## 239. *The Active Principles of Leguminous Fish-poison Plants. Part II. The Isolation of* l-*Elliptone from* Derris elliptica.

By STANLEY H. HARPER.

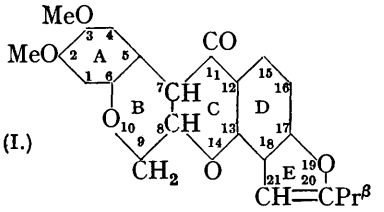
An optically active substance, l-*elliptone*, isolated from the neutral rotenone-free resin from *Derris elliptica* (var. Sarawak creeping), is shown to be the precursor in the resin of Buckley's substance. From a study of its reactions and by comparison of these with the reactions of *iso*rotenone, structure (II, R = H) is suggested for *l*-elliptone.

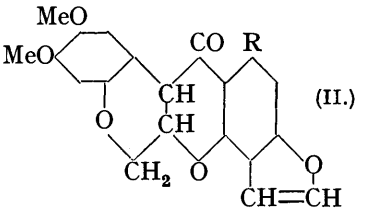
ALTHOUGH rotenone, as a constituent of the resin from *Derris elliptica* root, has been known for many years, little progress has been made towards elucidating the chemical constitution of the remainder of the resin. *D. elliptica* resin is characterised by a constant content of rotenone (*ca.* 40%), and the absence of sumatrol and *l*-α-toxicarol, substances which have only been reported from *D. malaccensis* root (Cahn and Boam, *J. Soc. Chem. Ind.*, 1935, **54**, 42T; Tattersfield and Martin, *ibid.*, 1937, **56**, 77T; Cahn, Phipers, and Boam, J., 1938, 513; Harper, this vol., p. 812). A portion of the resin (*ca.* 10%) is soluble in alkali and appears to consist solely of emulsifying agents. Fifty % of the resin, to which the term " deguelin " concentrate has been given, remains unaccounted for. Clark (*J. Amer. Chem. Soc.*, 1931, **53**, 313), by treating this concentrate with alcoholic sodium hydroxide, obtained a small yield of *dl*-deguelin and suggested that deguelin occurred as the lævo-form in the resin. The analogous racemisations by alkali of *l*-α-toxicarol and of *l*-elliptone (see p. 1104) make this probable. Later Haller and LaForge (*ibid.*, 1934, **56**, 2415), by catalytic hydrogenation of this fraction, obtained *l*-dihydrodeguelin in crystalline form. As yet *l*-deguelin has not been isolated in crystalline form. The claims of Takei, Miyijima, and Ono (*Ber.*, 1933, **66**, 1826) to have done this have not been confirmed by Haller and LaForge (*loc. cit.*). It is evident that *l*-deguelin is only a part, probably not more than half, of this so-called " deguelin " concentrate. Cahn, Phipers, and Boam (*J. Soc. Chem. Ind.*, 1938, **57**, 200T) have obtained evidence for the presence of a small proportion of a wax-like constituent, which the author has confirmed (*Chem. and Ind.*, 1938, **57**, 1059). Inasmuch as this " deguelin " concentrate contributes appreciably to the toxicity of the whole resin a knowledge of its constituents is desirable.

Some years ago Buckley (*J. Soc. Chem. Ind.*, 1936, **55**, 285T) treated an ethereal solution of *D. elliptica* resin repeatedly with 5% potassium hydroxide solution. On standing, the ethereal solution deposited crystalline material, from which a substance, m. p. 183°, was

obtained. He reported it as optically inactive, so it was unlikely that it occurred in the resin as such. The substance gave a positive Durham test,* was not isomerised by sulphuric acid, and the formation of an oxime and a dehydro-compound showed it to be distinct from rotenone and deguelin. Buckley, however, did not make any suggestion as to its nature. Recently, the author attempted to fractionate a " deguelin " concentrate by chromatographic adsorption on alumina (*Chem. and Ind., loc. cit.*). A small yield of crystalline solid was obtained which, by comparison with a specimen kindly sent by Dr. Buckley, was shown to be identical with his substance. Analysis established the formula $C_{20}H_{16}O_6$, which has now been confirmed. From the similarity in properties to *iso*rotenone ($C_{23}H_{22}O_6$) (I) and the fact that the formulæ differ by $C_3H_6$, it was suggested that the *iso*propyl group attached to ring E of *iso*rotenone is absent, *i.e.*, the substance has the structure (II, R = H).

