actions, gram-scale reactions afforded the corresponding products in analogously excellent yields.

Under the above-described condition, olefins were recovered unchanged as exemplified by the competitive reaction of 1-dodecyne (**1b**) and 1-dodecene. Treatment of an equimolar mixture of **1b** and 1-dodecene under the above-described condition for 1 h afforded 2-dodecanone (**2b**) in 96% yield and 1-dodecene was recovered almost quantitatively. Other products could not be detected by ^{1}H NMR analysis of the crude product.

A gold(I) complex was not effective for the hydration of acetylenes; upon substituting $KAu(CN)_2$ in place of $NaAuCl_4$, alkynes were not hydrated and were recovered unchanged.

Alkynes **1** were directly converted to dimethyl acetals **4** and **5** in excellent yields by the addition of 2 equiv of methanol, when the reaction was carried out in anhydrous methanol (Scheme II). The dimethyl acetal of the methyl ketone is obtained exclusively from 1-alkyne. Examples are shown in Table II. Acetal formation from 1-alkynes described here can be applied to gram-scale reaction; 2,2-dimethoxydodecane (**4b**) was obtained in 89% yield from 5 g (30.1 mmol) of 1-dodecyne (**1b**).

Although dimethyl acetals were successfully obtained by the reaction as above, direct conversion of alkynes to cyclic acetals even by the same treatment with 1 equiv of diols was not successful. However, as dimethyl acetals can be converted into other cyclic acetals, including acetals derived from optically active diols,[17-19] the above-described acetal preparation from acetylene should be useful in organic synthesis.

Experimental Section

^{1}H NMR were measured at 200 MHz.

Hydration of an Alkyne (General Procedure). To a stirring solution of an alkyne (6 mmol) and water (1 mL) in 10 mL of methanol was added $NaAuCl_4 \cdot 2H_2O$ (48 mg, 0.12 mmol, 0.02 equiv), and the mixture was heated at reflux for 1 to 10 h. The reaction mixture was concentrated under reduced pressure and the residue was diluted with ether and washed with a 1:1 mixture of brine and aqueous ammonia. The ethereal solution was dried over Na_2SO_4 and concentrated to give the product.

1-(7-Octynyl)-1-cyclohexanol (1d): bp 140 °C (2 mmHg, Kugelrohr); ^{1}H NMR ($CDCl_3$) δ 1.20–1.75 (20 H, m), 1.94 (1 H, t, J = 2.5 Hz), 2.20 (2 H, dt, J = 2.5, 6.8 Hz); IR (neat) 3550–3100, 3250 cm^{-1}. Anal. Calcd for $C_{14}H_{24}O$: C, 80.71; H, 11.61. Found: C, 80.62; H, 11.86.

8-(1-Hydroxycyclohexyl)-2-octanone (2d): bp 145 °C (2 mmHg, Kugelrohr); ^{1}H NMR ($CDCl_3$) δ 1.10–1.68 (20 H, m), 2.04 (3 H, s), 2.33 (2 H, t, J = 6.1 Hz); IR (neat) 3620–3100, 1710 cm^{-1}. Anal. Calcd for $C_{14}H_{26}O_2$: C, 74.29; H, 11.58. Found: C, 74.31, H, 11.78.

1-Ethynylcyclohexyl acetate (1g): bp 100 °C (2 mmHg, Kugelrohr); ^{1}H NMR ($CDCl_3$) δ 1.25–2.23 (10 H, m), 2.05 (3 H, s), 2.61 (1 H, s); IR (neat) 3280, 2105, 1744, 1368, 1264, 1230, 1145, 1043, 1025, 956 cm^{-1}. Anal. Calcd for $C_{10}H_{14}O_2$: C, 72.26; H, 8.48. Found: C, 72.26; H, 8.54.

1-Acetoxycyclohexyl methyl ketone (2g): bp 105 °C (2 mmHg, Kugelrohr); ^{1}H NMR ($CDCl_3$) δ 1.40–1.78 (10 H, m), 2.10 (3 H, s), 2.13 (3 H, m); IR (neat) 1738, 1732, 1715, 1369, 1266, 1138 cm^{-1}. Anal. Calcd for $C_{10}H_{16}O_3$: C, 65.19; H, 8.75. Found: C, 65.30; H, 9.00.

3-Acetoxy-1-octyne (1i): bp 80 °C (2 mmHg, Kugelrohr); ^{1}H NMR ($CDCl_3$) δ 0.90 (3 H, t, J = 6.0 Hz), 1.26–1.90 (8 H, m), 2.07 (3 H, s), 2.46 (1 H, d, J = 2.3 Hz), 5.36 (1 H, dt, J = 2.3, 6.6 Hz); IR (neat) 3280, 2120, 1740, 1372, 1236, 1120, 1020 cm^{-1}. Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.29; H, 9.54.

