

LONG CHAIN ESTERS OF *AESCULUS INDICA*¹

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In continuation of our chemical investigation on Indian horse chestnuts, seeds of *Aesculus indica* L. (Hippocastanaceae) (1,2), we have now isolated two unsaturated and two saturated aliphatic esters, designated as compounds A, B, C, and D, from the CHCl_3 extract.

Compound A, a viscous liquid, had its absorption bands at 2910, 2850, and 715 cm^{-1} for its long chain, at 1735 cm^{-1} for ester carbonyl, and at 1685 cm^{-1} for an isolated double bond. Its ^1H nmr exhibited a pair of olefinic methine

signals around 970 cm^{-1} in the ir spectrum. An oxymethylene quartet ($J = 6.0$ Hz) at δ 4.04 in addition to a broad triplet ($J = 6.0$ Hz) at δ 0.81 due to methyl groups (one terminal) led us to predict the presence of an OCH_2CH_3 substituent as an esterifying residue (5).

Its mass spectrum had a $[\text{M}]^+$ at m/z 310 revealing the molecular formula $\text{C}_{20}\text{H}_{38}\text{O}_2$. The ion at m/z 45 and the loss of 45 mass units from the $[\text{M}]^+$ resulting in the formation of an ion at m/z 265 were characteristic of a terminal

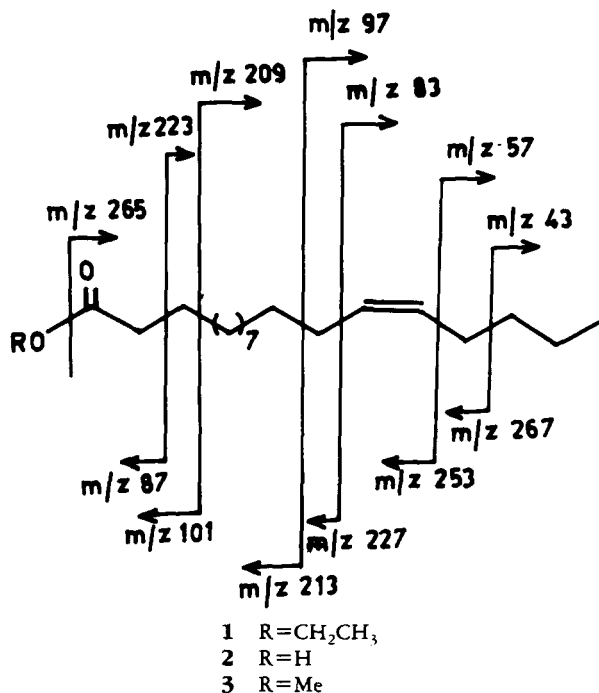


FIGURE 1. Mass Fragmentation Pattern of 1, 2, and 3.

signals at δ 5.25 as broad doublets ($J = 11$ Hz) of triplets ($J = 5.5$ Hz), hence revealing the *cis* geometry of the olefinic bond (3,4) which is moreover supported by the absence of an absorp-

tion around 970 cm^{-1} in the ir spectrum. This conclusion was further substantiated by the presence of an ion at m/z 87 corresponding to $\text{CH}_2\text{COOCH}_2\text{CH}_3$ (5). The location of the double bond at C-13 was determined from prominent β -fission (6) ions obtained at m/z 57, 253, 83, and 227 and

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α -fission (6) ions at 43, 267, 97, and 213 (Figure 1). There were fragments corresponding to the sequential loss of 14 mass units between m/z 223 and m/z 83 which revealed the existence of a straight chain up to C-12 followed by double bond at C-13.

On alkaline hydrolysis compound A yielded an acid **2**, which showed a carboxylic group absorption band at 1710 cm^{-1} in its ir spectrum and the absence of a quartet at δ 4.04 and the presence of a sharp triplet at δ 0.85 in its $^1\text{H-nmr}$ spectrum. Its ms exhibited $[\text{M}]^+$ m/z 282 corresponding to $\text{C}_{18}\text{H}_{34}\text{O}_2$, fragments due to the loss of 45 and 60 mass units, and remaining fragments which were quite similar to compound A. This indicated a C_{18} straight chain with olefinic unsaturation at C-13 which was in accordance with the appearance of both olefinic methines at δ 5.30 ($J_{13,14} = 11\text{ Hz}$, $J_{12,13} = J_{14,15} = 5.5\text{ Hz}$). Thus, **2** could be identified as octadeca-(13Z)-enoic acid and consequently compound

A as ethyl octadec-(13Z)-enoate [**1**], which was in full accordance with its ^{13}C shielding data.

