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REACTIONS OF DITERPENOIDS ON SOLID SUPPORTS.
I. OXIDATION OF METHYL ABIETATE ON THE SORBENTS Al_2O_3 AND SiO_2 CONTAINING POTASSIUM PERMANGANATE

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The oxidation of methyl abietate on the sorbents Al_2O_3 and SiO_2 containing potassium permanganate has been studied. It has been shown that the following are formed under the conditions selected: compounds of the dehydroabietane series, stereoisomeric mono- and diepoxides of methyl abietate, and the products of their transformation on the sorbents. The structures and stereochemistries of the compounds isolated have been established with the aid of spectral methods and XSA.

Abietic acid (**1a**) is the most readily available and widely distributed resin acid. It has been the object of numerous investigations over several decades and the literature devoted to its reactions is voluminous [1]. One of the types of reactions in the chemistry of abietic acid (**1a**) that is attracting intense interest is its oxidation by various reagents. Detailed studies have been made of its autooxidation [2], its epoxidation [3-5], and its interaction with $KMnO_4$, CrO_3 [6], and other oxidants [7]. The interest in these reactions is due to the fact that, thanks to its structure, (**1a**) readily undergoes oxidative transformations, forming polyfunctional compounds that frequently possess biological activity.

On the basis of literature information [3-6], it may be concluded that the action of oxidants ($KMnO_4$, CrO_3) on (**1a**) forms mainly the products of allyl oxidation and dehydroabietane derivatives, while, under severe conditions, destruction of the carbon skeleton of the (**1a**) molecule may take place. Abietic acid epoxides are unstable and, on being kept on sorbents or subjected to chromatography, they form various products with breakdown of the oxirane rings [4, 5].

Recently, interest has arisen in reactions on solid supports and, in particular, on sorbents impregnated with various oxidants [8-10], but there is practically no information in the literature on the chemical transformations of polycyclic compounds, especially diterpenoids, on solid supports.

We have studied the behavior of methyl abietate (**1b**) on alumina and silica gel containing potassium permanganate. This method provided the possibility of obtaining the reaction products by eluting the reaction mixture with a polar solvent, without any additional working up procedure. Furthermore, as is well known, the use of chemosorbed reagents frequently increases selectivity, thanks to a moderation of the strength of the oxidants, and permits the avoidance of difficulties connected with the choice of solvents for the reactants and with the isolation of the products by ordinary extraction [9, 10].

From a reaction mixture obtained after keeping methyl abietate on the sorbent $Al_2O_3/KMnO_4$ (5 h, in acetone) we isolated products of two structural types: the dehydroabietane and the abietane types. From among the compounds of the first type we obtained in the individual form methyl dehydroabietate (**2**) and methyl 7-ketodehydroabietate (**3**), identified from their spectral characteristics and by a comparison with authentic samples.

Then we isolated products of the second type — known epoxides of the ester (**1b**): methyl $13\alpha,14\alpha$-epoxy-$\Delta^{7,8}$-abietate (**4**) and methyl $7\alpha,8\alpha;13\alpha,14\alpha$- and $7\alpha,8\alpha;13\beta,14\beta$-diepoxyabietates (**5**) and (**6**), which have not been obtained previously by the oxidation of the ester (**1b**) with potassium permanganate. Nevertheless, examples of an anomalous reaction of potassium permanganate with conjugated dienes, leading to epoxides, are known in the literature [11]. The rate of formation of epoxides in the case of a sterically hindered intermediate — a bicyclic diester of manganic acid, formed from a conjugated diene — was far higher than the rate of conversion of this diester into the usual products — tetraols or acyloins.

