EXPERIMENTS ON THE SYNTHESIS OF THE PYRETHRINS. XIV.*—Rethrins and the Cyclopentadienone Related to 3-Methylcyclopent-2-enone

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Dimeric 3-methylcyclopentadienone was obtained by dehydrobromination of 4-bromo-3-methylcyclopentenone and by hydrolysis of 4-hydroxy-3-methylcyclopentenone formate. Four structures for the dimer were possible. Synthesis and spectroscopic evidence showed that the dimer obtained was formed by addition to the unsubstituted double bond, with the methyl group on the norbornene ring in the position more remote from the carbonyl group of the cyclopentenone. Decarbonmonoxylation of the dimer gave 3,5-dimethylindanone, synthesised for comparison by another route.

Contrary to an earlier report, pyrolysis of 9,10-dihydro-9,10(4,5-3-methylcyclopent-2-enono)anthracene (obtained by alkaline cyclisation of the adduct of anthracene and diacetyl ethylene) gave mainly 3,5-dimethylindanone and not 3-methylcyclopentadienone.

Rethrins with no side chain in the alcoholic part of the molecule were synthesised from 4-bromo-3-methylcyclopent-2-enone. Allethrolone cyclopropane carboxylate was made for comparison of its insecticidal activity with allethrolone chrysanthemate.

Introduction

This paper describes some simple compounds related to 3-methylcyclopentenone[1] (I) synthesised to determine the minimum number of structural features of the natural pyrethrins necessary for insect toxicity.[2] The formation and properties of 3-methylcylopentadienone were investigated.

Experimental

Ultraviolet spectra were measured in ethanol on a Unicam S.P. 500 Spectrophotometer. Infra-red spectra were determined for liquid films. Nuclear magnetic resonance (NMR) spectra were determined for carbon tetrachloride or deuterochloroform solutions with tetramethylsilane as internal standard using a Perkin Elmer R 10 spectrometer.

4-Bromo-3-methylcyclopent-2-enone (**IIa**). 3-Methylcyclopent-2-enone[1] (14·4 g, 0·15 mol.), freshly recrystallised *N*-bromosuccinimide (26·7 g, 0·16 mol.), benzoyl peroxide, (0·15 g) and carbon tetrachloride (50 ml) were refluxed together. Reaction started after 5 min. and was complete in 30 min. The product was chilled in ice, and succinimide (14·7 g, 98% recovery) was separated by filtration. The solvent was evaporated from the filtrate to give the light yellow product (26 g, 98%, n_D^{20} 1·5425).

4-Acetoxy-3-methylcyclopent-2-enone (**IId**). By a procedure similar to that used by Crombie *et al.*,[3] for dihydrocinerolone acetate, the crude bromoketone (26 g, 0·15 mol.) silver acetate (31 g, 25% excess) and glacial acetic acid (80 ml) gave, by distillation and redistillation the product (12 g, 52%), b.p. 63°–65°/0·05 mm, n_D^{20} 1·4844, λ_{max} 220 mμ, ε 15,000. (Found: C, 61·3; H, 6·75. $C_8H_{10}O_3$ requires C, 62·3; H, 6·5%). The 2,4-dinitrophenylhydrazone had m.p. 198° (from ethanol) after purification by chromatography on alumina with benzene. (Found: C, 49·9; H, 4·0. $C_{14}H_{14}N_4O_6$ requires C, 50·3; H, 4·2%).

4-Hydroxy-3-methylcyclopent-2-enone (**IIe**). The foregoing acetate (10 g) potassium hydroxide (3·8 g) water (25 ml) and methanol (40 ml) were set aside for 12 h at room temperature. The alcohol was evaporated and the residue was extracted into ether. The ethereal solution was washed, dried (Na_2SO_4), evaporated, and distilled to give *4-hydroxy-3-methylcyclopent-2-enone* (3 g, 33%), b.p. 80°–81°/0·07 mm, n_D^{20} 1·5112; λ_{max} 221 mμ, ε 10,050. (Found: C, 63·8; H, 6·8. C_6H_8O requires C, 64·3; H, 7·2%.)

