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# A PHENOLIC GLYCOSIDE FROM *PSILOTUM NUDUM* (L) GRISEB

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**Abstract**—A new phenolic β-glucoside has been isolated from *Psilotum nudum* shoots, and given the trivial name psilotin. The latter yields glucose and the aglycone psilotinin on hydrolysis with emulsin. Chemical, IR and PMR studies have established that the aglycone is 6-[4′-hydroxyphenyl]-5,6-dihydro-2-oxo-2H-pyran, and psilotin is 6-[4′-β-D-glucopyranosyloxyphenyl]-5,6-dihydro-2-oxo-2H-pyran. The synthesis of 6-phenyl-5,6-dihydro-2-oxo-2H-pyran enabled the signals for the protons in the αβ-unsaturated δ-lactone moiety of the aglycone to be assigned correctly. Although the aglycone contains an asymmetric center it is *not* optically active. A quinone methide mechanism has been suggested for the biosynthesis of psilotinin.

## INTRODUCTION

ALTHOUGH the Psilotaceae differ morphologically from other living vascular plants, surprisingly little work has been carried out on the chemical constituents of the two genera *Psilotum* and *Tmesipteris*. However, some work has been carried out on the occurrence of auxin,[1] and it is known that *Psilotum* contains syringic and sinapic acids in a combined form.[2] In the present communication, we wish to report the isolation of a new phenolic glucoside (I, R = β-D-glucopyranosyl), 6-[4′-β-D-glucopyranosyloxyphenyl]-5,6-dihydro-2-oxo-2H-pyran, which has been given the trivial name psilotin. The αβ-unsaturated δ-lactone ring of I is present in parasorbic acid (6-methyl-5, 6-dihydro-2-oxo-2H-pyran) which has been isolated from the unripe berries of *Sorbus aucuparia*,[3] and in massoilactone (6-n-amyl-5,6-dihydro-2-oxo-2H-pyran) which occurs in the bark of *Massoia aromatica*.[4] It is believed that lactones of this type may be growth inhibitors.[3]

## DISCUSSION

Psilotin (I, R = β-D-glucopyranosyl) analysed for $C_{17}H_{20}O_8$, and gave an equimolar mixture of glucose and the aglycone psilotinin (I, R = H) on hydrolysis with emulsin. The aglycone ($C_{11}H_{10}O_3$) gave a colour reaction with diazotized *p*-nitroaniline when analysed by paper chromatography, whereas the parent glucoside did not react with this spray reagent or with reagents used to detect reducing sugars. This evidence suggested that psilotinin possessed a free phenolic hydroxyl which was involved in the formation of a β-glucosidic linkage in psilotin.

The presence of a 1,4-disubstituted benzene ring in psilotinin was suggested by the presence of the characteristic aromatic C—H stretching vibration at 3060 $cm^{-1}$ and the C—H out of plane vibration in the IR at 844 $cm^{-1}$ together with the ring skeletal

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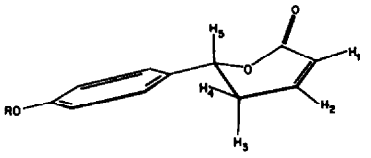
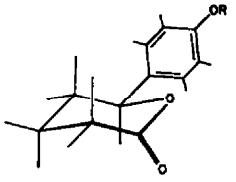
[1] W. P. Jacobs, *Science* **122**, 597 (1955).
[2] R. K. Ibrahim, G. H. N. Towers and R. D. Gibbs, *J. Linn. Soc., Bot.* **58**, 223 (1962).
[3] L. J. Haynes and E. R. H. Jones, *J. Chem. Soc.* 954 (1946).
[4] L. Crombie, *J. Chem. Soc.* 2535 (1955).



