12-HENTRIACONTANOL FROM MYRICARIA ALOPECUROIDES

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Myricaria alopecuroides Schrenk. (family Tamaricaceae) is a poisonous plant which is widely distributed in the USSR [1] and is used in folk medicine in the treatment of women's diseases [2] and rheumatism [3]. This plant contains a considerable amount of tannins [3].

The chromatography on alumina of a petroleum ether extract of the epigeal part of the plant gave a mixture of paraffins, β-sitosterol, and a substance with mp 84.5°-85.5° C, composition $C_{31}H_{64}O$, whose IR spectrum had absorption bands corresponding to hydroxy (3600 cm^{-1}), methylene (2940, 2920, 2860, 1480 cm^{-1}) and methyl groups (1390 cm^{-1}). The compound isolated formed an acetyl derivative with mp 46.0°-47.0° C and a 3, 5-dinitrobenzoate with mp 48.0°-49.0° C. These results show that the compound is an alcohol.

Oxidation of the alcohol gave a ketone, $C_{31}H_{62}O$; Wolf-Kishner reduction of this gave a hydrocarbon with a molecular weight of 434 ± 10 (by mass spectrometry), which corresponds to the empirical formula $C_{31}H_{64}$. The Bechmann rearrangement of the oxime gave an amide with mp 85.0° -86.0° C apparently consisting of a mixture of two isomeric substances, since its hydrolysis gave two acids: dodecanoic and eicosanoic.

To establish the position of the keto group in the chain, the ketone was oxidized with perbenzoic acid (Baeyer-Villiger reaction) [4]. The acid fraction of the products yielded dodecanoic and eicosanoic acids and the neutral fraction undecyl alcohol and 1-nonadecanol.

From these results, the secondary alcohol that we isolated may be assigned the structure of 12-hentriacontanol

$$CH_3-(CH_2)_{10}-CH(OH)-(CH_2)_{18}-CH_3.$$

12-Hentriacontanol is a substance having zero optical rotation.

By reducing the ketone obtained from the oxidation of 12-hentriacontanol we obtained the authentic racemic alcohol with mp 80.0°-82.0° C. In view of the difference in the melting points of the two alcohols (the racemic form and that isolated from the plant) it may be concluded that the 12-hentriacontanol from the plant is one of the enantiomorphs. A difference in the IR spectra of the enantiomorphs and the racemates of the hydrogen phthlates of some asymmetrical alcohols in the crystalline state has been reported by Eliel and Kofron [5].

The hydrogen phthalates of natural 12-hentriacontanol and its racemate that we prepared differed in their melting points and IR spectra (in potassium bromide). Consequently, the 12-hentriacontanol is one of the enantiomorphs.

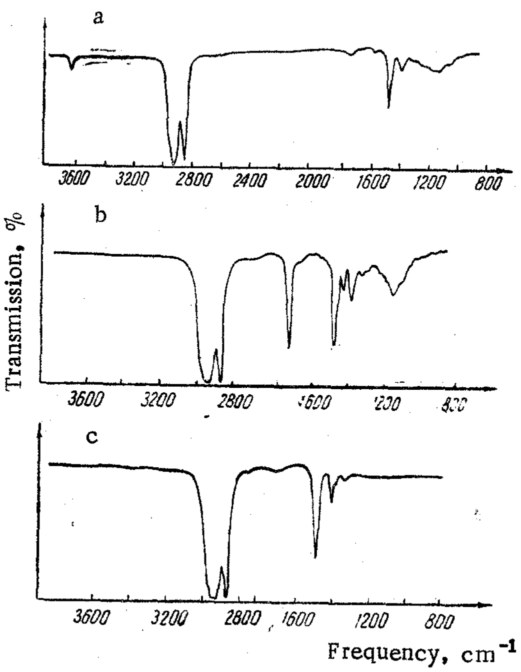

Fig. 1. IR spectra of the isolated alcohol: 12-hentriacontanol (a); the product of the oxidation of the alcohol-12-hentriacontanone (b); and the product of the reduction of 12-hentriacontanone-hentriacontane (c).

