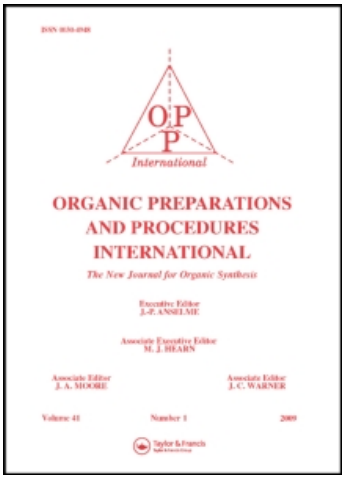


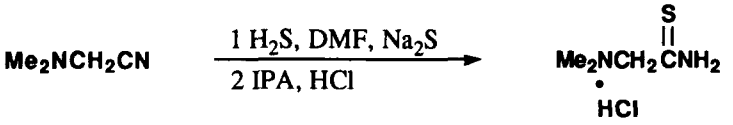

**Organic Preparations and Procedures International**
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t902189982

# A NEW ROUTE FOR SYNTHESIS OF 1-TRIACONTANOL

B. V. S. K. Rao[a]; R. Supharao[a]
[a] Oils and Fats Division, Indian Institute of Chemical Technology, Hyderabad, INDIA

**To cite this Article** Rao, B. V. S. K. and Supharao, R.(1992) 'A NEW ROUTE FOR SYNTHESIS OF 1-TRIACONTANOL', Organic Preparations and Procedures International, 24: 1, 67 — 70
**To link to this Article: DOI:** 10.1080/00304949209356703
**URL:** http://dx.doi.org/10.1080/00304949209356703

affords the product in 85 to 90% yield.




## EXPERMENTAL SECTION

**N,N-Dimethylaminothioacetamide.**- A 1 L stainless steel Parr reactor vessel was charged with dimethylaminoacetonitrile (53.4 g, 0.636 mol), a catalytic amount of sodium sulfide (5.46 g, 0.07 mol), and dry DMF (100 mL). The reactor vessel was sealed and hydrogen sulfide introduced to 60 psi pressure. The mixture was agitated at ambient temperature for 48 hrs while the reactor pressure was maintained at 60 psi with hydrogen sulfide. The reactor was carefully vented and the contents filtered through filter-aid to remove the catalyst. The filtrate was diluted with isopropyl alcohol (100 mL) and the pH was adjusted to < 1.0 with anhydrous HCl (g) while the temperature of the reaction mixture was maintained below 30°. The resulting slurry was agitated while being cooled to 0° and was maintained at 0° for 2 hrs. The crystals were collected and washed with isopropyl alcohol (100 mL). The product was dried at 50° for 24 hrs to provide 86.9 g (88%) of product (purity 99.2%) as a colorless to light green solid, mp. 171-172°, lit.[3] mp. 169-173°.

## REFERENCES

1. R. P. Pioch, U. S. Patent No. 4,375,547; *Chem Abst.*, **99**, 43548 (1983).

2. R. A. Cherkasov, G. A. Kutyrev, and A. N. Pudovik, *Tetrahedron*, **41**, 2567 (1985); M. P. Cava and M. 1. Levinson, *ibid.*, **41**, 5061 (1985).

