s). The 3,5-dinitrobenzoate, prepared by refluxing with 3,5-dinitrobenzoyl chloride in pyridine, crystallized from hexane–EtOAc as yellow needles, mp 135–136° (lit. 136–137° [3]).

Acknowledgements—We thank Mr. M. D. Webber, City Arboriculturist and Dr. W. J. Dale, of Bristol City Council for plant material, Mr. D. J. Puckey and Miss Tessa M. Coe of the Meat Research Institute, Langford, for mass spectrometry and Dr. G. A. Carter and Mrs. S. Kendall for bioassays.

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Phytochemistry, Vol. 22, No. 4, pp. 1040–1042, 1983.
Printed in Great Britain.

0031–9422/83/041040–03$03.00/0

HELIANTHOL A, A SESQUITERPENE ALCOHOL FROM *HELIANTHUS TUBEROSUS**

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(*Revised received* 25 *September* 1982)

Key Word Index—*Helianthus tuberosus*; Compositae; essential oil; helianthol A; sesquiterpene alcohol.

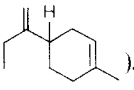
Abstract—A new sesquiterpene alcohol, helianthol A, was isolated from the aerial parts of *Helianthus tuberosus*. The structure of this compound has been established as (+)-2-methyl-6-[4-methyl-3′-cyclohexen-1′-(*R*)-yl]-3,6-heptadien-2-ol by chemical and spectroscopic methods.

INTRODUCTION

Helianthus tuberosus L. has been analysed chemically and the sesquiterpene heliangine was found [1–4]. We have now isolated a new sesquiterpene alcohol from the essential oil of the aerial parts.

RESULTS AND DISCUSSION

The essential oil was obtained by steam distillation of the aerial parts of *H. tuberosus* which were collected from the outskirts of Osaka, Japan. The compound (helianthol A) (**1**), 18.0% of the essential oil, was isolated by alumina column chromatography and by prep. GC, using Celite 545 as the stationary phase. Helianthol A, $[\alpha]_D^{20}$ +61.0° (EtOH; *c* 0.3), has the molecular formula $C_{15}H_{24}O$ (M^+, *m/z* 220, 0.2%), based on mass spectrometry and the following physical properties. IR ν_{max} cm^{-1}: 3360 1140 (tertiary hydroxyl), 3080, 1635, 890 (terminal olefin). ^1H NMR: δ ($CDCl_3$, TMS) 1.33 (6H, *s*, Me_2–C–OH), 1.65 (3H, *s*, Me–C=CH–), 2.02 (4H, *m*, $-CH_2-CH=$), 2.15 (1H, *m*,



), 2.75 (2H, *dd*, *J* = 15 Hz, $=CH-CH_2-C=$), 4.75 (2H, *m*, $CH_2=$), 5.38 (1H, *m*, –CH=C–), 5.64 (2H, *m*, –CH=CH–), 1.45 (1H, *s*, –OH, on deuteration shows no signal). MS: *m/z* 220 (M^+, 0.2%), 79 (100), 91(82), 93 (73), 119 (71), 105 (69), 202 (22), 187 (13). This compound has a similar skeleton to β-bisabolene the main component of this oil. Its structure as a related alcohol was confirmed by the following procedures. When the compound was heated with 10% aqueous oxalic acid for 4 hr, the dehydration product (**2**) was obtained. These results confirmed that the position of the hydroxy group was at C-2. In addition, the dehydration product **2**, was reduced with hydrogen on platinum oxide and was identified as a bisabolane, **3**. The ^{13}C NMR figure and the data on the ^{13}C-signals which were assigned by ^1H off-resonance are summarized in Table 1. The appearance of the carbon signal of the solvent ($CDCl_3$) at δ 78.30–75.76 (*t*) and another 15 signals are shown in Table 1. The signals of C-1 and C-8 were found at a high magnetic field at δ 29.87 and appeared equal in value to each other. Also observed was the appearance of a carbon (δ 70.72), on C-2, attached to a hydroxyl group in **1** which supported the partial structure

*Part X in the series "Chemical Constituents of Naturalized Plants of Japan".