Experimental

The comminuted air-dry epigeal part of *M. alopecuroides* (42 kg) was extracted with petroleum ether (bp 40°-70 °C). After the bulk of the solvent had been distilled off, 45 g of a yellow green precipitate deposited, which was chromatographed on alumina (activity grade III). Elution with petroleum ether yielded about 2 g of paraffins in the form of a viscous oil, and petroleum ether-benzene (1:1) gave 30 g of 12-hentriacontanol with mp 84.5°-85.5° C (from petroleum ether) and 0.1 g of β-sitosterol, identified by a mixed melting point with an authentic sample.

12-Hentriacontanol dissolves in most organic solvents but is insoluble in water, $[\alpha]_D^{20}$ 0° (c 1; chloroform); IR spectrum: 3640 cm^{-1} (OH group), 2940-2920, 2860 ($-CH_2-$), 1390 cm^{-1} ($-CH_3$) (Fig. 1a).

Found, %: C 82.21, 82.24; H 14.14, 14.27. Calculated for $C_{31}H_{64}O$, %: C 82.22; H 14.25.

12-Hentriacontanol acetate. A mixture of 12-hentriacontanol (0.1 g), acetic anhydride (0.5 ml), and pyridine (1.5 ml) was heated at 80°–85° C for 3 hr. After cooling, the reaction mixture was poured into cold water, and the precipitate that deposited was filtered off, washed with water, and dried. The acetate (0.11 g) had mp 46.0°–47.0° C (from methanol). IR spectrum: 1740, 1250 cm^{-1} (acetyl group).

Found, %: C 79.71, 79.71; H 13.35, 13.43. Calculated for $C_{33}H_{66}O_2$, %: C 80.09, H 13.44.

3, 5-Dinitrobenzoyl derivative of 12-hentriacontanol. A mixture of 12-hentriacontanol (0.5 g), freshly-prepared 3, 5-dinitrobenzoyl chloride (0.8 g), and pyridine (8 ml) was heated in a boiling water bath for 1 hr. The reaction mixture was poured into cold water, and the precipitate was filtered off and washed with water, with 5% sodium hydrogen carbonate solution, and with water again. This gave a dinitrobenzoate with mp 48.0°–49.0° C (from a mixture of petroleum ether of bp 40°–70° C and methanol).

Found, %: C 70.81, 70.92; H 10.27, 10.16; N 4.57, 4.55. Calculated for $C_{38}H_{66}O_6N_2$, %: C 70.55; H 10.28; N 4.33.

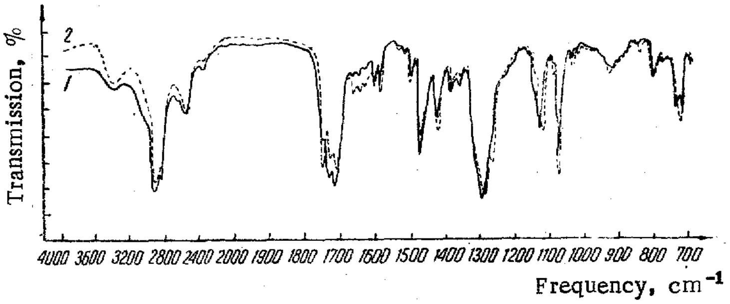

Fig. 2. IR spectra of the hydrogen phthalates of the racemic alcohol (1) and 12-hentriacontanol (2).

12-Hentriacontanone. A solution of 1.10 g of chromic anhydride in 250 ml of glacial acetic acid was added over 3 hr with stirring at 52°–55° C to a solution of 12-hentriacontanol (5.0 g) in 700 ml of glacial acetic acid. After 16 hr, the white crystals of 12-hentriacontanone that had separated out were filtered and washed with acetic acid, water, and alcohol. Weight, 4.5 g, mp 76.0°–77.0° C (from methanol). IR spectrum: 1730 cm^{-1} (keto group) (Fig. 1b).

