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SYNTHETIC STUDIES OF JASMININ[1]

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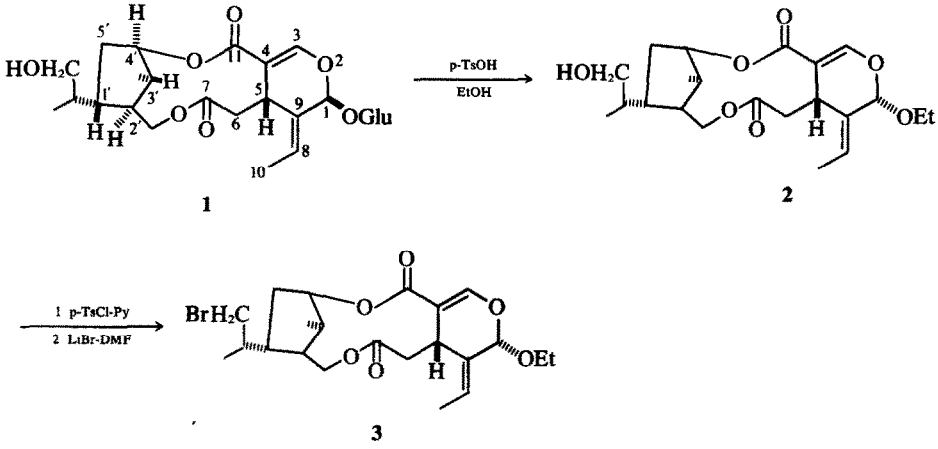
Abstract—The synthesis of the methyl ester hexaacetate **4** is described. This synthesis constitutes an unambiguous proof of the structure of jasminin **1**.

In a previous publication[2] we described the structure of jasminin **1**, the bitter principle isolated from *Jasminium primulinum* Hemsl. The structure of jasminin was inferred from that of aglycone ethyl ether **2** which was obtained by means of ethanolysis of jasminin. Final structure determination of **2** was accomplished by the x-ray crystal analysis[3] of the bromide **3**, obtained by the sequence of reactions shown in the Scheme 1.



1 **2** **3**

SCHEME 1

Though the structure of **2** was confirmed by the X-ray method, the structure of jasminin itself was once questioned because of the possibility of skeletal transformation during ethanolysis. The reactivities of **1** contrast with that of **2**. The lactones of **1** were easily cleaved but those of **2** were only partially cleaved even under forcing conditions. Epoxidation of the double bond of **1** was easy but that of **2** was difficult. Furthermore, the inertness of the primary OH group of jasminin tetraacetate, which was obtained by acetylation, was also inexplicable.[2] Considering the unique structure, reactions and biogenesis, we report here the synthetic confirmation of the structure of jasminin.

Mild alkaline hydrolysis (0·5 N NaOH, 30°, 3 h) of jasminin followed by methylation and acetylation gave the methyl ester hexaacetate **4**. To confirm the structure of jasminin, it was planned to obtain the methyl ester hexaacetate **4**, by direct esterification of the iridane alcohol **6** and the seco-iridoid carboxylic acid **7**.

Synthesis of the iridane alcohol **6**. Our initial goal was the construction of hydroxy carboxylic acid **9**, which would serve as the immediate procursor of **6**, from easily available terpene. The first solution to this problem involved a Favorskii rearrangement of (+)-carvone monoepoxide **8**.[4] Thus, oxidation of l-carvone with alkaline hydrogen peroxide gave (+)-carvone monoepoxide **8**,[4] which upon treatment with sodium ethoxide yielded two hydroxy acids **9** (20%) and **10** (2%), and 6-hydroxycarvone **11** (23%).

