STRUCTURE AND CONFIGURATION OF EDPETILIDINE

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Edpetilidine (I) [1], $C_{28}H_{47}O_2N$ (corrected) has absorption bands in the IR spectrum at (cm^{-1}): 3420, 3210, 1050 (OH), 2930, 2870, 1460–1430 (CH_3), 2790 (—N—CH_3), 1620–1700 and 975 (HC=CH). The acetylation of substance I with acetic anhydride in pyridine forms diacetyledpetilidine (II) with R_f 0.7 [Al_2O_3–$CaSO_4$ (9 : 1) in the toluene–petroleum ether–methanol (5 : 5 : 0.5) system] (a). IR spectrum of II (cm^{-1}): 2950, 2850, 2870, 1460–1440 (CH_3), 2780 (N—CH_3), 1730, 1725, 1260–1230, 1028, 1050 ($COOCH_3$), 1650 and 980 (CH=CH). The oxidation of I with chromic acid in acetic acid gave edpetilidinedione (III), with mp 227–228° C, R_f 0.56 (a). The IR spectrum of III has absorption bands at (cm^{-1}) 2950-2850, 1455, 1420 (CH_3), 2775 (N—CH_3), 1700, 1705 (CO), 1620, 1660, and 980 (HC=CH). The formation of a diketone shows that both oxygen atoms in I are in the form of secondary hydroxyl groups. The features of the NMR spectra of II and III are given in the table.

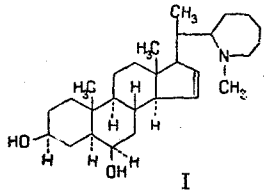
Substance	Chemical shifts, τ								
	s, 3H; 19–CH_3	s, 3H; 18–CH_3	d, 3H; 21–CH_3	s, 3H; $COOCH_3$ (a)	s, 3H; $COOCH_3$ (e)	s, 3H; N–CH_3	m, H (a) HCOCOCH$_3$	m, H (e) HCOCOCH$_2$	t, 2H; Olefin
II	9.05	9.45	9.21	9.05	9.07	7.86	5.40	5.15	4.70
III	9.11	9.45	9.21	—	—	7.87	—	—	4.70

Note. s) singlet; d) doublet; m) multiplet; t) triplet.

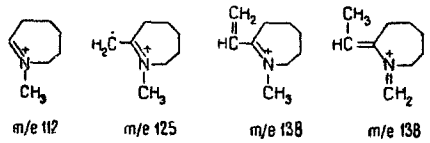
The mass spectrum of I exhibits peaks of ions with m/e 112 (100%), 125 (42%), 138 (29%), $(M-18)^+$, $(M-15)^+$, 429 (28%) (M^+), and the mass spectrum of III peaks with m/e 112 (100%), 125 (32%), 138 (27%), $(M-18)^+$, $(M-15)^+$, 425 (73%) M^+).

The presence in I of a N-methyl group and the formation in the fragmentation mass spectrometry of I and III of a characteristic fragment with a mass number of 112 [4], and the absence from the NMR spectra of II and III of a signal from the 26-CH_3 show that I has an α-substituted hexamethylenemethylamino group.

On the basis of the facts presented, I has the following structural formula and partial configuration [2, 3]:



I



m/e 112 m/e 125 m/e 138 m/e 138

The main characteristic peaks I and III corresponds to the fragments shown in the Scheme [4].

The NMR spectra were taken in deuteriochloroform on a JNM-4H-100 instrument (with hexamethyldisiloxane as internal standard), the IR spectra (moulded into tablets with KBr) on a UR-20 instrument, and the mass spectrum on a MKh-1303 instrument with a glass inlet system.

REFERENCES

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