Further Synthetic Investigations in the Eremophilane Sesquiterpene Group. Synthesis of (±)-Isovalencenic Acid, (±)-Isovalencenol, and their (*Z*)-Isomers, and Experiments directed towards the Synthesis of Tessaric acid

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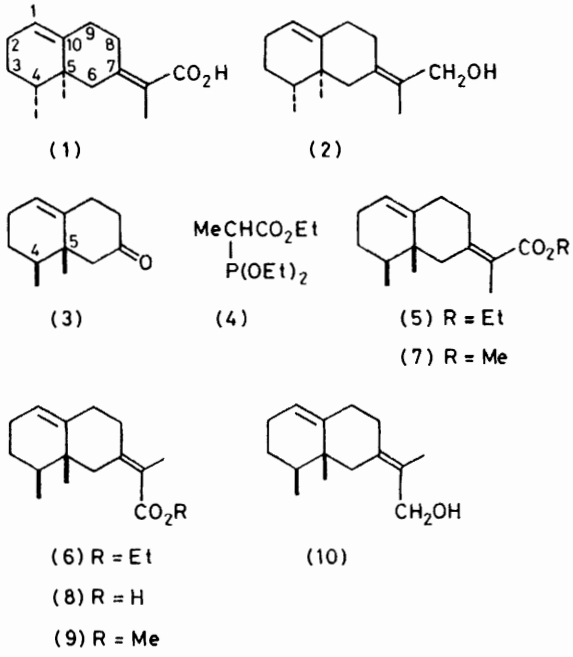
Stereospecific total syntheses of racemic isovalencenic acid and isovalencenol, two eremophilanoid sesquiterpenes of vetiver oil, along with their geometric isomers, are described. Details are also presented concerning a synthetic approach to tessaric acid, a similarly constituted natural sesquiterpene.

(+)-Isovalencenic acid is a sesquiterpene of the non-isoprenoid eremophilane family, which is a minor component of vetiver oil. It has been assigned structure and absolute configuration (1) on spectral evidence and by correlations with other members of the group. The (*E*)-geometry of the tetrasubstituted double bond was established by oxidation of the 1,10-dihydro-acid with selenium dioxide to a γ-lactone, shown by n.m.r. spectroscopy to be formed by a cyclisation *via* C-8 rather than C-6.[1] (+)-Isovalencenol is a similarly constituted allylic primary alcohol (2) occurring in North Indian vetiver oil. Its structure and stereochemistry have likewise been settled on the basis of correlations within the group and by spectral studies.[2] Another bicyclic primary alcohol isolated from a Japanese vetiver oil[3] is probably identical with isovalencenol, although it is a liquid whereas the Indian alcohol has m.p. 89—90 °C, and their specific rotations differ somewhat. (+)-Isovalencenic acid has been converted into (+)-isovalencenol by reduction of its methyl ester using lithium aluminium hydride,[1] which transformation reveals that the alcohol also has (*E*)-stereochemistry.

We describe here total syntheses of the racemic forms of the acid and alcohol, and of their (*Z*)-isomers.† The starting point was the octalone (3), the synthesis of which has been outlined earlier.[4] We have established, by n.m.r. analysis using a shift reagent, that in this ketone the methyl groups at positions 4 and 5 are *cis*.[4] The ketone was subjected to a Wadsworth–Emmons reaction[5] with triethyl α-phosphonopropionate (4), which furnished, as anticipated, a mixture of the unsaturated esters (5) and (6), as evidenced by g.l.c. and n.m.r. spectroscopy. These were eventually separated by careful column chromatography on neutral alumina. Their u.v. and n.m.r. spectra were virtually indistinguishable, but their i.r. spectra showed noticeable differences in the 800—1 500 cm^{-1} region. Hydrolysis of the ester with the longer g.l.c. retention time yielded a crystalline acid, m.p. 168 °C, whilst similar treatment of the ester with the shorter retention time generated another acid, m.p. 174 °C; on admixture these acids showed a marked m.p. depression. It was not possible to compare either acid with natural isovalencenic acid because of the lack of a sample of the latter and of its i.r. spectrum taken in solution. Consequently they were converted separately into their methyl esters by treatment with diazomethane. These two esters also had closely similar spectral properties, but differed significantly in the i.r. 'fingerprint region.' The i.r. spectrum of the ester derived from the