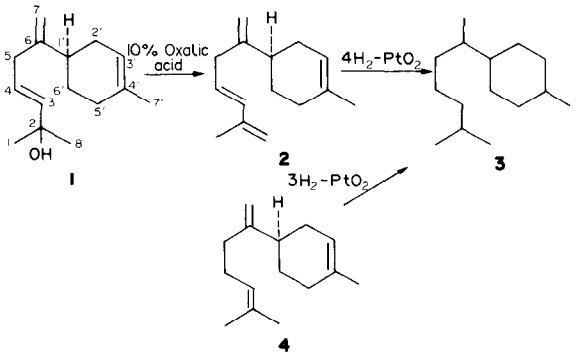
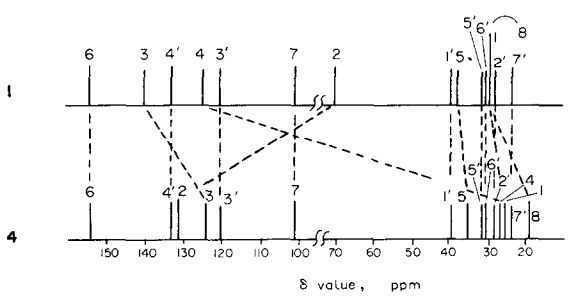


Fig. 1.

of a hydroxy group attached to a quarterly carbon. The carbon shift of helianthol A can be assigned by the use of β-bisabolene as a model and the δ-values of the carbons in an analogous monoterpene [5]. In the comparison of the ^{13}C NMR spectra between helianthol A and β-bisabolene, helianthol A was similar to that of β-bisabolene except for four signals at δ 29.87 (*q*), 70.72 (*s*), 125.16 (*d*) and 139.75 (*d*). The signals of δ 23.51 (*q*), 28.24 (*t*), 30.70 (*t*), 31.31 (*t*), 37.84 (*t*), 39.67 (*d*), 108.54 (*t*), 120.70 (*d*), 133.78 (*s*) and 153.06 (*s*) were similar to that of the limonene skeleton of β-bisabolene; also, it is clear that helianthol A has a cyclohexene skeleton. Furthermore, it should be noted that the signal of C-4 at δ 26.88 (*t*) in β-bisabolene is shifted to a low magnetic field (the corresponding olefinic field), δ 125.16 in helianthol A. Similarly, the signal of C-3 [δ 139.75 (*d*)] in helianthol A is shifted to a low magnetic field, δ 15.40, compared with the signal of C-3 [δ 124.35 (*d*)] in β-bisabolene. The signals of C-5–C-7 in helianthol A compared with β-bisabolene are more or less the same. Accordingly, the position of the carbon-carbon double bond is between C-3 and C-4. The signals of C-1 and C-8 in the methyl group appeared equal in value at a low magnetic field compared with β-bisabolene. From the results, there may be a single bond between C-2 and C-3 and, due to this, there may be free rotation. If these shift values were due to a hydroxyl group attached to C-2, C-2 would be shifted to a high magnetic field. From the above ^{13}C NMR spectral data, the planar structure of helianthol A was determined to be 2-methyl-6-(4′-methyl-3′-cyclohexenyl)-3,-6-heptadien-2-ol.

Table 1. ^{13}C NMR chemical shift assignments for **1** and **4**.