The hydroxy acid **9** showed NMR signals for a secondary Me group[δ 1·10 (3 H, d, J 6 Hz), δ 2·15 (1 H, m)], an isopropenyl group[δ 1·72 (3 H, s), δ 4·72 (2 H, m)], a secondary OH group[δ 3·75 (1 H,

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ddd, J 5, 6 and 6 Hz, H_3)], two methine protons [δ 3·06 (1 H, ddd, J 7, 9 and 10 Hz, H_5), δ 2·21 (1 H, dd, J 7 and 10 Hz, H_1)] and methylene protons [δ 1·85 (2 H, m, H_4 and $H_{4'}$)]. These NMR assignments were supported by decoupling experiments. Irradiation of the C-2 proton located at δ 2·15 collapsed the C-2 Me signal to a singlet and simultaneously collapsed the quartet pattern for C-3 proton to a triplet (J = 5 Hz). Subsequent irradiation of the centre of two C-4 protons at δ 1·85 collapsed the C-3 proton signal to a doublet (J = 6 Hz) and the C-5 proton to a doublet (J = 10 Hz). In the reverse experiment, irradiation of the C-1 proton reduced the H-5 to a double-doublets (J = 7 and 9 Hz). From these results, the coupling constants were determined as follows: $J_{3,4\alpha} = J_{3,4\beta}$ = 5 Hz, J_{23} = 6 Hz. A molecular model shows that if it takes an envelope form and the secondary OH group takes *quasi-axial* conformation, the dihedral angles between H-2 and H-3, H-3 and H-4α, and H-3 and H-4β are about 60°. This requires coupling constants of *ca* 6 Hz. The IR spectrum shows a strong H-bonding (ν_{max} 3260 and 1670 cm^{-1}). The stereochemistry was further demonstrated unambiguously by the following transformation.

The methyl ester **12** was hydrogenated and after oxidation with Jones' reagent gave the keto ester **14**. The same compound was derived from the stereochemically established tosylate **15** by the following sequence of reagents: (a) LAH, (b) Jones' reagent and (c) CH_2N_2 (Scheme 2). The keto esters derived from both routes are identical with respect to IR spectra, mp's, optical rotations and ORD curves.

The configuration of the secondary OH group was confirmed by the transformation shown in the Scheme 2. The derived diacetates **16** both from **15** and from **12** are identical in all respects. The hydroxy acid **9** was probably formed via an intermediate **17** followed by the cleavage at a.[5]

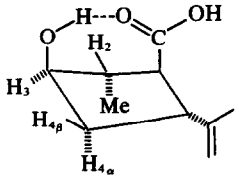
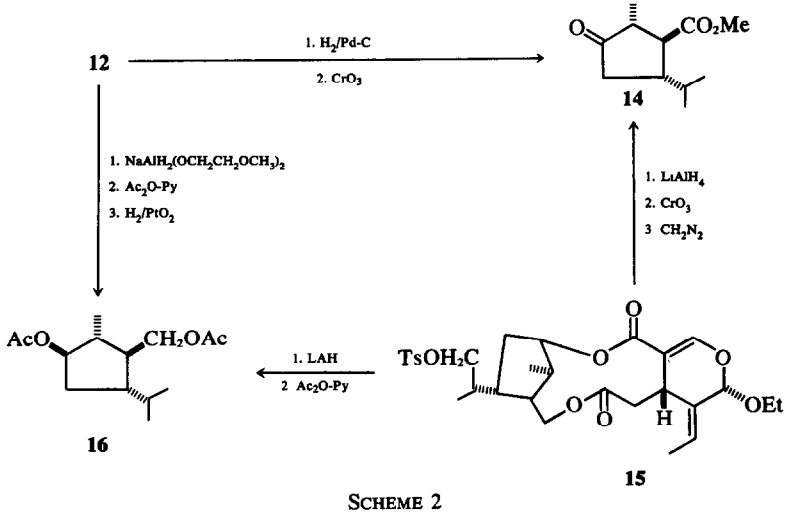


Fig 1.

The second product of a Favorskii rearrangement was an oil which on methylation gave a monomethyl ester **13**. The NMR signals of **13** show the presence of a quaternary Me group [δ 1·23 (3 H, s)], an isopropenyl group [δ 1.72 (3 H, s), δ 4·63 (2 H, m)] and a secondary OH group [δ 3·87 (1 H, t, J 4 Hz), δ 3·65 (1 H, s, exchangeable with D_2O)]. These spectroscopic properties coupled with the results of NMDR experiments are consistent with the structure **13**. This compound presumably formed via the intermediate **17** with the cleavage at b.

The third product was found to be 6-hydroxycarvone on the basis of physical data. And the structure was confirmed by the following transformation. Methylation of **11** with diazomethane, reduction with sodium bis-(2-methoxyethoxy)aluminium hydride followed by acid treatment gave DL-carvone.

