Phytochemistry, Vol. 23, No. 3, pp. 607–610, 1984.
Printed in Great Britain.

0031–9422/84 $3.00 + 0.00

DITERPENOIDS FROM *SIDERITIS PUSILLA* SUBSP. *FLAVOVIRENS**

ANDRÉS GARCÍA-GRANADOS, ANTONIO MARTÍNEZ, M. ESTHER ONORATO and OSWALDO SOCORRO

Departamentos de Química Orgánica y Botánica de la Universidad de Granada, Spain

(*Revised received* 20 *June* 1983)

Key Word Index—*Sideritis pusilla* subsp. *flavovirens*; Labiatae; new *ent*-beyer-15-ene derivatives; ^{13}C NMR data.

Abstract—Several new 14-hydroxybeyerene acetates have been isolated from the aerial parts of *Sideritis pusilla* subsp. *flavovirens*. In addition, an *ent*-kaur-15-ene (siderol) and a new *ent*-7α,18-dihydroxybeyer-15-ene (flavovirol) have been obtained from the same source. The structures of these new acetates have been established by chemical and spectroscopic means and the structure of flavovirol has been confirmed by ^{13}C NMR.

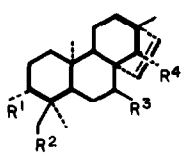
INTRODUCTION

In continuance of our work on the diterpenoids of the genus *Sideritis*, we have now studied the minor diterpenoids from *S. pusilla* (Lange) Pau subsp. *flavovirens* (Rouy) Malagarriga. Previously [1], we isolated the known diterpenoids *ent*-14β-acetoxy-18-hydroxybeyer-15-ene (tartesol, **1**) [2], *ent*-7α-acetoxy-14β,18-dihydroxybeyer-15-ene (**2**) [3], *ent*-7α,14β,18-trihydroxybeyer-15-ene, (**3**) [4], and the new natural acetate *ent*-14β-acetoxy-7α,18-dihydroxybeyer-15-ene (**4**). Only *ent*-kaurenes have been obtained from the apparently synonymous plant. *S. leucantha* Cav. var. *flavovirens* Rouy [1] and from *S. flavovirens* Rouy [5]; our present results show that this plant is quite different chemically.

RESULTS AND DISCUSSION

TLC of the terpenoid mixture from *S. pusilla* subsp. *flavovirens* revealed three fractions. Firstly, a neutral fraction containing mainly tartesol (**1**). Siderol (**5**) was isolated from this first fraction as well as two new *ent*-beyerene naturally occurring diacetates. Diacetate **6** ($C_{24}H_{36}O_5$) showed IR bands indicative of a hydroxyl function (3500 cm^{-1}), an acetate function (1735 and 1250 cm^{-1}) and a double bond (3070, 1660 and 740 cm^{-1}). Characteristic signals of an AB system (δ 5.70 and 5.50, J = 5.5 Hz), two acetate singlets and three methyl singlet signals (δ 0.76, 0.80 and 0.98) were observed in the ^1H NMR spectrum. In addition, an AB system (J = 12 Hz) with doublets at δ 4.20 and 3.85, a singlet (δ 4.50, 1H) and a broad signal (δ 3.40, $W_{1/2}$ = 18 Hz, 1H) were detected. Treatment of product **6** with acetic anhydride–pyridine led to a triacetate identified as triacetylisopusillatriol (**7**) [4]. Hence, product **6** can be identified as *ent*-14β,18-diacetoxy-3β-hydroxybeyer-15-ene, a new natural diacetate. Diacetate **8** showed similar polarity, identical molecular formula and similar IR spectrum as those described for diacetate **6**. Its ^1H NMR spectrum gave a broad signal (δ 4.85, *dd*, J_1 = 7, J_2 = 9 Hz, 1H), attributable to an axial proton, geminal to an acetoxyl group, a singlet signal at δ 4.50 (1H) and an AB system with doublets at δ 3.40 and 2.90 (J = 12 Hz). Acetylation of product **8** yields the above mentioned triacetylisopusillatriol (**7**). Thus, the structure *ent*-3β,14β-diacetoxy-18-hydroxybeyer-15-ene can be assigned to **8**, a new natural diacetate.

