*Methyl-substituted αβ-Unsaturated Acids. Part II.**

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In connection with studies of mycolipenic acid several long-chain methyl-substituted αβ-unsaturated acids have been prepared and converted, *via* the amides and dimethylamides, into the amines and dimethylamines, respectively.

In previous communications (Bailey, Polgar, and Robinson, *J.*, 1953, 3031; Polgar, *J.*, 1954, 1008) mycolipenic acid, from the lipids of tubercle bacilli, was shown to be (+)-2 : 4 : 6-trimethyltetracos-2-enoic acid. It was of interest to study the effect of modifications in the structural features of this acid on the biological activity, and the present paper describes syntheses of 2-methyloctadec-2-enoic (I; $n = 14$), 2-methyleicos-2-enoic (I; $n = 16$), 2 : 4-dimethyleicos-2-enoic (II; $n = 15$), and 2 : 4-dimethyldocos-2-enoic acid (II; $n = 17$). The acids were obtained from the corresponding saturated acids by α-bromination, followed by reaction with methanol and dehydrobromination of the resulting bromo-ester by means of pyridine according to the procedure given in Part I.* Of the requisite saturated acids, the preparations of 2-methyleicosanoic and 2 : 4-dimethyldocosanoic acid have already been reported (Bailey, Polgar, and Robinson, *loc. cit.*), and 2-methyloctadecanoic and 2 : 4-dimethyleicosanoic acid were obtained by analogous procedures.

(I) $CH_3 \cdot [CH_2]_n \cdot CH{:}CMe \cdot CO_2H$ $\qquad$ $CH_3 \cdot [CH_2]_n \cdot CHMe \cdot CH{:}CMe \cdot CO_2H$ (II)

It has been shown in Part I* that dehydrobromination of methyl (—)-2-bromo-2 : 4 : 8-trimethylnonanoate (optically active in respect of $C_{(4)}$) by pyridine, followed by hydrolysis of the resulting unsaturated ester, gave an optically active acid which, judged by its extinction coefficient in the ultraviolet, appeared to be essentially αβ-unsaturated. The formation of a βγ-ethylenic linkage would result in the loss of the original asymmetric centre at $C_{(4)}$. Since a βγ-unsaturated acid is more readily esterified than the αβ-unsaturated isomer (cf. Sudborough and Thomas, *J.*, 1911, **99**, 2307), we have submitted a specimen of the above optically active acid to partial esterification with a view to examine the optical rotation of the remaining acidic fraction. The latter exhibited the same rotatory power as the initial product, thus indicating that the pyridine dehydrobromination yielded only the αβ-unsaturated isomer. In comparative studies with the bromo-ester from 2-methyloctadecanoic acid, pyridine dehydrobromination, followed by hydrolysis of the resulting unsaturated ester, gave 2-methyloctadec-2-enoic acid (I; $n = 14$), m. p. 64° (log $\varepsilon_{max.}$ 4·11 at 2160 Å), whereas dehydrobromination by means of quinoline yielded the acid with a somewhat lower m. p. of 63·5° (log $\varepsilon_{max.}$ 4·07 at 2160 Å), and diethylaniline dehydrobromination gave an acid having m. p. 58° (log $\varepsilon_{max.}$ 3·90 at 2180 Å) which, thus, appeared only partly αβ-unsaturated. Therefore, pyridine seemed the most satisfactory of the organic

* Part I, *J.*, 1953, 132.

bases employed. Some dehydrobrominations involving the action of ethanolic potassium hydroxide are included in the Experimental section.

It was of interest to examine the physiological properties of water-soluble derivatives of the synthetic acids. For comparative studies 2-methyleicos-2-enoic, 2 : 4-dimethyldocos-2-enoic, and the corresponding saturated acids were converted into the amides and dimethylamides which, on reduction with lithium aluminium hydride, afforded the corresponding amines. It has been reported (Uffer and Schlittler, *Helv. Chim. Acta*, 1948, **31**, 1397) that α-ethylcrotonamide on treatment with lithium aluminium hydride for 20 hr. yields the corresponding saturated amine. However, in the present work refluxing ethereal solutions of the αβ-unsaturated amides with lithium aluminium hydride for periods not exceeding 2 hr. (Brown, " Organic Reactions," John Wiley & Sons, Inc., New York, 1951, Vol. VI, p. 469; Micovic and Mihailovic, *J. Org. Chem.*, 1953, **18**, 1190) did not appear to affect the double bond.

