3. R. Scartazzini and H. Bickel, *Heterocycles*, **7**, 1165 (1977).
4. O. Zak, W. A. Vischer, C. Schenk, W. Tosch, W. Zimmermann, J. Regos, E. R. Suter, F. Kradolfer and J. Gelzer, *J. Antibiot.*, **29**, 653 (1976).
5. J. Gosteli, *Chimia*, **30**, 13 (1976).
6. M. Gorman and C. W. Ryan, *"Cephalosporins and Penicillins-Chemistry and Biology"*, ed. E. H. Flynn, Academic Press, New York, p. 532 (1972).
7. M. Charton, *"The Chemistry of Alkenes"*, ed. J. Zabicky, Interscience, New York, Vol. 2, pp. 511-610 (1970).
8. S. D. Burke and P. A. Grieco, *Org. React.*, **26**, 361 (1979).
9. M. Suda, *Synthesis*, 714 (1981).
10. H. Yamanaka, T. Chiba, K. Kawabata, H. Takasugi, T. Masugi and T. Takaya, *J. Antibiot.*, **38**, 1738 (1985).
11. C. H. Lee, C. J. Moon, K. S. Kim, J. H. Kim and D. W. Kim, *Bull. Korean Chem. Soc.*, **8**, 336 (1987).
12. C. N. Herbschwerlen and G. Schmid, EP 73061; *Chem. Abstr.*, **99**, 38291 C (1983).
13. R. Bucourt, R. Heymes, A. Lutz, L. Penasse and J. Perronet, *Tetrahedron*, **34**, 2233 (1978).

A Convenient Synthesis of 1-Triacontanol, A Plant Growth Regulator

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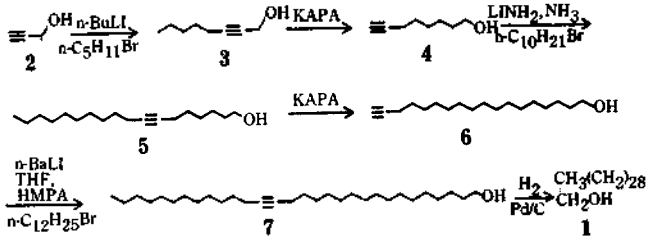
1-Triacontanol (1) is a naturally occuring fatty alcohol with extremely long chain length isolated as a principal contituent of wax derived from alfalfa leaves (*Medicago sativa L.*).[1] It was reported by Ries *et al.*[2] that 1-triacontanol (1) is a plant growth regulator for several crop species including rice. Recently, triacontyn-1-ols and triaconten-1-ols which have double or triple bond in the straight carbon skeleton have been reported[3] to be better plant growth regulators. Other higher saturated alcohols (C-26 and C-28) were also reported to possess biological activity such as insect feeding stimulant[4]. Several syntheses of 1 have been reported.[5]

We have investigated a general and practical procedure for the synthesis of the long chain saturated and unsaturated alcohols. Herein, we wish to report a convenient synthesis of 1-triacontanol (1) which is simple, uses cheap raw mateials, and is well suited for large scale preparations for 1 and other saturated and unsaturated long chain alcohols.

By the conventional method, 7-octyn-1-ol (4) was easily prepared. Alkylation of dianion of propargyl alcohol (2) with 1-bromopentane gave 2-octyn-1-ol (3), which was converted to 7-octyn-1-ol (4)[6] using Brown's acetylene-zipper KAPA in which the triple bond was shifted to the terminal position in 77% overall yield from propargyl alcohol (2) (Scheme 1). Chain elongation of 7-octyn-1-ol (4) by alkylation with 1-bromodecane furnished 7-octadecyn-1-ol (5) in 75% yield. The acetylenic alcohol 5 was subjected to another acetylene-zipper reaction using potassium hydride in 1,3-diaminopropane (KAPA) to provide 17-octadecyn-1-ol (6) in 88% yield. Further alkylation of dianion of the terminal acetylene 6 with 1-bromododecane gave 17-triacontyl-1-ol (7) having the desired number of carbon atoms (C-30 unit), which was directly subjected to catalytic hydrogenation in ethyl acetate using 10% Pd/C at room temperature for 24h to afford 1-triacontanol (1) (Scheme 1). The synthetic compound 1 was identical in every respect (mp, ^{1}H-NMR, IR, MS) with an authentic sample purchased from Aldrich Chem. Co.,



Scheme 1

Thus, the above synthetic sequence of 1 does not involve protection and deprotection and thus offers a facile route for the synthesis of other inaccessible long chain fatty alcohols.

