120. *The Active Principles of Leguminous Fish-poison Plants. Part VII. The Reduction of Elliptone.*

By Stanley H. Harper.

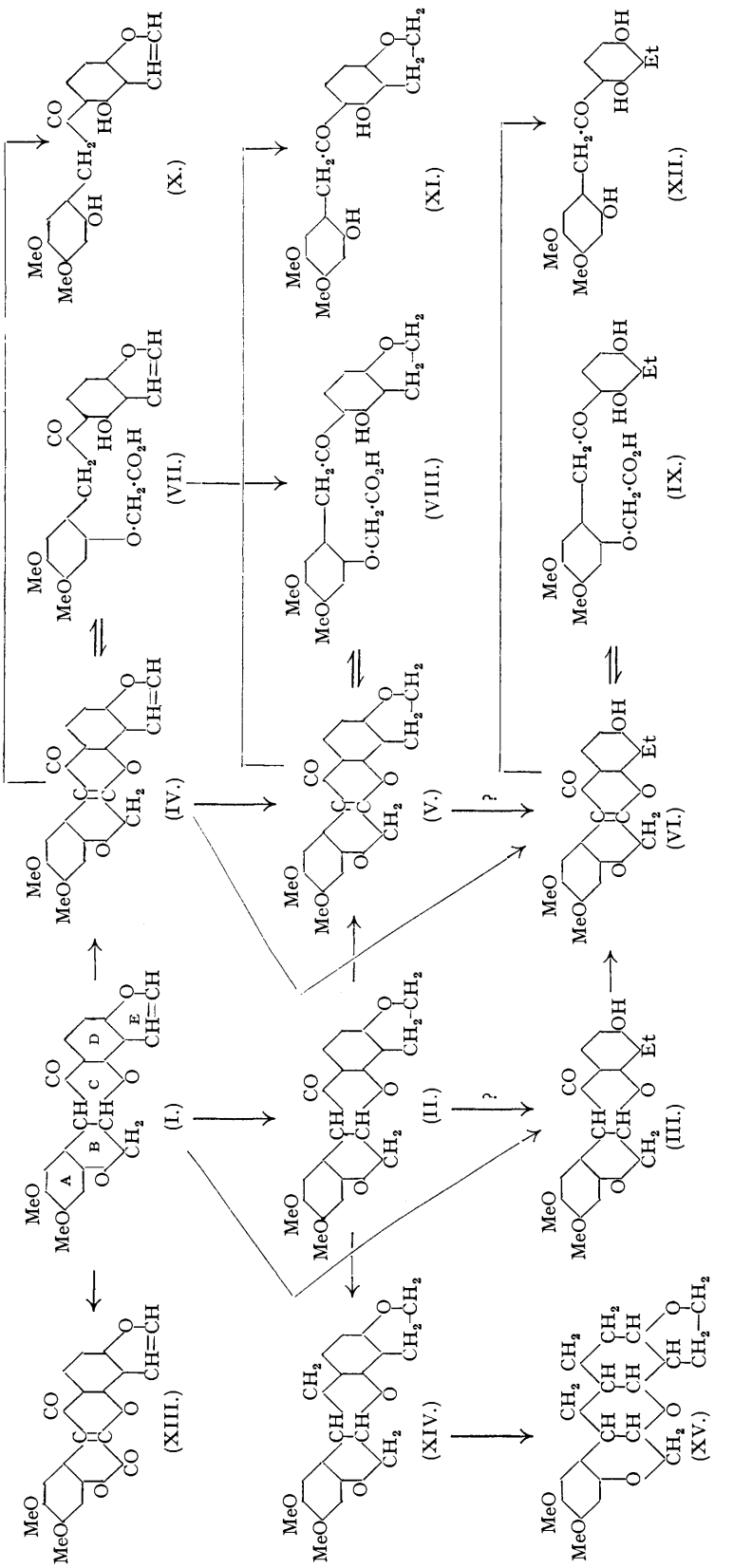
The course of the reduction of *l*- and *dl*-elliptones in acetic acid over platinum oxide catalyst has been elucidated, and the following stages characterised : dihydroelliptone, dihydrodeoxyelliptone, octahydrodeoxyelliptone, and perhydroelliptone.

The zinc–alkali reduction of the dehydro-compounds has been shown to give, in addition to acids of the derrisic acid type, phenols analogous to derritol.

Oxidation of elliptone with nitrous acid has given elliptononе, a diketone, whose structure has been established by a partial synthesis from elliptol, the phenol obtained in the zinc–alkali reduction of dehydroelliptone.

