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SYNTHESIS OF DIHYDROCHALCONES OF *MYRICA GALE**

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Key Word Index—*Myrica gale*; Myricaceae; dihydrochalcones; 2′,6′-dihydroxy-4′-methoxy-3′,5′-dimethyldihydrochalcone; 2′-hydroxy-4′,6′-dimethoxy-3′-methyldihydrochalcone; 4,4,6-trimethyl-2-(3-phenylpropionyl)-cyclohexane-1,3,5-trione; 2,2,5-trimethyl-4-(3-phenylpropionyl)cyclopent-4-ene-1,3-dione.

Abstract—4,4,6-Trimethyl-2-(3-phenylpropionyl)cyclohexane-1,3,5-trione, 2′-hydroxy-4′,6′-dimethoxy-3′-methyldihydrochalcone,2′,6′-dihydroxy-4′-methoxy-3′,5′-dimethyldihydrochalcone and 2,2,5-trimethyl-4(3-phenylpropionyl)cyclopent-4-ene-1,3-dione, constituents of *Myrica gale*, have been synthesized.

INTRODUCTION

Myrica gale L. (sweet gale, bog myrtle, 'pors') was used in Scandinavian brewing practice as a substitute for, or together with, hops (*Humulus lupulus* L.) as preservative or flavouring agent [1, 2]. From the fruit of *M. gale* three constituents, **1**–**3**, were isolated [3], one of which **2** was an analogue of the hop β-acids or lupulones [4] in which methyl groups replaced the 3-methylbut-2-enyl (isoprenyl) side chains. Alternatively, on account of their β-phenylpropionyl side chains these compounds may be regarded as dihydrochalcones [5]. Subsequently the Norwegian workers have isolated from *M. gale* three cyclophane derivatives [6, 7], a chalcone **4** and a further dihydrochalcone **5** [8]. We report the synthesis of compounds **1**, **2**, **3** and **5**. The Norwegian workers have also synthesized compounds **1** and **2** but by different routes and their work is the subject of the accompanying communication [9]. They have previously described the synthesis of **4** and **5** [8].

RESULTS AND DISCUSSION

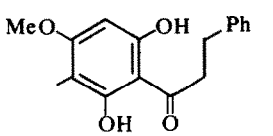
4,4,6 - Trimethyl - 2 - (β - phenylpropionyl)cyclohexane-1,3,5-trione (**2**) (*Scheme* 1)

As we had a supply of 2-acetyl-4,4,6-trimethylcyclohexane-1,3,5-trione **6** available from other work [10] we attempted to condense it with benzaldehyde to give the chalcone **7** in an analogous manner to the reported [11] synthesis of ceroptene (**8**). Reduction of the chalcone **7** should then have afforded the required compound **2**. However, no condensation occurred when **6** was heated at 100° with molar quantities of benzaldehyde. When **6** was heated with an excess of benzaldehyde using piperidine as catalyst, a product $C_{25}H_{22}O_5$ was isolated resulting from the condensation of two molecules of benzaldehyde with **6**. We regard this compound as 3 - benzylidene - 3,4,6,7 - tetrahydro - 5 - hydroxy - 6,6,8 - trimethyl - 2 - phenyl - 2H - benzopyran - 4,7 - dione (**10**); the chalcone **7** formed initially cyclizes to the flavanone **9** which then condenses with a further molecule of benzaldehyde. This structure **10** is favoured over **11**, resulting from the alternative mode of cyclization, as only **10** shows conjugate chelation [12]. The NMR and mass spectra are in agreement with this assignment [13].

The synthesis of **2** was achieved by hydrolysis [14] of **6** to 2,2,4-trimethylcyclohexane-1,3,5-trione (**12**) followed by Friedel-Crafts acylation using 3-phenylpropionyl chloride with aluminium chloride. The synthetic product was identical with the material isolated from *M. gale* (mp and mmp, IR spectrum and co-TLC).

