Pergamon

PII: S0031-9422(98)00044-2

Phytochemistry, Vol. 48, No. 3, pp. 561–563, 1998

Printed in Great Britain
0031-9422/98 $19.00+0.00

NERIIFOLIONE, A TRITERPENE FROM *EUPHORBIA NERIIFOLIA*

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(*Received in revised form* 1 *December* 1997)

Key Word Index—*Euphorbia neriifolia*; Euphorbiaceae; cycloartenol; 9,19-cyclolanost-20(21)-en-24-ol-3-one.

Abstract—A novel triterpene, 9,19-cyclolanost-20(21)-en-24-ol-3-one, named neriifolione, and cycloartenol were isolated from the latex of *Euphorbia neriifolia*. Their structures were elucidated with the help of chemical and physical data (^{1}H NMR, ^{13}C NMR, IR and mass spectra). © 1998 Elsevier Science Ltd. All rights reserved

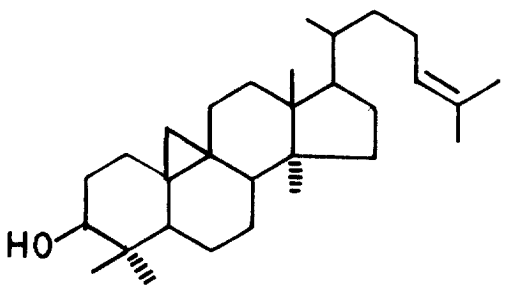
INTRODUCTION

The plant *Euphorbia neriifolia*, especially the latex, has been reported to possess a wide range of medicinal properties [1–11] which has prompted a comprehensive investigation of latex of *E. neriifolia*. A number of compounds have already been isolated from this plant [12–16]. We now report the isolation and characterization of a novel triterpene cyclolanost-20(21)-en-24-ol-3-one, named neriifolione (**2**), along with cycloartenol (**1**) from the latex of *E. neriifolia*.

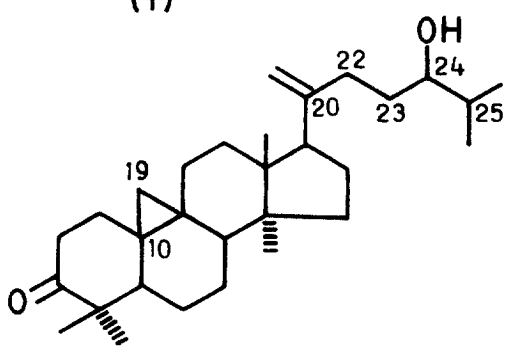
RESULTS AND DISCUSSION

The dried latex of *E. neriifolia*, collected from A.M.U. Campus, Aligarh, India, was extracted successively with petrol, benzene and acetone. The petrol and benzene extract on concentration gave a very small amount of the residue. The acetone extract was concentrated and chromatographed on a silica gel column. Elution of the column with petrol–benzene (1:1) afforded grannular white crystals mp, 86–90°C labelled as "compound A". The ^{1}H NMR spectrum of compound A indicated it to be a mixture of two compounds. Repeated column chromatography followed by preparative TLC (benzene–chloroform 1:1) resolved it into two pure compounds EN-1 (major) and EN-2 (minor).

EN-1 (200 mg) was crystallized from chloroform–methanol as white shining crystals, mp 95°C, analyzed for $C_{10}H_{50}O$, the molecular ion peak at *m/z* 426. It was characterized as cycloartenol (**1**) by comparison of its IR, ^{1}H NMR and mass spectra with those of an authentic sample [17, 18].



(1)



(2)

EN-2 (70 mg) was crystallized from chloroform–methanol as white shining crystals m.p. 92°C, analyzed for $C_{30}H_{48}O_2$. The IR spectrum showed the absorption maxima at 3400 (OH), 3040 (cyclopropane ring), 1705 (C=O), 1380, 1360 (geminal dimethyl) and 880 cm^{-1} (terminal methylene group =CH$_2$). The ^{1}H NMR spectrum exhibited two doublets at δ 0.15 and δ 0.39 (J = 5 Hz) characteristic of a cyclopropane ring in 9,19-cyclotriterpenoids [18]. A positive Zimmerman

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Table 1. ^{13}C NMR chemical shift [δc values (ppm)] of neriifolione