3-Acetoxy-2-octanone (2i): bp 98 °C (8 mmHg); ^{1}H NMR ($CDCl_3$) δ 0.87 (3 H, t, J = 6.0 Hz), 1.23–1.80 (8 H, m), 2.12 (3 H, s), 2.13 (3 H, s), 4.98 (1 H, dd, J = 5.0, 7.4 Hz); IR (neat) 1743, 1736, 1241, 1120, 1078, 1040 cm^{-1}. Anal. Calcd for $C_{10}H_{18}O_3$: C, 64.49; H, 9.74. Found: C, 64.35; H, 9.79.

Hydration of Alkyne in Gram-Scale Reaction. To a solution of 1-dodecyne (5 g, 30.1 mmol) and water (6 mL) in methanol (60 mL) was added $NaAuCl_4 \cdot 2H_2O$ (240 mg, 0.60 mmol, 0.02 equiv), and the whole was heated at reflux for 1 h. After removal of methanol under reduced pressure from the reaction mixture, the residue was diluted with ether and washed with a 1:1 mixture of brine and aqueous ammonia. The ethereal solution was dried over Na_2SO_4 and concentrated. Distillation [bp 107 °C (8 mmHg)] of the concentrate gave 4.6 g of 2-dodecanone (25 mmol, 83% yield).

By the analogous treatment of 3-acetoxy-1-octyne (5 g, 29.8 mmol) with $NaAuCl_4 \cdot 2H_2O$ (237 mg, 0.60 mmol, 0.02 equiv) in a refluxing mixture of methanol (60 mL) and water (6 mL) for 1 h, 4.8 g of 3-acetoxy-2-octanone (25.8 mmol, 87% yield) was isolated by distillation [bp 98 °C (8 mmHg)].

Competitive Hydration of 1-Dodecyne and 1-Dodecene. A mixture of 415 mg (2.5 mmol) of 1-dodecyne and 420 mg (2.5 mmol) of 1-dodecene was treated with 20 mg of $NaAuCl_4 \cdot 2H_2O$ (0.05 mmol, 0.02 equiv) in refluxing methanol (10 mL, containing ca. 10% H_2O) for 1 h. The reaction mixture was worked up as described above to give 817 mg of oily product, which contained 441 mg (95% yield) of 2-octanone and 376 mg (90% recovery) of 1-dodecene.

Direct Formation of Dimethyl Acetal from an Alkyne (General Procedure). A solution of an alkyne (5 mmol) and $NaAuCl_4 \cdot 2H_2O$ (40 mg, 0.1 mmol, 0.02 equiv) in anhydrous methanol (10 mL) was heated at reflux for 1 h to 10 h. To the cooled reaction mixture was added triethylamine (1 mL), and the solution was then concentrated in vacuo. The residue was diluted with ether and washed with a 1:1 mixture of brine and aqueous ammonia. The ethereal solution was dried over Na_2SO_4 and concentrated to afford the product.

1-(7,7-Dimethoxyoctyl)cyclohexanol (4d): bp 140 °C (1 mmHg, Kugelrohr); ^{1}H NMR ($CDCl_3$) δ 1.16 (3 H, s), 1.20–1.75 (22 H, m), 3.09 (6 H, s); IR (neat) 3650–3200 cm^{-1}. Anal. Calcd for $C_{16}H_{32}O_3$: C, 70.54; H, 11.84. Found: C, 70.53; H, 11.87.

7,7-Dimethoxytetradecane (4i = 5i): bp 160 °C (2 mmHg, Kugelrohr); ^{1}H NMR (C_6D_6) δ 0.89 (3 H, t, J = 6.5 Hz), 0.90 (3 H, t, J = 6.5 Hz), 1.15–1.80 (22 H, m), 3.10 (6 H, s); IR (neat), 1380, 1275, 1090 cm^{-1}. Anal. Calcd for $C_{16}H_{34}O_2$: C, 74.36; H, 13.26. Found: C, 74.49; 13.39.

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Synthesis of Methyl- and Methoxy-Substituted β-D-Ribofuranosylnaphthalene Derivatives by Lewis Acid Catalyzed Ribofuranosylation

Norimitsu Hamamichi*[,1] and Tadashi Miyasaka

School of Pharmaceutical Sciences, Showa University, Hatanodai 1-5-8, Shinagawa-ku, Tokyo 142, Japan

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Lewis acid catalyzed C-ribofuranosylation is an important synthetic introduction to naturally occurring *C*-

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Table I. ^{1}H NMR Spectral Data for Sugar Moieties of 4 and 9 in $CDCl_3$ ppm (Hz)

compd	H-1′	H-2′	H-3′	H-4′	H-5′	OH	=C(Me)$_2$ (Δδ)
4a	5.61 (d, J = 4)	4.73–5.61 (m)		4.22 (m)	3.88–3.99 (m)	1.74 (s)	1.35 1.69 (0.34)
4b	5.79 (d, J = 4)	5.13 (dd, J = 6, 4)	4.85 (d, J = 6)	4.46 (t, J = 4)	3.79 (d, J = 6)	1.71 (s)	1.23 1.36 (0.13)
9a	6.25 (br s)	4.69 (dd, J = 6, 2)	4.47 (t, J = 6)	3.89–4.24 (m)		1.78 (s)	1.30 1.64 (0.34)

