important when the nucleus under consideration is not directly involved in the bonding. In fact a meaningful interpretation of the NMR. data in complexes is not possible unless intra-ligand interactions are also taken into account.

Thanks are due to Dr. *S. Shupack*, Villanova University of Philadelphia, Penna. for the loan of compounds **3** and **4**.

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171. Piperaceae Alkaloids: Part I. Structure of Piperstachine; ^{13}C- and ^{1}H-NMR. Studies[1])

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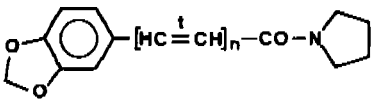
Dedicated to Prof. *T. R. Govindachari* on the occasion of his 60th Birthday

(22. V. 75)

Summary. From the stem of *Piper trichostachyon C. DC.* a new alkaloid designated piperstachine (VII) has been isolated. Its structure is derived on the basis of spectral data and synthesis of hexahydropiperstachine (X).

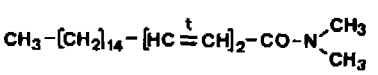
[1]) Contribution No 392 from *Ciba-Geigy Research Centre*; ^{13}C-NMR.-Spectroscopy, Part 7. Part 6 see [1].

Piper trichostachyon C. DC. (family *Piperaceae*) is a twining climber growing in the evergreen forests of Western Ghats of India. Earlier chemical investigations of this plant reported the isolation of trichostachine (I) [2] (=piperylin) [3], trichonine (II) [4] and 1-piperettyl pyrrolidine (III) [5].



I: n = 2

III: n = 3



II

We wish to report in this communication the structure determination of a new alkaloid isolated from the hexane extract of the stem and designated as piperstachine. The alkaloid, $C_{22}H_{29}NO_3$, m.p. 152°, exhibited in the UV. λ_{max} 216, 283, 293 and 315 nm (log ε 4.54, 4.34, 4.39 and 4.26) and in the IR. ν_{max}^{KBr} 3300 (NH or OH), 1662, 1620 (conjugated amide carbonyl), 1260, 930 (methylenedioxy) and 985 cm^{-1} (olefinic *trans* double bond). In its ^{1}H-NMR. spectrum (Fig. 1) piperstachine showed nine olefinic and aromatic protons in the region 5.6–6.9 ppm, a two proton singlet at 5.92 ppm due to the methylene group of a methylenedioxybenzene and the NH group at 5.8 ppm which exchanged on addition of D_2O. A two proton apparent triplet at 3.13 ppm ($J = 6.5$ Hz) which collapsed to a doublet ($J = 6.5$ Hz) on deuteration showed the presence of a methylene group flanked by an amide nitrogen and a methine. The four proton multiplet at ~2.2 ppm suggested the presence of two allylic or benzylic methylene groups, and a multiplet integrating for four protons centered at 1.47 ppm should be assigned to two saturated methylene groups. A six proton

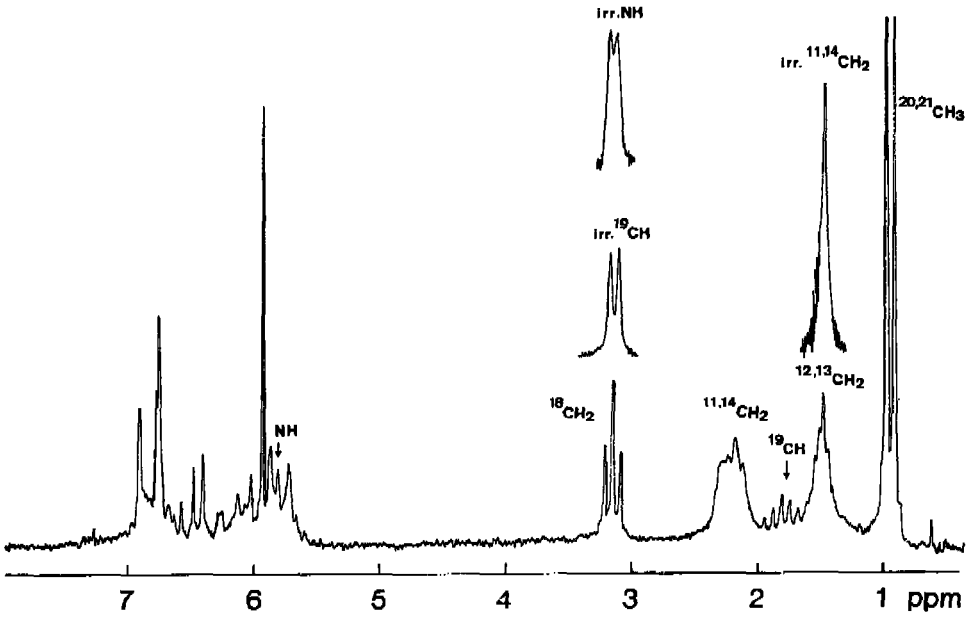
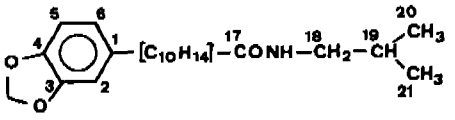