We also attempted (Scheme 2) to introduce three *C*-methyl groups into 3-phenylpropionylphloroglucinol (**13**) to form **2** by methods analogous to those used in the synthesis of the hop β-acids [4, 14, 15] but using three

*Part 3 in the series "β-Tricarbonyl Compounds". For Part 1 see ref. [10]. Part 2 in preparation.



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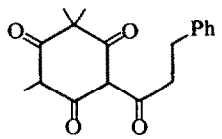

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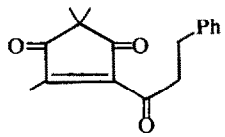

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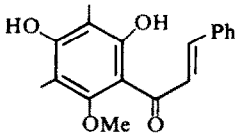

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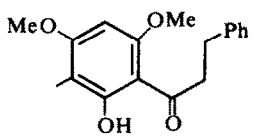

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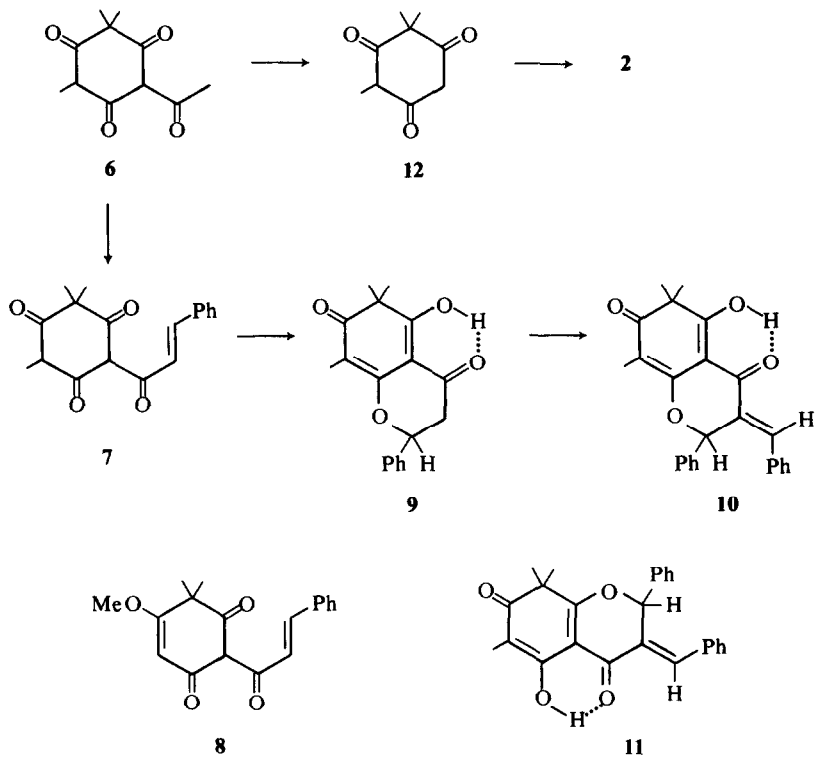
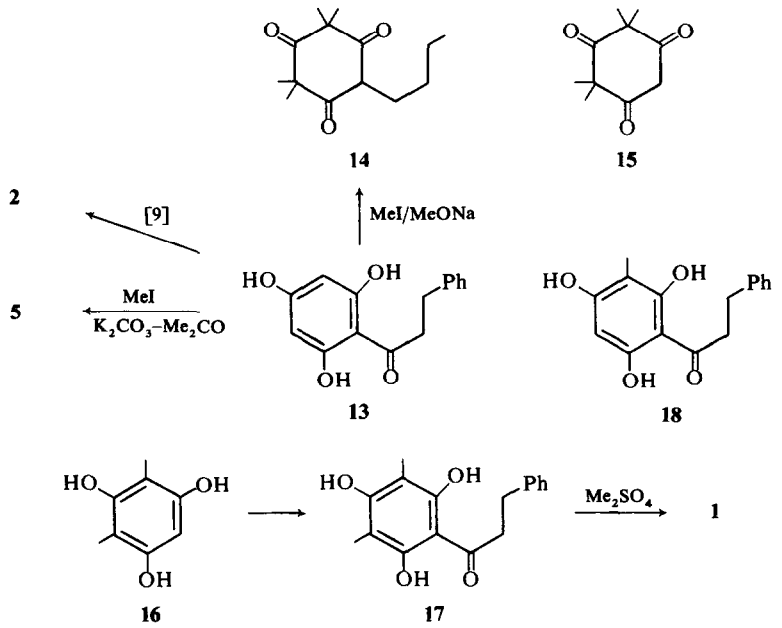