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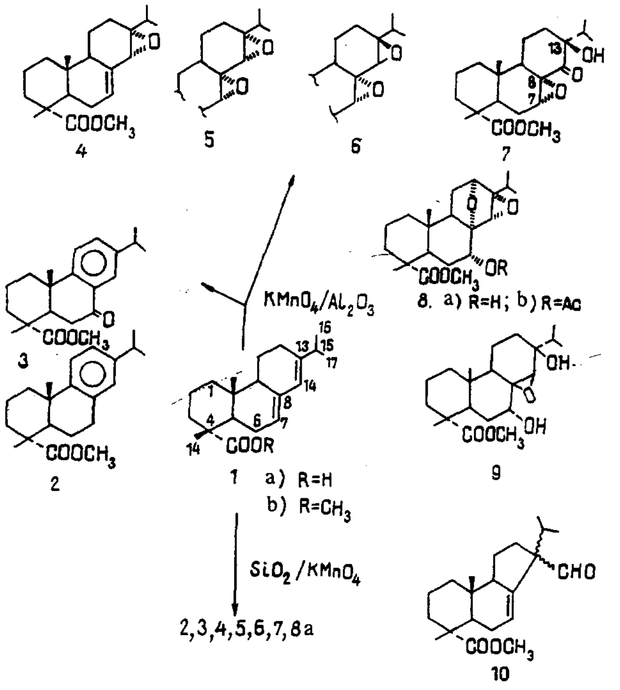
Therefore, in this case one would normally expect the presence in the reaction mixture of products of the degradation or isomerization of the corresponding epoxides. Thus, together with the diepoxides (**5**) and (**6**, compounds were isolated, which, according to IR and NMR spectroscopy, contained — in addition to the $-COOCH_3$ fragment — hydroxy and keto groups and also an oxirane ring presumably present at carbon atoms 7 and 8 (according to the literature [5]). With the aim of establishing the structure and relative configuration of the compound obtained, we subjected it to x-ray structural analysis (XSA), which indicated that this product was methyl 13β-hydroxy-14-keto-7α,8α-epoxyabietate (**7**), which has not been described in the literature. The structure of the molecule of compound (**7**) is shown in Fig. 1. Ring C has an unusual conformation — intermediate between "boat" and "twist" (angles of pseudorotation: $\psi_2 = -41°$, $\theta = 74°$ [12]). In the crystal, the molecules are linked into chains by $O_{13}-H...O_{19}{}^1$ hydrogen bonds with the parameters 1.01, 2.04 Å, 145°. The same hydroxy group forms a weaker intramolecular hydrogen bond $O_{13}-H...O_{14}$ (1.01, 2.35 Å, 100°).

Compound (**7**) was present in an equilibrium mixture before chromatography, as was confirmed by GLC results. Its formation is most probably to be explained by the opening, during the reaction, of the 13,14-oxirane ring in epoxide (**6**), only trace amounts of which remained in the reaction mixture.

The following compound, more polar than (**7**), formed an amorphous powder. Its PMR spectrum contained signals characteristic for protons present in the α-position to an epoxide (3.23 ppm) and to a hydroxy group (3.67 ppm, multiplet), and also the signal of a proton with a chemical shift of 4.48 ppm. In the ^{13}C NMR spectrum no signals corresponding to olefinic carbon atomds were observed, but in the weak-field part of the spectrum, in addition to the signal of a carbon atom bearing a hydroxy group (77.43 ppm, doublet), there were a doublet at 84.24 ppm and a singlet at 84.82 ppm. Such chemical shifts are characteristic for carbon atoms bound with the oxygen fragments of ketals or oxide rings [13]. According to the results of mass spectrometry, the empirical formula of the compound was $C_{21}H_{32}O_5$; an ion with *m/z* 346 (M — 18) had the maximum (100%) intensity. In the PMR spectrum of the acetylation product (**8b**) there was a change in the chemical shift of only one proton, present in the α-position to the hydroxy group in the initial compound. According to the IR spectrum of the acetate, its molecule lacked a tertiary hydroxy group.



