^{13}C AND ^{1}H NMR SPECTRA OF ALL METHYL O-BENZOYL-β-D-XYLOPYRANOSIDES. NONADDITIVITY OF ACYLATION EFFECTS ON ^{13}C CHEMICAL SHIFTS IN DEUTERIOCHLOROFORM SOLUTIONS

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All methyl O-benzoyl-β-D-xylopyranosides have been prepared and their ^{1}H and ^{13}C NMR spectra measured in deuteriochloroform solutions. The ^{1}H NMR spectra were analysed to the first order and assigned with the aid of homonuclear decoupling. The ^{13}C chemical shifts were assigned through heteronuclear selective decoupling experiments. Some of the ^{13}C chemical shifts observed in di- and tri-O-benzoyl derivatives differ considerably from those calculated according to the direct additivity rule from the shifts in the mono derivatives. It is shown that the nonadditivity is due to a conformational heterogeneity of the series of investigated compounds dissolved in deuteriochloroform. The heterogeneity is evidenced by the vicinal ^{1}H–^{1}H coupling constants and by ^{13}C chemical shifts of $C_{(1)}$ methoxyl carbon atoms.

One of the main advantages of ^{13}C NMR spectroscopy is the possibility to predict the relatively large ^{13}C chemical shifts with considerable accuracy according to a simple direct additivity rule[1,2]. Application of this rule requires knowledge of the chemical shifts in a parent unsubstituted molecule and of the so-called substituent chemical shifts (SCS) of all the substituents present in the given compound. In NMR spectroscopy of carbohydrates it has become customary to use, instead of the chemical shifts of tetrahydropyran or tetrahydrofuran, the chemical shifts in a suitably chosen monosaccharide derivative (most frequently, unsubstituted monosaccharide or its methyl glycoside) as the parent or reference molecule. The corresponding SCS values are then specific for the given system and cannot be easily adopted for other skeletons or compared with the true SCS values of the same substituent. For this reason, values of substituent effects will be refered here as the derivatization chemical shifts (DCS). (If the additivity rule were valid exactly, the DCS values would be equal to the difference of the SCS values of the given substituent and of the substituent present in the reference compound, *e.g.* the usual acetylation shifts should be equal to the difference between the SCS values of acetoxy and hydroxy groups).

Even with this simplification, the application of the additivity rule still requires knowledge of the DCS values of all substituents. Lack of such values severly limits routine applications. The present work has aimed at providing benzoylation DCS values for methyl β-D-xylopyranosides dissolved in deuteriochloroform. This particular choice of solvent was dictated by our concurrent studies of NMR spectra of other derivatives, namely trimethylsilylated methyl β-D-xylopyranosides.

To serve this purpose all mono O-benzoyl derivatives of methyl β-D-xylopyranoside were prepared. Since a test of the validity of the additivity rule was highly desirable in the case of multiple substitution, we have prepared also all possible di-O-benzoyl derivatives and the tri-O-benzoylated compound.

RESULTS AND DISCUSSION

Syntheses. Of all methyl O-benzoyl-β-D-xylopyranosides only 3-O-benzoyl[3-5] and 2,3,4-tri-O-benzoyl[6] derivatives had been described before. Mono O-benzoyl derivatives of methyl β-D-xylopyranoside were prepared by benzoylation of the corresponding di-O-acetyl derivatives followed by deacetylation. Methyl di-O-benzoyl--β-D-xylopyranosides were obtained from the corresponding mono-O-benzyl-β-D--xylopyranosides by benzoylation and subsequent catalytic hydrogenation.

^{13}C NMR *Spectra.* The chemical shifts in all methyl O-benzoyl-β-D-xylopyranosides are summarized in Table I. Almost all the shifts were assigned to individual xylopyranoside carbon atoms by selective coherent heteronuclear decoupling $^{13}C\{^1H\}$ experiments[7] without any recourse to additivity or other empirical rule. With the exception of four pairs of lines, all the assignments were unambiguous. In each of the four cases the chemical shifts of two protons were so close that sufficient selectivity of heteronuclear decoupling could not be achieved (*e.g.* the chemical shifts of protons H-3 and H-4 differ only only by 6 Hz in methyl 2-O-benzoyl-β-D--xylopyranoside which precludes the asignment within the pair of $C_{(3)}$ and $C_{(4)}$ lines in this compound). In these four cases, that assignment was adopted which led to a smaller sum of deviations from additivity.

