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DIRECT AMINATION OF CERAMIDONINES*

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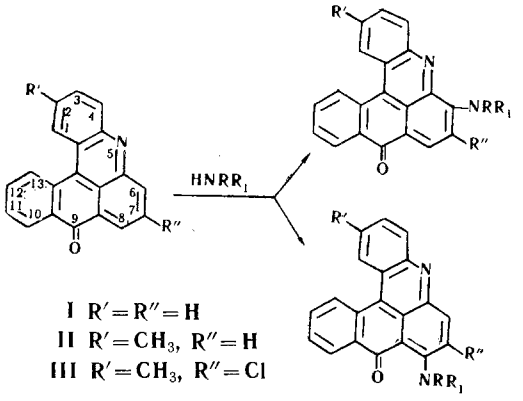
Direct amination of ceramidonine, 2-methylceramidonine, and 2-methyl-7-chloroceramidonine is investigated. It is shown that aromatic amines react with ceramidonines at 120°–150° C, to give 6- and 8-arylaminoceramidonines, the amino group entering preferentially at position 6. Strongly basic amines, (cyclohexylamine, methylamine) react with 2-methylceramidonines under mild conditions, giving mainly 8-aminoceramidonines.

Replacement of a hydrogen atom in ceramidonines by an amino group is a reaction which has not previously been studied. All that is known is that heating ceramidonines with aniline gives bases [1]. However, the reaction products were not isolated pure, and their structures remained unestablished.

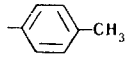
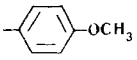
A study has now been made of the conversion of an unsubstituted ceramidonine (I), 2-methyl- (II), and 2-methyl-7-chloroceramidonine (III) under the action of aromatic and aliphatic amines.

Table 1

Results of Aminating Ceramidonines



I R′=R″=H
II R′=CH3, R″=H
III R′=CH3, R″=Cl

1. R1=H, R= 
2. R1=H, R= 
3. R1=H, R= −CH3
4. R1=H, R= 
5. R1=H, R= 
6. R1=H, R= 
7. R1=CH3, R= 

Reagent		I, 1	II, 1	II, 2	III, 1	III, 2	III, 5	III, 6	III, 7	II, 3	II, 4
Temperature, ° C		120	150	120	120	140	140	120	140	20	60
Reaction time hr		0.1	2	2	2	1.5	6	3	4.5	2	2
8 isomer	Yield, %	8	28	4	13			1		44	60
6 isomer		46	53	32	46	42	77	44	27		18

Aryl amination of ceramidonines was effected with excess aryl amine at 120°–150° C with addition of copper acetate, and, in some cases, air was passed to accelerate the reaction [2–4]. Table 1 shows that aniline reacts with I, II, and III, to give 6- and 8-anilinoceramidonines, the 6 isomer being formed preferentially. p-Toluidine and II also react to give a mixture of isomers, whereas it reacts with III to give practically only 2-methyl-6-(p-toluidino)-7-chloroceramidonine. III also gives 6-arylaminoceramidonines with other aromatic amines (p-anisidine, p-chloroaniline, and N-methylaniline).

A different isomer ratio is found when 2-methylceramidonine is treated with cyclohexylamine and methylamine.

* The nomenclature used is that of the Ring Index, Patterson and Capell, 1960.

The former gives a mixture of 6- and 8- isomers in the ratio 1:3, while the latter gives only 2-methyl-8-methylaminoceramidonine. In respect of ease of reaction with aliphatic amines, 2-methylceramidonine can compare with α-naphthaquinone [5]. Evidently the Δ^6 and Δ^8 double bonds in ceramidonines I, II, and III are fixed, and their properties approximate to those of an ethylenic double bond, which is responsible for the orientation on direct amination at position 6 or 8. The causes of change in substitution orientation, which are connected with the amine's basicity, are the subject of further research.

