74. *Catalytic Hydrogenation of Unsaturated Compounds. Part II. The Step-wise Reduction of Conjugated Acids.*

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INGOLD and SHAH (J., 1933, 885) state that, according to their experiments, sorbic acid, β-vinylacrylic acid, and ethyl muconate yield each only an equimolecular mixture of fully reduced derivative and unchanged conjugated compound when submitted to 50% hydrogenation in the presence of a platinum catalyst, although the degree of quantitative accuracy attained does not exclude the production of very small proportions (ranging from 0·1% to 3%) of dihydro-compounds. Their experimental work, which was " commenced with the theoretical preconception that the formation of considerable quantities of dihydro-products would not be the general rule," is thus in direct opposition to the results of Farmer and Galley (J., 1932, 430; *Nature*, 1933, **131**, 60; J., 1933, 687).

That the results recorded by Farmer and Galley for sorbic acid are true in all particulars, we have now proved by the simple method of isolating the dihydro-products or their simple derivatives and weighing them; it has been still easier to show by precisely similar means that muconic acid, which was not examined by Farmer and Galley, also yields (when hydrogenated in the form of its sodium salt) both of the possible dihydro-derivatives.

With regard to the proportions of the various acids in the hydrogenation product, Farmer and Galley found, and we confirm, that the figure for unchanged conjugated acid (which in 50% hydrogenation is equal to that for the fully saturated acid produced) is fairly reproducible from experiment to experiment, provided that (1) a rigorous separative technique is adhered to* (see p. 305) and (2) catalyst specimens of comparable activity are employed. The figures recorded by Farmer and Galley for the unchanged conjugated acid and for the fully reduced acid isolated (and consequently for the total of dihydro-acids) have repeatedly been reproduced by them and by us in experiments carried out with " new " catalyst preparations. Furthermore, no appreciable change in these figures has been observed in experiments in which the catalyst has been poisoned by the addition of carbon disulphide in increasing quantities up to the point of suppression of the reaction. Where, however, the catalyst has become partially deactivated with use (compare the " aged " catalyst of Farmer and Galley, J., 1933, 687) the percentage of dihydro-acids increases above the normal figure, but the increase affects mainly the yield of Δ^{α}-dihydro-acid. The deactivation becomes very noticeable during the later stages of reductions which have been unduly prolonged by the use of a small amount of catalyst (*e.g.*, 0·2 g.) to reduce a relatively large amount (*e.g.*, 50 g. or more) of conjugated acid, and in the following table the extent to which sorbic acid suffers conversion into dihydro-derivatives during such an operation is compared with that recorded by Farmer and Galley for reduction carried out with a " new " catalyst.

	50% Hydrogenation of Sorbic Acid.		50% Hydrogenation of Muconic Acid (with catalyst in low concentration) (%).
	" Ageing " catalyst (%).	" New " catalyst (F. and G.) (%).	
Unchanged acid	38·5	44·0	40·3
Fully reduced acid......	39·5	44·0	40·3
Δ^{α}-Dihydro-acid	18·0	7·0	11·3
Δ^{β}-Dihydro-acid	4·1* } 4·6	} 5·0	7·5
Δ^{γ}-Dihydro-acid	0·5		

* This figure was obtained by difference.

The corresponding figures for a reduction of muconic acid (sodium salt) effected with a relatively small proportion of catalyst are also shown, and it is seen that terminal reduction occurs here, as with sorbic acid, to quite an important extent.

From the muconic acid product, Δ^{α}-dihydromuconic acid (*trans*) has been obtained for the first time in the homogeneous condition : the descriptions of this acid by Rupe (*Annalen,*

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* By the separative procedure outlined by Ingold and Shah much of the Δ^{α}-dihydro-acid produced from sorbic acid would doubtless be mistaken for unchanged sorbic acid and would not be present in the dihydro-acid fraction submitted to ozonolysis.

1890, **256**, 26) and Ingold (J., 1921, **119**, 965) clearly refer to mixtures (possibly equilibrium mixtures) of the Δ^{α}- and the Δ^{β}-acid* (see Part III).

It is unlikely that Ingold and Shah's results were due to a peculiar quality of their catalyst, for in nearly four years' continuous work by one of us with platinum catalysts, prepared repeatedly and by different workers from Adams and Shriner's hydrated platinum oxide (*J. Amer. Chem. Soc.*, 1923, **45**, 2171; " Organic Syntheses," VIII, 92)—which Ingold and Shah also employed—no single departure from the partially step-wise mode of reduction of conjugated compounds described by Farmer and Galley has been encountered; furthermore, recent evidence indicates that conjugated tri-olefinic acids suffer (in part) step-wise reduction in an analogous way to that of sorbic acid and its homologues. We have no doubt that the ozonolytic degradative procedure employed by Ingold and Shah (which Farmer and Galley had rejected after trial as unsuitable for the estimation, or even the detection, of small proportions of the dihydro-products) is responsible for their failure to detect any of the eight dihydro-derivatives of the three acids they examined.

