

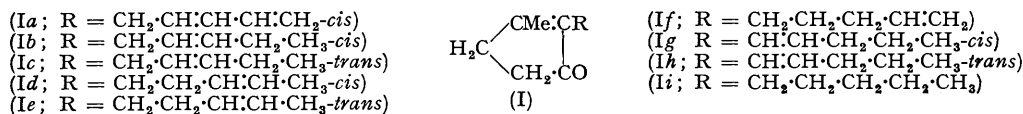
157. Experiments on the Synthesis of the Pyrethrins. Part VIII.* Stereochemistry of Jasmone and Identity of Dihydropyrethronone.

By LESLIE CROMBIE and STANLEY H. HARPER.

Five 3-methyl-2-*n*-pentenylcyclopent-2-en-1-ones having the structures possible for dihydropyrethronone, a degradation product of pyrethrolone, have been synthesised. Two of these, the *cis*- and *trans*-*n*-pent-2'-enyl ketones, are the previously unrecognised *cis*- and *trans*-forms of jasmone. Natural jasmone from *Jasminum grandiflorum* is shown to be the *cis*-ketone. The configurations assigned are based on the modes of synthesis and on infra-red spectra. Comment is made on the stereochemistry of synthetic jasmones previously described in the literature. The *cis*- and *trans*-*n*-pent-3'-enyl and *n*-pent-4'-enyl structures are excluded for dihydropyrethronone, which must be *cis*- or *trans*-jasmone.

(±)-*n*-Pent-4-enylpyrethrolone has also been synthesised and converted into its (±)-*cis*- and (±)-*trans*-chrysanthemic esters, for assessment of their insecticidal potencies.

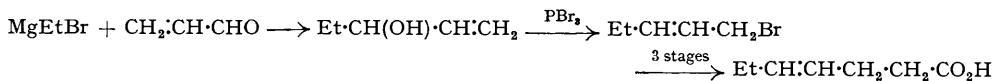
WHEN pyrethronone (Ia; the evidence for this structure is summarised in Part VII,* and references are cited therein) is catalytically hydrogenated addition of one mol. of hydrogen was found by LaForge and Haller (*J. Org. Chem.*, 1938, 2, 546) to give a mixture of tetrahydropyrethronone (dihydrojasmone) (Ii) and starting material. However, addition of one mol. of hydrogen bromide followed by zinc reduction yielded dihydropyrethronone, which was characterised by a semicarbazone (m. p. 202°). The same compound was obtained by West (*J.*, 1945, 412) by reduction of pyrethrolone with aluminium amalgam. Dihydropyrethronone semicarbazone gave dihydrojasmone semicarbazone on hydrogenation, but LaForge and Haller stated that it was not identical with jasmone semicarbazone, although no mixed melting point was recorded. Their experiments favoured structures (Id) or (Ie) for dihydropyrethronone which West supported. For a variety of reasons (cf. Crombie, Edgar, Harper, Lowe, and Thompson, Part V, *J.*, 1950, 3552, and below) we regarded this assignment as improbable and the non-identity with jasmone as unproven.



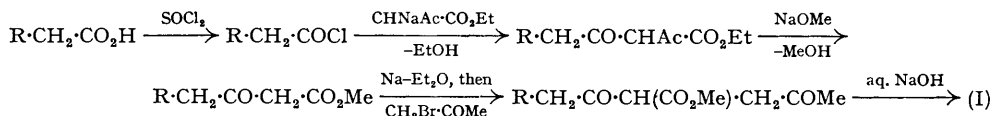
Of the seven structures (Ib—h) possible for dihydropyrethronone the cross-conjugated structures (Ig) and (Ih) are eliminated by West's light-absorption results. Structure (If) is also excluded, for G.P. 658 920 (Heine A. G.) describes 3-methyl-2-*n*-pent-4'-enylcyclopent-2-en-1-one semicarbazone, prepared by an unstated method, as having m. p. 164—165°. Hence in an attempt to elucidate the structure of dihydropyrethronone we have synthesised the remaining four ketones (Ib—e). Ketones (Ib) and (Ic) are of additional interest as they are the *cis*- and *trans*-forms of jasmone, which occurs in the essential oil of *Jasminum grandiflorum*, and whose stereochemistry has been in a state of confusion. Jasmone has been synthesised by Treff and Werner (*Ber.*, 1935, 68, 640) and by Hunsdiecker (*Ber.*, 1942, 75, 460) and the specimens obtained were all claimed to be identical with the natural ketone, the criterion of identity being the mixed melting point of the semicarbazones. Consideration of the methods used for the synthesis of the *n*-pent-2-enyl side-chain indicated that, in fact, the configuration was not the same in each case and as a corollary to our main purpose we have clarified the stereochemistry of jasmone.

