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NMR STUDIES OF TATRIDIN A AND SOME RELATED SESQUITERPENE LACTONES FROM *TANACETUM VULGARE*

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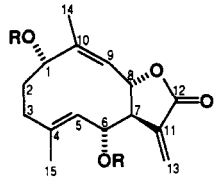
ABSTRACT.—The aerial parts of specimens of *Tanacetum vulgare* growing in Germany yielded several sesquiterpene lactones with germacrane and eudesmane framework. The nmr spectra of tatridin A [**1**], tatridin B [**2**], tanachin (= 1-*epi*-tatridin B [**3**]), and tamirin [**4**] are discussed.

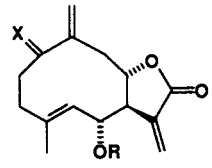
The common tansy, *Tanacetum vulgare* L. (Compositae), is widespread in many countries of Europe, Asia, and North America. Various preparations and decoctions of the plant have long been used in popular medicine because of their applications as expectorants, vermifuges, antiseptics, and spasmolytics (1–3). For this reason, *T. vulgare* has undergone many chemical investigations in the past. While some investigations have referred to the composition of the essential oil and its relation to the geographical location of the species (1, 4–7), many others have centered upon the study of the nonvolatile components, especially sesquiterpene lactones (2, 8–10). Among the latter, no fewer than 20 have been isolated from diverse chemotypes of the plant. In the present paper, we report on the isolation of fifteen sesquiterpene lactones and a sesquiterpene alcohol from specimens of *T. vulgare* collected in Germany. One of the lactones **1** was identified with tatridin A. The structure of this compound is still uncertain; moreover, no reliable nmr data have previously been published in the literature. This paper presents high-resolution ^{1}H- and ^{13}C-nmr data of this and other related compounds, as well as a discussion of nOe measurements.

Extraction and chromatographic fractionation of aerial parts of *T. vulgare* yielded the germacranolides tatridin A [**1**], tatridin B [**2**], tanachin (=deacetyldihydrochrysanolide, 1-*epi*-tatridin B) [**3**] (11,12), tamirin (=deacetylchrysanolide) [**4**] (2,12), parthenolide, costunolide diepoxide (2,13), anhydroverlotorin 4α,5β-epoxide (14), artemorin (2), and artemorin 4α,5β-epoxide (14); the eudesmanolides 1-*epi*-ludovicin C (=armexifolin) (2,15), armefolin (15), 1β-hydroxyarbusculin A (2), reynosin (2), santamarin (2), and magnolialide (16); and the germacrane derivative tanacetol B (8). Among these compounds, anhydroverlotorin 4α,5β-epoxide, artemorin 4α,5β-epoxide, armefolin, and magnolialide were found in *T. vulgare* for the first time.

The spectral data (ir, ms, nmr) of compound **1** and its acetate **1a** clearly suggest that **1** is a germacranolide with two hydroxyl groups at C-1 and C-6, a 12,8-lactone ring, two endocyclic dou-



1 R=H
1a R=Ac



2 X=H, βOH; R=H
2a X=H, βOAc; R=Ac
3 X=H, αOH; R=H
3a X=H, αOAc; R=Ac
4 X=O, R=H

ble bonds at C-4 and C-9, and an exocyclic double bond conjugated with the lactone carbonyl (Tables 1–3). The stereochemistry of the endocyclic double bonds was inferred from the nOe observed between the signals of H-9 and H-14 and from the absence of an nOe between H-5 and H-15. The double bonds were therefore defined as 4,5-trans (*E*) and 9,10-cis (*Z*). Because of the size of the coupling constants of H-6 with H-5 and H-7 (Table 1), which suggests an anti relationship between them, the configuration at C-6 was assigned as 6α-OH (H-6β). Furthermore, the lactone ring fusion is shown to be trans, as the nOe observed between the hydrogens H-6 and H-8 indicates that both atoms are on the same side of the medium cyclodecane ring.

