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SYNTHESIS OF TRIACONTAN-1-OL FROM DODECANEDIOIC ACID

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A method has been developed for obtaining triacontan-1-ol — a natural plant growth stimulator. Synthesized triacontan-1-ol has an appreciable influence on the growth and crop yield of tomatoes and on the flowering of asters.

Triacontan-1-ol (I) is an effective natural plant growth stimulator [1, 2]. The influence on the growth activity of homologues of (I) differing in their chain lengths (C_{16}-C_{32}) has been investigated, and not one of them causes an increase in the growth of plants [3]. A number of complex syntheses of the alcohol (I) have been published [4-7]. We have developed a simpler method of obtaining the alcohol (I) from the readily available dodecanediodic acid (II) and 1-bromooctadecane, by the following scheme:

$$\underset{\text{II}}{HOOC(CH_2)_{10}COOH} \rightarrow \underset{\text{III}}{OH(CH_2)_{12}OH} \rightarrow \underset{\text{IV}}{Cl(CH_2)_{12}OH} \rightarrow$$

$$\xrightarrow[2.\ Mg,\ THF]{1.\ n\text{-}PrMgCl} \underset{\text{V}}{ClMg(CH_2)_{12}OMgCl} \xrightarrow[2.\ H_3O^{\oplus}]{1.\ n\text{-}C_{14}H_{29}Br} \underset{\text{I}}{CH_3(CH_2)_{29}OH}$$

Dodecanedioic acid (II) was converted through its diester by a known method [8] into dodecane-1,12-diol (III), which, on treatment with hydrochloric acid by a modified method [8], gave 12-chlorododecan-1-ol (IV) in high yield. Using the method of Cahier et al. [9], the Grignard reagent (V) was obtained from the chlorohydrin (IV) by treating it with an equimolecular amount of n-C_3H_7-MgCl in tetrahydrofuran solution followed by the treatment of the magnesium alcoholate formed with magnesium. The reaction of (V) at −5 to 0°C with 1-bromooctadecane in the presence of catalytic amounts of Li_2CuCl_4 formed the magnesium derivative of the alcohol (I) which, on treatment with hydrochloric acid, gave the alcohol (I). The total yield of the alcohol (I) calculated on the initial acid (II) was 68%. The

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influence of the synthesized tricontan-1-ol on the growth, generative development, and crop yield of tomatoes of the early-ripening low-growing variety Alpat'evskii and on the later-ripening tall variety Moskovskii has been tested. In a concentration of 20 mg/liter, triacontan-1-ol had an appreciable effect on morphogenesis only in the case when the plant was subjected to treatment for a long time. Under these conditions, the ripening of the fruit was accelerated and its size and yield were increased.

The influence of triacontan-1-ol on large-flowered asters of two varieties was also tested. The plants were sprayed with triacontan-1-ol in a concentration of 10 mg/liter. The opening of the flowers was accelerated and a larger number of buds was formed. Thus, triacontan-1-ol obtained by this method had a favorable influence on the rates and intensity of generative morphogenesis.

EXPERIMENTAL

Dodecane-1,12-diol was obtained from dodecanedioic acid as described previously [8].

1-Chlorododecan-12-ol (IV). A 0.35-liter round-bottomed flask fitted with a funnel and inlet tube reaching to the bottom, with a condenser for downward distillation, and with a receiver was charged with 100 ml of 32% HCl, 30 g of dodecane-1,12-diol, and 300 ml of heptane. The reaction mixture was heated to 95-100°C, heptane was added slowly, and a current of gaseous HCl was passed. Heating with the slow distillation of the solvent into the receiver was continued for 12 h. The solvent was evaporated in vacuum and the residue was washed with potassium carbonate solution, extracted with ether, and dried over Na_2SO_4. After evaporation of the ether, 26.8 g (85%) of (IV) was obtained, with mp 29-30°C. According to the literature [8]: mp 29-30°C.

Triacontan-1-ol (I). At −20°C, 17 ml of a tetrahydrofuran solution of 2.7 g of n-propylmagnesium chloride was added to a solution of 5.5 g of (IV) in 20 ml of absolute tetrahydrofuran, in the presence of phenanthroline to monitor the reaction, until a cherry-red coloration had been formed, and then 0.9 g of magnesium was added and the reaction mixture was stirred at the boil for 6 h. The resulting solution of (V) was added slowly at −5 to 0°C to a solution of 5.65 g of 1-bromooctadecane and 0.3 g of Li_2CuCl_4 in 25 ml of absolute tetrahydrofuran, and the mixture was stirred at this temperature for 4 h. Then the temperature was raised to 20°C, and after the addition of 50 ml of 10% hydrochloric acid and 50 ml of hexane the resulting mixture was boiled for 10 min. The hot reaction mixture was filtered, the precipitate was washed with hot hexane, and the hexane solution was evaporated. This gave 7.4 g (68%) of (I) with mp 87-88°C. According to the literature [5]: mp 87-88°C. IR (ν, cm^{-1}): 3350 (OH). Found %: C 82.14; H 14.34. $C_{30}H_{62}O$. Calculated %: C 82.19; H 14.00.

CONCLUSION

A convenient method for the synthesis of triacontan-1-ol from the readily available dodecanedioic acid and 1-bromooctadecane has been worked out.

A trial has been made of the physiological activity of triacontan-ol on tomatoes and asters and it has been shown that it possesses growth activity.

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