Condensation of 4-Bromo-1-Naphthyl Acetic acid with Aldehydes

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THE results of the condensation of 1-naphthyl acetic acid with substituted aldehydes have already been reported.[1] In the present investigation 4-bromo-1-naphtyl acetic acid has been condensed with salicylaldehyde, 5-bromo and 3:5 dibromo salicylaldehydes in presence of different bases. No condensation occurred with benzaldehyde, anisaldehyde, *p*-nitrobenzaldehyde, *o*-nitrobenzaldehyde, *p*-hydroxybenzaldehyde and *p*-chlorobenzaldehyde.

Experimental

4-Bromo-1-naphthyl acetic acid: 1-Naphthyl acetic acid (10 g) was dissolved in 15 ml. glacial acetic acid; bromine (5.4 ml) was added and the mixture was heated on a water bath at 60°-80° for 3 hr. After standing overnight crude 4-Bromo-1-naphthyl acetic acid was precipitated. Crystallisation from aqueous acetic acid yielded the pure acid, m.p. 174°-175°.

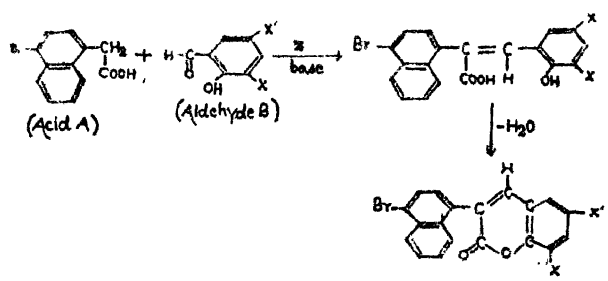
3-(4'-bromo-1'-naphthyl) coumarin: 4-Bromo-1-naphthyl acetic acid (.26 g) and salicylaldehyde (.12 g) were heated under reflux at different temperatures viz. 120°, 140° and 160°, for different durations of time viz., 6, 12 and 18 hr. in the presence of traces of different bases viz, pyridine, piperidine, α-picoline, mixture of pyridine and acetic anhydride and mixture of triethylamine and acetic anhydride. The condensed product, so obtained was extracted with 10% $NaHCO_3$ solution and filtered. The filtrate on neutralisation with conc. HCl yielded the unreacted 4-bromo-1-naphthyl acetic acid. The residue on crystallisation with dioxane was found to be 3-(4'-bromo-1'-naphthyl)-coumarin m.p. 240° (Found : Br 22.5%. Calc. for $C_{19}H_{11}O_2Br$ 22.7%). A maximum yield of 31.5% of condensed product was obtained when the reactants were heated at 160° for 12 hr, in presence of traces of piperidine and also when heated for 6 hr in the presence of a mixture of triethylamine and acetic anhydride.

Condensation with 5-bromo-salicylaldehyde : The neutral product was found to be 3-(4'-bromo-1'-naphthyl)-6-bromo coumarin m.p. 265°-266° (Found Br 36.9%. Calc. for $C_{19}H_{10}O_2Br_2$ 37.2%). A maximum yield of 55.8% was obtained when the reactants were heated at 160° for 6 hr in the presence of a mixture of pyridine and acetic anhydride.

Condensation with 3:5-dibromo-salicylaldehyde : The neutral product was found to be 3-(4'-bromo-1'-naphthyl)- 6:8-dibromo coumarin m.p. 217°-218° (Found Br 46.9%. Calc. for $C_{19}H_9O_2Br_3$ 47.1%). A

5-Bromo and 3:5-dibromo-salicylaldehydes : These were prepared as reported earlier.[2]

