CHAPTER IV

SUMMARY AND CONCLUSION

Reduction of 4,4-dimethylcholest-5-en-3-one oxime with lithium aluminum hydride or sodium and butanol-1 has afforded 3β-amino-4-4-dimethylcholest-5-ene as the major product. The ratio of 3β : 3α-amines in the lithium aluminum hydride reduction is considerable greater than in the corresponding sodium and butanol-1 reduction, and this suggests steric approach control in the metal hydride reduction. The different steric outcome in this reduction as compared with metal hydride reduction of steroidal oximes had been suggested to be due to a boat conformation of ring A.

The configurations of 3α-and 3β-amino-4,4-dimethylcholest-5-ene hydrochlorides have been determined by means of NMR and circular dichroism. The NMR spectra of the hydrochlorides, when determined in trifluoroacetic acid, show some interesting chemical shifts for the tertiary methyl protons attached to C_{19}, C_{30}, and C_{31}. Signals have been assigned to these protons, and evidence is provided which suggests that the ammonium group has shielding effect on protons. Further investigation of this effect is suggested.

Attempts to prepare 3-carboxy-4,4-dimethylcholest-5-ene by means of substitution reactions have failed. The results obtained show that elimination and rearrangement of ring A occurs more readily in this compound than substitution.

3β-Amino, 4,4-dimethylcholestane hydrochloride has been

prepared from 4,4-dimethylcholest-5-en-3-one and by catalytic hydrogenation of 3β-amino-4,4-dimethylcholest-5-ene hydrochloride. A 3β-configuration has been assigned to this hydrochloride on the basis of our findings on the reduction of 3-oximino-4,4-dimethylcholest-5-ene. In addition, we have suggested a 3β-configuration for the dimethylamino group of 3β-dimethylamino-4,4-dimethylcholestane which has been prepared by Djerassi.

3α-Amino-4,4-dimethylcholest-5-ene hydrochloride resisted hydrogenation on palladium charcoal, but afforded an isomer when shaken in ethanol with Raney nickel under an atmosphere of hydrogen. The formation of this compound is suggested to involve a carbonium ion rearrangement; support for this postulate has been found in the acid catalysed rearrangement of 3β-acetoxy-4,4-dimethylcholest-5-ene. This latter rearrangement affords two isomeric acetates and possible structures for these compounds are discussed. Evidence suggests that the acetates formed by a "back-bone" rearrangement and a Westphalen's diol type rearrangement are the most likely products of this reaction.

