

LXXVIII.—*Oxonitin*.

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OXONITIN was first obtained by Carr (J., 1912, **101**, 2241) by the decomposition of aconitine permanganate with sulphuric acid. It was subsequently examined by Brady (J., 1913, **103**, 1821), Barger and Field (J., 1915, **107**, 231), Majima and Sugimoto (*Ber.*, 1925, **58**, 2047), and Späth and Galinovsky (*Ber.*, 1930, **63**, 2994). The earlier workers suggested formulæ containing 23 to 25 atoms of carbon. The work of Späth and Galinovsky, however, indicates that the compound is much more complex and they have suggested the formula  $C_{32}H_{43}O_{12}N$  as being in better agreement with their analytical results. We had occasion to examine this substance about 6 years ago in connexion with our work on pseudoaconitine, which is probably closely related to aconitine. As we had no direct interest in oxonitin, the results then obtained were not published, but in view of Späth and Galinovsky's results we offer the information we have in the hope that it may be useful to other workers in this field. These results support the view of Späth and Galinovsky to some extent in that we also find oxonitin to be more complex than was originally thought. The formula  $C_{32}H_{43}O_{12}N$  suggested by Späth and Galinovsky implies the loss of only two atoms of carbon from aconitine ( $C_{34}H_{47}O_{11}N$ ). Carr has shown that acetaldehyde is produced along with oxonitin and our analyses indicate that the methyl group attached to nitrogen in aconitine has been lost in oxonitin, a fact which has also been pointed out by Majima and Sugimoto (*loc. cit.*); so, unless the group attached to nitrogen is not indeed a methyl but an ethyl group, oxonitin cannot contain more than 31 atoms of carbon. So far as we are aware, ethyl groups attached to nitrogen have not been found in naturally occurring substances. It is of course impossible definitely to fix the formula of such a complex substance by analysis alone without the confirmation afforded by a number of derivatives, which in the case of oxonitin are not available. Our earlier analyses agree with the formula  $C_{31}H_{41}O_{12}N$ , but later analyses performed by Pregl's micro-method are higher in carbon and lower in hydrogen and agree better with the formula  $C_{31}H_{39}O_{12}N$ . We prefer the former, as it is occasionally found in micro-analysis that some water escapes absorption in the collecting apparatus and so tends to give high carbon and low hydrogen figures. This formula differs from that of aconitine in having three carbon atoms and six hydrogen atoms less; these are accounted for by the loss of acetaldehyde and the methyl group attached to nitrogen, and it contains one additional atom of oxygen, the function of which is not yet

known. The numbers found for methoxyl are not in good agreement with this formula, although they agree, *e.g.*, with the numbers found by Barger and Field, by Brady, and by Majima and Suginome. Our nitrogen figures are in agreement with those of Späth and Galinovsky, but much lower than those of the earlier workers. This is probably accounted for by the fact that methane may be evolved from aconitine derivatives (Dunstan and Carr, P., 1896, **12**, 48), and so give high results. This is obviated by using the newer method devised by Pregl (compare Henry and Sharp, J., 1928, 1109). Our oxonitin was prepared by Barger and Field's method (*loc. cit.*), had m. p. 277° (decomp.),  $[\alpha]_D^{16} -48.18^\circ$  ( $c=0.4048$  in chloroform), and gave the following analytical figures: Found (by macro-analysis): C, 60.13, 60.13; H, 6.7, 6.7; OMe, 18.2; NMe, nil. Found (by micro-analysis): C, 60.57, 60.33; H, 6.32, 6.14; N, 2.34, 2.28, 2.27, 2.26; OMe, 19.2, 18.6, 18.67, 18.75, 18.73; NMe, nil.  $C_{31}H_{41}O_{12}N$  requires C, 60.04; H, 6.67; N, 2.26; 4OMe, 20.05.  $C_{31}H_{39}O_{12}N$  requires C, 60.25; H, 6.37; N, 2.27; 4OMe, 20.1%.

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