

A NOTE ON THE SYNTHESIS OF SOME NEW COUMARINS, BENZOCOUMARIN, CARBOSTYRIL AND QUINOLONE FROM N- α -NAPHTHYL MALONAMIC ACID AND SOME OF ITS DERIVATIVES

THE importance of coumarins^{1,2}, benzocoumarins, carbostyrils³ and quinolones⁴ in the field of medicine and in synthetic Organic Chemistry is well known. Earlier workers^{5,6} in this laboratory prepared a number of such compounds and studied their properties. This note deals with the synthesis of some new coumarins, benzocoumarin, carbostyril and quinolone. The coumarins and benzocoumarin were prepared by the condensation of N- α -naphthyl malonamic acid with salicylaldehyde, substituted salicylaldehydes and 2-hydroxy-1-naphthaldehyde respectively. Various condensing agents like pyridine, piperidine, etc., were used as catalysts but pyridine in traces was found to be the most effective. The general method has been to heat equimolecular mixture of the acid and the aldehyde along with a drop or two of the catalyst at 105-110° C for 5 h. The mass, which first melted to a clear liquid, soon set to a solid. After completion of heating, this was extracted with NaHCO₃ solution and the residue after washing with ethanol was recrystallised from glacial acetic acid. All the compounds thus prepared were found to be yellow to orange in colour.

The analytical results, m.p., etc., of these coumarins and benzocoumarin are given in Table I.

7,8-Benzo-4-phenyl-3,4-dihydro carbostyril: Cinnam- α -naphthylamide (0.5 g) and polyphosphoric acid (10 g) was heated at 120° C for 30 min. After heating, the product was poured over crushed ice, extracted with chloroform and was dried over anhydrous MgSO₄. After filtering off the MgSO₄, chloroform was distilled off. The solid thus obtained was purified by repeated washing with hot ethanol, m.p. 225° C, Yield, 0.25 g (50%) (Found N, 5.54%; C₁₉H₁₅NO requires N, 5.13%). IR spectrum (KBr-pellets) showed bands at 1661 (amide I-ring CO), 3300 (ν NH), 3030 (ν CH), 1618 and 1572 cm⁻¹ (aromatic ring) in agreement with the structure.

N- α -naphthyl malonamic acid and cinnam- α -naphthylamide used in the above condensations were prepared according to the procedure recommended by Banerji and Ittyerah⁷.

2-Quinolone-3-carboxy- α -naphthylamide: A mixture of *o*-amino benzaldehyde (0.3 g), ethyl-N- α -naphthyl malonamate (0.6 g) and piperidine (0.1 ml) was heated on a steam bath for 3 h. The product was washed with hot water (20 ml) and the yellow crystalline residue was filtered and further purified by repeatedly washing with hot ethanol. Yield, 0.6 g (81.9%), the compound did not melt upto 360° C (Found C, 76.02%; H, 4.84%; N, 8.95%; C₂₀H₁₄N₂O₃ requires C, 76.42%; H, 4.45%; N, 8.91%). IR spectrum (KBr-pellets) showed bands at 3436 (ν NH), 3096 and 2994 (ν CH), 1675 (amide I-ring CO), 1621 (α -B-unsaturated amide CO), 1592 (C=C), and 1550 cm⁻¹ (amide II) in agreement with the structure.

TABLE I

Sl. No.	Name	Formula	M.P. °C	Yield %	Found	Calc.
1.	R	C ₂₀ H ₁₃ NO ₃	227	48.5	N : 4.60	4.44
2.	6-Chloro-R	C ₂₀ H ₁₂ NO ₃ Cl	227	27.3	N : 4.52 Cl : 10.32	3.98 10.15
3.	6,8-Dichloro-R	C ₂₀ H ₁₁ NO ₃ Cl ₂	284 (d)	39.8	N : 3.83 Cl : 18.64	3.64 18.49
4.	6-Bromo-R	C ₂₀ H ₁₂ NO ₃ Br	202	38.7	N : 3.99 Br : 19.86	3.55 20.31
5.	6,8-Dibromo-R	C ₂₀ H ₁₁ NO ₃ Br ₂	>284	32.3	N : 3.31 Br : 33.58	2.96 33.83
6.	6,8-Di-iodo-R	C ₂₀ H ₁₁ NO ₃ I ₂	236 (d)	26.9	N : 2.63	2.47
7.	5,6-Benzo-R	C ₂₄ H ₁₅ NO ₃	255 (d)	20.9	N : 3.75	3.84

R = Coumarin-3-carboxy- α -naphthylamide,

Ethy-N- α -naphthyl malonamate used in the above experiment was prepared in the following manner:

A mixture of α -naphthylamine (7 g) and diethylmalonate (16 g) was gently refluxed for 2 h. The malondi- α -naphthylamide formed was filtered and the filtrate after evaporation to dryness was extracted with petroleum ether (b.p. 80–100°C). On evaporation of the solvent, a pink mass was obtained and this after recrystallisation from the same solvent yielded a white crystalline product, m.p. 83°C (Found: C, 70.21%, H, 5.76%, N, 5.61%; $C_{15}H_{15}NO_3$ requires C, 70.03%, H, 5.83%, N, 5.45%).

