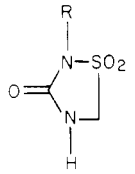
Table I. Properties of 1,2,4-Thiadiazolin-3-one 1,1-Dioxides[a]



compd	R	mp, °C	% yield
5	benzyl	125–127	40
6	*tert*-octyl	138–140	40
7	*tert*-butyl	140–141	50
8	*n*-butyl	89–91	33
9	cyclohexyl	109–111	34
10	2-pyrimidinyl	183–186	34
11	4-chlorophenyl	128–130	39

[a] Satisfactory analytical data (± 0.4% for C, H, N, and S) were reported for all compounds.

recorded with a JEOLCO Model C-60-HL spectrometer, using tetramethylsilane (Me_4Si) as internal standard. Infrared spectra were taken with either a Perkin-Elmer Model 257 or Model 281B spectrophotometer. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

2-*tert*-Butyl-1,2,4-thiadiazolin-3-one 1,1-Dioxide (7). To a cold (−10 °C) stirred mixture of 0.98 g (4.7 mmol) of (*N*-*tert*-butylsulfamoyl)acetic acid hydrazide,[1] 5 mL of H_2O, and 50 mL of Et_2O was added 0.52 mL (6.2 mmol) of 12 N HCl in 5 mL of H_2O and 0.36 g (5.3 mmol) of sodium nitrite in 5 mL of H_2O. Stirring and cooling were continued for 10 min. The Et_2O layer was separated and the aqueous layer was extracted with Et_2O (4 × 40 mL). The combined Et_2O extracts were kept cold, washed with 10 mL of saturated NaCl solution, and dried (Na_2SO_4). The extract was filtered through cotton into 70 mL of dry benzene and the mixture was concentrated in vacuo at room temperature to 40 mL. The concentrated solution was transferred to a 250-mL three-necked flask fitted with a condenser, drying tube, and stirrer. This flask was then immersed in an oil bath which had been preheated to 135 °C. The temperatue of the oil bath dropped to 92 °C over 1 h.[4] The solvent was evaporated in vacuo to obtain 0.56 g of a white solid. Recrystallization of this solid from benzene–petroleum ether gave 0.45 g (50%) of **7**: mp 140–141 °C; IR ($CHCl_3$) 3450 (NH), 1725 (CO), 1340 and 1150 (SO_2) cm^{-1}; NMR ($CDCl_3$) δ 1.66 (s, 9, *tert*-C_4H_9), 4.57 (s, 2, CH_2SO_2), 5.20 (br signal, 1, NH).

***tert*-Butyl (*N*-*tert*-Butylsulfamoylmethyl)carbamate (3, R = R′ = *tert*-butyl).** The same quantities and procedures as given above for **7** were used except that the 40-mL solution remaining after concentration in vacuo was immersed in an oil bath (preheated to 135 °C) for 2.5 min, prior to the addition of 4 mL of dry *tert*-butyl alcohol. This mixture was heated under reflux for 1.5 h and evaporated in vacuo to obtain 0.58 g of a white solid. Recrystallization of this solid from benzene gave 0.36 g (29%) of **3** (R = R′ = *tert*-butyl): mp 128–130 °C [lit.[1] mp 130–132 °C]; IR ($CHCl_3$) 3450, 3390 (NH), 1720 (C=O), 1370 and 1130 (SO_2) cm^{-1}; NMR ($CDCl_3$) δ 1.36 (s, 9 *N*-*tert*-C_4H_9), 1.47 (s, 9, *O*-*tert*-C_4H_9), 4.43 (d, 2, CH_2SO_2), 5.60 (br signals, 2, NHCO and $NHSO_2$).

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(4) This experiment was repeated with the addition of *tert*-butyl alcohol after the benzene solution of the azide was heated for 30 min. No carbamate was obtained under these conditions. In some experiments the initial Et_2O extract was dried for 1 to 12 h at room temperature and workup with or without the addition of *tert*-butyl alcohol gave **7**. Therefore it is likely that **7** is formed at room temperature in ether. We have used 1 h of heating in benzene to be sure complete rearrangement of the azide and cyclization of the isocyanate occurred.

