

α -BISABOLOL-6-DESOXY- β -ALTROPYRANOSIDE FROM *CARTHAMUS TURKISTANIKUS**

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(Received 26 September 1980)

Key Word Index—*Carthamus turkistanicus*; Compositae; sesquiterpene glycoside; 6-desoxy-altropyranoside; α -bisabolol-6-desoxy- β -altropyranoside.

Abstract—A sesquiterpene glycoside has been isolated from the aerial parts of *Carthamus turkistanicus* and identified as α -bisabolol-6-desoxy- β -altropyranoside.

The aerial parts of *Carthamus turkistanicus* (Compositae, tribe Cynareae) afforded, in addition to taraxasterol, a glycoside, which on acetylation gave a triacetate. The spectroscopic data showed that the α -bisabolol-glycoside **1** was present. The mass spectrum showed a molecular ion at m/z 368 ($C_{21}H_{36}O_5$) and a strong fragment at m/z 204 ($C_{15}H_{24}$), while the fragment of the sugar residue at m/z 147 ($C_6H_{11}O_4$) had a low intensity. These data indicated the presence of a desoxyhexose derivative, which was supported by the 1H NMR data of the corresponding triacetate **2** (Table 1). However, the spectrum could only be interpreted when determined at 400 MHz in C_6D_6 , when all the signals due to the glycoside moiety were separated. Irradiation of the H-1' doublet at δ 4.42 ($J = 7.5$ Hz) allowed the assignment of the H-2' signal, which was a double doublet at 5.57 ($J = 10.5, 7.5$ Hz), indicating an equatorial orientation of the oxygen functions at C-1' through C-3'. Further spin decoupling showed that the H-4' signal was a broadened doublet at 5.21 ($J = 3.5$ Hz), while the signal of H-5' was a broadened quartet at 2.96. The latter was coupled with the methyl doublet at 0.92. This sequence showed that a 6-desoxy- β -altropyranoside triacetate was present. The signals of the sesquiterpene part were nearly identical with those of bisabolol. Consequently the structure of the natural compound is **1**. The ^{13}C NMR spectrum of **1** also

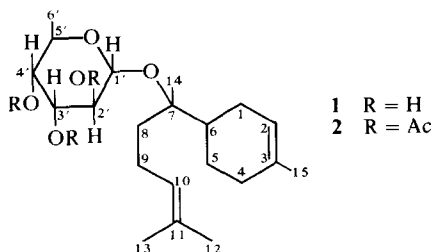
supported this structure. However, the question whether a D- or L-pyranoside is present could not be solved. 6-Desoxyaltropyranosides seem to be rare. From a *Strophanthus* species a cardiac glycoside with this sugar was isolated [1]. From *Carthamus oxyacantha* we have isolated a glycoside of hinesol where the glycoside part was the isomeric β -fucopyranoside [2]. These unusual glycosides may be more widespread in this genus.

EXPERIMENTAL

The air-dried plant material (250 g) was extracted with Et_2O at room temp. The extract was treated with MeOH to remove saturated hydrocarbons. Separation by CC (Si gel, act. grade II) and TLC (Si gel) afforded 50 mg taraxasterol and 50 mg **1** (Et_2O -petrol, 3:1), colourless gum. IR $\nu_{max}^{CHCl_3}$ cm^{-1} : 3580, 3450 (OH); MS m/z (rel. int.): 368.256 (M^+ , 2), ($C_{21}H_{36}O_5$) 350 ($M - H_2O$, 0.5), 332 ($350 - H_2O$, 0.3), 204.188 (M -sugar, 66) ($C_{15}H_{24}$), 147 ($C_6H_{11}O_4$, 13), 119 (C_9H_{11} , 100), 69 ($C_5H_9^+$, 90); CI (*iso*-butane): 369 ($M + 1$, 5), 205 (M -sugar + 1, 100).

$$[\alpha]_{24}^{25} = \frac{589}{-6.5} \quad \frac{578}{-7.0} \quad \frac{546}{-7.5} \quad \frac{436 \text{ nm}}{-13.0} \quad (c = 1.0, CHCl_3).$$

Compound **1** (20 mg) was heated in 1 ml Ac_2O for 1 hr at 70°. After evapn and TLC (Et_2O -petrol, 1:1) 15 mg **2** were obtained as a colourless gum. For 1H NMR data see Table 1.



