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)

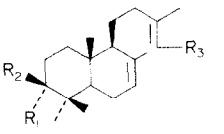
Key Word Index—*Solidago sempervirens*; Compositae; diterpene acid; sempervirenic acid; 3β-acetoxy-labda-7,13-diene-15-oic acid.

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

3 [3] in the labdane skeleton and it is β-equatorial as the C-3 proton is axial (*dd*, $J = 9$, 5 Hz). The structure was further confirmed by reduction of the methyl ester to yield labda-7,13-diene-3,15-diol (**5**) [4] and comparison of its ^{13}C NMR spectrum and $[\alpha]_D$ value with the reported values. Sempervirenic acid is, therefore, assigned the structure 3β-acetoxy-labda-7,13-diene-15-oic acid (**1**).

EXPERIMENTAL

All mps are uncorr. ^1H NMR recorded in $CDCl_3$ at 90 MHz with TMS as internal standard, chemical shifts are expressed in δ-values.

Isolation of sempervirenic acid (**1**). *Solidago sempervirens*, Compositae (whole plant) collected from Madras City in August, was dried (3 kg), coarsely powdered and extracted successively by the cold percolation method with hexane, $CHCl_3$ and MeOH.

The hexane extract on CC over Si gel gave *n*-triacontanol and sitosterol.

The $CHCl_3$ extract (20.5 g) was chromatographed over Si gel by gradient elution with hexane, C_6H_6, $CHCl_3$ and EtOAc. The $CHCl_3$–EtOAc (10%) eluate was crystallized from MeOH to give **1**, mp 185°. ^{13}C NMR: δ 36.9 (C-1), 23.8 (C-2), 81 (C-3), 37.6 (C-4), 54.2 (C-5), 25.3 (C-6), 122.4 (C-7), 134.6 (C-8), 49.7 (C-9), 36.6 (C-10), 23.3 (C-11), 43.5 (C-12), 16.3 (C-13), 115.4 (C-14), 172.1 (C-15), 19.3 (C-16), 21.9 (C-17), 13.6 (C-18), 27.8 (C-19), 16.2 (C-20), 171 (acetoxy carbonyl) and 21.3 (acetoxy methyl).

Methylation of **1**. Sempervirenic acid (100 mg) was methylated with excess CH_2N_2 in Et_2O overnight. After usual work-up it was chromatographed over a short column of Si gel. M^+ at *m/z* 376. (Found: C, 73.20; H, 9.3. $C_{23}H_{36}O_4$ requires: C, 73.4; H, 9.57%.) ^1H NMR: δ 0.74, 0.81, 0.89 (3H, *s*, tertiary methyl), 2.0 (6H, two vinylic methyl groups), 3.68 (3H, *s*, OMe). ^{13}C NMR: δ 36.5 (C-1), 23.8 (C-2), 80.9 (C-3), 37.5 (C-4), 54.17 (C-5), 25.29 (C-6), 122.39 (C-7), 134.6 (C-8), 49.7 (C-9), 36.6 (C-10), 23.28 (C-11), 43.19 (C-12), 160 (C-13), 115.35 (C-14), 167.19 (C-15), 18.9 (C-16), 21.9 (C-17), 13.6 (C-18), 27.8 (C-19), 16.2 (C-20), 170.1 (acetoxy carbonyl), 21.28 (acetoxy methyl) and 50.8 (methoxy methyl).

Hydrolysis of **1**. Sempervirenic acid (200 mg) in EtOH (3 ml) was refluxed with 5 N alcoholic KOH (10 ml) for 1 hr. The EtOH was removed and the remaining soln acidified and extracted with $CHCl_3$. The product was purified by chromatography and crystallized from Et_2O–hexane to yield the alcohol (**3**). mp 162°, $[\alpha]_D + 40°$ ($CHCl_3$; *c* 1). (Found: C, 75.01; H, 9.5%. $C_{20}H_{32}O_3$ requires: C, 75.01; H, 9.5%.) ^1H NMR: δ 0.75, 0.85, 0.98 (3H, *s*, tertiary methyl groups), 2.18 (6H, *s*, two vinylic methyl groups), 3.2 (1H, *dd*, $J = 9$, 5 Hz, H-3), 5.4 (1H, H-7), 5.7 (1H, H-14).

Jones' oxidation of **3**. Compound **3** (100 mg) in dry Me_2CO was oxidized with Jones' reagent (four drops) with stirring at room temp. After 5 min the excess reagent was destroyed with MeOH. The product was purified by chromatography to yield **4**. M^+ at *m/z* 318. (Found: C, 75.23; H, 9.2. $C_{20}H_{30}O_3$ requires: C, 75.44; H, 9.43%.) ^1H NMR: δ 1.0, 1.05, 1.08 (3H, *s*, tertiary methyl groups), 2.15 (6H, *s*, two vinylic methyl groups), with C_6H_6 0.15, 0.60, 0.32 (3H, *s*, C-18–C-20).

Hydrogenation of **1**. Sempervirenic acid (100 mg) in MeOH (10 ml) was hydrogenated in the presence of 5% Pd–C (50 mg) at atmospheric pressure until there was no further uptake of H_2. The soln was filtered and after removal of the solvent the tetrahydro compound, was obtained. M^+ at *m/z* 366. (Found: C, 72.0; H, 10.45. $C_{22}H_{38}O_4$ requires: C, 72.13; H, 10.39%.) ^1H NMR: δ 0.85 (15H, methyl groups); 2.0 (3H, OCOMe), 4.4 (1H, H-3).

Reduction of **2**. To a suspension of $LiAlH_4$ in Et_2O, a soln of **2** (100 mg) in Et_2O (9 ml) was gradually added with stirring and the mixture left overnight. Moist Et_2O was added and the product was extracted with CH_2Cl_2. The organic layer was coned and purified by chromatography to yield labda-7, 13-diene-3, 15-diol (**5**). M^+ at *m/z* 306. $[\alpha]_D - 2°$ ($CHCl_3$; *c* 1). (Found: C, 78.20; H, 11.08. $C_{20}H_{32}O_2$ requires: C, 78.43; H, 11.11%.) ^{13}C NMR: δ 37.2 (C-1), 27.2 (C-2), 78.9 (C-3), 38.6 (C-4), 54.3 (C-5), 25.5 (C-6), 122.1 (C-7), 134.9 (C-8), 49.5 (C-9), 36.5 (C-10), 23.4 (C-11), 41.9 (C-12), 139.4 (C-13), 123.6 (C-14), 59.1 (C-15), 15.0 (C-16), 21.9 (C-17), 13.5 (C-18), 27.8 (C-19) and 16.3 (C-20). These values are in agreement with those reported. However, the assignments of the methyl groups have been changed taking into consideration the residual splitting which distinguishes the vinyl methyls from the other tertiary methyl groups.

Acknowledgements—The authors wish to thank the Central Council for Research in Ayurveda and Siddha for financial support. The plant was identified and collected by Mrs. P. Brindha and Mrs. B. Sasikala.

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