Having established the stereospecific construction of the iridane skeleton, we turned our attention to the synthesis of the diacetate **6**. Jones' oxidation of the hydroxy ester **12** gave the keto ester **18**. The keto ester **18** was transformed, employing the following sequence of reactions: (a) ketalisation, (b) hydroboration-oxidation, (c) deketalisation with aqueous acetic acid and (d) acetylation, into the keto diacetate **19** as an inseparable mixture of epimers. Reduction of **19** with sodium borohydride gave a mixture of alcohols **6**, $[\alpha]_D$ −11·2 and **20**, $[\alpha]_D$ +30·3°. In both physical properties,

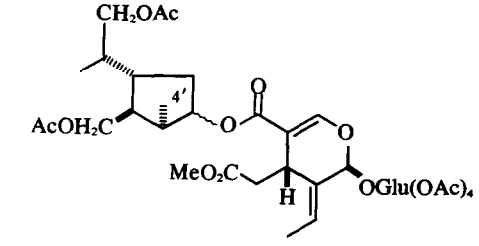


SCHEME 2

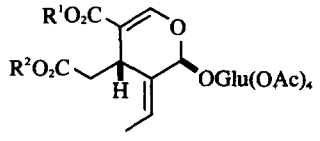
except optical rotations, are very similar. Acetylation of the (−)-alcohol **6** gave the triacetate **21**, which was identical with the triacetate (IR, VPC, $[\alpha]_D$) derived from **2** by reduction with LAH followed by acetylation. The triacetate **21** was also obtained from the hydroxy ester **12** by hydroboration, oxidation and acetylation.

Synthesis of the secoiridoid **7**. Recently it has been demonstrated that loganin **22** is the key intermediate for the biosynthesis of seco-iridoids and indole alkaloids.[6] In this connection, many useful syntheses of loganin have been reported.[7] Since the derivation of the seco-iridoid **23** from loganin **22** has been reported,[8] the seco-iridoid **23** has been formally synthesised. Because of the long reaction sequence and very low yield, the utilization of jasminin as a source of the seco-iridoid **7** was considered. When jasminin was treated with 0·5 N NaOH at 30° for 18 h followed by acetylation with acetic anhydride, the anhydride **24** was obtained in 70% yield. The anhydride (ν_{max} 1815 and 1750 cm^{-1}) showed NMR signals at δ 1·82 (3 H, *J* 2 and 7 Hz), 2·67 (1 H, dd, *J* 14 and 16 Hz, $H_{6\alpha}$), 3·37 (1 H, dd, *J* 5 and 16 Hz, $H_{6\beta}$), 3·64 (1 H, m, H_5), 5·52 (1 H, s, H_1), 6·00 (1 H, dq, *J* 2 and 7 Hz, H_8) and 7·70 (1 H, d, *J* 2 Hz, H_3). These assignments were confirmed by NMDR experiments.

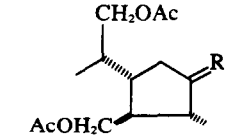
Hydrolysis of **24** gave the dicarboxylic acid **25**,

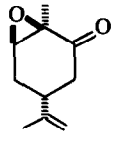


4: $H_{4'}\alpha$
27: $H_{4'}\beta$



7: $R^1 = H$, $R^2 = CH_3$
23: $R^1 = R^2 = CH_3$
25: $R^1 = R^2 = H$





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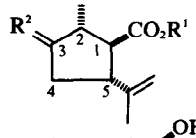
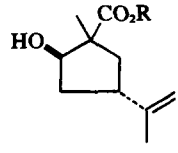
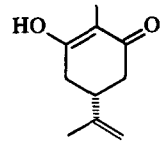


9: $R^1 = H$, $R^2 = \overset{OH}{\underset{H}{\diagup\!\!\diagdown}}$
12: $R^1 = CH_3$, $R^2 = \overset{OH}{\underset{H}{\diagup\!\!\diagdown}}$
18: $R^1 = CH_3$, $R^2 = O$

