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NOTE

Cetyl triacontanoate and other constituents from *Acacia jacquemontii* and *Kigelia pinnata*

Pahup Singh*, Poonam Khandelwal, Kuldeep K. Sharma and M. C. Sharma

Centre of Advanced Studies, Department of Chemistry, University of Rajasthan, Jaipur-302 004, Rajasthan, India

E-mail : pahupsingh@yahoo.co.uk

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Abstract : Leaves of *Acacia jacquemontii* on chemical investigation afforded a new aliphatic ester - cetyl triacontanoate along with *n*-triacontanol, *n*-octacosanol, β-sitosterol and stigmasterol while the heartwood of *Kigelia pinnata* gave lapachol, dehydro-α-lapachone, tecomaquinone-I, D-sesamin, paulownin, wodeshiol (kigeliol), kigelinone, β-sitosterol and stigmasterol on reinvestigation. The structures of isolated compounds were ascertained using various spectral (IR, ^{1}H, ^{13}C NMR, MS) techniques.

Keywords : *Acacia jacquemontii, Kigelia pinnata*, cetyl triacontanoate, naphthoquinones, lignans.

Introduction

Acacia jacquemontii (Fabaceae), an erect shrub usually 6 to 10 feet in height, is distributed over various parts of India but frequently occurs in Rajasthan[1]. Two cassane type diterpenes were earlier reported from its heartwood[2], however no work has been done on its leaves. *Kigelia pinnata* DC. (Bignoniaceae), a small spreading tree with a long-stalked large gourd like fruit, is an African tree introduced to India[3,4]. The bark is used as a remedy for syphilis and gonorrhoea[5] and fruit is traditionally used as dressing for ulcers and purgative[6]. Some studies on anti-implantation[7], molluscicidal[8], antimicrobial[9] and cytotoxic activities[10] on this plant have been cited in the literature. The isolation of isocoumarins from its roots[11], norviburtinal and pinnatal from its root bark[12,13], naphthoquinones, lignan[14], monoterpenes, naphthoquinones[15,9], iridoids[16] from stem bark, flavonoids from leaves[17] and iridoid and furanone derivatives[18] from its fruits, were earlier mentioned in the literature.

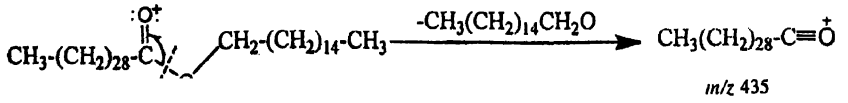
The present report deals with the isolation and characterization of cetyl triacontanoate, *n*-triacontanol, *n*-octacosanol, β-sitosterol and stigmasterol from the leaves of *Acacia jacquemontii* and lapachol, dehydro-α-lapachone, tecomaquinone-I, D-sesamin, paulownin, wodeshiol (kigeliol), kigelinone, β-sitosterol and stigmasterol from the heartwood of *Kigelia pinnata*.

Results and discussion

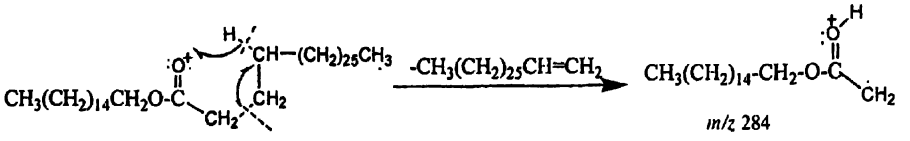
Five compounds were obtained from petroleum ether extract of the leaves of *Acacia jacquemontii* as described in the experimental section.

The compound **1**, $C_{46}H_{92}O_2$, M^+ 676 from its FAB mass spectrum. Its IR spectrum showed absorption bands at 1745, 1205 (COO), a doublet at 735 and 725 cm^{-1} due to $(CH_2)_n$ bending where n is > 4. ^{1}H NMR spectrum displayed a downfield triplet at δ 4.05 for oxymethylene moiety of an ester which was substantiated by the appearance of a ^{13}C signal at δ_c 64.41. Methylene group adjacent to keto group of ester appeared at δ 2.28 as triplet along with its corresponding ^{13}C signal at δ_c 34.43. ^{13}C signal at δ_c 31.95 was assigned to methylene carbon adjacent to oxymethylene group. A down field ^{13}C signal at δ_c 174.05 was assigned to carbonyl carbon of ester group. Both terminal methyl groups appeared as triplet at δ_H 0.88 was confirmed from their ^{13}C signal at δ_c 14.14. A broad singlet at δ_H 1.25 in ^{1}H NMR spectrum corresponded to 39 methylene groups. From the above spectral data it was clear that compound is an ester of a long chain alcohol with a long chain fatty acid.

