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Chemical Constituents Isolated from Seed Oil of *Jatropha curcas*

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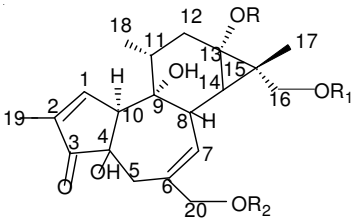
In present investigation seed oil of *Jatropha curcas* was examined and ten phorbol esters were isolated from it. Six of them were novel natural product (**2**, **3**, **4**, **5**, **6** and **7**). All the isolated compounds possess the same diterpene moiety, namely, 12-deoxy-16-hydroxyphorbol (**1**) (Fig. 1). The structures **2-11** were elucidated by spectroscopic methods.

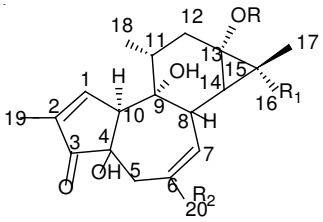
Key Words: *Jatropha curcas*, Euphorbiaceae, Diterpene, Phorbol esters, 12-Deoxy-16-hydroxyphorbol ester.

INTRODUCTION

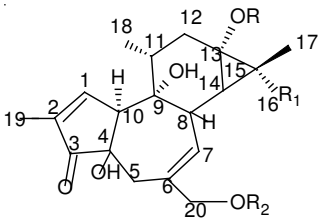
Jatropha curcas L. (Euphorbiaceae) is an oil bearing shrub widely distributed in American and African countries[1]. It grows wild in different parts of India[2]. The seed kernels contains up to 46-50 % oil having similar fatty acid composition to common edible oils, but the seeds and seed oil are toxic to human and animals due to which it is not used nutritionally[3-7]. The toxicity of the seeds of *J. curcas* is ascribed mainly due to presence of a group having diterpene esters termed as phorbol esters[8]. Chemical studies of seed oil of *J. curcas* have shown that it contains four different phorbol esters[9,10]. These substances are found in plants of Euphorbiaceae and Thymelaeaceae family and their structure is based on a tetracyclic carbon skeleton known as tigliane[11]. These class of compounds are known to cause many biological effects including antileukemic activity[12], tumor promotion and inflammation[13-16]. The cancerous growth has been treated by this plant ethno-medicinally[17]. These compounds provide a powerful biochemical tool for the study of the inflammation process in mammalian systems as well as a series of standard irritants for testing antiinflammatory drugs[18,19]. Seed extract of *Jatropha curcas* showed high molluscicidal activity[20-24]. Besides diterpines other chemical constituents such as sesquiterpenoids and triterpenes, lignins, coumarins, flavonoids, alkaloids, phytosterols *etc*., are also reported in *Jatropha curcas*[25] and this is also proved to be an opportunistic crop for production of biofuel[26]. In present paper the isolation and structure elucidation of ten phorbol esters (**2-11**) (Fig. 1) from seed oil of *Jatropha curcas* is reported. Six of them



1. R = R_1 = R_2 = H; **2**. R = $COCH_3$, R_1 = $COCH_2CH_2(CH{=}CH)_5CH_3$, R_2 = H; **3**. R = $COCH_3$, R_1 = $COCH{=}CH_3$, R_2 = H; **4**. R = $COCH_3$, R_1 = $CO(CH{=}CH)_3CH_2CH_2CH_3$, R_2 = $COCH_3$; **5**. R = $COCH_3$, R_1 = $CO(CH_2)_4CH{=}CHCH_3$, R_2 = H; **6**. R = $COCH_3$, R_1 = $CO(CH{=}CH)_6CH{=}CH_2$, R_2 = H; **7**. R = $COCH_2CH_3$, R_1 = $CO(CH_2)_{11}CH_2CH_3$, R_2 = H



8. R = $COCH(CH_3)_2$, R_1 = R_2 = CH_3; **9**. R = $COC(CH_3){=}CHCH_3$, R_1 = R_2 = CH_3



10. R = $CO(CH_2)_{10}CH_3$, R_1 = CH_3, R_2 = $COCH_3$; **11**. R = $CO(CH_2)_6CH_3$, R_1 = CH_3, R_2 = $COCH_3$

Fig. 1. Compounds isolated from *Jatropha curcas* seed oil

(**2**, **3**, **4**, **5**, **6** and **7**) are novel natural products. All isolated substances are diesters of the same diterpene, 12-deoxy-16-hydroxyphorbol (**1**)[8,27].

