other hydrolytically unstable and corrosive products along with a smaller amount of perfluorinated fragments. The yield of the hydrofluoro ethers in most cases exceeded the yield of perfluoro ethers owing to incomplete reaction. These products were removed by aqueous alkali hydrolysis and the hydrolytically stable ethers fractionated. The bulk of the desired products was collected in the −95 and −130° traps (combined weight 2.48 g, 20.6%). Final purification was accomplished using gas–liquid chromatography using a fluorosilicone (QF-1-0065, 13% on Chromosorb p, 80–100 mesh) column.

Perfluoro-1,2-dimethoxyethane is a gas at room temperature (bp 16.7°). The molecular weight determined by the ideal gas method was 269 (*cf.* 270 for $C_4F_{10}O_2$). The ^{19}F nmr consisted of a triplet at +59.54 and a quartet at +94.19 ppm relative to $CFCl_3$[5] with coupling constant 9.2 Hz and relative intensities of 3:2. The ir spectrum exhibited bands at 1410 (w), 1295 (s), 1250 (s), 1200 (w), 1170 (sh), 1155 (s), 1105 (w), 923 (w), 887 (m), 865 (w), 819 (w), 690 (w) wavenumbers. The mass spectrum contained no parent peak but showed strong peaks at *m/e* 135 corresponding to the symmetrical cleavage of the molecule, (CF_3–O–CF_2). Other strong peaks were at *m/e* 119 (C_2F_5), 100 (C_2F_4), 69 (CF_3), 50 (CF_2), 47 (CFO). *Anal.* Calcd for $C_4F_{10}O_2$: F, 70.36. Found: C, 17.41; F, 70.08. The yield was 21%.

1-Hydrononafluoro-2,5-dioxahexane.—If the products of the previously described reaction were not hydrolyzed, a second major product may be isolated which in some cases exceeds the amount of perfluoro-1,2-dimethoxyethane. This ether was a liquid with a disagreeable odor and may be quite toxic. Its molecular weight was determined to be 251 (*cf.* 252 for $C_4HF_9O_2$). Its ^{19}F nmr spectrum exhibited a triplet at +59.22 and a quartet at +93.63 with a coupling constant of 9.4 hz and relative intensities of 2:2, a doublet centered at +88.36 (J = 70.0 Hz) split into triplets (J = 4.4 Hz), and a triplet at +92.47 ppm (J = 4.6 Hz) relative to $CFCl_3$ with relative integrals of 2:2. The proton nmr consisted of a triplet at −6.26 ppm relative to TMS (external standard) with coupling constant equal to 68.6 Hz, in good agreement with the doublet splitting in the ^{19}F nmr. If the proton was irradiated, the ^{19}F doublet decayed into a singlet. This information is consistent with a structure containing a proton in the 1 position (Chart I). The mass spectrum supports this conclusion. The two peaks corresponding to "symmetrical" cleavage at *m/e* 135 (C_2F_5O) and 117 (C_2HF_4O) were both strong with relative intensities of 1:1.5 as were the very strong peaks at *m/e* 69 (CF_3) and 51 (CHF_2) of relative intensties of 1:1.5. Other, less intense peaks support this conclusion. The ir spectrum contained a weak proton absorption at 3028 cm⁻¹ in addition to carbon–fluorine and carbon–oxygen bands at 1400 (w, b), 1370 (w), 1295 (s), 1250 (s), 1192 (m), 1179 (sh), 1159 (s), 1125 (s), 1040 (m), 910 (m), 853 (w), 818 (w), 700 (w) cm⁻¹. The yield was 0–25%.

CHART I

^1H AND ^{19}F NUCLEAR MAGNETIC RESONANCE SPECTRA[a]

Perfluoro-1,2-dimethoxyethane

CF_3—O—CF_2—CF_2—O—CF_3
+59.54 +94.19
(9.2)

1-Hydrononafluoro-2,5-dioxahexane

CF_3——O——CF_2——CF_2——O——CF_2——H
+59.22 +93.63 +92.47 +88.36 −6.26[b]
(9.2) (<1) (4.5) (69.3)

Perfluorobis(2-methoxyethyl) Ether

CF_3—O—CF_2——CF_2—O—CF_2—CF_2—O—CF_3
+59.30 +93.84 +91.64
(9.4) (<1)

[a] ϕ in parts per million (J in hertz). $\phi_{CFCl_3(ext)} = 0$. [b] ^1H [TMS (external standard)].

