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Preparation of enantiopure inherently chiral calix[5]arenes

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Abstract—Enantiopure inherently chiral calix[5]arenes were successfully prepared by separation of their (*R*)-BINOL diastereomeric derivatives of the corresponding racemates by column chromatography instead of HPLC. A new type of inherently chiral calix[5]-arene was obtained.

1. Introduction

Chiral recognition and asymmetric catalysis are key goals in host–guest chemistry. Chiral calixerenes or their derivatives are frequently reported as host molecules or building blocks based on their unique cavity-shaped architecture and preorganized binding sites.[1,2] Compared with the simple attachment of chiral groups, it is difficult to obtain inherently chiral calixerenes involving asymmetric arrangements of achiral substituents on their lower or upper rims.[3–5]

There are few reports on inherently chiral calix[5]arenes due to the labor required to synthesize calix[5]arenes.[6–10] It is mainly limited to separating enantiopure inherently chiral calix[5]arenes with HPLC using a chiral column.[6] While some enantiopure inherently chiral calix[4]arenes have been prepared with column chromatography by Dieleman et al. and preparative TLC in our laboratory,[1,11] we herein report the first preparation of enantiopure inherently chiral calix[5]arenes by separation of the diastereomers formed with (*R*)-BINOL and their racemates with column chromatography and hydrolysis of the diastereomers. A new type of inherently chiral calix[5]arene was obtained.

2. Results and discussion

Starting from racemic **1** synthesized by Pappalardo and co-workers,[7] racemic acid **2** was obtained by hydrolysis of **1** in the presence of $Me_4N^+OH^-$ aqueous solution (Scheme 1). It was confirmed that **2** exists as a cone conformation by the information of bridging methylene carbon signals at $\delta \sim 30$ ppm in ^{13}C NMR spectrum.[12–14] Owing to the asymmetric structure, molecular asymmetry is reflected almost in every region of its ^1H NMR spectrum: aromatic protons show five pairs of peaks (partly overlapping each other), bridging methylene protons show five pairs of peaks in AX systems (partly overlapping with the signals of crown ether protons), the protons of $ArOCH_2CO_2$ show a pair of peaks as an AB system (partly overlapping with the signals of crown ether protons) and *tert*-butyl protons show five single peaks (Fig. 1, *tert*-butyl protons are not included).

Encouraged by the methods of separation of the diastereomers in Dieleman's work and our previous work,[1,11] we produced diastereomers **3a** and **3b** through esterifications of **2** with (*R*)-BINOL in the presence of DCC and DMAP in dry CH_2Cl_2 and separated them, respectively, with column chromatography (Scheme 1).

The ^1H NMR spectra of **3a** and **3b** are very similar to that of **2** in the splitting patterns. The chemical shifts of bridging methylene carbon in ^{13}C NMR spectra are at $\delta \sim 30$ ppm, which proves that they all adopt a cone conformation. Due to the bulky volume of the binaphthyl moiety of **3a**, the binaphthyl moiety is forced to leave from the crown ether by the repulsion between them. As a result, the phenyl ring moiety connecting the binaphthyl group inclines into the calixarene cavity and the relative chemical shift of its corresponding *tert*-butyl moiety moves upfield (0.17 ppm) in the ^1H NMR of **3a**. The same case occurs to **3b** and the relative chemical shift of its

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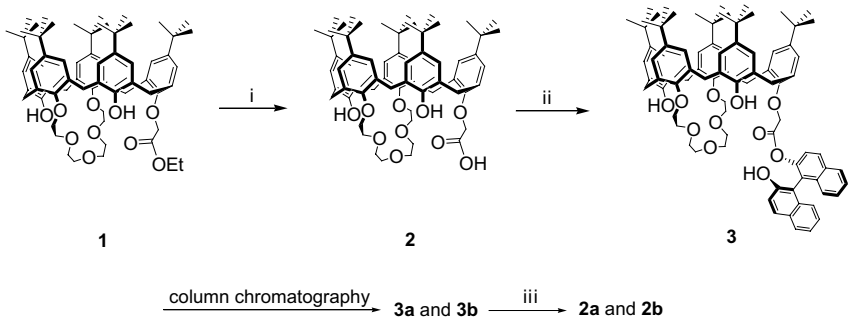

Scheme 1. Reagents and conditions: (i) Me_4N^+ OH^-, THF, 60 °C, 8 h; (ii) (*R*)-BINOL, DCC, DMAP, CH_2Cl_2, rt, 10 h; (iii) $Me_4N^+OH^-$, THF, 60 °C, 8 h.

