The structure was determined by the direct method using the MULTAN-78 programs [5] and was refined by the method of least squares in the full-matrix anisotropic approximation to R = 0.09. The positions of the hydrogen atoms in the molecule were determined from difference syntheses. The coordinates of the C and O atoms and their anisotropic thermal parameters are given in Table 5, while Table 6 gives the coordinates of the hydrogen atoms.

SUMMARY

The crystal and molecular strueture of methyl β-L-arabinopyranoside has been determined. The geometric parameters of the glycosidic bond have been found and the presence of a O(2)—H...O(1) intramolecular hydrogen bond in the molecule has been established. Differences are observed in the geometric parameters of the molecules of methyl β-L-arabinopyranoside, β-D-arabinose, and β-DL-arabinose which are expressed in smaller values of the lengths of the C(4)—C(5) and C(5)—O(6) bonds and in changes in the conformational angles of the molecule except for the angle at the C(3)—C(4) bond.

LITERATURE CITED

1. S. Furberg and A. Hordvik, Acta Chem. Scand., 11, 159 (1957).
2. A. Hordvik, Acta Chem. Scand., 15, 16 (1961).
3. S. H. Kim and G. A. Jeffrey, Acta Crystallogr., 22, 537 (1967).
4. S. Arnott and W. E. Scott, J. Chem. Soc., Perkin Trans., II, 324 (1972).
5. P. Main, S. E. Hull, L. Lessinger, G. Germain, J. P. Leclerq, and M. M. Woolfson, MULTAN 78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-Ray Diffraction Data. Universities of York, England, and Louvain, Belgium (1978).

^{13}C NMR SPECTRA OF BIOLOGICALLY ACTIVE COMPOUNDS.

II. 11-DEOXY-16- AND 17-ARYLOXYPROSTAGLANDINS

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UDC: 543.422.25+547.915

The ^{13}C NMR spectra of the initial ω-aryloxy chains and the final 16- and 17-aryloxyprostaglandins of the 11-deoxy series have been investigated, and stereochemical assignments have been made for the diastereomeric pairs. A weakening of the diastereotopic effects in the spectra of the 15- and 16-methyl-substituted 16- and 17-phenoxypropstaglandins to 0.1 ppm has been shown.

Aromatic fragments in the molecules of synthetic prostaglandins impart new properties to them: resistance to biological breakdown, and increased activity and selectivity of biological action [1]. With the aim of the stereochemical monitoring and study of diastereotopic effects in aryloxyprostaglandin derivatives we have as before [2], used the method of ^{13}C NMR spectroscopy. In the literature on aryloxyprostaglandins only the ^{13}C NMR spectrum of 16-phenoxy-11-deoxyprostaglandin has been described [3]. In this paper, erroneous assignments of some stereochemically important C_{13}—C_{16} signals of the ω-chain are given. In this connection, we have made a detailed study of ^{13}C NMR spectra of the final 16- and 17-aryloxy-11-deoxy-PGE_1's and their initial ω-chains, have made spectral and stereochemical assignments, and have estimated the diastereotopic effects according to the types of chiral centers and the distance between them.

Table 1 gives the chemical shifts (CSs) and multiplicities of some signals and (in the case of the fluorine-substituted derivatives) the $J_{^{13}C-^{19}F}$ spin-spin coupling constants

Institute of Chemistry, Bashkir Branch, Academy of Sciences of the USSR, Ufa. Translated from Khimiya Prirodnykh Soedinenii, No. 5, pp. 610-618, September-October, 1985. Original article submitted November 19, 1984.

 0009-3130/85/2105-0570$09.50

TABLE 1. ^{13}C NMR Spectra of the ω-Chains for 16- and 17-Aryloxyprostaglandin ($CDCl_3$, δ, ppm, $J_{^{13}C-^{19}F}$, Hz)