(I.)



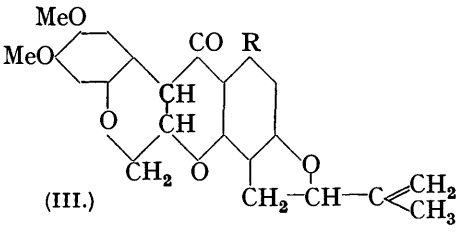

(II.)

The fact that this substance was optically inactive suggested that it was derived by a process of racemisation, caused by the conditions under which it was isolated, from an optically active precursor in the resin. A search for this precursor has now been successful. An ethereal extract of *D. elliptica* (var. Sarawak creeping) root was extracted with 5% potassium hydroxide solution to remove phenolic substances, the operation being carried out as quickly as possible to prevent racemisation. The neutral resin from the ethereal layer, on solution in carbon tetrachloride, deposited rotenone as the carbon tetrachloride solvate. The filtrate on evaporation gave a yellow resin, which was dissolved in a small volume of ether. This solution rapidly deposited a colourless crystalline solid, which crystallised from alcohol in needles, m. p. 160°, $[\alpha]_D^{20°}$ − 18° in benzene and + 53° in acetone. This substance, for which the name l-*elliptone* is suggested, has the formula $C_{20}H_{16}O_6$. Racemisation by sodium acetate in boiling alcohol led to a nearly quantitative yield of dl-*elliptone*. A mixture of this with Buckley's substance showed no depression of melting point, indicating their identity. In addition, Buckley's substance gives derivatives identical with those from *dl*-elliptone. *l*-Elliptone is therefore the optically active precursor of Buckley's substance.

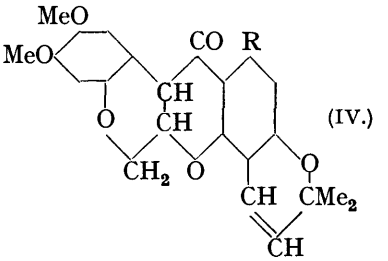
When the work described in this paper was nearly completed, the author's attention was drawn to a paper in which Meyer and Koolhaas (*Rec. Trav. chim.*, 1939, **58**, 207) describe the isolation of Buckley's substance, and a substance, crystallising from alcohol in needles, m. p. 162—163°, $[\alpha]_D$ − 19° in benzene and + 14° in acetone, for which they establish the formula $C_{20}H_{16}O_6$. This would appear to be *l*-elliptone. Although they do not establish any relationship, they suggest that it is possibly the optically active precursor of Buckley's substance. The rotations recorded for *l*-elliptone and this substance in benzene are the same, but those in acetone differ markedly. A similar difficulty was encountered by the author with regard to *l*-α-toxicarol (this vol., p. 815), in which preparations of the same specific rotation in benzene gave varying rotations in acetone. It was thought that the variation may have been due to fluctuation of the water content of the acetone. It is not believed that the differences recorded above indicate the non-identity of the two substances. Meyer and Koolhaas have suggested the name " derride " for this substance, somewhat unfortunately, as it has already been used by Greshoff (*Ber.*, 1890, **23**, 3538) for a resinous extract from *D. elliptica* root. Inasmuch, too, as the substance is shown to be a ketone, the suffix " ide " is inappropriate. Their work is important, for it shows that

* An intense red colour reaction with a drop of concentrated nitric acid which contact with a drop of aqueous ammonia changes to an evanescent deep blue or green; given by rotenone and substances of similar structure (*Ann. Appl. Biol.*, 1923, **10**, 5).

there are varieties of *Derris* root in the Dutch East Indies in which the rotenone is replaced by *l*-elliptone. For this reason a determination of the insecticidal activity of the latter with respect to the former will be of great interest. It is regrettable that they do not give more details as to the botanical and analytical characteristics of this root. Meyer and Koolhaas describe too the isolation in small yield of a phenol, $C_{20}H_{16}O_7$, from Sumatra type *Derris* root to which they ascribe formula (II, R = OH). It would appear, then, that elliptone and this phenol constitute a similar pair of compounds, as do rotenone (III,



(III.)



