

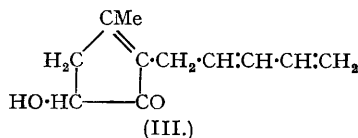
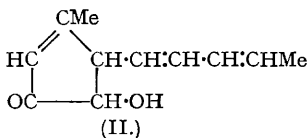
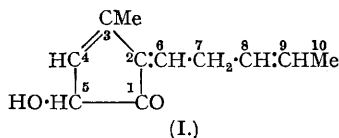
175. *The Structure of Pyrethrolone and Related Compounds. Part III.*

By T. F. WEST.

On hydrogenation the two methyl ethers derived from pyrethrolone (West, this vol., p. 239) were converted into the corresponding *tetrahydro*-compounds (cf. LaForge and Haller, *J. Amer. Chem. Soc.*, 1936, **58**, 1779). Attempts were made to remove one of the double bonds in the side chain in order to throw light upon the most probable position of the remaining double bond in relation to the unsaturation in the nucleus. *Dihydro-*

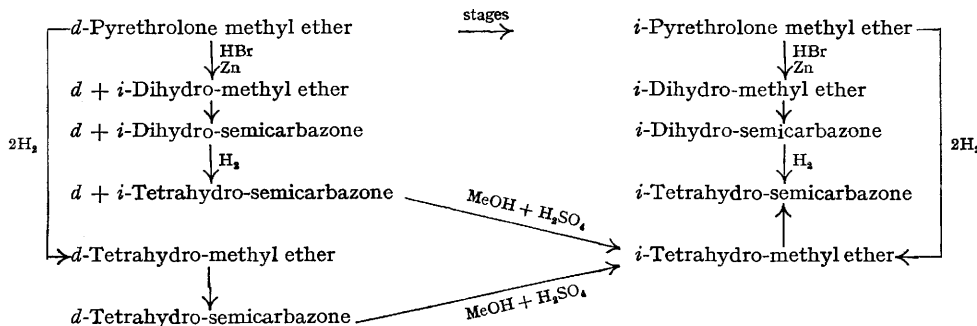
derivatives were obtained from both the *d*- and the *i*-pyrethrolone methyl ether by treatment with hydrogen bromide, followed by zinc reduction. Although the light absorption data for these compounds did not permit differentiation between the formulæ advanced for pyrethrolone during the past few years (Gillam and West, *J.*, 1942, 671; 1944, 49; LaForge and Acree, *J. Org. Chem.*, 1942, 7, 418; LaForge and Barthel, *ibid.*, 1944, 9, 242; West, this vol., pp. 51, 239), they indicated that the two pairs of dihydro- and tetrahydro-derivatives contained similar chromophoric systems and with other analytical data it was possible to infer that in the dihydro-compounds it was the double bond nearest the nucleus which had been eliminated. The terminal methyl values for the two pyrethrolone methyl ethers and their derivatives appeared to lend support to the conclusion of LaForge and Barthel (*loc. cit.*) that pyrethrolone may not be a homogeneous compound.

In Part II (this vol., p. 239) the relationship between the dextrorotatory methyl ether prepared from pyrethrolone and methyl sulphate and the optically inactive ether obtained from pyrethrolone semicarbazone with methyl-alcoholic sulphuric acid was examined. Arising mainly out of a study of the behaviour of these ethers towards dienophiles in the Diels-Alder reaction, a tentative structure (I) was suggested for pyrethrolone because of the chemical difficulties raised by the structures (II) and (III) which were suggested as possibilities by Gillam and West (*J.*, 1942, 671) in an attempt to accommodate the light absorption data.



In order to test the correctness or otherwise of these postulated formulæ attempts have been made to eliminate one of the double bonds in the side chain. The methyl ethers of pyrethrolone were utilised in these experiments because of the tendency for migration of the double bonds in pyrethrolone itself—due no doubt to the juxtaposition of the $>CO$ and $>CH\cdot OH$ groups in the cyclopentenolone ring (Gillam and West, *loc. cit.*; West, *loc. cit.*). For comparison as an end product *d*-pyrethrolone methyl ether was hydrogenated to *d*-tetrahydropyrethrolone methyl ether and the *i*-ether, under similar conditions, gave the *i*-tetrahydropyrethrolone methyl ether. *d*-Tetrahydropyrethrolone methyl ether semicarbazone was converted into the inactive tetrahydro-ether by refluxing with methyl-alcoholic sulphuric acid.