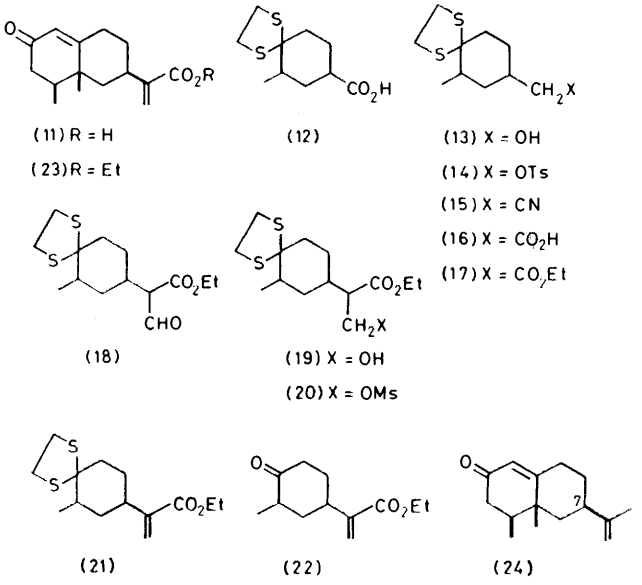
acid, m.p. 168 °C, proved to be identical with that of an authentic specimen of (+)-methyl isovalencenate (both as liquid films). It follows that the lower-melting acid is (±)-isovalencenic acid (1), its ethyl ester is (5), and its methyl ester (7), whilst the higher-melting acid is (8), its ethyl ester (6), and its methyl ester (9).

Reduction of the methyl ester (7) with lithium aluminium hydride afforded an alcohol which proved to be racemic isovalencenol (2); similar reduction of the methyl ester (9) yielded the (*Z*)-alcohol (10), the geometric isomer of (±)-isovalencenol.

(−)-Tessaric acid is another eremophilanoid sesquiterpene which occurs in the Argentinian plant *Tessaria absinthoides*. On spectral evidence it has been assigned the structure and configuration (11).[6]

† Most of the appended structures, including (3), represent racemates, only one enantiomer being shown.

We have explored a synthetic route to the racemic form of structure (11) as follows. The starting point was the crystalline dithioacetal (12) (presumably the *cis*-isomer) described earlier,[7] reduction of which with lithium aluminium hydride furnished the alcohol (13) which was converted into its tosylate (14) in the usual way. The latter with sodium cyanide afforded the nitrile (15) which on hydrolysis yielded the homologous acid (16). The ethyl ester (17) of the latter on reaction with ethyl formate afforded the α-formyl ester (18) as



the expected tautomeric equilibrium. Reduction with sodium borohydride under mild conditions gave the alcohol (19), mesylation of which yielded the ester (20). Heating the latter in γ-collidine effected elimination to the acrylic ester (21), hydrolysis of which generated the keto-ester (22). There was reason to anticipate that (22) on annulation with (*Z*)-pent-3-en-2-one would yield the desired all-*cis*-octalone (23), by analogy with the stereochemical result of annulation, with the same Michael acceptor, of 4-isopropenyl-2-methylcyclohexanone, which led to 7-*epi*-nootkatone (24).[7] Unfortunately, however, attempted annulation of (22) using a variety of conditions gave complex mixtures of products including polymeric material. Spectral examination of the distillable part of the product revealed that the side-chain double bond had undergone extensive migration into the exocyclic position, as evidenced by the absence of an i.r. band in the 900 cm^{-1} region characteristic of a $C{=}CH_2$ group, and by the almost total absence of olefinic hydrogen signals in the n.m.r. spectrum. Efforts to effect the desired annulation are continuing.

