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NOTES

Lochnericine—A new alkaloid from *Lochnera rosea*

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THIS paper reports the isolation of a new alkaloid, Lochnericine, from the root bark of *Lochnera* (Vinca) *rosea*, from which alkaloids of the Rauwolfia type have previously been isolated.[1-6]

Lochnericine has the molecular formula $C_{21}H_{24 \text{ or } 26}N_2O_3$ and contains one OCH_3 group as ester and one C—CH_3 group. The ultra-violet spectrum in alcohol shows maxima at 227 mμ (log ε 4·10), 299 mμ (log ε 4·15) and 328 mμ (log ε 4·32) and minima at 214, 258 and 306 mμ. The infra-red spectrum shows medium absorptions at 2·96 μ, 3·39 μ, (free >NH or —OH group?) and C—H. absorption at 3·57 μ. An ester group is definitely indicated by strong absorptions at 5·98 μ and 6·21 μ and is supported by hydrolytic evidence. Indole nucleus appears to be indicated by strong absorptions at 6·21 μ and 6·80 μ.

Lochnericine gives only a very slight blue-violet colouration with Keller reagent unlike the β-carboline serpentina bases. It gives a green colour with concentrated nitric acid, and no colour with concentrated sulphuric acid. Erdmann's reagent gives a persistent intense prussian blue colour.

The melting point, U.V. and I.R. data and colour reactions suggest that it is a new alkaloid.

EXPERIMENTAL

The dry root bark (6 kilos) was percolated repeatedly with cold methanol, evaporated at 100 mm to 1 l., and shaken out with petroleum-ether b.p. 60–80° (5 l.). The volume was reduced to 100 ml, cooled and extracted with 5% HCl (900 ml). The clear aqueous portion was made ammoniacal (pH just above 7) and the curdy light yellow precipitate filtered (3·5 g), washed well with a little ice-cold 50% methanol to remove colouring matter. The residue was crystallised repeatedly, first from petroleum ether, then from ethanol, and finally from methanol. Lochnericine (0·5 g), long, prismatic rods from all three solvents, m.p. 188–189° was obtained, yield 0·008% on dry root bark.

Chromatography of lochnericine 0·1 g was done by the method of "Divided columns"[7] (10 g Mercks' chromatographic alumina, 3 columns, length of each column 8 cm and diameter 7 mm). On elution with absolute alcohol, all the lochnericine was obtained in fractions 2, 3 and 4 (15 ml each). The melting point of the residue before and after crystallisation was 188–189°.

$$[\alpha]_D^{18^\circ} = -36{\cdot}1 \ (c, 12{\cdot}47 \text{ in alcohol.})$$

Paper-strip chromatography (ascending type) with *n*-butanol: hydrochloric acid: water: 100 : 4 : 30 showed a single dull violet band under U.V. light with an average *Rf* of 0·94. (Found: C, 71·7, 71·3; H, 7·4, 6·8; O, 13·6, 13·6; N, 8·3, 7·8, OCH_3, 9·3; CCH_3, 3·7 active H, 0·51, 0·52, Calc. for

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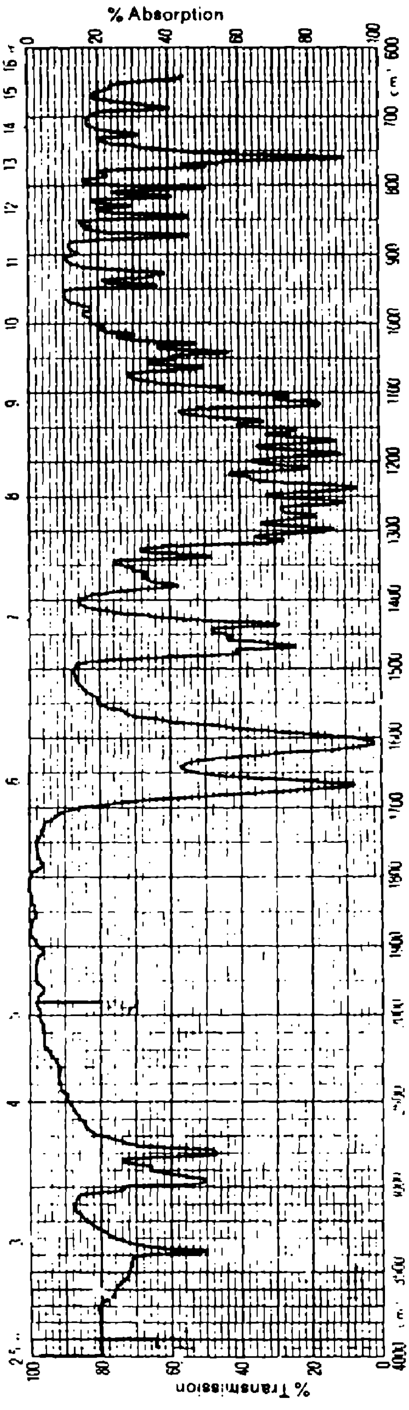