Scheme 1

moles of base a complex mixture of products was indicated by TLC. We did not isolate **2** from this mixture but the Norwegian workers have done so [9]. With an excess of MeI–NaOMe, **13** was converted to grandiflorone (**14**) [16]. This is essentially a repetition of the published [16] synthesis of grandiflorone from phloroglucinol but the earlier workers did not isolate **13**. We also tried to synthesize grandiflorone by acylation of 2,2,4,4-tetramethylcyclohexane-1,3,5-trione (**15**) but without success. Methylation of **13** using $MeI/K_2CO_3/Me_2CO$ gave 2′-hydroxy-4′,6′-dimethoxy-3′-methyldihydrochalcone **5** (dihydroaurentiacin [17]), which was subsequently isolated from *M. gale* and has been synthesized by two other routes [8].



Scheme 2

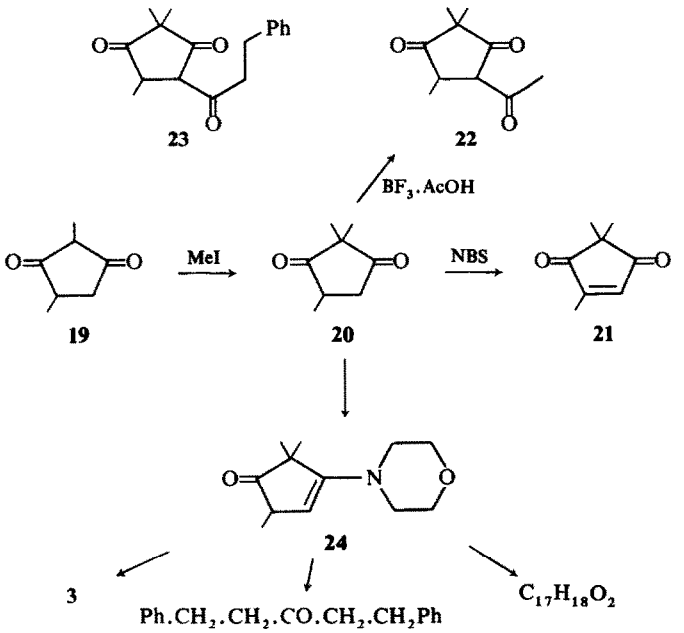
2'6'-Dihydroxy-4'-methoxy-3',5'-dimethyldihydrochalcone (**1**) (*Scheme* 2)

2',4',6'-Trihydroxy-3',5'-dimethyldihydrochalcone (**17**) was synthesized by Friedel-Crafts acylation of dimethylphloroglucinol (**16**) with 3-phenylpropionyl chloride. Selective methylation of the unchelated hydroxyl group was achieved using Me_2SO_4 in toluene containing $KHCO_3$ to give **1** which was identical with the natural product. We also prepared 2',4',6'-trihydroxy-3'-methyldihydrochalcone (**18**) in the analogous manner; thus the mono-(**18**), di-(**17**), tri-(**2**), and tetra-(**14**)-*C*-methylated derivatives of β-phenylphloropropiophenone (**13**) are now available.

