Anal. Calcd for $C_{14}H_{19}O_2P$: C, 67.19; H, 7.65; P, 12.38. Found: C, 67.30; H, 7.74; P, 12.42.

The syn isomer **6** was purified by recrystallization from acetonitrile (mp 198–201°): ir (KBr) 3350, 1150, 1110 cm^{-1}; NMR (TFA) 8.1–7.6 (5 H), 5.3–4.7 (1 H), 3.6–1.4 ppm (12 H).

Anal. Calcd for $C_{14}H_{19}O_2P$: C, 67.19; H, 7.65; P, 12.38. Found: C, 67.36; H, 7.59; P, 12.21.

In separate experiments pure **3** was reduced to **6** (91% yield) and pure **5** was reduced to **7** (95% yield).

***syn*-9-Phenyl-9-phosphabicyclo[3.3.1]non-2-ene 9-Oxide (8).** A solution of 1.18 g (4.75 mmol) of syn-endo hydroxy oxide **6** in 60 ml of concentrated hydrobromic acid was refluxed for 6 h, then allowed to cool to room temperature overnight, cooled in an ice–salt bath, and basicified with 25% aqueous sodium hydroxide. The resulting solution was extracted with methylene chloride and the combined extracts were dried (Na_2SO_4) and concentrated to provide 0.96 g (88%) of **8** (mp 160–163°): ir 1640, 1590, 1160, 1120 cm^{-1}; NMR 8.0–7.3 (5 H), 6.4–5.3 (2 H), 3.4–1.2 ppm (10 H).

Anal. Calcd for $C_{14}H_{17}OP$: C, 72.40; H, 7.38; P, 13.34. Found: C, 72.35; H, 7.47; P, 13.13.

***anti*-9-Phenyl-9-phosphabicyclo[3.3.1]non-2-ene 9-Oxide (9).** The above procedure was employed to provide a 77% yield of **9** (mp 145–148°) from **7**: ir 1640, 1590, 1150, 1120 cm^{-1}; NMR 8.0–7.3 (5 H), 6.4–5.5 (2 H), 3.4–1.1 ppm (10 H).

Anal. Calcd for $C_{14}H_{17}OP$: C, 72.40; H, 7.38; P, 13.34. Found: C, 72.24; H, 7.26.

Dehydration of *endo-syn*-3-Hydroxy-9-phenyl-9-phosphabicyclo[3.3.1]nonane 9-Oxide (6) with Sulfuric Acid. A solution of 10.00 g (0.042 mol) of syn hydroxy phosphine oxide **6** in 57% sulfuric acid (prepared from 120 ml of water and 160 ml of concentrated sulfuric acid) was heated to boiling for 12 hr. The solution was cooled, saturated with sodium chloride, and extracted several times with dichloromethane. The dichloromethane extracts were combined and evaporated to yield 6.55 g (71% yield) of a slightly yellow solid. The NMR spectrum of the solid was identical with that of *anti*-9-phenyl-9-phosphabicyclo[3.3.1]non-2-ene 9-oxide (**9**) (see previous experiment).

In a similar experiment starting with 7.08 g of anti hydroxy phosphine oxide **7**, 4.025 g (61%) of olefin **9** was produced.

The acidic aqueous solutions from both of the above experiments were combined and extracted repeatedly with dichloromethane. Evaporation of the dichloromethane extracts yielded an additional 2.76 g of **9** bringing the combined yields for the two experiments to 84%.

9-Ethyl-9-phosphabicyclo[3.3.1]nonane 9-Oxide (14). To a mixture of 234 mg (1.0 mmol) of phosphine oxide **1** in 10 ml of ether (freshly distilled from lithium aluminum hydride) cooled in an ice bath was added 2 mmol of methyllithium in ether. After 15 min (during which time the solution became yellow), excess methyl iodide was added and the reaction mixture was allowed to warm to room temperature. The mixture was then poured into water, the layers were separated, and the aqueous layer was extracted with methylene chloride. The combined organic phases were dried (Na_2SO_4) and concentrated to give 143 mg of yellow solid material. Preparative VPC (4% SE-30 on Chromosorb G, 3 ft × 0.25 in.) afforded 30 mg of **14** (mp 131–133°): ir 1150 cm^{-1}; NMR 3.0–1.1 ppm; MS *m/e* 186.

