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CHROMONES AND FLAVANS FROM *MARSHALLIA OBOVATA*

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Key Word Index—*Marshallia obovata*; Compositae; new chromones; new flavan derivatives; new thymol derivative; new inositol ester.

Abstract—An investigation of *Marshallia obovata* afforded, in addition to known thymol derivatives, one new ester. Furthermore six new chromone derivatives, all prenylated, were present together with the known spathelia chromene. The main constituent was a flavan already isolated from *M. grandiflora* but five new flavans were also isolated. Besides other widespread compounds a tetraester of inositol was isolated in minute amounts. All the structures were elucidated by spectroscopic methods or chemical transformations. Surprisingly, even the main 4-methoxyflavan could be split by periodic acid.

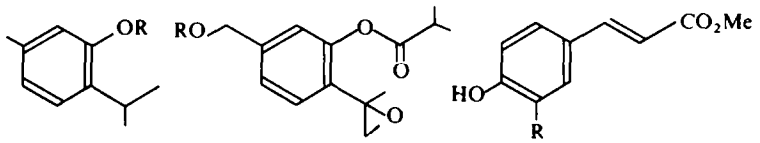
INTRODUCTION

Although the North American genus *Marshallia* has always been placed in the Heliantheae (Compositae), some authors have proposed that it should be put in the Eupatorieae instead. It appeared to us that an examination of its chemistry might be helpful to reach a clear decision on this point. So far, only one species, *M. grandiflora*, has been investigated chemically but the amount of material was very limited [1] and a more precise investigation was thus desirable. We have now studied *M. obovata* (Walt.) Beadle et Baynt. and found that the main constituent was a flavan derivative previously isolated from *M. grandiflora* [1]. However, in addition, some widely distributed compounds and several new ones are present. These include six new chromone derivatives and five further flavans, an inositol tetraester and a new thymol epoxide.

RESULTS AND DISCUSSION

The roots of *M. obovata* contain the thymol derivatives **1**–**5** [5, 6] of which only **3** is new and its structure clearly follows from the spectral data (see Experimental). Furthermore we isolated euphol acetate, together with some unidentified triterpenes, **8** [7], dehydrocostus lactone (**9**) [8], the sesquiterpene acids **10** [9] and **11** [10] as well as methyl *p*-coumarate. In addition to the known flavan derivatives **21** and **22** [1], a new one (**23**), with the positions of the hydroxy and methoxy groups at C-3 and C-4 reversed, was present. The structure follows from the ^{1}H NMR data (see Table 1). The protons at C-3 and C-4 show small differences in chemical shift compared with those of **22**. A second unknown flavan was obviously closely related to **21**. The ^{1}H NMR spectrum (see Table 1) shows that the prenyl side chain must be cyclized and dehydrogenated, since the typical signals of a chromene are visible. Hence, only the structure **27** seems likely for this compound. The relative position of the prenyl side chain in these flavans could be assigned by comparison with known compounds and from the results of the Eu(fod)$_3$-shift measurements [1], but further proof was desirable. We therefore degraded these compounds with periodate. The reaction of **21** with sodium periodate under neutral conditions afforded **29** from ring B and the aldehyde **28** whose structure was established by acid-catalysed cyclization to **30**, which on acetylation yielded **31**. The ^{1}H NMR data, and especially the observed Eu(fod)$_3$-shifts in the spectrum of **31**, clearly indicated the position of the prenyl side chain. The observed splitting of the dihydropyran ring requires hydrolysis at C-2. Surprisingly compound **22** could also be transformed to **30**. However, addition of dilute acid was necessary indicating that hydrolysis at C-4 was effected only in acidic medium under very mild conditions.

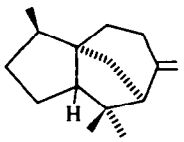
Compounds **21**–**23** and **27** could only be separated with difficulty from a complex mixture of chromone derivatives. Seven compounds of this type were finally isolated, only one of which, **13**, being previously known from *Spathelia sorbifolia* [2] (Rutaceae). A second chromone (**17a**) was prepared by the methylation of peucenine (**17b**), isolated from *Ptaeroxylon obliquium* (f.Sapidinaceae) [3]. The presence of the free 5-hydroxy group in **17a** follows from the observed ^{1}H-NMR signal at 12.76, which clearly indicates a hydrogen-bonded hydroxyl. The structures of two further chromones could be assigned by comparison of the ^{1}H-NMR data with those of **13** (see Table 2). To establish the position of the chromene ring in all these compounds we acetylated **13**. and the observed Eu(fod)$_3$-shifts of the resulting acetate (see Table 2) indicate that its structure is **14** and not the possible isomeric structure, present in ptaerochromeniol [4], with a C-C-bond at C-8. Three further chromones. which could not be separated, only differ in the acyloxy group at C-5′, which clearly follows from the ^{1}H NMR data (see Table 2). Their spectra further show that compounds closely related to peucenine must be present. The molecular formulae indicate that the corresponding