EXPERIMENTAL

I.r. spectra were determined with Perkin-Elmer 137 and Beckman 4250 (grating) instruments. U.v. spectra were obtained using a Perkin-Elmer 202 spectrophotometer. N.m.r. spectra were recorded using a Varian A-60 instrument. Gas chromatographic analyses were conducted on an F and M model 810 Research Chromatograph using SE-30 and OV-17 stationary phases.

4β,5β-Dimethyl-Δ$^{1(10)}$-octalin-7-one (3).—This ketone was synthesised from furfuraldehyde as described earlier.[4] It had b.p. 135 °C at 17—18 mmHg and was homogeneous by g.l.c.

Triethyl α-Phosphonopropionate (4).—The ester was prepared from ethyl α-bromopropionate and triethyl phosphite *via* a modified Michaelis–Arbuzov reaction.[5b] It had b.p. 135—138 °C at 13 mmHg.

Ethyl 2-(4aβ,5β-Dimethyl-1,2,3,4,4a,5,6,7-octahydro-3-naphthylidene)propionate [(5) *and* (6)].—Sodium hydride (0.20 g of a 50% dispersion in mineral oil) was washed thrice by decantation with light petroleum (b.p. 30—60 °C) and then covered with dry 1,2-dimethoxyethane (5 ml). The suspension was cooled to 0 °C and stirred in an atmosphere of dry nitrogen during the gradual addition over a few minutes of triethyl α-phosphonopropionate (1.2 g) in dry dimethoxyethane (5 ml). The mixture was stirred at this temperature for 1 h. Then the foregoing octalone (3) (0.45 g) in the same solvent (5 ml) was added under the same conditions. The resulting mixture was refluxed on a water-bath for 46 h, then cooled, and poured into ice–water. The product was extracted with ether (3×), and the combined extracts were washed with water, dried (Na_2SO_4), and concentrated. G.l.c. of the residue (0.60 g) showed it to be (>90%) a mixture of the two geometrically isomeric *unsaturated esters* (5) and (6) together with small amounts of reactants. The latter were eliminated by a fractional distillation, the major fraction (0.5 g, 75%) having b.p. (bath) 100—110 °C at 0.025 mmHg. G.l.c. (SE-30, 200 °C) showed this to contain the two isomers in a *ca.* 2 : 3 ratio.

The product was chromatographed on Camag neutral alumina (30 g, Brockmann No. 1) with elution with light petroleum (b.p. 30—60 °C)–ether (9 : 1) (100-ml portions). Fractions 4, 5, and 6 afforded a homogeneous ester (0.2 g) which corresponded to the component (A) with the longer g.l.c. retention time. Fractions 2 and 3 were re-chromatographed as above but with elution with the same solvents mixed in a 19 : 1 ratio. This furnished the unsaturated ester component (B) (0.15 g) with the shorter g.l.c. retention time. The ester (A) distilled at (bath) 105 °C and 0.04 mmHg (Found: C, 77.7; H, 9.9. $C_{17}H_{26}O_2$ requires C, 77.8; H, 10.0%); $\nu_{max.}$ (film) 1 718, 1 645, 1 635, 1 461, 1 450, 1 380, 1 276, 1 230, 1 200, 1 181, 1 096, and 845 cm^{-1}; δ ($CDCl_3$) 0.83 (3 H, s, Me), 0.90—1.00 (6 H, m, 2 × Me), 1.86 (3 H, s, allylic Me), 4.15 (3 H, q, OCH_2), and 5.20 (1 H, br, =CH); $\lambda_{max.}$ (EtOH) 225 nm (ε 9 100). The ester (B) distilled at (bath) 100—195 °C and 0.04 mmHg (Found: C, 77.5; H, 10.1. $C_{17}H_{26}O_2$ requires C, 77.8; H, 10.0%); $\nu_{max.}$ (film) 1 720, 1 645, 1 638, 1 464, 1 450, 1 440, 1 380, 1 374, 1 365, 1 298, 1 278, 1 210, 1 175, 1 132, 1 098, and 846 cm^{-1}; $\lambda_{max.}$ (EtOH) 225.5 nm (ε 8 590); δ ($CDCl_3$) 0.83 (3 H, s, Me), 0.90—1.00 (6 H, m, 2 × Me), 1.88 (3 H, s, allylic Me), 4.15 (3 H, q, OCH_2), and 5.30 (1 H, br, =CH).