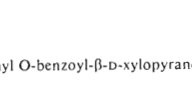
The aromatic carbon chemical shifts were omitted from Table I since they bear little significance here. Similarly as in other benzoyl derivatives the lines of *para*--carbon atoms occur around $\delta = 133{\cdot}4$, those of *ortho* and *meta*-carbon atoms in the interval $\delta = 128{\cdot}2 - 130{\cdot}0$ and the lines of the substituted carbon atoms in the interval $\delta = 128{\cdot}9 - 129{\cdot}6$.

The chemical shifts reported here for the parent compound, methyl β-D-xylopyranoside, in dimethyl sulfoxide–deuteriochloroform mixture agree satisfactorily with those found in deuterium oxide solutions[8]. It should be stressed, however, that all the benzoyl derivatives were measured in a different solvent (deuteriochloroform).

Benzoylation-induced chemical shifts and their additivity. Changes in ^{13}C chemical shifts induced by O-benzoylation (*i.e.* ^{13}C DCS values for O-benzoylation) given in Table II were calculated by subtracting the corresponding shift in the parent compound *1* from the chemical shift in a monobenzoate. The benzoylation shifts found here are in agreement with the general esterification shifts of alcohols[9,10] and acetylation (of secondary OH) shifts in other saccharides[11–13]. Benzoylation of an OH group has a deshielding effect (positive DCS values) on the appended (α) carbon atom and a shielding effect on the adjacent (β) carbon. The magnitude of these effects strongly depends on the site of benzoylation. In view of polar or inductive effects of benzoyl and methyl groups (as expressed by their polar or inductive substituent constants[14]) it might appear surprising that methylation has qualitatively the sameeffe cts in alcohols[9] and in other saccharides[15] as benzoylation. However, when the substituent groups are considered as a whole, the electronic effects of methoxy and benzoyloxy groups are not dissimilar[14]. If the parallelism with the methylation shift can be extended further, the large effects observed on ad-

TABLE I

^{13}C NMR chemical shifts of methyl O-benzoyl-β-D-xylopyranosides[a]



Compound	R^2	R^3	R^4	$C_{(1)}$	$C_{(2)}$	$C_{(3)}$	$C_{(4)}$	$C_{(5)}$	CH_3	C=O
1[b]	H	H	H	103·25	71·89	75·23	68·38	64·36	55·10	—
2	Bz	H	H	101·61	73·38	74·03[c]	69·82[c]	64·30	56·66	166·12
3	H	Bz	H	103·65	70·95	77·21	68·59	64·65	56·87	167·53
4	H	H	Bz	103·53	72·64	72·80	71·89	61·86	56·82	165·95
5	Bz	Bz	H	101·70	70·64[c]	76·12[c]	68·89	64·77	56·72	165·20; 167·26
6	Bz	H	Bz	99·63	70·62[c]	67·98	70·27[c]	58·94	56·17	165·92; 165·64
7	H	Bz	Bz	104·17	71·95	73·96	69·78	62·50	57·13	165·54; 166·21
8	Bz	Bz	Bz	101·25	70·41[c]	70·55	69·34[c]	61·38	56·59	165·16; 165·50

[a] Chemical shifts in δ scale, approximate error ±0·02 ppm. Measured in $CDCl_3$ solutions. Bz = benzoyl. [b] Measured with dimethyl sulfoxide added. [c] Assignment of the two lines within the labelled pair could not be made by selective decoupling.

jacent carbons in compound *4* would be suggestive of axial C—O bond on the adjacent carbons[15].

The chemical shifts calculated according to the direct additivity rule (by adding the appropriate DCS's values to the shift of the equivalent carbon in the parent compound *1*) for the di- and tribenzoates (Table II) differ considerably from those found experimentally.It should be noted that all significant deviations are negative (*i.e.* the predicted shifts are larger than the experimental ones), positive deviations are all small (less than 0·54 ppm).

