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ALKALOIDS OF *GLYCOSMIS PENTAPHYLLA* (RETZ.) CORREA

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Abstract—The isolation of skimmianine and three new acridone alkaloids from the root bark of *Glycosmis pentaphylla* (Retz.) Correa is reported. Based on the spectral evidence and chemical correlations, these are shown to be hitherto naturally unknown noracronycine (IIb), des-N-methylacronycine (IXa) and des-N-methylnoracronycine (IXb). Evidence is also presented to show that of the two possible structures, 1-methoxy-2',2',10-trimethylpyrano(5',6'-2,3 or 3,4) acridone (Ia or IIa) for acronycine, the angular structure IIa is correct.

Glycosmis pentaphylla (Retz.) Correa (Fam: Rutacea) is shrub or a small tree distributed in Malaya, India and Australia.[1] From the leaves and twigs collected in Australia, McKenzie and Price[2] have reported the isolation of the furoquinoline alkaloids kokusaginine and skimmianine, whereas Chakravarti *et al.*[3] have recorded the isolation of the quinazolone alkaloid arborine from the corresponding material collected in South India. We have now investigated the yellow root bark of this plant and report the isolation of skimmianine and three new yellow acridone alkaloids. For convenience these three bases have been designated as alkaloids A, B and C and evidence is presented below to show that they are respectively noracronycine (IIb), des-N-methylacronycine (IXa) and des-N-methylnoracronycine (IXb). Noracronycine (IIb) has not been hitherto reported to occur in nature and since at no stage of our isolation acid conditions were employed, alkaloids A and C could not be artefacts.

Alkaloid A (*noracronycine*)

Alkaloid A, m.p. 200°, has been isolated from the petroleum ether extracts as a bright yellow crystalline solid. It is a very weak base and forms no stable salts. It has the molecular formula $C_{19}H_{17}O_3N$ (mol. wt. 307 by mass spectrum) and contains one methylimino group and no methoxyl group. Its UV (Fig. 1) and IR (strong bands at 1630, 1590 and 1550 cm^{-1} in Nujol) spectra are strongly reminiscent of an acridone alkaloid.[5–7] The presence of a phenolic hydroxyl is suggested by the deep green ferric

* CIBA Research Centre, Goregaon, Bombay 62.

[1] V. Narayanaswami, *Records of the Botanical Survey of India* **14**, No. 2 (1941).
[2] A. W. McKenzie and J. R. Price, *Austral. J. Sci. Res.* **A5**, 579 (1952).
[3] D. Chakravarti, R. N. Chakravarti, L. A. Cohen, B. Dasgupta, S. Datta and H. K. Miller, *Tetrahedron* **16**, 224 (1961). These authors have also clarified the botanical position of the plant material referred to as *Glycosmis pentaphylla* (Retz.) Correa by Chatterjee and Majumdar (Ref. 4); botanical specimens received from the latter authors have been identified by Chakravarti *et al.* as *Glycosmis arborea* Correa.
[4] A. Chatterjee and S. G. Majumdar, *J. Amer. Chem. Soc.* **76**, 2459 (1954) and Refs cited therein.
[5] R. D. Brown and F. N. Lahey, *Austral. J. Sci. Res.* **A3**, 593 (1950).
[6] A. W. Sangster and K. L. Stuart, *Chem. Rev.* **65**, 69 (1965).
[7] L. E. Orgel, *The Chemistry of Heterocyclic Compounds, Acridines* (Edited by A. Weissberger) p. 289. Interscience, London (1956).