* Part VII, *J.*, 1951, 2906.

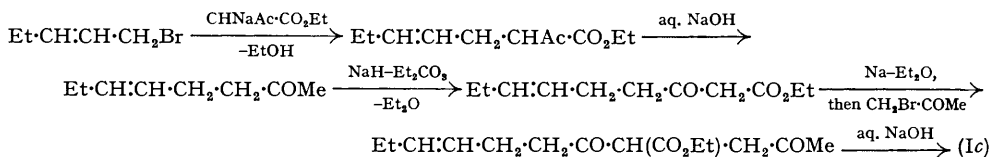
n-Pent-2-enyl bromide was prepared by Bouis's procedure (*Ann. Chim.*, 1928, **9**, 403), as follows, and converted into *n*-hept-4-enoic acid* by ethyl malonate chain extension:



This halide has the *trans*-configuration for Grédy (*Bull. Soc. chim.*, 1936, **3**, 1093, 1101; 1937, **4**, 415) has shown on Raman spectroscopic evidence that this is the configuration of halides prepared by the Bouis rearrangement. It is likely that this configuration would be retained in the subsequent reaction with ethyl sodiomalonate. Hence the resultant *n*-hept-4-enoic acid should have the *trans*-configuration. This is supported by the infra-red spectrum of the acid which shows strong absorption at 10.3 μ (cf. Crombie and Harper, *J.*, 1950, 873) and by its non-identity with *cis*-*n*-hept-4-enoic acid (see below). *trans*-*n*-Hept-4-enoic acid was converted into *trans*-jasmone (Ic) by the following generalised route which is known not to cause stereomutation (Harper, Part II, *J.*, 1946, 829; Crombie and Harper, Part IV, *J.*, 1950, 1152; Part V, *loc. cit.*):



A second specimen of *trans*-jasmone was prepared by this route from the *n*-hept-4-enoic acid prepared from the predominantly *trans*-*n*-hex-3-en-1-ol obtained on ring scission of the mixed *cis*- and *trans*-3-chloro-2-ethyltetrahydrofurans (Crombie and Harper, *J.*, 1950, 1715). A third specimen of *trans*-jasmone, identical with the above (mixed m. p.s), was prepared from *trans*-*n*-pent-2-enyl bromide by the following sequence (cf. Part V, *loc. cit.*):



As the intermediary *trans*-*n*-oct-5-en-2-one showed some absorption at 10.93 μ , as well as that expected at 10.33 μ , the possibility of contamination with 4-ethylhex-5-en-2-one (*i.e.*, vinyl absorption) derived from the secondary form of the bromide, could not be discounted at this stage. Nevertheless the infra-red spectrum of the *trans*-jasmone (see figure) obtained from it shows the virtual absence of any branched-chain isomer containing a vinyl group, whilst the strong absorption at 10.33 μ substantiates the *trans*-configuration. Hunsdiecker prepared a specimen of jasmone by the first of the above routes and it is evident that both the intermediary *n*-hept-4-enoic acid and the final ketone had the *trans*-configuration.

We have recently shown unequivocally that "leaf alcohol" is *cis*-*n*-hex-3-en-1-ol (Crombie and Harper, *J.*, 1950, 873) which may be converted through the bromide and cyanide (cf. Crombie, Harper, Stedman, and Thompson, Part VI, *J.*, 1951, 2445) or by carboxylation of the Grignard reagent into what is evidently the previously unrecognised *cis*-*n*-hept-4-enoic acid. As expected, and in contrast to the *trans*-acid, *cis*-*n*-hept-4-enoic acid shows only slight absorption at 10.3 μ . These two acids are indistinguishable by physical properties (Table 1) and have not previously been characterised by derivatives; we now find that the anilides and *p*-bromophenacyl esters differ appreciably in melting point. *cis*-*n*-Hept-4-enoic acid was converted by the route outlined above into *cis*-jasmone (Ib).† Again the infra-red spectrum of *cis*-jasmone (see figure)

* Geneva numbering, CO₂H = 1.

