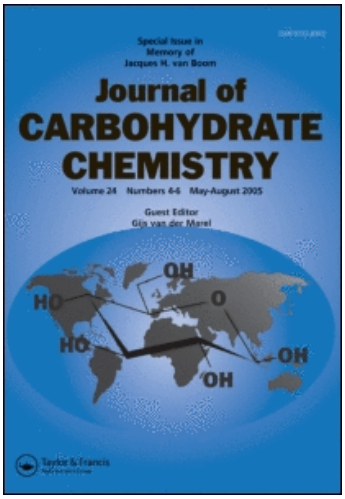


Journal of Carbohydrate Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713617200

Negativeion, Chemical-Ionization Mass Spectrometry of Sulfonic Acid Esters of Carbohydrates

Boyu Zhong[a]; Roger W. Binkley[a]; Edith R. Binkley[b]; Michael J. S. Tevesz[a]; Witold Winnik[a]
[a] Department of Chemistry, Cleveland State University, Cleveland, Ohio [b] Center For Carbohydrate Study, Oberlin, Ohio

To cite this Article Zhong, Boyu , Binkley, Roger W. , Binkley, Edith R. , Tevesz, Michael J. S. and Winnik, Witold(1998) 'Negativeion, Chemical-Ionization Mass Spectrometry of Sulfonic Acid Esters of Carbohydrates', Journal of Carbohydrate Chemistry, 17: 6, 823 — 834
To link to this Article: DOI: 10.1080/07328309808007458
URL: http://dx.doi.org/10.1080/07328309808007458

J. CARBOHYDRATE CHEMISTRY, 17(6), 823-834 (1998)

NEGATIVE-ION, CHEMICAL-IONIZATION MASS SPECTROMETRY OF SULFONIC ACID ESTERS OF CARBOHYDRATES

Boyu Zhong,[#] Roger W. Binkley,[#] Edith R. Binkley,[+]
Michael J. S. Tevesz,[#] and Witold Winnik[#]

[#]Department of Chemistry, Cleveland State University, Cleveland, Ohio 44115
[+]Center For Carbohydrate Study, 19 Hawthorne Dr., Oberlin, Ohio 44074

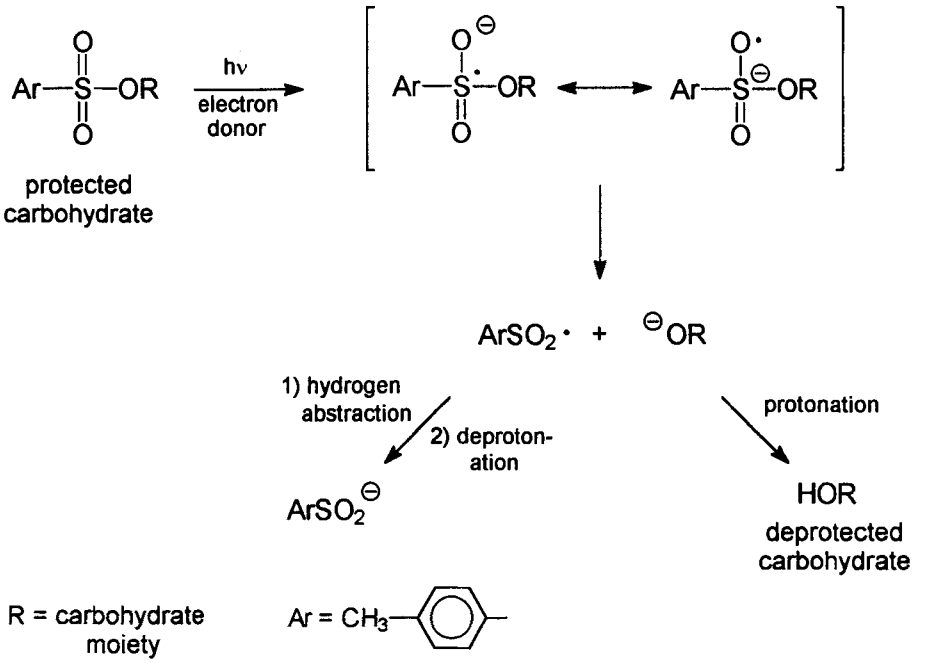
Received August 4, 1997 - Final Form March 17, 1998

