



- 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 %).

- 1 Dahlbom, R. *Acta Chem. Scand.* **3** (1949) 247.
- 2 Dahlbom, R., and Ekstrand, T. *Acta Chem. Scand.* **5** (1951) 102.
- 3 Smith, N. L. *J. Org. Chem.* **15** (1950) 1125.

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## 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

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form "humus substances" which are responsible for the values of Klason lignin found.

The publication of Kratzl and Eibl prompted us to record some results obtained during the investigation of *Sphagnum balticum* Russow and *Sphagnum fuscum* W. Klinggr. Both species gave about 5 % Klason lignin, containing only about 1 % of methoxyl. Both species were carefully extracted with organic solvents and water and then submitted to nitrobenzene oxidation. The resulting products were worked up, following the procedure used by Leopold and Malmström<sup>5</sup>, and a 0.6 % yield of aldehydes (calculated as *p*-hydroxybenzaldehyde) was obtained. Paper chromatography revealed that the major constituent of the aldehyde fraction was, indeed, *p*-hydroxybenzaldehyde, and this compound was isolated in a pure state (corresponding to 90 % of the aldehyde groups). Traces of vanillin (about 4.0 %), syringic aldehyde (about 0.6 %) and formyl vanillin (about 0.1 %) were identified on the paper

chromatograms, and three further substances as yet unidentified were present.

The investigations of Bland<sup>6</sup> and Leopold and Malmström<sup>5</sup> have shown that *p*-hydroxybenzaldehyde is obtained by nitrobenzene oxidation of lignin from various sources, and it follows that *p*-hydroxyphenyl groups occur in most lignins, although to a very small extent. *Sphagnum* species apparently contain a lignin which is built up chiefly from *p*-hydroxyphenyl units and thus differs from all lignins previously investigated. This investigation is being continued.

1. Stadnikow, G., and Baryschewa, A. *Brennstoff-Chem.* **2** (1930) 21.
2. Holmberg, B. *Ing. Vetenskapsakad. Handl.* **131** (1934) 26.
3. Lange, P. Private communication.
4. Kratzl, K., and Eibl, J. *Mitt. österr. Ges. Holzforsch. Intern. Holzmarkt* **3** (1951) 77.
5. Leopold, B., and Malmström, I. *Acta Chem. Scand.* **6** (1952) 49.
6. Bland, D. E. *Nature* **164** (1949) 1093.

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