INVESTIGATING THE APPLICATION OF BARIUM CHLORIDE CATALYST FOR SYNTHESIS OF PHTHALIC ACID ESTERS FROM *Gmelina arborea* leaves

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Abstract:
An investigation to determine the value-added materials and the green manage method of handling waste leaves was carried on *Gmelina arborea*. Hydrothermal decomposition of the plant leaves was carried out using barium chloride catalysts of concentration 0.25 and 0.50 g at 60, 70, 80, and 90 °C. The products were filtered and dehydrated with magnesium sulphate and then separated using a separating funnel. The results were analyzed using Gas Chromatography and Mass Spectroscopy (GC-MS). Two phthalates: 1, 2-benzene dicarboxylic butyl undecyl phthalic acid ester (butyl undecyl phthalate) and 1, 2-benzene dicarboxylic diisooctyl phthalic acid ester (diisooctyl phthalate) were identified in all the products. The highest quantity of butyl undecyl phthalate obtained was 30.43 g at 70 °C with 0.25 g (0.5%) catalyst loading and that of diisooctyl phthalate was 78.92 g at 60 °C with 0.50 g (1.0%) catalyst loading respectively. The *Gmelina arborea* is a potential source for the production of high-molecule phthalates.

Keywords: Application, Barium Chloride Catalyst, *Gmelina arborea* Waste leave, investigating, Phthalic Acid Esters, Synthesis

Introduction

Phthalic acid esters (PAEs) are a class of lipophilic chemicals widely used as plasticizers and additives to improve mechanical properties such as the extensibility and flexibility of material products for workability (Hung *et al*., 2021). These plasticizers are useful in extending the life span of materials and in the dissolution of other substances (Godwin, 2024: Ma *et al*., 2020). They have wide applications in the chemical industry due to their excellent plasticization, adhesion, stabilization, and softness properties (Jarosova, 2006; Godwin, 2000). The major products of phthalic esters include lubricating oil, plastic packaging, garden hoses, medical tubing, and personal care like soaps, shampoos, and hair sprays (Al-Horani & Ayyad, 2023: Meenu2022: Erkeko*et al., 2021*). Plasticizers also reduce the brittleness of the mixture/blend by interfering with the hydrogen bonding that exists between the lipid and hydrocolloid molecules which increases the flexibility and volume of the polymer due to the weakening of the internal hydrogen bonding (Kormin *et al*., 2019). Some of the products made from plasticizers include packaging, epoxy resins, water pipe lining, thermal printing papers, implanted medical devices, CDs and DVDs, mobile phones, plastic food containers, eyeglass lenses, drinking bottles, food packaging, and dental sealants (Wilkinson *et al*., 2017). Phthalates are also used to increase plastics' transparency, durability, and longevity (Dimassi *et* al., 2023: Bajracharya *et al*., 2021: Luís *et* al., 2021: Jayaweera *et al*., 2020). A claim by Olympia, 2023: Bajracharya *et al*. (2021), and Baloyi *et al*., 2021) that phthalates are used as stabilizers, binders, and adhesives for the manufacture of toys, textiles, paints, medical devices, and cosmetics, among others. They are used in personal care such as perfumes, eye shadow, nail polish, and hair spray (Pagoni *et al*., 2022: Srinivasulu *et al*., 2022).

1, 2-benzene dicarboxylic acid butyl decyl phthalate (DBDP)

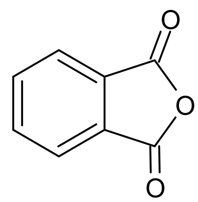
Butyl decyl phthalate with i.U.P.A.C. name, 1, 2-benzene dicarboxylic acid butyl decyl phthalate (DBDP) ($C_{22}H_{34}O_4$) is also known as phthalic acid, butyl decyl ester; Decyl butyl phthalate (Kang *et* al., 2023: KETEMA, 2022: Saad, 2021). It has a molecular weight of 262.5 g/mol and a CAS number of 89-19-0. It is mostly used as a plasticizer (Estévez-Danta *et al*., 2021). In addition to its use as a plasticizer, it is also used to soften polyvinyl chloride (Cao, 2010: Farajzadeh *et al.*,2018).