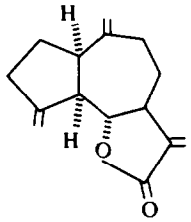
1 R = *i*-Bu [5]
2 R = Mebu [5]

3 R = *i*-Val
4 R = *i*-Bu [6]
5 R = Mebu [6]

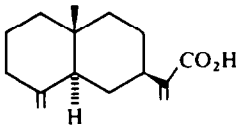
6 R = H
7 R = OH



8 [7]



9 [8]



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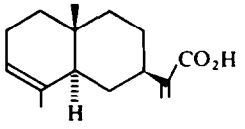

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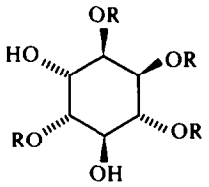
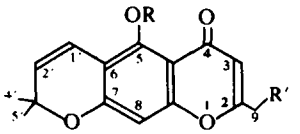
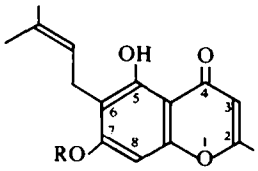


12 R = Ac, Ang, Ang, Ang

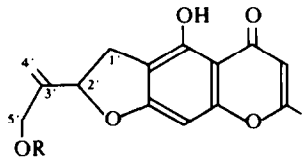


13 R = H, R′ = H
14 R = Ac, R′ = H



15 R = H, R′ = O-*i*-Bu
16 R = H, R′ = OH

17a R = Me
17b R = H



18 R = *i*-Bu
19 R = *i*-Val
20 R = Mebu

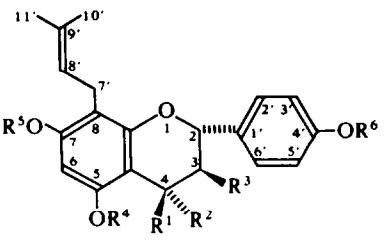
alcohol is isomeric with **16**, while the ^{1}H NMR data require that these compounds are dihydrofurans bearing an isopropenyl group substituted with different acyloxy groups (**18**–**20**: see Table 2), we have named the corresponding alcohol *marshallia chromone*.

Biogenetically, all the chromones are most probably formed from **17b** as a common precursor. Transformation to the 2,3-epoxide could be followed by cyclization in two different ways, which, after elimination of water, would lead to a chromene or a dihydrofuran. Further simple oxidation steps and esterification would lead to the compounds isolated.

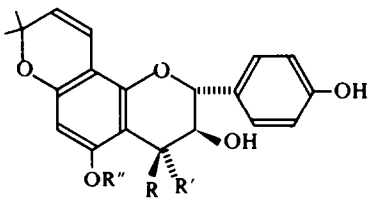
The aerial parts of the plant contain compounds **6**, **7** and **21**–**23** and three new flavan derivatives. The ^{1}H NMR data show that these latter compounds have the structures **24**–**26** (see Table 1). In the NMR spectrum of **24**, signals of 2-, 3- and 4-H clearly indicate that no function is present at C-3. The position of the methoxy group follows from the observed shift for 6-H, and from the typical splitting of the signals for 7′-H induced by the neighbouring methoxy group. The ^{1}H NMR spectrum of **25** indicates that the 4-hydroxy group must be replaced by a keto group, consequently the 3-H signal is shifted downfield when compared with the chemical shift in the spectrum of **21**.

The presence of a chromene ring in **26** also follows from the ^{1}H NMR data; the other signals of this compound are very similar to those of **25**, indicating the same stereochemistry at C-2 and C-3. The NMR data of **27** clearly show that this is the corresponding 4-hydroxy derivative of **26**. The observed coupling constants indicate that again the stereochemistry at C-2, C-3 and C-4 is the same as those of **21**. Compounds **26** and **27** are presumably biogenetically derived from **25** via **21**.