Ingold and Shah's method of experimentally testing the truth of the proposition that " either there is but a single reaction leading directly to the tetrahydro-derivative, or the dihydro-compound is produced as an intermediate product in two consecutive reactions, of which the second proceeds more rapidly than the first " is based on an unwarranted assumption. They apparently suppose that, if a substance A is reduced more rapidly than a substance B when each is taken separately, A will be reduced preferentially to B in a mixture of the two. That this assumption is invalid, or is not generally valid, was shown by Farmer and Galley in the case of allyl alcohol and Δ^{α}-hexenoic acid, and is indicated by an observation concerning pinene and cinnamic acid (*J. Amer. Chem. Soc.*, 1929, **51**, 3418) to which Professor H. Adkins has recently drawn our attention. It appears necessary to make a clear distinction between the *selectivity* of reduction in mixtures of substances and the *relative speeds* of reduction of the separate substances.

In respect of the specificity of catalysts in promoting the hydrogenation of this or that type of double-bonded centre in a multi-unsaturated molecule, we have proceeded further in the direction of clear-cut step-wise reduction of simple conjugated acids by producing nearly complete (at least 95%) reduction of sorbic acid and extensive reduction of muconic acid to dihydro-forms (mainly Δ^{α}-) at the stage of 50% hydrogenation by using an active nickel catalyst. The experiments will be described in a later paper.

EXPERIMENTAL.

50% *Hydrogenation of Sorbic Acid.*

In order to demonstrate with greater definiteness the formation of dihydro-derivatives as a normal result of the partial hydrogenation of conjugated acids, the degradative method used by Farmer and Galley (*loc. cit.*) for the determination of the components of the reaction mixtures has been replaced by a direct method dependent on the quantitative isolation of the latter. All the operations referred to in the introduction were carried out at least twice, and in many cases three or four times; since, however, they involved for the most part repetition of the same procedure, only one reduction of sorbic acid and one of sodium muconate are described below. In these reductions a relatively small proportion of catalyst was employed, with the result that the time of operation was greatly prolonged and the proportions of dihydro-product resembled those recorded by Farmer and Galley for an " aged " catalyst.

Separation of Sorbic Acid.—The reduction product obtained by shaking 44·8 g. of sorbic acid, dissolved in 250 c.c. of rectified spirit, with hydrogen and 0·2 g. of platinum oxide (PtO_2,H_2O) was freed from catalyst and solvent and *very slowly* distilled through a short column under reduced pressure (glycerol-bath) until crystals began to separate in the condenser. (In the subsequent distillations the same procedure was employed and the operation continued

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* Ingold and Shah (*loc. cit.*, p. 889) use such a *mixture* (supposedly the homogeneous Δ^{α}-acid), after esterification, in comparing the rates of reduction of ethyl Δ^{α}- and Δ^{β}-dihydromuconate and ethyl muconate. They make the form of the various absorption curves the basis of a calculation which leads to the conclusion that " if the hydrogenation of the butadiene were a two-stage process in which the intermediate dihydro-compound or mixture of compounds undergoes further reduction with the velocities illustrated, then, after the absorption of one molecule of hydrogen, the dihydro-derivatives should be present in proportions of the order of 50%."

until sorbic acid *just* began to crystallise in the condenser.) The residue in the flask solidified. By redistillation of the distillate from a smaller flask fitted with a short column, a liquid distillate of b. p. 110—120°/18 mm. was obtained and a solid residue remained. The two solid residues, which *apparently* consisted of sorbic acid, contained some Δ^{α}-hexenoic acid : they were taken up in boiling petroleum (b. p. 60—80°), and the solution cooled in ice. Sorbic acid (13·2 g.) separated in (*dry*) crystalline condition, and from the petroleum solution there were obtained, on evaporation of the solvent and slow distillation of the residue, 6·7 g. of liquid distillate and 3·3 g. of solid residue. This liquid distillate was combined with that previously obtained and with the acid derived from the washings of the apparatus (total, 27·6 g.), and the whole slowly redistilled as before : a liquid distillate (25·3 g.; b. p. 110—120°/19 mm.) and a further solid residue (2·3 g.) were thus obtained. The last two solid residues (2·3 g. and 3·3 g.) were combined and taken up in petroleum : the solution deposited 1·8 g. of sorbic acid and there remained dissolved a residue which when isolated and distilled yielded 2·6 g. of liquid distillate and 1·2 g. of sorbic acid. During these distillations Δ^{α}-hexenoic acid usually crystallised in part in the condenser, but could easily be distinguished from sorbic acid by its low melting point (33°) and its distinctive crystalline form; there was no difficulty in separating a considerable proportion of the Δ^{α}-acid in crystalline condition by careful fractionation, but a more elegant and less troublesome method of separation was available (see below). The separation effected is expressed by the following figures, which represent actual yields: unchanged sorbic acid, 17·3 g. (38%); total distillates, 27·8 g. (61%); loss, 0·5 g. (1·0%).