EXPERIMENTAL

The UV spectra were taken in Perkin-Elmer Lambda 15 UV/vis spectrophotometer. The IR spectra were taken in Perkin-Elmer Spectrum RX1 (4000-450 cm^{-1}). The ^1H NMR spectra were scanned using TMS as internal reference, on Bruker DRX-300 using solvent $CDCl_3$, δ values are in ppm. The mass spectra were recorded on Jeol SX-102 (FAB^+). *Jatropha curcas* seeds were collected from Medicinal & Aromatic Plants Research & Development Centre, G.B. Pant University of Agriculture and Technology, Pantnagar, India in 2003.

General procedure: A total of 3 kg dried finely powdered seeds (with seed coat) of *Jatropha curcas* were Soxhlet extracted successively in hexane, chloroform and methanol (5 L each) at their boiling points. Each extract was concentrated under reduced pressure below 45 ºC. The crude concentrated extract obtained from hexane, chloroform and methanol fraction was 1014.95, 31.90 and 77.12 g, respectively. The hexane fraction (non saponifiable 6 g) was subjected to column chromatography over silica gel (60-120 mesh) for gross fractionation, eluting with various percentage in increasing polarity of petroleum ether, benzene and ethyl acetate. Rechromatography over silica gel (230-400 mesh) with petroleum ether:benzene (30-45 %) fraction gave compound **2** and hexane:ethyl acetate (1-7 %) fraction gave compound **3**. The chloroform and methanol fraction (8 g each) over silica gel (60-120 mesh) after rechromatography over silica gel (230-400 mesh) gave compounds **4**, **5**, **6** and **7-11**, respectively.

Detection method: The structure for each compound isolated was determined by IR, ^1H NMR and MS studies carried out at Central Drug Research Institute, Lucknow, India. All compounds (**2-11**) are given below:

12-Deoxy phorbol-[4, 9,20-trihydroxy tigliadiene-(1,6)-16-O-myristyl-(4',6',8',10',12')-pentene-13-O-acetyl-one-3] (2): m.f. $C_{36}H_{46}O_8$. Yellowish viscous oil (hexane); R_f 0.28, hexane:ethyl acetate; 8:2; UV (methanol): 206 and 224 nm; IR (nujol, cm^{-1}): 3462, 3008, 2927, 2856, 1747, 1629, 1462, 1363, 1238, 1020, 723; ^1H NMR: (300 MHz, $CDCl_3$): 0.88 (3H, d, C_{18}), 1.15 (1H, d, C_{14}), 1.25 (3H, s, C_{17}), 1.50 (2H, s, C_{20}), 1.68 (3H, d, C_{19}), 2.18 (17H, m, C_{16}), 2.28 (3H, m, C_{11} and C_{12}), 2.70 (2H, s, C_5), 3.53 (2H, m (br), C_8, C_{10}), 4.01 (1H, s, OH-4), 4.10 (2H, q, C_{16}), 5.12 (1H, s (br), OH-9), 5.35 (1H, d, C_7), 7.20 (1H, s, C_1) ppm; MS: m/z: 606 (M^+), 604, 578, 552, 491, 476, 449,416, 393, 367, 339, 281, 261, 207, 194, 144, 128, 105.

12-Deoxy phorbol-[4,9,20-trihydroxy tigliadiene-(1,6)-16-O-butyl-2'-ene-13-O-acetyl-one-3] (3): m.f. $C_{26}H_{34}O_8$. White viscous oil; R_f 0.21, hexane:ethyl acetate; 5:5; IR (nujol, cm^{-1}): 3440, 2924, 2850, 1740, 1630, 1460, 1260, 1021, 723; ^1H NMR: (300 MHz, $CDCl_3$): 0.90 (3H, d, C_{18}), 1.25 (3H, s, C_{17}), 1.43 (3H, m (br), C_{11} and C_{12}), 1.68 (3H, d, C_{19}), 1.83 (H, dd, C_8), 2.28 (5H, m, C_{16}), 3.70 (1H, s, OH-4), 5.12 (1H, S (br), OH-9), 5.35 (1H, d, C_7), 7.26 (1H, s, C_1) ppm; MS: m/z 474 (M^+), 456, 396, 381, 368, 355, 297, 279, 249, 231, 207, 144, 128, 105.

