

## 198. "Green" Ethyl Tartrate.

By T. S. PATTERSON and ALEXANDER H. LAMBERTON.

It was suggested by Patterson (J., 1922, 121, 1042) that the slight yellow colour sometimes acquired by ethyl tartrate when hot, and lost after a few hours (Lowry and Cutter, *ibid.*, p. 537), might be due to an oxidation product, since it could easily be produced in colourless ethyl tartrate by passage of air through the hot ester. We have investigated this matter further.

Various experiments were made to concentrate this oxidation product as far as possible. About 250 g. of ethyl tartrate were heated to 200° in a Claisen flask, the side neck of which was lengthened, and contained a rod and disc fractionating column. Air was sucked through the hot ester for some 5 minutes at ordinary pressure. Then, at reduced pressure, a small first fraction, which was highly coloured (brownish-yellow), was carefully distilled off. The whole process was repeated some 20 times, until about 150 g. of distillate had been collected. This had  $\alpha_{D}^{20}$  (100 mm.) + 10°. On redistillation, a colourless, inactive liquid (A) (about 7 g.) was first collected. It gave a strong positive reaction with the fuchsine aldehyde reagent, but was not further examined. The second fraction (B) consisted of some 35 g. of greenish-yellow material, the rotation of which was  $\alpha_{D}^{20}$  (100 mm.) = + 8.4°. It gave a moderate fuchsine aldehyde reaction—possibly because it still contained some of fraction (A)—and reduced Fehling's solution; in direct contrast, in both respects, to the original ethyl tartrate. The succeeding fractions, which, since they all consisted of ethyl tartrate containing but a small proportion of an impurity boiling at only a slightly lower temperature than the ethyl tartrate itself, showed no appreciable temperature range, gave the following results for  $l = 100$  mm.: (C), 25 g., greenish,  $\alpha_{D}^{17}$  + 10.5°; (D) 25 g., almost colourless,  $\alpha_{D}^{18}$  + 11.55°; (E) 42 g., colourless,  $\alpha_{D}^{18}$  + 11.4°. The second fraction (B) gradually lost most of its colour on standing for a month in a stoppered flask, but the colour returned again on heating. The colour was immediately destroyed by addition of a drop of water to 0.5 c.c. of the product.

At this point, Sir Gilbert Morgan having mentioned, in conversation, that glyoxal turns green on heating, we added to a sample of colourless ethyl tartrate a small quantity (1%) of glyoxal; when the solution was heated, a colour, similar to that which had been observed in our earlier experiments, developed, and faded again on cooling. The formation of glyoxal itself from ethyl tartrate by oxidation seemed unlikely, but the observation supported the idea, originally held, that the colouration might be due to a ketosuccinic ester. The experiment with glyoxal also gave some notion of the amount of impurity sufficient to cause the green colour in the ethyl tartrate, and also suggested some experiments on its recognition.

To ethyl tartrate containing 1% of glyoxal, absolute alcohol (3 vols.) was added, and then a solution in alcohol of 2 : 4-dinitrophenylhydrazine sulphate. This gave an orange precipitate which was practically insoluble in glacial acetic acid and did not melt below 280°.

With 2 : 4-dinitrophenylhydrazine, a portion of the fraction (B) also yielded a precipitate (1.1 g. from 4.84 g. of green ester), which, however, was lighter in colour than that due to glyoxal. Crystallised from acetic acid, it decomposed at 180—200°, and after five crystallisations from chloroform, formed small lemon-yellow needles, decomposing gradually above 180° [Found : C, 42.6; H, 3.25; N, 20.1.  $\{C_6H_3(NO_2)_2 \cdot NH \cdot N : C(CO_2Et)_2\}_2$  requires C, 42.7; H, 3.2; N, 19.9%]. The first crop of crystals contained also a small quantity of bright red crystals, which could not be isolated for further examination.

It seems very probable, therefore, that the substance present in the ethyl tartrate, to which the green colouration on heating is due, is ethyl diketosuccinate, although there is a possibility that, if ethyl hydroxyketosuccinate were the active agent, it might be oxidised, by the 2 : 4-dinitrophenylhydrazine, to diketosuccinic ester, which then could yield the *bis*-2 : 4-dinitrophenylhydrazone. This view appears to be corroborated by the experiments of Astin and Riley (J., 1934, 845), who oxidised ethyl tartrate by means of selenium dioxide and isolated ethyl hydroxyketosuccinate, which was found to form, not a mono-, but a bis-hydrazone with phenylhydrazine. This bis-hydrazone, on boiling with glacial acetic acid, as was observed by Anschütz and Parlatto (*Ber.*, 1892, 25, 1979) gave the 4-phenylhydrazone of ethyl 4 : 5-diketo-1-phenyl-4 : 5-dihydropyrazole-3-carboxylate, m. p. 153.5°.