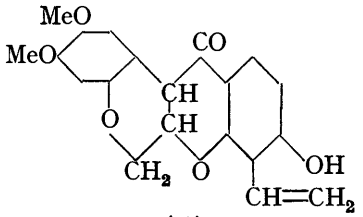
(IV.)

R = H) and sumatrol (III, R = OH), and deguelin (IV, R = H) and toxicarol (IV, R = OH). The existence of such a closely related group of substances in *Derris* root is of great interest and indicates the need for some knowledge of their biochemical origin.

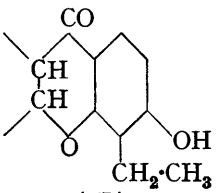
The positive Durham test given by *l*-elliptone indicates that rings A, B, and C are the same as in rotenone (III, R = H). This, with the fact that there are two methoxyl groups and a keto-group, accounts for five of the six oxygen atoms; the sixth is therefore probably attached to ring D. Treatment with sodium acetate in boiling alcohol, a process which is known to racemise only $C_7$–$C_8$ (Cahn, Phipers, and Boam, J., 1938, 513), yields inactive *dl*-elliptone, proving that the only asymmetric centres in the molecule are $C_7$–$C_8$. This is confirmed by the inactivity of dehydroelliptone obtained by the removal of the hydrogen atoms attached to $C_7$–$C_8$. *l*-Elliptone gives an *oxime* (m. p. 222°), distinct from that given by *dl*-elliptone (m. p. 259°), with hydroxylamine hydrochloride and sodium acetate in alcohol. The fact that racemisation does not occur indicates that it proceeds through enolisation of the keto-group. Meyer and Koolhaas (*loc. cit.*) describe a different oxime (m. p. 240°), prepared in pyridine solution. It seemed likely that this oxime corresponded to the *iso*oxime, which exhibits the properties of a phenol, obtained from rotenone in alkaline solution (Butenandt, *Annalen*, 1928, **464**, 253). LaForge, Haller, and Smith (*Chem. Reviews*, 1933, **12**, 199) have suggested a mechanism for the formation of this *iso*-oxime involving the opening of ring C. Repetition of Meyer and Koolhaas's preparation has confirmed the individuality of this oxime (m. p. 236°), but it exhibits no phenolic properties. Moreover *dl*-elliptone in pyridine gives a non-phenolic but different *oxime* (m. p. 261°). The fact that *l*- and *dl*-elliptone give different oximes shows that ring opening for the formation of an *iso*oxime has not occurred, as this would lead to racemisation. The relationship between these two pairs of oximes is not yet clear, but it may be of a *cis-trans* nature. Acetylation of *l*-elliptone in boiling acetic anhydride gives an inactive *monoacetate*, identical with that prepared from *dl*-elliptone. This is probably an enol acetate, inasmuch as *iso*rotenone under the same conditions gives an inactive enol acetate owing to racemisation of $C_7$–$C_8$.

Cahn and Boam (J., 1938, 1818) in support of their formula $C_{20}H_{18}O_6$ (V), which, however, is not supported by the analytical evidence, assert that *dl*-elliptone has cryptophenolic properties, Buckley's substance in acetone solution, on addition to an ether–aqueous sodium hydroxide mixture, being gradually transferred to the aqueous layer. The author has been unable to confirm this observation. Repeated extraction led to no measurable transference, although acidification gave a faint opalescence. Controls with rotenone and *iso*rotenone also gave similar opalescences, indicating that any transference was due to solubility in the acetone–water. Further negative tests for phenolic properties are described in the experimental section. Moreover, no intermediate iodo-compound was formed in the preparation of dehydroelliptone, as claimed by Cahn and Boam (*loc. cit.*),

thus distinguishing elliptone from substances containing a hydroxyl group attached to ring D. The absence of a phenolic group suggests that the remaining oxygen atom is part of a ring, which on the formulation $C_{20}H_{16}O_6$ will be of furan type and thus resemble that in *iso*rotenone (I). By analogy, structure (II, R = H) is suggested for elliptone, but it must be borne in mind that ring E could have other points of attachment to ring D and still agree with the experimental results described here. On the basis of this formula catalytic hydrogenation should lead to the taking up of four atoms of hydrogen with the fission of ring E to give a phenol (VI) [formula (V) would require only two atoms of hydrogen]. Hydrogenation over Adams's catalyst confirmed this view, approximately four atoms being taken up, though only slowly. The difficulty of reduction is in accord with the *iso*rotenone structure (cf. LaForge *et al.*, *loc cit.*, p. 190); with the same catalyst, rotenone was rapidly reduced. *l*- and *dl*-Elliptone gave l- and dl-*tetrahydroelliptone* respectively, substances



(V.)