The 3,5-dinitrobenzoate had m.p. 165°–167° after two crystallisations from ethanol. (Found: C, 51·0; H, 3·4%. $C_{13}H_{10}N_2O_7$ requires C, 51·0; H, 3·5%.)

When the reaction mixture was refluxed for 2 h, only crude dimeric 3-methylcyclopentadienone was obtained.

($\pm$)-H-*rethronylcyclopropane carboxylate* The silver salt of cyclopropane carboxylic acid,[4] made by the method of Crombie *et al.*,[3] (8·0 g), with the 4-bromoketone from 3-methylcyclopent-2-enone (4 g) gave[3] the ester (2·2 g, 30%). This was identical with the product (2·1 g, 65%) obtained by esterification of 4-hydroxy-3-methylcyclopent-2-enone (2 g) (below) with cyclopropane carboxylic acid chloride (2·2 g, b.p. 119°–122°) in benzene (10 ml) and pyridine (1 ml) by the method described.[3] The ester had b.p. 94°–96°/0·1 mm, n_D^{20} 1·5020, λ_{max} 219·5 mμ, ε 15,700. (Found: C, 66·0; H, 6·6%. $C_{10}H_{12}O_3$ requires C, 66·0; H, 6·7%.)

($\pm$)-H-*rethronyl*($\pm$)-trans-*chrysanthemate* (**IIc**). Similarly silver ($\pm$)-*trans* chrysanthemate and the crude bromoketone (8 g) gave the ester (6·0 g, 50%) b.p. 133°–136°/0·15 mm, n_D^{20} 1·5056; λ_{max} 217 mμ, ε 21,800. (Found: C, 71·8; H, 8·6%. $C_{16}H_{22}O_3$ requires C, 73·2; H, 8·65%.)

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(±)-*Allylrethronyl cyclopropanecarboxylate* By the usual procedure, allethrolone[5] (5·8 g) and cyclopropane carboxylic acid chloride (4 g) with pyridine (2·5 ml) in benzene (30 ml) gave the ester (5·5 g, 60%), b.p. 103°–107°/0·09 mm, n_D^{20} 1·5050, λ_{max} 227 mμ, ε 15,300. (Found: C, 71·2; H, 7·65. $C_{13}H_{16}O_3$ requires C, 70·9; H, 7·35%.)

3-Methylcyclopentadienone dimer (III). (*a*) *via* 4-formyloxy-3-methylcyclopent-2-enone. The crude bromoketone from 3-methylcyclopent-2-enone (9·6 g) and *N*-bromo-succinimide (17·8 g) was heated with a solution of sodium formate (13·6 g) in 98% formic acid (40 ml) for 3 h. Formic acid was then evaporated at reduced pressure and the residue was dissolved in ether, washed, dried (Na_2SO_4), and evaporated. The residue decomposed when distillation was attempted and was therefore stirred with sodium carbonate (11 g) in water (75 ml) and methanol (75 ml) for 15 h at room temperature. After evaporation of solvents, the residue was taken into ether, washed, dried (Na_2SO_4) and distilled to give *dimeric 3-methylcyclopentadienone*, b.p. 110°–112°/0·1 mm, n_D^{20} 1·5380, which crystallised. After being washed to remove adhering oil, the product (4·6 g, 50% based on 3-methylcyclopentenone) had m.p. 80°–82°, λ_{max} 229 mμ, ε 10,340. (Found: C, 76·1; H, 6·6; mol. wt. (Rast) 197. $C_{12}H_{12}O_2$ requires C, 76·5; H, 6·4%, mol. wt. 188. NMR spectrum ($CDCl_3$): CH_3 on ethylenic bond, 8·25 τ, doublet, J = 2 c/s; CH_3 on ethylenic bond, 7·9 τ, singlet; olefenic H, 4·05 τ, complex; olefenic H, 3·98 τ, complex; 4H, 6·5–7·3 τ, complex.)

