440. *Investigations of the Olefinic Acids. Part XIII.* Δ^{γ}-n-*Hexenoic Acid and " Hydrosorbic " Acid.*

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The " hydrosorbic " acid prepared by the reduction of sorbic acid with sodium amalgam has been proved to be a mixture of Δ^{β}- and Δ^{γ}-*n*-hexenoic acid (Goldberg and Linstead, J., 1928, 2343; Evans and Farmer, *ibid.*, p. 1644), but neither component has been separated from it. As the Δ^{γ}-acid was required for synthetic purposes, its isolation from hydrosorbic acid was attempted.

It was not found possible to effect a separation of the Δ^{β}- and the Δ^{γ}-acid either by taking advantage of the difference in velocity of formation of the amides from the esters of the component acids (compare Philippi and Galter, *Monatsh.*, 1929, **51**, 253) or by the method of partial esterification. The two acids are esterified at practically the same rate, which, in view of the difference between their dissociation constants—Δ^{β} 3·05, Δ^{γ} 1·91 ($\times 10^{-5}$)—confirms Sudborough's contention that there is no simple connexion between the two phenomena. The rapid esterification of the Δ^{γ}-acid, however, led to the following indirect method of separation.

Hot alkali converts the Δ^{β}-acid into a mixture containing 74% of the Δ^{α}- and 26% of the Δ^{β}-acid, but has no effect on the Δ^{γ}-isomeride (Eccott and Linstead, J., 1929, 2153). Similar treatment of hydrosorbic acid, assumed to be a 50% mixture of the Δ^{β}- and the Δ^{γ}-acid, should yield 37% of the Δ^{α}-, 13% of the Δ^{β}-, and 50% of the Δ^{γ}-acid. Such a mixture on controlled esterification should yield the Δ^{β}- and the Δ^{γ}-acid as esters and leave the Δ^{α}-acid unchanged. By hydrolysing the esters and repeating the whole process of equilibration and partial esterification twice, the Δ^{γ}-acid should be obtained almost free from its isomerides.

This process was successful in practice and yielded Δ^{γ}-hexenoic acid almost identical in properties with that prepared by other methods (see table below); the method seems the simplest available for the preparation of the acid in quantity. From the amounts of acids and esters isolated, the proportion of the Δ^{γ}-isomeride in " hydrosorbic " acid prepared by the reduction of sorbic acid by sodium amalgam in slightly acid solution is estimated to be 55—60%, in agreement with Burton and Ingold's figure of 55% (J., 1929, 2022).

Δ^{γ}-Hexenoic acid has previously been prepared (i) by decarboxylating the lactonic acid obtained by the reduction of α-acetylglutaric acid (Fichter, *Ber.*, 1896, **29**, 2370), (ii) by the pyrolysis of α-hydroxy-α-methyladipic acid (when the Δ^{δ}-isomeride also is formed; Fichter and Langguth, *Annalen*, 1900, **313**, 375; *Ber.*, 1897, **30**, 2051), and (iii) by decarboxylating Δ^{β}-butenylmalonic acid (Eccott and Linstead, *loc. cit.*). The product of the third method differed in physical properties from Fichter's acid, but yielded the same derivatives. In view of this discrepancy, all three processes have been re-examined and are now found to give essentially the same material with the properties shown below:

Δ^{γ}-*n*-Hexenoic acid from	M. p.	B. p.	$d^{20°}_{4°}$.	$n^{20°}_{D}$.	Anilide, m. p.	Dibromide, m. p.
" Hydrosorbic " acid	+1°	107°/16 mm.	0·9610	1·4385	87°	84°
Acetylglutaric acid..............	0	110/20 mm.	0·9647	1·4380	87	84
Hydroxymethyladipic acid ...	0	107/16 mm.	—	—	—	—
Butenylmalonic acid	+1	102/12 mm.	0·9658	1·4367	87	84

The Δ^{β}-butenylmalonic acid which yielded this hexenoic acid was prepared by a new method described in the following paper. The cause of the difference previously observed is unknown, but there is no longer any reason to assume the existence of a definite stereoisomeride.

Eijkmann (*Rec. trav. chim.*, 1893, **12**, 160) states that by crystallising the (Fichter) acid from cold petroleum an acid of m. p. 13° is obtained, but we have been unable to confirm this and from the concordance in properties of the products of four totally different preparative methods we regard the acid of m. p. 0—1° as being pure Δ^{γ}-*n*-hexenoic acid.

EXPERIMENTAL.

