SYNTHESIS OF SACCHAROSE ESTERS

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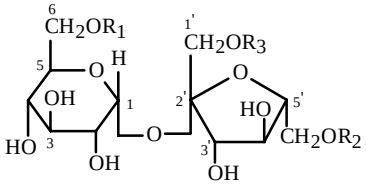
Di- and triesters of saccharose with aromatic acids are synthesized by transesterification of the methyl esters of the corresponding acids with saccharose. The structures of the resulting compounds are confirmed by IR spectroscopy, PMR, and ^{13}C NMR.

Key words: synthesis, saccharose esters, aromatic acids.

Aromatic acids (phenolcarboxylic, cinnamic, hydroxycinnamic, etc.) play an important role in the life cycle of plants and are widely distributed in nature. Their esters with carbohydrates are observed in many plants. Thus, di- and triesters of saccharose with ferulic and sinapic acids were isolated from *Tulipa* species and *Polygala chamaebuxus* [1, 2]. The glucose esters of *p*-coumaric and ferulic acids were observed in many vegetables (tomatoes, pepper, eggplant, peas, etc.) [3]. At present, natural esters of aromatic acids with carbohydrates are little used owing to their poor availability (minor components) as a result of the difficulty of isolating them from plants. Therefore, it seemed interesting to synthesize analogs of the natural esters of saccharose with aromatic acids.



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1. $R_1 = R_2 = -C(=O)-C_6H_5$, $R_3 = H$;

2. $R_1 = R_2 = -C(=O)-C_6H_4OH$-*o*, $R_3 = H$;

3. $R_1 = R_2 = -C(=O)-C_6H_4OCH_3$-*o*, $R_3 = H$;

4. $R_1 = R_2 = -C(=O)-CH=CH-C_6H_5$, $R_3 = H$;

5. $R_1 = R_2 = -C(=O)-CH_2-C_6H_5$, $R_3 = H$;

6. $R_1 = R_2 = -C(=O)-C_6H_4NH_2$-*o*, $R_3 = H$;

7. $R_1 = R_2 = -C(=O)-C_6H_4NO_2$-*n*, $R_3 = H$;

8. $R_1 = R_2 = R_3 = -C(=O)-C_6H_5$;

9. $R_1 = R_2 = R_3 = -C(=O)-C_6H_4OH$-*o*;

10. $R_1 = R_2 = R_3 = -C(=O)-CH=CH-C_6H_5$;

11. $R_1 = R_2 = R_3 = -C(=O)-CH_2-C_6H_5$;

12. $R_1 = R_2 = R_3 = -C(=O)-C_6H_4NH_2$-*o*;

13. $R_1 = R_2 = R_3 = -C(=O)-C_6H_4NO_2$-*n*

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The present article reports data on the synthesis of di- and triesters via the reaction of saccharose with methyl esters of salicylic, benzoic, *o*-methyoxybenzoic, cinnamic, anthranilic, phenylacetic, and *p*-nitrobenzoic acids in DMF catalyzed by K_2CO_3.

The aromatic C=C stretching vibrations in the IR spectra of the di- and triesters (**1-13**) are located at 1600 and 1500 cm^{-1}; the ester C=O at 1685-1725 cm^{-1}. The IR spectra also contain absorption bands at 990 and 935 cm^{-1} that are characteristic of the saccharose (atomic sequence –OCOCOC–) and 3000-3600 cm^{-1} (–OH).

The PMR spectra of the esters (**1-13**) exhibit signals for the CH and $–CH_2$ groups of the saccharose at 3.3-4.8 ppm; the anomeric proton of D-glucose at 5.2-5.5 ppm; and the aromatic protons at 6.8-8.3 ppm.

The positions of the acyl substituents in the di- and triesters (**1-13**) were determined using ^{13}C NMR spectra. The fact that the signals of C-6, C-6′, and C-1′ shift to weak field by 2-4 ppm confirms that the primary hydroxyls of the glucose (C-6) and the fructose (C-6′ and C-1′) parts of saccharose are acylated. The positions C-5, C-5′, and C-2′ undergo a diamagnetic shift by 1.2-2.5 ppm compared with the chemical shifts of the corresponding atoms in the unsubstituted saccharose. The chemical shifts of C-2, C-3, C-4, C-3′, and C-4′ change insignificantly ($\Delta\delta = \pm 0.5$ ppm) compared with those of the corresponding C atoms of saccharose. The chemical shifts of the aromatic C atoms of **1-13** are consistent with those of the C atoms in the starting methyl esters.