† The odour of *cis*-jasmone, although of similar type to that of *trans*-jasmone, has an exotic subtlety which the latter does not possess. Synthetic dihydrojasmone is used as a substitute for natural jasmone but in our opinion is distinctly inferior to *cis*-jasmone.

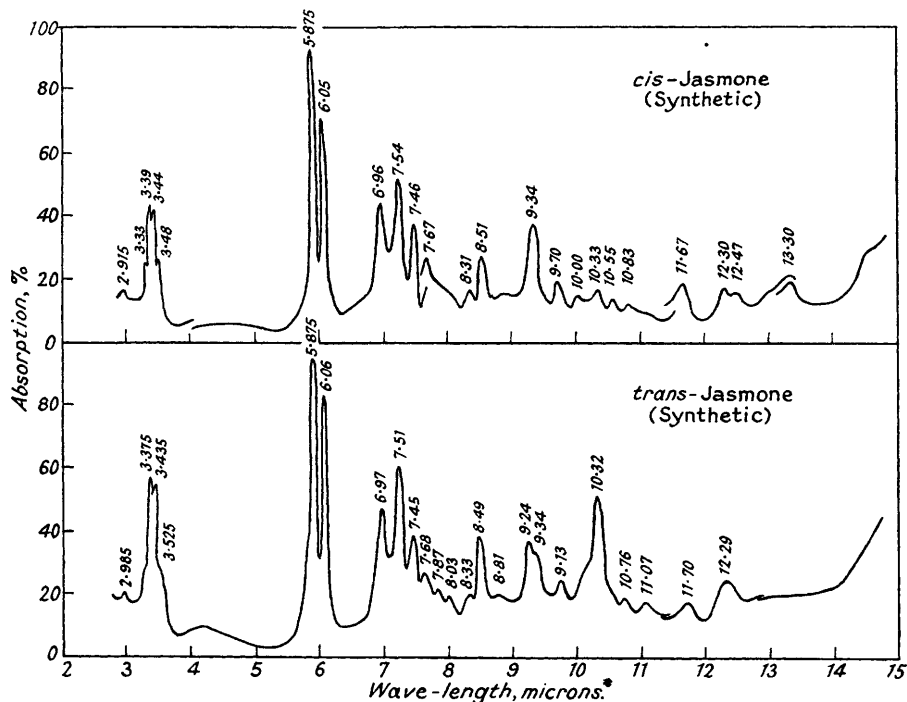
TABLE I.

	B, p./mm.	n_D^{20}	Anilide, m. p.	<i>p</i> -Bromophenacyl ester, m. p.
<i>cis</i> - <i>n</i> -Hept-4-enoic acid	116°/12	1.4400	Oil *	46°
<i>trans</i> - <i>n</i> -Hept-4-enoic acid	105°/8	1.4400	93°	79

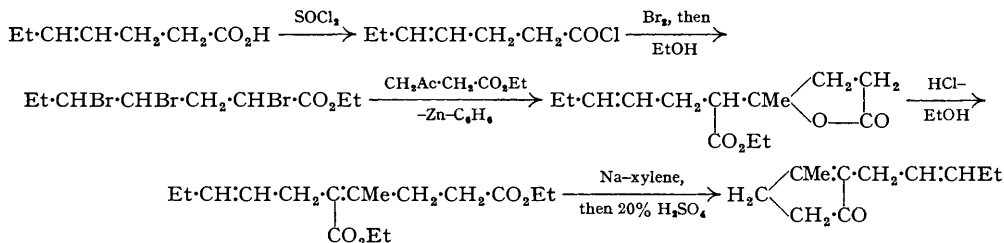
* Crystallises from light petroleum at -80° .

substantiates our stereochemical conclusion, absorption at 10.33μ being very slight. Hunsdiecker prepared a second specimen of jasmone by this route; it was evidently *cis*-jasmone. Other infra-red structural correlations common to both isomers (cf. Parts VI and VII, *loc. cit.*) are: unsaturated aliphatic C-H stretching, 3.33; saturated C-H stretching, 3.39, 3.44, 3.48; C=O stretching, 5.875; C=C stretching, 6.05; C-H bending in CH_2 and CH_3 , 6.96, 7.24 μ .

