

# CXXIV.—Di-Sec.-Octyl Tartrate and Di-sec.-Octyl Dibenzoyletartrate.

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It has already been explained (Trans., 1901, 79, 1103) that by the action of an acid chloride on a tartaric ester containing alkyl groups high in the series it was anticipated that it would be easy to obtain a monoacyl derivative. When one ethyl group of diethyl tartrate is replaced by an octyl group (*loc. cit.*), no indication could be found that the latter exerts any "surrounding" influence to prevent the easy introduction of two acyl groups. The second ethyl group has also been replaced by the octyl radicle, but even then there is no evidence of a hindering influence exerted by the alkyl groups on the reactivity of the hydroxyl radicles of the tartaric molecule.

In the preparation of the dioctyl tartrate, the same *sec.*-octyl alcohol was used as formerly.

## *Dioctyl Tartrate.*

Ethyl octyl tartrate was prepared by the method already described and 35 grams of it were dissolved in 150 grams of octyl alcohol; the solution was saturated in the cold with dry hydrogen chloride, and after standing at the ordinary temperature for three days the hydrogen chloride was extracted under reduced pressure and the residue distilled.

The fraction distilling above  $215^{\circ}$  under 15 mm. pressure had a rotation of  $4.15^{\circ}$  in a 50 mm. tube at  $20^{\circ}$ . This fraction was rectified and the oil which passed over at  $215\text{--}225^{\circ}$  under 19 mm. pressure showed a rotation of  $4.05^{\circ}$  in the same tube at  $18.5^{\circ}$ . The whole of the distillate which had passed over above  $200^{\circ}$  was washed with water, and after drying was dissolved in octyl alcohol; the solution was then saturated with hydrogen chloride and treated as before. On distilling the oil left after the extraction of the hydrogen chloride, a fraction was obtained which boiled at  $225^{\circ}$  under 20 mm. pressure and had a rotation of  $3.60^{\circ}$  in the 50 mm. tube at  $18^{\circ}$ . This rotation was not altered by redistillation of the ester, and the same rotation was obtained with different fractions of the same distillation.

Diocetyl tartrate is a viscous, slightly yellow oil with a rancid odour.

The following density determinations were made:

$$d_{32^{\circ}/4^{\circ}} = 1.0077.$$

$$d_{45^{\circ}/4^{\circ}} = 0.9967.$$

The density at  $18^{\circ}$  would be 1.0195; consequently

$$[\alpha]_D^{18^{\circ}} = \frac{3.6}{0.5 \times 1.0195} = 7.06^{\circ}, \text{ and } [M]_D^{18^{\circ}} = 26.30^{\circ}.$$

#### *Diocetyl Dibenzoyltartrate.*

Preliminary experiments showed that by the action of benzoyl chloride on diocetyl tartrate a levorotatory product was formed, and this, in analogy with the results which have been obtained for diethyl tartrate (Frankland and Wharton, *Trans.*, 1896, 69, 1586), dibutyl tartrate (Freundler, *Ann. Chim. Phys.*, 1894, [vii], 3, 479), and ethyl octyl tartrate (*Trans.*, 1901, 79, 1106), indicated that two acyl groups may easily be introduced into the molecule. It was evident, too, that the introduction of a single acyl group would be a matter of some difficulty, and consequently the original view was not realised.

The dibenzoyl derivative was prepared by heating 40 grams of benzoyl chloride to  $140^{\circ}$  and slowly dropping in 9 grams of diocetyl tartrate with repeated shaking. The mixture was heated at the same temperature for two days until there was no further evolution of hydrogen chloride. It was then poured into water and thoroughly shaken during two days with sodium carbonate solution. The oil was dissolved in ether, and the ethereal solution shaken with aqueous sodium carbonate solution until the odour of acid chloride completely disappeared. The ethereal solution was washed, dried over ignited potassium carbonate, then filtered, after which the ether was distilled off. A dark, oily residue was left which was dissolved in alcohol and shaken with charcoal. After filtering off the charcoal, the solution was quickly

heated and water was added until there was just a permanent turbidity. On cooling, a slightly yellow oil was precipitated which, after drying, gave a rotation of  $-22^{\circ}50'$  in a 50 mm. tube. The oil was further purified by dissolving in alcohol and precipitating with water; it was then dissolved in ether, dried over potassium carbonate, and the ether distilled off. The oil, which was yellowish and possessed a slightly rancid odour, was dried over sulphuric acid under reduced pressure, and gave a rotation of  $-23^{\circ}59'$  in a 50 mm. tube at  $25^{\circ}$ . Further treatment by the same method did not alter the rotation:

0.1320 gave 0.3390  $\text{CO}_2$  and 0.0856  $\text{H}_2\text{O}$ .  $\text{C} = 70.04$ ;  $\text{H} = 7.20$ .