The configuration at C-1 is less straightforward to assign. In fact, the coupling constants of H-1 (Table 1) with the vicinal hydrogens ($J = 11$ and 5.5 Hz) indicate an anti coplanar relationship between H-1 and one of these hydrogens (H-2 or H-2′), i.e., an axial-like orientation for H-1. The conformation of germacrane derivatives, however, is often very difficult to determine, due to the flexibility of medium-sized rings (17–19). In the case of compound **1**, for instance, an axial-like orientation of H-1 can be reached with both possible configurations at C-1. Thus, in order to determine the stereochemistry, nOe measurements were performed on the acetylated derivative **1a**, the ^{1}H-nmr spectrum of which displays well separated signals for H-1, H-6, and H-8 when C_6D_6 is used as the solvent. In this experiment, a marked Overhauser effect was observed between the signals of H-1 and H-8. Inspection of molecular models reveals that this nOe can only be explained by the presence of a 1α-hy-

TABLE 1. ^{1}H-nmr Data of Compounds **1**–**4**.[a]

Proton	Compound			
	1[b]	**2**[c]	**3**[c]	**4**[c]
H-1	4.38 br dd	3.84 br dd	4.02 br d	—
H-2/2′	2.05–1.85 m			3.27 m
H-3	2.29 br dd	2.30–2.00 m	2.30–1.90 m	2.60–2.30 m
H-3′	1.78 m[d]			
H-5	4.99 br d	5.04 br d	5.25 br d	5.07 br d
H-6	4.50 ddd	4.37 ddd	4.41 ddd	4.15 dd
H-7	2.80 dddd	2.82 dddd	2.88 dddd	2.73 ddddd
H-8	4.54 dd	3.96 ddd	3.94 ddd	3.95 ddd
H-9	5.32 br d	2.96 dddd	3.05 dddd	3.40 ddddd
H-9′		2.38 dd	2.41 dd	2.15 dd
H-13	6.30 dd	6.37 dd	6.30 dd	6.37 dd
	6.21 dd	6.20 dd	6.18 dd	6.17 dd
H-14	1.83 d	5.16 br s	5.29 br s	5.83 d
		5.11 d	5.16 d	5.78 d
H-15	1.78 br s	1.70 d	1.70 d	1.65 d

[a]Coupling constants in Hz: **1** $J_{1,2} = 11$, $J_{1,2'} = 5.5$, $J_{2,3} = 6$, $J_{2',3} = 1$, $J_{3,3'} = 12$, $J_{5,6} = 10.5$, $J_{6,7} = J_{7,8} = 9$, $J_{6,OH} = 3$, $J_{8,9} = 10$, $J_{7,13} = J_{7,13'} = 3$, $J_{13,13'} = 1$, $J_{9,14} = 1.5$; **2** $J_{1,2} = 9.5$, $J_{1,2'} = 6.5$, $J_{5,15} = 1$, $J_{5,6} = J_{6,7} = 10$, $J_{7,8} = 6.5$, $J_{8,9} = J_{9,14} = J_{9,14'} = 2$, $J_{8,9'} = 10$, $J_{9,9'} = 14$, $J_{7,13} = J_{7,13'} = 3$, $J_{13,13'} = 1$; **3** $J_{1,2} = 10$, $J_{5,15} = 1.5$, $J_{5,6} = J_{6,7} = 10$, $J_{7,8} = 6.5$, $J_{8,9} = J_{9,14} = J_{9,14'} = 2$, $J_{9,9'} = 14$, $J_{8,9'} = 10$, $J_{7,13} = J_{7,13'} = 3$, $J_{13,13'} = 1$; **4** $J_{5,6} = J_{6,7} = 10$, $J_{5,15} = 1$, $J_{7,8} = 5$, $J_{8,9} = 3$, $J_{8,9'} = 11$, $J_{9,9'} = 13$, $J_{7,13} = J_{7,13'} = 2.5$, $J_{7,9} = 1.5$, $J_{9,14} = 1$, $J_{9,14'} = 2$.

[b]At 400 MHz in $CDCl_3/CD_3OD$ (25°).

[c]At 400 MHz in $CDCl_3/CD_3OD$ (57°).

[d]Overlapped by other signals.