Fig. 1. *^{1}H-NMR. spectrum (100 MHz) of piperstachine (VII) in $CDCl_3$ and effect of double resonance experiments*

doublet at 0.91 ppm ($J = 7$ Hz) and the one proton multiplet at 1.79 ppm could be attributed to an isopropyl grouping. All the 29 protons of piperstachine are thus accounted for, indicating an isobutylamide group attached to a methylenedioxyphenyl-decatriene. Double resonance experiments (Fig. 1) have confirmed these assignments. Thus, irradiation of the methine proton simplified the triplet at 3.13 ppm to a doublet which must be due to spin coupling with the amide NH proton located as a broad resonance at ~5.8 ppm in the aromatic region, as shown by another decoupling experiment. Irradiation at 2.2 ppm (allylic and/or benzylic methylene) simplified the CH_2 resonance at ~1.5 ppm, *i.e.* the non-conjugated methylene groups. At the same time, some simplification occurred in the olefinic region at 6.0–6.4 ppm. This data indicated a partial structure (IV) for piperstachine wherein the $C_{10}H_{14}$



IV

aliphatic unit contains three olefinic double bonds and four contiguous methylene groups. Some information about the position and stereochemistry of one of the olefinic double bonds of the triene system could be obtained from the ^{1}H-NMR. spectrum measured in the presence of the shift reagent Pr(fod)$_3$ [Tris(1,1,1,2,2,3,3-heptafluoro-7,7-dimethyl-4,6-octane-dionato) praseodymium]. This reagent caused upfield shifts of the following resonances (Fig. 2): NCH_2 (−0.65 ppm), NH (−0.65), CH–$(CH_3)_2$

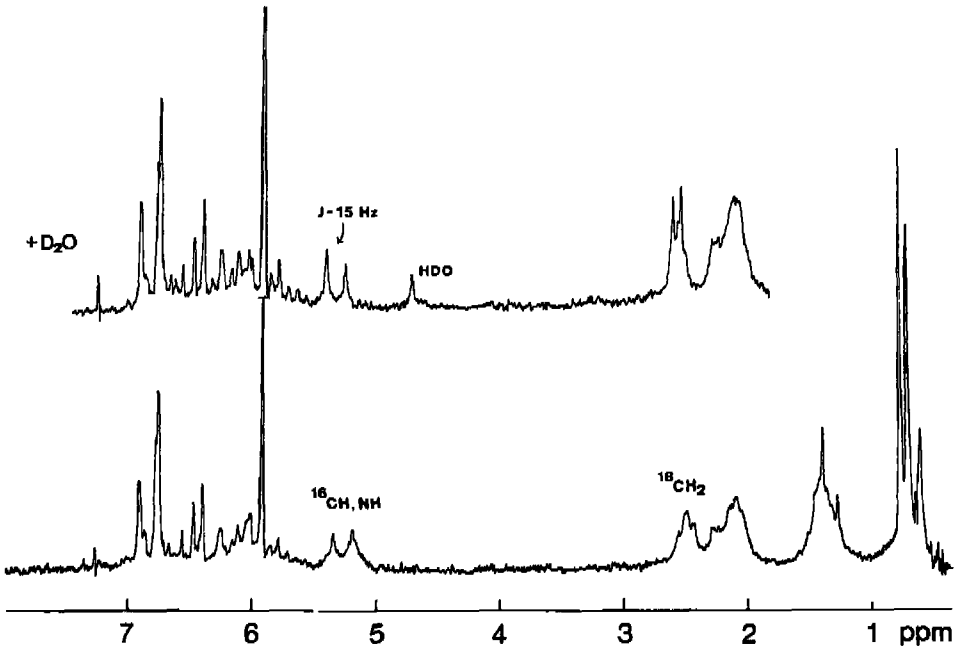
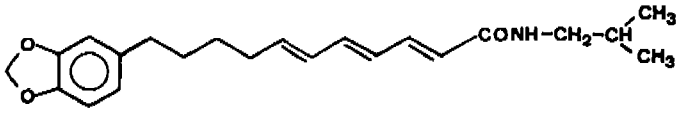