Biological trials using the chrysanthemum aphis as test insect have shown that *l*-elliptone is, next to rotenone, the most toxic insecticidal substance to be isolated from *Derris* resin in an optically active form. In the order of decreasing toxicity : *l*-elliptone > *dl*-elliptone > *l*-dihydroelliptone > *dl*-dihydroelliptone.

l-Dihydrorotenone has gained some prominence in recent years in the United States as a substitute for rotenone in insecticide sprays. This use appears to be based on two considerations, first, its stability, and secondly its high toxicity. Jones *et al.* (*J. Econ. Entomol.*, 1933, **26**, 451) have shown that *l*-dihydrorotenone is more resistant to atmospheric oxidation and is at least as toxic as rotenone to culicine mosquito larvæ. More recently Sullivan *et al.* (*Soap*, 1939, **15**, No. 7, 107) have shown that *l*-dihydrorotenone is only slightly less toxic than rotenone to the housefly (*Musca domestica* L.). Biological trials on *l*-elliptone have shown that it is the next most toxic optically active substance to rotenone to be isolated from *Derris* resin (this paper and see also


(I.)
(II.)
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(XIII.)
(XIV.)
(XV.)
MeO
MeO
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CH₂
CH₂·CO
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A
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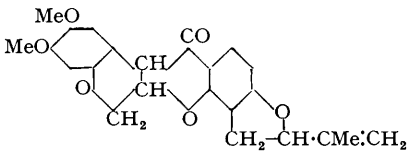
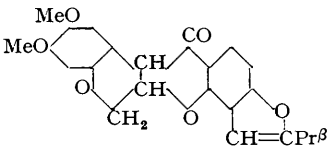
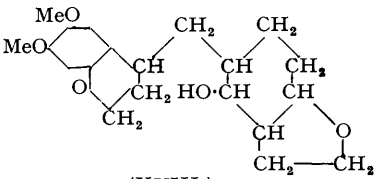
Martin, *Ann. Appl. Biol.*, **1942**, **29**, 75). For this reason the preparation of optically active and inactive dihydroelliptones was considered of interest so that their relative toxicities to elliptone and rotenone could be determined. In view also of conflicting statements in the literature, the reduction of elliptone under various conditions has been examined in some detail.



(XVI.)



(XVII.)



(XVIII.)

The exocyclic double bond of rotenone (XVI) can be hydrogenated under very mild conditions and, by suitable choice of solvent and catalyst, with the virtual absence of other hydrogenation products (Haller and Schaffer, *Ind. Eng. Chem.*, **1933**, **25**, 983). Elliptone (I), with its cyclic double bond, is, however, analogous to *iso*rotenone (XVII), which is known to be difficult to reduce. LaForge and Smith (*J. Amer. Chem. Soc.*, **1929**, **51**, 2574) were unable to reduce *iso*rotenone, but Butenandt and Hildebrandt (*Annalen*, **1930**, **477**, 261) effected reduction over platinum-black in acetic acid to give a product which they did not characterise. Re-examination of this (see p. 593) has shown it to be impure *l*-dihydrodeoxy*iso*rotenone and there was no evidence of the formation of *l*-dihydro*iso*rotenone. Hence the use of more active catalysts for the reduction of elliptone would at the same time facilitate the formation of by-products.

The reduction of elliptone by means of platinum oxide in ethyl acetate with fission of the furan ring to give tetrahydroelliptone (III) has already been described by the author (J., **1939**, 1099). The only other reduction recorded is that by Meijer and Koolhaas (*Rec. Trav. chim.*, **1939**, **58**, 875), in which elliptone (described there as derride) was hydrogenated in acetic acid in the presence of platinum oxide. About 5 molecules of hydrogen were absorbed, and a crystalline product isolated, to which the formula $C_{20}H_{26}O_5$ was given. It was stated to be insoluble in aqueous sodium hydroxide but gave a brown colour with ferric chloride, and was formulated as (XVIII). This formula, however, requires $C_{20}H_{28}O_5$ and is not consistent with the ferric chloride colour.

The hydrogenation of elliptone in acetic acid has therefore been examined. The initial absorption of hydrogen was fairly rapid, with a break between 1 and 2 molecules, after which hydrogenation proceeded slowly until the hydrogenation curve was asymptotic to an absorption of 10 molecules of hydrogen. This corresponds to the reduction of the keto-group, the furan ring, and both aromatic rings. The reaction mixture gave a small yield of a neutral crystalline substance, $C_{20}H_{26}O_5$, and with the same melting point as the substance described by Meijer and Koolhaas (*loc. cit.*). Although they are considered to be identical, this substance gave no colour with ferric chloride and was recovered unchanged from attempted acetylation and oximation. It therefore contains neither a keto-group nor hydroxyl-groups. It was optically active, so C_7–C_8, the seat of asymmetry in the molecule, was unchanged, *i.e.*, ring C could not have suffered fission (cf. the rotenols, in which C_7–C_8 is inactive). The substance is therefore considered to be *octahydrodeoxyelliptone* (XV). The non-crystalline portion of the reduction product is probably a mixture of stereoisomeric perhydroelliptones.

To obtain *l*-dihydroelliptone experiments were made, the reduction being stopped when one molecule of hydrogen had been absorbed. Products were obtained, however, that varied in melting point and optical rotation and no homogeneous product could be obtained. It was evident that the reduction was not wholly stepwise, *i.e.*, some reduction of the dihydroelliptone was taking place while elliptone remained unreduced. By stopping the reaction at 2 molecules absorption, this was overcome, and l-*dihydroelliptone* (II) was obtained in good yield, its high specific rotation in benzene providing a ready check on its purity. That it was the true dihydro-compound and not a deoxyelliptone was established by characterisation of the keto-group through an *oxime*, an enolic *acetate*, and oxidation with iodine to a dehydro-compound. In all hydrogenations in acetic acid over platinum oxide there was little if any fission of the furan ring to tetrahydroelliptone (III), in marked contrast to reduction in ethyl acetate over the same catalyst, in which reduction appears to proceed directly to the ring-open tetrahydro-product (J., **1939**, 1099). dl-*Dihydroelliptone* was obtained (1) by reduction of *dl*-elliptone under the above conditions, and (2) by racemisation of *l*-dihydroelliptone with sodium acetate in alcohol, the products being identical. This method of racemising C_7–C_8 has already been used for the preparation of *dl*-elliptone (*loc. cit.*). The same dehydro-compound, *dehydrodihydroelliptone* (V), was obtained by oxidation of both *l*- and *dl*-dihydroelliptones with iodine.