Perfluorobis(2-methoxyethyl) Ether.—Bis(2-methoxyethyl) ether (1.79 g, 0.0134 mol) was evaporated at 50° into the four-zone cryogenic factor (zone 1, −40°; zones 2, 3, and 4 at −78°) using a 80–100-cc/min flow of helium gas. After 6 to 8 hr the helium flow was reduced to 20 cc/min and a 0.5-cc/min flow of fluorine was started. A similar procedure to that used for 1,2-dimethoxyethane was used to complete the reaction. The raw products were fractionated through −63, −78, −95, and −196° traps. Perfluorobis(2-methoxyethyl) ether was collected from the −78 and −95° traps (yield 0.83 g, 16.1%). Perfluorobis(2-methoxyethyl) ether is a volatile liquid, bp 60–63°). Its molecular weight was determined to be 385 (*cf.* 386 for $C_6F_{14}O_3$). The ^{19}F nmr exhibited a triplet at +59.30 and a quartet at +93.84 (J = 9.4 Hz) and a singlet at +91.64 ppm relative to $CFCl_3$. The relative integrals of the absorptions are 3:2:2. The spectrum exhibited bands at 1385 (w), 1295 (s), 1250 (s), 1220 (sh, w), 1200 (w), 1165 (s), 1145 (s), 920 (sh), 910 (m), 770 (m), 697 (w), 681 (sh) wavenumbers. The mass spectrum exhibited strong peaks at *m/e* 185 (C_3F_7O), 135 (C_2F_5O), 119 (C_2F_5), 100 (C_2F_4), 69 (CF_3), 50 (CF_2). *Anal.* Calcd for $C_6F_{14}O_3$: C, 18.67; F, 68.90. Found: C, 18.64; F, 69.94. The yield was 16%.

Discussion

The yields of perfluorinated ethers reported are not to be considered optimum. Obviously the partially fluorinated material could be recycled. A new variable temperature reactor[6] which enables reactions to be studied at temperatures other than −78° may also greatly improve the yields.

Acknowledgment.—This work was supported by the National Science Foundation and the U. S. Air Force Materials Laboratory. The authors would like to thank Miss Norma Maraschin for assistance with instrumentation.

Registry No.—Perfluoro-1,2-dimethoxyethane, 378-11-0; 1,2-dimethoxyethane, 110-71-4; fluorine, 7782-41-4; 1-hydrononafluoro-2,5-dioxahexane, 40891-98-3; perfluorobis(2-methoxyethyl) ether, 40891-99-4; bis(2-methoxyethyl) ether, 111-96-6.

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(5) Nmr samples were condensed into capillary tubes, sealed, and immersed in a solution of $CFCl_3$ (30%), tetramethylsilane (5%), and carbon tetrachloride (65%) contained in a standard nmr tube.

(6) To be published.

Carbon-13 Magnetic Resonance Study of Terpenoids. I. An Application of Heteronuclear Selective Decoupling Experiments to the Spectral Assignments of Nonproton-Bearing Carbon-13 Resonances of a Germacranolide, Melampodin

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We recently reported[2] the isolation and structure elucidation of melampodin, a new sesquiterpene lactone from *Melampodium leucanthum* Torr. & Gray. Single-crystal X-ray diffraction[3] and neutron diffraction[4] of this highly oxygenated medium-ring compound revealed that melampodin represents a new and novel germacranolide-type sesquiterpene lactone, which, in contrast to the well-known *trans,trans*-cyclodeca-1,5-