Our sample of "green" ethyl tartrate (B), with phenylhydrazine acetate in aqueous solution, gave a pasty yellow precipitate, which, on boiling with glacial acetic acid, and then dilution with water, yielded a substance, m. p. 153—154°, identical with that described by Anschütz and Parlatto (Found : N, 16.6. Calc. : N, 16.7%).

Astin and Riley do not refer to any green colour in their esters, but Astin, Moulds, and Riley (J., 1935, 902) mention a yellow colour produced by selenium dioxide oxidation of ethyl malate to ethyl diketosuccinate; ethyl tartrate was oxidised only to ethyl hydroxyketosuccinate. We obtained no green product on aerating ethyl malate in the same way that we had adopted with ethyl tartrate.

In corroboration of these results we found that, when a mixture of ethyl tartrate with a small quantity of ethyl diketosuccinate (Anschütz and Parlato, *Ber.*, 1892, 25, 1976) was heated, a green colour developed, which faded on cooling; and, on treatment with 2:4-dinitrophenylhydrazine, the mixture behaved in a manner similar to that of the "green" ethyl tartrate of fraction (B), yielding a hydrazone (Found: C, 42.55; H, 3.3; N, 19.7%). In addition, the pyrazole obtained with phenylhydrazine, as described above, from "green" ethyl tartrate, was identical (m. p. and mixed m. p.) with a synthetic specimen prepared from ethyl diketosuccinate and phenylhydrazine.

*Experiments with Other Analogous Esters.*—Methyl tartrate and isobutyl tartrate behaved like ethyl tartrate, but only a weakly coloured specimen could be obtained from the former, owing to decomposition.

In the case of isobutyl tartrate the colouration was concentrated as in the ethyl ester, but without the rod and disc; by some twelve aerations and distillations, 60 g. of isobutyl tartrate yielded 23 g. of moderately "green" ester. The concentration was not so effective as in the case of the ethyl ester; the colouration could be removed by crystallisation from benzene, and concentrated to some extent in the mother-liquors.

With an alcoholic solution of the aerated ester, 2:4-dinitrophenylhydrazine sulphate gave the yellow bis-2:4-dinitrophenylhydrazone of isobutyl diketosuccinate (Found: N, 18.4. Calc. for  $C_{24}H_{26}O_{12}N_8$ : N, 18.1%). It had no definite m. p., but decomposed about 180°.

5 G. of the "green" isobutyl ester were boiled for 15 minutes with 0.5 g. of phenylhydrazine acetate in glacial acetic acid. The orange-coloured solid (mainly isobutyl tartrate) obtained by precipitation with water was dried and crystallised from carbon disulphide. The mother-liquor, after removal of isobutyl tartrate, was evaporated, and the residue, after two recrystallisations from methylated spirit, yielded a few mg. of felted, orange needles, m. p. 127—128°, identical with a synthetic specimen of the 4-phenylhydrazone of isobutyl 4:5-diketo-1-phenyl-4:5-dihydropyrazole-3-carboxylate, prepared from isobutyl diketosuccinate, which, in turn, was obtained, by Anschütz and Parlato's method (*loc. cit.*), from sodium dihydroxytartrate and isobutyl alcohol. The isobutyl diketosuccinate was a viscous red oil, b. p. 109—112°/3 mm. It was not analysed as such, since v. Auwers reported (*Ber.*, 1918, 51, 1121) that the corresponding ethyl diketosuccinate could not be obtained pure by distillation. Its identity was, however, amply confirmed by the formation of the bisphenylhydrazone (Found: N, 18.1. Calc.: N, 18.1%) and the above-mentioned pyrazole (Found: C, 65.8; H, 5.6; N, 15.2. Calc.: C, 65.9; H, 5.5; N, 15.4%). With a little water, a colourless oil was obtained which ultimately yielded a white solid, m. p. 87—90° (from carbon disulphide). This, of which we had only a small quantity, gave analytical results approximating to those required for a monohydroxide (Found: C, 53.0; H, 7.0. Calc.: C, 52.1; H, 7.2%). When either this substance or the original isobutyl diketosuccinate was added to hot colourless isobutyl tartrate, the colouration of the "green" ester was exactly imitated.

The foregoing experiments appear to show that, when air is aspirated through hot ethyl tartrate, an easily volatile, optically inactive, aldehydic compound is produced (which was not further examined), along with some ethyl diketosuccinate (formed probably *via* the ethyl hydroxyketosuccinate); and that to this diketosuccinate is owing the appearance and disappearance of a greenish-yellow colour on heating and cooling respectively. The mechanism of the change of colour with heating and cooling remains, however, obscure, although there is some evidence in favour of its being due to hydration (Wahl, *Bull. Soc. chim.*, 1908, 3, 24). With this view our observations are not inconsistent; since (1) the green colouration in ethyl tartrate disappeared immediately on addition of water, and (2), when the colourless solid obtained from isobutyl diketosuccinate and water was added to hot molten isobutyl tartrate, a green colour was produced.

The authors express their thanks to the Carnegie Trustees for the Universities of Scotland for assistance towards the cost of this investigation, and one of them, in addition, for a Carnegie Scholarship.