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LIPID CONSTITUENTS OF *TRIDAX PROCUMBENS*

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Key Word Index—*Tridax procumbens*; Compositae; methyl 14-oxooctadecanoate; methyl 14-oxononacosanoate; 3-methylnonadecyl benzene; heptacosanyl cyclohexane carboxylate; 1-(2,2-dimethyl-3-hydroxypropyl)-2-isobutyl phthalate; 12-hydroxytetracosan-15-one; 32-methyl-30-oxotetratriacont-31-en-1-ol; 30-methyl-28-oxodotriacont-29-en-1-oic acid; Δ^{12}-dehydrolupen-3-one; β-amyrone; β-amyrin; lupeol; fucosterol.

Abstract—Eight new compounds, isolated from *Tridax procumbens*, have been characterized as methyl 14-oxooctadecanoate, methyl 14-oxononacosanoate, 3-methylnonadecylbenzene, heptacosanyl cyclohexane carboxylate, 1(2,2-dimethyl-3-hydroxypropyl)-2-isobutyl phthalate, 12-hydroxytetracosan-15-one, 32-methyl-30-oxotetratriacont-31-en-1-ol and 30-methyl-28-oxodotriacont-29-en-1-oic acid by spectral data and chemical studies. Nine known compounds isolated for the first time from the plant, were identified as dotriacontanol, β-amyrone, Δ^{12}-dehydrolupen-3-one, β-amyrin, lupeol, fucosterol, 9-oxoheptadecane, 10-oxononadecane and sitosterol. Although Δ^{12}-dehydrolupen-3-one is reported synthetically, this is the first report of this compound from a natural source.

INTRODUCTION

Tridax procumbens L. a wild herb distributed throughout India, is used [1] in the treatment of bronchial catarrh, dysentery and diarrhoea. The leaf juice possess antiseptic, insecticidal and parasiticidal properties and is used also to check haemorrhage from cuts, bruises and wounds. Luteolin, glucoluteolin, quercetin and isoquercetin have been reported from its flowers [2]. The occurrence of fumaric acid [3], β-sitosterol and tannin [4] has also been reported in the plant. Since no detailed work has been done on the hexane soluble fraction of this plant, it was of interest to investigate the compounds from the hexane extract of the plant.

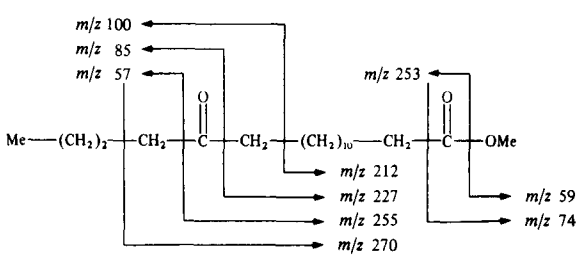
RESULTS AND DISCUSSION

The following 17 compounds were isolated by silica gel chromatography of a *n*-hexane extract of *T. procumbens*.

Compound **1**, viscous mass, had IR absorption bands at 1735 (ester CO), 1715 (CO) and 715 cm^{-1} (long chain), and gave a positive 2,4-dinitrophenylhydrazine (2,4-DNP) test, suggesting it to be a long chain saturated keto ester. The $[M]^+$ at *m/z* 312 suggested the molecular formula as $C_{19}H_{36}O_3$. The location of the carbonyl group was deduced to be at C-14 from the prominent α-fission ions at *m/z* 255, 227, 85, 57 and β-fission ions, involving McLafferty rearrangement, at *m/z* 270, 212 and 100 [5]. The ion at *m/z* 58 is characteristic of a ketone having a γ-hydrogen in both alkyl fragments. α and β-Fission fragments, characteristic of a methyl ester moiety were observed at *m/z* 253, 59 and 74 (base peak), respectively. The absence of an $[M-15]^+$ ion suggested its straight chain nature [6] whereas the presence of an $[M+1]^+$ was characteristic for its unsymmetrical nature [7, 8]. The ^1H NMR spectrum of the compound showed a singlet at δ3.66 for –OMe protons. The four protons of the $-CH_2-$ groups adjacent to the free carbonyl function and two protons adjacent to ester carbonyl function appeared as a triplet at δ2.30.