The physiological studies were carried out by Dr. J. Ungar of Glaxo Laboratories Ltd. On intraperitoneal injection into guinea pigs, 2-methyloctadec-2-enoic acid (I; $n = 14$) produced discrete nodules of cheesy consistency in the organs of the peritoneal cavity; the effects were transitory. 2 : 4-Dimethyleicos-2-enoic acid (II; $n = 15$) acted as a non-specific irritant. 2 : 4-Dimethyldocos-2-enoic acid (II; $n = 17$) showed very low activity in producing a non-specific reaction.

Of the unsaturated amines, the hydrochlorides of 2-methyleicos-2-enylamine (III) and 2 : 4-dimethyldocos-2-enylamine (V) were very active in producing lesions of the granulomatous type in abdominal organs with marked lymphatic spread. 2-Methyleicos-2-enyldi-

(III) $CH_3{\cdot}[CH_2]_{16}{\cdot}CH{:}CMe{\cdot}CH_2{\cdot}NH_2,HCl$ $CH_3{\cdot}[CH_2]_{17}{\cdot}CHMe{\cdot}CH{:}CMe{\cdot}CH_2{\cdot}NH_2,HCl$ (V)

(IV) $CH_3{\cdot}[CH_2]_{16}{\cdot}CH{:}CMe{\cdot}CH_2{\cdot}NMe_2,HCl$ $CH_3{\cdot}[CH_2]_{17}{\cdot}CHMe{\cdot}CH{:}CMe{\cdot}CH_2{\cdot}NMe_2,HCl$ (VI)

methylamine hydrochloride (IV) was only an irritant, and 2 : 4-dimethyldocos-2-enyldimethylamine hydrochloride (VI) was inactive.

The hydrochlorides of the saturated amines corresponding to (III)—(VI) were all active.

Experimental

The absorption spectra were measured by Mr. F. Hastings and Dr. F. B. Strauss. Ultraviolet spectra were determined in methanol.

Partial Esterification of (−)-2 : 4 : 8-*Trimethylnon-2-enoic Acid*.—For the preparation of the acid the procedure described in Part I (*loc. cit.*) was employed, except that the starting material, (+)-citronellal, was purified by Tiemann's procedure (*Ber.*, 1899, **32**, 812), and the intermediate bromo-ester, *methyl* (−)-2-*bromo*-2 : 4 : 8-*trimethylnonanoate* was isolated by distillation. It had b. p. 136—139°/9 mm., $[\alpha]_D^{15}$ −6·7° (homog.), d_4^{15} 1·139, n_D^{19} 1·4627 (Found : C, 53·0; H, 8·4; Br, 27·2. $C_{13}H_{25}O_2Br$ requires C, 53·2; H, 8·5; Br, 27·3%), and gave on pyridine dehydrobromination, followed by hydrolysis of the resulting unsaturated ester, (−)-2 : 4 : 8-trimethylnon-2-enoic acid (Found : C, 72·9; H, 11·2. Calc. for $C_{12}H_{22}O_2$: C, 72·7; H, 11·1%) having $[\alpha]_D^{17}$ −25·6° (*c*, 10·07 in ether; *l*, 0·5), a slightly higher value than that previously found (*loc. cit.*). The acid (2·7 g.) was kept with 5% (w/v) methanolic sulphuric acid (30 c.c.) at the room temperature for 0·5 hr. The mixture was then diluted with water and extracted with ether from which the acidic fraction was removed with 5% aqueous potassium carbonate. Acidification of the alkaline extract and ether-extraction, followed by distillation, gave the unesterified portion of the original acid (2 g.), $[\alpha]_D^{14}$ −25·8° (*c*, 9·99 in ether; *l*, 0·5). The recovered acid (1 g.) was refluxed with 2·5% (w/v) methanolic sulphuric acid (30 c.c.) for 8 min., and the acidic product separated from the ester fraction (0·21 g.) as above. The acid had $[\alpha]_D^{15}$ −25·7° (*c*, 10·20 in ether; *l*, 0·5).

2-*Methyloctadec-2-enoic Acid* (I; $n = 14$).—2-Methyloctadecanoic acid was obtained essentially as described previously for the preparation of 2-methyleicosanoic acid (Bailey, Polgar, and Robinson, *loc. cit.*). Hexadecan-1-ol (97 g.; b. p. 166°/2 mm.) was converted by reaction with iodine (52 g.) and red phosphorus (5 g.) into the iodide (122·5 g.), b. p. 206—207°/10 mm., which was condensed with the sodio-derivative of ethyl methylmalonate (from 8·4 g. of sodium, 66 g. of ethyl methylmalonate, and 205 c.c. of ethanol), the mixture being heated under reflux for 9 hr. The usual successive stages (hydrolysis, decarboxylation) afforded the acid (80 g.), b. p. 200—201°/2 mm., m. p. 55° (Found : C, 76·0; H, 12·7. Calc. for $C_{19}H_{38}O_2$: C, 76·5; H, 12·8%).