Found, %: C 82.56, 82.25; H 13.71, 13.67. Calculated for $C_{31}H_{62}O$, %: C 82.59; H 13.86.

Hentriacontane. A mixture of 12-hentriacontanone (0.24 g), sodium methoxide (from 0.113 g of sodium), and hydrazine hydrate (0.5 ml) was heated in a sealed tube at 200 °C for 19 hr. The reaction mixture was treated with water and extracted with ether. The residue after the ether had been driven off (0.2 g) was chromatographed on alumina (activity grade I). Petroleum ether eluted 0.1 g of hentriacontane in the form of lustrous colorless scales with mp 67.0°–68.0 °C. Literature data: mp 68.0° C.

Found, %: C 85.49, 85.40; H 14.45, 14.42; mol. wt 434 ± 10 (mass spectrometry). Calculated for $C_{31}H_{64}$, %: C 85.23; H 14.77. Mol. wt. 437 (Fig. 1c).

Oxime of 12-hentriacontanone. A solution of 12-hentriacontanone (5.0 g) in 100 ml of alcohol was treated with 4.0 g of hydroxylamine hydrochloride and 35 ml of 10% alcoholic alkali. The mixture was boiled for 2 hr and diluted with water, and the precipitate which separated was filtered off and washed with water. Weight 5.0 g, mp 53.5°–54.5° C (from alcohol).

Found, %: C 79.64, 79.91; H 13.54, 13.67; N 3.47, 3.57. Calculated for $C_{31}H_{63}ON$, %: C 79.93; H 13.63; N 3.01.

Beckmann rearrangement of 12-hentriacontanone oxime. A solution of 12-hentriacontanone oxime (5.0 g) in glacial acetic acid (380 ml) was mixed with 60 ml of sulfuric acid and the mixture was boiled for 1.5 hr. The crystals that deposited after cooling were filtered off and were washed with acetic acid and water. Weight 4.7 g, mp 85.0°–86.5° C (from methanol).

Hydrolysis of the mixture of amides. The amides (4.7 g) were mixed with alcoholic alkali (66 g of caustic potash in 470 ml of water) and heated in an autoclave at 200° C for 15 hr. After cooling, the reaction mixture was diluted with water and extracted with ether. The aqueous solution was then acidified with hydrochloric acid to a Congo Red color and was extracted with ether again. The mixture of acids remaining after the solvents had been distilled off was analyzed by two methods.

A. The mixture of acids (0.03 g) was methylated with diazomethane, and the mixture of methyl esters was analyzed in a Chrom-1 chromatograph (stationary phase polyethylene glycol adipate on INZ-600 brick (0.28–0.40 mm)) at 200° C. The method of additives showed two peaks corresponding to dodecanoic and eicosanoic acids.

B. The mixture of acids (0.2 g) was sublimed at 85°–100° C (3–5 mm). The sublimate, in the form of lamellar crystals, had mp 43.0°–44.0° C. Literature data for dodecanoic acid: mp 44.0° C [7]. A mixture with an authentic sample of dodecanoic acid had mp 43.0°–44.0° C.

The p-bromophenacyl ester was prepared: mp 75.0°–76.0° C. The melting point of a mixture with an authentic sample of p-bromophenacyl dodecanoate was 75.0°–76.0° C.

The residue after the sublimation of the dodecanoic acid was chromatographed on a column of silica gel. An acid with mp 74.0°–75.0° C was isolated. Eicosanoic acid has mp 75.0° C [8]. The p-bromophenacyl ester had mp 92.0° C and a mixture with an authentic sample of p-bromophenacyl eicosanoate had mp 92.0° C.