1, 2-benzene dicarboxylic acid diisooctyl phthalate (DIOP)

Diisobutyl phthalate has I.U.P.A.C name as, 1, 2-benzene dicarboxylic acid diisooctyl phthalate (DIOP) ($C_{24}H_{38}O_4$) (Hareesh, 2021: Benjamin *et al*., 2015) has a molecular weight of 390.56 g/mol and a CAS number of 27554-26-3. It is a clear oily colourless viscous liquid with a slight ester odor insoluble in water but soluble in alcohol such methanol (Bekkar *et al.,* 202: You *et al*., 2021: Omkaramurthy *et al*., 2020). It is one of the phthalates used primarily as a plasticizer for synthetic rubber and vinyl, cellulosic, and acrylate resins in a variety of consumer products (Liu, 2022: Bocqué *et al*., 2016).

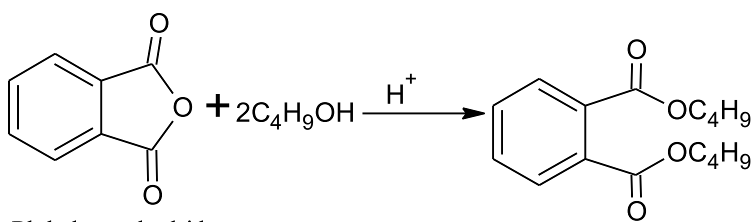
Rahman *et al*. (2006) isolated diisooctyl phthalate from the roots of Plumbago zeylanica to study its effect on antifungal activity against six phytopathogenic fungi: Alternaria alternata, Botryodiplodia theobromae, Curvularia lunata, Fusarium equiseti, Macrophomina phaseolina and Colktotrichum corchori. The results showed that the diisooctyl phthalate (DIOP) inhibited the radial mycelial growth of all the tested fungi to varied degrees. They also have good insulation, high strength, excellent corrosion resistance, low cost, and ease of fabrication (Huang *et al*., 2021). From the test carried out by Saillenfait et al., (2013), DIOP displayed an antiandrogenic activity and disrupted male reproductive development. Ahmed (2013), described phthalate esters as having carcinogenic, teratogenic, hepatotoxic, and endocrine effects.

Diisooctyl phthalate and other phthalates have been extracted and identified from natural sources Vijayakumar *et al*., 2018). They can be produced by esterification of phthalate anhydrides as presented in reaction schemes 1 and 2. Figure 1 shows the structure of a phthalic acid anhydride (2-benzofuran-1,3-dione). Studies have revealed that phthalates can be biosynthesized from algae (Huang *et al*., 2021). Bajracharya *et al*. (2021) reported that phthalic acid esters were used to be produced by esterification of phthalate anhydrides with alcohols using mineral acids such as sulphuric acid, hydrochloric acid, and phosphoric acid as shown in reaction Scheme 1 in the formation of dibutyl phthalate (DBP). But due to the corrosive action of the mineral acids and colour formation on the products by the effect of the co-products of the reaction, ferric chloride is under consideration as the alternative catalyst as presented in reaction Scheme 2 illustrating the formation of diethyl phthalate (DEP). These synthetic products are found to cause potential hazards to ecosystem functioning and public health, that have been detected in the atmosphere, water, soil, and sediments (Liang *et* al., 2024: Li *et* al., 2023: Huang *et al*., 2021). It is reported that the Phthalates obtain from natural plant sources are relative safe compared to that leached from synthetic products such as plastics, fertilizer and other synthetic materials (Caldeirão *et al.*, 2021).