ABSTRACT

Negative-ion, chemical-ionization mass spectra of *p*-toluenesulfonates **1-6**, 2-naphthalenesulfonates **7-10**, and *p*-nitrobenzenesulfonate **11** show that these compounds readily form radical anions in the gas phase. Regardless of the structure of the carbohydrate portion of the molecule, tosylate radical anions fragment by cleavage of the sulfur–carbon bond. Changes in the sulfonic acid portion of the molecule open new reaction pathways. The radical anions derived from compounds **7-10** break carbon–oxygen and sulfur–oxygen bonds in addition to the sulfur–carbon bond cleavage observed for *p*-toluenesulfonates.

INTRODUCTION

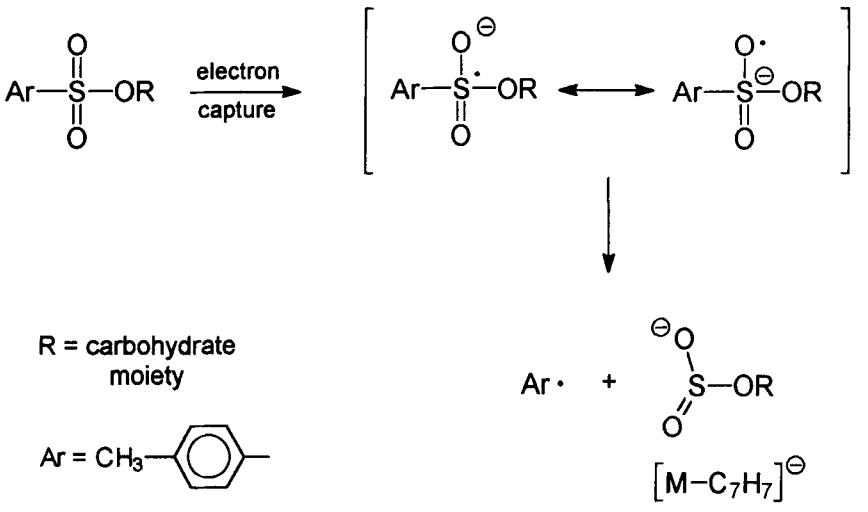
We have been investigating the mechanism of the photochemical reactions of carbohydrate tosylates for a number of years.[1-4] One of our early findings about these reactions was that irradiation of a tosylate in the presence of an electron donor produces a radical anion.[2,4] The radical anion then fragments to give the *p*-tolylsulfonyl radical and an alkoxide ion (Scheme 1). During these investigations we realized that tosylate radical anions could be generated in the gas phase by negative-ion, chemical-ionization mass spectrometry (NICI-MS); consequently, mass spectrometry provided a tool for studying the reactivity of these radical anions in the absence of solvent.



