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TRANSFORMATIONS OF TERPENOIDS ON SYNTHETIC ZEOLITES

I. REACTIONS OF LABDANE ALCOHOLS ON ZEOLITE HY

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The transformations on zeolite HY of epimanool and of 13-hydroxylabd-8(17),14-dien-6-one and its $\Delta^{7,8}$ isomer have been studied.

Catalysts based on synthetic zeolites are widely used in various petrochemical processes (cracking, hydrocracking, etc.) [1]. Recently, interest in synthetic zeolites as catalysts of fine organic reactions – the isomerization of organic compounds and substitution reactions in them – has intensified [2, 3].

Extremely interesting in view of the promising nature of zeolites as ecologically pure catalysts is an attempt to use zeolites for transformations of terpene compounds with the aim of obtaining new substances. There is little information in the literature on the use of solid catalysts in the chemistry of natural compounds. We must mention studies on the cyclization and isomerization of monoterpenes on solid acids [3], on zeolites [4], and on sorbents impregnated with chromic acid [5-7]. Zeolites of various brands have been used for hydration of sesquiterpenes [8, 9].

A large number of studies have been devoted to the chemistry of the labdane diterpenoids [10-12], which is explained by the wide distribution and availability of these compounds; although they form a raw material for obtaining valuable industrial products, we have found no reports of reactions of diterpenoids on zeolites. A large amount of experimental material has accumulated that is devoted to the study of the transformations of bicyclic diterpenoids in acid media over a very wide range of acidities (from weak acid media to "superacids") [13, 14]. In view of this, the task of a systematic study of the reactions of diterpenoids on zeolites in comparison with their transformations taking place in a liquid-phase acid medium is extremely urgent.

The present work was devoted to a study of the transformations of diterpenes of the labdane type – epimanool (I) and 13-hydroxylabda-8(17),14-dien-6-one (below, 6-oxolarixol) (II) and its $\Delta^{7,8}$ isomer (13-hydroxylabda-7,14-dien-6-one) – on zeolite HY.

Epimanool (I), isolated from the oleoresin of the Siberian larch, was deposited on the zeolite in solution in diethyl ether (DE), and the mixture was kept at 40°C for 4.5 h (see the Experimental part). The reaction products consisted of a difficultly separable multicomponent mixture of hydrocarbons (five components, according to GLC) from which it was possible by chromatography on silica gel with silver nitrate to isolate only two individual compounds, (IV) and (V). According to GLC and IR and PMR spectroscopy, compound (IV) was identical with pimara-8,9-diene, and hydrocarbon (V) with isopimara-8,9-diene.*

*Specimens of pimara-8,9-diene and isopimara-8,9-diene were kindly supplied by P. F. Vlad.

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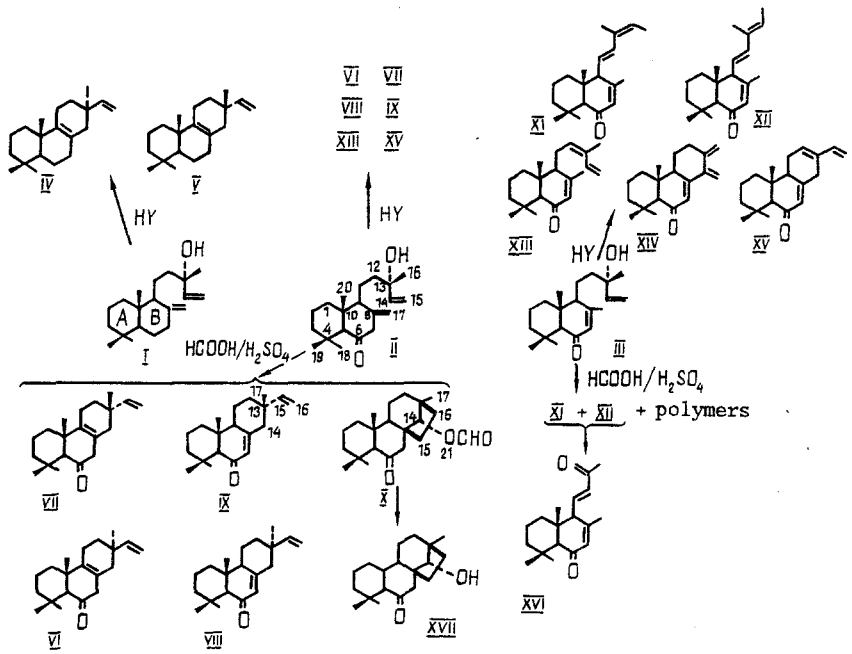
It is known that, in acid media, epimanool (or its epimer – manool) readily cyclizes with the formation of tricyclic compounds [15, 16]. This fact has found reflection in many hypothetical biogenetic schemes describing the interrelationship of bi-, tri-, and tetracyclic terpenoids. The mechanism of the formation of tricyclic diterpenoids from bicyclic precursors via intermediate carbocations has been described in fairly great detail [13, 17, 18].