Hunsdiecker prepared further specimens of jasmone in which the side-chain double bond was introduced either by dehydration of 2-3'-hydroxy-*n*-hexyl-5-methylfuran or by



semihydrogenation of *n*-hexa-2:4-dien-1-ol; these were probably mainly *trans*-jasmone contaminated with structural isomers (cf. Crombie, *Quart. Reviews*, in the press). The remaining and earliest synthesis of jasmone (Treff and Werner, *loc. cit.*) utilised (*cis*-)*n*-hept-4-enoic acid, prepared from "leaf alcohol" as described above, which was converted into jasmone as follows:



* Errata in Fig.: for 7.54 read 7.24; for 7.51 read 7.21; for 9.13 read 9.73.

The bromine addition to the *cis*-acid chloride would give a substantially *threo*-4 : 5-dibromide which on debromination with zinc, during the Reformatsky reaction, would give mainly a *cis*-lactone, although some inversion of configuration is liable to occur (cf. Crombie, *loc. cit.*). Hence it is probable that Treff and Werner's product was *cis*-jasmone, possibly containing *trans*-contaminant.

It is evident (Table 2) that *cis*- and *trans*-jasmone are not distinguishable with certainty by their physical properties or by the melting points of their semicarbazones. Furthermore mixed melting points of the semicarbazones, as a criterion of non-identity, are uncertain; decomposition precedes melting and the depressions are small. In this connection it is noteworthy that although Hunsdiecker considered his preparations of jasmone identical, he observed that, as judged by their semicarbazones, the (*trans*-) jasmone prepared from *n*-pent-2-enyl bromide was "less pure" than the (*cis*-) jasmone prepared from "leaf alcohol." However the 2 : 4-dinitrophenylhydrazones differ appreciably in melting point and give well-marked depressions on admixture. Fortunately for the elucidation of the configuration of natural jasmone the 2 : 4-dinitrophenylhydrazone has been described by Naves and Grampoloff (*Helv. Chim. Acta*, 1942, **25**, 1500) and direct comparison of our synthetic 2 : 4-dinitrophenylhydrazones with a specimen kindly provided by Dr. Y.-R. Naves established unequivocally the identity of *cis*-jasmone with the natural ketone. Furthermore, within the limitations described above, direct comparison of our synthetic semicarbazones with a specimen of natural jasmone semicarbazone, kindly provided by Prof. L. Ruzicka (cf. Ruzicka and Pfeiffer, *ibid.*, 1933, **16**, 1208), bore out this conclusion. Thus "leaf alcohol" and natural jasmone each contain the *cis*-*n*-pent-2-enyl group and it is possible that the latter is formed biosynthetically from the former. Relevant to this is the isolation by Schmidt (*Chem. Ber.*, 1947, **80**, 538) of jasmone from peppermint oils previously known to contain "leaf alcohol."

Ketones (*Id*) and (*Ie*), together with (*If*), whose properties are summarised in Table 2, were synthesised from the appropriate *n*-heptenoic acids by the route generalised above. *trans*-*n*-Hept-5-enoic acid was prepared from *trans*-*n*-hex-4-en-1-ol (Crombie and Harper, *J.*, 1950, 1707), and *cis*-*n*-hept-5-enoic acid was similarly prepared from *cis*-*n*-hex-4-en-1-ol, itself obtained by semi-hydrogenation of *n*-hex-4-yn-1-ol; but a full description of these and other *n*-heptenoic acids is reserved for a future communication. Although we find that the semicarbazone of 3-methyl-2-*n*-pent-4'-enylcyclopent-2-en-1-one (*If*) melts nearly 10° higher than recorded in G.P. 658,920 our previous conclusion is not invalidated.

Structures (*Id*) and (*Ie*) must be rejected for dihydropyrethronone since the melting points of their semicarbazones are some 30° too low. By elimination, dihydropyrethronone, contrary to previous views, must be (*Ib*) or (*Ic*), *i.e.*, a jasmone. The recorded melting points of dihydropyrethronone semicarbazone (Table 2) do not permit of any certain stereochemical prediction, though since present evidence points to a *cis*-configuration for pyrethronone, dihydropyrethronone, a product of "1 : 2"-hydrogenation might be expected to be predominantly *cis*. Mixed melting points with derivatives of dihydropyrethronone, which would settle this point, have not been possible for the only specimen extant (that of Dr. T. F. West) had seriously deteriorated on storage and we are at present unable to undertake the lengthy reisolation of this compound.