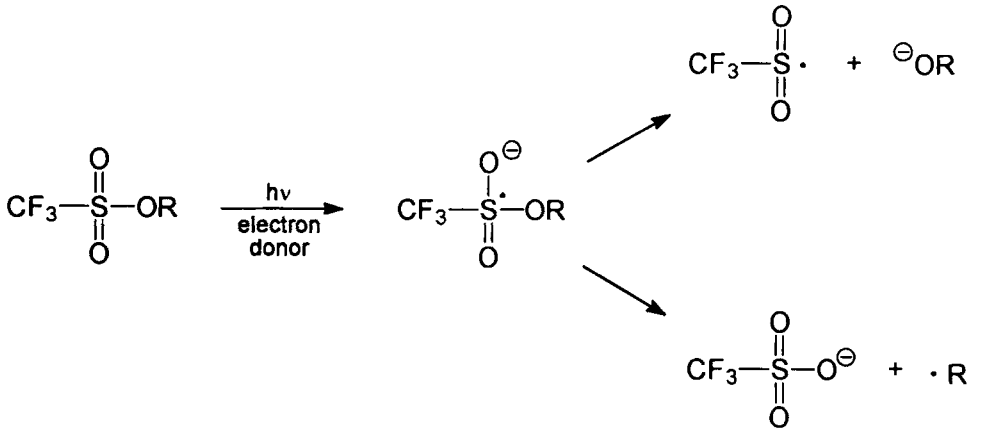
Scheme 1

When we investigated several carbohydrate tosylates by NICI-MS, we found that their radical anions reacted quite differently in the gas phase than in solution. Reaction in solution caused sulfur–oxygen bond cleavage, as pictured in Scheme 1, but in the absence of solvent, bond cleavage was exclusively between sulfur and carbon (Scheme 2).[2,4] This difference in reactivity was attributed to the difference in stability of an alkoxide ion when generated under different reaction conditions.[2] Alkoxide ions form readily in polar solvents because solvation stabilizes the negative charge, but in the gas phase without solvent stabilization alkoxide ions form with difficulty.[5]

One characteristic of solution phase reactivity of tosylate radical anions is that the same reaction occurs regardless of the structure of the carbohydrate portion of the molecule (Scheme 1).[1-4,6,7] In contrast, change in the structure of the noncarbohydrate substituent attached to the sulfonyl group can cause different reactions to occur.[8,9] For example, bonding of a trifluoromethyl[8] (Scheme 3) or pentafluorophenyl[9] substituent to the sulfonyl group opens

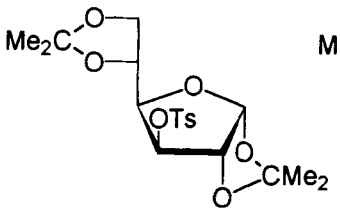


Scheme 2

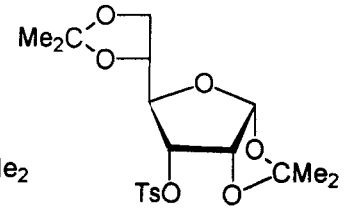


Scheme 3

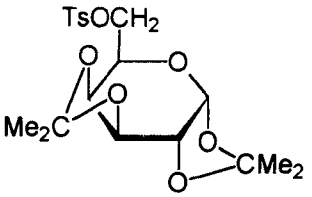
new reaction pathways. These findings raised the possibility that structural changes in the sulfonic acid portion of carbohydrate sulfonates also might cause new reactions in the gas phase. When we conducted the necessary experiments to test this possibility, we found that new reactions did occur.



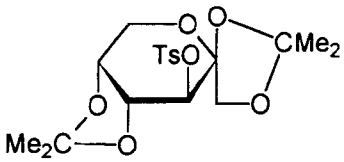
1



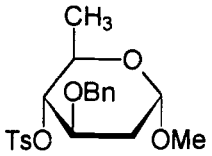
2



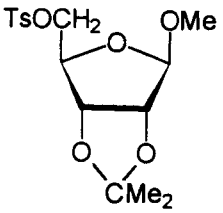
3



4



5



6

Ts = $CH_3C_6H_5SO_2-$ Bn = $C_6H_5CH_2-$

RESULTS AND DISCUSSION

The NICI mass spectra of tosylates **1-6**, given in tabular form in Table 1, have several features in common. First, the molecular ions from these compounds are sufficiently unstable that their relative abundances are quite low. Also, the base peak in the spectrum of each compound arises from loss of a tolyl radical (C_7H_7 •) from the molecular ion. The structure assigned to the $[M\text{-}C_7H_7]^-$ ion is shown in Scheme 2. This assignment is supported by collisionally activated dissociation (CAD), which in each case causes the loss of sulfur dioxide to give an $[M\text{-}C_7H_7\text{-}SO_2]^-$ ion (Table 2). This ion is the anion of the alcohol from which the tosylate originally was synthesized. The further fragmentation of the $[M\text{-}C_7H_7\text{-}SO_2]^-$ ion produces the same ions as those formed by NICI-MS of anions generated from the alcohols themselves. Since the molecular ions from compounds **1-6** all fragment in the same way, the structural changes found within the carbohydrate portions of these molecules have no effect on the basic fragmentation pattern.

