

listed in the last column of the table; they are of the same order of magnitude as those of authentic salts in benzene solution<sup>3</sup>.

B. EISLER  
A. WASSERMANN

William Ramsay and Ralph Forster Laboratory,  
University College,  
Gower Street,  
London, W.C.1.  
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<sup>1</sup> Eisler, Farnsworth, Schnurmann and Wassermann, *Nature*, **168**, 459 (1951).

<sup>2</sup> Weiss, *J. Chem. Soc.*, 245 (1942).

<sup>3</sup> cf. Fuoss and Krauss, *J. Amer. Chem. Soc.*, **55**, 27 (1933).

### Preparation of Aluminium Tri-Soaps

THE aluminium salts of higher fatty acids find considerable use for various industrial purposes. Their nature and composition are, however, surprisingly obscure. Even the existence of the tri-soaps has been doubted by a number of workers<sup>1</sup>, whereas Lawrence<sup>2</sup> believes that tri-soaps of aluminium do exist, and Glazer, McRoberts and Schuman<sup>3</sup> have reported the preparation of aluminium tri-laurate by the reaction between aluminium tri-methyl and lauric acid.

In this communication is described the preparation of the tri-palmitate and tri-stearate of aluminium by the following reaction in the presence of benzene, the isopropanol produced being removed azeotropically with the solvent:



1.51 gm. of freshly distilled aluminium isopropoxide (1 mole) and 6.30 gm. of double-distilled stearic acid (3 moles) in 80 c.c. of dry benzene were refluxed at a bath temperature of 140–150° C. under a column (60 cm. long filled with Fenske helices) fitted to a total-condensation variable take-off stillhead. 3.6 gm. of distillate was collected in one hour at 72–73° C. and on analysis was found to contain 1.05 gm. of isopropanol; 20 gm. of distillate collected between 77° and 80° C. was found to contain about 0.2 gm. of isopropanol. Refluxing was continued for another four hours and the distillate was collected at 80° C. under a high reflux ratio (1:20). The remaining benzene (about 10 c.c.) was removed by distillation under reduced pressure and the product (a white solid) was heated at 200–220° C. under 0.2 mm. pressure for one hour. The hard white solid thus obtained was analysed: found: Al, 3.09; C, 74.13; H, 12.02 per cent. Al(stearate)<sub>3</sub> requires Al, 3.07; C, 73.92; H, 12.07 per cent.

Aluminium tri-palmitate prepared by a similar procedure was a slightly yellow solid which on analysis gave Al, 3.42; C, 72.64; H, 11.90 per cent; Al(palmitate)<sub>3</sub> requires Al, 3.40; C, 72.68; H, 11.81 per cent.

The method of preparation appears to be a general one and has been extended to the soaps of titanium and zirconium. Further work on the physical characteristics of these soaps is planned to establish their constitution.

The carbon and hydrogen analyses were carried out by Messrs. Weiler and Strauss, Oxford.

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R. C. MEHROTRA

Chemistry Department,  
University of Allahabad.  
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<sup>1</sup> McBain, J. W., and McLatchie, W. L., *J. Phys. Chem.*, **36**, 2567 (1932); *J. Amer. Chem. Soc.*, **54**, 3266 (1932). Gray, V. R., and Alexander, A. E., *J. Phys. Chem.*, **53**, 23 (1949).

<sup>2</sup> Lawrence, A. S. C., *J. Inst. Petroleum*, **31**, 303 (1945).

<sup>3</sup> Glazer, J., McRoberts, T. S., and Schuman, J. H., *J. Chem. Soc.*, 2082 (1950).

### A Possible Common Biogenetic Origin of the Nicotine, Tropane and Hygrine Bases

THE isolation of both hyoscyne and nicotine from a genotype of *Duboisia myoporoides*<sup>1</sup> suggests the possibility of a close biosynthetic relation between these bases, and is consequently of interest in connexion with the classical schemes of alkaloid biogenesis<sup>2</sup>. However, a synthesis of nicotine or a related compound under so-called physiological conditions has not yet been effected, and it seems desirable to consider a possible alternative mechanism.

Since the publication of a review by R. F. Dawson<sup>3</sup> on alkaloid biogenesis, the metabolic pathway to nicotinic acid from tryptophane has become better known, and evidence that the conversion proceeds by way of the intermediates kynurenine, 3-hydroxykynurenine (I), and 3-hydroxyanthranilic acid (II) is accumulating<sup>4</sup>. It would now seem feasible that the simple 3-substituted pyridine derivatives trigonelline, ricinine and the areca nut alkaloids may likewise be products of this mode of tryptophane metabolism, and result from 3-hydroxyanthranilic acid, which itself occurs in the form of the methyl ester of its O,N-dimethyl derivative as the alkaloid damascenine. In nicotine and related bases, the pyridine ring may have a similar origin, arising by cleavage of the benzene ring in (I) or (II), followed by recyclization. The pyrrolidine ring of *nor*-nicotine could be built up from all or part of the carbon chain already present in (I), or by condensation of (II) or a metabolite of (II) with, for example, acetic acid and glycine, followed by decarboxylation. Such an origin permits the formation of both D<sub>5</sub> and L<sub>5</sub> *nor*-nicotine; both isomers are found, *nor*-nicotine in *Nicotiana* spp.<sup>5,6</sup> being mainly of the L<sub>5</sub> form but the D<sub>5</sub> isomer predominating in *D. hopwoodii*<sup>7-8</sup>. The occurrence of both isomers would suggest that the pyrrolidine ring does not arise directly from L<sub>5</sub> proline<sup>9</sup>. Apparently nicotine occurs in the L<sub>5</sub> form only, even in *D. hopwoodii*<sup>8,10</sup>. This is possibly due to failure of biological methylation to take place with D<sub>5</sub> *nor*-nicotine.

This speculation receives added interest from the fact that cleavage of the benzenoid ring of (II) between C<sub>1</sub> and C<sub>2</sub> would lead to a C<sub>7</sub>N intermediate such as (III), which, on appropriate cyclization, would give rise to the *nor*-tropane skeleton (IV). The oxygen atoms in (III) are suitably placed to accommodate the naturally occurring oxygenated tropanes. In dihydroxytropane and valeroidins, the oxygen on C<sub>3</sub> is retained as a hydroxy group; in hyoscyne it is present in an epoxide ring; in meteloidine the epoxide ring, probably of the diastereoisomer of hyoscyne, is opened to form the *cis*-glycol. In addition, the side-chains in ecgonine and dioscorine are accounted for as being possibly derived from the side-chain of (I).