$\text{C}_{84}\text{H}_{46}\text{O}_8$  requires  $\text{C} = 70.11$ ;  $\text{H} = 7.90$  per cent.

The following density determinations were made:

$d\ 21^{\circ}/4^{\circ} = 1.0953$ .  $d\ 30.5^{\circ}/4^{\circ} = 1.0860$ .  $d\ 45^{\circ}/4^{\circ} = 1.0725$ .

The density at  $25^{\circ}$  would therefore be 1.0913; consequently  $[\alpha]_D^{25} = -\frac{23.98}{0.5 \times 1.0913} = -43.94^{\circ}$ , and  $[M]_D^{25} = -255.7^{\circ}$ .

As the polarimeter used was not fitted with a heating arrangement, it was not possible to determine the influence of temperature on the rotation to find whether, in the case of the benzoyl compound, this passes through a maximum, as Frankland and Wharton (*Trans.*, 1896, 69, 1586) found to be the case with diethyl dibenzoyl tartrate.

### Conclusions.

The ester described above extends the series of tartaric esters, and for comparison the following table may be given:

Dimethyl tartrate *	$[\alpha]_D^{18} = 1.83^{\circ}$	$[M]_D^{18} = 3.26^{\circ}$
Diethyl tartrate *	$[\alpha]_D^{20} = 7.66$	$[M]_D^{20} = 15.78$
Di- <i>n</i> -propyl tartrate *	$[\alpha]_D^{20} = 12.44$	$[M]_D^{20} = 27.37$
Di- <i>isopropyl</i> tartrate *	$[\alpha]_D^{20} = 14.89$	$[M]_D^{20} = 32.76$
Di- <i>n</i> -butyl tartrate †	$[\alpha]_D^{19} = 10.3$	$[M]_D^{19} = 13.80$
Di- <i>isobutyl</i> tartrate *	$[\alpha]_D^{100} = 19.87$	$[M]_D^{100} = 26.62$
Di- <i>sec</i> -octyl tartrate .....	$[\alpha]_D^{18} = 7.06$	$[M]_D^{18} = 26.30$
Ethyl <i>sec</i> -octyl tartrate ‡	$[\alpha]_D^{20} = 7.78$	$[M]_D^{20} = 22.55$

The similarity of the specific rotations of diethyl and dioctyl tartrates is striking, and may possibly be due to a rise of rotatory power to a maximum, with subsequent rapid fall as the series of esters is ascended (see Frankland, *Trans.*, 1899, 75, 547). The relationship

\* Pictet, *Jahresber.*, 1882, 856.

† Freundler, *Ann. Chim. Phys.*, 1894, [vii], 3, 447.

‡ McCrae, *Trans.*, 1901, 79, 1106.

between the rotations of diethyl and dioctyl tartrates is very similar to that between the rotations of ethyl glycerate and octyl glycerate, or to that between the rotations of ethyl acetylglycerate and octyl acetylglycerate quoted by Frankland (*loc. cit.*, 354 and 355).

Taking the view previously expressed, that substitution effected sufficiently far removed from the asymmetric carbon atom scarcely modifies the rotatory power, we may here find a confirmation of Guye's proposition (Trans., 1901, 79, 476), inasmuch as substitution of a methylene hydrogen atom in the ethyl group of ethyl octyl tartrate by *n*-hexyl causes only a small increase in the molecular rotation, and the increase is only small even if we consider the replacement of a methylene hydrogen atom of each of the ethyl groups of diethyl tartrate by *n*-hexyl.

The comparatively high negative rotation of dioctyl dibenzoyl-tartrate shows that the introduction of two aromatic acyl groups into the tartaric molecule changes the dextrorotation into a levorotation (Frankland and Wharton, Freundler, McCrae, *loc. cit.*), and it would therefore appear that this is quite general and is independent of the nature of the alkyl groups present.

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