Carbon No.	1	4
1	25.71 (*q*)	29.87 (*q*)
2	131.47 (*s*)	70.72 (*s*)
3	124.35 (*d*)	139.75 (*d*)
4	26.88 (*t*)	125.16 (*d*)
5	34.94 (*t*)	37.84 (*t*)
6	154.28 (*s*)	153.06 (*s*)
7	107.13 (*t*)	108.54 (*t*)
8	17.72 (*q*)	29.87 (*q*)
1′	39.84 (*d*)	39.67 (*d*)
2′	28.39 (*t*)	28.24 (*t*)
3′	120.85 (*d*)	120.70 (*d*)
4′	133.71 (*s*)	133.78 (*s*)
5′	31.48 (*t*)	31.31 (*t*)
6′	30.80 (*t*)	30.70 (*t*)
7′	23.47 (*q*)	23.51 (*q*)



The spectra were recorded in $CDCl_3$ at 25.05 MHz. Chemical shifts in δ-values (ppm) from TMS as int. standard.

In order to determine the absolute configuration, helianthol A was compared in specific rotation with (+)-β-atlantone and (+)-α-atlantone [6, 7]. These compounds were indicated as $[\alpha]_D^{30}$ +65.0° and +77.0° respectively, and the absolute configuration of each compound has the *R* configuration. Also, helianthol A has $[\alpha]_D^{20}$ +61.0° and the dehydration product, **2**, has $[\alpha]_D^{20}$ +68.0°. Helianthol A (**1**) has the absolute configuration as shown in Fig. 1. In addition, these facts support the coupling constant of gate decoupling for C–H of the C-1′ position which was 148 Hz. This is the first example of the occurrence of **1** in nature.

EXPERIMENTAL

IR spectra were taken in liquid films and the ^1H NMR spectra were measured in $CDCl_3$ on a 100 MHz apparatus with TMS as the int. standard. ^{13}C NMR spectra were recorded in 5 mm tubes on a JEOL FX-100 NMR spectrometer operating at 25.05 MHz. Spectra were obtained under the following conditions. Observed with 47 KHz: data point, 8192; pulse width, 5 μsec; pulse interval, 1 sec; sample concn, 30 mg in 0.4 ml $CDCl_3$; accumulation time, 1500–2000. Chemical shifts are expressed in δ-values (ppm), downfield from the int. TMS. GC/MS analyses were made with a Shimadzu Model LKB 9000B. Spectra were obtained under the following conditions: ionization electron energy, 70 eV; ion source temp., 240°.

Plant material and essential oil. The plants were collected from un-occupied ground in Higashiosaka-shi in Sept. 1978. They were divided into three parts: flowers (10.0 kg), leaves (21.0 kg) and stalks (35.2 kg). After steam distillation of each part, the essential oil was obtained by extraction of the distillate with Et_2O and evaporation under N_2 and yielded 7.8 g, 0.078%, 9.9 g, 0.047% and 8.8 g, 0.025%, respectively.

Isolation of helianthol A (**1**). The essential oil (9.0 g) of the leaves was chromatographed on deactivated alumina with *n*-hexane, C_6H_6, Et_2O and MeOH divided into four fractions. Elution with Et_2O and MeOH gave helianthol A(**1**) (1.6 g) which was then isolated by prep. GC (Carbowax-20M 5%, 80–100 mesh, 4 mm × 3.00 m, H_2 0.5 kg/cm², 220°). The proportions were: 4.2% in flower oil, 18.7% in leaf oil and 14.0% in stalk oil on GC.

Isolation of β-bisabolene (**4**). Elution with *n*-hexane gave β-bisabolene (**4**) (1.4 g) which was then isolated by prep. GC (Carbowax-20M 5%, 80–100 mesh, 4 mm × 3.0 m, H_2 0.5 kg/cm², 150°). Obtained: 24.2% in flower oil, 15.8% in leaf oil and 40.5% in stalk oil on GC. $[\alpha]_D^{20}$ +73° (EtOH; *c* 0.5). IR, ^1H NMR and mass spectral values agreed with published values.

Dehydration of helianthol A (**1**). Compound **1** (30 mg) in 10% aq. oxalic acid (1.5 ml) was refluxed for 4 hr. An oily product was obtained. Prep. GC afforded one main product, identified by comparison of its NMR and mass spectra as **2**. $[\alpha]_D^{20}$ +68° (EtOH; *c* 0.6).