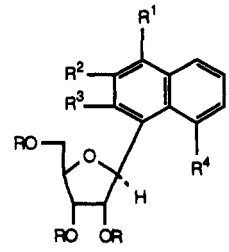
furanosides as well as their analogues. It is known that *C*-ribofuranosyl derivatives of benzene[2] and naphthalene[3] are prepared mainly as the β anomer by a stannic chloride catalyzed ribofuranosidic coupling reaction. Occasionally, however, the β anomer does not predominate. For instance, the reaction of 8-ethyl-1-methoxybenzo[*d*]naphtho[1,2-*b*]pyran-6-one with 1,2,3,5-tetra-*O*-acetyl-β-D-ribofuranose in the presence of stannic chloride gave the α- and β-*C*-ribosides as a 1:1 anomeric mixture.[4] Martin et al.[5] have reported an alternative method for the preparation of *C*-furanosides using the reaction of substituted sugars with organosilyl reagents in the presence of stannic chloride. The reaction of substituted naphthalenes with 1-*O*-acetyl-2,3,5-tri-*O*-benzoyl-β-D-ribofuranose (**1**) in the presence of stannic chloride has not, however, been described, although recently Suzuki et al.[6] reported a Friedel–Crafts coupling reaction of four methoxy-substituted naphthalenes and glycosyl fluoride.

In a previous publication, we described the synthesis of 3-phenyl-4-(β-D-ribofuranosyl)pyrazole and the reaction of ribosyl bromide with heavy metal acetylides.[7] In the present paper, we describe the synthesis of *C*-ribofuranosides from the reaction of methyl- and methoxy-substituted naphthalenes with **1** in the presence of stannic chloride (Chart I).

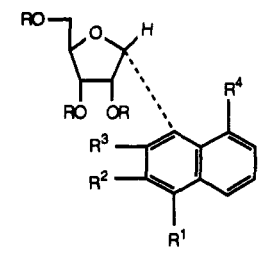
Results and Discussion

Reaction of α-methylnaphthalene with **1** in the presence of 1 M stannic chloride in benzene for 14 h at room temperature gave 4-(2,3,5-tri-*O*-benzoyl-β-D-ribofuranosyl)-1-methylnaphthalene (**2a**) in 79% yield as the major product and its α anomer **2b** in 8.3% yield as the minor product after purification by column chromatography. Subsequent deprotection of the benzoyl groups with sodium methoxide gave the corresponding 1-methyl-4-(β-D-ribofuranosyl)-naphthalene (**3a**) in 73% yield and its α anomer **3b** in 83% yield. In the ^{1}H NMR spectrum, the H-2 signals of **3a** and **3b** appeared as a doublet at δ 7.32 (J = 7 Hz) and at δ 7.35 (J = 7 Hz), respectively. Also, it is known that the Friedel–Crafts acylation of α-methylnaphthalene gave 1-acetyl-4-methylnaphthalene.[8] On the basis of the ^{1}H NMR spectra and Friedel–Crafts acylation, it is indicated that the ribofuranosyl moieties in both **2a** and **2b** are at position 4 on the naphthalene ring. The anomeric configuration was confirmed by means of the difference in the chemical shifts (Δδ) of the two methyl groups of the 2′,3′-*O*-isopropylidene.[9] Thus, reaction of **3a** and **3b** with acetone in the presence of *p*-toluenesulfonic acid gave the corresponding 2′,3′-*O*-isopropylidene derivatives **4a** and **4b**. In the ^{1}H NMR spectrum, the chemical shift difference (Δδ) between the two methyl signals of the 2′,3′-*O*-isopropylidene group was 0.34 ppm for **4a** and 0.13 ppm for **4b** (Table I). From the high value (Δδ = 0.34) for **4a** the naphthyl moiety at the anomeric carbon of **2a** was concluded to be in the β configuration.

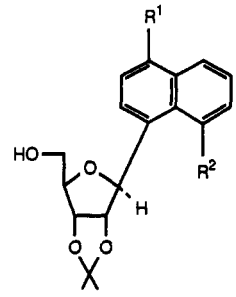
Chart I



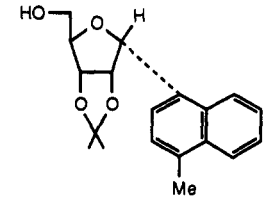
2a: R=Bz, R^1=Me, R^2=R^3=R^4=H
3a: R=H, R^1=Me, R^2=R^3=R^4=H
5a: R=Bz, R^1=R^4=H, R^2=R^3=Me
6a: R=H, R^1=R^4=H, R^2=R^3=Me
7a: R=Bz, R^1=R^4=OMe, R^2=R^3=H
8a: R=H, R^1=R^4=OMe, R^2=R^3=H