I



II

vibrations[5a] at 1616, 1600, 1520 and 1455 $cm^{-1}$. (All spectra were obtained on KBr disks unless specified otherwise.) Furthermore, psilotinin monoacetate (I, R = $CH_3CO$) gave *p*-hydroxybenzoic acid monoacetate, in approximately 80% yield, when oxidized with chromium trioxide in acetic acid containing 2% sulphuric acid. The aromatic acid was converted with diazomethane to the corresponding methyl ester which was subsequently purified and isolated by preparative gas–liquid partition chromatography (GLPC). Since the IR and PMR spectra of this ester were identical to those obtained with an authentic sample of methyl *p*-hydroxybenzoate monoacetate, psilotinin must contain the group *p*-$HOC_6H_5C\equiv$. Characteristic absorption, in the UV ($\lambda\lambda_{max}$ 278 and 280 m$\mu$) for the aglycone[6a] together with PMR data provided supporting evidence for this conclusion. Psilotinin monoacetate gave a typical $A_2B_2$ multiplet[7a] for the four aromatic protons at an average $\tau$ value of 2·78 (see Fig. I) with values of 18·0 c/s for $\delta_{AB}$, 9·0 c/s for $J_{AB}$, and $\approx$1·6 c/s for $J_{AA} = J_{BB}$. Moreover, the three protons of a phenolic acetoxyl group appeared as a singlet at 7·75. These data are only consistent with the presence of the 1,4-disubstituted benzene ring shown in I.

Hydrogenation of psilotinin monoacetate, using a Pd catalyst, resulted in the consumption of hydrogen corresponding to the saturation of one C=C bond with the concomitant formation of dihydropsilotinin monoacetate (II, R = $CH_3CO$—). IR absorption for psilotinin at 3030 (olefinic C—H stretch), 1380 (olefinic in plane C—H deformation) and 817 $cm^{-1}$ (olefinic out of plane C—H deformation), and for psilotinin monoacetate at 3030, 1643 (olefinic C=C stretch), 1386 and 820 $cm^{-1}$, provided supporting evidence for the presence of a *cis*-disubstituted double bond[5b] in the compounds, and the high value for the out of plane deformation frequency further indicated that the double bond was conjugated with an ester carbonyl group.[8a]

[5] R. N. Jones and C. Sandorfy, *Technique of Organic Chemistry* (Edited by Weissberger) Vol. IX, (a) pp. 397–400, (b) pp. 375–384. Interscience, New York (1956).

[6] E. A. Braude, *Ann. Reports* **42**, (1945); [a] p. 124. [b] p. 114.

[7] J. H. Pople, W. G. Schneider and H. J. Berstein, *High Resolution Nuclear Magnetic Resonance* [a] p. 142; [b] p. 193; [c] p. 132. McGraw-Hill, New York (1959).

[8] L. J. Bellamy, *The Infrared Spectra of Complex Molecules* [a] p. 48; [b] p. 186; [c] p. 179; [d] p. 22 Methuen, London (1954).

Supporting evidence for the presence of an $\alpha\beta$-unsaturated carbonyl group in psilotinin was provided by typical absorption in the UV ($\lambda\lambda_{max}$ 320 and 218 m$\mu$) for this group.[8b,9] The corresponding IR spectrum of dihydropsilotinin monoacetate, as expected, did not absorb at the above frequencies. Moreover, psilotinin monoacetate absorbed in the C=O stretching region at 1724 cm$^{-1}$, and saturation of the olefinic