Catalytic hydrogenation of (**1**). Catalytic hydrogenation of the dehydration product, **2** (20 mg), in EtOH (5 ml) over PtO_2 (15 mg) was carried out at room temp. for 2.5 hr. The product was purified by prep. GC and was obtained as a colorless oil, **3** (13 mg). The IR and mass spectra of this hydrocarbon were identical with those of authentic bisabolene from reduction of **4** from cotton oil [8] and this oil. Its IR spectrum was also identical with the reported spectrum of bisabolane (**3**) [9].

Catalytic hydrogenation of (**4**). Catalytic hydrogenation of the β-bisabolene (**4**) (25 mg) in EtOH (5 ml) over PtO_2 (2.0 mg) was carried out at room temp. for 2.5 hr. The product was purified by prep. GC and was obtained as a colorless oil, **3** (24 mg). Its IR and mass spectra were also identical with the reported spectrum of bisabolane (**3**) [8, 9].

Acknowledgment—This work was supported in part by a Grant-in-Aid for Organic Chemistry of Natural Products from the Ministry of Education, Science and Culture of Japan.

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Phytochemistry, Vol. 22, No. 4, pp. 1042–1043, 1983.
Printed in Great Britain.

0031-9422/83/041042-02$03.00/0
Pergamon Press Ltd.

SEMPERVIRENIC ACID, A DITERPENE ACID FROM *SOLIDAGO SEMPERVIRENS*

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(*Revised received* 30 *July* 1982)

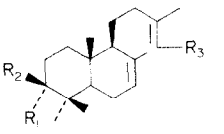
Key Word Index—*Solidago sempervirens*; Compositae; diterpene acid; sempervirenic acid; 3β-acetoxy-labda-7,13-diene-15-oic acid.

Abstract—Sempervirenic acid, a new diterpene has been isolated from *Solidago sempervirens* and its structure determined by spectroscopic methods and chemical conversions to be 3β-acetoxy-labda-7,13-diene-15-oic acid.

Chemical examination of *Solidago sempervirens* resulted in the isolation of a diterpene acid (**1**) which has not been reported by previous investigators of this plant [1] or isolated from any one of the several other *Solidago* species examined [2]. The new diterpene has been given the trivial name sempervirenic acid mp 185°, M^+ at *m/z* 362, $C_{22}H_{34}O_4$, $[\alpha]_D$ +70°. IR $\nu_{max}^{CCl_4}$ cm^{-1}: 3450 (*br*, OH), 1729 (ester), 1688 (α, β-unsaturated acid), 1638 (olefinic bond), 1250 (OAc). ^1H NMR: δ 0.9, 1.02 and 1.05 (3H, *s* each, tertiary methyl groups); 2.01 (6H, vinylic methyl groups); 2.17 (3H, *s*, O–CO–Me); 4.5 (*dd*, *J* = 9, 5 Hz, H-3); 5.4 (*br t*, H-7) and 5.7 (1H, *s*, H-14).

Compound **1** readily formed a methyl ester (**2**) and on hydrolysis gave a hydroxy acid $C_{20}H_{32}O_3$ (**3**), confirming the presence of an acetate and carboxylic acid grouping. On catalytic hydrogenation it absorbed 2 mol of hydrogen.

Jones' oxidation of **3** resulted in the ketone, **4**. The methyl signals in the ^1H NMR spectrum of **4** taken in deuterochloroform underwent a general upfield shift on addition of benzene. However, the C-19 and C-20 methyl signals became well resolved with a shift difference of δ 0.28 between them. Hence, the hydroxyl is placed at C-



1 R_1=H, R_2=OCOMe, R_3=COOH
2 R_1=H, R_2=OCOMe, R_3=COOMe
3 R_1=H, R_2=OH, R_3=COOH
4 R_1=R_2=O, R_3=COOH
5 R_1=H, R_2=OH, R_3=CH_2OH