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**SHORT COMMUNICATION**

# SOLVENT FREE PREPARATION OF *N*-SUBSTITUTED MALEANILIC ACID

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**ABSTRACT**. Six N-maleanilic acids namely N-(4-carboxy)maleanilic acid (CAMAA), N-(4-bromo)maleanilic acid (BMAA), N-(4-hydroxy)maleanilic acid (HMAA), N-(3-hydroxy)maleanilic acid (mHMAA), N-(4-chloro)maleanilic acid (CMAA) and N-(4-methyl)maleanilic acid (MMAA) were prepared by solvent free reaction between maleic anhydride and a 4-carboxy, 4-bromo, 4-hydroxy, 3-hydroxy, 4-chloro and 4-methyl aniline derivatives in good to excellent yield. FT-IR, $^{1}$H-NMR and $^{13}$C-NMR spectra revealed the confirmation of these compounds in good agreement.

**KEYWORDS**: Solvent free, Maleanilic acids, Maleic anhydride, Aniline derivatives

## INTRODUCTION

The reaction of aniline or its derivatives with maleic anhydride is well-known, because the product maleanilic acid or *N*-substituted maleanilic acid can be used to prepare the maleimides which are an important class of substrates for biological as chemical probes of protein structure [1], as a protective and curative fungicide [2] and in polymer chemistry as photoinitiators for free-radical polymerization [3, 4] and monomers in polymaleimides or their copolymers synthesis.

The literature contains a large number of publications regarding to the synthesis of maleanilic acids mostly consisting of the reaction of equimolar of aniline or its derivatives with maleic anhydride in the presence of a solvent. Different solvents can be used, ether [5], acetic acid [6], acetone [7], nitrobenzene [8], chloroform [9] or mixed solvents such as equal volume of ethyl alcohol and water [10]. The reactions were carried out at 0-5 $^{o}$C [11], room temperature [12, 13] or at 70-75 $^{o}$C [14].

Also, it may be noted that the amount of used solvent is a large one for any of these preparations. For example; to obtain about ninety grams of *N*-(*p*-chloro)maleanilic acid more than half liter of methylene chloride had been used [15, 16].

In this article, six *N*-maleanilic acids CMAA, BMAA, HMAA, MMAA, mHMAA and CAMAA were prepared by solvent free reaction between maleic anhydride and a 4-chloro, 4-bromo, 4-hydroxy, 4-methyl, 3-hydroxy and 4-carboxy aniline derivatives at room temperature.

## EXPERIMENTAL

*Materials*. All chemicals were purchased from Merck Chemical Co. (Germany). 4-Chloroaniline, 4-bromoaniline, 4-aminophenol, 3-aminophenol, and 4-aminobenzoic acid were used as received. Maleic anhydride was recrystallized from acetone.

*Instrumental analysis*. The IR spectra were recorded on a Shimadzu FTIR 8300 series spectrometer using KBr pellets. The $^{1}$H and $^{13}$C NMR spectra were recorded on Bruker 500

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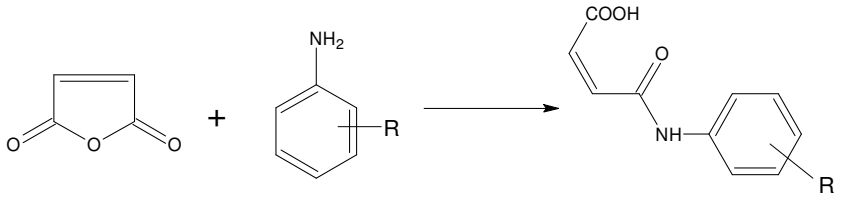
MHz spectrometer in solutions of $CDCl_3$ or DMSO-$d_6$. The elemental analysis was taken by a Carlo Erba Model NA 500 series analyzer. The melting points were determined by Stuart (SMP3) Melting Point Apparatus.