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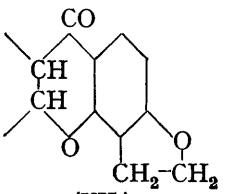

(VII.)

which, although giving no colour with ferric chloride, were readily soluble in alkali solution (cf. tetrahydrorotenone). The presence of a phenolic group was further shown by the formation of a *diacetate* with acetic anhydride. In one reduction of *l*-elliptone the experiment was stopped when only two atoms of hydrogen had been absorbed: the product was entirely a neutral compound, which had the same melting point as the initial material, but differed from it, and was probably impure l-*dihydroelliptone* (VII).

In one attempted reduction (not reproducible) of *l*-elliptone no hydrogen was absorbed, probably owing to poisoning of the catalyst; the recovered material, however, was not *l*-elliptone but Buckley's substance (m. p. 181°). This sample of Buckley's substance had a slight optical activity ($[\alpha]_D^{20°}$ — 7° in benzene). Meyer and Koolhaas (*loc. cit.*) state that their material had a slight rotation ($[\alpha]_D$ — 3° in benzene), as do Cahn and Boam (*loc. cit.*), but Buckley (*loc. cit.*) himself describes his material as being optically inactive. Buckley's substance is essentially *dl*-elliptone, as has been shown previously. That the optical activity of the above sample was due to incomplete racemisation of the *l*-elliptone was shown by treatment with sodium acetate in boiling alcohol, which completed the racemisation to give *dl*-elliptone, m. p. 177°. The slight difference in melting points (177° and 181°) may well be due to dimorphism. *l*-Elliptone, when shaken with platinum-black, is converted into what appears to be a dimorphic form crystallising in plates, m. p. 173° after softening at 160°.

Although the evidence described here makes the formula put forward for elliptone very probable, final proof can only be afforded by degradation to compounds of known structure. Experiments to this end are in progress.

## Experimental.

The *D. elliptica* (var. Sarawak creeping) used was received in the form of short lengths of air-dried root, which were chopped and finely ground. It then gave 8·8% of ethereal extract. Microanalyses are by Drs. Weiler and Strauss, Oxford. Methoxyl determinations are by the author, using Clark's semimicro-method (*J. Assoc. Off. Agric. Chem.*, **1932**, **15**, 136). Melting points are uncorrected.

The finely ground air-dried root (1000 g.) was extracted with ether (Soxhlet). Rotenone separated, and was removed (15·1 g.) after standing overnight in a refrigerator. The filtrate was concentrated to 1000 c.c., extracted with two portions of 5% potassium hydroxide solution (200 and 100 c.c.) as rapidly as possible (5 mins.), washed, dried over sodium sulphate, and evaporated, finally in a vacuum. The neutral resin was dissolved in carbon tetrachloride

(250 c.c.) and kept in a refrigerator overnight after being seeded with rotenone–carbon tetrachloride complex. The crop of complex (31·9 g.) was filtered off, and the filtrate evaporated, finally in a vacuum. The residue of resin (63 g.) was dissolved in ether (400 c.c.) and kept in a refrigerator with occasional scratching. A colourless solid separated, which could be filtered off after 48 hours (6·0 g.); occasionally, however, crystallisation took a longer time. By concentration of the filtrate and keeping for some weeks further small crops could be obtained, making a total of 8·9 g.