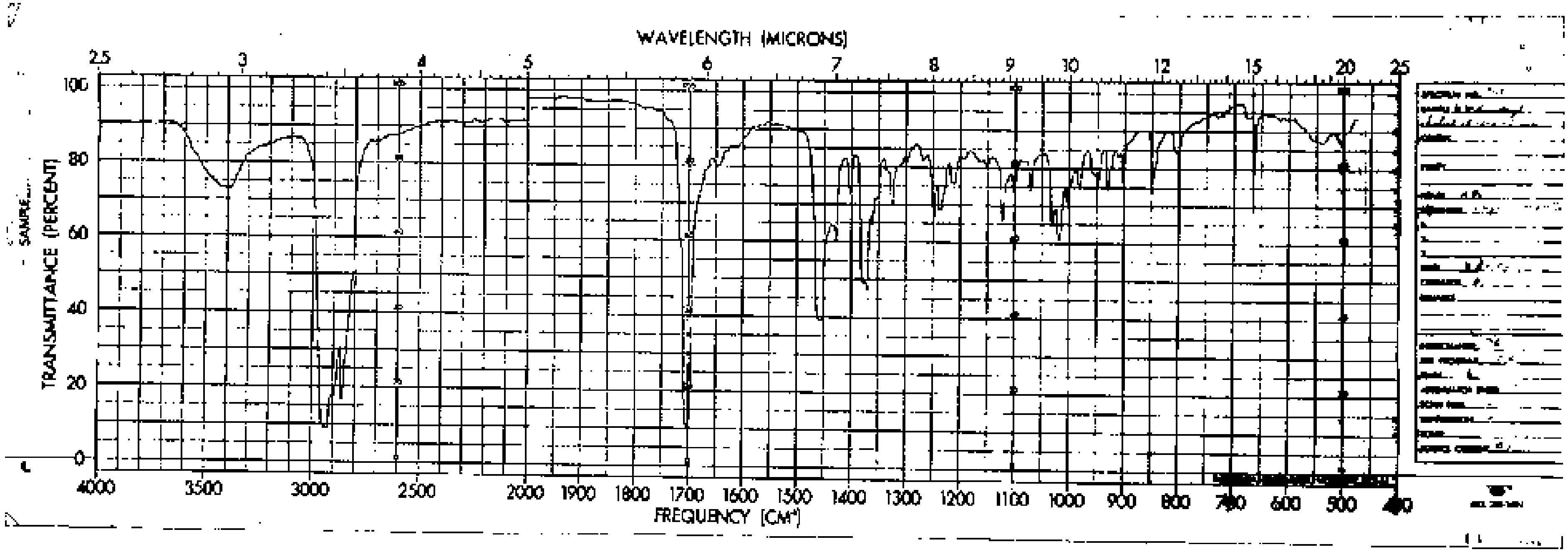

Fig. 1. Infra-red Spectrum of 4,4-Dimethylcholest-5-en-3-one M.P. 170-172°

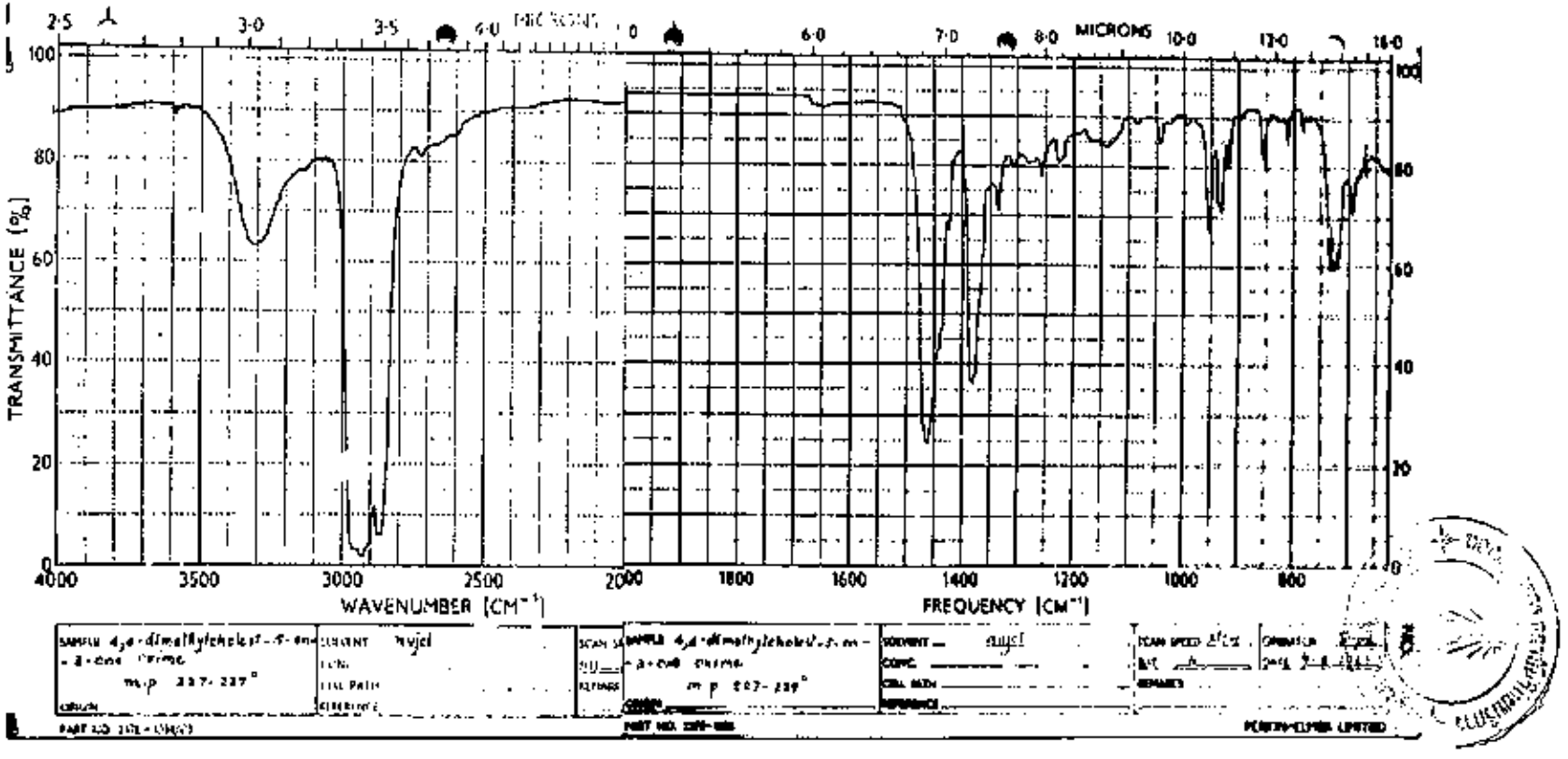

Fig. 2. Infra-red Spectrum of 4,4-Dimethylcholest-5-en-3-one Oxime M.P. 227-229°

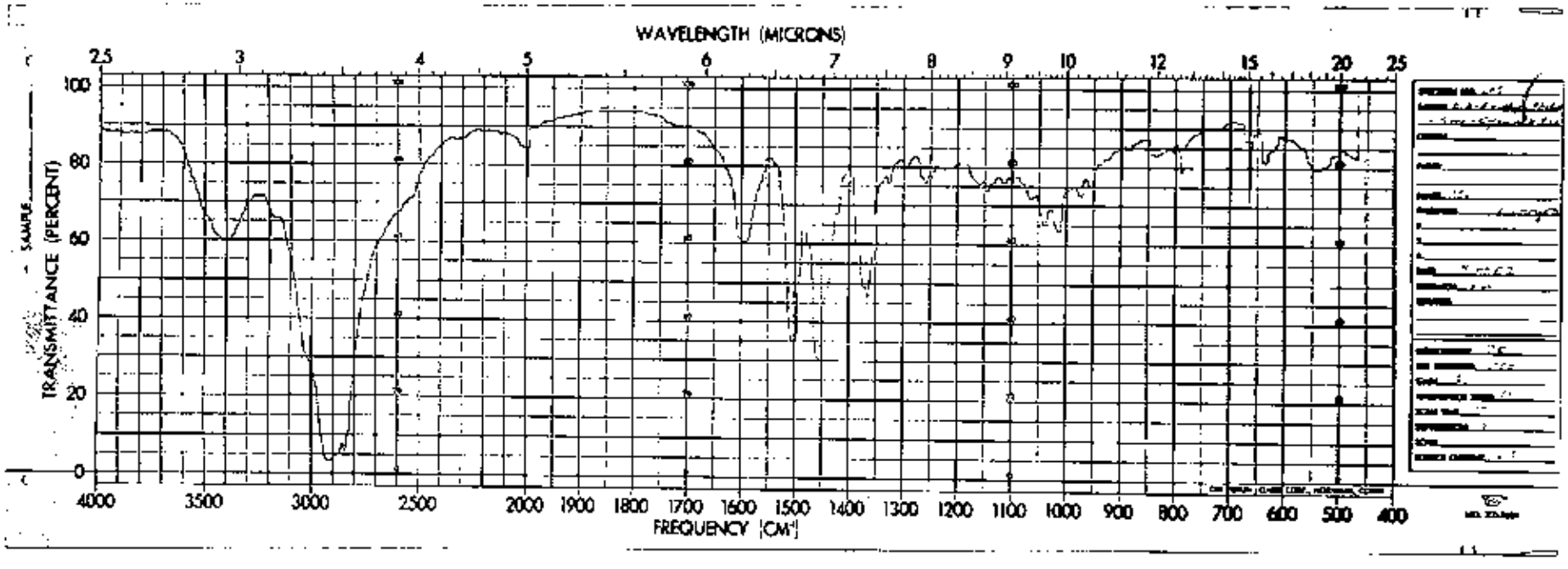

Fig. 3. Infra-red Spectrum of 4,4-Dimethylcholest-5-en-3α-ylamine Hydrochloride M.P. 255° dec.

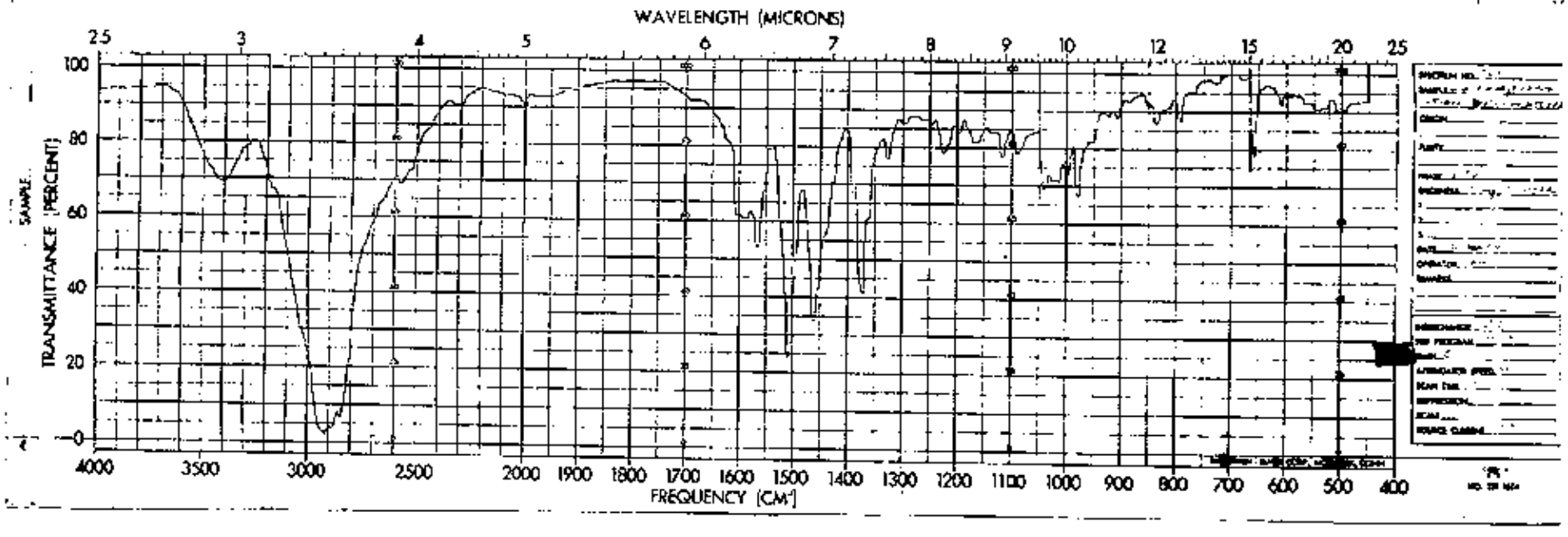

Fig. 4. Infra-red Spectrum of 4,4-Dimethylcholest-5-en-3β-ylamine Hydrochloride M.P. 265° dec.

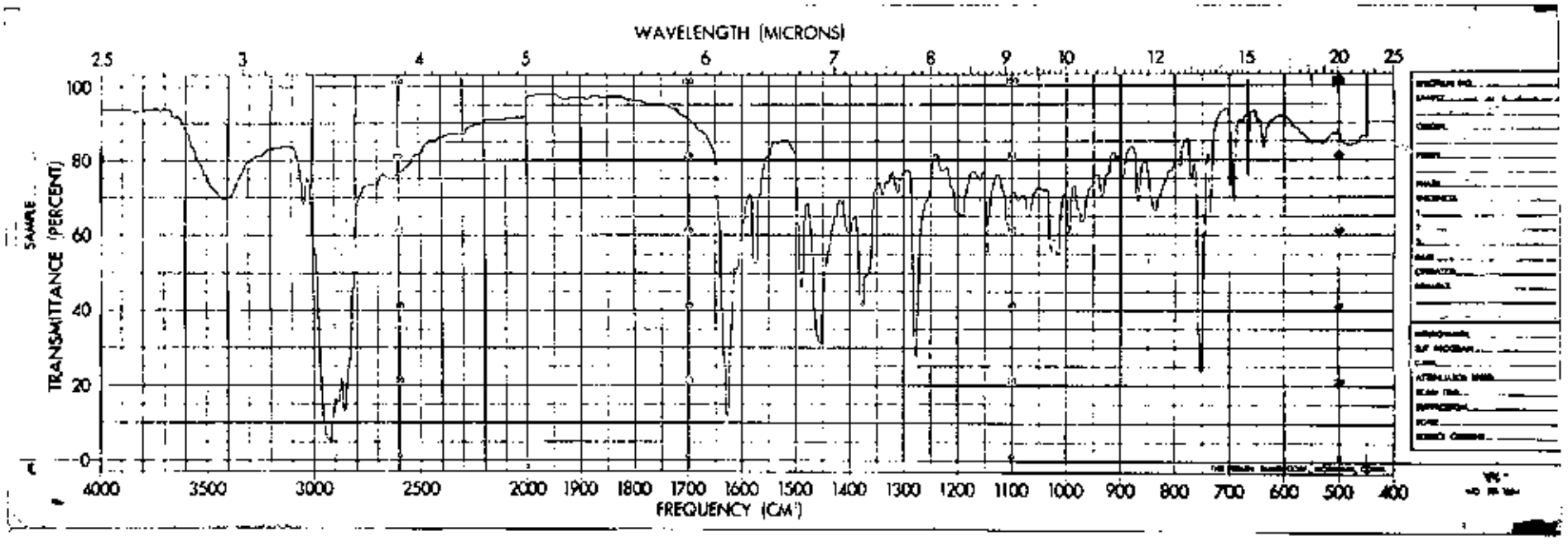

Fig. 5. Infra-red Spectrum of N-Salicylidene Derivative of 4,4-Dimethylcholest-5-en-3α-ylamine M.P. 117-118°

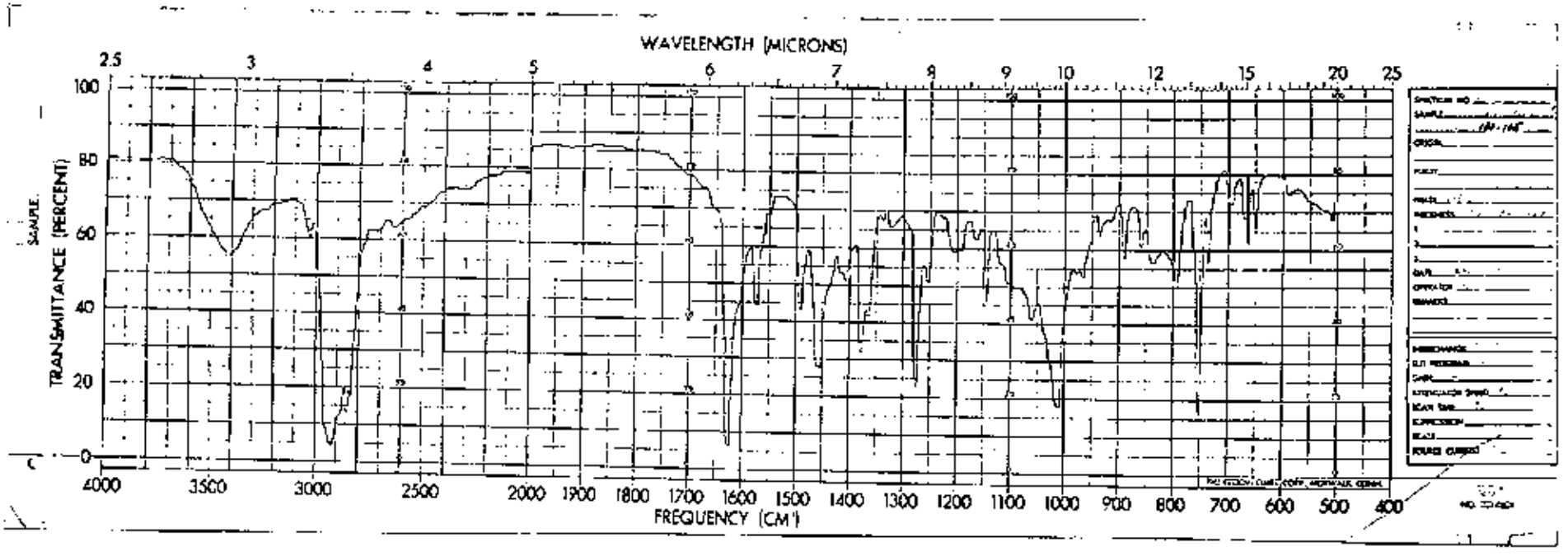

Fig. 6. Infra-red Spectrum of N-Salicylidene Derivative of 4,4-Dimethylcholest-5-en-3β-ylamine M.P. 164-165°

