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STRUCTURE OF SAWARANIN: A DECARBOXYLATED ASCORBIGEN IN THE HEARTWOOD OF *CHAMAECYPARIS PISIFERA*

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IN MEMORY OF TONY SWAIN, 1922–1987

Key Word Index—*Chamaecyparis pisifera*; Cupressaceae; heartwood; ascorbigen; sawaranin.

Abstract—The structure of sawaranin which had been isolated from the heartwood of *Chamaecyparis pisifera* was re-examined. The structure as a decarboxylated ascorbigen, (3*S*,4*R*,6*R*,7*S*)-5,8-epoxy-3-*p*-hydroxyphenyl-5,6,7-trihydroxyoctan-1,4-olide, was determined by spectral analyses of sawaranin and its derivatives and by chemical degradation of monomethylsawaranin into *d*-*p*-anisylsuccinic acid and L-threose. Further, sawaranin was synthesized by decarboxylative hydrolysis of the product of the reaction of L-ascorbic acid with methyl 3-hydroxy-3-*p*-hydroxyphenylpropionate.

INTRODUCTION

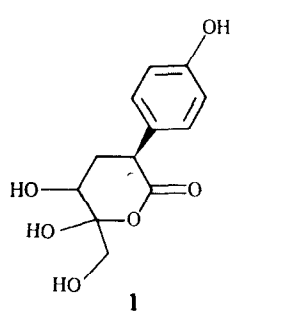
Sawaranin is a phenolic substance isolated from the heartwood of *Chamaecyparis pisifera* (Japanese name 'Sawara'), the structure of which was proposed as **1** by Imamura [1] in 1962. Our recent interest in phenolic constituents in this heartwood led to the isolation of sawaranin identical with an authentic sample, kindly supplied by Imamura, by mmp and by direct comparisons of the IR spectrum and TLC behaviour. However, the assignments of the ^{1}H and ^{13}C NMR spectra obtained by us did not agree with the structure proposed for sawaranin by Imamura. In addition, the molecular formula analysed by HRMS was found to be $C_{14}H_{16}O_7$, not $C_{12}H_{14}O_6$ which had been proposed by him. Hence, we re-examined the structure, and conclude that it should be revised from **1** to **3**.

RESULTS AND DISCUSSION

Sawaranin had a carbonyl group (ν_{max} 1760 cm^{-1}, ^{13}C NMR: 177 ppm) appropriate for γ-lactone and four hydroxyl groups (ν_{max} 3600, 3400 cm^{-1}), affording tetraacetylsawaranin by acetylation. One of the hydroxyl groups was ascribed to that of a *p*-substituted phenol by the UV (λ_{max} 278 nm) and ^{1}H NMR [δ 6.98 and 6.68 ppm (A_2B_2, J = 8.8 Hz)] spectra. In the ^{1}H NMR spectrum (in DMSO), the four hydroxyl protons resonated as four pairs of one-proton signals [δ 9.27 and 9.24 (each *s*); 5.91 and 5.56 (each *s*); 5.30 and 5.46 (each *d*); 5.15 and 5.39 ppm (each *d*)] with the relative peak area of 7:2, which suggested that sawaranin exists in solution as a mixture of two equilibrium forms, having one phenolic, one tertiary and two secondary hydroxyl groups. The fact was also supported by the ^{13}C NMR spectrum, in which all the carbon signals appeared as double lines except for those of the phenolic ring (see Table 1). Sawaranin had no primary hydroxyl group. Nevertheless, Imamura demonstrated the formation of one mole of formaldehyde as well as 'methyl*nor*sawaranonic acid' by periodate oxidation of monomethylsawaranin. This discrepancy was resolved by the finding that a primary hydroxyl group took part in the formation of a hemiacetal moiety in sawaranin, since two carbon signals due to a tertiary carbon bearing two oxygen atoms [102.1 ppm (*s*)] and an oxy-methylene carbon [69.8 ppm (*t*)] were observed in the ^{13}C NMR spectrum. As for Imamura's 'methyl*nor*sawaranonic acid', $C_{12}H_{12}O_5$, he showed that the compound contained a butyrolactone and carboxylic and anisyl groups, affording *d*-*p*-anisylsuccinic acid on oxidation; hence he proposed the structure as **2**. However, the ^{1}H NMR spectrum of 'monomethyl*nor*sawaranonic acid' prepared by us showed proton signals at δ 5.33 (*d*, J = 5.0 Hz, 4-H), 4.11 (*ddd*, J = 5.0, 6.2, 8.8 Hz, 3-H), 3.28 (*dd*, J = 8.8, 17.7 Hz, 2-H) and 2.86 ppm (*dd*, J = 6.2, 17.7 Hz, 2-H) in addition to signals of *p*-anisyl and carboxyl groups, indicative of the presence of a β,γ-disubstituted butyrolactone moiety. Thus the structure of this compound should be represented by **9** and not by **2**.

