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# HIRSUDIOL, A TRITERPENOID FROM *COCCULUS HIRSUTUS*

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**Key Word Index**—*Cocculus hirsutus*; Menispermaceae; triterpenoid alcohol; hirsudiol; 2α,3α-dihydroxyolean-13(18)-ene; nonacosan-10-ol.

**Abstract**—A new triterpenoid alcohol, hirsudiol, has been isolated from *Cocculus hirsutus*. Its structure was determined as 2α,3α-dihydroxyolean-13(18)-ene through spectroscopic studies. Nonacosan-10-ol was also isolated.

## INTRODUCTION

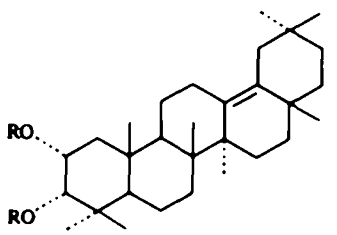
*Cocculus hirsutus* (Syn: *C. villosus*) DC., locally called Jamti-ki-bel, is a climbing shrub and is commonly found in Karachi, Sind and Kutch. Its various parts are highly reputed for their medicinal properties in the indigenous systems of medicine [1–3]. Earlier investigations on various parts of this plant led to the isolation of trilobine, isotrilobine, coclaurine, magnoflorine and sitosterol [4–6].

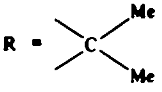
In this paper we report the isolation and structure determination of a new triterpenoid alcohol, hirsudiol (**1**), and nonacosan-10-ol (**2**) from this plant.

## RESULTS AND DISCUSSION

Compound **1** showed a molecular ion peak at *m/z* 442.38159 (HRMS) which corresponded to the molecular formula $C_{30}H_{50}O_2$ and indicated that **1** may be a triterpenoid. Its UV spectrum showed only end absorption. Its IR spectrum ($CHCl_3$) revealed absorption peaks at 3420 (OH) and 1640 cm$^{-1}$ (C=C). There was no peak due to a carbonyl group.

The $^1$H NMR ($C_5D_5N$, 300 MHz) spectrum of **1** showed singlets due to eight tertiary methyl groups at δ0.75, 0.90, 0.94, 0.98, 0.99, 1.07, 1.11 and 1.29. In addition, there were signals due to carbinylic protons at δ3.78 (*d*, *J* = 2 Hz, H-3) and 4.35 (*ddd*, *J* = 11, 3.0, 3.0 Hz, H-2). The chemical shift and the coupling constant of the H-3 signal showed that the hydroxyl group at C-3 was axial. The coupling constant of H-2 indicated that it had one *trans*-diaxial coupling with H-1 axial and therefore the hydroxyl group at C-2 was equatorial. The $^1$H NMR also showed signals of protons at allylic positions at δ2.07 (*dd*, *J* = 12.4, 4.2 Hz, H-12α), 2.31 (*d* (*br*), *J* = 13.7 Hz, H-19α) and 2.65 (*dd* (*br*), *J* = 15, 3 Hz, H-12β). The last two signals were very similar in chemical shift and coupling constant to those reported for heliantriol-$A_1$ [7].



**1** R = H
**1a** R = Ac
**1b** R =

$>C(Me)_2$

The mass spectrum of **1** showed strong peaks at *m/z* 218, 205 and 191, indicating that **1** could have a similar structure to δ-amyrin [8, 9] with a double bond between C-13 and C-18. This was confirmed by the presence of peaks at δ133.41 and 134.25 ppm in the $^{13}$C NMR spectrum, both of them being due to quaternary carbons as indicated by DEPT experiments.

On acetylation, **1** gave a 2,3-diacetate (**1a**, $[M]^+$ at *m/z* 526), the IR spectrum of which showed no hydroxyl absorption. The $^1$H NMR spectrum of the diacetate ($CDCl_3$) revealed singlets for six tertiary methyl groups at δ0.71, 0.86, 0.87, 0.94, 0.97, 1.01, 1.20 and 1.25. The carbinylic proton signals were shifted to δ5.26 (*ddd*, *J* = 12, 4.5, 3 Hz, H-2) and 4.97 (*d*, *J* = 2.4 Hz, H-3).

In the presence of acetone and a catalytic amount of sulphuric acid, **1** formed an acetonide. All of the spectroscopic data cited above led to the structure 2α,3α-dihydroxyolean-13(18)-ene. The corresponding 2β,3β-derivative has already been isolated from *Salvia horminum* [10].