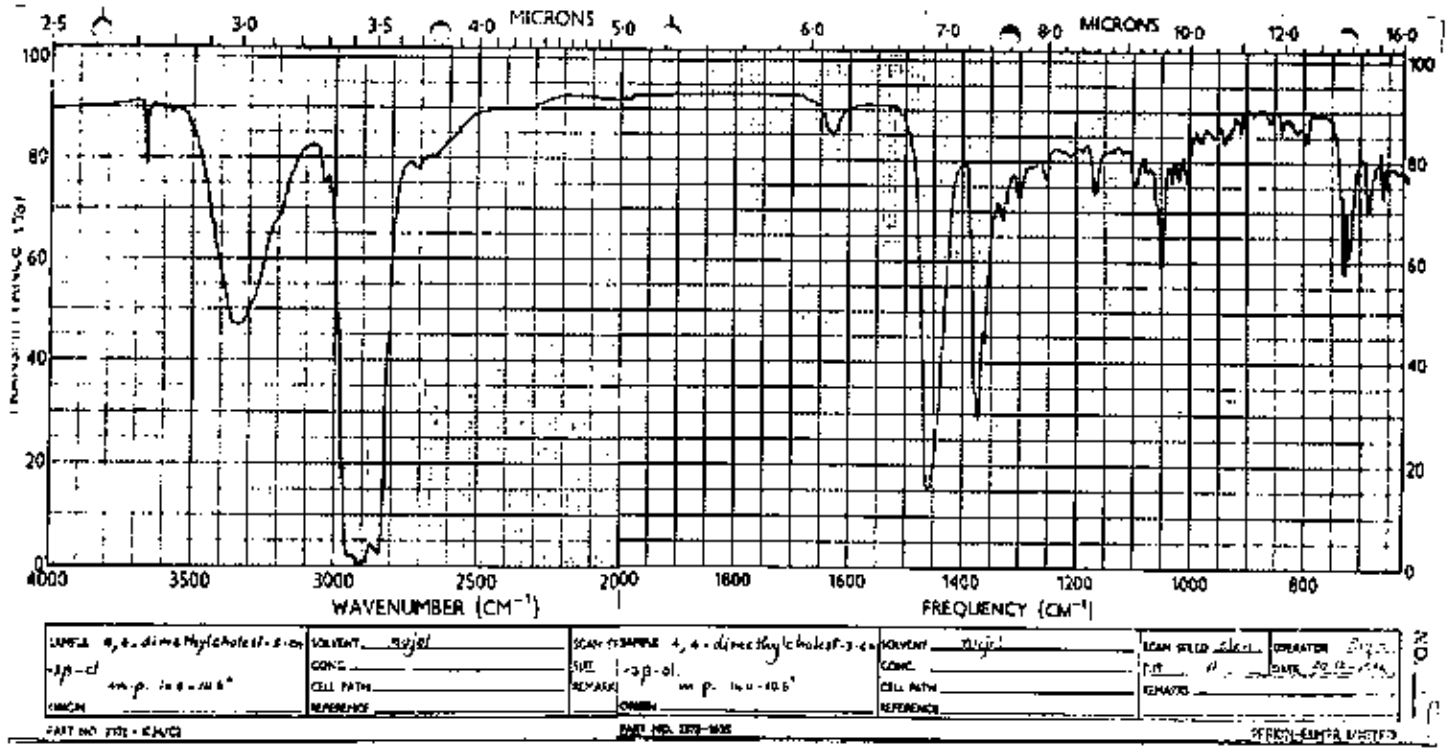

Fig. 7. Infra-red Spectrum of 4,4-Dimethylcholest-5-en-3β-ol M.P. 144–146°

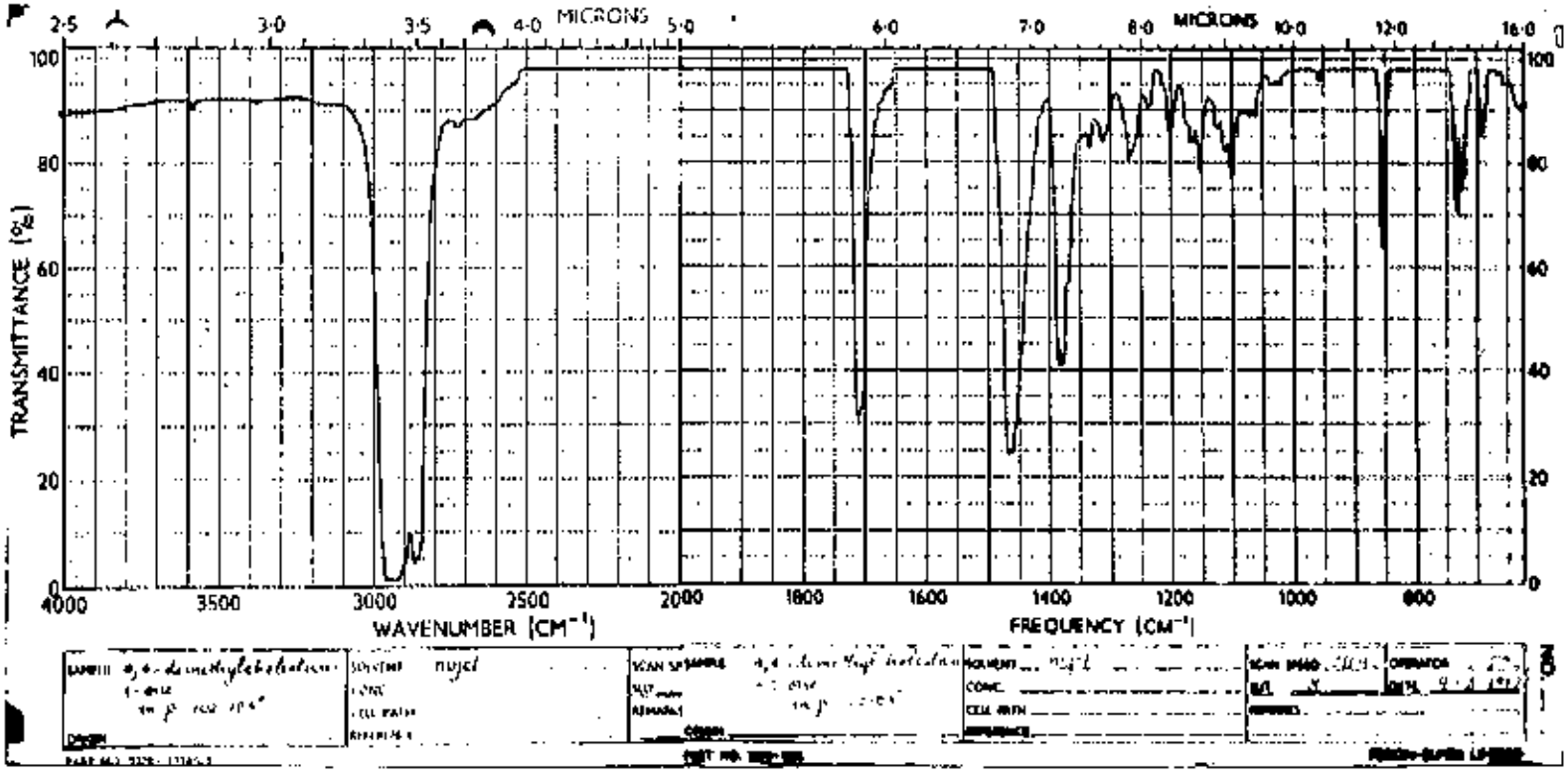

Fig. 8. Infra-red Spectrum of 4,4-Dimethylcholestan-3-one M.P. 102-103°

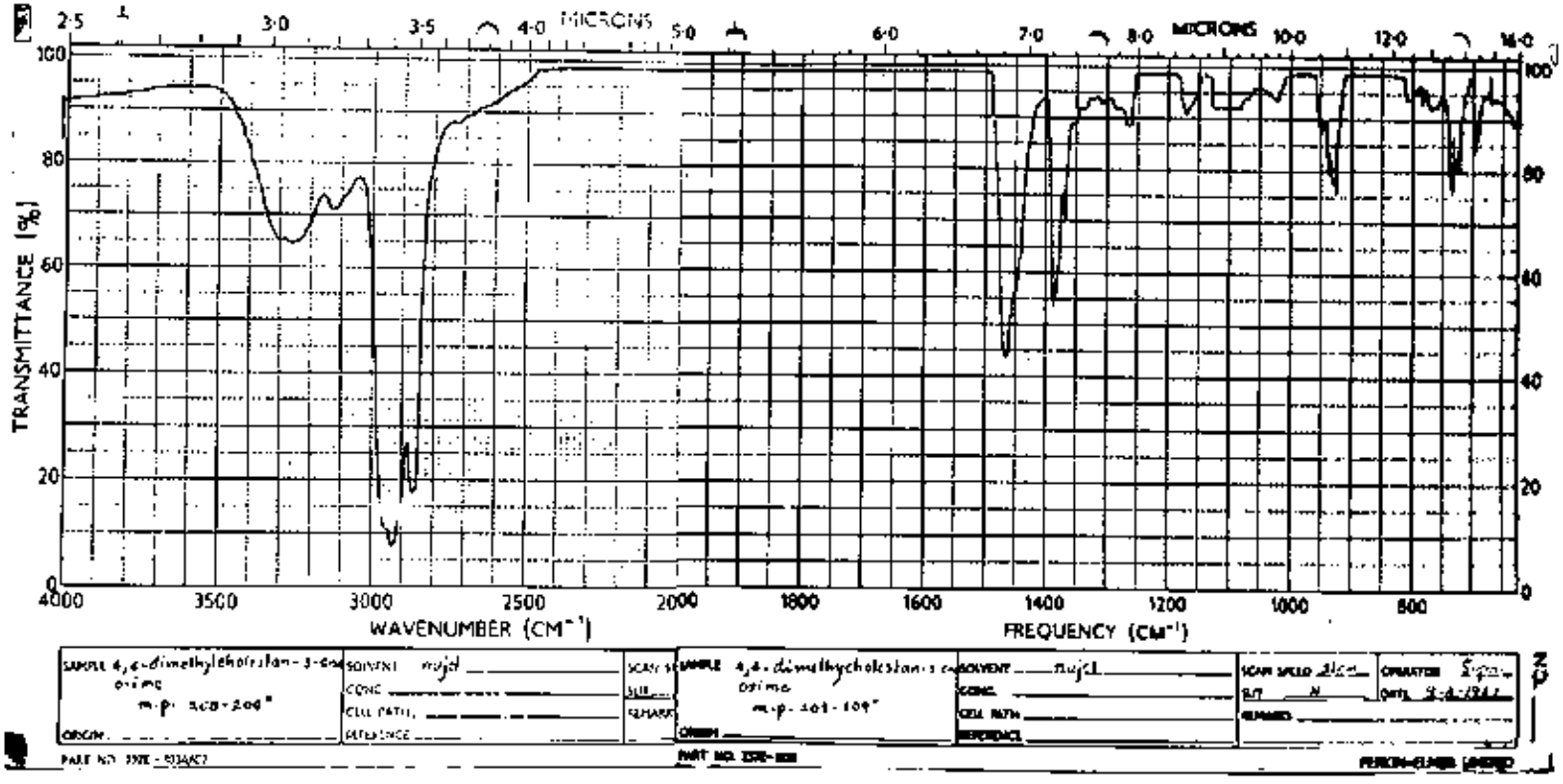

Fig. 9. Infra-red Spectrum of 4,4-Dimethylcholestan 3-one Oxime M.P. 208-209°

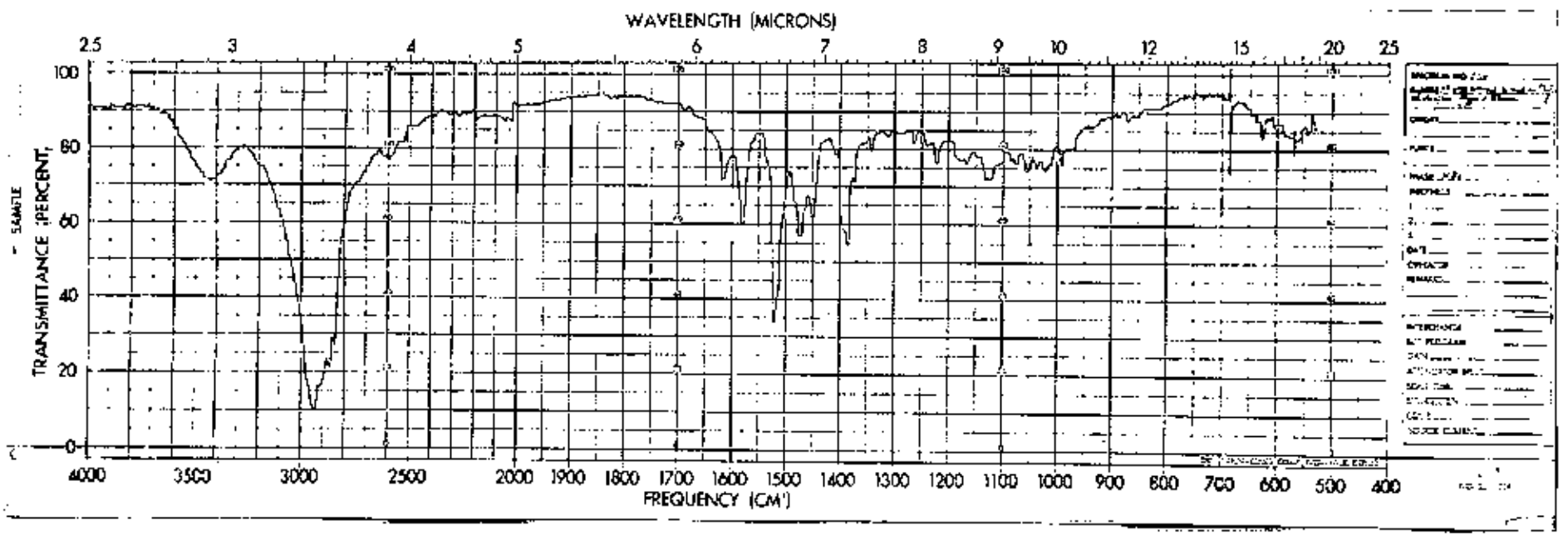