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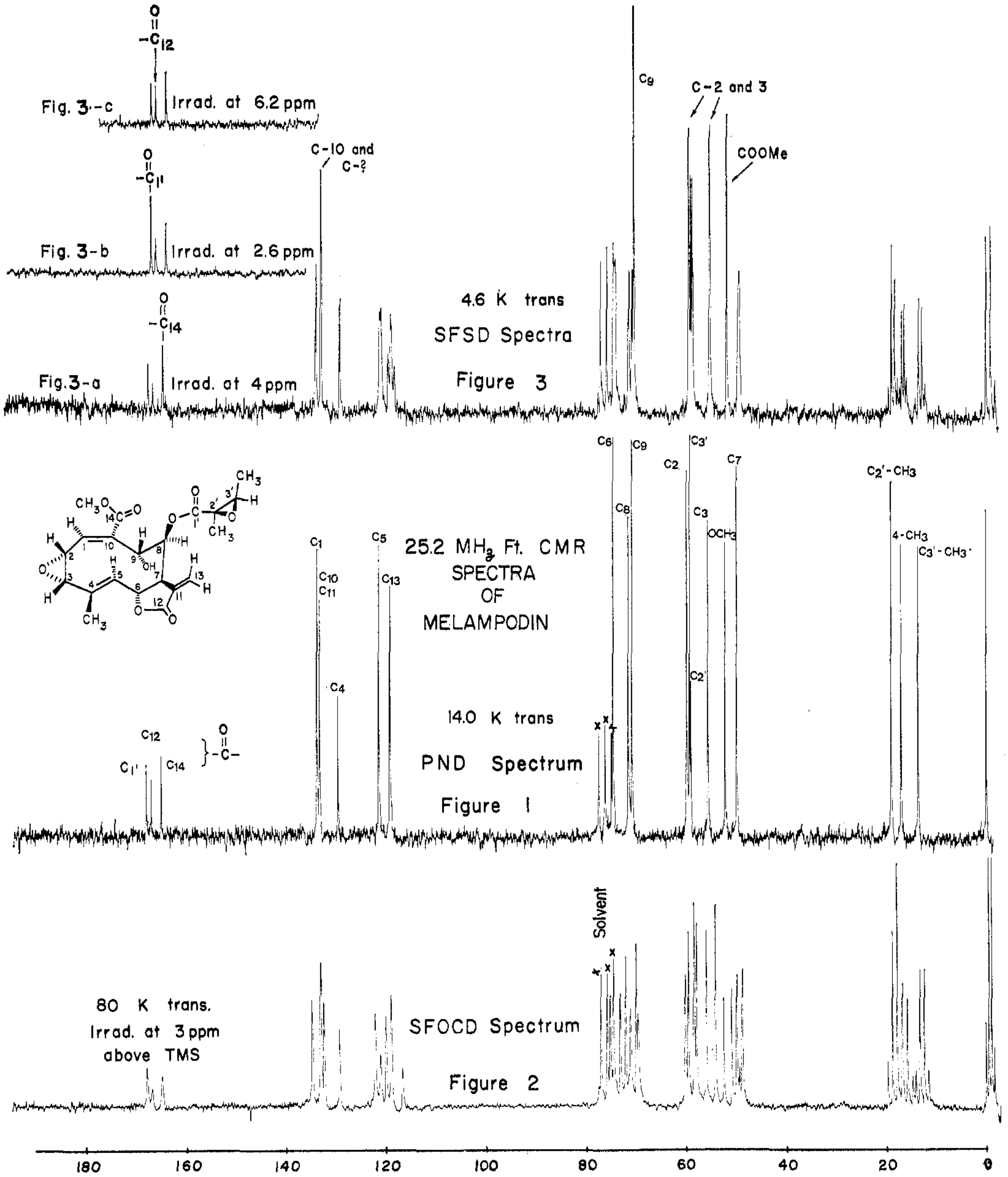
(1) (a) Louisiana State University. (b) Varian AG.

(2) N. H. Fischer, R. Wiley, and J. D. Wander, *J. Chem. Soc. Chem. Commun.*, 137 (1972).

(3) S. Neidle and D. Rogers, *J. Chem. Soc. Chem. Commun.*, 140 (1972).

(4) I. Bernal and S. F. Watkins, *Science*, **178**, 1282 (1972).



Figures 1–3.

diene germacrolides, represents a *cis,trans*-cyclodeca-1,5-diene melampolide ($\Delta^{1(10)}$ cis double bond).[5] Limited amounts of material and inconclusive results in a number of chemical reactions of melampodin and other new, highly oxygenated sesquiterpene lactones suggest that nuclear magnetic resonance (nmr) studies in general and ^{13}C magnetic resonance (cmr) in particular offered the best prospects for the structural elucidation of new malampolides and their derivatives. The cmr investigation of melampodin was conducted by dissolving the compound in $CDCl_3$ containing $\sim$2% tetramethylsilane to act as an internal reference, and then recording cmr spectra of the sample under the experimental conditions as described below.

