A NEW ANTHRAQUINONE FROM THE ROOTS OF MORINDA CITRIFOLIA LINN.

KALPNA RUSIA and SANTOSH K. SRIVASTAVA
Department of Chemistry, Dr H. S. Gour Vishwavidyalaya, Sagar 470 003, India.

MORINDA CITRIFOLIA Linn. (N. O. Rubiaceae) is used in the Indian system of medicine. This anthraquinone has not been reported so far from this plant. We report here the isolation and characterization of a new anthraquinone (7-hydroxy-8-methoxy-2-methyl anthraquinone) by its colour reactions, spectral data and chemical methods.

The powdered roots of M. citrifolia (3 kg) was extracted with ethanol under reflux for 180 h on a water bath. The ethanol from the percolates (20 l) was removed under reduced pressure on a water bath to get a solid mass which was then successively extracted with petroleum ether and benzene.

The benzene extract was concentrated and examined by thin layer chromatography, which showed the presence of a single entity. It was then passed through a column of neutral alumina and eluted with benzene: chloroform (5:5 v/v) and crystallized as red colour needles from ether:chloroform mixture (yield 900 mg).

The new anthraquinone, m.p. 240–241° C., C_{12}H_{12}O_4 (M^+ 268) showed uv-visible maxima at 225, 255, 385 and 410 nm and gave a positive Borntrager reaction, a characteristic for an anthraquinone. The IR (KBr) spectrum of (I) showed characteristic absorptions for hydroxyl (3560–3320), methoxyl (2860 and 1170), methyl (2920 and 1460) and unchelated carbonyl (1680) cm\(^{-1}\) respectively. The \(^1\)H-NMR spectrum (DMSO-\(d_6\), \(\delta\), 90 MHz) of the compound displayed signal for a unchelated hydroxyl (11.0, s, 1 × OH), one methoxyl (3.88, s, 3H, 1 × OMe) and one methyl (2.70, s, 3H, 1 × Me). Further, the compound showed three ortho coupled doublets at \(\delta\) 8.16, 8.08 and 7.80 for one proton each at positions H-4, H-5 and H-6 respectively and a meta coupled doublet at \(\delta\) 7.04 for one proton at position H-1 and a doublet centred at \(\delta\) 6.80–6.90 for one proton at position H-3.

The compound formed a monomethyl ether (Me_2SO_4-K_2CO_3), m.p. 120–122° C [found C, 72.33; H, 4.95; (OMe Zeisels method) 21.97; calculated for C_{17}H_{14}O_4:C, 72.34; H, 4.96; (OCl_4), 21.98%] and monoacetate (Ac_2O C_5H_4NO), m.p. 127 128 [found: C, 69.63; H, 4.50; calculated for C_{18}H_{14}O_4:C, 69.67; H, 4.51%] confirming the presence of one hydroxyl and one methoxyl group in the compound. Chronic acid oxidation of methylated compound gave 3,4-dimethoxy phthalic acid, m.p. 174–175° (lit m.p. 177°, m.m.p. and Co-TLC)\(^3\) as one of the oxidation products showing the presence of OMe at C-8 and hydroxyl at C-7 positions in the compound. The major MS fragment ions of the compound were as follows: MS: m/z: 268 (M\(^+\)), 253, 251, 250, 240, 239, 212, 156, 151, 123, 119 and 91 respectively, which confirms the structure of the new anthraquinone:

![Chemical Structure](attachment:image)

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LITHIATION OF AROMATIC ETHERS WITH ULTRASOUND: SOME SYNTHETIC APPLICATIONS

A. BANERJI and S. K. NAYAK
Bio-Organic Division, Bhabha Atomic Research Centre, Bombay 400 085, India.

In recent years dramatic effects of ultrasound on several chemical reactions have been reported. We have observed significant increase in the yields under ultrasonic irradiation in reactions of synthetic importance, such as \(O\)-alkylation of phenols, Reformatsky reaction, oxidative degradation, etc. A recent communication on lithiation of different substrates using ultrasound prompts us to report
our results on the use of ultrasound in ortho-lithiation of alkyl aryl ethers.