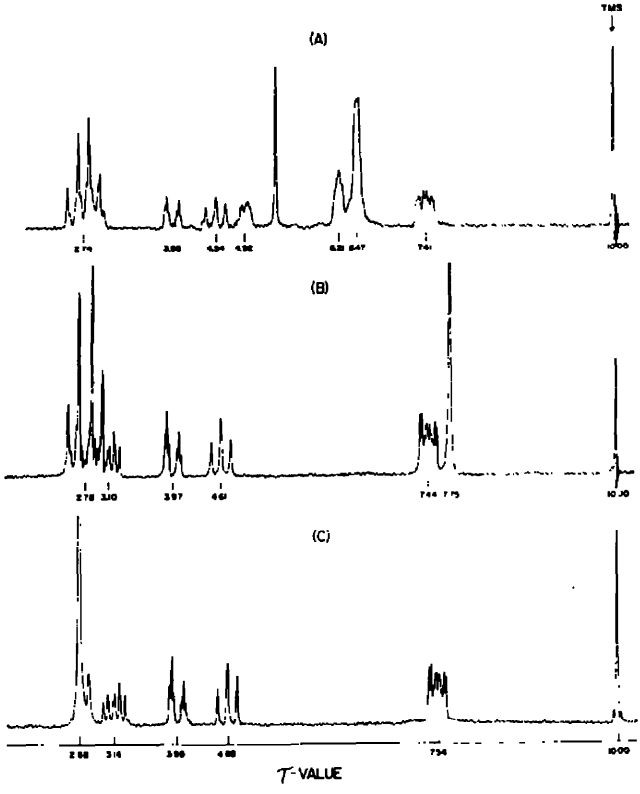


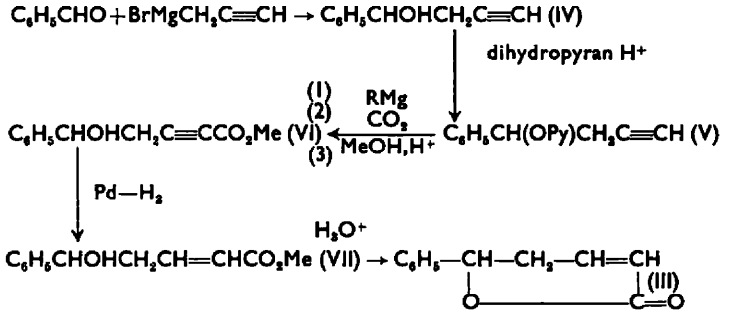

FIG. 1. The PMR spectra of 6-phenyl-5,6-dihydro-2-oxo-2H-pyran (C) and psilotinin monoacetate (B) in $CDCl_3$ using tetramethylsilane (TMS) as an internal standard, and the spectrum of psilotin (A) in $D_2O$ using TMS as an external reference. The sharp undesignated signal to the high field side of the signal at $\tau$ 4·92 in spectrum (A) is due to residual $H_2O$ in the $D_2O$.

bond conjugated with the carbonyl group resulted in the carbonyl frequency increasing to 1735 cm$^{-1}$ for the dihydro derivative. This behaviour was consistent with the $\alpha\beta$-unsaturated carbonyl group in the former compound, and consequently in the aglycone, being present in the form of an $\alpha\beta$-unsaturated $\delta$-lactone[8b] ring as shown in I. The low value for the carbonyl frequency (1695 cm$^{-1}$) for psilotinin itself was undoubtedly due to the formation of an intermolecular hydrogen bond between the lactone carbonyl and phenolic hydroxyl groups which absorbed in the O—H stretching region at 3310 cm$^{-1}$. Of course, the IR spectra of psilotinin and dihydropsilotinin

[9] A. R. Pinder, *J. Chem. Soc.* 2236 (1952).

monoacetates also possessed the characteristic bands for an acetate group.[8c] The final piece of IR evidence was the presence of a weak band at 1420 $cm^{-1}$ ($CH_2$ deformation) in psilotinin, and its monoacetyl derivative, which suggests that these compounds possess an allylic methylene group in a cyclic system.[8d] All of the above information provided strong evidence that psilotinin had structure I, and this conclusion was supported by PMR data, and the synthesis of 6-phenyl-5,6-dihydro-2-oxo-2H-pyran (III).