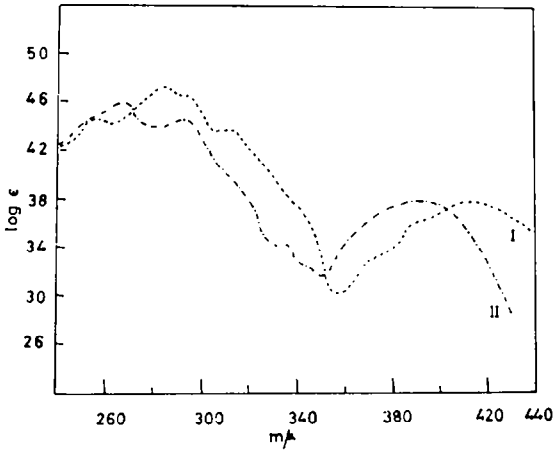


FIG. 1. U.V. spectrum of: I, Noracronycine (Alkaloid A); II. Des-N-methylacronycine (Alkaloid B).

reaction of the alkaloid. Further, this hydroxyl group must be situated *peri* to the carbonyl group since the alkaloid is insoluble in alkali, could not be methylated by diazomethane and no band attributable to the hydroxyl group is present in its IR spectrum.[8] The complete structure of the alkaloid A as noracronycine[9] (Ib or IIb) became evident from its NMR and mass spectra. The latter exhibits a peak at *m/e* 292 (M-15) which is three times as intense as that of the parent ion with no other peaks of comparable intensity; this is characteristic of the ready formation of stable benzopyrylium ions from 2,2-dimethylchromenes.[10,11] The NMR spectrum (Fig. 2) shows the following peaks: The sharp singlet at 1·49 δ (6H) and the doublets at 5·41 and 6·45 δ (each 1H, J = 9·5 c/s) are typical of a 2,2-dimethylchromene system.[10,12] The sharp singlet at 3·79 δ (3H) is due to the N-methyl group. The complex series of peaks centred around 7·35 δ (3H) can be assigned to the aromatic hydrogens at C-5, C-6 and C-7 while the multiplet centred at 8·17 δ (1H) is attributable to the C-8 hydrogen.[13] The very low field signal at 14·56 δ (1H) is due to the strongly hydrogen bonded phenolic proton. The sharp singlet at 6·14 δ (1H) must be assigned to the lone aromatic proton at C-4 (or C-2) consistent with the observations of Pakrashi *et al.*[13] that such rather far upfield shifts have been noted with single aromatic protons flanked by oxygen atoms or by nitrogen and oxygen. Finally, methylation of alkaloid A with dimethyl sulphate–acetone–potassium carbonate afforded acronycine (Ia or IIa) identical with an authentic specimen, thereby confirming the structure Ib or IIb assigned to it.

[8] R. M. Acheson, Ref. 7, p. 203.
[9] R. D. Brown, L. J. Drummond, F. N. Lahey and W. C. Thomas, *Austral. J. Sci. Res.* A2, 622 (1949).
[10] C. S. Barnes, J. L. Occolowitz, N. L. Dutta, P. Madhaven Nair, P. S. Phadke and K. Venkataraman, *Tetrahedron Letters* 281 (1963).
[11] C. S. Barnes and J. L. Occolowitz, *Austral. J. Chem.* 17, 975 (1964).
[12] B. F. Burrows, W. D. Ollis and L. J. Jackman, *Proc. Chem. Soc.* 177 (1960).
[13] Cf. S. C. Pakrashi, S. K. Roy, L. F. Johnson, T. George and C. Djerassi, *Chem. & Ind.* 464 (1961).