Alkaline hydrolysis of **1** afforded a compound having IR bands at 3300–2500 (broad), 1705 and 915 cm^{-1} for a carboxyl group and 1710 cm^{-1} for a carbonyl group, suggesting it to be a keto acid. It had a $[M]^+$ at *m/z* 298 ($C_{18}H_{34}O_3$) and also α and β-fission ions with respect to the C-14 carbonyl group at *m/z* 241, 213, 85, 57 and 256 and 100, respectively. These data suggested the structure of this acid to be 14-oxooctadecanoic acid. On the basis of above data, **1** was characterized as methyl 14-oxooctadecanoate.

Compound **2**, viscous mass, showed a positive 2,4-DNP test and had a similar IR and NMR spectrum to that of **1**. It possessed a $[M]^+$ peak at *m/z* 466 ($C_{30}H_{58}O_3$). The carbonyl group was at C-14 since α and β-fission ions were seen at *m/z* 255, 239, 227, 211 and 270, 254, 212 and 196, respectively. As in **1** it had a base peak at *m/z* 74, characteristic of a methyl ester. On alkaline hydrolysis it afforded 14-oxononacosanoic acid, $[M]^+$ *m/z* 452 ($C_{29}H_{56}O_3$) which had prominent α and β-fission ions for carbonyl groups at *m/z* 241, 239, 211 and 256, 254 and 196, respectively. Thus **2** was characterized as methyl 14-oxononacosanoate.



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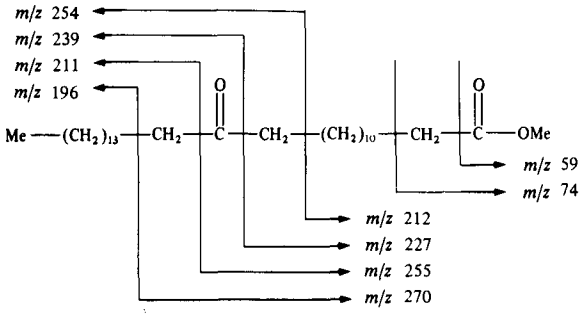

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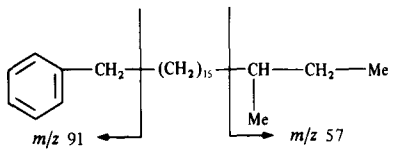

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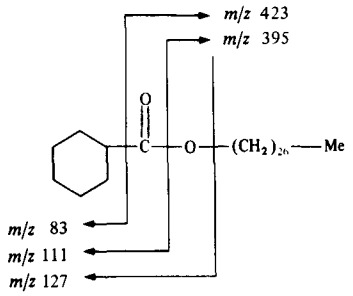

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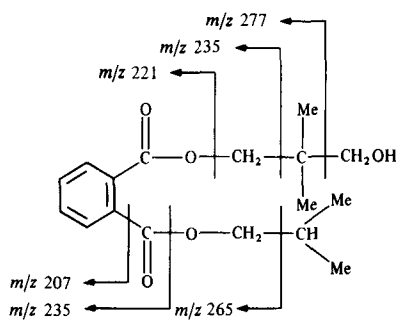
Compound **3**, viscous mass, obtained in traces had IR bands at 1580, 750, 700 cm^{-1} and ^1H NMR signals at δ7.3 (*m*, 5H), suggesting it was a singly substituted aromatic hydrocarbon [9]. It had a $[M]^+$ ion at *m/z* 358 ($C_{26}H_{46}$) with the base peak at *m/z* 91, the tropylium ion formed by cleavages β to the aromatic ring [10]. The presence of a $[M-15]^+$ ion at *m/z* 343 and a doublet at δ0.88 (3H) suggested the branched chain nature of the compound. A strong peak at *m/z* 57 favoured the branching at C-3. Thus, the compound **3** was identified as 3-methyl nonadecyl benzene.