Its amide, after crystallisation from ethanol, had m. p. 105° (Found : C, 76·1; H, 13·1; N, 4·9. Calc. for $C_{19}H_{39}ON$: C, 76·6; H, 13·2; N, 4·7%). The p-*bromophenacyl ester*, crystallised from ethanol–methanol, had m. p. 83—83·5° (Found : C, 65·3; H, 8·8; Br, 16·4. $C_{27}H_{43}O_3Br$ requires C, 65·5; H, 8·7; Br, 16·1%). Schneider and Spielman (*J. Biol. Chem.*, 1942, **142**, 345) give m. p. 54·55° for the acid, and m. p. 104·5° for the amide.

The preceding acid (50 g.) was heated with bromine (98 g.) in the presence of red phosphorus (5·2 g.) for 7·5 hr., as already described for similar cases (Part I, *loc. cit.*), and the resulting crude acid bromide converted, by means of methanol (50 c.c.), into *methyl 2-bromo-2-methyloctadecanoate* (55·7 g.), b. p. 190—192°/0·5 mm., n_D^{19} 1·4656 (Found : C, 61·9; H, 9·9; Br, 20·2. $C_{20}H_{39}O_2Br$ requires C, 61·4; H, 10·0; Br, 20·45%).

A 7-g. portion of this bromo-ester was refluxed with anhydrous pyridine (33 g.) for 19 hr. *Methyl 2-methyloctadec-2-enoate* was obtained as an oil (4·4 g.), b. p. 159—163°/0·2 mm., n_D^{17} 1·4599, log $\varepsilon_{max.}$ 4·08 at 2180 Å (Found : C, 77·7; H, 12·3. $C_{20}H_{38}O_2$ requires C, 77·4; H, 12·3%). The corresponding *acid*, obtained by refluxing the unsaturated ester (3·2 g.) with a solution of potassium hydroxide (2 g.) in ethanol (30 c.c.) and water (5 c.c.) for 75 min., distilled at 195—197°/0·35 mm. (2·8 g.) and had m. p. 64° (Found : C, 77·4, H, 12·5. $C_{19}H_{36}O_2$ requires C, 77·0; H, 12·3%). Ultraviolet absorption : log $\varepsilon_{max.}$ 4·11 at 2160 Å. Infrared absorption : 1647 and 1697 cm.$^{-1}$ (–C:C–C:O). The *amide*, after crystallisation from ethanol, had m. p. 82° (Found : C, 77·0; H, 12·2; N, 4·5. $C_{19}H_{37}ON$ requires C, 77·3; H, 12·5; N, 4·7%).

When the above bromo-ester (7 g.) was heated with pyridine (26·5 g.) on a steam-bath for 6 hr., and kept at the room temperature for another 36 hr., the product was found on analysis to contain considerable amounts of bromine (Found : C, 64·0; H, 10·5; Br, 15·7%).

Comparative Dehydrobromination Experiments.—(i) Methyl 2-bromo-2-methyloctadecanoate (7 g.) and quinoline (25 g.; freshly distilled over potassium hydroxide) were gently refluxed for 0·5 hr. After dilution with water, the product was collected with ether, and distilled in steam until free from quinoline. The residue, isolated with the aid of ether, had been partly hydrolysed to the acid. It was refluxed with potassium hydroxide (3 g.) in ethanol (50 c.c.) and water (7 c.c.) for 2 hr., and the product worked up in the usual manner. Distillation afforded 2-methyloctadec-2-enoic acid (4·7 g.), log $\varepsilon_{max.}$ 4·07 at 2160 Å, m. p. 63·5° after crystallisation from methanol (Found : C, 77·2; H, 12·1%).