Experimental Section

All chemicals and solvents were analytical grade. IR spectra were recorded on a Shimadzu IR-440 spectrophotometer and were calibrated with the 1601 cm^{-1} absorption of polystyrene. ^{1}H-NMR spectra were taken in chloroform-d at 80MHz on a Bruker WP 80 SY spectrometer. Chemical shifts are reported in ppm relative to internal tetramethylsilane. ^{13}C-NMR spectra (^{1}H-decoupled) were taken in $CDCl_3$ solutions at 22.6MHz using Me_4Si as an internal standard. Mass spectra were obtained using Hewlett-Packcard 5890 GC/MS system at 70 eV. Column chromatography was performed using silica gel (Merck 60, 70-230 mesh) as adsorbent. 7-Octadecyn-1-ol (5)-To a suspension of lithium (1.40g, 200mmol) in liquid ammonia (ca, 200m*l*) in the presence of ferric nitrate (0.50g) was added 7-octyn-1-ol (4) (12.6 g, 100mmol) in THF (100m*l*) followed by 1-bromodecane

(2.32g, 105mmol). The reaction mixture was stirred at reflux for 8h. The ammonia was allowed to evaporated at room temperature, and saturated ammonium chloride solution (100 m*l*) was added. The residue was extracted with ether, and washed with water and saturated sodium chloride solution. The organic layer was dried over anhydrous magnesium sulfate and concentrated *in vacuo*. The crude product was recrystallized from light petroleum ether to give **5** (19.9g, 75%) as a white solid, mp. 32–33 °C, lit[6b]. mp. 30–31 °C. TLC: SiO_2, EtOAc/CH_2Cl_2(1:5), R_f~0.68. IR(KBr): 3300, 2250, 1050cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 0.90 (t, 3H, J = 7Hz), 1.00–1.88(m, 22H), 1.90–2.21 (m, 4H), 3.55(t, 2H, J = 7Hz).

17 – Octadecyn – 1 – ol (6). Potassium hydride (*ca* 35% suspension in mineral oil, 13.3 m*l*, 0.115 mol) was washed two times with dry pentane. Dry 1.3-diaminopropane (99.4m*l*, 1.19 mol) was then added at room temperature, and th reaction mixture was stirred for 2h at room temperature. The reaction mixture was cooled to −15 °C and to this was added 7-octadecyn-1-ol (**5**) (3.00g, 12.6mmol) rapidly and allowed to room temperature and stirred for 1h. The reaction mixture was cooled again to 0 °C and quenched with water (50 m*l*) and 6N hydrochloric acid, and extracted with ether, and washed with water and then brine. The organic layer was dried over anhydrous magnesium sulfate, and evaporated *in vacuo*. The crude product was recrystallized from hexanes to give 17-octadecyn-1-ol (**6**) (2.80g, 87%) as a white plate, mp 56–57 °C. TLC: SiO_2, EtOAc/CH_2Cl_2 (1:5), R_f~0.54. IR(KBr): 3300, 2200 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 1.20–1.70(m, 28H), 1.90(t, 1H, J = 3Hz), 2.10–2.25(m, 2H), 3.01(bs, 1H), 3.60(t, 2H, J = 7Hz).

^{13}C-NMR ($CDCl_3$): 84.74, 67.98, 62.97, 33.17, 29.79, 29.59, 29.08, 28.87, 28.73, 28.62, 28.49, 25.81, 18.37.

MS(m/e): 226(M^+), 248, 225, 109, 97, 83.

Anal. Calcd. for $C_{18}H_{34}O$: C, 81.14: H, 12.86 Found: C, 80.79; H, 13.02.

17 – Triacontyn – 1 – ol (7). A solution of *n*-butyllithium (1.6M, 12.9m*l*, 20.6mmol) was added dropwise to 17-octadecyn-1-ol (**6**) (2.50g, 9.38mmol) in dry THF (9.6 m*l*) and HMPA (8.0 m*l*) under nitrogen atmosphere at −50~−55 °C. The reaction mixture was allowed to 0 °C and stirred for 1h at this temperature. To this solution was added 1-bromododecane (2.45g, 9.96mmol) in dry HMPA (8.0m*l*) at −10 °C. After addition, the temperature was raised to room temperature and stirred for 1h. To the reaction mixture, a small amount of water was added and THF was evaporated under reduced pressure. The residue was extracted with ether, and washed with water and then brine. The organic layer was dried over anhydrous magnesium sulfate, and evaporated *in vacuo*. The crude product was separated by column chromatography using hexanes/EtOAc (6:1) as eluent to afford 17-triacontyn-1-ol (**7**) (3.01g, 63%) as a white solid, mp. 66–67 °C (from hexanes). TLC:SiO_2, EtOAc/CH_2Cl_2 (1:5), R_f~0.69. IR(KBr): 3200, 2200 cm^{-1} ^{1}H-NMR ($CDCl_3$): δ 0.90 (t, 3H, J = 7Hz), 1.10–1.70 (m, 54H), 2.12–2.30 (m, 4H), 3.60 (t, 2H, J = 7Hz). ^{13}C-NMR($CDCl_3$): 80.24, 63.09, 32.83, 31.93, 29.65, 29.20, 28.90, 25.77, 22.66, 20.69, 20.38, 18.78, 14.00, MS(*m/e*): 434(M^+), 418(M^+-18), 321, 282, 223, 195, 111, 97.