Compound **4**, viscous mass, had IR bands at 1740 (ester CO) and 730, 720 cm^{-1} (long chain). The $[M]^+$ at *m/z* 506 suggested the molecular formula as $C_{34}H_{66}O_2$. It showed a triplet at δ4.02 for $-CH_2-O-\overset{O}{\overset{\|}{C}}-$ protons, a multiplet at δ1.5 for methylene protons of cyclohexane and a multiplet at δ2.6 for a $-CH-\overset{O}{\overset{\|}{C}}-O-$ proton. On hydrolysis it afforded cyclohexane carboxylic acid and heptacosanol. Thus on the basis of above data compound **4** was characterized as heptacosanyl cyclohexanoate. The mass spectral fragments at *m/z* 423, 395, 127, 111 and 83 in **4** were consistent with the proposed structure.

Compound **7**, viscous mass, showed IR bands at 3440, 1070 (hydroxyl group), 1728 (ester CO) and 1610, 1580 (aromatic). It had a $[M]^+$ ion at *m/z* 308 ($C_{17}H_{24}O_5$). The presence of the base peak at *m/z* 149 suggested it to be a phthalic acid ester [11]. Strong ions at *m/z* 265 [M − isopropyl group]$^+$, 207 $\left[M-\overset{O}{\overset{\|}{C}}-O-CH_2CH\begin{matrix}Me\\Me\end{matrix}\right]^+$ and 235 $\left[M-O-CH_2CH\begin{matrix}Me\\Me\end{matrix}\right]^+$ suggested the presence of isobutyl group in the compound. The second part of the ester should be 2,2-dimethyl-3-hydroxypropanol due to the prominent ions at *m/z* 290 $[M-H_2O]^+$, 277 $[M-CH_2OH]^+$, 235 $[M-\overset{Me}{\overset{|}{C}}-CH_2OH]^+$ and 221 $[M-CH_2-\overset{Me}{\overset{|}{C}}-CH_2OH]^+$. In the ^1H NMR spectrum two methyls of a isobutyl group were observed at δ0.98 as a doublet. A multiplet was centered at δ4.1 for $-O-CH_2-$ protons. A singlet, corresponding to $-CH_2-OH$ protons, was observed at δ3.62; $-\overset{Me}{\overset{|}{C}}-CH_2OH$ protons resonated at δ1.22. Aromatic protons were observed, δ7.3–7.75 ppm. On hydrolysis the ester yielded phthalic acid (identical with authentic material) which led to the characterization of compound **7** as 1-(2,2-dimethyl-3-hydroxypropyl)-2-isobutyl phthalate.

Compound **10**, viscous mass, exhibited IR absorption bands at 3430, 1720, 720, 710 cm^{-1} and gave a positive 2,4-DNP test for a long chain saturated hydroxy ketone [12]. It had a $[M]^+$ ion at *m/z* 368 ($C_{24}H_{48}O_2$). The assignment of the CO group to C-15 was made from the presence of prominent α-fission ions at *m/z* 241, 213, 155, 127 and β-fission ions at *m/z* 256, 198, 170 and 112. A double rearrangement ion at *m/z* 58 is characteristic for ketone having a γH in both the alkyl fragments. The location of the hydroxyl group at C-12 was deduced by the significant α-fission ions at *m/z* 213, 185, 183 and 155. The absence of an $[M-15]^+$ ion indicated the straight chain nature of the ketone whereas the presence of an $[M+1]^+$ is characteristic for its unsymmetrical nature. In the ^1H NMR spectrum a –CH–OH proton was observed at δ3.70. A triplet was observed at δ2.25 for $-CH_2-\overset{O}{\overset{\|}{C}}-CH_2-$ protons. Thus, the data obtained above suggested the structure of **10** as 12-hydroxytetracosan-15-one.