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 DMSO-d_6, CD_3OD, and $CDCl_3$. The course of the reactions was monitored by TLC on Silufol UV-254 plates using $CHCl_3$—CH_3OH (9-4:1). Compounds **1-13** were isolated by column chromatography on silica gel L.

Di- and triesters of saccharose with aromatic acids were synthesized by the literature method [4]. Diesters were prepared at a saccharose—methyl ester mole ratio of 1:2; triesters, 1:3, respectively.

Compound 1: 4.82 g (17.5%), mp 89-91°C, R_f 0.20. Found, %: C 56.66, H 5.48. $C_{26}H_{30}O_{13}$. Calc., %: C 56.73, H 5.45.

IR spectrum (ν, cm^{-1}): 1720 (CO, ester), 1600, 1580 (C=C), 3100-3600 (–OH).

PMR (δ, ppm, CD_3OD): 3.42-4.78 (13H, m, sacch.), 5.44 (1H, anom., d, J = 4 Hz), 7.34-8.03 (10H, m, Ar).

^{13}C NMR (δ, ppm, DMSO-d_6), carbohydrate: C-1 92.98 ($\Delta\delta = +0.1$), C-2 71.91 (-0.30), C-3 73.58 (+0.26), C-4 71.30 (+0.42), C-5 71.56 (-2.20), C-6 65.16 (+3.83), C-1′ 63.42 (+0.34), C-2′ 105.20 (+0.48), C-3′ 78.41 (+0.35), C-4′ 74.18 (+0.11), C-5′ 80.27 (-2.07), C-6′ 66.22 (+3.39); arom. C: 129.03, 129.15, 130.28, 130.71, 133.81; COO: 167.27, 167.64.

Compound 2: 8.15 g (28%), mp 125-128°C, R_f 0.38. Found, %: C 53.53, H 5.18. $C_{26}H_{30}O_{15}$. Calc., %: C 53.61, H 5.15.

IR spectrum (ν, cm^{-1}): 1685 (CO, ester), 1635, 1500, 1450 (C=C), 3100-3600 (–OH).

PMR (δ, ppm, DMSO-d_6): 3.28-4.62 (13H, m, sacch.), 5.25 (1H, d, anom., J = 4 Hz), 6.86-7.84 (8H, m, Ar), 10.45 (2H, OH, d, J = 4.5 Hz).

^{13}C NMR (δ, ppm), carbohydrate: C-1 93.30 (+0.42), C-2 71.43 (+0.15), C-3 73.46 (+0.14), C-4 70.65 (-0.23), C-5 71.60 (-2.16), C-6 64.36 (+3.03), C-1′ 63.28 (+0.20), C-2′ 104.92 (-0.20), C-3′ 78.35 (+0.27), C-4′ 74.42 (+0.35), C-5′ 80.20 (-2.14), C-6′ 65.60 (+2.77); arom. C: 112.29, 116.91, 118.94, 119.05, 129.66, 135.39, 159.76, 159.89; COO: 168.25, 168.54.

Compound 3: 5.26 g (18.1%), mp 177-180°C, R_f 0.38. Found, %: C 54.96, H 5.51. $C_{28}H_{34}O_{15}$. Calc., %: C 55.08, H 5.57.

IR spectrum (ν, cm^{-1}): 1715 (CO, ester), 1600, 1495 (C=C), 3100-3600 (–OH).

PMR (δ, ppm, DMSO-d_6): 3.78 (3H, m, OCH_3), 3.79 (3H, m, OCH_3), 3.38-4.55 (13H, m, sacch.), 5.22 (1H, anom., d, J = 3.5 Hz), 6.94-7.72 (3H, m, Ar).

^{13}C NMR (δ, ppm), carbohydrate: C-1 93.12 (+0.24), C-2 72.46 (+0.18), C-3 73.58 (+0.26), C-4 71.06 (+0.16), C-5 71.92 (-1.84), C-6 64.47 (+3.16), C-1′ 62.49 (-0.34), C-2′ 104.38 (-0.24), C-3′ 77.87 (-0.20), C-4′ 73.85 (-0.22), C-5′ 79.07 (-2.08), C-6′ 65.96 (+3.56); arom. C: 112.25, 119.81, 119.88, 130.60, 133.35, 158.16, 158.25; $–OCH_3$: 55.45; COO: 165.47, 165.05.