It was difficult to analyse fully the ^{1}H NMR spectrum of sawaranin itself because of its anomeric nature, but tetraacetylsawaranin displayed clearly separated signals in the ^{1}H NMR as it was obtained as a single product. The ^{1}H NMR spectrum revealed the presence of two structural units with the same proton system, $-CH_2-\underset{|}{CH}-\underset{|}{CH}-$, attributable to a β,γ-disubstituted butyrolactone and a C(1)-substituted triacetylfuranose moiety by considering their chemical shifts (see Experimental). Consequently, structure **3** is apparent for sawaranin.

To confirm this structure including the absolute stereochemistry, we performed the cleavage of the C(4)–C(5) bond of monomethylsawaranin (**8**) as follows. Tetrahydropyranylation of **8** which was prepared from sawaranin via isopropylidenesawaranin (now represen-



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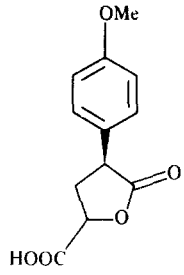

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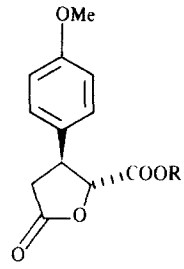
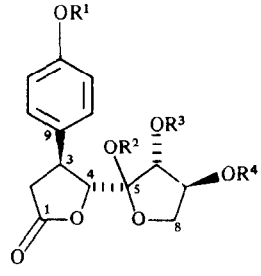
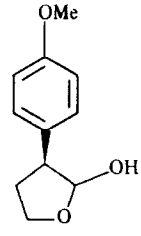


9 R = H
10 R = Et



3 $R^1 = R^2 = R^3 = R^4 = H$
4 $R^1 = R^2 = R^3 = R^4 = Ac$
5 $R^1 = H$; $R^2, R^3 = >CMe_2$; $R^4 = H$
6 $R^1 = Me$; $R^2, R^3 = >CMe_2$; $R^4 = H$
7 $R^1 = Me$; $R^2, R^3 = >CMe_2$; $R^4 = Ac$
8 $R^1 = Me$; $R^2 = R^3 = R^4 = H$
11 $R^1 = Me$; $R^2 = H$; $R^3 = R^4 = THP$



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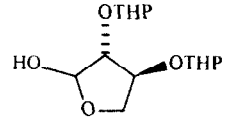


13

ted by the structure **5**, see Experimental) according to Imamura's method, gave the bistetrahydropyranyl derivative **11**. Compound **11** was reduced with lithium aluminium hydride and then oxidized with sodium periodate to yield the fragments **12** and **13**. The former was further oxidized with potassium permanganate to give *d-p*-anisylsuccinic acid [1], $[\alpha]_D + 115°$, while the latter was treated in aqueous acid to give L-threose [2], $[\alpha]_D + 11°$. The absolute configurations at C-3, C-6 and C-7 of sawaranin were thus determined. As for the configuration at C-4 of sawaranin, 3,4-*trans* was suggested by the ^{1}H NMR spectrum of the ethyl ester (**10**) of **9**, because the chemical shifts [δ 4.27 (*q*) and 1.30 ppm (*t*)] of the ethyl protons were unaffected by an anisotropic effect of the aromatic ring [3], indicating that the ethoxycarbonyl group was *trans* to the phenolic ring. This was also consistent with small *vicinal* coupling constants, 3–5 Hz, between 3–H and 4–H of **3** and its derivatives (**4**–**10**) [4].