3. Z. A. Vasil'eva, *J. Org. Chem. USSR*, **6**, 882 (1970), *Chem Abst.*, **73**, 15213 (1970).

**********

## A NEW ROUTE FOR SYNTHESIS OF 1-TRIACONTANOL†

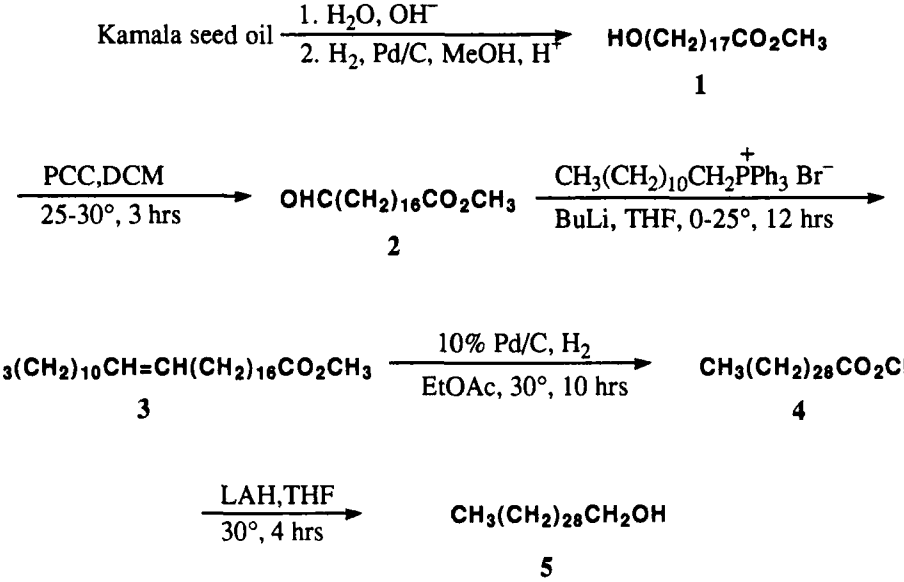
*Submitted by* (05/23/91) B. V. S. K. Rao and R. Subbarao*

*Oils and Fats Division*
*Indian Institute of Chemical Technology*
*Hyderabad-500007, INDIA*

1-Triacontanol is the principal component of alfalfa *(Medicago sativa* L) which has been

shown to promote growth of plants and higher yields of crops.[1] This observation has prompted the development of synthetic routes[2] for 1-triacontanol. The present communication describes a new route based on methyl 18-hydroxyoctadecanoate, derived from *Kamala seed oil*, to afford 1-triacontanol in 68% overall yield.

The synthesis of 1-triacontanol starts with *Kamala seed oil* for the preparation of methyl 18-hydroxyoctadecanoate (**1**)[3] which is oxidized to the aldehyde (**2**) using pyridinium chlorochromate,




and then coupled with the required $C_{12}$ fragment *via* a Wittig reaction and then reduced in 2 steps to yield 1-triacontanol (**5**).

## EXPERIMENTAL SECTION

Melting points were determined on a Mettler FP 51 instrument and are uncorrected. IR spectra were recorded on a Perkin-Elmer Model 283 B spectrophotometer. $^1H$ NMR spectra were recorded on a JEOL FX 90 Q and $^{13}C$ NMR spectra were obtained on a Varian Gemini 200 instruments in $CDCl_3$ using TMS as an internal standard. Chemical shifts are given as δ values. Mass spectra were recorded on a V. G. Micromass 7070 H mass spectrometer at 70 ev. The reactions involving organometallic reagents were conducted under argon atmosphere and the solvents or reagents were transferred with the help of syringes. The anhydrous solvents were freshly prepared prior to use. Dodecyl bromide, triphenylphosphine and pyridinium chlorochromate were obtained from Aldrich Chemical Company, Inc., Milwaukee, WI, USA. Kamala *(Mallotus philippinensis)* seed was purchased from Prakash Nursery, Dehradun, Uttar Pradesh, India.

**Methyl 18-Hydroxyoctadecanoate (1).**- Kamala seed oil, which contains more than 50% 18-hydroxyoctadeca-*cis*-9, *trans*-11, *trans*-13 trienoic acid, was obtained by extraction of the ground seed with ether. The oil (50 g) was saponified with ethanolic potassium hydroxide (0.5 N, 500 mL), the unsaponifiable matter was removed by extraction with diethyl ether and the soap solution was

acidified with dilute hydrochloric acid to liberate the total fatty acids. The mixture of fatty acids on repeated precipitation from petroleum ether (40-60°) and subsequent crystallization of the precipitate from ethyl acetate gave pure 18-hydroxyoctadecatrienoic acid (23 g), mp. 79-80°, lit.[3] 78-79°. The hydroxytrienoic acid (10 g) on hydrogenation in ethyl acetate using 10% Pd/C followed by crystallization of the product from ethyl acetate at -5° provided pure 18-hydroxyoctadecanoic acid (9.7 g), mp. 98-99°, lit.[3] 99-100°. Methyl 18-hydroxyoctadecanoate, mp. 61-62°, lit.[3] 62-62.5°, was obtained from the hydroxy acid in 95% yield by the usual esterification procedure using 2% sulfuric acid in methanol.