Compound **12** mp 80–82°, showed IR bands at 3380, 1050 (OH group) and 1700, 1650, 1620 characteristic of a



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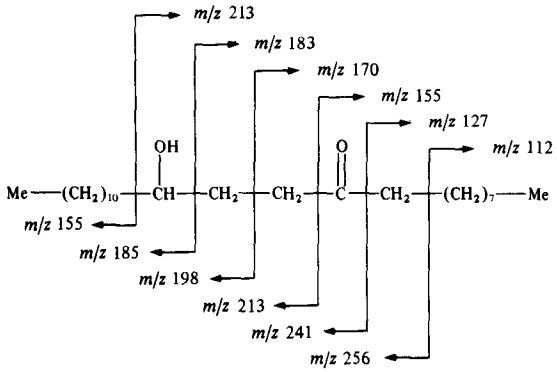

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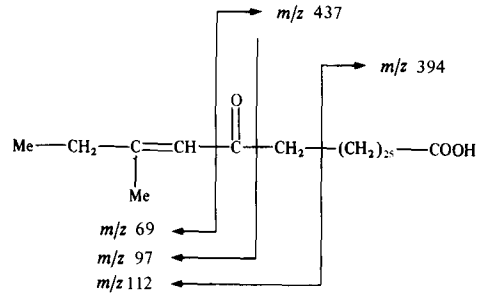

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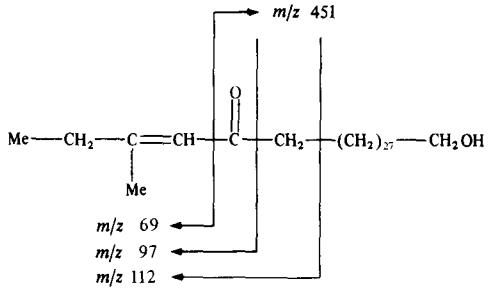

12

α,β-unsaturated ketone [13]. A $[M]^+$ ion was absent from its mass spectrum but it had a $[M-H_2O]^+$ at *m/z* 502 suggesting the molecular formula as $C_{35}H_{68}O_2$. An ion at *m/z* 505 $[M-15]^+$ suggested [6] the compound to be branched having the methyl group (δ1.55) attached to the olefinic carbon atom. The downfield shift of the olefinic proton (δ5.70) suggested that it was in the vicinity of the carbonyl group. A triplet was observed at δ3.6 for $-C\underline{H}_2-OH$ protons. The presence of strong ions at *m/z* 69, 97, 451 (α-fission) and 112 (β-fission) suggested the position of the carbonyl at C-30 in the molecule. On acetylation **12** afforded a monoacetate, $[M]^+$ *m/z* 562 which showed a triplet at δ4.02 for $-C\underline{H}_2-OAc$ protons and a singlet at δ2.01 for the –OAc group. On the basis of the above data, the compound was characterized as 32-methyl-30-oxotetratriacont-31-en-1-ol (**12**).

Compound **17**, mp 74–75°, had IR bands at 3300–2500, 1700, 920 (–COOH), 1690, 1650, 1610 (α,β-unsaturated ketone) and 730, 720 (long chain). It had a $[M]^+$ at *m/z* 506 which corresponded with the molecular formula $C_{33}H_{62}O_3$. The occurrence of a $[M-15]^+$ ion at *m/z* 491 suggested its branched chain nature. Similarly to compound **12** it had singlets at δ1.55 and 5.7 for a Me O | ‖ –C=CH–C– moiety. The position of the carbonyl group at C-28 was obtained by the observation of prominent α and β-fission ions at *m/z* 69, 97, 437 and 112, 394, respectively. The ions at *m/z* 45 and 60 indicated the presence of a terminal –COOH group. On methylation it gave a methyl ester, $[M]^+$ 520, $C_{34}H_{64}O_3$ which had ions at *m/z* 59 and 74 and a singlet at δ3.68 in its ^{1}H NMR spectrum, characteristic of a Me ester group. Thus, the compound **17** was identified as 30-methyl-28-oxodotriacont-29-en-1-oic acid.