The initial cmr spectrum of melampodin was obtained on an nmr spectrometer operating at 23.4 kG or 25.2 MHz for ^{13}C and simultaneous proton noise decoupling (PND) at 100 MHz. The utilization of this technique leads to the elimination of all ^{13}C–^{1}H spin–spin splittings yielding just one line per carbon atom. The resultant cmr spectrum of the compound ($C_{21}H_{24}O_9$) consists of 20 sharp singlets representing 21 carbon atoms in the molecule (Figure 1).

The singlet resonances occurring in the PND spectrum were assigned to methyl, methylene, and methine groups and nonproton-bearing carbons by obtaining a second ^{13}C spectrum of the sample under slightly modified conditions. Namely, in the place of a PND frequency, a single-frequency (coherent) decoupling field was applied which was tuned to a frequency several hundred hertz (usually 300 to 500 Hz) farther away from all proton resonances that are coupled to the ^{13}C nuclei under observation. Since $J_{^{13}C-^1H}$ values are relatively large (120–250 Hz), a partially decoupled spectrum results under single-frequency off-center decoupled (SFOCD) experimental conditions. This spectrum (Figure 2) exhibits small residual splittings in the form of a quartet for methyl carbons, a triplet for methylene carbons, a doublet for tertiary carbons, and unchanged singlets for nonproton-bearing carbon

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[5] D. Rogers, G. P. Moss, and S. Neidle, *J. Chem. Soc. Chem. Commun.*, 142 (1972).

Table I[a]

Chemical shift (PND spectrum)	No. of lines (SFOCD spectra)	Inference deduced from PND and SFOCD spectra	Comparison of ^{13}C resonances in PND and SFSD spectra)	^{13}C assignment
167.0	Singlet	Lowest field resonances, carbonyl signals	SE when C-2′ Me or C-3′ PM are irradiated (Figure 3b)	C-1′
166.0	Singlet		SE when C-13 pm is irradiated (Figure 3c)	C-12
164.0	Singlet		SE when COOMe PM is irradiated (Figure 3a)	C-14
133.0	Doublet	Lowest field $^{\mathrm{H}}{>}\mathrm{C}{=}$, β to carbonyl, ∴ C-1		C-1
132.5	Singlet	Two $>\mathrm{C}{=}$, ∵ twice the intensity of singlet at 128.9	SE when COOMe, or C-13 PM are irradiated (Figure 3a)	C-10 and C-11
128.9	Singlet	One $>\mathrm{C}{=}$	SE when C-4 PM is irradiated	C-4
120.7	Doublet	$^{\mathrm{H}}{>}\mathrm{C}$, by process of elimination C-5	SE when C-5 PM is irradiated	C-5
118.5	Triplet	$\genfrac{}{}{0pt}{}{\mathrm{H}}{\mathrm{H}}{>}\mathrm{C}{=}$, ∴ C-13		C-13
74.2	Doublet	$\mathrm{H{-}\overset{\mid}{\underset{\mid}{C}}{-}O}$ probably present in medium ring	SE when C-6 PM is irradiated	C-6
71.2	Doublet		SE when C-8 PM is irradiated	C-8
70.2	Doublet		SE when C-9 PM is irradiated (Figure 3a)	C-9
59.5	Doublet	$\mathrm{H{-}\overset{\mid}{\underset{\mid}{C}}{-}O}$ probably present in the epoxide ring	SE when C-2 and C-3 PM are irradiated (Figure 3a)	C-2 or 3
59.0	Doublet		SE when C-3′ PM is irradiated	C-3′
58.7	Singlet	$\mathrm{{-}\overset{\mid}{\underset{\mid}{C}}{-}O}$, ∴ C-2′	SE when C-3′ PM is irradiated	C-2′
55.3	Doublet	$\mathrm{H{-}\overset{\mid}{\underset{\mid}{C}}{-}O}$ (probably epoxide)	SE when C-2 and C-3 PM are irradiated (Figure 3a)	C-3 or C-2
51.9	Quartet	Me at $\mathrm{O{-}\overset{\mid}{C}{=}O}$, ∴ COOMe		COOMe
49.7	Doublet	$\mathrm{H{-}\overset{\mid}{\underset{\mid}{C}}{-}O}$ or $\mathrm{H{-}\overset{\mid}{\underset{\mid}{C}}{-}}$	SE when C-7 PM is irradiated	C-7
18.9	Quartet	Me, ∴ C-2′ Me, C-3′ Me, or C-4 Me	SE when C-2′ methyl PM is irradiated	C-2′ Me
16.9	Quartet		SE when C-4 methyl PM is irradiated	C-4 Me
13.4	Quartet		SE when C-3′ Me PM is irradiated	C-3′ Me

