CHAPTER II
EXPERIMENTAL

2.1 Instruments and Equipment

Melting points were determined with a Fisher-Johns melting point apparatus and uncorrected. Thin layer chromatography (TLC) was performed on aluminium sheets precoated with silica gel (Merck Kieselgel 60 F_{254}). Column chromatography was performed on silica gel (Merck Kieselgel 60 G).

The FT-IR spectra were recorded on a Nicolet Fourier Transform Infrared spectrophotometer: Impact 410. Solid samples were incorporated into a pellet of potassium bromide. Liquid samples were dropped on sodium chloride cells. The ^{1}H- and ^{13}C-NMR spectra were obtained in deuterated chloroform ($CDCl_3$) or deuterated dimethylsulfoxide (DMSO-d_6) with tetramethylsilane (TMS) as an internal reference on a Bruker: ACF200 spectrometer and a Jeol: JNM-A500 FTNMR which operated at 200.13 MHz for ^{1}H and 50.32 MHz for ^{13}C nuclei, and 500.00 MHz for ^{1}H and 125.00 MHz for ^{13}C nuclei, respectively. The chemical shifts (δ) are assigned by comparison with residue solvent protons. $CDCl_3$/DMSO-d_6 means that DMSO-d_6 is added dropwise to a suspension of the compound in $CDCl_3$ until a clear solution is obtained. Mass spectra (70 eV) were acquired from a Fissons Instrument mass spectrometer: VG TRIO 2000 in EI mode.

2.2 Chemicals

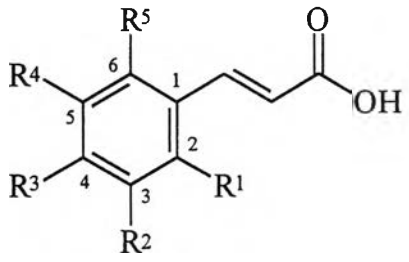
All solvents used in this research were purified prior to use by standard methodology except for those which were reagent grades. The reagents used for synthesizing the precursors were purchased from Fluka Chemical Company or otherwise stated and were used without further purification.

2.3 Synthesis of Substituted *trans*-Cinnamic Acids

General Procedure [30]

Malonic acid 3.12 g (0.03 mol) was dissolved in 5.20 mL of anhydrous pyridine, selected aromatic aldehyde (0.03 mol) and 0.28 mL of piperidine were added. The solution was refluxed approximately 1.5 hour, cooled to room temperture, then poured into a mixture of 16 g of ice, 8 mL of conc HCl and 26 mL of H_2O, precipitating the acid as a colorless solid. The product was filtered, washed with ice water and recrystallized with dilute ethanol.

Forty-seven substituted *trans*-cinnamic acids were synthesized and their structures are displayed as shown in Fig 2.1.



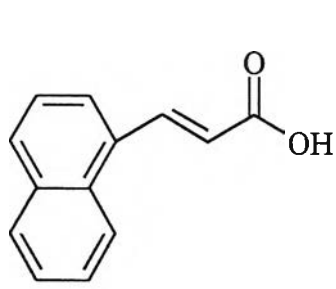
Cpds	R^1	R^2	R^3	R^4	R^5
C	H	H	H	H	H
C1	H	F	H	H	H
C2	H	H	F	H	H
C3	Cl	H	H	H	H
C4	H	Cl	H	H	H
C5	H	H	Cl	H	H
C6	Br	H	H	H	H
C7	H	Br	H	H	H
C8	H	H	Br	H	H
C9	Cl	H	Cl	H	H
C10	Cl	H	H	H	Cl
C11	H	Cl	Cl	H	H
C12	Cl	H	H	H	F

Fig 2.1 Structures of synthesized substituted *trans*-cinnamic acids

Cpds	R^1	R^2	R^3	R^4	R^5
C13	OCH_3	H	H	H	H
C14	H	OCH_3	H	H	H
C15	H	H	OCH_3	H	H
C16	H	H	OC_4H_9	H	H
C17	H	H	OC_6H_{13}	H	H
C18	H	H	OC_8H_{17}	H	H
C19	H	H	$OC_{12}H_{25}$	H	H
C20	H	H	OCH_2Ph	H	H
C21	H	H	OPh	H	H
C22	H	OCH_3	OC_4H_9	H	H
C23	H	OCH_3	OC_6H_{13}	H	H
C24	H	OCH_3	OC_8H_{17}	H	H
C25	H	OCH_3	$OC_{12}H_{25}$	H	H
C26	H	OCH_3	OCH_2Ph	H	H
C27	OCH_3	OCH_3	H	H	H
C28	OCH_3	H	OCH_3	H	H
C29	OCH_3	H	H	OCH_3	H
C30	H	OCH_3	OCH_3	H	H
C31	H	OCH_3	H	OCH_3	H
C32	H	OCH_3	OCH_3	OCH_3	H
C33	H	-OCH_2O-		H	H
C34	NO_2	H	H	H	H
C35	H	NO_2	H	H	H
C36	H	H	NO_2	H	H
C37	Cl	H	H	NO_2	H
C38	H	NO_2	Cl	H	H
C39	NO_2	H	H	Cl	H
C40	H	H	CH_3	H	H
C41	H	H	$CH(CH_3)_2$	H	H
C42	H	H	$C(CH_3)_3$	H	H
C43	H	H	CF_3	H	H

Fig 2.1 (cont.)

Cpds	R^1	R^2	R^3	R^4	R^5
C44	H	CN	H	H	H
C45	H	H	CN	H	H



C46

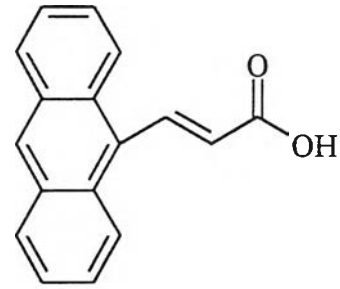


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Fig. 2.1 (cont.)

Halocinnamic Acids

3-Fluorocinnamic acid (**C1**): Light white solid (57%), m.p. 165-167°C (ethanol) (lit.[31] 166.5°C), R_f 0.62 (ethanol); IR (KBr, cm^{-1}): 3596-3320, 1690, 1636, 1583, 1491, 1446, 1419, 1354, 1250 and 1150; ^{1}H-NMR (DMSO-d_6) δ (ppm): 7.57 (*d*, *J* = 15.95 Hz, 1H, Ar-C**H**=), 7.22-7.50 (Ar-H, 4H) and 6.60 (*d*, *J* = 16.04 Hz, 1H, =C**H**-COOH); ^{13}C-NMR (DMSO-d_6) δ (ppm): 167.3 (-**C**OOH), 164.8, 136.8, 130.8, 124.6, 116.8 and 114.3 (aromatic carbons), 142.5 and 120.8 (olefinic carbons).

4-Fluorocinnamic acid (**C2**): White mirror-like crystal (67%), m.p. 209-210°C (ethanol) (lit.[32] 202°C), R_f 0.78 (ethanol); IR (KBr, cm^{-1}): 3648-3250, 1685, 1634, 1598, 1511, 1432, 1350, 1310, 1280, 1250, 1150 and 1050; ^{1}H-NMR (DMSO-d_6) δ (ppm): 7.48 (*d*, *J* = 16.00 Hz, 1H, Ar-C**H**=), 6.88-7.40 (Ar-H, 4H) and 6.20 (*d*, *J* = 15.91 Hz, 1H, =C**H**-COOH); ^{13}C-NMR (DMSO-d_6) δ (ppm): 168.6 (-**C**OOH), 161.1 130.7, 129.8 (2x1C) and 115.9 (2x1C) (aromatic carbons), 143.2 and 118.5 (olefinic carbons).

2-Chlorocinnamic acid (**C3**): Light white solid (56%), m.p. 210-212°C (ethanol) (lit.[31] 212°C), R_f 0.88 (ethanol); IR (KBr, cm^{-1}): 3604-3320, 1685, 1620, 1567, 1470, 1419, 1350, 1300, 1290, 1220 and 1040; ^{1}H-NMR (acetone-d_6) δ (ppm): 8.07 (*d*, *J* = 15.87 Hz, 1H, Ar-C**H**=), 7.48-7.89 (Ar-H, 4H) and 6.58 (*d*, *J* = 16.17 Hz, 1H, =C**H**-COOH); ^{13}C-NMR (acetone-d_6) δ (ppm): 167.3 (-**C**OOH), 135.1, 133.4, 132.3, 130.9, 128.9 and 128.5 (aromatic carbons), 142.5 and 120.8 (olefinic carbons).

3-Chlorocinnamic acid (**C4**): Light white solid (77%), m.p. 162-164°C (ethanol) (lit.[31] 165°C), R_f 0.65 (ethanol); IR (KBr, cm^{-1}): 3654-3280, 1675, 1640, 1562, 1475, 1432, 1330, 1310, 1280, 1230 and 1190; ^{1}H-NMR (DMSO-d_6) δ (ppm): 7.56 (*d*, *J*= 16.05 Hz, 1H, Ar-C**H**=), 7.40-7.88 (Ar-H, 4H) and 6.60 (*d*, *J* = 16.04 Hz, 1H, =C**H**-COOH); ^{13}C-NMR (DMSO-d_6) δ (ppm): 167.0 (-**C**OOH), 136.5, 133.7, 130.6, 129.8, 127.8 and 126.7 (aromatic carbons), 142.3 and 121.0 (olefinic carbons).

4-Chlorocinnamic acid (**C5**): White solid (75%), m.p. 250-251°C (ethanol) (lit.[33, 34] 248-250°C), R_f 0.74 (ethanol); IR (KBr, cm^{-1}): 3590-3300, 1685, 1629, 1601, 1572, 1491, 1472, 1306, 1286, 1230, 1180 and 1086; ^{1}H-NMR (DMSO-d_6) δ (ppm): 7.75-7.44 (Ar-H, 4H), 7.57 (*d*, *J* = 16.07 Hz, 1H, Ar-C**H**=) and 6.54 (*d*, *J* = 16.05 Hz, 1H, =C**H**-COOH); ^{13}C-NMR (DMSO-d_6) δ (ppm): 167.4 (-**C**OOH), 134.7, 133.2, 129.9 (2x1C) and 128.9 (2x1C) (aromatic carbons), 142.5 and 120.0 (olefinic carbons).

2-Bromocinnamic acid (**C6**): White crystal (93%), m.p. 208-209°C (ethanol) (lit.[31] 215-216°C), R_f 0.66 (ethanol); IR (KBr, cm^{-1}): 3664-3300, 1685, 1625, 1567, 1475, 1419, 1350, 1325, 1290 and 1224; ^{1}H-NMR (acetone-d_6) δ (ppm): 8.04 (*d*, *J* = 15.87 Hz, 1H, Ar-C**H**=), 7.34-7.88 (Ar-H, 4H) and 6.54 (*d*, *J* = 16.17 Hz, 1H, =C**H**-COOH); ^{13}C-NMR (acetone-d_6) δ (ppm): 167.2 (-**C**OOH), 135.2, 134.2, 132.4, 129.0 and 125.5 (aromatic carbons), 143.2 and 122.4 (olefinic carbons).

3-Bromocinnamic acid (**C7**): Pale yellow crystal (73%), m.p. 179-180°C (ethanol) (lit.[31] 178-179°C), R_f 0.85 (ethanol); IR (KBr, cm^{-1}): 3624-3310, 1685, 1635, 1572, 1470, 1424, 1316, 1280, 1219 and 1180; ^{1}H-NMR (acetone-d_6) δ (ppm): 7.64 (*d*, *J* = 15.87 Hz, 1H, Ar-C**H**=), 7.34-7.88 (Ar-H, 4H) and 6.60 (*d*, *J* = 16.17 Hz, 1H, =C**H**-COOH); ^{13}C-NMR (acetone-d_6) δ (ppm): 167.4 (-**C**OOH), 138.0, 133.7, 131.6, 131.6, 127.8 and 123.4 (aromatic carbons), 143.6 and 121.1 (olefinic carbons).

