563. *The Alkaloids of the* Leguminosae. *Part I. The Structure of Calpurnine from* Calpurnia subdecandra.

By A. Goosen.

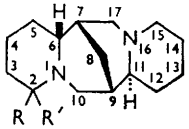
A new alkaloid calpurnine (II), is shown to be an ester of pyrrole-2-carboxylic acid and (+)-13-hydroxylupanine which was characterised by reduction to (—)-13-hydroxysparteine and by a comparison of these bases and their known derivatives. New derivatives have been prepared.

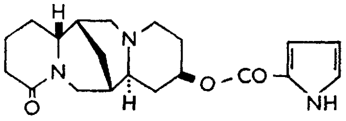
Calpurnine, $C_{20}H_{27}N_3O_3$, the major alkaloid from the aerial portion of *Calpurnia subdecandra,* forms a monoperchlorate and monomethiodide. A chloroform solution of the alkaloid shows infrared absorption bands at 3480, 1710, 1695, and 1615 cm.$^{-1}$. The band at 3480 cm.$^{-1}$ was attributed to an NH group which was either acidic or neutral since the alkaloid could not be acetylated. The ultraviolet spectrum had a maximum at 268 mμ (log ε 1·55).

Reduction of calpurnine by lithium aluminium hydride gave a base " A," $C_{15}H_{26}N_2O$, with infrared absorption (3600 cm.$^{-1}$) (OH) and giving an acetyl derivative. The absence in base " A " of the infrared absorption bands of calpurnine at 1710 and 1695 cm.$^{-1}$, and the diminished band at 1630 cm.$^{-1}$, indicated the reduction of an ester and an amide since calpurnine did not possess a double bond.

Alkaline hydrolysis of calpurnine gave a base " B," $C_{15}H_{24}N_2O_2$, and an acid, $C_5H_5NO_2$, which gave a red colour on an acid-treated pine splint. A solid-state infrared spectrum of the acid showed a sharp band at 3400 cm.$^{-1}$ (NH) and a broad band at 1670 cm.$^{-1}$ (αβ-unsaturated C=O). The acid was identified as pyrrole-2-carboxylic acid by comparison with a synthetic sample,[1] and appears not to have been reported previously as an ester component in alkaloids.

(I)





(II)

Base " B " contained a hydroxyl group which was acetylated and benzoylated and showed infrared bands at 3600 and 1630 cm.$^{-1}$, the latter being attributed to an amide carbonyl. Reduction by lithium aluminium hydride gave base " A."

Base " B " was identified with (+)-hydroxylupanine.[2,3] The hydrochloride, aurichloride, picrolonate, methiodide, and benzoyl derivative agree in melting point with the corresponding (+)-hydroxylupanine derivatives. The hydriodide, m. p. 234—238°, was obtained anhydrous. The reported (+)-hydroxylupanine hydriodide, m. p. 91—93°, is a hydrate. Base " A " and its dipicrate agree in melting point with (—)-13-hydroxysparteine, but our methiodide had m. p. 258—260° (lit., m. p. 230—232°).[2] Further, the infrared spectrum of base " A " is identical with that of (—)-13-hydroxysparteine published by Bohlmann.[4]

The relative configurations of (+)-lupanine and (—)-sparteine have been fully established,[4-6] and the experiments of Okuda and Tsuda[7] relating (—)-anagyrine to (+)-epilupine permit definition of the absolute configuration of (+)-lupanine (I; R + R′ = O)

---

[1] McCay and Schmidt, *J. Amer. Chem. Soc.*, 1935, **48**, 1333.
[2] Manske, " The Alkaloids," Vol. III, Academic Press Inc., 1953.
[3] Manske, " The Alkaloids," Vol. VII, Academic Press Inc., 1960.
[4] Bohlmann, Winterfeldt, and Brackel, *Chem. Ber.*, 1958, **91**, 2194.
[5] Leonard and Beyler, *J. Amer. Chem. Soc.*, 1950, **72**, 1316.
[6] Marion and Leonard, *Canad. J. Chem.*, 1951, **29**, 355.
[7] Okuda and Tsuda, *Chem. and Ind.*, 1961, 1115.

and (—)-sparteine (I; R = R′ = H). Bohlmann and his co-workers[4] converted (+)-13-hydroxylupanine into (—)-13-hydroxysparteine and from comparative infrared studies of synthetic isomeric hydroxysparteines postulated that (—)-13-hydroxysparteine contained an equatorial hydroxyl group.