A second fraction of medium polarity contained mainly 7-acetylpusillatriol (**2**) and 14-acetylpusillatriol (**4**) [1]. Another product (**9**) isolated from fraction was a monoacetate ($C_{22}H_{34}O_3$) with IR bands of a hydroxyl group (3400 cm^{-1}), an acetoxyl group (1740 and 1250 cm^{-1}) and an olefinic system (3060, 1660 and 740 cm^{-1}). The ^1H NMR spectrum of **9** shows a 2H signal at δ 5.68 and 5.45 (AB quartet, J = 6 Hz), a 1H broad signal at δ 4.90 ($W_{1/2}$ = 18 Hz), an AB system (δ 4.15 and δ 3.70, J = 12 Hz), a 1H singlet at δ 2.95, an acetoxyl singlet at δ 2.05 and methyl signal singlets at δ 1.05 (3H)



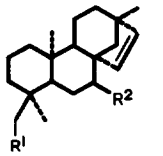
	R¹	R²	R³	R⁴
	H	OH	H	OAc
2	H	OH	OAc	OH
3	H	OH	OH	OH
4	H	OH	OH	OAc
6	OH	OAc	H	OAc
7	OAc	OAc	H	OAc
8	OAc	OH	H	OAc
9	OAc	OH	H	OH
10	OAc	OH	OAc	H
11	OAc	OAc	OAc	OAc
12	OH	OAc	OAc	OH
13	OH	OAc	OH	OAc

*Part 15 in the series "Terpenoid Components of Spanish Labiatae". For part 14 see García-Granados, A., Martínez, A. and Onorato, E. *An. Quim. C* (in press).

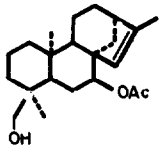
and 0.79 (6H). Since acetylation of **9** leads to isopusillatrioltriacetate (7), we conclude that **9** is *ent*-3β-acetoxy-14β,18-dihydroxybeyer-15-ene, a new natural acetate.

Product **10** has a polarity similar to that of **9**, and is a diacetate ($C_{24}H_{38}O_6$) with an IR spectrum indicating the presence of a hydroxyl group, a C–C double bond and an acetoxyl group. The ^{1}H NMR spectrum of **10** shows a collapsed AB system centred at δ 5.55, a narrow signal at δ 5.05 (1H, $W_{1/2}$ = 7 Hz), a broad signal centred at δ 4.80 (1H, $W_{1/2}$ = 18 Hz), a narrow 1H signal at δ 3.25 and a Q_{AB} (J = 12 Hz) with signals at δ 3.18 and 2.86. Two acetoxyl singlet signals at δ 2.10 (6H) and methyl singlet signals at δ 1.10, 0.85 and 0.72 (3H each) were also registered. In accordance with these data, we propose that **10** is *ent*-3β,7α-diacetoxy-14β,18-dihydroxybeyer-15-ene, a new natural diacetate. Acetylation of **10** leads to tetraacetylpusillatetrol (**11**) [4], confirming thereby the proposed structure. Product **12** is a natural product which is another diacetylpusillatetrol whose ^{1}H NMR spectrum presents a collapsed Q_{AB} at δ 5.48, the signal of a geminal proton to an axial acetoxyl group, presumably at C-7, (δ 5.05, *m*, $W_{1/2}$ = 6 Hz, 1H) an AB system with signals centred at δ 4.20 and 3.48 (J = 12 Hz) attributable to an acetoxymethylene group at C-18 and two superimposed signals at δ 3.15 and 3.10 of geminal protons to possible hydroxyl groups at C-3 and C-14. Acetylation yields tetraacetylpusillatetrol (**11**). Consequently, we conclude that **12** must be the new natural diacetate *ent*-7α,18-diacetoxy-3β,14β-dihydroxybeyer-15-ene. Product **13** is another natural diacetate which yielded tetraacetylpusillatetrol (**11**) after acetylation although, in this case, the natural acetylated hydroxyl groups were situated at C-14 and C-18. The ^{1}H NMR spectrum of **13** shows, inter alia, a singlet signal at δ 4.65 (1H), a poorly resolved collapsed Q_{AB} and narrow signal at δ 3.95 (3H in total), as well as a double doublet (J_1 = 7, J_2 = 9 Hz) centred at δ 3.50. Since the acetylation of **13** yields tetraacetylpusillatetrol (**11**), we assume that it must be the new natural diacetate *ent*-3β,7α-dihydroxy-14β,18-diacetoxybeyer-15-ene.