2b: R=Bz, R^1=Me, R^2=R^3=R^4=H
3b: R=H, R^1=Me, R^2=R^3=R^4=H
5b: R=Bz, R^1=R^4=H, R^2=R^3=Me
7b: R=Bz, R^1=R^4=OMe, R^2=R^3=H
8b: R=H, R^1=R^4=OMe, R^2=R^3=H



4a: R^1=Me, R^2=H
9a: R^1=R^2=OMe



4b

Reaction of 2,3-dimethylnaphthalene with **1** using 0.5 M stannic chloride in benzene for 18 h at room temperature gave 1-(2,3,5-tri-*O*-benzoyl-β-D-ribofuransoyl)-2,3-dimethylnaphthalene (**5a**) in 60.3% yield as the major product and its α anomer **5b** in 15% yield as the minor product. Subsequent deprotection of **5a** with sodium methoxide gave 2,3-dimethyl-1-(β-D-ribofuranosyl)-naphthalene (**6a**) in 80% yield. In the ^{1}H NMR spectrum an aromatic signal appeared at δ 7.59 (1 H, s). Also, Gore et al.[10] have reported that Friedel–Crafts benzoylation of 2,3-dimethylnaphthalene gave 1-benzoyl-2,3-dimethylnaphthalene as the major product. Therefore, the position of the ribofuranosyl linkage of **5** was concluded to be at

(1) Present address: Department of Chemistry, University of Virginia, McCormick Road Charlottesville, VA 22901.
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position 1 in the naphthalene ring.

Reaction of 1,5-dimethoxynaphthalene with 1 in the presence of 0.5 M stannic chloride in benzene for 4 h at room temperature gave 4-(2,3,5-tri-*O*-benzoyl-β-D-ribofuranosyl)-1,5-dimethoxynaphthalene (**7a**) in 50% yield and its α anomer **7b** in 10% yield. When 1,5-dimethoxynaphthalene was reacted with 2,3,5-tri-*O*-benzoyl-D-ribofuranosyl bromide using zinc oxide, only **7a** was obtained in 5% yield. Subsequent deprotection of the benzoyl groups of **7a** and **7b** with sodium methoxide gave the corresponding 1,5-dimethoxy-1-(β-D-ribofuranosyl)-naphthalene (**8a**) and its α anomer **8b**. In the ^{1}H NMR spectrum, the H-2 signals of **8a** and **8b** were observed at δ 6.9 and at 7.0,[4a] respectively. Therefore, the position of the glycosidic linkage in both **8a** and **8b** was assigned as position 4 on the naphthalene ring. The anomeric configuration was determined by means of the difference in the chemical shifts of the two methyl signals (Δδ) of the 2′,3′-*O*-isopropylidene. Thus, reaction of **8a** with acetone using *p*-toluenesulfonic acid gave the isopropylidene (**9a**) in 59% yield. In the ^{1}H NMR spectrum the chemical shift difference (Δδ) of the two methyl signals of the 2′,3′-*O*-isopropylidene was found to be 0.34 ppm, indicating that the major product, compound **7a**, has the β configuration.

In conclusion, the reaction of α-monosubstituted naphthalene with 1 gave mainly the β-*C*-riboside in good yield and the α anomer was obtained in ca. 8% yield. In the case of the β-substituted 2,3-dimethylnaphthalene, the yield of α-*C*-riboside increased, while the yield of β-*C*-riboside decreased. This may be due to steric hindrance between the methyl group of the naphthyl moiety and the $C_{5'}$ and $C_{2'}$ protons of the ribofuranose. In the reaction of 1 with 1,5-dimethoxynaphthalene, the yield of β-*C*-riboside was lower than that obtained from the reaction of α-methylnaphthalene, again suggesting the possibility of steric hindrance between the methoxy group of the naphthyl moiety and the $C_{1'}$, $C_{2'}$, and $C_{5'}$ protons of the ribofuranose.

Experimental Section

All melting points are uncorrected. IR spectra were taken on a JASCO A-102 spectrophotometer. UV spectra were measured on a Hitachi EPS-3T spectrophotometer. ^{1}H NMR spectra were recorded on a JEOL JNM-FX 100 spectrometer, using tetramethylsilane as an internal standard. Mass spectra were measured with a JEOL JMS-D300 spectrometer.