TABLE 1



S. NO.	X	X'	A:B	t_0	T	Yield %	t_1	Z
1	H	H	1:1	120	6	31.5	240	$(C_2H_5)_3N+Ac_2O$
2	H	H	1:1	160	12	31.5	240	Piperidine
3	H	H	1:1	160	12	15.8	240	Piperidine+Ac_2O
4	Br	H	1:1	160	6	10.8	265	Piperidine
5	Br	H	1:1	160	6	55.8	265	Py+Ac_2O
6	Br	Br	1:1	140	6	9.2	217	Piperidine
7	Br	Br	1:1	140	6	20.3	217	Pyridine-Ac_2O

t_0 = temperature of oil bath in degree centigrade, T = Time in hr,
t_1 = melting point of the products in degree centigrade and
Z = base used.

maximum yield of 20.3% was obtained when the reactants were heated at 140° for 6 hr in presence of a mixture of pyridine and acetic anhydride

Acknowledgement

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A New Method for Resolution of Racemic forms of α-Amino acids and Related Compounds

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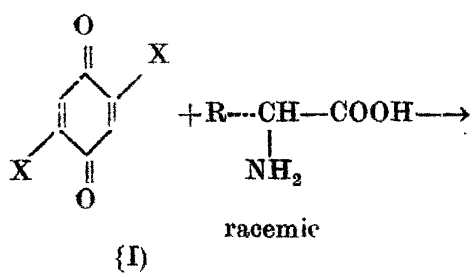
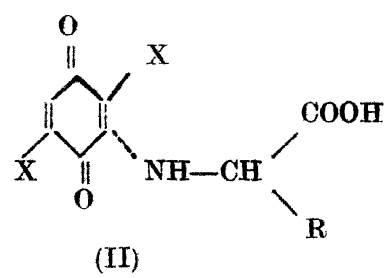
IT has now been discovered that racemic forms of α-amino acids, their esters and in general, compounds containing an active amino group (e.g. threoamine) can be resolved by interaction with simple quinone molecules under suitable conditions to give monosubstituted quinonoid products of which the *d*-form separates completely during the reaction period leaving the l-form in solution.[1]



(I)

X = H or halogen



(II)

l-form in solution
d-form insoluble

It is to be pointed out that interaction of amino-compounds with quinones of the type (I) gives normally the 2,5-disubstituted products and in no case could the monosubstituted products be isolated[2,3]. However, with racemic forms or with single optically active compounds only monosubstituted quinonoid products are formed under suitable ratios of reactants, probably because the optically active quinonoid molecule of type (II) is chemically less reactive, that it does not react further under the applied reaction conditions. The monosubstituted reaction products (II) were hydrolysed to give pure *d*- or l-α-amino acids by refluxing with concentrated mineral acids.

Verification of the above results was accomplished by interaction of *p*-quinones with pure *d*-or l-forms and comparison with the above results using thin layer chromatographic technique, m ps, mixed m ps and optical rotation measurements The reactions were carried out with *dl*-alanine, *dl*-valine, *dl*-isoleucine, *dl*-aspartic acid, and *dl*-tryptophane, and d-alanine on large scale laboratory amounts. with dl-alanine, to assure its successfulness as a new method for resolution of racemic forms of α-amino acids and related amino compounds.

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Isolation of an Antibacterial compound, Xanthumin from the leaves of *Xanthium strumarium* Linn.

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XANTHIUM strumarium Linn (Compositae), commonly known as 'Chhota Gokharu' in Hindi and 'Cocklebar' in English is an annual herb which grows wildly throughout India upto an altitude of 7,000 ft. The plant is used as diaphoretic and sedative. Its root is used as a bitter tonic and in the treatment of cancer and strumous diseases[1].

The seed fat of this plant has been thoroughly investigated by several workers[2,3,4]. Plourde and Mockle[5] have isolated Xanthinin from the leaves of Canadian *X. strumarium* while Minnato and Horibe[6] have reported the isolation of a stereoisomer of Xanthinin from Japanese *X. strumarium* which they named as Xanthumin. No phytochemical work seems to have been done on the leaves of Indian *X. strumarium*, the petroleum ether extract of which was reported earlier to be active against gram positive