Registry No. **1** (R = benzyl), 74965-40-5; **1** (R = *tert*-octyl), 74965-41-6; **1** (R = *tert*-butyl), 74965-42-7; **1** (R = butyl), 74965-43-8; **1** (R = cyclohexyl), 74965-44-9; **1** (R = 2-pyrimidinyl), 74965-45-0; **1** (R = 4-chlorophenyl), 74965-46-1; **3** (R = R′ = *tert*-butyl), 67542-05-6; **5**, 74965-47-2; **6**, 74965-48-3; **7**, 74965-49-4; **8**, 74965-49-4; **9**, 74965-50-7; **10**, 74965-51-8; **11**, 74965-52-9.

A Novel Synthesis of 1,21-Heneicosanedioic Acid[1]

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The synthesis of polymethylene dibasic acids has been accomplished mainly by the alkylation of malonic esters with polymethylene dibromides followed by hydrolysis and decarboxylation.[2] The synthesis of long-chain diacids requires long-chain dibromides, usually synthesized by reduction of long-chain diesters to diprimary alcohols followed by conversion to dibromides. If uneven-numbered dibasic acids are desired uneven dibasic esters are needed and these often require multistep synthesis. Another route involves electrolytic coupling of half-esters of dibasic acids,[3] but this route gives only even-numbered diesters.[4]

Because of interest in the synthesis of polymethylene dibasic acids for a study of how compounds with two polar end groups separated by a long polymethylene chain (even and odd numbered) would behave in surface films,[5] we have developed a new synthesis of heneicosane-1,21-dioic acid, **8**. The steps are outlined in Scheme I.

The crude tetraacid **4** was heated to effect decarboxylation to **5** which, on treatment with a solution of HCl in methanol at room temperature, afforded good yields of diester **6**. This ready preferential esterification can be explained by noting that the six numbers[6] (number of atoms in the six position from the carbonyl oxygen as one) of the terminal carboxyl groups are each three whereas the six number of the middle carboxyl group is six. The rates of esterification of comparable acids are those obtained[6] by esterification at 40 °C. However, when esterification is allowed to take place at room temperature an even greater ratio for rates of acids having a six number of three to acids with a six number of six is expected.

Brominative decarboxylation of **6** followed by reduction and hydrolysis afforded the desired heneicosane-1,21-dioic acid, **8**,[7] in good yield.

Experimental Section[8]

Ethyl ω-Bromoundecylenate,[9] **1.** Into a solution of 146 g of undecylenic acid, mp 21.0–22.5 °C in 1.4 L of petroleum ether, bp 65–80 °C, was passed HBr to saturation at 15 °C (about 45 min). The resulting solution was washed with saturated NaCl

(1) The work herein reported was contained in the Ph.D. thesis of Khi Ruey Tsai, The Ohio State University, 1950, supervised by Edward Mack and Preston Harris. Dr. K. R. Tsai is now Professor of Chemistry at Amoy University, Xiamen, Fukien, Peoples Republic of China. The delay in publication was caused by a lack of communication.

(2) Chuit, P. *Helv. Chim. Acta* **1926**, *9*, 264.

(3) (a) Brown, A. C.; Walker, J. *Justus Liebigs Ann. Chem.* **1891**, *261*, 107. (b) Zeigler, K., Hechelhammer, W. *Ibid.* **1937**, *528*, 115. (c) Fairweather, D. A. *Proc. R. Soc. Edinburgh* **1925**, *45*, 23, 283. (d) Ruzicka, L.; Stoll, M.; Schinz, H. *Helv. Chim. Acta* **1928**, *11*, 670, 1174.

(4) Difficulty in electrolysis of mixed half-esters is mentioned in ref 3b.