The *bis*-semicarbazone (decomp. above 290°) (sodium acetate method) was almost insoluble in all organic solvents and was purified by boiling with methanol. (Found; C, 56·3; H, 6·0; N, 27·6. $C_{14}H_{18}N_6O_2$ requires C, 55·7; H, 6·2; N, 27·8%.)

The *bis*-2,4-dinitrophenylhydrazone (decomp. at 238°) was recrystallised from alcohol-nitrobenzene. (Found: C, 52·8; H, 3·7. $C_{24}H_{20}N_8O_8$ requires C, 52·5; H, 3·7%.)

(*b*) *via* 4-bromo-3-methylcyclopentenone. The undistilled bromo-ketone was treated with trimethylamine by the method of Crombie *et al.*[3] The product (52%, λ_{max} 227 mμ, ε 10,240) was identical with that obtained by alkaline hydrolysis of the formate.

Decarbonmonoxylation The crystalline dimer (0·13 g) was heated at 200° until no more carbon monoxide (burnt with a blue flame) was eliminated (5 min.) to give a residue (0·11 g, equivalent to 15·4% weight loss. Calculated for $C_{12}H_{12}O_2$ to $C_{11}H_{12}O$, 15%). Similarly, heating the dimer (1·0 g) and distillation and redistillation of the residue gave 3,5-dimethylindanone (0·5 g, 59%), b.p. 80°–81°/0·2 mm, n_D^{20} 1·5540; λ_{max} 252, 293 mμ; ε 13,800, 3100. (Found: C, 81·6; H, 7·4%. Calculated for $C_{11}H_{12}O$: C, 82·4; H, 7·1 calculated for $C_{12}H_{15}N_3O$: C, 66·3; H, 7·0%.)

The semicarbazone, (pyridine, ethanol) twice crystallised from ethanol, had m.p. 218°–219°. (Found: C, 66·0; H, 7·1. Calculated for $C_{12}H_{15}N_3D$: C, 66·3; H, 7·0%.)

The 2,4-dinitrophenylhydrazone was twice crystallised from benzene as orange-red crystals, m.p. 224°–225°. (Found: C, 59·6; H, 4·6; N, 16·7. Calculated for $C_{17}H_{16}N_4O_4$: C, 60·0; H, 4·7; N, 16·5%.)

The same 2,4-dinitrophenylhydrazone (m.p. and mixed m.p.) was obtained when undistilled 4-bromo-3-methylcyclopentenone was treated with sodium methoxide in methanol and the reaction product was heated until carbon monoxide elimination was finished.

The oxime of 3,5-dimethylindanone had m.p. 111·5–113·5°. (Found: C, 74·8; H, 7·4; N, 6·6. Calculated for $C_{11}H_{13}NO$: C, 75·4; H, 7·5; N, 8·0%.) Pavolini *et al.*[6] claimed, without analytical data, that the oxime of 3-methylcyclopentadienone had m.p. 143°–145°.

Pyrolysis of the dimer of 3-methylcyclopentadienone in the presence of anthracene gave only 3,5-dimethlyindanone, identified as the 2,4-dinitrophenylhydrazone.

3,6-Dimethylindanone (V), synthesised by the method of Pines *et al.*,[7] had b.p. 83°–84°/0·1 mm, n_D^{20} 1·5510, λ_{max} 211, 247, 298 mμ, ε 24,000, 10,700, 2500. Semicarbazone, m.p. 222° (decomp.) from ethanol. The m.p. was not depressed by the semicarbazone of 3,5-dimethylindanone from 3-methylcyclopentadienone. 2,4-Dinitrophenylhydrazone, m.p. 273°–274° (from benzene). (Found: C, 59·3; H, 5·0. Calculated for $C_{17}H_{16}N_3O_4$: C, 60·0; H, 4·7%.) The melting point was depressed on admixture with the derivative of 3,5-dimethylindanone.

