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GUTIERREZIAL AND FURTHER DITERPENES FROM *GUTIERREZIA SAROTHRAE*

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Key Word Index—*Gutierrezia sarothrae*; Compositae; diterpenes; *ent*-labdane derivatives; new diterpene skeleton.

Abstract—The aerial parts of *Gutierrezia sarothrae* afforded in addition to polyalthic acid, daniellic acid and nivenolide, 14 new diterpenes, most of them closely related to polyalthic acid. One of these compounds has a new carbon skeleton. The structures were elucidated by spectroscopic methods and by some chemical transformations.

INTRODUCTION

Gutierrezia (Compositae, tribe Astereae) is a genus with about 20 species present only in North and South America [1, 2]. So far six species have been studied chemically. In addition to widespread compounds [3, 4], acetylenes [5] and labdane derivatives were isolated [4, 6, 7]. From the roots of *G. sarothrae* (Pursh.) Britt. et Rusby only baccharis oxide was isolated [7], while the essential oil of the aerial parts gave common mono- and sesquiterpenes [8]. We now have studied the aerial parts of *G. sarothrae* in more detail. The results are discussed in this paper.

RESULTS AND DISCUSSION

The aerial parts of *G. sarothrae* afforded in addition to germacrene D, 1,10-epoxycaryophyllene and the C_{17}-acetylenic compound **22** [9], several diterpenes including the known compounds polyalthic acid (**1**) [10], daniellic acid (**2**) [11] and nivenolide (**16**) [12]. The structure of **1** was established by comparing the physical data with those reported in the literature and by rigorous ^{1}H NMR spectroscopy including NOE difference spectra. The latter allowed the assignment of the complete stereochemistry, while the absolute configuration followed from the optical rotation which agreed with that of polyalthic acid with known configuration [10]. The ^{1}H NMR data of **2** were close to those of **1**. However, the stereochemistry at C-4 clearly followed from the chemical shift of H-5. The latter is deshielded if the carboxy group is equatorial. Again the optical rotation indicated that an ent-labdane was present. The data of **16** also agreed with those reported in the literature [12] and the structure was further established by spin decoupling of the ^{1}H NMR spectrum.

The main constituent of this species was a hydroxy acid which was purified as its methyl ester. The spectral data indicated that **3a**, the methyl ester of 3α-hydroxy polyalthic acid was present (Table 1). The stereochemistry at C-3 followed from the couplings observed, while the equatorial carbomethoxy group led to the expected down field shift of the H-5 signal. Spin decoupling allowed the assignment of nearly all signals, though a few were overlapped multiplets. Furthermore, the structure was supported by the ^{13}C NMR spectrum (see Experimental), where the signals were assigned by selective heterodecoupling.

The ^{1}H NMR spectral data of the methyl esters of **4**–**6** (Table 1) indicated the presence of esters of **3a**. The nature of the ester group at C-3 followed from the typical signals in the ^{1}H NMR spectra. The structures were further supported by the ^{13}C NMR spectrum of **5a** which agreed well with the proposed formula. The ^{1}H NMR spectrum of **7a** was close to that of **3a** (Table 2). However, the changed stereochemistry at C-4 led to an expected difference in the chemical shift of the H-5 signals, indicating that the compound was 3α-hydroxydaniellic acid.

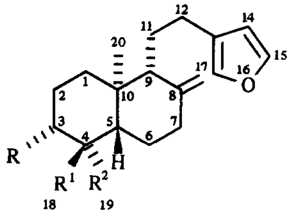
In the ^{1}H NMR spectrum of **8** (Table 2) the presence of a labdane with hydroxy groups at C-18 and 19 followed from the corresponding pairs of doublets around δ 4. Spin decoupling indicated the presence of W-couplings between H-3α and 19 and between H-18 and H-19′ which allowed a clear assignment of the signals.

The structure of the diol **9** followed from the ^{1}H NMR spectrum (Table 2) and was established by reduction of **3a** with lithium aluminium hydride which afforded a diol identical with the natural compound. Reduction of **7a** gave **10**, the ^{1}H NMR of which typically differing from that of **9**.