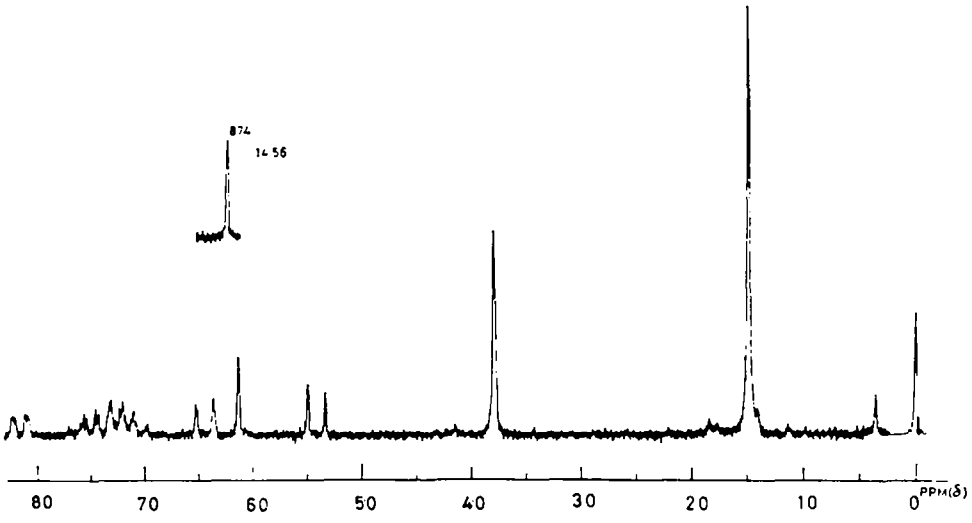


FIG. 2. NMR spectrum of Noracronycine (60 Mc; solvent $CDCl_3$)

Structure of acronycine

Acronycine has been assigned the structure Ia or IIa by the Australian workers[9,14] on the basis of their elegant degradative sequence. A preliminary statement[15] indicated a preference for the linear structure Ia. The evidence detailed below has now enabled us to formulate acronycine as the angular IIa, i.e. as 1-methoxy-2′,2′,10-trimethylpyrano (5′,6′-3,4) acridone in preference to Ia. Tosylation of noracronycine gave the tosyl derivative (Ic or IIc). Desulphurization of this tosylate with Raney nickel in a current of hydrogen afforded a colourless deoxycompound which we expected to be desoxydihydroacronycine (III or IV). However, the molecular formula $C_{19}H_{23}O_2N$ (mol. wt. by mass spectrum 297) for the desoxycompound suggested that in addition to saturation of the chromene double bond, one of the aromatic rings also was saturated[16] during desulphurization. This was strongly supported by its UV spectrum (Fig. 4) which was no longer characteristic of an acridone but typical of a 4-quinolone.[6,18] The primary problem then was to decide which of the two aromatic rings (A or C) had undergone hydrogenation. The NMR spectrum (Fig. 3) of the desoxycompound served admirably to prove that ring A was saturated and also to define it as 2′,2′,10-trimethyldihydropyrano (5′,6′-3,4) 5,6,7,8-tetrahydroacridone (VIII). In agreement with the analysis the integrated spectrum shows a total of 23 protons. Apart from the sharp singlet at 1·4 δ (6H) and 3·6 δ (3H) which must be ascribed to the *gem*-dimethyl[19]

[14] L. J. Drummond and F. N. Lahey. *Austral. J. Sci. Res.* **A2**, 630 (1949).

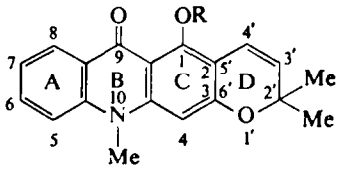
[15] Ref. 5. Footnote on p. 607.

[16] This is not surprising in view of the several reports[17] involving saturation of an aromatic ring during Raney nickel desulphurization.

[17] For a collective Ref. see G. R. Pettit and E. E. van Tamelen, *Organic Reactions* (Edited by A. C. Cope) **12**, 356 (1962).

[18] R. D. Brown and F. N. Lahey. *Austral. J. Sci. Res.* **A3**, 615 (1950).

[19] The chemical shift of the *gem*-dimethyl groups in noracronycine (1·49 δ) and the desoxycompound (1·4 δ) differ in a manner consistent with the change in their environment on reduction of an allylically placed carbon-carbon double bond. See eg. J. S. P. Schwarz, A. I. Cohen, W. D. Ollis, E. A. Kaczka and L. M. Jackman, *Tetrahedron* **20**, 1317 (1964).