Crystallisation was best effected from ethyl alcohol, from which l-*elliptone* separated in colourless needles or occasionally as a gel which changed into the crystalline form; m. p. 160° (largely depressed by rotenone or *dl*-deguelin), $[\alpha]_D^{20°}$ − 18° in 1·00% benzene solution and + 55° in 1·00% acetone solution. By fractional crystallisation from benzene, crops were obtained having identical physical constants, indicating the homogeneity of the substance. From this solvent, *l*-elliptone, in contrast to *dl*-elliptone, separated in unsolvated rectangular prisms. It gave no colour with ferric chloride, but in the Durham test an intense blue colour was produced (Found : C, 67·9; H, 4·55; OMe, 17·5; *M*, Rast, 352. $C_{20}H_{16}O_6$ requires C, 68·2; H, 4·55; 2OMe, 17·6%; *M*, 352).

α-*Oxime*. *l*-Elliptone (250 mg.), hydroxylamine hydrochloride (250 mg.), and anhydrous sodium acetate (300 mg.) were refluxed for 8 hours in alcohol (20 c.c.). The mixture was poured into water, and the precipitate crystallised from methyl alcohol, the *oxime* (111 mg.) forming felted needles, m. p. 222° (Found : N, 3·4. $C_{20}H_{17}O_6N$ requires N, 3·8%).

β-*Oxime* (cf. Meyer and Koolhaas, *loc. cit.*). *l*-Elliptone (100 mg.), hydroxylamine hydrochloride (200 mg.), and sodium carbonate (150 mg.) in pyridine (10 c.c.) were heated on the water-bath for 3 hours. The solution was poured into water and extracted with ether, and the extract washed with water, dried, and evaporated. The gum obtained crystallised when rubbed with methyl alcohol. Recrystallisation from methyl alcohol–water gave the β-*oxime* (64 mg.) in needles, m. p. 236°. It gave no colour with ferric chloride and was not extracted from ethereal solution by alkali (Found : N, 3·6. $C_{20}H_{17}O_6N$ requires N, 3·8%). A mixture with the α-oxime softened at 210° and became fluid at 230°, indicating that the two may not be dimorphous.

*Monoacetate*. *l*-Elliptone (250 mg.) and sodium acetate (75 mg.) in acetic anhydride (4 c.c.) were refluxed for 1 hour and poured into water. The precipitate crystallised from ethyl alcohol in hexagonal prisms of the *monoacetate* (72 mg.), m. p. 200°, not depressed by the acetate prepared from *dl*-elliptone [Found : C, 67·0; H, 4·6; OMe, 15·9. $C_{20}H_{15}O_6(CO{\cdot}CH_3)$ requires C, 67·0; H, 4·6; OMe, 15·8%].

*Dehydroelliptone*. *l*-Elliptone (1 g.) and sodium acetate (2 g.) were dissolved in ethyl alcohol (40 c.c.), and iodine (1 g.) in alcohol (10 c.c.) added in portions to the boiling solution. Refluxing was continued for 30 minutes, and the solution kept overnight. Dehydroelliptone separated in very pale yellow prisms and could be recrystallised from chloroform–ethyl alcohol (1 : 2), occasionally separating in the needle form described by Buckley (*loc. cit.*), m. p. 264°, $[\alpha]_D \pm 0°$ in chloroform (Found : C, 68·2; H, 4·1; OMe, 17·9. Calc. for $C_{20}H_{14}O_6$ : C, 68·55; H, 4·0; OMe, 17·7%). There was no depression of m. p. in admixture with the dehydro-compound from *dl*-elliptone. On melting, a purple colour developed, which may have been mistaken by Cahn and Boam (*loc. cit.*) for the evolution of iodine. Tests for iodine were negative and reduction with zinc in acetic acid gave the dehydro-compound unchanged.

