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COLLINUSIN, A NEW LIGNAN LACTONE FROM CLEISTANTHUS COLLINUS (Roxb.)*

T.R. Govindachari, S.S. Sathe and N. Viswanathan

CIBA Research Centre, Goregaon, Bombay 63, India

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In a previous communication[1] we reported the isolation of diphyllin[2] from the leaves of Cleistanthus collinus (Roxb.). Benth. & Hook. f. (Family : Euphorbiaceae) and furnished evidence leading to the revision of the structures of diphyllin and justicidin A[3] to (Ia) and (Ib) respectively from those assigned earlier for these compounds.

Besides these two compounds, the acetone extract of the leaves furnished ellagic acid, m.p. 360° (identical with an authentic sample) and a new lactone which we have named collinusin. We present below evidence leading to structure (IIa) for collinusin.

Collinusin, m.p. 196°, $[\alpha]_D$ + 132.48° ($CHCl_3$, c, 2.04), $C_{21}H_{18}O_6$ (molecular weight by mass spectrum 366) has λ_{max}^{EtOH} 247 and 347 mμ (log ε 4.19, 4.02), ν_{max}^{KBr} 1750 (γ-lactone), 1650, 1615 (aromatic) and 925 cm^{-1} (methylenedioxy group). Its UV spectrum is very similar to that of γ-apopicropodophyllin[4] (IIb). Zeisel determination showed the presence of two methoxyl groups and a positive chromotropic acid test supported the presence of a methylenedioxy group. The NMR spectrum of collinusin, determined in $CDCl_3$ solution at 100 mc, shows the presence of two methoxyl groups (δ 3.62, 3.86 p.p.m.), a methylenedioxy group (δ 5.94) and five aromatic protons (δ 6.50 - 6.87). The region

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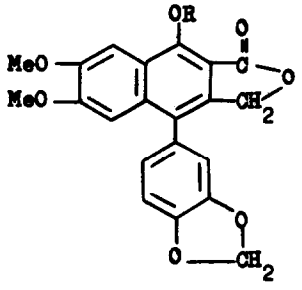
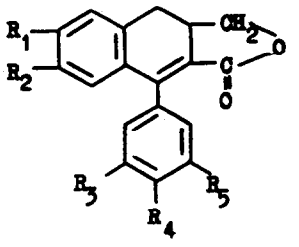
from δ 2.54 - 4.70 p.p.m. bears a striking similarity to the reported NMR spectrum of the synthetic lactone (IIc)[5].



I

a : R = H

b : R = Me



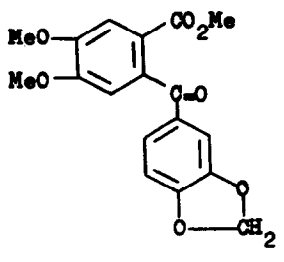
II

a : $R_1 = R_2 = OMe$; $R_3 = H$; $R_4R_5 = -O.CH_2.O-$

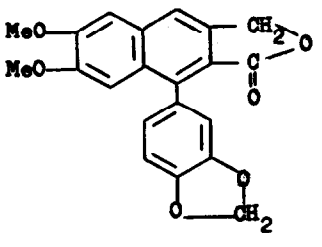
b : $R_1 = R_2 = -O.CH_2.O-$; $R_3 = R_4 = R_5 = OMe$

c : $R_1 = R_2 = R_3 = R_4 = R_5 = H$

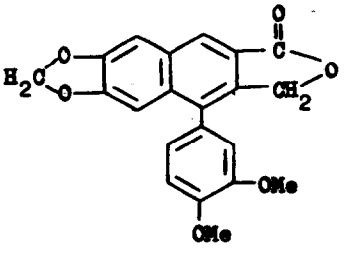
Controlled oxidation of collinusin with acetone-potassium permanganate followed by esterification of the acidic product with diazomethane yielded the keto-ester (III) identical (mixed m.p., TLC, IR and NMR spectra) with a synthetic sample[1]. Oxidation of collinusin with sodium hypobromite under vigorous conditions yielded piperonylic acid identical with an authentic sample.



III



IV



V

Dehydrogenation of collinusin with palladised charcoal yielded optically inactive dehydrocollinusin, m.p. 235-236°, $C_{21}H_{16}O_6$ (molecular weight by mass spectrum 364) $\lambda_{max}^{CHCl_3}$ 261, 296, 312 and 352 mμ (log ε 4.78, 4.03, 4.03 and 3.74), ν_{max}^{KBr} 1762 (γ-lactone), 1618 (aromatic) and 930 cm^{-1} (methylenedioxy group). Its NMR spectrum ($CDCl_3$, 60 mc) shows the presence of two methoxyl groups (δ3.84, 4.07), a methylenedioxy group (δ 6.12), six aromatic protons (δ 6.90 - 7.75) and a methylene (δ5.40) assigned to the group $-CH_2-O-\overset{\overset{O}{\|}}{C}-$ of the lactone ring.

Structures (IIa) and (IV) are evident for collinusin and dehydrocollinusin respectively. The physical properties of dehydrocollinusin are strikingly close to those reported for justicidin B by Munakata et al.[3]. The latter authors have assigned structure (V) for justicidin B. Apart from the incorrect disposition of the alkoxyl groups a structure with such a reversed placement of the lactone carbonyl and methylene groups is untenable for dehydrocollinusin since it should then reveal a low-field proton with $\delta > 8.0$ p.p.m.[5,6]. Direct comparison of dehydrocollinusin with justicidin B has not been possible so far due to non-availability of the latter sample.

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