6: $R = \overset{OH}{\underset{H}{\diagup\!\!\diagdown}}$
19: R = O
20: $R = \overset{H}{\underset{OH}{\diagup\!\!\diagdown}}$
21: $R = \overset{OAc}{\underset{H}{\diagup\!\!\diagdown}}$
26: $R = \overset{OTs}{\underset{H}{\diagup\!\!\diagdown}}$
28: $R = \overset{H}{\underset{OTs}{\diagup\!\!\diagdown}}$



10: R = H
13: $R = CH_3$



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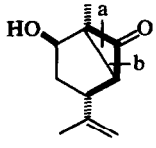

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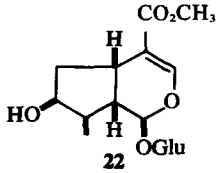

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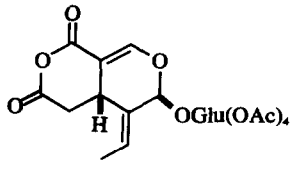
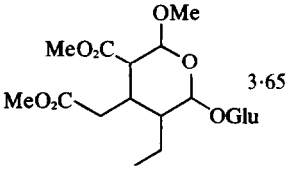
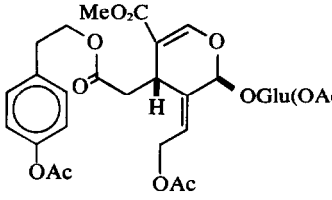
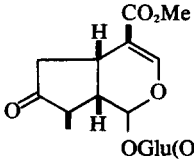


24

Fig 2.

which on treatment with phosgene regenerated **24**. Heating the anhydride **24** in methanol gave the half ester **7**. Esterification of the C-11 carboxylic group rather than C-7 was inferred from the chemical shifts of carbomethoxy groups (Table 1).

Table 1. Chemical shifts in $CDCl_3$

Compounds	$-C_{(7)}O_2Me$	$-C_{(11)}O_2Me$	Ref
7	3·60		
23	3·62	3·73	
	3·65		2
		3·70	9
		3·70	10

Synthesis of the methyl ester hexaaceta **4**. With the alcohols **6** and **20**, and the secoiridoid **7** in hand, our efforts were directed toward condensation of the both components. As all attempts at direct esterification [DCC, $(CF_3CO)_2O$, $COCl_2$, $SOCl_2$ etc.] failed, the (−)-alcohol **6** was converted into the tosylate **26**, which was treated with the sodium salt of the half-ester **7** in DMF to give the methyl ester hexaacetate **27**. The IR spectrum of **27** was superimposable on that of **4**, however, the Me signals in the NMR spectrum were different. Thus, the tosylate of (+)-alcohol **28** was treated with the sodium salt of **7** in DMF to give the crystalline methyl ester hexaacetate, identical in all respects with the compound **4** derived from jasminin (mp. mixed mp, IR, NMR).

Although the many attempts to convert **4** into jasminin were unsuccessful, this synthesis constitutes an unambiguous proof of the structure of jasminin.

EXPERIMENTAL

M.ps and b.ps were uncorrected. IR spectra were taken on a Japan Spectroscopic IRA-I spectrometer. NMR spectra were recorded on a JEOL PS-100 spectrometer, using TMS as internal standard. Optical rotations were determined in $CHCl_3$ on a Rex Optical Works NEP-2 phtoelectric polarimeter. Silica gel (Merck) was used for column chromatography, and silica gel GF_{254} (Merck) was used for TLC.

Favorskii rearrangement of (+)-carvone monoepoxide **8**. (+)-Carvone monoepoxide[4] **8** (16·6 g) was heated in a sodium ethoxide soln (prepared from 11·5 g of Na in 250 ml of abs EtOH) at 80° for 2 h. After removal of the solvent under reduced pressure, the residue was diluted with water and extracted with ether. The aqueous phase was acidified with conc HCl. The precipitated **11** was filtered off (4·4 g), and the filtrate was extracted with light petroleum and subsequently with ether. The light petroleum extract was washed with brine and dried. Removal of the solvent gave an oil (0·9 g), which was methylated with diazomethane. The crude product was purified by chromatography on silicic acid and eleution with benzene-EtOAc (95:5) afforded **13**, b.p. 90°/0·1 mm Hg, ν_{max} (liquid film) 3400, 1720, 1640, 1140 and 890 cm^{-1}, MS *m/e* 180 ($M^+ - 18$).