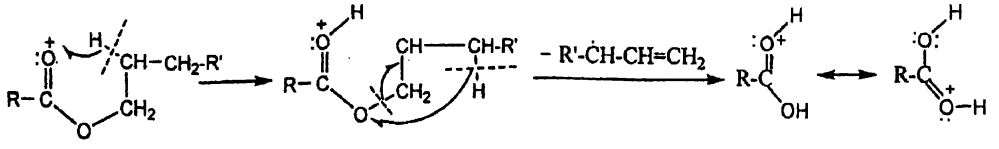
The molecular ion peak was very weak but the appearance of an abundant ion peak at *m/z* 435 on account of acylium ion[19] in its mass spectrum confirming the acid moiety of an ester.



The most characteristic peak at *m/z* 284 was due to Mc Lafferty rearrangement[20].



It also showed a diagnostic peak at *m/z* 453 due to transfer of two hydrogen atoms to the fragment containing the oxygen atoms[21].



R = -$(CH_2)_{28}$-CH_3

R' = -$(CH_2)_{12}$-CH_3

The above mass spectral data suggested it to be acetyl triacontanoate. Further on hydrolysis with methanolic KOH it gave cetyl alcohol as colourless gum and triacontanoic acid as colourless solid, m.p. 90–91 °C confirming its identity.

The compound **2** was obtained as colourless flakes, m.p. 136–137 °C, and gave positive Liebermann-Burchard test. It was characterized as β-sitosterol from its spectral data. The compound **3** was also isolated as colourless needles, m.p. 168–170 °C and also gave positive test for sterols. It was identified as stigmasterol. The compound **4** was separated as white granules, m.p. 82–83 °C and formed an acetyl derivative, m.p. 67–68 °C. Its spectral data were consistent with those reported for *n*-triacontanol[2]. The compound **5** was isolated as white microcrystalline solid, m.p. 80–82 °C and its acetate has m.p. 62–63 °C. Its analytical and spectral data led to its confirmation as *n*-octacosanol[22].

Chloroform extract of heartwood of *Kigelia pinnata*, after separation into alkali soluble and insoluble fractions gave seven compounds (**6-12**) in addition to β-sitosterol and stigmasterol. The compound **6** was separated as fine yellow needles, m.p. 139–140 °C from alkali soluble fraction. It gives a violet red colour with ferric chloride and a red colour with magnesium acetate. It dissolves in aqueous sodium hydroxide giving a deep red solution which turns light yellow on addition of sodium dithionite and the red colour can be restored or shaking for some time in air. From analytical and spectral data it was characterized as lapachol[23]. The compound **7** was obtained as blue green crystals, m.p. 194–195 °C. Its methanolic solution was blue and displayed strong absorption band at 578 nm in UV-VS spectrum. On refluxing with zinc dust it gave tectol, m.p. 215–216 °C and was characterized as tecomaquinone-I[24]. The compound **8** was isolated as orange red needles, m.p. 142–143 °C and confirmed as dehydro-α-lapachone from its spectral data[25]. The compound **9** was obtained as colourless prisms, m.p. 122–123 °C. It gave red colour with phloroglucinol and sulphuric acid[26] and blue green colour with gallic acid and H_2SO_4[27] indicating the presence of methylenedioxy group. It was identified as D-sesamin[28]. The compound **10** was separated as colourless needles, m.p. 104–105 °C and gave positive Labat test[27] for -OCH_2O-. Its identity was assured by preparing its methanolate[29], m.p. 84–85 °C. The compound **11** was isolated as colourless needles, m.p. 152–153 °C, [α]-12° and gave positive colour reactions for -OCH_2O- groups. It has a highly symmetrical structure and confirmed as wodeshiol[14,30] by preparing

its diacetate, m.p. 169–170 °C. The compound **12** was obtained as yellow needles, m.p. 154–155 °C. Its molecular formula $C_{14}H_{10}O_5$ was established from its mass spectrum and characterized as kigelinone[31-33].