12-Deoxy phorbol-[4,9-dihydroxy tigliadiene-(1,6)-16-O-decanyl-(2',4',6')-triene-13,20-diacetyl-one-3] (4): m.f. $C_{34}H_{44}O_9$. Yellowish red viscous oil (chloroform); R_f 0.19, hexane:ethyl acetate; 9:1; UV (methanol): 204 and 279 nm; IR (nujol, cm^{-1}): 3465, 3011, 2927, 2856, 1741, 1656, 1461, 1377, 1217, 1166, 1099, 764; ^1H NMR: 300 MHz, $CDCl_3$: 0.89 (3H, d, C_{18}), 1.30 (3H, s, C_{17}), 1.56 (3H, d, C_{19}), 2.03 (3H, dd, C_{11}, C_{12}), 2.28 (1H, s, OH-4), 2.70 (2H, s, C_5), 4.17 (13H, m, C_{16}), 5.19 (1H, s, OH-9), 5.36 (1H, d, C_7), 7.26 (1H, s, C_1) ppm; MS: m/z: 596 (M^+), 578, 518, 503, 462, 436, 397, 382, 266, 248, 207, 194, 144, 128, 105.

12-Deoxy phorbol-[4,9,20-trihydroxy tigliadiene-(1,6)-16-O-octanyl-(6')-ene-13-O-acetyl-one-3] (5): m.f. $C_{30}H_{42}O_8$. Pale yellow viscous oil (chloroform); R_f 0.22, hexane:ethyl acetate; 8:2; IR (nujol, cm^{-1}): 3451, 2926, 2858, 1741, 1459, 1375, 1218, 1161, 1026, 767; ^1H NMR: 300 MHz, $CDCl_3$: 0.87 (3H, d, C_{18}), 1.03 (3H, s, C_{17}), 1.59 (3H, d, C_{19}), 1.67-2.30 (3H, m, C_{11}, C_{12}), 2.77 (2H, s, C_5), 2.92 (1H, m, C_8), 3.19 (1H, s, OH-4), 3.73 (1H, d, C_{10}), 3.80-4.10 (13H, m, C_{16}), 4.43 (1H, s, OH-20), 5.11 (1H, s, OH-9), 5.35 (1H, d, C_7), 7.35 (1H, d, C_1) ppm; MS: m/z: 530 (M^+), 512, 452, 434, 406, 379, 337, 279, 261, 246, 231, 207, 194, 128, 105.

12-Deoxy phorbol-[4,9,20-trihydroxy tigliadiene-(1,6)-16-O-pentadecanyl-(2',4',6',8',10',12',14')-heptene-13-O-acetyl-one-3] (6): m.f. $C_{37}H_{44}O_8$. White viscous oil (chloroform); R_f 0.17, hexane:ethyl acetate; 8.5:1.5; IR (nujol, cm^{-1}): 3429, 3011, 2922, 2854, 1713, 1656, 1462, 1376, 1281, 1217, 1025, 762; ^1H NMR: 300 MHz, $CDCl_3$: 0.88 (3H, d, C_{18}), 1.11 (3H, s, C_{17}), 1.25 (3H, d, C_{19}), 2.02 (1H, s, OH-4), 2.29 -2.37 (3H, m, C_{11}, C_{12}), 2.77 (2H, s, C_5), 3.39 (1H, d, C_{10}), 4.22 (15H, m, C_{16}), 4.68 (1H, s, OH-20), 5.34 (1H, s, OH-9), 6.90 (1H, d, C_7), 7.35 (1H, d, C_1) ppm; MS: m/z: 616 (M^+), 598, 538, 520, 506, 480, 454, 428, 402, 376, 350, 337, 279, 261, 248, 233, 207, 194, 144 , 128, 105.

12-Deoxy phorbol-[4,9,20-trihydroxy tigliadiene-(1,6)-16-O-myristyl-13-O-acetyl methyl-one-3] (7): m.f. $C_{37}H_{58}O_8$. Reddish brown viscous oil (methanol); R_f 0.18, chloroform:methanol ; 9:1; UV (methanol): 224 nm; IR (nujol, cm^{-1}): 3419, 3016, 2927, 2856, 1724, 1657, 1461, 1377, 1220, 1120, 1048, 764; ^1H NMR: 300 MHz, $CDCl_3$: 0.88 (3H, d, C_{18}), 1.25 (3H, s, C_{17}), 1.63 (3H, d, C_{19}), 1.88 (1H, m, C_8), 2.00-2.10 (3H, m, C_{11} and C_{12}), 2.53 (2H, s, C_5), 2.77 (1H, s, OH-4), 3.41 (1H, d, C_{10}), 3.50-3.99 (27H, m, C_{16}), 4.30 (1H, s, OH-20), 5.34 (1H, s, OH-9), 6.95 (1H, d, C_7), 7.26 (1H, s, C_1) ppm; MS: m/z: 630 (M^+), 601, 573, 559, 531, 517, 461, 425, 351, 336, 332, 264, 246, 216, 207, 194, 144, 128, 105.