Fig. 10. Infra-red Spectrum of 4,4-Dimethylcholestan-3β-ylamine Hydrochloride M.P. 285°dec.

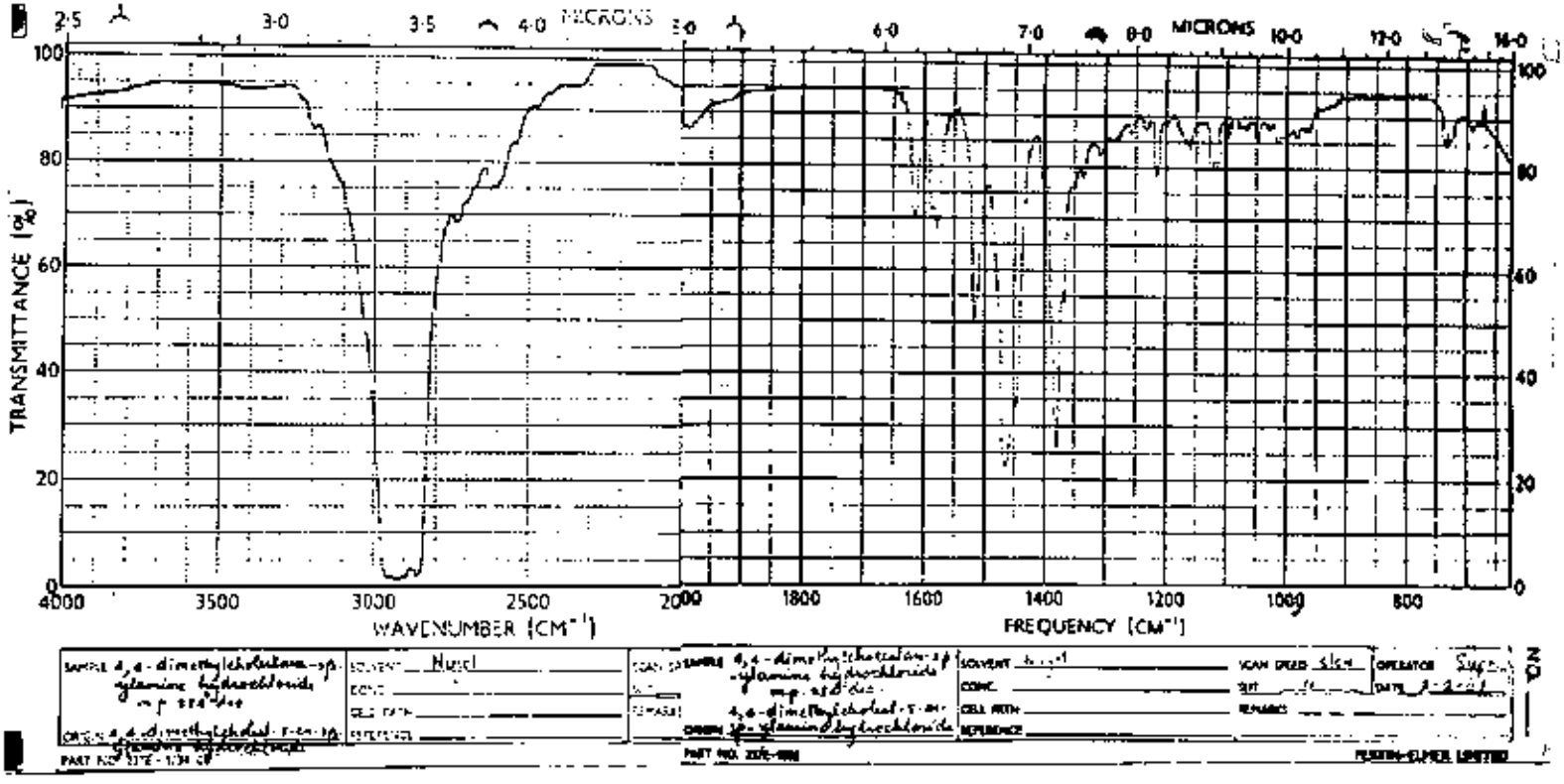

Fig. 11. Infra-red Spectrum of 4,4-Dimethylcholestan-3β-ylamine Hydrochloride M.P. 284°dec. Derived from 4,4-Dimethylcholest-5-en-3β-ylamine Hydrochloride

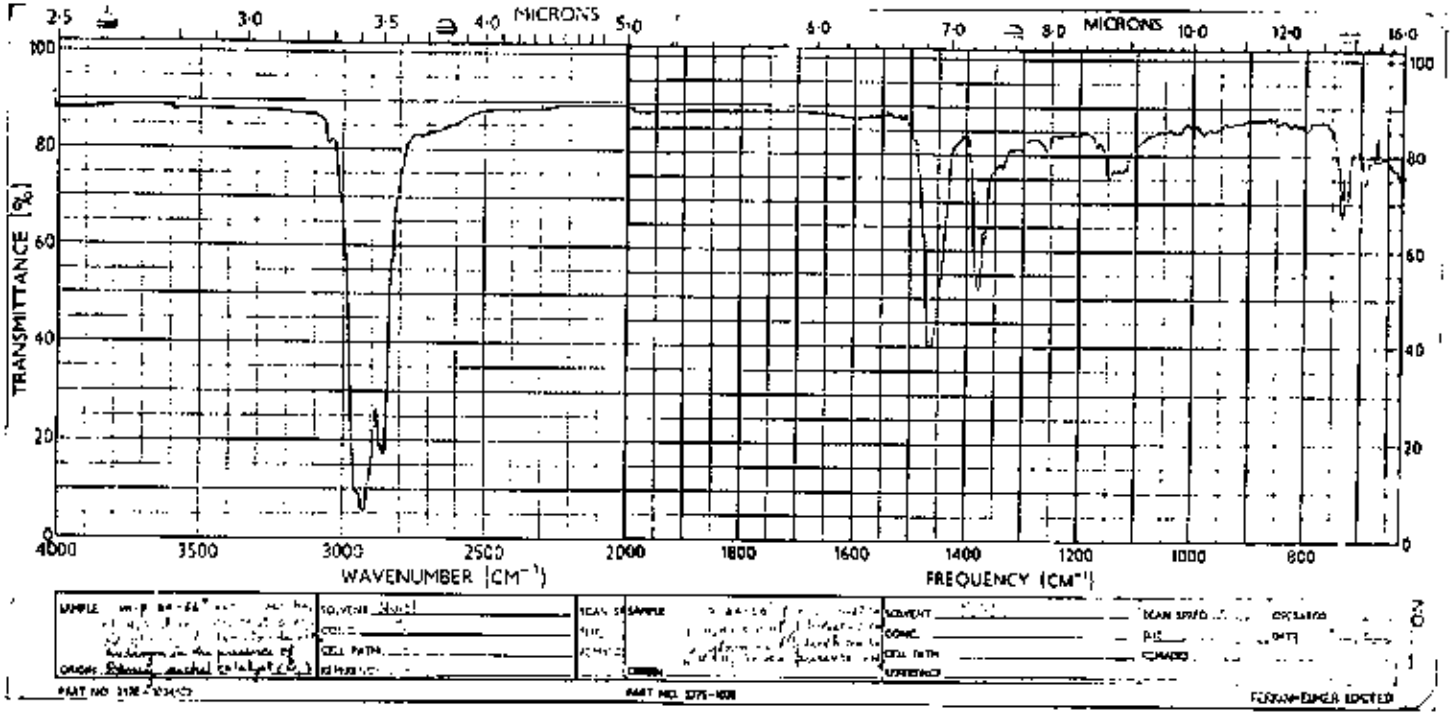

Fig. 12. Infra-red Spectrum of a Compound M.P. 64-66° Derived from 4,4-Dimethylcholest-5-en-3α-ylamine Hydrochloride