l-*Tetrahydroelliptone*.—*l*-Elliptone (1 g.) in ethyl acetate (20 c.c.) was reduced catalytically in the presence of Adams's catalyst (150 mg.). Reduction was slow, but a volume (146 c.c. of $H_2$ at N.T.P.) corresponding to 4 atoms of hydrogen (128 c.c.) was taken up. The filtered solution was diluted with ether and extracted with 5% aqueous potassium hydroxide to separate acid and neutral fractions. The alkaline layer on acidification and recovery through ether gave l-*tetrahydroelliptone* (444 mg.), which crystallised from alcohol in solvated rectangular plates, m. p. 217° (softening at 205°), $[\alpha]_D^{20°}$ + 61° in 1·00% acetone; it was only slightly soluble in benzene or chloroform [Found for material dried in a vacuum at room temperature : C, 65·4; H, 6·5; OMe, 23·0. $C_{20}H_{20}O_6,C_2H_5{\cdot}OH$ requires C, 65·65; H, 6·5; OMe (2OMe + EtOH), 23·1%]. The unsolvated phenol, m. p. 217°, was obtained by prolonged heating in a vacuum at 100° (Found : Loss in weight, 11·5. Calc. for loss of EtOH, 11·5%. Found : OMe, 17·5. Calc. for $C_{20}H_{20}O_6$ : OMe, 17·4%). Although soluble in alkali, this phenol gave no colour with ferric chloride. Methylation with diazomethane was unsuccessful. Attempted oximation in alcoholic sodium acetate was unsuccessful, but racemisation occurred to give *dl*-tetrahydroelliptone. Acetylation in acetic anhydride gave the *diacetate*, crystallising from ethyl alcohol–water in prisms, m. p. 140—142° [Found : C, 65·05; H, 5·8. $C_{20}H_{18}O_6(CO{\cdot}CH_3)_2$ requires

C, 65·4; H, 5·5%]. The neutral ethereal solution on evaporation, and crystallisation of the residue from alcohol, gave *dl*-elliptone (110 mg.), m. p. 173—175°, showing that some racemisation occurs as the result of a secondary reaction.

In one reduction of *l*-elliptone (500 mg.) the experiment was stopped when only 2 atoms of hydrogen had been absorbed. The neutral layer then gave a substance (294 mg.) crystallising from alcohol in clusters of prisms, m. p. 159° (depressed by *l*-elliptone), $[\alpha]_D^{20°}$ − 97° in 1·00% acetone. This substance gave no colour with ferric chloride and was probably l-*dihydroelliptone* (Found : C, 69·0; H, 5·2; OMe, 18·1. $C_{20}H_{18}O_6$ requires C, 67·8; H, 5·1; OMe, 17·5%).

dl-*Elliptone*.—*l*-Elliptone (1 g.) and sodium acetate (2 g.) were refluxed in alcohol (50 c.c.) for 2 hours. dl-*Elliptone* (922 mg.), which separated on cooling, was filtered off, washed with hot water to remove sodium acetate, and recrystallised from alcohol, separating in needles, m. p. 176—177°, $[\alpha]_D \pm 0°$ in benzene (Found : C, 68·0; H, 4·85. $C_{20}H_{16}O_6$ requires C, 68·2; H, 4·6%). The solid separating from the first filtrate on dilution was optically inactive, indicating the absence of impurities such as rotenone. A mixed m. p. determination with Buckley's substance showed no depression (176—179°); a mixture with *l*-elliptone (5 : 1) melted indefinitely at 176° and cleared at 181°. From benzene, *dl*-elliptone separated in solvated prisms, confirming Cahn and Boam's (*loc. cit.*) observation for Buckley's substance, m. p. 176° (after resolidifying, 181°) (Found : OMe, 15·9. Calc. for $2C_{20}H_{16}O_6,C_6H_6$ : OMe, 15·9%).

α-*Oxime*. *dl*-Elliptone (100 mg.), hydroxylamine hydrochloride (100 mg.), and sodium acetate (120 mg.) were refluxed in alcohol (5 c.c.) for 8 hours. The oxime (57 mg.) separated on cooling and crystallised from methyl alcohol (less soluble than the *l*-α-oxime) in the characteristic triangular leaflets, m. p. 259°, described by Buckley (*loc. cit.*) (Found : N, 4·0. Calc. for $C_{20}H_{17}O_6N$ : N, 3·8%).

β-*Oxime*. *dl*-Elliptone (100 mg.), hydroxylamine hydrochloride (200 mg.), and sodium carbonate (150 mg.) in pyridine (10 c.c.) were heated on the water-bath for 3 hours. The solution was poured into water and extracted with ether, and the extract washed with water, dried, and evaporated. Crystallisation of the residue from methyl alcohol, in which it was sparingly soluble (cf. *l*-β-oxime), gave the β-*oxime* in thin prisms, m. p. 261° (Found : N, 3·8. $C_{20}H_{17}O_6N$ requires N, 3·8%). It gave no colour with ferric chloride. The m. p. was depressed by the α-oxime, indicating that the two oximes may not be dimorphous forms.

