The first hydrocarbon ($C_{10}H_{16}$) showed a molecular peak at m/z 136 and the base peak was at m/z 93. Another peak at m/z 92 was important due to the formation of toluene which is possible with the direct loss of a C_3H_8 fragment without rearrangement of the double bond. This type of fragmentation is shown by bicyclic monoterpenes α-pinene and α-thuyene [4]. Therefore this hydrocarbon can be assigned to the class of bicyclic monoterpenes.

The second unknown compound, $C_{10}H_{18}O$, had a molecular ion peak at m/z 154 and base peak at m/z 119 and it is probably an ether derivative of a monocyclic monoterpene.

EXPERIMENTAL

The gum-resin produced by *Boswellia frereana* was collected near Bari and Sanaag (Somaly). Frankincense (50 g) was extracted with EtOAc by percolation. After removal of the solvent, the residue was steam distilled. The distilled oil was separately extracted with *n*-hexane, dried over Na_2SO_4 and the solvent removed at low temp. yielding 1.3 g (2.6%) of oil.

Analytical GC employed the following columns: (a) Stainless steel, (2 m × 3 mm o.d.) packed with 3% OV-1 on Chromosorb W 80–100 mesh; (b) Stainless steel, (2 m × 3 mm o.d.) packed with 2.5% SE-30 on Chromosorb W 80–100 mesh. The MS were obtained by GC/MS analysis using column (b) temp. programmed from 70° to 250° (rate 4°/min) with N_2 as carrier gas. The mass spectrometer operating conditions were as follows: ionization voltage 75 eV; filament emission 200 A; source temp. 250°; resolving power 1000 (10% valley).

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α-BISABOLOL β-D-FUCOPYRANOSIDE FROM *CARTHAMUS LANATUS*

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Key Word Index—*Carthamus lanatus*; Compositae; sesquiterpene glycoside; α-bisabolol β-D-fucopyranoside.

Abstract—A sesquiterpene glycoside has been isolated from the aerial parts of *Carthamus lanatus* and identified by its spectroscopic and chemical properties as α-bisabolol β-D-fucopyranoside.

The major component of the hexane extract from the aerial parts of *Carthamus lanatus* L. (Compositae; tribe Cynereae) is a sesquiterpene glycoside, **1**. This type of compound seems to be characteristic of the genus *Carthamus* because two other isomeric glycosides have been described from *C. oxyacantha* [1] and *C. turkistanikus* [2].

The IR spectrum of the product shows absorptions of double bonds and hydroxyl groups, and interpretation of the signals due to the glycoside in the ^1H NMR spectrum (60 MHz) was not possible. On acetylation it gave a triacetate, **2**, with no absorption of hydroxyl groups in the IR. The mass spectrum showed no molecular ion but two peaks at m/z 289 (10%) $C_{12}H_{17}O_8$ and 204 (99%) $C_{15}H_{24}$ and their respective fragmentation sequences (289, 273, 213, 153, 111 and 204, 134, 119) were readily assigned to the acetylated glycoside and the sesquiterpene moieties.

The ^1H NMR spectrum of the triacetate, **2**, shows a methyl doublet at δ 1.15 and a broad quartet at 3.70

Table 1. ^{1}H NMR of compounds **1**–**5** (60 MHz, $CDCl_3$, TMS as internal standard)

	1	**2**	**3**	**4**	**5**
H-2	5.35 *m*	4.8–5.4 *m*	5.35 *m*	5.38 *m*	—
H-10	5.02 *t* $J = 7$ Hz		5.06 *t* $J = 7$ Hz	5.13 *t* $J = 7$ Hz	—
H-12, H-13, H-15	1.62–1.67 *m*	1.60 *m*	1.58 *m*	1.51 *m*	—
H-14	1.15 *s*	1.05 *s*	0.98 *s*	1.12 *s*	—
H-1′	3.3–4.5	4.35 *d* $J = 7$ Hz	—	—	4.85–5.30 *m*
H-2′, H-3′, H-4′		4.8–5.4 *m*	—	—	
H-5′		3.70 *q* $J = 6$ Hz	—	—	4.07 *q* $J = 6$ Hz
H-6′	1.28 *d* $J = 7$ Hz	1.15 *d* $J = 7$ Hz	—	—	1.15 *d* $J = 7$ Hz
OH-3	3.3–4.5	—	—	—	—
OAc-3	—	1.93, 1.99, 2.11	—	—	1.97, 2.07, 2.16
OMe	—	—	3.07 *s*	—	3.36

that agree with the existence of a ω-desoxysugar, and the pattern of absorptions between δ 4.5 and 5.4 indicated a β-fucopyranoside structure for the sugar. The signals of the sesquiterpene moiety (Table 1) were very similar with those α-bisabolol; consequently the structure of the natural compound is **1**.

To confirm the structure and to determine the absolute configuration, **2** was treated with *p*-toluenesulfonic acid in methanol. The resulting terpenoid fraction, after chromatography, yielded a mixture of α-, β- and γ-bisabolenes, (−)-7-epi-bisabolol methyl ether (**3**) and (−)-α-bisabolol (**4**) [3]. The major sugar component from the aqueous fraction after acetylation and chromatography was **5**, identical with an authentic sample.