Experimental

IR spectra were recorded on FTIR Nicolet Magna 550 and Shimadzu 8400 s spectrometers. ^1H and ^{13}C NMR spectra were measured on Jeol AL 300 MHz FTNMR instrument. Mass spectra (FAB MS) were recorded on a Jeol SX-102 spectrometer. UV-VS spectra were recorded in ethanol (95%) on Perkin-Elmer model 2R automatic recording. Optical rotations were measured on JAS CODIP-370 digital polarimeter. Qualitative and quantitative TLC were conducted on aluminium sheets Kieselgel $60F_{254}$ (E. Merck). Melting points were determined in soft glass capillaries in an electrothermal melting point apparatus and are uncorrected.

Extraction of leaves of Acacia jacquemontii Roxb. :

The leaves of *A. jacquemontii* were collected from nearby Jaipur region. The air dried and coarsely powdered leaves (5 kg) were extracted with petroleum ether (60–80°) on boiling water bath for 3 × 12 h. The solvent was removed under reduced pressure and the resulting dark green semisolid mass was taken in $CHCl_3$ and decolourized with activated charcoal. Pale green mass (10 g) was column chromatographed over silica gel and collected following fractions. Fraction eluted with pet-ether (100%) gave compound **1** as white solid, 60 mg, which was recrystallised from *n*-hexane. Fraction eluted with pet-ether-benzene (1 : 1) afforded colourless flakes, 110 mg as compound **2** while fraction eluted with pet-ether-benzene (2 : 3) gave colourless needles, 90 mg as compound **3**. Fraction eluted with pet-ether-benzene (1 : 3) and followed by prep. TLC gave white solid, 30 mg as compound **4**. Fraction obtained after eluting benzene (100%) gave white granules, 60 mg as compound **5**.

Cetyl triacontanoate : White granules, m.p. 60–62 °C; IR (KBr) ν $(cm)^{-1}$: 2910–2850 (C–H, stretch), 1745, 1205 (C=O), 735 and 725 $(CH_2)_n$; ^1H NMR (300 MHz, $CDCl_3$) δ : 0.88 t (*J* 6.78 Hz, 2 × CH_3), 1.25 sbr (78H), 1.61 m (2 × CH_2), 2.28 t (*J* 7.5 Hz, -CH_2-), 4.05 t (*J* 6.78 Hz, -OCH_2-); ^{13}C NMR (75.45 MHz, $CDCl_3$) δ : 14.14 (2 × CH_3), 22.71, 25.05, 25.96, 28.67, 29.18, 29.30, 29.38, 29.50, 29.56, 29.61, 29.63, 29.68, 29.72, 31.95, 64.41 (OCH_2), 174.05 (COO); MS : *m/z* 676 $[M^+]$ ($C_{46}H_{92}O_2$), 661, 647, 633, 619, 605, 453 ($C_{30}H_{61}O_2$), 435 ($C_{30}H_{59}O$), 284 ($C_{18}H_{36}O_2$); 20 mg of compound **1** was treated with methanolic KOH at 80 °C at boiling water bath. Prep. TLC gave 7 mg triacontanoic acid and 8 mg cetyl alcohol.

β-Sitosterol : Colourless flakes, m.p. 136–137 °C (MeOH); IR (KBr) ν (cm^{-1}) : 3400 (OH), acetate (Ac_2O/pyridine), m.p. 126–127 °C; MS : *m/z* 414 $[M^+]$ ($C_{29}H_{50}O$).