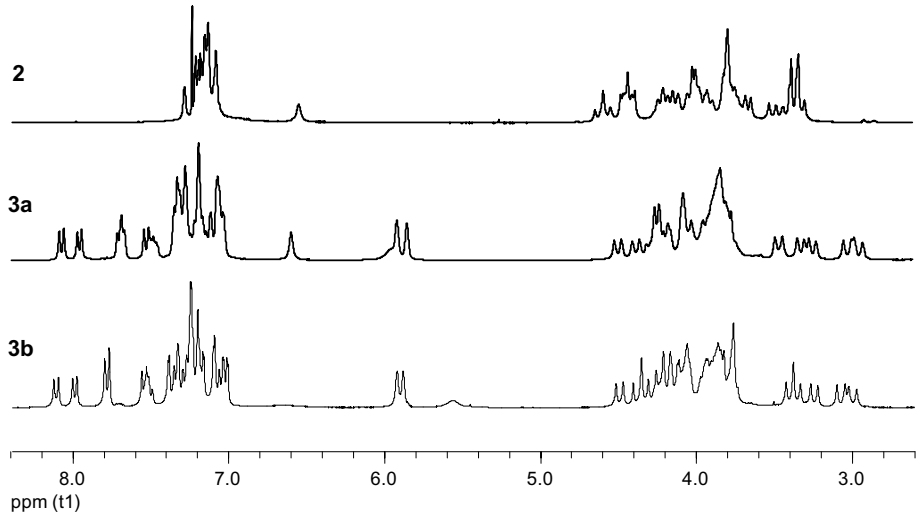

Figure 1. Partial ^1H NMR ($CDCl_3$) spectra of **2**, **3a** and **3b**.

corresponding *tert*-butyl moiety also moves to upfield (0.18 ppm) in the ^1H NMR of **3b**.

However, there is an obvious difference in ^1H NMR spectra of the two diastereomers of **3a** and **3b**. The protons of the two phenolic hydroxy group of **3a** resonate at 5.91 ppm and 5.85 ppm, whilst those of **3b** resonate at 5.92 ppm and 5.88 ppm. The relative chemical shifts of equatorial hydrogen of bridging methylene of **3a** (3.46, 3.32, 3.24, 3.02, 2.95 ppm) distribute wider compared with those of **3b** (3.40, 3.35, 3.24, 3.07, 3.00 ppm). The phenomena show that the distortion of calix[5]arene backbones of **3a** may be more serious than that of **3b** due to the repulsion of an outer bulky rigid stereogenic center. The obvious difference between them may be the most important factor in separating them. Moreover, the proton of the binaphthyl hydroxy of **3a** (6.59 ppm) resonates more downfield than that of **3b** (5.56 ppm) in their ^1H NMR. This can be attributed to the different steric positions of the binaphthyl hydroxy groups of the diastereomers.

The optically active calix[5]arene derivatives **2a** and **2b** were obtained by hydrolysis of **3a** and **3b** according to the method of preparing **2**. They are a new type of inherently chiral calix[5]arene. Circular dichroism (CD) spectroscopy of **2a** ($[\alpha]_D^{25} = +4.8$) and **2b** ($[\alpha]_D^{25} = -4.9$) shows a mirror image, which proves they are indeed a pair of enantiomers (Fig. 2).[11]

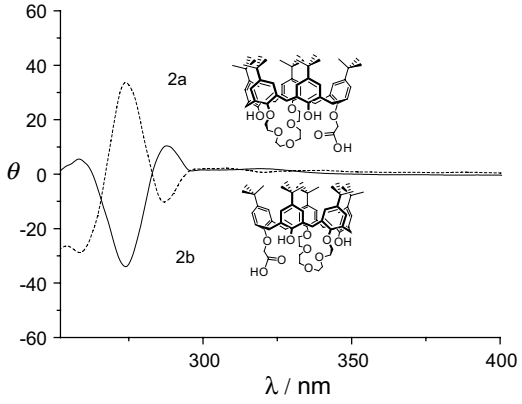

Figure 2. CD spectra of **2a** (dot line) and **2b** (solid line) in CH_2Cl_2.