The ether extract gave a crystalline residue which was recrystallised from ether–light petroleum to give **9**, m.p. 127°, ν_{max} (Nujol) 3260, 2520, 1670 and 900 cm^{-1}, $[\alpha]_D$ −57·8° (*c* = 1·23), (Found: C, 65·39; H, 8·81. $C_{10}H_{16}O_3$ requires: C, 65·19; H, 8·75%).

Treatment of **9** with diazomethane gave **12**, b.p. 81–82°/0·15 mm Hg, $[\alpha]_D$ − 26·2° (*c* = 1·26), ν_{max} ($CHCl_3$) 3450, 1735, 1640 and 890 cm^{-1}, δ 1·15 (3 H, d, *J* 6 Hz), 1·76 (3 H, s), 2·75 (1 H, S, exchangeable with D_2O), 3·77 (3 H, s) and 4·84 (2 H, m). The methyl ester **12** was hydrolysed with N NaOH to give **9**.

Methyl 5-isopropenyl-2-methyl-3-oxocyclopentane-carboxylate **18**. A soln of the hydroxy ester **12** (2 g) in acetone (30 ml) was treated with slight excess of Jones' reagent at 0°. The soln was diluted with water, then extracted with ether. The ethereal extracts were combined, washed with brine, dried and concentrated to give **18** (1·77 g), b.p. 71°/0·2 mm Hg, m.p. 42–42·5°, $[\alpha]_D$ −117·9° (*c* = 1·50), ν_{max} ($CHCl_3$) 1740, 1730, 1640 and 895 cm^{-1}, δ 1·13 (3 H, d, *J* 6 Hz), 1·75 (3 H, s), 3·74 (3 H, s) and 4·85 (2 H, m) ORD (MeOH), $[\phi]_{400}$ − 1300, $[\phi]_{320}$ −8590, $[\phi]_{310}$ − 9150, $[\phi]_{270}$ + 10150, $[\phi]_{230}$ + 5790, and a = −194. (Found: C, 67·43; H, 8·26. $C_{11}H_{16}O_3$ requires: C, 67·32; H, 8·22%).

The ester **18** (588 mg) in MeOH (25 ml) was treated with $NaBH_4$ (228 mg) for 1 h at room temp. The mixture was diluted with water and extracted with ether. The extract was washed with brine, dried and evaporated to give **12** (540 mg).

Methyl 5-isopropyl-2-methyl-3-oxocyclopentane-carboxylate **14**. The ester **12** (233 mg) in EtOH (20 ml) was hydrogenated over 10% Pd-C (45 mg) in H_2 atmosphere for 4 h. The crude product in acetone (15 ml) was treated with a slight excess of Jones' reagent at 0° for 5 min. The mixture was diluted with water and extracted with ether. The extract was washed successivly with $NaHCO_3$ aq and brine and dried. The resulting ester **14** (238 mg) crystallised from pentane as needles, m.p. 53°, $[\alpha]_D$ − 141·5° (*c* = 1·16), ORD (MeOH) $[\phi]_{400}$ − 1092, $[\phi]_{320}$ − 7862, $[\phi]_{310}$ − 8480, $[\phi]_{270}$ + 9354, $[\phi]_{230}$ + 5920, a = 179. The IR spectrum and ORD curve were superimposable with those of the corresponding keto ester[2] derived from jasminin.

3 - Hydroxy - 5 - isopropyl - 2 - methylcyclopentanemethanol diacetate **16**. A soln of 70% $NaAlH_2$

