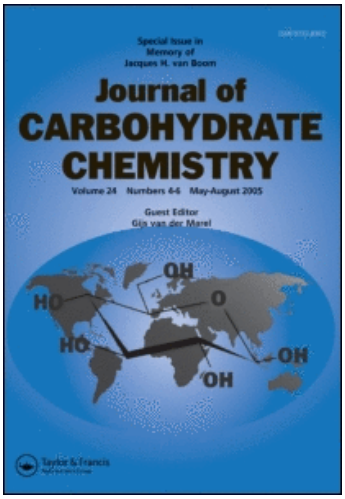

Journal of Carbohydrate Chemistry

Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713617200

Assignment of Anomeric Configuration and Identification of Carbohydrate Residues by ^{13}C NMR: Arabino- and Ribopyranosides and Furancsides

Ross C. Beier[a]; Bradford P. Mundy[b]
[a] U.S. Department of Agriculture, Veterinary Toxicology and Entomology Research Laboratory Agricultural Research Service, College Station, TX [b] Department of Chemistry, Montana State University, Bozeman, Montana

To cite this Article Beier, Ross C. and Mundy, Bradford P.(1984) 'Assignment of Anomeric Configuration and Identification of Carbohydrate Residues by ^{13}C NMR: Arabino- and Ribopyranosides and Furancsides', Journal of Carbohydrate Chemistry, 3: 2, 253 — 266
To link to this Article: DOI: 10.1080/07328308408058819
URL: http://dx.doi.org/10.1080/07328308408058819

J. CARBOHYDRATE CHEMISTRY, 3(2), 253-266 (1984)

ASSIGNMENT OF ANOMERIC CONFIGURATION AND IDENTIFICATION OF CARBOHYDRATE RESIDUES BY ^{13}C NMR:

ARABINO- AND RIBOPYRANOSIDES AND FURANOSIDES

Ross C. Beier

Veterinary Toxicology and Entomology Research Laboratory
Agricultural Research Service
U.S. Department of Agriculture
College Station, TX 77841

Bradford P. Mundy

Department of Chemistry, Montana State University
Bozeman, Montana 59715

Received May 31, 1983

ABSTRACT

A ^{13}C NMR fingerprint method previously developed for galactosides and glucosides is extended to arabinosides and ribosides. This approach demonstrates the capability of ^{13}C NMR to determine ring size and anomeric configuration in four isomeric arabinosides and ribosides.

INTRODUCTION

Due to the frequent incorporation of carbohydrates into complex natural products, it is desirable to have methods for

0732-8303/84/0302-0253$3.50/0

their structure determination that do not require degradation of the sample. Recent renewed interest in carbohydrate-containing natural products is being generated because of the impact of these molecules on man. Although commonly thought of as simply carriers of the active aglycone moieties, a developing theme may place a much greater emphasis on the role of the carbohydrate portion for the actual biological activity.

Thus, it is becoming increasingly important to be able to examine the total complex molecule (often isolated in minute quantity) by spectroscopic methods that will accurately define the sugar, ring form, and anomeric configuration. Because of the ubiquitous nature of carbohydrates in natural products chemistry, and the increasing number of research personnel with extremely varied backgrounds that are becoming involved with structural determinations, it is of importance to develop simple, accurate and consistent methods to help analyze spectral data on these compounds.

In a previous study,[1] correlation of the ^{13}C NMR resonances for α- and β-D-galacto- and glucopyranosides and furanosides permitted all of the possible isomers to be identified. By simultaneously observing resonances for all of the carbons in the carbohydrate moiety of the galacto- and glucosides, correlation diagrams (referred to as **fingerprints**) were constructed. These fingerprint diagrams could then be used to identify the carbohydrate moiety, ring size and anomeric configuration of "unknown"

carbohydrates. We now present the necessary data and means for applying this technique to glycosides of arabinose and ribose.