3. Conclusion

A practical and convenient method was successfully designed to obtain enantiopure inherently chiral calix[5]arenes through separation of the diastereomers synthesized with (*R*)-BINOL and their racemates with column chromatography and hydrolysis of the diastereomers. A new type of inherently chiral calix[5]arene was obtained. This can be used to help prepare more significant inherently chiral calix[5]arene derivatives and probabilities to study chiral recognition and asymmetric catalysis involving inherently chiral calix[5]arenes.

4. Experimental

Column chromatography was conducted with 160–200 mesh silica gel. Melting points were measured with an X-4 digital indicating melting point apparatus. Optical rotations were recorded using an AA-10R polarimeter. CD spectra were recorded on a JASCO *J*-810 spectropolarimeter. IR spectra were obtained using JASCO FT/IR-480 plus spectrometer (KBr pellets). Mass spectra were recorded in MALDI-TOF MS using Bruker BIFLEXIII instrument or in high resolution FT-ICR MS using Bruker APEX II instrument. NMR spectra were recorded on Bruker AV 300 spectrometer. Chemical shifts of NMR are given in ppm relative to tetramethylsilane.

4.1. 31,33-Dihydroxy-32,35-crown-5-34-carboxy-methoxy-*t*-butylcalix[5]arene and 31,34-dihydroxy-32,35-crown-5-33-carboxymethoxy-*t*-butylcalix[5]arene 2

To a mixture of $Me_4N^+OH^-$ (910 mg, 10 mmol) aqueous solution (9.1 mL) and THF (100 mL) was added **1** (1054 mg, 1 mmol). The solution was heated at 60 °C for 8 h. After removal of the solvent in vacuo, the residue was acidified by 10% HCl and partitioned between water and CH_2Cl_2. **2** was isolated with column chromatography (petroleum ether/ethyl acetate, 1:1 v/v) as a white powder (677 mg, yield 66%): mp 147–149 °C; IR (KBr) 3402, 2958, 1740, 1482; ^{1}H NMR ($CDCl_3$) δ 7.29 (d, 1H, J = 2.1 Hz, ArH), 7.23–7.20 (m, 2H, ArH), 7.18 (d, 1H, J = 2.3 Hz, ArH), 7.16–7.09 (m, 6H, ArH), 6.56 (s, 2H, OH), 4.62 (d, 1H, J = 15.4 Hz, $ArOCH_2CO_2$), 4.57 (d, 1H, J = 13.9 Hz, $ArCH_2Ar$), 4.48–3.65 (m, 21H, $ArOCH_2CO_2$, $ArCH_2Ar$ and polyether chain), 3.51 (d, 1H, J = 13.6 Hz, $ArCH_2Ar$), 3.36 (d, 3H, J = 13.5 Hz, $ArCH_2Ar$), 3.32 (d, 1H, J = 12.0 Hz, $ArCH_2Ar$), 1.33 (s, 9H, $C(CH_3)_3$), 1.28 (s, 9H, $C(CH_3)_3$), 1.15 (s, 9H, $C(CH_3)_3$), 1.12 (s, 9H, $C(CH_3)_3$), 1.07 (s, 9H, $C(CH_3)_3$); ^{13}C NMR ($CDCl_3$) δ 170.9 (CO), 150.8, 150.6, 150.3, 149.7, 149.5, 147.1, 146.9, 146.5, 142.4, 141.3, 133.8, 133.3, 132.7, 132.6, 132.2, 131.9, 127.1, 127.0, 126.9, 126.5, 126.4, 126.2, 126.1, 126.0, 125.9, 125.8, 125.7, 125.6, 125.5, 125.3 (ArC), 74.4, 71.7, 70.8, 70.7, 70.3, 70.1, 70.0 ($ArOCH_2CO_2$ and polyether chain), 34.2, 34.0, 33.9 ($C(CH_3)_3$), 31.7, 31.6, 31.4, 31.3, 31.2 ($C(CH_3)_3$), 32.0, 30.4, 29.5, 29.0, 28.6 ($ArCH_2Ar$); MALDI-TOF MS *m*/*z* 1049 ($[M + Na]^+$), 1065 ($[M + K]^+$). Anal. Calcd for $C_{65}H_{86}O_{10}$: C, 75.99; H, 8.44. Found: C, 76.12; H, 8.77.

