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TRITERPENES FROM *RHUS TAITENSIS*

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Key Word Index—*Rhus taitensis*; Anacardiaceae; triterpenes; new lupane derivative; 3β,20,25-trihydroxy lupane.

Abstract—A new lupane type triterpene, 3β,20,25-trihydroxy lupane, was isolated from the petrol extract of the leaves of *Rhus taitensis* together with the known compounds 3,20-dihydroxylupane, 20-hydroxylupane-3-one, 20,28-dihydroxylupane-3-one, 3,16-dihydroxy lup-20(29)-ene and 28-hydroxy-β-amyrone. Their structures were determined by means of spectral methods. © 1998 Published by Elsevier Science Ltd. All rights reserved

INTRODUCTION

In the course of our studies on medicinal plants from Papua New Guinea, the chemical content of *Rhus taitensis* Guill. was investigated. This plant is used in the traditional medicine of Papua New Guinea to treat boils [1]. Phenolic compounds [2, 3], essential oil [4] and triterpenes [5–8] have previously been isolated from several plant species of the genus *Rhus*. In this paper, we report on the isolation and structure elucidation of one new (**1**) and five known triterpenes: **2** [9, 10], **3** [9–11], **4** [10], **5** [12, 13] and **6** [14, 15] from *R. taitensis*. Although **2**, **4**, **5**, and **6** are known compounds their complete spectroscopic data have not been reported in the literature. They are included in Table 1 and in the experimental part of this communication.

RESULTS AND DISCUSSION

Dried leaves of *R. taitensis* were extracted with petrol by percolation at room temperature to give, after evaporation of solvent, a crude extract. Fractionation of this extract using VLC, MPLC and HPLC as described in the experimental section led to the isolation of triterpenes **1**–**6**.

The IR spectrum of **1** showed absorption for hydroxyl groups (3300 cm^{-1}). Its ^1H NMR spectrum showed signals for seven tertiary methyl groups as sharp singlets at δ 0.77, 0.85, 0.98, 0.99, 1.10, 1.19 and 1.21, a methine double doublet at δ 3.17 (J = 11.7, 4.5 Hz) along with a methylene singlet at δ 3.92. The 30 carbon signals observed in the ^{13}C NMR spectrum were characterized by a DEPT experiment (Table 1). The carbon signals observed at δ 79.9 (*d*), 74.0 (*s*) and 62.7 (*t*) indicated the presence of a secondary, a tertiary and a primary hydroxyl group, respectively. Formation of the diacetate **1a** by acetylation established that there was one hydroxyl group which could not be acetylated, thus the occurrence of a tertiary hydroxyl group was further substantiated. These data, along with the EI mass fragment peaks at m/z 189, 163, 147, 81 and 59, suggested that **1** had a 20-hydroxy lupane skeleton. This assumption was further verified by 2D NMR experiments, in particular HMQC and HMBC measurements of **1** and **1a**. By using these methods, all carbons with the exception of C-2, C-6, C-11, C-12, and C-21 could be associated with one or more of the methyl groups on the basis of $^2J_{CH}$, $^3J_{CH}$ correlations (Table 2). Carbon signals resonating at δ 34.8 (*t*), 79.9 (*d*), 19.2 (*t*), 57.2 (*d*) and 74.0 (*s*) were assigned to C-1, C-3, C-6, C-5 and C-20, respectively (Table 1). Comparison of the ^{13}C NMR shifts of **1** with those of some lupane derivatives [13] showed some differences particularly for the carbons of the A and B rings. Based on this fact and the HMBC correlations from H_2-25 to C-1, C-5, C-9 as well as C-10, the primary hydroxyl group was assigned to C-25. The structure of **1** was thus established as 3β,20,25-trihydroxy-lupane.

The ^{13}C NMR data of compound **2** showed the presence of eight tertiary methyl groups and two oxygenated carbons [δ 79.0 (*d*), C-3 and δ 73.5 (*s*), C-20]. From these data and also from the identical ^1H NMR and EI mass data with the reported values [9, 10], **2** was identified as 3β,20-dihydroxylupane (= monogynol).

