal reference) and of the coupling constants are from first-order analysis. The CD spectra were recorded in cells of 2.00 to 0.02 cm path length at room temperature with the dichrographs model 185 (Roussel-Jouan) and Mark III (Jobin-Yvon).

RESULTS AND DISCUSSION

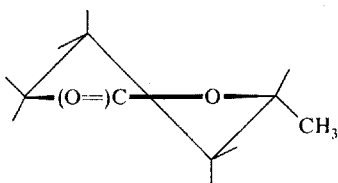
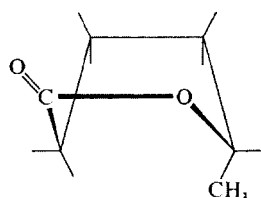
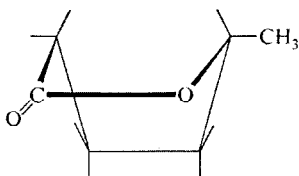
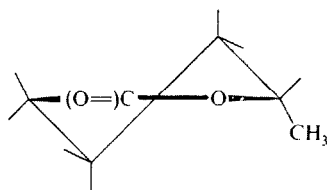
Nuclear Magnetic Resonance Spectra

The following assumptions were made for determining of the prevailing conformation of lactones *I–IV* from their ¹H-NMR spectra: 1) The accuracy of first-order analysis in connection with decoupling technique was considered satisfactory for the determination of values of the spin-spin coupling constants. With regard to the fact that in most cases the ratio $\Delta\nu/J$ is higher than 5–6, this assumption is obviously justified. 2) We neglected the influence of polarity of the lactone grouping on the magnitude of the absolute value of the vicinal coupling constants in dependence on the torsion angle. This assumption can also be accepted because the differences in J_{vic} values for diversely situated protons were considerable and because the interactions of protons in various positions of the ring were always taken into account. 3) Nearly planar arrangement of the segment C₍₂₎—CO—O—C₍₅₎ in the lactone molecules is assumed on the basis of X-ray studies^{7–9} of the δ -lactone rings.

* With respect to the way of their preparation¹, compounds *V–VII* are in D-series, the other compounds measured are in L-series.

On the other hand, some different results obtained by other authors^{18,19} could make the correctness of the last assumption questionable. However, the possible deviation of the $C_{(5)}$ atom from the plane of the remaining three ring atoms of the lactone group could cause some distortion of the conformation, but does not cause the change of the adopted type of conformation. With respect to this, when the third assumption is accepted, we can only expect that the determination of the prevailing type of conformation (*i.e.*, near to boat or near to half-chair) will represent the maximum information which is obtainable from the analysis of the $^1\text{H-NMR}$ spectra.

The assignment of conformation using $^1\text{H-NMR}$ spectra is usually based on values of the vicinal coupling constants of ring protons. However, the observed coupling constants, as well as the values of chemical shift, could represent either a time averaged spectrum of the different conformers in a rapid equilibrium, or the spectrum of a single stable conformation²⁰. As a test of conformational homogeneity, the spectra of lactone *III* were examined between -90°C to $+50^\circ\text{C}$ of the solution in hexadeuterioacetone. In this temperature range, the values of the vicinal coupling constants of the methine protons on $C_{(2)}$, $C_{(3)}$ and $C_{(5)}$ were found to be temperature independent. The same conclusions resulted from the analysis of the spectra of lactone *II* measured in hexadeuterioacetone – hexadeuteriodimethyl sulfoxide (1 : 1) in the temperature range from 0°C to $+45^\circ\text{C}$. To know the influence of the solvent polarity on the conformational equilibrium, the spectra of lactones *I–III* were also measured in deuterium oxide and hexadeuteriodimethyl sulfoxide. The values of the coupling constants were practically identical with those obtained from the measurements of solution in CDCl_3 .