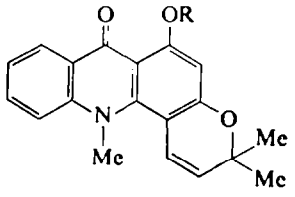


I

Ia R = Me

Ib R = H

Ic R = Tosyl

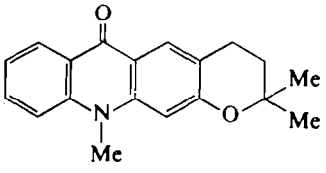


II

IIa R = Me

IIb R=H

IIc R = Tosyl



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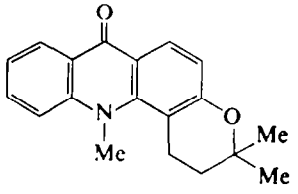

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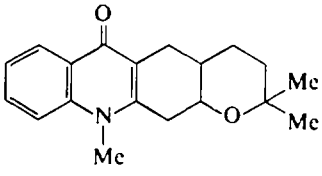

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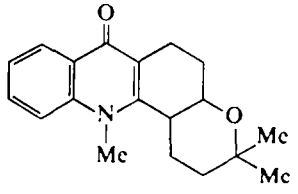

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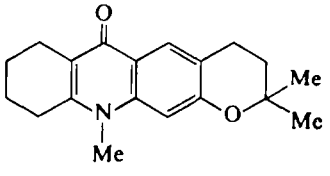

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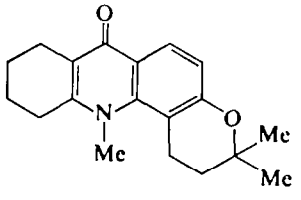
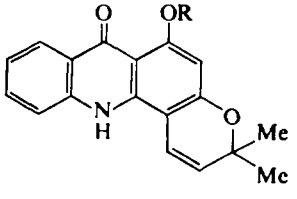


VIII



IX a: R = Me

b: R = H

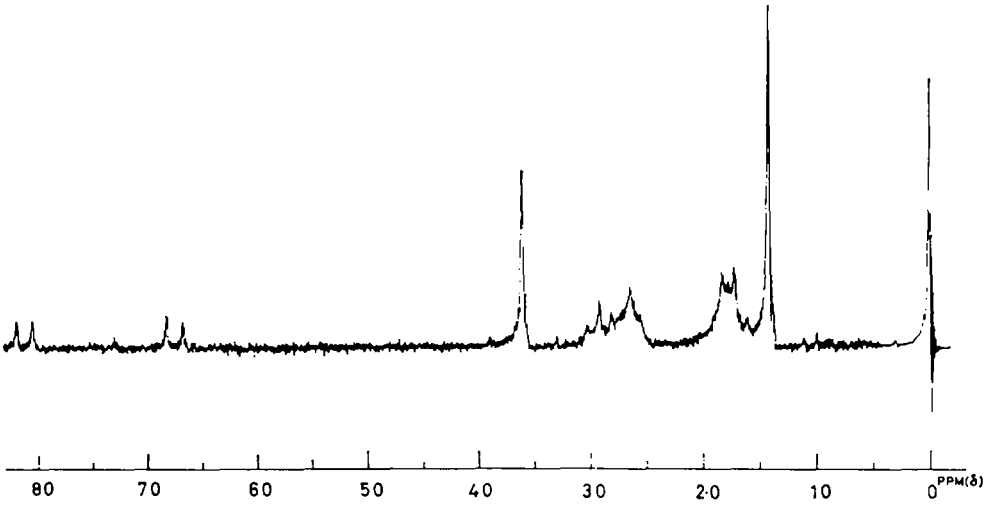


FIG. 3. NMR spectrum of 2′,2′,10-trimethyldihydropyrano-(5′,6′-3,4)-5,6,7,8-tetrahydroacridone.