The absolute stereochemical structure for calpurnine is thus (II) provided that the 13-hydroxyl group of (+)-13-hydroxylupanine is equatorial and the unlikely inversion did not occur at C-13 during the hydrolysis and lithium aluminium hydride reduction of calpurnine.

EXPERIMENTAL

Calpurnine (II).—Calpurnine crystallised from ethyl acetate as prisms, m. p. 152—154°, $[\alpha]_D^{22}$ +59° (*c* 1 in $CHCl_3$) (Found: C, 67·4; H, 7·5; N, 11·5. Calc. for $C_{20}H_{27}N_3O$: C, 67·2; H, 7·6; N, 11·8%). The *perchlorate* crystallised from hot methanol as prisms, m. p. 255—260° (Found: C, 52·1; H, 6·3. $C_{20}H_{28}ClN_3O_7$ requires C, 52·5; H, 6·2%). The *methiodide* crystallised from acetone as rods, m. p. 230—233° (Found: C, 50·1; H, 6·5. $C_{21}H_{30}O_3N_3I$ requires C, 50·5; H, 6·1%).

(—)-13-*Hydroxysparteine*.—Calpurnine (250 mg.) in tetrahydrofuran (30 ml.) was treated with an excess of lithium aluminium hydride and refluxed for 10 hr. The mixture was poured into ice–water, then acidified, and the tetrahydrofuran distilled off under reduced pressure. The aqueous solution, when basified and extracted with chloroform, gave a gum. The gum in chloroform was chromatographed on alumina. Chloroform eluted a gum which crystallised from acetone as prisms of (—)-13-hydroxysparteine, m. p. 155—157°, $[\alpha]_D^{22}$ —21·3° (*c* 1 in $CHCl_3$) (Found: C, 72·6, 71·9; H, 10·3, 10·3; N, 11·0, 10·6. Calc. for $C_{15}H_{26}N_2O$: C, 72·0; H, 10·5; N, 11·1%). The *acetate*, formed with acetic anhydride in pyridine, sublimed at 100°/0·5 mm. to give crystals, m. p. 135—138° (Found: C, 69·8; H, 9·6. $C_{17}H_{28}N_2O_2$ requires C, 69·8; H, 9·65%). The *acetate picrate* crystallised from acetone–ethanol in needles, m. p. 224—226° (Found: C, 46·7, 46·2; H, 4·5, 4·0. $C_{23}H_{31}N_5O_9$ requires C, 46·1; H, 4·5%). The *acetate methiodide*, crystallised from ethyl acetate, had m. p. 260—264° (Found: C, 49·6; H, 7·4. $C_{18}H_{31}IN_2O_2$ requires C, 49·0; H, 7·5%).

(+)-13-*Hydroxylupanine*.—Calpurnine (250 mg.) in methanolic sodium methoxide (25 ml. of methyl alcohol and 1·0 g. of sodium) was refluxed under nitrogen for 13 hr. The mixture was concentrated, poured into water, and extracted with chloroform which gave a gum. The gum crystallised from acetone as prisms of (+)-13-hydroxylupanine, m. p. 174°, $[\alpha]_D^{22}$ +51·8° (*c* 1 in EtOH) (Found: C, 68·1; H, 9·2; N, 10·1. Calc. for $C_{15}H_{24}N_2O_2$: C, 68·15; H, 9·15; N, 10·6%). The aqueous solution was acidified and extracted with chloroform which gave a solid. The solid sublimed at 120°/0·5 mm. to crystals which recrystallised from water as prisms of pyrrole-2-carboxylic acid, m. p. 206—209° (Found: C, 54·3; H, 4·6; N, 12·9. Calc. for $C_5H_5NO_2$: C, 54·05; H, 4·5; N, 12·6%). (+)-13-*Acetoxylupanine*, m. p. 103—105°, crystallised from light petroleum (Found: C, 66·9; H, 8·5. $C_{17}H_{26}N_2O_3$ requires C, 66·6; H, 8·5%).

The author thanks Professor F. L. Warren for his interest and Smith, Klyne, and French (Philadelphia) for information of their survey on South African plants.

C.S.I.R., NATURAL PRODUCTS RESEARCH UNIT,
DEPARTMENT OF CHEMISTRY, UNIVERSITY OF NATAL,
PIETERMARITZBURG, SOUTH AFRICA.

[*Received, November* 19*th*, 1962.]