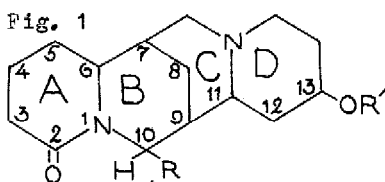


NEW QUINOLIZIDINE ALKALOIDS FROM CADIA PURPUREA

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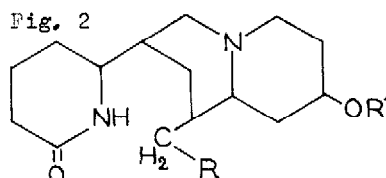
From *Cadia purpurea* (Picco., Ait.), Caesalpiniaceae, a poisonous shrub from Ethiopia (Dire Dawa-Harrar), we earlier isolated spartein, lupanin, 13-hydroxylupanin and esters of the last compound.<sup>1,2</sup> We now isolated four new alkaloids, which are unknown in nature as far as we know.



I R = R' = H (13-hydroxylupanin)

II R = OH R' = H

III R = OH R' =



IV R = OH R' = H (Cadiamin<sup>2</sup>)

V R = OH R' =

VI R = OH R' =

TABLE 1

	M <sup>+</sup>	[M-R'OH] <sup>+</sup>			
		A	B	C	D
I	264 (51 %) C <sub>15</sub> H <sub>24</sub> N <sub>2</sub> O <sub>2</sub>	246 (54 %) C <sub>15</sub> H <sub>22</sub> N <sub>2</sub> O	152 (100 %) C <sub>9</sub> H <sub>14</sub> NO	112 (33 %) C <sub>6</sub> H <sub>10</sub> NO	134 (41 %) C <sub>9</sub> H <sub>12</sub> N
II	280 (31 %) C <sub>15</sub> H <sub>24</sub> N <sub>2</sub> O <sub>3</sub>	262 (62 %) C <sub>15</sub> H <sub>22</sub> N <sub>2</sub> O <sub>2</sub>	152 (100 %) C <sub>9</sub> H <sub>14</sub> NO	128 (17 %) C <sub>6</sub> H <sub>10</sub> NO <sub>2</sub>	134 (31 %) C <sub>9</sub> H <sub>12</sub> N
III	373 (1 %) C <sub>20</sub> H <sub>27</sub> N <sub>3</sub> O <sub>4</sub>	262 (100 %) C <sub>15</sub> H <sub>22</sub> N <sub>2</sub> O <sub>2</sub>		128 (3 %) C <sub>6</sub> H <sub>10</sub> NO <sub>2</sub>	134 (24 %) C <sub>9</sub> H <sub>12</sub> N

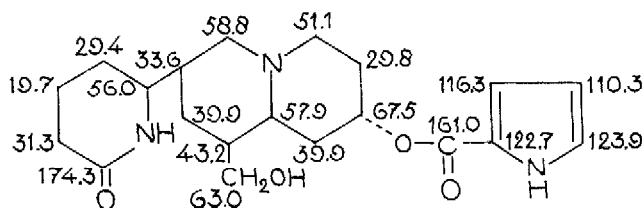
According to their ion abundances and fragmentation pattern the mass spectra of I and II are roughly similar. Both the molecular ion of II and its fragment ions A and C contain one oxygen atom more than the corresponding ions of I. Fragment ions B and D of I and II have the same elemental composition (Table 1). From this we deduced the presence of an OH-group situated in either ring A or ring B. From the MS data of III we concluded that this alkaloid is an ester of 2-pyrrolicarboxylic acid and II.

In the IR spectra of II and III we found an amide C=O absorption band of  $1595\text{ cm}^{-1}$  of.  $1625\text{ cm}^{-1}$  in I. This shift is attributed to an intramolecular hydrogen bond. The above data result in the conclusion that II and III have an extra -OH at  $C_{10}$ .

TABLE 2

	$M^+$	$[M-R'OH]^+$	$[M-\text{C}_6\text{H}_9\text{N}_2\text{O}]^+$	$[\text{C}_6\text{H}_9\text{N}_2\text{O}]^+$	$[M-R'OH-\text{C}_6\text{H}_9\text{N}_2\text{O}]^+$
IV	282 (22 %) $C_{15}H_{26}N_2O_3$	264 (3 %) $C_{15}H_{24}N_2O_2$	184 (100 %) $C_{10}H_{18}NO_2$	98 (17 %) $C_5H_8NO$	166 (14 %) $C_{10}H_{16}NO$
V	375 (5 %) $C_{20}H_{29}N_3O_4$	264 (66 %) $C_{15}H_{24}N_2O_2$	277 (31 %) $C_{15}H_{21}N_2O_3$	98 (33 %) $C_5H_8NO$	156 (100 %) $C_{10}H_{16}NO$
VI	416 (41 %) $C_{23}H_{32}N_2O_5$	264 (59 %) $C_{15}H_{24}N_2O_2$	318 (66 %) $C_{18}H_{24}NO_4$	98 (37 %) $C_5H_8NO$	166 (100 %) $C_{10}H_{16}NO$

In our first publication on cadiamin (IV, 2) no structure proposal was made. The isolation of V however enabled us to elucidate the structures of the compounds mentioned above. Comparison of the spectroscopic (IR, NMR and MS) data of compounds IV, V and VI with those of the known spartein type alkaloids, indicated that we are dealing with the same skeleton. Acid hydrolysis provided evidence that V and VI are esters of IV. From the presence of an amide C=O absorption in the IR spectra and the 2 H atoms extra in the molecular formula of the new alkaloids, we conclude that one ring of the skeleton must be open. The easy loss of fragment  $C_5H_8NO$  from IV, V and VI in the mass spectrometer and the amide -NH absorption at  $3400\text{ cm}^{-1}$  in the IR spectrum of the silyl derivative of IV (2 TMS), lead to the conclusion that ring B is open between  $N_1$  and  $C_{10}$ . The value of the C=O absorption,  $1640-1650\text{ cm}^{-1}$  (sec. amide) in the IR spectra of IV, V and VI and the proton signals at 3.55 ppm (-CH<sub>2</sub>O-) and 5.25 ppm (-CH-O-CO-) of V confirm the proposed structures. The  $C_{13}$  NMR spectrum of V (Fig. 3) was in agreement with spectra of similar compounds.<sup>3)</sup>



## References :

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The NMR spectra were obtained with Perkin Elmer 257 and 377 instruments; low and high resolution mass spectra were recorded with an AEI-MS 902/Argus 500 computer combination (See H.A. van 't Klooster, Org.Mass Spectrom. 8, 303-316(1974).