Anal. Calcd. for $C_{30}H_{59}O$: C, 82.68; H, 13.65 Found: C, 82.44; H, 13.63.

1 – Triacontanol (1). 17-Triacontyl-1-ol (**1**) (2.00 g, 4.92mmol) was dissolved in dry ethyl acetate (20m*l*) and to this was added 10% Pd/C (50 mg) and hydrogenated at room temperature at atmospheric pressure for 24h. The reaction mixture was filtered through Celite and then concentrated *in vacuo*. The crude product was purified by silica gel column chromatography using 5% acetone in benzene as eluent to afford 1-triacontanol (**1**) (1.80g, 89%). The crude product also can be recrystallized from hexanes to get the pure **1**, mp. 86–88 °C (lit[5g]. mp. 87–88 °C), mixed mp with an authentic sample (from Aldrich Chem. Co.,) remained undepressed. TLC: SiO_2, EtOAc/CH_2Cl_2 (1:5), R_f~0.71. IR (KBr): 3300cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ 0.90 (t, 3H, J = 7Hz), 1.10–1.30 (m, 58H), 3.65(t, 2H, J = 7Hz). MS(*m/e*): 438 (M^+), 420(M^+-18), 392, 153 (base peak).

References

1. A. C. Chibnall, EF. Williams, A. L. Latner, and S. H. Piper, *Biochem. J.*, **27**, 1885 (1933).
2. (a) S. K. Ries, V. Wert, C. C. Sweely, and R. A. Leavitt, *Science*, **195**, 1339 (1977); (b) R. G. Laughlin, R. L. Munyon, S. K. Ries, and V. F. Wert, *Science*, **219**, 1219 (1983).
3. R. R. Iyer and V. R. Mamdapur, *Indian J. Chem., Sect. B*, **25B**, 1216 (1986).
4. M. Mori, *J. Insect. Physiol.*, **28**, 969 (1982).
5. (a) R. M. Robinson, *J. Chem. Soc.*, 1543 (1934); (b) R. G. Jones, *J. Am. Chem. Soc.*, **69**, 2350 (1947); (c) D. E. Ames, R. E. Bowman, and R. G. Mason, *J. Chem. Soc.*, 174 (1950); (d) A. Watanabe, *Bull. Chem. Soc. Japan*, **34**, 398 (1961); (e) K. Maruyama, K. Terada, and Y. Yamamoto, *J. Org. Chem.*, **45**, 737 (1980); (f) N. R. Hunter, T. L. Charlton, N. C. Green, W. J. Fritz, and B. M. Addison, *Org. Prep. Proced. Int.*, **13**, 19 (1981); (g) A. V. R. Rao, M. N. Deshmukh, and M. Kamalan, *Tetrahedron*, **37**, 227 (1981); (h) T. Gibson, *Tetrahedron Lett.*, **23**, 157 (1982); (i) D. Villemin, *Tetrahedron Lett.*, **24**, 2855 (1983); (j) A. V. R. Rao, J. S. Yadav, and G. S. Annapurna, *Synthetic Communications*, **13**, 331 (1983); (k) A. V. R. Rao, K. Ravichandran, N. L. Reddy, *Synthetic Communications*, **14**, 1779 (1984); (l) U. T. Bhalerao, S. J. Rao, and B. D. Tilak, *Tetrahedron Lett.*, **25**, 5439 (1984); (m) U. R. Joshi and A. H. Kapadi, *Synthetic Communications*, **14**, 681 (1984); (n) G. Kirchner and H. Weidmann, *Liebigs Ann. Chem.*, **214** (1985); (o) R. R. Iyer and V. R. Mamdapur, *Chem. Ind.* (London), 398 (1986).
6. (a) C. A. Brown and E. Negishi, *J. Chem. Soc. Chem. Comm.*, 318 (1977); (b) D. E. Ames and T. G. Goodburn, *J. Chem. Soc.;* (C), 1556 (1967).
7. C. A. Brown and A. Yamashita, *J. Am. Chem. Soc.*, **97**, 891 (1975).