RESULTS AND DISCUSSION

Published ^{13}C NMR data for arabinosides and ribosides have been collected.[2-15] The ^{13}C NMR chemical shift resonances were used to construct a fingerprint diagram. The actual literature data for the carbohydrate residues in α- and β-D(L)-arabinopyranosides are presented in Table 1; the α- and β-D(L)-ribopyranosides are presented in Table 2; α- and β-D(L)-arabinofuranoside data are found in Table 3, and the information on the α- and β-D-ribofuranosides are found in Table 4. For each reported compound a value was tabulated for each carbon of the carbohydrate moiety (C-1 through C-5). Since downfield shifts from 7-10 ppm can be expected for carbons with O-methylation or O-glycosylation,[16] all carbons (C-2 - C-5) involved in these substitutions were not used in the determination of resonance intervals or means; however, carbons adjacent to these positions where substitution occurred were included in the resonance intervals and means. Data were also included from materials run in DMSO-d_6 and pyridine-d_5, since resonance values obtained using these solvents were within 1 ppm of the values obtained in D_2O.[2]

The fingerprint diagram incorporating the data from Tables 1-4 is presented in Figure 1. A rectangular box is drawn to enclose the maximum and minimum resonance values for each carbon

TABLE I. Reported ^{13}C Chemical Shift for the Carbohydrate Residues in α and β D(L)- Arabinopyranosides

Compound (reference)	Chemical shift[a]				
	C1	C2	C3	C4	C5
α-D(L)-arabinopyranosides					
methyl α-D(L)-arabinopyranoside (2)	105.1	71.8	73.4	69.4	67.3
methyl α-D-arabinopyranoside (3)	107.0	73.75	75.35	71.15	68.9
methyl α-D-arabinopyranoside (4)	104.05	70.85[b]	75.5[c]	68.35	66.15
methyl α-D-arabinopyranoside (5)	104.75	71.61	73.29	69.15	66.95
α-L-arabinopyranosyl in proacaciberin (17)[d]	104.4	71.5	73.0	68.9	66.9
methyl α-L-arabinoside (6)[e]	105.8	72.1	74.2	69.0	66.5
propyl α-L-arabinoside (6)[e]	104.7	72.1	74.1	69.1	66.5
isopropyl α-L-arabinoside (6)[e]	103.0	72.1	74.1	69.3	66.6
tert-butylcyclohexyl α-L-arabinoside (6)[e]	103.0	72.1	74.2	69.1	66.4
tert-butyl α-L-arabinoside (6)[e]	99.1	72.1	74.2	69.2	66.3
d-menthyl α-L-arabinoside (6)[e]	106.3	72.6	74.3	69.1	66.4
l-menthyl α-L-arabinoside (6)[e]	101.4	72.2	74.4	69.2	66.6
methyl α-L-arabinopyranoside (7)[e]	105.9	72.2	74.4	69.1	66.6
Mean	104.2	72.1	74.0	69.2	66.8
Standard Deviation	2.2	0.7	0.7	0.6	0.7

β-D-(L)-arabinopyranosides					
methyl β-D(L)-arabinopyraoside (2)	101.0	69.4	69.92	69.96	63.8
methyl β-D-arabinopyranoside (3)	102.65	70.95[b]	71.7	71.7[c]	65.35
methyl β-D-arabinopyranoside (4)	99.95	68.35[b]	69.05	69.05[c]	62.6
methyl β-D-arabinopyranoside (5)	100.74	69.15[b]	69.8	69.80[c]	63.39
β-arabinopyranosyl in quercetin 3-O-arabinopyranoside (8)[d,f]	101.8	65.9[b]	70.8	71.7[c]	64.1
methyl β-L-arabinopyranoside (6)[e]	102.1	70.0	70.5	70.9	63.9
propyl β-L-arabinopyranoside (6)[e]	100.9	70.1	70.7	71.0	64.1
isopropyl β-L-arabinopyranoside (6)[e]	99.0	70.1	70.6	71.1	64.1
tert-butylcyclohexyl β-L-arabinopyranoside (6)[e]	99.0	70.1	70.6	71.0	64.1
tert-butyl β-L-arabinopyranoside (6)[e]	95.1	70.0	70.7	71.1	63.8
d-menthyl β-L-arabinopyranoside (6)[e]	96.8	70.0	70.6	71.2	64.6
l-menthyl β-L-arabinopyranoside (6)[e]	102.8	70.0	71.0	71.0	64.4
methyl β-L-arabinopyranoside (7)[e]	102.0	70.1	70.4	70.8	63.9
Mean	100.3	69.6	70.5	70.8	64.0
Standard Deviation	2.3	1.2	0.6	0.8	0.6

[a]Relative to external TMS.
[b]These numbers have been interchanged with those designated c to conform with assignments by Gorin and Mazuerk (2).
[d]Assignments were made according to Gorin and Mazurek (2).
[e]Measurement was made in solutions of pyridine-d_5.
[f]Note: Original assignment considered this compound to be in the α-pyranoside form.