Nine known compounds, 9-oxoheptadecane (**5**), 10-oxononadecane (**6**), β-amyrone (**8**), Δ^{12}-dehydrolupen-3-one (**9**), dotriacontanol (**11**), fucosterol (**13**), sitosterol (**14**), β-amyrin (**15**) and lupeol (**16**) were also isolated and characterized by their spectral analysis and comparison with authentic materials. Although Δ^{12}-dehydrolupen-3-one was synthesized earlier [14], this communication constitutes the first report of this compound from a natural source.

Oxo acids are commonly found in fat, lipid, oil, epicuticular wax, latex and rhizomes. Most natural straight chain acids whether saturated or unsaturated, have an even number of carbon atoms in the molecule [15]. In the even acids oxo groups are rare but are more likely to be situated on a odd carbon atom. Both these observations can be explained in terms of biosynthesis. Compound **17** isolated in the present investigation does not fit in with these generalizations. However, some unusual oxo acids are reported in the literature [15–19]. Fatty acid esters serve as an essential source of energy for plant growth. The aliphatic alcohols are reported to play important roles in the metabolic pathways of a number of organisms since they can generate fatty acids [20].

EXPERIMENTAL

Mps: uncorr. IR spectra were recorded in KBr and the 80 MHz NMR spectra were measured in $CDCl_3$ with TMS as int. std. TLC was carried out on silica gel G and the spots were visualized by exposure to I_2 vapour or spraying with 2,4-DNP. The homogeneity of compounds was checked on $AgNO_3$–silica gel TLC in at least four different solvent systems. Plant material was collected locally and a voucher specimen has been deposited in the Botany Department of our Institute.

Extraction and isolation. The plant was air-dried (1.7 kg dry wt) and extd with MeOH (5 × 10 l). The MeOH ext was concd to 250 ml, dild with H_2O (500 ml) and extracted with *n*-hexane (5 × 500 ml), $CHCl_3$ (5 × 500 ml) and *n*-BuOH (5 × 250 ml), respectively. The hexane extract was evapd and the residue (33.7 g) chromatographed over silica gel (1400 g, 60–120 mesh, BDH). Elution was carried out in hexane, hexane–C_6H_6 (3:1, 1:1, 1:3) and C_6H_6. Fractions (250 ml each) were collected and monitored by TLC.

Methyl-14-oxooctadecanoate (**1**). Fractions (30–32) of hexane–C_6H_6 (3:1) were purified by prep. TLC (hexane–C_6H_6, 9:1) to give compound **1**, 8 mg. IR ν_{max} cm^{-1}: 2920, 2850, 1735, 1715, 1460, 1430, 1380, 1240, 1160, 715. ^{1}H NMR: δ0.90 (3H, *t*,

J = 8 Hz), 1.25 [$(CH_2)_n$, *br s*], 2.30 (6H, *t*, J = 8 Hz), 3.66 (3H, *s*, –C(=O)–OMe). MS *m/z* (rel. int): 312 $[M]^+$ ($C_{19}H_{36}O_3$) (0.2), 270 (20), 255 (2), 253 (0.2), 227 (8), 212 (6), 100 (10), 85 (10), 74 (100), 59 (8), 58 (6), 57 (15), 43 (30).

Hydrolysis of **1**. Compound **1** (4 mg) was refluxed with 5% alcoholic KOH (5 ml) for 4 hr. The vol. was then reduced and the reaction mix. dild with H_2O (10 ml) and acidfied with dil HCl. It was extd with Et_2O (4 × 10 ml) washed with H_2O (2 × 10 ml) and dried (Na_2SO_4). Removal of solvent gave 14-oxooctadecanoic acid, 2 mg. IR ν_{max} cm^{-1}: 2920, 2850, 3300–2500, 1710, 1705, 1450, 1420, 1380, 1280, 1160, 915, 720. MS *m/z* (rel. int.) 298 $[M]^+$ (1), 256 (40), 241 (15), 213 (10), 100 (15), 85 (12), 60 (65), 58 (6), 57 (100), 45 (5), 43 (85).