TABLE 2. ^{1}H-nmr Data of Compounds **1a–3a**.[a]

Proton	Compound					
	1a[b]	**1a**[c]	**2a**[d]	**2a**[e]	**3a**[d]	**3a**[e]
H-1	5.48 br dd	5.50 br dd	5.07 br dd	5.05 br dd	4.91 br dd	4.69 br dd
H-2/2′	2.30 m (1H)	1.90–1.50 m	2.25–2.00 m	1.90–1.70 m	2.30–2.00 m	1.90–1.70 m
H-3/3′	2.10–1.80 m (3H)	(4H)	(4H)	(4H)	(4H)	(4H)
H-5	4.90 br d	4.58 br d[f]	4.96 br d	4.72 br d	5.17 br d	4.77 br d
H-6	5.45 dd	5.24 dd	5.24 dd	5.11 dd	5.35 dd	5.20 dd
H-7	3.02 dddd	2.62 dddd	3.00 dddd	2.65 dddd	3.10 dddd[f]	2.62 dddd
H-8	4.75 dd	4.58 dd[f]	4.12 ddd	3.93 ddd	3.97 ddd	3.58 ddd
H-9	5.37 br d	4.97 br d	2.81 dddd	2.74 dddd	3.06 dddd[f]	2.94 dddd
H-9′			2.32 dd	1.95 dd	2.36 ddd	2.02 ddd
H-13	6.25 d	6.16 d	6.31 d	6.28 dd	6.27 d	6.21 dd
	5.70 d	5.41 d	5.81 d	5.55 dd	5.75 d	5.46 dd
H-14	1.82 d	1.56 d	5.27 br s	4.91 br s	5.32 br s	5.01 t
			5.24 br s	4.82 d	5.20 d	4.87 d
H-15	1.95 br s	1.78 br s	1.85 d	1.60 d	1.74 d	1.41 d
OAc	2.07 s	1.62 s	2.05 s	1.65 s	2.08 s	1.65 s
	2.00 s	1.59 s	2.02 s	1.63 s	2.02 s	1.63 s

[a]Coupling constants in Hz (essentially the same values are observed in $CDCl_3$ and in C_6D_6): **1a** $J_{1,2}=10.5$, $J_{1,2'}=4$, $J_{5,6}=10.5$, $J_{6,7}=9.5$, $J_{5,15}=1$, $J_{7,8}=J_{8,9}=9.5$, $J_{7,13}=3.3$, $J_{7,13'}=3$, $J_{9,14}=1.5$; **2a** $J_{1,2}=7.5$, $J_{1,2'}=6.5$, $J_{5,6}=10$, $J_{6,7}=11$, $J_{5,15}=1$, $J_{7,8}=6.5$, $J_{8,9}=J_{9,14}=J_{9,14'}=2$, $J_{8,9'}=10$, $J_{9,9'}=14.5$, $J_{7,13}=3$, $J_{7,13'}=2.7$; **3a** $J_{1,2}=J_{1,2'}=5$, $J_{5,15}=1.5$, $J_{5,6}=J_{6,7}=10$, $J_{7,8}=8.5$, $J_{8,9}=J_{9,14}=J_{9,14'}=2.5$, $J_{9',14}=1$, $J_{8,9'}=6.5$, $J_{9,9'}=16$, $J_{7,13}=3.2$, $J_{7,13'}=2.8$.

[b]At 200 MHz in $CDCl_3$ (25°).

[c]At 200 MHz in C_6D_6 (25°).

[d]At 200 MHz in $CDCl_3$ (57°).

[e]At 200 MHz in C_6D_6 (57°).

[f]Overalpped signals.

droxyl group. The alternative configuration would demand a considerable transannular tension in order to bring both hydrogens into close proximity.

The structure thus proposed for **1** corresponds to that of deacetyltulirinol (20). The limited resolution of the published ^{1}H-nmr spectrum of this compound, however, especially as regards the signal of H-1, does not permit a reliable comparison with our data. Furthermore, the available data suggest that compound **1** might also be identical with tatridin A, which had already been found in *T. vulgare* (21). The structure of this lactone, however, has not yet been definitively established, although there is evidence that it may be identical with deacetyltulirinol (20). Direct comparison of **1** (tlc, nmr) with an authentic sample of tatridin A confirmed the identity of both compounds. Our results therefore support the idea that tatridin A is identical with deacetyltulirinol. [After this manuscript had been submitted for publication, we learned that the structure of tatridin A has recently been confirmed by X-ray crystallography (22).] Structure **1** has also been assigned to a compound isolated from diverse plant sources in recent years (23–25) but for which also no nmr data have previously been given. It is possible that tatridin A is identical with tavulin, also isolated from one chemotype of *T. vulgare* (26). The low resolution of the ^{1}H-nmr data reported for the latter compound, however, precludes any confirmation of this.