4-Bromocinnamic acid (**C8**): White needle crystal (98%), m.p. 258-259°C (ethanol) (lit.[31] 257°C), R_f 0.85 (ethanol); IR (KBr, cm^{-1}): 3704-3200, 1688, 1629, 1587, 1567, 1485, 1424, 1380, 1325, 1300, 1285, 1210 and 1074; ^{1}H-NMR (acetone-d_6) δ (ppm):), 7.66-7.61 (Ar-H, 4H), 7.65 (*d*, *J* = 15.87 Hz, 1H, Ar-C**H**=) and 6.56 (*d*, *J* = 15.87 Hz, 1H, =C**H**-COOH); ^{13}C-NMR (acetone-d_6) δ (ppm): 167.5 (-**C**OOH), 134.8, 132.9 (2x1C), 130.7 (2x1C) and 124.6 (aromatic carbons), 143.9 and 120.2 (olefinic carbons).

2,4-Dichlorocinnamic acid (**C9**): Light pale green solid (75%), m.p. 233-235 °C (ethanol) (lit.[33] 235-236°C), R_f 0.66 (ethanol); IR (KBr, cm^{-1}): 3634-3320, 1690, 1619, 1582, 1475, 1285, 1200 and 1090; ^{1}H-NMR (DMSO-d_6) δ (ppm): 7.85 (*d*, *J* = 16.07 Hz, 1H, Ar-C**H**=),), 7.11-7.47 (Ar-H, 3H) and 6.27 (*d*, *J* = 15.87 Hz, 1H, =C**H**-COOH); ^{13}C-NMR (DMSO-d_6) δ (ppm): 167.9 (-**C**OOH), 135.9, 135.2, 131.4, 129.8, 128.4 and 127.5 (aromatic carbons), 138.9 and 122.0 (olefinic carbons).

2,6-Dichlorocinnamic acid (**C10**): Pale yellow needle crystal (33%), m.p. 195-197°C (ethanol) (lit.[33, 34] 194-196°C), R_f 0.66 (ethanol); IR (KBr, cm^{-1}): 3594-3320, 1693, 1650, 1587, 1434, 1316, 1224 and 1185; ^{1}H-NMR (DMSO-d_6) δ (ppm): 7.49 (*d*, *J* = 16.36 Hz, 1H, Ar-C**H**=), 7.18-6.97 (Ar-H, 3H) and 6.31 (*d*, *J* = 16.33 Hz, 1H, =C**H**-COOH); ^{13}C-NMR (DMSO-d_6) δ (ppm): 170.8 (-**C**OOH), 135.1, 131.6 (2x1C), 130.1, and 128.9 (2x1C) (aromatic carbons), 140.4 and 15.9 (olefinic carbons).

3,4-Dichlorocinnamic acid (**C11**): White solid (75%), m.p. 219-221°C (ethanol) (lit.[34] 218-220°C), R_f 0.56 (ethanol); IR (KBr, cm^{-1}): 3594-3320, 1680, 1624, 1553, 1471, 1424, 1385, 1310 and 1290; ^{1}H-NMR (DMSO-d_6) δ (ppm): 7.60-7.99 (Ar-H, 3H), 7.54 (*d*, J = 16.05 Hz, 1H, Ar-C**H**=) and 6.62 (*d*, J = 16.05 Hz, 1H, =C**H**-COOH); ^{13}C-NMR (DMSO-d_6) δ (ppm): 167.2 (-**C**OOH), 135.1, 132.4, 131.7, 130.9, 129.9 and 128.1 (aromatic carbons), 141.2 and 121.6 (olefinic carbons).

2-Chloro-6-fluorocinnamic acid (**C12**): Pale yellow solid (48%), m.p. 210-212°C (ethanol) (lit.[31] 212°C), R_f 0.68 (ethanol); IR (KBr, cm^{-1}): 3624-3340, 1700, 1624, 1601, 1568, 1455, 1419, 1300, 1285, 1230 and 1215; ^{1}H-NMR ($CDCl_3$) δ (ppm): 8.00 (*d*, *J* = 16.17 Hz, 1H, Ar-C**H**=), 7.29-7.02 (Ar-H, 3H) and 6.74 (*d*, *J* = 16.38 Hz, 1H, =C**H**-COOH); ^{13}C-NMR ($CDCl_3$) δ (ppm): 171.3 (-**C**OOH), 136.9, 131.2, 131.0, 126.1, 124.3 and 114.7 (aromatic carbons), 136.2 and 115.2 (olefinic carbons).

Alkoxy Cinnamic Acids

2-Methoxycinnamic acid (**C13**): Pale yellow needle crystal (80%), m.p. 185-186°C (ethanol) (lit.[31] 185-186°C), R_f 0.67 (ethanol); IR (KBr, cm^{-1}): 3614-3320, 1685, 1620, 1485, 1475, 1427, 1345, 1250, 1220, 1150 and 1100; ^{1}H-NMR (acetone-d_6) δ (ppm): 8.00 (*d*, *J* = 16.17 Hz, 1H, Ar-C**H**=), 6.98-7.66 (Ar-H, 4H) and 6.56 (*d*, *J* = 16.17 Hz, 1H, =C**H**-COOH); ^{13}C-NMR (acetone-d_6) δ (ppm): 168.3 (-COOH),

159.2, 132.5, 129.3, 124.0, 121.5 and 112.3 (aromatic carbons), 140.6 and 119.3 (olefinic carbons).

3-Methoxycinnamic acid (**C14**): White mirror-like needle crystal (59%), m.p. 120-122°C (ethanol) (lit.[33, 34] 117-118°C), R_f 0.69 (ethanol); IR (KBr, cm^{-1}): 3650-3350, 1680, 1640, 1582, 1491, 1320, 1285, 1250, 1150 and 1050; ^{1}H-NMR (DMSO-d_6) δ (ppm): 7.55 (*d*, *J* = 16.08 Hz, 1H, Ar-C**H**=), 6.95-7.27 (Ar-H, 4H) and 6.54 (*d*, *J* = 15.92 Hz, 1H, =C**H**-COOH); ^{13}C-NMR (DMSO-d_6) δ (ppm): 167.5 (-**C**OOH), 159.6, 135.6, 129.9, 120.7, 116.2 and 112.9 (aromatic carbons), 143.9 and 119.5 (olefinic carbons).

4-Methoxycinnamic acid (**C15**): White mirror-like needle crystal (62%), m.p. 173-174°C (ethanol) (lit.[33, 34, 35] 172-175°C), R_f 0.62 (ethanol); IR (KBr, cm^{-1}): 3650-3300, 1690, 1630, 1598, 1516, 1446, 1432, 1250, 1210 and 1175; ^{1}H-NMR (acetone-d_6) δ (ppm): 7.64 (*d*, *J* = 15.87 Hz, 1H, Ar-C**H**=), 6.97-7.64 (Ar-H, 4H) and 6.40 (*d*, *J* = 16.17 Hz, 1H, =C**H**-COOH); ^{13}C-NMR (acetone-d_6) δ (ppm): 168.2 (-**C**OOH), 162.5, 130.6 (2x1C), 128.0 and 115.2 (2x1C) (aromatic carbons), 145.3 and 116.5 (olefinic carbons).

4-Butyloxycinnamic acid (**C16**): Pale yellow solid (73%), m.p. 164-165°C (ethanol) (lit.[36] 153-154°C), R_f 0.73 (ethanol); IR (KBr, cm^{-1}): 3594-3320, 2955, 2868, 1675, 1603, 1568, 1519, 1475, 1429, 1385, 1350, 1200 and 1185; ^{1}H-NMR (DMSO-d_6) δ (ppm): 7.60 (*d*, *J* = 8.78 Hz, 2H), 7.52 (*d*, *J* = 15.97 Hz, 1H, Ar-C**H**=), 6.93 (*d*, *J* = 8.72 Hz, 2H), 6.47 (*d*, *J* = 15.98 Hz, 1H, =C**H**-COOH), 3.99 (*t*, *J* = 6.41 Hz, 2H), 1.27-1.71 (*m*, br, 4H) and 0.91 (*t*, *J* = 7.23 Hz, 3H); ^{13}C-NMR (DMSO-d_6) δ (ppm): 167.8 (-**C**OOH), 160.4, 129.9 (2x1C), 126.6 and 114.8 (2x1C) (aromatic carbons), 143.7 and 116.4 (olefinic carbons), 67.3, 30.6, 18.7 and 13.6.

4-Hexyloxycinnamic acid (**C17**)[37]: Pale yellow solid (90%), m.p. 160-162°C (ethanol), R_f 0.70 (ethanol); IR (KBr, cm^{-1}): 3625-3319, 2935, 2873, 1675, 1603, 1582, 1511, 1471, 1432, 1300, 1285, 1250, 1225 and 1185; ^{1}H-NMR (DMSO-d_6) δ (ppm): 7.73 (*d*, *J* = 15.85 Hz, 1H, Ar-C**H**=), 7.48 (*d*, *J* = 8.56 Hz, 2H), 6.88 (*d*, *J* = 8.51 Hz, 2H), 6.31 (*d*, *J* = 16.00 Hz, 1H, =C**H**-COOH), 3.97 (*t*, *J* = 6.48 Hz, 2H), 1.25-1.83 (*m*, br, 8H) and 0.89 (*t*, *J* = 6.49 Hz, 3H); ^{13}C-NMR (DMSO-d_6) δ (ppm): 174.0 (-**C**OOH), 166.2, 135.7 (2x1C), 132.1 and 120.6 (2x1C) (aromatic carbons), 149.9 and 121.6 (olefinic carbons), 73.4, 36.6, 34.1, 30.7, 27.7 and 19.5.

4-Octyloxycinnamic acid (**C18**)[37]: Pale yellow mirror-like crystal (70%), m.p. 142-144°C (ethanol), R_f 0.66 (ethanol); IR (KBr, cm^{-1}): 3650-3350, 2823, 1675, 1640, 1603, 1577, 1555, 1475, 1437, 1315, 1300, 1250, 1220 and 1175; ^{1}H-NMR (DMSO-d_6) δ (ppm): 7.74 (*d*, *J* = 15.90 Hz, 1H, Ar-C**H**=), 7.48 (*d*, *J* = 8.70 Hz, 2H), 6.89 (*d*, *J* = 8.70 Hz, 2H), 6.30 (*d*, *J* = 15.87 Hz, 1H, =C**H**-COOH), 3.97 (*t*, *J* = 6.54 Hz, 2H), 1.28-1.82 (*m*, br, 12H) and 0.88 (*t*, *J* = 6.92 Hz, 3H); ^{13}C-NMR (DMSO-d_6) δ (ppm): 172.9 (-**C**OOH), 161.4, 130.1 (2x1C), 126.5 and 114.9 (2x1C) (aromatic carbons), 146.8 and 114.5 (olefinic carbons), 68.2, 31.8, 29.3, 29.2, 29.1, 26.0, 22.7 and 14.1.

4-Dodecyloxycinnamic acid (**C19**)[37]: Small white solid (67%), m.p. 122-125 °C (ethanol); IR (KBr, cm^{-1}): 3525-3300, 2919, 2854, 1675, 1630, 1603, 1511, 1470, 1429, 1325, 1250, 1210 and 1185; ^{1}H-NMR (DMSO-d_6) δ (ppm): 7.60 (*d*, *J* = 8.76 Hz, 2H), 7.52 (*d*, *J* = 16.07 Hz, 1H, Ar-C**H**=), 6.93 (*d*, *J* = 8.74 Hz, 2H), 6.35 (*d*, *J* = 15.96 Hz, 1H, =C**H**-COOH), 3.98 (*t*, *J* = 6.41 Hz, 2H), 1.23-3.38 (*m*, br, 20H) and 0.84 (*t*, *J* = 6.70 Hz, 3H); ^{13}C-NMR (DMSO-d_6) δ (ppm): 167.8 (-**C**OOH), 160.4, 126.6 (2x1C), 116.3 and 114.0 (2x1C) (aromatic carbons), 143.8 and 129.9 (olefinic carbons), 67.6, 31.3, 29.0, 28.7 (6x1C), 28.5, 25.4, 22.1 and 13.9.

4-Benzyloxycinnamic acid (**C20**): Pale yellow solid (92%), m.p. 200-203°C (ethanol) (lit.[38] 208-209°C), R_f 0.67 (ethanol); IR (KBr, cm^{-1}): 3650-3300, 1665, 1603, 1577, 1509, 1451, 1429, 1310, 1250 and 1185; ^{1}H-NMR (DMSO-d_6) δ (ppm): 7.64 (*d*, *J* = 8.69 Hz, 2H), 7.40 (*d*, *J* = 15.15 Hz, 1H, Ar-C**H**=), 7.33-7.62 (Ar-H, 5H), 7.04 (*d*, *J* = 8.77 Hz, 2H), 6.38 (*d*, *J* = 15.94 Hz, 1H, =C**H**-COOH) and 5.15 (*s*, 2H); ^{13}C-NMR (DMSO-d_6) δ (ppm): 167.8 (-**C**OOH), 160.0, 136.9, 130.0 (2x1C), 128.5 (2x1C), 127.9, 127.7 (2x1C) and 127.0 (aromatic carbons), 143.7 and 116.6 (olefinic carbons) and 69.3 (-**C**H_2).