*N-(Substituted) maleanilic acids preparation*. *p*-Chloroaniline 12.75 g (0.1 mol) was mixed and ground at room temperature with maleic anhydride 9.8 g (0.1 mol) in an agate mortar. As a crunching preceeded a nice greenish-yellow color appeared. The grinding was continued for 30 more min. The crude product was crystallized from ethanol and the collected greenish-yellow crystals were dried. Melting point: 197-199 $^{o}$C, yield 92%. The other five *N*-substituted maleanilic acids were prepared on the same procedure. Time of grinding, melting point and elemental analysis of the prepared *N*-(substituted) maleanilic acids are listed in Tables 1. Pure and dry samples of prepared *N*-maleanilic acids were characterized by FT-IR (Table 2), $^{1}$H-NMR (Table 3) and $^{13}$C-NMR (Table 4).

## RESULTS AND DISCUSSION

A series of *N*-substituted maleanilic acids (MAA) have been prepared using a solid phase (new approach) reaction between solid maleic anhydride and various solid *N*-substituted anilines at room temperature. The prepared maleanilic acids are depicted in Scheme 1. The synthetic method used to prepare the series is simple, clean, economic and nearly quantitative or high yields (Table 1).

The FT-IR spectra of the compound CMAA exhibited no anhydride C=O stretching band at 1870-1725 cm$^{-1}$ region indicating that the maleanilic acids have been successfully prepared. The FT-IR spectrum showed several characterization bands. The broad -OH stretching band associated with the carboxylic group between 3275-2877 cm$^{-1}$, the weak –NH amide stretching band at 3198 cm$^{-1}$ and the C-H aromatic stretching absorption band at 3076 cm$^{-1}$ have generally been seen. The band at 1701 cm$^{-1}$ are due to the carboxylic C=O stretching band expected to α-β-unsaturated system for the dimers [15]. The absorption band at 1630 cm$^{-1}$ is assigned to amide I. The band at 1545 cm$^{-1}$ are due to the interaction of the N-H bending and C-N stretching vibration, also referred to as the amide II bands and are characterized to primary and secondary amide [16]. The bands at 1392 cm$^{-1}$ are assigned to the O-H bending of the carboxylic acid. The CO stretching at 1317 cm$^{-1}$ are those associated with the OC-OH carboxylic group. The stretching absorption at 1088 cm$^{-1}$ has been assigned to the aromatic C-Cl band. The structures of the other prepared compounds have been confirmed by FT-IR (Table 2).




MA MAA

where R = 4-Cl (CMAA) R = 4-Br (BMAA) R = 4-OH (HMAA) R = 4-$CH_3$ (MMAA) R = 3-OH (mHMAA) R = 4-COOH (CAMAA)

Scheme 1. Preparation of *N*-Substituted maleanilic acids.

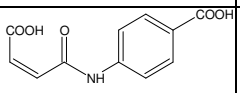
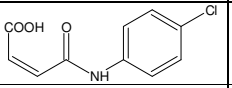
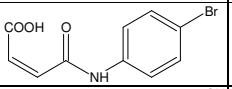
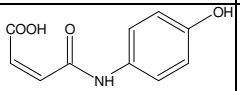
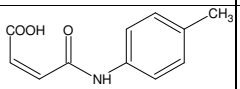
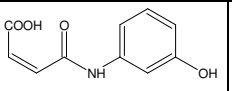
Table 1. Mixing time, melting point, yield% and elemental analysis of prepared N-substituted maleanilic acids.