$^1$H NMR: δ 3.62 (s, 5H, -$OCH_2$, -$OCH_3$), 2.25 (t, 2H, -$CH_2$-C=O), 1.57 (s, 1H, $D_2O$ exchangeable), 1.25 [bs, 30H, -$(CH_2)_{15}$].

*Anal.* Calcd. for $C_{19}H_{28}O_3$: C, 72.61; H, 12.10. Found : C, 72.26; H, 11.90

**Methyl 18-Oxooctadecanoate (2).**- Methyl 18-hydroxyoctadecanoate (**1**) (3.14 g, 10 mmol.) in dichloromethane (10 mL) was added rapidly to a stirred suspension of pyridinium chlorochromate (3.22 g, 15 mmol) in dichloromethane (15 mL) at room temperature. Further reaction for 3 hrs, at RT followed by usual work-up gave the oxo ester, mp. 51-52°, in quantitative yield. IR (KBr): 1705 (C=O of aldehyde), 1735 cm$^{-1}$ (C=O of ester). $^1$H NMR: δ 9.69 (t, 1H, -CHO), 3.63 (s, 3H, -$OCH_3$) 2.44-2.19 [m, 4H, (-$CH_2$-C=O)$_2$], 1.29 [bs, 3H, -$(CH_2)_{14}$].

$^{13}$C NMR: δ 202.8 (C=O of aldehyde), 174.21 (C=O of ester).

*Anal.* Calcd. for $C_{19}H_{36}O_3$: C, 73.08; H, 11.54. Found : C, 72.95; H, 11.37

**Methyl 18-Triacontenoate (3).**- To a stirred solution of dodecyl triphenylphosphonium bromide (2.29 g, 4.5 mmol)[4] in dry THF (10 mL) at 0°, 15% BuLi in hexane (1.9 mL, 4.5 mmol) was added dropwise. The orange-red ylide was allowed to stir for 15 min at 0°. Then methyl 18-oxooctadecanoate (**2**) (1.17 g, 3.75 mmol) in dry THF (5 mL) was added slowly. The temperature of the reaction mixture was allowed to reach room temperature (25°) and the mixture was stirred for 12 hrs. Water (5 mL) was added, and after a further 30 min stirring, the organic layer was dried and the solvent was removed under reduced pressure. Silica gel (60-120 mesh) column chromatographic purification of the crude material using hexane: diethyl ether (95:5, v/v) as eluent gave 1.29 g (74%) of the title product, mp. 44-45°. NMR data showed that methyl 18-triacontenoate consisted of 90% of *cis*-isomer and 10% *trans*-isomer. IR (KBr): 1745 (C=O of ester); 1640 (C=C), 965 cm$^{-1}$ (HC=CH *trans*, very weak band). $^1$H NMR: δ 5.36 (t, 2H, J = 4.47, -CH=CH-), 3.68 (s, 3H, -$OCH_3$), 2.31 (t, 2H, -$CH_2$-C=O), 2.28-1.98 (m, 4H, -$CH_2$-C=C-$CH_2$), 1.27 [bs, 46H, -$(CH_2)_{23}$], 0.89 (t, 3H, -$CH_3$). Mass: m/z (%) 464 ($M^+$, 0.8), 433 (M-31, 15.0), 432 (M-32, 28.3), 74 (MLRF, 51.7), 55 (100).