To gain further insight into the structural features responsible for the insecticidal activity of the pyrethrins, in conjunction with Mr. R. E. Stedman, we have prepared (\pm)-*n*-pent-4-enylrethrolone (for an exposition of this nomenclature, see Harper, *Chem. and Ind.*, 1949, 636) and thence its esters with (\pm)-*cis*- and (\pm)-*trans*-chrysanthemic acids. Alkenylation of ethyl sodioacetoacetate with *n*-pent-4-enyl bromide (cf. route D, Part V, *loc. cit.*) followed by ketonic fission gave *n*-oct-7-en-2-one, which on carbethoxylation with ethyl carbonate and sodium hydride yielded ethyl 2-keto-*n*-oct-7-ene-1-carboxylate. Hydrolysis of this ester and condensation of the sodium salt with pyruvaldehyde in aqueous solution gave 3-hydroxy-*n*-undec-10-ene-2 : 5-dione, cyclised by aqueous sodium hydroxide to (\pm)-*n*-pent-4-enylrethrolone. This keto-alcohol was esterified with the appropriate acids to give (\pm)-*n*-pent-4-enylrethronyl (\pm)-*cis*- and (\pm)-*trans*-chrysanthemates.

TABLE 2.

	B. p./mm.	n_D^{20} *	Terminal methyl groups	$\lambda_{max.}$, Å.	ϵ
<i>Naturally derived</i>					
Dihydropyrethron 1, 2	115—118°/11	1.5010	1.74	2350	14 300
Jasmone 3, 4, 5, 6	111—113°/2.5 108—110°/5 134—135°/12	1.4987 1.4997 —	— — —	— — —	— — —
<i>Synthetic 3-methyl-2-n-pentenylcyclopent-2-en-1-ones</i>					
<i>cis-n-Pent-2'-enyl</i> Ib	146°/27	1.4978	1.52	2350	12 000
<i>trans-n-Pent-2'-enyl</i> ... Ic	142°/23	1.4974	1.12	2340	12 300
<i>cis-n-Pent-3'-enyl</i> Id	—	—	—	—	—
<i>trans-n-Pent-3'-enyl</i> ... Ie	130°/20	1.4946	1.67	2360	12 100
<i>n-Pent-4'-enyl</i> If	126°/15	1.4955	0.90	2350	13 700
Semicarbazone					
	2 : 4-Dnph, † m. p.	M. p.	$\lambda_{max.}$, Å	ϵ	
Dihydropyrethron 1, 2	—	202°, 203—205°	2665	23 600	
Jasmone 3, 4, 5, 6	121.0—122.5°	204—206 208 210	— — —	— — —	
<i>cis-n-Pent-2'-enyl</i> Ib	117.5	204—206	2650	21 900	
<i>trans-n-Pent-2'-enyl</i> ... Ic	128.5	200—202	2650	25 700	
<i>cis-n-Pent-3'-enyl</i> Id	—	174—175	2660	20 000	
<i>trans-n-Pent-3'-enyl</i> ... Ie	165	171—172	2650	22 100	
<i>n-Pent-4'-enyl</i> If	118	173	2650	21 000	

¹ LaForge and Haller, *J. Org. Chem.*, 1938, **2**, 546. ² West, *J.*, 1945, 412. ³ Treff and Werner, *Ber.*, 1933, **66**, 1521. ⁴ Ruzicka and Pfeiffer, *Helv. Chim. Acta*, 1933, **16**, 1208. ⁵ Naves and Grampoloff, *ibid.*, 1942, **25**, 1500. ⁶ Specimens from *Jasminum grandiflorum*.

* n adjusted to 20°, if necessary, by means of -0.0004 per degree, within a range $\pm 5^\circ$.

† 2 : 4-Dnph = 2 : 4-Dinitrophenylhydrazone.

EXPERIMENTAL

Most of the microanalyses, all of the terminal methyl determinations, and a few of the ultra-violet light-absorption measurements (all in purified ethanol) are by Drs. Weiler and Strauss, Oxford. The remainder were determined in the microanalytical (Mr. F. H. Oliver) and the spectrographic (Mrs. A. I. Boston) laboratories of the Organic Chemistry Dept., Imperial College. The infra-red absorption spectra were determined with a Grubb Parsons single-beam spectrometer (rock-salt prism) coupled to a Brown recorder, capillary films of pure liquids (*ca.* 5- μ thickness) being used; we are indebted to Dr. W. C. Price for this facility.