3-Phenoxycinnamic acid (**C21**): Pale yellow solid (83%), m.p. 108-109°C (ethanol) (lit.[39] 111-113°C), R_f 0.73 (ethanol); IR (KBr, cm^{-1}): 3610-3370, 1690, 1635, 1578, 1491, 1445 and 1250; ^{1}H-NMR(DMSO-d_6) δ (ppm): 7.56 (*d*, *J* = 16.05 Hz, 1H, Ar-C**H**=), 7.40 (*t*, *J* = 8.36 Hz, 6H), 7.38 (*d*, *J* = 8.27 Hz, 1H), 7.36 (*s*, 1H), 7.18 (*t*, *J* = 8.36 Hz, 3H), 7.02 (*d*, *J* = 7.64 Hz, 2H) and 6.50 (*d*, *J* = 16.00 Hz, 1H, =C**H**-COOH); ^{13}C-NMR (DMSO-d_6) δ (ppm): 167.4 (-**C**OOH), 157.0, 156.4, 136.3, 130.5, 130.1 (2x1C), 123.6, 123.3, 120.2 (2x1C), 118.6 and 118.2 (aromatic carbons), 143.1 and 119.3 (olefinic carbons).

4-Butyloxy-3-methoxycinnamic acid (**C22**): Pale yellow solid (82%), m.p. 155-156°C (ethanol) (lit.[40] 153-154°C), R_f 0.63 (ethanol); IR (KBr, cm^{-1}): 3650-3325, 2955, 2955, 2865, 2827, 1680, 1624, 1521, 1466, 1350, 1250, 1200, 1180 and 1125; ^{1}H-NMR(DMSO-d_6) δ (ppm): 7.73 (*d*, *J* = 15.87 Hz, 1H, Ar-C**H**=), 7.08 (*d*, *J* = 2.13 Hz, 1H), 7.11 (*d*, *J* = 8.54 and 2.13 Hz, 1H), 6.87 (*d*, *J* = 8.24 Hz, 1H), 6.32 (*d*, *J* = 15.87 Hz, 1H, =C**H**-COOH), 3.90 (*s*, 3H), 4.06 (*t*, *J* = 6.71 Hz, 2H), 1.47-1.87 (*m*, br, 4H) and 0.98 (*t*, *J* = 7.63 Hz, 3H); ^{13}C-NMR (DMSO-d_6) δ (ppm): 172.7 (-**C**OOH), 151.2, 147.0, 126.8, 123.1, 112.2 and 110.2 (aromatic carbons), 149.5 and 114.7 (olefinic carbons), 56.0 (-O**C**H_3), 68.7, 31.0, 19.1 and 13.8.

4-Hexyloxy-3-methoxycinnamic acid (**C23**): Light white solid (93%), m.p. 124-125°C (ethanol) (lit.[40] 127-127.5°C), R_f 0.64 (ethanol); IR (KBr, cm^{-1}): 3625-3325, 2955, 2868, 2827, 1680, 1624, 1603, 1521, 1466, 1437, 1350, 1250 and 1200; ^{1}H-NMR ($CDCl_3$) δ (ppm): 7.73 (*d*, *J* = 15.87 Hz, 1H, Ar-C**H**=), 7.12 (*dd*, *J* = 8.24 and 2.13 Hz, 1H), 7.08 (*d*, *J* = 1.83 Hz, 1H), 6.87 (*d*, *J* = 8.24 Hz, 2H), 6.32 (*d*, *J* = 15.56 Hz, 1H, =C**H**-COOH), 4.05 (*t*, *J* = 6.72 Hz, 2H), 3.91 (*s*, 3H), 1.32-1.89 (*m*, br, 8H) and 0.91 (*t*, *J* = 7.01 Hz, 3H); ^{13}C-NMR ($CDCl_3$) δ (ppm): 172.4 (-**C**OOH), 151.2, 147.0, 126.8, 123.1, 112.3 and 110.2 (aromatic carbons), 149.5 and 114.7 (olefinic carbons), 56.0 (-O**C**H_3), 69.0, 31.5, 29.0, 25.6, 22.5 and 14.0.

4-Octyloxy-3-methoxycinnamic acid (**C24**): White solid (81%), m.p. 115-118 °C (ethanol), R_f 0.70 (ethanol); IR (KBr, cm^{-1}): 3625-3325, 2955, 2930, 1675, 1629, 1598, 1516, 1465, 1424, 1270, 1200 and 1150; ^{1}H-NMR($CDCl_3$) δ (ppm): 7.73 (*d*, *J* = 15.90 Hz, 1H, Ar-C**H**=), 7.11 (*dd*, *J* = 8.24 and 1.83 Hz, 1H), 7.08 (*d*, *J* = 1.83 Hz, 1H), 6.87 (*d*, *J* = 8.24 Hz, 1H), 6.32 (*d*, *J* = 15.86 Hz, 1H, =C**H**-COOH), 4.05 (*t*, *J* = 7.02 Hz, 2H), 3.90 (*s*, 3H), 1.25-1.90 (*m*, br, 12H) and 0.89 (*t*, *J* = 7.01 Hz, 3H); ^{13}C-NMR ($CDCl_3$) δ (ppm): 172.6 (-**C**OOH), 151.2, 147.0, 126.8, 123.1, 112.2 and 110.2 (aromatic carbons), 149.5 and 114.7 (olefinic carbons), 56.0 (-O**C**H_3), 69.0, 31.8, 29.3, 29.2, 28.9, 25.0, 22.6 and 14.1; MS *m/z* (% rel. int.): 306, 194, 179 and 133.

The FT-IR, ^{1}H-NMR, ^{13}C-NMR and mass spectra of **C24** are shown in Fig B.1, B.2, B.3 and B.4, respectively. (see Appendices B)

4-Dodecyloxy-3-methoxycinnamic acid (**C25**): Pale yellow solid (60%), m.p. 60-62°C (ethanol), R_f 0.80 (ethanol); IR (KBr, cm^{-1}): 3625-3325, 2935, 2868, 1683, 1624, 1603, 1514, 1470, 1427, 1250 and 1150; ^{1}H-NMR(DMSO-d_6) δ (ppm): 7.71 (*d*, *J* = 15.87 Hz, 1H, Ar-C**H**=), 7.11 (*dd*, *J* = 8.24 and 1.84 Hz, 1H), 7.07 (*d*, *J* = 1.83

Hz, 1H), 6.87 (*d*, *J* = 8.24 Hz, 1H), 6.32 (*d*, *J* = 15.87 Hz, 1H, =C**H**-COOH), 4.08 (*t*, *J* = 7.02 Hz, 2H), 3.93 (*s*, 3H), 1.23-1.91 (*m*, br, 20H) and 0.88 (*t*, *J* = 6.72 Hz, 3H); ^{13}C-NMR (DMSO-d_6) δ (ppm): 171.4 (-**C**OOH), 154.2, 146.7, 129.8, 126.8, 111.3 and 109.2 (aromatic carbons), 149.8 and 114.8 (olefinic carbons), 56.0 (-O**C**H$_3$), 69.2, 31.9, 29.6 (2x1C), 29.6, 29.5, 29.3, 29.0, 28.9, 25.9, 22.7 and 14.1; MS *m/z* (% rel. int.): 320, 152 and 123.

The FT-IR, ^{1}H-NMR, ^{13}C-NMR and mass spectra of **C25** are shown in Fig B.5, B.6, B.7 and B.8, respectively. (see Appendices B)

4-Benzyloxy-3-methoxycinnamic acid (**C26**): Pale yellow needle crystal (93%), m.p. 185-187°C (ethanol) (lit.[41] 191°C), R_f 0.63 (ethanol); IR (KBr, cm^{-1}): 3625-3300, 1675, 1624, 1598, 1511, 1471, 1429, 1285, 1200 and 1125; ^{1}H-NMR ($CDCl_3$) δ (ppm): 7.70 (*d*, *J* = 15.87 Hz, 1H, Ar-C**H**=), 7.36-7.45 (Ar-H, 5H), 7.33 (*d*, *J* = 8.54 Hz, 1H), 7.09 (*d*, *J* = 1.83 Hz, 1H), 6.89 (*d*, *J* = 8.54 Hz, 1H), 6.31 (*d*, *J* = 15.87 Hz, 1H, =C**H**-COOH), 5.20 (*s*, 2H) and 3.98 (*s*, 3H); ^{13}C-NMR ($CDCl_3$) δ (ppm): 171.1 (-**C**OOH), 150.6, 149.8, 136.5, 128.7 (2x1C), 128.1, 127.2 (2x1C), 122.8, 133.4 and 110.3 (aromatic carbons), 146.9 and 114.7 (olefinic carbons) and 70.8 (-**C**H2-), 56.0 (-O**C**H$_3$).

2,3-Dimethoxycinnamic acid (**C27**): Pale yellow crystal (64%), m.p. 186-188 °C (ethanol) (lit.[35] 180-181°C), R_f 0.60 (ethanol); IR (KBr, cm^{-1}): 3650-3350, 1680, 1690, 1624, 1588, 1475, 1413, 1310, 1285 and 1225; ^{1}H-NMR (acetone-d_6) δ (ppm): 7.99 (*d*, *J* = 16.17 Hz, 1H, Ar-C**H**=), 7.10-7.31 (Ar-H, 3H) and 6.53 (*d*, *J* = 16.48 Hz, 1H, =C**H**-COOH); ^{13}C-NMR (acetone-d_6) δ (ppm): 168.0 (-**C**OOH), 154.2, 140.0, 129.1, 125.0, 120.0 and 115.4 (aromatic carbons), 149.3 and 119.9 (olefinic carbons).

2,4-Dimethoxycinnamic acid (**C28**): Yellow crystal (78%), m.p. 188-189°C (ethanol) (lit.[33, 34] 187-189°C), R_f 0.75 (ethanol); IR (KBr, cm^{-1}): 3625-3325, 1675, 1598, 1506, 1460, 1420, 1340, 1275, 1210, 1150 and 1110; ^{1}H-NMR (DMSO-d_6) δ (ppm): 7.75 (*d*, *J* = 16.07 Hz, 1H, Ar-C**H**=), 6.54-7.62 (Ar-H, 3H) and 6.37 (*d*, *J* = 16.06 Hz, 1H, =C**H**-COOH); ^{13}C-NMR (DMSO-d_6) δ (ppm): 168.2 (-**C**OOH), 162.5, 159.3, 129.9, 115.4, 106.1 and 98.3 (aromatic carbons), 138.7 and 116.3 (olefinic carbons).

2,5-Dimethoxycinnamic acid (**C29**): Small yellow crystal (77%), m.p. 147-148°C (ethanol) (lit.[35] 148-149°C), R_f 0.74 (ethanol); IR (KBr, cm^{-1}): 3650-3350, 1680, 1624, 1582, 1501, 1429, 1291 and 1200; ^{1}H-NMR (DMSO-d_6) δ (ppm): 7.80

(*d*, *J* = 16.20 Hz, 1H, Ar-C**H**=), 6.98-7.24 (Ar-H, 3H) and 6.54 (*d*, *J* = 16.12 Hz, 1H, =C**H**-COOH); ^{13}C-NMR (DMSO-d_6) δ (ppm): 167.8 (-**C**OOH), 153.1, 152.0, 123.0, 117.5, 112.9 and 112.5 (aromatic carbons), 138.4 and 119.5 (olefinic carbons).

3,4-Dimethoxycinnamic acid (**C30**): Pale yellow crystal (69%), m.p. 182-183 °C (ethanol) (lit.[33, 34] 183°C), R_f 0.72 (ethanol); IR (KBr, cm^{-1}): 3625-3350, 1680, 1639, 1598, 1516, 1460, 1432, 1420, 1380, 1275 and 1130; ^{1}H-NMR (acetone-d_6) δ (ppm): 7.62 (*d*, *J* = 15.87 Hz, 1H, Ar-C**H**=), 6.98-7.31 (Ar-H, 3H) and 6.41 (*d*, *J* = 15.87 Hz, 1H, =C**H**-COOH); ^{13}C-NMR (acetone-d_6) δ (ppm): 168.2 (-**C**OOH), 152.5, 150.6, 128.4, 123.5, 112.5 and 111.3 (aromatic carbons), 145.7 and 116.7 (olefinic carbons).