[a] Chemical shift recorded in parts per million relative to TMS. PND, proton noise-decoupled spectrum; SFOCD, single-frequency off-center decoupled spectrum; SFSD, selectively decoupled spectrum; SE, signal enhanced; PM, proton–carbon-13 multiplet.

atoms. The spectral data obtained from these two experimental conditions and the interpretation of these data are recorded in the first three columns of Table I.

The definitive designation of the unassigned and partially assigned ^{13}C resonances of melampodin was obtained from selective single-frequency heteronuclear-decoupled (SFSD) cmr spectra[6] and the correlation of chemical shifts of the ^{13}C signals from the PND spectrum with the assigned proton signals in the proton magnetic resonance (pmr) spectrum (Figure 4). In a SFOCD spectrum, all ^{13}C–^{1}H splittings caused by the direct spin–spin interactions of ^{13}C and ^{1}H nuclei are greatly reduced. The magnitude of this residual splitting (J_{res}) may be described by the following expression: $J_{\mathrm{res}}^{\mathrm{obsd}}$ in a given ^{13}C resonance $= \Delta f J/(\gamma_{\mathrm{H}_2}/2\pi)$, where J = the magnitude of true ^{13}C–^{1}H coupling, $\gamma_{\mathrm{H}_2}/2\pi$ = the strength of the decoupling field in hertz, and Δf = the frequency difference (in hertz) between the decoupling frequency and the resonance frequency of proton(s) attached to the ^{13}C nucleus under investigation.

In the SFSD experiment, $\Delta f = 0$ for the ^{13}C nucleus under investigation and the value of $\gamma_{\mathrm{H}_2}/2\pi$ was reduced by approximately one half or one third of the intensity employed during the SFOCD experiments. The strength of $\gamma_{\mathrm{H}_2}/2\pi$ employed in the SFSD experiments depends upon the width of the multiplet of the proton that is directly bonded to the carbon atom to be assigned. The irradiated proton spectral region is not a relative narrow multiplet composed of ^{1}H–^{1}H couplings, but a spectral pattern caused by the combined ^{1}H–^{1}H and ^{1}H–^{13}C splittings and thus may be ~120 to 250 Hz wide. Although in the pmr spectra of even moderately complex molecules ^{1}H–^{1}H–^{13}C multiplets inevitable overlap, the SFSD technique may still be successfully employed to assign ^{13}C resonances, provided that their corresponding ^{1}H–^{1}H multiplets are separated from each other by at least 5 Hz. Therefore, when the single frequency decoupling radiofrequency field was centered at the absorption frequency of H-9 at δ 4.00 in the pmr spectrum of melam-

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[6] (a) A. J. Jones, T. D. Alger, D. M. Grant, and W. M. Lichtman, *J. Amer. Chem. Soc.*, **92**, 2396 (1970); (b) H. J. Reich, M. Jautelat, M. T. Messe, F. J. Weigert, and J. D. Roberts, *ibid.*, **91**, 7445 (1969).