The $^{13}\text{C-nmr}$ spectrum of compound A (Table 1) displayed resonances at δ 173.42 for ester carbonyl, δ 129.73 and δ 129.51 for olefinic methines, δ 33.97 for a methylene adjacent to an ester carbonyl group, and δ 59.98 and δ 14.01 corresponding to an OCH_2CH_3 grouping. The definitive ^{13}C signal assignments were made by comparison with the related n -alkane (7,8) and with other similar esters (9–11). The Z configuration of the olefinic bond (12–14) was indicated by the appearance of an allylic methylene at δ 27.01. The remaining thirteen methylene signals were observed between δ 31.71 and 24.76 together with the signals at δ 22.46 and 14.01 due to a terminal CH_2CH_3 group. This confirmed the presence of a C_{18} straight chain acid with an olefinic unsaturation at C-13 and an ethyl group as an ester moiety, thus unequivocally

TABLE 1. $^{13}\text{C-nmr}$ Data for Ethyl Octadec-(13Z)-enoate [**1**], Methyl octadec-(13Z)-enoate [**3**], Ethyl Heptadecanoate, and Methyl Heptadecanoate.

Carbon	Compound			
	1	3	ethyl heptadecanoate	methyl heptadecanoate
1	175.68	173.42	175.77	173.46
2	33.97	33.91	33.95	33.66
3	24.76	24.78	24.66	24.66
4	28.81	28.91	28.91	28.91
5	29.55 ^a	29.49 ^a	29.83 ^a	29.69 ^a
6	29.47 ^a	29.49 ^a	29.03 ^a	29.03 ^a
7	29.32 ^a	29.49 ^a	29.23 ^a	29.23 ^a
8	29.11 ^a	29.14 ^a	29.44 ^a	29.44 ^a
9	29.06 ^a	29.14 ^a	29.44 ^a	29.44 ^a
10	28.94 ^a	28.96 ^a	29.44 ^a	29.44 ^a
11	29.11 ^a	28.96 ^a	29.44 ^a	29.44 ^a
12	27.01	27.02	29.44 ^a	29.44 ^a
13	129.73	129.79	29.12 ^a	29.12 ^a
14	129.51	129.54	29.91 ^a	29.91 ^a
15	27.01	27.02	31.68	31.68
16	31.71	31.73	22.39	22.39
17	22.46	22.48	12.68	13.68
18	13.87	13.87	—	—
OCH_2CH_3	59.98	—	59.58	—
OCH_2CH_3	14.01	—	13.86	—
OMe	—	51.15	—	50.76

^aAssignments may be reversed in any vertical column.

supporting the proposed structure **1** for compound A.

Compound B, $C_{19}H_{36}O_2$ ($[M]^+$ m/z 296), exhibited a close resemblance of its ir, 1H -, and ^{13}C -nmr spectral data with those for compound A. However, instead of ethoxymethylene at δ 4.04, it showed a sharp singlet at δ 3.62 due to carboxymethyl group in its 1H -nmr spectrum; we therefore inferred that it was a methyl ester. The presence of a strong peak at m/z 74 arose by McLafferty rearrangement, and a fragment ion at m/z 222, due to the rest of the molecule, moreover confirmed its methyl ester behavior. This was further supported by the presence of the signals at δ 175.68 and δ 51.15 assignable to a carboxymethyl group in its ^{13}C -nmr spectrum, whereas remaining ^{13}C spectral data (Table 1) was quite similar to that of compound A. Alkaline hydrolysis yielded an acid identified as **2**. Hence, compound B can be identified as methyl octadec-(13Z)-enoate [**3**].

Compound C, a colorless viscous liquid, analyzed for $C_{19}H_{38}O_2$ and showed ir absorption bands at 1732 and 1270 cm^{-1} for the ester group. The presence of a quartet at δ 4.01 and a broad triplet at δ 0.80 suggested it to be an ethyl ester. This was supported by its ms, which exhibited $[M]^+$ at m/z 298 and fragment ions due to the loss of m/z 45 and m/z 73 and other fragments consistent with its identity as ethyl heptadecanoate.

Compound D, $C_{18}H_{34}O_2$ ($[M]^+$ m/z 284), exhibited significant resemblance of its ir, 1H -, and ^{13}C -nmr spectral data with those for compound C except for the replacement of an ethoxyl group by a methoxyl group (1H nmr δ 3.55, 3H; ^{13}C nmr, δ 50.76). Based on its ms and ^{13}C -nmr spectral data, it was identified as methyl heptadecanoate.

EXPERIMENTAL

GENERAL EXPERIMENTAL PROCEDURES.—

Melting points were taken on a Toshniwal melting point apparatus and are not corrected. Spectra were recorded with the following instruments: ir,

Perkin-Elmer 399B model; 1H nmr and ^{13}C nmr, Varian Ft-80A in $CDCl_3$ with TMS as an internal standard. Si gel (60–120 mesh, BDH) was used for cc. All R_f values were reported on tlc using Si gel G. Plates (0.075 mm) were used for preparative layer chromatography.