	Compound	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}	C_{11}	C_{12}	C_{13}	C_{14}	C_{15}
I*	trans-3-Hydroxy-1-iodo-4-phenoxybut-1-ene	79,8	143,7	72,5	70,6	158,2	114,7	129,5	121,3	129,5	114,7					
II*	cis-3-Hydroxy-1-iodo-4-phenoxy-but-1-ene	84,4	139,4	73,3	69,8	158,2	114,7	129,5	121,3	129,5	114,7					
III.	trans-4-Phenoxy-1-tributylstannyl-3-trimethylsiloxybut-1-ene	129,2	147,0	74,4	72,0	158,7	114,5	129,2	120,5	129,2	114,5	9,4	29,1	27,2	13,7	0,2
IV.	trans-4-(p-Fluorophenoxy)-3-hydroxy-1-iodobut-1-ene; $J_{^{13}C\ ^{19}F}$	79,9	143,3	72,6	71,3	154,2 (d 2)	115,7 (d 9)	115,8 (d 22)	157,4 (d 238)	115,8 (d 22)	115,7 (d 9)					
V.	trans-4-(p-Flurophenoxy)-1-tributylstannyl-3-trimethylsiloxybut-1-ene	129,6	147,6	74,5	72,8	154,7	115,1	115,3	156,7	115,3	115,1	9,6	29,2	27,3	13,8	0,5
VI.	trans-3-Hydroxy-1-iodo-4-(m-trifluoromethylphenoxy)but-1-ene; $J_{^{13}C-^{19}F}$	80,1	143,1	72,6	70,9	158,2	111,4 (q 4)	131,9 (q 31)	118,0 (q 4)	130,1	118,2					
VII.	trans-1-Tributylstannyl-4-(m-trifluoromethylphenoxy)-3-trimethylsiloxybut-1-ene; $J_{^{13}C-^{19}F}$	129,8	146,5	74,5	72,5	159,1	111,4 (q 4)	131,3 (q 32)	117,3 (q 4)	130,4	118,2	9,5	29,1	27,3	13,7	0,2
VIII.	trans-4-(m-Chlorophenoxy)-3-hydroxy-1-iodobut-1-ene	80,0	143,3	72,3	70,6	158,7	114,9	134,7	121,4	130,2	112,9					

TABLE 1 (continued)

Compound	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}	C_{11}	C_{12}	C_{13}	C_{14}	C_{15}	C_{16}	$SiMe_3$
IX. cis-4-(m-Chlorophenoxy)-3-hydroxy-1-iodobut-1-ene	84,7	139,0	73,1	69,9	158,7	114,9	134,7	121,4	130,2	113,0							
X. trans-4-(p-Chlorophenoxy)-1-tributylstannyl-3-trimethylsiloxybut-1-ene	130,2	146,7	74,4	72,6	157,6	115,9	129,2	125,2	129,2	115,9	9,5	29,1	27,3	13,7			0,26
XI. trans-3-Hydroxy-1-iodo-3-methyl-4-phenoxybut-1-ene	78,4 d	148,7 d	75,0	74,1 t	158,2 s	114,6 d	129,5 d	121,4 d	129,5 d	114,6 d	24,2						
XII. trans-3-methyl-4-phenoxy-1-tributylstannyl-3-trimethylsiloxybut-1-ene	126,6 d	152,1 d	76,8 d	75,5 t	159,1 s	114,8 d	129,3 d	120,6 d	129,3 d	114,8 d	9,5 t	29,2 t	27,2 t	13,7 q	24,7 q		2,5
XIII. trans-1-Iodo-4-methyl-5-phenoxy-4-trimethylsiloxypent-1-ene	77,1 d	142,1 d	46,3 t	74,5 s	73,9 t	158,5 s	114,4 d	129,4 d	121,0 d	129,4 d	25,0 d	2,4 q					
XIV. cis-1-Iodo-4-methyl-5-phenoxy-4-trimethylsiloxypent-1-ene	84,4 d	137,4 d	45,2 *	74,2 s	73,9 t	158,5 s	114,4 d	129,4 d	121,0 d	129,4 d	114,4 d	25,1 q					
XV. trans-4-Methyl-5-phenoxy-1-tributylstannyl-4-trimethylsiloxypent-1-ene	131,6 d	144,8 d	48,7 t	75,1 s	74,3 t	158,9 s	114,4 d	129,3 d	120,6 d	129,3 d	114,4 d	9,4 t	29,2 t	27,3 t	13,7 q	25,1 q	2,5 q
XVI. cis-5-Phenoxy-1-tributylstannyl-4-trimethylsiloxypent-1-ene	130,7 d	144,3 d	47,1 t	75,2 s	74,5 t	158,9 s	114,4 d	129,3 d	120,6 d	129,3 d	114,4 d	10,2 t	29,2 t	27,3 t	13,7 q	25,1 q	2,5 q

*Spectra taken in the Institute of Chemical and Biological Physics, Tallin.