We then studied the behavior of 6-oxolarixol (II) and its $\Delta^{7,8}$ isomer (III) on the zeolite. Compound (II) has been obtained previously by the oxidation of larixol with chromic anhydride; on chromatographic purification, (II) partially isomerized into compound (III) [19]. The chemical properties of these substances have not been studied. On its interaction with the zeolite, from compound (II) we obtained a difficultly separable multicomponent mixture.

In view of the closeness of the structures of (I) and (II) and of the results obtained in the reactions of epimanool on the zeolite and also with formic acid [15, 16], we performed the acid isomerization of 6-oxolarixol (II) in a mixture of formic and sulfuric acids (9:1). In this case, as was to be expected, we obtained epimeric pairs of the tricyclic diterpene ketones (VI and VII) and (VIII and IX). The structures of the compounds isolated were established on the basis of their IR and ^1H and ^{13}C NMR spectra, and also of an x-ray structural analysis (XSA) of compound (VIII). The acid isomerization of compounds (VIII) and (IX) (with gaseous HCl) gave products (VI) and (VII), respectively. Compounds (VI), (VII), (VIII), and (IX) have not previously been described. The reaction mixture was also found to contain oxo-α-hibanol formate (X). The structure of α-hibanol and the mechanism of its formation have been described [13], but its oxo derivative was unknown. The reaction of compound (II) in an acid medium took place in a short time (5 min), with the formation of ≈80% of tricyclic ketones; it is known that compounds of similar structural types possess biological activity [20]. As a result of the transformation of compound (II) on the zeolite we detected in the reaction products – together with the tricyclic compounds (VI-IX) – two substances, (XIII) and (XV), the formation of which can be explained by the migration of the 8(17) double bond into a position of conjugation with the keto group and the impossibility of cyclization; only dehydration takes place.



After being kept on the zeolite, the hydroxyketone (III) gave a reaction mixture containing, according to GLC, not less than three components, in a ratio of 2:1:2. The mixture was separated by adsorption chromatography. We isolated in very small amount (fraction 1) a mixture of the isomeric ketones (XI) and (XII) in a ratio of 1:4 (according to PMR results); their retention times were identical with one another and with that of compound (XIV). An analysis of spectral characteristics and a comparison of them with the spectra of cis- and trans-neoabienols permitted the assumption that the hydrocarbon skeletons and the configurations of the side chains of (XI) and (XII) were similar to those of the isomeric neoabienols [21].

Then fraction 2 (see the Experimental part) was dissolved in pentane, and the precipitate that deposited was recrystallized from methanol to give a crystalline compound with mp 148-151°C. Its UV spectrum contained an absorption maximum at 240 nm, while its IR spectrum lacked the absorption band of a free hydroxy group. The PMR spectrum showed the presence of five methyl groups, two of which were present at double bonds (1.80 and 1.83 ppm). In the weak-field region of the spectrum there were the signals of the protons at a vinyl double bond – 5.12 ppm (1H, dd), 5.22 ppm (1H, dd), and 6.74 ppm (1H, dd) – and also the signals of protons on trisubstituted double bonds at 5.36 and 5.75 ppm. On the basis of the spectral results, the compound isolated was ascribed the structure of labda-7,12,14-trien-6-one (XIII), the configuration of the side chain and the positions of the double bonds in it being the same as in the cis-abienol molecule [23].