LaForge and Haller (*J. Org. Chem.*, 1938, 2, 546) found that on treatment with aluminium amalgam pyrethrolone was converted into its deoxy-derivative, pyrethron, but when treated under the same conditions both the *d*- and the *i*-pyrethrolone methyl ether were recovered substantially unchanged. Reduction of the *d*-ether with sodium and alcohol gave products which possessed negligible light-absorbing properties. However, on addition of one molecule of hydrogen bromide in acetic acid solution, followed by zinc reduction, the *d*-ether was converted into *d*-dihydropyrethrolone methyl ether, the semicarbazone of which gave the corresponding tetrahydro-derivative on hydrogenation. The melting points of the semicarbazones were somewhat indefinite and the optical rotation of the tetrahydro-compound indicated that this was due to partial conversion into the inactive modifications during the reaction. This tetrahydro-compound was converted into *i*-tetrahydropyrethrolone methyl ether by treating the semicarbazone with methyl-alcoholic sulphuric acid. Under the same conditions the *i*-pyrethrolone methyl ether gave *i*-dihydropyrethrolone methyl ether, the semicarbazone of which was hydrogenated to the corresponding *i*-tetrahydro-derivative. In this case one fraction gave a semicarbazone, m. p. 202—204°, which was shown to be dihydropyrethron semicarbazone by conversion into dihydrojasmon (tetrahydropyrethron) on hydrogenation. (The formation of this compound was not observed in the earlier experiments with *d*-pyrethrolone methyl ether, but as it appeared to have no bearing upon the structure of pyrethrolone the experiment with the active ether was not repeated.)



The λ_{max} and ϵ values for the two dihydro-ethers and the two tetrahydro-derivatives were practically identical and presumably each pair contained similar chromophoric systems. The terminal methyl values for the dihydro-derivatives indicated that the unsaturated group at the end of the chain was present in these compounds. Therefore, it was not possible to use this result to differentiate between the formulæ advanced mainly to bridge the gap between the somewhat conflicting chemical evidence (West, this vol., p. 239) and the requirements of light absorption data (Gillam and West, *J.*, *loc. cit.*). It is, however, clear that (a) if (I) is

correct, then reduction to the dihydro-derivative involved addition to the ends of the conjugated system between carbon atoms 4 and 6 with the formation of a double bond between atoms 2 and 3, (b) if (II), then addition was made to the ethylenic linkage between carbon atoms 6 and 7, and (c) if III, then addition was made to the ends of the conjugated system between carbon atoms 7 and 10. In spite of the great difficulty involved in accepting (III) on the chemical evidence LaForge and Barthel (*loc. cit.*) consider that this formulation, first put forward by Gillam and West (J., 1942, 671), cannot be excluded from consideration. In connection with the various alternative formulæ advanced, the terminal methyl values for samples of the *d*- and the *i*-pyrethrolone methyl ether and their dihydro-derivatives—in spite of the similar absorption data—appear to lend support to the conclusion of LaForge and Barthel (*loc. cit.*) that pyrethrolone may not be a homogeneous substance as previously supposed but a mixture of components differing in the nature of the side chain. This indication that these derivatives of pyrethrolone which show almost identical absorption data can differ in respect to the unsaturation in the side chain appears to be a significant observation and would seem to permit considerable reconciliation of the chemical reactions with the light absorption data. LaForge and Barthel (*loc. cit.*) found that fractions from pyrethrolone, "pyrethrolone methyl ether," and pyrethrolone acetate had terminal methyl values which indicated heterogeneity, but unfortunately absorption data were not recorded.

The various data are summarised in Table I.

TABLE I.

Absorption Spectra (Alcoholic Solutions) and Terminal Methyl Values for Some Pyrethrolone Derivatives.