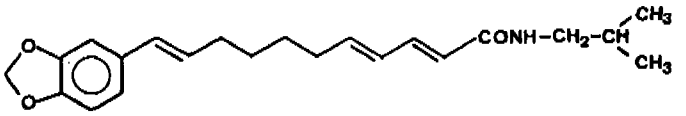
Fig. 2. *^{1}H-NMR. spectrum of piperstachine (20 mg) in ~ 0.3 ml $CDCl_3$ after addition of 4 mg of Pr(fod)$_3$. Solution measured also after shaking with D_2O to exchange H(N).*

(−0.4), CH_3 (−0.14) and of one olefinic proton which in the shifted spectrum appeared as a doublet (J = 15 Hz) at 5.26 ppm ($\Delta\delta$ −0.53). This doublet coincides with the shifted resonance of the amide NH proton and is more clearly resolved after deuterium exchange of the NH proton. The doublet structure of this vinyl proton proves that it must be attached to the terminal carbon of the olefinic system in α-position to the amide carbonyl. Then, the value of the vicinal coupling constant (15 Hz) establishes the *trans* configuration of the C(15)–C(16) double bond [6].

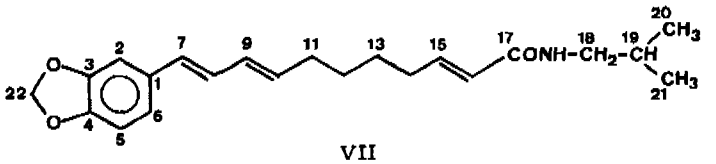
Piperstachine readily afforded the *Diels-Alder* addition product with maleic anhydride indicating a *trans*-diene system of two olefinic double bonds [7]. Only three structures (V), (VI) and (VII) should then be considered for the alkaloid.



V

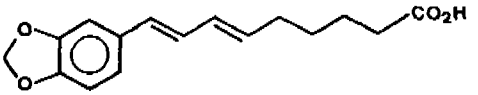


VI

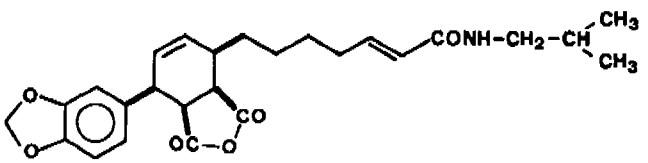


VII

The UV. spectrum of V would be expected to show maxima at 286 nm due to the methylenedioxyphenyl group [8] and 297 nm due to the conjugated triene amide [9]. Structure VI has two UV. chromophore systems of which the methylenedioxystyryl group would show maxima at 260, 268, 305 nm as in pipataline [10] and the second chromophore, the conjugated diene amide would show a maximum at 258 nm [11]. The diene acid (VIII) [12] was found to resemble closely the spectrum of piperstachine (Fig. 3). The alkaloid has therefore been formulated as (VII) and the maleic anhydride addition product as (IX). The UV. and IR. spectra of (IX) are in accord with this formulation.