In one reduction of *dl*-elliptone in acetic acid the experiment was stopped when 2·5 molecules of hydrogen had been absorbed. Crystallisation failed to give a homogeneous product, but by making use of the sparing solubility of the benzene *solvate* of *dl*-dihydroelliptone a more soluble constituent was isolated in about 10% yield. Analysis showed this to be dl-*dihydrodeoxyelliptone* (XIV). In the light of this, the substance previously described as *l*-dihydroelliptone (J., **1939**, 1099) was re-examined. Fresh analyses supported the formula $C_{20}H_{20}O_5$ and it was not oximated under conditions which sufficed for *l*-dihydroelliptone. There is little doubt that it is impure l-*dihydrodeoxyelliptone*. Butenandt (*Annalen*, **1928**, **494**, 266) has recorded the formation of dihydrodeoxyrotenone in the reduction of rotenone when carried to 3 molecules absorption under similar conditions. It is evident that the reduction of elliptone over platinum in acetic acid proceeds through the

following stages: elliptone (I) ⟶ dihydroelliptone (II) ⟶ dihydrodeoxyelliptone (XIV) ⟶ octahydrodeoxyelliptone (XV) ⟶ perhydroelliptone.

The zinc–alkali reduction of dehydroelliptone (IV) was used previously (J., 1939, 1424) for the preparation of elliptic acid (VII). It was observed at that time that the crude acid had m. p. 140—145° and needed repeated crystallisation for purification (m. p. 190°). Fractional crystallisation later showed that a second phenolic constituent was present and the method has therefore been modified to enable the phenol, *elliptol*, to be separated chemically. From its formula, $C_{18}H_{16}O_6$, insolubility in sodium bicarbonate, and solubility in potassium hydroxide solution this substance is analogous to derritol. Hence it is ascribed the structure (X), this being confirmed by the formation of a *monomethyl* ether with methyl sulphate and alkali. This ether was exactly analogous to derritol methyl ether in being insoluble in potassium hydroxide solution but still giving a ferric chloride colour. The di-*o*-substituted hydroxyl group has therefore remained unmethylated, as would be expected under such conditions. In like manner dehydrodihydroelliptone gave *dihydroelliptic acid* (VIII), also obtained by the hydrogenation of elliptic acid over platinum oxide in dioxan, and *dihydroelliptol* (XI). *Dehydrotetrahydroelliptone* (VI), obtained from *l*- or *dl*-tetrahydroelliptone by oxidation with iodine and also by the hydrogenation of dehydroelliptone over platinum oxide in ethyl acetate, gave on zinc–alkali reduction *tetrahydroelliptic acid* (IX) and *tetrahydroelliptol* (XII). The formation of elliptol was unexpected, as no parallel formation of derritol in the zinc–alkali reduction of dehydrorotenone had been reported. Nevertheless the repetition of this reaction with dehydrorotenone led in one experiment to a good yield of derritol. A number of experiments have been made, both the time and the method of addition of the reagents being varied, but so far with no clue as to the factors governing the formation of derritol and of elliptol in this reaction.

Meijer and Koolhaas (*loc. cit.*) by the chromic acid oxidation of elliptone obtained a diketone, derridenone, $C_{20}H_{12}O_7$, analogous to rotenonone. The same diketone, for which the name elliptonone is preferred, has now been obtained by treatment of elliptone with nitrous acid (cf. dihydrorotenone ⟶ dihydrorotenononone; LaForge and Smith, *J. Amer. Chem. Soc.*, 1930, **52**, 1091). The structure (XIII) assigned to it by Meijer and Koolhaas has been confirmed by a partial synthesis from elliptol. Elliptol readily condensed with a molecule of methyl oxalate in the presence of sodium acetate to give elliptonone in good yield (cf. the synthesis of rotenonone from derritol; Takei, *Ber.*, 1932, **65**, 1041).

TABLE I.

Test Insect: *Macrosiphoniella sanborni* Gill (Chrysanthemum aphis) (viviparous parthogenetic females).
Carrying Medium: 0·1% sulphonated lorol + 10% acetone.
The pressure and the gap at the bottom of the spray tower were adjusted to give a deposit of approximately 500 mg. on a 9 cm. Petri dish. Temp. 68° F. Rel. humidity 58%. Sprayed in triplicate, fifteen insects per dish.

Substance.	Concn., mg./l.	% Kill.	Substance.	Concn., mg./l.	% Kill.	Substance.	Concn., mg./l.	% Kill.
l-Elliptone	20	96	*l*-Dihydroelliptone	40	38	Rotenone	4	100
	10	84		20	40		2	89
	5	36		10	33		1	18
dl-Elliptone	20	89	*dl*-Dihydroelliptone	40	39		0·5	11
	10	70		20	16	Control	—	4
	5	9		10	4			

With the co-operation of Dr. C. Potter some of the substances described in this paper have been compared with rotenone for their relative toxicities as insecticides. The general technique has been described by Potter (*Ann. Appl. Biol.*, 1941, **28**, 142). From the percentage kills *l*-elliptone is approximately one-fifth as toxic as rotenone, a result closely in accord with the more accurate figure published by Martin (*ibid.*, 1942, **29**, 75) for a comparison using the same insect but in an alcohol–saponin medium. This potency of *l*-elliptone places the compound second in importance to rotenone among the optically active principles so far separated from *Derris* resin.