(ii) The above bromo-ester (7 g.) was refluxed with diethylaniline (25 g.; freshly distilled over potassium hydroxide) for 2 hr., and then added to 10% hydrochloric acid (300 c.c.). The product was isolated by means of ether and freed from diethylaniline by washing with 10% hydrochloric acid, and then with water. Distillation gave the unsaturated ester (4·1 g.), b. p. 155—161°/0·15 mm., n_D^{17} 1·4569, log $\varepsilon_{max.}$ 3·93 at 2180 Å (Found : C, 77·1; H, 12·6%). The corresponding acid, obtained by refluxing the ester with 5% ethanolic potassium hydroxide for 1·5 hr., and isolated by distillation, had m. p. 58° (Found : C, 77·4; H, 12·2%). It exhibited log $\varepsilon_{max.}$ 3·90 at 2180 Å, and its infrared spectrum showed absorption bands at 1647 and 1697 cm.$^{-1}$ with an inflection at 1718 cm.$^{-1}$.

(iii) The bromo-ester (8 g.) was added to a solution of potassium hydroxide (8 g.) in ethanol (36 c.c.) and water (4 c.c.), and the mixture kept at the room temperature for 20 hr. The solution, containing a voluminous precipitate of potassium bromide, was diluted with water, acidified (10% hydrochloric acid), and extracted with ether. The product (5·7 g.), b. p. 180—195°/0·07 mm., was a wax-like solid, m. p. 44—48° (Found : C, 75·1; H, 12·1%), log $\varepsilon_{max.}$ 3·71 at 2140 Å, representing a mixture of unsaturated acids and the α-hydroxy-acid. Accordingly, it gave on oxidation with lead tetra-acetate octadecan-2-one, isolated as its semicarbazone, m. p. 125·5—126° after crystallisation from ethanol (Found : C, 70·4; H, 12·1; N, 12·7. Calc. for $C_{19}H_{39}ON_3$: C, 70·15; H, 12·0; N, 12·9%).

(iv) A solution of methyl (–)-2-bromo-2 : 4 : 8-trimethylnonanoate (4 g.) and potassium hydroxide (4 g.) in ethanol (18 c.c.) and water (2 c.c.) was kept at the room temperature for 18 hr. (within a few minutes there was a considerable precipitate of potassium bromide). Acidification with 5% hydrochloric acid, followed by extraction with ether and distillation, gave a product (2·7 g.), b. p. 150—165°/14 mm., which had no measurable rotation (*c*, 54 in ether; *l*, 0·5). Light absorption : log $\varepsilon_{max.}$ 3·66 at 2100 Å. It was chromatographed in light petroleum (b. p. 40—60°; 100 c.c.) on a silica column (35 × 1 cm.), prepared in the same solvent. Two main fractions were obtained; the first (0·8 g.) was eluted by light petroleum, and the second (0·7 g.) by methanol–benzene (1 : 10). The former, a mixture of unsaturated acids, distilled at 165°(bath)/12 mm. as an oil (Found : C, 72·6; H, 11·2. Calc. for $C_{12}H_{22}O_2$: C, 72·7; H, 11·1%), light absorption : log $\varepsilon_{max.}$ 3·88 at 2140 Å, and had no rotation in ethereal solution. The second fraction, a wax-like solid, was a hydroxy-acid [Found : active hydrogen

(Zerewitinoff), 0·8. Calc. for $C_{12}H_{24}O_3$: 0·9%]. It showed no high-intensity absorption in the ultraviolet (2050—2400 Å).

2-*Methyleicos*-2-*enoic Acid* (I; $n = 16$).—2-Methyleicosanoic acid (20 g.; Bailey, Polgar, and Robinson, *loc. cit.*) was heated with bromine (30 g.) in the presence of red phosphorus (1·61 g.) for 8 hr. in the manner already described. Next day anhydrous methanol (100 c.c.) was added, and the mixture refluxed for 3 hr. The crude bromo-ester was then refluxed with pyridine (100 c.c.) for 16 hr. and the resulting mixture poured into dilute hydrochloric acid. Isolation with ether gave *methyl* 2-*methyleicos*-2-*enoate* (16 g., 77%) as a colourless liquid, b. p. 172°/0·08 mm. (Found: C, 77·8; H, 12·5. $C_{22}H_{42}O_2$ requires C, 78·2; H, 12·4%). This was refluxed with a solution of potassium hydroxide (6 g.) in water (30 c.c.) and ethanol (60 c.c.) for 5 hr. On cooling, the potassium salt of the acid separated and was collected. It was then dissolved in hot water, and the solution acidified with hydrochloric acid, yielding 2-*methyleicos*-2-*enoic acid* which crystallised from ethanol in fine needles, m. p. 70—70·8° (Found: C, 77·3; H, 12·2. $C_{21}H_{40}O_2$ requires C, 77·8; H, 12·4%). Light absorption: log $\varepsilon_{max.}$ 4·13 at 2180 Å. The *amide*, prepared *via* the acid chloride (obtained by means of purified thionyl chloride) in the usual manner, had m. p. 88—88·5° (Found: C, 78·2; H, 12·7; N, 4·2. $C_{21}H_{41}ON$ requires C, 78·0; H, 12·7; N, 4·3%). The *dimethylamide*, obtained from the acid chloride by reaction with 33% aqueous dimethylamine, distilled at 203—210°(bath)/0·04 mm., and had m. p. 27—27·5° (Found: C, 78·0; H, 12·6; N, 4·2. $C_{23}H_{45}ON$ requires C, 78·6; H, 12·9; N, 4·0%).