Hydrolysis of Ester (A).—The foregoing ester (A) (0.1 g) was mixed with an 85 : 15 mixture (10 ml) of dimethyl sulphoxide and 2N-aqueous sodium hydroxide and kept at room temperature for 21 h.[8] The mixture was poured into a large excess of ice–dilute HCl and extracted thrice with ether. The combined extracts were washed with water, dried (Na_2SO_4), and concentrated. The residual (±)-(E)-2-(4aβ,5β-*dimethyl*-1,2,3,4,4a,5,6,7-*octahydro*-3-*naphthylidene*)*propionic acid* (1) (0.09 g) solidified readily and crystallized from ether in glistening needles, m.p. 168 °C

(Found: C, 76.7; H, 9.5. $C_{15}H_{22}O_2$ requires C, 76.9; H, 9.5%); $\lambda_{max.}$ (EtOH) 226 nm (ε 8 200) [lit.,[1] $\lambda_{max.}$ (MeOH) 225 nm (ε 8 000)]; δ (CCl_4) 0.83 (3 H,s, Me), 0.93 (3 H, d, Me), 1.98 (3 H, s, allylic Me), and 5.35 (1 H, br, =CH).

Hydrolysis of Ester (B).—An identical procedure applied to the ester (B) (0.1 g) effected its hydrolysis to (±)-(Z)-2-(4aβ,5β-*dimethyl*-1,2,3,4,4a,5,6,7-*octahydro*-3-*naphthylidene*)-*propionic acid* (8) (0.09 g), which also separated from ether in glistening needles, m.p. 174 °C (Found: C, 76.95; H, 9.3%); $\lambda_{max.}$ (EtOH) 225 nm (ε 7 900); δ (CCl_4) 0.84 (3 H, s, Me), 0.93 (3 H, d, Me), 1.96 (3 H, s, allylic Me), and 5.35 (1 H, br, =CH). A mixture of the two acids had m.p. 137—143 °C.

Methylation of the (E)-*Acid*.—The foregoing (*E*)-acid (0.1 g) was dissolved in ether (15 ml) and treated with an excess of ethereal diazomethane, with ice-cooling. After 30 min the ethereal solution was washed with aqueous sodium hydrogencarbonate and water, and then dried (Na_2SO_4), and concentrated. The residual (±)-*methyl ester* (7) (100% yield) distilled at (bath) 100 °C and 0.02 mmHg (Found: C, 77.3; H, 9.75. $C_{16}H_{24}O_2$ requires C, 77.4; H, 9.7%); $\lambda_{max.}$ (EtOH) 224 nm (ε 9 500) [lit.,[1] $\lambda_{max.}$ (MeOH) 224 nm (ε 9 150)]; $\nu_{max.}$ (film) 1 718, 1 635, 1 458, 1 432, 1 380, 1 370, 1 355, 1 340, 1 330, 1 310, 1 280, 1 232, 1 202, 1 188, 1 155, 1 146, 1 132, 1 120, 1 098, 1 070, 1 060, 1 043, 996, 980, 938, 881, 842, 810, 773, and 725 cm^{-1}; i.r. spectrum identical with that of an authentic sample of (+)-methyl isovalencenate; [1] δ (CCl_4) 0.83 (3 H, s, Me), 0.95 (3 H, d, Me), 1.80 (3 H, s, allylic, Me) 3.63 (3 H, s, OMe), and 5.25 (1 H, br, =CH).