In investigating the direct amination, an unusual side reaction was observed in a number of cases. This was splitting of the ceramidonines to the corresponding 1-arylaminoanthraquinone derivatives. Thus when 2-methylceramidonine was reacted with p-toluidine or cyclohexylamine, the main reaction products were accompanied by 1% of 1-(p-toluidino) anthraquinone, while 2-methyl-7-chloroceramidonine and aniline gave 1(p-toluidino)-3-chloroanthraquinone in 7% yield. The structures of these 1-arylaminoanthraquinones were proved by comparing their IR spectra with those of known compounds, as well as by undepressed mixed melting points with authentic specimens. When 2-methyl-7-chloroceramidonine was reacted with aniline, p-toluidine, or m-chloroaniline, the impurities were the corresponding diarylaminoceramidonines, as elementary analyses showed. Probably they were 6, 8-diarylaminoceramidonines.

To demonstrate the structures of direct amination of ceramidonines, a number of 8-aryl(alkyl)aminoceramidonines were retro-synthesized: 8-anilino- and 2-methyl-8-(p-toluidino) ceramidinones were prepared by a known method [8] from 1,4-dianilno- and 1,4-di(p-toluidino) anthraquinones respectively. 2-Methyl-8-cyclohexylamino- and 2-methyl-8-anilinoceramidonines were prepared from 2-methyl-8-hydroxyceramidonine by heating with the appropriate amine in the presence of boric acid [9].

2-Methyl-6-(p-toluidino) ceramidonine was prepared by reacting alizarin with p-toluidine [10], 6-anilinoceramidonine is described in the literature. Other 6- and 8-aminoceramidonines obtained in the course of the present work were identified by their elementary analyses and by the differences in physicochemical properties between the 6 and 8 isomers. 6-Aminoceramidonines are violet-blue solids, and give solutions in organic solvents which have the

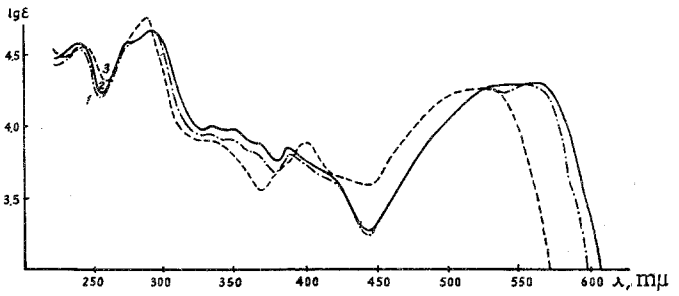


Fig. 1. Absorption spectra (in n-pentane): 1) 6-methylanilinoceramidonine; 2) 2-methyl-6-(p-toluidino)ceramidonine; 3) 2-methyl-6-(m-chloroanilino)-7-chloroceramidonine.

same color, while the 8 substituted compounds are red and give red solutions. With concentrated sulfuric acid 8-aminoceramidonines give orange or red solutions, while the 6 derivatives give bluish green ones. The color change occurring when pyridine solutions of these compounds are treated with methanolic potassium hydroxide vary: orange solutions of 8 amino derivatives become pinkish-violet, while the color of the 6 amino ones changes from violet to green.

When chromatographing on paper (using 3 systems, see Table 2), or on alumina, 8-aminoceramidonines gave higher R_f values than the corresponding 6 isomers.

Experimental

When aminating ceramidonines, the end of the reaction was established by chromatographing the reaction products to ascertain whether the starting ceramidonine had disappeared. Preparative chromatography was carried out with Al_2O_3, grade II activity, and benzene or $CHCl_3$ was used for developing. The absorption spectra were measured (200–700 mμ) with SF-4 and SF-5 spectrophotometers (C 0.5×10^{-4} M, l 0.5 and 0.2 cm). IR spectra (3800–2600 and 1800–400 cm^{-1}) were observed with a UR-10 spectrophotometer after tabletting with KBr (4 mg substance in 800 mg KBr).

Amination of ceramidonine I with aniline. 1 g (0.0035 mole) I, 0.5 g $Cu(OAc)_2$, and 5 ml (0.05 mole) aniline were stirred together for 6 min at 120° C. The yellowish-brownish solution became bluish-violet. The reaction products were cooled to 100° C, and poured into 5% HCl. The precipitate was filtered off, washed with 5% HCl, and