*Monoacetate*. In acetic anhydride (as described above, p. 1103), *dl*-elliptone gave a monoacetate, m. p. 202° [Found : C, 66·8; H, 4·55. Calc. for $C_{20}H_{15}O_6(CO\cdot CH_3)$ : C, 67·0; H, 4·6%], identical with that from *l*-elliptone.

*Dehydroelliptone*.—This was prepared from *dl*-elliptone by the method described under *l*-elliptone and crystallised from chloroform–ethyl alcohol in pale yellow prisms or needles, m. p. 264° (Buckley, *loc. cit.*, gives 264°) (Found : C, 68·3; H, 4·0. Calc. for $C_{20}H_{14}O_6$ : C, 68·55; H, 4·0%).

dl-*Tetrahydroelliptone*.—*dl*-Elliptone (1 g.) in ethyl acetate (20 c.c.) was catalytically reduced in the presence of Adams's catalyst (150 mg.), 132 c.c. (N.T.P.) of hydrogen being absorbed, though slowly (4 atoms of hydrogen require 128 c.c.). The solution, diluted with ether, was extracted with 5% potassium hydroxide solution to remove phenols. The ethereal solution on evaporation, and crystallisation of the residue from alcohol, gave *dl*-elliptone (177 mg.). dl-*Tetrahydroelliptone* (468 mg.) was obtained from the alkaline layer on acidification and isolated by means of ether. It crystallised from alcohol in rectangular plates with 1 mol. of alcohol, m. p. 205° (softening at 197°), and gave no colour with ferric chloride [Found : OMe, 23·1. $C_{20}H_{20}O_6,C_2H_5\cdot OH$ requires OMe (2OMe + EtOH), 23·1%]. The unsolvated phenol, m. p. 205°, was obtained by prolonged heating at 100° in a vacuum (Found : Loss in weight, 11·9. Calc. for loss of EtOH, 11·5%. Found : C, 66·9; H, 5·85; OMe, 17·4. Calc. for $C_{20}H_{20}O_6$ : C, 67·3; H, 5·65; OMe, 17·4%).

*Buckley's Substance*.—In one attempted reduction of *l*-elliptone over platinum no absorption took place. The filtered solution was evaporated; the residue crystallised from alcohol to give a substance, m. p. 181°, identical with a specimen kindly sent by Dr. Buckley (Found : C, 68·0; H, 4·55. Calc. for $C_{20}H_{16}O_6$ : C, 68·2; H, 4·55%). The former had $[\alpha]_D^{20°}$ − 7° in 1·00% benzene. As described by Buckley (*loc. cit.*), with hydroxylamine in alcohol it gave *dl*-elliptone α-oxime. On refluxing with sodium acetate in alcohol, it gave *dl*-elliptone (m. p. 176—177°).

*Tests for Phenolic Properties*.—(a) Buckley's substance (50 mg.) was suspended in ether (10 c.c.) and vigorously shaken with 5% potassium hydroxide solution for 10 minutes. There was no precipitate on acidification of the alkaline layer. In a control experiment with *dl*-α-toxicarol (similarly insoluble in ether), solution in the alkali took place immediately.

(b) A few mg. were dissolved in acetone, and sufficient water added to produce a turbidity.

Addition of a drop of 5% aqueous potassium hydroxide did not effect solution, indicating that Buckley's substance has no cryptophenolic properties. On standing, a yellow colour slowly developed owing to oxidation.

(c) Buckley's substance (20 mg.) in acetone (3 c.c.) was poured into a mixture of ether (25 c.c.) and 2% potassium hydroxide solution (10 c.c.). After shaking, the alkaline layer gave a faint opalescence on acidification. Further extractions with portions of alkali gave similar opalescences. Controls with rotenone and *iso*rotenone also gave opalescences, showing that the transfer was due to solubility in the acetone–water (cf. Cahn and Boam, *loc. cit.*).

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ROTHAMSTED EXPERIMENTAL STATION, HARPENDEN, HERTS. [*Received, May 30th,* 1939.]