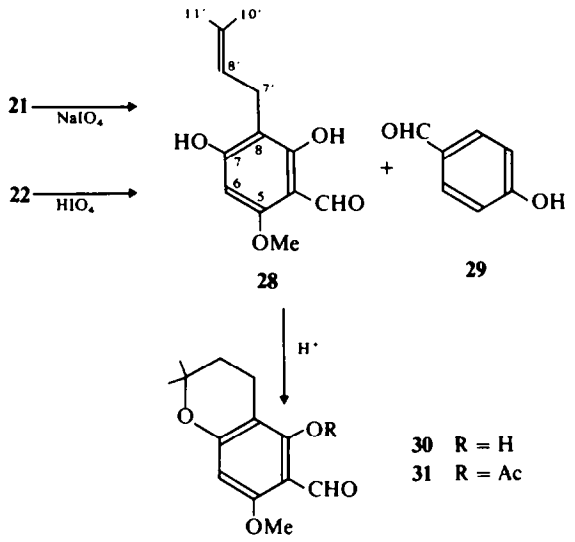
Finally we isolated a tetraester in minute amounts which turned out to be a derivative of inositol. The sterochemistry of the compound **12** clearly follows from



	21 [1]	22 [1]	23	24	24a	25
R^1	OH	OMe	OH	OH	OH	=O
R^2	H	H	H	H	H	
R^3	OH	OH	OMe	H	H	OH
R^4	Me	Me	Me	H	H	H
R^5	H	H	H	Me	Me	H
R^6	H	H	H	H	Ac	H



	26	27
R	=O	OH
R′		H
R″	H	Me



28 **29**

30 R = H
31 R = Ac

the observed coupling constants, but the relative position of the four ester residues has not been established; the ^{1}H NMR data (see Experimental) only show that, in addition to three angelicates, one acetate group must be present.

The compounds isolated from this *Marshallia* species show that this genus bears no close relationship to other genera in the tribe Heliantheae. The overall picture, however, is very uniform since biogenetically most of the compounds are derivatives of phloroglucinol, all prenylated. While the flavans **21**–**27** are surely condensation products with activated coumarate, the chromones must be formed by condensation of the same phloroglucinols with acetoacetate. The latter pathway seems to be rare in composites. The proposed position as a separate tribe Marshalliinae [11] therefore seems to be supported by the chemistry of the genus. Furthermore, a relationship with the Inuleae is very likely, since prenylated phloroglucinol derivatives are widespread in the genus *Helichrysum* [12].

EXPERIMENTAL

IR: CCl_4 or $CHCl_3$; ^{1}H NMR: 270 MHz, TMS as int. standard; MS: 70 eV. The air-dried plant material (79/1337) was cut and extracted with Et_2O–petrol (1:2). The resulting extracts were first separated by column chromatography (Si gel: grade II) and further by repeated TLC (on Si gel GF 254). Known compounds were identified by comparison of their IR and ^{1}H NMR spectra with those of authentic compounds. Roots (50 g) afforded 8 mg euphol acetate, 2 mg **1**, 3 mg **2** (Et_2O–petrol, 1:10),

Table 1. ^{1}H NMR data of compounds **23**–**28**, **30** and **31***

Position of H	**23** $(CD_3)_2CO$	**24** $(CDCl_3)$	**25** $((CD_3)_2CO)$	**26** $(CDCl_3)$	**27** $((CD_3)_2CO)$	**28** $(CDCl_3)$	**30** $(CDCl_3)$	**31** $(CDCl_3)$	Δ†
2	4.69 *d*	5.42 *dd*	4.62 *d(br)*	4.53 *d*	4.91 *d*				
3	4.20 *dd*	2.57 *ddd* 3.21 *dd*	5.08 *d(br)*	5.00 *d*	4.90 *dd*				
4α	4.49 *d*	4.22 *d*	—	—	4.23 *d*				
6	6.19 *s*	5.73 *s*	6.09 *s*	5.96 *s*	6.05 *s*	5.89 *s*	5.83 *s*	6.30 *s*	0.16
2′,6′	7.28 *d(br)*	7.23 *d(br)*	7.45 *d(br)*	7.42 *d(br)*	7.35 *d(br)*	—	—	—	
3′,5′	6.82 *d(br)*	6.76 *d(br)*	6.92 *d(br)*	6.89 *d(br)*	6.87 *d(br)*	—	—		—
7′	3.24 *d(br)*	3.13 *dd(br)* 3.03 *dd(br)*	3.20 *d(br)*	6.63 *d*	6.45 *dd*	3.35 *d(br)*	2.60 *t*	2.54 *t*	0.22
8′	5.22 *tqq*	5.10 *tqq*	5.18 *t(br)*	5.53 *d*	5.44 *d*	5.26 *tqq*	1.80 *t*	1.80 *t*	0.10
10′	1.53 *s(br)*	1.64 *s(br)*	1.61 *s(br)*	1.45 *s*	1.37 *s*	1.84 *s(br)*	1.37 *s*	1.36 *s*	0.07
11′	1.52 *s(br)*	1.56 *s(br)*	1.57 *s(br)*		1.36 *s*	1.79 *s(br)*			
OMe	3.76 *s* 3.36 *s*	3.73 *s*	—	—	3.83 *s*	3.84 *s*	3.81 *s*	3.85 *s*	0.15
OH			11.65 *s* 10.79 *s*	11.43 *s*	8.34 *s*	12.80 *s* 6.27 *s*	12.75 *s*	2.39 *s* (OAc)	0.38
CHO	—	—	—	—	—	10.10 *s*	10.07 *s*	10.25 *s*	0.39