3,5-Dimethoxycinnamic acid (**C31**): Pale yellow needle crystal (77%), m.p. 176-177°C (ethanol) (lit.[35] 175-176°C), R_f 0.69 (ethanol); IR (KBr, cm^{-1}): 3650-3275, 1690, 1634, 1598, 1480, 1429, 1285, 1210 and 1150; ^{1}H-NMR (DMSO-d_6) δ (ppm): 7.50 (*d*, *J* = 16.00 Hz, 1H, Ar-C**H**=), 653-6.86 (Ar-H, 3H) and 6.55 (*d*, *J* = 15.74 Hz, 1H, =C**H**-COOH); ^{13}C-NMR (DMSO-d_6) δ (ppm): 167.6 (-**C**OOH), 160.6 (2x1C), 136.0, 106.0 (2x1C) and 102.4 (aromatic carbons), 143.9 and 119.8 (olefinic carbons).

3,4,5-Ttrimethoxycinnamic acid (**C32**): Pale yellow solid (40%), m.p. 124-126°C (ethanol) (lit.[35] 126-127°C), R_f 0.65 (ethanol); IR (KBr, cm^{-1}): 3650-3250, 1696, 1629, 1583, 1511, 1455, 1390, 1350, 1300, 1250 and 1115; ^{1}H-NMR (DMSO-d_6) δ (ppm): 7.51 (*d*, *J* = 15.94 Hz, 1H, Ar-C**H**=), 7.01 (s, 2H) and 6.52 (*d*, *J* = 16.02 Hz, 1H, =C**H**-COOH); ^{13}C-NMR (DMSO-d_6) δ (ppm): 167.6 (-**C**OOH), 153.0 (2x1C), 139.2, 129.8 and 105.8 (2x1C) (aromatic carbons), 144.4 and 118.5 (olefinic carbons).

3,4-Methylenedioxycinnamic acid (**C33**): Pale yellow mirror-like crystal (57%), m.p. 244-245°C (ethanol) (lit.[31, 35] 242-244°C), R_f 0.62 (ethanol); IR (KBr, cm^{-1}): 3650-3320, 1696, 1629, 1611, 1496, 1450, 1427, 1310, 1250, 1210 1100 and 1125; ^{1}H-NMR (DMSO-d_6) δ (ppm): 7.49 (*d*, *J* = 15.99 Hz, 1H, Ar-C**H**=), 6.91-7.45 (Ar-H, 2H) and 6.37 (*d*, *J* = 15.92 Hz, 1H, =C**H**-COOH); ^{13}C-NMR (DMSO-d_6) δ (ppm): 167.8 (-**C**OOH), 149.1, 148.0, 128.6, 124.6, 108.4 and 106.6 (aromatic carbons), 143.8 and 117.1 (olefinic carbons).

Nitrogen-containing Cinnamic Acids

2-Nitrocinnamic acid (**C34**): Brown solid (67%), m.p. 237-239°C (ethanol) (lit.[31] 240°C), R_f 0.66 (ethanol); IR (KBr, cm^{-1}): 3650-3250, 1716, 1634, 1577, 1524, 1446, 1424, 1354, 1285, 1250 and 1200; ^{1}H-NMR (DMSO-d_6) δ (ppm): 7.85 (*d*, *J* = 16.33 1H, Ar-C**H**=), 7.62-8.08 (Ar-H, 4H) and 6.52 (*d*, *J* = 15.77 Hz, 1H, =C**H**-COOH); ^{13}C-NMR (DMSO-d_6) δ (ppm): 166.9 (-**C**OOH), 148.2, 133.8, 130.8, 129.2, 124.6 and 123.8 (aromatic carbons) and 138.8 (olefinic carbons).

3-Nitrocinnamic acid (**C35**): Yellow needle crystal (59%), m.p. 204-206°C (ethanol) (lit.[31] 200-201°C), R_f 0.70 (ethanol); IR (KBr, cm^{-1}): 3625-3358, 1690, 1634, 1529, 1442, 1419, 1364, 1300 and 1210; ^{1}H-NMR (DMSO-d_6) δ (ppm): 7.70 (*d*, *J* = 16.06 Hz, 1H, Ar-C**H**=), 7.64-8.48 (Ar-H, 4H) and 6.72 (*d*, *J* = 16.09 Hz, 1H, =C**H**-COOH); ^{13}C-NMR (DMSO-d_6) δ (ppm): 167.1 (-**C**OOH), 148.2, 136.1, 134.0, 130.3, 124.4 and 122.8 (aromatic carbons), 141.5 and 122.2(olefinic carbons).

4-Nitrocinnamic acid (**C36**): Brown solid (77%), m.p. 283-285°C (ethanol) (lit.[31] 286°C), R_f 0.66 (ethanol); IR (KBr, cm^{-1}): 3625-3225, 1690, 1634, 1611, 1527, 1429, 1347, 1306 and 1210; ^{1}H-NMR (DMSO-d_6) δ (ppm): 7.69 (*d*, *J* = 16.11 Hz, 1H, Ar-C**H**=), 7.95-8.26 (Ar-H, 4H) and 6.74 (*d*, *J* = 16.07 Hz, 1H, =C**H**-COOH); ^{13}C-NMR (DMSO-d_6) δ (ppm): 167.0 (-**C**OOH), 147.9, 140.7, 129.3 (2x1C) and 123.9 (2x1C) (aromatic carbons), 141.3 and 123.6 (olefinic carbons).

2-Chloro-5-nitrocinnamic acid (**C37**): Green solid (83%), m.p. 216-218°C (ethanol) (lit.[42] 220-221°C), R_f 0.74 (ethanol); IR (KBr, cm^{-1}): 3650-3350, 1716, 1640, 1625, 1511, 1450, 1419, 1358, 1281 and 1219; ^{1}H-NMR (DMSO-d_6) δ (ppm): 7.78 (*d*, *J* = 15.76 Hz, 1H, Ar-C**H**=), 7.77-8.59 (Ar-H, 4H) and 6.78 (*d*, *J* = 15.91 Hz, 1H, =C**H**-COOH); ^{13}C-NMR (DMSO-d_6) δ (ppm): 172.5 (-**C**OOH), 152.5, 142.5, 139.2, 137.1, 131.2 and 131.0 (aromatic carbons), 145.4 and 128.6 (olefinic carbons).

4-Chloro-3-nitrocinnamic acid (**C38**): Yellow solid (68%), m.p. 182-183°C (ethanol) (lit.[31] 184-185°C), R_f 0.68 (ethanol); IR (KBr, cm^{-1}): 3650-3350, 1696, 1639, 1601, 1536, 1480, 1424, 1352 and 1219; ^{1}H-NMR (DMSO-d_6) δ (ppm): 7.62 (*d*, *J* = 15.09 Hz, 1H, Ar-C**H**=), 7.77-8.41 (Ar-H, 3H) and 6.71 (*d*, *J* = 15.98 Hz, 1H, =C**H**-COOH); ^{13}C-NMR (DMSO-d_6) δ (ppm): 167.0 (-**C**OOH), 159.0, 140.4, 135.0, 132.8, 132.0 and 124.6 (aromatic carbons), 148.5 and 122.8 (olefinic carbons).

5-Chloro-2-nitrocinnamic acid (**C39**): Pale yellow solid (85%), m.p. 172-173 °C (ethanol) (lit.[31] 174-175°C), R_f 0.72 (ethanol); IR (KBr, cm^{-1}): 3675-3350, 1742, 1696, 1644, 1611, 1568, 1524, 1429, 1342, 1306 and 1150; ^{1}H-NMR (DMSO-d_6) δ (ppm): 7.80 (*d*, *J* = 15.81 Hz, 1H, Ar-C**H**=), 7.66-8.11 (Ar-H, 3H) and 6.60 (*d*, *J* = 15.77 Hz, 1H, =C**H**-COOH); ^{13}C-NMR (DMSO-d_6) δ (ppm): 166.7 (-**C**OOH), 138.6, 137.7, 131.6, 130.4, 128.9 and 126.7 (aromatic carbons), 146.6 and 125.1 (olefinic carbons).

Alkyl Cinnamic Acids and Others

4-Methylcinnamic acid (**C40**): White needle mirror-like crystal (63%), m.p. 196-197°C (ethanol) (lit.[33, 34] 196-198°C), R_f 0.64 (ethanol); IR (KBr, cm^{-1}): 3680-3150, 1675, 1629, 1600, 1419, 1312, 1281, 1200 and 1185; ^{1}H-NMR (DMSO-d_6) δ (ppm): 7.49 (*d*, *J* = 16.15 Hz, 1H, Ar-C**H**=), 7.15-7.48 (Ar-H, 4H), 6.36 (*d*, *J* = 16.01 Hz, 1H, =C**H**-COOH) and 2.25 (*s*, 3H); ^{13}C-NMR (DMSO-d_6) δ (ppm): 168.2 (-**C**OOH), 140.6, 131.1, 129.6 (2x1C) and 128.1 (2x1C) (aromatic carbons), 144.5 and 117.4 (olefinic carbons).

4-iso-Propylcinnamic acid (**C41**): Pale yellow needle crystal (56%), m.p. 156-157°C (ethanol) (lit.[33] 157-159°C), R_f 0.80 (ethanol); IR (KBr, cm^{-1}): 3680-3200, 1675, 1624, 1567, 1519, 1424, 1380, 1350 and 1219; ^{1}H-NMR (DMSO-d_6) δ (ppm): 7.67 (*d*, *J* = 15.87 Hz, 1H, Ar-C**H**=), 7.31-7.60 (Ar-H, 4H), 6.48 (*d*, *J* = 15.87 Hz, 1H, =C**H**-COOH), 2.95 (*m*, br, 1H), 1.26 (*s*, 3H) and 1.24 (*s*, 3H); ^{13}C-NMR (DMSO-d_6) δ (ppm): 167.9 (-**C**OOH), 152.2, 133.1, 129.1 (2x1C) and 127.8 (2x1C) (aromatic carbons), 145.4 and 118.2 (olefinic carbons).

4-tert-Butylcinnamic acid (**C42**): Pale yellow needle crystal (96%), m.p. 202-205°C (ethanol), R_f 0.60 (ethanol); IR (KBr, cm^{-1}): 3625-3400, 1675, 1624, 1611, 1567, 1524, 1424, 1312, 1281, 1219 and 1085; ^{1}H-NMR (DMSO-d_6) δ (ppm): 7.78 (*d*, *J* = 15.98 Hz, 1H, Ar-C**H**=), 7.40-7.51 (Ar-H, 4H), 6.41 (*d*, *J* = 16.01 Hz, 1H, =C**H**-COOH) and 1.32 (*s*, 9H); ^{13}C-NMR (DMSO-d_6) δ (ppm): 168.2 (-**C**OOH), 153.6, 131.1, 128.0 (2x1C) and 125.8 (2x1C) (aromatic carbons), 144.3 and 117.6 (olefinic carbons).

4-Trifluoromethylcinnamic acid (**C43**): White solid (72%), m.p. 225-226°C (ethanol) (lit.[43] 230°C), R_f 0.78 (ethanol); IR (KBr, cm^{-1}): 3625-3375, 1675, 1624, 1600, 1480, 1424, 1300, 1285 and 1215; ^{1}H-NMR (DMSO-d_6) δ (ppm): 7.75 (*d*, *J* =

16.17 Hz, 1H, Ar-C**H**=), 7.77-7.92 (Ar-H, 4H) and 6.68 (*d*, *J* = 16.17 Hz, 1H, =C**H**-COOH); ^{13}C-NMR (DMSO-d_6) δ (ppm): 167.3 (-**C**OOH), 139.4, 131.9, 129.5 (2x1C) and 126.1 (2x1C) (aromatic carbons), 143.5 and 122.2 (olefinic carbons).