$(OCH_2CH_2OCH_3)_2$ (3·5 ml) in dry benzene (10 ml) was added dropwise to a stirred soln of **12** (1 g) in benzene (10 ml) and the mixture was refluxed for 4 h. After cooling, the excess of the reagent was decomposed with 10% H_2SO_4 (20 ml). The mixture was extracted with benzene, and the extract was dried over K_2CO_3. Removal of the solvent gave the crystalline material (842 mg), m.p. 58–60° (from ether–light petroleum), $[\alpha]_D$ − 29·5° (c = 1·24), ν_{max} (Nujol) 3300, 1640, 1095 and 890 cm^{-1}, δ 1·04 (3 H, d, J 6 Hz), 1·72 (3 H, s), 2·77 (1 H, dd, J 9 and 9 Hz), 3·22 (2 H, s, exchangeable with D_2O), 3·62 (2 H, d, J 4 Hz), 3·80 (1 H, dd, J 4 and 4 Hz) and 4·73 (2 H, m). (Found: C, 70·24; H, 10·65. $C_{18}H_{18}O_2$ requires: C, 70·54; H, 10·66%). Acetylation gave a diacetate. The crude diacetate in EtOH (20 ml) was hydrogenated over PtO_2 (110 mg) under an atmosphere of H_2 for 3 h. The product was chromatographed on silicic acid. Elution with light petroleum–EtOAc (97:3) gave **16**, b.p. 81–82°/0·2 mm Hg, (583 mg), $[\alpha]_D$ − 49·6° (c = 1·27), ν_{max} ($CHCl_3$) 2980, 1735, 1460 and 1230 cm^{-1}. The Ir spectrum was identical with that of the corresponding diacetate[2] derived from jasminin.

4 - *Hydroxy* - 2 - *hydroxymethyl* - 3,β - *dimethylcyclopentaneethanol triacetate* **21**. The ester **12** (2 g) was treated with diborane and oxidised as before. The mixture was continuously extracted with ether. The extract was dried and evaporated to give a viscous oil (1·23 g). Acetylation gave **21** (1·26 g), b.p. 126°/0·18 mm Hg, $[\alpha]_D$ − 22·5° (c = 1·52), ν_{max} ($CHCl_3$) 2980 and 1730 cm^{-1}, δ 0·98 (3 H, d, J 6 Hz), 1·01 (3 H, d, J 6·5 Hz), 1·98, 2·08 (9 H, each s), 3·96 (4 H, m). (Found: C, 61·05; H, 8·50. $C_{16}H_{26}O_6$ requires: C, 61·13; H, 8·34%). The IR spectrum, optical rotation and the retention time of VPC were identical with that of the corresponding triacetate[2] derived from jasminin.

2 - *Acetoxymethyl* - 4 - *hydroxy* - 3,β - *dimethylcyclopentaneethanol acetate* **6** *and* **20**. A mixture of **18** (4·4 g), ethylene glycol (10 ml), p-TsOH (60 mg) and benzene (250 ml) was refluxed under a Dean-Stark water separator for 20 h. After cooling, the benzene layer was separated and washed with $NaHCO_3$ aq and brine and dried. Removal of the solvent gave a ketal, b.p. 85–86°/0·2 mm Hg.

The above ketal (3 g) was treated with disborane and oxidised as before. The crude product was deketalised by refluxing with 80% aqueous AcOh (20 ml) for 1 h. A viscous oil obtained after removal of the solvent under reduced pressure was acetylated by the usual manner. The crude product was chromatographed on silicic acid. Elution with benzene–EtOAc (9:1) afforded **19** (1·5 g), b.p. 119·5–120°/0·08 mm Hg ν_{max} (liquid film) 1740 cm^{-1}, δ 1·00 (3 H, d, J 7 Hz) 1·11 (3 H, d, J 7 Hz), 2·00 (3 H, s) and 2·04 (3 H, s), $[\alpha]_D$ + 17·4° (c = 1·21).

The diacetate **19** (702 mg) in MeOH (15 ml) was treated with $NaBH_4$ (40 mg) for 1·5 h at room temp. After neutralisation with dil HCl, the mixture was extracted with $CHCl_3$. The extract was washed with sat brine and dried. An oil obtained after removal of the solvent was chromatographed on silicic acid. Elution with $CHCl_3$–MeOH (99:1) gave two epimeric alcohols **6** (372 mg) and **20** (183 mg). The (+)-alcohol **29**, $[\alpha]_D$ + 30·3° (c = 1·02), ν_{max} ($CHCl_3$) 3500, 1730, 1240, 1070, 1030 and 980 cm^{-1}, δ 0·97 (3 H, d, J 6 Hz), 1·00 (3 H, d, J 6 Hz), 1·99 (6 H, s) and 2·10 (1 H, br s, exchangeable with D_2O).