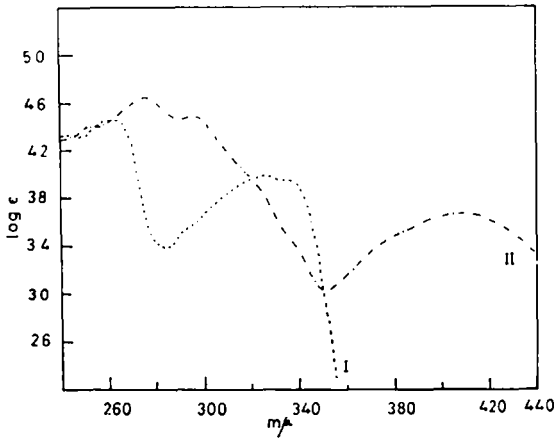


FIG. 4. U.V. spectrum of: I. 2′,2′,10-trimethyldihydropyrano-(5′,6′-3,4)-5,6,7,8-tetrahydroacridone; II. Des-N-methylacronycine (Alkaloid C).

and N-methyl protons respectively, there are present signals which can be grouped as methylenic (complex multiplet at 1·55–1·95 δ, 6H), benzylic (complex multiplet at 2·5–3·1 δ, 6H) and aromatic (doublets at 6·75 and 8·13 δ, each 1H, J = 9 c/s) protons. Of the four possible structures (V–VIII) for the desoxycompound, V and VI were readily ruled out on the ground that their spectra should display signals for four aromatic protons. Of the remaining two possibilities (VII and VIII) a choice could be made based on the two doublets at 8·13 and 6·75 δ which comprise an aromatic AB system. By virtue of its low field, the signal at 8·13 δ indicates that it could be due only to a proton ortho to the carbonyl i.e. on C-1 of the acridone nucleus. Further, the adjacent C-2 position must bear the other aromatic proton to account for the magnitude of the coupling (J = 9 c/s) between the two.[20] Hence the desoxycompound must be formulated as VIII and acronycine must be IIa.

[20] Cf. S. Goodwin, J. N. Schoolery and L. F. Johnson, *J. Amer. Chem. Soc.* **81**, 3065 (1959).

Alkaloid B (*des*-N-*methylacronycine*)

This new alkaloid m.p. 268–270°), which is the major constituent of *G. pentaphylla*, has been isolated from the acetone extracts. It forms a stable picrate and a perchlorate and gives no colour with ferric chloride. It has the same molecular formula $C_{19}H_{17}O_2N$ (mol. wt. by mass spectrum 307) as alkaloid A, but contains one methoxyl group and no methylimino group. Its IR spectrum is similar to that of acronycine (IIa). The sharp band at 3300 cm^{-1} is attributed to a NH group. The UV spectrum (Fig. 1) is typical of an acridone alkaloid and its mass spectrum with the base peak at *m/e* 292 (M-15, 100%) reveals the presence of a 2,2-dimethylchromene system. Demethylation of the alkaloid by heating its hydrochloride affords a *nor*compound (green ferric reaction), m.p. 246°, showing thereby that the methoxyl group must be located at C-1. The sum of evidence is thus in favour of structure IXa to alkaloid B and structure IXb to its *nor*compound; this has been confirmed by methylation of both to acronycine (IIa) by means of methyl iodide, potassium carbonate and acetone.[21]

Alkaloid C (*des*-N-*methylnoracronycine*)

Alkaloid C, m.p. 246°, has been isolated from the mother liquors of alkaloid B by chromatography over silica gel. It is evidently a 'nor' alkaloid as is shown by its green ferric reaction. It contains neither methoxyl nor methylimino group and its molecular formula $C_{18}H_{15}O_2N$ (mol. wt. by mass spectrum 293) is less by one CH_2 than those of alkaloids A and B. This evidence coupled with its UV (Fig. 4), IR (bands at 3300, 1640, 1585, 1535 cm^{-1}) and mass (intense base peak at M-15) spectra and TLC strongly suggested its being identical with des-N-methylnoracronycine. A direct comparison of alkaloid C with the *nor*compound from alkaloid B established their complete identity.

After the conclusion of this work a paper by MacDonald and Robertson[22] appeared in which independent evidence was furnished for the angular structure IIa for acronycine. These authors synthesized 1,3-dimethoxy-2-methoxycarbonyl-10-methylacridone and found it to be different from the degradation product obtained from acronycine through ozonolysis, methylation, oxidation and esterification.

