Phytocatalytic Utility of Unripe Banana Peel Water as a Novel Matrix for Benzoylation of Amino Containing Functionality

Abstract
We herein report unripe banana peel water as an alternate medium for benzoylation of aromatic amino containing functionality especially aniline, further concluded that same methodology could be used for benzoylation purposes of other aromatic compounds containing similar functionality. Compared to conventional methodology, the catalytic system we reported here is superior in multiple aspects and devoid of using any non-eco-friendly hazardous organic/inorganic alkaline matrix.

Keywords: Benzoylation; Unripe banana peel water; Phytocatalytic

Introduction
It is now a well evident fact that catalyst and solvent affects both the reaction rate as well as outcome of a chemical reaction. On the basis of practical and industrial applicability, numerous techniques were evaluated for substitution/modification of later [1-3] although the same could not be true for former comparatively, owing to its specificity and selectivity towards a particular type of chemical reaction or desired product needed from same along with decisive direct influence on outcomes of a chemical phenomenon (reaction rate, product purity, its yield, and economic value etc.) and its kinetics (Figure 1).

Benzoylation, a phenomenon involves introduction of ArCO-functionality (Scheme-01) is an effective, economic, and handy technique, not only used to protect and identify amino as well as hydroxyl group present in an aromatic as well as aliphatic organic compounds, but is also equally important in their synthetic...
hence a comparative study between synthesized and reported compound was done to enumerate its practicability (Table 1). The melting point for synthesized compounds was recorded by open capillary method in triplicate and is uncorrected. The progression of reaction was monitored in PET ether:ethylacetate (8:2) as a binary solvent system on a pre-prepared TLC plate.

**Experimental**

**Preparation of banana water**

The unripe, matured (banana with green peel color), and healthy bananas were selected carefully for making banana peel water. Sufficient communication before selecting banana for experimentation was established with shopkeepers. The unripe banana so obtained were washed thoroughly from distilled water, dried suitably at lower temperature, and carefully peeled-off with knife such that the outer covering of banana could be separated from inner white edible (body) portion. The peels (20 g) were then transferred into a beaker (500 ml) and were cold macerated (with distilled water; 300 ml) at room temperature for 72-hours. On completion peels were separated from mother liquid (black in color), which is further filtered off carefully to remove any suspended or un-dissolved particle.

**Evaluation of benzoylating efficiency of banana peel water**

The efficiency of unripe banana peel water as a medium for synthesizing benzoylated derivatives was evaluated by dissolving or suspending equimolar quantity (0.01 M) of reactant (aniline) and benzoyl chloride in banana peel water (15 ml; Figure 3). The content was shaken for the sufficient period of time (under fuming hood), yielding crude product, was further washed thoroughly from cold water and finally recrystallized from ethanol.

**Results and Discussion**

The phytocatalytic technique for benzoylation we herein develop and reports is unique and advantageous over traditional methodology (Table 2) in terms of cost effectiveness, eco-
Physiochemical/qualitative parameters | Reference benzanilide (Commercially available) | Benzanilide Synthesize in traditional catalyst | Benzanilide Synthesize in unripe banana peel water | Inferences
--- | --- | --- | --- | ---
Physical appearance Before recrystalization | Yellowish white White/colorless crystal | Yellowish white White/colorless crystal | Yellowish white White/colorless crystal | Synthesized product having similar appearance as that of reference

Solubility
Water (cold) | - | - | - | Differences in Solubility of reactants & products in nonpolar organic solvent indicates addition of aromatic ring (lipophilic character).
Water (hot) | + | + | + | 
Methanol | ++ | ++ | ++ |
Ethanol | +++ | +++ | +++ |
Chloroform | - | - | - |

Melting point (°C) | 163 | 162 | 166 | Within the range Melting point indicates synthesis of benzanilide

Qualitative detection of residual benzoyl chloride in product
-Silver nitrate test | Negative | Negative | Negative | Chlorine absent, benzoyl chloride exhausted; benzoylation done