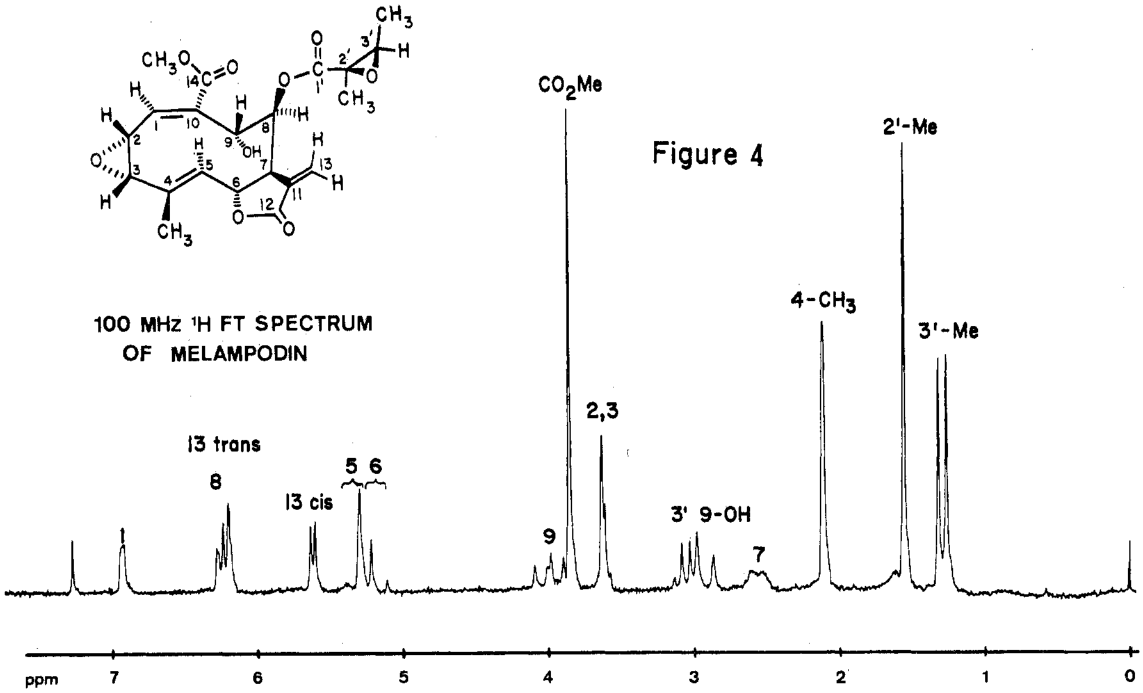

Figure 4.

podin (see Figure 4), the $^{13}C-^{1}H$ splittings associated with the respective interacting nuclei were totally eliminated and the completely decoupled ^{13}C resonance of C-9 appeared as the sharpest singlet in the SFSD spectrum (Figure 3a). Comparison of this SFSD spectrum with those obtained under PND and SFOCD spectra (Figures 1 and 2) showed that, besides the C-9 multiplet, other $^{13}C-^{1}H$ multiplets occurring in the SFOCD spectrum as shown in Figure 2 also collapsed into singlets in the SFSD spectrum (Figure 3a). The magnitude of intensities and the degree of sharpness observed in these ^{13}C singlets in the SFSD spectrum are directly related to the proximity of the resonance frequencies of the protons attached to the corresponding ^{13}C nuclei, to the proton frequency at which the maximum intensity of the perturbing radiofrequency field is aligned. Thus, when the decoupling radiofrequency field was aligned at the center of the H-9 $^{13}C-^{1}H$ multiplet at δ 4.00, other $^{13}C-^{1}H$ multiplets representing COOMe and H-2 and H-3 in the pmr spectrum were also considerably perturbed. As a direct consequence of this irradiation the quartet at 51.9 ppm and the doublets at 55.3 and 59.5 ppm observed in the SFOCD spectrum of melampodin were transformed into singlets in the SFSD trace (Figure 3a). In the SFSD spectrum the COOMe singlet was sharper than the two C-2 and C-3 singlets because the COOMe pmr signal at 3.94 ppm is nearer to the maximum intensity of the perturbing radiofrequency field at δ 4.00 than the overlapping absorptions of H-2 and H-3 at 3.63 ppm. Previously partially designated methyl ^{13}C signals at 13.4, 16.9, and 18.9 ppm as well as the methine ^{13}C resonances at 49.7, 59.0, and 71.2 ppm were assigned to C-3′ Me, C-4 Me, C-2′ Me, C-7, C-3′, C-8, and C-6, respectively, by performing similar selective decoupling experiments. (See the last two columns in Table I.)