3-Cyanocinnamic acid (**C44**): Pale yellow solid (82%), m.p. 245-247°C (ethanol) (lit.[43] 247-248°C), R_f 0.68 (ethanol); IR (KBr, cm^{-1}): 3650-3350, 2228, 1696, 1635, 1548, 1427, 1301, 1250 and 1200; ^{1}H-NMR (DMSO-d_6) δ (ppm): 7.60 (*d*, *J* = 15.93 Hz, 1H, Ar-C**H**=), 7.56-8.21 (Ar-H, 4H) and 6.69 (*d*, *J* = 16.06 Hz, 1H, =C**H**-COOH); ^{13}C-NMR (DMSO-d_6) δ (ppm): 167.2 (-**C**OOH), 135.6, 133.3, 132.6, 131.7, 130.0 and 112.1 (aromatic carbons), 141.6 and 121.8 (olefinic carbons).

4-Cyanocinnamic acid (**C45**): White crystal (67%), m.p. 254-255°C (ethanol) (lit.[43] 255-256°C), R_f 0.82 (ethanol); IR (KBr, cm^{-1}): 3650-3300, 2228, 1690, 1624, 1567, 1509, 1424, 1312, and 1243; ^{1}H-NMR (DMSO-d_6) δ (ppm): 7.63 (*d*, *J* = 16.01 Hz, 1H, Ar-C**H**=), 7.85-7.95 (Ar-H, 4H) and 6.69 (*d*, *J* = 16.09 Hz, 1H, =C**H**-COOH); ^{13}C-NMR (DMSO-d_6) δ (ppm): 167.1 (-**C**OOH), 138.8, 132.7 (2x1C), 128.8 (2x1C) and 112.1 (aromatic carbons), 141.9 and 122.8 (olefinic carbons).

3-(1-Naphthalene)-propenoic acid (**C46**): Pale yellow solid (76%), m.p. 210-212°C (ethanol) (lit.[44] 208-210°C), R_f 0.67 (ethanol); IR (KBr, cm^{-1}): 3650-3350, 1685, 1625, 1424, 1354, 1300, 1296 and 1229; ^{1}H-NMR (DMSO-d_6) δ (ppm): 8.38 (*d*, *J* = 15.72 Hz, 1H, Ar-C**H**=), 7.55-8.02 (Ar-H, 7H) and 6.55 (*d*, *J* = 16.73 Hz, 1H, =C**H**-COOH); ^{13}C-NMR (DMSO-d_6) δ (ppm): 167.4 (-**C**OOH), 133.3, 131.0, 130.7, 128.7, 127.1, 126.3, 125.7, 125.2 and 123.0 (aromatic carbons), 140.1 and 121.9 (olefinic carbons).

3-(9-Anthracene)-propenoic acid (**C47**): Yellow-brown solid (83%), m.p. 245-248°C (ethanol) (lit.[45] 246-247°C), R_f 0.64 (ethanol); IR (KBr, cm^{-1}): 3620-3350, 1645, 1625, 1552, 1500, 1445, 1255, 1166 and 1050; ^{1}H-NMR (DMSO-d_6) δ (ppm): 7.64 (*d*, *J* = 16.75 Hz, 1H, Ar-C**H**=), 7.56-9.03 (Ar-H, 9H) and 6.35 (*d*, *J* = 16.22 Hz, 1H, =C**H**-COOH); ^{13}C-NMR (DMSO-d_6) δ (ppm): 167.0 (-**C**OOH), 135.2, 131.3, 130.6, 129.3, 129.2, 125.8 and 124.3 (aromatic carbons), 145.0 and 123.4 (olefinic carbons).

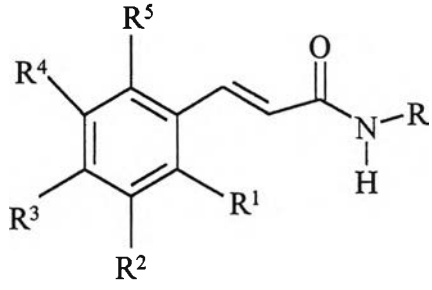
2.4 Synthesis of *trans*-Cinnamic Acid Derivatives

2.4.1 Synthesis of Cinnamamides

General Procedure[18]

Appropriate substituted *trans*-cinnamic acids (0.01 mol) and 5 mL of thionyl chloride were put into a round bottom flask and stirred under heating at a temperature of 60-70°C for 2 hours. The mixture was then concentrated to remove excess thionyl chloride and obtain the desired cinnamoyl chlorides. Selected amine (0.01 mol) in 10 mL of tetrahydrofuran was added to a solution of the desired cinnamoyl chloride (0.01 mol) in 8 mL of tetrahydrofuran at 0-5°C. After the mixture was stirred for 1 hour, the solvent was removed, and the residue thus obtained was dissolved in ethyl acetate and 5 % sodium hydroxide solution. After extraction, the organic phase was washed with water, followed by separation, drying, and crystallized from a mixture of dichloromethane-hexane to give the desired compound.

Twelve cinnamamides were synthesized and their structures are displayed as shown in Fig 2.2.



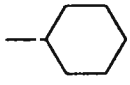
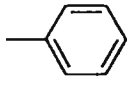
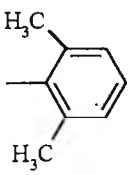
Cpds	R	R^1	R^2	R^3	R^4	R^5
D1	$-(CH_2)_3CH_3$	H	H	CH_3	H	H
D2		H	H	CH_3	H	H
D3		H	H	CH_3	H	H
D4		H	H	CH_3	H	H

Fig 2.2 Structures of synthesized cinnamamides

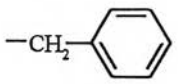
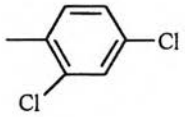
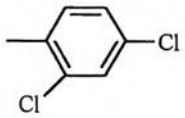
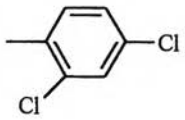
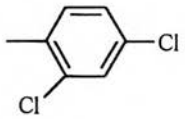
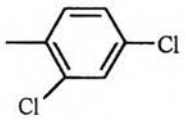
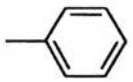
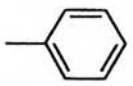
Cpds	R	R^1	R^2	R^3	R^4	R^5
D5		H	H	CH_3	H	H
D6		H	H	CH_3	H	H
D7		H	H	C_3H_7	H	H
D8		NO_2	H	H	H	H
D9		H	NO_2	H	H	H
D10		H	$-OC_2H_2O-$		H	H
D11		H	NO_2	H	H	H
D12		H	$-OC_2H_2O-$		H	H

Fig 2.2 (cont.)

(N-Butyl)-4-methylcinnamamide (**D1**): Pale yellow crystal (95%), m.p. 175-177°C (dichloromethane-hexane), R_f 0.68 (ethyl acetate); IR (KBr, cm^{-1}): 3452, 3293, 2955, 2930, 2848, 1660, 1624, 1562, 1427, 1342 and 1250; ^{1}H-NMR ($CDCl_3$) δ (ppm): 7.57 (*d*, *J* = 15.62 Hz, 1H, Ar-C**H**=), 7.35 (*d*, *J* = 8.15 Hz, 2H), 7.09 (*d*, *J* = 8.02, 2H), 6.42 (*d*, *J* = 15.67 Hz, 1H, =C**H**-CONHR), 6.23 (*s*, 1H), 3.36 (*q*, *J* = 7.04 Hz, 2H), 2.31 (*s*, 3H), 1.29-1.57 (*m*, br, 4H) and 0.90 (*t*, *J* = 7.19 Hz, 3H); ^{13}C-NMR ($CDCl_3$) δ (ppm): 166.4 (-**C**ONHR), 129.6, 129.5 (2x1C), 128.2 and 127.7 (2x1C)

(aromatic carbons), 140.7 and 119.9 (olefinic carbons), 39.6, 31.7, 21.4, 20.1 and 13.8.

(N-Cyclohexyl)-4-methylcinnamamide (**D2**): Pale yellow crystal (94%), m.p. 168-170°C (dichloromethane-hexane), R_f 0.64 (ethyl acetate); IR (KBr, cm^{-1}): 3452, 3288, 2925, 2848, 2655, 1630, 1552, 1445, 1353 and 1250; ^{1}H-NMR ($CDCl_3$) δ (ppm): 7.56 (*d*, *J* = 15.62 Hz, 1H, Ar-C**H**=), 7.36 (*d*, *J* = 8.13 Hz, 2H), 7.13 (*d*, *J* = 8.02, 2H), 6.32 (*d*, *J* = 15.55 Hz, 1H, =C**H**-CONHR), 3.80-4.00 (*m*, br, 1H), 2.33 (*s*, 3H), and 1.13-1.99 (*m*, br, 10H); ^{13}C-NMR ($CDCl_3$) δ (ppm): 165.1 (-**C**ONHR), 139.7, 132.2, 129.5 (2x1C) and 127.7 (2x1C) (aromatic carbons), 140.6 and 120.1 (olefinic carbons), 48.3, 33.3 (2x1C), 24.9 (2x1C), 25.6 and 21.4.

(N-Phenyl)-4-methylcinnamamide (**D3**): White needle crystal (34%), m.p. 185-186°C (dichloromethane-hexane) (lit.[46] 183-184°C), R_f 0.72 (ethyl acetate); IR (KBr, cm^{-1}): 3452, 3293, 1655, 1624, 1601, 1532, 1439, 1337, 1245 and 1190; ^{1}H-NMR ($CDCl_3$) δ (ppm): 7.71 (*d*, *J* = 15.51 Hz, 1H, Ar-C**H**=), 7.64 (*t*, *J* = 7.13 Hz, 1H), 7.62 (*d*, *J* = 8.07 Hz, 2H), 7.31 (*t*, *J* = 6.90 Hz, 2H), 7.26 (*d*, *J* = 6.77 Hz, 2H), 7.14 (*d*, *J* = 8.09, 2H), 6.53 (*d*, *J* = 15.49 Hz, 1H, =C**H**-CONHR) and 2.35 (*s*, 3H) and; ^{13}C-NMR ($CDCl_3$) δ (ppm): 161.1 (-**C**ONHR), 140.3, 138.1, 131.9, 129.6 (2x1C), 129.1 (2x1C), 129.1 (2x1C), 128.0 (2x1C) and 124.4 (aromatic carbons), 142.4 and 120.0 (olefinic carbons) and 21.4.

(N-2,6-Dimethylphenyl)-4-methylcinnamamide (**D4**): White mirror-like solid (43%), m.p. 218-220°C (dichloromethane-hexane), R_f 0.65 (ethyl acetate); IR (KBr, cm^{-1}): 3452, 3247, 1650, 1619, 1521, 1465, 1332, 1224 and 1190; ^{1}H-NMR ($CDCl_3$) δ (ppm): 7.69 (*d*, *J* = 15.49 Hz, 1H, Ar-C**H**=), 7.43 (*d*, *J* = 8.07 Hz, 2H), 7.18 (*d*, *J* = 8.42, 2H), 6.60 (*d*, *J* = 15.55 Hz, 1H, =C**H**-CONHR), 7.08-7.10 (Ar-H, 3H), 2.37 (*s*, 3H) and 2.25 (*s*, 6H); ^{13}C-NMR ($CDCl_3$) δ (ppm): 164.5 (-**C**ONHR), 140.2, 135.5, 131.8, 129.6 (2x1C), 128.2 (2x1C), 128.1 (2x1C), 127.9 (2x1C) and 127.4 (aromatic carbons), 142.1 and 119.1 (olefinic carbons), 21.45 and 18.55 (2x1C).

(N-Benzyl)-4-methylcinnamamide (**D5**): Pale yellow crystal (43%), m.p. 138-139°C (dichloromethane-hexane), R_f 0.65 (ethyl acetate); IR (KBr, cm^{-1}): 3457, 3288, 3050, 2950, 2850, 1650, 1619, 1529, 1449, 1374, 1355 and 1250; ^{1}H-NMR ($CDCl_3$) δ (ppm): 7.62 (*d*, *J* = 15.54 Hz, 1H, Ar-C**H**=), 7.36 (*d*, *J* = 8.06 Hz, 2H), 7.23-7.30 (Ar-H, 5H), 7.14 (*d*, *J* = 7.95 Hz, 2H), 6.36 (*d*, *J* = 15.52 Hz, 1H, =C**H**-CONHR), 4.54 (*d*, *J* = 5.63 Hz, 2H) and 2.34 (*s*, 3H); ^{13}C-NMR ($CDCl_3$) δ (ppm): 166.0 (-**C**ONHR),

140.0, 138.3, 132.0, 129.5 (2x1C), 128.7 (2x1C), 127.9 (2x1C), 127.8 (2x1C) and 127.6 (aromatic carbons), 141.4 and 119.4 (olefinic carbons), 43.8 and 21.4.