TABLE 2. ^{13}C NMR Spectra of the 16- and 17-Aryloxyprostaglandins of the 11-Deoxy-PGE_1 Series and Their Analogs ($CDCl_3$, δ, ppm, $J_{^{13}C-^{19}F}$, Hz)

Compound	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}	C_{11}	C_{12}	C_{13}	C_{14}
XVII. Butyl ester of 11-deoxy-16-phenoxy-17,18,19,20-tetranorhomo-PGE_1, 15S(α)OH	174,0	24,9	29,0	29,0	29,6	26,7	27,7	54,5	219,7	37,7	27,7	45,6	135,6	128,7
XVIII. ", 15R(β)OH	173,9	24,9	29,0	29,0	29,6	26,7	27,7	54,5	219,7	37,7	27,8	45,5	135,0	129,2
XIX. ", 8-iso	173,9	24,9	29,0	29,0	29,6	26,7	25,3	53,6	219,7	35,5	27,3	42,4	130,3	130,8
XX. Ethyl ester of 16-p-fluorophenoxy-11-deoxy-17,18,19,20-tetranor-PGE_1, $J_{^{13}C-^{19}F}$, 15S(α)OH	173,9	34,3	24,9	28,9	29,4	26,6	27,8	54,5	219,3	37,6	27,8	45,6	135,7	129,2
XXI. 15R(β)OH	173,9	34,3	24,9	28,9	29,4	26,6	27,8	54,5	219,3	37,6	27,8	45,6	135,4	129,2
XXII. ", 8-iso	173,9	34,3	24,9	28,9	29,2	26,6	25,3	53,6	219,6	35,5	27,1	42,5	130,4	131,3
XXII. Ethyl ester of 16-m-trifluoromethylphenoxy-11-deoxy-17,18,19,20-tetranor-PGE_1 15S(α)OH $J_{^{13}C-^{19}F}$	174,0	34,3	24,8	28,9	29,4	26,6	27,8	54,5	219,5	37,7	27,8	45,7	136,1	128,5
XXIV. ", 15R(β)OH $J_{^{13}C-^{19}F}$	174,0	34,3	24,7	28,8	29,3	26,4	27,7	54,5	219,5	37,7	27,2	45,6	135,8	128,8
XXV. ", 8-iso	174,0	34,3	24,7	28,8	29,3	26,4	25,2	53,7	219,5	35,5	27,0	42,5	131,6	129,9

TABLE 2 (continued)

Compound	C_{15}	C_{16}	C_{17}	C_{18}	C_{19}	C_{20}	C_{21}	C_{22}	C_{23}	C_{24}	C_{25}	C_{26}	C_{27}
XVII	70,6 d	71,8 t	158,4	114,6	129,5	121,1	129,5	114,6	34,3	64,1	30,6	19,1	13,7
XVIII	70,3 d	71,9 t	158,6 t	114,6	129,4	121,1	129,4	114,6	34,3	64,0	30,8	19,1	13,7
XIX	70,3	71,9	158,6	114,6	129,4	121,1	129,4	114,6	34,3	64,0	30,8	19,1	13,7
XX	70,6	72,9	154,9	115,9	115,9	157,6	115,9	115,9	60,2	14,2			
XXI	70,5	72,9	154,9 d, 2	115,9 d 8	115,9 d 23	157,6 d 23	115,9 d 23	115,9 d 8	60,2	14,2			
XXII	70,5	72,9	154,9	115,9	115,9	157,6	115,9	115,9	60,2	14,2			
XXIII	70,6 d	72,1 t	158,6	111,5 q 4	131,9 q 31	117,8 q 4	130,1	118,0	60,3	14,2			
XXIV	70,5 d	72,1 t	158,7	111,5 q 4	131,9 q 31	117,8 q 4	130,1	118,0	60,3	14,2			
XXV	70,5	72,1	158,7	111,5	131,9	117,8	130,1	118,0	60,3	14,2			

TABLE 2 (continued)