Anal. Calcd for $C_{10}H_{19}OP$: C, 64.49; H, 10.28; P, 16.63. Found: C, 64.30; H, 10.28; P, 16.72.

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Registry No.—**1**, 57458-74-9; **3**, 37759-01-6; **3**-d_4, 57495-99-5; **5**, 57458-75-0; **5**-d_4, 57458-76-1; **6**, 37759-02-7; **7**, 57458-77-2; **8**, 57458-78-3; **9**, 57458-79-4; **14**, 57458-80-7.

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Potamogetonin, a New Furanoid Diterpene. Structural Assignment by Carbon-13 and Proton Magnetic Resonance

Cecil R. Smith, Jr.,* Richard V. Madrigal, David Weisleder, and Kenneth L. Mikolajczak

Northern Regional Research Laboratory, Agricultural Research Service, U.S. Department of Agriculture, Peoria, Illinois 61604

Robert J. Highet*

National Heart and Lung Institute, Bethesda, Maryland 20014

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Potamogetonin (**1**), a new furanoid diterpene with a labdane skeleton, has been isolated from seeds of *Potamogeton ferrugineus* Hagstr. The structure of **1** has been assigned on the basis of its spectral characteristics, particularly by nuclear magnetic resonance. The proton and carbon-13 chemical shifts of two related diterpenes of known structure, sciadin (**3**) and nepetaefuran (**4**), are correlated with shifts of **1**.

We wish to report the isolation and structure of potamogetonin (**1**), a new member of the growing group of furanoid labdane derivatives.[1] Potamogetonin was isolated from seeds of *Potamogeton ferrugineus* (family Potamogetonaceae).[2] Gas–liquid phase chromatographic (GLC) analysis of the petroleum ether extract of these seeds revealed, in

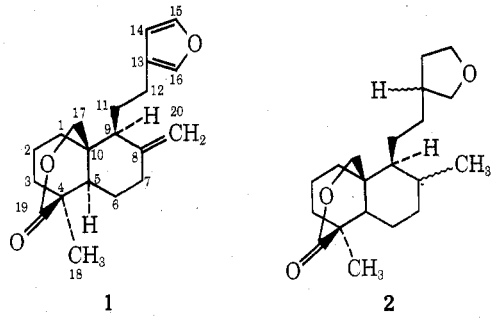
Table I
Selected Proton Chemical Shifts of Potamogetonin, Sciadin, and Nepetaefuran[a]

Protons	Potamogetonin (1)	Sciadin (3)	Nepetaefuran (4)
H-14	6.26, 1 H, dd ($J_{14,15}$ = 1.6, $J_{14,16}$ = 0.9)	6.43, 1 H, dd ($J_{14,15}$ = 1.8, $J_{14,16}$ = 0.9)	6.27, 1 H, dd ($J_{14,15}$ = 1.8, $J_{14,16}$ = 0.9)
H-15	7.33, 1 H, dd ($J_{14,15}$ = $J_{15,16}$ = 1.6)	7.38, 1 H, dd ($J_{14,15}$ = $J_{15,16}$ = 1.8)	7.38, 1 H, dd ($J_{14,15}$ = $J_{15,16}$ = 1.8)
H-16	7.18, 1 H, m	7.47, 1 H, m ($J_{12,16}$ = 0.9)	7.27, 1 H, m
H-17	3.95, 4.15, 2 H, AB q (J = 11)[b]	5.52, d, 1 H (J = 1.3)[c]	4.05, 5.02, 2 H, AB q (J = 12)[d]
H-18	0.87, 3 H, s	1.23, 3 H, s	1.12, 3 H, s
H-20	4.82, 4.94, 2 H, AB q (J = 1)	4.80, 5.05, 2 H, AB q (J = 1)	2.32, 2.70, 2 H, AB q (J = 14)

[a] Spectra were determined in $CDCl_3$. Chemical shifts (δ) are expressed in parts per million from tetramethylsilane and couplings (J) in hertz. Letters following the shifts indicate the multiplicities observed without decoupling. [b] The δ 4.15 doublet shows further splitting (J = 1.8 Hz). [c] Irradiation at δ 1.40 eliminates this coupling. [d] The δ 5.02 doublet shows further splitting (J = 1.7 Hz), decoupled by irradiation at δ 2.15.

addition to the expected triglycerides, 25% of an unfamiliar component (1) which subsequently was isolated by thin layer chromatography (TLC).