The main conformation of compound **1** most probably resembles a boat-chair geometry, as in melampolides, with C-14 below and C-15 above the plane of the medium ring. The evidence for this geometry, which has already been observed in tulirinol (20), is supported by the fact that, in addition to the nOe's mentioned above, there is another one

TABLE 3. ^{13}C-nmr Data of Compounds **1–4** and **1a–3a**.

Carbon	Compound						
	1[a]	**2**[b]	**3**[b]	**4**[b]	**1a**[c]	**2a**[d]	**3a**[d]
C-1	66.85	70.57	76.60[e]	203.13	68.98	71.46	77.83
C-2	27.21	31.15	36.27[f]	36.40	25.10	27.96	33.42
C-3	35.26	34.30	36.47[f]	35.62	35.24	34.61	36.69
C-4	135.25[e]	135.51[e]	138.19[g]	136.45[e]	137.35[e]	138.65[e]	140.63
C-5	129.89	130.77	127.85	131.51	126.33	126.86	124.72
C-6	71.06	70.57	71.38[e]	70.21	73.15	72.70	73.05
C-7	52.31	52.04	58.06	50.48	49.53	48.81	50.37
C-8	74.15	79.23	83.46	76.75	74.46	78.22	82.26
C-9	126.80	41.41	41.92	40.17	128.78	42.26	42.72
C-10	142.47	147.07	152.90	146.64	137.89[e]	142.31	148.50
C-11	137.55[e]	137.00[e]	137.30[g]	136.33[e]	138.14[e]	136.22[e]	137.16
C-12	169.92	170.16	170.09	169.57	169.73[f]	170.34[f]	169.96[f]
C-13	123.67	125.09	124.50	124.15	122.26	124.80	123.42
C-14	16.80	114.41	113.02	125.95	17.42	117.92	116.14
C-15	15.69	17.32	17.79	17.25	15.67	17.38	17.62
OAc	—	—	—	—	169.67[f]	169.42[f]	169.60[f]
					168.94[f]	168.85[f]	169.09[f]
					20.96	21.00	21.09
					(×2)	20.80	20.92

[a]At 50.32 MHz in $CDCl_3/CD_3OD$ (25°).
[b]In $CDCl_3/CD_3OD$ (57°).
[c]In $CDCl_3$ (25°).
[d]In $CDCl_3$ (57°).
[e–g]The signals with these superscripts may be interchanged within the same column.

between the signals of H-6 and H-15. This conformational preference might be explained by the tendency of the molecule to place the 1-hydroxy group in a pseudo-equatorial orientation, thus minimizing transannular interactions (12). Table 3 gives the ^{13}C-nmr data of **1** and **1a**.

Tables 1–3 also contain the nmr data of compounds **2–4**. While the identity of tatridin B [**2**] was affirmed by comparison with an authentic sample, tamirin [**4**] (26) was identified by acetylation, which gave the known chrysanolide (23,27). Structure **3** (1-*epi*-tatridin B) has been attributed to several compounds, among these tanachin, a compound isolated from *T. vulgare* and *Tanacetum pseudoachillea* (23–26, 28). Although the structures of **3** and **4** have very recently been confirmed by X-ray crystallography (29), no high-resolution nmr data have been published. In contrast to **1**, the nmr spectra of **2–4** display broad, unresolved signals at room temperature, due to slow conformational movement which produces coalescence of the signals. This reflects the much higher flexibility of cyclodecane rings bearing exocyclic rather than endocyclic C=C bonds. The data of compounds **2–4** and of the acetylated derivatives **2a** and **3a** were thus recorded at 57°, where sharp and defined signals are observed. Note here the values of the coupling constants of H-1 in the pairs of compounds **2**/**3** and **2a**/**3a** (Tables 1 and 2). Because the conformation of both molecules cannot be assumed a priori, the observed *J* values are difficult to relate to the configuration at C-1. Also noteworthy are the differences in some carbon chemical shift values (Table 3), which undoubtedly reflect the conformational differences caused by the opposite configuration at C-1 (12).