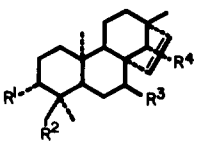
The last natural product isolated from the fraction of medium polarity is **14**, a dihydroxylated diterpene



	R¹	R²
14	OH	OH
16	OAc	OAc



5



	R¹	R²	R³	R⁴
15	H	OH	H	OH
17	-O-CMe$_2$-O-		H	OH
18	-O-CMe$_2$-O-		OH	OH
19	-O-CMe$_2$-O-		OAc	OH
20	-O-CMe$_2$-O-		OH	OAc
21	H	OAc	OAc	OAc
22	H	H	H	H

($C_{20}H_{32}O_2$) which shows IR bands for a hydroxyl group (3400 cm^{-1}) and a C–C double bond (3060, 1650 and 740 cm^{-1}). The ^{1}H NMR spectrum of this product was similar to those previously described. It shows a collapsed AB system at δ 5.55 assigned to a *cis* olefin with no hydrogens at the vecinal carbon atoms. A Q_{AB} system, with J = 12 Hz and signal centred at δ 3.45 and 2.85, suggests the existence of a –CH_2OH group, presumably situated at C-18. A signal attributable to an equatorial hydrogen ($W_{1/2}$ = 7 Hz), geminal to a hydroxyl group can be observed at δ 3.5. In addition, three methyl singlet signals (δ 1.07, 0.81 and 0.73) can be observed. The chemical shift and form of the equatorial proton, geminal to the hydroxyl group described, may be due to an equatorial proton at the C-7 position. On the other hand, this product is clearly distinguishable from the saponification product (**15**) of tartesol (**1**). In the case of **15**, the *ent*-14α proton, geminal to the characteristic *ent*-14β-hydroxyl group, produces a ^{1}H NMR narrow signal at δ 2.90. The acetylation of **14** yields a diacetate (**16**) which has two signals due to geminal protons to the acetoxyl groups: a narrow 1H signal at δ 4.85 ($W_{1/2}$ = 7 Hz) and a collapsed Q_{AB} system at δ 3.72. Product **14** must be *ent*-7α,18-dihydroxybeyer-15-ene. This was confirmed by ^{13}C NMR spectral measurements (Table 1), which also provided conclusive proof of the structure of this new diterpenoid. The chemical shifts assigned to the carbon of diacetate **15** are in agreement to those calculated [6] for an axial acetoxyl group at C-7. We propose the trivial name of flavovirol for **14**.

Finally, the most polar fraction of diterpenoids from *S. pusilla* subsp. *flavovirens* was acetonated for 8 hr in acetone–copper sulphate, and chromatographed repeatedly. In this way, the previously described *ent*-3β,18-isopropylidenedioxy-14β-hydroxybeyer-15-ene (**17**) and *ent*-3β,18-isopropylidenedioxy-7α,14β-dihydroxybeyer-15-ene (**18**) were isolated and identified [4]. Similarly, *ent*-3β,18-isopropylidenedioxy-7α-acetoxy-14β-hydroxybeyer-15-ene (**19**) was isolated and identified. The last acetonide (**20**) isolated from the mixture shows IR bands of a hydroxyl group, an acetate group and a C–C double bond. The ^{1}H NMR spectrum of product **20** shows a collapsed Q_{AB} system at δ 5.45, and 1H singlet signal at δ 4.60, and a narrow signal at δ 3.80 (1H, $W_{1/2}$ = 6 Hz). The two last described signals can be respectively attributed to an axial proton at C-14 (geminal to an