Compound 4: 5.15 g (17.1%), mp 103-105°C, R_f 0.44. Found, %: C 59.92, H 5.61. $C_{30}H_{34}O_{13}$. Calc., %: C 59.80,

H 5.65.

IR spectrum (ν, cm^{-1}): 1720 (CO, ester), 1635, 1500, 1450 (C=C), 3100-3600 (–OH).

PMR (δ, ppm, DMSO-d_6): 3.28-4.71 (13H, m, sacch.), 5.41 (1H, anom., d, J = 3.5 Hz), 6.56 (2H, dd, J = 16 Hz, CH=), 7.34-7.39 (8H, m, Ar), 7.56-7.59 (2H, m, Ar), 7.69 (2H, dd, J = 16 Hz, CH=).

^{13}C NMR (δ, ppm), carbohydrate: C-1 93.06 (+0.18), C-2 72.46 (+0.18), C-3 73.56 (+0.24), C-4 70.47 (-0.41), C-5 72.19 (-1.57), C-6 64.54 (+3.21), C-1′ 63.22 (+0.14), C-2′ 104.85 (-0.32), C-3′ 78.35 (+0.28), C-4′ 73.84 (-0.23), C-5′ 80.54 (-1.80), C-6′ 66.55 (+2.72); arom. C: 128.84, 129.63, 131.17, 135.28; CH=: 118.31, 146.05; COO: 168.19, 167.48.

Compound 5: 4.2 g (14.5%), mp 63-65°C, R_f 0.33. Found, %: C 63.96, H 6.41. $C_{28}H_{34}O_{13}$. Calc., %: C 63.88, H 6.46.

IR spectrum (ν, cm^{-1}): 1700 (CO, ester), 1590, 1500 (C=C), 3100-3600 (–OH).

PMR (δ, ppm, CD_3OD): 3.29 (4H, d, J = 1.5 Hz, Ar–CH_2CO–), 3.50-4.56 (13H, m, sacch.), 5.33 (1H, anom., d, J = 4 Hz), 7.15-7.32 (10H, m, Ar).

^{13}C NMR (δ, ppm), carbohydrate: C-1 92.66 (-0.22), C-2 72.46 (+0.18), C-3 73.54 (+0.22), C-4 70.65 (-0.23), C-5 71.80 (-1.96), C-6 64.34 (+3.01), C-1′ 63.13 (+0.05), C-2′ 104.90 (+0.18), C-3′ 78.27 (+0.20), C-4′ 73.88 (-0.18), C-5′ 80.19 (-1.26), C-6′ 65.39 (+2.56); Ar–CH_2COO: 41.31, 41.52; COO: 173.16, 172.33.

Compound 6: 6.52 g (22.5%), mp 107-109°C, R_f 0.40. Found, %: C 53.65, H 5.46, N 4.76. $C_{26}H_{32}N_2O_{13}$. Calc., %: C 53.79, H 5.52, N 4.83.

IR spectrum (ν, cm^{-1}): 1690 (CO, ester), 1615, 1590, 1490 (C=C), 3100-3600 (–OH), 3380, 3470 (–NH_2).

PMR (δ, ppm, CD_3OD): 3.41-4.65 (13H, m, sacch.), 5.49 (1H, anom., d, J = 4 Hz), 6.55 (4H, t, J = 7.5 Hz, –NH_2), 6.61-7.92 (8H, m, Ar).

^{13}C NMR (δ, ppm), carbohydrate: C-1 93.07 (+0.19), C-2 72.56 (+0.28), C-3 73.46 (+0.14), C-4 70.66 (-0.20), C-5 71.94 (-1.82), C-6 64.75 (+3.42), C-1′ 63.26 (+0.18), C-2′ 104.92 (+0.20), C-3′ 78.31 (+0.24), C-4′ 73.86 (-0.21), C-5′ 80.21 (-2.13), C-6′ 66.07 (+3.14); arom. C: 110.72, 116.31, 117.41, 131.91, 134.89, 152.25; COO: 168.69, 169.01.

Compound 7: 5.05 g (15.8%), mp 85-87°C, R_f 0.41. Found, %: C 48.67, H 4.42, N 4.31. $C_{26}H_{32}N_2O_{17}$. Calc., %: C 48.75, H 4.38, N 4.38.