2,2,5 - *Trimethyl* - 4 - (3 - *phenylpropionyl*)*cyclopent* - 4 - *ene*-1,3-*dione* (**3**) (*Scheme* 3)

The third compound isolated from *M. gale* could be obtained formally by the exclusion of formaldehyde from **2** but until very recently [18] there was no analogy for this reaction among the hop resins. Related compounds have also been obtained by oxidative degradation of a constituent of Dragon's blood [19]. In the literature 2,2,5-trimethylcyclopent-4-ene-1,3-dione (**21**) has been prepared by two routes [20, 21] but we chose an alternative route cf [22]. Condensation of methylsuccinic acid with propionyl chloride in the presence of $AlCl_3$ gave the mono enol of 2,4-dimethylcyclopentane-1,3-dione (**19**). The preparation and properties of this compound have not been described although its MS has been reported [23]. Methylation of **19** gave 2,2,4-trimethylcyclopentane-1,3-dione (**20**) which with *N*-bromosuccinimide was converted into **21**. Numerous attempts were made to acylate this compound with 3-phenylpropionyl chloride without success. Using $AlCl_3$ in dichloromethane dichloroethane, nitrobenzene, or nitromethane only, indanone, formed by internal cyclization of the acid chloride, was isolated. Such internal cyclizations do not occur with stannic chloride but none of the required compound **3** was obtained using this reagent. Acylation using acetic anhydride with boron trifluoride–acetic acid complex was also unsuccessful.

In contrast, acylation of 2,2,4-trimethylcyclopentane-1,3-dione (**20**) using acetic anhydride and the boron trifluoride acetic acid complex was successful giving **22**. However, attempts to condense 3-phenylpropionic acid with **20** in the presence of the boron trifluoride–diethyl etherate were unsuccessful; ethyl 3-phenylpropionate was isolated. At the same time 2,2,4-trimethylcyclopentane-1,3-dione (**20**) was condensed with morpholine to give the enamine **24**. This reacted with 3-phenylpropionyl chloride to give an oil which analysed for $C_{17}H_{20}O_3$, as required for **23**. It was therefore treated with 2,3-dichloro-5,6-dicyanobenzoquinone(DDQ)andtherequiredcompound **3** isolated. However, GLC established that the enamine condensation product was a mixture. It was therefore subjected to GC–MS when four peaks were resolved: (i) $C_{17}H_{20}O_2$, $C_{17}H_{18}O_2$; (ii) $C_{17}H_{18}O_3$; (iii) $C_{17}H_{18}O_2$: and (iv) $C_{17}H_{18}O$; none of which corresponds to the expected **23**. Peak (ii) gave a mass spectrum identical with that of **3** either obtained by treatment of the above mixture with DDQ or isolated from *M. gale* [3]. Peak (iv) was readily identified as 1,5-diphenylpentan-3-one (**25**) from its mass spectrum. The mass spectrum of peak (iii) was more complex and showed prominent ions at *m/e* 254, 163 and 91. It would appear that DDQ treatment of this mixture oxidized the other components of the mixture and facilitated the isolation of **3**, which was then homogeneous by GLC. On storage **3** crystallized and after recrystallization from petrol had mp 80°. Nevertheless, in all other respects it was identical with the oil isolated from *M. gale* [3, 9].



Scheme 3

EXPERIMENTAL

Unless otherwise stated UV spectra were recorded in EtOH, IR spectra as thin films or Nujol mulls and PMR at 60 MHz. TLC was carried out on 0.25 mm thick plates of Kieselgel PF_{254} R_fs are quoted for the solvent system petrol (bp 60–80°)–EtOAc–HCO_2H (69:30:1). Elsewhere petrol bp 40–60° was used. Mps are uncorrected.