The remaining substances tested can qualitatively be placed in the following order of decreasing toxicity: *l*-Elliptone > *dl*-Elliptone > *l*-Dihydroelliptone > *dl*-Dihydroelliptone. In marked contrast to *l*-dihydrorotenone, *l*-dihydroelliptone is distinctly much less toxic than *l*-elliptone. Further the optically active forms are distinctly more toxic than the corresponding racemic forms of each pair of compounds tested, a conclusion in agreement with other workers' observations in this series of compounds. Fink and Haller (*J. Econ. Ent.*, 1936, **29**, 594) have observed that *l*-> *dl*-*iso*rotenone and *l*-> *dl*-dihydrodeguelin to culicine mosquito larvæ. Sullivan *et al.* (*loc. cit.*) have also observed that *l*-> *dl*-dihydrodeguelin to the housefly. Tattersfield and Martin (*Ann. Appl. Biol.*, 1938, **25**, 411) have shown that *l*-> *dl*-toxicarol to the bean aphis.

EXPERIMENTAL.

Before analysis all substances in this and the following two papers were dried for 1 hour at 100° in a high vacuum. Microanalyses are by Drs. Weiler and Strauss, Oxford. Methoxyl determinations are by the author, using Clark's semi-micro-method (*J. Assoc. Off. Agric. Chem.*, 1932, **15**, 136). Melting points were observed in Mason's apparatus (*Chem. and Ind.*, 1925, **577**), soft glass tubes being used, and are uncorrected.

Under the same conditions that rotenone forms a 1 : 1 solvate with dichloroacetic acid [Jones, *Ind. Eng. Chem.* (*Anal.*), 1938, **10**, 684] *l*-elliptone forms a similar *solvate*, crystallising in needles, m. p. 108° (67·1 mg. required 6·90 c.c. of 0·02N-potassium hydroxide. Calc. for $C_{20}H_{16}O_6,CHCl_2{\cdot}CO_2H$: 6·96 c.c.). If present, therefore, in crude rotenone, elliptone would interfere in the estimation of the purity of the latter by this proposed volumetric method. *dl*-Elliptone

does not, however, form a solvate with dichloroacetic acid. Neither *l*- nor *dl*-elliptone forms a solvate with carbon tetrachloride, though both are only sparingly soluble in that solvent.

Relative Stability of Rotenone and Elliptone.—100 Mg. of each in acetone (25 c.c.) were aerated side by side in bright sunlight intermittently for several days. At 4 hours the rotenone solution was yellow. After 12 hours, when the elliptone solution was still colourless, the solutions were evaporated. The rotenone gave a non-crystalline red gum, but the elliptone was recovered in crystalline form with unchanged m. p. Acetone was used as the solvent because Jones (*Ind. Eng. Chem.*, 1931, **23**, 387) has shown that, of the solvents he examined, rotenone was least decomposed in acetone on aeration in sunlight.

Relative Goodhue Values.—*l*- and *dl*-Elliptones gave the Goodhue test (*J. Assoc. Off. Agric. Chem.*, 1936, **19**, 118) with equal intensity, but more strongly than rotenone.

l-Elliptone exhibits dimorphism on crystallisation from alcohol; when first isolated (*Chem. and Ind.*, 1939, **58**, 292) it had m. p. 159° but subsequent preparations have had a higher m. p. 171—172° but with unchanged specific rotation (J., 1941, 878). The influence of the type of glass used for the m. p. determinations has recently been reported (*loc. cit.*).

Isolation of dl-*Elliptone and* dl-*Deguelin from* D. malaccensis (cf. J., 1940, 1182).—The alkali-washed neutral resin (100 g.) from 4 kg. of " Kinta type " root was dissolved in carbon tetrachloride (250 c.c.) and seeded with rotenone complex. On refrigeration rotenone–carbon tetrachloride solvate (20 g.) separated. The soluble resin was recovered by evaporation and dissolved in ether (500 c.c.). A crop (9 g.) slowly separated which by fractional crystallisation gave small quantities of *dl*-elliptone, m. p. 183°, not depressing the m. p. of an authentic specimen (Found : OMe, 17·5. Calc. for $C_{20}H_{16}O_6$: OMe, 17·6%), and of *dl*-deguelin, m. p. 174°, not depressing the m. p. of an authentic specimen (Found : OMe, 15·9. Calc. for $C_{23}H_{22}O_6$: OMe, 15·7%). From this it is concluded that *l*-elliptone and *l*-deguelin were present in the original resin, but were racemised during the alkali treatment and the prolonged crystallisation. The bulk of the crystalline material could not be separated into any chemical entities and without doubt contained dehydro-compounds formed by aerial oxidation during the crystallisation.