IR spectrum (ν, cm^{-1}): 1720 (CO, ester), 1605, 1450 (C=C), 1530, 1350 (–NO_2), 3000-3650 (–OH).

PMR (δ, ppm, CD_3OD): 3.35-4.71 (13H, m, sacch.), 5.43 (1H, anom., d, J = 4 Hz), 7.96-8.30 (8H, m, Ar).

^{13}C NMR (δ, ppm), carbohydrate: C-1 92.66 (-0.22), C-2 72.15 (-0.13), C-3 73.46 (+0.16), C-4 70.56 (-0.32), C-5 71.50 (-2.26), C-6 65.53 (+4.20), C-1′ 63.50 (+0.42), C-2′ 104.39 (-0.33), C-3′ 77.83 (-0.24), C-4′ 73.84 (-0.23), C-5′ 80.02 (-2.03), C-6′ 66.98 (+4.15); arom. C: 124.08, 124.26, 131.53, 135.95, 136.21, 151.46; COO: 165.31, 165.66.

Compound 8: 6.86 g (21%), mp 89-92°C, R_f 0.45. Found, %: C 60.43, H 5.24. $C_{33}H_{34}O_{14}$. Calc., %: C 60.55, H 5.20.

IR spectrum (ν, cm^{-1}): 1715 (CO, ester), 1600, 1490 (C=C), 3100-3600 (–OH).

PMR (δ, ppm, DMSO-d_6): 3.41-4.72 (13H, m, sacch.), 5.52 (1H, anom., d, J = 4 Hz), 7.29-8.12 (15H, m, Ar).

^{13}C NMR (δ, ppm): C-1 92.73 (-0.15), C-2 71.72 (-0.46), C-3 73.63 (+0.31), C-4 71.28 (+0.40), C-5 71.63 (-2.13), C-6 64.05 (+2.72), C-1′ 66.20 (+3.12), C-2′ 103.28 (-1.44), C-3′ 78.36 (+0.30), C-4′ 74.46 (+0.39), C-5′ 80.38 (-1.96), C-6′ 65.17 (+2.34); arom. C: 129.02, 129.10, 130.29, 130.55, 133.76; COO: 166.86, 167.30, 167.65.

Compound 9: 8.9 g (25.4%), mp 88-90°C, R_f 0.54. Found, %: C 57.32, H 4.76. $C_{33}H_{34}O_{17}$. Calc., %: C 57.41, H 4.84.

IR spectrum (ν, cm^{-1}): 1685 (CO, ester), 1615, 1585 (C=C), 3100-3600 (–OH).

PMR (δ, ppm, $CDCl_3$): 3.42-4.70 (13H, m, sacch.), 5.45 (1H, anom.), 6.50-7.80 (12H, m, Ar), 10.36, 10.42, 10.44 (3H, –OH, salic.).

^{13}C NMR (δ, ppm): C-1 93.06 (+0.16), C-2 72.56 (+0.28), C-3 73.64 (+0.32), C-4 70.96 (+0.08), C-5 71.34 (-2.42), C-6 64.78 (+3.45), C-1′ 66.16 (+3.08), C-2′ 103.08 (-1.64), C-3′ 77.92 (0.15), C-4′ 74.41 (+0.34), C-5′ 80.17 (-2.17), C-6′ 65.35 (+2.52); arom. C: 111.43, 111.53, 117.30, 118.92, 119.12, 129.54, 135.81, 161.01, 161.42; COO: 169.16, 169.51, 169.77.

Compound 10: 3.08 g (8.4%), mp 83-85°C, R_f 0.48. Found, %: C 63.93, H 5.42. $C_{39}H_{40}O_{14}$. Calc., %: C 63.93, H 5.46.

IR spectrum (ν, cm^{-1}): 1715 (CO, ester), 1580, 1500 (C=C), 3100-3600 (–OH).

PMR (δ, ppm, DMSO-d_6): 3.33-4.56 (13H, m, sacch.), 5.39 (1H, anom., d, J = 9 Hz), 6.59 (1H, d, J = 16 Hz, –CH=),

7.32-7.62 (15H, m, Ar), 7.69 (1H, d, J = 16 Hz, –CH=).