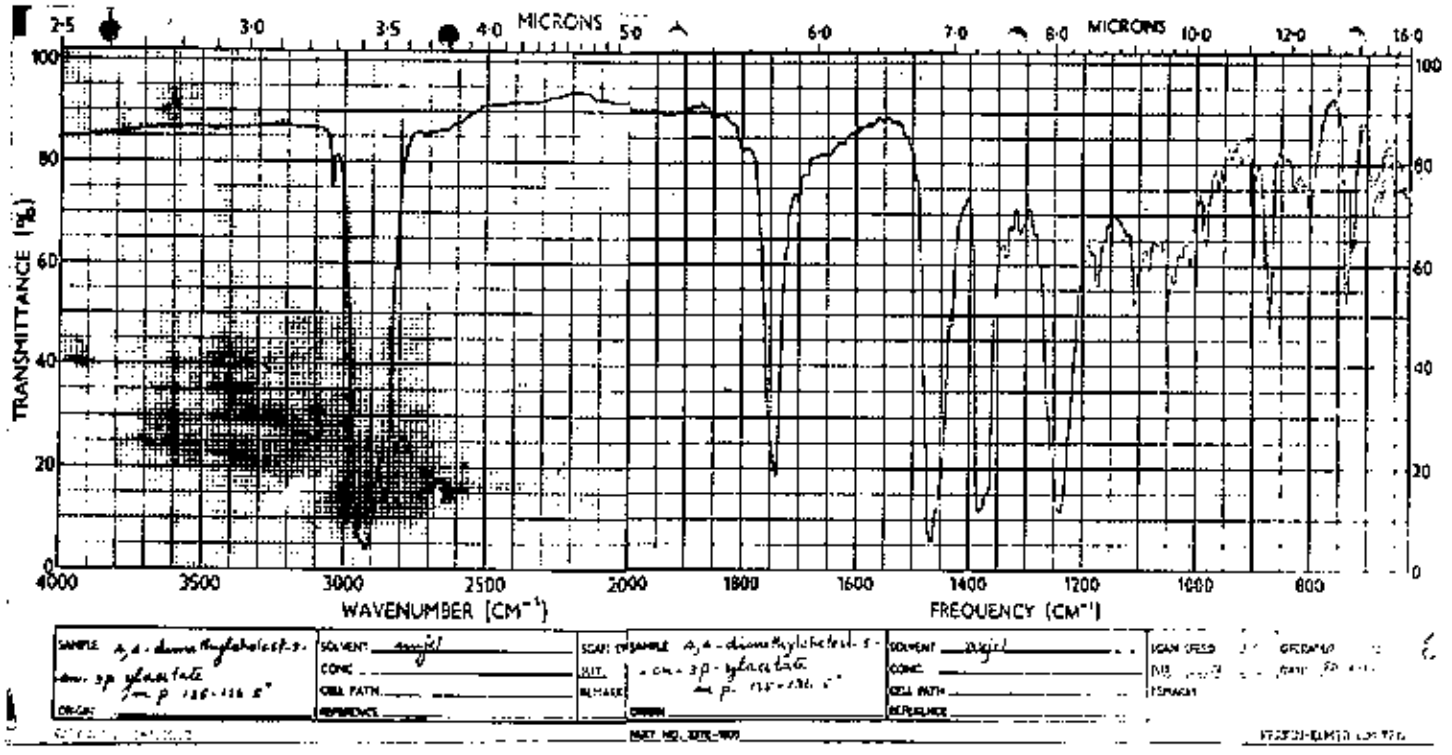

Fig. 13. Infra-red Spectrum of 4,4-Dimethylcholest-5-en-3β-ylacetate M.P.. 135-136.5°

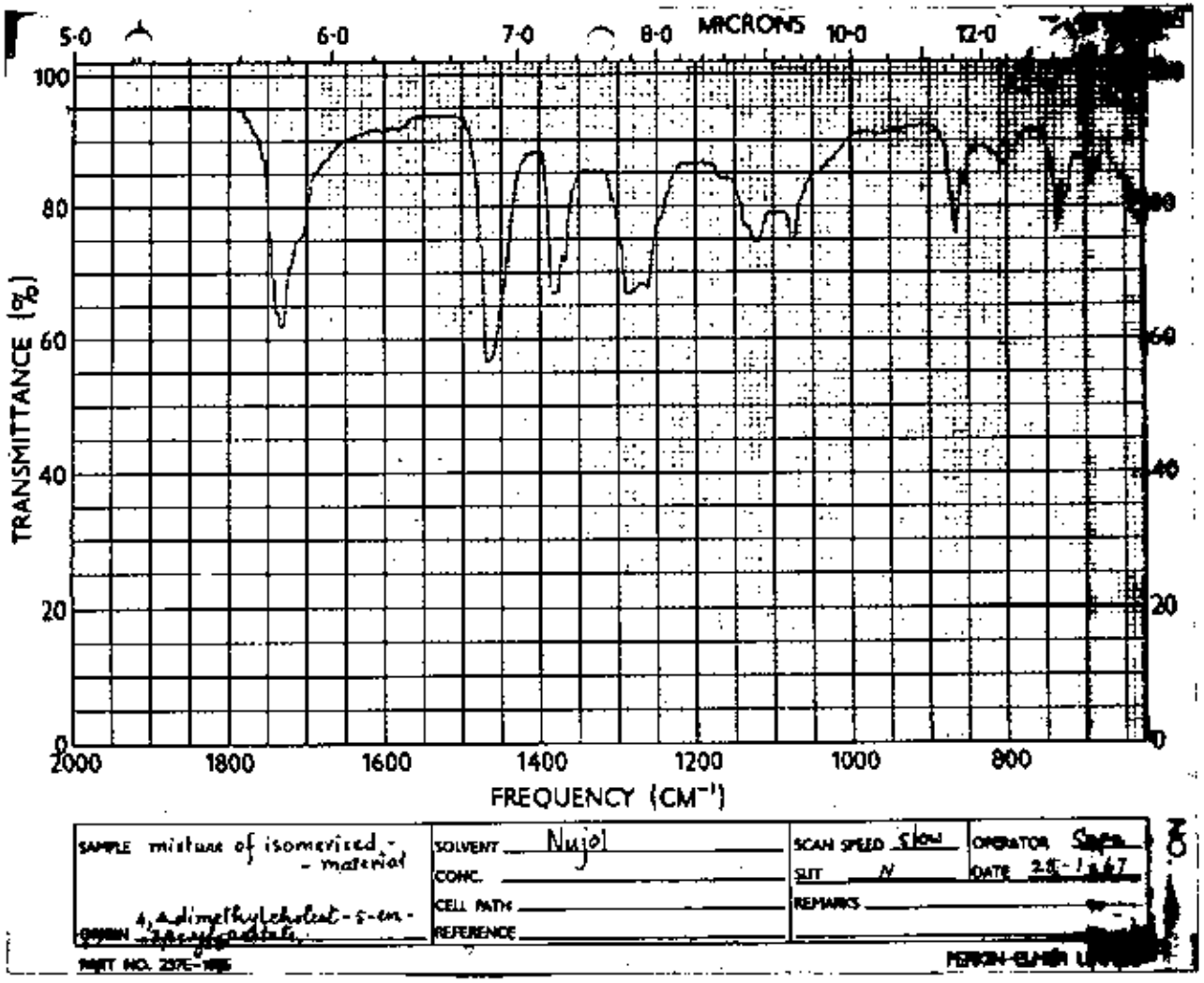

Fig. 14. Infra-red Spectrum of Isomerized Material Derived from 4,4-Dimethylcholest-5-en-3β-ylacetate

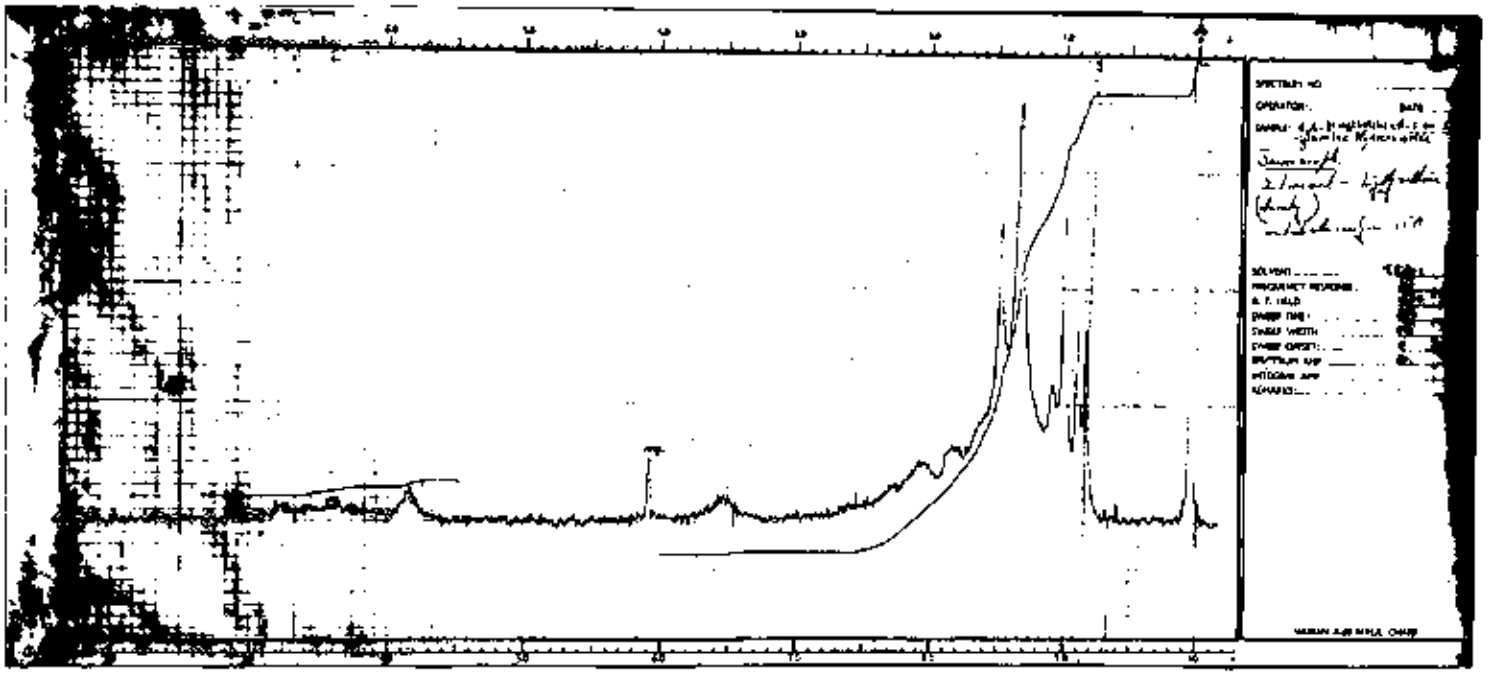

Fig. 15. Nuclear Magnetic Resonance Spectrum of 4,4-Dimethylcholest-5-en-3α-ylamine Hydrochloride M.P. 235° dec.

