

ISOLATION OF DEACETYLVIGUIESTENIN AND ERIOFLOLIN FROM *HELIANTHUS TUBEROSUS*

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In the previous papers (1), the authors elucidated the structure of heliangine (1), a plant growth regulator isolated from *Helianthus tuberosus* L. (Compositae) by Shibaoka (2). Recently, we have isolated two other heliangolides (2 and 3) from the same plant.

The ^1H nmr, ^{13}C nmr spectra and optical rotation of 2 indicated that it was deacetylviguiestenin (tagitinin E) (3, 4). The ^1H nmr spectrum of 2 was superimposable upon that of an authentic sample.

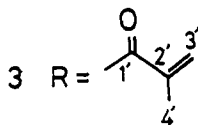
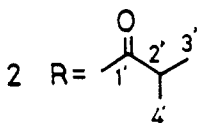
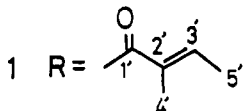
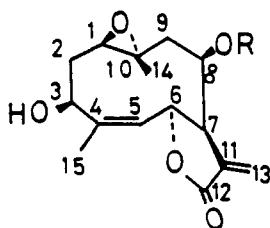
It was deduced that 3 was also a heliangolide containing a methacrylate moiety from its ^1H nmr and ^{13}C nmr spectra; 3 afforded 11,13-dihydro-

deacetylviguiestenin on hydrogenation. The rotation of 3 was significantly close to that of erioflorin reported by Torrance *et al.* (5). These findings show that the structure of 3 coincides with erioflorin.

TABLE. ^{13}C nmr data of heliangolides in CDCl_3 (δ).

Comp.	1	2	3
C-atom			
1.....	60.6	60.5	60.5
2.....	32.6	32.6	32.6
3.....	72.0	72.0	71.9
4.....	141.5	141.5	141.6
5.....	126.1	126.1	125.9
6.....	74.1	74.0	74.1
7.....	48.4	48.2	48.2
8.....	76.1	75.5	76.5
9.....	43.5	43.8	43.4
10.....	58.6	58.6	58.6
11.....	137.2	137.2	137.1
12.....	169.4	169.3	169.3
13.....	124.5	124.5	124.6
14.....	19.7	19.9	19.6
15.....	22.9	22.9	22.8
1' ^a	166.4	175.6	165.7
2' ^a	127.6	34.1	135.1
3' ^a	138.7	18.9 ^a	126.6
4' ^a	11.8	18.5 ^a	18.0
5' ^a	14.5		

^aAssignments are interchangeable.



EXPERIMENTAL

ISOLATION OF HELIANGOLIDES.—Dry leaves of *Helianthus tuberosus* L. (43 kg), collected at Fukuchiyama Experimental Farm, Takeda Chemical Ind., in September 1975, were extracted with methanol for 4 days. After concentration *in vacuo*, the extract was mixed with water, methanol and hexane, then the lower layer was concentrated until organic solvent was evaporated. The aqueous solution was extracted with chloroform. The chloroform extract (76 g) was chromatographed over silica gel and eluted with chloroform-methanol (9:1) to afford a mixture of heliangolides (22.4 g). From the methanol solution of this mixture, crystals of 1 (10.8 g) were precipitated.

The mother liquor was chromatographed over silica gel, impregnated previously with glycerol (10%), and eluted with chloroform to give **1** (2.2 g) and a mixture of **1**, **2** and **3** (3.8 g). The latter mixture (2.2 g) was chromatographed repeatedly through Sephadex LH-20 column and eluted with hexane-chloroform-ethanol (4:5:1) to afford **1** (310 mg), **2** (273 mg) and **3** (769 mg).

HELIANGINE (1).—Recrystallization from methanol gave colorless needles, mp 240–243° (6). It was identical with an authentic sample (mmp, ir and ¹H nmr spectra).

DEACETYLVIQUESTENIN (2).—Recrystallization from methanol gave colorless needles, mp 218–219°; $[\alpha]^{25}_D -97^\circ$ (CHCl₃); ir (KBr) 3450 (OH), 1750 (lactone), 1730 (ester), 1660 cm⁻¹ (C=C); ¹H nmr (CDCl₃) δ 1.11 (6H, d, *J*=7.0 Hz, 3'-H and 4'-H). It was identical with an authentic sample (¹H nmr spectrum).

ERIOFLORIN (3).—Recrystallization from methanol gave colorless needles, mp 227–230°; $[\alpha]^{25}_D -117^\circ$ (CHCl₃); ir (KBr) 3420 (OH), 1750 (lactone), 1708 (ester), 1660, 1630 cm⁻¹ (C=C); ¹H nmr (CDCl₃) δ 1.89 (3H, broad s, 4'-H), 5.57 (1H, m, 3'-H), 6.08 (1H, m, 3'-H).

HYDROGENATION OF 3 TO 11,13-DIHYDRO-DEACETYLVIQUESTENIN.—Compound **3** (159 mg) in methanol was hydrogenated over 5% Pd-C until 2 mol of hydrogen was taken-up.

The product gave colorless prisms, mp 191–192°, (100 mg) on recrystallization from methanol. It was identical with 11,13-dihydrodeacetylviquestenin (mmp, ir and ¹H nmr spectra).

ACKNOWLEDGMENTS

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6. We wish to correct the mp of heliangine (1) cited in lit. 1 (227–229°).