Attempted synthesis of 2-cinnamoyl-4,4,6-trimethylcyclohexane-1,3,5-trione (**7**). A soln of 2-acetyl-4,4,6-trimethylcyclohexane-1,3,5-trione (**6**) [10, 15] (1 g) in benzaldehyde (1 g) containing piperidine (2 drops) was heated on a steam bath for 30 min; TLC indicated that no reaction had occurred. When the excess benzaldehyde was distilled off at 20 mm pressure the residue obtained was triturated with Et_2O to give 3-benzylidene-3,4,6,7-tetrahydro-3-hydroxy-6,6,8-trimethyl-2-phenyl-2H-benzopyran-4,7-dione (**10**) as yellow prisms from cyclohexane mp 139–140° (Found: C, 77.4; H, 5.6; M^+, 386.1498. $C_{25}H_{22}O_4$ requires: C, 77.7; H, 5.75%; M, 385.1518); ν_{max} (CCl_4) 3100, 3000, 2950, 2880, 1660, 1616, 1570, 1505, 1470, 1450, 1385, 1370, 1350, 1260, 1135, 1080, 1065, 1030, 1000, 965, 930, 910, and 690 cm^{-1}, PMR δ (CCl_4) 1.12 (3H, *s*, 6-Me), 1.28 (3H, *s*, 6-Me), 1.85 (3H, *s*, 8-Me), 6.50 (1H, *s*, 2-H), 7.28 (*s*) and 7.36 (*s*) (10H, 10 × ArH), 7.88 (1H, *s*, =CHPh), 15.30 (1H, *s*, chelated OH) [13].

2,2,6-*Trimethyl*-4-(3-*phenylpropionyl*)*cyclohexane*-1,3,5-*trione* (**2**) (*General Friedel-Crafts procedure*). A mixture of 2,2,4-trimethylcyclohexane-1,3,5-trione (**12**) [14] (1 g) and dry $AlCl_3$ (7 g) in CS_2 (10 ml) was stirred for 30 min, nitrobenzene (6 ml) was added, and the mixture heated under reflux for a further 30 min. To the boiling soln 3-phenylpropionyl chloride (3 g) in nitrobenzene (4 ml) was added over 30 min and heating was then continued for 1 hr. The mixture was decomposed with ice-H_2O and CS_2 and nitrobenzene removed by steam distillation. Recrystallization of the oily residue from aq. MeOH gave **2** as pale yellow cryst. mp 142°, undepressed on admixture with the natural product, yield 2.2 g 41%, R_f 0.3, (Found: C, 71.8; H, 6.7. $C_{18}H_{20}O_4$ requires: C, 72,0; H, 6.7%). λ_{max} nm (ε) 353 (20400) with NaOH 353 (21300); ν_{max} 1670, 1575, 1520, 1328, 1260, 1165, 1035, 998, 750 and 700 cm^{-1}; PMR δ (CD_3OD) 1.33 (6H, *s*, CMe_2), 1.80 (3H, *s*, =CMe), 2.95 and 3.30 (4H, A_2B_2, $ArCH_2CH_2CO$), 7.18 (5H, *s*, ArH).

2,2,4,4-*Tetramethyl*-4-(3-*phenylpropionyl*)*cyclohexane*-1,3,5-*trione* (*Grandiflorone*) (**14**). To a soln of Na (1.4 g) in MeOH (40 ml) was added β-phenylphloropropiophenone (13) [24] (2.0 g) and MeI (17 g) and the mixture set aside at room temp. for 5 days. After the removal of solvent, H_2O was added, the mixture acidified to congo red and extracted with Et_2O. The ethereal extract was then extracted into a soln of $KHCO_3$, which after acidification and extraction into C_6H_6 gave grandiflorone (**14**) as pale yellow needles from aq. MeOH, yield 0.25 g 10%, mp 31°, lit. [16] 32° R_f 0.60 (Found: C, 72.5; H, 7.0. Calc. for $C_{19}H_{22}O_4$: C, 72.6, H, 7.1%) λ_{max} nm (ε) 278 (26900), with NaOH 276 (27800); ν_{max} 3030, 2985, 2940, 1722, 1670, 1570, 1380, 1215, 1050, 965, 840, 745, and 700 cm^{-1}; PMR δ(CCl_4) 1.23 (6H, *s*, CMe_2), 1.43 (6H, *s*, CMe_2), 2.97 and 3.28 (4H, A_2B_2, $ArCH_2CH_2CO$), 7.20 (5H, *s*, ArH).