The synthesis of compound III was accomplished by the series of reactions shown below:




Phenylbut-1-yn-4-ol (IV) was prepared by the interaction of benzaldehyde and propargyl magnesium bromide. Compound IV was then converted into its tetrahydropyranyl ether (V) largely to increase the solubility of the acetylenic Grignard reagent prepared in the next step. The latter after carboxylation was heated with methanolic sulphuric acid to esterify and remove the tetrahydropyranyl residue with the concomitant formation of VI. This compound on reduction with hydrogen gave the *cis*-ethylenic hydroxy ester VII which in turn formed III on hydrolysis with aqueous acid. All of the intermediates described above gave IR and PMR spectra which agreed with the postulated structures.

The IR spectrum of a liquid film of compound III was similar to that for psilotinin monoacetate and only differed significantly in the spectral regions associated with the aromatic ring (Experimental) and acetoxyl group. Moreover, the PMR spectra of the two compounds were identical (Fig. I) except for the absence of the phenolic acetoxyl protons at 7·75 in the spectrum of compound III, and the presence of a singlet for five aromatic protons at 2·68 in the spectrum of the latter compound instead of the $A_2B_2$ multiplet, centred at 2·78, present in the spectrum of psilotinin monoacetate. Since the synthesis of compound III was completed by an unambiguous route these data provided final proof that psilotinin had structure I (R = —H). It was now possible to assign the PMR signals to the protons in the $\alpha\beta$-unsaturated $\delta$-lactone moiety of the two molecules (Fig. I). The two olefinic protons appear as doublets centred at 3·14 for $H_2$ and 3·99 for $H_1$, and have a common coupling constant $J_{H_1H_2}$ of 9·8 c/s which is characteristic of protons on a *cis*-disubstituted double bond.[7b] Since each olefinic proton forms the X part of an ABX system,[7c] with the methylene protons $H_3$ and $H_4$ the individual lines of the doublets appear as triplets with a spacing between the outer lines ($J_{AX} + J_{BX}$) of 8·4 c/s for $H_2$ and 3·6 c/s for $H_1$. It should be noted that one triplet of the $H_2$ signal is hidden under the $A_2B_2$ multiplet for the aromatic protons, and it was because of this feature compound III was

synthesized, instead of psilotinin, in order to observe the complete spectrum for this proton. The magnitude of the triplet spacings confirm the assignments for $H_1$ and $H_2$ because the value of $J_{AX} + J_{BX}$ would be greater for the case in which the allylic protons and one olefinic proton are on adjacent carbon atoms.[10a] In a similar manner the triplet centred at 4·68 with an outer spacing ($J_{AX} + J_{BX}$) of 16·0 c/s could be assigned to proton $H_5$ which also forms the X part of an ABX system with the allylic protons. Furthermore, the spectrum of dihydropsilotinin monoacetate provided further evidence in favour of the above assignments. Saturation of the double bond in psilotinin monoacetate resulted in the disappearance of the signals for the olefinic hydrogens with the concomitant appearance of an ill-defined triplet, broadened by long range coupling, at 7·39 for a methylene group adjacent to a carbonyl group[10b] and a complex multiplet for the four methylenic protons[10c] at 8·04. The single methine hydrogen $H_5$ in psilotinin monoacetate appeared as an ill-defined quartet at 4·68 in the dihydro derivative. Of course, the spectrum of the latter also contained the characteristic $A_2B_2$ pattern for the four aromatic protons at 2·76, and a singlet for the three methyl protons of the phenolic acetoxyl group at 7·70.