Stigmasterol : Colourless needles, m.p. 168–170 °C (MeOH); IR (KBr) ν (cm^{-1}) : 3450 (OH), acetate (Ac_2O/pyridine), m.p. 144–145 °C; MS : *m/z* 412 $[M^+]$ ($C_{29}H_{48}O$).

n-Triacontanol : White granules, m.p. 82–83 °C; IR (nujol) ν (cm^{-1}) : 3289, 1063, 733 and 723; ^1H NMR (300 MHz, $CDCl_3$) δ : 3.63 t (*J* 6.0 Hz, -OCH_2-), 2.16 sbr (OH), 1.26 sbr (56H), 0.88 t (*J* 6.6 Hz, 3H); ^{13}C NMR (75.45 MHz, $CDCl_3$) δ : 63.1 (C-l), 32.9 (C-2), 32.0 (C-28), 29.7 (C-5 to C-27), 29.4, 25.8, 27.7, 14.1 (C-30); CIMS : isobutane *m/z* 439 $[M^+ + 1]$.

n-Octacosanol : White microcrystalline solid, m.p. 80–82 °C; IR (nujol) ν (cm^{-1}) : 3279, 1058, 730 and 720; ^1H NMR (300 MHz, $CDCl_3$) δ : 3.62 t (*J* 6.0 Hz, -OCH_2-), 1.25 sbr (52H), 0.85 t (*J* 6.6 Hz, 3H); EIMS : *m/z* 392 $[M\text{-}18]^+$, 377, 363, 349, 335, 321, 139.

Extraction of heartwood of Kigelia pinnata DC. :

The heartwood of *Kigelia pinnata* was collected from the Rajasthan University campus, Jaipur. Air-dried and finely powdered heartwood shavings (5 kg) were extracted with chloroform over a boiling water-bath for 3 × 12 h. Extract was concentrated to dryness *in vacuo* and dissolved in ether and then extracted with 2 *N* Na_2CO_3 aqueous solution. Deep red sodium carbonate soluble fraction was acidified with 2 *N* HCl to give lapachol as yellow mass, 50 g as compound **6**.

Lapachol : Bright yellow needles, m.p. 139–140 °C; UV-VS λ_{max} (EtOH) : 251, 278, 333 nm; IR (KBr) ν (cm^{-1}) : 3350, 1660, 1637, 1591; ^1H NMR (300 MHz, $CDCl_3$) δ : 1.68 s (CH_3), 1.78 s (CH_3), 3.30 dbr (*J* 7 Hz, -CH_2-), 5.20 tq (*J* 7.1 Hz, =CH), 7.32 s (OH), 7.67 dd (*J* 8.8 Hz, 2 × ArH), 8.07 dd (*J* 8.2 Hz, 2 × ArH); MS : *m/z* 242 $[M^+]$ ($C_{15}H_{14}O_3$).

Alkali insoluble fraction was chromatographed over neutral alumina (deactivated with 10% aq. AcOH) and eight fractions were collected. First fraction upon elution with petroleum ether gave blue green solid, 50 mg of tecomaquinone-I as compound **7**. Second fraction, when

eluted with petroleum ether-benzene (3 : 1) afforded orange needles, 45 mg of dehydro-α-lapachone as compound **8**. Third and fourth fractions were eluted with pet-ether-benzene (1 : 1) to obtain colourless solids, 80 mg and 70 mg of compounds **2** and **3**. Fifth fraction eluted with pet-ether-benzene (2 : 3) was further purified by prep. TLC to get colourless solid, 40 mg of D-sesamin as compound **9**. Sixth fraction eluted with pet-ether-benzene (1 : 3) was purified by prep. TLC to give colourless needles, 80 mg of paulownin as compound **10**. Seventh fraction eluted with benzene gave white needles, 200 mg of wodeshiol as compound **11**. The last fraction eluted with benzene-ethyl acetate (3 : 1) yielded yellow solid which was purified by prep. TLC to give yellow needles, 80 mg of kigelinone as compound **12**.

Tecomaquinone-I : Blue green crystals, m.p. 194–195 °C; UV-VS λ_{max} (EtOH) : 271, 343, 422, 578 nm; IR (nujol) ν (cm^{-1}) : 1664, 1650; ^1H NMR (300 MHz, $CDCl_3$) δ : 1.64 sbr (CH_3), 1.66 sbr (CH_3), 1.60 d (*J* 1.28 Hz, CH_3), 2.05 d (*J* 1.33 Hz, CH_3), 5.58 d (*J* 9.65 Hz, =CH), 6.16 d (*J* 9.65 Hz, =CH), 6.42 d (*J* 9.34 Hz, =CH), 5.45 dm (*J* 9.34, 1.33, 1.28 Hz, CH), 7.51 m (2 × ArH), 7.75 m (2 × ArH), 8.17 m (4 × ArH); MS : *m/z* 448 [M^+] ($C_{30}H_{24}O_4$). On refluxing its 15 mg in AcOH with zinc dust gave tectol, 10 mg, m.p. 215–216 °C.