Recently, Poss *et al.* [5] synthesized two phenolic ascorbigens, dilaspirolactone aglycone (**16**) and leucodrin (**17**), from compound **14** prepared by the C–C coupling reaction of L-ascorbic acid with methyl 3-hydroxy-3-*p*-hydroxyphenylpropionate. In the reaction, they also obtained the C(3)-epimer **15**. By treatment with aqueous base, we successfully converted **15** into sawaranin and 4-*epi*-sawaranin (**20**), which suggested that sawaranin might be produced biogenetically by decarboxylative hydrolysis of an ascorbigen such as the 5-oxo-derivative (**19**) of conocarpin (**18**) [6], as shown in the Scheme. In fact, 4-*epi*-sawaranin was also found to occur in this wood extract and the details will be reported soon, together with other phenolic constituents.

So far several ascorbigens have been found to occur in various plants and their biogeneses have been discussed [6–9], whereas sawaranin is the first example of a decarboxylated ascorbigen.

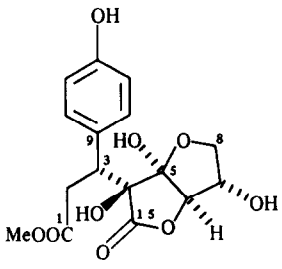
EXPERIMENTAL

General. Mps: uncorr; ^{1}H (100 MHz) and ^{13}C NMR (25.1 MHz): δ ppm from TMS; The sawaranin derivatives **4**–**10** were prepared by methods described by Imamura [1].

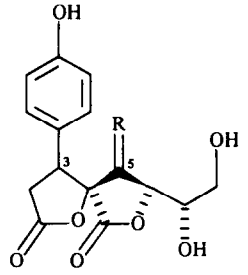
Table 1. ^{13}C NMR spectral data of sawaranin (3) and its derivatives

	3	3	4§	6‖	7¶	10**
C	in DMSO-d_6	in C_5D_5N		in $CDCl_3$		
1	176.6 (176.9)*	177.6 (178.1)*	175.3	176.3	176.6	175.0
2	36.2 (36.7)	37.3 (37.9)	37.0	36.2	36.3	35.3
3	38.2 (†)	39.8 (40.1)	40.5	40.1	40.2	43.8
4	86.1 (85.3)	88.0 (87.0)	84.5	86.6	87.0	82.3
5	102.1 (105.7)	103.9 (107.6)	107.1	113.6	114.1	169.1
6	76.9‡ (79.8)‡	79.0‡ (81.1)‡	77.3	87.2	84.4	
7	74.0‡ (76.6)‡	76.3‡ (78.2)‡	77.3	75.2	76.9	
8	69.8 (73.2)	71.5 (75.0)	73.3	75.1	71.4	
9	134.2 (134.3)	135.4 (†)	139.9	134.9	135.4	131.6
10, 14	127.4	128.3 (128.4)	127.8	127.4	127.3	127.6
11, 13	115.4	116.7	122.4	114.5	114.5	114.7
12	156.0	157.8	150.2	158.8	158.8	159.3

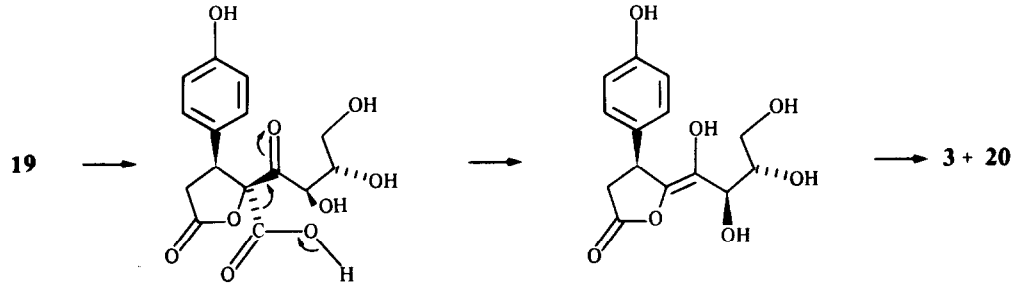
*Carbon signals due to a minor anomer.
†Carbon signals might be buried in a solvent signal.
‡Assignments may be interchanged.
§ —OAc: 170.4, 169.3, 169.2, 168.0, 21.1, 21.0, 20.6, 20.4 ppm.
‖ —OMe: 55.3; $>CMe_2$: 112.5, 27.1, 26.4 ppm.
¶ —OMe: 55.3; $>CMe_2$: 112.7, 27.1, 26.4; —OAc: 170.7, 20.8 ppm.
** —OMe: 55.3; -OEt: 62.1, 14.1 ppm.