	$\lambda_{\max.}$, A.	ϵ .	Terminal methyl value, ¹	M.W. used.
<i>d</i> -Pyrethrolone methyl ether ⁶	2275	23,000	0.76	192
<i>d</i> -Dihydropyrethrolone methyl ether ²	2285	10,900	1.62	194
<i>d</i> -Tetrahydropyrethrolone methyl ether ²	2305	10,300	—	196
<i>i</i> -Pyrethrolone methyl ether ⁶	2270	21,700	0.37	192
<i>i</i> -Dihydropyrethrolone methyl ether ²	2335	10,800	1.31	194
<i>i</i> -Tetrahydropyrethrolone methyl ether ²	2305	10,600	—	196
Tetrahydropyrethrolone ^{3, 2}	2320	12,000	—	182
4 <i>d</i> -Pyrethrolone methyl ether semicarbazone ⁵	{ 2320	{ 17,300	—	249
	{ 2665	{ 19,000		
<i>d</i> -Dihydropyrethrolone methyl ether semicarbazone	2660	19,800	—	251
<i>d</i> -Tetrahydropyrethrolone methyl ether semicarbazone	2650	21,400	—	253
<i>i</i> -Pyrethrolone methyl ether semicarbazone ⁵	{ 2320	{ 21,000	—	249
	{ 2655	{ 19,000		
<i>i</i> -Dihydropyrethrolone methyl ether semicarbazone	2665	20,150	—	251
<i>i</i> -Tetrahydropyrethrolone methyl ether semicarbazone	2660	19,300	—	253
Tetrahydropyrethrolone semicarbazone	2650	22,000	—	239

¹ Expressed as mol. of acetic acid per mol. of the ether. ² The fact that the light absorption data on these five different compounds are so closely alike points clearly to the presence of the same chromophoric system in the same molecular environment (cf. Gillam and West, J., 1942, 486). Since the dihydro- and the tetrahydro-derivatives are not different, it is clear also that the extra ethylene linkage in the dihydro-derivatives must be isolated from the conjugated system. ³ Gillam and West, J., 1942, 671. ⁴ The absorption data here are clearly indicative of the presence of the C=C=C=N chromophore (Evans and Gillam, J., 1943, 565), but this band is less susceptible to the effect of molecular environment than that due to C=C=C=O. ⁵ West, this vol., p. 239. ⁶ Data for the samples actually used in preparing the dihydro-ethers (cf. West, this vol., p. 239).

EXPERIMENTAL.

(Analyses are by Drs. Weiler and Strauss, Oxford.)

d-Tetrahydropyrethrolone Methyl Ether.—*d*-Pyrethrolone methyl ether (1.1 g.) (West, this vol., p. 241) having b. p. 103°/0.8 mm., n_D^{20} 1.5034, $[\alpha]_D^{20} + 88^\circ$ (c, 5 in alcohol), OMe 15.85%, dissolved in a mixture of ethyl acetate (45 ml.) and methyl alcohol (45 ml.), was hydrogenated, a platinum oxide catalyst (0.25 g.) being used, absorbing 164 ml. of hydrogen at N.T.P. (Calc. for $C_{12}H_{16}O_2$, 2 double bonds, 256.8 ml.). The filtered solution was concentrated by distillation under reduced pressure, and the residue steam-distilled. The *d*-tetrahydropyrethrolone methyl ether obtained by extraction of the distillate with light petroleum and purified by distillation (0.87 g.) had b. p. 92–93°/1.1 mm., n_D^{20} 1.4731, d_{4}^{25} 0.966, $[\alpha]_D^{20} + 88^\circ$ (c, 8.37 in alcohol), $\lambda_{\max.}$ 2305 A., $\epsilon = 10,300$ (Found: OMe, 15.1. $C_{12}H_{20}O_2$ requires OMe, 15.8%).

