Chemistry of Natural Compounds, Vol. 36, No. 4, 2000

SYNTHESIS OF D-MANNITE ESTERS

A. F. Artamonov, F. S. Nigmatullina,
M. T. Aldabergenova, and B. Zh. Dzhiembaev

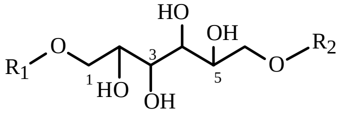
UDC 661.725:547.58

Mono- and diesters of D-mannite with aromatic acids are synthesized. The structures of the resulting compounds are confirmed by IR spectroscopy, PMR, and ^{13}*C NMR.*

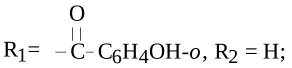
Key words: synthesis, D-mannite esters, aromatic acids.

In continuation of research on the modification of natural and synthetic carboxylic acids with polyols [1-3], the present article reports the synthesis of mono- and diesters of D-mannite with phenolcarboxylic and cinnamic acids.

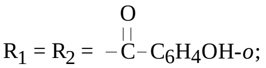
Mono- and diesters of D-mannite and aromatic acids [1-8] were prepared via transesterification of the methyl esters of the corresponding acids by D-mannite in DMF catalyzed by K_2CO_3.



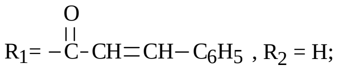
1 - 8

1. 

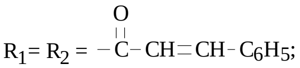
$R_1 = -\overset{\text{O}}{\overset{\|}{\text{C}}}-C_6H_4OH\text{-}o$, $R_2 = H$;

5. 

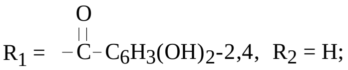
$R_1 = R_2 = -\overset{\text{O}}{\overset{\|}{\text{C}}}-C_6H_4OH\text{-}o$;

2. 

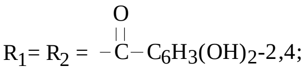
$R_1 = -\overset{\text{O}}{\overset{\|}{\text{C}}}-CH{=}CH-C_6H_5$, $R_2 = H$;

6. 

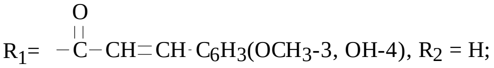
$R_1 = R_2 = -\overset{\text{O}}{\overset{\|}{\text{C}}}-CH{=}CH-C_6H_5$;

3. 

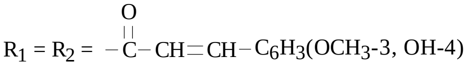
$R_1 = -\overset{\text{O}}{\overset{\|}{\text{C}}}-C_6H_3(OH)_2\text{-}2,4$, $R_2 = H$;

7. 

$R_1 = R_2 = -\overset{\text{O}}{\overset{\|}{\text{C}}}-C_6H_3(OH)_2\text{-}2,4$;

4. 

$R_1 = -\overset{\text{O}}{\overset{\|}{\text{C}}}-CH{=}CH\cdot C_6H_3(OCH_3\text{-}3,\ OH\text{-}4)$, $R_2 = H$;

8. 

$R_1 = R_2 = -\overset{\text{O}}{\overset{\|}{\text{C}}}-CH{=}CH-C_6H_3(OCH_3\text{-}3,\ OH\text{-}4)$

Mono- (**1-4**) and diesters (**5-8**) of D-mannite with aromatic acids were isolated by column chromatography on silica gel. They are finely crystalline substances that are soluble in alcohol, DMF, and DMSO and insoluble in benzene and $CHCl_3$. The monoesters, in contrast with the diesters, are very soluble in water.

The PMR spectra of the synthesized compounds (**1-8**) exhibit a group of signals for the –CH and $–CH_2$ protons of D-mannite at 4.6-5.1 ppm. The protons of the aromatic ring appear at 6.5-8.0 ppm. The spectra of the mono- and diesters of D-mannite with cinnamic (**2** and **6**) and ferulic (**4** and **8**) acids contain two doublets at 6.4-6.6 and 7.7-7.9 ppm (J = 16 Hz) due to the *trans*-orientation of the olefin protons.

The ^{13}C NMR spectra confirm that the primary hydroxyls of D-mannite are acylated because the C atoms C-1 and C-6 in the α-positions relative to the esters undergo a weak-field shift of 3.0-4.0 ppm whereas those in the β-positions experience a strong-field shift of 1.5-3.0 ppm compared with the corresponding atoms in unsubstituted D-mannite.

A. B. Bekturov Institute of Chemical Sciences, Ministry of Education and Science, Republic of Kazakhstan, Almaty, fax (3272) 91 57 65. Translated from Khimiya Prirodnykh Soedinenii, No. 4, pp. 280-281, July-August, 2000. Original article submitted March 6, 2000.