TABLE 2. Reported ^{13}C Chemical Shift Values for the Carbohydrate Residues in α - and β -D- Ribopyranosides

Compound (reference)	Chemical shift[a]				
	C1	C2	C3	C4	C5
α -D-Ribopyranosides					
Methyl α -D-ribopyranoside (5)	100.41	69.18	70.41	67.40	60.78
β -D-Ribopyranosides					
Methyl β -D-ribopyranoside (5)	103.07	71.0	68.6	68.6	63.9
Methyl β -D-ribopyranoside (3)	103.85	72.65[b]	70.4[c,d]	69.85[d]	65.55
Methyl β -D-ribopyranoside (9)	103.85	72.65[b]	69.85[d]	70.4[c,d]	65.55
Mean	103.6	72.1	69.6	69.6	65.0

[a] Relative to external TMS.
[b] These numbers have been interchanged with those designated to conform with assignments by Bock and Pedersen (5).
[d] These numbers may be interchangxed due to lack of positive assignments.

atom of the carbohydrate moiety (C-1 - C-5). A vertical line within the box shows the position of the mean value, and a horizontal bar expresses the standard deviation about the mean value. It becomes clear from examination of Figure 1 that each arabinoside isomer has a different set of intervals, as does each riboside isomer. There is only one compound representing the α-D-ribopyranosides, and as a result, only one value for each carbon was used in the construction of the correlation diagram. Without defined intervals for these compounds, the difference between methyl α- and β- D-ribopyranosides must be considered as marginal.

By using these intervals, one might be able to determine the anomeric configuration and ring size of the carbohydrate moieties for arabinosides and ribosides. Admittedly, the data are not as well-defined as those found in the galactosides and glucosides;[1] however, they should provide some help in examination of carbohydrate structure. We must comment that since the resonance intervals for the β - D-ribo- and arabino- pyranosides are so small, the fingerprint method should not be used as the sole evidence for structure.

In conclusion, the ^{13}C NMR chemical shift method for fingerprinting carbohydrates can be extended to other systems. A fingerprint derived from resonance intervals can be used to determine the difference between most isomeric forms of arabinosides and ribosides. It appears that all isomeric forms of arabinosides are

TABLE 3. Reported ^{13}C Chemical Shift Values for the Carbohydrate Residues in α- and β-D (L)-Arabinofuranosides

Compound (reference)	Chemical shift[a]				
	C1	C2	C3	C4	C5
α-D(L)-Arabinoranosides					
Methyl α-D-arabinofuranoside (2)	109.3	81.9	77.5	84.9	62.4
Methyl α-L-arabinofuranoside (10)	109.2	81.8	77.5	84.9	62.4
Methyl 2-O-methyl-α-D-arabinofuranoside (11)	107.3	91.6[d]	75.5	84.3	62.0
Methyl 3-O-methyl-α-D-arabinofuranoside (11)	109.6	78.8	87.8[d]	84.3	62.7
Methyl 5-O-methyl-α-D-arabinofuranoside (11)	109.3	81.7	77.8	83.1	73.0[d]
Methyl 2-O-isopropyl-α-D-arabinofuranoside (11)	108.2	87.7[d]	76.3	84.0	62.1
Methyl α-L-arabinofuranoside (12)	109.5	82.0	77.9	84.8	62.5
α -L-Arabinofuranosyl in avicularin (9)	108.1	82.1	77.2	86.22	61.0
Mean	108.8	81.4	77.1	84.6	62.2
Standard Deviation	0.8	1.3	0.9	0.9	0.6

β-D(L)-arabinofuranosides

Methyl β-D-arabinofuranoside (2)	103.2	77.5	75.7	83.1	64.2
Methyl β-L-arabinofuranoside (10)	103.1	77.4	75.7	82.9	62.4
Methyl 2-O-methyl-β-D-arabinofuranoside (11)	101.7	86.1[d]	74.6	83.3	64.2
Methyl 3-O-methyl-β-D-arabinofuranoside (11)	103.6	77.1	85.8[d]	82.5	64.8
Methyl 5-O-methyl-β-D-arabinofuranoside (11)	103.3	77.2	75.9	81.0	75.1[d]
Methyl 2-O-isopropyl-β-D-arabinofuranoside (11)	102.3	82.8[d] 82.6	74.8	82.8 82.6	64.4
Methyl β-L-arabinofuranoside (12)	103.3	77.9[b]	76.3[c]	83.1	64.3
Mean	102.9	77.4	75.5	82.7	64.1
Standard Deviation	0.7	0.3	0.7	0.7	0.8

[a]Relaative to external TMS.
[b]These numbers have been interchanged with those designated c to conform with assignments by Gorin and Mazurek (2).
[d]The downfield shift of this resonance is due to substitution.

