7. L. A. Golovina, A. I. Sandkhodzhaev, V. M. Malikov, and S. Melibaev, Khim. Prir. Soedin., 787 (1982).
8. T. Kh. Khasanov, A. I. Sandkhodzhaev, and G. K. Nikonov, Khim. Prir. Soedin., 807 (1972).
9. A. Sh. Kadyrov, T. Kh. Khasanov, A. I. Sandkhodzhaev, and G. K. Pikonov, Khim. Prir. Soedin., 808 (1972).
10. A. I. Sandkhodzhaev, Khim. Prir. Soedin., 437 (1979).
11. L. A. Golovina, A. I. Sandkhodzhaev, and V. M. Malikov, Khim. Prir. Soedin., 712 (1978).

CONVERSION OF CARYOPHYLLENE α-OXIDE INTO 1R,10R-SELINA-4,6-DIEN-1-OL

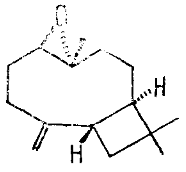
G. A. Nisnevich, A. V. Tkachev,
D. V. Korchagina, V. P. Gatilova,
V. A. Barkhash, and Zh. V. Dubovenko

UDC 547.91

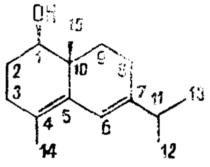
It is generally accepted that the immediate precursors in the biosynthesis of selinane compounds are sesquiterpenoids with the carbon skeleton of germacrene [1]. There is information on rearrangements of humulene [2] and of spirovetivane [3] into selinane compounds. At the same time, caryophyllene and the elinanes are not biogenetically connected with one another and all known rearrangements of caryophyllene lead to carbon skeletons differing from the bicyclic system of selinane [4]. In an investigation of the behavior of caryophyllene α-oxide (I) in superacids, we unexpectedly obtained a compound that was a derivative of δ-selinene — 1R,10R-selina-4,6-dien-1-ol (II).

When 1 g of the oxide (I) with $[\alpha]_D^{20}$ −62.3° (c 2.67; $CHCl_3$) was dissolved in the acid system HSO_3F (2 ml)–SO_2FCl (16 ml) at −130°C and the solution was rapidly neutralized (CH_3OH–$(C_2H_5)_2O$, −125°C, then treatment with sodium carbonate followed by chromatography on SiO_2, the secondary alcohol (II) was isolated in a yield of 35% with mp 83-86°C (hexane) and $[\alpha]_D^{20}$ +254! (c 3.41; $CHCl_3$). The alcohol (II) was unstable, and readily polymerized during crystallization. The p-nitrobenzoate of the alcohol (II) had mp 112-114°C (hexane). ^1H NMR spectrum of the alcohol (II) (200 MHz); $CDCl_3 + CCl_4$ (1:1); δ, ppm; internal standard $CHCl_3$, δ 7.24 ppm): 0.88 (3 H, singlet, $CH_3C\langle$); 1.05 (6 H, doublet, J = 7 Hz, $(C\underline{H}_3)_2CH-$); 1.66 (3 H, broadened singlet, $CH_3-\underset{|}{C}=C-$; 1.70-2.20 (8 H, superposed multiplets, $-C\underline{H}_2-$); 2.28 (1 H, septet, J = 7 Hz, $(CH_3)_2C\underline{H}-$); 3.43 (1 H, doublet of doublets, J = 11 Hz and 5.5 Hz, $>C\underline{H}OC$); 6.03 (1 H, broadened singlet, $-\underset{|}{C}=CH-C-\underset{|}{C}=\underset{|}{C}-$). ^{13}C NMR spectrum ($CDCl_3 + CCl_4$, 1:1; ppm from TMS; internal standard $CDCl_3$, δ 76.9 ppm): 142.8 s (C^7); 132.0 s (C^5); 124.7 s (C^4); 117.0 d (C^6); 76.0 s (C^1); 37.1 s (C^{10}); 35.4 d (C^{11}); 33.2 t (C^9); 31.8 t and 26.7 t (C^2 and C^3); 22.7 t (C^8); 21.7 q and 21.2 q (C^{12} and C^{13}); 18.1 q (C^{14}); 16.3 q (C^{15}).