Compound **2**, $[M]^+$ at *m/z* 424 and $[M-H_2O]^+$ at *m/z* 406, was identified as nonacosan-10-ol (mp [11], IR, $^1$H NMR, $^{13}$C NMR and MS [12]).

## EXPERIMENTAL

*General procedures*. The DEPT expts were carried out with θ = 45°, 90° and 135°; the quaternary carbons were determined by subtraction of these spectra from the broad-band $^{13}$C NMR spectrum. The EI and FD MS were recorded on a Finnigan MAT 312 double focusing mass spectrometer coupled with a PDP 11/34 computer system. Silica gel 60 (70–230 mesh Merck) was used for CC. TLC was performed on silica gel plates (Silica gel SIF-254 precoated Al cards) using the following solvent systems: (a) $C_6H_6$-EtOAc (17:3); (b) $C_6H_6$ EtOAc (10:0) (c) $C_6H_6$-EtOAc (19:1).

*Plant material*. The plant material was collected from the Karachi region and was identified by the Department of Botany, University of Karachi. A voucher specimen has been deposited at the herbarium of the Department of Botany, University of Karachi.

*Extraction and isolation*. The plant material was chopped into small pieces and extracted exhaustively with EtOH. The ethanolic extract was evaporated under red. pres. and the residue thus obtained was partitioned between EtOAc and $H_2O$. The EtOAc layer was evaporated and was then subjected to CC on silica gel. Elution was carried out with a gradient of increasing polarity in the order *n*-hexane, $C_6H_6$, EtOAc and MeOH.

*2α,3α-Dihydroxyolean*-13(18)-*ene* (**1**) was eluted from the column with $C_6H_6$-EtOAc (7:3) and purified by repeated recrystallization from MeOH, whereby fine needles of **1** were obtained, mp 238°, $[\alpha]_D -25°$ (*c* 0.25; $CHCl_3$). UV $\lambda_{max}^{MeOH}$ 208 nm; IR $\nu_{max}^{KBr}$ $cm^{-1}$: 3420 (OH), 1640 (C=C); $^1H$ NMR ($C_5D_5N$, 300.13 MHz): see Results and Discussion; $^{13}C$ NMR ($CDCl_3$, 75.43 MHz): δ17.38 (C-25), 17.67 (C-26), 21.56 (C-24), 21.95, 23.65, 24.18, 28.73 (C-23), 32.39 (methyls); 18.81 (C-6), 21.60 (C-11), 24.98, 26.57, 34.62 (C-7), 35.52, 36.70, 38.77, 39.47, 42.36 (C-1) (methylenes); 48.35 (C-9), 50.45 (C-5), 66.96 (C-2), 79.33 (C-3) (methynes); 33.65, 38.36, 41.27, 44.84, 133.41, 134.25 (quaternary carbons); EIMS *m/z* (rel. int.): 422.38159 (calc. for $C_{30}H_{50}O_2$: 422.38106) (42), 427 $[M - Me]^+$ (12), 409 (4), 337 (8), 295 (2), 257 (6), 223 (12), 218 (44), 205 (100), 155 (24), 109 (84), 95 (74), 81 (32), 69 (36); FAB MS *m/z*: 442 $[M]^+$; FDMS *m/z*: 443 $[M + 1]^+$.

*Acetylation of* **1**. **1** (10 mg) was treated with $Ac_2O$ (5 ml) in $C_5H_5N$ (1 ml) at room temp. overnight. Ice was added to the reaction mixture and a white ppt. was obtained which was filtered, washed with $H_2O$, dried, and crystallized from MeOH, yielding colourless crystals (2.3 mg) of diacetate **1a**, mp 112°. UV $\lambda_{max}^{MeOH}$ 220 nm; IR $\nu_{max}^{CHCl_3}$ $cm^{-1}$: 1740, 1370 (geminal dimethyl), 1250 (ester), 1040; $^1H$ NMR ($CDCl_3$, 300.13 MHz): δ0.71, 0.86, 0.87, 0.94, 0.97, 1.01, 1.20, 1.25 (*s*, 3H, 8 × Me), 1.96 (3H, *s*, OAc), 2.13 (3H, *s*, OAc), 4.97 (*d*, *J* = 2.4 Hz, H-3), 5.26 (*ddd*, *J* = 12, 4.5, 3 Hz, H-2); MS *m/z* (rel. int.): 526 $[M]^+$ (20), 511 $[M - Me]^+$ (10), 484 $[M - HOAc]^+$ (8), 406 (6), 391 (4), 257 (4), 205 (100), 189 (38), 135 (16), 119 (18), 109 (78), 95 (56), 84 (30), 69 (38).