Phthalate anhydrate (2-Benzofuran-1, 3-dione)

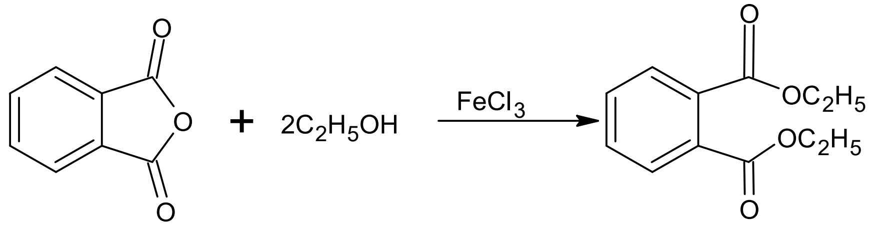
Figure 7: A sample of phthalate anhydrate



Phthalate anhydride

1,2-Benzenedicarboxylic acid dibutyl phthalate

Scheme 1: Conventional production of phthalate by esterification



Phthalate anhydride

1, 2-benzenedicarboxylyc acid diethyl phthalate
(Diethy phthalte)

Scheme 2: Esterification of Phthalate anhydride using ferric chloride catalyst

Diisooctyl phthalate and other phthalates have been isolated from Lythrum salicaria (Omidpana *et* al., 2018: Piwowarski *et al.*, 2015). It can also be extracted from Hibiscus rosa-sinensis (Yasmin *et* al., 2023: Sidhu *et al.*, 2023: Firdous *et al.*, 2021). Diisooctyl phthalate and many other phthalates have been obtained from microalgae and bacteria (Abbasian *et al.*, 2024: Pace *et al.*, 2024). It is interesting to note that *Lythrum salicaria* is used as an herb for diarrhea, dysentery (Dadi *et al.*, 2020: Granica *et al.*, 2020) and its dried powder leaves are used to cure ulcers, sores and wounds (Al-Snafi, 2021). Hibiscus rosa-sinensis has many applications such as feed, food, industrial, and medicinal preparations (Suprabha *at* al., 2024: Valdivié & Martínez, 2022). Hibiscus is also used as colorant, and component of food in salads, tea and flavour (Santos *et al.*, 2022: Apaliy *et al.*, 2021).

The natural sources of phthalates listed here are good sources for other important uses that deserved to be reserved for such known applications. The use of Hibiscus for phthalates production may affect foods and medicines supply from it. Also, its production from *Lythrum salicIaria* may affect the availability of *Lythrum salicaria* for medicine. The quantity of phthalates that can be produced from microalgae and bacteria would not be sufficient enough to meet its wider demand. Therefore, a renewable, sustainable and commercial able source require investigation. In this study, *Gmelina arborea* waste leaves were hydrothermally treated with barium chloride catalyst to investigate its suitability for phthalates production.

Materials and Methods

Materials

The materials used in this study include dried pulverized *Gmelina arborea* leaves, ceramic mortar and pestle, 300-400 µm sifters, hot plate magnetic stirrer, thermometer, 250- and 500-mL beakers, 500- and 1000-mL conical flasks, nylon sieve, spatula, 500 mL separating funnel. The reagents were barium chloride catalyst and anhydrous magnesium sulphate.