The ether (0.59 g.), dissolved in ethyl alcohol (6 ml.), was mixed with a solution of semicarbazide hydrochloride (0.89 g.) and sodium acetate crystals (1.2 g.) in warm water (1.2 ml.) and kept overnight. Water (50 ml.) was then added, and the mixture refrigerated for 2 hours. The semicarbazone (0.67 g., m. p. 125–130° indef.) crystallised from methyl alcohol (20 ml.) to give 0.15 g., m. p. 137–139°. After one further recrystallisation the *d*-tetrahydropyrethrolone methyl ether semicarbazone had m. p. 141–142°, $[\alpha]_D^{20} - 68^\circ$ (c, 0.26 in pyridine), $\lambda_{\max.}$ 2650 A., $\epsilon = 21,400$ (Found: N, 15.3. $C_{13}H_{23}O_2N_3$ requires N, 16.6%).

i-Tetrahydropyrethrolone Methyl Ether.—*i*-Pyrethrolone methyl ether (1 g.) (West, J., *loc. cit.*) having b. p. 107–109°/1.5 mm., n_D^{20} 1.5132, d_{4}^{25} 1.007, $[\alpha]_D^{20} + 0.1^\circ$, OMe 16.3%, in methyl alcohol (60 ml.), was hydrogenated with a platinum oxide catalyst (0.26 g.), absorbing 215 ml. of hydrogen at N.T.P. (Calc. for $C_{12}H_{16}O_2$ two bonds, 233.5 ml.). The *i*-tetrahydropyrethrolone methyl ether (0.83 g.) (worked up as described for the active ether) had b. p. 95–96°/1.7 mm., n_D^{20} 1.4732, d_{4}^{25} 0.965, $[\alpha]_D \pm 0^\circ$ (c, 7.55 in alcohol), $\lambda_{\max.}$ 2305 A., $\epsilon = 10,600$ (Found: OMe, 15.5. $C_{12}H_{20}O_2$ requires OMe, 15.8%).

By the method given for the active compound this ether (0.5 g.) yielded a semicarbazone (0.52 g.), m. p. 115–117°, which was recrystallised from methyl alcohol (15 ml.) to give 0.25 g., m. p. 120–121°. After one further recrystallisation the *i*-tetrahydropyrethrolone methyl ether semicarbazone had m. p. 122–123°, $[\alpha]_D \pm 0^\circ$ (c, 0.927 in pyridine), $\lambda_{\max.}$ 2660 A., $\epsilon = 19,300$ (Found: N, 15.6. $C_{13}H_{23}O_2N_3$ requires N, 16.6%).

Conversion of the d- into the i-Form.—The *d*-semicarbazone (1.5 g.), m. p. 140—142°, was refluxed on the water-bath for 2½ hours with a solution of sulphuric acid (0.9 g.) in methyl alcohol (15 ml.); water (15 ml.) was then added, and the bulk of the methyl alcohol removed by distillation under reduced pressure. The residue was saturated with sodium chloride, and the reddish oil extracted with light petroleum. This solution was washed until it was neutral, the solvent removed, and the residue steam-distilled. The oil (0.7 g.) extracted from the distillate with light petroleum had b. p. 90°/1.2 mm., n_D^{20} 1.4747, d_{15}^{20} 0.968, $[\alpha]_D^{20} \pm 0^\circ$ (*c*, 2 in alcohol), of which the semicarbazone, after recrystallisation from methyl alcohol, had m. p. 122—124°, $[\alpha]_D^{20} \pm 0^\circ$ (*c*, 1 in pyridine); the m. p. was not depressed by admixture with the semicarbazone, m. p. 122—123°, prepared from *i*-tetrahydropyretrolone methyl ether.