FIG. 1. Infra-red spectrum of "Lochnericine", Medium: KBr.

$C_{21}H_{24}N_2O_3$; C, 71·58; H, 6·82; O, 13·64; N, 7·95; one OCH_3 8·8%; one CCH_3 4·3%; two active H, 0·57. Calc. for $C_{21}H_{26}N_2O_3$: C, 71·19; H, 7·32; O, 13·56; N, 7·91; one OCH_3 8·7%; one CCH_3 4·2; two active H, 0·56%).

Hydrolysis of Lochnericine. Lochnericine (11 mg) and 10% alcoholic sodium hydroxide (0·6 ml) was sealed and heated in the water-bath for 30 min. The deep orange yellow solution on careful additions of sulphuric acid gave at the isoelectric point of about 7 pH, a sparingly soluble yellowish brown amorphous solid, soluble in and forming salts with acids and alkalies.

Acknowledgement—For the analytical results, U.V. and I.R. spectra we are indebted to Dr. A. Hofmann, Vize Direktor Der Sandoz A.G. Basel, Switzerland.

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A novel trans-glycosylation reaction

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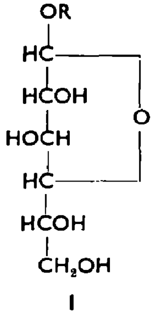
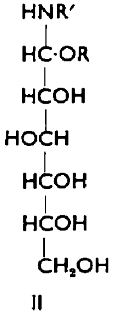
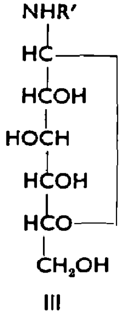
The replacement of one aglycone in an O- or N-glycoside by another aglycone has been variously termed 'transglycosidation'[1] or 'transglycosylation'.[2,3] Such a process has been found to occur only with difficulty when one O-aglycone replaces another,[1] but proceeds readily under mildly acidic conditions for the replacement of one N-aryl group by another in the N-aryl-glycosylamines.[2,3] So far no case has been recorded of the replacement of an O-aglycone by a N-aglycone. In the course of an investigation of some colour reactions of arylamines and sugars, we have noted such a replacement, and shown that in certain cases it may proceed readily under mildly acidic conditions. Treatment of methyl-glucofuranoside (I, R = CH_3) with *p*-nitroaniline in anhydrous methanol containing 0·01 to 0·1 mol of hydrogen chloride, leads to rapid formation of a mixed O- and N-glycoside (II, R = CH_3: R′ = $pNO_2{\cdot}C_6H_4$) which on prolonged treatment yields the N-*p*-nitrophenyl-D-glucosylamine (III, R′ = $pNO_2{\cdot}C_6H_4$).



I



II



III

Similarly *p*-chloroaniline under the same conditions reacts with methyl-glucofuranoside to yield a compound II, (R = CH_3:R′ = $pCl{\cdot}C_6H_4$). In contrast methyl-α-D-glucopyranoside was recovered unchanged even on prolonged boiling under these conditions. Similar results were observed with the ethyl- and *n*-propyl- glucosides, and with the corresponding galactose compounds.

When methyl-3:6-anhydro-α-D-glucopyranoside was added to a methanolic solution of *p*-nitroaniline or *p*-chloroaniline containing catalytic proportions of hydrochloric acid, a similar reaction occurred.

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