Methylation of the (Z)-*Acid*.—Similar methylation of the foregoing (*Z*)-acid (0.1 g) afforded the (±)-*methyl ester* (9), b.p. (bath) 100—102 °C at 0.02 mmHg (Found: C, 77.25; H, 9.6%) (100% yield); $\lambda_{max.}$ [EtOH] 224.5 nm (ε 9 000); $\nu_{max.}$ (film) 1 720, 1 645, 1 640, 1 465, 1 450, 1 381, 1 373, 1 365, 1 300, 1 278, 1 210, 1 176, 1 165, 1 132, 1 098, 1 070, 1 062, 1 030, 1 000, 980, 845, 810, 770, and 725 cm^{-1}; δ (CCl_4) 0.83 (3 H, s, Me), 0.94 (3 H, d, Me), 1.82 (3 H, s, allylic Me), 3.61 (3 H, s, OMe), and 5.28 (1 H, br, =CH). The i.r. spectrum of this ester (liquid film) was noticeably different in the ' fingerprint region ' from that of authentic (+)-methyl isovalencenate.[1]

(±)-*Isovalencenol* (2).—The foregoing (*E*)-methyl ester (0.08 g) in dry ether (10 ml) was stirred at 0 °C during the gradual addition of a solution/suspension of lithium aluminium hydride (0.05 g) in dry ether (10 ml) (few min). The mixture was stirred at 0 °C for 3½ h, then treated with a little Celite and decomposed with ice–water. The ether solution was decanted from the sludge, dried (Na_2SO_4), and concentrated. The residual (±)-*isovalencenol* (0.06 g) distilled at (bath) 130 °C and 0.04 mmHg (Found: C, 81.9; H, 10.9. $C_{15}H_{24}O$ requires C, 81.8; H, 11.0%); $\nu_{max.}$ (film) 3 350, 1 670, 1 630, 1 460, 1 440, 1 380, 1 005, 990, 890, 843, and 810 cm^{-1}; δ (CCl_4) 0.80 (3 H, s, Me), 0.93 (3 H, d, Me), 1.78 (3 H, br, allylic Me), 4.10 (2 H, s, CH_2OH), and 5.27 (1 H, br, =CH). These spectra were identical with those of an authentic sample of (+)-isovalencenol.

Reduction of Ester (9).—An identical reduction procedure applied to the ester (9) (0.1 g) furnished the racemic (*Z*)-isomer (10) of isovalencenol (0.07 g), b.p. (bath) 130 °C at 0.03 mmHg (Found: C, 81.8; H, 11.1%); $\nu_{max.}$ (film) 3 365, 1 670, 1 632, 1 440, 1 380, 1 010, 980, 880, and 840 cm^{-1}; n.m.r. spectrum (CCl_4) closely similar to that of (+)- and (±)-isovalencenol; i.r. spectra noticeably different in the fingerprint region.

1,1-*Ethylenedithio*-4-*hydroxymethyl*-2-*methylcyclohexane* (13).—A solution/suspension of lithium aluminium hydride (1.5 g) in dry ether (50 ml) was stirred with ice-cooling during the gradual addition (few min) of the acid (12) (4.64 g) in dry ether (50 ml). The mixture was stirred at ambient temperature overnight, then refluxed on a water-bath for 16 h, cooled in ice, treated with Celite, and decomposed with ice–water. The ethereal solution was decanted and the residue leached several times with ether. Evaporation of the combined, dried (Na_2SO_4) extracts yielded the *alcohol* (13) as an oil, b.p. (bath) 145—150 °C at 0.04 mmHg (4.04 g, 93%) (Found: C, 55.2; H, 8.4. $C_{10}H_{18}OS_2$ requires C, 55.0; H, 8.3%); $\nu_{max.}$ (film) 3 413, 1 264, and 1 036 cm^{-1}.