EXPERIMENTAL[23]

1. *Extraction of* Glycosmis pentaphylla (*Retz.*) *Correa*

(a) *With petroleum ether.* The milled root bark[24] (3 kg) was percolated in the cold with pet. ether. The brownish yellow oil obtained by distilling off the solvent, on being kept in the ice-chest overnight deposited *noracronycine* (alkaloid A) as a crystalline yellow solid. It was collected, washed free from the oil with pet. ether and dried (1·8 g). A second crop (0·4 g) of this alkaloid was obtained on leaving the oil in the ice-chest for two more days.

After isolating noracronycine, the residual oil and the pet. ether washings were left in the ice-chest for three weeks when skimmianine was thrown out as a pale yellow solid contaminated with traces of alkaloid A. Repeated crystallization from alcohol afforded the pure base (0·4 g). Extraction of the oil with 5% HCl aq. yielded more of skimmianine.

[21] J. R. Cannon, G. K. Hughes, K. G. Neill and E. Ritchie, *Austral. J. Sci. Res.* **A5**, 406 (1952).
[22] P. L. MacDonald and A. V. Robertson, *Austral. J. Chem.* **19**, 278 (1966).
[23] M.ps are uncorrected. UV spectra: 95% EtOH using a Beckmann model DU spectrophotometer. NMR spectra: $CDCl_3$ on a 60 m.c. Varian instrument with TMS as an internal standard. Kieselgel G. (E. Merck) was used for TLC and pet. ether refers to b.p. 40–60°.
[24] The plant material was collected from the Rajbhavan forests, Guindy, Madras.

(b) *With acetone.* After extraction with pet. ether the plant material was air dried and extracted with acetone in the cold. Acetone was distilled off and the semi-solid residue on being refluxed with benzene and filtered hot gave *des*-N-*methylacronycine* (alkaloid B) as a gritty yellow solid (42 g) insoluble in benzene. The pure alkaloid was obtained by repeated crystallization from dry acetone.

The benzene washings and the acetone mother liquor from the first crystallization of crude alkaloid B above were combined, concentrated to a small volume, and treated with pet. ether to give a partially crystalline solid (6 g). A TLC examination of this material in benzene–AcOEt–MeOH (50:10:1) showed it to be a mixture of noracronycine, *des*-N-*methylnoracronycine* (alkaloid C) and des-N-methylacronycine (in the order of decreasing R_f) contaminated with other impurities. This crude alkaloid mixture (0·2 g) was dissolved in the minimum amount of AcOEt, put on the top of a column of silica gel (Kiezelgel G; 20 g) in benzene and eluted with a mixture of benzene–AcOEt–MeOH (50:10:1). Fractions (5 ml) were cut and analysed by TLC. The pure fractions were combined separately, while the mixed fractions were recycled to the above operation. The yield of the pure alkaloid C from 0·2 g of the crude mixture was 46 mg.[25]

2. *Skimmianine*

It crystallized from alcohol as colourless prisms, m.p. 178°, undepressed on admixture with an authentic specimen, λ_{max} 250, 320, 335 mμ (log ε 4·86, 3·98, 3·97). (Found: C, 64·90; H, 5·20. Calc. for $C_{14}H_{13}O_4N$. C, 64·86; H, 5·02%.)

The *picrate*, yellow needles from alcohol, melted at 196–198°. (Found: C, 49·23; H, 3·22. Calc. for $C_{20}H_{16}O_{11}N_4$. C, 49·18; H, 3·28%.)