2′-*Hydroxy*,4′,6′-*dimethoxy*-3′-*methyldihydrochalcone* (**5**). β-Phenylphloropropiophenone (3.1 g), MeI (8 ml) and K_2CO_3 (6 g) in Me_2CO (40 ml) were heated under reflux for 5 hr. After filtration **5** crystallized from the filtrate as white needles, yield 0.6 g 17%, mp 148° lit. [8] 146–147°, R_f 0.40 (Found: C, 71.9; H, 6.7. $C_{18}H_{20}O_4$ requires: C, 72.0; H, 6.7%) λ_{max} nm (ε) 291 (23300); ν_{max} 1632, 1596, 1292, 1280, 1230, 1210, 1130, 790, and 695 cm^{-1}; PMR δ ($CDCl_3$) 2.02 (3H, *s*, ArMe) 2.90 and 3.25 (4H, A_2B_2, $ArCH_2CH_2CO$) 3.90 (6H, *s*, 2 × OMe), 6.02 (1H, *s*, ArH), 7.32 (5H, *s*, ArH).

2′,4′,6′-*Trihydroxy*-3′,5′-*dimethyldihydrochalcone* (**17**). By the general Friedel-Crafts procedure, 1,3-dimethylphloroglucinol (**16**) [25] (7.0 g) was condensed with β-phenylpropionyl chloride (7.6 g). After steam distillation the residue was extracted with Et_2O and the ethereal extract chromatographed on Si gel. Elution with Et_2O–petrol (1:1) gave **17** as pale yellow needles from cyclohexane, yield 1.2 g 9%, mp 125° R_f 0.25 (Found: C, 71.2; H, 6.3 $C_{17}H_{18}O_4$ requires: C, 71.3; H, 6.3%). λ_{max} nm (ε) 296 (17200), with NaOH 338 (20900); ν_{max} 3580, 1640, 1582, 1250, 1195, 1128, 895, 758, 718, and 700 cm^{-1}; PMR δ ($CDCl_3$) 2.07 (6H, *s*, 2 × ArMe), 3.08 and 3.42 (4H, A_2B_2, $ArCH_2CH_2CO$) 7.20 (5H, *s*, ArH), 9.67 (*s*, OH).

2′,4′,6′-*Trihydroxy*-3′-*methyldihydrochalcone* (**18**). In a similar manner methylphloroglucinol (8 g) gave **18** as light brown cryst. from MeOH, yield 9.0 g 58%, mp 175° R_f 0.2 (Found: C, 70.4; H, 5.9. $C_{16}H_{16}O_4$ requires: C, 70.6; H, 5.9%). λ_{max} nm (ε) 293 (18700), with NaOH 329 (23300); ν_{max} 3360, 1622, 1607, 1568, 1335, 1278, 1215, 1141, 1095, and 820 cm^{-1}; PMR δ($(CD_3)_2CO$) 2.0 (3H, *s*, ArMe), 3.05 and 3.40 (4H, A_2B_2, CH_2CH_2), 6.05 (1H, *s*, ArH), 7.22 (5H, *s*, ArH_5).

2′,6′-*Dihydroxy*-4′-*methoxy*-3′,5′-*dimethyldihydrochalcone* (**1**). A soln of **17** (1 g) in Et_2O (3 ml) was mixed with toluene (10 ml) dimethyl sulphate (0.5 g) and $KHCO_3$ (1.5 g). The mixture was heated under reflux for 24 hr, a further portion of Me_2SO_4 (0.5 g) added and heating continued for a further 24 hr. Concn to 5 ml and cooling to 0° gave **1** as yellow needles from cyclohexane, identical with compound from *M. gale*, yield 0.3 g 29%, mp 121° lit. [3] 116–117° R_f 0.4 (Found: C, 71.6; H, 6.7. $C_{18}H_{20}O_4$ requires: C, 72.0; H, 6.7%). λ_{max} nm (ε) 280 (16400), with NaOH 296 (12500); ν_{max} 3420, 1622, 1598, 1308, 1198, 1125 cm^{-1}; PMR δ ($CDCl_3$) 2.10 (6H, *s*, 2 × ArMe), 3.05 and 3.40 (4H, A_2B_2, $ArCH_2CH_2CO$—), 3.71 (3H, *s*, OMe), 7.30 (5H, *s*, ArH), 9.48 (2H, *s*, OH).