14 3*R*
15 3*S*



16 R = O; 3*R*
17 R = H,OH; 3*R*,5*R*
18 R = H,OH; 3*S*,5*R*
19 R = O; 3*S*



Scheme 1. Postulated biogenesis of sawaranin and 4-*epi*-sawaranin.

Sawaranin **3**. The eartwood (5.2 kg) of *Chamaecyparis pisifera* was extracted with MeOH (72 l × 2) to give a brown oil (980 g), which was treated with hexane (1 l × 2) and then hot H_2O (500 ml × 3). The H_2O-soluble part (29 g) was then treated with Me_2CO (500 ml × 2). The Me_2CO extract was concd and left to stand, giving a ppt. of a crystalline material, which was recrystallized from H_2O to afford pure **3** (1.1 g), mp 214–222° (dec.) (fine needles) (lit. mp 200–226°), mmp 213–224°; UV λ_{max}^{MeOH} nm (log ε): 278 (3.24) (lit. λ_{max}^{MeOH} 279 nm); IR ν_{max}^{KBr} cm^{-1}: 3600, 3400, 3035, 2995, 2955, 2900, 1760, 1615, 1600, 1520, 1455, 1400, 1365, 1330, 1270, 1230, 1180, 1115, 1060, 1020, 1000, 955, 940, 880, 835, 815, 760; HRMS *m/z* (rel. int.): 296.0887 $[M]^+$

(calc. for $C_{14}H_{16}O_7$: 296.0896) (3), 236 $[C_{12}H_{12}O_5]^+$ (13), 207 $[C_{11}H_{11}O_4]^+$ (26), 178 $[C_{10}H_{10}O_3]^+$ (31), 165 $[C_9H_9O_3]^+$ (49), 133 $[C_9H_9O]^+$ (40), 123 $[C_7H_7O_2]^+$ (79), 120 $[C_8H_8O]^+$ (100), 119 (46), 107 (41), 91 (37), 77 (32), 32 (38), 31 (42), 29 (35), 28 (99).

Tetraacetylsawaranin **4**. Acetylation of **3** with Ac_2O–pyridine at room temp. for 15 hr gave **4**, mp 137–138° (prisms from MeOH) (lit. mp 134–135°); IR ν_{max}^{KBr} cm^{-1}: 2960, 1790, 1760, 1740, 1510, 1430, 1370, 1230, 1190, 1135, 1060, 1040, 1025, 1005, 980, 910, 855, 805, 650; ^1H NMR ($CDCl_3$): δ 7.17 (2H, *d*, *J* = 8.8 Hz, 10- and 14-H), 7.03 (2H, *d*, *J* = 8.8 Hz, 11- and 13-H), 5.73 (1H, *d*, *J* = 5.0 Hz, 6-H), 5.49 (1H, *dt*, *J* = 7.3, 5.0, 5.0 Hz, 7-H), 4.82 (1H, *d*, *J* = 4.0 Hz, 4-H), 4.71 (1H, *dd*, *J* = 9.1, 7.3 Hz, 8-H), 3.84 (1H, *ddd*, *J* = 10.0, 5.4, 4.0 Hz, 3-H), 3.79 (1H, *dd*, *J* = 9.1, 5.0 Hz, 8-H), 3.12 (1H, *dd*, *J* = 18.0, 10.0, 2-H), 2.55 (1H, *dd*, *J* = 18.0, 5.4 Hz, 2-H), 2.28, 2.08, 2.04 and 1.92 (each 3H, *s*, -OAc); ^1H NMR (C_6D_6): δ 6.84 (2H, *d*, *J* = 8.8 Hz, 10- and 14-H), 6.76 (2H, *d*, *J* = 8.8 Hz, 11- and 13-H), 6.11 (1H, *d*, *J* = 4.8 Hz, 6-H), 5.72 (1H, *dt*, *J* = 7.3, 4.8, 4.8 Hz, 7-H), 4.91 (1H, *d*, *J* = 4.1 Hz, 4-H), 4.75 (1H, *dd*, *J* = 9.2, 7.3 Hz, 8-H), 3.78 (1H, *dd*, *J* = 9.2, 4.8 Hz, 8-H), 3.63 (1H, *ddd*, *J* = 9.8, 7.0, 4.1 Hz, 3-H), 2.70 (1H, *dd*, *J* = 17.8, 9.8 Hz, 2-H), 2.14 (1H, *dd*, *J* = 17.8, 7.0 Hz, 2-H), 1.75, 1.57, 1.54 and 1.50 (each 3H, *s*, -OAc); HRMS *m/z* (rel. int.): 404.1087 $[M-HOAc]^+$ (calc. for $C_{20}H_{20}O_9$: 404.1107) (7), 302 $[C_{16}H_{14}O_6]^+$ (3), 218 $[C_{12}H_{10}O_4]^+$ (17), 203 $[C_8H_{11}O_6]^+$ (18), 177 $[C_{10}H_9O_3]^+$ (12), 176 $[C_{10}H_8O_3]^+$ (21), 120 $[C_8H_8O]^+$ (14), 43 (100), 28 (16).