Thus, according to spectral results, the molecule of the compound contained: an epoxide ring (presumably in the 13,14-position), a secondary hydroxy group, and an oxide ring. The configurations of the epoxide ring and of the hydroxy group were determined on the basis of [5] and, in particular, the chemical shifts of the C-5 and C-9 atoms present in the γ-position to the oxygen atom (γ-*gauche* effect). The oxide ring was probably in the 8,12 position since similar compounds with an oxygen bridge (in the 8,12-position) have been obtained previously only on the oxidation of levopimaric acid with potassium permanganate [14]. In our case, apparently, partial isomerization of the ester (**1b**) into methyl levopimarate took place on the sorbent and was accompanied by the further oxidation of the methyl levopimarate by the potassium permanganate. On the basis of its spectral characteristics, structure (**8a**) is proposed for the compound isolated.

TABLE 1

Eluent	Amount, g	Composition of the fraction
1. Hexane/DE (95:5)	0.06	Methyl dehydroabietate (2)
2. "	0.005	Methyl 13α,14α-epoxy-$\Delta^{7,8}$-abietate (4)
3. Hexane/DE (90:10)	0.03	Methyl 7-ketodehydroabietate (3)
4. "	0.01	Methyl 7α,8α;13α,14α-diepoxyabietate (5)
5. "	0.02	Methyl 13β-hydroxy-14-keto-7α,8α-epoxyabietate (7)
6. Hexane/DE (85:15)	0.003	Methyl 7α,8α;13β,14β-diepoxyabietate (6)
7. Hexane/DE (80:20)	0.02	Methyl 7α-hydroxy-8α,12α;13α,14α-diepoxyabietate (8a)
8. Hexane/DE (60:40)	0.01	Methyl 7α,13β-dihydroxy-8β,14β-epoxyabietate (9)
Total yield	0.158	

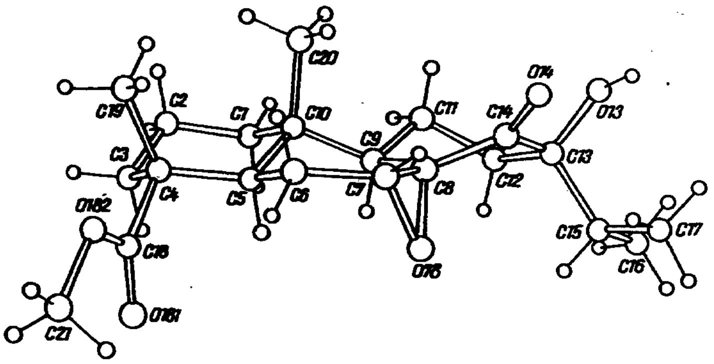


Fig. 1. Crystal structure and relative configuration of methyl 13β-hydroxy-14-keto-7α,8α-epoxyabietate (7).

From its ^{1}H and ^{13}C NMR spectra, the most polar compound of the reaction mixture was identified as methyl 7α,13β-dihydroxy-8β,14β-epoxyabietate (**9**), the tert-butyl ester of which had been synthesized previously by the epoxidation of methyl abietate derivatives [5].

On the interaction of the ester (**1b**) with the reagent $SiO_2/KMnO_4$ the yield of reaction products was somewhat higher, but dehydroabietane derivatives predominated in the reaction mixture (70% of methyl dehydroabietate, 10% of methyl 7-ketodehydroabietate, and trace amounts of methyl 7α-hydroxydehydroabietate), and it contained only 20% of abietane derivatives. From them we isolated the monoepoxide (**4**), the diepoxides (**5**) and (**6**), the epoxyketoalcohol (**7**), and compound (**8a**).

Then from this mixture we isolated a small amount of a compound containing an aldehyde group (according to its PMR spectrum), which was probably an artefact formed during the chromatography of the monoepoxide (**4**) on silica gel. Judging from its ^{13}C NMR spectrum, the structure of the aldehyde obtained corresponded to a product with a changed abietane skeleton (**10**). The PMR spectrum contained, in addition to the signals of an aldehyde proton at 9.33 ppm, a multiplet (6.73 ppm) which we assigned to the H-7 proton. The large chemical shift of this proton can be explained by the influence of the oxygen atom of the carbonyl group, since the PMR spectrum of the alcohol obtained by reducing the aldehyde (**10**) showed a "reversion" of this signal* to the 5.60 ppm region (in the spectrum of the ester (**1b**) its chemical shift is 5.34 ppm).