2,4-*Dimethylcyclopentane*-1,3-*dione* (**19**). To a soln of $AlCl_3$ (200 g) in dry nitrobenzene (200 ml) methylsuccinic acid (66 g) was added in small portions while cooling to room temp. Propionyl chloride (140 g) was added and the mixture heated at 80° for 3 hr. After cooling the mixture was poured on to ice (400 g) and stored overnight in an ice chest. The solid was recovered by filtration and washed with 10% NaCl soln and toluene. Recrystallization from water gave **19** as white prisms (26 g, 41%), mp 132° (Found: C, 66.6; H, 8.0. $C_7H_{10}O_2$ requires: C, 66.7; H, 8.0%). λ_{max} nm (ε) 271 (15000); ν_{max} 1575, 1350, 1260, 1120, 1080, 920, 703 cm^{-1}; PMR δ ($CDCl_3$) 1.25 (3H, *d*, J = 6 Hz, CHMe), 1.70 (3H, *s*, =CMe), 2.5 (3H, *m*, 4, 4, 5-H), 11.64 (1H, *s*, OH).

2,2,4-*Trimethylcyclopentane*-1,3-*dione* (**20**). A mixture of **19** (22.4 g) KOH (10 g), and CH_3I (27 g) in dioxan (150 ml) and H_2O (50 ml) was heated under reflux for 5 hr and KOH (4 g), CH_3I (10.5 g) in dioxan (30 ml) water (10 ml) added. After a further 3.5 hr heating further aliquots of KOH and CH_3I were added and heating was continued for a further 5 hr. Extraction with Et_2O gave an oil which was heated to boiling with 10% HCl (100 ml), cooled and neutralized with an excess of 10% Na_2CO_3 soln. Extraction with $CHCl_3$ and distillation gave 2,2,4-trimethylcyclopentane-1,3-dione (**20**) as a yellow oil (14.5 g 58%) bp 54°/1 mm, n_D^{20} 1.4519 (Found: C, 68.4; H, 8.6. $C_8H_{12}O_2$ requires: C, 68.6; H, 8.6%). λ_{max} nm (ε) 229 (20600) with NaOH 228 (26300) ν_{max} 1767, 1727, 1461, 1379, 1281, 1100 cm^{-1}; PMR δ (CCl_4) 1.12 (6H, *s*, CMe_2), 1.30 (3H, *d*, J = 6.8 Hz, CHMe), 7.65 (1H, *m*, CHMe), 2.80 (2H, *d*, J = 7 Hz, $CHCH_2$).

2,2,4-*Trimethylcyclopent*-4-*ene*-1,3-*dione* (**21**). A soln of **20** (14.5 g) and *N*-bromosuccinimide (18.2 g) in CCl_4 (300 ml) was heated with a 100 watt incandescent bulb for 4 hr. After cooling and filtration the filtrate was washed with $NaHCO_3$ soln, dried, and evapd. Fractional distillation gave **21** (11.2 g 78%) bp 46–48° 0.7 mm, lit. [20] 75°/8 mm, n_D^{23} 1.4762 (Found: C, 69.2; H, 7.5. Calc. for $C_8H_{10}O_2$: C, 69.5; H, 7.3%) λ_{max} nm (ε) 231 (13270) and 272 (11280) with NaOH 231 (13800) and 272 (11400); ν_{max} 1745, 1710, 1620, 1465, 1381, 1320, 1288, 1168, 1130, 900 cm^{-1}; PMR CCl_4) 1.09 (6H, *s*, CMe_2), 2.08 (3H, *d*, J = 2 Hz, =CHMe), 6.82 (1H, *br*, =CH).