The technique for the isolation of *l*-elliptone described previously (J., 1939, 1102), being utilised, *l*-elliptone has been isolated (0·5% calc., on root) from *D. elliptica* (Changi type) (ethyl acetate extract 27%, rotenone 9%) and from further specimens of *D. elliptica* (var. Sarawak creeping). Elliptone could not be isolated from a sample of cube of unknown origin (ethereal extract 14%), but no opportunity has occurred of examining an authentic specimen of *Lonchocarpus utilis*.

Fractionation of Elliptone-free D. elliptica *Resin.*—The ethereal solution from 5 kg. of *D. elliptica* root from which *l*-elliptone no longer crystallised (for details, see J., 1939, 1102) was washed with 5% potassium hydroxide solution, dilute acid, and water, and the neutral resin obtained by evaporation. This resin (216 g.) was dissolved in benzene (500 c.c.) and precipitated with successive portions of light petroleum (b. p. 40—60°, 2 × 750 c.c.). The first precipitate (123 g.) was redissolved in benzene (350 c.c.), and divided into two fractions by light petroleum (450 c.c.). The following fractions were obtained in order of increasing solubility :

			$[\alpha]_D^{19°}$ in benzene (c = 4).	OMe, %.
Ppte. A.	Sticky red resin	26 g.	−32°	13·7
Ppte. B.	Hard red resin	81 g.	−53	15·4
Ppte. C.	Hard red resin	58 g.	−56	15·9
Soln. D.	Yellow opaque wax	51 g.	−48	11·5

Fraction B in ether gave a small yield of *dl*-elliptone (1·02 g.) after prolonged refrigeration, but no further crystals. Fraction D on treatment with light petroleum gave a soluble fraction nearly free from rotenoids (OMe, 4·2%. Durham test, very faint). No crystalline material could be obtained from any of the other fractions. These results closely parallel those obtained with a column of activated alumina by which *dl*-elliptone was first isolated (Harper, *Chem. and Ind.*, 1938, **57**, 1059).

Reduction of l-*Elliptone in Acetic Acid* (cf. Meijer and Koolhaas, *Rec. Trav. chim.*, 1939, **58**, 878).—*l*-Elliptone (1 g.) in " AnalaR " acetic acid (20 c.c.) was reduced in the presence of platinum oxide (100 mg.). After absorption of 2 mols. of hydrogen reduction was slow, the final absorption being 9·7 mols. after 100 hours, which corresponds to complete reduction of the keto-group and of the aromatic rings. The solution was filtered and poured into water, and the product taken out in ether. The extract was washed with 5% potassium hydroxide solution (nothing soluble), and the neutral gum recovered. In contact with methyl alcohol part crystallised, and was recrystallised from that solvent to give *octahydrodeoxyelliptone* (XV) (160 mg.), m. p. 160° (Found : C, 69·2; H, 7·5. $C_{20}H_{26}O_5$ requires C, 69·3; H, 7·5%). $[\alpha]_D^{18°}$ −10° in acetone (c = 1·0) and −8° in benzene (c = 1·0). This substance is without doubt the same as that described by Meijer and Koolhaas, and, as they found, nothing crystalline could be obtained from the alcoholic filtrate, the gum probably consisting of a mixture of stereoisomeric perhydroelliptones.

In another experiment octahydrodeoxyelliptone was isolated in what is presumably a dimorphic form, m. p. 139°, $[\alpha]_D^{17°}$ −8° in benzene (c = 1·0) (Found : C, 69·5; H, 7·6%).

By interrupting the reduction when 2 mols. of hydrogen had been absorbed it was possible to obtain optically pure l-*dihydroelliptone* (II) in good yield. It crystallised from alcohol in needles, m. p. 191°, $[\alpha]_D^{18°}$ −132° in benzene (c = 1·0) (Found : C, 67·7; H, 5·1; OMe, 17·4. $C_{20}H_{18}O_6$ requires C, 67·8; H, 5·1; 2OMe, 17·5%).

The *oxime*, prepared as described for elliptone β-oxime (J., 1939, 1103), had m. p. 250° (Found : N, 3·9. $C_{20}H_{19}O_6N$ requires N, 3·8%). The *monoacetate*, prepared as described for elliptone (*loc. cit.*), had m. p. 208° (Found : C, 66·6; H, 5·1; OMe, 15·7. $C_{22}H_{20}O_7$ requires C, 66·6; H, 5·1; 2OMe, 15·7%).

Reduction of dl-*Elliptone in Acetic Acid.*—dl-*Dihydroelliptone* (II), crystallising from alcohol in prisms, m. p. 188°, was obtained in good yield by the reduction of *dl*-elliptone in acetic acid following the conditions outlined for *l*-dihydroelliptone above (Found : C, 67·2; H, 5·1; OMe, 17·8%). From benzene, in which it was sparingly soluble, *dl*-dihydroelliptone separated as a *solvate* (cf. *dl*-elliptone, *loc. cit.*), in hard prisms, m. p. 188° (Found : OMe, 15·5. $2C_{20}H_{18}O_6,C_6H_6$ requires OMe, 15·7%).

In one reduction of *dl*-elliptone in acetic acid in the presence of platinum oxide, slightly more than 2 mols. of hydrogen were absorbed before the reduction was interrupted. Repeated crystallisation failed to yield a homogeneous product of sharp m. p. Separation was eventually effected by means of cold benzene, in which the solvate of *dl*-dihydroelliptone remained undissolved. Crystallisation from alcohol of the material soluble in benzene gave dl-*dihydrodeoxyelliptone* (XIV) in fine plates, m. p. 157—159° (Found : C, 70·6; H, 6·0; OMe, 18·3. $C_{20}H_{20}O_5$ requires C, 70·6; H, 5·9; 2OMe, 18·2%), in about 10% yield.