Lithiation of alkyl aryl ethers is the key step in our programme on the synthesis of bioactive compounds. Effects of ultrasound irradiation on α-lithiation of anisole and 1,3-dimethoxybenzene are reported here. A mixture of lithium metal, butyl chloride and aromatic ether in tetrahydrofuran at 20°C was irradiated with ultrasound under dry and inert atmosphere. Initiation of the reaction was indicated by the slow disappearance of lithium. The progress of the lithiation could be monitored by quenching aliquots with acetone and analysing the products by thin layer chromatography. Under similar conditions but in the absence of ultrasound, no lithiation took place. Reactions of lithiated aromatic ethers with different electrophiles such as dialkyl and alkyl aryl ketones, aroyl chlorides, alkyl chlorofomates, aryl esters, aryl aldehydes, etc. have been studied and the products analysed in the usual way.

Anisole was lithiated in 30 min to 2-methoxyphenyllithium (I) at 20°C. Carbinol IIIa was obtained in 75% yield when acetone was added to I at −78°C. Similarly, good yields of carbinol IIIb were obtained using acetophenone. Reaction of I with
aromatic esters in 1:1 proportion gave mixtures of benzophenones and triarylmethanols (Va and Vb). Formation of V suggests that benzophenone formed in the first step reacts further with I to give carbinol. Thus, a mixture of IVa and Va was obtained when methyl o-methoxybenzoate was added to I at -78°C. Similarly reaction of I with benzoyl chloride gave benzophenone (IVb) and carbinol (Vb) in the ratio of 1:1. Formation of Va and Vb necessarily means that a part of the electrophile remains unreacted. In fact when a reaction was carried out with limited amount (0.5 equivalent) of ethyl chloroforate better yield of carbinol Va was obtained. The reaction of I with aryl aldehydes has also been studied and good yields of benzhydrols have been obtained. Using o-methoxybenzaldehyde, 2,2'-dimethoxybenzhydrol (IIIc) was prepared.

Lithiation of 1,3-dimethoxybenzene under ultrasonic irradiation was complete in 15 min. Reaction of II with 0.5 equivalent of ethyl chloroforate gave ethyl 2,6-dimethoxybenzoate (VI) as the sole product. Thus, unlike with I, in the case of II the reaction does not proceed beyond the ester stage. Advantage has been taken of this for the synthesis of benzophenones. Good yields of benzophenones (IVc and IVd) were obtained when II was quenched with methyl 2-methoxybenzoate and benzoyl chloride. Absence of the formation of triarylcabinol could be explained by the fact that in II the reactive centre is crowded by two adjacent methoxyl groups, which offer steric hindrance to subsequent reaction. 2,2'-Dialkoxybenzophenones are important intermediates because of their ready conversion to xanthones. Benzhydrol (IIIc), which was obtained in excellent yield, could be oxidized to IVa by PCC. Benzophenones (IVa and IVc) were converted into xanthones (VII and VIII) by heating with pyridine hydrochloride. Thus this constitutes a convenient synthesis of xanthones.

Table I gives a summary of the results of the use of lithiated compounds in synthesis.

**Synthesis of 2,2'-dimethoxybenzophenone (IVa) and tris(o-methoxyphenyl) carbinol (Va); Typical procedure:**

A mixture of anisole (0.54 g, 5 mmol), lithium (70 mg, 10 mg-atom) and n-butyl chloride (0.47 g, 5 mmol) in THF (10 ml) was sonicated in an ultrasonic cleaning bath (40 kHz) at 20°C under dry and inert atmosphere. When lithium had reacted as evidenced by the disappearance of lithium pieces, the flask was cooled to -78°C and methyl o-methoxybenzoate (0.83 g, 5 mmol) in 10 ml of THF was added slowly.

After completion of the reaction (30 min, monitored by TLC) the reaction mixture was diluted with ether, acidified with 1:1 HCl, extracted with ether and dried (Na₂SO₄). Removal of solvent gave a mixture of IVa and Va, which were separated by column chromatography (SiO₂). On successive elution of the column with petroleum ether-ethyl acetate mixtures (95:5 and 9:1) two fractions A and B were obtained. Colourless crystals (hexane) of IVa were isolated from fraction A; 300 mg, m.p. 103°C (lit. m.p. 104°C); DNP (+); IR (KBr): 1640, 1600, 1490 cm⁻¹; 60 MHz

