## PRELIMINARY CHEMICAL INVESTIGATIONS ON EMINIUM SPICULATUM

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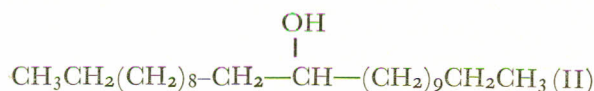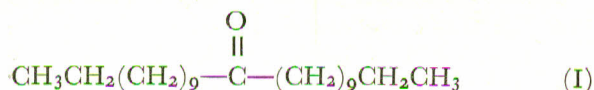*Department of Chemistry, Mosul University, Mosul, Iraq*

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*Eminium spiculatum* is one of the most common members of the Aracea family which grows wild in Iraq. The plant, when taken fresh, is known to be fatal,[1] but boiling of the plant for a prolonged time in water, in the presence of tartaric acid, removes its toxicity. Isolation of the toxic principle is the concern of the present studies.

The dried powdered plant material was defatted with petroleum spirit and subsequently extracted with chloroform and finally with alcohol. The components of the alcoholic extract are under investigation and will be reported elsewhere. The concentration of the chloroform extract and repeated chromatography on silica gel column using chloroform–petroleum ether mixtures and then methanol as eluents, afforded a brown gum which crystallised from methanol m.p. 62–63°C.

The combustion data and mass spectrum of the compound established the molecular formula as $C_{23}H_{46}O$. The IR absorption at 1715 cm$^{-1}$ suggested the presence of a carbonyl function in a saturated system. This was confirmed by its formation of monoxime[2] and semicarbazone derivatives The UV spectrum was also consistent with a carbonyl group in a completely saturated system. The NMR spectrum of the compound was extremely simple showing a single resonance line at 8.9τ, characteristic of methylenic protons in a highly symmetrical system.
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$$CH_3CH_2(CH_2)_9{-}\overset{\displaystyle O}{\overset{\displaystyle \|}{C}}{-}(CH_2)_9CH_2CH_3 \qquad (I)$$

$$CH_3CH_2(CH_2)_8{-}CH_2{-}\overset{\displaystyle OH}{\overset{\displaystyle |}{CH}}{-}(CH_2)_9CH_2CH_3 \text{ (II)}$$

$$CH_3CH_2(CH_2)_8CH_2CH(CH_2)_9CH_2CH_3 \qquad (III)$$

Reduction of I with Raney nickel and also with sodium in ethanol resulted in a carbinol[4] (II) which was dehydrated by β-toluene-sulphonic acid to an olefln[4] (III) Potassium permanganate oxidation of olefln (III) yielded lauric acid as one of the components. The only symmetrical ketone for louric acid could be 12-tricosanone (I). Direct comparison of the natural product with a synthetic specimen [5–7] left on dubt in establishing the struc-

true of the compound as I. Previously 12-tricosanone has been isolated from *Polytrichum juniperimum*.

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## THE CRYSTAL STRUCTURE OF HARMIDINE (HARMALINE)

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Harmaline (I)[1] is a major alkaloid of *Peganum harmala*. There has been some confusion in the literature regarding the structure of 'harmidine', a higher melting base isolated by Siddiqui from the mature seeds of the same plant.[2,3] Siddiqui suggested that 'harmidine' (m.p. 258°C) may be isomeric to harmaline (m.p. 235–238°C). Robinson subsequently showed that 'harmidine' was identical to harmaline and suggested that the higher melting point of 'harmidine' observed by Siddiqui may have been due to its dependency on the mode and rate of heating.[4] However, Ahmad and Rizvi, on the basis of X-ray powder data of 'harmidine'

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later suggested that the substance may be different from harmaline.[5]



I
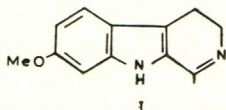
One of us (A.u.R.) during investigation of the chemistry of harmaline, found that pure harmaline could be separated into two different moving spots on thin layer chromatography and attibuted them to the imine and enamine tautomers of harmaline.[6] Convincing evidence for the existence of imine–enamine tautomerism in solutions of harmaline came from NMR studies of deuteriated harmaline.[7] Studies on the reactions of harmaline with electrophilic reagents further demonstrated that there was a significant contribution of the enamine tautomer and a number of pharmacologically interesting indolic compounds were synthesized by utilization of this chemical reactivity.[7]

During the investigation of harmaline, repeated crystallisation afforded well-formed orthorhombic crystals m.p. 254°C. Since the melting point of these crystals corresponded closely with that of 'harmidine' reported by Siddiqui, it was suspected that this higher melting compound may be the enamine tautomer of harmaline. Since conjugative stabilization is available to both the imine and enamine species, such a possibility did not appear unreasonable. Since NMR studies were unsuccessful on account of the low solubility of these crystals in nonpolar solvents and the rapid equilibration between the imine and enamine tautomers in polar solvents,[7] X-ray diffraction methods were used to demonstrate the equality or isomerism of the two substances.

Harmidine, $C_{13}H_{14}N_2O$, mol wt 214, m.p. 254°C, thick orthorhombic crystals, $a = 10.702 \pm 5$, $b = 13.579 \pm 7$, $c = 7.535 \pm 5\text{Å}$, $V = 1095\text{Å}^3$, $Z = 4$, $D_{calc} = 1.29$ g. c$^{-3}$. Space group $P2_12_12_1$ from extinctions. 1209 intensities were collected by Weissenberg method, measured by visual comparison against a standard scale and corrected by usual factors, including absorption.
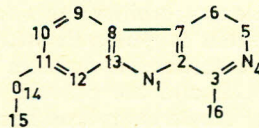
The structure was solved by direct methods using a programme written in Cambridge.[8,9] The right phase set was soon recognised by the low value of $R_{karle}$ and the Fourier map gave all the non-hydrogen atoms. The least squares refinement was terminated at an agreement factor of 0.128 when the chemical problem was solved with certainty. The distance $C_3$–$N_4$ is definitely

a double bond $(1.283 \pm 8°\text{A})$ while $C_3$—$N_4$ is definitely a double bond $(1.283 \pm 8\text{Å})$ while $C_3$—$C_{16}$ is a single bond $(1.449 \pm 9\text{Å})$. The resulting structure for 'harmidine' is, therefore, identical with that known for harmaline (Table 1).



TABLE 1.—FRACTIONAL ATOMIC POSITIONS ($\times 10^4$).*

| | X | Y | Z | | X | Y | Z |
|---|---|---|---|---|---|---|---|
| $N_1$ | 4899 | 3764 | 4913 | $C_9$ | 9774 | 3799 | 1511 |
| $C_2$ | 1166 | 1312 | 4508 | $C_{10}$ | 945 | 3376 | 1274 |
| $C_3$ | 7059 | 2974 | 5002 | $C_{11}$ | 1947 | 3983 | 501 |
| $N_4$ | 3180 | 2057 | 4354 | $C_{12}$ | 1744 | 4928 | 91 |
| $C_5$ | 3420 | 1272 | 3094 | $C_{13}$ | 9453 | 311 | 4782 |
| $C_6$ | 2853 | 246 | 3478 | $C_{14}$ | 3027 | 3544 | 527 |
| $C_7$ | 1515 | 453 | 3885 | $C_{15}$ | 4043 | 4047 | —5 |
| $C_8$ | 9546 | 4782 | 991 | $C_{16}$ | 6724 | 2162 | 3818 |

* The numbering of atoms is arbitrary.

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