

phenothiazine compounds. The new carbazole derivatives were isolated as oxalates, which were also used in the pharmacological tests. These were carried out on isolated guinea pig intestine (S. Wiedling), and it was found that the aminoacylcarbazoles were devoid of spasmolytic and antihistaminic activity. It is of interest to note that an analogous replacement of the phenothiazine nucleus by carbazole in the aminoalkylphenothiazine series greatly reduced the strong antihistaminic activity of the parent compounds<sup>3,4</sup>.

**EXPERIMENTAL.** *9-(Chloroacetyl)-carbazole.* Chloroacetyl chloride (11.3 g, 0.1 mole) in toluene (20 ml) was added to a solution of carbazole (16.7 g, 0.1 mole) in boiling toluene (250 ml). The mixture was refluxed for twenty-four hours, most of the solvent was evaporated, and the residue was cooled. The precipitate which formed (18.4 g, 76 % yield) was collected and recrystallised from ethanol; m.p. 98–100°. (Found: C 68.7; H 4.11; Cl 14.4.  $C_{14}H_{10}ClNO$  (243.7) requires C 69.0; H 4.14; Cl 14.6 %).

*9-(Diethylaminoacetyl)-carbazole oxalate.* The above chloro compound (2.43 g, 0.01 mole) was dissolved in benzene (20 ml) and refluxed with diethylamine (1.9 g, 0.026 mole) for four hours. The reaction mixture was filtered and washed with water and the oxalate of the reaction product was precipitated by the addition of an ethereal solution of oxalic acid. The crude oxalate (1.9 g, 46 %) was recrystallised from acetone; m.p. 155–157° (dec.). Analysis indicated that three moles of oxalic acid were associated with two moles of the base. (Found: C 60.9; H 5.72; N 6.82;  $H_2C_2O_4$  33.0.  $2C_{18}H_{20}N_2O \cdot 3H_2C_2O_4$  (830.8) requires C 60.7; H 5.58; N 6.74;  $H_2C_2O_4$  32.5 %).

The percentage of oxalic acid was determined as follows: A sample of the oxalate was decomposed with alkali, the base was removed by extraction with ether, and the aqueous solution was acidified and titrated with permanganate.

*9-(Piperidinoacetyl)-carbazole oxalate.* This compound was prepared in 67 % yield from 9-(chloroacetyl)-carbazole and piperidine in an analogous way to the diethylamino compound. M.p. 228–229° (dec.) after recrystallisation from acetone-water (1:1). (Found: C 66.0; H 5.70; N 7.36.  $C_{19}H_{20}N_2O \cdot H_2C_2O_4$  (382.4) requires C 65.9; H 5.80; N 7.33 %).

*9-( $\alpha$ -Diethylaminopropionyl)-carbazole oxalate.* Prepared similarly, in 56 % yield, from 9-( $\alpha$ -bromopropionyl)-carbazole<sup>5</sup> and diethylamine. M.p. 174–175° (dec.) after recrystallisation from acetone. (Found: C 65.7; H 6.17; N 7.10.  $C_{19}H_{22}N_2O \cdot H_2C_2O_4$  (384.4) requires C 65.6; H 6.29; N 7.29 %).

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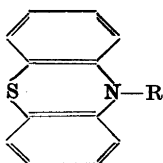
Received February 1, 1952.

## 10-Hydroxyalkylphenothiazines

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In a previous communication on antihistamine agents the synthesis of 10-( $\beta$ -hydroxypropyl)-phenothiazine (III) was described<sup>1</sup>. In connection with this work another two compounds of this class hitherto unreported (I, II) were prepared. Compound I was prepared by the addition of ethylene oxide to the sodium salt of



- R =
- I.  $-\text{CH}_2 \cdot \text{CH}_2\text{OH}$
  - II.  $-\text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2\text{OH}$
  - III.  $-\text{CH}_2 \cdot \text{CHOH} \cdot \text{CH}_3$

phenothiazine and compound II by the reduction of  $\beta$ -(10-phenothiazine)-propionic acid with lithium aluminium hydride. Attempts were also made to obtain 10-(hydroxymethyl)-phenothiazine by the reduction of methyl phenothiazine-10-carboxylate. However, this compound decomposed when treated with lithium aluminium hydride giving phenothiazine as the only identifiable product. Phenothiazine derivatives with a carbonyl group attached to the nitrogen atom in the 10-position have previously been shown to be sensitive to lithium aluminium hydride<sup>2</sup>.

**EXPERIMENTAL.** *10-( $\beta$ -Hydroxyethyl)-phenothiazine (I).* Phenothiazine (39.8 g, 0.2 mole) was added to a suspension of sodium amide (prepared from sodium (4.6 g, 0.2 mole) and liquid ammonia) in toluene (100 ml) and the mixture was refluxed with stirring for three hours. After cooling to room temperature, ethylene oxide (17.6 g, 0.4 mole) in toluene (50 ml) was added in portions, whereupon the temperature rose to 70°. The mixture was refluxed for one hour, cooled to room temperature and washed with water. The solvent was then evaporated and the residue was distilled *in vacuo* giving a viscous oil (26.9 g, 55 %) of b.p. 210–213°/0.3 mm. (Found: C 68.8; H 5.47; N 5.68.  $\text{C}_{14}\text{H}_{13}\text{NOS}$  (243.3) requires C 69.1; H 5.39; N 5.76 %).

*10-( $\gamma$ -Hydroxypropyl)-phenothiazine (II).* Lithium aluminium hydride (0.57 g, 0.015 mole) was suspended in dry ether (50 ml) and the mixture was stirred for half an hour. A solution of  $\beta$ -(10-phenothiazine)-propionic acid<sup>3</sup> (3.0 g, 0.011 mole) was added portionwise and the mixture was stirred at the reflux temperature for another half hour. Excess of hydride was destroyed with ethyl acetate (2 ml) and N hydrochloric acid (50 ml) was then cautiously added to the reaction mixture. The organic

layer was separated, washed with water and dried and the solvent was evaporated. The residue was distilled *in vacuo* giving a very viscous oil (1.4 g, 50 %) boiling at 0.01 mm at 160° (bath temperature). (Found: C 70.2; H 5.68; N 5.57.  $\text{C}_{15}\text{H}_{15}\text{NOS}$  (257.3) requires C 70.0; H 5.88; N 5.45 %).

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- 2 Dahlbom, R., and Ekstrand, T. *Acta Chem. Scand.* **5** (1951) 102.
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Received February 1, 1952.

## Studies on Sphagnum Peat

### II. \* Lignin in Sphagnum

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Although various groups of workers have sought to demonstrate the presence of lignin in *Sphagnum* species, their results have been rather indecisive. Thus, Stadnikow and Baryschewa<sup>1</sup> found 9 % of hydrochloric acid lignin in *S. parvifolium* but Holmberg<sup>2</sup> found only traces of thio-glycolic acid lignin in *S. subsecundum* Nees. Lange<sup>3</sup> studied *Sphagnum* moss with the ultraviolet microscope and concluded that it probably contained lignin, while Kratzl and Eibl<sup>4</sup>, recently, working on similar material, found about 7 % of Klason lignin, which, however, contained only 1 % of methoxyl. As nitrobenzene oxidation of the moss yielded a product, containing only 0.1 % of methoxyl, from which they were unable to isolate any vanillin, Kratzl and Eibl concluded that the moss contains no lignin, but does contain some partly methoxylated carbohydrates which easily

\* Part I. *Svensk Kem. Tid.* In press.

Also part XIII in the series *Studies on Lignin*.