* 270 MHz, TMS as internal standard.

† Shifts after addition of 0.1 equivalents of $Eu(fod)_3$.

J (Hz): 2′,3′ = 8.5; **23**: 2, 3 = 3, 4 = 4.5; 7, 8′ = 7; 8′, 10′ = 8′, 11′ = 1; **24**: 2′, 3_1 = 11.5; 2, 3_2 = 3; 3_1, 4 = 3; 3_1, 3_2 = 15; 7′, 8′ = 7; 8_1, 8_2 = 13; **25**: 2, 3 = 12; 7′, 8′ = 7; **26**: 2, 3 = 12; 7′, 8′ = 10; **27**: 2, 3 = 9; 3, 4 = 3.5; 6, 7′ = 0.5; 7′, 8′ = 10; **28**: 7′, 8′ = 7; **30/31**: 7′, 8′ = 7.

Table 2. ^{1}H NMR data of compounds **13**–**17a** and **18**–**20***

Position of H	**13** ($CDCl_3$)	**14** ($CDCl_3$)	Δ†	**15** ($CDCl_3$)	**16** ($CDCl_3$)	**17a**	**18 20**
3	6.00 *s(br)*	5.93 *q*	1.37	6.19 *t*	6.30 *t*	6.03 *q*	6.02 *s(br)*
8	6.27 *s(br)*	6.65 *d*	0.75	6.29 *d*	6.28 *s(br)*	6.36 *s*	6.31 *s*
9	2.33 *d*	2.29 *d*	0.22	4.96 *s(br)*	3.86 *d* 3.77 *d*	2.34 *s(br)*	2.34 *d*
1′	6.70 *d(br)*	6.48 *dd*	1.17	6.70 *dd*	6.70 *dd*	3.34 *d(br)*	3.46 *dd* 3.18 *dd*
2′	5.60 *d*	5.74 *d*	0.53	5.62 *d*	5.61 *d*	5.21 *t(br)*	5.44 *dd*
4′	1.40 *s*	1.48 *s*		1.47 *s*	1.48 *s*	1.79 *s(br)*	5.36 *s(br)* 5.29 *s(br)*
5′			0.39			1.68 *s(br)*	4.73 *d(br)* 4.65 *d(br)*
OMe	—	—	—	—	—	3.88 *s*	
OCOR	—	—	—	2.68 *qq* 1.25 *d*	— —		‡
OAc	—	2.45 *s*	2.31	—	—		
OH	13.0 *s*	—	—	12.80 *s*	12.80 *s*	12.76 *s*	12.92 *s*

*270 MHz, TMS as internal standard.
† Δ values after addition of 0.2 equivalents $Eu(fod)_3$.
‡ OCOR: **18**: 2.57 *qq*, 1.18 *d*, 1.15 *d*; **19**: 0.96 *d*; **20**: 2.40 *tq*, 0.90 *t*, 1.44 *d*.
J(Hz): 3,9 ~ 1; 8,1′ ~ 1; 1′,2′ = 10 (**17a**: 7); **18**–**20**: $1'_1,2 = 9.5$; $1',2 = 7.5$; $1'_1,1'_2 = 14.5$; $5'_1,5'_2 = 13$.