Method

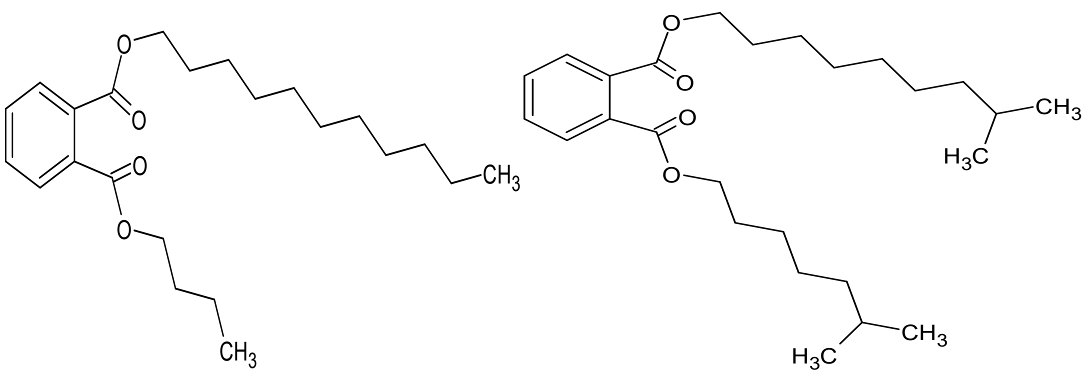
Dried *Gmelina arborea* leaves were collected from the premises of Kaduna Polytechnic, Kaduna-Nigeria. The leaves were pretreated i.e., handpicked foreign material, washed and sundried, pulverized with ceramic mortar and pestle into powder, and sieved with 300-400 µm sifters. A solution of 0.25 g (0.5%) barium chloride in 500 mL of distilled water was prepared and placed on GallenKamp hot plate equipped with a magnetic stirrer. It was followed by the addition of 50 g of the pulverized *Gmelina arborea* leaves (Magaji and Ibrahim, 2020). It was then heated to 60 ^{o}C and maintained at this temperature for 30 minutes with the followers constantly stirring the mixture at 200 rpm. The product was filtered, weighed, and dehydrated using 0.2% anhydrous magnesium sulphate and allowed to settle in a separating funnel (Atatdashi et al., 2011). The organic portion was separated from the aqueous layer and weighed. Four grams (4 g) of the organic product were then analyzed using a GC-MS machine to determine the chemical components and composition. The phthalate compounds in the products were identified and their quantities were estimated. This procedure was repeated with 0.5 g (1.0%) barium chloride catalyst at the same temperature (60 ^{o}C) and time (30 minutes). The process was repeated at temperatures of 70, 80, and 90 ^{o}C.

Results and Discussion

In all the eight products obtained, two phthalates were produced which were 1, 2-benzene dicarboxylic acid butyl decyl phthalate (DBDP) and 1, 2-benzene dicarboxylic acid diisooctyl phthalate (DIOP) also known as Bis (6-methyl heptyl) phthalate as shown in Figure 2. The yields (%) of butyl undecyl phthalate and diisoctyl phthalates at the operating temperature as revealed by GC-MS are presented in Table 1. At all catalyst loadings and reaction temperatures, diisoctyl phthalate had higher yields that butyl undecyl phthalate.

Table 1: Phthalate yields obtained from hydrothermal processing of *Gmelina arborea* leaves

Products yields	**Reaction Temperature (^{o}C)**			
	60	70	80	90
0.5% Catalyst loading				
Butyl undecyl phthatalate (%)	7.12	8.84	3.49	2.39
Diisooctyl Phthalate (%)	17.15	18.40	21.42	11.97
1.0% Catalyst loading				
Butyl undecyl phthatalate (%)	3.21	3.50	2.0	3.83
Diisooctyl Phthalate (%)	18.43	18.39	12.44	17.53



1, 2-benzenedicarboxylyc acid buttyl decyl phthalate   1, 2-benzenedicarboxylyc acid diisooctyl phthalate

Figure 8: Structural formulas of the two phthalates synthesized from* Gmelina arborea *leaves