The nature of the signals for the protons $H_1$, $H_2$ and $H_5$ in psilotinin monocaetate or compound III were dependent on the magnitude of the applied magnetic field. At 100 Mc/s the triplets were replaced by quartets with the same value for $J_{AX} + J_{BX}$. This implies that the triplet structure of the signals for these protons was not due to the equality of $J_{AX}$ and $J_{BX}$ in the three ABX systems, since the magnitude of coupling constants are independent of the applied field, but rather to the fact that $J_{AB} \gg (\delta_{AB}) + (J_{AX} - J_{BX})/2$.[11] The signal for the allylic methylene protons $H_3$ and $H_4$ appears as a multiplet at 7·54, and is a composite of six overlapping quartets representing the three AB portions of the ABX systems discussed above. It has not been possible to obtain values for the coupling constants between the various protons in the $\alpha\beta$-unsaturated $\delta$-lactone ring, with the exception of $J_{H_1H_2}$, because the complexity of the signal for $H_3$ and $H_4$ does not permit the calculation of a value for $J_{H_3H_4}$ ($J_{AB}$), and subsequently values for the other coupling constants.

All of the PMR spectral assignments for psilotinin monoacetate have been confirmed by "field sweep" double-resonance experiments.[12] The signals for $H_1$ or $H_2$ collapse to a single triplet when one proton is being observed while the other is irradiated, and each proton appears as a simple doublet, with a spacing corresponding to $J_{H_1H_2}$ of 9·8 c/s, if the allylic methylene protons are decoupled from the olefinic protons one at a time. In a similar manner the triplet signal for the methine proton $H_5$ collapses to a singlet when the methylene protons $H_3$ and $H_4$ are irradiated. The multiplet for the methylene protons at 7·54 is modified in a different manner when each of the protons $H_1$, $H_2$ and $H_5$ are decoupled from the appropriate ABX system. These data are once again only consistent if psilotinin has structure I (R = −H).

It can be seen from Fig. I that the PMR spectrum of the parent glucoside psilotin in deuterium oxide contains the characteristic signals for the aromatic protons and protons associated with the $\alpha\beta$-unsaturated $\delta$-lactone ring of the aglycone. However,

[10] J. B. Stothers, *Technique of Organic Chemistry* (Edited by Weissberger) Vol. XI; [a] p. 215; [b] p. 201; [c] p. 199. Interscience, New York (1963).

[11] K. B. Wiberg and B. J. Nist, *The Interpretation of NMR spectra* p. 21. W. A. Benjamin, New York (1962).

[12] L. D. Hall and L. F. Johnson, *Tetrahedron* **20**, 883-889 (1964).

the two triplets for proton $H_2$ of the aglycone are hidden to a greater extent under the $A_2B_2$ multiplet for the aromatic protons. No signal was obtained for the hydroxyl protons since they had been exchanged with deuterium prior to analysis. The signals centred at 6·25 and 6·51 are due to all the protons in the pyranose ring of the glucose moiety except the proton at the anomeric position. Since the latter occurs as an ill-defined doublet at 4·96 with an average spacing of 5·5 c/s the glucoside must have the $\beta$-configuration at the anomeric position.[13] It follows, therefore, that psilotin must be 6-[4′-$\beta$-D-glucopyranosyloxyphenyl]-5,6-dihydro-2-oxo-2H-pyran (I, R = $\beta$-D-glucopyranosyl).

Although the aglycone psilotinin contains an asymmetric centre, optical rotatory dispersion studies have established that this compound is *not* optically active. Parasorbic acid and massoilactone,[14] on the other hand, which contain a similar centre of asymmetry occur naturally in an optically active form. Psilotin, however, was isolated as a pure compound, and consequently cannot be a mixture of the diastereo-isomeric glucosides of the two possible enantiomers of psilotinin. The diastereoisomers would have different physical properties, and could be separated by crystallization. It follows, therefore, that the enantiomer of psilotinin, which occurs as the aglycone in psilotin must have racemized during the isolation procedure subsequent to the enzymatic hydrolysis of psilotin. The racemization of psilotinin is not surprising in view of its structure and could occur *via* a quinone methide type intermediate.