EXPERIMENTAL

Carthamus lanatus was collected in July near Almenara de Tormes (Salamanca, Spain). Dried aerial parts (1300 g) were extracted with hexane, defatted with MeOH and fractionated with aq. NaOH. By chromatography of 11 g of the neutral fraction (total yield 35.1 g) 480 mg of **1** were isolated as an oil, $[\alpha]_D = -20.6°$ ($CHCl_3$; *c* 0.97). IR ν_{max} cm^{-1}: 3400, 3060, 1640, 1100, 1030, 840. Triacetate, **2**, colourless oil, $[\alpha]_D = -20.6°$ ($CHCl_3$; *c* 0.31). IR ν_{max} cm^{-1}: 3060, 1750, 1250, 1230, 1075, 840. EIMS 70 eV, *m/z*: 289 (10), 273 (60), 213 (24), 205 (50), 204 (99), 153 (74), 119 (100), 111 (40).

Methanolysis of **1**. 2.39 g of **1** in MeOH (61 ml) were treated with TsOH (0.6 g) at 46° for 3 hr, worked-up as usual and after chromatography the organic phase yielded bisabolenes (71 mg); **3** (123 mg) $[\alpha]_D = -62.2°$ ($CHCl_3$; *c* 1.19). IR ν_{max} cm^{-1}: 3060, 1650, 1085, 840; and **4** (745 mg) $[\alpha]_D = -38.8°$ ($CHCl_3$; *c* 2.45). The aq. layer after neutralization, acetylation and prep. TLC yielded **5** (41 mg) $[\alpha]_D = +112.6°$ ($CHCl_3$; *c* 0.31). IR and ^{1}H NMR superimposable with those of an authentic sample obtained through the same reaction from commercial *p*-nitrophenyl-β-D-fucopyranoside.

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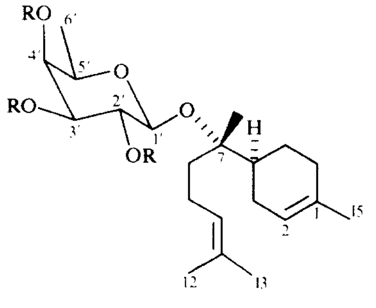
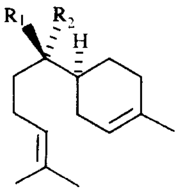


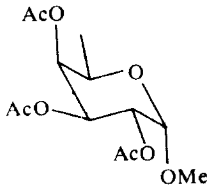
1 R = H

2 R = Ac



3 $R_1 = OMe$, $R_2 = Me$

4 $R_1 = Me$, $R_2 = OH$



5

facilities and Professor Navarro, of this Faculty for identifying the plant material.

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TWO FURANOHELIANGOLIDES FROM *CALEA ANGUSTA**

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Key Word Index—*Calea angusta*; Compositae; sesquiterpene lactones; furanoheliangolides.

Abstract—*Calea angusta* afforded, in addition to known compounds, two new furanoheliangolides closely related to those of *Calea pilosa*.

So far chemical investigation of *Calea* species has shown that furanoheliangolides may be characteristic for this genus (see ref. [1]). This finding supports the view that most of the *Calea* genus needs to be transferred from the subtribe Galinsoginae to the subtribe Neurolaeninae [2], while the remainder, re-established as the genus *Alloisospermum*, should be retained in the Galinsoginae [3]. The results on *Calea angusta* Blake again support this conclusion.

Table 1. ^{1}H NMR spectral data of compounds **13** and **14** (400 MHz, $CDCl_3$ TMS as internal standard)

	13	**14**
H-2	5.60 *s*	5.62 *s*
H-5	6.00 *dq*	6.04 *dq*
H-6	5.28 *ddq*	5.22 *ddq*
H-7	3.28 *dd*	3.38 *dd*
H-8	5.08 *ddd*	5.01 *ddd*
H-9α	2.34 *dd*	—
H-9β	2.14 *dd*	3.95 *dd*
H-13	3.30 *d*	3.32 *d*
H-13′	3.25 *d*	3.30 *d*
H-14	1.44 *s*	1.53 *s*
H-15	2.09 *dd*	2.08 *dd*
OMeBu	2.32 *ddq*	2.35 *ddq*
	1.60 *ddq*	1.62 *ddq*
	1.40 *ddq*	1.43 *ddq*
	1.08 *d*	1.10 *d*
	0.85 *t*	0.86 *t*

J(Hz): 5, 6 = 4; 5, 15 = 6, 15 = 1.5; 6, 7 = 4; 7, 8 = 2; 8, 9α = 6; 8, 9β = 3; 9α, 9β = 15; 13, 13′ = 4.5 (**14**: 8, 9 = 5; 9, OH = 6); OMeBu: 2′,3′ = 2′,5′ = 3′,4′ = 7; $3_1'$, $3_2'$ = 14.

The roots afforded zingiberene, caryophyllene, the thymol derivatives **3** [4] and **4** [5], isocomene (**5**) [6], β-isocomene (**6**) [7] and silphinene (**7**) [8], while the aerial parts gave germacrene D, α-humulene, caryophyllene, bicyclogermacrene, squalene, **1** [9], **2** [10], **3**, the furanoheliangolides **8** [1], **9** [11], **10** [1], **11** [1] and **12** [12] as well as two further ones, the epoxides **13** and **14**. In the ^{1}H NMR spectrum (Table 1) of **13** the signals of the exomethylene proton were replaced by a pair of doublets at $\delta = 3.25$ and 3.30, indicating the presence of 11, 13-epoxide, while a singlet at 5.60 together with a double quartet at 5.28 supported the presence of a furanoheliangolide. The nature of the ester residue followed from the typical signals of a methyl butyrate. Spin decoupling allowed the as-

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*Part 448 in the series "Naturally Occurring Terpene Derivatives". For Part 447 see Bohlmann, F., Zdero, C., King, R. M. and Robinson, H. (1982) *Phytochemistry* **21** (in press).