Reaction of 1-Methylnaphthalene with 1. A solution of 1 (1.50 g, 2.97 mmol) and 1-methylnaphthalene (0.820 g, 5.77 mmol) in a 1 M solution of stannic chloride in benzene (15 mL) was stirred for 14 h at room temperature. The solution was diluted with ethyl acetate (10 mL) and then water (5 mL) was added to the solution. The organic layer was washed with 20% aqueous acetic acid (3 × 30 mL) and water, dried over Na_2SO_4, and evaporated in vacuo. The residue was purified by column chromatography with benzene as eluent, and the solvent was evaporated in vacuo to give a solid. Recrystallization from CH_2Cl_2–EtOH gave 4-(2,3,5-tri-*O*-benzoyl-β-D-ribofuranosyl)-1-methylnaphthalene (**2a**) (1.370 g, 79%) as colorless needles: mp 117–118 °C; $[\alpha]^{20}_D$ −40.4° (*c* 0.5, $CHCl_3$); IR ($CHCl_3$) 1720 (CO), 1265, 1120 cm^{-1}; UV (MeOH) λ_{max} (ε) 227 (35 900), 267 (2400), 275 (3470), 286 (3160), 299 (2140), 317 (210) nm; ^{1}H NMR ($CDCl_3$) δ 2.68 (3 H, s, Me), 4.68–4.90 (3 H, m, H-4′, H-5′), 5.87 (2 H, m, H-2′, H-3′), 6.08 (1 H, d, $J_{1',2'}$ = 4 Hz, H-1′), 7.21–8.18 (21 H, m, aromatic H); MS *m*/*z* 586 (M$^+$), 464. Anal. Calcd for $C_{37}H_{30}O_7$: C, 75.75; H, 5.16. Found: C, 75.43; H, 5.12.

Further elution with benzene gave 4-(2,3,5-tri-*O*-benzoyl-α-D-ribofuranosyl)-1-methylnaphthalene (**2b**) (0.260 g, 8.3%) as a solid: $[\alpha]^{20}_D$ −7° (*c* 0.5, $CHCl_3$); IR ($CHCl_3$) 1720 (CO), 1267, 1123 cm^{-1}; UV (MeOH) λ_{max} (ε) 227 (13 500), 267 (3710), 275 (10 900), 286 (10 700), 299 (7240), 317 (1440) nm; ^{1}H NMR ($CDCl_3$) δ 2.65 (3 H, s, Me), 4.64–4.99 (3 H, m, H-4′, H-5′), 6.06 (1 H, m, H-3′), 6.30 (2 H, m, H-1′, H-2′), 7.25–8.09 (21 H, m, aromatic H); MS *m*/*z* 586 (M$^+$), 464. Anal. Calcd for $C_{37}H_{30}O_7 \cdot H_2O$: C, 75.49; H, 5.48. Found: C, 75.16, H, 5.34.

1-Methyl-4-(α-D-ribofuranosyl)naphthalene (3a). A solution of **2a** (0.900 g, 1.53 mmol) and sodium methoxide (0.414 g, 7.6 mmol) in MeOH–THF (2:1 v/v, 10 mL) was stirred for 24 h at room temperature. The solution was neutralized with AcOH and evaporated in vacuo. The residue was extracted with AcOEt (3 × 50 mL) and the combined organic layers were evaporated in vacuo. The residue was purified by column chromatography on silica gel (20 g) with 3% MeOH in CH_2Cl_2 as eluent and the solvent was evaporated in vacuo to give a solid. Recrystallized from MeOH–benzene gave **3a** (0.308 g, 73%) as colorless needles: mp 128–130 °C; UV (MeOH) λ_{max} (ε) 227 (75 800), 267 (3550), 278 (6030), 288 (8910), 298 (5500), 317 (760) nm; ^{1}H NMR (DMSO-d_6–D_2O) δ 2.64 (3 H, s, Me), 3.61–4.34 (5 H, m, H-2′, H-3′, H-4′, H-5′), 5.73 (1 H, br s, H-1′), 7.35 (1 H, d, *J* = 7 Hz, H-2), 7.50–8.05 (5 H, m, naphthalene H); MS *m*/*z* 274 (M$^+$), 171. Anal. Calcd for $C_{16}H_{18}O_4 \cdot H_2O$: C, 65.74; H, 6.90. Found: C, 65.35; H, 6.72.

1-Methyl-4-(α-D-ribofuranosyl)naphthalene (3b). A solution of **2b** (0.350 g, 0.59 mmol) and sodium methoxide (0.160 g, 2.9 mmol) in MeOH–THF (3:1 v/v, 8 mL) was stirred for 24 h at room temperature. The solution was neutralized with acetic acid and evaporated in vacuo. The residue was extracted with AcOEt (4 × 30 mL) and the extracted organic layers were evaporated in vacuo. The residue was purified by column chromatography on silica gel (10 g) with 3% MeOH in CH_2Cl_2 as eluent, and the solvent was evaporated in vacuo to give a solid. Recrystallization from MeOH–benzene gave **3b** (0.135 g, 83%) as colorless needles: mp 151–153 °C; UV (MeOH) λ_{max} (ε) 227 (58 900), 267 (3470), 278 (6460), 288 (7940), 298 (5620), 317 (590) nm; ^{1}H NMR (DMSO-d_6–D_2O) δ 2.64 (3 H, s, Me), 3.70–3.89 (5 H, m, H-2′, H-3′, H-4′, H-5′), 5.38 (1 H, d, *J* = 3 Hz, H-1′), 7.32 (1 H, d, *J* = 7 Hz, H-2), 7.52–8.24 (5 H, m, naphthalene H); MS *m*/*z* 274.1186 (M$^+$, calcd $C_{16}H_{18}O_4$, 274.1204).