(N-2,4-Dichlorophenyl)-4-methylcinnamamide (**D6**): White solid (48%), m.p. 179-181°C (dichloromethane-hexane), R_f 0.68 (ethyl acetate); IR (KBr, cm^{-1}): 3442, 3250, 1654, 1629, 1587, 1516, 1481, 1410, 1350, 1200 and 1180; ^{1}H-NMR ($CDCl_3$) δ (ppm): 8.49 (*d*, *J* = 8.92 Hz, 1H), 7.73 (*d*, *J* = 15.47 Hz, 1H, Ar-C**H**=), 7.37 (*s*, 1H), 7.26 (*d*, *J* = 7.38 Hz, 2H), 7.25 (*d*, *J* = 8.95 Hz, 2H), 7.18 (*d*, *J* = 8.07 Hz, 2H), and 6.51 (*d*, *J* = 5.45 Hz, 1H, =C**H**-CONHR); ^{13}C-NMR ($CDCl_3$) δ (ppm): 164.0 (-**C**ONHR), 140.8, 133.6, 131.2, 129.8 (2x1C), 128.8, 128.7, 128.1, 128.0 (2x1C), 122.3 and 120.0 (aromatic carbons), 143.4 and 119.1 (olefinic carbons) and 21.5.

(N-2,4-Dichlorophenyl)-4-i-propylcinnamamide (**D7**): Pale yellow solid (44 %), m.p. 148-150°C (dichloromethane-hexane), R_f 0.71 (ethyl acetate); IR (KBr, cm^{-1}): 3447, 3250, 2980, 1665, 1629, 1582, 1527, 1475, 1400 and 1350; ^{1}H-NMR ($CDCl_3$) δ (ppm): 8.49 (*d*, *J* = 8.94 Hz, 1H), 7.74 (*d*, *J* = 15.44 Hz, 1H, Ar-C**H**=), 7.48 (*d*, *J* = 8.24 Hz, 2H), 7.38 (*s*, 1H), 7.26 (*d*, *J* = 8.37 Hz, 2H), 7.25 (*d*, *J* = 7.99 Hz, 2H), 6.52 (*d*, *J* = 15.45 Hz, 1H, =C**H**-CONHR), 2.92 (*h*, *J* = 6.76 Hz, 1H), 1.26 (*s*, 3H) and 1.23 (*s*, 3H); ^{13}C-NMR ($CDCl_3$) δ (ppm): 164.0 (-**C**ONHR), 151.7, 133.6, 131.9, 129.0, 128.7, 128.3, 128.0, 127.1 (2x1C), 127.1 (2x1C) and 122.3 (aromatic carbons), 143.5 and 119.1 (olefinic carbons), 34.1 and 23.8 (2x1C).

(N-2,4-Dichlorophenyl)-2-nitrocinnamamide (**D8**): Pale yellow solid (42%), m.p. 212-214°C (dichloromethane-hexane), R_f 0.66 (ethyl acetate); IR (KBr, cm^{-1}): 3447, 3370, 1696, 1659, 1629, 1587, 1514, 1470, 1393, 1359, 1301 and 1210; ^{1}H-NMR ($CDCl_3$) δ (ppm): 8.75 (*d*, *J* = 9.03 Hz, 1H), 8.08 (*d*, *J* = 16.38 Hz, 1H, Ar-C**H**=), 8.07 (*d*, *J* = 8.03 Hz, 1H), 7.51-7.67 (Ar-H, 3H), 7.45 (*s*, 1H), 7.29 (*d*, *J* = 8.94 Hz, 2H) and 6.48 (*d*, *J* = 15.44 Hz, 1H, =C**H**-CONHR); ^{13}C-NMR ($CDCl_3$) δ (ppm): 161.1 (-**C**ONHR), 145.0, 138.7, 133.5, 133.0, 132.5, 130.3, 129.2, 128.8, 128.1, 128.1, 125.5 and 125.1 (aromatic carbons), 140.5 and 122.5 (olefinic carbons).

(N-2,4-Dichlorophenyl)-3-nitrocinnamamide (**D9**): Pale yellow solid (40%), m.p. 246-248°C (dichloromethane-hexane), R_f 0.73 (ethyl acetate); IR (KBr, cm^{-1}): 3650-6110 (br), 1703, 1639, 1587, 1470, 1358, 1320, 1180 and 1150; ^{1}H-NMR ($CDCl_3$) δ (ppm): 8.48 (*s*, 1H), 8.24 (*d*, *J* = 8.22 Hz, 1H), 8.05, (*t*, *J* = 8.97 Hz, 1H), 7.75 (*d*, *J* = 8.18 Hz, 1H), 7.69 (*s*, 1H), 7.68 (*d*, *J* = 8.10 Hz, 1H), 7.44 (*dd*, *J* = 8.79 and 2.42 Hz, 1H), 7.33 (*d*, *J* = 15.77 Hz, 1H, Ar-C**H**=) and 6.73 (*d*, *J* = 16.08 Hz, 1H,

=C**H**-CONHR); ^{13}C-NMR ($CDCl_3$) δ (ppm): 163.4 (-**C**ONHR), 148.3, 136.5, 134.4, 134.0, 130.6, 129.1, 128.9, 127.6, 126.2, 126.0, 124.5 and 124.1 (aromatic carbons), 138.7 and 121.6 (olefinic carbons).

(N-2,4-Dichlorophenyl)-3,4-methylenedioxycinnamamide (**D10**): Pale yellow crystal (48%), m.p. 199-201°C (dichloromethane-hexane), R_f 0.72 (ethyl acetate); IR (KBr, cm^{-1}): 3452, 3247, 1670, 1630, 1603, 1531, 1501, 1451, 1399, 1368, 1248, 1180 and 1100; ^{1}H-NMR ($CDCl_3$) δ (ppm): 8.48 (*d*, *J* = 8.92 Hz, 1H), 7.66 (*d*, *J* = 15.34 Hz, 1H, Ar-C**H**=), 7.38 (*s*, 1H), 7.26, (*d*, *J* = 8.00 Hz, 1H), 7.05 (*s*, 1H), 7.03 (*d*, *J* = 7.49 Hz, 1H), 6.80 (*d*, *J* = 7.52 Hz, 1H), 6.38 (*d*, *J* = 15.35 Hz, 1H, =C**H**-CONHR) and 6.00 (*s*, 2H, -OC**H**$_2$O-); ^{13}C-NMR ($CDCl_3$) δ (ppm): 161.1 (-**C**ONHR), 148.4, 143.2, 133.6, 129.0, 128.7, 128.0, 124.6, 122.3, 108.6 and 106.5 (2x1C) (aromatic carbons), 143.2 and 118.1 (olefinic carbons) and 101.6 (-O**C**H$_2$O).

(N-Phenyl)-3-nitrocinnamamide (**D11**): Pale yellow crystal (43%), m.p. 187-189°C (dichloromethane-hexane), R_f 0.62 (ethyl acetate); IR (KBr, cm^{-1}): 3447, 3372, 3091, 1687, 1640, 1598, 1546, 1499, 1447, 1358, 1254 and 1179; ^{1}H-NMR ($CDCl_3$) δ (ppm): 8.40 (*s*, 1H), 8.20 (*d*, *J* = 8.05 Hz, 1H), 8.00 (*d*, *J* = 7.73 Hz, 1H), 7.78 (*d*, *J* = 15.11 Hz, 1H, Ar-C**H**=), 7.74 (*t*, *J* = 8.37 Hz, 1H), 7.59 (*d*, *J* = 8.25 Hz, 2H), 7.54 (*d*, *J* = 7.95 Hz, 2H), 7.35 (*t*, *J* = 7.76 Hz, 1H) and 6.71 (*d*, *J* = 15.57 Hz, 1H, =C**H**-CONHR); ^{13}C-NMR ($CDCl_3$) δ (ppm): 161.1 (-**C**ONHR), 148.3, 138.8, 137.5, 136.8, 134.0, 129.9, 128.6 (2x1C), 125.3, 123.6 and 121.1 (2x1C) (aromatic carbons), 141.6 and 119.6 (olefinic carbons).

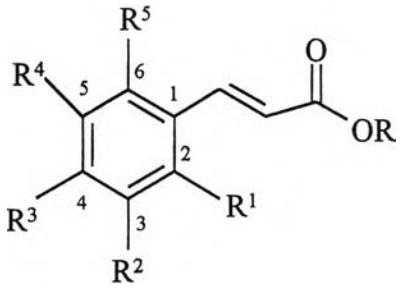
(N-Phenyl)-3,4-methylenedioxycinnamamide (**D12**): White solid (44%), m.p. 145-147°C (dichloromethane-hexane) (lit.[47] 158°C), R_f 0.65 (ethyl acetate); IR (KBr, cm^{-1}): 3419, 3259, 2922, 2854, 1668, 1621, 1541, 1499, 1447, 1329, 1259, 1200 and 1047; ^{1}H-NMR ($CDCl_3$) δ (ppm): 7.63 (*d*, *J* = 15.43 Hz, 1H, Ar-C**H**=), 7.61 (*d*, *J* = 7.71 Hz, 2H), 7.31 (*t*, *J* = 7.52 Hz, 2H), 7.09 (*t*, *J* = 7.49 Hz, 1H), 6.98 (*s*, 1H), 6.96 (*d*, *J* = 7.66 Hz, 1H), 6.76 (*d*, *J* = 7.61 Hz, 1H), 6.38 (*d*, *J* = 15.44 Hz, 1H, =C**H**-CONHR) and 5.97 (*s*, 2H, -OC**H**$_2$O-); ^{13}C-NMR ($CDCl_3$) δ (ppm): 163.8 (-**C**ONHR), 149.3, 148.3, 138.1, 129.1 (2x1C), 129.0, 124.4, 124.2, (2x1C), 108.6, 106.4 and 101.5 (aromatic carbons), 142.1 and 118.9 (olefinic carbons) and 91.3 (-O**C**H$_2$O-).

2.4.2 Synthesis of Cinnamate Esters

General Procedure[30]

Selected alcohol (0.01 mol) was dissolved in 10 mL of benzene and then substituted *trans*-cinnamic acids (0.01 mol) were added thereto. After that 0.3 mL of conc. sulfuric acid was added and the mixture was refluxed for 5 hours. The reaction mixture was concentrated to remove benzene and the residue was poured into 8 mL of ice water. The mixture was extracted three times with 10 mL of ether. The combined extracts were washed twice with 10 mL of H_2O, dried over Na_2SO_4, evaporated in vacuum and the residue fractionally distilled to give the desired compound.

Fifteen cinnamate esters were synthesized and their structures are displayed as shown in Fig 2.3.



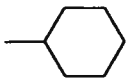
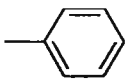
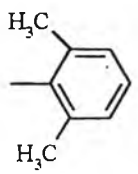
Cpds	R	R^1	R^2	R^3	R^4	R^5
E1	$-CH_2CH_3$	H	H	CH_3	H	H
E2	$-CH_2CH_3$	H	H	C_3H_7	H	H
E3	$-CH_2CH_3$	NO_2	H	H	H	H
E4	$-CH_2CH_3$	H	NO_2	H	H	H
E5	$-CH_2CH_3$	H	$-OC_2H_2O-$		H	H
E6	$-(CH_2)_3CH_3$	H	H	CH_3	H	H
E7		H	H	CH_3	H	H
E8		H	H	CH_3	H	H
E9		H	H	CH_3	H	H

Fig 2.3 Structures of synthesized cinnamate esters

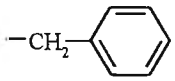
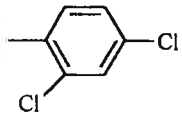
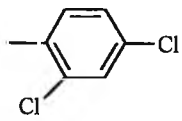
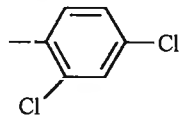
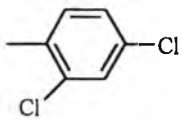
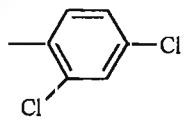
Cpds	R	R^1	R^2	R^3	R^4	R^5
E10		H	H	CH_3	H	H
E11		H	H	CH_3	H	H
E12		H	H	C_3H_7	H	H
E13		NO_2	H	H	H	H
E14		H	NO_2	H	H	H
E15		H	$-OC_2H_2O-$		H	H

Fig 2.3 (cont.)

