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UNUSUAL HOMOLOGOUS LONG-CHAIN ALKANOIC ACID ESTERS OF LUPEOL FROM *KOELPINIA LINEARIS*

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Key Word Index—*Koelpinia linearis*; Compositeae; pentacyclic triterpenoid esters.

Abstract—An unusual series of five long-chain alkanoic acid (C_{14}–C_{18}) esters of lupeol was isolated from the methanol extract of *koelpinia linearis* and characterized by chemical and spectroscopic methods, including ^{13}C NMR. The spectral assignments were achieved by APT and DEPT techniques.

INTRODUCTION

Following our earlier report [1] that *Koelpinia linearis* [2] is a rich source of triterpenoids, we describe the isolation and characterization of an unusal homologous series of five long-chain alkanoic acid esters of lupeol, in addition to lupeol and lupenone, from the methanolic extract of the aerial parts of the plant.

RESULTS AND DISCUSSION

The chromatography of the methanolic extract of the aerial parts of *Koelpinia linearis* yielded seven crystalline compounds (**1**–**7**). The positive LB, TNM, TCA [3], Baeyer's tests and HR mass spectra of **1**–**5** ($[M]^+$ at *m/z* 636.5859, $C_{44}H_{76}O_2$ (**1**); 650.6025, $C_{45}H_{78}O_2$ (**2**); 664.6187, $C_{46}H_{80}O_2$ (**3**); 678.6387, $C_{47}H_{82}O_2$ (**4**); and 690.6490, $C_{48}H_{84}O_2$ (**5**) indicated that they belonged to a homologous series of triterpenoids, carrying a long side-chain and two centres of unsaturation (ν_{max} cm^{-1} 1690, 880; exocylic disubstituted double bond [4], 1750–O–C=O). Their ^1H NMR contained resonance signals characteristic of lup-20(29)-ene [5, 6] with a 3β-ester moiety (δ_H4.40, 1H, *dd*, J = 9.6, 8 Hz, H-3) [7]. On alkaline hydrolysis the compounds yielded the corresponding fatty acid and lupeol (**6**) which was confirmed by oxidation to lupenone (**7**) and comparison of their spectra and co-TLC with authentic samples.

The 70 eV mass spectra of **1**–**5** confirmed the lup-20(29)-ene skeleton [8] with the base peak at *m/z* 189, like that of lupeone [10]. But the 12 eV mass spectra contained the molecular ion peak as the base peak. The high-mass region of **1**–**5** and their acids showed the loss of methyl from $[M]^+$ and the fragment ion spacings at 56 amu which is typical of unbranched long-chain alkanoic acids [9].

The ^{13}C NMR signals, assigned by known techniques, including APT and DEPT (90°) [11–16] confirmed the structures of **1**–**5** (δ_C 150.9 (C-20), 109.3 (C-29), 173.3 (C-1′)) [6], and revealed that the long-chain ester moiety has an effect on the ^{13}C NMR shifts of C-2, C-4 and C-24. The spectral study and an examination of molecular models suggested that the long-chain ester moiety flattened the ring *A* to a quasi-chair conformation.

Compounds **1**–**5** were thus characterized as lup-20(29)-en-3-tetradecanoate (myristate) (**1**), 3-pentadecanoate (**2**), 3-hexadecanoate (palmitate) (**3**), 3-heptadecanoate (margarate) (**4**) and 3-octadecanoate (stearate) (**5**). The ratio of lupeol margarate to lupeol stearate has been determined as 1 : 3. The major ester was lupeol myristate. The coexistence of this homologous series of long-chain alkanoic acid esters in a plant is intriguing because the odd carbon containing alkanoic acids are seldom encountered in the plant kingdom.

EXPERIMENTAL

Mps: uncorr. IR spectra were recorded on KBr discs; ^1H NMR at 250 MHz; MS was run at 70 eV and 12 eV. ^{13}C NMR, APT and DEPT (90°) experiments were done on a Brucker instrument.

Isolation of Compounds. The MeOH extract of the aerial parts of *K. linearis* (U. Dhar; V. No. 102/88; CCRUM, K-U) was chromatographed on a silica gel column. The petrol (60–80°) frs showed positive for tests

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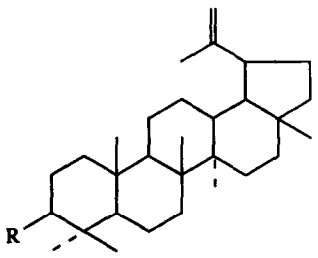

R	
1	$OCOC_{13}H_{27}$
2	$OCOC_{14}H_{29}$
3	$OCOC_{15}H_{31}$
4	$OCOC_{16}H_{33}$
5	$OCOC_{17}H_{35}$
6	OH
7	O

for triterpenoids. One of these fractions (20 g) was resolved by repeated CC over 5% $AgNO_3$–silica gel followed by chromatography, on silica gel-G discs, using petrol–$CHCl_3$ (19 : 1) to yield **1–5** purified by crystallization from C_6H_6–EtOH.