## EXPERIMENTAL

*Isolation of psilotin* (I, R = $\beta$-D-glucopyranosyl). The residue from a hot ethanolic extract (4·1 g of *Psilotum nudum* shoots (485 g) was dissovled in water and continuously extracted first with ether (500 ml for 48 hr) and then ethyl acetate 1 l. for 14 days). Removal of the solvent, from the ethyl acetate solution (red. press.) gave a residue of psilotin which crystallized from EtOH as long colourless needles (5·9 g) m.p. 130–131°, $[\alpha]_D^{25}$ −145·3° (*c*, 5% in water) and mol. wt. 380 (Rast method). (Found: C, 57·17; H, 6·36. $C_{17}H_{20}O_8 \cdot C_2H_5OH$ requires: C, 57·28; H, 6·58%.)

Reaction of psilotin with acetic anhydride in pyridine at room temp gave psilotin tetraacetate (I, R = 2,3,4,6-tetra-O-acetyl-$\beta$-D-glucopyranosyl) in quantitative yield. This compound crystallized from ethyl acetate–petroleum ether as long colourless needles, m.p. 155·5–156·5°, $[\alpha]_D^{24}$ −101·0° (*c*, 3·5% in $CHCl_3$). (Found: C, 57·81; H, 5·40. $C_{25}H_{28}O_{12}$ requires: C, 57·69; H, 5·42%.)

*Hydrolysis of psilotin.* When psilotin (3·22 g) was hydrolysed with emulsin (0·25 g) in distilled water (100 ml) at 30° for 12 hr the aglycone psilotinin (I, R = —H; 1·62 g) precipitated from solution and was isolated by filtration. The latter compound crystallized from ethyl acetate as needles, m.p. 136–138° and then recrystallized almost immediately as leaflets, m.p. 151–153°. (Found: C, 69·52; H, 5·42. $C_{11}H_{10}O_3$ requires: C, 69·46; H, 5·30%.) This compound absorbed in the IR* at 3310 *s*, 3060 *w*, 3030 *w*, 2950 *w*, 1697 *s*, 1616 *m*, 1600 *m*, 1520 *m*, 1455 *m*, 1425 *w*, 1380 *m*, 1355 *m*, 1287 *w*, 1274 *w*, 1262 *s*, 1206 *m*, 1176 *m*, 1158 *m*, 1115 *w*, 1066 *m*, 1030 *m*, 1012 *w*, 974 *w*, 962 *w*, 913 *m*, 844 *m*, 817 *m*, 729 *w* and 700 *m* $cm^{-1}$. MeOH $\lambda\lambda_{max}$ 218 ($\varepsilon$ 15,686), 280 ($\varepsilon$ 1480), 278 ($\varepsilon$ 1680) and 320 m$\mu$ ($\varepsilon$ 43).

Acetylation of psilotinin with acetic anhydride in pyridine yielded psilotinin monoacetate (I, R = —$OCCH_3$) which crystallized from ethyl acetate–pet. ether as needles, m.p. 111–112° and mol. wt. 233 (osmometer method). (Found: C, 67·23; H, 5·40. $C_{13}H_{12}O_4$ requires: C, 67·23; H, 5·29%.) IR absorption at 3100 *w*, 3060 *w*, 3010 *w*, 2960 *w*, 2925 *w*, 1750 *s* (sh. 1765), 1725 *s* (sh. 1712), 1643 *w*, 1625 *w*, 1614 *w*, 1600 *w*, 1517 *m*, 1425 *w*, 1420 *w*, 1386 *m*, 1372 *m*, 1345 *w*, 1290 *m*, 1260 *s*, 1230 *s*, 1200 *s*, 1170 *m*, 1110 *w*, 1060 *s*, 1033 *s*, 1020 *s*, 982 *w*, 966 *w*, 924 *w*, 917 *s*, 860 *m*, 820 *s*, 795 *w*, 737 *w*

* The intensities of the bands are indicated by *w* = weak, *m* = medium, and *s* = strong.