Methyl-14-oxononacosanoate (**2**). Fractions (34–40) of hexane–C_6H_6 (3:1), purified by prep. TLC (hexane–C_6H_6, 9:1), gave compound **2**, 10 mg. IR ν_{max} cm^{-1}: 2920, 2840, 1735, 1710, 1460, 1430, 1370, 1235, 1165, 725, 715. ^1H NMR: δ0.90 (3H, *t*, J = 8 Hz), 1.25 [$(CH_2)_n$, *br s*], 2.30(6H, *t*, J = 8 Hz), 3.65 (3H, *s*, –C(=O)–OMe). MS *m/z* (rel. int.): 466 $[M]^+$ ($C_{30}H_{58}O_3$) (0.1), 270 (7), 255 (1), 254 (8), 239 (3), 227 (5), 212 (5), 211 (2), 196 (4), 74 (100), 59 (8), 58 (3), 57 (22), 43 (45).

Hydrolysis of **2**. Compound **2** (5 mg) was hydrolysed with 5% alcoholic KOH (5 ml) for 4 hr. After usual work-up it gave 14-oxononacosanoic acid, 3 mg. IR ν_{max} cm^{-1}: 2910, 2850, 3300–2500, 1715, 1700, 1450, 1410, 1380, 1260, 1140, 920, 715. MS *m/z* (rel. int.): 452 (2), 256 (30), 254 (10), 241 (12), 239 (5), 211 (10), 196 (2), 60 (70), 58 (5), 58 (5), 57 (100), 45 (4), 43 (80).

3-Methyl nonadecyl benzene (**3**). Fractions (42–45) of hexane–C_6H_6 (3:1) gave **3** after purification by prep. TLC (hexane–C_6H_6, 4:1), 3 mg. IR ν_{max} cm^{-1}: 2920, 2845, 1580, 1380, 750, 700. ^1H NMR: δ0.90 (3H, *t*, J = 8 Hz), 0.88 (3H, *d*, J = 8 Hz), 1.20 [$(CH_2)_n$, *br s*], 2.4 (2H, *m*), 7.3 (5H, *m*). MS *m/z* (rel. int.): 358 $[M]^+$ ($C_{26}H_{46}$] (6), 343 (45), 91 (100), 65 (10), 57 (55), 43 (8).

Heptacosanyl cyclohexanoate (**4**). Fractions (50–55) of hexane–C_6H_6 (3:1) were purified by prep. TLC (hexane–C_6H_6, 4:1) to give compound **4**, 8 mg. IR ν_{max} cm^{-1}: 2910, 2850, 1740, 1460, 1380, 1240, 1170, 730, 720. ^1H NMR: δ0.90 (3H, *t*, J = 8 Hz), 1.25 [$(CH_2)_n$ *br s*], 2.6 (1H, *m*, –CH–C(=O)–O–), 1.5 [$(CH_2)_5$, *m*], 4.02 (2H, *t*, J = 8 Hz). MS *m/z* (rel. int.): 506 $[M]^+$ ($C_{34}H_{66}O_2$) (0.5), 423 (1), 395 (2), 127 (3), 111 (25), 83 (50), 57 (80), 43 (100).

Hydrolysis of **4**. Compound **4** (5 mg) was refluxed with 5% alcoholic KOH (5 ml) for 4 hr. After usual work-up it afforded cyclohexane carboxylic acid, viscous mass, $[M]^+$ 128 and heptacosanol, mp 74–75°, $[M]^+$ 396.

9-Oxoheptadecane (**5**). Fractions (60–70) of hexane–C_6H_6 (3:1) were purified by prep. TLC to give 9-oxoheptadecane, 7 mg, identified by its spectral analysis (MS, IR, NMR).