[Recorded densities and refractive indices are for $d_{4^\circ}^{20^\circ}$ and $n_D^{20^\circ}$ respectively. Iodine additions (J) are for a 10-minute reaction at 20°. All the esterifications were conducted at room temperature, a 1·2*N*-solution of hydrogen chloride in methyl alcohol being used.]

Hydrosorbic acid was prepared in 75% yield by reducing sorbic acid with sodium amalgam, sufficient sulphuric acid being added periodically to keep the solution acid. 10 G. were treated with 7·5 c.c. of methyl-alcoholic hydrogen chloride and 19·5 c.c. of methyl alcohol for 2 hours. Conversion into the ester (b. p. 57°/16 mm.) was almost complete and this was hydrolysed to an acid of J 65·4%. In another experiment the acid (10 g.) with J 65·7% was treated with 1 c.c. of alcoholic acid and 3 c.c. of methyl alcohol for 5 hours. The unesterified acid had J 65·1% and that obtained by hydrolysis of the ester had J 67·7%. This proves that there is no appreciable separation of the Δ^{β}- and the Δ^{γ}-acid by esterification.

Hydrosorbic acid (40 g.) was equilibrated over-night (steam-bath) with 40 g. of caustic potash and 80 c.c. of water, and the crude acidic product (35 g.) treated with 27 c.c. of alcoholic acid and 70 c.c. of methyl alcohol for 1·5 hours. The unesterified acid (10 g.), which was separated in the usual way (Eccott and Linstead, *loc. cit.*), was almost pure Δ^{α}-*n*-hexenoic acid, m. p. 32°. The ester (30 g.) was hydrolysed and equilibrated by heating it (steam-bath, 15 hours) with 30 g. of caustic potash in 60 c.c. of water and a little alcohol. The recovered acid (18 g.) was esterified with 13 c.c. of alcoholic acid and 35 c.c. of methyl alcohol for 1·5 hours, to yield a small amount of an acid and 16 g. of an ester. The acid was a semi-solid mixture of (mainly) the Δ^{α}- and the Δ^{γ}-acid with J 25·4%. The ester was hydrolysed and equilibrated as before to an acid (11 g.), which was esterified (9 c.c. alcoholic acid, 23 c.c. alcohol, 1·5 hours) to almost pure methyl Δ^{γ}-*n*-hexenoate, b.p. 54°/20 mm., d 0·9136, n 1·4244, whence $[R_L]_D = 35{\cdot}73$ (calc., 35·71). A trace of unesterified acid with J 54·2% remained. This ester on hydrolysis yielded 10 g. of Δ^{γ}-*n*-hexenoic acid with the properties tabulated above (whence $[R_L]_D = 31{\cdot}16$; calc., 30·98). A mixture of this acid and a sample prepared from acetylglutaric acid melted at 0—1°.

The above figures show that 35 g. of equilibrated hydrosorbic acid gave 10 g. of the Δ^{α}-acid and 30 g. of the Δ^{β}- and the Δ^{γ}-ester, equivalent to 24 g. of acids. If x is the amount of the Δ^{β}-acid in 35 g. of hydrosorbic acid, then after equilibration the mixture will contain $(35 - x)$ g. of the Δ^{γ}-, $26x/100$ g. of the Δ^{β}-, and $74x/100$ g. of the Δ^{α}-acid.

$$\text{From } 74x/100 = 10,\ x = 13{\cdot}5 \text{ g.}$$
$$\text{From } 35 - x + 26x/100 = 24,\ x = 14{\cdot}8 \text{ g.}$$

The Δ^{β}-acid content of hydrosorbic acid is thus about 14/35 or 40%. The true amount will probably be a little greater than this owing to the formation of β-hydroxy-acid during equilibration, which will occur solely at the expense of the Δ^{β}-acid. By a similar calculation the proportion of the Δ^{β}-acid in the Δ^{γ}-acid finally isolated is estimated to be about 1%.

The other preparative methods do not call for special comment. All the products gave the characteristic cadmium salt (Fichter) and anilide, m. p. 87° (Eccott and Linstead). Treated with bromine in carbon disulphide, they all yielded an oily dibromide which solidified (vacuum) to the same *γδ-dibromo-*n*-hexoic acid*, white needles from benzene–petrol, m. p. 84° (Found: Br, 58·2. $C_6H_{10}O_2Br_2$ requires Br, 58·4%). The identity of the derivatives of the various preparations was confirmed by mixed m. p. determinations.

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