Table 1. ^{13}C NMR chemical shifts of diterpenoid **16** in ppm relative to TMS

Carbon No.	**22** [6]	**16**
1	39.3	38.31
2	18.7	17.64
3	42.2	35.70
4	33.3	36.15
5	56.1	42.23
6	20.3	25.30
7	37.4	75.68
8	49.1	52.79
9	53.0	47.91
10	37.4	37.17
11	20.5	19.85
12	33.7	32.80
13	43.6	43.88
14	61.3	56.54
15	135.2	132.42
16	136.1	138.01
17	25.0	24.73
18	33.8	72.61
19	22.0	17.64
20	15.1	15.08
Me–COO		21.27
		21.05
MeCOO		170.98
		170.55

acetoxyl group) and an equatorial proton at C-7 (geminal to a hydroxyl group). Moreover, a collapsed Q_{AB} at δ 3.40 superimposed to a broad signal (3H as a whole), as well as an acetoxyl singlet (δ 2.0), and methyl singlet signals [δ 1.45 (6H), 1.09 (3H), 1.03 (3H) and 0.85 (3H)] were observed. We believe that **20** is the 3,18-isopropylidene derivative of *ent*-3β,7α,18-trihydroxy-14β-acetoxybeyer-15-ene, another new natural acetate. Acetylation of an aliquot of the most polar fraction leads to a mixture from which triacetylpusillatriol (**7**) was isolated and characterized by comparison with published data [4].

EXPERIMENTAL

Mps were uncorr. ^{1}H NMR spectra were measured at 60 MHz in $CDCl_3$ soln with TMS as internal standard. ^{13}C NMR spectra were determined at 25.2 MHz, also in $CDCl_3$ soln (which also provided the lock signal) with TMS as internal reference. Assignment of ^{13}C chemical shifts were made with the aid of off-resonance and noise decoupled ^{13}C NMR spectra. The MS were determined on a Hewlett-Packard 5930 A instrument (direct inlet, 70 eV e.e.). Silica gel Merck 7729 (< 0.08 mm) was used for CC. Plant material was collected in May 1980 between Huercal Overa and Pulpí (Almería) and voucher specimens were deposited in the Herbarium of the Faculty of Pharmacy (Granada University).

Extraction and isolation of the diterpenoids. Dried and finely powdered *S. pusilla* subsp. *flavovirens* (3.2 kg aerial parts) were extracted with hexane (5 l.) in a Soxhlet. The extract was concd *in vacuo* to 1.5 l. and repeatedly extracted with 90% aq. MeOH (6 × 300 ml.). The methanolic extract was concd to 0.5 l., diluted with H_2O (3 l.) and extracted with $CHCl_3$ (6 × 250 ml). The $CHCl_3$ extracts were dried and concd to give a yellowish residue (80 g), 75 g of which was stepwise chromatographed on a silica gel column, and eluted with increasing polarity mixtures of CH_2Cl_2–Me_2CO. In addition to the previously reported [1] tartesol (**1**), 7-acetylpusillatriol (**2**), pusillatriol (**3**) and 14-acetylpusillatriol (**4**), repeated chromatography of the resulting mixtures led to the isolation of siderol (**5**, 148 mg), 14,18-diacetylisopusillatriol (**6**, 128 mg), 3,14-diacetylisopusillatriol (**8**, 50 mg), 3-acetylisopusillatriol (**9**, 24 mg), 3,7-diacetylpusillatetrol (**10**, 134 mg), 7,18-diacetylpusillatetrol (**12**, 308 mg), 14,18-diacetylpusillatetrol (**13**, 75 mg) and flavovirol (**14**, 186 mg). Moreover, a mixture of very polar products was obtained (4.6 g), 1.5 g of which were acetonated (Me_2CO–$CuSO_4$, 8 hr reflux), and chromatographed yielding the 3,18-acetonide of isopusillatriol (**17**, 74 mg), 3,18-acetonide of pusillatetrol (**18**, 78 mg), 3,18-acetonide of 7-acetylpusillatetrol (**19**, 248 mg) and 3,18-acetonide of 14-acetylpusillatetrol (**20**, 184 mg). After the acetylation of a certain part (838 mg) of this polar fraction, triacetylpusillatriol (**21**, 34 mg), tetracetylpusillatetrol (**11**, 87 mg) and triacetylisopusillatriol (**7**, 31 mg) were isolated.