10-Oxononadecane (**6**). Removal of solvent from the fractions (73–85) of hexane–C_6H_6 (3:1) gave 10-oxononadecane (5 mg) after purification by prep. TLC. It was identified by its spectral analysis (MS, IR, NMR).

1-(2,2-Dimethyl-3-hydroxypropyl)-2-isobutyl phthalate (**7**). Fractions (118–130) of hexane–C_6H_6 (1:1) were purified by prep. TLC (hexane–C_6H_6 (3:1) to give compound **7** as a viscous mass, 10 mg. IR ν_{max} cm^{-1}: 3440, 2940, 2860, 1728, 1610, 1580, 1465, 1375, 1280, 1125, 1070, 745. ^1H NMR: δ0.98 (6H, *d*, J = 8 Hz), 1.22 (6H, *s*), 4.1 (4H, *m*, –O–CH_2–), 3.62 (2H, *s*, –CH_2–OH), 7.3–7.75 (4H, *m*), MS *m/z* (rel. int.): 308 $[M^+]$ ($C_{17}H_{24}O_5$) (2), 293 (1), 290 (0.5), 277 (2), 265 (5), 235 (2), 207 (3), 221 (2), 149 (100), 57 (65), 43 (60).

Hydrolysis of **7**. Compound **7** (5 mg) was hydrolysed with 5% alcoholic KOH (5 ml) to give phthalic acid, identified by comparison with an authentic sample.

β-Amyrone (**8**). Eluted in hexane–C_6H_6 (1:1) fractions (140–171), 40 mg, mp 163–165°, identified by comparison with an authentic sample (mp, mmp, co-TLC).

Δ^{12}-Dehydrolupen-3-one (**9**). Eluted in hexane–C_6H_6 (1:1) fractions (172–188), 30 mg, mp 152–155°, identified by comparison with an authentic sample (IR, MS, mmp, co-TLC).

12-Hydroxytetracosan-15-one (**10**). Eluted in hexane–C_6H_6 (1:3) fractions (190–194), 5 mg. IR ν_{max} cm^{-1}: 3430, 2900, 2815, 1720, 1450, 1370, 1160, 720, 710. ^1H NMR: δ0.90 (6H, *t*, J = 8 Hz), 1.25 [$(CH_2)_n$, *br s*] 2.25 (4H, *t*, J = 8 Hz), 3.70 (1H, *m* –CH–OH). MS *m/z* (rel. int.): 368 $[M]^+$ ($C_{24}H_{48}O_2$) (1), 256 (10), 241 (2), 213 (8), 198 (4), 185 (6), 183 (2), 170 (5), 155 (3), 127 (4), 112 (8), 58 (6), 57 (85), 43 (100).

Dotriacontanol (**11**). Fractions (195–210) of hexane–C_6H_6 (1:3) afforded dotriacontanol, 50 mg, mp 87–89°, identified by IR and MS.

32-Methyl-30-oxotetratriacont-31-en-1-ol (**12**). Fractions (215–231) of hexane–C_6H_6 (1:3) afforded a solid, mp 80–82° (Me_2CO–MeOH), 20 mg. IR ν_{max} cm^{-1}: 3380, 2920, 2860, 1700, 1650, 1620, 1465, 1410, 1380, 1050, 820, 730, 710. ^1H NMR: δ0.87 (3H, *t*, J = 8 Hz), 1.55 (3H, *s*, Me–C=CH–), 2.15 (2H, *t*, J = 8 Hz, –C(=O)–CH_2), 3.6 (2H, *t*, J = 8 Hz), 5.70 (1H, *br s*), 1.22 [$(CH_2)_n$ *br s*]. MS *m/z* (rel. int.): 505 $[M-Me]^+$ (0.5), 502 $[M-H_2O]^+$ (1), 451 (4), 112 (8), 97 (60), 69 (55), 57 (100).

