Tetrahedron Letters No.27, pp. 2281-2283, 1965. Pergamon Press Ltd.
Printed in Great Britain.

ON 7:8-DIMETHOXY*ISO*CARBOSTYRIL. A CASE OF TRANS-ESTERIFICATION INVOLVING AN AROMATIC ALKOXYL GROUP

J. N. Chatterjea, B. K. Banerjee
and H. C. Jha
Department of Chemistry, Patna university, Patna

(Received 7 May 1965)

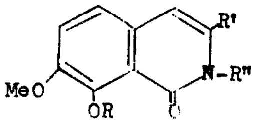
D. Bain, W. H. Perkin (Jun.) and R. Robinson[1] obtained a compound, m.p. 233° by heating 7:8-dimethoxy*iso*carbostyril-3-carboxylic acid (I) and regarded it as 7:8-dimethoxy*iso*carbostyril (II). The compound was not analysed and only recently L. I. Linevich[2] also regarded it as (II). The compound which is insoluble in sodium hydrogen carbonate gives a blue ferric reaction and analysed for $C_{10}H_5O_2N(OCH_3)_2$. In chloroform solution it showed i.r. absorption at 3380 cm^{-1} and 1730 cm^{-1} (associated OH and ester CO). On methylation with methyl iodide and potassium carbonate in acetone solution, the compound afforded N-methyl-7:8-dimethoxy*iso*quinolone-3-carboxylate (III), m.p. 160-61° (negative ferric reaction) which was also

---

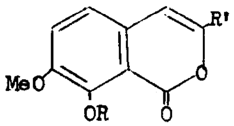
[1] D. Bain, W. H. Perkin (Jun.) and R. Robinson, *J. Chem. Soc.* 105, 239 (1914).

[2] L. I. Linevich, *Zhur. obshchei khim.* 28, 2510-14 (1958).

obtained by the methylation of methyl 7:8-dimethoxy*iso*carbostyril-3-carboxylate (IV). The compound m.p. 233°



I, R=Me, R'=COOH, R"=H
II, R=Me, R'=R"=H
III, R=Me, R'=COOMe, R"=Me
IV, R=Me, R'=COOMe, R"=H
V, R=H, R'=COOMe, R"=H
VI, R=H, R'=COOH, R"=H
VII, R=R'=R"=H



VIII, R=R'=H
IX, R=Me, R'=H
X, R=Me, R'=COOH
XI, R=Me, R'=COOMe
XII, R=H, R'=COOMe

must be regarded as methyl 7-methoxy-8-hydroxy*iso*carbostyril-3-carboxylate (V) which was further substantiated by hydrolysis with aqueous potassium carbonate to the related acid (VI), m.p. 315° followed by decarboxylation with copper bronze-quinoline to 7-methoxy-8-hydroxy*iso*carbostyril (VII), m.p. 209-10°. The latter was synthesised independently from 7-methoxy-8-hydroxy*iso*coumarin (VIII), m.p. 150-51° and ammonia.

It is pertinent to point out that P. K. Banerjee and D. N. Choudhury[3] have recently described a synthesis of 7:8-dimethoxy*iso*coumarin (IX), m.p. 149-50° from 7:8-dimethoxy-3:4-dihydro*iso*coumarin by bromination with N-bromosuccinimide followed by dehydrobromination.

---

[3] P. K. Banerjee and D. N. Choudhury, *J.Indian Chem. Soc.* **41**, 221 (1964).

C. Ribbens, c. Van der Stelt and W. Th. Nauta[4] reported melting point 105.5-107° for the same compound obtained by the decarboxylation of 7:8-dimethoxy*iso*coumarin-3-carboxylic acid (X). A careful reinvestigation of this decarboxylation has now led to the isolation of four products, viz., 7:8-dimethoxy*iso*coumarin (IX), m.p. 115°, 7-methoxy-8-hydroxy*iso*coumarin (VIII), m.p. 150-51°, methyl 7:8-dimethoxy*iso*coumarin-3-carboxylate (XI), m.p. 174-76° and methyl 7-methoxy-8-hydroxy*iso*coumarin-3-carboxylate (XII), m.p. 194°. P. K. Banerjee and D. N. Choudhury's product was obviously (VIII) arising from demethylation of 8-methoxyl group. The authentic 7:8-dimethoxy*iso*coumarin was converted into 7:8-dimethoxy-*iso*carbostyril (II), m.p. 178-79° and characterised by the picrate, m.p. 150-51°.

The formation of above esters in the *iso*carbostyril and *iso*coumarin series is unique and it is obviously a case of intermolecular trans-esterification involving an aromatic methoxyl group. The methoxyl group at the 8-position is labile on account of the participation of the neighbouring carbonyl group.

---

[4] C. Ribbens, c. Van der Stelt and W. Th. Nauta, *Rec. Trav. chim.* *79*, 78 (1960).