Scheme I



1 2

By high-resolution mass spectrometry, the empirical formula of 1 was established as $C_{20}H_{26}O_3$. The ^{1}H NMR spectrum of 1 indicated the presence of a β-substituted furan group (multiplets at δ 6.22, 7.18, and 7.30),[3] an exocyclic double bond (doublets at δ 4.82 and 4.94),[3] and a tertiary methyl group (singlet at δ 0.87). The uv spectrum exhibited a maximum at 201 nm (ϵ 8329), in accord with a furanoid structure.[3,4] The ir spectrum of 1 had maxima at 895 cm^{-1}, suggestive of an exocyclic double bond, and at 872 cm^{-1}, in harmony with a furan nucleus.[3] This ir spectrum also showed a peak at 1740 cm^{-1}, evidently due to an ester or δ-lactone grouping; no hydroxyl absorption was observed.

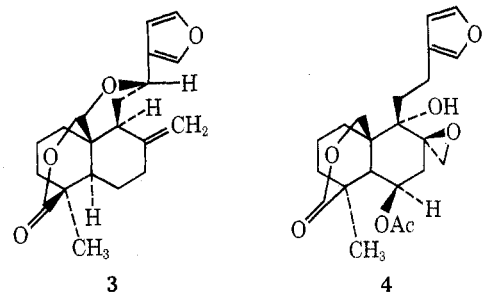
Catalytic hydrogenation of 1 provided a hexahydro derivative (2), $C_{20}H_{32}O_3$, and thus indicated that 1 probably contains three double bonds and four rings. In the ^{1}H NMR spectrum of 2, resonances at δ 4.82 and 4.94 were replaced by a doublet at δ 0.85, evidently associated with a new methyl substituent formed from the exocyclic methylene group. Low-field resonances attributable to a furan ring disappeared.

One of the three oxygens in 1 is allocated to a furan ring. Another oxygen must be in a carbonyl function; if this is assumed to be an ester or δ-lactone grouping, all three are accounted for. However, treatment with 0.5 M sodium methoxide in methanol followed by isolation under mild conditions left 1 unchanged, as did more rigorous reaction with 4 M potassium hydroxide. The new substance likewise was unaltered under conditions of acid-catalyzed methanolysis.

Additional chemical reactions on potamogetonin were precluded by our limited supply of plant material. However, as a working hypothesis, we adopted formula 1 for the constitution of potamogetonin on the basis of the spectral data and previously observed biogenetic patterns for furanoid labdane derivatives.[1] The apparent resistance of 1 to alkaline hydrolysis seemingly contradicts our proposed structure, since facile relactonization normally would be expected of a γ-lactone but not of a δ-lactone. Nevertheless, the chemistry of some related diterpenoid δ-lactones —derivatives of columbin,[5] nepetaefolin,[6] and nepetaefuran[6] (4)—provides parallels for the behavior of 1. In contrast, sciadin (3) can be saponified and isolated as a free acid;[7] perhaps its ether linkage makes the corresponding free acid relatively stable.

Structure 1 was validated by correlating its ^{1}H NMR and carbon-13 magnetic resonance (^{13}C NMR) spectra with those of two related furanoid diterpenes, sciadin (3) and nepetaefuran (4), which were selected as model compounds.[6,7] These correlations resulted in assignment of carbon-13 chemical shifts for 3 and 4, which had not been examined by ^{13}C NMR previously.