Table 1. Negative-Ion, Chemical-Ionization Mass Spectra of Tosylates **1-6**

m/z	**1**	**2**	**3**	**4**	**5**	**6**
414 (M)	0.42	2.09	0.68	2.33		
406 (M)					<0.10	
358 (M)						1.15
323	100.00[a]	100.00[a]	100.00[a]	100.00[a]		
315					100.00[a]	
267						100.00[a]
259	0.58	0.75	0.65	0.63		
240						15.46
201	1.25	21.47	3.10	0.37		

a. $[M\text{-}C_7H_7]^-$ ion

Several changes did occur in the NICI mass spectra of sulfonic acid esters when the tolyl group was replaced by a 2-naphthyl group. One change was that the radical anions from the 2-naphthalenesulfonates were more stable than those from the tosylates; consequently, molecular ions were present in greater relative abundances (Table 3). This meant that it was possible to verify by CAD the proposal (Scheme 2) that sulfonate radical anions fragment by loss of an aryl radical. (CAD of tosylate radical anions was not possible due to their low relative abundances.)

Another characteristic of naphthalenesulfonate radical anions is that they exhibit new fragmentation pathways. The exclusive reaction for tosylate radical anions is cleavage of the C–S bond in such a manner that the negative charge remains with the carbohydrate-containing fragment (Scheme 2). Although this type of reaction is observed for naphthalenesulfonates also, it is accompanied by two other modes of fragmentation (Scheme 4). One of these produces an ion with $m/z = 207$ and the other an ion with $m/z = 191$. The first of these ions was determined to be the 2-naphthalenesulfonate anion by comparison of the CAD spectrum

Table 2. Collisionally Activated Dissociation (CAD) of $[M\text{-}C_7H_7]^-$ Ions From Compounds **1-6**.

m/z	**1**	**2**	**3**	**4**	**5**	**6**
323	100.00[a]	100.00[a]	100.00[a]	100.00[a]		
315					100.00[a]	
267						100.00[a]
259	70.23[b]	96.97[b]	1.54[b]	92.57[b]		
251					55.93[b]	
203						40.57[b]
201	48.75	1.96	4.99	59.24		
171			19.50			11.56
145						19.50
143	7.78				2.08	
125				4.94		
113			10.26			65.49
111					39.21	
85			19.97			32.75
83	1.58		4.23		2.07	14.76
71				2.31		
65			21.14			64.79
59	3.94					

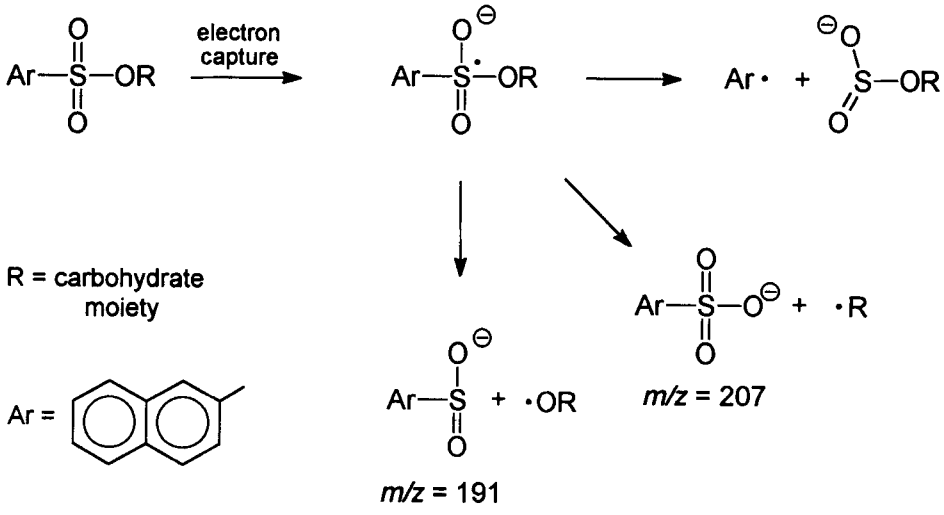
a. $[M\text{-}C_7H_7]^-$ ion.
b. $[M\text{-}C_7H_7\text{-}SO_2]^-$ ion.