C no.	Chemical shift	C no.	Chemical shift
C-1	35.5	C-16	26.52
C-2	33.53	C-17	52.10
C-3	215.10	C-18	18.70
C-4	39.4	C-19	29.61
C-5	50.63	C-20	138.25
C-6	20.91	C-21	113.21
C-7	28.30	C-22	34.50
C-8	47.51	C-23	25.10
C-9	20.02	C-24	76.30
C-10	26.00	C-25	30.51
C-11	25.91	C-26	22.50
C-12	36.24	C-27	22.71
C-13	45.31	C-28	19.42
C-14	48.60	C-29	24.71
C-15	32.71	C-30	20.52

reaction [19] indicated the presence of carbonyl group at C-3. Six methyl protons appeared as a multiplet in the range of δ 0.89–1.10. A doublet at δ 4.65 ($J = 8$ Hz) was assigned to a terminal methylene group placed at $\Delta^{20(21)}$ which was supported by the peaks at *m/z* 339, 353 and 367 in the mass spectrum. The carbinylic hydrogen appeared as a multiplet at δ 3.25. The chemical shift of the carbinylic hydrogen ruled out the placement of OH at C-22 position (as it would be α to oxygen and allylic). The presence of the fragments at *m/z* 339, 353 and 367 further suggested that the hydroxyl was not at C-22. This left the positions C-24 and C-25. The presence of hydroxyl at C-25 would shift the terminal methyl to below δ 1.1, which was not observed. Furthermore, the absence of the fragment at *m/z* 59 due to $>C{=}O^{+}H$ indicated that the hydroxyl group was not at C-25. In the high resolution ^1H NMR spectrum, signals near δ 1.01 and 1.03 indicated two methyl doublets due to isoprenyl units. This suggests the placement of the hydroxyl group at C-24. The mass spectrum showed the molecular ion peak at *m/z* 440. The ^{13}C NMR (Table 1) showed one carbonyl carbon at δ 215.10. The terminal methylene carbons (C-20 and C-21) appeared at δ 138.25 and 113.21 and C-24 was observed at δ 76.30.

On the basis of the above results, the compound EN-2 was characterized as 9,19-cyclolanost-20(21)-en-24-ol-3-one and named as nariifolione (**2**).

EXPERIMENTAL

Mps were determined on a Reichert microscope hot stage apparatus and are uncorr. IR spectra were measured on Shimadzo IR-408. Mass spectra were obtained by electron impact a 70 eV on a JEOL JMS-300 spectrometer. ^1H NMR and ^{13}C NMR spectra were recorded on Bruker WM-400 using $CDCl_3$ as solvent and TMS as internal standard. Chemical shifts are quoted in δ ppm.

Plant material

Latex of *E. neriifolia* was collected from A.M.U. campus and the plant was identified by Prof. Wazahat Hussain, Department of Botany, A.M.U., Aligarh-202002, India.

Extraction and isolation

The latex of *E. neriifolia* (500 g) was dried under red. pres., then extracted successively with petrol, benzene and Me_2CO. Petrol and benzene extracts showed similar behaviour on TLC examination. The Me_2CO extract was chromatographed over a silica gel column using petrol, petrol–benzene (1:1) as the eluting solvents. The fractions obtained from petrol–benzene (1:1) gave a solid mass, labelled as compound "A" (350 mg), crystallized from $CHCl_3$–MeOH as granular crystals m.p. 86–90°. Spectral analysis of compound "A" showed it to be a mixture of two components which were separated into individual compounds EN-1 and EN-2 by repeated CC followed by prep. TLC (benzene–chloroform, 3:1).

EN-2 (*70 mg*). Crystallized from $CHCl_3$–MeOH, shining crystals mp 92°C. It gave +ve Zimmerman test (violet colour with meta-dinitrobenzene in KOH), M^+ *m/z* 440 (Calc. for $C_{30}H_{48}O_2$), $[\alpha]_D^{27}$ −17.5°, IR ν_{max}^{KBr} cm^{-1}, 3400 (OH), 3040 (cyclopropane ring), 1750 ($>C{=}O$), 1380, 1360 (gem. dimethyl), 880 ($=CH_2$); ^1H NMR: δ 0.19 and 0.39 (2H, AB*q*, $J = 5$ Hz, cyclopropane ring), δ 0.89–1.1 (18 H, *m*, 6 × Me), 3.25 (1H, *m*, carbinylic hydrogen), 4.65 (2H, *d*, $J = 8$ Hz, $=CH_2$); ^{13}C NMR (Table 1). MS, *m/z* (rel. int.): 440 [M^+] (15), 425 [$M^+ - Me$] (12), 422 [$M^+ - H_2O$] (9) 367 (8), 353 (8.5), 339 (15), 313 [M^+ − side chain] (27.6), 302 (11), 175 (36).

Acknowledgement—One of us (M.P.) is thankful to U.G.C. for financial assistance.

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