This predominance of the negative deviations indicates a systematic error in the above approach (the origin of this error will be discussed later in this paper). Since the described calculations are very sensitive to any error in the chemical shifts of the chosen reference compound, and since the compound *1* could not be measured in chloroform as the rest of the investigated compounds, we have tried to improve the agreement by circumventing usage of *1* as the reference compound. This was achieved by evaluating "debenzoylation" shifts, *i.e.* the shifts due to the replacement of a benzoyl group of methyl 2,3,4-tri-O-benzoyl-β-D-xylopyranoside (*8*) by a hydroxyl group (similar procedure was used in refs[11,13]). The derived debenzoylation DCS

TABLE II

^{13}C DCS values for O-benzoylation of methyl β-D-xylopyranoside and the calculated chemical shifts[a,b]

Compound	$C_{(1)}$	$C_{(2)}$	$C_{(3)}$	$C_{(4)}$	$C_{(5)}$
2[a]	−1·64	1·49	−1·20	1·44	−0·06
3[a]	0·40	−0·94	1·98	0·21	0·29
4[a]	0·28	0·75	−2·43	3·51	−2·50
5[b]	102·01	72·44	76·01	70·03	64·59
	(−0·31)	(−1·80)	(0·11)	(−1·14)	(0·18)
6[b]	101·89	74·13	71·60	73·33	61·80
	(−2·26)	(−3·51)	(−3·62)	(−3·06)	(−2·86)
7[b]	103·93	71·70	74·78	72·10	62·15
	(0·24)	(0·25)	(−0·82)	(−2·32)	(0·35)
8[b]	102·29	73·19	73·58	73·54	62·09
	(−1·04)	(−2·78)	(−3·03)	(−4·20)	(−0·71)

[a] DCS Values calculated by subtracting the corresponding chemical shift in the parent compound *1* from that in monobenzoate. [b] The chemical shifts calculated as the sum of the corresponding chemical shift in the parent compound *1* and of the appropriate DCS values. Values in parentheses are the differences between the experimental and calculated chemical shifts.

values are given in Table III together with the chemical shifts calculated according to the additivity rule for monobenzoates. Obviously, this procedure has removed the negative bias in the deviations and led to a small improvement in the agreement with the experiment but many deviations have remained still too large.

In the two reported tests of additivity of substituent effect on pyranoside ring carbons[13,16] the deviations were much smaller. In other instances, when deviations were noted, they were attributed to substituent interactions, distorted molecular geometry and similar factors. In xylopyranosides one has to consider first the possibility of substituent induced changes in conformer populations. To evaluate the latter effect we have analysed ^{1}H NMR spectra of compounds *1*–*8* measured under the same conditions as the ^{13}C NMR spectra.

^{1}H NMR *spectra and conformer populations*. The results of analysis of the spectra of xylopyranoside protons are summarized in Table IV. The data for compounds *1* and *8* agree satisfactorily with the values published earlier for these compounds[17,18], other compounds appear not to have been investigated. On the basis of comparison of the coupling constants with those found in other aldopentopyranosides[19,20] one can conclude that the compounds *1*–*8* (with the exception of *6*) are predominant-

TABLE III

^{13}C DCS values for debenzoylation of methyl 2,3,4-tri-O-benzoyl-β-D-xylopyranoside and the calculated chemical shifts for methyl O-benzoyl-β-D-xylopyranosides[a,b]

Compound	$C_{(1)}$	$C_{(2)}$	$C_{(3)}$	$C_{(4)}$	$C_{(5)}$
7[a]	2·92	1·54	3·41	0·44	1·12
6[a]	−1·62	0·21	−2·57	0·93	−2·44
5[a]	0·45	0·23	5·57	−0·45	3·39
4[b]	102·55	72·16	71·39	70·71	60·06
	(0·98)	(0·48)	(1·41)	(1·18)	(1·80)
3[b]	104·62	72·18	79·53	69·33	65·89
	(−0·97)	(−1·23)	(−2·32)	(−0·74)	(−1·24)
2[b]	100·08	70·85	73·55	69·82	62·33
	(1·53)	(2·53)	(0·48)	(0·00)	(1·97)

[a] DCS values calculated by subtracting the corresponding shift in the reference compound *8* from that in dibenzoate. [b] The chemical shifts calculated as the sum of the corresponding shift in the compound *8* and the appropriate DCS values. Values in parentheses are the differences between the experimental and calculated chemical shifts.

ly in *C1* conformation and hence that the H-5 proton resonating at a higher field (H-5′ of Table IV) is axial.