2 mg **3**, 10 mg **4**, 5 mg **5**, 1 mg **6**, 7 mg **8**, 2 mg **9**, 1 mg **10**, 1 mg **11**, 12 mg **13**, 8 mg **15** (Et_2O–petrol 1:3), 4 mg **16** (Et_2O–petrol 1:1), 3 mg **17a** (Et_2O–petrol, 1:1), 4 mg **18–20** (Et_2O–petrol, 1:1, *ca* 1:1:1), 35 mg **21**, 90 mg **22**, 3 mg **23** (Et_2O–*tert*.-BuOH, 70:1), and 12 mg **27** (Et_2O), while 200 g aerial parts yielded 6 mg **6**, 5 mg **7**, 4 mg **12**, 140 mg **21**, 2.1 g **22**, 40 mg **23**, 8 mg **24** (Et_2O–petrol, 3:1), 3 mg **25** (Et_2O petrol, 3:1), 5 mg **26** (Et_2O–petrol, 3:1) and 30 mg **27** (Et_2O).

7-Isovaleryloxy-8,9-epoxythymolisobutyrate (**3**). Colourless oil, not free from **5**, IR cm^{-1}: 1760 (PhOCOR), 1740 (CO_2R); MS: M^+ *m/e* 334.178 (2%) ($C_{19}H_{26}O_5$); —O=C=CMe$_2$ 264 (20); O=C=CHCHMe$_2$ 250 (55); 264—RCO_2H 162 (100); ^1H NMR ($CDCl_3$): *d* 7.02 (2-H), *d* 7.45 (5-H), *dd* 7.21 (6-H), *s* 5.09 (7-H), *d* 2.85 (9-H), *d* 2.47 (9-H), *s* 1.59 (10-H), *m* 2.84, *d* 1.36 (OCOCHMe$_2$), *d* 2.24, *m* 2.05, *d* 0.94 (OCOCH$_2$CHMe$_2$).

O-Acetyl-inositol-triangelicate (**12**). Colourless oil; IR (CCl_4) cm^{-1}: 1240, 1760 (OAc), 1730 (OAc, OCOC=C), 1650 (C=C); 3620 (OH); ^1H NMR ($CDCl_3$): *dd* 5.25 (1-H), *s(br)* 4.26 (2-H), *dd* 5.58 (3-H), *dd* 5.52 (4-H), *dd* 5.44 (5-H), *m* 4.23 (6-H), *m* 2.44, *s(br)* 2.34 (OH), *s* 1.99 (OAc), *qq* 6.19, 6.17, 6.11 (3′-H), *dq* 2.06, 2.03, 1.98 (4-H), *dq* 2.00, 1.95, 1.88 (5′-H) [*J*(Hz) = 1, 2 = 3.5, 2, 3 = 10.5; 3, 4 = 3; 4, 5 = 10; 5, 6 = 9; 3′, 4′ = 7; 3′, 5′ = 4′, 5′ = 1.5]; MS: M^+ *m/e* 468 (20%) ($C_{23}H_{32}O_{10}$); $-H_2O$ 450 (52); $-HOAc$ 408 (14); $-OCOC_4H_7$ 369 (56); $-HO_2CC_4H_7$ 368 (64); $C_4H_7CO^+$ 83 (100).

9-Isobutyryloxy-spatheliachromene (**15**). Colourless crystals, mp 108°; IR ($CHCl_3$) cm^{-1}: 1750 (CO_2R), 1660, 1635, 1600 (chromone); MS: M^+ *m/e* 344.126 (18%) ($C_{19}H_{20}O_6$); $-Me$ 329 (100); 329 $-OCOR$ 242 (18).

9-Hydroxyspatheliachromene (**16**). Colourless gum; IR ($CHCl_3$) cm^{-1}: 3600 (OH), 1660, 1635, 1600 (chromone); MS: M^+ *m/e* 274.084 ($C_{15}H_{14}O_5$).

Peucenine-7-O-methyl ether (**17a**). Colourless gum; IR ($CHCl_3$) cm^{-1}: 1665, 1635, 1600 (chromone); MS: M^+ *m/e* 274.121 (25%) ($C_{16}H_{18}O_4$); $-C_4H_7$ 219 (35); 219 $-CH_2O$ 189 (4); 189 $-C_4H_3$ 149 (100) (RDA).