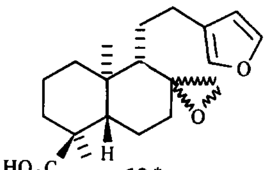
The structure of **11**, which was purified as its methyl ester **11a**, again could be easily deduced from the spectral data (Table 3). The relative position of the oxygen functions at C-4 followed from the chemical shift of H-5 and also from the presence of a W-coupling between H-3α and H-19.

The methyl esters of **12** and **13** differed in the ^{1}H NMR spectra (Table 2) by the presence of a W-coupling of H-17 in the spectrum of **13a**. Inspection of models showed that this required a 8β,17-epoxide. The remaining signals of **12a** and **13a** were close to those of **3a** though the H-7 signals were as expected, at higher fields. No pronounced differences were visible in the MS of **12a** and **13a**, only the relative intensities of the fragments differed slightly.

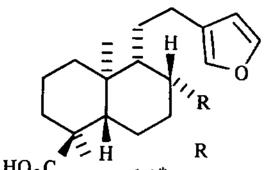
The structure of the aldehyde **14a** followed from its molecular formula ($C_{21}H_{20}O_4$), the characteristic signals in the ^{1}H NMR spectrum (Table 2), and from the product of



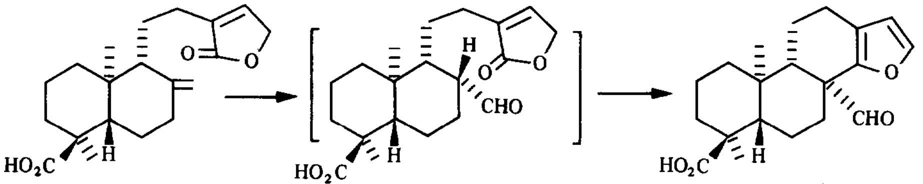
	1*	**2***	**3***	**4***	**5***	**6***	**7***	**8**	**9**	**10**	**11***
R	H	H	OH	OAng	OMebu	OiBu	OH	H	OH	OH	H
R^1	CO_2H	Me	CO_2H	CO_2H	CO_2H	CO_2H	Me	CH_2OH	CH_2OH	Me	CO_2H
R^2	Me	CO_2H	Me	Me	Me	Me	CO_2H	CH_2OH	Me	CH_2OH	CH_2OH



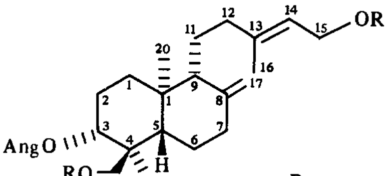
12* α – epoxide
13* β – epoxide



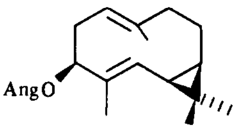
	R
14*	CHO
15*	CH_2OH



16 **17** **18***



	R
19	H
20	Ac



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$H_2C{=}CH\ CH(OH)\ [C{\equiv}C]_2\ CH(OAc)CH{=}CH(CH_2)_5CH{=}CH_2$ **22**

* **1a** – **7a**, **11a** – **15a** and **18a** are the corrosponding methyl esters

boranate reduction, the alcohol **15a**. The stereochemistry at C-4 could be deduced by comparing the ^1H NMR spectrum with that of **3a**, while the configuration at C-8 followed from the chemical shift of H-7α and the couplings of H-8 which required an equatorial proton at C-8. The very small coupling $J_{8,17}$ indicated a restricted rotation of the 8,17-bond. The ^1H NMR data of the corresponding alcohol **15a** further supported the structure.

The methyl ester of **18** showed no molecular ion in the MS. The highest fragment obviously was formed by loss of formyl radical leading to *m/z* 315 ($C_{20}H_{27}O_3$). However, by chemical ionization a clear M + 1 peak could be observed [*m/z* 345 (100 %)]. The ^1H NMR spectrum of **18a** (Table 2) clearly indicated the presence of a diterpene with only two furan protons (δ 7.25 *br s* and 6.22 *d*). These shifts showed that one of the α-furane protons were missing. Spin decoupling allowed the clear assignment of