The corresponding saturated acid, 2-methyleicosanoic acid (see above), gave an amide, m. p. 107—107·5° (from ethanol) (Found: C, 77·8; H, 13·2; N, 4·2. Calc. for $C_{21}H_{43}ON$: C, 77·5; H, 13·2; N, 4·3%). Its *dimethylamide* crystallised from methanol in fine needles, m. p. 56—57° (Found: C, 78·0; H, 13·2; N, 4·1. $C_{23}H_{47}ON$ requires C, 78·1; H, 13·3; N, 4·0%).

2 : 4-*Dimethyleicos*-2-*enoic Acid* (II; $n = 15$).—2 : 4-*Dimethyleicosanoic acid* was prepared from 2-methyloctadecanoic acid as described for the preparation of 2 : 4-dimethyldocosanoic acid (Bailey, Polgar, and Robinson, *loc. cit.*). The intermediate, 2-*methyloctadecan*-1-*ol*, b. p. 163—165°/0·1 mm., m. p. 48—48·5° (from aqueous ethanol) (Found: C, 80·1; H, 14·1. $C_{19}H_{40}O$ requires C, 80·3; H, 14·1%), was converted into the iodide which by condensation with ethyl methylmalonate afforded *ethyl* 2-*carbethoxy*-2 : 4-*dimethyleicosanoate*, b. p. 198—201°/0·15 mm. (Found: C, 74·3; H, 12·3. $C_{27}H_{52}O_4$ requires C, 73·6; H, 11·8%). This, by the usual successive stages, gave 2 : 4-dimethyleicosanoic acid, b. p. 195—198°/0·15 mm. (Found: C, 78·0; H, 12·9. $C_{22}H_{44}O_2$ requires C, 77·6; H, 12·9%). Its *amide*, after crystallisation from ethanol, had m. p. 79° (Found: C, 78·0; H, 13·4. $C_{22}H_{45}ON$ requires C, 77·9; H, 13·3%).

The preceding acid gave *via* the bromo-acid bromide by the procedure previously described *methyl* 2-*bromo*-2 : 4-*dimethyleicosanoate*, b. p. 194—199°/0·1 mm. (Found: C, 63·5; H, 10·3; Br, 18·7. $C_{23}H_{45}O_2Br$ requires C, 63·7; H, 10·4; Br, 18·3%). This, on pyridine dehydrobromination, followed by hydrolysis of the resulting unsaturated ester, afforded 2 : 4-*dimethyleicos*-2-*enoic acid*, b. p. 199—201°/0·1 mm., m. p. 53—54° (Found: C, 78·1; H, 12·3. $C_{22}H_{42}O_2$ requires C, 78·1; H, 12·4%), log $\varepsilon_{max.}$ 4·07 at 2140 Å. The *amide*, after crystallisation from ethanol, had m. p. 82° (Found: C, 78·4; H, 12·6; N, 4·1. $C_{22}H_{43}ON$ required C, 78·3; H, 12·8; N, 4·2%).

2 : 4-*Dimethyldocos*-2-*enoic Acid* (II; $n = 17$).—2 : 4-Dimethyldocosanoic acid (Bailey, Polgar, and Robinson, *loc. cit.*) on α-bromination, followed by pyridine dehydrobromination as described above for similar cases, afforded methyl 2 : 4-dimethyldocos-2-enoate, b. p. 172—176°/0·07 mm., which was hydrolysed to 2 : 4-*dimethyldocos*-2-*enoic acid*, m. p. 63·5—64° (from light petroleum, b. p. 40—60°) (Found: C, 78·9; H, 12·6. $C_{24}H_{46}O_2$ requires C, 78·7; H, 12·6%), log $\varepsilon_{max.}$ 4·13 at 2160 Å. The *amide* formed needles, m. p. 85—85·5° (from ethanol) (Found: C, 79·1; H, 12·5; N, 3·8. $C_{24}H_{47}ON$ requires C, 79·0; H, 12·9; N, 3·8%). The *dimethylamide*, which did not crystallise satisfactorily, distilled at 220° (bath)/0·04 mm. (Found: N, 3·6. $C_{26}H_{51}ON$ requires N, 3·6%).