Monomethylsawaranin **8**. A solution of **3** in Me_2CO was refluxed for 4 hr in the presence of *p*-TsOH to yield isopropylidenesawaranin **5**, mp 143.5–144° (needles from EtOAc–hexane) (lit. mp 143–143.5°), which was treated with an ethereal solution of CH_2N_2 for 12 hr, affording monomethylisopropylidene-sawaranin **6**, mp 121–122° (needles from Me_2CO–hexane) (lit. mp 121–122°); IR ν_{max}^{KBr} cm^{-1}: 3450, 2990, 2960, 1790, 1610, 1515, 1380, 1250, 1180, 1145, 1080, 1030, 850, 830; ^1H NMR ($CDCl_3$): δ 7.12 (2H, *d*, *J* = 8.8 Hz, 10- and 14-H), 6.84 (2H, *d*, *J* = 8.8 Hz, 11- and 13-H), 4.54 (1H, *d*, *J* = 3.0 Hz, 4-H), 4.45 (1H, *br s*, $W_{\frac{1}{2}}$ = 2 Hz, 6-H), 4.28–3.86 (4H, *m*, 3-, 7- and 8-H), 3.79 (3H, *s*, -OMe), 3.18 (1H, *dd*, *J* = 18.3, 10.0 Hz, 2-H), 2.65 (1H, *br d*, *J* = 10.2 Hz, -OH), 2.54 (1H, *dd*, *J* = 18.3, 4.0 Hz, 2-H), 1.49 and 1.23 (each 3H, *s*, $>CMe_2$); HRMS *m/z* (rel. int.): 350.1338 $[M]^+$ (calc. for $C_{18}H_{22}O_7$: 350.1366) (12), 335 $[C_{17}H_{19}O_7]^+$ (3), 219 $[C_{12}H_{11}O_4]^+$ (7), 190 $[C_{11}H_{10}O_3]^+$ (100), 162 $[C_{10}H_{10}O_2]^+$ (22), 134 $[C_9H_{10}O]^+$ (36) 121 $[C_8H_9O]^+$ (18), 91 (14), 59 (49), 43 (32).