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*Results of Yu. A. Silko.

TABLE 2. ^{13}C NMR Spectra of Compounds (**7**), (**8a**), and (**10**) ($CDCl_3$, δ_C, ppm)

C Atom	7	8a	9	10
1	38.26 t	39.90 t	37.84 t	37.60 t
2	17.45 t	17.40 t	17.52 t	17.55 t
3	36.74 t	36.93 t	37.68 t	36.66 t
4	46.08 s	45.92 s	46.71 s	46.07 s
5	39.43 d	39.90 d	41.69 d	40.55[a] d
6	23.90 t	24.40 d	30.33 t	42.34 s
7	56.16 d	77.43* d	72.80 d	152.01 d
8	58.28 s	84.82 s	63.95 s	144.15 s
9	53.38 d	55.18 d	46.17 d	49.77 d
10	34.20 s	33.19 s	37.01 s	35.53 s
11	18.60 t	48.52 t	17.52 t	20.62 t
12	33.35 t	84.24 d	30.62 t	26.63 t
13	80.15 s	62.83 s	70.16 s	37.60 s
14	211.75 s	57.66 d	62.61 d	194.66 d
15	36.28 d	33.07 d	36.87 d	43.00[a] d
16	15.87[a] q	17.65 q	16.70[a] q	18.10[b] q
17	16.05[a] q	17.65 q	17.74[a] q	18.21[b] q
18	178.05 s	178.09 s	178.79 s	178.40 s
19	17.28 q	17.28 q	16.22 q	16.89 q
20	15.25 q	15.17 q	14.70 q	14.07 q
21	51.95 q	51.95 q	51.94 q	51.94 q

The chemical shifts marked with identical letters should possibly change places within the limits of a given compound. *In C_6D_6.

We also isolated a certain amount of the aldehyde (**10**) from the mixture produced by the epoxidation of ester (**1b**) with *m*-chloroperbenzoic acid. No compounds containing a $-CHO$ group have been obtained previously by the oxidation of the acid (**1a**) or the ester (**1b**), but similar changes to the carbon skeleton, with the formation of an aldehyde function, taking place on sorbents have been reported by many researchers for a number of epoxides of the mono- and diterpene series [15].

We did not detect in the reaction mixtures any products of allyl or destructive oxidation, which are most characteristic for the reactions of the acid (**1a**) and its ester (**1b**) with potassium permanganate, and it is therefore appropriate in this case to note the considerable moderation of the strength of the oxidant due to its chemosorption, as has been reported previously [8, 9].

Thus, on the interaction of the ester (**1b**) with $Al_2O_3/KMnO_4$ and $SiO_2/KMnO_4$, two competing processes take place simultaneously: 1) the aromatization of ring C with the formation of dehydroabietane derivatives, and 2) the "anomalous" epoxidation of the molecule of the ester (**1b**), accompanied by a further transformation of the epoxides on the sorbents, as a result of which a series of polyfunctional compounds of the abietane type arises.

EXPERIMENTAL

Melting points were determined on a Kofler stage. PMR spectra were recorded on Bruker WP-200 (200.13 MHz) and AC-200 (200.13 MHz) instruments. The $CHCl_3$ (δ_H 7.24 ppm) present in the deuterochloroform was used as an internal standard. The chemical shifts of the signals are given in ppm, δ scale. ^{13}C NMR spectra were taken on an AC-200 (50.32 MHz) spectrometer in $CDCl_3$ solutions, the solvent being used as internal standard (δ_C 76.90 ppm). The assignment of the chemical shifts and multiplicities of the signals in the ^{13}C NMR spectra of the compounds was made on the basis of a comparison of them with those for related compounds [5, 16]. IR absorption spectra were recorded on a UR-20 instrument in CCl_4 solutions. High-resolution mass spectra were obtained on a Finnigan MAT instrument. Specific rotations were determined on a Polamat AA spectropolarimeter at 540 nm in $CHCl_3$ solutions. The x-ray structural analysis of a specimen was carried out on a SYNTEX $P2_1$ diffractometer.