Re-examination of the substance reported previously as *l*-dihydroelliptone (J., 1939, 1104), m. p. 159°, $[\alpha]_D^{20°}$ −97° in acetone (c = 1·0), has shown it to be impure l-*dihydrodeoxyelliptone* (Found : C, 70·2; H, 5·5; OMe, 18·1%). After recovery from an attempted oximation in sodium acetate–alcohol the substance had m. p. 170° (Found : C, 70·0; H, 5·9%); perhaps it was purer *l*-dihydrodeoxyelliptone, but insufficient material has prevented elucidation of this point.

Racemisation of l-*Dihydroelliptone.*—*l*-Dihydroelliptone (250 mg.) and sodium acetate (500 mg.) in alcohol (20 c.c.) were refluxed for 2 hours. On cooling, *dl*-dihydroelliptone separated and was recrystallised from alcohol, m. p. 188°,

$[\alpha]_D$ ±0° in chloroform (130 mg.), identical with that obtained by the reduction of *dl*-elliptone (cf. the racemisation of *l*-elliptone, *loc. cit.*).

Dehydrodihydroelliptone (V).—To *l*- or *dl*-dihydroelliptones (250 mg.) and sodium acetate (500 mg.) in boiling alcohol (20 c.c.), iodine (500 mg.) in alcohol (5 c.c.) was added slowly, and refluxing continued for 3 hours, during which time the *dehydro*-compound crystallised. It was recrystallised from chloroform–alcohol, separating in bright yellow plates (133 mg.), m. p. 264° (Found: C, 68·0; H, 4·6; OMe, 17·6. $C_{20}H_{16}O_6$ requires C, 68·2; H, 4·6; 2OMe, 17·6%). It was an apparently dimorphic form of that obtained by cyclisation of dihydroelliptic acid (see below).

Action of Zinc and Alkali on Dehydroelliptone.—Dehydroelliptone (1·5 g.), zinc dust (5 g.), and 15% aqueous potassium hydroxide (10 c.c.) in ethyl alcohol (30 c.c.) were refluxed for 2 hours. The filtered liquid was acidified (hydrochloric acid) and diluted till crystallisation commenced. The whole was extracted with ether, and the ethereal suspension shaken with saturated sodium bicarbonate solution. The aqueous layer containing suspended sodium elliptate was filtered. Solution of the sparingly soluble sodium salt in boiling water and acidification gave pure elliptic acid (VII) (750 mg.), m. p. 190°. The sodium bicarbonate filtrate was acidified to give elliptic acid (370 mg.) that required recrystallisation before purity was attained. Esterification with alcoholic sulphuric acid and recrystallisation from ethyl alcohol gave *ethyl elliptate*, m. p. 142°, in microcrystalline needles [Found: OMe, 22·1. $C_{22}H_{22}O_8$ requires 2OMe + OEt (calc. as 3OMe), 22·3%]. This ester gave a slight depression of m. p. (to 130—135°) with methyl elliptate (J., 1939, 1426) of the same m. p.

The ethereal layer was evaporated, and the gum crystallised from aqueous methyl alcohol to give *elliptol* (X) in narrow plates, m. p. 163° (Found: C, 65·6; H, 4·9; OMe, 18·9. $C_{18}H_{16}O_6$ requires C, 65·8; H, 4·9; 2OMe, 18·9%). It gave a deep blue ferric chloride colour.

Elliptol (100 mg.), dissolved in 2% potassium hydroxide solution (2 c.c.), was shaken with methyl sulphate (0·1 c.c.). Next day the precipitate was collected and crystallised from methyl alcohol to give *elliptol methyl ether* (78 mg.), m. p. 137° (Found: OMe, 26·7. $C_{19}H_{18}O_6$ requires 3OMe, 27·1%).

Following these observations the action of zinc and alkali on dehydrorotenone has been re-examined. In one experiment under the above conditions derritol was isolated in good yield (14·5 g. from 50 g. of dehydrorotenone). In another experiment in which the acidified alcoholic filtrate was concentrated before ether extraction, the main product from the ethereal layer was a substance, m. p. 95°, insoluble in 5% potassium hydroxide solution but giving a violet ferric chloride colour. Comparison with a sample prepared by direct esterification of derrisic acid with alcoholic sulphuric acid showed this substance to be ethyl derrisate [Found: OMe, 20·1. Calc. for $C_{25}H_{28}O_8$: 2OMe + OEt (as 3OMe), 20·3%].

Cyclisation of Elliptic Acid.—Elliptic acid (1 g.) and sodium acetate (500 mg.) in acetic anhydride (10 c.c.) and acetic acid (1 c.c.) were refluxed for 5 mins., then diluted with alcohol (40 c.c.) and left overnight. The yellow needles (120 mg.) were collected and recrystallised from chloroform–alcohol to give dehydroelliptone (IV), m. p. 262—264°, identical with an authentic specimen (J., 1939, 1103). The alcoholic filtrate was evaporated, and the gum rubbed with sodium carbonate solution. Acidification of the filtrate gave impure acetylelliptic acid (45 mg.), m. p. 120°, which could not be purified. Crystallisation from alcohol of the portion insoluble in sodium carbonate gave *ethyl acetylelliptate* (224 mg.), m. p. 151—153° [Found: C, 62·5; H, 5·0; OMe, 19·1. $C_{24}H_{24}O_9$ requires C, 63·1; H, 5·3; 2OMe + OEt (as 3OMe), 20·4%]. This ester was insoluble in 5% potassium hydroxide solution, and like the crude acid, gave no colour with ferric chloride.