Chemical Laboratories,
St. John's College, Agra,
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D. S. SETH.
B. C. BANERJI.
P. I. ITTYERAH.

1. Bose, P. K., *J. Indian Chem. Soc.*, 1958, 35, 365.
2. Arora, R. B. and Seth, S. D., *M.D. Thesis*, All India Institute of Medical Sciences, 1965.
3. Conley, R. T. and Knopa, W. N., *J. Org. Chem.*, 1964, 29, 406.
4. Fryer Brust *et al.*, *J. Chem. Soc.*, 1964, p. 3097.
5. Bhukta, M. J. and Ittyerah, P. I., *J. Indian Chem. Soc.*, 1965, 42, 454.
6. Singhal, O. P. and Ittyerah, P. I., *Curr. Sci.*, January 5, 1967, 36, 12.
7. Banerji, B. C. and Ittyerah, P. I., *Agra Univ. J. Res. (Sci.)*, 1964, 13, 61.

A NOTE ON THE RARE MINERALS BEARING GRANITE OF KANIGIRI IN PRAKASAM DISTRICT OF ANDHRA PRADESH

THE granite of Kanigiri-Podile tract of Nellore and Prakasam districts (Andhra Pradesh) has been under investigation¹, not only for their abnormal fluorine content and its environmental aspects (widespread fluorosis in the human population of the area) but also because of their interesting mineralogy. This note reports the occurrence of columbite-tantalite in the granite and its economic significance. To the best of our knowledge, this is the first time that such an economically viable occurrence of columbite-tantalite in granite is reported from India.

Kanigiri town (Lat. 15° 24' 30" N, Long. 70° 30' 00" E in toposheet No. 57 M/11) after which the granite is named is situated approximately 180 km NNW of Nellore (Nellore district) and 86 km WSW of Ongole (Prakasam district) of Andhra Pradesh. The granite forms the main hill mass just NE of the town and is extensively quarried. Results of airborne gamma-ray spectrometric data acquired in the flights conducted over these parts by the Atomic Minerals Division (AMD) in 1977 indicated high radioactivity, largely confined to the peripheries of the granitic body and prompted a detailed study by AMD,

The leuco-granite occurs as an intrusive in the meta-basic rocks, comprising sericite-chlorite-schists, exposed on the western flanks of the granite body and hornblende schists and gneisses on its eastern limits. The schists forming part of the Nellore schist belt (Dharwar) are considered equivalents of the Holenarsipur schists of the same age in Karnataka.

In thin sections the granite is seen to have typical holocrystalline-hypidiomorphic texture and composed mainly of orthoclase, microcline, perthite, albite and chloritoid biotite. Zircon is the chief accessory mineral. Fluorite, topaz, arsenopyrite and apatite are the other accessories observed in the rock. A few black and/or brown coloured, opaque mineral grains occur at the edges of the chloritised biotite clusters. The potash feldspars have been converted to perthite and at places also replaced by albite. The rock can be termed as essentially an albitised granite (apogranite).

A sample of the granite from the fresh quarry at the northern edge of Kanigiri town was pulverised to –35 μ size (Tyler screen) and deslimed. Heavy minerals were isolated by tabling, magnetic and heavy media separations yielding a crop mainly of zircon and other opaque mineral grains.

The above poly-mineral concentrate analysing radio-metrically 0.5% equivalent U_3O_8 , revealed the presence of samarskite, fergusonite, monazite and zircon in decreasing order of abundance. The concentrates were found by X-ray fluorescence analysis to contain 14.9% Nb_2O_5 and 2.2% Ta_2O_5 ². The presence of columbite-tantalite, samarskite, fergusonite with lesser amounts of zircon and monazite in the same fraction was confirmed by X-ray diffraction studies³.

The columbite-tantalite and samarskite bearing granite of Kanigiri is the first reported occurrence of non-pegmatitic source of these rare elements in the country. In mineralogy and mode of occurrence, this granite closely resembles the well-known Jos Bukuru granite of Nigeria⁴ and similar granites in USSR⁵. The soil resulting from the weathering of this granite may prove to be a major source of niobium and tantalum. The soil contains 100 to 200 gm of columbite-tantalite per tonne and may yield sizable reserve of columbite-tantalite⁶.

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Atomic Minerals Division, T. M. RAMACHAR,
Department of Atomic Energy, B. KRISHNAMCORTHY,
Begumpet, Hyderabad 500 016, K. M. V. JAYARAM,
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