12,20-Dideoxy phorbol-[4,9-dihydroxy tigliadiene-(1,6)-13-O-isobutyryl-one-3] (8): m.f. $C_{24}H_{34}O_5$. Viscous oil (methanol); R_f 0.65, chloroform:methanol; 9.5:0.5; IR (nujol, cm^{-1}): 3401, 2930, 2851, 1675, 1380, 1050; ^1H NMR: 300 MHz, $CDCl_3$: 0.98 (3H, s, C_{20}), 1.01 (3H, s, C_{16}), 1.13 (d, gem dimethyl proton, C_{13}) ppm; MS: m/z: 402 (M^+), 387, 384, 369, 351 and 314.

12,20-Dideoxy phorbol-[4,9-dihydroxy tigliadiene-(1,6)-13-O-angelate-one-3] (9): m.f. $C_{25}H_{34}O_5$. Viscous oil (methanol); R_f 0.62, chloroform: methanol; 9.5:0.5; IR (nujol,

cm^{-1}): 3394, 2929, 2848, 1675, 1039; ^1H NMR: 300 MHz, $CDCl_3$: 1.91 (3H, s, C_{13}), 2.01 (3H, d, C_{13}); MS: m/z: 414 (M^+), 396, 378 and 314.

12-Deoxy phorbol-[4,9-dihydroxy tigliadiene-(1,6)-13-O-dodecanyl-20-O-acetyl-one-3] (10): m.f. $C_{34}H_{52}O_7$. Viscous oil (methanol); R_f 0.80, $CHCl_3$: C_6H_6: $(C_2H_5)_2O$; 1:3:3; IR (nujol, cm^{-1}): 3380, 1725, 1695, 780; ^1H NMR: 300 MHz, $CDCl_3$: 0.89 (3H, d, C_{18}), 1.16 (6H, s, C_{16}, C_{17}), 1.80 (3H, s, C_{19}), 2.05 (3H, Me-CO), 2.47 and 5.58 (1H, s(br), OH-4, OH-9), 1.27 (s, side chain protons, C_{13}). MS: m/z: 572, (M^+), 512, 372, 312 and 294.

12-Deoxy phorbol-[4,9-dihydroxy tigliadiene-(1,6)-13-O-octenyl-20-O-acetyl-one-3] (11): m.f. $C_{30}H_{44}O_7$. Viscous oil (methanol); R_f 0.78, $CHCl_3$:C_6H_6:$(C_2H_5)_2O$; 1:3:3; ^1H NMR: 300 MHz, $CDCl_3$: 0.89 (3H, d, C_{18}), 1.17 (6H, s, C_{16}, C_{17}), 1.80 (3H, s, C_{19}), 2.45 and 5.59 (1H each, s(br), OH-4, OH-9), 1.20 (s, side chain protons, C_{13}); MS: m/z: 516 (M^+), 456, 372, 312 and 294.

RESULTS AND DISCUSSION

The compounds **2** and **3** were obtained from hexane fraction, having molecular formula $C_{36}H_{46}O_8$ and $C_{26}H_{34}O_8$, respectively. The UV spectra absorption was shown at 206 and 224 nm for the presence of ketonic group and α,β-unsaturation in the compounds. IR spectra of compounds **2** and **3** was very similar and gave peak at 3462 cm^{-1} for hydroxyl group, at 1747 cm^{-1} for keto group and at 1020 cm^{-1} for a cyclopropane group. The proton NMR spectra gave multiplet at 2.18 ppm for the protons of myristyl-(4',6',8',10',12')-pentene group present at C_{16} in compound **2** and it gave multiplet at 2.28 ppm for the protons of butyl(-2'-ene)-group in compound **3** at C_{16} (numbering is according to the diester **1** of Fig. 1). Presence of α,β-unsaturated ketone in both compounds was confirmed by the peaks obtained at 7.20 and 7.26 ppm, respectively. The mass spectra for the myristyl group present in the compound **2** at C_{16} gave fragments at m/z 449, 393, 367 and m/z 339. The butyl group present in compound **3** at C_{16} gave fragments at m/z 381, 368, 355 and m/z 297. In both compounds **2** and **3** an O-acetyl group was present at C_{13} which was confirmed by the MS peaks obtained at m/z 491 and 396, respectively. Thus compound **2** was identified as 12-deoxy-phorbol-[4,9,20-trihydroxy tigliadiene-(1,6)-16-O-myristyl-(4',6',8',10',12')-pentene-13-O-acetyl-one-3] and compound **3** as 12-deoxyphorbol-[4,9,20-trihydroxy tigliadiene-(1,6)-16-O-butyl-2',ene-13-O-acetyl-one-3].