4.2. 31,33-Dihydroxy-32,35-crown-5-34-(*R*)-[1,1′]-binaphthalenyl-2′-ol-2-oxy-carbonylmethoxy-*t*-butylcalix[5]arene 3a and 31,34-dihydroxy-32,35-crown-5-33-(*R*)-[1,1′]binaphthalenyl-2′-ol-2-oxy-carbonyl-methoxy-*t*-butylcalix[5]arene 3b

A mixture of **2** (1026 mg, 1 mmol), (*R*)-BINOL (572 mg, 2 mmol), DCC (309 mg, 1.5 mmol) and DMAP (18 mg, 0.15 mmol) in dry CH_2Cl_2 (50 mL) was stirred at rt for 10 h. The DCU was removed by filtration. After removal of solvent, the residue was purified with column chromatography (petroleum ether/ethyl acetate, 5:1 v/v) to afford **3a** (479 mg, yield 37%) and **3b** (440 mg, yield 34%).

Compound **3a**: mp 117–118 °C; $[\alpha]_D^{25} = +21$ (*c* 1, CH_2Cl_2); IR (KBr) 3384, 2957, 1782, 1481, ^{1}H NMR ($CDCl_3$) δ 8.07 (d, 1H, J = 8.8 Hz, binaphthylH), 7.95 (d, 1H, J = 8.1 Hz, binaphthylH), 7.71–7.02 (m, 20H, binaphthylH and ArH), 6.59 (s, 1H, OH), 5.91 (s, 1H, OH), 5.85 (s, 1H, OH), 4.49 (d, 1H, J = 13.6 Hz, $ArCH_2Ar$), 4.38 (d, 1H, J = 13.8 Hz, $ArCH_2Ar$), 4.31–3.76 (m, 21H, $ArOCH_2CO_2$, $ArCH_2Ar$ and polyether chain), 3.46 (d, 1H, J = 13.7 Hz, $ArCH_2Ar$), 3.32 (d, 1H, J = 13.5 Hz, $ArCH_2Ar$), 3.24 (d, 1H, J = 13.8 Hz, $ArCH_2Ar$), 3.02 (d, 1H, J = 15.6 Hz, $ArCH_2Ar$), 2.95 (d, 1H, J = 16.1 Hz, $ArCH_2Ar$), 1.40 (s, 9H, $C(CH_3)_3$), 1.37 (s, 9H, $C(CH_3)_3$), 1.25 (s, 9H, $C(CH_3)_3$), 1.15 (s, 9H, $C(CH_3)_3$), 0.17 (s, 9H, $C(CH_3)_3$); ^{13}C NMR ($CDCl_3$) δ 168.5 (CO), 152.2, 152.1, 150.7, 150.6, 150.0, 149.6, 147.5, 147.0, 146.7, 146.3, 141.7, 141.6, 134.5, 134.2, 133.6, 133.5, 133.0, 132.5, 132.4, 132.3, 132.2, 130.6, 130.5, 128.9, 128.4, 128.1, 127.6, 127.4, 127.3, 127.2, 127.0, 126.9, 126.7, 126.3, 126.2, 126.1, 126.0, 125.9, 125.6, 125.4, 125.2, 124.9, 124.6, 124.0, 123.9, 123.4, 123.2, 121.7, 118.4, 113.9 (binaphthylC and ArC), 75.3, 74.2, 71.6, 71.0, 70.5, 69.3 ($ArOCH_2CO_2$ and polyether chain), 34.4, 34.3, 34.0, 33.9, 33.4 ($C(CH_3)_3$), 31.9, 31.7, 31.4, 30.5 ($C(CH_3)_3$), 31.1 30.9, 30.8, 28.3 ($ArCH_2Ar$); HRMS: $C_{85}H_{98}O_{11}$ *m*/*z* calcd 1317.7007 ($[M + Na]^+$), found 1317.6988 ($[M + Na]^+$).