2 : 4-Dimethyldocosanoic acid (see above) gave an *amide* which crystallised from ethanol in needles, m. p. 77·5—79° (Found: C, 78·3; H, 13·1; N, 3·5. $C_{24}H_{49}ON$ requires C, 78·5; H, 13·4; N, 3·8%). Its *dimethylamide* distilled at 220—224° (bath)/0·04 mm. (Found: C, 78·4; H, 13·1; N, 3·8. $C_{26}H_{53}ON$ requires C, 79·0; H, 13·4; N, 3·5%).

Amines.—A solution of the requisite amide (2 g.) in ether or tetrahydrofuran (100 c.c.) was added dropwise to a suspension of lithium aluminium hydride (0·6 g.) in boiling ether (50 c.c.), the resulting mixture refluxed for 105 min., then cooled, and the excess of lithium aluminium hydride decomposed by the addition of ethyl acetate. A few c.c. of water were then added, followed by " Hyflosupercel " (1 g.). The ethereal solution was decanted from the precipitate, and the latter washed with ether; the solution and washing were combined, dried (Na_2SO_4) and

evaporated. The resulting crude amine was dissolved in light petroleum (b. p. 40—60°), and 10% ethanolic hydrogen chloride added until precipitation was complete. Thus were obtained: 2-*Methyleicosylamine hydrochloride*, fine needles (from acetone–alcohol), m. p. 107·5—108·5° (Found: C, 72·6; H, 13·3; N, 3·7; Cl, 10·3. $C_{21}H_{46}NCl$ requires C, 72·5; H, 13·2; N, 4·0; Cl, 10·2%), 2-*methyleicosyldimethylamine hydrochloride*, needles (from acetone), m. p. 176—178° (Found: C, 73·6; H, 13·3; N, 3·4; Cl, 8·8. $C_{23}H_{50}NCl$ requires C, 73·5; H, 13·3; N, 3·7; Cl, 9·4%), 2-*methyleicos*-2-*enylamine hydrochloride* (III), needles (from acetone), m. p. 109—110° (Found: C, 73·1; H, 13·0; N, 4·0; Cl, 10·1. $C_{21}H_{44}NCl$ requires C, 73·0; H, 12·7; N, 4·0; Cl, 10·3%), 2-*methyleicos*-2-*enyldimethylamine hydrochloride* (IV), needles (from acetone), m. p. 168—169° (Found: C, 73·5; H, 12·6; N, 3·8; Cl, 9·9. $C_{23}H_{48}NCl$ requires C, 73·9; H, 12·9; N, 3·7; Cl, 9·5%), 2 : 4-*dimethyldocosylamine hydrochloride*, needles (from acetone), m. p. 71—73° (Found: C, 73·7; H, 13·2; N, 3·4. $C_{24}H_{52}NCl$ requires C, 73·9; H, 13·4; N, 3·6%), 2 : 4-*dimethyldocosyldimethylamine hydrochloride*, m. p. 151—153° (from acetone) (Found: C, 74·8; H, 13·6; N, 3·2; Cl, 8·3. $C_{26}H_{56}NCl$ requires C, 74·7; H, 13·4; N, 3·4; Cl, 8·5%), 2 : 4-*dimethyldocos*-2-*enylamine hydrochloride* (V), m. p. 58—60° (from acetone) (Found: C, 74·3; H, 12·9; N, 3·4; Cl, 8·1. $C_{24}H_{50}NCl$ requires C, 74·3; H, 12·9; N, 3·6; Cl, 9·2%), and 2 : 4-*dimethyldocos*-2-*enyldimethylamine hydrochloride* (VI), m. p. 147—150° (from acetone) (Found: C, 75·0; H, 12·8; N, 3·3; Cl, 9·0. $C_{26}H_{54}NCl$ requires C, 75·1; H, 13·0; N, 3·4; Cl, 8·6%).

The infrared spectrum of 2 : 4-dimethyldocos-2-enylamine showed a weak band at 1660 cm.$^{-1}$ (C=C) which was absent in case of the corresponding saturated base.

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