d-Dihydropyretrolone Methyl Ether.—*d*-Pyrethrolone methyl ether (7.3 g.), b. p. 115—117°/1.8 mm., n_D^{20} 1.5136, d_{15}^{20} 1.004, $[\alpha]_D^{20} + 87.2^\circ$, OMe 15.7%, terminal methyl value 0.76 (expressed as mol. of acetic acid per mol. of ether), λ_{max} 2275 Å., $\epsilon = 23,000$, was dissolved in glacial acetic acid (36.5 ml.), and the solution cooled in ice. Hydrogen bromide (previously washed by passing through acetic acid and then over calcium chloride) was passed slowly through until the weight had increased by 3.3 g. (1 mol. of hydrogen bromide \equiv 3.1 g.). The apparatus was disconnected and kept at laboratory temperature overnight with calcium chloride tubes fixed at the exit points. Acetic acid (36 ml.) was added, followed by zinc dust (20 g.) in approximately 3 g. portions during 2 hours, to the mechanically stirred solution heated under reflux on the water-bath. Cold water (500 ml.) was added to the cooled solution, which was then saturated with sodium chloride, and the oil extracted with ether. The ethereal solution was washed with cold N/10-sodium carbonate until neutral (sodium chloride being added at each washing) and finally with water, and the solvent removed by distillation to leave an orange-coloured oil, which was steam-distilled. The practically colourless oil (5.0 g.) extracted from the distillate with light petroleum was carefully fractionated in a 10 ml. flask with a vacuum-sealed fractionating column (Shrader and Ritzer, *Ind. and Eng. Chem. Anal.*, 1939, **11**, 54).

Fraction.	B. p./0.7 mm.	n_D^{20} .	Wt. (g.).	λ_{max} , Å.	ϵ_{max} .	Mol. wt. taken.
1	<72°	1.4965	0.28	—	—	—
2	79—81	1.4965	2.55	2290	11,500	194
3	82—85	1.4983	0.58	—	—	—
4	86—95	1.5028	1.08	—	—	—
Residue	—	—	0.45	—	—	—

Fraction 2 (2.45 g.), dissolved in alcohol (25 ml.), was added to a solution of semicarbazide hydrochloride (3.67 g.) and crystalline sodium acetate (4.5 g.) in water (5 ml.). After refrigeration overnight the first crop of crystals (2.6 g.) had m. p. 156—170° (sintering at 145°) and a second crop (0.3 g.), obtained by adding water (25 ml.) and refrigeration, had m. p. 152—165° (sintering at 143°). Fraction 1 (0.17 g.) under similar conditions yielded a semicarbazone (0.15 g.), m. p. 156—170° (sintering at 145°). These semicarbazones were bulked (3.0 g.) and recrystallised from benzene (65 ml.) to give a first crop (2.2 g.), m. p. 161—167°. Recrystallised from benzene (50 ml.), the product (1.7 g.) had m. p. 163—168°. This was recrystallised from methyl alcohol (50 ml.) to give *d-dihydropyretrolone semicarbazone* (1.2 g.) as powdery white crystals, m. p. 175° (sintering at 169°), $[\alpha]_D^{20} - 51.8^\circ$ (*c*, 1.1 in pyridine), λ_{max} 2660 Å., ϵ_{max} 19,800 (Found: N, 16.0. $C_{13}H_{21}O_2N_3$ requires N, 16.7%). (The m. p.'s were indefinite and there is little doubt that partial conversion of the *d*-pyrethrolone methyl ether into the inactive ether was brought about by the acid treatment so that the *d*-dihydro-derivative and its semicarbazone were not optically pure.) This semicarbazone (0.47 g.) in ether (20 ml.) was shaken during 8 days in a mechanical shaker with a solution of potassium hydrogen sulphate (7 g.) in water (20 ml.) in an atmosphere of carbon dioxide. The ethereal solution was separated and washed successively with brine and water, the solvent removed, and the oil distilled to give regenerated *d-dihydropyretrolone methyl ether* (0.28 g.), b. p. 95—96°/2 mm., n_D^{20} 1.4947, d_{15}^{20} 0.980, $[\alpha]_D^{20} + 70.8^\circ$ (*c*, 6.75 in alcohol), λ_{max} 2285 Å., ϵ_{max} 10,900 (Found: OMe, 15.2. $C_{12}H_{18}O_2$ requires OMe, 16.0%). The terminal methyl value is 1.62, expressed as mol. of acetic acid per mol. of ether (LaForge and Barthel, *loc. cit.*). This product gave a semicarbazone which after recrystallisation from methyl alcohol had $[\alpha]_D^{20} - 60^\circ$ (*c*, 0.27 in pyridine), m. p. 176° (sintering at 171°), not depressed by admixture with the semicarbazone before regeneration treatment. Dihydropyretrolone methyl ether semicarbazone (0.5 g.) in methyl alcohol (120 ml.) was hydrogenated with a previously reduced platinum oxide catalyst (\equiv 0.1 g. of PtO_2), absorbing 51.9 ml. of hydrogen at N.T.P. in 3 minutes with no further absorption after 15 minutes ($C_{13}H_{21}O_2N_3$, one double bond, requires 44.6 ml. at N.T.P.). The filtered solution was concentrated by distillation under reduced pressure to 5 ml. and refrigerated to give white crystals (0.38 g.), m. p. 116° (sintering at 104°). Recrystallised twice from benzene, the product (0.22 g.) had m. p. 119° (sintering at 108°); recrystallisation from ether (4 ml.) then gave 0.17 g., m. p. 121° (sintering at 110°), $[\alpha]_D^{20} - 39^\circ$ (*c*, 1.1 in pyridine). This was shown to be optically impure *d*-tetrahydropyretrolone methyl ether semicarbazone by conversion into the *i*-semicarbazone. This *d*-semicarbazone with some second crop (0.4 g.) in methyl alcohol (5 ml.) containing sulphuric acid (0.25 g.) was heated on the water-bath during 2 hours. Water was added, the mixture saturated with sodium chloride, and the oil extracted with light petroleum. The oil recovered (0.13 g.), n_D^{20} 1.4731, gave by the usual method a semicarbazone (0.16 g.), m. p. 115—119°, which was raised by one recrystallisation from methyl alcohol to 121—122°, not depressed by admixture with the semicarbazone, m. p. 122—123°, of *i*-tetrahydropyretrolone methyl ether.