Table 2

Chromatographic Properties of Aminoceramidonines

Compound	R'_f spot color*		R''_f spot color		R'''_f spot color	
	6-isomer	8-isomer	6-isomer	8-isomer	6-isomer	8-isomer
Anilino-I	0.07, bl	0.51, r-v	0.32, g	0.77, y-v	0.30, bl-v	0.33, r-v
Anilino-II	0.05, bl-v	0.60, r-b	0.29, g	0.72, y-v	0.24, v	0.30 r
p-Toludino-II	0.06, bl	0.49, r-b	0.21, g	0.60, y-g	0.17, bl-v	0.25, r
Methylamino-II	0.29, v	0.80, r	0.60, y-g	0.86, v	0.47, r-v	0.54, r
Cyclohexylamino-II	0.07, v	0.66, p-r	0.28, g		0.18, r-v	0.25, r-v
Anilino-III	0.02, v	0.27, r-b	0.28, y-g	0.53, y-g	0.12, r-v	0.16, r
p-Toludino-III	0.02, v	—	0.21, y-g	—	0.09, r-v	—
p-Anisidino-III	0.02, bl-v	—	0.23, y-v	—	0.11, bl-v	—
m-Chloroanilino-III	0.02, r-v	0.16, o	0.20, y-v	0.42, y-v	0.11, p-v	0.13, r
N-methylanilino-III	0.03, r-v	—	0.29, y-v	—	0.12, v	—

I) Caramidonine II) 2-methylceramidonine III) 2-methyl-7-chloroceramidonine

* Color abbreviations are b = brown, bl = blue, g = green, o=orange p = pink, r = red, y = yellow, v = violet.

then with hot water. After drying, it was dissolved in benzene and chromatographed. The material split into two main zones, a red one, and a bluish-violet one, yellowish-brown impurities remaining at the top. The eluate was concentrated under reduced pressure, then filtered, and evaporated to dryness. Yields 0.11 g (8%) red and 0.59 g (46%) bluish-violet compounds.

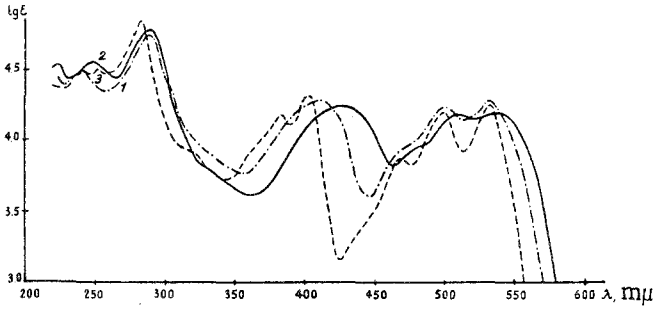


Fig. 2. Absorption spectra (in n-pentane): 1) 2-methyl-8-anilinoceramidonine; 2) 2-methyl-8-anilino-7-chloroceramidonine; 3) 2-methyl-8-cyclohexylaminoceramidonine.

The red compound, bunches of prisms mp 221°–222.5° C (ex $CHCl_3$) gives an undepressed mixed mp with a sample of 8-anilinoceramidonine, prepared by the method of [8]. The IR spectra of the two compounds were identical, λ_{max}, mμ (lg ε) ($CHCl_3$): 288 (4.81), 400 (4.23), 500 (4.22), 536 (4.29).

Bluish-violet compound, needles, mp 209°–210° C (ex acetone). The literature [10] gives for 6-anilinoceramidonine mp 203°–205° C, λ_{max} mμ (lg ε) (n-pentane): 236 (4.47), 290 (4.62), 334 (3.90), 386 (3.72), 536 (4.16), 560 (4.20). Found: N 7.07, 7.04%. $C_{26}H_{16}N_2O$: N 7.51%.

Amination of 2-methylceramidonine (II). A. With aniline. 1.5 g (0.005 mole) II, 0.08 g $Cu(OAc)_2$, and 10 ml (0.1 mole) aniline were heated together with stirring for 2 hr, at 150° C. The amination products were separated as described above, to give 1) 0.55 g (28%) of a red substance, mp 190°–193° C, which after two recrystallizations from $CHCl_3$-petrol ether (2:1) had mp 200°—201° C. Its IR spectrum was identical with that of 2-methyl-8-anilinoceramidonine; undepressed mixed mp with an authentic specimen. The amination products also gave 2) 1.03 g (53%) 2-methyl-6-anilinoceramidonine, bluish-violet prisms mp 191°–193° C (ex Et_2O), λ_{max}, mμ (lg ε) (n-pentane): 238 (4.55), 290 (4.66), 331 (3.94), p* 340 (3.90), p 364 (3.80), 390 (3.79), 528 (4.23), 558 (4.26). Found: C 83.73, 83.61; H 4.96, 4.87; N 7.54, 7.55%. Calculated for $C_{27}H_{18}N_2O$: C 83.93; H 4.70; N 7.25%.