Determination and Isolation of Dihydro-acids.—The final oily distillate was divided into three portions, which were treated as in (i)—(iii) below.

(i) 3·6 G. were oxidised with 3% alkaline permanganate at 0°. The amount required (145 c.c.) corresponded to the presence originally of 1·2 g. of mixed hexenoic acids. This figure agreed fairly well with the amount of hexoic acid obtained on working up the oxidation product. The amount of hexoic acid in the total distillate was thus 18·3 g. (representing 39·5% of the sorbic acid taken).

(ii) 11·8 G. were kept for 5½ hours with 12 c.c. of *N*-ethyl-alcoholic hydrogen chloride and 48 c.c. of absolute alcohol (compare Eccott and Linstead's modification of Sudborough's method of partial esterification, J., 1929, 2153; 1932, 125); the product was then poured into four times its bulk of water, and the whole made alkaline with sodium carbonate. The precipitated neutral ester was collected in a little ether and separated from the alkaline solution; the latter was entirely freed from alcohol by warming at 50° under reduced pressure and then thoroughly extracted with ether. The combined ethereal extracts yielded 6·2 g. of neutral ester. The alkaline solution yielded after acidification and extraction 6 g. of acidic material.

Since the completeness of partial esterification (in the sense that Δ^{β}- and Δ^{γ}-hexenoic and hexoic acids become esterified whilst Δ^{α}-hexenoic acid remains unchanged) was in doubt, the acidic portion was resubmitted to esterification for 5½ hours. The product then consisted of 1·9 g. of crude neutral ester and 5·2 g. of acidic material. Further treatment of the unesterified portion (5·2 g.) for 5½ hours yielded 1·1 g. of crude neutral ester and 4·5 g. of acidic material. These final products were separately submitted to careful examination before it was decided whether esterification had gone far enough. The neutral portion gave on distillation 7·9 g. of ester, b. p. 160—167°, which contained 0·8 g. of hexenoic acid as determined by oxidation with alkaline permanganate; moreover the oxidation product contained 0·1 g. of succinic acid (derived from 0·1 g. of Δ^{γ}-hexenoic acid) and *no oxalic acid.* Accordingly, no Δ^{α}-hexenoic acid had suffered esterification. The acidic material which had escaped esterification was largely solid, even in crude condition : recrystallisation from light petroleum yielded 3·2 g. of Δ^{α}-hexenoic acid (m. p. and mixed m. p. 33°) and there remained 0·5 g. of oily acid which was found by oxidation with permanganate to contain 0·3 g. of ethylenic acid and to yield by the oxidation oxalic acid, some volatile acid which consisted partly of butyric acid as shown by the smell, but no isolable quantity of succinic acid. The oily portion of the unesterified material, therefore, was adjudged to consist of 0·3 g. of Δ^{α}-hexenoic acid and 0·2 g. of hexoic acid. The total amount of Δ^{α}-hexenoic acid found was 3·5 g. and it was apparent that suitable conditions of esterification had been attained.

(iii) For quantitative purposes, 12·2 g. were submitted to partial esterification with 12 c.c. of *N*-ethyl-alcoholic hydrogen chloride and 50 c.c. of absolute alcohol for 16 hours. The products were (a) 8·9 g. of crude ester and (b) 6·0 g. of crude unesterified acid. The ester gave, on bromination in chloroform at 0°, a mixture which yielded on distillation 2·8 g. of dibromo-esters (equivalent to 1·06 g. of Δ^{β}- or Δ^{γ}-hexenoic acid) and a residue of saturated (hexoic) acid. The dibromo-esters yielded smoothly, on debromination with zinc and acetone, a mixture of Δ^{β}-

and Δ^{γ}-hexenoic acid: no attempt to separate the compounds was made owing to the great similarity in physical properties of the acids themselves and of their corresponding simple derivatives. Ozonolysis of the ester mixture yielded a mixture of aldehydes, which was dissolved in aqueous dimethyldihydroresorcinol: the corresponding mixture of dimethones was obtained in good yield, but the adequate separation of the individual compounds by fractional crystallisation and sublimation proved so difficult that only propaldehyde dimethone (the major constituent) could be separated in tolerably pure condition (m. p. 151—153°; mixed m. p. 151—155°); comparison of the lowest-melting fraction (m. p. 130—140°), however, with authentic acetaldehyde dimethone (m. p. 139—140°) indicated that the latter substance was its main constituent.