Qualitative detection of nitrogen in product
-Ferrous sulphate test | Positive | Positive | Positive | Nitrogen present

Qualitative detection of sulphur in product
-Sodium nitroprusside test | Negative | Negative | Negative | Sulphur absent

Qualitative detection of free phenolic group in product
-Ferric chloride test | Negative | Negative | Negative | Phenolic group absent/ test not applicable

Qualitative detection of free NH group in product
-Dye test | Negative | Negative | Negative | Free –NH group absent; benzoylation done

Table 1 Comparative physiochemical characteristic of benzyolated derivative synthesised in unripe banana peel water with that of standard.

Figure 3 Optimized quantity of unripe banana peel water and it effect on product yield at constant concentration of reactants (0.1 M).
compatibility, and is entirely free from using any harmful alkaline catalytic medium to assist the reaction. The unripe banana peel water was successfully evaluated to elucidate its synthetic harmony for benzoylating monocarbocyclic aromatic ring system containing amino functionality (Figure 4). We further claims (on the basis of our experimentation result) that the technique we herein reported can equally be applied for yielding benzoylated derivatives of polycarbocyclic aromatic as well as aliphatic compounds containing hydroxyl and amino groups including protecting N-terminal ends of amino acids for peptide synthesis however the same was reserved as a future workup plan of ours. The benzoylated derivative of aniline by this methodology was yielded practically in excellent yield, and is comparable with the product obtained by traditional chemical pathway. Furthermore, the quantity of unripe banana peel water used for benzoylation against particular quantity of reactants were optimized, was found that even a quantity less than 15 ml is appropriate (Figure 3) for normal yield of benzoylated product however any quantity
Table 2 Catalyst used for industrial applicability.

| Reaction conditions          | Conventional benzylation pathway | Phytocatalytic benzylation pathway |
|------------------------------|----------------------------------|-----------------------------------|
| Host reactant                | Aniline (0.1 M)                  | Aniline (0.1 M)                   |
| Benzylation agent            | Benzoyl chloride (0.1 M)         | Benzoyl chloride (0.1 M)          |
| Catalyst used                | Sodium hydroxide (10%)           | Unripe banana peel water          |
| Catalyst preparation         | Tedious                          | Easy                              |
| Catalyst handling            | Need special care                | Easy                              |
| Catalyst effect on human     | Harmful                          | None                              |
| Catalyst effect on environment | Harmful                       | None                              |
| Catalyst biodegradability    | Non-biodegradable                | Biodegradable                     |
| Catalyst cost                | Costlier                         | Cheap; even none                  |
| Catalyst quantity used       | 15 ml                            | 15 ml* (see Figure 4)             |
| Reaction temperature (°C)    | RT                               | RT                                |
| Reaction time                | 20-minutes                       | 12-minutes                        |
| Product yield (%)            | 85                               | 78                                |
| Recrystallization requirement | Yes                              | Yes                               |
| Recrystallization solvent    | Ethanol                          | Ethanol                           |

*quantity even less is effective.

**Conclusion**

Though overall yield of benzoylated derivatives we found in unripe banana peel water is not comparable with traditional alkaline solvents nevertheless its practicability in terms of cost effectiveness and eco-compatible is unquestionable. Furthermore the unripe banana peel water alone or used in combination with other alkaline solvent the net cost for industrial production of benzoylated derivatives could efficiently be minimized. Since the unripe banana peel water is comparatively less/no basic than conventional alkaline solvents thus the same could be used for benzoylation of amino acid without causing their racemization. However as per our prediction, the unripe peel banana peel water could be used efficiently for yielding benzoylated derivative of aniline.

Beyond a particular amount (10-8 ml) affects the yield of product as well as its purity. Likewise volume of unripe banana peel water greater than 15 ml is equally effective to yield product although a volume next to 20 ml is wastage to medium.
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