ent-14β,18-*Diacetoxy*-3β-*hydroxybeyer*-15-*ene* (14,18-*diacetylisopusillatriol*, **6**). Mp 95–97°. $[\alpha]_D^{20}$ +9° (*c* 1.25, $CHCl_3$). IR ν_{max}^{KBr} cm^{-1}: 3500, 3080, 1740, 1650, 1250, 750. ^{1}H NMR: δ 5.70 and 5.50 (Q_{AB}, J = 5.5 Hz, H-15 and H-16), 4.5 (1H, *s*, H-14), 4.20 and 3.85 (Q_{AB}, J = 12 Hz, 2H-18), 3.4 (1H, *m*, $W_{1/2}$ = 18 Hz, H-3), 2.02 and 1.97 (3H each, AcO–groups), 0.98, 0.80 and 0.76 (3H each, C–Me singlets). MS *m/z* (rel. int.): 404 [M]$^+$ (9), 387 (3), 364 (4), 344 (50), 326 (49), 316 (25), 303 (19), 285 (100), 266 (42), 253 (45). Found: C, 70.92; H, 9.06. $C_{24}H_{36}O_5$ requires: C, 71.26; H, 8.97%.

ent-3β,14β-*Diacetoxy*-18-*hydroxybeyer*-15-*ene* (3,14-*diacetylisopusillatriol*, **8**). Mp 143–145° $[\alpha]_D^{20}$ +39° (*c* 1.5, $CHCl_3$). IR ν_{max}^{KBr} cm^{-1}: 3500, 3075, 1735, 1650, 1260, 750. ^{1}H NMR: δ 5.70 and 5.48 (Q_{AB}, J = 6 Hz, H-15 and H-16), 4.85 (1H, *dd*, J_1 = 7, J_2 = 9 Hz, H-3), 4.5 (1H, *s*, H-14), 3.40 and 2.90 (Q_{AB}, J = 12 Hz, 2H-18), 2.05 and 2.0 (3H each, AcO– groups), 0.94, 0.82 and 0.69 (3H each, C–Me singlets). MS *m/z* (rel. int.): 404 [M]$^+$ (2), 386 (0.5), 374 (0.3), 344 (13), 332 (17), 330 (15), 326 (9), 316 (66), 302 (4), 300 (35), 284 (12), 272 (13), 266 (10), 254 (100). Found: C, 70.87; H, 9.10. $C_{24}H_{36}O_5$ requires: C, 71.26; H, 8.97%.

ent-3β-*Acetoxy*-14β,18-*dihydroxybeyer*-15-*ene* (3-*acetylisopusillatriol*, **9**). Colorless oil. $[\alpha]_D^{20}$ +41.5° (*c* 0.24, $CHCl_3$). IR ν_{max}^{film} cm^{-1}: 3400, 3060, 1740, 1660, 1250, 740. ^{1}H NMR: δ 5.68 and 5.45 (Q_{AB}, J = 6 Hz, H-15 and H-16), 4.9 (1H, *m*, $W_{1/2}$ = 18 Hz, H-3), 4.15 and 3.70 (Q_{AB}, J = 12 Hz, 2H-18), 2.95 (1H, *s*, H-14), 2.05 (3H, AcO– group), 1.05 (3H) and 0.79 (6H) (C–Me singlets signals). MS *m/z* (rel. int.): 362 [M]$^+$ (81), 332 (39), 315 (35), 302 (28), 285 (44), 274 (100), 272 (64), 257 (79), 254 (98), 241 (100).

ent-3β,7α-*Diacetoxy*-14β,18-*dihydroxybeyer*-15-*ene* (3,7-*diacetylpusillatetrol*, **10**). Mp 183–185°. $[\alpha]_D^{20}$ +68.2° (*c* 1.13, $CHCl_3$). IR ν_{max}^{KBr} cm^{-1}: 3500, 3060, 1735, 1660, 1250, 740. ^{1}H NMR: δ 5.55 (collapsed Q_{AB}, H-15 and H-16), 5.05 (1H, *m*, $W_{1/2}$ = 7 Hz, H-7), 4.80 (1H, *m*, $W_{1/2}$ = 18 Hz, H-3), 3.25 (1H, *s*, H-14), 3.18 and 2.86 (Q_{AB}, J = 12 Hz, 2H-18), 2.10 (6H, *s*, 2AcO– groups), 1.03, 0.85 and 0.72 (3H each, C–Me singlet signals). MS *m/z* (rel. int.): 420 [M]$^+$ (0.5), 361 (76), 360 (88), 342 (13), 332 (100), 302 (59), 300 (45), 299 (42), 282 (33), 274 (55), 273 (44). Found: C, 68.73; H, 8.73. $C_{24}H_{36}O_6$ requires: C, 68.55; H, 8.63%.