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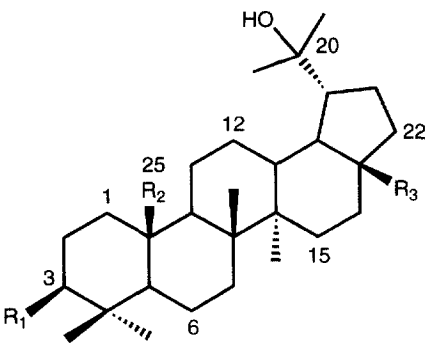
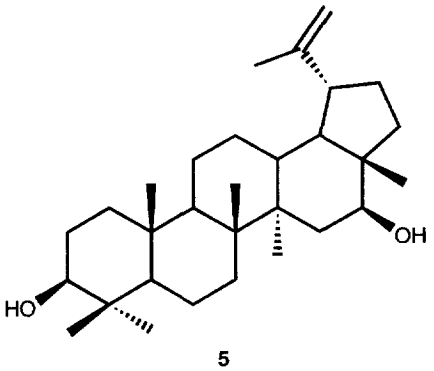


	R_1	R_2	R_3
1	β-OH	CH_2OH	CH_3
1a	OAc	CH_2OAc	CH_3
2	β-OH	CH_3	CH_3
3	=O	CH_3	CH_3
4	=O	CH_3	CH_2OH



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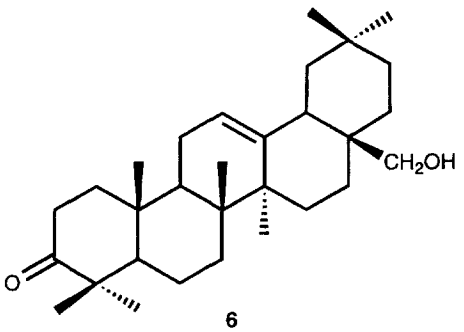

6

The ^1H NMR, ^{13}C NMR and mass spectral data for **3** were quite similar to those for **2**. The absence of the H-3 signal in the ^1H NMR spectrum and the presence of a signal at δ 218.2 (*s*) for a carbonyl group in the ^{13}C NMR spectrum suggested a ketone functionality in this position for **3**. The structure of **3** was established as 20-hydroxylupane-3-one by comparison of its spectral data with those reported in the literature [9–11].

On comparison with the NMR features of **3**, compound **4** showed the spectral properties of 20-hydroxylupane-3-one with an additional primary hydroxyl group [δ 3.33 and 3.86 (each 1H, *d*, J = 10.5 Hz) and 60.8 (*t*]. This CH_2OH group was assigned to C-28 based on HMQC and HMBC experiments and compound **4** was identified as 20,28-dihydroxylupane-3-one, a compound which was reported from *Betula alleghaniensis* (Betulaceae) [10].

Compound **5** gave the $[M]^+$ peak at *m/z* 442 in the EI mass spectrum in agreement with the molecular formula $C_{30}H_{50}O_2$. The ^1H NMR spectra revealed characteristic signals of lupane-type triterpenes such as those of an isopropenyl group, seven tertiary methyl groups and also two secondary hydroxyl groups. Based on these data and the ^{13}C NMR data identical with those reported in the literature [13], **5** was identified as 3β,16-dihydroxy lup-20(29)-ene.

Compound **6** showed signals for seven tertiary methyl groups, the signals of a primary hydroxyl group (δ 3.23 and 3.56, each 1H, *d*, J = 10.9 Hz) and a signal at δ 5.22 (*brt*, J = 3.5 Hz), which was indicative of an olefinic proton attached to a trisubstituted double bond. These data together with the ^{13}C NMR spectral data (Table 1) identified **6** to be 28-hydroxy-β-amyrone [14, 15].

Although some lupane, oleane and dammarane type triterpenes (semimoronic acid [5, 6], benulin [6], rhuslactone [7] and semialatic acid [8]) have been previously reported from the genus *Rhus*, this is the first report on the isolation of compounds **2**–**6** from this genus.

EXPERIMENTAL

General

^1H NMR and ^{13}C NMR: 300 MHz and 75 MHz, respectively. Solvent resonances were used as int. refs and chemical shifts (δ) are reported in ppm. EIMS: 70 eV: VLC and MPLC: Silica gel 40–63 μm (Merck); RP-MPLC: R-Sil C18, 15–30 μm; HPLC: 250 mm × 8 mm column packed with Spherisorb ODS 5 μm.

Plant material

Leaves of *R. taitensis* were collected from Lae-Wau road, Morobe Province, Papua New Guinea, in April 1991. A voucher specimen has been deposited at the Rijksherbarium (ETH 91/19 6-04-91), University of Leiden (The Netherlands).