Evaluation of conformer populations from the observed time-averaged chemical shifts or coupling constants requires knowledge of their values in the two considered (*C1* and *1C*) conformers of each compound[19-21]. Since the chemical shifts depend strongly on the substituent effects and on the measuring conditions we have chosen to estimate the conformer populations by the method of average coupling constants[21] which is generally prefered[20,21]. We have made two independent estimates (I and II) of populations P (in %) of conformer *C1* in compounds *1*–*8* (Table V). The first estimates are based on the measured $J_{1,2}$ coupling constants in conjunction with the values of $J_{1,2}$ = 8·1 Hz and 1·0 Hz which were derived by Durette, Horton, and Bhacca[21] for *C1* and *1C* conformers of β-D-xylopyranose tetraacetate, respectively. The second estimate uses the observed $J_{4,5}$, and the values of $J_{4a,5a}$ = 11·1 Hz and $J_{4e,5e}$ = 1·5 Hz found by Durette and Horton[18] in tribenzoates of methyl aldopentopyranosides. Of course, both estimates suffer from inadequacy of the model values. But since the correction of Karplus equation for electronegativity

TABLE IV

^{1}H NMR data on methyl O-benzyl-β-D-xylopyranosides

Compound[a]	Chemical shifts[b]							Coupling constants[c]					
	H-1	H-2	H-3	H-4	H-5[d]	H-5′[d]	CH_3O	$J_{1,2}$	$J_{2,3}$	$J_{3,4}$	$J_{4,5}$	$J_{4,5'}$	$J_{5,5'}$
1[e]	4·13	3·21	3·36	3·52	3·88	3·19	3·47	7·14	8·3	8·5	5·0	10·0	−11·3
2	4·48	4·96	3·72[f]	3·75[f]	4·04	3·36	3·45	6·38	6·9	8·5[g]	3·9	7·8	−11·7
3	4·35	3·67	5·09	3·89	4·11	3·43	3·53	6·35	8·0	8·0	4·7	8·5	−11·7
4	4·34	3·56	3·87	5·07	4·20	3·46	3·53	6·29	7·8	8·0	4·7	8·1	−11·9
5	4·61	5·36[f]	5·29[f]	4·04	4·22	3·53	3·51	6·23	7·5[g]	7·5[g]	4·8	8·3	−11·9
6	4·82	5·10[h]	4·18[i]	5·11[h]	4·32	3·78	3·52	3·18	5·0[g]	5·0[g]	3·1	3·9	−12·6
7	4·41	3·78	5·60	5·30	4·32	3·52	3·56	7·14	9·0	9·0	5·2	9·4	−11·5
8	4·73	5·39	5·78	5·31	4·43	3·70	3·53	5·61	7·5	7·5	4·4	7·2	−12·0

[a] Measured in $CDCl_3$ solutions for numbering of compounds see Table I. [b] Chemical shifts in δ-scale, maximum error ±0·01 ppm. Protons numbered as the skeleton carbon atoms. [c] Coupling constants in Hz, approximate error ±0·1 Hz except for $J_{1,2}$ where the error is ±0·03 Hz. [d] The proton on $C_{(5)}$ carbon resonating at the higher magnetic field is designated H-5′. [e] Measured with dimethyl sulfoxide-d_6 added. [f] Strongly coupled protons, approximate error ±0·05 ppm. [g] Approximate error ±1·0 Hz. [h] Accidentally degenerate, possible maximum error ±0·10 ppm. [i] Unresolved broad band.

effects has the form $(1 - \sum f_i \Delta X_i)$ where the correction factor f varies within 0·05 – 0·15 (ref.[22,23]) the different electronegativity X of hydroxy, methoxy, acetoxy, or benzoxy substituents on $C_{(1)}$ and $C_{(2)}$ carbons (for estimates I) and on $C_{(4)}$ carbon (for estimates II) cannot cause changes larger than 0·1 – 0·2 Hz in the model coupling constants. The actual effect of substituent electronegativity on the calculated populations would be reduced since the electronegativity influences both model couplings in parallel unless a correction for relative orientation of the substituents is made. With such correction[24] the $J_{4c,5c}$ coupling constant would not be appreciably affected by substituent electronegativity changes. An increase in the substituent electronegativity by 0·3 units would cause a decrease in the $J_{4a,5a}$ coupling by some 0·5 Hz with concomitant increase in *C1* population by 3 – 4% which is within the considered precision of the estimates.