The (−)-alcohol **6**, b.p. 137°/0·07 mm Hg, $[\alpha]_D$ − 11·2° (c = 1·02), ν_{max} ($CHCl_3$) 3500, 1730, 1240 and 980 cm^{-1}, δ 0·94 (3 H, d, J 6 Hz), 1·00 (3 H, d, J 6 Hz), 2·00 (6 H, s) and 1·97 (1 H, s, exchangeable with D_2O). The (−)-alcohol **6** was acetylated to give the triacetate **21**. The IR spectrum and the retention time of VPC were identical with those of the corresponding triacetate derived from jasminin.

2 - *Acetoxymethyl* - 3,β - *dimethyl* - 4 - *tosyloxycyclopentaneethanol acetates* **26** *and* **28**. To a soln of the (−)-**6** (248 mg) in dry pyridine (1 ml) at 0° was added p-TsCl (210 mg) and the mixture was kept in a refrigerator overnight. The mixture was poured onto ice and extracted with ether. The extract was washed with dil HCl, $NaHCO_3$ aq, sat brine and dried. The crude product was chromatographed on silicic acid. Elution with $CHCl_3$ gave **26** (246 mg) as a viscous oil, ν_{max} ($CHCl_3$) 1740, 1600, 1190, 1175 and 850 cm^{-1}, δ *n*2·01, 2·02 (6 H, each s), 2·22 (3 H, s)and 7·24 (4 H, m).

The (+)-alcohol **20** was also treated as before to give **28**, ν_{max} 1740, 1600, 1190, 1175, and 850 cm^{-1}, δ 2·01, 2·02 (6 H, each s), 2·22 (3 H, s) and 7·24 (4 H, m).

Partial hydrolysis of jasminin. Jasminin **1** (5 g) was dissolved in 0·5 N NaOH (200 ml) and the soln was allowed to stand at 30° for 3 h. The mixture was acidified with Amberlite IR-120 and concentrated to dryness under reduced pressure. The residue was dissolved in MeOH and treated with diazomethane followed by acetylation gave a gum (8·4 g). Chromatography of the crude product on silicic acid and elution with $CHCl_3$–MeOH (98:2) gave **4** (3·06 g), needles, m.p. 83–85° (from EtOH). ν_{max} ($CHCl_3$) 1740, 1720, 1700, 1690, 1630 and 1220 cm^{-1}, δ 1·01 (3 H, d, J 6·7 Hz), 1·09 (3 H, d, J 6·7 Hz), 1·78 (3 H, dd, J 7·0 and 1·5 Hz), 2·05, 2·10 (18 H, each s), 3·64 (3 H, s), 2·43 (1 H, dd, J 14 and 14 Hz), 2·78 (1 H, dd, J 5 and 14 Hz), 5·72 (1 H, m), 6·05 (1 H, dq, J 1·5 and 7·5 Hz) and 7·49 (1 H, s).

Hydrolysis of jasminin. Jasminin (3 g) was dissolved in 0·5 N NaOH (200 ml) and the mixture was allowed to stand at 30° for 18 h. The mixture was acidified with Amberlite IR-120 and continuously extracted with ether. The aqueous soln was concentrated to dryness under reduced pressure. The residue was acetylated with AC_2O and pyridine. The mixture was poured onto ice and the resulting gum solidified on scratching the wall of the flask. The crude product was recrystallised from chloroform-light petroleum to give **24**, m.p. 190°, ν_{max} (Nujol) 1815, 1750, 1620, 1230, 1060 and 1040 cm^{-1}. (Found: C, 53·03; H, 5,38. $C_{24}H_{28}O_{14}$ requires: C, 53·33; H, 5·22%).

Treatment of **24** (550 mg) with boiling MeOH gave the amorphous **7** (613 mg), ν_{max} ($CHCl_3$) 3400–2400, 1740, 1680, 1630, 1430, 1360, 1240, 1160, 1065, 1035, and 905 cm^{-1}, δ 1·74 (3 H, dd, J 1·5 and 7 Hz), 2·02, 2·06 (12 H, each s), 2·40 (1 H, dd, J 10 and 14 Hz), 2·72 (1 H, dd, J 5 and 14 Hz), 3·60 (3 H, s), 4·30 (1 H, dd, J 5 and 14 Hz), 5·70 (1 H, br s), 6·00 (1 H, dq, J 1·5 and 7 Hz), 7·54 (1 H, s) and 8·10 (1 H, br s).