Reduction of Elliptic Acid.—Elliptic acid (3·5 g.) in dioxan (100 c.c.) was shaken with hydrogen in the presence of platinum oxide (0·5 g.). After 12 hours (absorption 400 c.c., including that of the catalyst) the reaction mixture was filtered and evaporated. The residue, sparingly soluble in alcohol or ethyl acetate, crystallised in hard irregular tablets (2·2 g.), m. p. 200°. Analysis showed it to be *dihydroelliptic acid* (VIII) (Found: C, 61·7; H, 5·2; OMe, 15·7. $C_{20}H_{20}O_8$ requires C, 61·8; H, 5·2; 2OMe, 15·9%). With alcoholic ferric chloride it gave a wine-red colour. The acid gave no depression of m. p. with elliptic acid. Its identity as dihydroelliptic acid was finally established by comparison with an authentic specimen prepared from dehydrodihydroelliptone (see below). Esterification of a suspension of the acid in benzene–ether with diazomethane gave the *methyl* ester, crystallising from alcohol in prisms, m. p. 149° (Found: OMe, 23·1. $C_{21}H_{22}O_8$ requires 3OMe, 23·1%). With alcoholic ferric chloride it gave a wine-red colour, thus distinguishing it from methyl elliptate (m. p. 143°), with which it gave no depression of m. p. Esterification with ethyl alcohol–sulphuric acid and crystallisation from ethyl alcohol gave *ethyl dihydroelliptate* in needles, m. p. 147° [Found: OMe, 22·1. $C_{22}H_{24}O_8$ requires 2OMe + OEt (as 3OMe), 22·3%].

Neither elliptic acid nor methyl elliptate could be reduced in ethyl acetate suspension in the presence of platinum oxide. Dihydroelliptic acid could not be further reduced in dioxan in the presence of platinum oxide.

Cyclisation of Dihydroelliptic Acid.—Dihydroelliptic acid (500 mg.) and sodium acetate (250 mg.) in acetic anhydride (5 c.c.) and acetic acid (0·5 c.c.) were refluxed for 15 mins. The orange solution was poured into water, and the yellow solid ground with sodium bicarbonate. The neutral insoluble portion was sparingly soluble in alcohol and crystallised in straw-coloured needles, m. p. 248—250°. This form of *dehydrodihydroelliptone* (V) would appear to be a dimorph of that described above (Found: C, 68·3; H, 4·7; OMe, 17·6. $C_{20}H_{16}O_6$ requires C, 68·2; H, 4·6; 2OMe, 17·6%). Acidification of the sodium bicarbonate filtrate gave crude acetyldihydroelliptic acid, m. p. 185—190°, which could not be effectively purified.

Action of Zinc and Alkali on Dehydrodihydroelliptone.—Following the modified conditions used for dehydroelliptone (see above), dehydrodihydroelliptone (1 g.) gave dihydroelliptic acid (275 mg.), m. p. 200°, identical with that prepared by the reduction of elliptic acid (see above), and *dihydroelliptol* (XI) (336 mg.), crystallising from alcohol in plates, m. p. 190° (Found: C, 66·0; H, 5·6; OMe, 18·9. $C_{18}H_{18}O_6$ requires C, 65·5; H, 5·5; 2OMe, 18·8%). This substance was insoluble in sodium bicarbonate solution and gave a wine-red colour with alcoholic ferric chloride.

Dehydrotetrahydroelliptone (VI).—To *l*- or *dl*-tetrahydroelliptone (*loc. cit.*) (500 mg.) and sodium acetate (500 mg.) in boiling alcohol (20 c.c.), iodine (500 mg.) in alcohol (5 c.c.) was added slowly. After 6 hours' refluxing no crystals had separated; the solution was therefore concentrated and precipitated with water. The solid, after drying in a vacuum, was refluxed in acetic acid (10 c.c.) with zinc dust (500 mg.) for 2 hours. At the end of 1 hour a further 500 mg. of zinc dust were added. The solution was filtered, and the zinc washed with hot acetic acid (2 × 5 c.c.), yellow needles separating on cooling. *Dehydrotetrahydroelliptone* (240 mg.) was recrystallised from alcohol to give pale yellow needles, m. p. 260° (decomp.) (Found: C, 67·4; H, 5·0. $C_{20}H_{18}O_6$ requires C, 67·8; H, 5·1%). The dehydro-compound gave no colour with ferric chloride but was soluble in 5% potassium hydroxide solution.