*Acetonide of* **1**. 10 mg **1** was dissolved in 2 ml dry $Me_2CO$, 1 drop of $H_2SO_4$ was added and the reaction mixture stirred for 3 hr at room temp. Solid $K_2CO_3$ was then added and the mixture filtered. Removal of the solvent from the filtrate yielded colourless crystals of **1b**, mp 98°. $^1H$ NMR ($CDCl_3$, 300 MHz): δ0.69 (3H, *s*, Me), 0.83 (*s*, 6H, 2 × Me), 0.89, 0.92, 0.99, 1.01, 1.15 (each 3H, *s*, 5 × Me), 1.24 (*s*, 6H, 2 × methyls of acetonide); MS *m/z* (rel. int.): 482 $[M]^+$ (absent), 424 $[M - Me_2C{=}O]^+$ (22), 409 (10), 391 (2), 316 (4), 225 (6), 205 (96), 189 (30), 109 (80), 95 (82), 81 (46), 64 (100).

*Nonacosan*-10-*ol* (**2**) was eluted from the column with $C_6H_6$-EtOAc (19:1) and purified by repeated crystallization from EtOAc. Mp 82° (lit. [11] 83-84°), $[\alpha]_D \pm 0$ (*c* 0.25); IR $\nu_{max}^{CHCl_3}$ $cm^{-1}$: 3400 (OH), 2820, 1590, 1100-1000; $^1H$ NMR ($CDCl_3$, 300.13 MHz): δ0.88 (*t*, *J* = 6.8 Hz, 6H, 2 × Me), 1.25 (*br*), 24H, $CH_2$), 1.42 (*m*, 4H, $CH_2$), 3.60 (*br*, 1H, H-9); $^{13}C$ NMR ($CDCl_3$, 75.43 MHz): δ14.08 (C-1 and C-29), 22.70 (C-2 and C-28), 25.69 (C-8 and C-12), 29.36 (C-4 and C-26), 29.71 (C-5,6,7, C-13,14,15), 37.57 (C-9 and C-11), 31.94 (C-3 and C-27), 72.08 (C-10); FDMS *m/z* (rel. int.): 424 $[M]^+$ (18), 423 $[M - 1]^+$ (26), 407 $[M - OH]^+$ (38), 406 $[M - H_2O]^+$ (100), 379 (4); EIMS *m/z*: 406.45342 $[M - H_2O]^+$ (calc. for $C_{29}H_{58}$, 406.45385) (12), 297.31448 (calc. for $C_{20}H_{41}O$, 291.31572) (26), 157.15803 (calc. for $C_{10}H_{21}O$, 157.159232) (30), 139 (14), 125 (22), 111 (38), 97.101046 (calc. for $C\,H_{13}$, 97.10172) (72), 83 (100).

## REFERENCES

1. Chopra, R. N., Chopra, I. C., Handa, K. L. and Kapoor, L. D. (1958) *Indigenous Drugs of India*, p. 501. U. N. Dhar, Calcutta.
2. Kirtikar, K. R. and Basu, B. D. (1933) *The Indian Medicinal Plants*, Vol. 1, p. 86. L. M. Basu, Allahabad.
3. Nadkarni, K. M. (1976) *Indian Materia Medica*, Vol. 1, p. 362. Popular Prakashan.
4. Rao, K. V. J. and Rao, L. R. C. (1981) *J. Sci. Ind. Res.* **20B**, 125.
5. Tripathi, V. J. R. and Dasgupta, A. B. (1976) *Indian J. Chem.* **14B**, 62.
6. Chughtai, M. I. D. and Khokhar, I. (1979) *Pak. J. Sci. Ind. Res.* **31**, 79.
7. Pyrek, J. St. (1979) *Pol. J. Chem.* **53**, 2463.
8. Heupel, R. C. (1985) *Phytochemistry* **24**, 2929.
9. Bhutani, K. K., Kapoor, R. and Atal, C. K. (1984) *Phytochemistry* **23**, 407.
10. Ulubelen, A., Brieskorn, C. H. and Ozdemir, N. (1977) *Phytochemistry* **16**, 790.
11. Buckingham, J. (ed.) (1982) *Dictionary of Organic Compounds*, p. 4303. Chapman & Hall, London.
12. Luo, S., Gong, X., Gao, Z. and Tan, J. (1983) *Yunnan Zhiwu Yanjiu* **5**, 315.