EXPERIMENTAL

IR spectra were recorded on a UR-20 instrument (KBr pellets); PMR and ^{13}C NMR, on a Mercury-300 instrument at working frequencies 300 and 75 MHz, respectively, with TMS as an internal standard in deuteropyridine. The course of the reactions was monitored by TLC on Silufol UV-254 plates using $CHCl_3$—CH_3OH.

Mono- and diesters of aromatic acids with D-mannite were synthesized by the literature method [2]. The mole ratio of methyl ester of the corresponding acid and D-mannite was 1:3 for preparation of the monoesters and 2:1 for the diesters. Compounds **1-8** were obtained.

Compound 1: 10.04 g (50.6%), mp 145-146°C, R_f 0.28. Found, %: C 51.62, H 5.93. $C_{13}H_{18}O_8$. Calc., %: C 51.65, H 5.96.

IR spectrum (KBr, ν, cm^{-1}): 1670 (CO, ester), 1610, 1580, 1490 (C=C), 3000-3600 (–OH).

PMR (δ, ppm): 4.20-5.16 (8H, m, mannite), 6.58-7.81 (4H, m, Ar).

^{13}C NMR (δ, ppm), mannite: C-1 68.84 (+3.78), C-2 69.49 (-2.67), C-3 70.75 (-0.78), C-4 70.93 (-0.60), C-5 72.53 (-0.29), C-6 64.98 (-0.08); Ar: C-1′ 112.90, C-2′ 161.28, C-3′ 117.21, C-4′ 135.46, C-5′ 118.91, C-6′ 130.21; COO: 170.18.

Compound 2: 7.36 g (40.2%), mp 175-176°C, R_f 0.34. Found, %: C 57.62, H 6.43. $C_{15}H_{20}O_7$. Calc., %: C 57.69, H 6.41.

IR spectrum (KBr,ν, cm^{-1}): 1690 (CO, ester), 1635, 1580, 1500 (C=C), 3100-3600 (–OH).

PMR (δ, ppm): 4.30-5.20 (8H, m, mannite), 6.51 (1H, d, J = 16 Hz, CH=), 7.20-7.42 (4H, m, Ar), 7.78 (1H, d, J = 16 Hz, CH=).

^{13}C NMR (δ, ppm), mannite: C-1 67.97 (+2.93), C-2 (69.86 (-2.96), C-3 70.77 (-0.76), C-4 71.01 (-0.51), C-5 72.63 (-0.19), C-6 65.04 (-0.02); Ar: C-1′ 134.37, C-2′, C-6′ 128.79, C-3′, C-5′ 128.00, C-4′ 130.12; Ar–CH= 144.13; –OOC–CH= 118.57; COO: 166.99.

Compound 3: 2.86 g (15.1%), mp 179-180°C, R_f 0.19. Found, %: C 49.13, H 5.71. $C_{13}H_{18}O_9$. Calc., %: C 49.05, H 5.66.

IR spectrum (KBr,ν, cm^{-1}): 1664 (CO, ester), 1512, 1600, 1640 (C=C), 3000-3600 (–OH).

PMR (δ, ppm): 4.29-5.17 (8H, m, mannite), 6.47 (1H, dd, J = 9 Hz, Ar), 6.77 (1H, d, J = 3 Hz, Ar).

^{13}C NMR (δ, ppm), mannite: C-1 68.38 (+3.32), C-2 69.65 (-3.17), C-3 70.77 (-0.76), C-4 71.00 (-0.52), C-5 72.60 (-0.17), C-6 65.07 (+0.01); Ar: 165.31, 163.90, 132.11, 108.45, 104.65, 102.92; COO: 170.44.

Compound 4: 5.05 g (30.4%), mp 158-159°C, R_f 0.23. Found, %: C 53.60, H 6.10. $C_{16}H_{22}O_9$. Calc., %: C 53.63, H 6.14.

IR spectrum (KBr,ν, cm^{-1}): 1688 (CO, ester), 1512, 1600, 1632 (C=C), 3100-3600 (–OH).

PMR (δ, ppm): 3.74 (3H, s, $–OCH_3$), 4.30-5.16 (8H, m, mannite), 6.42 (1H, d, J = 16 Hz, CH=), 7.00-7.16 (3H, m, Ar), 7.81 (1H, d, J = 16 Hz, CH=).

^{13}C NMR (δ, ppm), mannite: C-1 67.79 (+2.73), C-2 69.93 (-2.90), C-3 70.79 (-0.74), C-4 70.96 (-0.57), C-5 72.60 (-0.22), C-6 65.03 (-0.03); Ar: C-1′ 125.94, C-2′ 116.22, C-3′ 150.44, C-4′ 148.42, C-5′ 114.88, C-6′ 121.93, Ar–CH= 144.92, –OOC–CH= 110.91; COO: 167.61.