Dehydro-α-lapachone : Orange needles, m.p. 142–143 °C; UV-VS λ_{max} (EtOH) : 267, 276, 333 and 434 nm; IR (KBr) ν (cm^{-1}) : 1680, 1640, 1632 and 1580; ^1H NMR (300 MHz, $CDCl_3$) δ : 1.54 s (2 × CH_3), 5.76 d (*J* 11 Hz, =CH), 6.73 d (*J* 11 Hz, =CH), 7.72 m (2 × ArH), 8.13 m (2 × ArH); MS : *m/z* 240 [M^+] ($C_{15}H_{12}O_3$).

D-Sesamin : Colourless prisms, m.p. 122–123 °C; [α] + 71°; IR (nujol) ν (cm^{-1}) : 1610, 1255, 1185, 1100, 930 (OCH_2O); ^1H NMR (300 MHz, $CDCl_3$) δ : 3.04 m (H-1 and H-5), 4.71 d (*J* 4.2 Hz, H-2 and H-6), 3.87 dd (*J* 3.66, 9.16 Hz, H-4a and H-8a), 4.23 dd (*J* 6.9, 9.16 Hz, H-4e and H-8e), 5.95 s (2 × OCH_2O), 6.78 m (6 × ArH); MS : *m/z* 354 [M^+] ($C_{20}H_{18}O_6$).

Paulownin : Colourless needles, m.p. 104–105 °C, $[\alpha]_D$ + 28°; IR (nujol) ν (cm^{-1}) : 3300, 1610, 1260, 1040, 940; ^1H NMR (300 MHz, $CDCl_3$) δ : 3.04 m (H-5), 4.80 s (H-2), 4.83 d (*J* 5.1 Hz, H-6), 3.81 dd (*J* 9.6 Hz, H-4a), 3.90 d (*J* 9.6 Hz, H-8a), 4.47 dd (*J* 8.4, 9 Hz, H-4e), 4.01 d (*J* 9.6 Hz, H-8e), 5.90 s (OCH_2O), 5.88 s (OCH_2O), 6.6–6.9 m (6 × ArH); MS : *m/z* 370 [M^+] ($C_{20}H_{18}O_7$); acetate (Ac_2O/pyridine), m.p. 145–146 °C.

Wodeshiol : Colourless needles, m.p. 152–153 °C; $[\alpha]_D$ −12°; IR (nujol) ν (cm^{-1}) : 3480 (OH), 1615 (arom.), 930 (-OCH_2O-); ^1H NMR (300 MHz, $CDCl_3$) δ : 2.41 sbr (OH), 4.04 s (H-8a, H-8e, H-4a, H-4e), 4.96 s (H-2 and H-6), 5.95 s (2 × OCH_2O), 6.7–6.88 m (6 × ArH); ^{13}C NMR (75.45 MHz, $CDCl_3$) δ : 87.53 (C-1, C-5), 76.30 (C-4, C-8), 86.83 (C-2, C-6), 107.56 (C-2′, C-2″), 108.28 (C-5′, C-5″), 120.31 (C-6′, C-6″), 101.15 (OCH_2O), 147.67 and 147.92 (C-3′, C-3″, C-4′, C-4″); MS : *m/z* 386 [M^+] ($C_{20}H_{18}O_8$).

Kigelinone : Yellow needles, m.p. 153–154 °C; UV-VS λ_{max} (MeOH) : 233, 247, 300 and 396 nm; IR (KBr) ν (cm^{-1}) : 1674, 1640; ^1H NMR (300 MHz, $CDCl_3$) δ : 1.65 d (*J* 6.5 Hz, -CH_3), 2.03 sbr (OH), 5.05 q (*J* 6.5 Hz, >CHOH), 6.84 s (H-3), 7.26 dd (*J* 8.4, 1.2 Hz, H-6), 7.60 dd (*J* 8.4, 6.6 Hz, H-7), 7.76 dd (*J* 7.5, 1.2 Hz, H-8), 12.18 s (OH); MS : *m/z* 258 [M^+] ($C_{14}H_{10}O_5$).

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