3,5-Dimethylindanone (IV), prepared by the method of Entel *et al.*,[8] was purified by way of the semicarbazone. It had b.p. 78°/0·08 mm, n_D^{20} 1·5550, λ_{max} 211, 251, 293 mμ, ε 23,000, 14,800, 3230. (Found: C, 83·1; H, 7·75. Calculated for $C_{11}H_{12}O$: C, 82·5; H, 7·6%. NMR spectrum: Aliphatic CH_3, doublet, J = 6 c/s, 8·64 τ; CH_3 on ethylenic bond 7·58 τ, singlet; 3H atoms, diffuse humps at 7·9, 7·25 and 6·7 τ.)

The semicarbazone (ethanol, pyridine) had m.p. 218°–219·5° (from ethanol), not depressed on admixture with the derivative from decarbonmonoxylation of the dimer. (Found: C, 66·3; H, 7·1. Calculated for $C_{12}H_{15}N_3O$: C, 66·3; H, 7·0%.)

The 2,4-dinitrophenylhydrazone had m.p. 225°–226° (from benzene), not depressed on admixture with the derivative from decarbonmonoxylated dimer. λ_{max} 290, 314, 386 mμ, ε 8850, 6050, 31,650: λ_{inf} 255,300, ε 14,850, 7190 (in EtOH). (Found: C, 66·6; H, 4·8. Calculated for $C_{17}H_{16}N_3O_4$: C, 66·0; H, 4·7%.)

9,10-Dihydro-9,10(4,5-3-methylcyclopentenono)anthracene By the method described,[6] anthracene and diacetylethylene gave 9,10-dihydro-9,10-(11,12-diacetylethano)anthracene which showed only low intensity aromatic absorption at 252, 258, 261, 269 and 273 mμ. (Found: C, 81·7; H, 6·4. Calculated for $C_{20}H_{18}O_2$: C, 82·8; H, 6·2%.) Cyclisation[6] gave 9,10-dihydro-9,10(4,5-3-methylcylopentenono)anthracene, m.p. 236·5°–239°. (Found: C, 88·1; H, 5·7. Calculated for $C_{20}H_{16}O$: C, 88·2; H, 5·9%.) This cyclopentenone was characterised as the 2,4-dinitrophenylhydrazone, m.p. 268° (from ethanol, ethyl acetate). (Found: C, 69·0; H, 4·3; N, 11·7. $C_{26}H_{20}N_4O_4$ requires C, 69·0; H, 4·5; N, 12·4%.)

Pyrolysis The cyclopentenone (V) (9·53 g) was heated in the vapour of refluxing diethyl phthalate for 1 h (when evolution of gas was very slow). The product was taken into ether, and anthracene was separated by filtration. The residue was concentrated and distilled at 2 × 10^{-2}mm. After rejection of low boiling product (0·034 g), two fractions were collected: (a) b.p. 84°–88° (0·637 g), n_D^{20} 1·5581; λ_{max} 252, 286, 294 mμ; ε 13,600, 2800, 3050. (Found: C, 80·1; H, 7·2%.) (b) 120°–142°, with decomposition (0·213 g), n_D^{20} 1·5567. (a) gave a semicarbazone, m.p. 222°–224° (from 95% ethanol), (found: C, 66·2; H, 7·1; N,17·5. Calculated for $C_{12}H_{15}N_3O$: C, 66·3; H, 7·0; N, 19·3%) and a 2,4-dinitrophenylhydrazone, m.p. 210°–211°, mixed m.p. with derivative of 3,5-dimethylindanone, 221°–222°.

In another experiment, the cyclopentenone (3·11 g) was heated gently whilst gas evolution was just maintained and the gas evolved (104 ml; calculated, 129 ml) was collected over saturated salt solution. The gas gave a positive reaction for carbon monoxide with Manchot-Scherer's reagent,[9] and carbon monoxide was detected spectroscopically by reaction with rabbit's blood. The reaction product was taken into ethanol (20 ml) and anthracene was removed by filtration. After concentration the following fractions were collected: (a) b.p. 144°/17 mm, 0·088 g; (b) 140°/15 mm, 0·327 g, λ_{max} 252, 285 (inflexion) 292 mμ; ε 13,340, 2500, 2760 (found: C, 79·9; H, 7·4. $C_{11}H_{12}O$ requires C, 82·5; H, 7·6%); (c) 140°–150°/2 mm, 0·089 g.