| Compound | Name of compound | Mixing time (min) | m.p. (ºC) | Yield (%) | Formula (M.Wt.) | Elemental Analysis | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | C % | | H % | | N % | |
| | | | | | | Found | Cal. | Found | Cal. | Found | Cal. |
| CMMA | *N*-(-4-chloro) maleanilic acid | 30 | 197-199, Lit. 195-198 [9] | 92.0 | $C_{10}H_8NO_3Cl$ (225.55) | 53.28 | 53.25 | 3.51 | 3.55 | 6.24 | 6.21 |
| BMAA | *N*-(-4-bromo) maleanilic acid | 40 | 187-190, Lit. 192-193.5 [10] | 90.3 | $C_{10}H_8NO_3Br$ (270.00) | 44.50 | 44.48 | 2.95 | 2.96 | 5.24 | 5.19 |
| HMAA | *N*-(-4-hydro-xy) male-anilic acid | 30 | 207-208 | 92.4 | $C_{10}H_9NO_4$ (207.10) | 58.01 | 57.99 | 4.37 | 4.35 | 6.81 | 6.76 |
| MMAA | *N*-(-4-methyl) male anilic acid | 40 | 195-197 Lit. 201-202 [11] Lit. 174-175 [12] Lit. 186-188 [9] | 94.1 | $C_{11}H_{11}NO_3$ (205.11) | 64.45 | 64.41 | 5.33 | 5.36 | 6.79 | 6.83 |
| HMAA | *N*-(-3-hydroxy)mal eanilic acid | 30 | 186-189 | 91.0 | $C_{10}H_9NO_4$ (207.10) | 57.98 | 57.99 | 4.39 | 4.35 | 6.73 | 6.76 |
| CAMAA | *N*-(-4-carboxy)mal eanilic acid | 30 | 219-221 Lit. 225-226 [13] Lit. 222 [14] | 86.7 | $C_{11}H_9NO_5$ (235.11) | 56.15 | 56.19 | 3.81 | 3.83 | 5,97 | 5.95 |

The $^1$H-NMR data of compound CMAA, HMAA and mHMAA are shown in Table 3, exhibit signals at 13.2 ppm and 10.44 ppm attributed to the carboxylic acid –OH and H-(NCO) amide protons. The expanded $^1$H-NMR of the compound CMAA shows distinguished doublets due to aromatic protons ; protons that are ortho to amide group show a doublet signal 7.65-7.67 ppm and that are *ortho* to chloride appear at 7.36-7.38 ppm . These two doublet signals have the same coupling constant (*J*) and the same integrated area, indicating the presence of four protons with two couples that are chemically but not magnetically equivalent [15]. The vinylic protons resonate at 6.47-6.50 ppm as doublet. The integrated area of the aromatic region to that of vinylic region in the $^1$H-NMR spectrum of the compound CMAA, indicated that aromatic protons to vinylic protons are in the ratio of 3.893:2, which is in the region of theoretical value 4:2. The $^1$H-NMR spectra for the other maleanilic acids show typical signals which confirm their structures (Table 3).

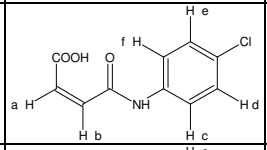
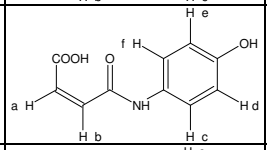
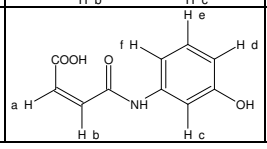
$^{13}$C-NMR has also been useful to confirming some of the N-maleanilic acids, $^{13}$C-NMR spectrum of compound CMAA exhibits two peaks at 167.54 ppm and 164.28 ppm for carboxylic and amide carbons. The two vinylic carbons, adjacent to the carboxylic and amide groups resonate at 131.11 and 128.44 ppm, respectively. The aromatic carbon signals appeared as four different peaks; the carbon that is substituted with amide group resonates at 138.35 ppm and that is substituted with chloride resonates at 132.76 ppm. The two carbon atoms *ortho* to amide group resonate at 122.02 ppm and that which is *ortho* to chloride group resonates at 129.53 ppm. The other compounds show their own signals which are confirmed there chemical structures (Table 4).