Retro-synthesis of 2-methyl-8-anilinoceramidonine. 1.24 g (0.004 mole) 2-methyl-8-hydroxyceramidonine, 0.27 g (0.04 mole) boric acid, and 6 ml (0.06 mole) aniline, were stirred together for 2 hr 30 min at 120° C. Chromatography ($CHCl_3$ developer) gave 1.41 g (91%) reddish-brown crystalline material mp 162°–174° C, which after three recrystallizations from $CHCl_3$ gave needles mp 199°–200° C, λ_{max} mμ (lg ε) (n-heptane): 240 (4.48), 287 (4.74), 410 (4.27), p 461 (3.95), 498 (4.22), 530 (4.26). Found: C 84.02, 83.75; H 4.92, 4.76; N 7.58, 7.54%. Calculated for $C_{27}H_{18}N_2O$: C 83.93; H 4.70; N 7.25%.

B. p-Toluidine. 3 g (0.01 mole) II, 0.15 g $Cu(OAc)_2$, and 16 g (0.15 mole) p-toluidine were stirred together for 2 hr at 120° C. Chromatography ($CHCl_3$ developer) gave 4 zones, reddish-violet, yellow, bright reddish-orange, and a wide bluish-violet one. The first fraction gave, on evaporation of the solvent, 0.03 g (1%) substance, mp 154°–155° C, R_f** 0.06. Mixed mp with 1-(p-toluidino) anthraquinone, prepared as in [7], undepressed. The IR spectra of the compounds were identical. The second fraction gave 0.24 g (8%) substance mp 164° C, R_f 0.74. Undepressed mixed mp with 2-methylceramidonine. The 3rd and 4th fractions were bulked, evaporated to dryness, dissolved in benzene, and chromatographed again, to give: 1) 0.14 g (4%) 2-methyl-8-(p-toluidino) ceramidonine, mp 237°–240° C; red prisms mp 241°–242° C (ex benzene). Undepressed mixed mp with 2-methyl-8-(p-toluidino) ceramidonine, prepared as described in [8]. The IR spectra of the two compounds were the same, λ_{max}, mμ (lg ε) ($CHCl_3$): 288 (4.79), 416 (4.30), 502 (4.20), 534 (4.25): 2) 1.26 g (32%), bluish-violet compound mp 185°–193° C; needles mp 198° C (ex benzene). Undepressed mixed mp with a specimen of 2-methyl-6-(p-toluidino) ceramidonine prepared as in [10]. The IR spectra of the compounds were identical, λ_{max} (lg ε) (n-pentane): 238 (4.57), p 276 (4.59), 291

*Here and elsewhere, p = an inflection.

**The R_f values in this Experimental were for system I (Table 2).

(4.66), 334[3.99), p 346(3.96), p 366(3.86), 389(3.83), 558–568(427).

C. Methylamine. Into a flask fitted with an efficient coil condenser was put a solution of 2-methylceramidonine (0.7 g) in pyridine (20 ml) and $MeNH_2$ passed in at a rate of 2–3 bubbles/sec for 2 hr, at room temperature. The yellow solution became dark red, it was left overnight, the pyridine vacuum-distilled off, water added to the tarry mass in the flask, and the whole evaporated to dryness. The residue was chromatographed (developer benzene), to give 0.34 g (44%) 2-methyl-8-methylaminoceramidonine, mp 228°–230° C; needles mp 230°–231.5° C (ex benzene), λ_{max} mμ (lg ε) ($CHCl_3$): 260(4.78), 286(4.83), 370(4.03), 388(4.16), 410(4.32), 470(3.83), 500(4.19), 536(4.28). Found: C 81.33, 81.57; H 4.98, 5.13; N 8.67, 8.80%. Calculated for $C_{22}H_{16}N_2O$: C 81.45; H 4.97; N 8.63%.