Acetylation of **12**. To **12** (10 mg) was added pyridine and Ac_2O (1 ml each) and the mixt left overnight at room temp. It was then dil. with H_2O (25 ml) and extracted with Et_2O (4 × 25 ml). The Et_2O extract was washed successively with dil HCl, H_2O, $NaHCO_3$ and soln and H_2O (each 2 × 50 ml) and then dried (Na_2SO_4). Removal of solvent gave a residue, mp 78–80° (Me_2CO–MeOH), 8 mg. IR ν_{max} cm^{-1}: 2910, 2860, 1730, 1700, 1650, 1460, 1410, 1380, 1240, 820, 730, 720. ^1H NMR: δ0.87 (3H, *t*, J = 8 Hz), 1.55 (3H, *s*), 2.15 (3H, *t*, J = 8 Hz), 5.70 (1H, *br s*), 4.02 (2H, *t*, J = 8 Hz, –CH_2–OAc), 2.01 (3H, *s*, OAc), 1.22 [$(CH_2)_n$, *br s*]. MS: $[M]^+$ *m/z* 562.

Fucosterol (**13**). Eluted in (233–236) fractions from benzene, 10 mg, mp 122–123° and identified by comparison with an authentic specimen (mmp, co-TLC, MS).

Sitosterol (**14**). Eluted from (238–290) fractions of benzene, mp 136–137°, 200 mg. Identified by comparison with an authentic sample (mmp, co-TLC, IR, MS).

β-Amyrin (**15**). Eluted from (292–295) fractions of benzene and purified by prep. TLC to afford 5 mg, mp 195–197°, which was identified by comparison with authentic material (mmp, co-TLC, IR, MS).

Lupeol (**16**). Eluted from (292–295) fractions of benzene, purified by prep. TLC, 4 mg, mp 215–217°. Identified by comparison with authentic material (co-TLC, mmp, IR, MS).

30-Methyl-28-oxodotriacont-29-en-1-oic acid (**17**). Fractions (297–341) of benzene afforded a solid, mp 74–75° (Me_2CO–MeOH), 20 mg, IR γ_{max} cm^{-1}: 2920, 2850, 3300–2500, 1700, 1690, 1650, 1610, 1460, 1410, 1375, 1300, 920, 830, 730, 720. ^1H NMR: δ0.87 (3H, *t*, J = 8 Hz), 1.55 (3H, *s*, Me–C=CH), 2.15 (4H, *t*, J = 8 Hz, –C(=O)–CH_2, CH_2–COOH), 5.70 (1H, *br s*), 1.22 [$(CH_2)_n$, *br s*]. MS *m/z* (rel. int.): 506 $[M]^+$ ($C_{33}H_{62}O_3$) (0.5), 491 (0.5), 437 (1), 394 (4), 112 (6), 97 (30), 69 (35), 60 (45), 57 (100), 45 (35).

Methylation of **17**. Compound **17** (10 mg) in Me_2CO (0.5 ml) was mixed with dry $NaHCO_3$ (4 mg) and Me_2SO_4 (0.1 ml) and the mixt. heated gently under reflux for 20 hr. Solvent was then removed under red. pres., H_2O (25 ml) added and extracted with

Et_2O (4 × 25 ml) and dried (Na_2SO_4). It was purified by prep. TLC (hexane–C_6H_6, 9 : 1) to provide a viscous residue, 4 mg. IR ν_{max} cm^{-1}: 2910, 2860, 1700, 1690, 1650, 1450, 1410, 1370, 1260, 830, 730, 720. ^1H NMR: δ0.87 (3H, *t*, J = 8 Hz), 1.55 (3H, *s*), 2.15 (4H, *t*, J = 8 Hz), 5.70 (1H, *br s*), 3.68 (3H, *s*, –C(=O)–O–Me), 1.22 [$(CH_2)_n$ *br s*]. MS *m/z*: 520 $[M]^+$, 74, 59.

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