Table 2. FT-IR measurements of the prepared *N*-substituted maleanilic acids.

| Comp-ound | Structure | Band frequencies* | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | νCOO-H | $\nu NH_3$ (amide) | νar.C-H | νC=O (C=C-OOH) | νC=O (amide I) N-C=O | νsy.-NHCO- (amide II) | σ O-H | νC-O | Others |
| CAMAA |  | 3500-2500 | 3307 | 3034 | 1699 | 1626 | 1545 | 1415 | 1298 | σC-H 846 |
| CMAA |  | 3275-2877 | 3198 | 3076 | 1701 | 1630 | 1545 | 1392 | 1317 | νar.C-Cl 1088 |
| BMAA |  | 3271-2870 | 3193 | 3074 | 1706 | 1628 | 1546 | 1394 | 1321 | νar.C-Br 1076 |
| HMAA |  | 3292-2821 | 3126 | 3072 | 1697 | 1625 | 1541 | 1412 | 1329 | νar.C-O (pphenol) 1229, 1246 |
| MMAA |  | 3277-2837 | 3205 | 3078 | 1699 | 1633 | 1531 | 1398 | 1309 | |
| mHMAA |  | 3336-2696 | 3282 | 3078 | 1699 | 1616 | 1568 | 1407 | 1302 | νar.C-O (phenol) 1356, 1261 |

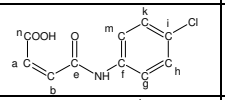
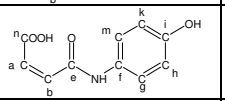
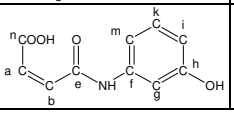
(*) ν = stretching band, σ = bending band, sy. = symmetric vibration mode.

Table 3. $^1$H-NMR measurements for some prepared *n*-substituted maleanilic acids.

| Comp-ound | Structure | Chemical shifts (σ/ppm) relative to TMS* | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | O-H | N-H | $H_a$ | $H_b$ | $H_c$ | $H_d$ | $H_e$ | $H_f$ | Others |
| CMAA |  | 13.20 (s) | 10.43 (s) | 6.47-6.50 (d) | 6.30-6.34 (d) | 7.65-7.67 (d) | 7.36-7.38 (d) | 7.36-7.38 (d) | 7.65-7.67 (d) | |
| HMAA |  | 13.20 (s) | 10.43 (s) | 6.47-6.50 (d) | 6.26-6.29 (d) | 7.42-7.43 (d) | 6.74-6.75 (d) | 6.74-6.75 (d) | 7.42-7.43 (d) | 6.62-6.63 H-(ar.OH) |
| mHMAA |  | 13.20 (s) | 10.30 (s) | 6.46-6.31 (d) | 6.28-6.31 (d) | 7.25 (s) | 6.52 (d) | 7.09-7.12 (d) | 6.99-7.00 (d) | H-(ar.OH) 9.44 broad |

(*)Multiplicity: s = singlet; m = multiplet; t = triplet; d = doublet.

Table 4. Spectral $^{13}$C-NMR data of some prepared *n*-substituted maleanilic acids.

| Compound | Structure | Chemical shifts (σ/ppm) relative to TMS | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | $C_a$ | $C_b$ | $C_n$ | $C_e$ | $C_f$ | $C_g$ | $C_h$ | $C_i$ | $C_k$ | $C_m$ |
| CMAA |  | 131.11 | 128.44 | 167.54 | 164.28 | 138.35 | 122.02 | 129.35 | 132.76 | 129.35 | 122.02 |
| HMAA |  | 132.96 | 132.36 | 166.96 | 163.23 | 130.49 | 122.58 | 116.14 - 116.67 | 155.80 | 116.14 - 166.67 | 122.58 |
| mHMAA |  | 132.83 | 131.37 | 167.55 | 164.10 | 140.25 | 107.77 | 158.50 | 113.37 | 130.33 | 112.10 |

## CONCLUSIONS

This work involved preparation of six *N*-maleanilic acids CMAA, BMAA, HMAA, MMAA, mHMAA and CAMAA by solvent free reaction between maleic anhydride and a 4-chloro, 4-bromo, 4-hydroxy, 4-methyl, 3-hydroxy and 4-carboxy aniline derivatives at room temperature. This new approach, solvent free preparation method is simple, clean, economic and nearly quantitative or high yields.

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