^{13}C HMR (δ, ppm), carbohydrate: C-1 93.07 (+0.19), C-2 72.56 (+0.28), C-3 73.68 (+0.36), C-4 70.66 (-0.20), C-5 71.44 (-2.32), C-6 64.70 (+3.37), C-1′ 66.56 (+3.48), C-2′ 103.05 (-1.67), C-3′ 78.27 (+0.20), C-4′ 74.28 (+0.21), C-5′ 80.27 (-2.07), C-6′ 65.28 (+2.45); arom. C: 128.54, 129.82, 131.10, 135.38; –CH=: 118.34, 135.38; COO: 166.94, 167.48, 168.19.

Compound 11: 9.1 g (26.1%), mp 43-45°C, R_f 0.53. Found, %: C 62.12, H 5.72. $C_{36}H_{40}O_{14}$. Calc., %: C 62.07, H 5.75.

IR spectrum (ν, cm^{-1}): 1700 (CO, ester), 1600, 1490 (C=C), 3100-3600 (–OH).

PMR (δ, ppm, CD_3OD): 3.28 (6H, t, J = 2 Hz, Ar–CH_2 CO–), 3.46-4.52 (13H, m, sacch.), 5.28 (1H, anom., d, J = 3.5 Hz), 7.16-7.32 (15H, m, Ar).

^{13}C NMR (δ, ppm), carbohydrate: C-1 93.18 (+0.30), C-2 72.44 (+0.16), C-3 73.68 (+0.36), C-4 70.66 (-0.20), C-5 71.45 (-2.31), C-6 64.46 (+3.13), C-1′ 66.38 (+3.30), C-2′ 103.65 (-1.33), C-3′ 78.28 (+0.21), C-4′ 74.16 (+0.09), C-5′ 80.64 (-1.70), C-6′ 65.37 (+2.54); arom. C: 127.59, 127.69, 129.08, 130.00, 134.96, 135.08; Ar–CH_2–CO–: 41.26, 41.50; COO: 172.15, 172.88, 173.12.

Compound 12: 1.47 g (4.2%), mp 88-90°C, R_f 0.60. Found, %: C 56.58, H 5.24, N 5.95. $C_{33}H_{37}N_3O_{14}$. Calc., %: C 56.65, H 5.29, N 6.01.

IR spectrum (ν, cm^{-1}): 1695 (CO, ester), 1620, 1590, 1490 (C=C), 3100-3600 (–OH), 3470, 3370 (–NH_2).

PMR (δ, ppm, CD_3OD): 3.45-4.64 (13H, m, sacch.), 5.57 (1H, anom.), 6.57 (6H, t, J = 7 Hz, –NH_2), 6.63-7.98 (12H, m, Ar).

^{13}C NMR (δ, ppm): C-1 93.25 (+0.37), C-2 72.56 (+0.28), C-3 73.72 (+0.40), C-4 71.25 (+0.37), C-5 71.67 (-2.09), C-6 64.51 (+3.18), C-1′ 66.18 (+3.35), C-2′ 103.15 (-1.57), C-3′ 78.25 (+0.18), C-4′ 74.26 (+0.19), C-5′ 80.27 (-2.07), C-6′ 65.75 (+2.92); arom. C: 110.37, 116.15, 117.33, 132.25, 134.57, 152.33; COO: 168.27, 168.69, 169.01.

Compound 13: 2.21 g (8.4%), mp 94-96°C, R_f 0.53. Found, %: C 50.12, H 3.98, N 5.26. $C_{33}H_{31}N_3O_{20}$. Calc., %: C 50.19, H 3.93, N 5.32.

IR spectrum (ν, cm^{-1}): 1725 (CO, ester), 1610, 1450 (C=C), 1525, 1350 (–NO_2), 3100-3600 (–OH).

PMR (δ, ppm, CD_3OD): 3.35-4.76 (13H, m, sacch.), 5.50 (1H, anom., d, J = 4 Hz), 8.08-8.30 (12H, m, Ar).

^{13}C NMR (δ, ppm), carbohydrate: C-1 93.29 (+0.41), C-2 72.62 (+0.24), C-3 73.82 (+0.50), C-4 71.22 (+0.34), C-5 71.32 (-2.44), C-6 65.15 (+3.82), C-1′ 67.03 (+3.95), C-2′ 103.02 (-1.70), C-3′ 78.34 (+0.27), C-4′ 74.38 (+0.31), C-5′ 79.94 (-2.40), C-6′ (66.30 (+3.47); arom. C: 124.06, 124.21, 131.51, 135.91, 136.20, 151.42; COO: 165.08, 165.30, 165.64.

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