VIII



IX

The noise decoupled ^{13}C-NMR. spectrum of piperstachine exhibited 21 strong lines as expected for the 22 carbon atoms (Fig. 4). The highest field signal is double in intensity and originates from the isopropyl methyl carbon atoms. From the off-resonance decoupled spectrum and a careful inspection of the frequency output of both spectra the multiplicities can be determined and these are written above each singlet in the noise decoupled spectrum. There are as expected 4 singlets (s), 10 doublets (d), 6 triplets (t) and one quartet (q). Since the sp^2-carbon region contains

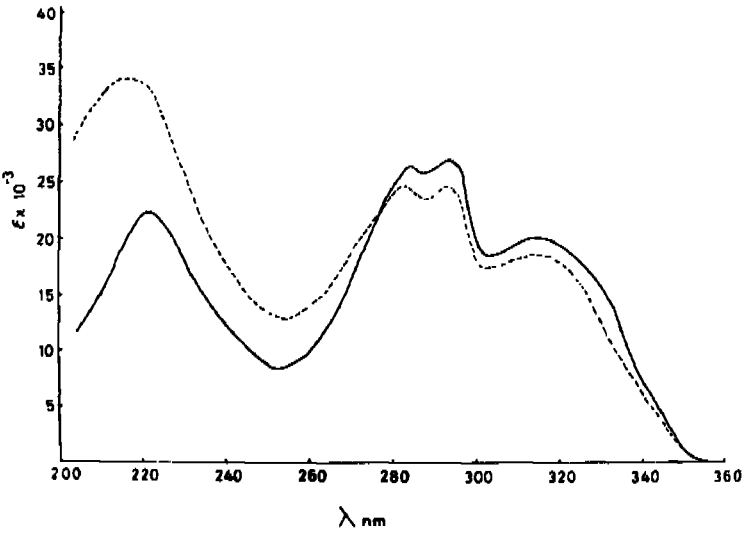


Fig. 3. *UV. spectra of piperstachine (VII)* – – – – – – *and 9-(3,4-methylenedioxyphenyl)-nona-6,8-*trans,trans-*dien-oic acid (VIII)* ————