n-Heptenoyl Chlorides.—Thionyl chloride (1.25 mols.) was added dropwise with shaking to the *n*-heptenoic acid (1 mol.), and the mixture set aside. Next day, after brief refluxing, the heptenoyl chloride was isolated by distillation. In this way there were obtained: *cis*- (89%), b. p. 72—76°/35 mm., n_D^{20} 1.4500, and *trans-n*-hept-4-enoyl chloride (97%), b. p. 69—71°/12 mm., n_D^{20} 1.4473; *cis*- (93%), b. p. 65°/11 mm., n_D^{20} 1.4417 (Found: Cl, 24.2. $C_7H_{11}OCl$ requires Cl, 24.2%), and *trans-n*-hept-5-enoyl chloride (80%), b. p. 65.5—68°/16 mm., n_D^{20} 1.4490 (Found: C, 57.8; H, 7.75. $C_7H_{11}OCl$ requires C, 57.35; H, 7.55%); and *n*-hept-6-enoyl chloride (94%), b. p. 69°/17 mm.

Methyl 2-Keto-n-octene-1-carboxylates.—By the procedure of Part II (*J.*, 1946, 892) the heptenoyl chloride was treated with ethyl sodioacetoacetate, prepared from powdered sodium or sodium hydride, in ether and the undistilled ethyl 2 : 4-diketo-*n*-decene-3-carboxylate so formed was treated with methanolic sodium methoxide, to give the methyl 2-keto-*n*-octene-1-carboxylate. In this way there were obtained: methyl 2-keto-*cis*-, b. p. 131—137°/30 mm., n_D^{20} 1.4524, and methyl 2-keto-*trans-n*-oct-5-ene-1-carboxylate (56%), b. p. 109—115°/7 mm., n_D^{20} 1.4488; methyl 2-keto-*cis*- (43%), b. p. 122—126°/15 mm., n_D^{20} 1.4436 (Found: C, 65.05; H, 9.2. $C_{10}H_{16}O_3$ requires C, 65.2; H, 8.75%), and methyl 2-keto-*trans-n*-oct-6-ene-1-carboxylate (46%), b. p. 90—94°/0.85 mm., n_D^{20} 1.4472 (Found: C, 64.9; H, 8.7%); and methyl 2-keto-*n*-oct-7-ene-1-carboxylate (56%), b. p. 95—102°/0.5 mm. (Found: C, 65.5; H, 8.9%). Each of these keto-esters gave a deep red colour with alcoholic ferric chloride.

trans-n-Oct-5-en-2-one.—*trans-n*-Pent-2-enyl bromide (75 g.; b. p. 69—74°/114 mm.; prepared by Bouis's procedure, *Ann. Chim.*, 1928, **9**, 403) was treated with ethanolic ethyl sodioacetoacetate, by the procedure of route D (Part V, *J.*, 1950, 3552), to give after ketonic hydrolysis *trans-n*-oct-5-en-2-one (28 g.), b. p. 169—173°, n_D^{20} 1.4316 (Found: C, 76.4; H, 11.2.

$C_8H_{14}O$ requires C, 76.15; H, 11.2%. The 2:4-dinitrophenylhydrazone formed orange-red needles (from ethanol), m. p. 60° (Found: C, 55.55; H, 6.0; N, 18.75. $C_{14}H_{18}O_4N_4$ requires C, 54.9; H, 5.9; N, 18.3%).

Ethyl 2-Keto-trans-n-oct-5-ene-1-carboxylate.—As further described in Part V, *trans-n-oct-5-en-2-one* was caused to interact with sodium hydride and ethyl carbonate in ether, to give ethyl 2-keto-*trans-n-oct-5-ene-1-carboxylate* (62%), b. p. 69—76°/0.05 mm., n_D^{20} 1.4488.