Oxidation of 12-hentriacontanone with perbenzoic acid. A solution of 12-hentriacontanone (1.0 g) in 70 ml of chloroform was treated with 5.5 g of perbenzoic acid in 120 ml of chloroform. The mixture was kept at room temperature for 13 days. After being washed with 10% potassium carbonate solution and water, the chloroform layer was dried, and the solvent was distilled off. The residue was chromatographed on alumina (activity grade III). Petroleum ether eluted a crystalline product (0.4 g), and this was boiled with 10% alcoholic alkali (25 ml) for 4 hr.

The neutral fraction of the saponification products was chromatographed on alumina (activity grade III).

Petroleum ether eluted 0.1 g of unchanged ketone and an alcohol. The fraction containing the alcohol was analyzed on a LKhM-5 gas-liquid chromatograph (stationary phase—SKTNF silicone) at 185° C.

The alcohol was identified by the correlation method as undecyl alcohol.

Benzene eluted a second alcohol with mp 62.0°–63.0° C from ethanol. The alcohol was characterized as the phenylurethane with mp 78.0°–80.0° C. Literature data for 1-nonadecanol: mp 62.0°–63.0° C; and for its phenylurethane: 79.0°–80.0° C [9–10].

The mixture of acids was separated by sublimation. This gave dodecanoic and eicosanoic acids, which were identified by their mixed melting points with the acids obtained by the saponification of the amides.

Racemic 12-hentriacontanol. A solution of 12-hentriacontanone (2.0 g) in 450 ml of absolute ether was boiled with 2 g of lithium aluminum hydride for 4 hr. The reaction mixture was decomposed with ice and was acidified with hydrochloric acid to a Congo Red color. The ethereal extract was washed with sodium carbonate solution and water and dried. The melting point of the residue after the elimination of the solvent (1.7 g) was 80.0°–82.0° C (petroleum ether).

Found, %: C 82.08, 82.01; H 14.08, 14.17. Calculated for $C_{31}H_{64}O$, %: C 82.22; H 14.25.

Preparation of the hydrogen phthalates of natural 12-hentriacontanol and racemic 12-hentriacontanol. The hydrogen phthalates of the two alcohols were prepared in the same way. The 12-hentriacontanol (1.17 g) was heated with phthalic anhydride (1.0 g) in pyridine solution (1.5 ml) in an oil bath at 120° C for 18 hr. To eliminate the pyridine, the hot reaction mixture was poured into dilute hydrochloric acid. The cooled mixture was extracted with ether. The residue after the ether had been distilled off was transferred to a column of silica gel and was eluted with petroleum ether. The substance eluted from the column (0.9 g) had mp 53.0°–54.0° C in the case of the natural alcohol and 48.0°–50.0° C in the case of the racemate. The IR spectra of both hydrogen phthalates were recorded (DS-300 instrument). The IR spectra in carbon tetrachloride solution agreed completely, while the spectra taken in potassium bromide tablets differed by displacements of the peaks at 725–745, 1125–1135, 1285–1300, and 1470–1475 cm^{-1} (Fig. 2).

For the hydrogen phthalate of the natural alcohol, found, %: C 78.54, 78.53; H 11.40, 11.20. Calculated for $C_{39}H_{68}O_4$, %: C 77.94; H 11.41.

For the hydrogen phthalate of the racemic alcohol, found, %: C 78.38, 78.45; H 11.18, 11.30. Calculated for $C_{39}H_{68}O_4$, %: C 77.94; H 11.41.

The chromatography was carried out with neutral alumina and with silica gel of grade KSK (70–100 mesh). All the melting points were determined on a Kofler block. The IR spectra were recorded on a UR-10 spectrophotometer. The molecular weights were determined in a MI-1305 mass spectrometer.

Summary

A new secondary aliphatic alcohol, 12-hentriacontanol, has been isolated from the epigeal part of the plant Myricaria alopecuroides Schrenk.

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