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3α,20-DIHYDROXY-3β,25-EPOXYLUPANE, A TRITERPENE FROM *RHUS TYPHINA*

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Key Word Index—*Rhus typhina* L.; Anacardiaceae; flowers; triterpene; 3α,20-dihydroxy-3β,25-epoxylupane.

Abstract—A new triterpene, 3α,20-dihydroxy-3β,25-epoxylupane, was isolated and structurally elucidated from flowers of the sumach tree *Rhus typhina* (Anacardiaceae).

INTRODUCTION

The genus *Rhus*, belonging to the Anacardiaceae family, is phytochemically mainly characterised by the occurrence of phenolics including flavanoid compounds [1, 2]. *Rhus typhina* L. being a widely distributed shrub in Northern America and Europe was mainly investigated with respect to the occurrence of phytosterols [3], volatile constituents [4], gallotannins, phenolics including catechins [5, 6] as well as cynarine [7]. Furthermore, plants of the genus *Rhus* represent a source of triterpenoids with a hemiketal bridge in ring A [8–10]. We describe in this paper the isolation and structure elucidation of a new lupane-type triterpene from flowers of *R. typhina*.

RESULTS AND DISCUSSION

After partition and repeated silica gel chromatography of the methanolic extract of flowers of *R. typhina* a lupane-type triterpene (**1**) with an elemental composition of $C_{30}H_{50}O_3$ (M^+ at m/z 458.3782) could be isolated. The mass spectral behaviour shows complementary key ions at m/z 400 (**a**, $[M-C_3H_6O]^+$) and 59 (**b**) indicating the presence of a hydroxylated isopropyl group. This is supported by the appearance of the **b**-type ion at m/z 131 (base peak) in the EIMS of the bistrimethylsilyl ether **2** (M^+ at m/z 602). The IR-spectrum shows absorptions assignable to hydroxyl functions.

The ^{1}H NMR spectrum of **1** shows 7 methyl singlets (δ 1.221, 1.108, 1.016, 0.969, 0.970, 0.935, 0.798) and two double doublets (δ 4.244 *J* 8.8/2.8; 3.723 *J* 8.8/1.8) due to the oxymethylene group at ring A. One of the oxymethylene protons (δ 3.723, H-25 pro-*R*) has a W type coupling with H-5α, the other one (δ 4.244, H-25 pro-*S*) a similar coupling with H-1α. The ^{1}H NMR data of this function as well as the ^{13}C chemical shift (δ 98.2) of the hemiacetal carbon C-3 correspond to that of lantabetulic acid and other triterpenes with a 3α-hydroxy-3β,25-epoxy system [8, 9]. Furthermore, a HMBC correlation found for H-25 pro-*R* with C-3 proves the existence of an oxide bridge between C-3 and C-25. The ^{1}H NMR signals of both methyl groups, Me-29 and Me-30, show heteronuclear long-range (HMBC) correlations with the methine signal at δ 49.7 (C-19) and the lowfield quaternary carbon signal at δ 73.5 (C-20). This finding clearly indicates a 20-hydroxylated lupane structure. The ^{13}C chemical shifts of the carbons C-19 and C-20 as well as the two connected methyl groups (C-29 and C-30) are in good agreement with corresponding data of other 20-hydroxylated lupane derivatives described in the literature [11]. A complete assignment of all proton and carbon NMR signals, including stereochemical assignment of all methylene protons, was attained by combined use of homo- and heteronuclear shift correlation experiments including APT, ^{1}H-^{1}H-COSY, NOESY, HSQC and HMBC. From