The compounds **4**, **5** and **6** were obtained from the chloroform fraction. The molecular formula for these compounds were $C_{34}H_{44}O_9$, $C_{30}H_{42}O_8$ and $C_{37}H_{44}O_8$, respectively. In the UV spectrum absorption was shown at 204 and 279 nm for the compound **4**. The IR spectra of compounds **4**, **5** and **6** was similar to each other. The bands for hydroxyl group and =CH stretching were obtained at 3465 and 3011 cm^{-1}, respectively. Bands at 2927 and 2856 cm^{-1} were obtained for $-CH_2$ asymmetric and symmetric stretching band at 1741 and 1656 cm^{-1} were for β-ketoester group, respectively. Band at 1099 cm^{-1} in IR spectrum was shown for a cyclopropane ring. The ^1H NMR spectra of compounds **4**, **5** and **6** only differ for protons present at C_{16} and C_{20}; other protons in these compounds were similar and gave a singlet at 7.26 ppm for C_1 protons. A doublet was obtained at 5.36 ppm for the protons present at C_7. A singlet was obtained at 2.70 ppm for two protons at C_5. Two hydroxyl groups present at C_4 and C_9 gave broad singlet at 2.28 and 5.19 ppm, respectively. Three protons each at C_{18} and C_{19} gave doublet at 0.89 and 1.56 ppm. In compound **4**, thirteen protons of side chain, -16-O-decanyl-(2'-4'-6')-triene at C_{16} gave multiplet at 3.80-4.17 ppm. In compound **5** protons of side chain -16-O-octanyl-(6')-ene at C_{16} gave multiplet at 3.80-4.10 ppm. A broad singlet was obtained at 4.43 ppm for a hydroxyl group present at C_{20}. In compound **6** protons of side chain, -16-O-pentadecanyl-(2',4',6',8',10',12',14')-heptene gave multilpet at 4.22 ppm. At 4.68 ppm a singlet was obtained for hydroxyl group present at C_{20}. Molecular ion peak obtained for compound **4** in mass spectra was at m/z 596. Peaks at m/z 578, 518 were due to loss of a water molecule and a $-CH_3COOH$ group from C_9 and C_{13}, respectively. Peaks at m/z 503, 382, 462, 436 and 397 were due to loss of fragments from side chain present at C_{16}. Thus compound **4** was identified as 12-deoxy phorbol- [4, 9-dihydroxy tigliadiene-(1,6)-16-O-decanyl-(2',4',6')-triene-13,20-diacetyl-one-3]. The mass spectra of compound **5** gave molecular ion peak at m/z 530. Peaks at m/z 406, 379, 337, 246 and 231 were due to loss of various fragments from side chain at C_{16}. So, compound **5** was identified as 12-deoxy phorbol-[4,9,20-trihydroxy tigliadiene-(1,6)-16-O-octanyl-(6')-ene-13-O-acetyl-one-3]. Mass spectra of compound **6** gave a molecular ion peak at m/z 616. Peaks at m/z 598, 520 and 261 were due to loss of three water molecules from C_9, C_4 and C_{20}, respectively. Peaks at m/z 506, 480, 454, 428, 402 and m/z 376 were obtained due to cleavage of the side chain present at C_{16}. So, compound **6** was 12-deoxy phorbol-[4,9,20-trihydroxy tigliadiene-(1,6)-16-O-pentadecanyl-(2',4', 6',8',10',12',14')-heptene-13-O-acetyl-one-3]. Compounds **7**, **8**, **9**, **10** and **11** were obtained from methanol fraction. Compound **7** was obtained as reddish brown viscous oil with molecular formula $C_{37}H_{58}O_8$. The UV spectra at 224 nm show the presence of ketonic α,β-unsaturation which on addition of alkali did not showed any bathochromic shift indicating absence of any carboxyl and phenolic group. The ^1H NMR spectra gave multiplet at 3.50-3.99 ppm for the protons present at C_{16}. Other ^1H NMR peaks were similar to compound **5**. The mass spectra gave molecular ion peak at m/z 630. Peak at m/z 351 was obtained for the loss of a acetyl methyl group present at C_{13}. Peaks obtained due to loss of fragments from side chain present at C_{16} were at m/z 601, 573, 559, 517 and m/z 531. So, compound **7** was identified as 12-deoxyphorbol-[4,9,20-trihydroxy tigliadiene-(1,6)-16-O-myristyl-13-O-acetyl methyl-one-3]. Compounds **8** and **9** were obtained as viscous oil with molecular formula $C_{24}H_{34}O_5$ and $C_{25}H_{34}O_5$, respectively. The IR spectra of compound **8** and **9** was similar to compound **7**. ^1H NMR spectra of compound **8** were also similar to compound **7** only with the difference in the protons present at C_{16} and C_{20}. Three protons of methyl group present each at C_{16} and C_{20} gave a singlet at 1.01 and 0.98 ppm, respectively. A doublet at 1.13 ppm was obtained for gem dimethyl groups of the isobutyric acid. The isobutyric acid was present at C_{13} and this was confirmed by mass spectrometry, which gave peak at m/z 314 (M^+-88) after loss of a