Reduction of Dehydroelliptone.—An attempt to reduce dehydroelliptone (1·3 g.) in ethyl acetate suspension in the presence of platinum oxide was partly successful. After absorption had apparently ceased, the solid was treated with 2% potassium hydroxide solution and collected. Acidification of the filtrate and crystallisation from alcohol gave dehydrotetrahydroelliptone (140 mg.), m. p. 260° (decomp.), identical with that prepared above. The main insoluble portion (1·07 g.), m. p. 264° (Found: C, 67·9; H, 4·2%), appeared to consist of a mixture of dehydro- and dehydrodihydro-elliptone. The substance gave no depression of m. p. with either of these compounds. There was no evidence of the reduction of the dehydro-linkage (cf. the reduction of dehydrorotenone to dehydrotetrahydrorotenone; Haller and LaForge, *J. Amer. Chem. Soc.*, 1931, **53**, 3426).

Action of Zinc and Alkali on Dehydrotetrahydroelliptone.—Following the modified conditions used for dehydroelliptone (see p. 592), dehydrotetrahydroelliptone (300 mg.) gave *tetrahydroelliptic acid* (IX) (130 mg.) crystallising from alcohol in prisms, m. p. 202° (Found : C, 61·1 : H, 5·4; OMe, 15·9. $C_{20}H_{22}O_8$ requires C, 61·5; H, 5·6; 2OMe, 15·9%), and giving a brownish-red colour with alcoholic ferric chloride. In an attempt to prepare the methyl ester the acid (50 mg.) in benzene suspension was treated overnight at 0° with excess of diazomethane. The product crystallised from alcohol in prisms (15 mg.), m. p. 123°, and was insoluble in 5% potassium hydroxide solution. It was evidently impure *methyl ester methyl ether* of tetrahydroelliptic acid (Found : OMe, 27·4. $C_{22}H_{26}O_8$ requires 4OMe, 29·6%. $C_{21}H_{24}O_8$ requires 3OMe, 23·0%), methylation occurring at the *p*-hydroxyl group of ring D.

Crystallisation of the phenolic fraction from aqueous alcohol gave *tetrahydroelliptol* (XII) in plates (60 mg.), m. p. 225° after evolution of solvent at 135—140°, but in a bath at 200° it melted immediately with effervescence (Found : C, 64·2; H, 5·7. $C_{18}H_{20}O_6$ requires C, 65·0; H, 6·1%), *i.e.*, solvent retention.

Elliptonone (XIII) (cf. Meijer and Koolhaas, *loc. cit.*).—*l*-Elliptone (500 mg.) in acetic acid (4 c.c.) and amyl nitrite (1·7 c.c.) was cooled to 0°, and a mixture of hydrochloric acid (1 c.c.) and acetic acid (1 c.c.) added during 5 minutes. After warming to room temperature the bright yellow precipitate was collected, washed with cold acetic acid, and dried over potash pellets in a vacuum. Elliptonone crystallised from xylene in yellow prisms, m. p. 315° (Found : OMe, 17·0%); it sublimed in a high vacuum at 250° and then had m. p. 325° (Found : C, 66·1; H, 3·6; OMe, 17·1. Calc. for $C_{20}H_{12}O_7$: C, 65·9; H, 3·3; 2OMe, 17·0%).

Partial Synthesis of Elliptonone (cf. synthesis of rotenonone; Takei, *Ber.*, 1932, **65**, 1047).—Elliptol (100 mg.), methyl oxalate (100 mg.), and sodium acetate (50 mg.) were heated at 160° for 1 hour. The reaction mixture was treated with boiling methyl alcohol (2 × 5 c.c.), and the residue sublimed to give elliptonone in yellow prisms, m. p. 325°, not depressing that described above.

No crystalline products could be isolated from the Clemmensen reduction of *l*- and *dl*-elliptones and of *dl*-dihydroelliptone, under conditions similar to those in which Haller and LaForge (*J. Amer. Chem. Soc.*, 1931, **53**, 3430) reduced *iso*rotenone to deoxy*iso*rotenone.

l-Elliptone could not be reduced in dioxan with either platinum oxide or a palladium–barium sulphate catalyst, although rotenone was readily reduced in the presence of the latter catalyst to dihydrorotenone in good yield (cf. Haller and Schaffer, *J. Amer. Chem. Soc.*, 1933, **55**, 3494).

Reduction of l-iso*Rotenone in Acetic Acid* (cf. Butenandt and Hildebrandt, *Annalen*, 1930, **477**, 261),—*l-iso*Rotenone (5 g.) in " AnalaR " acetic acid (100 c.c.) was hydrogenated slowly in the presence of platinum oxide (0·5 g.). There was no break in the absorption curve at 1 or 2 molecules absorption. By interrupting the reduction at 2 molecules absorption and repeatedly crystallising the product from alcohol, the substance described by Butenandt and Hildebrandt was obtained in needles, m. p. 168°, $[\alpha]_D^{17}$ −107° in benzene (c = 1·0), in 30% yield. Despite its apparent homogeneity this substance contained unreduced *l-iso*rotenone. Oxidation with iodine in alcoholic sodium acetate and fractional crystallisation of the product gave dehydro*iso*rotenone, m. p. 195°, not depressed by an authentic specimen. Crystallisation of the more soluble fraction gave l-*dihydrodeoxy*iso*rotenone*, m. p. 158°, in needles from alcohol and giving no colour in the Durham test; $[\alpha]_D^{19°}$ −113° in benzene (c = 1·0) (Found : C, 71·8; H, 6·2; OMe, 16·4. $C_{23}H_{26}O_5$ requires C, 72·2; H, 6·8; OMe, 16·3%).

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