The evidence of the 4,5-*O*-isopropylidene structure for **6** was shown by the observation that the ^1H NMR signal of a free hydroxyl group appeared as a doublet both in $CDCl_3$ (δ 2.65, *J* = 10.2 Hz) and in DMSO-d_6 (δ 5.26, *J* = 3.2 Hz), and by the ^1H NMR ($CDCl_3$) of the acetate **7**: δ 7.10 (2H, *d*, *J* = 8.8 Hz, 10- and 14-H), 6.84 (2H, *d*, *J* = 8.8 Hz, 11- and 13-H), 5.01 (1H, *dt*, *J* = 2.9, 1.0, 1.0 Hz, 7-H), 4.61 (1H, *t*, *J* = 1.0 Hz, 6-H), 4.48 (1H, *d*, *J* = 2.2 Hz, 4-H), 4.21 (1H, *dd*, *J* = 10.6, 2.9 Hz, 8-H), 4.04 (1H, *dt*, *J* = 10.6, 1.0, 1.0 Hz, 8-H), 3.88 (1H, *ddd*, *J* = 9.8, 2.7, 2.2 Hz, 3-H), 3.78 (3H, *s*, -OMe), 3.18 (1H, *dd*, *J* = 17.8, 9.8 Hz, 2-H), 2.48 (1H, *dd*, *J* = 17.8, 2.7 Hz, 2-H), 2.15 (3H, *s*, -OAc), 1.52 and 1.26 (each 3H, *s*, $>CMe_2$).

A soln of **6** in 5% HCl was refluxed for 30 min to yield monomethylsawaranin **8**, mp 175–178° (dec.) (fine needles from water) (lit. mp 175–176°); IR ν_{max}^{KBr} cm^{-1}: 3560, 3440, 2950, 2900, 1760, 1510, 1250, 1170, 1110, 1060, 1000, 830, 760; HRMS *m/z* (rel. int): 310.1048 $[M]^+$ (calc. for $C_{15}H_{18}O_7$:310.1053) (10), 179 $[C_{10}H_{11}O_3]^+$ (81), 137 $[C_8H_9O_2]^+$ (99), 134 $[C_9H_{10}O]^+$ (100), 121 $[C_8H_9O]^+$ (52), 119 (54), 91 (60), 32 (85), 31 (54), 28 (100).

'*Monomethyl*norsawaranonic acid' **9**. Oxidation of **8** with HIO_4 in water gave **9**, mp 144–145° (prisms from $CHCl_3$, anhydrous form) (lit. mp 142–143°); IR ν_{max}^{KBr} cm^{-1}: 3200, 2970, 1770, 1745, 1515, 1260, 1205, 1170, 1060, 1030, 830, 690; ^1H NMR (C_5D_5N): δ 7.39 (2H, *d*, *J* = 8.8 Hz, 10- and 14-H), 6.97 (2H, *d*, *J* = 8.8 Hz, 11- and 13-H), 5.33 (1H, *d*, *J* = 5.0 Hz, 4-H), 4.11 (1H, *ddd*, *J* = 8.8, 6.2, 5.0 Hz, 3-H), 3.68 (3H, *s*, -OMe), 3.28 (1H, *dd*, *J* = 17.7, 8.8 Hz, 2-H), 2.86 (1H, *dd*, *J* = 17.7, 6.2 Hz, 2-H); HRMS *m/z* (*rel. int.*): 236.0681 $[M]^+$ (calc. for $C_{12}H_{12}O_5$: 236.0685) (12), 208 $[C_{11}H_{12}O_4]^+$ (26), 134 $[C_9H_{10}O]^+$ (100), 133 $[C_9H_9O]^+$ (17), 121 $[C_8H_9O]^+$ (12), 119 $[C_8H_7O]^+$ (19), 91 (22), 77 (11), 65 (12).

'*Ethyl monomethyl*norsawaranonate' **10**. A soln of **9** in EtOH was refluxed for 2 hr in the presence of conc H_2SO_4 to yield **10**, mp 73–74° (needles from aq. MeOH) (lit. mp 73–73.5°); IR ν_{max}^{KBr} cm^{-1}: 2950, 1785, 1750, 1515, 1195, 1140, 1055, 825; ^1H NMR ($CDCl_3$): δ 7.13 (2H, *d*, *J* = 8.8 Hz, 10- and 14-H), 6.18 (2H, *d*, *J* = 8.8 Hz, 11- and 13-H), 4.81 (1H, *d*, *J* = 5.0 Hz, 4-H), 4.27 (2H, *q*, *J* = 7.3 Hz, $-COOCH_2Me$), 3.80 (3H, *s*, -OMe), 3.72 (1H, *ddd*, *J* = 8.8, 6.2, 5.0 Hz, 3-H), 3.05 (1H, *dd*, *J* = 17.7, 8.8 Hz, 2-H), 2.64 (1H, *dd*, *J* = 17.7, 6.2 Hz, 2-H), 1.30 (3H, *t*, *J* = 7.3 Hz, $-COOCH_2\underline{Me}$).