of this ion with the spectrum of the anion produced by deprotonation of 2-naphthalenesulfonic acid (Scheme 5).[10] The 2-naphthalenesulfinate structure was assigned to the second ion on the basis of its mass to charge ratio [*m/z* = 191] and its collisionally activated dissociation to form $[SO_2]^-$ and $[C_{10}H_7]^-$ (Scheme 6).

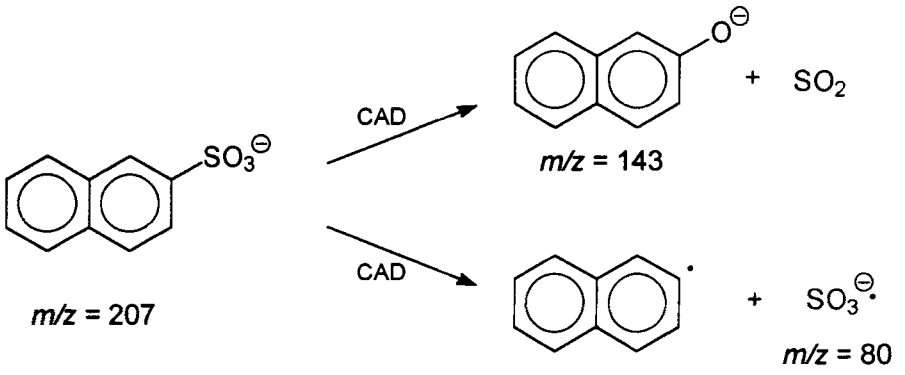
Table 3. Negative-Ion, Chemical-Ionization Mass Spectra of Compounds 7-11

m/z	7	8	9	10	11
450 (M)	8.06				
445 (M)					100.00
442 (M)		85.44	1.54	83.46	
323	100.00[a]				
315		100.00[a]	26.62[a]	100.00[a]	
207	20.14	56.56	100.00	66.23	
191		4.01	34.41	2.27	