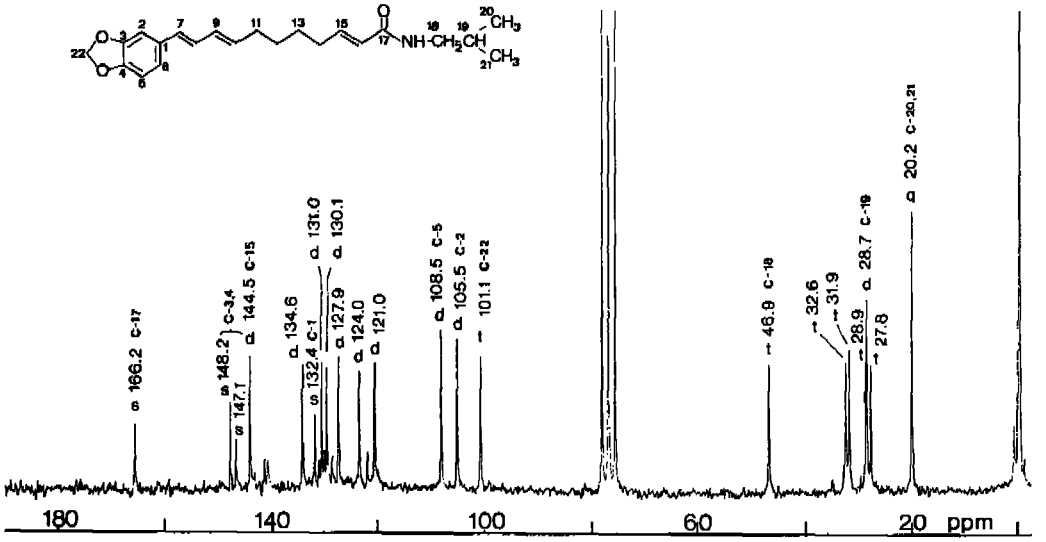
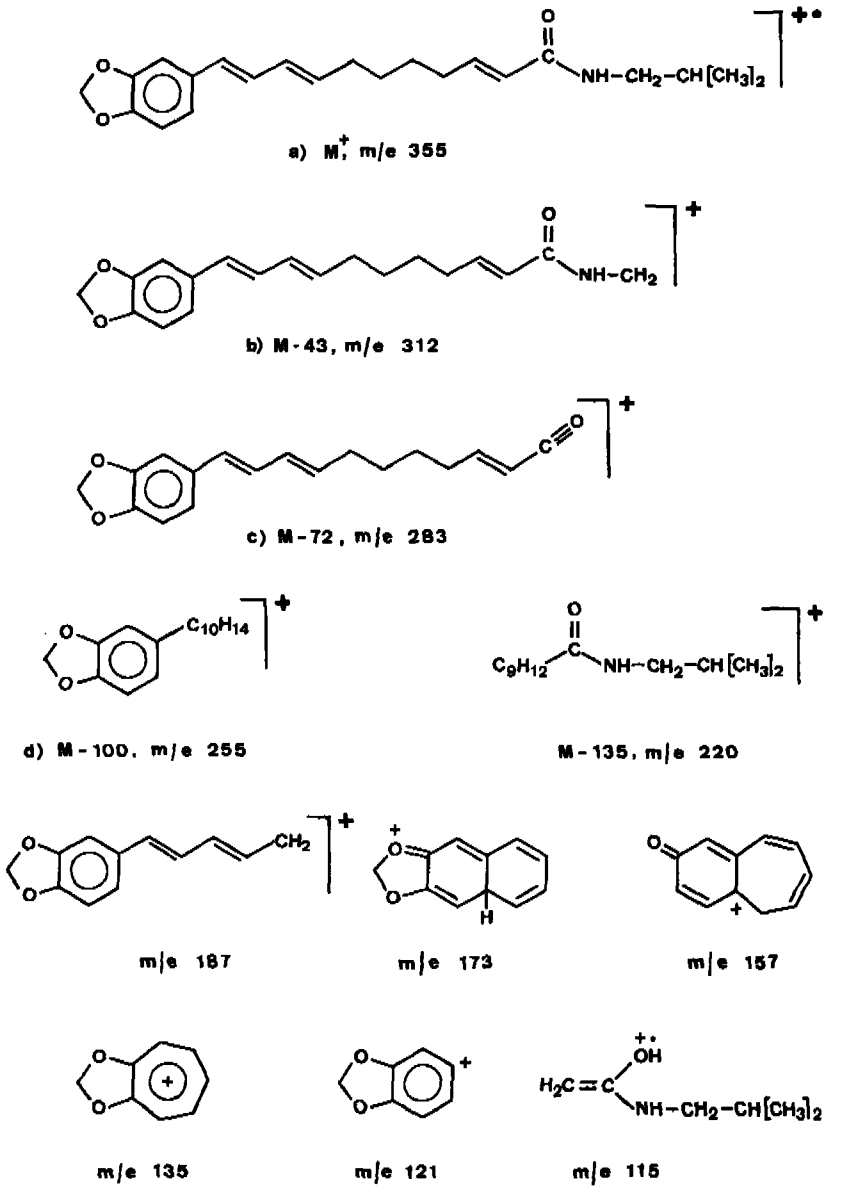


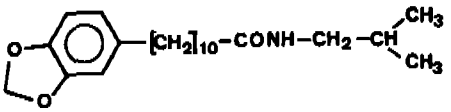
Fig. 4. *Proton noise-decoupled ^{13}C-NMR. spectrum of VII in $CDCl_3$* (conc. 47 mg/2 ml, 118000 transients)

nine doublets and three of these originate from the aromatic ring, there are six vinyl =CH carbon atoms from the three olefinic double bonds. Assignments to individual carbon atoms are given (Fig. 4) as far as possible at the present state of the investigation. It could be noticed that six additional weak signals are observed in the olefinic region. These are probably due to an isomer originating from hindered rotation about the amide bond or due to stereo-isomerism at the olefinic double bonds.