 3H_4  $B_{2,5}$  $^{2,5}B$  4H_3

The data obtained from the measurements in deuteriochloroform solutions at 37°C are summarized in Tables I and II. The derivatives of *ribo* configuration *I*, *VIII*, *XI* and *XV* show a great coupling constant between axial proton at C₍₄₎ (whose signal is situated at higher field) and proton at C₍₅₎ ($J_{4,5} = 10.5 - 11$ Hz). The other spin-spin coupling constants have very similar values lying in the interval of 2–4 Hz. Assuming the planarity of the lactone group we are able to explain all values of the spin-spin constants only when the half-chair conformation 3H_4 of the measured lactones is preferred.* Analogous result was obtained by the analysis of the data from the spectra of compounds of *xyló* configuration *II*, *V*, *VI*, *VII*, *XII* and *XVI*, whose coupling constants have the following approximate values: $J_{2,3} \sim 9 - 10$ Hz, $J_{3,4} \sim 9 - 10$ Hz,

TABLE I

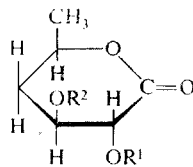
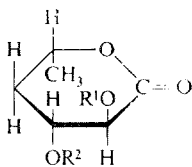
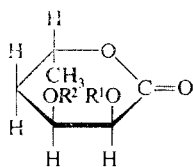
Chemical Shifts of Protons in Molecules of the Lactones *I–XVIII*

Measured at 37°C in deuteriochloroform with the exception of *XIII* which has been measured in hexadeuterioacetone; chemical shifts are presented in δ -values (p.p.m.) relative to tetramethylsilane. The signals of H-2 and H-6 are doublets, the others are multiplets. Single chemical shift values refer to midpoints of multiplets if the signals of the respective protons are clearly discernible. In the case of overlapping multiplets the overall range is given.

Compound	H-2	H-3	H-4	H-4'	H-5	H-6
<i>I</i>	4.11	4.33	1.65–2.0	2.10–2.40	4.90	1.41
<i>II</i>	3.90–4.20		1.60–2.10	2.15–2.40	4.45	1.46
<i>III</i>	4.29	3.98	1.80–2.30		4.70	1.38
<i>IV</i>	4.30–4.60		1.62–2.0	2.30–2.60	4.50	1.47
<i>V</i>	4.08	3.50–3.75	1.60–1.80	2.20–2.40	4.43	1.43
<i>VI</i>	3.60	3.80–4.16	1.55–1.90	2.17–2.40	4.44	1.41
<i>VII</i>	3.56–3.80		1.57–1.80	2.18–2.45	4.49	1.40
<i>VIII</i>	3.77	3.85–4.0	1.56–2.0	2.12–2.40	4.74	1.37
<i>IX</i>	3.85	3.50–3.70	1.80–2.30		4.61	1.38
<i>X</i>	3.85–4.05		1.66–1.99	2.15–2.46	4.45	1.39
<i>XI</i>	5.56	4.45	1.90	2.26	4.93	1.42
<i>XII</i>	5.25	4.18–4.66	1.88	2.34	4.18–4.66	1.43
<i>XIII</i>	5.59	4.42	2.00–2.26		4.96	1.40
<i>XIV</i>	5.62	4.44–4.72	1.80	2.54	4.44–4.72	1.42
<i>XV</i>	5.80–5.94		2.15	2.52	4.90	1.48
<i>XVI</i>	5.55	5.69	1.90	2.60	4.68	1.45
<i>XVII</i>	6.0	5.53–5.74	2.05–2.65		4.95	1.48
<i>XVIII</i>	5.83–6.04		1.80–2.20	2.60–2.90	4.74	1.48

* The symbols submitted²¹ to IUPAC are used here for designation of conformations.

$J_{3,4'} \sim 2.5-4$ Hz, $J_{4,5} \sim 10-11$ Hz, $J_{4',5} \sim 2.5-3.5$ Hz. All these values are explainable only when half-chair conformation is assigned to these lactones.



I; $R^1 = R^2 = H$
VIII; $R^1 = R^2 = CH_3$
XI; $R^1 = COC_6H_5$, $R^2 = H$
XV; $R^1 = R^2 = COC_6H_5$

II; $R^1 = R^2 = H$
XII; $R^1 = COC_6H_5$, $R^2 = H$
XVI; $R^1 = R^2 = COC_6H_5$

V; $R^1 = CH_3$, $R^2 = H$
VI; $R^1 = H$, $R^2 = CH_3$
VII; $R^1 = R^2 = CH_3$

TABLE II

The Vicinal Coupling Constants of the Protons in Molecules of the Lactones *I*–*XVIII*

Experimental conditions of measurements are described in the Table I. The values of coupling constants are presented in Hz. The constants $J_{5,6} \sim 6.5$ Hz and $J_{4,4'} \sim 13.5-15$ Hz could be found in spectra of all measured compounds in addition to those which are presented below.