TABLE 4. Reported ^{13}C Chemical Shift Values for the Carbohydrate Residues in α- and β-D-Ribofuranosides

Compound (reference)	Chemical shift[a]				
	C1	C2	C3	C4	C5
α-D-Ribofuranosides					
Methyl α-D-ribofuranoside (2)	104.2	72.1	70.8	85.8	62.2
Methyl α-D-ribofuranoside (10)	103.1	71.1	69.8	84.6	61.9
Methyl 2-O-methyl-α-D-ribofuranoside (11)	103.1	81.0[b]	69.4	86.3	62.6
Methyl 3-O-methyl-α-D-ribofuranoside (11)	104.1	71.8	80.1[b]	83.6	62.8
Methyl 5-O-methyl-α-D-ribofuranoside (11)	104.1	71.9	70.8	83.5	73.2[b]
Methyl 2-O-isopropyl-α-D-ribofuranoside (11)	103.6	77.1[b]	70.0	86.2	62.7
Methyl 3-O-isopropyl-α-D-ribofuranoside (11)	104.2	71.4	75.9[b]	84.0	62.3
Methyl α-D-ribofuranoside (18)	104.6	72.8	72.6	84.0	63.3
Methyl α-D-ribofuranoside (12)	104.3	72.5	72.3	83.7	63.0
Mean	103.9	71.9	70.8	84.6	62.6
Standard Deviation	0.5	0.6	1.2	1.1	0.4
β-D-Ribofuranosides					
Methyl β-D-ribofuranoside (2)	109.0	75.3	71.9	83.9	63.9
β-D-Ribofuranosyl in ribostamycin (13)	109.1	75.7	70.5	83.4	62.6
β-D-Ribofuranosyl in ribostamycin, pD=9.5 (13)	109.6	75.9	70.5	83.3	62.5
β-D-Ribofuranosyl in ribostamycin, $(H_2SO_4)_{3/2}$ (13)	111.0	76.1	70.0	83.3	62.1

Methyl β-D-ribofuranoside 910)	108.0	74.3	70.9	83.0	62.9
Methyl 2-O-methyl-β-D-ribofuranoside (11)	106.6	84.5[b]	71.1	84.5	63.6
Methyl 3-O-methyl-β-D-ribofuranoside (11)	109.2	72.8	81.3[b]	82.3	64.0
Methyl 5-O-methyl-β-D-ribofuranoside (11)	109.1	75.0	72.2	81.9	74.9[b]
Methyl 2-O-isopropyl-β-D-ribofuranoside (11)	108.0	80.7[b]	71.2	84.6	63.6
Methyl 3-O-isopropyl-β-D-ribofuranoside (11)	109.1	73.6	77.0[b]	82.4	63.5
Robofuranosyl in N-hexaacetyl-neomycin B (14)[c]	109.3	74.5	77.2[b]	82.4	62.2
Methyl β-D-ribofuranoside (18)	109.5	75.9	71.3	86.1	64.7
Ribofuranosyl in neomycin C (18)	110.3	74.6	82.5[b]	85.9	61.6
Methyl β-D-ribofuranoside (12)	109.2	75.6	71.0	85.8	64.4
Methyl β-D-ribofuranoside (15)[d]	108.3	74.42	71.13	83.79	63.31
Methyl β-D-ribofuranoside (9)	108.0	74.35	70.85	82.95	62.9
Mean	109.0	74.9	71.0	83.7	63.2
Standard Deviation	1.0	1.0	0.6	1.3	0.9

[a]Relative to external TMS.
[b]The downfield shift of this resonance is due to substitution.
[c]1,4-dioxane was the internal standard.
[d]Chemical shifts were obtained in DMSO-d_6 relative to internal TM.