Hydrolysis of **1–5**. Compounds **1–5** (40 mg) were dissolved separately in $CHCl_3$ (25 ml) and refluxed with 1.2 N NaOH (20 ml) for 2–3 hr. After usual work up, the acids and **6** were recovered, dried and chromatographed on silica gel pencil columns. The acids were analysed directly by MS and **6** was recrystallized from MeOH.

^{1}H NMR of **1–5** ($CDCl_3$). δ0.74–0.78 (3H, *s*, H-24), 0.80–0.83 (3H, *s*, H-28), 0.82–0.86 (3H, *s*, H-25), 0.88 (3H, *s*, H-23), 0.92–0.98 (3H, *s*, H-27), 1.03 (3H, *s*, H-26), 1.26 (3H, *s*, term. CH_3 ester), 1.68 (3H, *s*, H-30), 2.29 (1H, *t*, *d*, J = 11.5, 6; 9 Hz, H-19), 2.50–2.60 (2H, *m*, $-COCH_2-$), 4.42 (1H, *dd*, J = 9.6, 8 Hz, H-3), 4.58 (1H, *br d*, J = 6 Hz, H-29a), 4.69 (1H, *br d*, J = 6 Hz, H-29b).

Lupeol-20(29)-en-3-tetradecanoate (**1**). Mp 102–103°, $[\alpha]_D^{25}$ + 34.2[9] ($CHCl_3$; *c* 0.1), MS *m/z*; 636.5859 $[M]^+$ (calc. for $C_{44}H_{76}O_2$ 636.5844). MS *m/z*: 636 $[M]^+$), 621, 580, 524, 468, 429, 413 $[M - C_{14}H_{28}O_3]^+$, 409, 408, 406, 393, 365, 298, 257, 229, 218, 204, 189 (100%). 150.9 (C-20). On hydrolysis gave myristic acid semisolid, mp 56–57° (lit. 58° [16]. $[M]^+$ at *m/z* 228.2084 (calc. for $C_{14}H_{28}O_2$, 228.2076 (100%).

Lupeol-20(29)-en-3-pentadecanoate (**2**). Mp 122–123° $[\alpha]_D^{25}$ + 34.3° ($CHCl_3$; *c* 0.1). $[M]^+$ at *m/z* 650.6025 (Calc. for $C_{45}H_{78}O_2$, 650–6001), 635, on hydrolysis gave pentadecanoic acid, semisolid, mp 50–51° (lit. 52.1° [16]). $[M]^+$ at *m/z* 242.2240 (calc. for $C_{15}H_{30}O_2$, 242.2223) (100% 12 eV).

Lupeol-20(29)-en-3-hexadecanoate (**3**). Mp 124–125° $[\alpha]_D^{20}$ + 34.0° ($CHCl_3$; *c* 0.09). $[M]^+$ at *m/z* 664.6187 (Calc. for $C_{46}H_{80}O_2$, 664.6157). On hydrolysis gave palmitic acid, semisolid mp 60–61° (lit. mp 63.1° [16]). $[M]^+$ at *m/z* 256.2389 (calc. for $C_{16}H_{32}O_2$, 256.2386) (100% 12 eV).

Lupeol-20(29)-en-3-heptadecanoate (**4**). Mp 135–136° $[\alpha]_D^{20}$ + 34.3° ($CHCl_3$; *c* 0.1). $[M]^+$ at *m/z* 678.6387 (Calc. for $C_{47}H_{82}O_2$, 678.6315). On hydrolysis gave margaric acid, semisolid, mp 58–59° (lit. mp 61.3° [16]). $[M]^+$ at *m/z* 270.2544 (calc. for $C_{17}H_{34}O_2$, 270.2542) (100% 12 eV).

Lupeol-20(29)-en-3-octadecanoate (**5**). Mp 146.147° $[\alpha]_D^{20}$ + 34.2° ($CHCl_3$; *c* 0.1). $[M]^+$ at *m/z* 692.6490 (Calc. for $C_{48}H_{84}O_2$, 692.6470). On hydrolysis gave stearic acid, crystals mp 68–68.5° (lit. 70.5° [16]). $[M]^+$ at *m/z* 284.2700 (calc. for $C_{18}H_{36}O_2$, 284.2697) (100% 12 EeV);

Lupeol-20(29)-en-3-ol (**6**). Mp. 212°. $[\alpha]_D^{20}$ (EtOH) + 23° (*c* 0.5) IR ν_{max} Cm^{-1}: 3510, 1680, 810. MS: $[M]^+$ at *m/z* 426; $C_{30}H_{50}O$.

Lupeol-20(29)-en-3-one (**7**) Mp. 170° *IR* ν_{max} cm^{-1}: 1705, 1680, 1365, 1340, 1240, 880. MS *m/z*: 424, $C_{30}H_{48}O$.

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