Monomethylbistetrahydropyranylsawaranin **11**. A mixture of **8** (204 mg), 2,3-dihydropyran (283 mg) and pyridinium *p*-toluenesulphonate (20 mg) in dry dioxane (10 ml) was stirred at room temp. for 18 hr. The mixture was diluted with Et_2O (50 ml), washed with H_2O and dried over Na_2SO_4. The product was chromatographed on a silica gel column eluting with EtOAc–hexane (2:3) to yield **11** (267 mg) as a gum: IR $\nu_{max}^{CCl_4}$ cm^{-1} 3530, 2950, 1785, 1515, 1245, 1175, 1120, 1065, 1035, 730; ^1H NMR ($CDCl_3$): δ 7.14 (2H, *d*, *J* = 8.8 Hz, 10- and 14-H), 6.85 (2H, *d*, *J* = 8.8 Hz, 11- and 13-H), 3.79 (3H, *s*, -OMe), 4.90–2.25 (15H), 1.64 (12H, *br s*, methylene protons of two THP groups).

d-p-*Anisylsuccinic acid and* L-*threose from* **11**. To a soln of **11** (200 mg) in dry THF (20 ml) was added dropwise a soln of $LiAlH_4$ (160 mg) in THF (10 ml) at room temp. and then refluxed for 1 hr. The reaction mixture was diluted with H_2O-satd Et_2O and a ppt. was filtered off. Without purification the reduction product was oxidized with $NaIO_4$ (210 mg) in water–dioxane (1:1) for 2 hr at room temp. and the soln was extracted with Et_2O. The crude product was then treated in 5% HCl–dioxane (1:1) for 11 hr. After extraction with Et_2O, the Et_2O layer was washed with 5% $NaHCO_3$, dried over $MgSO_4$, and evapd to give an oil (163 mg), which was chromatographed on a silica gel column eluting with EtOAc–hexane (1:1) to yield **12** (34 mg), mp 62–63° (fine needles from Et_2O–hexane) (lit. mp 63–64°). Upon permanganate oxidation the compound **12** afforded *d-p*-anisylsuccinic acid, mp 193–194° (lit. mp 197–198°), $[\alpha]_D$ +115° (EtOH; *c* 1.0) (lit. $[\alpha]_D$ +126°) as described by Imamura.

The residual aq. soln of the acid hydrolysate was evapd to yield a syrupy oil (24 mg), $[\alpha]_D$ +11° (c 2.0, water), which was refluxed in Me_2CO in the presence of conc H_2SO_4 to afford 1,2-*O*-isopropylidene-β-L-threofuranose, mp 84–85° (needles from Et_2O–hexane) (lit. mp 84–85°), $[\alpha]_D$ +13° (*c* 0.73, Me_2CO) (lit. $[\alpha]_D$ +13°). The spectral data: IR ν_{max}^{KBr} cm^{-1}: 3450, 2990, 2970, 2940, 2890, 1465, 1395, 1375, 1330, 1280, 1210, 1160, 1110, 1065, 1015, 980, 915, 850, 770; ^1H NMR ($CDCl_3$, 60 MHz): δ 5.90 (1H, *d*, *J* = 4 Hz), 4.45 (1H, *br d*, *J* = 4 Hz), 4.22 (1H, *m*), 4.03–3.73 (2H, *m*), 2.25 (1H, *br s*, OH), 1.48, 1.30 (each 3H, *s*), were in agreement with those of the D-isomer prepared from commercially available D-threose.