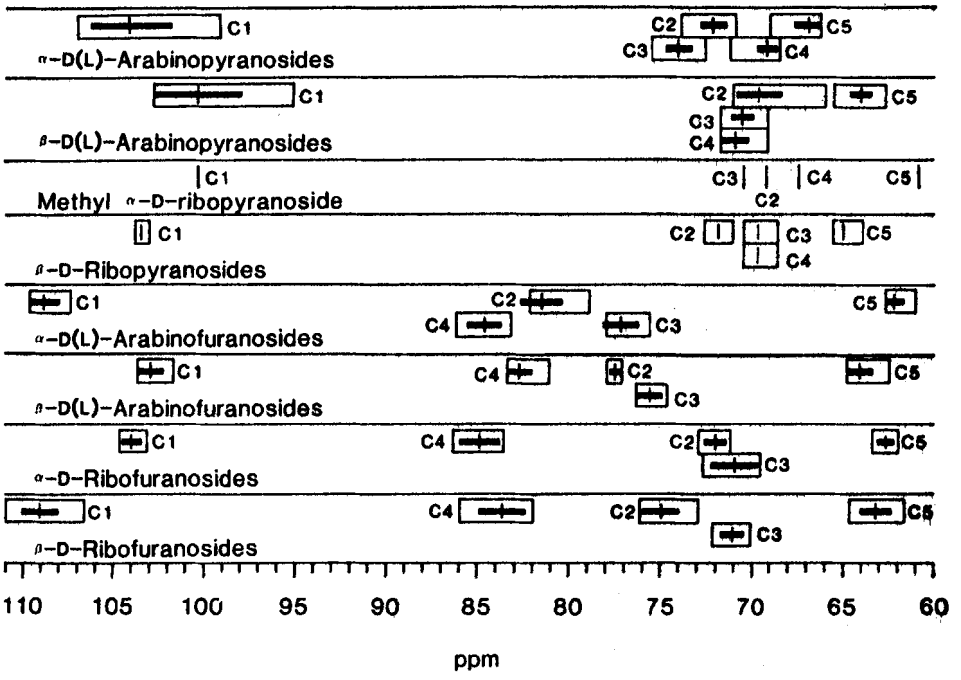

Figure 1. Chemical Shift Fingerprint Map

distinguishable. Since carbons adjacent to sites of O-substitution were included in this study, the method may be applicable to substituted carbohydrates; however, the large downfield shifting of the substituted carbon may preclude its direct assignment by this method.

ACKNOWLEDGMENTS

B.P.M. acknowledges the partial support of the Montana Agricultural Experimental Station and the NSF (ISP-8Ø1149) for his part of this work.

REFERENCES

1. R. C. Beier, B. P. Mundy and G. A. Strobel, Can. J. Chem., 58, 2800 (1980).
2. P. A. J. Gorin and M. Mazurek, Can. J. Chem., 53, 1212 (1975).
3. E. Breitmaier, W. Voelter, C. Jung and C. Tanzer, Chem. Ber., 104, 1147 (1971).
4. E. Breitmaier and W. Voelter, Tetrahedron, 29, 227 (1973).
5. K. Bock and C. Pedersen, Acta Chem. Scand. Ser. B, 29, 258 (1975).
6. K. Mizutani, R. Kasai and O. Tanaka, Carbohydr. Res., 87, 19 (1980).
7. S. Seo, Y. Tomita, K. Tori and Y. Yoshimura, J. Am. Chem. Soc., 100, 3331 (1978).
8. K. R. Markham, B. Ternai, R. Stanley, H. Geiger and T. J. Mabry, Tetrahedron, 34, 1389 (1978).
9. E. Breitmaier, G. Jung and W. Voelter, Chimia, 26, 136 (1972).
10. R. G. S. Ritchie, N. Cyr, B. Korsch, H. J. Koch and A. S. Perlin, Can J. Chem., 53, 1424 (1975).
11. P. A. J. Gorin and M. Mazurek, Carbohydr. Res., 48, 171 (1976).
12. T. Usui, S. Tsushima, N. Yamaoka, K. Matsuda, K. Tuzimura, H. Sugiyama, S. Seto, K. Fujieda and G. Miyajima, Agr. Biol. Chem., 38, 1409 (1974).
13. S. Omoto, S. Inouye, M. Kojima and T. Niida, J. Antibiot., 26, 717 (1973).

14. K. L. Rinehart, Jr., J. M. Malik, R. S. Nystrom, R. M. Stroshane, S. T. Truitt, M. Taniguchi, J. P. Rolls, W. J. Haak and B. A. Ruff, J. Am. Chem. Soc., 96, 2263 (1974).

15. Y. Wang and H. P. C. Hogenkamp, Carbohydr. Res., 76, 131 (1979).

16. D. E. Dorman and J. D. Roberts, J. Am. Chem. Soc., 93, 4463 (1971).

17. F. Nartey, L. Brimer and S. B. Christensen, Phytochemistry, 20, 1311 (1981).

18. N. Yamaoka, T. Usui, H. Sugiyama and S. Seto, Chem. Pharm. Bull., 22, 2196 (1974).