*Anal.* Calcd. for $C_{31}H_{60}O_2$: C, 80.17; H, 12.93. Found: C, 80.01; H, 12.65

**Methyl n-Triacontanoate (4).**- Methyl 18-triacontenoate (**3**) (0.928 g, 2 mmol) in ethyl acetate (20 mL), was hydrogenated using 10% Pd/C (90 mg) for 10 hrs at room temperature. The usual work-up gave 0.90 g (97%) of the saturated ester, mp. 70-71°, lit.[2] 71°. IR ($CHCl_3$): 1740 cm$^{-1}$ (C=O of ester). $^1$H NMR: δ 3.63 (s, 3H, -$OCH_3$), 2.29 (t, 2H, -$CH_2$-C=O), 1.31 [bs, 54 H, -$(CH_2)_{27}$] 0.91 (t, 3H, -

$CH_3$). Mass: m/z (%) 466 ($M^+$, 24.2), 74 (MLRF, 100).
*Anal.* Calcd. for $C_{31}H_{62}O_2$: C, 79.83; H, 13.30. Found: C, 79.98; H, 13.48

**1-Triacontanol (5).**- A solution of methyl triacontanoate (4) (0.466 g, 1 mmol) in dry THF (15 mL) was added dropwise to a stirred suspension of LAH (18.8 mg, 0.5 mmol) in dry THF (5 mL) at -10°. The contents were allowed to reach room temperature (25°) over a period of 1 hr and stirred at this temperature for 4 hrs. After the usual work-up with ethyl acetate, the fine precipitate was filtered and washed with THF. The filtrate was dried over anhydrous sodium sulfate, and the solvent was removed on a rotary evaporator. The crude 1-triacontanol on crystallization from petroleum ether (60-80°) furnished 0.44 g (95%) of the pure product, mp. 86-87°, lit.[7] 87-88°. IR (KBr): 3300 cm (-OH): H NMR: δ 3.66 (t, 2H, $-CH_2OH$), 1.58 (s, 1H, $D_2O$ exchangeable), 1.27 [bs, 56H, $-(CH_2)_{28}$], 0.90 (t, 3H, $-CH_3$). Mass: m/z (%) 438 (M), 420 (M-18, 7.5).
*Anal.* Calcd. for $C_{30}H_{62}O$: C, 82.19; H,14.16. Found: C, 81.98; H, 13.98

**Acknowledgennt.**- The authors thank Dr. S. Y. Mhaskar for help in the Wittig reaction.



## REFERENCES

† I. I. C. T. Communication No. 2806

1. S. K. Ries, V. Wert, C. C. Sweeley and R. A. Leavitt, *Science*, **195**, 1339 (1977).

2. A. V. Rama Rao, M. N. Deshmukh and M. Kamalam, *Tetrahedron*, **37**, 227 (1981); A. V. Rama Rao, J. S. Yadav and G. S. Annapurna, *Synth. Commun.*, **13**, 331 (1983); A. V. Rama Rao, K. Ravichandran and N. Laxma Reddy, *ibid.*, **14**, 779 (1984); U. T. Bhalerao, S. Jagadishwar Rao and B. D. Tilak, *Tetrahedron Lett.*, **25**, 5439 (1984); K. Maruyama, K. Terada and Y. Yamamoto, *J. Org. Chem.*, **45**, 737 (1980); J. Penninger, M. Bierman and H. J. Krause, *Fette Seifen Anstrichm.*, **85**, 239 (1983), CA **99**, 139264 b (1983); D. Villemin, *Tetrahedron Lett.*, **24**, 2855 (1983).

3. R. C. Calderwood and F. D. Gunstone, *J. Sci. Food Agric.*, **5**, 382 (1954); J. S. Aggarwal, S. S. Bhatnagar, P. Narain and Karimullah, *J. Sci. Industr. Res.*, **7 B**, 136 (1948); S. C. Gupta, V. N. Sharma and J. S. Aggarwal, *ibid.*, **11 B**, 463 (1952).

4. P. C. Wailes, *Australian J. Chem.*, **12**, 173 (1959).

********