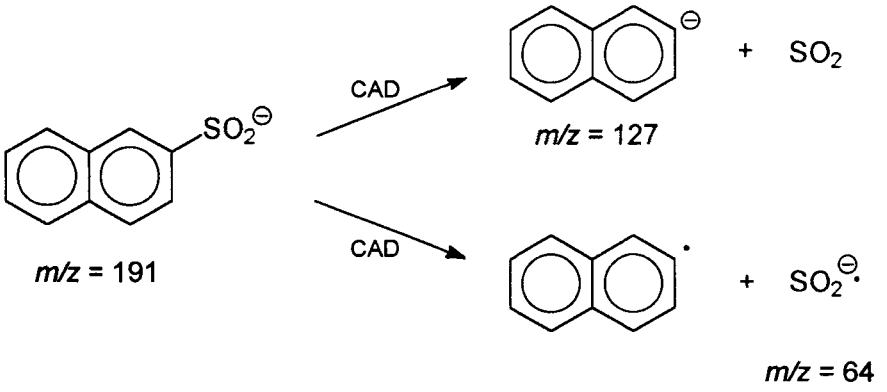
a. $[M\text{-}C_7H_7]^-$ ion



Scheme 4

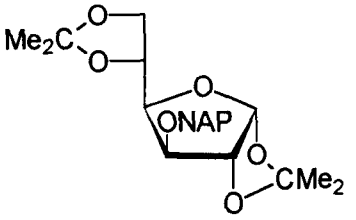


Scheme 5

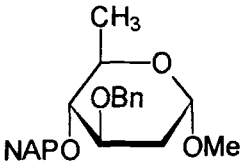


Scheme 6

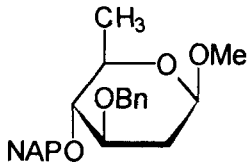
The difference in gas-phase reactivity between the radical anions of carbohydrate sulfonates is related to radical-anion stability. From information gathered on a wide variety of compounds, Bartmess concluded that the necessary conditions for stable radical-anion formation are met by a variety of compounds, including those with aromatic rings that have at least one, good electron-accepting group (e.g., a nitro group) and by polycyclic aromatic hydrocarbons.[11] The ability of the naphthalenesulfonates **7**-**10** and of the *p*-nitrobenzenesulfonate **11** to form stable radical anions, therefore, is consistent with the Bartmess generalizations.



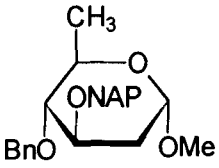
7



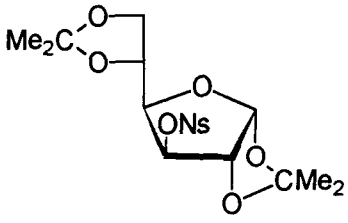
8



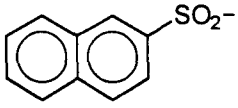
9



10



11

NAP = 

Ns = *p*-$NO_2C_6H_4SO_2$-

The stability of daughter ions is critical in determining the pathway for radical anion fragmentation. Daughter ion formation is favored by strong electron-withdrawing groups and by structures effectively stabilized by ion polarizability. (Ion polarizability is the ability of atoms to undergo electronic distortion to accommodate charge and is especially important in gas phase reactions where solvent is not available to help stabilize charge.) Since the more atoms that are available to accept a negative charge the more stable an anion will be,[12] the greater number of carbon atoms in the 2-naphthyl group, when compared to the *p*-tolyl group, offers greater possibility for anion stabilization due to polarizability. The 2-naphthyl π-system provides a pathway for charge delocalization in addition to that created by the σ-framework. The fragmentation of 2-naphthalenesulfonate radical anions to produce the corresponding sulfonate (m/z = 207) and sulfinate (m/z = 191) ions, when similar fragmentation of *p*-toluenesulfonate radical ions does not occur, is a result of the greater stabilizing effect of the 2-naphthyl group.

In summary, the results from the study of NICI-MS of compounds **1-11** provide new understanding of the fragmentation of radical anions of carbohydrate sulfonates in the gas phase. They show that simple changes in the structure of the carbohydrate portion of a radical anion have no effect on the basic fragmentation of the molecular ion, but changes in the structure of the sulfonic acid portion of the radical ion can cause new reactions to occur.

EXPERIMENTAL

General Procedures. Mass spectra were obtained with a Finnigan TSQ-45 triple quadrupole mass spectrometer under the following conditions: source temperature, 120 °C; ammonia gas pressure, 0.35 Torr; electron energy 70 eV. The collision cell pressure was 1.3 mTorr and the collision energy was 10 eV. ^{1}H NMR (300 MHz) and ^{13}C NMR (75 MHz) spectra were determined in $CDCl_3$.

Preparation of Compounds 1-11. Compounds **1-11** were prepared according to the indicated literature procedures: **1**,[13] **2**,[14] **3**,[15] **4**,[16] **5**,[17] **6**,[18] **7**,[19] **8-10**,[20] **11**.[21] NMR data for compounds **7-10** are included because these data are not given in the references describing their preparation.

NMR Spectra of Naphthalenesulfonates 7-10.