1-(2,3-*O*-Isopropylidene-β-D-ribofuranosyl)-4-methylnaphthalene (4a). A solution of **3a** (0.100 g, 0.36 mmol) and absolute *p*-toluenesulfonic acid (10 mg, 0.058 mmol) in acetone (10 mL) was stirred for 2.5 h at room temperature. The solution was diluted with acetone (3 mL) and Ag_2O (26 mg) was added to the solution. The resulting precipitate was filtered off, and the filtrate was evaporated in vacuo to give a solid. Recrystallization from acetone–hexane gave **4a** (0.107 g, 94%) as colorless needles: mp 82–83 °C; $[\alpha]^{20}_D$ +20° (*c* 1, $CHCl_3$); IR (KBr) 3450 (OH), 1381, 1372 (gem Me) cm^{-1}; MS *m*/*z* 314 (M$^+$), 170. Anal. Calcd for $C_{19}H_{22}O_4$: C, 72.59; H, 7.05. Found: C, 72.53; H, 7.36.

1-(2,3-*O*-Isopropylidene-α-D-ribofuranosyl)-4-methylnaphthalene (4b). A solution of **3b** (0.122 g, 0.44 mmol) and *p*-toluenesulfonic acid (10 mg, 0.058 mmol) in acetone (12 mL) was stirred for 2.5 h at room temperature. The solution was diluted with acetone (3 mL) and Ag_2O (26 mg) was added to the solution. The resulting precipitate was filtered off, and the filtrate was evaporated in vacuo to give **4b** (0.116 g, 83%) as a solid: $[\alpha]^{20}_D$ −102.3° (*c* 0.4, $CHCl_3$); IR ($CHCl_3$) 3450 (OH), 1370, 1380 (gem Me) cm^{-1}; MS *m*/*z* 314 (M$^+$), 170. Anal. Calcd for $C_{19}H_{22}O_4 \cdot {}^1/_2H_2O$: C, 70.58; H, 7.16. Found: C, 70.87; H, 7.27.

Reaction of 2,3-Dimethylnaphthalene with 1. A solution of 1 (0.200 g, 0.39 mmol) and 2,3-dimethylnaphthalene (93 mg, 0.6 mmol) in a 0.5 M solution of stannic chloride in benzene (4 mL) was stirred for 18 h at room temperature. The solution was diluted with benzene (5 mL), washed with water, dried over Na_2SO_4, and evaporated in vacuo. The residue was purified by column chromatography on silica gel (25 g) with benzene as eluent, and the solvent was evaporated in vacuo. The residue was recrystallized from EtOH to give 2,3-dimethyl-1-(2,3,5-tri-*O*-benzoyl-β-D-ribofuranosyl)naphthalene (**5a**) (0.143 g, 60%) as colorless needles: mp 138–139 °C; IR (KBr) 3060, 1720 (CO) cm^{-1}; UV (MeOH) λ_{max} (ε) 227 (102 300), 265 (6030), 275 (9120), 297 (5490) nm; ^{1}H NMR ($CDCl_3$) δ 2.45 (3 H, s, Me), 2.62 (3 H, s, Me), 4.59 (1 H, m, H-5′), 4.86–4.96 (2 H, m, H-4′, H-5′), 6.07–6.25 (3 H, m, H-1′, H-2′, H-3′), 7.01–8.47 (20 H, m, aromatic H); MS *m*/*z* 600 (M$^+$), 478, 235. Anal. Calcd for $C_{38}H_{32}O_7$: C, 75.95; H, 5.37. Found: C, 75.92; H, 5.42.

Further elution with benzene gave a solid, which was recrystallized from EtOH to give 2,3-dimethyl-1-(2,3,5-tri-*O*-benzoyl-α-D-ribofuranosyl)naphthalene (**5b**) (36 mg, 15%) as colorless needles: mp 145–146 °C; IR (KBr) 2950, 1725 (CO) cm^{-1}; UV

(MeOH) λ_{max} (ϵ) 227 (112200), 265 (6760), 275 (8910), 297 (4900) nm; ^{1}H NMR ($CDCl_3$) δ 2.40 (3 H, s, Me), 2.52 (3 H, s, Me), 4.77 (2 H, d, J = 4 Hz, H-5'), 5.04 (1 H, m, H-4'), 6.07-6.30 (2 H, m, H-2', H-3'), 6.46 (1 H, d, J = 3 Hz, H-1'), 7.14-8.64 (20 H, m, aromatic H); MS m/z 600.2151 (M^+, calcd $C_{38}H_{32}O_7$, 600.2121).