Extraction and isolation

The air-dried and powdered leaves (800 g) were continuously percolated with petrol, CH_2Cl_2 and

Table 1. ^{13}C NMR spectral data of triterpenes **1**, **1a**, **2**, **4**, and **6**

C	1	1a*	2	4	6
1	34.8 *t*	33.4 *t*	38.7 *t*	39.6 *t*	39.3 *t*
2	29.0 *t*	23.6 *t*	27.6 *t*	34.1 *t*	34.1 *t*
3	79.9 *d*	80.5 *d*	79.0 *d*	218.2 *s*	217.8 *s*
4	39.8 *s*	37.5 *s*	38.9 *s*	47.3 *s*	47.5 *s*
5	57.2 *d*	55.5 *d*	55.2 *d*	54.8 *d*	55.3 *d*
6	19.2 *t*	18.0 *t*	18.3 *t*	19.7 *t*	19.6 *t*
7	36.1 *t*	34.5 *t*	34.6 *t*	33.8 *t*	34.2 *t*
8	42.7 *s*	40.1 *s*	41.4 *s*	41.4 *s*	39.8 *s*
9	53.4 *d*	51.0 *d*	50.3 *d*	49.6 *d*	46.8 *d*
10	42.9 *s*	41.4 *s*	37.1 *s*	36.8 *s*	37.0 *s*
11	25.2 *t*	23.9 *t*	21.4 *t*	21.9 *t*	23.7 *t*
12	29.2 *t*	28.7 *t*	27.4 *t*	27.2 *t*	122.1 *d*
13	39.3 *d*	37.6 *d*	37.5 *d*	36.3 *d*	144.2 *s*
14	45.0 *s*	43.9 *s*	43.6 *s*	43.5 *s*	41.9 *s*
15	28.5 *t*	27.8 *t*	28.8 *t*	28.3 *t*	25.5 *t*
16	36.9 *t*	35.6 *t*	35.6 *t*	33.4 *t*	22.0 *t*
17	45.5 *s*	44.5 *s*	44.7 *s*	40.2 *s*	36.7 *s*
18	49.8 *d*	48.4 *d*	48.3 *d*	48.7 *d*	42.4 *d*
19	51.4 *d*	50.0 *d*	50.0 *d*	49.7 *d*	46.4 *t*
20	74.0 *s*	73.4 *s*	73.5 *s*	73.5 *s*	31.0 *s*
21	30.5 *t*	29.4 *t*	29.1 *t*	29.0 *t*	32.1 *t*
22	41.1 *t*	40.1 *t*	40.2 *t*	29.7 *t*	31.0 *t*
23	29.4 *q*	28.6 *q*	28.0 *q*	26.7 *q*	26.5 *q*
24	16.5 *q*	16.9 *q*	16.2 *q*	21.1 *q*	21.5 *q*
25	62.7 *t*	64.0 *t*	15.4 *q*	16.0 *q*	15.3 *q*
26	17.3 *q*	16.5 *q*	16.3 *q*	16.09 *q*	16.7 *q*
27	15.9 *q*	15.2 *q*	14.9 *q*	15.0 *q*	25.8 *q*
28	19.8 *q*	19.2 *q*	19.2 *q*	60.8 *t*	69.7 *t*
29	25.3 *q*	24.7 *q*	24.8 *q*	24.6 *q*	33.2 *q*
30	31.5 *q*	31.7 *q*	31.6 *q*	31.8 *q*	23.6 *q*

*Additional signals for **1a** 171.1, 171.0 ($CH_3\underline{C}O$), 21.3, 21.0 ($\underline{C}H_3CO$) ppm.

Table 2. Two and three bond connectivities revealed by HMBC spectrum of **1**

C-1	H-25
C-3	H-23, H-24
C-4	H-23, H-24
C-5	H-23, H-24, H-25
C-7	H-26
C-8	H-26, H-27
C-9	H-25, H-26
C-10	H-25
C-13	H-27
C-14	H-26, H-27
C-15	H-27
C-16	H-28
C-17	H-28
C-18	H-28
C-19	H-29, H-30
C-20	H-19, H-29, H-30
C-22	H-28
C-24	H-3, H-23
C-29	H-30
C-30	H-29