Compound	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9	C_{10}	C_{11}	C_{12}	C_{13}	C_{14}
XXVI. 15-Methyl-16-phenoxy-11-deoxy-17,18,19,20-tetranor-PGE_1, 15(β)OH	179,3	33,9	24,5	28,7	29,2	26,5	27,9	54,5	219,9	37,7	27,6	45,8	134,34	132,1
XXVII. ", 15(α)OH	179,3	33,9	24,5	28,7	29,2	26,5	27,9	54,5	219,9	37,7	27,6	45,8	134,43	132,1
XVIII. Butyl ester of 16-hydroxy-16-methyl-17-phenoxy-11,15-dideoxy-18,19,20-trinor-PGE_1, 16(β)OH	173,9	24,9	29,0	29,0	29,7	26,7	27,7	54,7	219,8	37,7	28,1	46,0	136,9	125,8
XXIX. ", 16(α)OH	173,9	24,9	29,0	29,0	29,7	26,7	27,7	54,7	219,8	37,7	28,1	46,0	136,9	125,8

TABLE 2 (continued)

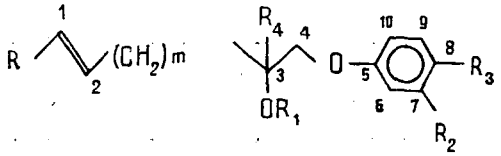
Compound	C_{15}	C_{16}	C_{17}	C_{18}	C_{19}	C_{20}	C_{21}	C_{22}	C_{23}	C_{24}	C_{25}	C_{26}	C_{27}
XXVI	72,1 s	74,9 t	158,5	114,6	129,5	121,2	129,5	114,6	24,81 q				
XXVII	72,1 s	74,9 t	158,5	114,6	129,5	121,2	129,5	114,6	24,8 q				
XXVIII	42,2 t	71,7 s	74,15 t	158,6	114,5	129,5	121,1	34,3	23,9 q	64,1	30,7	19,1	13,7
XXIX	42,2 t	71,7 s	74,25 t	158,6	114,5	129,5	121,1	34,3	23,9 q	64,1	30,7	19,1	13,7

(SSCCs) for the cis and trans isomers of a series of 4- or 5- aryloxy-3-hydroxy-1-iodobut-(or pent-)-1-enes and their synthetic precursors: 4- or 5- aryloxy-3-hydroxy-1-tributyl-stannyl-and -1-tributylstannyl-3-trimethylsiloxybut-(or pent-)-1-enes.

The spectrum of 3-hydroxy-1-iodo-4-phenoxybut-1-ene (I) contains eight nonequivalent signals. The signals of the C_1 double-bond carbon atom directly attached to an iodine atom experience a considerable diamagnetic shift through the heavy-atom effect [4].

The determination of the configuration of the C_1—C_2 double bond caused some difficulties, since the signals of the carbon atoms of a double bond and of the groups directly attached to it are usually observed in a weaker field for the trans isomer than for the cis isomer [5]. In the spectrum of compound (II), however, of the above-mentioned signals only the C_2 signal was present in a stronger field. Bringing in literature information on the CS values of 1-bromoprop-1-ene [6], which are given in the scheme, shows that in halogen-substituted double

bonds the signal of the C_1 carbon atom for the cis isomer is located in a weaker field than that for the trans isomer as a result of the redistribution of electron density, and the shift of the C_2 signal has the opposite tendency. The signal of the C_3 atom, bearing a hydroxy group in compound (II) is also shifted downfield in comparison with the corresponding signal of compound (I).



I—XII m=0, XIII—XVI m=1

R=I, R_1, R_2, R_3, R_4=H (I); R=$SnBu_3$, R_1=$SiMe_3$, R_2, R_3, R_4=H (III)

R=I, R_1, R_2, R_4=H, R_3=F (IV); R=$SnBu_3$

R_1=$SiMe_3$, R_2, R_4=H, R_3=F (V); R_1, R_3, R_4=H, R_2=CF_3 (VI);

R=$SnBu_3$, R_1=$SiMe_3$, R_2=CF_3, R_3, R_4=H (VII);

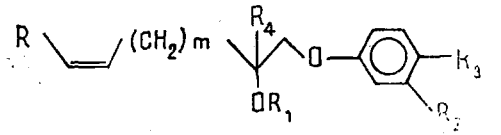
R=I, R_1, R_3, R_4=H, R_2=Cl (VIII); R=$SnBu_3$

