Tetrahedron Letters No.8, pp. 607-608, 1969. Pergamon Press. Printed in Great Britain.

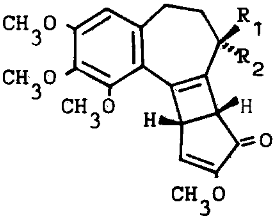
DIRECT EVIDENCE FOR THE STEREOISOMERIC RELATIONSHIP BETWEEN β- AND γ-LUMICOLCHICINE

L.Canonica, B.Danieli, P.Manitto and G.Russo

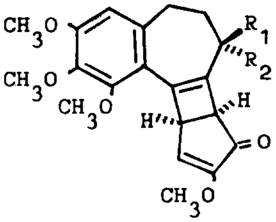
Istituto di Chimica Organica dell'Università - Via Saldini 50 - Milano(Italy)

(Received in UK 27 December 1968; accepted for publication 14 January 1969)

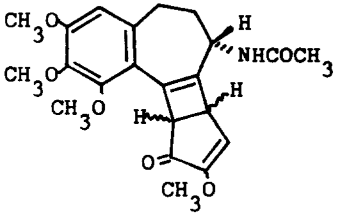
When a solution of colchicine is exposed to light in the absence of air, two isomeric products, β- and γ-lumicolchicine,can be obtained in varying amounts, depending on the conditions used(1). Although structure Ia for β-lumicolchicine was rigorously established by chemical and spectral evidence(2,3), no unequivocal proof has as yet been reported to distinguish between three possible structures for γ-lumicolchicine : IIa and the two stereoisomers of III.



I



II



III

a $R_1 = H$ $R_2 = NHCOCH_3$
b $R_1 = H$ $R_2 = NHCHO$
c $R_1 = H$ $R_2 = NH_2$
d $R_1 = R_2 = O$

Structure IIa is regarded as the more plausible one, particularly on the basis of the reasonably interpreted spectral analogies between β- and γ-lumicolchicine and their derivatives(2,4). However, Chapman et al.(3)have pointed out that structure III cannot be excluded, since the photoisomerization of tropolones frequently involves more than simple alterations(6). For the same reason, the observation of a photochemical conversion of β- to γ-lumicolchicine(5) cannot be considered direct evidence in support of structure IIa. Furthermore, in agreement with Chapman et al.(3),we were not able to reproduce the base-catalyzed conversion of β-lumicolchicine to the γ-isomer, which was reported by Gardner et al.(2) as a strong evidence for the hypothesis of a stereoisomeric relationship between the two.

In this paper we wish to report a chemical correlation between the two N-formyldesacetyllumicolchicines, Ib and IIb, which were previously related to β- and γ-lumicolchicine respectively(7) : such a correlation provides evidence for structure IIa for γ-lumicolchicine.

During our investigations on the constituents of Gloriosa superba L.(Liliaceae) we isolated, beside colchicine and other new alkaloids of this group(7), a nitrogen-free product,which we named β-lumicolchicone(Id)(8). Id (m.p. 195°; $[\alpha]_D^{20}$ = + 346°, c=1.0 in $CHCl_3$) was shown to be identical with the product obtained by oxidation of N-desacetyl-β-lumicolchicine (Ic)(9) with ninhydrin(8). Similar oxidation of N-desacetyl-γ-lumicolchicine (IIc)(9)(.HCl , m.p. 233-5° dec.; $[\alpha]_D^{20}$= - 351°, c=1.0 in MeOH) afforded γ-lumicolchicone (IId), which resulted identical with Id in m.p. and spectral data, but showed opposite optical rotation ($[\alpha]_D^{20}$ = - 342° , c=1.0 in $CHCl_3$).

The enantiomeric relationship of Id and IId confirms structure IIa for γ-lumicolchicine.

REFERENCES and NOTES

1. For a recent review see W.C.Wildman and B.A.Pursey in " *The Alkaloids*", vol. XI, R.H.F. Manske, Ed., Academic Press, New York, 1968, pp 407-457.
2. P.D.Gardner, R.L.Brandon and G.R.Haynes, *J. Am. Chem. Soc.*, **79**, 6334 (1957).
3. O.L.Chapman, H.G.Smith and R.W.King, *J. Am. Chem. Soc.*, **85** , 803 (1963).
4. J.Hrbek,Jr., J.P.Jennings, W.Klyne and F.Šantavý, *Collection Czech. Chem. Commun.*, **29** , 2822 (1964).
5. G.O.Schenk, H.J.Kuhn and O.A.Neumüller, *Tetrahedron Letters*, **1** ,12 (1961).
6. W.G.Dauben, K.Koch, O.L.Chapman and S.L.Smith, *J. Am. Chem. Soc.*,**83**, 1768(1961)
7. L.Canonica, B.Danieli, P.Manitto, G.Russo and E.Bombardelli, *La Chimica e l'Industria*(Milan) , **49** , 1304 (1967).
8. *Gazz. Chim. Ital*. in the press.
9. Ic and IIc were obtained by deformylation of the corresponding N-formyl-derivatives (Ib and IIb , respectively) in methanolic HCl 0.1 N at r.t. for 24hrs.