[13] G. H. N. Towers, A. G. McInnes and A. C. Neish, *Tetrahedron* **20**, 72 (1964).

[14] W. Karrer, *Konstitution und Vorkommen der organischen Pflanzenstoffe* p. 451. Birkhäuser, Basel (1958).

and 705 *w* $cm^{-1}$. The shoulders at 1765 and 1712 $cm^{-1}$ were not present when the spectrum of a solution of psilotinin monoacetate in $CHCl_3$ was taken.

Psilotinin monoacetate (0·2321 g) absorbed 24·9 ml $H_2$ (theory for one double bond was 25·2 ml) when reduced in ethyl acetate solution (20 ml) using 5% Pd–C as catalyst, at 26° and one atm. press., to give dihydropsilotinin monoacetate. This compound (0·2180 g) crystallized from ethyl acetate–pet. ether as needles, m.p. 111·5–112·5°. (Found: C, 66·72; H, 6·05. $C_{13}H_{14}O_4$ requires: C, 66·65 H, 6·02%.) IR absorption at 3100 *w*, 3060 *w*, 2950 *w*, 2875 *w*, 1755 *s*, 1732 *s*, 1610 *w*, 1595 *w*, 1510 *m*, 1463 *w*, 1440 *w*, 1425 *w*, 1370 *m*, 1341 *w*, 1328 *w*, 1300 *w*, 1285 *m*, 1245 *s*, 1224 *s*, 1200 *s*, 1165 *m*, 1110 *w*, 1048 *s*, 1022 *m*, 970 *w*, 935 *w*, 920 *m*, 880 *w*, 852 *m*, 785 *w*, 766 *w* and 733 *w* $cm^{-1}$.

The filtrate from the aqueous reaction solution (see above) was taken to dryness (red. press.) and glucose (1·59 g) was extracted from the residue with anhydrous MeOH. Glucose was identified by paper chromatography,[15] GLPC of appropriate derivatives,[16] and by its specific rotation.

Optical rotatory dispersion curves of psilotinin and psilotinin monoacetate in MeOH throughout all of the accessible region established that the compounds were *not* optically active.

*Oxidation of psilotinin monoacetate.* Psilotinin monoacetate (116 mg) was oxidized in acetic acid (5 ml) containing 2% conc. $H_2SO_4$ with $CrO_3$ (200 mg). The reaction mixture was worked up, and the product of oxidation treated with diazomethane in ether to yield methyl *p*-hydroxybenzoate monoacetate (79·5 mg). The IR and PMR spectra of this compound were identical to those obtained for an authentic sample of methyl *p*-hydroxybenzoate monoacetate.

*4-Phenylbut-1-yn-4-ol* (IV). Propargyl magnesium bromide (0·5 M) was prepared by the procedure of Gaudemar,[17] and subsequently reacted at 0–2° with benzaldehyde (0·4 M). After working up in the usual manner the product of the reaction was distilled (red. press.) to give 4-phenylbut-1-yn-4-ol (0·29 M), b.p. 89–95°/0·6 mm. (Found C, 82·05; H, 6·81. Calc. for $C_{10}H_{10}O$: C, 82·16; H, 6·90%.)

*4-Tetrahydropyranyloxy-4-phenylbut-1-yne* (V). The above compound was prepared from 4-phenylbut-1-yn-4-ol (0·125 M) and dihydropyran (0·25 M), using *p*-toluene sulphonic acid as catalyst, in the manner described for similar compounds by Robertson.[18] Distillation (red. press.) gave the pure reaction product (0·082 M), b.p. 114–120°/0·3 mm. (Found: C, 78·27; H, 8·02. Calc. for $C_{15}H_{18}O_2$: C, 78·26; H, 7·83%.)