4-*Cyanomethyl*-1,1-*ethylenedithio*-2-*methylcyclohexane* (15).—The foregoing alcohol (2.84 g) in dry pyridine (20 ml) was mixed with toluene-*p*-sulphonyl chloride (3.7 g) in dry pyridine (20 ml) with ice-cooling. The mixture was kept in a refrigerator overnight, then poured into an excess of dilute HCl–ice. The tosylate (14) was isolated with ether, the extracts being washed with water, dried (Na_2SO_4), and concentrated under reduced pressure at about 40 °C. The residual ester (5.3 g, 100%) was dissolved in dimethyl sulphoxide (30 ml) and the solution stirred during the gradual addition (few min) of powdered sodium cyanide (3.0 g), and then overnight. The mixture was poured into ice–water and the *nitrile* isolated with ether. It distilled at (bath) 150 °C and 0.05 mmHg (3.2 g, 100%) (Found: C, 58.3; H, 7.6; N, 6.1. $C_{11}H_{17}NS_2$ requires C, 58.15; H, 7.5; N, 6.2%); $\nu_{max.}$ (film) 2 247 cm^{-1} (CN).

4-*Ethoxycarbonylmethyl*-1,1-*ethylenedithio*-2-*methylcyclohexane* (17).—The foregoing nitrile (15) (8.4 g) was refluxed for 21 h with a solution of KOH (40 g) in water (250 ml). The homogeneous product was cooled, acidified with 5N-HCl, and extracted thrice with ether. The combined extracts were washed with water, dried (Na_2SO_4), and concentrated. The residual acid (16) (8.8 g, 97%) was dissolved in absolute ethanol (160 ml). The solution was cooled in ice and concentrated sulphuric acid (8 ml) added cautiously. The mixture was refluxed for 17 h, then cooled and poured into a large volume of ice–water. The *ethyl ester* (17) was isolated by several extractions with ether, the extracts being washed with sodium hydrogencarbonate and water, and then dried (Na_2SO_4) and concentrated. The residual ester distilled at (bath) 125—130 °C and 0.05 mmHg (8.8 g, 90%) (Found: C, 57.1; H, 8.2. $C_{13}H_{22}O_2S_2$ requires C, 56.9; H, 8.1%); $\nu_{max.}$ (film) 1 727 cm^{-1}.

4-*Ethoxycarbonyl*(*formyl*)*methyl*-1,1-*ethylenedithio*-2-*methylcyclohexane* (18).—Potassium hydride (25 g of a 22% suspension in mineral oil) [9] was washed thrice under dry nitrogen by decantation with pentane, then covered with dry tetrahydrofuran (60 ml) and stirred at 0 °C during the gradual addition (20 min) of a solution of the foregoing ethyl ester (17) (6.85 g) and ethyl formate (15.0 g) in dry tetrahydrofuran (60 ml). The mixture was stirred at room temperature for 4 d, then cooled to 0 °C and decomposed with ice–water. Ether was added and the aqueous layer separated, the ethereal layer being extracted twice with a little dilute sodium hydroxide. The combined aqueous layers were cooled in ice and acidified with dilute HCl. The liberated product was extracted with ether (2×), the combined extracts being washed with sodium hydrogencarbonate and water, then dried (Na_2SO_4) and concentrated. The residual *formyl ester* (18) (4.82 g, 64%) was used in the next step; it distilled at (bath) 15 °C and 0.04 mmHg with

some decomposition (Found: C, 55.9; H, 7.7. $C_{14}H_{22}O_3S_2$ required C, 55.6; H, 7.35%). The product was soluble in dilute aqueous alkali, gave an intense dark purple colour with ferric chloride, and reduced ammoniacal silver nitrate.