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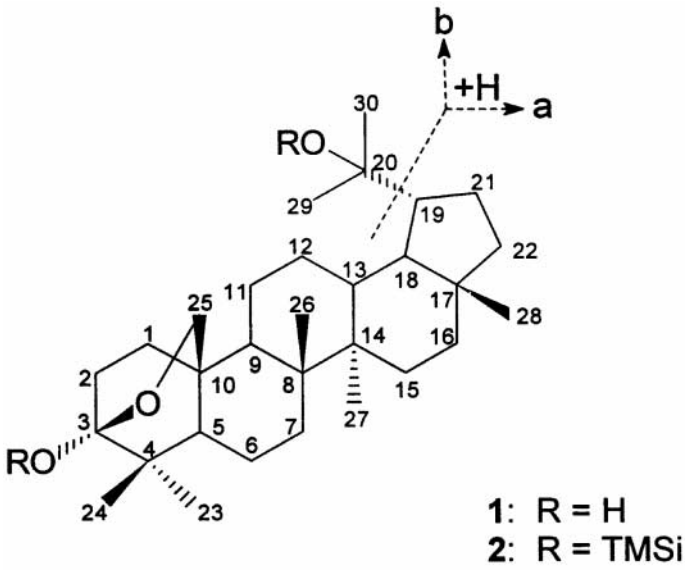

the above mentioned data triterpene **1** can be regarded as 3α,20-dihydroxy-3β,25-epoxylupane.

Other triterpenes with a hemiacetal bridge in ring A could be found with different triterpene skeletons. The lupane-type triterpene benulin (lantabetulic acid) was isolated from *Lantana camara* (Verbenaceae) [12], *Bursera arida* (Burseraceae) [13] and *Rhus semialata* [9], whereas the oleanane type semimoronic acid could be identified only from leaves of *Rhus semialata* [9]. Dammarane-type triterpenes are rhuslactone from *Rhus javanica* [8], semialatic acid from *Rhus semialata* [10] as well as the cordialins A and B from *Cordia verbenacea* (Boraginaceae) [14].

EXPERIMENTAL

General methods

Mps. uncorr.; $[\alpha]_D$: JASCO DIP 1000 polarimeter; ^{1}H and 2D NMR: VARIAN UNITY 500, 499.83 MHz, solvent $CDCl_3$, TMS as int. standard (δ 0); ^{13}C NMR: VARIAN Gemini 2000–300, 75.5 MHz, $CDCl_3$ as int standard (δ 77.0), solvent $CDCl_3$; electrospray (ES)-MS: TSQ 7000 (Finnigan); MS (AMD 402, AMD Intectra): 70 eV EIMS (DIS), HR-EIMS (resolution 7.500); IR (Bruker IFS 28): KBr discs; GC-MS (MD-800, Fisons Instruments): 70 eV EI, source temp. 200°C, column DB-5MS (J and W, 15m × 0.32 mm, 0.25 μm film thickness), inj. temp. 260°C, interface temp. 300°C, carrier gas He, flow rate 1 ml min^{-1}, splitless injection, column temp. program: 170°C for 1 min, then raised to 270°C at a rate of 25°C min^{-1} and then to 290°C at a rate of 2°C min^{-1}. The trimethylsilylation was carried out with a mixture of *N*,*O*-bis(trimethylsilyl)acetamide/trimethylchlorosilane (4:1 v/v) at room temp.

Plant material

Flowers of R. *typhina* L. were collected near Halle in May 1995. The sumach species was identified by Dr. Hanelt. A voucher specimen is deposited in the GAT-herbarium, Institute of Plant Genetics and Crop Plant Research, Gatersleben.

Extraction and purification

The dried flowers (280 g) were extracted 3× with MeOH (1.5 l) at room temperature. The corresponding extracts were combined and evaporated to dryness *in vacuo*. The residues were partitioned 3× between H_2O and $CHCl_3$. The residues (8.9 g) obtained after drying the $CHCl_3$ phase with Na_2SO_4 and evaporation of the solvent were partitioned between *n*-hexane and 80% MeOH. The *n*-hexane phase was partitioned a second time with 80% MeOH, and the combined 80% MeOH fractions were concentrated (5.2 g).