1,2:5,6-Di-*O*-isopropylidene-3-*O*-(2-naphthylsulfonyl)-α-D-glucofuranose (7). ^{1}H NMR ($CDCl_3$): δ 0.84, 0.90, 1.32, 1.40 (CH_3), 3.84-4.06 (H_4, H_5, H_6, H_6), 4.85 (H_3, $J_{2,3}$ < 1.0 Hz), 4.91 (H_2, $J_{1,2}$ = 3.5 Hz), 5.95 (H_1, $J_{1,2}$ = 3.5 Hz), 7.60-8.02. 8.54 (aromatic). ^{13}C NMR: δ 24.39, 26.21, 26.32, 26.61 (CH_3), 67.02 (C_6), 71.65 (C_5), 79.78 (C_4), 82.31 (C_3), 83.48 (C_2), 105.11 (C_1), 108.97, 112.56 (OCO), 123.04, 127.76, 127.89, 129.36, 129.45, 129.54, 130.29, 131.92, 132.42, 135.48 (aromatic).

Methyl 3-*O*-Benzyl-2,6-dideoxy-4-*O*-(2-naphthylsulfonyl)-α-D-*arabino*-hexopyranoside (8). ^{1}H NMR ($CDCl_3$): δ (1.36 (H_6, $J_{5,6}$ = 6.3 Hz), 1.65 (H_{2a}, $J_{1,2a}$ = 3.7 Hz, $J_{2a,3}$ = 11.3 Hz, $J_{2a,2e}$ = 13.1 Hz), 2.17 (H_{2e}, $J_{1,2e}$ = 1.0 Hz, $J_{2e,3}$ = 5.2 Hz), 4.48 (H_4, $J_{3,4}$ = 9.4 Hz, $J_{4,5}$ = 9.4 Hz), 3.27 (CH_3O), 3.80 (H_5), 3.80 (H_3), 4.71 (H_1), 4.12 (CH_2, J_{CH2} = 11.9 Hz), 6.87-7.88, 8.46 (aromatic). ^{13}C NMR: δ 18.02 (C_6), 35.78 (C_2), 54.72 (CH_3O), 65.79 (C_5), 71.08 (CH_2), 85.20 (C_4), 73.91 (C_3), 97.90 (C_1), 122.86, 127.18, 127.34, 127.48, 127.93, 128.04, 128.97, 129.02, 129.33, 131.87, 135.06, 137.85 (aromatic).

Methyl 3-*O*-Benzyl-2,6-dideoxy-4-*O*-(2-naphthylsulfonyl)-β-D-*arabino*-hexopyranoside (9). ^{1}H NMR ($CDCl_3$): δ 1.39 (H_6, $J_{5,6}$ = 6.2 Hz), 1.58 (H_{2a}, $J_{1,2a}$ = 9.8 Hz, $J_{2a,3}$

= 11.8 Hz, $J_{2a,2e}$ = 12.7 Hz), 2.21 (H_{2e}, $J_{1,2e}$ = 2.0 Hz, $J_{2e,3}$ = 5.2 Hz), 4.46 (H_4, $J_{3,4}$ = 9.2 Hz, $J_{4,5}$ = 9.2 Hz), 3.45 (CH_3O), 3.47 (H_5), 3.48 (H_3), 4.29 (H_1), 4.03, 4.20 (CH_2, J_{CH2} = 12.1 Hz), 6.86-7.91, 8.49 (aromatic). ^{13}C NMR: δ 18.04 (C_6), 36.81 (C_2), 56.62 (CH_3O), 70.15 (C_5), 70.81 (CH_2), 84.79 (C_4), 75.35 (C_3), 100.36 (C_1), 122.92, 127.41, 127.57, 127.94, 128.16, 129.03, 129.07, 129.36, 131.89, 135.11, 137.38 (aromatic).