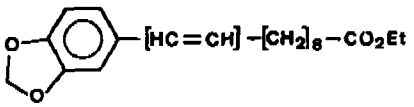
Mass spectral fragmentation of piperstachine

Piperstachine (VII) on hydrogenation absorbed three moles of hydrogen to afford hexahydropiperstachine (X). The structure X was confirmed by an unambiguous synthesis. The chloride [13] of ethyl hydrogen sebacate was reduced with sodium borohydride to the corresponding alcohol [14] [15] which on treatment with phos-

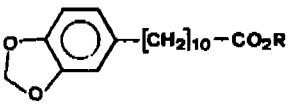


X

phorus tribromide gave ethyl 10-bromodecanoate. The triphenylphosphonium bromide derivative from the bromo-ester on *Wittig* reaction with piperonal afforded ethyl 11-(3,4-methylenedioxyphenyl)-10-undecenoate (XI). The same compound was also obtained by *Wittig* reaction of piperonyltriphenylphosphonium bromide with methyl 9-formylnonanoate [16], ester exchange taking place in presence of sodium



XI



XII : R = Et

XIII : R = H

ethoxide. Hydrogenation of (XI) yielded the saturated ester (XII) which on hydrolysis gave the crystalline acid (XIII) m.p. 76–77°. The acid (XIII) on condensation with isobutylamine in ethylchloroformate and triethylamine gave the amide (X) identical in all respects with hexahydropiperstachine.

The mass spectrum of piperstachine shows the molecular ion peak (a) at *m/e* 355 which loses the isopropyl group to give fragment (b). Loss of isobutylimino and isobutylamide groups from the molecular ion lead to fragment ions (c) and (d) respectively. Some of these fragment ions have been depicted in the following chart.

We wish to thank Professor *T. R. Govindachari* for his interest in the work and Dr. *S. Selvavinayakam* and associates for the analytical data. Part of this work was supported by the *Swiss National Research Foundation.*

Experimental Part

UV. and IR. spectra were determined on *Beckman* model DK-2A and *Perkin-Elmer* model 421 spectrophotometers. MS. were recorded on an *Atlas Varian* Mat CH-7 spectrometer using direct inlet system. ^{13}C-NMR. spectra were measured on an XL-100-15 spectrometer at 25.2 MHz in the pulsed mode, ^{1}H-NMR. spectra including double resonance on an HA-100 instrument. Deuteriochloroform as a solvent and tetramethylsilane as an internal reference were used for both ^{13}C- and ^{1}H-NMR. spectra. To obtain the praseodymium-shifted proton spectrum, 4 mg of the shift reagent Pr(fod)$_3$ were dissolved together with ca. 20 mg of the alkaloid in 0.3 ml of $CDCl_3$.

Isolation of piperstachine (VII). Powdered stem of *Piper trichostachyon* (6 kg) was extracted in the cold with hexane (3 × 30 l). The greenish black oil (80 g) obtained after evaporation of the solvent was chromatographed over neutral alumina (2 kg). The column was gradient eluted with

hexane, hexane/benzene and benzene/chloroform. Fractions (300 ml each) were collected and the chromatographic separation monitored by T.L.C. Fractions eluted with benzene (22–27) gave a solid which crystallised from hexane/ether as colourless plates (TLC., silica gel, $CHCl_3$: 2% MeOH; Rf 0.5) (140 mg), m.p. 152°. – IR. (ν_{max}^{KBr}): 3300, 1662, 1620, 1540, 1500, 1450, 1340, 1260, 1220, 1200, 1160, 1100, 1040, 985, 930, 860, 855, 820, 790 and 720 cm^{-1}. – MS.: *m/e* 355 (M^+, 50%), 312 (5), 283 (5), 272 (5), 256 (35), 255 (60), 240 (25), 220 (75), 213 (10), 211 (8), 194 (12), 187 (100), 173 (28), 157 (65), 154 (38), 135 (85), 128 (95), 121 (80), 115 (45).