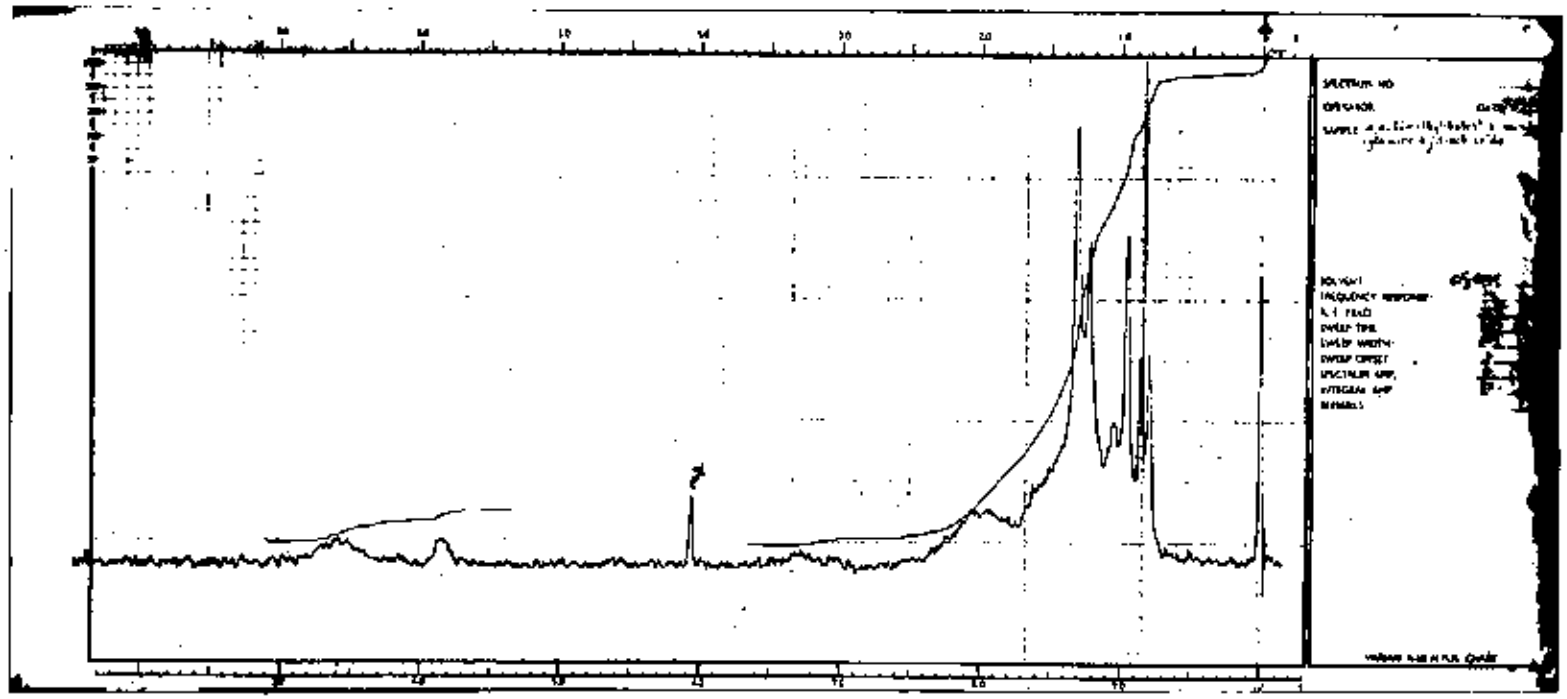

Fig. 16. Nuclear Magnetic Resonance Spectrum of 4,4-Dimethylcholest-5-en-3β-ylamine Hydrochloride M.P. 265° dec.

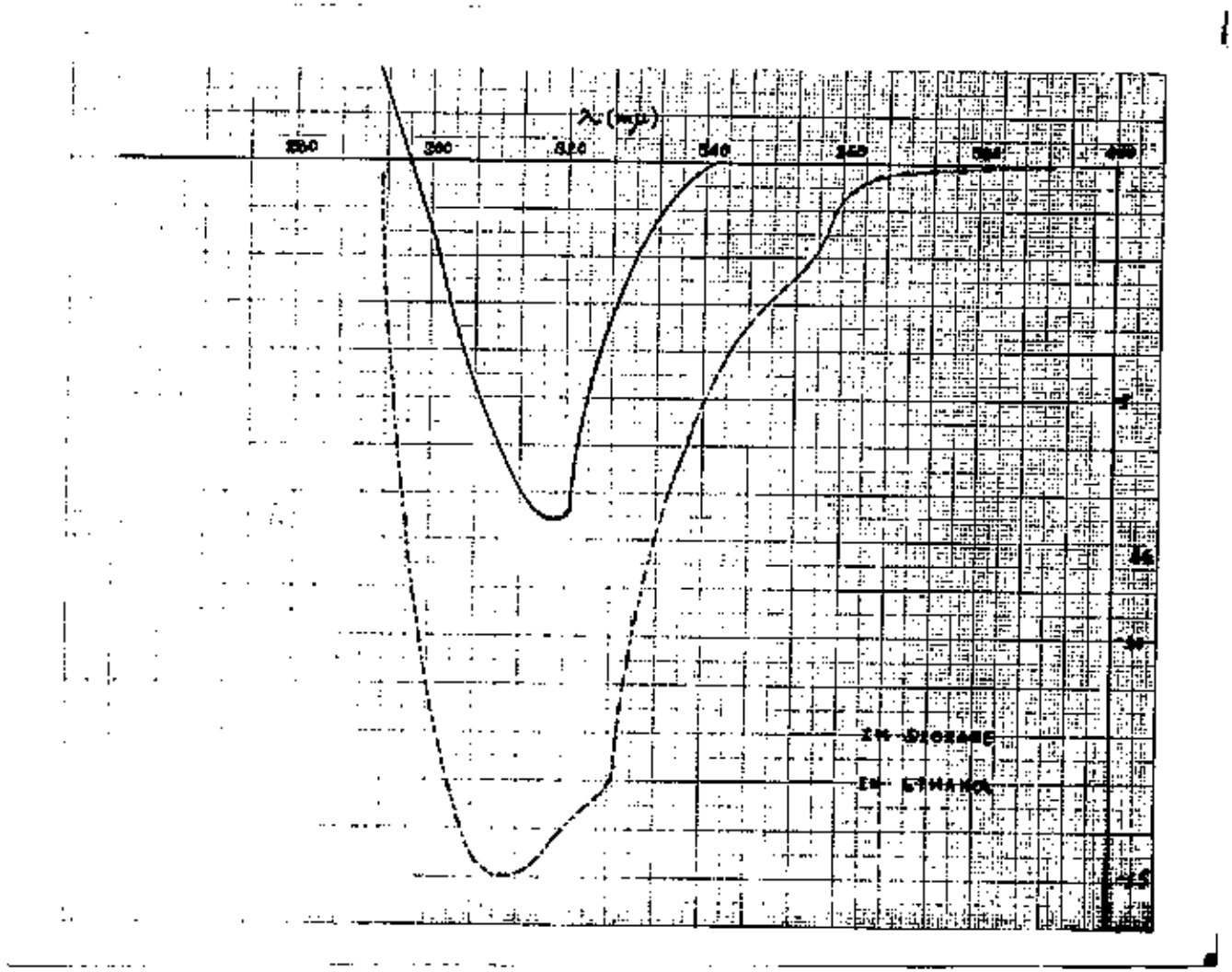

Fig 17. Circular Dichroism Curve of N-Salicylidene Derivative of 4,4-Dimethylcholest-5-en-3α-ylamine M.P. 117-118°

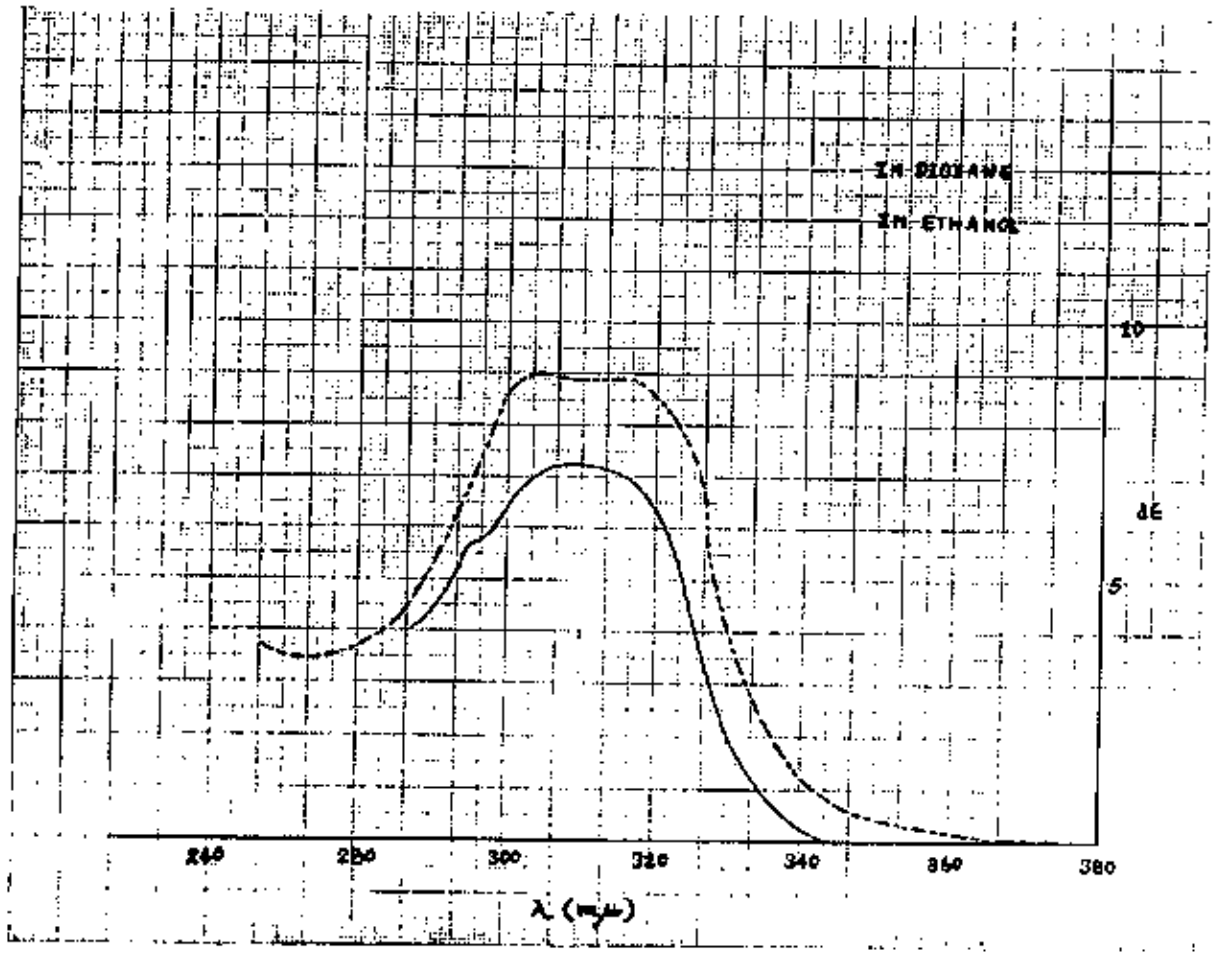

Fig. 18. Circular Dichroism Curve of N-Salicylidene Derivative of 4,4-Dimethylcholest-5-en-3β-ylamine M.P. 164-165°