Ethyl 4-methylcinnamate (**E1**): Yellowish liquid (72%), R_f 0.70 (ethyl acetate); IR (neat, cm^{-1}): 3075, 2980, 2950, 1720, 1635, 1616, 1569, 1513, 1451, 1367, 1300, 1250 and 1175; ^{1}H-NMR ($CDCl_3$) δ (ppm): 7.68 (*d*, *J* = 15.99 Hz, 1H, Ar-C**H**=), 7.38 (*d*, *J* = 8.11 Hz, 2H), 7.14 (*d*, *J* = 8.02 Hz, 2H), 6.36 (*d*, *J* = 16.04 Hz, 1H, =C**H**-COOR), 4.23 (*q*, *J* = 7.09 Hz, 2H), 2.33 (*s*, 3H) and 1.31 (*t*, *J* = 7.08 Hz, 3H); ^{13}C-NMR ($CDCl_3$) δ (ppm): 167.1 (-**C**OOR), 140.6, 131.7, 129.6 (2x1C) and 128.0 (2x1C) (aromatic carbons), 144.6 and 117.1 (olefinic carbons), 60.4, 21.4 and 14.3.

Ethyl 4-i-propylcinnamate (**E2**): Yellowish liquid (77%), R_f 0.70 (ethyl acetate); IR (neat, cm^{-1}): 2970, 2925, 2900, 2875, 1715, 1630, 1602, 1574, 1515, 1466, 1423, 1367, 1277, 1174 and 1052; ^{1}H-NMR ($CDCl_3$) δ (ppm): 7.66 (*d*, *J* = 15.99 Hz, 1H, Ar-C**H**=), 7.42 (*d*, *J* = 7.98 Hz, 2H), 7.20 (*d*, *J* = 7.99 Hz, 2H), 6.38 (*d*,

J = 15.95 Hz, 1H, =C**H**-COOR), 4.23 (*q*, *J* = 7.14 Hz, 2H), 2.81-2.94 (*m*, br, 1H), 1.30 (*t*, *J* = 7.16 Hz, 3H), 1.19 (*s*, 3H) and 1.16 (*s*, 3H); ^{13}C-NMR ($CDCl_3$) δ (ppm): 167.1 (-**C**OOR), 151.4, 132.1 128.2 (2x1C) and 127.0 (2x1C) (aromatic carbons), 144.6 and 117.2 (olefinic carbons), 60.3, 34.1, 23.7 (2x1C) and 14.3.

Ethyl 2-nitrocinnamate (**E3**): Brownish liquid (83%), R_f 0.64 (ethyl acetate); IR (neat, cm^{-1}): 3071, 2989, 2925, 2910, 1875, 1727, 1645, 1611, 1582, 1529, 1475, 1451, 1350, 1275 and 1180; ^{1}H-NMR ($CDCl_3$) δ (ppm): 8.00 (*d*, *J* = 15.84 Hz, 1H, Ar-C**H**=), 7.94 (*d*, *J* = 9.98 Hz, 1H), 7.60-7.46 (Ar-H, 3H), 6.29 (*d*, *J* = 15.76 Hz, 1H, =C**H**-COOR), 4.20 (*q*, *J* = 7.11 Hz, 2H) and 1.26 (*t*, *J* = 7.11 Hz, 3H); ^{13}C-NMR ($CDCl_3$) δ (ppm): 165.0 (-**C**OOR), 148.2, 133.6, 130.4, 130.3, 139.1 and 124.8 (aromatic carbons), 139.8 and 123.2 (olefinic carbons), 60.9 and 14.2.

Ethyl 3-nitrocinnamate (**E4**): White needle crystal (78%), m.p. 72-74°C (ethanol) (lit.[31] 78-79°C) R_f 0.74 (ethyl acetate); IR (KBr, cm^{-1}): 3078, 2981, 1721, 1644, 1533, 1358, 1325 and 1185; ^{1}H-NMR ($CDCl_3$) δ (ppm): 8.35 (*s*, 1H), 8.19 (*d*, *J* = 8.20 Hz, 1H), 7.80 (*d*, *J* = 7.37 Hz, 1H), 7.68 (*d*, *J* = 16.04 Hz, 1H, Ar-C**H**=), 7.56 (*t*, *J* = 7.92 Hz, 1H), 6.53 (*d*, *J* = 16.04 Hz, 1H, =C**H**-COOR), 4.26 (*q*, *J* = 7.11 Hz, 2H) and 1.32 (*t*, *J* = 7.20 Hz, 3H); ^{13}C-NMR ($CDCl_3$) δ (ppm): 166.1 (-**C**OOR), 148.7, 136.2, 133.6, 130.0, 124.5 and 122.4 (aromatic carbons), 141.7 and 121.4 (olefinic carbons), 60.9 and 14.3.

Ethyl 3,4-methylenedioxycinnamate (**E5**): White solid (59%), m.p. 69-71°C (ethanol) (lit.[31] 67-68°C) R_f 0.69 (ethyl acetate); IR (KBr, cm^{-1}): 2990, 2880, 1701, 1644, 1619, 1496, 1450, 1379, 1245 and 1173; ^{1}H-NMR ($CDCl_3$) δ (ppm): 8.88 (*d*, *J* = 8.13 Hz, 1H), 7.68 (*d*, *J* = 7.77 Hz, 1H), 7.44 (*d*, *J* = 15.92 Hz, 1H, Ar-C**H**=), 6.89 (*s*, 1H), 6.12 (*d*, *J* = 15.91 Hz, 1H, =C**H**-COOR), 5.88 (*s*, 2H, -OC**H**$_2$O-), 4.11 (*q*, *J* = 7.12 Hz, 2H), and 1.19 (*t*, *J* = 7.10 Hz, 3H); ^{13}C-NMR ($CDCl_3$) δ (ppm): 167.0 (-**C**OOR), 149.5, 148.3, 128.7, 124.3, 108.4 and 106.4 (aromatic carbons), 144.2 and 116.1 (olefinic carbons), 101.5 (-O**C**H$_2$O-), 60.3 and 14.3.

Butyl 4-methylcinnamate (**E6**): Yellowish liquid (95%), R_f 0.68 (ethyl acetate); IR (neat, cm^{-1}): 3010-2860, 1706, 1645, 1608, 1569, 1518, 1466, 1400, 1380, 1311, 1174 and 1071; ^{1}H-NMR ($CDCl_3$) δ (ppm): 7.62 (*d*, *J* = 15.99 Hz, 1H, Ar-C**H**=), 7.36 (*d*, *J* = 7.89 Hz, 2H), 7.12 (*d*, *J* = 7.90 Hz, 2H), 6.34 (*d*, *J* = 15.97 Hz, 1H, =C**H**-COOR), 4.16 (*q*, *J* = 6.58 Hz, 2H), 2.31 (*s*, 3H), 1.68-1.33 (*m*, br, 4H) and 0.92 (*t*, *J* = 7.19 Hz, 3H); ^{13}C-NMR ($CDCl_3$) δ (ppm): 167.3 (-**C**OOR), 140.6, 131.7, 129.5

(2x1C) and 128.0 (2x1C) (aromatic carbons), 144.6 and 117.1 (olefinic carbons), 64.3, 30.8, 21.4, 19.18, and 13.7.

Cyclohexyl 4-methylcinnamate (**E7**): Yellow liquid (21%), R_f 0.72 (ethyl acetate); IR (neat, cm^{-1}): 2931, 2868, 1775, 1732, 1712, 1635, 1524, 1452, 1250, 1224 and 1171; ^{1}H-NMR ($CDCl_3$) δ (ppm): 7.63 (*d*, *J* = 15.99 Hz, 1H, Ar-C**H**=), 7.40 (*d*, *J* = 8.15 Hz, 2H), 7.14 (*d*, *J* = 8.00 Hz, 2H), 6.37 (*d*, *J* = 15.93 Hz, 1H, =C**H**-COOR), 3.34 (*t*, *J* = 8.95 Hz, 1H), 2.32 (*s*, 3H) and 1.87-1.21 (*m*, br, 10H); ^{13}C-NMR ($CDCl_3$) δ (ppm): 166.7 (-**C**OOR), 137.4, 134.0, 131.8 (2x1C) and 129.6 (2x1C) (aromatic carbons), 140.5 and 117.7 (olefinic carbons), 72.6, 31.8 (2x1C), 25.4, 23.8 (2x1C) and 21.0.

Phenyl 4-methylcinnamate (**E8**): Yellow liquid (45 %), R_f 0.58 (ethyl acetate); IR (neat, cm^{-1}): 3025, 2931, 1761, 1711, 1626, 1517, 1489, 1456, 1422, 1350, 1290, 1231 and 1141; ^{1}H-NMR ($CDCl_3$) δ (ppm): 7.29-6.95 (Ar-H, 10H), 7.10 (*d*, *J* = 14.84 Hz, 1H, Ar-C**H**=), 6.75 (*d*, *J* = 14.42 Hz, 1H, =C**H**-COOR) and 2.33 (*s*, 3H); ^{13}C-NMR ($CDCl_3$) δ (ppm): 167.9 (-**C**OOR), 151.7, 137.4, 137.2, 129.8 (2x1C), 128.7 (2x1C), 127.5 (2x1C) and 124.7 (2x1C) (aromatic carbons), 137.3 and 117.1 (olefinic carbons) and 21.1.

2,6-Dimethyl 4- methylcinnamate (**E9**): Yellow liquid (45%), R_f 0.68 (ethyl acetate); IR (neat, cm^{-1}): 3018, 2926, 1708, 1640, 1611, 1514, 1490, 1437, 1321, 1214 and 1147; ^{1}H-NMR ($CDCl_3$) δ (ppm): 7.95 (*d*, *J* = 16.03 Hz, 1H, Ar-C**H**=), 7.29-6.70 (Ar-H, 7H), 6.74 (*d*, *J* = 16.04 Hz, 1H, =C**H**-COOR), 2.32 (*s*, 3H) and 2.28 (*s*, 6H); ^{13}C-NMR ($CDCl_3$) δ (ppm): 165.1 (-**C**OOR), 148.4, 141.3, 140.4, 130.3 (2x1C), 129.8 (2x1C), 128.7 (2x1C), 128.6 (2x1C) and 125.9 (aromatic carbons), 146.9 and 115.8 (olefinic carbons) 21.6 and 16.6 (2x1C).

Benzyl 4-methylcinnamate (**E10**): Yellowish liquid (95%), R_f 0.74 (ethyl acetate); IR (neat, cm^{-1}): 3025, 2931, 2866, 1708, 1631, 1607, 1519, 150/8, 1456, 1358, 1311, 1250, 1200, 1161 and 1080; ^{1}H-NMR ($CDCl_3$) δ (ppm): 8.15 (*d*, *J* = 16.04 Hz, 1H, Ar-C**H**=), 7.76-7.42 (Ar-H, 9H), 6.84 (*d*, *J* = 16.02 Hz, 1H, =C**H**-COOR), 5.61 (*s*, 2H) and 2.64 (*s*, 3H); ^{13}C-NMR ($CDCl_3$) δ (ppm): 167.8 (-**C**OOR), 141.0, 138.8, 130.1, 129.5 (2x1C), 128.9 (2x1C), 128.6, 128.2 (2x1C), 126.5 (2x1C) and 125.9 (aromatic carbons), 141.1 and 117.0 (olefinic carbons) 72.5 and 21.9.

2,4-Dichlorophenyl 4-methylcinnamate (**E11**): Yellowish liquid (58%), R_f 0.69 (ethyl acetate); IR (neat, cm^{-1}): 1706, 1584, 1480, 1414, 1338, 1287, 1193, 1104

and 1061; ^{1}H-NMR ($CDCl_3$) δ (ppm): 7.19-6.51 (Ar-H, 7H), 7.10 (*d*, *J* = 16.27 Hz, 1H, Ar-C**H**=), 6.89 (*d*, *J* = 15.59 Hz, 1H, =C**H**-COOR) and 2.09 (*s*, 3H); ^{13}C-NMR ($CDCl_3$) δ (ppm): 165.5 (-**C**OOR), 147.5, 140.3, 136.2, 129.4 (2x1C), 129.4, 129.4, 128.7, 128.6, 127.7 and 126.6 (aromatic carbons), 143.6 and 117.2 (olefinic carbons) and 21.0.