Scheme II



3 4

The ^{1}H NMR spectra of all three compounds (Table I) show similar signals for the furanoid protons at C-14, C-15, and C-16 as well as for the C-18 methyl group. The exocyclic methylene group at C-20 gives similar peaks in the spectra of 1 and 3. The AB quartet associated with the C-17 methylene group is comparable for 1 and 4, although one doublet of 1 is shifted downfield by about 1 ppm in 4 by the deshielding effect of the epoxy and 6β-acetoxy groups.

The ^{13}C NMR spectra of 1, 3, and 4 (Table II) provide strong support for both the aromatic and the alicyclic portions of the structure postulated for 1. Thus, for each of the furanoid peaks of 3 and 4, there is a corresponding peak in the spectrum of 1 within approximately 1 ppm. Inspection of the alicyclic portion of 1 suggests that C-1, C-2, and C-3 should have chemical shifts very similar to those of both 3 and 4, while carbons 6, 7, 8, 18, and 20 should have similar shifts in 1 and 3, for these carbon atoms are distant from

Table II
Carbon-13 Chemical Shifts of Potamogetonin, Sciadin, and Nepetaefuran[a]

Carbon	Potamogetonin (1)	Sciadin (3)	Nepetaefuran (4)
1	41.1 t	40.9 t	41.2 t
2	20.9 t	20.8 t	20.5 t
3	25.8 t	25.0 t	25.8 s/t
4	33.5 s	37.8 s	32.6 s
5	49.5 d	45.0 d	46.5 d
6	28.1 t	28.5 t	68.0 d
7	36.1 t	35.6 t	42.1 t
8	145.2 s	145.1 s	*b*
9	51.7 d	48.4 d	74.6 s
10	51.1 s	44.9 s	56.7 s/t
11	23.7 t	33.1 t	32.3
12	37.0 t	69.4 d	39.9 t
13	125.1 s	125.8 s	124.2 s
14	110.0 d	108.8 d	110.6 d
15	142.6 d	143.2 d	143.5 d
16	138.9 d	139.2 d	138.8 d
17	76.4 t	100.4 d	73.5 dd
18	23.7 q	22.3 q	22.4 q
19	173.0 s	174.4 s	*b*
20	108.3 t	110.0 t	46.8 t
Acetyl			170.5, 21.0 q

[a] Chemical shifts (δ) were measured in parts per million from tetramethylsilane in $CDCl_3$ solution. [b] Not observed.

sites that differ among the structures compared. Peaks with suitable shifts and off-resonance multiplicities are found for each of these carbon atoms. This correspondence of signals provides a satisfying demonstration of the power of ^{13}C NMR to elucidate structural features that are not otherwise readily accessible to spectroscopic examination.

Comparison of the ^{13}C NMR spectra of **1**, **3**, and **4** allows a reasonable assignment of the chemical shifts for all of the observed peaks, although the differentiation of some closely grouped peaks remains uncertain. Of the three high-field triplets allocated to C-1, C-2, and C-3 in each of the compounds, those at highest field are associated with C-2 because it has the fewest β substituents and should be shifted farther upfield by the C-17 and C-19 axial substituents.[8] They occur 1–2 ppm upfield from the C-2 of 10-methyl-*trans*-decalin.[9] Differentiation of the peaks for C-1 and C-3 is tentative and is based on assignments by Grover and Stothers[9] for *trans*-decalin systems.

Two singlets at high field, from C-4 and C-10, are anticipated in the spectrum of **4**. That of C-10 should be the lower of the two because of the larger number of β substituents. The same order can be retained for **1** and **3**, leading to the following correlations: the 6β-acetoxy group of **4** shifts C-4 slightly upfield by a gauche interaction, while the effect of the oxygen bridge of **3** upon C-9 affords an example of a heteroatom producing an upfield shift of a β-carbon atom.[10]

Only one high field doublet, due to C-5, is anticipated from **4**, but differentiation of the two doublets appropriate to C-5 and C-9 in **1** and **3** is difficult. The present assignments indicate a consistent effect of attaching the oxygen bridge to **3**, since each γ carbon is shifted upfield relative to the same carbons in **1** and **4**.[10]

The triplets at δ 28 and 36 can be grouped together because they occur in spectra of **1** and **3**, but not in that of **4**. Gauche interactions with C-17 and C-19 should shift the C-6 resonance upfield. Nepetaefuran's doublet at δ 68.0 is related to C-6, and it shows an appropriate downfield shift of 40 ppm under the influence of the acetoxyl substituent. Accordingly, we attribute the remaining upfield triplet for **4** to C-7.