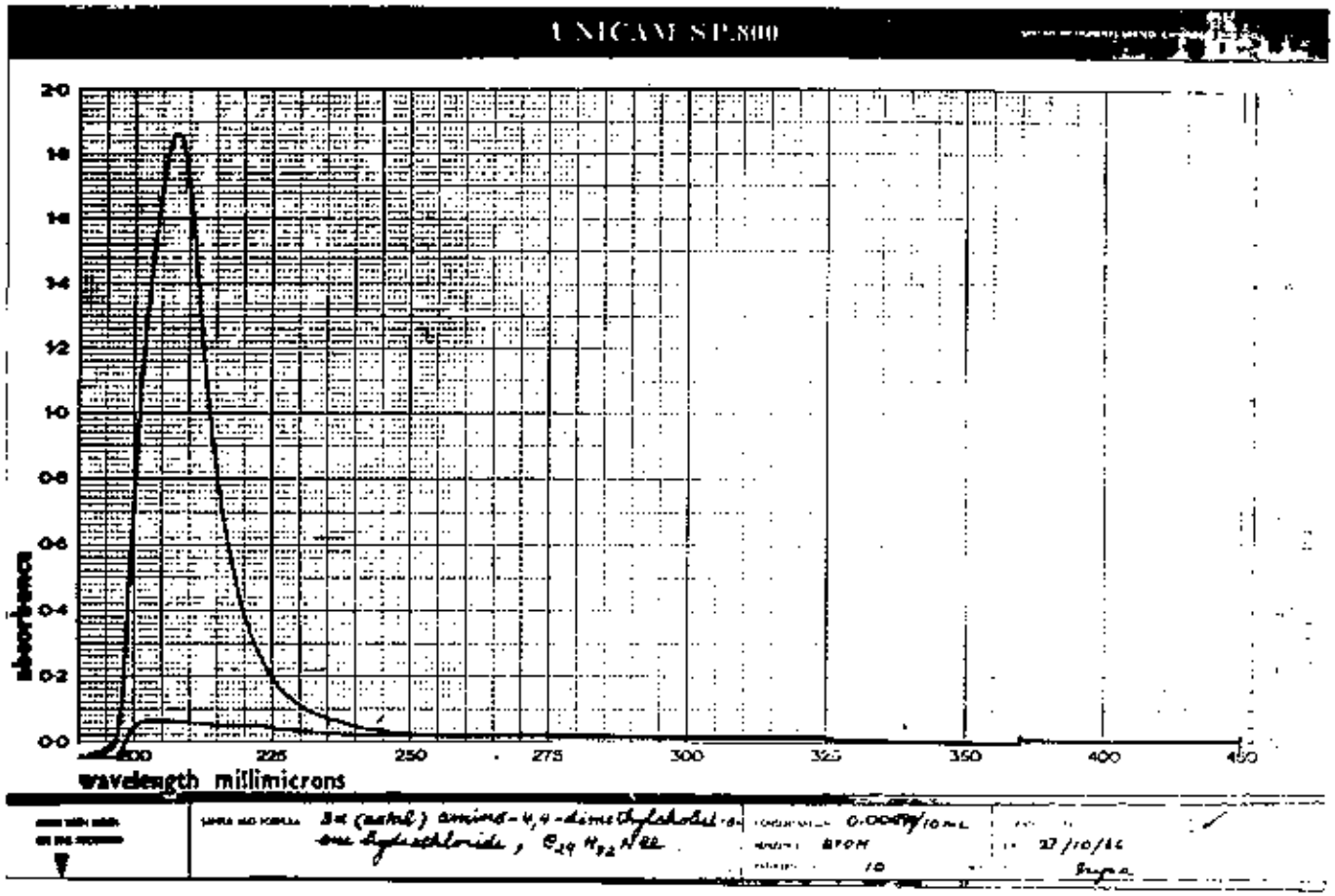

Fig. 19. Ultraviolet Spectrum of 4,4-Dimethylcholest-5-en-3α-ylamine Hydrochloride M.P. 255° dec.

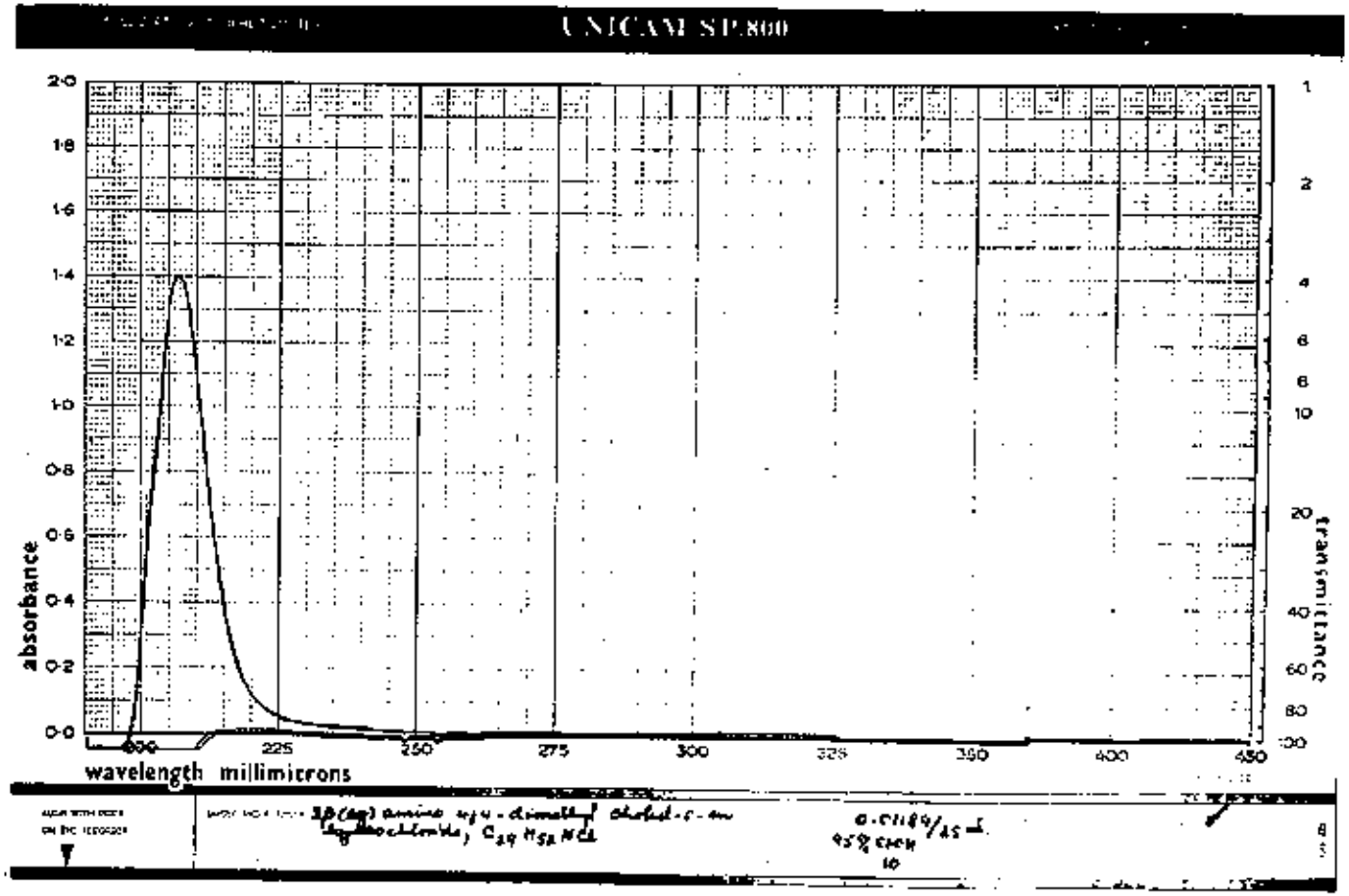

Fig. 20. Ultraviolet Spectrum of 4,4-Dimethylcholest-5-en-3β-ylamine Hydrochloride M.P. 265° dec.