The unesterified acid yielded on recrystallisation 2·0 g. of pure hexenoic acid and a residue of oily acid. The latter consisted of only slightly impure Δ^{α}-acid, since it yielded on ozonolysis almost pure butaldehyde (dimethone, m. p. 132°; authentic specimen, 134—135°; mixed m. p. 133—135°) (compare Kao and Yen, *Sci. Rep., Nat. Tsing Hua Univ.*, 1932, **1**, 185).

The proportions of materials present in the hydrogenation mixture are shown on p. 304.

50% *Hydrogenation of Muconic Acid.*

Muconic acid (21·3 g.) was exactly neutralised with sodium bicarbonate solution, and the solution of the sodium salt (diluted with water to 500 c.c.) hydrogenated in the presence of 0·4 g. of freshly reduced platinum catalyst (from platinum oxide). When 1 mol. of hydrogen had been absorbed, the catalyst was removed from the product, and the filtrate acidified with a *slight* excess of hydrochloric acid; the precipitated muconic acid was filtered off, washed with water, and dried (yield, 7·9 g.). The combined filtrate and washings were evaporated to dryness on a steam-bath and the residue of reduced acids and sodium chloride (31·2 g.) was directly submitted to partial esterification.

Isolation of Δ^{α}-Hydromuconic Acid.—Partial esterification was effected by keeping the residue for 16 hours with 50 c.c. of absolute methyl alcohol and 13 c.c. of *N*-methyl-alcoholic hydrogen chloride. The product, worked up as described above, yielded (a) a neutral oil (10·1 g.) and (b) an acidic oil (4·1 g.) which completely solidified in characteristic radial aggregates on cooling. The latter product, which was a half-ester, was extracted with light petroleum, from which it separated in colourless plates, m. p. 58°; there was a residue (0·7 g.), insoluble in petroleum, of slightly impure muconic acid. The half-ester was identified as methyl hydrogen Δ^{α}-dihydromuconate, $MeO_2C{\cdot}CH_2{\cdot}CH_2{\cdot}CH{:}CH{\cdot}CO_2H$, the production of which in pure form from Δ^{β}-dihydromuconic acid was investigated for the purpose (see Part III). Yield, 2·7 g. Hydrolysis of the half-ester to the corresponding Δ^{α}-acid can be effected by boiling *for several minutes* with 25% (by vol.) sulphuric acid or for a short time with dilute alkali.

Isolation of Δ^{β}-Dihydromuconic Acid and Adipic Acid.—The neutral product derived by partial esterification was brominated at 0° in chloroform (1·83 g. of bromine absorbed, the quantity required for the production of 3·8 g. of methyl ββ′-dibromoadipate). The chloroform solution was washed with thiosulphate solution, dried, and freed from solvent by warming under reduced pressure. The oily residue yielded on partial distillation (i) pure methyl adipate (6·1 g.), b. p. 108—111°/8 mm., which was quantitatively hydrolysable to adipic acid, and (ii) an oily bromide which consisted mainly of the higher-melting form of methyl ββ′-dibromoadipate (m. p. 93°; mixed m. p. 93°), but partly of the lower-melting form of the same compound (m. p. 43°; see Farmer, J., 1923, **123**, 2542). No other substance was found. The dibromo-esters were capable of quantitative debromination with zinc and alcohol to yield pure methyl Δ^{β}-dihydromuconate.

Recovery Table.

	Yield, g.	Equiv. of muconic acid, g.	Yield, %.	
Muconic acid	8·6	8·6	40·3	
Methyl hydrogen Δ^{α}-dihydromuconate	2·7	2·4	11·3	
Methyl ββ′-dibromoadipate	3·8	1·6	7·5	
Methyl adipate	6·1	5·0	23·5	40·9
Loss		3·7*	17·4	

* This loss was an accidental loss due almost entirely to volatilisation of methyl adipate during incautious warming of the bromination mixture under reduced pressure to expel the solvent; no significant portion of it represented dihydro-acid in excess of that shown.

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