3-Methyl-2-n-pentenylcyclopent-2-en-1-ones.—By the procedure of Part II the methyl or ethyl sodio-2-keto-*n-octene-1-carboxylate*, prepared with powdered sodium or sodium hydride in ether, was treated with bromoacetone, and the crude 2:5-diketo-*n-undecene-4-carboxylic ester* so formed was stirred in aqueous sodium hydroxide, to give the 3-methyl-2-*n-pentenylcyclopent-2-en-1-one*, isolated by distillation. The crude ketones (40—60% yields) obtained in this way were converted into their semicarbazones in pyridine-ethanol and these were recrystallised from ethanol. In this way there were obtained: *cis*-, prisms or small plates (Found: C, 65.8; H, 8.6. $C_{12}H_{19}ON_3$ requires C, 65.1; H, 8.65%), and *trans-jasmone semicarbazone*, needles, the specimen prepared from *trans-n-pent-2-enyl bromide* via *trans-n-hept-4-enoic acid* having m. p. 200°, that prepared from "*trans*"-*n-hex-3-en-1-ol* via "*trans*"-*n-hept-4-enoic acid* having m. p. 204° after softening at 199° (Found: C, 65.5; H, 8.7; N, 19.0; 1.71 terminal Me. $C_{12}H_{19}ON_3$ requires N, 19.0%), and that prepared from *trans-n-oct-5-en-2-one* having m. p. 200—202° when crystallised from methanol (Found: C, 65.05; H, 8.55%; 1.21 terminal Me); together with 3-methyl-2-*cis*- (Found: C, 65.4; H, 8.95%; 1.42 terminal Me), and 3-methyl-2-*trans-n-pent-3'-enylcyclopent-2-en-1-one semicarbazone*, iridescent plates (Found: C, 64.9; H, 8.65%); and 3-methyl-2-*n-pent-4'-enylcyclopent-2-en-1-one semicarbazone* (Found: C, 65.05; H, 8.55%). Further data are given in Table 2. The semicarbazones, in capillary tubes, were placed in a bath at 160° which was heated rapidly (6—7° per minute) to minimise decomposition; even so the *jasmone semicarbazones* became yellow before melting and fused to a brown liquid. The other semicarbazones melted without decomposition. Distinctly lower m. p.s were observed microscopically on a Kofler hot stage.

The 3-methyl-2-*n-pentenylcyclopent-2-en-1-ones* were regenerated from their semicarbazones by the procedure of Part II in 81—90% yield, and portions converted into the 2:4-dinitrophenylhydrazones. In this way there were obtained: *cis-jasmone* (Found: C, 80.5; H, 9.8. $C_{11}H_{16}O$ requires C, 80.45; H, 9.8%), 2:4-dinitrophenylhydrazone (Found: C, 59.3; H, 5.9; N, 16.2. $C_{17}H_{20}O_4N_4$ requires C, 59.0; H, 5.85; N, 16.25%); *trans-jasmone* (Found: C, 80.3; H, 9.6%), 2:4-dinitrophenylhydrazone (Found: C, 59.4; H, 5.85; N, 16.1%); 3-methyl-2-*trans-n-pent-3'-enylcyclopent-2-en-1-one* (Found: C, 79.7; H, 9.95%), 2:4-dinitrophenylhydrazone (Found: C, 59.3; H, 5.85%), and 3-methyl-2-*n-pent-4'-enylcyclopent-2-en-1-one* (Found: C, 79.65; H, 9.8%), 2:4-dinitrophenylhydrazone (Found: C, 59.35; H, 5.65%). Further properties are given in Table 2. As the preparation of 3-methyl-2-*cis-n-pent-3'-enylcyclopent-2-en-1-one* was carried out on a small scale, insufficient of its semicarbazone was obtained to permit of regeneration; the crude ketone had b. p. 120—122°/12 mm.

Mixed m. p.s of *jasmone derivatives*.

Semicarbazones, m. p.	<i>trans</i> -, 200—202°	197—200°	<i>cis</i> -, 204—206°
Semicarbazones, m. p.*	natural, 200—202°	197—198°	<i>cis</i> -, 197°
2:4-Dinitrophenylhydrazones, m. p.	<i>trans</i> -, 128.5°	111°	<i>cis</i> -, 117.5°
2:4-Dinitrophenylhydrazones, m. p.	natural, 119.5°	117—118°	<i>cis</i> -, 117°
2:4-Dinitrophenylhydrazones, m. p.	natural, 119.5°	110—112°	<i>trans</i> -, 128.5°

* Determined by placing the specimen on a Kofler hot stage at 170° and heating it with the rheostat at the 250° calibration. The other mixed m. p.s were determined in capillaries as described above.