(5) See the thesis of Khi R. Tsai for a discussion of the desirability of studying even- and odd-numbered dibasic acids in various ways.

(6) Newman, M. S. "Steric Effects in Organic Chemistry"; J. Wiley and Sons Inc.: New York, 1956; p 205. Note acids 3 and 21 in Table I.

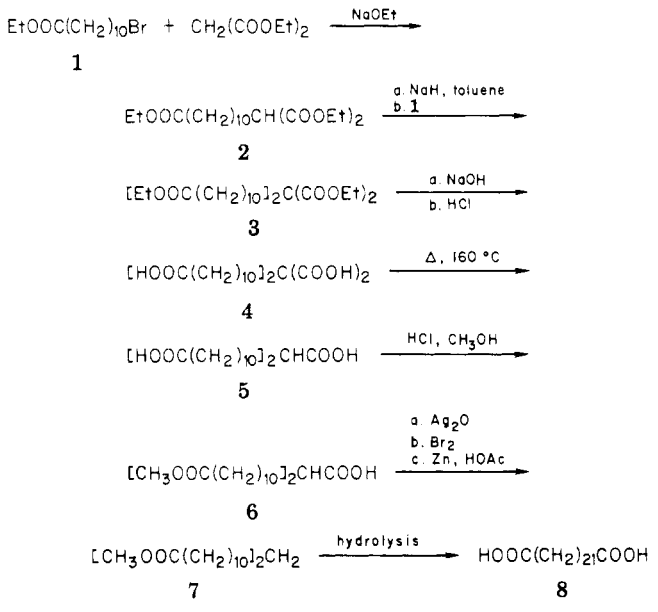
(7) Flaschentrager, B.; Halle, F. *Z. Physiol. Chem.* **1930**, *190*, 120.

(8) All temperatures are uncorrected.

(9) Chuit, P.; Boelsing, F.; Hausser, J.; G. B. *Helv. Chim. Acta* **1927** *10*, 167.

0022-3263/80/1945-4785$01.00/0

Scheme I



and cooled to -5 °C. The crystals which separated, mp 50–55 °C, 142 g (67%), were collected.[9] This acid was converted into the ethyl ester,[9] L, in 93% yield via the acid chloride prepared with thionyl chloride.

Dimethyl 11-Carboxy-1,21-heneicosanedioate, 6. To the solution prepared by reacting 9.0 g (0.39 mol) of sodium with 250 mL of absolute ethanol was added 80 mL (ca. 0.5 mol) of diethyl malonate and 115 g (0.39 mol) of **1**. After 6 h at reflux the alcohol was largely distilled and the residue was diluted with water and extracted with ether–benzene. After the solution was washed with saturated brine, the solvents were removed by heating and then about 20 mL of diethyl malonate was distilled at 75 °C (2.3 mm), leaving crude reaction product, mainly **2**. To a mixture prepared by reacting 7.3 g (0.30 mol) of sodium hydride in 300 mL of toluene with the above **2** for 0.5 h was added 97 g (0.33 mol) of **1**. The stirred mixture was held at reflux for 40 h (titration showed all base had been used up), cooled, and taken up in ether. After the solution was washed with water, dilute acetic acid, and brine, the solvents were removed and the residue, mainly **3**, was heated for 1 h at reflux with a solution of 10 g of NaOH in 250 mL of 95% ethanol and then with excess 6% NaOH while allowing most of the alcohol to distill. After 1 day at reflux the solution was treated with dilute HCl until the solid which formed just redissolved. After extraction with benzene the aqueous layer was added to excess aqueous HCl. The solid product was collected, washed with water and ether, and dried in a vacuum desiccator over concentrated H_2SO_4 for 12 h. The crude acid, **4**, mp 116–118 °C, was heated at 160 °C for 85 min to effect decarboxylation to yield 88 g (28% based on **1**) of heneicosane-1,11,21-tricarboxylic acid, **5**, mp 89.0–90.5 °C, neutralization equivalent 143.4 (theory 142.7). A solution of 21 g of **3** in 400 mL of dry methanol and 30 mL of 0.38 N HCl in methanol was held at room temperature for 1 h and then in the icebox for 15 h. By filtration there was obtained crude **6** and additional **6** on allowing the mother liquor to stand for 4 days in the icebox. Recrystallization afforded 14 g (69%) of pure **6**, mp 62.5–63.5 °C (corr). Anal.[10] Calcd for $C_{26}H_{48}O_6$: C, 68.4; H, 10.6. Found: C, 68.4; H, 10.3. Additional **6** was present in the mother liquor which was useful in recrystallizing material from another run. The remaining material in the mother liquor was mainly **5**.