D. Cyclohexylamine. a) 0.3 g (0.001 mole) II and 3 ml (0.03 mole) cyclohexylamine were stirred together for 2 hr at 60°–65° C, to give 0.27 g reddish-brown material. On chromatographing this gave (developer $CHCl_3$) 0.19 g (60%) of a red substance mp 140°–160° C, and 0.07 g (18%) of a dark violet powder which melted indefinitely below 100° C. The first of these substances was reprecipitated from benzene with high-boiling petrol ether, when it had mp 162°–163° C. Mixed mp with 2-methyl-8-cyclohexylaminoceramidonine, undepressed. The IR spectra of the two compounds were identical. 2-Methyl-6-cyclohexylaminoceramidonine was repeatedly precipitated from acetone or benzene with low-boiling petrol ether, when it had mp 121°–124° C, λ_{max}, mμ (lg ε) (EtOH): 236(4.51), 298(4.59), 386(3.85), 544(4.12), 566(4.13). Found: N 6.83, 7.23%. Calculated for $C_{27}H_{24}N_2O$: N 7.13%.

b) 0.89 g II and 7 ml cyclohexylamine were refluxed together for 40 min, to give 0.23 g (24%) 2-methyl-8-cyclohexylaminoceramidonine, 0.07 g (7%) 2-methyl-6-cyclohexylaminoceramidonine, and 0.01 g (~ 1%) of a reddish violet substance, mp 154°–158° C (ex MeOH), R_f 0.06. Mixed mp with 1-(p-toluidino)anthraquinone [7] undepressed.

Retro-synthesis of 2-methyl-8-cyclohexylaminoceramidonine. 0.94 g (0.003 mole) 2-methyl-8-hydroxyceramidonine, 0.2 g (0.003 mole) $B(OH)_3$, and 5 ml (0.05 mole) cyclohexylamine were refluxed together for 30 min. The reaction products were poured into 5% HCl, the precipitate filtered off, repeatedly washed with 5% HCl and hot water, then dried, to give 1.1 g (93%) powder mp 140°–150° C. After reprecipitating three times from benzene with petrol ether, it had mp 161°–162.5° C. λ_{max}, mμ (lg ε) (n-heptane): 240(4.48), 250(4.49), 284(4.86), 382(4.17), 402 (4.31), 468(3.85), 498(4.19), 532(4.24). Found: C 82.38, 82.29; H 5.98, 6.02; N 7.15, 7.00%. Calculated for $C_{27}H_{24}N_2O$: C 82.62; H 6.16; N 7.13%.

Amination of 2-methyl-7-chloroceramidonine (III). A. Aniline. a) Through a solution of III (2.5 g) in aniline (15 ml) at 120° C, air was passed, at the rate of 4–5 bubbles/sec, for 2 hr. The product obtained by working up in the usual way was dried, dissolved in benzene, and column chromatographed on silica gel, eluting the main zone with benzene, to remove bluish-violet impurities. The red eluate was evaporated to dryness, the residue (2.3 g) chromatographed over Al_2O_3 ($CHCl_3$), to give: 1) 1.47 g (46%) 2-methyl-6-anilino-7-chloroceramidonine, mp 254°–257° C; reddish-violet needles mp 257°–258° C (ex benzene), λ_{max}, mμ (lg ε) ($CHCl_3$): 294(4.81), 340(3.89), 400(3.88), 434(3.68), 540(4.31). Found: Cl 8.46, 8.72; N 6.66, 6.77%. Calculated for $C_{27}H_{17}ClN_2O$: Cl 8.43; N 6.66%. 2) 0.29 g (9%) 2-methyl-7-chloro-7 anilinoceramidonine, mp 239°–246° C; dark red plates mp 250°–252° C (ex benzene). λ_{max}, mμ (lg ε) (n-heptane): 224(4.51), 248(4.56), 290(4.79), 426(4.23), 508(4.17), 540(4.19). Found: Cl 8.93, 8.90; N 6.86, 6.92%. Calculated for $C_{27}H_{17}ClN_2O$: Cl 8.43; N 6.66%.