Compound **3b**: mp 158–159 °C; $[\alpha]_D^{25} = +60$ (*c* 1, CH_2Cl_2); IR (KBr) 3408, 2868, 1766, 1481; ^{1}H NMR (CDCl3) δ 8.11 (d, 1H, J = 8.8 Hz, binaphthylH), 7.99 (d, 1H, J = 8.1 Hz, binaphthylH), 7.78 (d, 2H, J = 8.6 Hz, binaphthylH), 7.56–7.00 (m, 18H, binaphthylH and ArH), 5.92 (s, 1H, OH), 5.88 (s, 1H, OH), 5.56 (s, 1H, OH), 4.49 (d, 1H, J = 13.7 Hz, $ArCH_2Ar$), 4.38 (d, 1H, J = 16.0 Hz, $ArOCH_2CO_2$), 4.33 (d, 1H, J = 12.9 Hz, $ArCH_2Ar$), 4.26–3.74 (m, 20H, $ArOCH_2CO_2$, $ArCH_2Ar$ and polyether chain), 3.40 (d, 1H, J = 14.0 Hz, $ArCH_2Ar$), 3.35 (d, 1H, J = 13.6 Hz, $ArCH_2Ar$), 3.24 (d, 1H, J = 13.8 Hz, $ArCH_2Ar$), 3.07 (d, 1H, J = 15.6 Hz, $ArCH_2Ar$), 3.00 (d, 1H, J = 15.2 Hz, $ArCH_2Ar$), 1.39 (s, 9H, $C(CH_3)_3$), 1.36 (s, 9H, $C(CH_3)_3$), 1.25 (s, 9H, $C(CH_3)_3$), 1.14 (s, 9H, $C(CH_3)_3$), 0.18 (s, 9H, $C(CH_3)_3$); ^{13}C NMR ($CDCl_3$) δ 168.5 (CO), 152.0, 151.9, 150.6, 150.5, 149.9, 149.5, 147.4, 146.8, 146.7, 146.2, 141.6, 141.5, 134.6, 134.0,

133.4, 133.3, 132.8, 132.3, 132.2, 132.1, 132.0, 130.8, 130.4, 128.8, 128.3, 128.0, 127.5, 127.4, 127.1, 126.9, 126.8, 126.7, 126.6, 126.3, 126.2, 126.1, 125.8, 125.7, 125.6, 125.2, 125.0, 124.9, 124.5, 123.8, 123.5, 123.4, 123.2, 121.6, 118.4, 113.9 (binaphthylC and ArC), 75.2, 74.2, 71.8, 71.4, 71.0, 70.5, 69.4, 69.3 (ArO*C*H_2-CO_2 and polyether chain), 34.3, 34.1, 33.9, 33.8, 33.3 (*C*$(CH_3)_3$), 31.7, 31.6, 31.5, 31.3, 30.4 (C(*C*$H_3)_3$), 31.0, 30.6, 28.2 ($ArCH_2Ar$); HRMS: $C_{85}H_{98}O_{11}$ *m/z* calcd 1317.7007 ($[M + Na]^+$), found 1317.6999 ($[M + Na]^+$).

4.3. 31,33-Dihydroxy-32,35-crown-5-34-carboxy-methoxy-*t*-butylcalix[5]arene 2a and 31,34-dihydroxy-32,35-crown-5-33-carboxymethoxy-*t*-butylcalix[5]arene 2b

According to the method of preparing **2**, **2a** and **2b** were respectively obtained by hydrolyzation of **3a** and **3b** as white solids (**2a**, yield 72%; **2b**, yield 74%). The ^1H NMR and ^{13}C NMR data of **2a** and **2b** are almost equal to those of racemic mixture **2**.