The anhydride **24** was hydrolysed with water to give **25**, m.p. 190° (from EtOH), ν_{max} (Nujol) 3200–2400, 1750, 1720 and 1635 cm^{-1}, δ 1·62 (3 H, d, J 7 Hz), 2·04, 2·07, (12 H, each s), 2·40 (1 H, dd, J 9 and 15 Hz), 2·86 (1 H, dd, J 4 and 15 Hz), 4·03 (1 H, dd, J 4 and 9 Hz), 5·75 (1 H, br s), 6·05 (1 H, q, J 7 Hz), 7·62 (1 H, s) and 11·13 (2 H, br s). (Found: C, 51·54; H, 5·41. $C_{24}H_{30}O_{15}$ requires: C, 51·61; H, 5·41%).

To a stirred soln of **25** (500 mg) and Et_3N (14 ml) in $CHCl_3$ (20 ml) was added a soln of phosgene (10 g) in benzene (30 ml) at 0° and the stirring was continued for 1 h at the same temp. The mixture was washed with dil HCl, $NaHCO_3$ aq and satd brine and dried. Removal of the solvent gave the anhydride **24**.

The methyl ester hexaacetates **4** *and* **27**. A soln of the sodium salt of **7** in DMF [prepared from **7** (89 mg) in

1·5 ml of dry DMF and sodium hydride (8 mg)] was added to a soln of **28** (66 mg) in DMF (0·5 ml). The mixture was heated at 130° for 24 h under N_2. After cooling, the solvent was removed under reduced pressure and the residue was extracted with ether. The extract was washed with $NaHCO_3$ aq, satd brine and dried. The crude product was chromatographed on silicic acid and elution with $CHCl_3$–MeOH (98:2) gave the methyl ester hexaacetate (30 mg), m.p. 83° (from EtOH), no m.p. depression on admixture with **4**. The IR and NMR spectra were superimposable to that of the authentic sample.

Similarly, the tosylate **26** was condensed with the sodium salt of **7**. The crude product was chromatographed on silicic acid. Elution with $CHCl_3$–MeOH (98:2) gave **27** (52 mg).

REFERENCES

[1]Preliminary communication, Y. Asaka, T. Kamikawa and T. Kubota, *Tetrahedron Letters* 1597 (1972)
[2]T. Kamikawa, K. Inoue, T. Kubota and M. C. Woods, *Tetrahedron* **26**, 4561 (1970)
[3]A. Shimada and M. Fukuyo, *Abstracts of the 22nd Annual Meeting of the Chemical Society of Japan* pp. 60 (1969)
[4]E. Klein, G. Ohloff, *Tetrahedron* **19**, 1091 (1963)
[5]R. B. Loftfield, *J. Am. Chem. Soc.* **72**, 632 (1950)
[6]J. M. Bobbitt, K.-P. Segebarth, *Cyclopentanoid Terpene Derivatives* (Edited by W. I. Taylor and A. R. Battersby) pp. 122. Marcel Dekker, New York (1967); A. I. Scott, *Accounts Chem. Res.* **3**, 151 (1970); H. Inouye, S. Ueda, K. Inoue and Y. Takeda, *Tetrahedron Letters* 4073 (1971); D. V. Banthorpe, B. V. Charlwood and M. J. O. Francis, *Chem. Revs* **72**, 115 (1972)
[7]G. Büchi, J. A. Carlson, J. E. Powell, Jr. and L.-F. Tietze, *J. Am. Chem. Soc.* **95**, 540 (1973); J. F. Partridge, N. K. Chadka and M. R. Uskoković, *Ibid.*, **95**, 532 (1973)
[8]H. Inouye, T. Yoshida, S. Tobita, K. Tanaka and T. Nishida, *Tetrahedron Letters* 2459 (1970)
[9]Y. Asaka, T. Kamikawa, T. Kubota and H. Sakamoto, *Chemistry Letters* 141 (1972)
[10]*Y. Asaka, T. Kamikawa, T. Tokoroyama and T. Kubota, Tetrahedron* **26**, 2365 (1970)