TABLE 3. Coordinates (× 10^4, in fractions of the cell) and Temperature Factors ($Å^2$, × 10^3) of the Nonhydrogen Atoms of Compound (7)

Atom	x	y	z	Ueq.
C-1	8483	8330	10959	36
C-2	9819(10)	8572(8)	12091(5)	45
C-3	8554(10)	6753(9)	12916(5)	42
C-4	7919(8)	4567(8)	12317(4)	34
C-5	6649(8)	4345(7)	11100(5)	29
C-6	5976(9)	2191(8)	10452(5)	38
C-7	4795(9)	1904(8)	9278(5)	37
C-8	4840(9)	3702(8)	8704(5)	30
C-9	5976(8)	5929(8)	9302(5)	26
C-10	7776(8)	6221(8)	10246(4)	28
C-11	6730(9)	7572(8)	8325(5)	38
C-12	4758(10)	7132(9)	7512(5)	39
C-13	3934(9)	5055(8)	6755(4)	32
C-14	4643(9)	3605(8)	7346(5)	32
C-15	1372(9)	3891(10)	6597(5)	47
C-16	632(10)	5344(12)	6018(6)	68
C-17	466(10)	1761(12)	5900(6)	74
C-18	6207(9)	2878(9)	13107(5)	37
C-19	9992(9)	4278(9)	12210(5)	42
C-20	9755(9)	6278(9)	9589(5)	41
C-21	5012(10)	—365(10)	14065(5)	58
O-7,8	2837(7)	2150(8)	9265(4)	44
O-13	4987(8)	5639(8)	5625(4)	41
O-14	5042(9)	2385(8)	6760(4)	56
O-18$_1$	4640(9)	2973(9)	13515(5)	52
O-18$_2$	6584(8)	1275(8)	13305(5)	49

Gas–liquid chromatograms were recorded on a Chrom-5 instrument, using a 0.3 × 125 cm column with 5% of SE-30 as the stationary phase and nitrogen as the carrier gas at an evaporator temperature of 180°C. For the isolation of individual compounds from mixtures we used absorption column chromatography on silica gel (40-63, 71-90, and 90-125 μm, KSK). The eluents used were mixtures of hexane and diethyl ether (DE) with increasing amounts of the diethyl ether. Monitoring the course of the reactions and of column chromatography and comparison with authentic samples were carried out on Silufol-254 (UV) plates. For detection we used UV light, the vapor of crystalline iodine, or concentrated H_2SO_4.

In the performance of the processes, the experimentally selected ratio of substrate to oxidant + sorbent of 1/10 was used, this being the optimum ratio permitting the avoidance of a large excess of oxidant and ensuring the complete conversion of the methyl abietate during the reactions.

Methyl Abietate (1b). A solution of diazomethane in diethyl ether was added dropwise to a solution of 5 g of the acid (**1a**) in 20 ml of diethyl ether until a permanent yellow coloration of the solution had appeared and the evolution of bubbles of gas had ceased. The solvent was driven off, and the reaction mixture (5.2 g) was chromatographed on SiO_2 (90-125 μm), the eluent being a solution containing 5% of DE in hexane. The yield of the ester (**1b**) was 4.02 g. PMR spectrum: 0.80 (s, 3H-20), 0.98 and 0.99 (d, J = 7 Hz, 3H-16, 3H-17), 1.24 (s, 3H-19), 3.60 (s, OCH_3), 5.34 (m, H-7), 5.74 (s, H-14).

Preparation of a Sorbent with an Oxidant (by analogy with the procedure described in [8]). A suspension of 10 g (0.1 mole) of neutral Al_2O_3 in a solution of 6.32 g (0.04 mole) of $KMnO_4$ in 250 ml of water was evaporated in a rotary evaporator at 80°C. The oxidant with the sorbent was dried at 70°C for 12 h.