Methyl 4-*O*-Benzyl-2,6-dideoxy-3-*O*-(2-naphthylsulfonyl)-α-D-*arabino*-hexopyranoside (10). ^1H NMR ($CDCl_3$): δ 1.21 (H_6, $J_{5,6}$ = 6.3 Hz), 1.90 (H_{2a}, $J_{1,2a}$ = 3.6 Hz, $J_{2a,3}$ = 11.5 Hz, $J_{2a,2e}$ = 12.9 Hz), 2.35 (H_{2e}, $J_{1,2e}$ = 1.4 Hz, $J_{2e,3}$ = 5.4 Hz), 3.15 (H_4, $J_{3,4}$ = 8.9 Hz, $J_{4,5}$ = 9.1 Hz), 3.25 (CH_3O), 3.67 (H_5), 4.96 (H_3), 4.66 (H_1), 4.45, 4.64 (CH_2, J_{CH2} = 10.9 Hz), 7.01-7.90, 8.50 (aromatic). ^{13}C NMR: δ 17.94 (C_6), 36.88 (C_2), 54.56 (CH_3O), 67.01 (C_5), 74.95 (CH_2), 81.80 (C_4), 80.80 (C_3), 97.56 (C_1), 122.52, 127.64, 127.66, 127.98, 128.18, 129.18, 129.40, 129.58, 131.93, 135.20, 137.50 (aromatic).

ACKNOWLEDGMENT

RWB wishes to thank the Oberlin College Affiliate Scholar Program for providing access to the college libraries during preparation of this manuscript.

REFERENCES

1. R. W. Binkley, *J. Org. Chem.*, **50**, 5646 (1985).
2. J. Masnovi, D. J. Koholic, R. J. Berki and R. W. Binkley, *J. Am. Chem. Soc.*, **109**, 2851 (1987).
3. R. W. Binkley and D. J. Kohleic, *J. Org. Chem.*, **54**, 3577 (1989).
4. R. J. Berki, E. R. Binkley, R. W. Binkley, D. G. Hehemann, D. J. Koholic and J. Masnovi, *J. Carbohydr. Chem.*, **15**, 33 (1996).
5. J. E. Bartmess, R. T. McIver in *Gas Phase Ion Chemistry*, Vol 2; M. T. Bowers, Ed; Academic Press, New York, 1979, pp 87.
6. R. W. Binkley, *Adv. Carbohydr. Chem. Biochem.*, **38**, 105 (1981).
7. R. W. Binkley and T. W. Flechtner in *Synthetic Organic Photochemistry;* W. M. Horspool, Ed.; Plenum, New York, 1984, p 377.
8. X.-G. Liu, R. W. Binkley and P. Yeh, *J. Carbohydr. Chem.*, **11**, 1053 (1992).
9. S. Daun, E. R. Binkley and R. W. Binkley, *J. Carbohydr. Chem.*, **14**, 1029 (1995).
10. R. W. Binkley, T. W. Flechtner, M. J. S. Tevesz, W. Winnik and B. Zhong, *Org. Mass. Spectrom.*, **28**, 769 (1993).
11. J. E. Bartmess, *Mass Spectrom. Rev.*, **8**, 297 (1989).
12. F. A. Carey and R. J. Sundberg, *Advanced Organic Chemistry;* Plenum Press, New York, 1990, p 242.
13. I. E. Muskat, *J. Am. Chem. Soc.*, **56**, 2449 (1934).

14. A. Nishida, T. Hamada and O. Yonemitsu, *Chem. Pharm. Bull.*, **38**, 2977 (1990).
15. A. L. Raymond and E. F. Schroeder, *J. Am. Chem. Soc.*, **70**, 2785 (1948).
16. M. Sarel-Imber and E. D. Bergmann, *Carbohydr Res.*, **27**, 73 (1973).
17. M. Hornyák, I. F. Pelyvás and F. J. Sztaricskai, *Tetrahedron Lett.*, **34**, 4087 (1993).
18. P. A. Levene and E. T. Stiller, *J. Biol. Chem.*, **106**, 421 (1934).
19. K. Freudenberg, O. Burkhart and E. Braun, *Ber.*, **59B**, 714 (1926).
20. H. Ohle, E. Euler and R. Lichtenstein, *Ber.*, **62B**, 2885 (1929).
21. B. Coxon and L. Hough, *J. Chem. Soc.*, 1643 (1961).