In the spectra of **1** and **3**, assignment of the low-field singlet to C-8 is straightforward and agrees well with similar structures.[11] Two "midfield" singlets are expected for **4**, but only one is observed. In the trichothecanes, an epoxy carbon similar to C-8 has a chemical shift of δ 65.[12] Accordingly, the one observed singlet (δ 74.6) is allocated to C-9; the deshielding effect of the hydroxyl group is only 22–26 ppm.

After five of the six high-field triplets for **3** have been assigned, the remaining one must represent C-11. Of the two high-field triplets left in the spectrum of **1**, the more highly shielded one is assigned to C-11 in order to allow the following correlations: C-11 in **3** is shifted downfield appropriately from the corresponding signal for **1** owing to the influence of the oxygen bridge, and likewise in **4** as a result of deshielding by the hydroxyl at C-9.

The triplets associated with C-12 are similar for **1** and **4**. The only midfield doublet exhibited by **3** (δ 69.4) must be that of C-12, shifted downfield ca. 30 ppm by the oxygen bridge.

Assignment of the low-field signals generated by the furanoid system is straightforward. For all three compounds, a singlet must result from C-13 since it is quaternary. Of the three sets of doublets, those at highest field are assigned to C-14; the ones at lowest field are associated with C-15 because of substitution at C-13 that shields C-16 slightly.[13]

The only triplets at midfield in the spectra of potamogetonin and nepetaefuran are generated by C-17, as is a doublet for sciadin that is deshielded by the oxygen bridge and appears at lower field. The C-18 methyl group appears as a similar highfield quartet in each of the compounds, and the C-19 (lactone) carbonyl of **1** and **3** gives similarly placed singlets.

The only low-field triplet possible for **1** and **3** must represent C-20. The triplet near δ 48 in the spectrum in **4** is chosen for C-20 to correspond with shifts observed for the trichothecanes.[12]

Aside from establishing their empirical formulas, mass spectra of **1** and **2** did not lend themselves to interpretations that facilitated structural elucidation. Prominent peaks at *m/e* 94 ($C_6H_6O^+$) and 81 ($C_5H_5O^+$), probably from cleavages of the β-furylethyl side chain, occurred in the spectrum of **1**. The complexity of fragmentation of related diterpenoids in mass spectrometry has been noted previously.[14]

Our representation of **1** is intended to suggest only its relative stereochemistry. For convenience, we show the absolute stereochemistry that corresponds to lambertianic acid, although we have no basis for excluding the enantiomeric spatial arrangement of daniellic acid.[1,3] Inspection of a molecular model of potamogetonin emphasizes that C-17 and C-19 must be cis and diaxial, as in sciadin,[7,15] in order to accommodate the lactone ring without excessive strain. An A/B cis ring juncture, although sterically possible, is unlikely because of observed ^{13}C NMR resonances and biogenetic precedents. The β configuration chosen for C-9 may be somewhat arbitrary, but is consistent with ^{13}C NMR data.

On the basis of our ^{13}C NMR data, it appears that sciadin must have the *S* configuration at C-12 as indicated in the accompanying stereoformula. In the alternative *R* configuration, the β-furyl group of **3** would interact severely with the *exo*-methylene group so that C-8 and C-20 surely would be shielded much differently than they are in **1**.