The cyclopentenone (1·0 g) was pyrolysed to give distillate (0·39 g), b.p. 139°–140°/15 mm, n_D^{20} 1·5539. This gave a red 2,4-dinitrophenylhydrazone, m.p. 218°–224° (from ethanol), mixed m.p. with 3,5-dimethylindanone 2,4-dinitrophenylhydrazone, 223°–225°, λ_{max} 290, 314, 386 mμ, ε 7980, 5290, 29,430; λ_{inf} 255, 300, ε 13,630, 6360. (Found: C, 59·6; H, 4·6; N, 16·7. $C_{17}H_{16}N_4O_4$ requires C, 60·0; H, 4·7; N, 16·5%.)

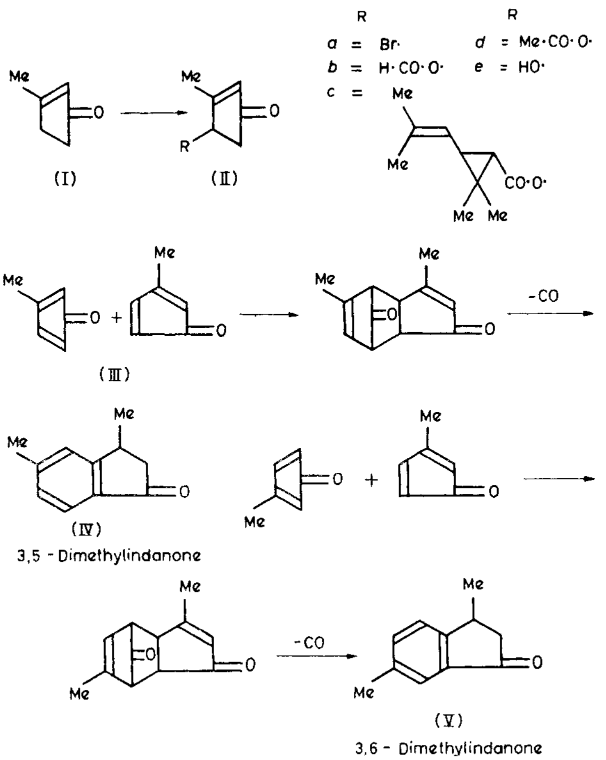
The infra-red spectra of the distilled product from pyrolysis of the cyclopentenone and from decarbonmonoxylation of 3-methylcyclopentadienone dimer were identical except in the carbonyl region, where a hump at 5·7 μ on the side of the conjugated carbonyl peak at 5·88 μ indicated the presence of some unconjugated carbonyl absorption (bridgehead carbonyl of 3-methyl cyclopentadienone dimer). In 2-allyl-3-methylcyclopentadienone dimer the bridge and conjugated carbonyl groups absorbed at 5·64 and 5·92 μ, respectively,[10] and in cyclopentadienone dimer, at 5·67 and 5·88 μ.[11]

The identity of the products from decarbonmonoxylation of 3-methylcyclopentadienone dimer (III) and from 9,10-dihydro-9,10-(4,5-3-methylcyclopentenono)anthracene (V) was proved by gas–liquid chromatography at 175° using a Pye Argon Chromatograph and a column of 10% polypropylene sebacate on Celite. 3-Methylcyclopentadienone dimer was retained by the column and gave no peak. After heating the dimer until decarbonmonoxylation was complete, a sharp peak emerged 8 min. after injection. 9,10-Dihydro-9,10-(4,5-3-methylcyclopentenono)anthracene gave no peak under similar conditions, but after heating, a sharp peak was obtained at the identical position to that obtained from 3-methylcyclopentadienone dimer, and anthracene came out at 57 min. Separate injection of pure constituents gave identical retention times.

When the crude mixture from pyrolysis of 9,10-dihydro-9,10-(4,5-3-methylcyclopentenono)anthracene was examined by NMR, absorption bands appeared at identical τ values to those found in the spectrum of the product from pyrolysis of 3-methylcyclopentadienone dimer. The aromatic region in the anthracene spectrum was clarified by filtering the spectroscopic solution in deuterochloroform.