*Methyl 5-hydroxy-5-phenylpent-2-ynoate* (VI). The above compound was synthesized by a procedure described by Crombie.[19]

The Grignard reagent prepared from the reaction of 4-tetrahydropyranyloxy-4-phenylbut-1-yne (0·04 M) with EtMgBr (0·08 M) was poured on to solid $CO_2$ (100 g) in a steel autoclave and kept sealed for 32 hr. At the end of this period the reaction mixture was treated with anhydrous MeOH (40 ml) containing conc. $H_2SO_4$ (7·2 ml) and left standing overnight. The solution was then reduced to ½ original volume and a further aliquot of MeOH (40 ml) was added and once again it was left standing overnight. After working up, the product was distilled (red. press.) to give a pure fraction of the desired product (0·025 M), b.p. 112°/0·2 mm. (Found: C, 70·41; H, 6·10. Calc. for $C_{12}H_{12}O_3$: C, 70·57; H, 5·92%.)

*Methyl 5-hydroxy-5-phenylpent-cis-2-ynoate* (VII). Methyl 5-hydroxy-5-phenylpent-2-ynoate (0·015 M) in ethyl acetate (20 ml) was hydrogenated, at room temp and 1 atm press., in the presence of 5% Pd–$BaSO_4$ (0·7 g). The desired product (0·011 M) was obtained on removing the catalyst and the solvent (red. press.), and finally collecting the material which distilled at 110°/0·15 mm. (Found: C, 69·71; H, 6·80. Calc. for $C_{12}H_{14}O_3$: C, 69·88; H, 6·84%.)

*6-Phenyl-5,6-dihydro-2-oxo-2H-pyran* (III). Methyl 5-hydroxy-5-phenlypent-*cis*-2-enoate (0·005 M) was refluxed with 2 N HCl (10 ml) for 40 min, cooled and extracted with ether. The extracts were washed with $NaHCO_3$ aq and water and subsequently dried ($Na_2SO_4$) and the lactone (0·003 M) distilled at 80°/0·15 mm. The latter crystallized from ether–pet. ether (60–80°) as needles, m.p. 59·2–60·1° which agrees with the reported value.[20] (Found: C, 75·80; H, 5·71. Calc. for $C_{11}H_{10}O_2$: C, 75·84; H, 5·79%.) IR absorption at 3095 *w*, 3060 *w*, 3035 *w*, 3025 *w*, 2945 *w*, 2895 *w*, 1768 *m*, 1725 *s*, 1690 *m*,

[15] L. Hough, J. K. N. Jones, P. W. H. Wadman, *J. Chem. Soc.* 1702 (1950).
[16] D. Rast, A. G. McInnes and A. C. Neish, *Phytochemistry* **3**, 103–108 (1964).
[17] M. Gaudemar, *Ann. Chim.* **1**, 190 (1956).
[18] D. N. Robertson, *J. Org. Chem.* **25**, 931 (1960).
[19] L. Crombie, *J. Chem. Soc.* 1007–1025 (1955).
[20] H. B. Henbest and E. R. H. Jones, *J. Chem. Soc.* 3628 (1950).

1640 *w*, 1615 *w*, 1590 *w*, 1504 *m*, 1467 *m*, 1420 *m*, 1388 *s*, 1348 *w*, 1291 *m*, 1257 *s*, 1193 *w*, 1150 *m*, 1088 *w*, 1071 *m*, 1038 *m*, 1029 *s*, 1006 *m*, 988 *m*, 966 *m*, 935 *w*, 918 *m*, 850 *w*, 820 *s*, 775 *s*, 717 *m*, and 707 *s* $cm^{-1}$. Methanol $\lambda\lambda_{max}$ 249 ($\varepsilon$ 420), 257 ($\varepsilon$ 400), 261 ($\varepsilon$ 325), 267 ($\varepsilon$ 215), 304 m$\mu$ ($\varepsilon$ 11).

The PMR spectra shown in Fig. 1 were recorded on a Varian A60 spectrometer, and all IR spectra were run on a Perkin–Elmer Model 237 spectrometer.

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