Experimental Section[16]

General Techniques. ^1H NMR spectra were measured with a Varian HA-100 instrument. For ^{13}C NMR spectra, the instrument was a Varian XL-100 equipped with a Digi-Lab Fourier transform

accessory. Multiplicity of the various signals was determined by off-resonance decoupling. Exciting pulses at approximately 200 Hz below the frequency of tetramethylsilane were used, the free induction decay being sampled at 12 kHz, to fill an 8K data table, giving an effective resolution of 1.5 Hz. Typically, 70 000 FID's were collected overnight. Spectra were obtained using both a 30 and 90° (60 μs) pulse, the latter showing saturation effects for fully substituted carbon atoms. The multiplicity of high-field signals was confirmed by partially relaxed Fourier transform spectra using a 180°, 2 s, 90° sequence. Ir spectra were determined with a Perkin-Elmer Model 137 instrument. Low-resolution mass spectra were obtained with a Du Pont (CEC) 21-492-1 spectrometer, and corresponding high-resolution data with a Nuclide 12-90G spectrometer. A Beckman DK-2A spectrophotometer was used to record uv spectra. Analytical TLC was carried out on silica gel G F-254 plates (E. Merck, Darmstadt) with the solvent system hexane–ethyl ether–acetic acid (80:20:2). For preparative TLC, the same solvent was used with regular silica gel G plates of 1 mm thickness. Components were located under uv light after spraying with ethanolic dichlorofluorescein solution. GLC analyses were performed with a Hewlett-Packard Model 5750 instrument equipped with a 24 × 0.125 in. stainless steel column packed with 3% OV-1 on Gas-Chrom Q (100/200 mesh) (Applied Science Laboratories); column temperatures were programmed at 6°/min with an initial temperature of 160°. Equivalent chain length values for components separated by GLC were determined as described by Miwa and co-workers.[17]

Isolation of Potamogetonin (1). Ground seed of *Potamogeton ferrugineus* Hagstr. collected in Uruguay (28.3 g) was extracted for 8 h in a Soxhlet apparatus with petroleum ether and provided 2.6 g of oil after evaporation of solvent. TLC analyses of this oil revealed major components at R_f 0.63 (triglycerides), 0.15 (potamogetonin), and 0.08 (not characterized). GLC analyses revealed a component representing 25% of the oil and more volatile than triglycerides; this substance had equivalent chain length 21.4 (OV-1 column).[17] The R_f 0.15 component (1), a liquid, was isolated by preparative TLC and was shown to have these same GLC retention characteristics: ux max (cyclohexane) 201 nm (ϵ 8329); ir (CCl_4) 1745 (ester or δ-lactone), 1133, 1050, 1025, 900, 872 cm^{-1}; ORD $[\alpha]^{30}D$ −23, $[\alpha]_{400}$ −50, $[\alpha]_{300}$ −140, $[\alpha]_{250}$ −290, $[\alpha]_{230}$ −340° (*c* 0.48, CH_3OH);[18] ^1H NMR spectral data are in Table I and ^{13}C NMR data in Table II. Anal. Calcd for $C_{20}H_{26}O_3$: M^+, *m/e* 314.188. Found: M^+, *m/e* 314.188.

Compound 1 was resistant to hydrolysis (solvolysis) when treated with each of the following reagents: 5% methanolic hydrogen chloride (reflux), 0.5 M methanolic sodium methoxide (ambient temperature), and aqueous 4 N potassium hydroxide (reflux). In each case, the product was recovered by conventional procedures and was unaltered 1, as judged by GLC, TLC, ir, or ^1H NMR.

Hydrogenation of Potamogenin (1). A 16-mg portion of **1**, dissolved in methanol, was hydrogenated with Adams catalyst for 4 h at ambient temperature and pressure. The product (2), mp 112–113° from hexane–chloroform, was isolated by filtration and evaporation of solvent: ir (CCl_4) 1735 (ester or δ-lactone), 1137, 908 cm^{-1}; ^1H NMR ($CDCl_3$) δ 4.25 (dd, 1 H, *J* = 11, 1 Hz, part of C-17 methylene), 4.00 (d, 1 H, *J* = 11 Hz, part of C-17 methylene), 0.87 (s, 3 H, H-18), 0.85 (d, 3 H, *J* = 8 Hz, H-20), 1.0–2.4 and 3.0–3.8, complex multiplets.

Anal. Calcd for $C_{20}H_{32}O_3$: M^+, *m/e* 320.235. Found: M^+, *m/e* 320.234.

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Registry No.—1, 57459-42-4; 2, 57459-43-5; 3, 6813-08-7; 4, 29461-24-3.

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