Results and Discussion

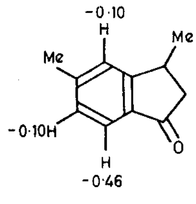
Like cyclopent-2-enone itself[12] and 2-alkyl-3-methylcyclopentenones,[3] 3-methylcyclopent-2-enone[1] (I) reacted smoothly with *N*-bromo-succinimide to give a crude bromo-compound (**IIa**) in 97% yield. This partly decomposed on attempted distillation but gave the acetate of 4-hydroxy-3-methylcyclopent-2-enone (**IId**) with silver acetate[3] and the formate with sodium formate in 95% formic acid (**IIb**).[13] As with dihydrocinerolone acetate,[3] 3-methylcyclopent-2-enolone acetate was hydrolysed to the corresponding alcohol with dilute aqueous methanolic potassium hydroxide; in contrast, allethrolone acetate[14] gave mainly the dimer of 2-allyl-3-methylcyclopentadienone with aqueous ethanolic sodium hydroxide. However, hydrolysis of the formate gave, as the principal product, a crystalline compound recognised as 3-methylcyclopentadienone dimer by its analysis, molecular weight, spectrum properties and the formation of *bis*-semicarbazone and *bis*-2,4-dinitrophenylhydrazone. Cyclopentadienones with fewer than 3-substituents[15] or without alkyl groups such as *tert*-butyl[16] exist as dimers which eliminate carbon monoxide on heating and rearrange to indanones. Cyclopentadienones with substituents at the 2 and 3 positions could dimerise in two ways by addition at the unsubstituted double bond. The dimers from 3-methylcyclopentadienone, which would give 3,5- or 3,6-dimethylindanone, are as shown:



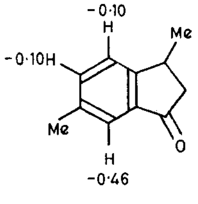
Addition might occur also in two ways at the substituted double bond, when aromatisation would necessitate methyl group migration from the bridgehead into the cyclopentenone ring, leading to 2,5- or 2,6-dimethylindanone (Allen's discussion[17] on phenyl group migration). There was no evidence that this occurred in the present work.

The direction of self-dimerisation of mono- and disubstituted cyclopentadienones has been considered only with 2-chlorocyclopentadienone, 2,3-dichlorocyclopentadienone and 2,3-dichloro-5-bromocyclopentadienone.[12,18] Carbon monoxide was eliminated from the crystalline 3-methylcyclopentadienone dimer on heating, as was expected, and a dimethyl indanone was obtained that appeared to be homogeneous. 3,5-(IV) and 3,6-Dimethylindanones (V) were synthesised for comparison, and the decarbonmonoxylated product was identical with the former. Therefore, as with 2-chlorocyclopentadienone,[12] dimerisation gave the compound (**III**) with the substituent on the norbornene ring in the more remote position from the carbonyl group of the cyclopentenone.

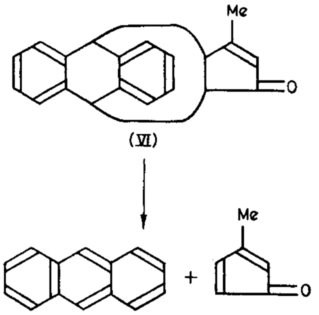
Besides the synthetical evidence, examination of the aromatic region by nuclear magnetic resonance spectroscope indicated that the product was 3,5- and not 3,6-dimethylindanone. The approximation to an aromatic quartet with centres at 2·43 and 2·83 τ respectively and a singlet centred over the doublet at higher field agreed with the pattern predicted for 3,5- but not for 3,6-dimethylindanone. Thus using the values of Corio and Dailey[19] (cf. Jackman[20]) to predict the shifts of the three aromatic protons from the value of benzene (see below), 3,5-dimethylindanone would be expected to show a quartet, with separation between the centres of about 0·36 τ (0·46–0·10) with a singlet superimposed on the higher member. In 3,6-dimethylindanone the singlet H should be isolated at lower field from the bands of the remaining two protons which, shifted to the same extent from the mean benzene value, should also be a singlet.