4-Ethoxycarbonyl(hydroxymethyl)methyl-1,1-ethylenedithio-2-methylcyclohexane (19).—The above formyl ester (3.02 g, crude) was dissolved in dry ethanol (60 ml) and stirred at 0 °C during the addition (10—15 min) of sodium borohydride (0.4 g). The mixture was stirred at the same temperature for an additional 1¼ h, then poured into an excess of ice–water and brine and extracted four times with ether. The combined extracts were washed with water, dried (Na_2SO_4) and concentrated *in vacuo*. The residual *alcohol* (19) (2.8 g, 92%) distilled at (bath) 160 °C and 0.02 mmHg (Found: C, 55.1; H, 8.0. $C_{14}H_{24}O_3S_2$ requires C, 55.25; H, 8.0%); $\nu_{max.}$ (film) 3 533, 1 727, and 1 036 cm^{-1}. The product gave no colour with ferric chloride.

Ethyl α-(4,4-Ethylenedithio-3-methylcyclohexyl)acrylate (21).—The above hydroxy-ester (3.04 g) in dry pyridine (50 ml) was cooled and mixed with a cooled solution of methanesulphonyl chloride (1.5 g) in dry pyridine (50 ml). After having been kept in the refrigerator overnight the mixture was poured into an excess of dilute HCl and ice. The mesylate (20) was isolated by three extractions with ether followed by washing with water, drying (Na_2SO_4), and evaporation (3.8 g, 100%). This mesylate (6.1 g) in freshly-distilled dry γ-collidine (100 ml) was heated in an oil-bath at 150 °C for 8 h. The mixture was cooled, poured into an excess of ice and dilute HCl, and extracted thrice with ether. The combined extracts were washed with water, dried (Na_2SO_4), and concentrated. The residual *acrylic ester* (21) distilled at (bath) 140 °C and 0.02 mmHg (3.7 g, 81%) (Found: C, 58.7; H, 7.75. $C_{14}H_{22}O_2S_2$ requires C, 58.7; H, 7.75%); $\lambda_{max.}$ (EtOH) 205 nm (ε 15 860); $\nu_{max.}$ (film) 1 706, 1 621, 1 266, 1 142, and 936 cm^{-1}; δ ($CDCl_3$) 1.20 (3 H, d, Me), 1.30 (3 H, t, Me), 3.30 (4 H, br d, SCH_2CH_2S), 4.35 (2 H, q, OCH_2), and 5.75 and 6.40 (both poorly resolved, 2 H, $=CH_2$).

Ethyl α-(3-Methyl-4-oxocyclohexyl)acrylate (22).—The above ester (20) (7.15 g) in acetonitrile (150 ml) and water (5 ml), together with mercuric chloride (12.3 g) and cadmium carbonate (7.5 g), was stirred at 50 °C under nitrogen for 22 h. The solvent was removed *in vacuo* and the residue leached several times with dichloromethane. The combined extracts were filtered and evaporated. The residual keto-ester was taken up in light petroleum (b.p. 30—60 °C) and filtered through a short plug of silica gel, with benzene as eluant. Evaporation of the benzene left the keto-ester (22), b.p. (bath) 100 °C at 0.03 mmHg and 110 °C at 0.07 mmHg (3.7 g, 71%) (Found: C, 68.2; H, 8.7. $C_{12}H_{18}O_3$ requires C, 68.5; H, 8.6%); $\nu_{max.}$ (film) 1 718, 1 626, and 942 cm^{-1}; δ ($CDCl_3$) 1.0 (3 H, t, Me), 1.25 (3 H, d, Me), 3.95 (2 H, q, OCH_2), 5.20 (1 H, s, =CH), and 5.80 (1 H, s, =CH); $\lambda_{max.}$ (EtOH) 204.5 nm (ε 12 000). G.l.c. showed the product to be homogeneous. The *2,4-dinitrophenylhydrazone* separated from ethanol in orange prisms, m.p. 75 °C (Found: C, 55.3; H, 5.7. $C_{18}H_{22}N_4O_6$ requires C, 55.4; H, 5.7%).

Attempts to annulate this ester with (*Z*)-pent-3-en-2-one under a variety of conditions commonly adopted for this type of reaction led to complex mixtures of products with little or no spectral evidence for the presence of a $C=CH_2$ group or olefinic H. Polymeric material was also encountered.

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