$C_{23}H_{29}NO_3$ (355.5) Calc. C 74.3 H 8.2 N 3.9% Found C 74.2 H 8.0 N 4.4%

Hexahydropiperstachine (X). Piperstachine (6 mg) was hydrogenated over 5% Pd/C (20 mg) in ethanol (5 ml). Removal of the solvent gave a gum which crystallised from hexane to give colourless needles, m.p. 78°. – UV. (λ_{max}^{EtOH}): 233, 287 nm (log ε 3.64, 3.60). – IR. (ν_{max}^{KBr}): 3320, 1645, 1550, 1500, 1490, 1470, 1445, 1385, 1370, 1350, 1300, 1260, 1250, 1235, 1220, 1190, 1160, 1120, 1100, 1040, 940, 920, 860, and 810 cm^{-1}. – MS. (*m/e*): 361 (M^+, 45%), 318 (5), 305 (4), 289 (14), 226 (7), 148 (7), 135 (100), 128 (40), 115 (50).

Maleic anhydride addition to piperstachine to give IX. Piperstachine (7 mg) and maleic anhydride (2 mg) were heated with benzene (0.5 ml) in a sealed tube at 80–85° for 3 h. The tube was cooled, opened and the crystalline residue collected and washed with benzene (5 mg), m.p. 185–187°. UV. (λ_{max}^{EtOH}): 286 nm (log ε 3.66). – IR. (ν_{max}^{KBr}): 3340, 1850, 1772, 1670, 1625, 1550, 1505, 1490, 1448, 1370, 1280, 1260, 1235, 1175, 1030, 980 and 940 cm^{-1}. – MS. (*m/e*): 453 (M^+, 20%), 438 (5), 410 (10), 381 (100), 353 (15), 335 (20), 307 (18), 281 (15), 266 (25), 211 (70), 183 (60).

Synthesis of hexahydropiperstachine (X). – 1. *Ethyl 10-hydroxydecanoate*: A solution of the chloride [13] of ethyl hydrogen sebacate (15 g) in dry dioxane (80 ml) was cooled in ice, stirred and treated with $NaBH_4$ (4 g) in portions. After keeping at 0–10° for 1 h, the solution was kept at room temperature (RT.) for 3 h and treated with ice and a few drops of dil. acetic acid. Extraction with methylene chloride gave the hydroxyester (13 g), b.p. 150°/2 mm. – IR. (ν_{max}^{neat}): 3420, 1730 cm^{-1}. – ^{1}H-NMR. (CCl_4): δ [ppm] 5.13 (1 H, br. *s*, OH); 4.08 (2 H, *q*, J = 7); 3.5 (2 H, *t*, J = 6); 2.23 (2 H, *t*, J = 7).

$C_{12}H_{24}O_3$ (216.3) Calc. C 66.6 H 11.2% Found C 66.4 H 11.2%

The ester has been prepared earlier by other methods [14] [15].

2. *Ethyl 10-bromodecanoate*. To the foregoing hydroxyester (13 g) in dioxane (50 ml) was added PBr_3 (5.2 g) and the solution refluxed for 1.5 h. Addition of ice and extraction with methylene chloride gave the bromoester (9 g), b.p. 140° (bath temp.)/0.5 Torr. – IR. (ν_{max}^{neat}): 1735 cm^{-1}. – ^{1}H-NMR. (CCl_4): δ [ppm] 4.1 (2 H, *q*, J = 7); 3,37 (2 H, *t*, J = 7); 2.22 (2 H, *t*, J = 7). – MS. (*m/e*): 278, 280 (M^+).

$C_{12}H_{23}BrO_2$ (279.2) Calc. C 51.6 H 8.3% Found C 51.4 H 8.5%

3. *Ethyl 11-(3,4-methylenedioxyphenyl)-10-undecenoate* (XI). a) A solution of triphenylphosphine (5.25 g) and the above bromoester (5.5 g) in benzene (60 ml) was refluxed for 3 h. The solvent was removed *in vacuo*, the residual gum washed with hexane, dried *in vacuo* at 80° and used as such for the *Wittig* reaction. The phosphonium bromide (5.41 g) in dimethyl formamide (15 ml) was added to a stirred solution of sodium (0.23 g) in ethanol (10 ml) in N_2 atm. After stirring at RT. for 5 min, piperonal (1.5 g) was added and the solution stirred overnight. The solution was evaporated *in vacuo* and the residue triturated with ether/hexane. The insoluble triphenylphosphine oxide was filtered off, the filtrate evaporated and the residue chromatographed over silica gel in hexane. Elution with hexane/ether 9:1 gave the ester (2.3 g), b.p. 250° (bath temp.)/1 Torr. – IR. (ν_{max}^{neat}): 1740, 1600, 1500, 1040, 965, 935 cm^{-1}. – ^{1}H-NMR. (CCl_4): δ [ppm] 6.5–6.8 (3 H, *m*, Ar-H); 5.2–6.4 (2 H, *m*, vinylic H); 5.85 (2 H, *s*, —O—CH_2—O—); 4.05 (2 H, *q*, J = 7); 2.2 (4 H, *t*, J = 6); 1–1.8 (15 H, *m*, aliph.).