Fractions 3 and 4 were converted into semicarbazones and worked up, but it was not possible to separate completely the mixture of *d*- and *i*-ethers and their dihydro-derivatives which appeared to comprise these fractions. No evidence was obtained in any experiments for the presence of an isomeric dihydro-ether, *i.e.*, one in which the double bond nearest the ring was intact.

i-Dihydropyretrolone Methyl Ether.—*i*-Pyrethrolone methyl ether (10 g.), b. p. 108—110°/1.8 mm., n_D^{20} 1.5106, $[\alpha]_D^{20} + 0.3^\circ$, OMe 15.7%, terminal methyl value 0.37 (expressed as mol. of acetic acid per mol. of ether), λ_{max} 2270 Å., $\epsilon = 21,700$, in acetic acid (50 ml.) was treated with hydrogen bromide (4.2 g.) (1 mol. $HBr \equiv$ 4.22 g.) and worked up as described for *d*-dihydropyretrolone methyl ether, but 25 g. of zinc dust were used. The steam-volatile oil (6.35 g.) was fractionated in a 20 ml. fractionating flask:

Fraction.	B. p./0.7 mm.	n_D^{20} .	Wt. (g.).
1	<72°	1.4895	0.1
2	79—81	1.4960	0.65
3	81—82	1.4975	0.61
4	82—86	1.4980	1.44
5	86—90	1.5007	0.47
6	90—98	1.5068	1.49
Residue	—	—	1.0

Fraction 1 yielded a semicarbazone, m. p. 155° (indef., sintering at 140°), which was not further examined.

Fraction 2 (0.58 g.) in alcohol (6 ml.) was added to a solution of semicarbazide hydrochloride (0.87 g.) and sodium acetate crystals (1.18 g.) in water (1.2 ml.), and the mixture refrigerated overnight. The white crystalline solid which separated (0.56 g.) had m. p. 174° (indef., sintering at 145°) and when recrystallised from methyl alcohol (35 ml.) the product (0.35 g.) had m. p. 185° (sintering at 171°). After two further recrystallisations from methyl alcohol the crystals (0.12 g.) had m. p. 202—204° (decomp.). This semicarbazone (50 mg.), dissolved in methyl alcohol (20 ml.), was hydrogenated with a reduced platinum catalyst (\equiv 30 mg. of PtO₂), absorbing 5.2 ml. of hydrogen at N.T.P. in 3 minutes with no further absorption after 20 minutes (Calc. for C₁₂H₁₉ON₃, one double bond, 5.1 ml.). The filtered solution was concentrated under reduced pressure to 5 ml., water (5 ml.) added, and the mixture refrigerated overnight. The white crystals which separated (40 mg.) had m. p. 173° (sintering at 169°), raised by one recrystallisation from benzene to 174—175°, not depressed by admixture with authentic dihydrojasnone semicarbazone, m. p. 175—176° [prepared from tetrahydropyretrolone *via* the corresponding chloro-compound as described by LaForge and Haller (*J. Amer. Chem. Soc.*, 1936, **58**, 1777)].