PLANT MATERIAL AND EXTRACTION.—The seeds of *A. indica* were collected from Kulu, Himachal Pradesh, India, during the autumn of 1983 and identified at the Botany Department of this Institute. A voucher specimen is deposited in CIMAP herbarium collection, No. 1851. The air-dried, powdered seeds (1 kg) were defatted with *n*-hexane (5×2.5 liters) and then extracted with $CHCl_3$ (5×3 liters). The total $CHCl_3$ extract was concentrated under reduced pressure to give a brown viscous mass (25 g), which was chromatographed over Si gel (500 g) and eluted with $CHCl_3$ and an increasing amount of MeOH in $CHCl_3$. The fractions 2–4 obtained by elution with $CHCl_3$ were combined and subjected to repeated cc followed by tlc [petroleum ether- C_6H_6 (8:2)] to yield compound A (105 mg), compound B (55 mg), compound C (85 mg), and compound D (42 mg).

Compound A [1].—Colorless viscous liquid, ir ν max (neat) 2930, 2855, 1735, 1460, 1440, 1365, 1240, 1170, 720 cm^{-1} ; 1H nmr δ 0.81 (6H, t, $J = 6$ Hz, OCH_2CH_3 , H_3 -18), 1.19 (24H, br s, $12 \times CH_2$), 1.95 (4H, m, H_2 -12, 15), 2.21 (2H, t, $J = 6$ Hz, H_2 -2), 4.04 (2H, q, $J = 6$ Hz, OCH_2CH_3), 5.25 (2H, dt, $J_{13,14} = 11$ Hz, $J_{12,13} = J_{14,15} = 5.5$ Hz, H-13, 14); ms m/z 310, 296, 284, 267, 264, 255, 253, 239, 227, 222, 213, 199, 185, 171, 157, 143, 129, 115, 100, 97, 87, 83, 69, 55, 43, 41; ^{13}C nmr see Table 1.

Alkaline hydrolysis of compound A.—Compound A [**1**] (50 mg) was refluxed with 5% aqueous KOH solution, worked up as usual, and on crystallization from a $CHCl_3$ /MeOH mixture yielded colorless crystals of the acid **2**: mp 56°; ir ν max (KBr), 2920, 2840, 1710, 1460, 1410, 720 cm^{-1} ; 1H nmr δ 0.85 (3H, t, $J = 6$ Hz, H_3 -18), 1.24 (24H, br s, $12 \times CH_2$), 1.98 (4H, m, H_2 -12, 15), 2.31 (2H, t, $J = 6$ Hz, H_2 -2), 5.30 (2H, t, $J = 6$ Hz, H-13, 14); ms m/z 282, 264, 256, 227, 222, 213, 219, 185, 171, 157, 143, 129, 115, 111, 101, 97, 86, 82, 73, 68, 57, 55, 43, 41.

Compound B [3].—Colorless liquid, ir ν max (neat) 2930, 2855, 1740, 1460, 1435, 1360, 1250, 1170, 720 cm^{-1} ; 1H nmr δ 0.86 (3H, t, $J = 6$ Hz, H_3 -18), 1.12 (24H, br s, $12 \times CH_2$), 1.98 (4H, m, H_2 -12, 15), 2.26 (2H, t, $J = 6$ Hz, H_2 -2), 3.62 (3H, s, COOMe), 5.28 (2H, t, $J = 5.5$ Hz, 6 Hz, H-13, -14); ms m/z 296, 271, 265, 239, 228, 223, 213, 200, 199, 185, 171, 157, 143, 129, 115, 111, 101, 97, 87, 83, 74, 69, 57, 55, 43, 41; ^{13}C nmr see Table 1.

Alkaline hydrolysis of compound B.—Compound B (20 mg) was hydrolyzed with 5% aqueous KOH solution and worked up as usual. The acid was identified as **2** (mp, co-tlc, ir, ^1H nmr).

Compound C (ethyl heptadecanoate).—Colorless liquid; ir ν max (neat) 2920, 2825, 1732, 1440, 1350, 1240, 1140, 670 cm^{-1} ; ^1H nmr δ 0.80 (6H, t, $J=6$ Hz, CH_2CH_3 , OCH_2CH_3), 1.58 (28H, br s, $14 \times \text{CH}_2$), 2.19 (2H, t, $J=6$ Hz, $\text{OCOCH}_2\text{CH}_2$), 4.01 (2H, q, $J=6$ Hz, OCH_2CH_3); ms m/z 298, 271, 256, 242, 226, 228, 212, 198, 184, 170, 156, 142, 128, 114, 100, 86, 74, 57, 55, 43; ^{13}C nmr see Table 1.

Compound D (methyl heptadecanoate).—Colorless liquid, ir ν max (neat) 2920, 2848, 1730, 1440, 1410, 1352, 1240, 1145, 670 cm^{-1} ; ^1H nmr δ 0.80 (3H, t, $J=6$ Hz, CH_2CH_3), 1.58 (28H, br s, $14 \times \text{CH}_2$), 2.19 (2H, t, $J=6$ Hz, $\text{OCOCH}_2\text{CH}_3$), 3.55 (3H, s, COOCH_3); ms m/z 284, 226, 212, 198, 184, 156, 142, 128, 100, 86, 74, 59, 43; ^{13}C nmr see Table 1.

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