3. *Noracronycine* (*alkaloid* A)

Repeated crystallization of the crude alkaloid from benzene or AcOEt gave bright yellow needles, m.p. 198–200°. It was insoluble in aq. alkali and formed no stable salts. With alcoholic $FeCl_3$ it produced an intense green colour and was identical (m.p., m.m.p., TLC and IR) with an authentic specimen, λ_{max} 255, 285, 293 (inflex) 305–310 (sh), 410–415 mμ (log ε 4·50, 4·75, 4·69, 4·41, 3·79). (Found: C, 74·39; H, 5·52; N, 4·73; NMe, 5·10; OMe, Nil; mol. wt. by mass spectrum 307. Calc. for $C_{19}H_{17}O_3N$. C, 74·27; H, 5·54; N, 4·56; NMe, 4·89%; mol.wt. 307.)

4. *Methylation of alkaloid* A

Alkaloid A (0·16 g) was methylated with Me_2SO_4 (1 ml) and K_2CO_3 (2 g) in acetone.[9] The product was purified by chromatography over alumina followed by recrystallization from AcOEt–pet. ether giving pale yellow needles, m.p. 174–175°, alone or when mixed with an authentic specimen of acronycine. Their IR spectra and TLC behaviour were identical λ_{max} 225, 280, 293, 305–310 (inflex), 395 mμ (log ε 4·21, 4·58, 4·54, 4·23, 3·82). (Found: C, 74·88; H, 6·00; N, 4·10; OMe, 4·83. Calc. for $C_{20}H_{19}O_3N$. C, 74·76; H, 5·92; N, 4·36; 1OMe, 4·76%.)

5. *Tosylation of noracronycine*

A mixture of noracronycine (0·5 g), tosyl chloride (1·2 g), ignited K_2CO_3 (4 g) and acetone (70 ml) was refluxed for 48 hr. The reaction mixture was filrered hot, the K- salts washed with hot acetone and the solvent distilled off. Recrystallization of the residue from benzene–pet. ether afforded the *tosyl derivative* as pale yellow stout needles (0·72 g), m.p. 176–178°. It gave no colour with $FeCl_3$. (Found: C, 67·75; H, 5·35. $C_{26}H_{23}O_5NS$ requires: C, 67·69; H, 4·99%.)

6. *Desulphurization of noracronycine tosylate*

To a soln of the tosyl derivative (0·6 g) in hot EtOH (126 ml) was added Raney Ni catalyst[26] (W-2, one day old) and the mixture heated under reflux with stirring for 6 hr in a flask through which a steady stream of purified H was bubbled. The reaction mixture was then filtered hot and the catalyst washed twice with warm alcohol. The colourless filtrate was evaporated *in vacuo* to dryness and the residue extracted with boiling benzene. The benzene soln was concentrated to a small volume and adsorbed on a column of silica (Kieselgel G) in benzene and eluted with AcOEt. Fractions (~6 ml) were cut and analysed by TLC. The first few fractions consisted of the unreacted starting material

[25] Later it was found that extraction of the plant material with ether instead of acetone after extracting with petroleum ether is preferable for the isolation of this alkaloid.

[26] R. Mozingo, *Org. Syntheses Coll.* Vol. 3, 181 (1955).

and were rejected. The latter fractions containing the pure desulphurized product were combined and crystallized from AcOEt giving colourless prisms (0·28 g), m.p. 218–220°, λ_{max} 245 (sh), 265, 325, 335 (inflex) mμ (log ε 4·34, 4·45, 3·99, 3·97). (Found: C, 76·77; H, 7·71; mol.wt. by mass spectrum 297. $C_{19}H_{23}O_3N$ requires: C, 76·76; H, 7·74%; mol.wt. 297.)

7. *Des*-N-*methylacronycine* (*alkaloid* B)

Alkaloid B crystallized from abs acetone as yellow needles, m.p. 268–270° (dec) with sintering at 260°, λ_{max} 265, 295, 333 (inflex) 395 mμ (log ε 4·60, 4·43, 3·43, 3·78). (Found: C, 74·66; H, 5·80; N, 4·05; OMe, 5·3; NMe, Nil; mol.wt. by mass spectrum 307. $C_{19}H_{17}O_3N$ requires: C, 74·27; H, 5·54; N, 4·56; 1OMe, 4·89%; mol.wt. 307.) It was sparingly soluble in benzene, chf and AcOEt and easily soluble in MeOH. An alcoholic solution showed a green fluorescene and gave no colour with $FeCl_3$. It dissolved in 10% HClaq on warming with the precipitation of its orange–red hydrochloride.