The residues resulting from the 80% MeOH fraction was chromatographed on a silica gel column (25 g silica gel Merck 0.063–0.2 mm) with 300 ml $CHCl_3$, 500 ml $CHCl_3$–MeOH (4:1, v/v, fraction 2) and 500 ml MeOH as eluent. Fr 2 (3.0 g) was further purified on a silica gel column (30 g) by stepwise elution with increased content of MeOH in $CHCl_3$ (0, 2, 3, 4, 5, 7, 10, 15, 30, 50% v/v). The fr eluted with 2% MeOH (798 mg) was further chromatographed on a silica gel column (40 g) with $CHCl_3$. The frs containing compound **1** were com-

Table 1. ^1H and ^{13}C NMR data (δ values) of compound **1** (in $CDCl_3$)

Carbon	^1H*	^{13}C
1	1.11/2.19	35.1
2	2.14/1.68	29.6
3	–	98.2
4	–	40.3†
5	1.17	49.7
6	1.46/1.55	19.7
7	1.32/1.46	32.3
8	–	40.2†
9	1.41	44.9
10	–	35.4
11	1.61/1.04	22.7
12	1.20/1.88	29.2
13	1.72	37.7
14	–	43.2
15	1.08/1.68	27.5
16	1.35/1.48	35.4
17	–	44.6
18	1.37	48.1
19	1.80	49.7
20	–	73.5
21	1.31/1.88	28.7
22	1.10/1.30	40.2
23	1.016 s	26.9
24	0.969 s	18.3
25	pro-R: 3.723 dd (8.8/1.8) pro-S: 4.244 dd (8.8/2.8)	68.0
26	0.963 s	16.7
27	0.935 s	14.5
28	0.798 s	19.2
29‡	1.221 s	31.6
30‡	1.108 s	24.7
3α-OH	2.837 s	–
20-OH	1.969 br s	–

*methylene protons: α/β; ^1H chemical shifts expressed with only two decimals are chemical shifts of HSQC correlation peaks.
†,‡May be interchanged.

bined (445 mg) and recrystallised from MeOH (226 mg).

α,20-Dihydroxy-3β,25-epoxylupane (**1**)

mp. 225–227°C; $[\alpha]_D = +78.5$ ($CHCl_3$, *c* 0.66); IR (KBr) ν_{max} cm^{-1}: 3446 (*br*, OH), 2958 (*br*, OH), 1465, 1380, 1333, 1292, 1172, 1120, 1092, 1064, 1031, 978, 926, 890; ES-MS: *m/z* 459 $[M + H]^+$; EIMS, *m/z* (rel. int.): 458.3782 M^+, (7, calc. for $C_{30}H_{50}O_3$ 458.3760), 440.3656 $[M-H_2O]^+$ (61, calc. for $C_{30}H_{48}O_2$ 440.3654), 425 (4), 400.3327 $[M-C_3H_6O]^+$ **a** (9, calc. for $C_{27}H_{44}O_2$ 400.3341), 397.3105 $[M-H_2O-C_3H_7]^+$ (4, calc. for $C_{27}H_{41}O_2$ 397.3107), 367 (5), 329.2491 (8, calc. for $C_{22}H_{33}O_2$ 329.2481), 275.2015 (4, calc. for $C_{18}H_{27}O_2$ 275.2011), 257 (8), 231 (5), 222 (7), 205 (8), 191 (11), 189 (14), 175 (10), 163 (20), 149 (20), 133 (18), 121 (24), 107 (24), 95 (29), 81 (28), 69 (30), 59 (**b**, 100). ^1H- and ^{13}C-NMR data see Table 1.

1-*Bistrimethylsilylether* (**2**)

$R_t = 12.83$ min, EIMS, *m/z* (rel. int.): 602 (M^+, 5), 587 (2), 544 (3), 512 ($[M\text{-}TMSiOH]^+$, 6), 497 (1), 422 ($[M-2TMSiOH]^+$, 4), 409 (7), 401 (1), 367 (2), 294 (2), 257 (4), 217 (5), 203 (6), 189 (5), 163 (5), 131 (**b**, 100), 107 (11), 95 (14), 73 (74).

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