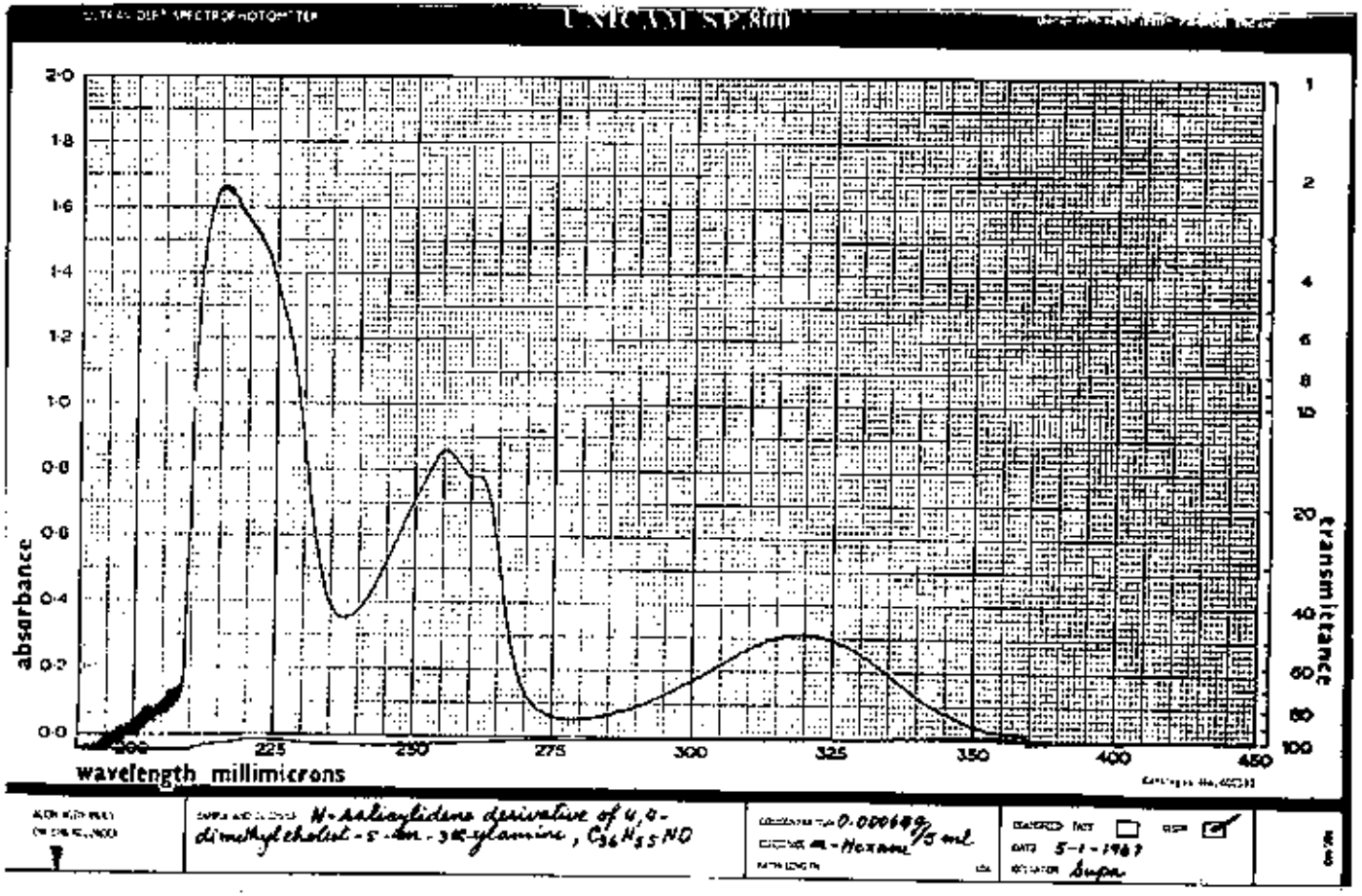

Fig. 21. Ultraviolet Spectrum of N-Salicylidene Derivative of 4,4-Dimethylcholest-5-en-3α-ylamine M.P. 117-118°

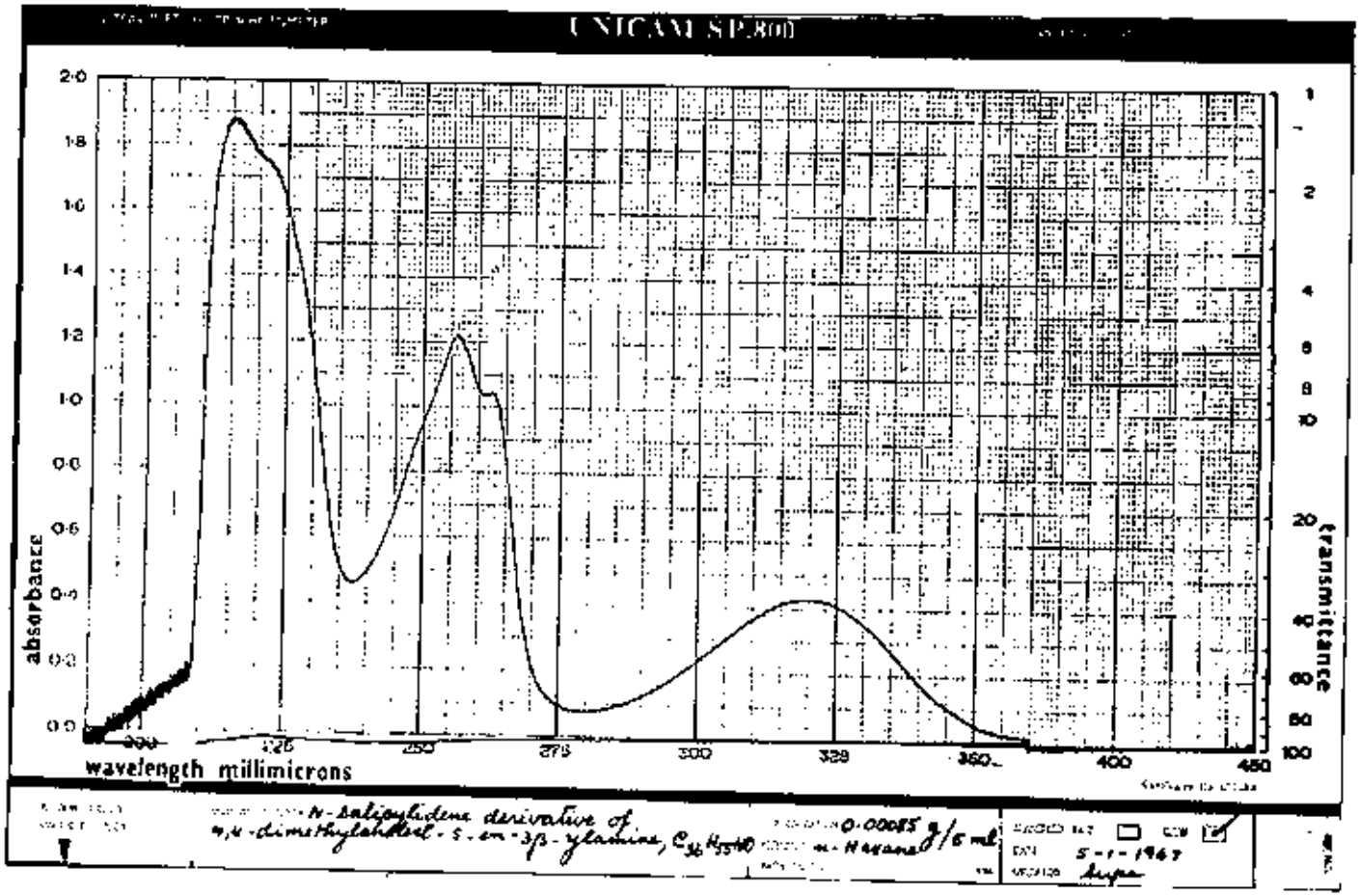

Fig. 22. Ultraviolet Spectrum of N-Salicylidene Derivative of 4,4-Dimethylcholest-5-en-3β-ylamine M.P. 164-165°

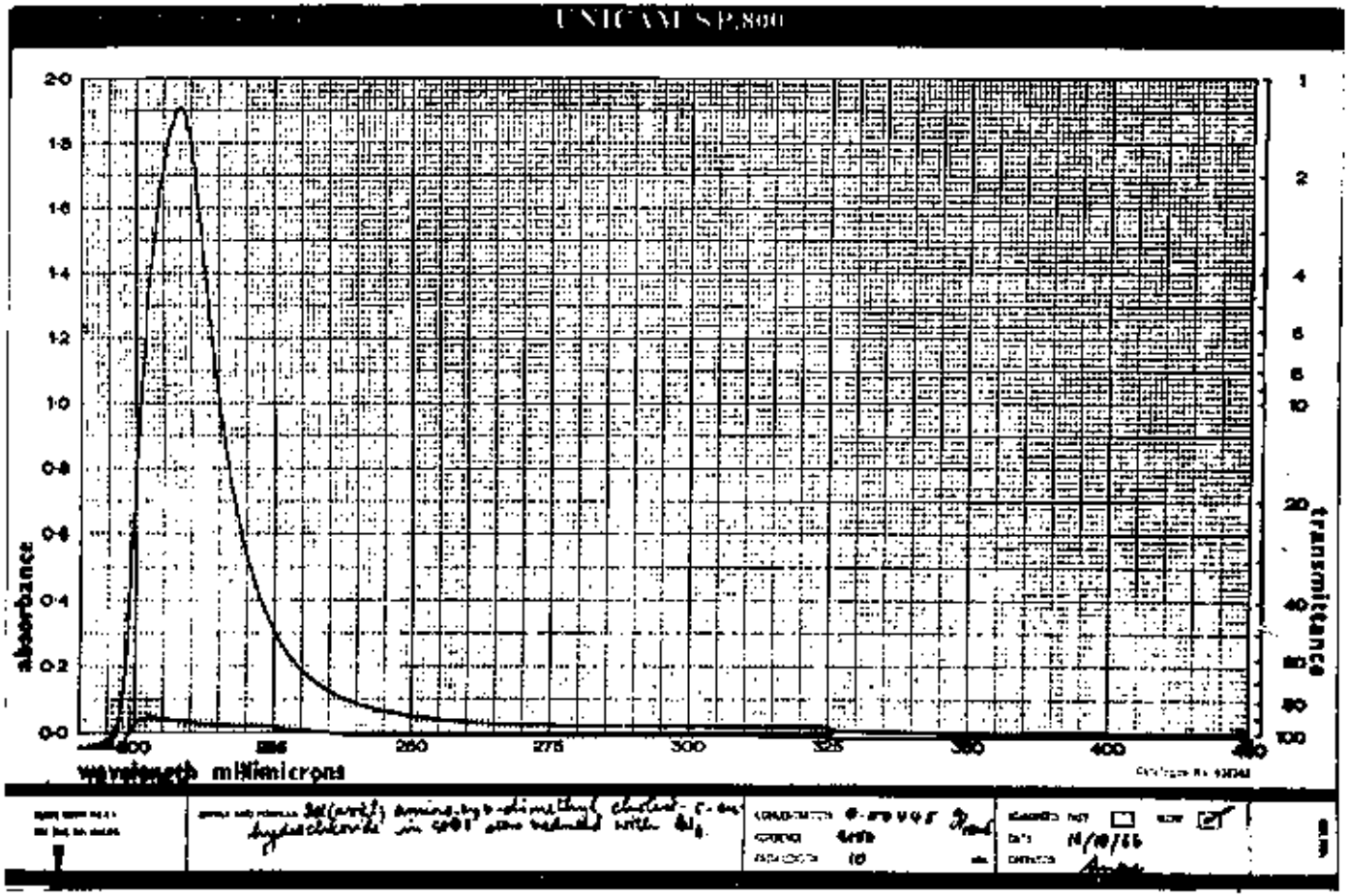

Fig. 23. Ultraviolet Spectrum of a Compound M.P. 64-66° Derived from 4,4-Dimethylcholest-5-en-3α-ylamine Hydrochloride