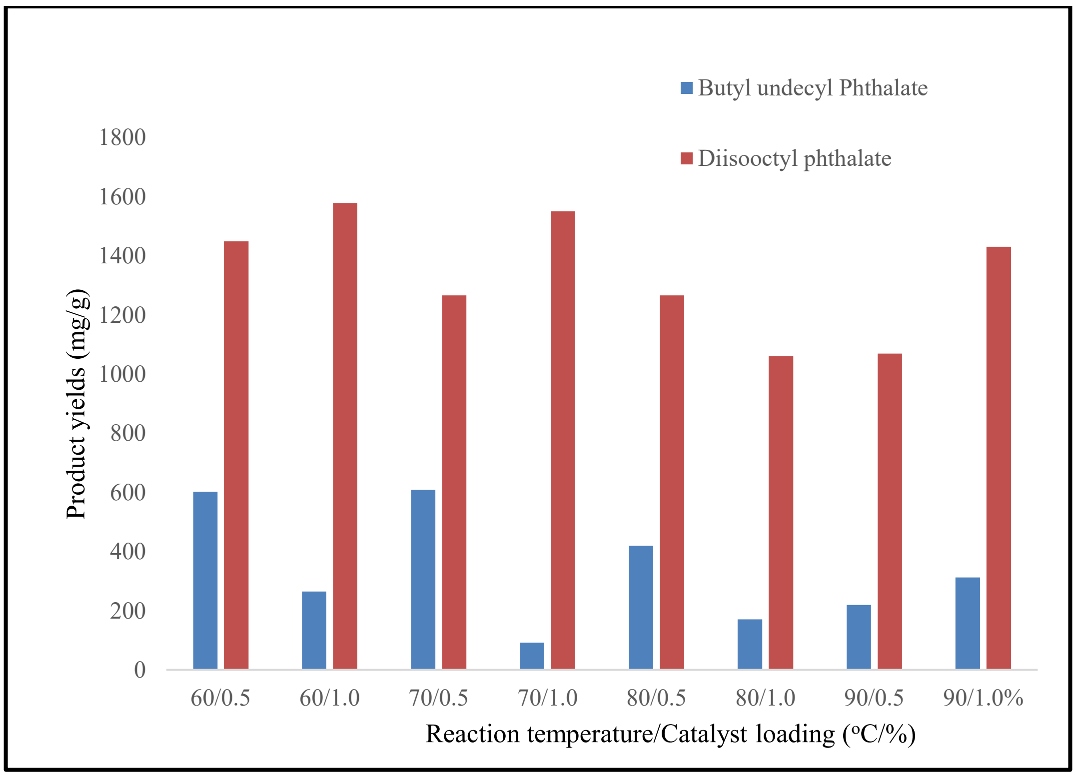


Figure 9: The yields (mg/g) of phthalates from Gmelina arborea leaves

Al-Gara *et al*. (2019) reported the extraction of many of bioactive phytochemicals including butyl undecyl phthalate from *Cyperus alternifolius L*. In the methanolic extraction of *Penicillium expansum*, 28 secondary metabolites were identified by Hamza *et al*. (2015) butyl undecyl phthalate was also produced and identified. Ezeamagu, (2021), carried out the acetone extraction of *Daedalea elegans,* a Nigerian wild non-edible plant and among the identified bioactive compounds was butyl undecyl phthalate. The methanolic extraction of *Morganella morganii* to determine its antifungal and antimicrobial activity butyl undecyl phthalate was also identified by Al–Khafaji, (2018). Serkerov *et al*., (2018) reported that among the 22 bioactive compounds extracted and identified with aid of GC-MS from the resins of the leaves and fruits of Laser trilobum (Apiaceae) was butyl undecyl phthalate. Butyl undecyl phthalic acid ester was found in the extract of *Metarhizium anisopliae extracted with ethyl acetate and methanol by* Kathiar *et al*. (2022). Despite the toxicity of phthalates, Huang *et al* (2021) classified them as essential oil as they are useful in cosmetics and drugs. The production of DIOP from *Gmelina arborea* waste leaves yields more quantity than those methods found in the literatures. This method is also more convenient than the use of the roots of Plumbago zeylanica employed by Rahman et at., (2006). DIOP is a potential pesticide, as Saillenfait et al. (2013) administered orally to rats, indicated antiandrogenic activity and disruption of male reproductive development.

Conclusion

Butyl undecyl phthalate and diisooctyl phthalate were produced from *Gmelina arborea* waste dry leaves with water using barium chloride catalyst. The highest quantity of butyl undecyl phthalate was 30.43g produced at 70 ^{o}C using 0.25 g $BaCl_2$ and the highest quantity of diisooctyl phthalate produced was 78.92 g 60 ^{o}C with 0.50 g $BaCl_2$. *Gmelina arborea* leaves is found to be a cheaper and better source for 1,2 benzene dicarboxylic butyl, undecyl phthalic acid ester (DBUP) and 1,2-benzene dicarboxylic diisooctyl phthalic acid ester (DIOP). These compounds are believed to be toxic yet are found useful in many industrial applications.

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