* Part 339 in the series "Naturally Occurring Terpene Derivatives". For Part 338 see Bohlmann, F., Gupta, R. K., Jakupovic, J., King, R. M. and Robinson, H. (1981) *Phytochemistry* **20**, (in press).

Table 1. ^1H NMR spectral data of compounds **1** and **2** (TMS as internal standard)

	1	2 (CDCl_3)	C_6D_6	$^{13}\text{C}^*$			
H-1	1.98 <i>m</i>	1.98 <i>m</i>	1.96 <i>m</i>	C-1	21.9 <i>t</i>	C-1'	97.2 <i>s</i>
H-2	5.36 <i>m</i>	5.33 <i>m</i>	5.38 <i>m</i>	C-2	120.5 <i>d</i>	C-2'	74.3 <i>d</i>
H-4 } H-9 }	1.98 <i>m</i> }	1.98 <i>m</i>	1.96 <i>m</i>	C-3	134.4 <i>s</i>	C-3'	72.4 <i>d</i>
			1.8 <i>m</i>	C-4	31.1 <i>t</i>	C-4'	71.8 <i>d</i>
H-10	5.05 <i>br.t</i>	5.02 <i>m</i>	5.16 <i>br.t</i>	C-5	23.6 <i>t</i>	C-5'	70.4 <i>d</i>
H-12	1.65 <i>br.s</i>	1.63 <i>br.s</i>	1.59 <i>br.s</i>	C-6	41.3 <i>d</i>	C-6'	20.2 <i>q</i>
H-13	1.61 <i>br.s</i>	1.60 <i>br.s</i>	1.58 <i>br.s</i>	C-7	81.9 <i>s</i>		
H-14	1.14 <i>s</i>	1.07 <i>s</i>	1.01 <i>s</i>	C-8	38.0 <i>t</i>		
H-15	1.68 <i>br.s</i>	1.67 <i>br.s</i>	1.67 <i>br.s</i>	C-9	27.0 <i>t</i>		
H-1'	4.37 <i>d</i>	4.62 <i>d</i>	4.42 <i>d</i>	C-10	125.0 <i>d</i>		
H-2' } H-3' }	3.29 <i>m</i>	5.21 <i>m</i> 5.02 <i>m</i>	5.57 <i>dd</i> 5.12 <i>dd</i>	C-11	131.1 <i>s</i>		
				C-12	26.7 <i>q</i>		
H-4'	3.71 <i>br.s</i>	5.21 <i>m</i>	5.21 <i>br.d</i>	C-13	17.8 <i>q</i>		
H-5'	3.34 <i>m</i>	3.76 <i>br.q</i>	2.96 <i>br.q</i>	C-14	16.5 <i>q</i>		
H-6'	1.28 <i>d</i>	1.18 <i>d</i>	0.92 <i>d</i>	C-15	23.4 <i>q</i>		
OAc	—	2.17 <i>s</i> 2.02 <i>s</i> 1.98 <i>s</i>	1.81 <i>s</i> 1.74 <i>s</i> 1.58 <i>s</i>				

* Assignments may be in part interchangeable.

$J(\text{Hz})$: 9,10 = 7 Hz; 1',2' = 7.5 Hz; 2',3' = 10.5 Hz; 3',4' = 3.5 Hz;
4',5' ~ 0.7 Hz; 5',6' = 6.5 Hz.

REFERENCES

1. Reichstein, T. and Weiss, E. (1962) *Adv. Carbohydr. Chem.* **17**, 65.
2. Rustaiyan, A., Behjati, B. and Bohlmann, F. (1976) *Chem. Ber.* **109**, 3953.