(IV)

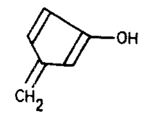


(V)



The synthesis of 3-methylcyclopentadienone as a yellow liquid, b.p. 218°–220°, by pyrolysis of the cyclised adduct of anthracene and diacetyl ethylene, (9,10-dihydro-9,10-(4,5-3-methylcyclopentenone(anthracene) (**VI**) was claimed.[6]

The known properties of 3-methylcyclopentadienone suggested that any monomeric dienone formed in the reaction would dimerise and under the pyrolysis conditions eliminate carbon monoxide to give 3,5-dimethylindanone as the volatile product. This reaction was investigated in connexion with the work described above, for it has since been suggested[21] that Pavolini's product[6] was:



rather than 3-methylcyclopentadienone or products from it.

Carbon monoxide was detected when the cyclised anthracene adduct (**VI**) was heated, and the distillate, although similar to that obtained directly from 3-methylcyclopentadienone, gave a 2,4-dinitrophenylhydrazone of lower and less sharp melting point. It was found difficult to complete the elimination and pyrolysis of the 3-methylcyclopentadienone, and traces of dimeric cyclopentadienone and of its adduct (**VI**) tended to be co-distilled. However, by gas–liquid chromatography, separation of the dimethylindanone from other products was easy, and no doubt remained that the indanone formed was 3,5-dimethylindanone (**IV**). Again, if present, other related isomeric compounds were below the limits of detection by the spectroscopic and chromatographic techniques available.

(±)-H-rethronyl(±)-*trans*-chrysanthemate (**IIc**)[22] (±)-H-rethronylcyclopropane carboxylate and (±)-allethronyl (±)-cyclopropane carboxylate were synthesised as indicated (see experimental) but were of very small insecticidal activity. The results are discussed in detail elsewhere.

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STUDIES ON POTASSIUM NUTRITION OF PLANTS.

I.—Effects of potassium concentration on growth and mineral composition of vegetable seedlings in sand culture.

By G. G. FREEMAN

The effect of potassium concentration in the nutrient medium on growth and mineral composition (N, K, P, Ca, Mg, Na) of red beet, cabbage, lettuce and Italian ryegrass in sand culture was investigated. It was shown that the results and those of some earlier workers can be interpreted as a simple linear relationship by means of the equation: $\frac{1}{y} = \mathrm{a} + \frac{\mathrm{b}}{x + \mathrm{x_0}}$ where y is plant weight or leaf potassium content, x is potassium concentration in the nutrient medium and a, b and $\mathrm{x_0}$ are constants. Sand-grown plants contained relatively high concentrations of sodium, which played an important part in the maintenance of cation balance under these conditions. In red beet, cabbage and ryegrass, changes in potassium content were almost completely balanced by corresponding changes in sodium content with relative constancy of calcium and magnesium, whereas in lettuce, calcium and magnesium also functioned in maintaining the balance.

Introduction

In a recent review of the metabolic role of potassium in plants, Evans and Sorger[1] took the view that a mechanism involving univalent cation-induced conformation changes in enzymes could account for most, if not all, of the recorded observations, including the high concentrations of potassium often present.

The present work is a study of the effect of potassium nutrition on growth and mineral composition of certain plants as an initial step in an investigation of its effects on the organic acids of leaves.[2] One of its objects was to establish the concentration of potassium in the nutrient medium which, while it produced pronounced deficiency, still afforded adequate quantities of tissue for determination of organic acids and other components. Preliminary experiments showed that sodium had an important rôle in maintaining constancy of cation equivalents in sand culture and this has been studied in some detail.

Experimental

Sand-culture experiments

Seedlings were grown in a glasshouse in 20 cm dia. earthenware pots which had received two coats of bitumastic paint to seal the pores; each pot contained 3·3 kg of sand which had been washed once with hot hydrochloric acid as described by Hewitt.[3] Seven seedlings were grown in each pot, evenly spaced over the surface. Nutrient solution