Fractions 3 and 4 were bulked (1.95 g.) and, when treated as above (addition of water and refrigeration), yielded a semicarbazone (2.2 g.), m. p. 168° (indef., sintering at 159°), which was recrystallised from methyl alcohol (40 ml.) to give white crystals (1.4 g.), m. p. 170° (sintering at 166°). After three further recrystallisations the *semicarbazone of i*-dihydropyretrolone methyl ether (0.95 g.) had m. p. 185° (sintering at 181°), $[\alpha]_D \pm 0^\circ$ (*c.* 1.0 in pyridine), λ_{max} 2665 Å., $\epsilon = 20,150$ (Found: N, 16.8%. C₁₂H₂₁O₂N₃ requires N, 16.7%). This semicarbazone (0.35 g.), dissolved in methyl alcohol (50 ml.), was hydrogenated in the presence of a platinum oxide catalyst (0.2 g.), previously reduced, absorbing 30.3 ml. of hydrogen at N.T.P. after 5 minutes, with no further absorption after 20 minutes (C₁₂H₂₁O₂N₃, one double bond, requires 31.2 ml. at N.T.P.). The filtered solution was concentrated under reduced pressure to 7 ml., water (10 ml.) added, and the mixture refrigerated. The crystalline product obtained (0.32 g.) had m. p. 118—120° (sintering at 116°), raised by one recrystallisation to 121—122°, not depressed by admixture with the semicarbazone of *i*-tetrahydropyretrolone methyl ether. An ethereal solution of the semicarbazone of *i*-dihydropyretrolone methyl ether (0.5 g.) was shaken with a concentrated aqueous solution of potassium hydrogen sulphate for 10 days in an atmosphere of carbon dioxide and worked up as described for the *d*-compound. The regenerated *i*-dihydropyretrolone methyl ether (0.18 g.) had b. p. 78—80°/1.8 mm., n_D^{20} 1.4976, d_{15}^{15} 0.985, $[\alpha]_D \pm 0^\circ$ (*c.* 4.0 in pyridine), λ_{max} 2335 Å., $\epsilon = 10,800$ (Found: OMe, 15.4%. C₁₂H₁₈O₂ requires OMe, 16.0%). The terminal methyl value is 1.31, expressed as mol. of acetic acid per mol. of ether. The semicarbazone derived from this product, after one recrystallisation from methyl alcohol, had m. p. 185° (sintering at 183°), $[\alpha]_D \pm 0^\circ$. The m. p. was not depressed by admixture with the parent semicarbazone, showing that no change had taken place during regeneration.

Fraction 5 (0.4 g.) gave a semicarbazone (0.42 g.), m. p. 178° (sintering at 166°). After four recrystallisations from methyl alcohol the product (0.14 g.) had m. p. 196—197°, not depressed by admixture with authentic *i*-pyrethrolone methyl ether semicarbazone, m. p. 197—198°.

Fraction 6 (1.4 g.), treated with semicarbazide in the usual manner, yielded a semicarbazone (1.4 g.), m. p. 167° (indef., sintering at 145°). After three recrystallisations from methyl alcohol the product (0.6 g.) had m. p. 195—196°, not depressed by admixture with authentic *i*-pyrethrolone methyl ether semicarbazone, m. p. 197—198°.