Reaction of Methyl Abietate on Al_2O_3 Impregnated with $KMnO_4$. A solution of 0.8 g (2.53 mmoles) of methyl abietate in 15 ml of acetone was added to 8 g of $KMnO_4/Al_2O_3$. The resulting suspension was stirred at room temperature for 5 h. The course of the reaction was monitored by TLC. After the disappearance of the initial ester (**1b**) the mixture was transfereed into a flask, the solvent was eliminated, and the dry residue was deposited on a column with a layer of SiO_2 (90-125 μm), ratio 1/10. The products were eluted with DE, and the solvent was driven off. Yield 0.2 g. The component composition was determined by GLC and TLC. The products were chromatographed on SiO_2 (71-90 μm) at a ratio of 1/30.

Methyl Dehydroabietate (2). PMR spectrum: 1.19 (s, 3H-20), 1.22 (d, J = 7 Hz, 3H-16, 3H-17), (s, 3H-19), 2.25 (m, 2H-7), 2.83 (septet, H-15), 3.65 (s, OCH_3), 6.83, 6.94, 7.12 (m, 3H, protons of an aromatic ring).

Methyl 7-Ketodehydroabietate (3). PMR spectrum: 1.21 (s, 3H-20), 1.23 (d, J = 7 Hz, 3H-16, 3H-17), 1.32 (s, 3H-19), 2.67 (m, 2H-6), 2.91 (septet, H-15), 3.64 (s, OCH_3), 7.27, 7.83 (m, 3H, protons of an aromatic ring).

Methyl 13α,14α-Epoxy-$\Delta^{7,8}$-abietate (4). This fraction, which consisted of a crystalline residue, was recrystallized from hexane. mp 56-58°C (lit. [3], 58-59°C). PMR spectrum: 0.77 (s, 3H-20), 0.94 (d, J = 7 Hz, 3H-16, 3H-17), 1.21 (s, 3H-19), 3.11 (s, H-14), 3.63 (s, OCH_3), 5.81 (m, H-7).

Methyl 7α,8α;13α,14α-Diepoxyabietate (5). PMR spectrum; 0.84 (s, 3H-20), 0.92 and 0.95 (d, J = 7 Hz, 3H-16, 3H-17), 1.21 (s, 3H-19), 2.27 (s, H-14), 3.14 (t, J = 3 Hz, H-7), 3.64 (s, OCH_3).

Methyl 13β-Hydroxy-14-keto-7α,8α-epoxyabietate (7). This fraction was recrystallized from hexane–ethyl acetate (9:1). Elimination of the solvent yielded crystals with mp 138-140°C, $[\alpha]_{540}^{21}$ + 97.5° (sec 1.892). IR spectrum (ν_{max}^{CCl4}, cm^{-1}): 1720 (C = O), 3520 (–OH). PMR spectrum: 0.90 (s, 3H-20), 0.72 and 0.94 (d, J = 7 Hz, 3H-16, 3H-17), 1.20 (s, 3H-19), 2.85 (m, H-9), 3.63 (s, OCH_3), 3.81 (t, J = 3 Hz, H-7). For the ^{13}C NMR spectrum, see Table 2.

X-Ray Structural Analysis of Compound (7). Triclinic crystals; a = 6.8946(8), b = 7.1715(9), c = 11.170(1)Å, α = 91.944(9), β = 89.970(9), γ = 118.824(8)°, V = 483.5(8) Å^3, space group P1, $C_{21}H_{32}O_5$, Z = 1, d_{calc} = 1.252 g/cm^3, μ = 6.73 cm^{-1}, λ CuK_α radiation (graphite monochromator) The intensities of 5440 reflctions in the $\theta/2\theta$ hemisphere were measured by the ω-scanning method. A correction for absorption was made by the DIFABS program. After the averaging of equivalent reflections, 1397 independent ones were obtained. The structure was interpreted by the direct method using the SHELX 86 program and was refined by the method of least squares in the anisotropic full-matrix approximation to R = 0.047, R_w = 0.050, where $W^{-1} = \sigma_F^2 + 0.013F^2$, S = 0.59. The positions of the hydrogen atoms were calculated geometrically after each cycle of refinement. The atomic coordinates obtained are given in Table 3.