MeOH at room temp. Solvents were removed *in vacuo* to yield the crude extracts. Half of the petrol extract (ca 13 g) was subjected to VLC with hexane containing increasing portions of EtOAc to afford 10 fractions (Frs 1–10). Fr. 3 was applied to MPLC (silica gel, hexane–EtOAc–methyl *t*-butyl ether (6.5 : 1 : 1)) to yield 7 Frs (3a–g). Rechromatography of Frs 3b and 3d gave **6** (10 mg) and **3** (13 mg), respectively. Fr. 6 was first applied to MPLC (silica gel, hexane–EtOAc–$CHCl_3$ (8 : 1 : 1–5 : 3 : 1)) and the obtained Frs were combined into 5 groups (Frs 6a–6e). Application of Frs 6b and 6c to HPLC (RP, MeOH) afforded **5** (13 mg) and **2** (20 mg). Fr. 7 was first subjected to MPLC (silica gel, petrol–EtOAc (10 : 2–5 : 2) to give 6 Frs (7a–7f). Rechromatography of Fr. 7d with MPLC (RP, 85% MeOH), followed by HPLC (RP, 85% MeOH) yielded **4** (26 mg). Fr. 9 was applied to MPLC using RP material and 85% MeOH to afford **1** (550 mg).

3*β*,20,25-*Trihydroxylupane* (**1**). Amorphous powder, $[\alpha]_D^{25}$ −4.2 (MeOH, *c* 0.12). IR_{max}^{ν} cm^{-1} 3300, 2957, 1455, 1359, 1133, 1018; ^1H NMR (CD_3OD): *δ* 0.77 (3H, *s*, H-24), 0.85 (3H, *s*, H-28), 0.98 (3H, *s*, H-23), 0.99 (3H, *s*, H-27), 1.10 (3H, *s*, H-29), 1.19 (3H, *s*, H-30), 1.21 (3H, *s*, H-26), 3.17 (1H, *dd*, *J* = 11.7, 4.5 Hz, H-3), 3.92 (2H, *s*, H-25); ^{13}C NMR (CD_3OD): Table 1; EIMS *m/z* (rel. int.): $[M]^+$ absent, 442 $[M-H_2O]^+$ (7.6), 424 $[(M-H_2O)-H_2O]^+$ (3.5), 412 $[(M-H_2O)-CH_3OH]^+$ (19), 411 (16), 393 (11), 205 (16), 203 (18.6), 191 (19.8), 189 (37.8), 175 (26), 163 (25), 149 (30), 147 (30), 135 (36), 121 (54), 107 (70), 95 (100), 81 (96), 69 (91), 59 (92); FAB-MS: 483.3 $[M+Na]^+$ (consistent with the MW calculated for $C_{30}H_{52}O_3$), 461.2 $[M+H]^+$, 443, 425.

3,25 *Diacetyl derivative of* **1** (**1a**). ^1H NMR ($CDCl_3$): *δ* 0.81 (3H, *s*, H-28), 0.85 (3H, *s*, H-24), 0.86 (3H, *s*, H-23), 0.96 (3H, *s*, H-27), 1.12 (6H, *s*, H-26 and H-29), 1.23 (3H, *s*, H-30), 2.04 (6H, *s*, CH_3CO), 4.33 (1H, *d*, *J* = 12.4 Hz, H-25), 4.49 (1H, *d*, *J* = 12.4 Hz, H-25), 4.53 (1H, *t*, *J* = 10.5 Hz, H-3); ^{13}C NMR ($CDCl_3$): Table 1; EIMS *m/z* (rel. int.): 526 $[M-H_2O]^+$ (18), 466 (22), 453 (14), 413 (14), 393 (49), 257 (37), 229 (32), 218 (22), 203 (58), 201 (70), 189 (100), 187 (70), 163 (47), 149 (56), 121 (55), 119 (52), 95 (10), 81 (56), 59 (53), 43 (50).

3*β*,20-*Dihydroxylupane* (**2**). $[\alpha]_D^{25}$ +4 ($CHCl_3$, *c* 0.05). IR_{max}^{ν} cm^{-1}: 3300, 2926, 1650, 1455; ^1H NMR: See Ref. [9]; ^{13}C NMR ($CDCl_3$): Table 1; EIMS: See Ref. [10].

20,28-*Dihydroxylupane*-3-*one* (**4**). $[\alpha]_D^{25}$ +32.5 ($CHCl_3$, *c* 0.04). ^1H NMR ($CDCl_3$): *δ* 0.94 (3H, *s*, H-25), 1.01 (3H, *s*, H-27), 1.03 (3H, *s*, H-24), 1.08 (3H, *s*, H-23), 1.09 (3H, *s*, H-26), 1.14 (3H, *s*, H-29), 1.25 (3H, *s* H-30), 3.33 (1H, *d*, *J* = 10.6 Hz, H-28), 3.86 (1H, *d*, *J* = 10.6 Hz, H-28); ^{13}C NMR ($CDCl_3$): Table 1; EIMS: See Ref. [10].