ent-3β,14β-*Dihydroxy*-7α,18-*diacetoxybeyer*-15-*ene* (7,18-*diacetylpusillatetrol*, **12**). Mp 178–180°. $[\alpha]_D^{20}$ +90° (*c* 1.55, $CHCl_3$). IR ν_{max}^{KBr} cm^{-1}: 3400, 3060, 1750, 1650, 1265, 735. ^{1}H NMR: δ 5.48 (collapsed Q_{AB}, H-15 and H-16), 5.05 (1H, *m*, $W_{1/2}$ = 6 Hz, H-7), 4.20 and 3.48 (Q_{AB}, J = 12 Hz, 2H-18), 3.15 (1H, *m*, $W_{1/2}$ = 18 Hz, H-3), 3.10 (1H, *s*, H-14), 2.03 (6H, 2AcO– groups), 1.03, 0.80 and 0.74 (3H each, C–Me singlet signals). MS *m/z* (rel. int.): 420 [M]$^+$ (3), 361 (39), 360 (29), 342 (17), 331 (25),

327 (23), 313 (15), 300 (10), 282 (98), 267 (49), 253 (100). Found: C, 68.10; H, 8.74. $C_{24}H_{36}O_6$ requires: C, 68.55; H, 8.63%.

ent-3β,7α-*Dihydroxy*-14β,18-*diacetoxybeyer*-15-*ene* (14,18-*diacetylpusillatetrol*, **13**). Mp 198–200°. $[\alpha]_D^{20}$ + 39° (*c* 1.28, $CHCl_3$). IR ν_{max}^{KBr} cm^{-1}: 3450, 3060, 1735, 1640, 1270, 740. ^1H NMR: δ 5.47 (collapsed Q_{AB}, H-15 and H-16), 4.65 (1H, *s*, H-14), 3.95 (collapsed Q_{AB}, 2H-18), 3.90 (1H, *m*, $W_{1/2}$ = 6 Hz, H-7), 3.50 (1H, *dd*, J_1 = 7, J_2 = 9 Hz, H-3), 2.03 (6H, 2AcO– groups), 0.98 (3H) and 0.80 (6H), C–Me singlet signals. MS *m/z* (rel. int.): 420 $[M]^+$ (0.5), 360 (33), 342 (37), 331 (22), 326 (100), 315 (20), 310 (16), 300 (72), 292 (70), 283 (70). Found: C, 70.80; H, 9.02. $C_{24}H_{36}O_5$ requires: C, 71.26; H, 8.97%.

ent-7α,18-*Dihydroxybeyer*-15-*ene* (*flavovirol*, **14**). Mp 107–109°. $[\alpha]_D^{20}$ + 42.8° (*c* 1, $CHCl_3$). IR ν_{max}^{KBr} cm^{-1}: 3400, 3060, 1650, 740. ^1H NMR: δ 5.55 (collapsed Q_{AB}, H-15 and H-16), 3.50 (1H, *m*, $W_{1/2}$ = 7 Hz, H-7), 3.45 and 2.85 (Q_{AB}, *J* = 12 Hz, 2H-18), 1.07, 0.81 and 0.73 (3H each, C–Me singlet signals). MS *m/z* (rel. int.): 304 $[M]^+$ (2), 286 (6), 270 (2), 257 (6), 256 (5), 242 (3), 228 (2), 227 (2), 200 (3), 185 (3), 176 (10), 174 (9), 172 (10), 157 (100). Found: C, 78.97; H, 10.76; $C_{20}H_{32}O_2$ requires: C, 78.90; H, 10.59%.