The ^{13}C signals at 128.9 and 132.5 ppm corresponding to nonproton-bearing olefinic carbon atoms as well as the carbonyl carbon atoms at 164.0, 166.0, and 167.0 ppm were sorted out during the SFSD experiments by observing the enhancements in the intensities of the resonances of the nonproton-bearing ^{13}C nuclei. When in the pmr spectrum of melampodin the maximum intensity of the decoupling field was set at the resonance frequency of the C-3′ methyl group at δ 1.3, not only the splittings of the directly bonded nuclei ($^{13}C-^{1}H$) of the C-3′ methyl multiplet and to a lesser extent the C-2′ methyl signal at δ 1.58 were perturbed, but the long range couplings ($^{13}C-C-^{1}H$ and $^{13}C-C-C-^{1}H$) occurring in their resonances were also affected. As a direct result of this decoupling, the intensities of the nonproton-bearing C-2′ carbon and the C-1′ carbonyl carbon singlets at 58.7 and 167.0 ppm, respectively, increased in the SFSD spectrum. Similarly, when in the pmr spectrum the decoupling frequency was aligned at δ 2.6, the proton resonances of the C-2′ methyl at δ 1.58 and H-3′ at δ 3.1 were perturbed and the C-1′ carbonyl ^{13}C signal exhibited even greater intensity enhancement (compare Figures 3b and 1). Thus by observing the small but definite increment in their intensity in the selectively decoupled spectra, the C-12 and C-14 carbonyl ^{13}C resonances (see Figures 3a and 3c) as well as the nonproton-bearing olefinic C-4, C-10, and C-11 ^{13}C signals were assigned. This appears to be the first reported example[7] for the assignment of the ^{13}C resonances representing nonproton-bearing carbonyl and olefinic carbon atoms in a complex natural product with the aid of SFSD experiments. This technique may be generally useful for the assignment of nonproton-bearing ^{13}C signals in other related systems.

The resonance of the epoxide carbon atoms 2 and 3 were distinguished on the basis of their distinctive chemical shifts. The model of melampodin derived

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(7) Jones, *et al.*,[6a] used in 1970 the same SFSD technique toward the spectral assignment of ^{13}C resonances in cmr spectra of nonalternating hydrocarbons.

from neutron diffraction data[4] indicates a definite steric interaction between the C-4 methyl protons and H-3, whereas no such interaction exists between H-2 and H-1. Since it is well known that such steric interaction causes an upfield shift in resonances of interacting ^{13}C nuclei, the high field signal at 55.3 is assigned to C-3 while the lower field absorption at 59.5 to C-2.

The above methodology employed for the cmr spectral analysis will be particularly useful in the structure elucidation of other new, structurally related melampolides and complex natural products in general. After accumulating data from other sesquiterpene lactones we hope to correlate the ^{13}C chemical shift data with stereochemical and conformational features of the melampolides. The availability of accurate conformational information of melampolides in solution will help to better understand the biogenesis of these highly strained medium rings. Furthermore, the newly obtained data will be used extensively in our biochemical systematic studies of the three white-rayed species of the genus *Melampodium*.[2,8]

Experimental Section

The nmr spectral data were obtained on a Varian XL-100-15 spectrometer operating Fourier transform mode with proton decoupling. Data were accumulated in a Varian 620F computer using 5000-Hz sweep width in 8192 points. Data acquisition and pulse delay times were 0.8 and 0.9 sec. The number of pulses (transients) employed were varied and are recorded on respective cmr traces. Melampodin (300 mg) dissolved in 2 ml of CDCl$_3$ was employed for the nmr study. The chemical shifts are relative to internal tetramethylsilane and are estimated to be accurate to ±0.04 ppm.

Acknowledgment is made to the University Council on Research, Louisiana State University, for partial support of this work. We thank Dr. T. F. Stuessy for collecting and authenticating the plant collections.

Registry No.—Melampodin, 35852-26-7.

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[8] T. F. Stuessy, *Brittonia*, **23**, 177 (1971).