R_1=$SiMe_3$, R_2, R_4=H, R_3=Cl (X); R=I, R_1, R_2, R_3=H

R_4=Me[II] (XI); R=$SnBu_3$, R_1=$SiMe_3$, R_2, R_3=H

R_4=Me[II] (XII); R=I, R_1=$SiMe_3$, R_2, R_3=H, R_4=Me (XIII)

R=$SnBu_3$, R_1=$SiMe_3$, R_2, R_3=H, R_4=Me (XV)



R=I, R_1, R_2, R_3, R_4=H (II); R=I, R_1, R_3, R_4=H, R_2=Cl (IX)

R=I, R_1=$SiMe_3$, R_2, R_3=H, R_4=Me (XIV)

R=$SnBu_3$, R_2, R_3=H, R_4=Me (XVI).

In contrast to the isomeric pairs of vinyl iodides (I and II; VIII, and IX; and XIII and XIV), slight screening of the C_1 and C_2 double-bond carbon atoms and of the C_3 allyl carbon atom for the tributylstannyl derivatives is observed, which is well seen, for example, in a comparison of the CSs of the cis isomer (XVI) and the trans isomer (XV). We have observed a similar effect previously for trimethylsilyl-substituted double bonds [7].

Definite interest is presented by the assignment of the signals of the sp^2-hybridized carbon atoms for the tributylstannyl derivatives (III), (V), (VII), (XII), (XV), and (XVI). In the first place, the decrease in the value of the $J_{^{13}C-^1H}$ SSCC, 146 Hz, in compound (III) for the carbon atom bound directly to the Sn atom as compared with the ethylene molecule ($J_{^{13}C-^1H}$ = 156.4 Hz [4]) must be mentioned. In the second place, on the attachment of a methyl

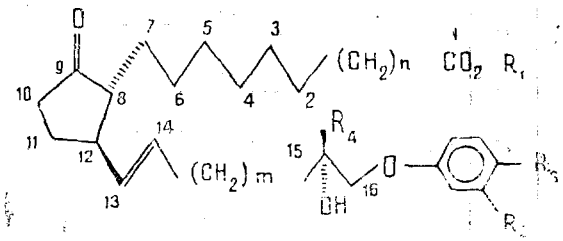
group to C_3 in compound (XII) there is a descreening of the C_2 atom (β-effect of the methyl group) and a screening of C_1 (β'-effect) in comparison, for example, with the analogous signals of compounds (III), (V), and (VII). In contrast to (IX), the position of the methyl and trimethylsilyloxy group at C_4 in compound (V) causes a screening of the C_2 carbon atom.

The multiplicities of the signals of the carbon atoms in the 69-77 ppm region unambiguously show that they belong to the C_3 and C_4 atoms in compounds (I)-(XII) and the C_4 and C_5 atoms in (XII)-(XVI), and, as a rule, the carbon atoms bearing hydroxy and trimethylsiloxy groups are the more screened.

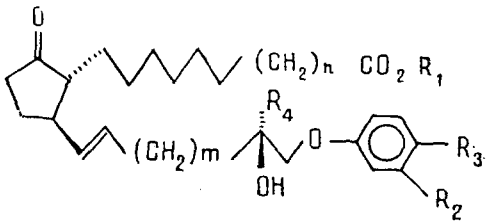
The positions of the signals of the aromatic carbon atoms of the para-F- (IV, V), meta-CF_3- (VI, VII), meta-Cl- (VIII, IX), and para-Cl-(X) -substituted phenoxy groups can easily be predicted by using figures calculated by additive schemes [6]. The magnitude of the splitting of the signals on the ^{19}F nucleus decreases monotonically with an increase in the number of bonds separating the ^{13}C nucleus observed and the ^{19}F nucleus. The direct (through a single bond) $^1J_{^{13}C-^{19}F}$ SSCC has the maximum value of 238-247 Hz. The constants through two bonds $^2J_{^{13}C-^{19}F}$ range between 21 and 32 Hz, and those (through three bonds - $^3J_{^{13}C-^{19}F}$ from 4 to 9 Hz.