ent-14β,18-*Dihydroxybeyer*-15-*ene* (**15**). Mp 183–185°. $[\alpha]_D^{20}$ + 15° (*c* 1.88, $CHCl_3$). IR ν_{max}^{KBr} cm^{-1}: 3400, 3060, 1645, 740. ^1H NMR: δ 5.70 and 5.48 (Q_{AB}, *J* = 6 Hz, H-15 and H-16), 3.45 and 3.12 (Q_{AB}, *J* = 12 Hz, 2H-18), 2.95 (1H, *s*, H-14), 1.0 (3H) and 0.77 (6H), C–Me singlet signals. MS *m/z* (rel. int.): 304 $[M]^+$ (30), 286 (3), 274 (40), 273 (57), 255 (66), 242 (27), 228 (15), 213 (24), 202 (18), 187 (21), 185 (21), 177 (75), 173 (100).

ent-7α,18-*Diacetoxybeyer*-15-*ene* (*diacetylflavovirol*, **16**). Mp 91–93°. $[\alpha]_D^{20}$ + 35° (*c* 1.37, $CHCl_3$). IR ν_{max}^{KBr} cm^{-1}: 3070, 1735, 1650, 1250, 740. ^1H NMR (CCl_4): δ 5.6 (collapsed Q_{AB}, H-15 and H-16), 4.85 (1H, *m*, $W_{1/2}$ = 7 Hz, H-7), 3.72 (collapsed Q_{AB}, 2H-18), 2.05 (6H, 2AcO– groups), 1.10, 0.91 and 0.88 (3H each, C–Me singlet signals). ^{13}C NMR: see Table 1. MS *m/z* (rel. int.): 388 $[M]^+$ (1), 328 (13), 301 (75), 269 (100), 256 (45), 254 (32), 241 (23), 240 (23), 226 (18), 212 (7), 199 (13), 186 (20), 172 (23), 160 (25). Found: C, 74.35; H, 9.65; $C_{24}H_{36}O_4$ requires: C, 74.19; H, 9.34%.

ent-3β,18-*Isopropilidenedioxy*-7α-*hydroxy*-14β-*acetoxybeyer*-15-*ene* (*acetonide of* 14-*acetylpusillatetrol*, **20**). Mp 198–200°. $[\alpha]_D^{20}$ + 30° (*c* 1.20, $CHCl_3$). IR ν_{max}^{KBr} cm^{-1}: 3500, 3060, 1740, 1250, 730. ^1H NMR: δ 5.45 (collapsed Q_{AB}, H-15 and H-16), 4.60 (1H, *s*, H-14), 3.80 (1H, *m*, $W_{1/2}$ = 6 Hz, H-7), 3.40 (3H, collapsed Q_{AB} superimposed to a broad signal, 2H-18 and H-3), 2.0 (3H, AcO– group), 1.32 (6H, *s*, isopropylidenedioxy group), 1.0, 0.92 and 0.79 (3H each, C–Me singlet signals). MS *m/z* (rel. int.): 418 $[M]^+$ (0.5), 403 (100), 385 (0.5), 361 (2), 360 (2), 359 (2), 358 (1), 344 (5), 343 (4), 330 (2), 327 (2), 301 (11), 292 (3), 291 (4), 284 (23), 283 (17), 266 (17). Found: C, 71.80; H 9.20; $C_{25}H_{38}O_5$ requires: C, 71.74; H, 9.15%.

Acknowledgements—We thank Dr. J. Santoro (C.S.I.C., Madrid) for recording ^{13}C NMR spectra. This work was supported by a grant from the Comisión Asesora de Investigación Científica y Técnica.

REFERENCES

1. García-Granados, A., Parra, A., Peña, A. and Socorro, O. *An. Quim.* (in press).
2. Rabanal, R. M., Rodríguez, B. and Valverde, S. (1974) *Experientia* **30**, 977.
3. Garcia de Quesada, T., Rodriguez, B. and Valverde, S. (1973) *An. Quim.* **69**, 1201.
4. Garcia de Quesada, T., Rodríguez, B. and Valverde, S. (1974) *An. Quim.* **70**, 239.
5. Escamilla, E. M. and Rodriguez, B. (1980) *An. Quim.* **76**, 189.
6. von Carsten-Lichterfelde, C., Pascual, C., Rabanal, R. M., Rodriguez, B. and Valverde, S. (1977) *Tetrahedron* **33**, 1989.