Compound	$J_{2,3}$	$J_{3,4}$	$J_{3,4'}$	$J_{4,5}$	$J_{4',5}$
<i>I</i>	3	2	3.5	10.5	3.5
<i>II</i>	^a	9	2.5	10	3
<i>III</i>	7.5	4	7.5	4.5	9
<i>IV</i>	^a	2.5	8	10.5	4
<i>V</i>	9	^a	4	10	3
<i>VI</i>	9	10	4	11	3.5
<i>VII</i>	^a	9	4	11	3
<i>VIII</i>	3	^a	4	10.5	4
<i>IX</i>	6	^a	^a	4	8.5
<i>X</i>	^a	3	7	10.5	4.5
<i>XI</i>	3	2	4.5	11	3.5
<i>XII</i>	9	9	^a	10	^a
<i>XIII</i>	7.5	3.5	6.5	4.5	8.5
<i>XIV</i>	4	2.5	8.5	10.5	4.5
<i>XV</i>	^a	2	4	11	4
<i>XVI</i>	10	9	4.5	11	2.5
<i>XVII</i>	7.5	2.5	6	3.5	10
<i>XVIII</i>	^a	2.5	7.5	11.5	4.5

^a Not obtainable from first-order analysis.

The spectra of lactones of the *arabino* configuration *III*, *IX*, *XIII* and *XVII* gave results differing from those described above. High value of the spin-spin coupling constant $J_{4',5}$ shows that the torsion angle between $C_{(5)}-H$ and $C_{(4)}-H$ is about 0° or 180° for one of both hydrogen atoms at $C_{(4)}$. The torsion angle $H-C_{(2)}-C_{(3)}-H$, however, because of rather high value (6–7.5 Hz) of the coupling constant $J_{2,3}$, cannot be near to 70° as it should be necessary for the half-chair conformation. This seeming contradiction is completely comprehensible when we assign to the discussed molecules the boat conformation $^{2,5}B$ in which the atoms $C_{(2)}$ and $C_{(5)}$ are situated above the plane of the remaining four atoms of the ring. This conclusions agree with the mentioned results¹¹ assuming the boat conformation as the more prevailing one for all the δ -lactones having no 1,4-interaction of bulky groups at $C_{(2)}$ and $C_{(5)}$ atoms. Whereas the deduced conformations of the lactones of *arabino* and *lyxo* configuration are in agreement with this demand, the lactones of *ribo* and *xylo* configuration have the more bulky substituent at one of the critical positions of the boat conformer. On the basis of these results, the preference of the boat conformation can also be expected in compounds of *lyxo* configuration *IV*, *X*, *XIV* and *XVIII*, because decisive positions on $C_{(2)}$ and $C_{(5)}$ in $^{2,5}B$ conformation of these compounds are also occupied by hydrogen atoms only. From the analysis of the obtained data it is obvious that the signal of the proton on $C_{(4)}$ which appears at higher field being eclipsed by the OH-group on $C_{(3)}$ is split owing to the neighbouring protons with the constants $J_{4,5} \sim 10.5-11$ Hz and $J_{4,3} \sim 2.5-3$ Hz. The other geminal proton with the signal at lower field gives the coupling constants $J_{4',5} \sim 4-4.5$ Hz, $J_{4',3} \sim 7$ to 8.5 Hz. These relations are not consistent with the half-chair conformation but, on the contrary, they are in good agreement with the boat conformation.

The following conclusions result from experimental data obtained by first-order analysis of 1H -NMR spectra: 1) In the 4,6-dideoxyhexonic acid lactones of *ribo* and *xylo* configurations the half-chair or, better, near to half-chair (*c.f.* note on p. 3326) conformation prevails, whereas the boat (or near to boat) conformation is preferred in *arabino* and *lyxo* diastereoisomers.

2) This conformational equilibrium is not significantly changed by the substitution of hydroxyl groups by more bulky substituents (methoxy-, benzoyloxy-) and does not undergo any remarkable change in dependence on solvent polarity; furthermore, as it was proved with lactones *II* and *III*, this equilibrium does not observably depend on temperature in the used range.