-COOHCH(CH_3)$_2$ group. The molecular ion peak for compound **8** was at m/z 402. Other major peaks were found at m/z 402 (M^+) 387 (M^+-CH_3), 384 (M^+-H_2O), 369 (M^+-H_2O-CH_3), 351 (M^+-H_2O-CH_3-H_2O). So, compound **8** was identified as 12,20-dideoxy phorbol-[4,9-dihydroxy tigliadiene-(1,6)-13-O-isobutyryl-one-3]. ^{1}H NMR for compound **9** was similar to compound **8** except a singlet and doublet found at 1.91 and 2.01 ppm for -CH_3 groups present at C_{13} as a side chain which was confirmed by the peak obtained in mass spectrum at m/z 314 (M^+-100) by loss of an (HOOC-C(CH_3)=CH-CH_3) group. Other major peaks were obtained at m/z 414 (M^+), 396 (M^+-H_2O), 378 (M^+-H_2O-H_2O). Thus the compound **9** was identified as 12,20-dideoxy phorbol-[4,9-dihydroxy tigliadiene-(1,6)-13-O-angelate-one-3]. Compounds **10** and **11** were obtained as viscous oil with molecular formula $C_{34}H_{52}O_7$ and $C_{30}H_{44}O_7$, respectively. ^{1}H NMR spectrum gave a doublet at 0.89 ppm for three protons at C_{18}. Six protons of C_{16} and C_{17} (3 protons each) gave a singlet at downfield value of 1.16 ppm, due to their attachment with a cyclopropane ring. Three protons at C_{19} gave a singlet at 1.80 ppm; the downfield value was due to its presence near, α,β-unsaturated ketone. Peak at 2.05 ppm was assigned for protons attached to ester group (Me-CO). Two broad singlets were found at 2.47 and 5.58 ppm for two hydroxyl groups present in the substance at C_4 and C_9. Singlet at 1.27 ppm was obtained for protons of side chain at C_{13}. The side chain present was a dodecanoate, which was confirmed by the mass spectrum obtained for the compound **10** which gave peak at m/z 372 (M^+-200). The molecular ion peak was obtained at m/z 572 (M^+), other peaks were obtained at m/z 512 (M^+-CH_3COOH), 312 (M^+- 60 + 200), 294 (M^+-60 + 200 + H_2O). So compound **10** was identified as 12-deoxyphorbol-[4,9-dihydroxy tigliadiene-(1,6)-13-O-dodecanyl-20-O-acetyl-one-3].

The ^{1}H NMR and of the compound **11** was very similar to compound **10**. The major difference found in ^{1}H NMR spectra of compound **11** in comparison to compound **10** was a singlet at 1.20 ppm for protons present at C_{13} as a side chain. The mass spectra gave a molecular ion peak at m/z 516 (M^+). Peak obtained by loss of a fragment at m/z 372 (M^+-144) indicated the presence of side chain as octenoate. Other peaks were found at m/z 456 (M^+-60) due to loss of -CH_3COOH present at C_{20}, 312 (M^+-60 + 144) and at m/z 294 (M^+-60 + 144 + H_2O). Thus compound **11** was identified as 12-deoxy phorbol-[4,9-dihydroxy tigliadiene-(1,6)-13-O-octenyl-20-O-acetyl-one-3].

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