Reduction of d-Pyrethrolone Methyl Ether with Sodium and Alcohol.—*d*-Pyrethrolone methyl ether (8.5 g.), b. p. 122—124°/4.5 mm., n_D^{20} 1.5113, $[\alpha]_D + 83.9^\circ$, λ_{max} 2260 Å., $\epsilon = 23,400$, was dissolved in alcohol (90 ml.), and sodium (11 g.) added under reflux during 25 minutes. Then alcohol (30 ml.) was added, and the flask heated on the water-bath until all the sodium had dissolved. Water (20 ml.) was added, and the alcohol removed by steam-distillation, followed by steam-distillation of the oil. This oil was extracted from the distillate with light petroleum, and the oil recovered therefrom (5.8 g.) treated with semicarbazide in the usual manner, but no semicarbazone was obtained. The oil, which was recovered quantitatively (5.76 g.), was distilled to give two fractions: (i) 4.2 g., b. p. 95—102°/5.5 mm., n_D^{20} 1.4715, d_{15}^{15} 0.9232, $[\alpha]_D + 1^\circ$ (Found: C, 74.2; H, 11.4; OMe, 6.25%), λ_{max} 2380 Å., $E_{1\text{cm}}^{1\%} = 21.3$, showing that no conjugated system was now present in the molecule but that absorption was due to a trace of conjugated material only. Under conditions similar to those employed for the preparation of *d*-pyrethrolone methyl ether with methyl sulphate (West, this vol., p. 239) this product gave a methylation product, b. p. 75—78°/2.5 mm., n_D^{20} 1.4610, λ_{max} 2380 Å., $E_{1\text{cm}}^{1\%} = 11.3$ (Found: OMe, 10.85%), and an acetylation product, b. p. 75—78°/2 mm., n_D^{20} 1.4564, λ_{max} 2360 Å., $E_{1\text{cm}}^{1\%} = 11.1$ (Found: C, 75.7; H, 10.8%). Fraction (ii) (0.5 g.) had b. p. 102—120°/5.5 mm., n_D^{20} 1.4700, $[\alpha]_D + 2^\circ$ (*c.* 2 in alcohol), λ_{max} 2380 Å., $E_{1\text{cm}}^{1\%} = 19.7$ (Found: C, 72.1; H, 11.3; OMe, 13.0%).

Treatment of d- and i-Ethers with Aluminium Amalgam.—*d*-Pyrethrolone methyl ether (2 g.), b. p. 115—117°/1.8 mm., $[\alpha]_D^{20} + 87.2$, OMe 15.7%, in ethereal solution (120 ml.) was poured on amalgamated aluminium (6 g.) prepared as described by LaForge and Haller (*J. Org. Chem.*, 1938, **2**, 552). By proceeding essentially as described by these authors, the following fractions were obtained:

Fraction.	B. p./0.8 mm.	n_D^{20} .	Wt. (g.).	M. p. of semicarbazone (after recrystallisation from methyl alcohol).
1	80—85°	1.5071	0.15	176—180°
2	85—86	1.5105	0.23	182—183
3	87—92	1.5172	0.27	182—183
4	92—94	1.5210	0.49	182—184
Residue	—	—	0.4	—

The m. p.'s of the semicarbazones were not depressed on admixture with the semicarbazone, m. p. 183—184°, prepared from the original *d*-pyrethrolone methyl ether.

i-Pyrethrolone methyl ether (5 g.), b. p. 108—110°/1.8 mm., $[\alpha]_D + 0.3^\circ$, OMe 15.7%, in ether (300 ml.), treated with amalgamated aluminium (15 g.), gave two fractions: (a) 2 g., b. p. 84—86°/0.9 mm., n_D^{20} 1.5090, (b) 2.4 g., b. p. 86—89°/0.9 mm., n_D^{20} 1.5110. Fraction (a) gave a semicarbazone, m. p. 196—198° after recrystallisation from methyl alcohol, and fraction (b) a semicarbazone, m. p. 197—198°, of which the m. p.'s were not depressed on admixture with the semicarbazone, m. p. 197—198°, prepared from the original *i*-pyrethrolone methyl ether.

Determinations of absorption spectra were made in ethyl alcohol solutions on a Hilger E₃ quartz spectrograph in conjunction with a Spekker photometer.

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