2,3-Dimethyl-1-(β-D-ribofuranosyl)naphthalene (6a). A solution of **5a** (0.100 g, 0.16 mmol) and sodium methoxide (45 mg, 0.8 mmol) in THF-MeOH (1:3 v/v, 2 mL) was stirred for 20 h at room temperature. The solution was neutralized with acetic acid and evaporated in vacuo. The residue was purified by column chromatography on silica gel with ethyl acetate as eluent, and the solvent was evaporated in vacuo to give **6a** (38 mg, 80%) as a foam: UV (MeOH) λ_{max} (ϵ) 234 (64600, sh), 238 (74100), 274 (3550), 285 (5370), 295 (6030), 304 (4470 sh), 331 (490 sh) nm; ^{1}H NMR (CD_3OD) δ 2.45, 2.52 (3 H, 2s, 2 x Me), 3.92 (3 H, m, H-4', H-5'), 4.30 (1 H, m, H-3'), 4.45 (1 H, t, H-2'), 5.58 (1 H, d, J = 7 Hz, H-1'), 7.31 (1 H, d, J = 6 Hz, naphthalene H), 7.34 (1 H, d, J = 6 Hz, naphthalene H), 7.59 (1 H, s, H-4), 7.69 (1 H, dd, J = 6 Hz, J = 3 Hz, naphthalene H), 8.35 (1 H, dd, J = 6 Hz, J = 3 Hz, naphthalene H); MS m/z 288.1317 (M^+, calcd $C_{17}H_{20}O_4$, 288.1359).

Reaction of 1,5-Dimethoxynaphthalene with 1. A solution of 1 (1.00 g, 2 mmol) and 1,5-dimethoxynaphthalene (0.530 g, 2.8 mmol) in a 0.5 M solution of stannic chloride in benzene (10 mL) was stirred for 4 h at room temperature. The solution was diluted with AcOEt (15 mL), washed with 10% acetic acid (3 × 10 mL) and water, dried over Na_2SO_4, and evaporated in vacuo. The residue was purified by column chromatography on silica gel (120 g) with benzene as eluent and the solvent was evaporated in vacuo to give a solid. Recrystallization from AcOEt-MeOH gave 4-(2,3,5-tri-O-benzoyl-β-D-ribofuranosyl)-1,5-dimethoxynaphthalene (**7a**) (0.620 g, 50%) as colorless needles: mp 169-171 °C; $[\alpha]^{20}_D$ +14.4° (c 0.52, $CHCl_3$); IR ($CHCl_3$) 1720 (CO), 1120 cm^{-1}; UV (MeOH) λ_{max} (ϵ) 228 (109600), 275 (7760), 285 (10200), 300 (12000), 310 (8710), 317 (9330), 330 (8130) nm; ^{1}H NMR ($CDCl_3$) δ 3.64 (3 H, s, OMe), 3.94 (3 H, s, OMe), 4.61-4.94 (3 H, m, H-4', H-5'), 5.72 (1 H, dd, J = 8 Hz, J = 4 Hz, H-3'), 5.96 (1 H, d, J = 4 Hz, H-2'), 6.53 (1 H, s, H-1'), 6.59 (1 H, d, J = 8 Hz, H-2), 6.82 (1 H, dd, J = 10 Hz, J = 1 Hz, H-6), 7.15-8.19 (18 H, m, aromatic H); MS m/z 632 (M^+), 510. Anal. Calcd for $C_{38}H_{32}O_9 \cdot {}^1/_8H_2O$: C, 71.89; H, 5.04. Found: C, 71.63; H, 5.16.

Further elution with benzene gave a solid, which was recrystallized from MeOH to give 4-(2,3,5-tri-O-benzoyl-α-D-ribofuranosyl)-1,5-dimethoxynaphthalene (**7b**) (0.130 g, 11%) as colorless needles: mp 129-130 °C; $[\alpha]^{20}_D$ -67.8° (c 0.5, $CHCl_3$); IR (KBr) 1720 (CO), 1265 cm^{-1}; UV (MeOH) λ_{max} (ϵ) 228 (131800), 275 (8710), 285 (10700), 300 (13800), 310 (9330), 317 (10700), 330 (8710) nm; ^{1}H NMR ($CDCl_3$) δ 3.89 (3 H, s, OMe), 3.98 (3 H, s, OMe), 4.61-4.93 (3 H, m, H-4', H-5'), 5.98 (1 H, dd, J = 6 Hz, J = 5 Hz, H-3'), 6.31 (1 H, t, J = 4 Hz, H-2'), 6.73 (1 H, d, J = 4 Hz, H-1'), 6.75 (1 H, d, J = 8 Hz, H-2), 6.87 (1 H, d, J = 8 Hz, H-6), 7.15-8.15 (18 H, m, aromatic H); MS m/z 632 (M^+), 510. Anal. Calcd for $C_{38}H_{32}O_9$: C, 72.14; H, 5.10. Found: C, 72.14; H, 4.98.