Compound **2a**: mp 226–228 °C; $[\alpha]_D^{25} = +4.8$ (*c* 2.6, CH_2Cl_2); IR (KBr) 3423, 2958, 1734, 1481; ^1H NMR ($CDCl_3$) δ 7.30 (d, 1H, $J = 2.1$ Hz, ArH), 7.23–7.21 (m, 2H, ArH), 7.18 (d, 1H, $J = 3.0$ Hz, ArH), 7.18–7.09 (m, 6H, ArH), 6.54 (s, 2H, OH), 4.63 (d, 1H, $J = 15.2$ Hz, $ArOCH_2CO_2$), 4.58 (d, 1H, $J = 14.2$ Hz, $ArCH_2Ar$), 4.50–3.64 (m, 21H, $ArOCH_2CO_2$, $ArCH_2Ar$ and polyether chain), 3.51 (d, 1H, $J = 13.7$ Hz, $ArCH_2$-Ar), 3.37 (d, 3H, $J = 13.1$ Hz, $ArCH_2Ar$), 3.32 (d, 1H, $J = 13.2$ Hz, $ArCH_2Ar$), 1.33 (s, 9H, C$(CH_3)_3$), 1.28 (s, 9H, C$(CH_3)_3$), 1.16 (s, 9H, C$(CH_3)_3$), 1.12 (s, 9H, C$(CH_3)_3$), 1.06 (s, 9H, C$(CH_3)_3$); ^{13}C NMR ($CDCl_3$) δ 170.7 (CO), 150.8, 150.6, 150.3, 149.8, 149.5, 147.1, 146.9, 146.4, 142.4, 141.3, 133.8, 133.3, 132.7, 132.6, 132.2, 131.9, 127.1, 127.0, 126.9, 126.5, 126.4, 126.2, 126.1, 126.0, 125.9, 125.8, 125.7, 125.5, 125.4, 125.3 (ArC), 74.4, 71.6, 70.8, 70.7, 70.3, 70.1, 69.9 (ArO*C*H_2-CO_2 and polyether chain), 34.1, 33.9 33.8 (*C*$(CH_3)_3$), 31.7, 31.6, 31.4, 31.3, 31.2 (C(*C*$H_3)_3$), 32.0, 30.3, 29.5, 29.1, 28.6 ($ArCH_2Ar$); MALDI-TOF MS *m/z* 1049 ($[M + Na]^+$), 1065 ($[M + K]^+$). Anal. Calcd for $C_{65}H_{86}O_{10}$: C, 75.99; H, 8.44. Found: C, 75.92; H, 8.81.

Compound **2b**: mp 225–227 °C; $[\alpha]_D^{25} = -4.9$ (*c* 2.6, CH_2Cl_2); IR (KBr) 3390, 2958, 1738, 1481; ^1H NMR ($CDCl_3$) δ 7.31 (d, 1H, $J = 2.1$ Hz, ArH), 7.24–7.21 (m, 2H, ArH), 7.18 (br s, 1H, ArH), 7.19–7.09 (m, 6H, ArH), 6.54 (s, 2H, OH), 4.64 (d, 1H, $J = 15.7$ Hz, Ar-OCH_2CO_2), 4.58 (d, 1H, $J = 14.5$ Hz, $ArCH_2Ar$), 4.49–3.63 (m, 21H, $ArOCH_2CO_2$, $ArCH_2Ar$ and polyether chain), 3.52 (d, 1H, $J = 13.7$ Hz, $ArCH_2Ar$), 3.37 (d, 3H, $J = 13.4$ Hz, $ArCH_2Ar$), 3.32 (d, 1H, $J = 13.9$ Hz, $ArCH_2Ar$), 1.33 (s, 9H, C$(CH_3)_3$), 1.28 (s, 9H, C$(CH_3)_3$), 1.17 (s, 9H, C$(CH_3)_3$), 1.12 (s, 9H, C$(CH_3)_3$), 1.06 (s, 9H, C$(CH_3)_3$); ^{13}C NMR ($CDCl_3$) δ 170.9 (CO), 150.8, 150.6, 150.4, 149.7, 149.5, 147.1, 146.9, 146.5, 142.4, 141.3, 133.9, 133.4, 132.7, 132.6, 132.2, 131.9, 127.2, 127.0, 126.9, 126.6, 126.5, 126.2, 126.1, 126.0, 125.9, 125.8, 125.7, 125.5, 125.4, 125.3 (ArC), 74.5, 71.7, 70.8, 70.7, 70.3, 70.1, 70.0 (ArO*C*H_2-CO_2 and polyether chain), 34.2, 33.9 33.8 (*C*$(CH_3)_3$), 31.8, 31.6, 31.4, 31.3, 31.2 (C(*C*$H_3)_3$), 32.1, 30.4, 29.4, 29.0, 28.5 ($ArCH_2Ar$); MALDI-TOF MS *m/z* 1049 ($[M + Na]^+$), 1065 ($[M + K]^+$). Anal. Calcd for $C_{65}H_{86}O_{10}$: C, 75.99; H, 8.44. Found: C, 76.14; H, 8.79.

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