Methyl 7α-Hydroxy-8α,12α;13α,14α-diepoxyabietate (8a). Amorphous powder, $[\alpha]_{540}^{21}$ + 20.2° (sec 0.896). PMR spectrum: 0.91 (s, 3H-20), 0.92 and 1.01 (d, J = 7 Hz, 3H-16, 3H-17), 1.19 (s, 3H-19), 3.23 (H-14), 3.61 (s, OCH_3). 3.67 (m, H-7), 4.48 (dd, J = 6 and 1.5 Hz, H-12). For the ^{13}C NMR spectrum, see Table 2. Empirical formula $C_{21}H_{32}O_5$ (found, *m/z* 364.2382, calculated, 364.4821).

Methyl 7α-Acetoxy-8α,12α;13α,14α-diepoxyabietate (8b). Viscous liquid. PMR spectrum: 0.92 (s, 3H-20), 0.96 and 1.00 (d, J = 7 Hz, 3H-16, 3H-17), 1.19 (s, 3H-19), 3.27 (1H-14), 3.62 (s, OCH_3), 4.47 (dd, J = 6.5 and 1.5 Hz, H-12), 4.69 (m, H-7).

Methyl 7α,13β-Dihydroxy-8β,14β-epoxyabietate (9). This fraction, consisting of a viscous oil, was dried under vacuum at 70°C. $[\alpha]_{540}^{21}$ – 7.9° (sec 0.892). PMR spectrum: 0.90 (s, 3H-20), 0.90 (d, J = 7 Hz, 3H-16, 3H-17), 1.16 (s, 3H-19), 2.25 and 2.33 (d, J = 2 Hz each, 2H-6), 2.42 (m, H-9), 2.74. (br. s, H-14), 3.27 (t, J = 3 Hz, H-7), 3.60 (s, OCH_3). For the ^{13}C NMR spectrum, see Table 2.

Reaction of Methyl Abietate on SiO_2 Impregnated with $KMnO_4$. The oxidant with the sorbent was prepared by the method described above. A solution of methyl abietate (0.4 g, 1.265 mmoles) in acetone (6 ml) was added to 4 g of $KMnO_4/SiO_2$, and the mixture was stirred for 4 h. After the end of the reaction, which was determined by TLC, 0.15 g of a mixture of products was isolated, and analyzed by GLC. Results of the analysis: methyl dehydroabietate (2) — 70%; methyl 7-ketodehydroabietate (3) — 10%; epoxidation products and others — about 20%. The following were isolated by chromatography on a column of SiO_2 (71-90 μm), the eluent being a solution of from 5 to 40% of DE in hexane: 1) 0.09 g of a fraction containing methyl dehydrobietate (2) and trace amounts of the monoepoxide (4); 2) 0.012 g of a fraction containing methyl 7-ketodehydroabietate (3); and 3) 0.02 g of a mixture of compounds (5), (6), (7) and (8a).

Methyl 13-Formyl-14-norabiet-7-en-18-oate (10). The chromatography of the mixture of products from the reaction of the ester (**1b**) with $SiO_2/KMnO_4$, using 10% of DE in hexane as the eluent gave 0.008 g of compound (**10**), an oily liquid, $[\alpha]_{540}^{21}$ – 37.2°*. PMR spectrum: 0.81 (s, 3H-20), 1.07 (d, J = 7 Hz, 3H-16, 3H-17), 1.21 (s, 3H-19), 3.60 (s, OCH_3), 6.73 (m, H-7), 9.33 (s, H-14). For the ^{13}C NMR spectrum, see Table 2.

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*Results due to Yu. A. Silko.

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