Compound 5: 6.39 g (46.1%), mp 181-182°C, R_f 0.69. Found, %: C 56.80, H 5.25. $C_{20}H_{22}O_{10}$. Calc., %: C 56.87, H 5.21.

IR spectrum (KBr,ν, cm^{-1}): 1700 (CO, ester), 1660, 1610, 1585 (C=C), 3100-3600 (–OH).

PMR (δ, ppm): 4.67-5.05 (8H, m, mannite), 6.60-7.88 (8H, m, Ar).

^{13} C NMR (δ, ppm), mannite: C-1, C-6 68.68 (+3.62); C-2, C-5 70.19 (-2.63); C-3, C-4 69.49 (-2.04); Ar: C-1′ 112.95, C-2′ 161.44, C-3′ 117.34, C-4′ 135.65, C-5′ 119.12, C-6′ 130.38; COO: 170.36.

Compound 6: 4.44 g (35.4%), mp 165-166°C, R_f 0.68. Found, %: C 65.20, H 5.83. $C_{24}H_{26}O_8$. Calc., %: C 65.16, H 5.88.

IR spectrum (KBr,ν, cm^{-1}): 1695 (CO, ester), 1645, 1500, 1450 (C=C), 3100-3600 (–OH).

PMR (δ, ppm): 4.75-5.20 (8H, m, mannite), 6.44 (2H, dd, J = 16 Hz, 2CH=), 7.73 (2H, d, J = 16 Hz, 2CH=), 7.23-7.38 (10H, m, Ar).

^{13}C NMR (δ, ppm), mannite: C-1, C-6, 67.99 (+2.93); C-2, C-5 70.32 (-2.50); C-3, C-4 69.82 (-1.71); Ar: C-1′ 134.32; C-2′, C-6′ 128.77; C-3′, C-5′ 127.98; C-4′ 130.12; Ar-CH= 144.11; –OOC–CH=, 118.50; COO: 166.98.

Compound 7: 1.39 g (10.3%), mp 171-172°C, R_f 0.48. Found, %: C 52.89, H 4.87. $C_{20}H_{22}O_{12}$. Calc., %: C 52.86, H 4.84.

IR spectrum (KBr,ν, cm^{-1}): 1664 (CO, ester), 1552, 1512, 1464 (C=C), 3000-3600 (–OH).

PMR (δ, ppm): 4.81-5.19 (8H, m, mannite), 6.45 (1H, dd, J = 9 Hz, Ar), 6.77 (2H, d, J = 3 Hz, Ar), 7.78 (2H, d, J = 9 Hz, Ar).

^{13}C NMR (δ, ppm), mannite: C-1, C-6 68.38 (+3.27); C-2, C-5 70.27 (-2.55); C-3, C-4 69.59 (-1.94); Ar: 165.29, 163.89, 132.08, 108.42, 104.59, 102.89; COO: 170.44.

Compound 8: 3.14 g (24.6%), mp 96-97°C, R_f 0.57. Found, %: C 58.49, H 5.68. $C_{26}H_{30}O_{12}$. Calc., %: C 58.43, H 5.62.

IR spectrum (KBr,ν, cm^{-1}): 1704 (CO, ester), 1632, 1616, 1600 (C=C), 3000-3600 (–OH).

PMR (δ, ppm): 3.76 (6H, s, $–OCH_3$), 3.56-5.22 (8H, m, mannite), 6.45 (2H, d, J = 16 Hz, 2CH=), 7.80 (2H, d, J = 16 Hz, 2CH=), 7.00-7.16 (6H, m, Ar).

^{13}C NMR (δ, ppm), mannite: C-1, C-6 67.89 (+2.83); C-2, C-5 70.40 (-2.42); C-3, C-4 69.91 (-1.62); Ar: C-1′ 125.93, C-2′ 116.24, C-3′ 150.50, C-4′ 148.45, C-5′ 144.86, C-6′ 122.93; Ar–**C**H= 144.94; $–OCH_3$ 55.45; –COO–**C**H= 110.90; COO: 166.98.

REFERENCES

1. A. F. Artamonov, L. F. Burkovskaya, and G. K. Nikonov, *Khim. Prir. Soedin.*, 561 (1994).
2. A. F. Artamonov, L. F. Burkovskaya, F. S. Nigmatullina, and B. Zh. Dzhiembaev, *Khim. Prir. Soedin.*, 735 (1997).
3. A. F. Artamonov, F. S. Nigmatullina, and B. Zh. Dzhiembaev, *Khim. Prir. Soedin.*, 452 (1998).