Circular Dichroism Spectra

Saturated lactones show one or two CD-bands in the accessible range of the spectrum²² and most authors agree now with the explanation that these are due to different conformers and both have their origin in an $n \rightarrow \pi^*$ transition. In addition to the specific solvent effect (usual hypsochromic shift by augmentation of the sol-

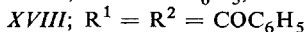
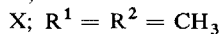
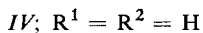
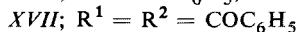
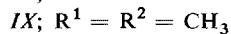
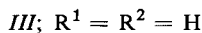
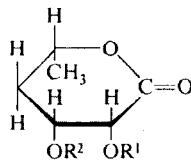
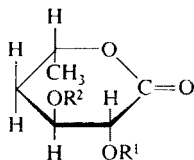
vent polarity) the band position depends also on the conformation of six-membered rings: for half-chair forms the CD maxima are at longer wavelengths than for boat forms^{11,23}.

As regards the correlation between the sign (and magnitude) of the Cotton effect and the stereochemistry of the lactone molecules different views have been expressed which can, however, be discussed from a general point of view²⁴. Okuda and co-workers²⁵ stressed the influence of the α -OH in sugar lactones, whereas Wolf¹¹ laid more emphasis on the ring chirality. A generalisation of his rule was put forward by Legrand and Bucourt²⁶ who claimed that the torsion angle around the C(=O)—C₍₂₎ bond within the lactone ring determines the sign of CD. Klyne and coworkers²² and Snatzke and coworkers^{27,28} put forward sector rules for the determination of contributions of different groups to the Cotton effect. Actually all effects will work simultaneously and we can estimate their relative importance from a general principle proposed²⁴, which states that that chiral sphere which is closest to the chromophore determines to a great extent the sign and magnitude of the Cotton effects. The first sphere is defined as the chromophore itself and becomes chiral *e.g.* in some α,β - and β,γ -unsaturated lactones²⁹; the second sphere is the lactone ring, and it is chiral in practically all five and six-membered lactones, whereas the third sphere comprises all other substituents in this series. Actually the essential factor of the second sphere is the torsion angle around the bond directly connected with the chromophore²⁴, and substituents at the C₍₂₎ atom which can act as strong perturbers (like OR, halogens, NR₂, *etc.*) have therefore also to be assumed as being part of the second sphere, when they are not (more or less) coplanar with the lactone grouping. This clearly explains the greater importance of the α -OH over the other substituents which fact has been mentioned by several authors (*e.g.* refs.³⁰⁻³⁷). Very recently, by semiempirical calculations Richardson and coworkers^{38,39} come to the same result, *viz.* that 1) the torsion angle around the C(=O)—C₍₂₎ governs the sign of the Cotton effect, and 2) that the OR group on C₍₂₎ outweighs contributions of other OR groups.

Benzoates give a CD within the "conjugation band" around 225 nm, for which a sector rule has been proposed⁴⁰⁻⁴¹. As this band comes, however, very close to the position of the lactone CD band we will refrain from a detailed discussion of this Cotton effect. On the other hand dibenzoates in a chiral arrangement give a very strong "CD-couplet"⁴² due to exciton splitting; for vicinal glycol derivatives the torsion angle between these two groups determines unequivocally the sign of this couplet^{43,44}, which appears at about 239 and 224 nm; at longer wavelengths benzoates and dibenzoates show also the ¹B_{2u}-band, for which, however, no rule exists in such cases hitherto.

Of the four different ring conformations ³H₄, B_{2,5}, ^{2,5}B and ⁴H₃ for (5*S*)-hexanolide half-chair ³H₄ and boat B_{2,5} according to their chirality^{11,26} give rise to positive Cotton effects, boat ^{2,5}B and half-chair ⁴H₃ negative ones. Conformation B_{2,5}

can be excluded because of the flagpole arrangement of the methyl group, the population of the others has been discussed for the four diastereoisomers in the first part of this paper. The *L-ribo* compound *I* and its *L-xylo* isomer *II* both adopt half-chair