5-*Acetyl*-2,2,4-*trimethylcyclopentane*-1,3-*dione* (**22**). A mixture of **20** (5.7 g), Ac_2O (8 ml) and $BF_3.CH_3COOH$ complex (20 ml) was stirred for 1 hr at 0° and then 4 hr at room temp. A soln of NaOAc (27 g) in H_2O (30 ml) was added and the mixture heated at 100°for 1 hr. After cooling the mixture was extracted with petrol and the extract washed with a saturated soln of $NaHCO_3$, dried and evapd. Fractional distillation gave **22**

(4.5 g 61%) bp 96°/3 mm (Found: C, 66.2; H, 7.8. $C_{10}H_{14}O_3$ requires: C, 65.9; H, 7.7%).

2,2,5-*Trimethyl-3-morpholinocyclopent-3-en-1-one* (**24**). A soln of **20** (8.6 g), morpholine (8 ml), toluene-4-sulphonic acid (0.1 g) in toluene (20 ml) was heated under reflux with a Dean and Stark adaptor until no further H_2O separated. Fractional distillation gave the enamine **24** (8.6 g 66%) bp 106°/1.3 mm (Found: C, 68.7; H, 9.0; N, 6.5 $C_{12}H_{19}NO_2$ requires: C, 68.9; H, 9.2; N, 6.7%) $\lambda_{max}^{Cyclohexane}$ nm (ε) 278 (10 500); ν_{max} 2970, 2855, 1745, 1610, 1450, 1310, 1121, 1038, 888 cm^{-1}; PMR δ (CCl_4) 1.10 (3H, *d*, J = 7 Hz, CHMe), 1.18 (6H, *s*, CMe_2), 2.50 (1H, *m*, CHMe), 2.90 (4H, *t*, J = 6 Hz, 2 × NCH_2—), 3.08 (4H, *t*, J = 6 Hz, 2 × OCH_2—), 4.62 (1H, *br*, =CH).

2,2,5 - *Trimethyl* - 4 - (3 - *phenylpropionyl)cyclopent* - 4 - *ene* - 1,3-*dione* (**3**). A soln of 3-phenylpropionyl chloride (22 g) in dry $CHCl_3$ (45 ml) was added slowly to a mixture of **24** (16 g) and triethylamine (12 ml). The mixture was heated for 2 hr on a steam bath, 5N HCl (48 ml) was added, and heating continued for a further 2 hr. After cooling the $CHCl_3$ layer was separated and washed with H_2O. The combined aq. layers were neutralized with 20% NaOH and extracted with $CHCl_3$. The combined $CHCl_3$ layers were dried, evapd and distilled, bp 162°/1 mm, to give a yellow oil (10 g). GC–MS analysis of the oil (5' × 2 mm i.d. glass column of 2.5% OV1 at 180° eluted with 35 ml He/min) gave 4 peaks (retention time): peak I (5.2 min) $M^{\cdot+}$ 256.1464, 254.1308 calc for $C_{17}H_{20}O_2$ 256.1463, calc for $C_{17}H_{18}O_2$ 254.1307; peak II (**3**) (6.0 min) $M^{\cdot+}$ 270.1254, calc for $C_{17}H_{18}O_3$ 270.1256 *m/e* 91, 105, 110, 138, 156, 166, 199, 242, 270; peak III (7.2 min) $M^{\cdot+}$ 254,1308 calc for $C_{17}H_{18}O_2$ 254.1307 *m/e* 91, 105, 163, 211, 239, 254; peak IV (**25**) (8.4 min) $M^{\cdot+}$ 238.1356 calc for $C_{17}H_{18}O$ 238.1358 *m/e* 91, 105, 133, 238. The oil (8 g) and DDQ (8 g) in C_6H_6 (300 ml) were heated under reflux for 15 hr. After filtration the filtrate was evapd and the residue chromatographed on Si gel. Elution with C_6H_6 petrol (1:1) gave **3**, bp 175–180°/4 mm. On storage at 0° the oil crystallized and recrystallization from petrol gave **3** as yellow prisms (1.2 g, 8%) mp 80° (Found: C, 75.6; H, 6.6%; $M^{\cdot+}$ 270.1250. $C_{17}H_{18}O_3$ requires: C, 75.5; H, 6.7%; $M^{\cdot+}$ 270.1256) otherwise identical with the oil isolated from *M. gale* [9].

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