1,5-Dimethoxy-4-(β-D-ribofuranosyl)naphthalene (8a). A solution of **7a** (1.00 g, 1.58 mmol) and sodium methoxide (0.341 g, 6.3 mmol) in MeOH-THF (1:2 v/v, 24 mL) was stirred for 20 h at room temperature. The solution was neutralized with acetic acid and evaporated in vacuo. Water (2 mL) was added to the residue and the resulting precipitate was collected by filtration, which was recrystallized from DMF-H_2O to give **8a** (0.458 g, 90%) as colorless needles: IR (KBr) 3350 (OH), 1600 cm^{-1}; UV (MeOH) λ_{max} (ϵ) 226 (61660), 288 (7940, sh), 299 (10470), 317 (8320), 331 (6920) nm; ^{1}H NMR (DMSO-d_6-D_2O) δ 3.80-4.13 (5 H, m, H-2', H-3', H-4', H-5'), 3.94 (6 H, s, 2 × Me), 5.91 (1 H, s, H-1'), 6.92 (1 H, d, J = 8 Hz, naphthalene H), 7.01 (1 H, d, J = 8 Hz, naphthalene H), 7.42 (1 H, t, J = 8 Hz, H-7), 7.78 (1 H, d, J = 8 Hz, naphthalene H), 7.92 (1 H, d, J = 8 Hz, naphthalene H); MS m/z 320 (M^+), 217 (naphthalene + 30). Anal. Calcd for $C_{17}H_{20}O_6$: C, 63.74; H, 6.29. Found: C, 63.49; H, 6.38.

1,5-Dimethoxy-4-(α-D-ribofuranosyl)naphthalene (8b). A solution of **7b** (90 mg, 0.14 mol) and sodium methoxide (32 mg, 0.59 mmol) in MeOH-THF (1:3 v/v, 4 mL) was stirred for 24 h at room temperature. The solution was neutralized with acetic acid and evaporated in vacuo. Water (2 mL) was added to the residue and the resulting precipitate was collected by filtration, which was recrystallized from DMF-ether to give **8b** (31 mg, 68%) as colorless needles: mp 172-173 °C; IR (KBr) 3400 (OH), 2935 cm^{-1}; UV (MeOH) λ_{max} (ϵ) 226 (49000), 288 (6020, sh), 299 (8510), 317 (7080), 331 (5890) nm; ^{1}H NMR (DMSO-d_6-D_2O) δ 3.56-4.32 (5 H, m, H-2', H-3', H-4', H-5'), 3.93 (3 H, s, OMe), 3.95 (3 H, s, OMe), 6.05 (1 H, d, J = 3 Hz, H-1'), 6.96 (1 H, d, J = 8 Hz, aromatic H), 7.37 (1 H, t, J = 8 Hz, aromatic H), 7.67 (1 H, s, J = 8 Hz, aromatic H), 7.78 (1 H, d, J = 8 Hz, aromatic H); MS m/z 320.1213 (M^+, calcd $C_{17}H_{20}O_6$, 320.1258).

1,5-Dimethoxy-4-(2,3-O-isopropylidene-β-D-ribofuranosyl)naphthalene (9a). A solution of **8a** (50 mg, 0.15 mmol) and absolute p-toluenesulfonic acid (20 mg, 0.11 mmol) in DMF-acetone (1:2 v/v, 6 mL) was stirred for 3 days at room temperature. The solution was neutralized with Ag_2O (52 mg), the resulting precipitate was filtered off, and the filtrate was evaporated in vacuo. The residue was recrystallized from MeOH-H_2O to give **9a** (33 mg, 59%) as colorless needles: mp 164-165 °C; MS m/z 360 (M^+), 216. Anal. Calcd for $C_{20}H_{24}O_6 \cdot {}^1/_5H_2O$: C, 65.99; H, 6.75. Found: C, 66.14; H, 6.80.

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Correlations between the Solvent Hydrogen Bond Acceptor Parameter β and the Calculated Molecular Electrostatic Potential

Jane S. Murray, Shoba Ranganathan,† and Peter Politzer*

Department of Chemistry, University of New Orleans, New Orleans, Louisiana 70148

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Introduction

In the course of an extended effort to separate, identify, and quantify various types of solvent effects,[1-5] it was found that a number of experimentally measurable solution properties (e.g., rate constants, equilibrium constants, and IR, NMR, ESR, and UV/vis absorption maxima and intensities) can be expressed as linear combinations of several "solvatochromic parameters".[5] This approach has now been used to characterize a large number of systems, including supercritical solutions.[6-8] One of the solvatochromic parameters, designated as β, has been interpreted as providing a measure of a solvent's ability to accept a proton in solute to solvent hydrogen bond.[5]

In this paper, we demonstrate that the calculated molecular electrostatic potentials within several different families of solvents, treated separately, correlate well with the corresponding β values. This further confirms the physical validity of β and provides a practical means for predicting its magnitudes.

The molecular electrostatic potential $V(r)$ has emerged over the past two decades as an effective analytical tool for interpreting and predicting the reactive behavior of molecules.[9-13] It is a real physical property, which expresses the net electrical effect of the nuclei and electrons

*To whom correspondence should be addressed.

†Department of Chemistry, Maitreyi College, University of Delhi, New Delhi 110 021, India.

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