The *hydrochloride*, prepared by passing HCl through a chf soln of the alkaloid followed by precipitation with ether, could be crystallized from MeOH–ether in orange–red needles, m.p. 137–141°, identical with the specimen obtained by dissolving the base in 10% HClaq.

The *picrate* crystallized from alcohol as orange needles m.p. 222–224° (dec). (Found: C, 56·44; H, 3·88; N, 10·72. $C_{25}H_{20}O_{10}N_4$ requires: C, 55·97; H, 3·73; N, 10·45%.)

The *perchlorate*, prepared from an alcoholic soln of the base with perchloric acid, crystallized from alcohol as aggregates of short orange needles, m.p. 251–252° (dec). (Found: C, 56·05; H, 4·44; N, 3·58; $C_{19}H_{16}O_7NCl$ requires: C, 55·95; H, 4·42; N, 3·44%.)

8. N-*Methylation of alkaloid* B

A mixture of alkaloid B (0·5 g), MeI (15 ml), ignited K_2CO_3 (20 g) and acetone (100 ml) was refluxed for 32 hr. After being filtered hot, acetone was distilled off and the residue extracted with hot AcOEt. Concentration of the AcOEt soln to a small volume followed by addition of pet. ether gave a pale yellow solid, which on crystallization from AcOEt– pet. ether afforded pale yellow needles (0·45 g), m.p. and m.m.p. with authentic acronycine 174–175°. The *picrate* formed orange crystals from abs alcohol m.p. 161–162°. Lahey and Thomas[37] have reported m.p. 150–154°. (Found: C, 57·19; H, 3·60; N, 9·71. $C_{26}H_{20}O_{10}N_4$ requires: C, 56·72; H, 4·00; N, 10·18%.)

9. *Demethylation of alkaloid* B

Dry alkaloid B hydrochloride (0·1 g) was heated in a test tube at 150–170° (oil bath) until effervescence ceased (~5 min). On cooling a bright yellow solid was obtained. The material from five such batches was dissolved in the minimum amount of ethyl acetate and chromatographed over a column of silica in benzene, the elution being carried out with a mixture of benzene and AcOEt (1:1). Recrystallization from AcOEt gave the *norcompound* as orange stout rods (0·28 g) or as bright yellow short needles from benzene–AcOEt, m.p. 245–246° (dec). An alcoholic soln gave an intense green colour and showed no fluoroescence. (Found: C, 73·27; H, 5·23; N, 4·96. $C_{18}H_{15}O_3N$ requires: C, 73·72; H, 5·12; N, 4·78%.)

10. *Methylation of nor-alkaloid* B

A mixture of nor-alkaloid B (0·1 g), MeI (5 ml), ignited K_2CO_3 (5 g) and acetone (40 ml) was refluxed for 36 hr. The methylated product crystallized from AcOEt–pet. ether as pale yellow needles (68 mg), m.p. 174–175°, identical in all respects with acronycine.

11. *Des*-N-*methylnoracronycine* (*alkaloid* C)

Alkaloid C formed orange stout rods from AcOEt or bright yellow needles from benzene–AcOEt, m.p. 245–246°, identical in all respects (m.m.p. IR and TLC) with *nor*-alkaloid B above, λ_{max} 252 (sh), 275, 295, 410 mμ (log ε 4·37; 4·63, 4·48, 3·66). (Found: C, 73·64; H, 5·20; N, 4·50; OMe, Nil; NMe, Nil; mol.wt. by mass spectrum 293. $C_{18}H_{15}O_3N$ requires: C, 73·72; H, 5·12; N, 4·78%; mol.wt. 293.)

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[37] F. N. Lahey and W. C. Thomas, *Austral. J. Sci. Res.* **A2**, 423 (1949).