The filtrates from recrystallizing the two solids were bulked, evaporated to dryness, dissolved in $CHCl_3$, and paper chromatographed. The colored zones were cut out, extracted with $CHCl_3$ in Soxhlet apparatus, and a further 0.11 g (4%) 2-methyl-7-chloro-8-anilinoceramidonine mp 247°–250° C, isolated, as well as 0.04 g (1%) 2-methyl-6,8(?)-dianilino-7-chloroceramidonine, mp 249°–259° C; red needles mp 265°–267° C (ex chlorobenzene), R_f 0.00, λ_{max}, mμ (lg ε) ($CHCl_3$): 296(4.68), 413(3.99), 464(4.06), 520(4.20), 552(4.27). Found: C 77.41, 77.23; H 4.33, 4.45; Cl 7.14, 7.31; N 7.95, 8.22%. Calculated for $C_{33}H_{22}ClN_3O$: C 77.41; H 4.33; Cl 6.92; N 8.20%.

b) 3.3 g (0.01 mole) III, 0.16 g $Cu(OAc)_2$, and 10 g (0.1 mole) aniline were heated together at 160° C for 1 hr, air being passed through the reaction mixture. After separating off the brownish-yellow impurities by chromatographing on Al_2O_3 ($CHCl_3$), the eluate was evaporated to dryness, then chromatographed twice more, the column being washed with benzene, to give 1) 0.23 g (7%) of a red substance mp 145°–150° C; plates mp 158°–160° C (ex acetone), R_f 0.04. Undepressed mixed mp with 1-(p-toluidino)-3-chloroanthraquinone [6]. The IR spectra of the compounds were identical; 2) 0.17 g (4%) 2-methyl-6-anilino-7-chloroceramidonine, and 0.7 g (14%) 2-methyl-6,8(?)-dianilino-7-chloroceramidonine.

B. p-Toluidine. 1.65 g (0.005 mole) III, 0.08 g $Cu(OAc)_2$, and 5.35 g (0.05 mole) p-toluidine were heated together for 1 hr 30 min at 140° C, air being passed through the reaction mixture. Chromatography (developer benzene) gave: 1) 0.18 g (7%) 2-methyl-6,8(?)-di(p-toluidino)-7-chloroceramidonine, red needles, mp 232°–234° C (ex benzene). λ_{max}, mμ (lg ε) (n-heptane): 244(4.57), 296(4.66), 382(3.95), 470(4.05), 520(4.22), 554(4.29). Found: C 78.07, 78.12; H 5.22, 5.13; Cl 6.46, 6.65; N 8.22, 7.95%. Calculated for $C_{35}H_{26}ClN_3O$: C 77.84; H 4.85; Cl 6.57; N 7.78%; 2) 0.41 g (42%) 2-methyl-6-(p-toluidino)-7-chloroceramidonine as violet needles, mp 258°–259° C

(ex benzene). λ_{max}, mμ (lg ε) (EtOH): 247 (4.81), 282 (4.86), 344 (4.08), 400 (3.98), p 432 (3.82), 551 (4.47). Found: C 77.82, 78.13; H 4.39, 4.63; Cl 8.10, 8.07%. Calculated for $C_{28}H_{19}ClN_2O$: C 77.31; H 4.40; Cl 8.15%.

C. p-Anisidine. 1.65 g (0.005 mole) III, 0.98 g (0.01 mole) Fused KOAc, and 8.92 g (0.075 mole) p-anisidine, were stirred together for 6 hr at 140° C. The products were cooled to 90°-100° C, diluted with 15 ml EtOH, the precipitate filtered off, washed with EtOH, and dried, to give 1.7 g (77%) 2-methyl-6-(p-anisidino)-7-chloroceramidonine, mp 223°-224° C. Repeated recrystallization from $CHCl_3$ gave dark violet needles, mp 234.5°-235.5° C. λ_{max}, mμ (lg ε) (ethanol): 249 (4.69), 292 (4.71), 351 (3.94), 401 (3.84), 558 (4.30). Found: C 74.75, 74.83; H 4.32, 4.32; Cl 8.11, 8.26; N 6.30, 6.40%. Calculated for $C_{28}H_{19}ClN_2O_2$: C 74.57; H 4.25; Cl 7.86; N 6.21%.