The spectroscopic parameters ^{13}C NMR obtained for the synthons studied have been used in the analysis of the spectra of the final 16- and 17-ω-aryloxyprostaglandins.

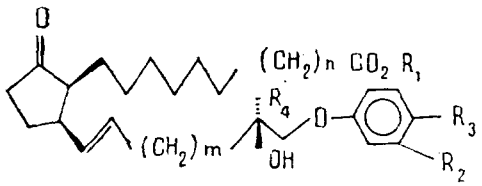
Table 2 gives the multiplicities of some signals and the CSs and $J_{^{13}C-^{19}F}$ SSCCs for the ω-aryloxyprostaglandins (XVII-XXIX) that we have studied. The assignment of the signals of the carbon atoms of the α-chain and of the five-membered ring was made in accordance with literature information and results obtained by ourselves previously [2, 3]. The assignment of the signals of the carbon atoms of the ω-chain was made independently of literature information, since some contradictions were detected in it. The multiplicities of the signals of the carbon atoms bound to oxygen atoms in the spectrum of prostaglandin (XVII) unambiguously show the assignment of the doublet at 70.6 ppm to the C_{15} atom and the triplet at 71.8 ppm to the C_{16} atom. In the



R_1=Bu, R_2, R_3, R_4=H, n=1, m=0 (XVII)
R_1=Et, R_2, R_4=H, R_3=F, n=0, m=0 (XX)
R_1=Et, R_2=CF_3, R_3, R_4=H, n=0, m=0 (XXIII)
R_1, R_2, R_3=H, R_4=Me, n=0, m=0 (XXVII)
R_1=Bu, R_2, R_3=H, R_4=Me, n=1, m=1 (XXIX).

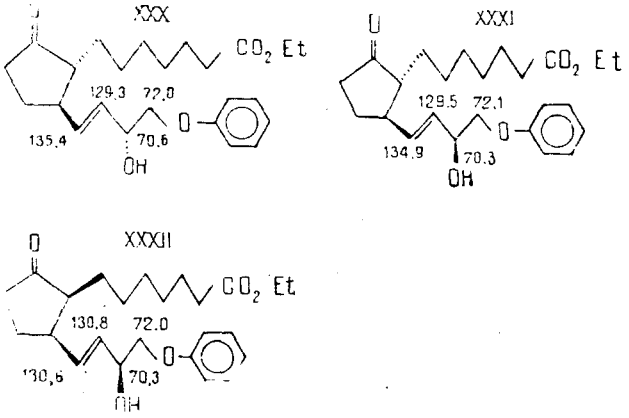


R_1=Bu, R_2, R_3, R_4=H, n=1, m=0 (XVIII)
R_1=Et, R_2, R_4=H, R_3=F, n=0, m=0 (XXI)
R_1=Et, R_2=CF_3, R_3, R_4=H, n=0, m=0 (XXIV)
R_1, R_2, R_3=H, R_4=Me, n=0, m=0 (XXVI)
R_1=Bu, R_2, R_3=H, R_4=Me, n=1, m=1 (XXVIII)



R_1=Bu, R_2, R_3, R_4=H, n=, m=0 (XIX)
R_1=Et, R_2, R_4=H, R_3=F, n=0, m=0 (XXII)
R_1=Et, R_2=CF_3, R_3, R_4=H, n=0, m=0 (XXV).

case of the 15β epimer (XVIII) some screening of the C_{12} and C_{15} carbon atoms (up to 0.3 ppm) in comparison with the corresponding atoms of compound (XVII) is observed. The diamagnetic shifts of the signals of the chiral centers are explained by erythro interactions of the substituents at these centers in the 15β epimer (XVIII).



A comparison of the signals of the carbon atoms of the double bond in the 8-cis isomer (XIX) with the signals of the trans isomer (XVII) and (XVIII) shows that the doublets at 130.3, 135.6, and 135.0 ppm belong to the C_{13} atom in the corresponding compounds. The screening of this carbon atom in the 8-cis isomer (IX) is caused by the interaction of the side chains [8]. The signals of the carbon atoms of the aromatic ring in the spectrum of each of the prostaglandins (XVII)-(XX) practically coincide with the values obtained for the ω-aryloxy chains of (I)-(XVI).