The populations derived by the two independent methods are in a reasonable agreement. Since the ^{13}C chemical shifts of methyl group on $C_{(1)}$ depend on conformer population[25] (axial OCH_3 being shielded by some 2 – 2·5 ppm more than equatorial OCH_3, ref.[25,26]) linear correlation of these chemical shifts with the derived average populations (correlation coefficient $r = 0{\cdot}949$) confirms that the population estimates are meaningful (this is important especially for compounds *6* and *8*).

^{13}C *Chemical shift additivity and conformer populations.* The observed chemical shifts are time averages and so must be the derived DCS (or SCS) calues. When the conformer populations of the reference or parent compound are different from the

TABLE V
Estimates of *C1* conformer populations in methyl β-D-xylopyranoside benzoates (*1*–*8*)[a]

Compound	Estimate *I*[b]	Estimate *II*[c]	Average *P*
1	86	89	87·5 ± 1·5
2	76	66	71 ± 5
3	75	73	74 ± 1
4	74	69	71·5 ± 2·5
5	74	71	72·5 ± 1·5
6	31	25	28 ± 4
7	86	82	84 ± 2
8	65	59	62 ± 3

[a] Conformer populations in %. [b] Estimated from Eq. $J_{1,2} = 8{\cdot}1P + 1{\cdot}0\,(1 - P)$. [c] Estimated from Eq. $J_{4,5'} = 11{\cdot}1P + 1{\cdot}5\,(1 - P)$.

populations in the monosubstituted derivatives, the calculated DCS values have little meaning, and, of course, when a polysubstituted derivative has yet another conformer populations, validity of the additivity rule could be only accidental. The data of Table V indicate that this is the case of benzoylated methyl β-D-xylopyranosides in chloroform solutions. The reference compound for benzoylation *1* has *C1* conformer population 10–15% higher than the monosubstituted derivatives *2–4*, di- and tribenzoates *5–8* have widely differing populations. Decreasing *C1* conformer population means that the substituent groups on methyl β-D-xylopyranoside are for a longer period of time in axial positions. Since the carbon atoms bearing an axial substituent (OH, OCH_3, $OCOCH_3$) are more shielded[25–27] than their counterparts with equatorial substituent we can expect that the chemical shifts calculated according to the additivity rule will be larger than observed (negative deviations) in compounds with decreased *C1* conformer population. This consideration combined with the data of Table V explains the predominance of negative deviations in calculated chemical shifts in Table II and the mentioned large DCS values for β carbons in compound *4*.

Practical considerations. The above results have an important practical consequence. They show that before an application of the additivity rule to ^{13}C chemical shifts is attempted (*e.g.* for line assignments), the average conformations of the model and investigated compounds should be determined in a given solvent and only such solvent should be used in which the average conformations are the same.

EXPERIMENTAL

Syntheses of mono-O-benzoyl derivatives of methyl β-D-*xylopyranoside.* Benzoylation of methyl 3,4-di-O-acetyl-β-D-xylopyranoside[28], methyl 2,4-di-O-acetyl-β-D-xylopyranoside[29], and methyl 2,3-di-O-acetyl-β-D-xylopyranoside[30] afforded the corresponding methyl 3,4-di-O-acetyl-2-O-benzoyl-β-D-xylopyranoside (*9*), methyl 2,4-di-O-acetyl-3-O-benzoyl-β-D-xylopyranoside (*10*), and methyl 2,3-di-O-acetyl-4-O-benzoyl-β-D-xylopyranoside (*11*), respectively. Deacetylation of these compounds gave the required products *2*, *3* and *4*. Benzoylation procedure: benzoyl chloride (1·3 equivalent) was added dropwise to the solution of the compound in a minimum amount of pyridine. After stirring for 3–4 h at room temperature, a solution of $NaHCO_3$ was added, and the product was extracted with chloroform. Deacetylation procedure: 1M-HCl solution in methanol (3·75 ml per each 0·001 mol of acetyl groups) was added to the compound, and the mixture was stirred for 3–4 h at room temperature. Then, methanol (1 : 1 V/V) and a weakly basic anion exchanger were added. Neutral reaction mixture was filtered off, evaporated, and crystallized.