D. m-Chloroaniline. Air was passed through a mixture of 1.65 g (0.005 mole) III, 0.08 g $(Cu(OAc)_2$, and 8 ml (0.07 mole) m. chloroaniline at 120° C, for 3 hr. Chromatographing of the products on Al_2O_3 ($CHCl_3$) gave: 0.02 g (1%) 2-methyl-8-(m-chloroanilino)-7-chloroceramidonine, flocs of red needles mp 215°-216° C (ex chlorobenzene). λ_{max}, mμ (lg ε) ($CHCl_3$): 292 (4.74), 440 (4.28), 510 (4.17), 544 (4.18). Found: Cl 16.18%. Calculated for $C_{27}H_{16}Cl_2N_2O$: Cl 15.57%. 2) 1 g (44%) 2-methyl-6-(m-chloroanilino)-7-chloroceramidonine, reddish-violet plates mp 255°-256° C (ex MeOH). λ_{max}, mμ (lg ε) (n-heptane): 243 (4.55), 287 (4.76), p 330 (3.90), 400 (3.87), 528 (4.24). Found: C 71.28, 71.50; H 3.62, 3.52; Cl 16.08, 15.85; N 6.34, 3.34%. Calculated for $C_{27}H_{16}Cl_2N_2O$: C 71.21; H 3.54; Cl 15.57; N 6.15%. 3) 0.026 g (1%) 2-methyl-6,8(?)-di(m-chloroanilino)-7-chloroceramidonine, dark red needles mp 278° C (ex chlorobenzene). R_f 0.01 λ_{max}, mμ (lg ε) ($CHCl_3$): 286 (4.76), 454 (4.16), 516 (4.29), 550 (4.36).

E. Monomethylaniline. 3.5 g (0.01 mole) III, 0.16 g $Cu(OAc)_2$, and 10 ml (0.1 mole) methylaniline were heated together at 140° C for 4 hr 30 min. Chromatographing on Al_2O_3 ($CHCl_3$) gave 1.15 g (27%) 2-methyl-6-(methylanilino)-7-chloroceramidonine mp 249.5°-252° C, reddish-brown needles mp 262°-263° C (ex benzene). λ_{max}, mμ (lg ε) ($CHCl_3$): 258 (4.74), 280 (4.54), 292 (4.51), p 330 (3.91), 400 (3.62), 542 (3.99). Found: C 77.20, 77.10; H 4.17, 4.14; Cl 8.22; N 6.32, 6.46%. Calculated for $C_{28}H_{19}ClN_2O$: C 77.31; H 4.40; Cl. 8.15; N 6.44%.

Properties of aminoceramidonines. All the 6- and 8-aminoceramidonines obtained were readily soluble in benzene, chlorobenzene, $CHCl_3$, and pyridine, less soluble in alcohols, insoluble in petrol ether. Almost all of the 8-aminoceramidonines were soluble in acetone and ether, in which 6-aminoceramidonines were almost insoluble.

Chromatographic data were obtained with filter paper from the Pure Salts Experimental Plant, impregnated with a 10% solution of α-bromonaphthalene in MeOH. The following systems were used as eluants: I – 80% AcOH saturated with α-bromonaphthalene; II – 80% AcOH saturated with α-bromonaphthalene-conc HCl (100:3); III – pyridine-water (2:1), saturated with α-bromonaphthalene. Table 2 gives the data relating to the chromatographic behavior of 6- and 8-aminoceramidonines.

REFERENCES

1. A. H. Cook and W. Waddington, J. Chem. Soc., 402, 1945.
2. R. Baltzyl and E. Lorz, J. Am. Chem. Soc., 70, 861, 1948.
3. Y. T. Pratt, J. Org. Chem., 27, 3905, 1962.
4. W. Bradley, J. Chem. Soc., 1091, 1937.
5. T. Zincke and Wulfing, Ber., 14, 92, 1881.
6. E. P. Fokin and R. P. Shishkina, ZhOKh, 33, 3674, 1963.
7. F. Ullmann and O. Fodor, Ann., 380, 317, 1911.
8. N. I. Grineva, V. V. Puchkova, and V. N. Ufimtsev, ZhOKh, 33, 597, 1963.
9. N. N. Vorozhtsov, Fundamental Syntheses of Intermediates and Dyes [in Russian], Goshkhimizdat, Moscow, p. 474, 1955.
10. BASF, German Patent no. 330 572, 1914; C., 11, 559, 1921.

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