Several nOe measurements were performed on the epimeric pair **2a**/**3a**. In the cases where the overlapping of sig-

nals prevented a selective saturation, the corresponding experiments were made in C_6D_6. Somewhat unexpectedly, a marked nOe was observed between the signals of H-1 and H-8 in **2a** but not in **3a**. The absence of this particular nOe in the latter compound is not too surprising, despite the fact that both hydrogens are formally on the same side of the medium ring surface. As mentioned above, the highly flexible cyclodecane ring tends to adopt the conformation that maintains the hydroxy group in a pseudo-equatorial position, away from the inner part of the cycle. The observance of the aforementioned nOe in **2a**, however, demands the existence of a somewhat tense conformation, which clearly differs from that observed for tatridin B dibenzoate in the solid state (12). Whether this is indeed the main conformation of **2a** or merely one which can be reached in solution by the molecule remains to be established. Further significant nOe's were observed between the pairs H-1/H-15, H-5/H-7, H-6/H-8, H-6/H-15, H-8/H-9, and H-8/H-15 in **2a**, and between the pairs H-1/H-9′, H-6/H-15, H-6/H-8, H-8/H-14, and H-8/H-15 in **3a**.

EXPERIMENTAL

GENERAL EXPERIMENTAL METHODS.—Nmr spectra were measured on Bruker nmr spectrometers WM-400 and AC-200 at the frequencies indicated in the tables. Mass spectra were run on a Varian MAT 711 system. Hplc was performed in the reversed-phase mode (LiChrosorb RP-8, length 250 mm, i.d. 8 mm) with elution by MeOH/H_2O mixtures (flow, 3 ml/min) and detection by refractive index. Medium pressure column chromatography (mpcc) was made on Si gel Merck (40–63μ).

EXTRACTION AND CHROMATOGRAPHY.—*T. vulgare* was collected in August 1989, in Mülheim, a district of Cologne, FRG. A voucher specimen is deposited in the Herbarium of the Department of Botany at the Faculty of Biology in Valencia. Fresh aerial parts of the plant (1100 g) were macerated three times at room temperature with MeOH (3 × 10 liters, 5 days). The extract (61.7 g) was defatted by dissolution in boiling MeOH (620 ml) and precipitation at − 15°. After elimination of the precipitate by filtration, the material obtained (35.7 g) was prefractionated by cc on Si gel: (A) hexane-Et_2O (3:1); (B) hexane-Et_2O (1:3); (C) Et_2O; and (D) Et_2O-MeOH (6:1) (column length, 70 cm, i.d. 5 cm, 4 liters of each solvent mixture).

Fraction A (3.5 g) consisted mainly of waxes, volatile terpenes, and sterols (tlc, ^{1}H nmr), and was discarded. Fraction B (1.18 g) was submitted to mpcc on Si gel [$CHCl_3$-Et_2O (30:1 to 4:1)]. This yielded parthenolide (9 mg), a mixture of santamarin and magnolialide (10 mg), and reynosin (15 mg). Fraction C (1.8 g) was separated by mpcc on Si gel [elution with hexane-Et_2O (1:3) to Et_2O]. The relevant fractions (monitored by tlc and ^{1}H nmr) were further purified by hplc [MeOH-H_2O (6:4), ca. 170 bar]. This gave more reynosin (3 mg), anhydroverlotorin epoxide (8 mg), **1** (7 mg), **4** (6 mg), artemorin (9 mg), and tanacetol B (40 mg).

Fraction D (3.7 g) was further fractionated by mpcc on Si gel [$CHCl_3$-MeOH (100:1 to 12:1)]. The relevant fractions were further purified by hplc [MeOH-H_2O (55:45), ca. 180 bar]. This gave costunolide diepoxide (6 mg), more tanacetol B (20 mg), artemorin epoxide (4 mg), 1-hydroxyarbusculin A (5 mg), 1-*epi*-ludovicin C (6 mg), more **1** (3 mg), **2** (7 mg), armefolin (4 mg), **3** (8 mg), and deacetyltanacetol B (8 mg), an artifact of tanacetol B deacetylation (8).

All compounds were identified by comparison with authentic samples or derivatives thereof. Tatridin A and tatridin B were supplied by Prof. G. Appendino, from the University of Torino, Italy. The other compounds were from either our or Prof. Bohlmann's collection.

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[1]The authors concluded, from a comparison of ^{1}H-nmr data, that tatridin A and deacetyltulirinol were probably identical, but they did not perform a direct comparison of both compounds.