(±)-*n-Pent-4-enylrethrolone* (4-Hydroxy-3-methyl-2-*n-pent-4'-enylcyclopent-2-en-1-one*) (with Mr. R. E. STEDMAN).—Interaction, by the procedure of route D (Part V, *loc. cit.*), of *n-pent-4-enyl bromide* (167 g.) and ethyl sodioacetoacetate, prepared from ethyl acetoacetate (148 g.) and sodium (27 g.) in ethanol (450 ml.), followed by treatment with 5% aqueous sodium hydroxide (1 l.), yielded *n-oct-7-en-2-one* (61.5 g., 58%), b. p. 172—179°, n_D^{15} 1.4324 (Found: C, 76.15; H, 11.25. $C_8H_{14}O$ requires C, 75.15; H, 11.2%). The yellow 2:4-dinitrophenylhydrazone had m. p. 65° (Found: C, 54.7; H, 5.9. $C_{14}H_{18}O_4N_4$ requires C, 54.9; H, 5.9%).

Addition of *n-oct-7-en-2-one* (30 g.) to sodium hydride (12 g.) and ethyl carbonate (59 g.) in refluxing ether (90 ml.) and then proceeding as in Part V gave *ethyl 2-keto-n-oct-7-ene-1-carboxylate* (25.5 g., 53%), b. p. 94—100°/0.6 mm., n_D^{20} 1.445—1.450 (Found: C, 66.95; H, 9.4. $C_{11}H_{18}O_3$ requires C, 66.7; H, 9.15%).

Hydrolysis of this keto-ester (27 g.) with 3% aqueous sodium hydroxide (200 ml.) during 24 hours, followed by condensation with aqueous pyruvaldehyde (42 ml.) by the procedure of Part V, yielded 3-hydroxy-*n*-undec-10-ene-2 : 5-dione (16.0 g., 55%), b. p. 120—127°/0.1 mm., n_D^{20} 1.466—1.471 (Found : C, 67.25; H, 9.25. $C_{11}H_{18}O_3$ requires C, 66.7; H, 9.15%).

3-Hydroxy-*n*-undec-10-ene-2 : 5-dione (16 g.) was stirred with 3% aqueous sodium hydroxide (100 ml.) during 1 hour and the product isolated by the procedure of Part V. Fractional distillation at 0.1 mm., as described, then gave (\pm)-*n*-pent-4-enylrethrolone (5.2 g., 32%), b. p. 126—134°/0.1 mm., n_D^{20} 1.504—1.505 (Found : C, 73.3; H, 9.05. $C_{11}H_{18}O_2$ requires C, 73.2; H, 8.95%).

Ozonisation of (\pm)-*n*-pent-4-enylrethrolone (150 mg.), by the procedure of Part VII (*J.*, 1951, 2906), yielded the formaldehyde dimedon derivative, m. p. 187—188° after one crystallisation from 50% aqueous ethanol.

(\pm)-*n*-Pent-4-enylrethronyl Chrysanthemates (with Mr. R. E. STEDMAN).—By the procedure of Part V (*loc. cit.*) the undistilled chloride from (\pm)-*trans*-chrysanthemic acid (1.2 g.) was caused to interact with (\pm)-*n*-pent-4-enylrethrolone (1.6 g.) and pyridine (1 ml.) in benzene (20 ml.). Distillation as described (Part V) gave (\pm)-*n*-pent-4-enylrethronyl (\pm)-*trans*-chrysanthemate (1.46 g., 61%), b. p. 154—164°/5 $\times 10^{-3}$ mm., n_D^{20} 1.5023—1.5026 (Found : C, 76.75; H, 9.5. $C_{21}H_{30}O_3$ requires C, 76.35; H, 9.4%).

In a similar manner interaction of the undistilled chloride from (\pm)-*cis*-chrysanthemic acid (1.7 g.) and (\pm)-*n*-pent-4-enylrethrolone (1.9 g.) gave (\pm)-*n*-pent-4-enylrethronyl (\pm)-*cis*-chrysanthemate (2.1 g., 62%), b. p. 152—161°/1 $\times 10^{-2}$ mm., n_D^{20} 1.5013—1.5030 (Found : C, 75.3; H, 9.3%). In contrast to our earlier experience (Part V, but cf. Part III, *J.*, 1950, 971) (\pm)-*cis*-chrysanthemic acid crystallised from the forerun (0.4 g.) of this distillation on storage and was identified by its m. p. and mixed m. p.

We are indebted to Mr. D. Thompson for the preparation of the methyl 2-keto-*cis*-*n*-oct-5-ene-1-carboxylate and to the Agricultural Research Council, the Central Research Fund of the University of London, and to the Chemical Society for grants. The initial experiments of this investigation were carried out at University College, Southampton, during 1946.

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[Received, October 15th, 1951.]