Syntheses of di-O-benzoyl derivatives of methyl β-D-*xylopyranoside.* Methyl 4-O-benzyl-β-D-xylopyranoside[30], methyl 3-O-benzyl-β-D-xylopyranoside[29], and methyl 2-O-benzyl-β-D-xylopyranoside[31] were benzoylated by the above mentioned procedure to yield methyl 2,3-di-O-benzoyl-4-O-benzyl-β-D-xylopyranoside (*12*), methyl 2,4-di-O-benzoyl-3-O-benzyl-β-D-xylopyranoside (*13*), and methyl 3,4-di-O-benzoyl-2-O-benzyl-β-D-xylopyranoside (*14*), respectively. Their hydrogenation provided the compounds *5*, *6* and *7*, respectively. Hydrogenation procedure:

the catalytic hydrogenation was carried out in methanol solution (or in an acetone–methanol mixture) using 5% Pd/C catalyst (approximately 20% of the compound weight) under normal hydrogen pressure at laboratory temperature.

Methyl 2,3,4-tri-O-benzoyl-β-D-xylopyranoside was prepared according to Fletcher[6], the unsubstituted methyl β-D-xylopyranoside was a commercial sample (Lachema, Brno).

TABLE VI

Analytical data and physical properties of methyl O-benzoyl-β-D-xylopyranosides

Compound	Formula	Calculated/Found % C	% H	Yield, % $[\alpha]_D$	M.p., °C (solvent)
2	$C_{13}H_{16}O_6$	58·20	6·01	100	122·0–122·5
		58·43	6·15	– 26	(2-propanol)
3	$C_{13}H_{16}O_6$	58·20	6·01	92	135·6–136·0[a]
		58·55	6·31	– 18[a]	(diethyl ether)
4	$C_{13}H_{16}O_6$	58·20	6·01	97	114·5–115·5
		58·45	6·22	– 92	(acetone, benzene)
5	$C_{20}H_{20}O_7$	64·51	5·41	95	–
		64·43	5·37	– 72	–
6	$C_{20}H_{20}O_7$	64·51	5·41	95	–
		64·47	5·31	– 40	–
7	$C_{20}H_{20}O_7$	64·51	5·41	96	85·5–87·0
		64·34	5·35	– 107	(diisopropyl ether, hexane) (1 : 1)
9	$C_{17}H_{20}O_8$	57·94	5·72	100	75·0–76·0
		58·04	5·91	– 17	(ethanol)
10	$C_{17}H_{20}O_8$	57·94	5·72	91	118·0–119·0
		58·18	5·88	– 24	(ethanol)
11	$C_{17}H_{20}O_8$	57·94	5·72	97	136·0–136·5
		58·04	6·07	– 127	(ethanol)
12	$C_{27}H_{26}O_7$	70·11	5·66	97	–
		70·27	5·92	– 67	–
13	$C_{27}H_{26}O_7$	70·11	5·66	93	119–120·0
		70·32	5·82	– 61	(2-propanol)
14	$C_{25}H_{26}O_7$	70·11	5·66	98	83·0–84·0
		70·16	5·86	– 70	(ethanol)

[a] Lit.[3] m.p. 138–139°C, $[\alpha]_D = -15°$.

Analytical data, melting points and specific optical rotations of all the prepared compounds *2–14* are gathered in Table VI, NMR spectra of the final products are in Tables I and IV, those of intermediate products (compounds *8–14*) are in Table VII. Melting points were determined on a Kofler hot-stage. Optical rotations (22°C, *c* 1, chloroform) were measured with a Perkin–Elmer Model 141 automatic polarimeter. Microanalyses were performed on a Perkin–Elmer Model 240 automatic analyzer. Chloroform extracts were dried with anhydrous sodium sulfate and evaporated at 40°C/2 kPa, the solvent used in crystallization is indicated in Table VI.

