

2. The stability of the oximes is discussed and shown to be contrary to Hantzsch's theory and not fully explained by Abegg's theory.

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[CONTRIBUTION FROM BUREAU OF CHEMISTRY AND SOILS, U. S. DEPARTMENT OF AGRICULTURE]

## PREPARATION AND PROPERTIES OF THE 2-METHYL-5-ISOPROPYL PHENYL AMIDES OF SOME HIGHER FATTY ACIDS

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The use of amides as a means of identification of acids is too generally recognized to require more than a passing mention. It is noteworthy, however, that the amides<sup>3</sup> of the higher fatty acids differ so slightly in melting point that it is questionable if the identification by this method is positive enough to be of much value. Phenyl amides and substituted phenyl amides show a greater increment between melting points of closely following members of the saturated series, but even here much is to be desired. Phenylene diamides have been prepared by De Conno,<sup>4</sup> and the differences in melting point between neighboring members of the series are of such magnitude as to be of use for differentiation.

It seemed possible that weighting of the phenyl nucleus and corresponding increase in the molecular weight would lead to some useful results. Accordingly cymidine (2 methyl-5-isopropylaniline) was prepared and coupled with the higher fatty acid chlorides. The resulting substituted phenyl amides were purified and their physical constants were determined. It was observed that up to arachidic acid the melting point of the amides increased with the molecular weight, but that arachidic and lignoceric cymidines are lower in melting point than myristyl cymidine. This condition finds an analogy in the behavior of the toluides, since palmitic toluides melt at 66, or 27° lower than myristic toluides, whereas in the phenylene diamides it has been observed that both stearic and arachidic *p*-phenylene diamides melt at lower temperatures than palmitic *p*-phenylene diamide.

### Experimental

Cymidine was prepared from cymene by nitration according to Phillips'<sup>5</sup> modification of Andrews'<sup>6</sup> procedure and subsequent reduction by tin and

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<sup>3</sup> Lewkowitsch and Warburton, sixth edition, Vol. I, p. 150.

<sup>4</sup> De Conno, *Gazz. chim. ital.*, **47**, I, 93 (1917).

<sup>5</sup> Phillips, *THIS JOURNAL*, **44**, 1777 (1922).

<sup>6</sup> Andrews, *J. Ind. Eng. Chem.*, **10**, 453 (1918).

hydrochloric acid as directed by Wheeler and Smithey.<sup>7</sup> The acid chlorides were obtained from the pure acids and thionyl chloride as stated for lower homologs by Meyer,<sup>8</sup> except that the reaction period was increased by refluxing in an all-glass reaction vessel for one-half hour before distillation. Lauryl chloride boiled at 175–176°, under a pressure of 47 mm., myristyl chloride at 179–180° under 22 mm. and palmityl chloride at 199–200° under 20 mm. A high boiling residue was obtained in each case which contained some of the corresponding ketone.

The arachidic and lignoceric acids used in this study were separated from peanut oil in connection with the investigation of peanut oil.<sup>9</sup> The arachidic acid melted at 76–77°. *Anal.* Calcd. for C<sub>20</sub>H<sub>40</sub>O<sub>2</sub>: H, 12.91; C, 76.85. Found: H, 12.90; C, 77.05. The lignoceric acid which melted at 80–85.5° gave by analysis: H, 13.01; C, 78.14. Calcd. for C<sub>24</sub>H<sub>48</sub>O<sub>2</sub>: H, 13.13; C, 78.18.

Due to the limited quantity of these acids, the procedure adopted was to treat 3g. portions of the acids with an excess of thionyl chloride and after the reaction had taken place the excess of thionyl chloride was removed by distillation under reduced pressure. The reaction product, without purification, was used for the preparation of the derivatives.

The compounds described were all prepared by treating the acid chloride (3 g.) dissolved in ether with an excess of cymidine. An exothermic reaction took place and the condensation product separated gradually from the ether solution in crystalline condition. The solid was filtered off, worked with ether and recrystallized two or three times from alcohol. All were obtained as glistening white crystals which were soluble in alcohol, acetone and acetic acid. Table I gives the characteristics of each compound.

TABLE I  
2-METHYL-5-ISOPROPYL AMIDES OF FATTY ACIDS

Amide of	Subs., g.	Analysis (KGA)			M. p., °C.
		0.1 N HCl, cc.	N found, %	N calc., %	
Lauric acid	0.1171	3.6	4.31	4.23	82–83
Myristic acid	.1056	2.8	3.71	3.69	88–89
Palmitic acid	.2062	5.4	3.67	3.44	90–91
Stearic acid	.1851	4.3	3.25	3.37	93–94
Arachidic acid	.1063	2.2	2.90	3.16	81–82
Lignoceric acid	.1097	2.2	2.81	2.97	84–85

### Summary

The 2-methyl-5-isopropyl phenyl amides of lauric, myristic, palmitic, stearic, arachidic and lignoceric acids have been prepared and analyzed.

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<sup>7</sup> Wheeler and Smithey, *THIS JOURNAL*, **43**, 2613 (1921).

<sup>8</sup> Meyer, *Monatsh.*, **22**, 417 (1901).

<sup>9</sup> Jamieson, Baughman and Brauns, *THIS JOURNAL*, **43**, 1372 (1921).