Marshalliachromone-isobutyrate and -isovalerate [*2-methylbutyrate*] (**18–20**). Not separated, colourless oil; IR ($CHCl_3$) cm^{-1}: 1745 (CO_2R), 1670, 1635, 1610 (chromone); MS: M^+ *m/e* 358.142 (36%) and 344.126 (28) ($C_{20}H_{22}O_6$ and $C_{19}H_{20}O_6$); $-RCO_2H$ 256 (55); 256 $-C_3H_4$ 216 (100); 216 $-C_4H_3O$ 149 (91).

4β,7,4′-Trihydroxy-3β,5-dimethoxy-8-[3,3-dimethylallyl]-flavan (**23**). Colourless gum: IR ($CHCl_3$) cm^{-1}: 3600 (OH), 1620, 1600, 1560 (aromatic); MS: M^+ *m/e* 386.173 (11%) ($C_{22}H_{26}O_6$); $-OH$ 369 (2); $-MeOH$ 356 (45); 356 $-CH_2O$ 326 (40); 326 $-Me$ 311 (15); $C_5H_9^+$ 69 (100).

4β,5,4′-Trihydroxy-7-methoxy-8-[3,3-dimethylallyl]-flavan (**24**). Colourless gum; IR ($CHCl_3$) cm^{-1}: 3600 (OH), 1620, 1600 (aromatic); MS: M^+ *m/e*—; $-H$, $-Me$ 340 (55); 340 $-CO$ 312 (60); 2 mg **24** were acetylated at room temp. (12 hr). 2 mg **24a** were obtained, colourless gum, MS: M^+ *m/e* —; $-H_2O$ 380.162 ($C_{23}H_{24}O_5$).

3β,5,7,4′-Tetrahydroxy-8-[3,3-dimethylallyl]-flavonone (**25**). Colourless gum; IR ($CHCl_3$) cm^{-1}: 3600 (OH), 1635 (C=O), 1610 (aromatic); MS: M^+ *m/e* 356.126 (21%) ($C_{20}H_{20}O_6$); $-OH$ 339 (58); 339 $-HOCH=CHC_6H_4OH$ (RDA) 203 (100).

4-Oxoobovatachromene (**26**). Colourless gum; IR ($CHCl_3$) cm^{-1}: 3600 (OH), 1640, 1625 (C=O), 1610 (aromatic); MS: M^+ *m/e* 354.110 (36%) ($C_{20}H_{18}O_6$); $-Me$ 339 (46); 339 $-H_2O$ 321 (11); 339 $-HOCH=CHC_6H_4OH$ 203 (100) (RDA).

4β-Hydroxyobovatachromene (**27**). Colourless gum: IR ($CHCl_3$) cm^{-1}: 3600 (OH), 1615, 1585, 1520 (aromatic); MS: M^+ *m/e* 370.142 (5%) ($C_{21}H_{22}O_6$); $-Me$ 355 (8); $-HOCH=CHC_6H_4OH$ 234 (10); $-Me$ 219 (100).

Acetylation of **13**. 10 mg **13** in 1 ml CH_2Cl_2 were heated with 0.1 ml Ac_2O and 10 mg 4-pyrrolidinopyridine [13]. TLC (Et_2O–petrol, 1:1) afforded 10 mg **14**, colourless gum, ^1H NMR see Table 2.

Degradation of **21**. To 5 mg **21** in 1 ml MeOH, 15 mg $NaIO_4$ in 0.2 ml H_2O were added. After 2 hr at room temp. H_2O was added and the product extracted with Et_2O. TLC (Et_2O–petrol, 1:1) afforded 1 mg **29** and 2 mg **28**, colourless gum. ^1H NMR see Table 1.

Degradation of **22**. To 30 mg **22** in 2 ml MeOH 50 mg $NaIO_4$ in 0.5 ml 2 N H_2SO_4 was added. After 2 hr stirring at room temp. the reaction products were isolated and separated by TLC. 5 mg **29** and 15 mg **28** were obtained. 15 mg **28** were refluxed in 2 ml C_6H_6 with 10 mg *p*-toluene sulphonic acid. After washing with $NaHCO_3$ soln and evapn of the organic phase, TLC afforded 10 mg **30**, which were acetylated as above yielding 8 mg **31**, colourless gum, MS: M^+ *m/e* 278.115 (4%) ($C_{15}H_{18}O_5$); —ketene 236 (35); 236 $-Me$ 221 (15); 221 $-CO$ 193 (13); 236 $-C_4H_7$ 181 (100).

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