The presence of a methyl group in position 15 (XXVI, XXVII) leads to some equalization of the molecular contributions of the α-atoms of the C_{15} chiral center which should apparently weaken the diastereotopic effects. In actual fact, the difference in the CSs of the signals for (XXVI) (15β) and (XXVII) (15α) is appreciable only for the C_{13} carbon atom and does not exceed 0.1 ppm. In the structures of compounds (XXVIII) and (XXIX) an additional methylene group increases the distance between the chiral centers to four carbon-carbon bonds. Nevertheless, the splitting of the C_{16} signal (by 0.1 ppm) permits the assumption of a difference in the stereochemistry of compounds (XXVIII) and (XXIX), which are formed in a mixture with a ratio of approximately 1:1.

The compounds (XVII)-(XIX) considered in this investigation differ from the stereoisomers of 16-phenoxy-11-deoxyprostaglandin (XXX)-(XXXII) described in the literature [3] by the fact that the α-chain is one carbon atom longer, and compounds (XVIII) and (XIX) are butyl esters, in contrast to the ethyl esters (XXX)-(XXXII). The complete analogy of compounds (XVIII) (XIX) and (XXX-XXXII) permits the assignment of the C_{13}-C_{16} signals given in [3] to be considered erroneous and the mutual inversion of the assignments of the C_{13} and C_{14} and the C_{15} and C_{16} signals to be proposed, as shown in the scheme.

EXPERIMENTAL

The ^{13}C NMR spectra were taken on a JEOL FX-90Q spectrometer (22.5 MHz) with broad-band and off-resonance suppression with respect to protons at room temperature. The samples were irradiated with 45-degree pulses every 3 sec. Field sweeps of 6024 and 4000 Hz; resolution

of the analog-digital converter 0.74 and 0.49 Hz. The samples were prepared in $CDCl_3$ (5-10 vol%) with TMS as internal standard. The field was stabilized with respect to the signal of deuterium (solvent). The syntheses of the compounds studied has been described in [9, 10].

SUMMARY

The structures of a number of initial ω-aryloxy chains of the prostaglandins have been established and the geometries of their double bonds have been determined. A stereochemical assignment has been made of the final 16-aryloxy-11-deoxyprostaglandins. It has been shown that the weakening of the diastereotopic effects for the 15- and 16-methyl-substituted 16- and 17-phenoxyprostaglandins reaches 0.1 ppm. A reassignment of the stereochemically important signals of the C_{13}-C_{16} carbon atoms of the 16-phenoxy-11-deoxyprostaglandins has been made.

LITERATURE CITED

1. A. K. Banerjee, B. J. Broughton, T. S. Burton, et al., Prostaglandins, 22, 167 (1982).
2. G. A. Tolstikov, L. M. Khalikov, A. A. Panasenko, et al., Khim. Prir. Soedin., 314 (1985).
3. T. Pekhk, T. Vilimyae, and N. Samel, Izv. Akad. Nauk ESSR, Khim., 31, No. 2, 85 (1982).
4. G. C. Levy, R. L. Lichter, and G. L. Nelson, Carbon-13 Nuclear Magnetic Resonance Spectroscopy, 2nd edn., Wiley-Interscience, New York (1980), p. 338.
5. G. B. Stothers, Carbon-13 NMR Spectroscopy, Academic Press, New York (1972), p. 559.
6. E. Pretsh, T. Clerc, J. Siebel, and W. Simon, Tabellen zur Strukturaufklärung Organischer Verbindungen mit Spektroskopischen Methoden, Springer, New York (1966), p. 95.
7. A. A. Panasenko, L. M. Khalilov, I. M. Salimgareeva, and V. N. Yur'ev, Izv. Akad. Nauk SSSR, Ser. Khim., 938 (1979).
8. M. Christl, H. J. Reich, and J. D. Roberts, J. Am. Chem. Soc., 93, No. 14, 3463 (1971).
9. G. A. Tolstikov, N. A. Danilova, and M. S. Miftakhov, in: Synthesis and Investigation of the Prostaglandins. Abstracts of Lectures of the Xth All-Union Conference [in Russian], Riga (1982), p. 54.
10. N. A. Danilova, G. A. Tolstikov, M. S. Miftakhov, M. I. Lopp, and Yu. E. Lille, Dokl. Akad. Nauk SSSR, 273, No. 3, 620 (1983).