The selinane carbon skeleton was confirmed by the dehydrogenation of the alcohol (II) in the presence of selenium to endesmane. The absolute configuration of C^{10} was deduced on the basis of a comparison of the specific rotations of the alcohol (II), of δ-selinene [3], and a number of selinane derivatives [3]. The equatorial nature of the hydroxy group followed from an analysis of the vicinal spin–spin coupling constants of the carbinol hydrogen atom (see [3]). The absolute configuration at C^1 was determined by the configuration of this center in the initial compound (I) [5].



I



II

Novosibirsk Institute of Organic Chemistry, Siberian Branch, Academy of Sciences of the USSR. Translated from Khimiya Prirodnykh Soedinenii, No. 3, pp. 413-414,, May-June, 1985. Original article submitted January 17, 1985.

0009-3130/85/2103-038S$09.50

Thus, this arrangement of a compound of the caryophyllene type into a compound of the selinane type, the first ever performed, has shown a possible biogenetic link of the sesquiterpenoids of these structural types.

LITERATURE CITED

1. A. P. S. Narula, J. Sci. Ind. Res., 35, 362 (1976).
2. G. Mehta and B. P. Singh, Tetrahedron Lett., 3961 (1975).
3. H. Itokawa, H.Nakanishi, and S. Minashi, Chem. Pharm. Bull., 31, 1991 (1983).
4. J. M. Robertson, MTP International Review of Science, Physical Chemistry. Series 1, Vol. 11, Chemical Crystallography, Butterworth, London (1975), p. 57.
5. D. H. R. Barton and A. Nickon, J. Chem. Soc., 4665 (1954).

TRITERPENOIDS OF THE BARK AND TWIGS OF Betula dahurica

L. E. Odinokova, G. V. Malinovskaya,
N. D. Pokhilo, and N. I. Uvatova

UDC 581.192+547.914

In connection with the complex utilization of raw material, a chemical study has been made of an extrract of the outer bark (0.5 kg) [1]. and of the twigs (0.7 kg) of Betula dahurica.

The bark was exhaustively extracted with diethyl ether. The combined ethereal extract was evaporated (24 g) and chromatographed on silica gel L 100/160 μm. Six substances of triterpene nature (I, II, IV-VII) and β-sitosterol (III) were isolated. All the compounds and also their derivatives, obtained by the usual methods, gave no depression of the melting points in admixture with authentic samples.

	Substance	mp, °C		Yield, %
I.	Oleanolic acid acetate	262-265	[2]	0.6
	Methyl oleanolate acetate	219-220	[2]	
II.	Lupeol	212-213	[2]	0.04
	Lupeol acetate	218-220	[2]	
III.	β-Sitosterol	138-139	[3]	0.03
	β-Sitosterol acetate	145-147	[3]	
IV.	Allobetulin	279-280	[4]	0.02
	Allobetulin acetate	284-284.5	[4]	
V.	Betulin	258-260	[2]	0.08
	Betulin diacetate	221-223	[2]	
VI.	Oleanolic acid	306-308	[2]	0.4
	Methyl oleanolate	198-200	[2]	

The structure of triterpene (VII) is being studied.

From an ethereal extract of the twigs we isolated and identified β-sitosterol (III) (0.07%), oleanolic acid acetate (I) (0.06%); oleanolic acid (VI) (0.002%), and fatty acids (0.01%). The fraction containing the fatty acids was methylated and studied by the GLC method. The methyl esters were identified on a Shimadzu LC-5A chromatograph with Supelcoport, 100-120 mesh, impregnated with 3% of Carbowax 20M, under isothermal conditions (215°C). It was established that the farry acid fraction consisted fo a mixture of three main acids: palmitic, oleic, and linoleic.

LITERATURE CITED

1. L. G. Matyukhina, A. A. Ryabinin, I. A. Seminkova, and T. B. Shakhvorostova, Khim. Prir. Soedin., 387 (1968).
2. H. W. Kircher, Phytochemistry, 19, 2707 (1980).
3. L. Fieser and M. Fieser, Steroids, Reinhold, New York (1959).
4. J. L. Simonsen and W. C. Ross, The Tempenes, Cambridge University Press (1957), p. 304.

Pacific Ocean Institute of Bioorganic Chemistry, Far Eastern Scientific Center, Academy of Sciences of the USSR, Vladivostok. Translated from Khimiya Prirodnykh Soedinenii, No. 3, pp. 414, May-June, 1985. Original article submitted July 11, 1984.

0009-3130/85/2103-0390$09.50