Nucleosides. LXXXIV. Total Synthesis of Pentopyranine C, a Nucleoside Elaborated by *Streptomyces griseochromogenes*[1]

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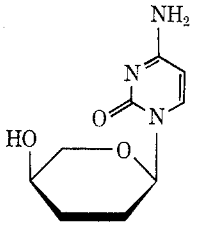
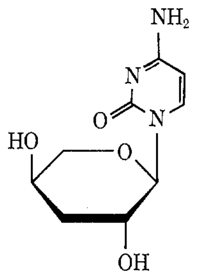
Received April 18, 1973

Recently, Seto, *et al.*,[2] isolated two cytosine nucleosides, pentopyranine A and C, from the fermentation broth of *Streptomyces griseochromogenes*, the blasticidin S-producing microorganism.[3] The structures of these nucleosides were given as 1-(2,3-dideoxy-α-L-*glycero*-pentopyranosyl)cytosine (**1**) and 1-(3-deoxy-α-L-*threo*-pentopyranosyl)cytosine (**2**). Pentopyranine A and C are therefore the first naturally occurring nucleosides possessing the α-L configuration.



1, pentopyranine A



2, pentopyranine C

We now report the total synthesis of pentopyranine C (**2**) and its furanosyl isomer (**13**) by condensation of bis(trimethylsilyl)-N^4-acetylcytosine with tri-*O*-acetyl-3-deoxy-L-*threo*-pentoses (**9** and **10**) in the presence of stannic chloride.[4]

The starting material, 3-deoxy-1,2-*O*-isopropylidene-α-L-*threo*-pentose (**6**), was prepared by the procedure of Prokop and Murray[5] as shown in Chart I from 3-deoxy-di-*O*-isopropylidene-α-D-*xylo*-hexofuranose (**3**).[5,6] Acid hydrolysis of **6** afforded the aldopentose (**8**) which was acetylated to give a mixture of **9** and **10**. This mixture of triacetates (**9** and **10**) was not separated, but condensed directly with bis(trimethylsilyl)-N^4-benzoylcytosine to afford the mixture **11a** and **12a**, which was saponified and acetylated to **11b** and **12b**. The latter mixture was separated easily by fractional crystallization from methanol. The physical constants (melting point, uv, ir, and nmr) of **11b** were identical with those reported[2] for the triacetyl derivative of pentopyranine C. After deacetylation of **11b**, a product (**2**) was obtained which was identical with pentopyranine C with respect to melting point, optical rotation, and uv, ir spectral characteristics.

The structure of compound **12b** was established by an unambiguous synthesis. Acetylation of **6** gave compound **7** which was acetolyzed to the triacetate (**9**). Condensation of **9** with bis(trimethylsilyl)-N^4-acetylcytosine gave a nucleoside identical in all respects with **12b**. After deacetylation of **12b**, the free nucleoside (**13**) was obtained. The α-L configuration for **13** was established by comparison of its ORD curve (in water) with that of 1-(α-L-arabinofuranosyl)cytosine (**14**).[7] Both **13** and **14** showed positive Cotton effects with two extrema at 273 and 218 mμ (the amplitudes being 180 and 230, respectively).

The total synthesis of pentopyranine C provides conclusive proof of the structure of this natural product which is believed to be a shunt pathway product[2] in the synthesis of the important anti rice blast disease agent, Blasticidin S.[3]

Experimental Section

Melting points are corrected. Analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

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[1] This investigation was supported in part by funds from the National Cancer Institute, National Institutes of Health, U. S. Public Health Service (Grant No. CA 08748).

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[3] S. Takeuchi, K. Hirayama, K. Ueda, H. Sakai, and H. Yonehara, *J. Antibiot. Ser. A*, **11**, 1 (1958); For recent reviews, see J. J. Fox, K. A. Watanabe, and A. Bloch, *Progr. Nucl. Acid Res. Mol. Biol.*, **5**, 251 (1966); R. J. Suhadolnik, "Nucleoside Antibiotics," Wiley, New York, N. Y., 1970).

[4] U. Niedballa and H. Vorbrüggen, *Angew. Chem., Int. Ed. Engl.*, **9**, 461 (1970); K. A. Watanabe, I. Wempen, and J. J. Fox, *Carbohyd. Res.*, **21**, 148 (1972).

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[6] T. Chiu, K. A. Watanabe, and J. J. Fox, *Carbohyd. Res.*, in press.

[7] N. Yamaoka, B. A. Otter, and J. J. Fox, *J. Med. Chem.*, **11**, 55 (1968).