Synthesis of sawaranin **3** *and* 4-epi-*sawaranin* **20**. Compound **15**, prepared by the method described by Poss *et al.*, existed in two forms, the hemiacetal from **15a** and the keto form **15b**, in a ratio of *ca* 3:2 in soln and showed the following spectral data: UV λ_{max}^{EtOH} nm (logε): 276 (3.05); IR ν_{max}^{KBr} cm^{-1}: 3400, 2955, 2925,

1775, 1715, 1615, 1518, 1440, 1225, 1125, 1035, 840, 825; ^{1}H NMR (DMSO-d_6): hydroxyl protons of **15a**: δ 9.33 (*s*), 6.91 (*s*), 5.84 (*s*), 5.38 (*d*, J = 4.0 Hz); hydroxyl protons of **15b**: δ 9.45 (*s*), 6.91 (*s*), 5.27 (*d*, J = 5.5 Hz), 4.83 (*t*, J = 5.5 Hz); aromatic protons of **15a**: δ 7.07, 6.64 (each *d*, J = 8.8 Hz); aromatic protons of **15b**: δ 6.85, 6.64 (each *d*, J = 8.8 Hz); other protons of **15a** and **15b**: δ 4.10–2.60 ppm; ^{13}C NMR (DMSO-d_6) (assignments: from C-1 to C-15): **15a**: 176.1 32.5, 46.9, 80.2, 107.6, 86.6, 73.8, 73.2, 126.0, 130.7, 114.6, 156.6, 172.6, 51.1 (OMe); **15b**: 173.8, 31.9, 47.2, 74.6, 209.4, 82.9, 69.9, 60.6, 124.4, 129.3, 115.4, 157.0, 171.5, 51.3 ppm (OMe); HRMS *m/z* (rel. int.): 354.0936 $[M]^+$ (calc. for $C_{16}H_{18}O_9$: 354.0950) (1), 179 $[C_{10}H_{11}O_3]^+$ (46), 178 $[C_{10}H_{10}O_3]^+$ (67), 147 $[C_9H_7O_2]^+$ (100), 137 $[C_8H_9O_2]^+$ (52), 120 $[C_8H_8O]^+$ (29), 119 (35), 116 (23), 91 (29).

To an ice-cold soln of **15** (120 mg) in H_2O (5 ml) was added dropwise 0.1 M Na_2CO_3 (4 ml) over 1 hr and stirred for further 30 min at room temp. The soln was acidified (pH 3) with HCl and stirred for 5 hr and extracted with *n*-BuOH. After removal of the solvent, the product (110 mg) was chromatographed on silica gel by prep. TLC developing with Me_2CO–C_6H_6 (1:1) to yield **3** (R_f 0.38, 21 mg), mp 215–224° (dec.), $[\alpha]_D$ +3° (c 3.1, pyridine) (lit. $[\alpha]_D$ +3.24°), identical in all respects [IR, ^{1}H NMR, TLC; the tetraacetate, mp 137–138°, $[\alpha]_D$ +24° (c 2.0, Me_2CO) (lit. $[\alpha]_D$ +23.7°)] with natural sawaranin, and **20** (R_f 0.29, 50 mg), mp 170–172° (dec.) (amorphous, from EtOAc–C_6H_6), $[\alpha]_D$ +127° (*c* 2.25, MeOH).

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REFERENCES

1. Imamura, H. (1962) *Bull. Gov. Forestry Exp. Sta.* (Japan) No. 138.
2. Morgenlie, S. (1972) *Acta Chem. Scand.* **26**, 2146.
3. Fukunishi, K., Inoue, Y., Kishimoto, Y. and Mashio, F. (1975) *J. Org. Chem.* **40**, 628.
4. Gaudemer, A. (1977), in *Stereochemistry* (Kagan, H. B., ed.) Vol. 1, p. 90, Georg Thieme, Stuttgart.
5. Poss, A. J. and Belter, R. K. (1987) *Tetrahedron Letters* **28**, 2555.
6. Glennie, C. W. and Perold, G. W. (1980) *Phytochemistry* **19**, 1463.
7. Couchman, R., Eagles, J., Hegarty, M. P., Laird, W. M., Self, R. and Synge, R. L. M. (1973) *Phytochemistry* **12**, 707.
8. Yvin, J.-C., Chevolot-Magueur, A.-M., Chevolot, L., Lallemand, J.-Y., Potier, P. and Guilhem, J. (1982) *J. Am. Chem. Soc.* **104**, 4498.
9. Iwagawa, T. and Hase, T. (1984) *Phytochemistry* **23**, 2299.