2,4-Dichlorophenyl 4-i-propylcinnamate (**E12**): Yellow brown liquid (47%), R_f 0.72 (ethyl acetate); IR (neat, cm^{-1}): 3091, 2960, 1727, 1591, 1480, 1413, 1330, 1287, 1190, 1085 and 1055; ^{1}H-NMR ($CDCl_3$) δ (ppm): 7.22-6.58 (Ar-H, 7H), 7.07 (*d*, *J* = 16.24 Hz, 1H, Ar-C**H**=), 6.76 (*d*, *J* = 16.31 Hz, 1H, =C**H**-COOR), 3.02-2.98 (*m*, br, 1H) and 1.21 (*s*, 6H); ^{13}C-NMR ($CDCl_3$) δ (ppm): 165.9 (-**C**OOR), 150.1, 147.9, 138.7, 133.1, 129.6, 128.7, 127.8, 127.5 (2x1C), 125.3 (2x1C) and 124.4 (aromatic carbons), 147.5 and 117.2 (olefinic carbons), 33.8 and 24.0 (2x1C).

2,4-Dichlorophenyl 2-nitrocinnamate (**E13**): Yellow brown liquid (41%), R_f 0.72 (ethyl acetate); IR (neat, cm^{-1}): 1722, 1630, 1587, 1480, 1413, 1330, 1292, 1185, 1098 and 1055; ^{1}H-NMR ($CDCl_3$) δ (ppm): 7.31-6.91 (Ar-H, 7H), 7.55 (*d*, *J* = 16.06 Hz, 1H, Ar-C**H**=) and 6.62 (*d*, *J* = 16.08 Hz, 1H, =C**H**-COOR); ^{13}C-NMR ($CDCl_3$) δ (ppm): 164.0 (-**C**OOR), 150.2, 147.8, 136.5, 136.0, 134.0, 128.8, 128.6, 128.5, 125.6 and 120.4 (aromatic carbons), 146.0 and 117.1 (olefinic carbons).

2,4-Dichlorophenyl 3-nitrocinnamate (**E14**): Yellow brown liquid (45%), R_f 0.74 (ethyl acetate); IR (neat, cm^{-1}): 1727, 1616, 1584, 1533, 1480, 1409, 1339, 1278, 1188, 1104 and 1056; ^{1}H-NMR ($CDCl_3$) δ (ppm): 7.55-6.73 (Ar-H, 7H), 7.75 (*d*, *J* = 16.04 Hz, 1H, Ar-C**H**=) and 6.60 (*d*, *J* = 16.02 Hz, 1H, =C**H**-COOR); ^{13}C-NMR ($CDCl_3$) δ (ppm): 151.7, 145.0, 134.5, 132.5, 130.0, 129.2, 127.6, 127.5, 124.2, 124.0, 122.5 and 121.1 (aromatic carbons), 144.5 and 117.5 (olefinic carbons).

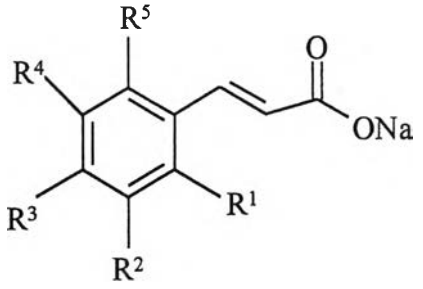
2,4-Dichlorophenyl 3,4-methylenedioxycinnamate (**E15**): Brownish liquid (34 %), R_f 0.76 (ethyl acetate); IR (neat, cm^{-1}): 1734, 1673, 1584, 1485, 1446, 1409, 1329, 1277, 1193, 1108 and 1056; ^{1}H-NMR ($CDCl_3$) δ (ppm): 7.20-6.81 (Ar-H, 7H), 7.32 (*d*, *J* = 16.04 Hz, 1H, Ar-C**H**=) and 6.42 (*d*, *J* = 16.06 Hz, 1H, =C**H**-COOR); ^{13}C-NMR ($CDCl_3$) δ (ppm): 161.0 (-**C**OOR), 151.3, 127.8, 124.5, 121.1, 116.5, 108.4 and 106.8 (aromatic carbons), 117.5 (olefinic carbons), 102.2 (-O**C**H_2O-).

2.4.3 Preparation of Sodium Cinnamate Derivatives

General Procedure[48]

Selected *trans*-cinnamic acids (0.003 mol), 0.03 mol of sodium hydroxide and 24 mL of toluene were put into a round bottom flask and stirred under reflux for 5 hours. The reaction solution was cooled, and then 24 mL of acetone was added thereto. The precipitate was collected by filtration, and the obtained crude crystals were washed with acetone and then dried to obtain the desired compound.

Six sodium cinnamate derivatives were synthesized and their structures are displayed as shown in Fig 2.4.



Cpds	R^1	R^2	R^3	R^4	R^5
S1	H	F	H	H	H
S2	H	Cl	H	H	H
S3	H	Br	H	H	H
S4	H	OCH_3	H	H	H
S5	H	NO_2	H	H	H
S6	H	$-OC_2H_2O-$		H	H

Fig 2.4 Structures of sodium cinnamate derivatives

Sodium 3-fluorocinnamate (**S1**): White solid (45%), m.p. at least 300°C; IR (KBr, cm^{-1}): 1639, 1587, 1552, 1486, 1451, 1414, 1250, 1200 and 1115.

Sodium 3-chlorocinnamate (**S2**): White solid (75%), m.p. at least 300°C; IR (KBr, cm^{-1}): 1644, 1552, 1471, 1422, 1404, 1250, 1185 and 1080.

Sodium 3-bromocinnamate (**S3**): White solid (94%), m.p. at least 300°C; IR (KBr, cm^{-1}): 1644, 1557, 1470, 1413, 1200, 1150 and 1050.

Sodium 3-methoxycinnamate (**S4**): White solid (89%), m.p. at least 300°C; IR (KBr, cm^{-1}): 1639, 1591, 1531, 1422, 1403, 1235, 1150 and 1115.

Sodium 3-nitrocinnamate (**S5**): Pale brown solid (64%), m.p. at least 300°C; IR (KBr, cm^{-1}): 1650, 1567, 1541, 1480, 1439, 1408, 1352 and 1075.

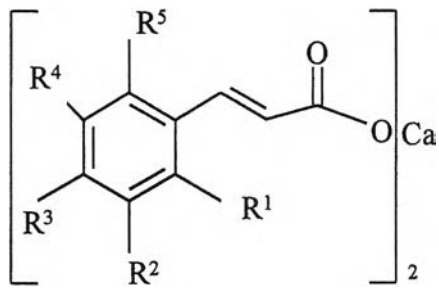
Sodium 3,4-methylenedioxycinnamate (**S6**): White solid (94%), m.p. at least 300°C; IR (KBr, cm^{-1}): 1645, 1616, 1553, 1456, 1413, 1359, 1250, 1100 and 1050.

2.4.4 Preparation of Calcium Cinnamate Derivatives

General Procedure[48]

Selected *trans*-cinnamic acids (0.03 mol) and 12.5 mL of a 1.0% sodium hydroxide aqueous solution were put into a round bottom flask and stirred at room temperature for one hour. Then, 5 mL of a 4.0% calcium chloride aqueous solution was dropwise added thereto at room temperature. Stirring was continued at room temperature for one hour. Then, the formed precipitated was collected by filtration, washed with water and hexane and then dried to obtain the desired compound.

Three calcium cinnamate derivatives were synthesized and their structures are displayed as shown in Fig 2.5.



Cpds	R^1	R^2	R^3	R^4	R^5
CS1	H	F	H	H	H
CS2	H	NO_2	H	H	H
CS3	H	$-OC_2H_2O-$		H	H

Fig 2.5 Structures of calcium cinnamate derivatives

Calcium 3-fluorocinnamate (**CS1**): White solid (77%), m.p. at least 300°C; IR (KBr, cm^{-1}): 1650, 1625, 1587, 1562, 1485, 1445, 1350, 1250 and 1125.

Calcium 3-nitrocinnamate (**CS2**): White solid (41%), m.p. at least 300°C; IR (KBr, cm^{-1}): 1644, 1542, 1450, 1432, 1353, 1250 and 1100.

Calcium 3,4-methylenedioxycinnamate (**CS3**): White solid (64%), m.p. at least 300°C; IR (KBr, cm^{-1}): 1639, 1557, 1506, 1445, 1480, 1275, 1100 and 1104.

2.5 Bioassay on Herbicidal Activity

2.5.1 General Procedure for Weed Growth Inhibition Test[49]

Tested compound was dissolved in a proper solvent[a] at concentration of 4500, 450, 45 and 4.5 ppm. The 3.0 mL of solution was poured into a glass tube (diameter 30 mm and length 120 mm) which contained 1.5 g of cellulose powder. The controlled tube was prepared by the same solvent using the same methodology. All tubes were covered with aluminum foil, dried up by heated at 50°C in vacuum oven for 10-12 hours, stirred until well-mix, followed by the addition of 4.5 mL of distilled water to each tube (concentrations of tested compound were 3000, 300, 30 and 3 ppm, respectively). Three seedlings of giant mimosa or barnyard grass with radical root length 1-2 mm (seeds of bioassay species were soaked for 6 hours and germinated in petri-dish one night before testing) were transplanted in each tube, 3 tubes for each concentration. The tubes were sealed with transparent vinyl film and kept in growth chamber at 30°C, 24 hours daylight. The seedlings were cleared from artificial food, the root and shoot length were recorded at 7 days after transplanting.[b] The growth inhibitory effect was calculated with the formula:

$$\% \text{ Growth Inhibition} = \{ 1 - (T / C) \} \times 100 \%$$

where 'T' is root (or shoot) length of treated seedlings and 'C' is root (or shoot) length of controlled set.

Growth inhibition of 100 % mean completely inhibitory effect.

---

a) acetone is solvent for most substituted *trans*-cinnamic acids

b) All of these experiments were performed at Weed Science Sub-Division, Botany and Weed Science Division, Department of Agriculture, Ministry of Agriculture and Cooperatives.

The results of weed growth inhibition of substituted *trans*-cinnamic acids against *M. pigra* and *E. crus-galli* are displayed in Tables C.1 and C.2, respectively. (see Appendices C)

The results of weed growth inhibition of cinnamamides, cinnamate esters, sodium cinnamate and calcium cinnamate derivatives against *M. pigra* are displayed in Tables C.3, C.4, C.5 and C.6, respectively. (see Appendices C)

2.5.2 General Procedure for Weed Germination Inhibition Test[50]

Tested compound was dissolved in a proper solvent[a] at concentration of 5000, 500, 50 and 5 ppm. The 3.0 mL of solution was poured in a plate (diameter 90 mm) which contained with a filter paper. The controlled plate was prepared using the same methodology with no tested compound. All plates were dried up for 10-12 hours, followed by the addition of 5.0 mL of distilled water to each plate (concentrations of tested compound were 3000, 300, 30 and 3 ppm, respectively). Fifty seeds of tested weed were transplanted in each plate, 3 plates for each concentration. All plates were covered and left at room temperature. The germinated seed numbers were recorded at 7 days after application. Five seedlings were randomly selected to measure root and shoot length.[b] The inhibitory effect of the substance on germination was calculated by:

$$\% \text{ Germination Inhibition} = \{ 1 - (T / C) \} \times 100\ \%$$

where 'T' is germination number of treated seedlings and 'C' is germination number of controlled set.

Germination inhibition 100 % mean completely inhibitory effect.

---

a) acetone is solvent for selected compound

b) All of these experiments were performed at Weed Science Sub-Division, Botany and Weed Science Division, Department of Agriculture, Ministry of Agriculture and Cooperatives.

The results of germination and root growth inhibition test of 3,4-methylene dioxycinnamic and 3-nitrocinnamic acids against various weeds, *Mimosa pigra* Linn., *Echinochloa crus-galli* Beauv., *Trianthema portulacastrum* Linn., *Celosia argentea* Linn., *Dactyloctenium aegyptium* Linn., *Euphorbia geniculata* Ort., *Tridax porcumbens* Linn., *Aeschynomene americana* Linn., *Cenchrus echinatus* Linn. and *Pennisetum pedicellatum* Trin., are displayed in Tables C.7 and C.8, respectively. (see Appendices C)

2.6 Herbicidal Activity of Commercially Available Herbicides

Two commercial herbicides, 2,4-D (**H1**), alachlor (**H2**) and atrazine (**H3**) were chosen to compare with tested compounds. The inhibitory effect of commercial herbicide and tested compounds were done in test tube by using *M. pigra* as bioassay species with the same procedure of inhibitory effect test. The results are shown in Table C.9. (see Appendices C)