524. *Adducts of Alantolactone and* iso*Alantolactone with Bases.*

By J. W. Steele, J. B. Stenlake, and W. D. Williams.

Formation of amides from alantolactone and *iso*alantolactone by the action of ethanolic ammonia on crude alantolactone was described by Bredt and Posth [1] and by Sprinz.[2] Hansen,[3] and Ruzicka and Pieth,[4] later showed these substances to be addition compounds and, contrary to the earlier workers, established the formula $(C_{15}H_{20}O_2)_2NH_3$ for the *iso*alantolactone adduct. The alantolactone adduct was not obtained pure. Ruzicka and Pieth [4] suggested that the adducts were probably formed by addition to the β-position

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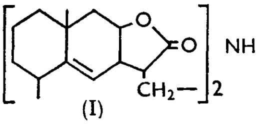
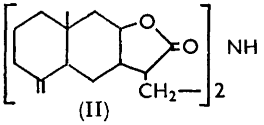
[1] Bredt and Posth, *Annalen*, 1895, **285**, 356.
[2] Sprinz, *Arch. Pharm.*, 1901, **239**, 201.
[3] Hansen, *Ber.*, 1931, **64**, 67.
[4] Ruzicka and Pieth, *Helv. Chim. Acta*, 1931, **14**, 1090.

of the lactone-conjugated double bonds, and this is supported by Hansen's observation [3] that dihydro*iso*alantolactone failed to form such an adduct.

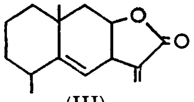
Pure samples of both alantolactone- and *iso*alantolactone–ammonia adduct have now been obtained by fractional crystallisation of the product from helenin and ethanolic ammonia, and are formulated as (I) and (II) respectively, in conformity with the recent structures for alantolactone (III) and *iso*alantolactone (IV).[5,6] Replacement of the typical ultraviolet absorption of the parent αβ-unsaturated lactones ($\lambda_{max.}$ 212 mμ, ε 9500) [6] by end absorption [ε 2770 at 210 mμ for the adduct (I) and ε 1213 at 210 mμ for the adduct (II)] confirms the mode of addition and agrees with the retention of trisubstituted and methylene double bonds in (I) and (II) respectively.



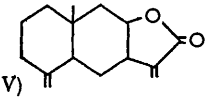
(I)



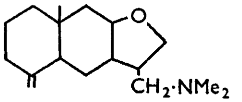
(II)



(III)



(IV)



(V)

Reaction of the same sample of helenin with dimethylamine under similar conditions gave only one crystalline product, a 1 : 1 adduct which yielded formaldehyde on ozonolysis. It is therefore formulated as (V), being derived from *iso*alantolactone. A second sample of helenin gave the same adduct, and no evidence of an isomer.

Experimental.—Alantolactone- and iso*alantolactone–ammonia adducts.* Helenin (1·07 g.) in 95% ethanol (10 ml.) was saturated with ammonia. Fractional crystallisation of the solid (0·7 g.) which separated after 16 hr. at room temperature gave fractions: I (102 mg.), m. p. 236—240°; II (56 mg.), m. p. 227—233°; III (276 mg.), m. p. 213—215°; and IV (124 mg.), m. p. 205—208°. Recrystallisation of fraction I from ethanol (charcoal) gave the *iso*alantolactone–ammonia adduct (32 mg.), m. p. 248—249° (decomp.) [Found: C, 74·7; H, 8·6; N, 2·9%; *M* (Rast), 545. Calc. for $C_{30}H_{43}O_4N$: C, 74·8; H, 9·0; N, 2·9%; *M*, 481]. Ruzicka and Pieth [4] gave m. p. 233—234°. Fraction IV from ethanol gave colourless needles of the *alantolactone–ammonia adduct*, m. p. 205—206° (decomp.) (Found: C, 74·8; H, 8·3; N, 2·9. $C_{30}H_{43}O_4N$ requires C, 74·8; H, 9·0; N, 2·9%).

iso*Alantolactone–dimethylamine adduct.* Helenin (0·5 g.) in absolute ethanol (10 ml.) was mixed with excess of dimethylamine. After 16 hr. at room temperature, colourless needles of the iso*alantolactone–dimethylamine adduct* separated, having m. p. 150° (block) (from aqueous ethanol), ε 1218 at 210 mμ (Found: C, 73·4; H, 9·25; N, 4·9. $C_{33}H_{27}O_2N$ requires C, 73·6; H, 9·8; N, 5·1%).

Ozonolysis of iso*alantolactone–dimethylamine adduct.* The adduct (0·3 g.) was ozonised in chloroform (10 ml.) for 1 hr. at 0°. The ozonide was decomposed by shaking it with acetic acid (2 ml.) and zinc powder (0·4 g.) for 1 hr., the mixture was filtered, and water-soluble compounds were extracted with water (30 + 20 ml.). The aqueous extracts were partially neutralised with 20% sodium hydroxide solution (5 ml.) and treated with excess of dimedone in ethanol, giving the formaldehyde–dimedone derivative (115 mg.), m. p. and mixed m. p. 189—190°.

THE SCHOOL OF PHARMACY, THE ROYAL COLLEGE OF SCIENCE AND TECHNOLOGY,
GLASGOW.
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[5] Tsuda, Tanabe, Iwai, and Funakoshi, *J. Amer. Chem. Soc.*, 1957, **79**, 5721.

[6] Asselineau and Bory, *Compt. rend.*, 1958, 1874.