conformation 3H_4 and should thus show positive Cotton effects, which is indeed the case (Table III). The small difference between the two $\Delta\epsilon_{\max}$ values may, of course, in part be caused by a direct contribution of OH on $C_{(3)}$ according to the sector rule, indirect influences by changing slightly ring conformation may, however, be even more important. The *L-arabino* isomer *III* according to the 1H -NMR studies is present in a rigid boat conformation ${}^{2,5}B$ and should, therefore, give a negative CD, furthermore the band position is expected to be at shorter wavelengths than in the spectra of *I* and *II*. The CD-spectrum is in full agreement with this prediction. Finally, for the *L-lyxo* isomer *IV* the same boat form ${}^{2,5}B$ seems to be preferred according to 1H -NMR measurements. The conformational analysis does not unequivocally distinguish between 3H_4 and ${}^{2,5}B$, but the CD is clearly in favour of ${}^{2,5}B$. The rotational strength is even larger for *IV* than for *III*, and the band position (215 nm)

TABLE III

Circular Dichroism Spectra of the Lactones *I*–*IV* at 20°C

Lactone	Wavelength, nm ($\Delta\epsilon_{\max}$)	
	methanol	water
<i>I</i>	224 (+2.10)	220 (+2.16)
<i>II</i>	224.5 (+1.81)	221 (+2.49)
<i>III</i>	218 (–2.42)	215 (–3.33)
<i>IV</i>	215 (–4.34) ^a	215 (–5.92)

^a Measured in ethanol.

is another indication of the presence of the boat form. For the difference in magnitude the same argumentation is valid as mentioned above for *I* and *II*.

The CD within the lactone $n \rightarrow \pi^*$ absorption is, therefore, in full agreement with the conclusions drawn from conformational analysis and $^1\text{H-NMR}$ measurements for these lactones. In all cases ring chirality is the dominating effect, because the OH group at the $\text{C}_{(2)}$ atom is equatorially arranged for *I* to *IV* and will thus neither contribute strongly to first nor to second chiral sphere.

The four monobenzoates *XI* through *XIV* (Table IV) all show CD-bands between 220 and 227 nm, which have the same sign as the lactone bands mentioned above. As, however, in CD spectrum the K-band of the benzoate moiety appears also in the same wavelength range, it is difficult to estimate which contribution comes from the benzoate and which from the lactone chromophore. We have, nevertheless, run the CD spectra of these compounds in order to proof that no anomalies occur which could obscure the dibenzoate exciton CD.

In the dibenzoates *XV* through *XVIII* because of the other steric requirements of the benzoate groups the conformation of the lactones must not necessarily be the same as that of free diols; the CD spectra (Table IV) of these compounds demonstrate, however, that benzylation does not significantly change the conformation of these lactones. Of the conformations discussed for *I-IV* those of the *L-ribo* and *L-arabino* isomers will lead to a positive torsion angle between the two OR groups at $\text{C}_{(2)}$ and $\text{C}_{(3)}$, and the dibenzoates *XV* and *XVII* indeed show a positive "CD-couplet". For the remaining dibenzoates *XVI* and *XVIII* this torsion angle is negative, as is the "CD-couplet" in their spectra. For *XVIII* only the long-wavelength wing of the "couplet" is clearly recognizable, the other one is mainly compensated by other,

TABLE IV
Circular Dichroism Spectra of the Lactones *XI-XVIII* in Ethanol (20°C)

Lactone	Wavelength, nm ($\Delta\epsilon_{\text{max}}$)
<i>XI</i>	278 (+0.12), 252 (-0.32), 227 (+3.73)
<i>XII</i>	275 (+0.10), 242 (-0.53), 220 (+1.74)
<i>XIII</i>	293 (-0.16), 269 (-0.23), 248 (+0.19), 225 (-5.03)
<i>XIV</i>	278 (-0.14), 247 (+0.85), 223 (-6.22)
<i>XV</i>	275 (-0.06), 237 (+27.86), 220 (-4.76)
<i>XVI</i>	237 (-25.64), 222 (+9.34)
<i>XVII</i>	238 (+24.54), 223 (-11.16)
<i>XVIII</i>	237 (-18.74), 221 (+1.16)

strongly negative bands like the lactone chromophore, nevertheless there is no doubt about the presence of such a negative "CD-couplet". The CD spectra of the 2,3-dibenzoates can thus be explained by assuming the same conformations for the ring as for the free diols.

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