3,16-*Dihydroxy*-*lup*-20(29)-*ene* (**5**). $[\alpha]_D^{25}$ +14

($CHCl_3$, *c* 0.05). IR^{ν}_{max} cm^{-1}: 3390, 2942, 1644, 1455, 1384, 1018, 883; ^1H NMR ($CDCl_3$): δ 0.77 (3H, *s*, H-28), 0.80 (3H, *s*, H-24), 0.84 (3H, *s*, H-26), 0.97 (3H, *s*, H-23), 0.99 (3H, *s*, H-25), 1.04 (3H, *s*, H-27), 1.69 (3H, *s*, H-30), 3.19 (1H, *dd*, J = 10.6, 5.1 Hz, H-3), 3.61 (1H, *dd*, J = 11, 4.6 Hz, H-16), 4.6 and 4.71 (each 1H, *brs*, H_2-29); ^{13}C NMR: See Ref. [13]; EIMS *m/z*: 442.4 $[M]^+$, 424.4, 409.

28-*Hydroxy-β-amyrone* (28-*hydroxyolean*-12-*en*-3-*one*) (**6**). IR^{ν}_{max} cm^{-1}: 3440, 2950, 1704, 1644, 1455, 1384, 1018; ^1H NMR ($CDCl_3$): δ 0.88, 0.89, 1.06, 1.07, 1.10, 1.18, 1.26 (each 3H, *s*, methyl × 7), 3.23 and 3.56 (each 1H, *d*, J = 10.9 Hz, H_2-28), 5.22 (1H, *t*, J = 3.3 Hz, H-12); ^{13}C NMR ($CDCl_3$): Table 1; EIMS *m/z*: 440 $[M]^+$ (0.6), 422 (1.6), 279 (3.7), 234 (2.7), 203 (23), 167 (99), 149 (24).

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REFERENCES

1. Woodley, E., *Medicinal Plants of Papua New Guinea*, Part 1: Morobe Province, Verlag Josef Margraf, D-6992 Weikersheim, 1991, p. 14.
2. El Sissi, H. I., Ishak, M. S. and Abd El Wahid, M. S., *Planta Med.*, 1972, **21**, 67.
3. Chen, F.-C., Lin, Y.-M. and Lin, Y.-C., *Heterocycles*, 1978, **9**, 663.
4. Kurucu, S., Koyuncu, M., Güvenç, A., Baser, K. H. C. and Özek, T., *J. Essent. Oil Res.*, 1993, **5**, 481.
5. Bagchi, A., Sahai, M., Sinha, S. C., Ray, A. B., Oshima, Y. and Hikino, H., *J. Chem. Research (S)*, 1985, 398.
6. Parveen, M., Khan, N. U., Achari, B. and Dutta, P. K., *Curr. Sci.*, 1989, **58**, 1326.
7. Sung, C.-K., Akiyama, T., Sankawa, U. and Iitaka, Y., *J.C.S. Chem. Commun.*, 1980, 909.
8. Parveen, N., Singh, M. P., Khan, N. U., Achari, B. and Logani, M. K., *Phytochemistry*, 1991, **30**, 2415.
9. Hui, W.-H. and Li, M.-M., *Phytochemistry*, 1977, **16**, 111.
10. Cole, B. J. W., Bentley, M. D., Hua, Y. and Bu, L., *J. Wood Chem. Tech.*, 1991, **11**, 209.
11. Dantanarayana, A. P., Kumar, N. S., Muthukuda, P. M. and Wazeer, M. I. M., *Phytochemistry*, 1982, **21**, 2065.
12. Baddeley, G. V., Bealing, A. J., Jefferies, P. R. and Retallack, R. W., *Aust. J. Chem.*, 1964, **17**, 908.
13. Wenkert, E., Baddeley, G. V., Burfitt, I. R. and Moreno, L. N., *Org. Mag. Reson.*, 1978, **11**, 337.
14. Monaco, P., Caputo, R., Palumbo, G. and Mangoni, L., *Phytochemistry*, 1973, **12**, 939.
15. Marner, F.-J., Freyer, A. and Lex, J., *Phytochemistry*, 1991, **30**, 3709.