NMR *Spectra*. The spectra were measured on a Varian XL-200 spectrometer operating at 200 MHz for ^{1}H NMR and at 50·3 MHz for ^{13}C NMR. The two spectra were measured in identical solutions (approximately 0·1M) in deuteriochloroform (Merck, Uvasol quality) to which 5% (V/V) of hexamethyldisilane (MHDS) were added. Because of solubility problem hexadeuteriodimethyl sulfoxide had to be added 1 : 1 to chloroform for the measurements of methyl β-D-xylopyranoside (24 hours accumulation of saturated chloroform solution did not yield a signal). ^{1}H NMR spectra were measured in 5 mm o.d. NMR tubes at 23°C using deuterium lock. The FIDs were recorded with 4 s acquisition time using spectral width of 2 000 Hz and 16 k memory zero filling to 32 k. The relationships among various signal groups were established by a series of homonuclear decoupling and tickling experiments based on H-1 proton signal appearing as an isolated doublet due to $J_{1,2}$ coupling. The spectra were referenced to the line of hexamethyldisilane, δ (HMDS) = 0·04 (ref.[32]). Most parts of the spectra were of the first order type, they were accordingly analysed and the calculated parameters were confirmed by simulation by LAOCOON program which was a part of the spectrometer system software. In the few cases of strongly coupled spin subsystems, the trial parameters were readjusted until a satisfactorily agreement between the experimental and simulated spectra was achieved. The resulting lower precission of calculated chemical shifts and coupling constants did not affect the values of $J_{1,2}$ and $J_{4,5}$, which were utilized in the discussion here. In principle, a different solvent or a shift reagent could be used to increase chemical shift difference and to remove accidental degeneracy of the subspectra.

TABLE VII

^{13}C NMR chemical shifts of intermediate products[a]

Compound	$C_{(1)}$	$C_{(2)}$	$C_{(3)}$	$C_{(4)}$	$C_{(5)}$	CH_3O	C=O		
9	101·56	70·96	70·82	68·88	61·82	56·63	165·03	169·82	169·92
10	101·51	70·52	71·72	68·89	62·00	56·63	165·52	169·38	169·78
11	101·59	70·63	71·12	69·55	61·98	56·66	165·36	169·42	170·00
12	101·95	71·26	73·09	74·65	63·23	56·80	[b]	—	—
13	100·52	70·39	75·30	69·94	60·12	56·20	165·17	165·56	—
14[c]	104·9	78·1	72·9	70·2	62·3	57·0	165·98	165·9	—

[a] Chemical shifts in δ-scale, approximate error ±0·02 ppm. Measured in $CDCl_3$ solutions. Lines assigned only by analogy with the data of Table I. [b] Not measured. [c] Measured on a Jeol FX-60 spectrometer.

Coupling constants derived from such solutions could not be transferred to chloroform solutions with a better precision since the coupling constants are solvent dependent. For example, in the case of compound 6 the coupling constant $J_{1,2}$ might appear anomalous, but similar value is found in C_6D_6 solution while a "normal" value (7·0 Hz) is observed in dimethyl sulfoxide. The error estimates given in Table III are conservative, the value of coupling constant $J_{1,2}$ could be read directly from the spectra in all cases with a precision higher than the other coupling constants determined by the analysis.

^{13}C NMR spectra were measured in 10 mm o.d. tubes also at 23 °C and with deuterium lock. The FIDs were recorded with 0·7 s acquisition time and 16 000 Hz spectral width using 22·4 k of memory with zero filling to 32 k. The measurements were run both with broad-band incoherent proton decoupling (square wave modulation) and with low-power selective coherent decoupling of protons. The spectra were referenced to the central line of deuteriochloroform $\delta(CDCl_3) = 76{\cdot}99$ the relative position of which was checked by monitoring the HMDS line, $\delta(HMDS) = -2{\cdot}49$ (in dimethyl sulfoxide–chloroform mixture $\delta(HMDS) = 3{\cdot}69$).

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