$C_{20}H_{28}O_4$ (332.4) Calc. C 72.3 H 8.5% Found C 71.9 H 8.5%

b) To a suspension of triphenylpiperonylphosphononium bromide [3] (4.9 g) (dried at 100°/1 Torr) in dimethyl formamide (10 ml), stirred in N_2 atm, was added a solution of sodium (0.23 g)

in ethanol (6 ml). After stirring for 3 min, a solution of methyl 9-formylnonanoate [16] (2.3 g) in dimethyl formamide (3 ml) was added. The solution was stirred overnight at RT. and worked-up as above to get the unsaturated ester (2.2 g) identical with the above product.

4. *Ethyl 11-(3,4-methylenedioxyphenyl)undecanoate* (XII). The above ester (2 g) in ethyl acetate (50 ml) was reduced with hydrogen at 1 atm and RT. in presence of platinum oxide (0.2 g) for 4 h to yield the saturated ester (2 g), b.p. 220° (bath temp./1 Torr). – IR. (ν_{max}^{neat}): 1740, 1600, 1040, 940 cm^{-1}. – ^{1}H-NMR. (CCl_4): δ [ppm] 6.4–6.8 (3 H, *m*); 5.8 (2 H, *s*); 4.05 (2 H, *q*, $J = 7$); 2–2.6 (4 H, *m*); 1–1.8 (19 H, *m*).

$C_{20}H_{30}O_4$ (334.5) Calc. C 71.8 H 9.0% Found C 71.6 H 9.2%

5. *11-(3,4-Methylenedioxyphenyl)undecanoic acid* (XIII). The above ester (1.5 g) was refluxed for 1 h with aqueous methanolic sodium hydroxide (10%; 15 ml), the solvent evaporated, acidified and extracted with ether to yield the acid (1.3 g), m.p. 76–77° (from ether/hexane). – IR. (ν_{max}^{nujol}): 2600–2800 (br), 1710 cm^{-1}. – MS. (*m/e*): 306 (M^+, 70%), 135 (100).

$C_{18}H_{26}O_4$ (306.4) Calc. C 70.6 H 8.6% Found C 70.8 H 8.8%

6. *Hexahydropiperstachine* (X). A solution of the above acid (0.9 g) in benzene (35 ml) was stirred at 0° in N_2 atm and treated with triethylamine (0.6 ml). After 10 min, ethyl chloroformate (0.4 ml) was added and stirred at 0–10° for 2 h. Isobutylamine (1.0 ml) was added, the solution stirred for 2 h at RT. and finally warmed at 50–60° for 15 min. The solution was washed with 1N hydrochloric acid and water, dried, evaporated and the residue crystallised from ether/hexane to yield the amide (0.9 g), m.p. 78–79° identical (TLC., mixed m.p., UV., IR., MS.) with hexahydropiperstachine. – ^{1}H-NMR. ($CDCl_3$): δ [ppm] 6.4 6.8 (3 H, *m*); 5.9 (3 H, *s*, —O · CH_2 · O–, NH); 3.1 (2 H, *t*, J = 6); (*d*, J = 6, after addition of D_2O) (· 11N—CH_2–); 2–2.7 (4 H, *m*); 1.1–1.9 (17 H, *m*); 0.9 (6 H, *d*, J = 6).

$C_{22}H_{35}NO_3$ (361.5) Calc. C 73.1 H 9.8 N 3.9% Found C 73.5 H 10.0 N 3.9%

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