1,21-Heneicosanedioic Acid, 8. A stirred mixture of 20 g of pure **6**, the silver oxide freshly prepared from 8 g of $AgNO_3$ and 2.5 g of NaOH in water, 100 mL of water, and 10 mL of ether was distilled. Addition of a little methanol caused the silver salt to coagulate and the brownish solid was collected, washed with methanol, and dried under vaccum at 60–70 °C. The silver salt, 24 g, was suspended in CCl_4 and treated with 5 mL of bromine.[11] After a few minutes the mixture was filtered and the filtrate was washed with cold aqueous K_2CO_3 and brine, and the CCl_4 was removed under vacuum to yield a soft waxy solid. This material was heated under reflux with stirring with 20 g of zinc dust and 150 mL of acetic acid for 2 h. The acetic acid was separated from the zinc dust and poured into ice water to yield 12 g (66% based on **6**, 13% based on **1**) of colorless dimethyl 1,21-heneicosanedioate, mp 73–74 °C (lit.[7] mp 70.8 °C). Alkaline saponification yielded pure **8**, mp 127–128 °C (lit.[7] mp 127.5 °C), in almost quantitative yield.

Registry No. 1, 6271-23-4; 2, 74965-67-6; 3, 74965-68-7; 4, 74965-69-8; 5, 74965-70-1; 6, 74965-71-2; 7, 42235-77-8; 8, 73292-43-0; $CH_2(COOEt)_2$, 105-53-3.

(10) Analysis by Mrs. E. H. Klotz.
(11) Cf.: Cristol, S. J.; Firth, W. C., Jr. *J. Org. Chem.* **1961** *26*, 280.

The Structure of Helminthogermacrene

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The coproduction of (-)-sativene (I) and (-)-longifolene (II) by *Helminthosporium* species[2] and the different stereospecificities of the crucial 1,3-hydride shifts occurring during biosynthesis of these compounds[3] have been interpreted in terms of a common precursor possessing a unique conformation (Scheme I).[4] According to this proposal cyclization of *cis,trans*-farnesyl PP[5] with the *re* face of the terminal double bond leads initially to medium-ring carbocycles containing one cis double bond[6] and conformationally well-suited for the hydrogen migrations.

We report here the isolation and structure verification by synthesis of a new hydrocarbon from *Helminthosporium sativum*; the structure of this hydrocarbon corresponds to the ten-membered-ring intermediate required for sativene biosynthesis and thereby provides indirect evidence in support of the biosynthetic proposal.

Careful analysis of the hydrocarbon fractions obtained from mycellium of *H. sativum* has revealed the presence of components other than I and II.[7] Repeated chromatography gave a levorotatory $C_{15}H_{24}$ hydrocarbon which exhibited spectroscopic properties requiring three olefinic methyl groups [δ 1.70 (3 H) and 1.74 (6 H)] and four vinyl hydrogens, two of which compose a terminal methylene [δ 4.70 (2 H) and 5.1–5.5 (2 H) and $\bar{\nu}$ 3065, 3020, 1640, and 890 cm^{-1}]. The properties of this substance did not correspond with those of any known sesquiterpene hydrocarbon and in particular ruled out (-)-germacrene-A (III)[8] as a possible structure. This fact and the biogenetic arguments summarized above suggested that the new hy-

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