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<th>Table I Synthetic application of sonochemical lithiation</th>
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| Compound lithiated | Conditions              | Substances                  | Product $|$ | Yield (%) | Ref. |
|--------------------|-------------------------|-----------------------------|-------------|-----------|------|
| Anisole            | Li/n-BuCl/THF           | Acetone                     | (IIIa)      | (75)      | 4    |
|                    | 20°C, Sono, 0.5 h       |                             |             |           |      |
|                    | "                      | Acetophenone                | (IIIb)      | (84)      | 5    |
|                    | "                      | Methyl o-methoxy            | (IVa) + (Va)| (25)      | 6    |
|                    | "                      | benzoate                    | (37)        | 7         |      |
|                    | "                      | Benzoyl chloride            | (IVb) + (Vb)| (33)      | 8    |
|                    | "                      | 1/2 CICO₂ Et                | (IVa) + (Va)| (19)      | 6    |
|                    | "                      | o-Methoxy benzaldehyde      | (IIIc)      | (75)      | 10   |
| 1,3-Dimethoxy-     | Li/n-BuCl/THF           | 1/2 CICO₂ Et                | (VI)        | (79)      | 11   |
| benzene            | 20°C, Sono, 0.25 h      |                             |             |           |      |
|                    | "                      | Methyl o-methoxy            | (IVc)       | (51)      | 12   |
|                    | "                      | benzoate                    | (IVd)       | (55)      | 13   |

$\dagger$ Physical and chemical data of compounds were in complete agreement with those reported in the literature; $\dagger$ Based on the substrate.
PMR (CDCl₃): δ 3.63 (s, 6H, 2x-OMe), 6.73–7.57 (m, 8H, Ar-H). Similarly, Va was obtained as colourless crystals (hexane) from fraction B; 320 mg, m.p. 180°C (lit. m.p. 181°C); IR (KBr): 3500, 1600, 1580 cm⁻¹; 60 MHz PMR (CDCl₃): δ 3.5 (s, 9H, 3x-OMe), 6.8–7.43 (m, 12H, Ar-H).

Cyclization of 2,2’-dimethoxybenzophenone (IVa) to xanthone (VII)

A mixture of IVa (50 mg) and pyridine hydrochloride in 1:5 proportion was heated in a dry flask in an oven at 180°C for 36 h. After cooling, water was added and the mixture extracted with ether and dried. Removal of ether gave crude product which on purification (prep. TLC) and crystallization from ethanol furnished colourless crystals of VII; 35 mg, m.p. 174°C (lit. m.p. 174°C)¹⁵. NMR and IR data are in agreement with those of xanthone.

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INDUCED SHY MUTANT OF LENTIL (LENS CULINARIS MED.)

R. P. Sinha

Tirhut College of Agriculture, Dholi, Musaffarpur 843 121, India.

During induced mutation studies in lentil, various types of mutants with altered morphological characteristics were isolated. In the present communication a morphological mutant with changed leaflet shape and size and shy in flowering and pod bearing is reported.

Dry seeds of a lentil variety Sehore 74–7 were irradiated with 5, 10, 15 and 20 krad of γ-ray at the Gamma Cell Laboratory of Indian Agricultural Research Institute, New Delhi. The M₁ and later generations were grown at the College Farm, Dholi of the Rajendra Agricultural University. In M₂ generation from 10 krad treated population one dwarf mutant with narrow leaflets and slight longitudinal bending was isolated. This had less flowers and fruits. The mutant was therefore named 'shy mutant'. In M₃ it did not segregate indicating recessiveness of the character induced. Some M₃ mutant plants were crossed with the parent variety. F₁ was like parent and F₂ segregated in the ratio of 3 tall-like parent:1 dwarf-like mutant. The ratio confirmed that shyness is a monogenically controlled recessive character. M₃ mutant was separately evaluated for other characteristics.

Though the mutant plants were dwarf there were no significant differences in flowering and maturity days (table 1). Mutant plants were erect and non-bushy whereas the parent was semisplaying and bushy. Rachis length, leaflets/leaf, leaflet length, leaflet breadth and stipule length of mutant plants were significantly lower than that of parent plants. Pod-bearing was significantly lower in the mutant compared to the parent. Seed weight and seed colour were almost the same as in the parent.