We then isolated from the reaction mixture compound (XV), with mp 142.5-144°C (UV spectrum: λ_{max} 238 nm). The PMR spectrum of (XV) was identical with that of (XIII), with the only difference that the signal of the H_{14} proton on the vinyl bond resonated in a stronger field (6.34 ppm), which is characteristic for trans-isomers. Consequently, the side chain of compound (XV) is similar to that in the trans-biformene or trans-abienol molecule, as was confirmed by UV and ^1H and ^{13}C NMR spectra [22, 24].

Thus, on the reaction of compound (III) with the zeolite under the conditions selected, no change in the carbon skeleton or cyclization of the ketone molecule took place, but the hydroxy group at C_{13} in the side chain was split out. The results obtained may be compared with those for the dehydration of manool [24], where the formation of cis- and trans-biformenes was shown.

It was of interest to compare the results obtained on the zeolite for (III) with the products formed on its acid isomerization. In this case, we obtained a mixture of the isomeric ketones (XI) and (XII), and also the diketone (XVI) (15,16-bisnorlabda-7,11-diene-6,13-dione), but the main products (80%) were polymeric. Compound (XVI) was, most probably, an artefact – a product of the autooxidation of the ketones (XI) and (XII) [25].

After studying the behavior of the labdadienes (I), (II), and (III) on zeolite HY we came to the conclusion that, under the conditions selected, different processes took place according to the position of the double bond in ring B. If the compound contained an exomethylene double bond the predominant process was acid-catalyzed cyclization with the formation of isomeric tricyclic diterpenoids. Where the most reactive semicyclic bond was absent, dehydration and polymerization processes took place but no compounds with a different type of carbon skeleton were formed.

EXPERIMENTAL

Melting points were determined on a Kofler stage. Specific rotations were measured on a Polamat A polarimeter. IR spectra were taken in CCl_4 solution on a UR-20 instrument. PMR spectra were recorded on $CDCl_3$ on Bruker AC-200 (200.13 MHz) and Bruker AM-400 (400.13 MHz) instruments (δ scale, internal standard chloroform, the signal of which was taken as 7.24 ppm). ^{13}C NMR spectra were recorded on Bruker AC-200 (50.32 MHz) and Bruker AM-400 (100.62 MHz) instruments (δ scale, internal standard $CDCl_3$, 76.9 ppm). The assignment of the signals and the multiplicities of the chemical shifts in the ^{13}C NMR spectra are given on the basis of a comparison with those for related compounds [26-28]. High-resolution mass spectra were obtained on a Finnigan MAT 8200, pW, instrument.

For the reactions we used a zeolite HY (composition: Na_2O 2.90%, Al_2O_3 19.65%, SiO_2 55.60%, Fe_2O_3 0.08%) synthesized by the ion-exchange of a suspension of zeolite NaY in a buffer solution of the following composition: 80 g of NH_4Cl + 75 ml of a 25% solution of NH_4OH + water (to a volume of 1500 ml). Exchange was performed at a weight ratio of zeolite to buffer solution of 1:100. The treatment was carried out at 60°C with stirring; after 1.5 h of contacting, the suspension was filtered, and the residue was washed with water until the anion of the salt had been completely eliminated, and it was dried in the air and calcined at 500°C for 1.5 h. This procedure was repeated 3 times. Immediately before the reaction, the zeolite, placed in a reactor of the flow-through type (a Pyrex tube with a volume of 10 cm^3), was calcined in a current of air at 500°C for 2 h.

After the catalyst had cooled to room temperature, the substrate dissolved in DE was deposited on it (zeolite:substrate ratio = 1:0.015). The solvent was driven off, and the reactor was placed in a thermostated cell. In all cases the reaction time was 4.5 h, and

TABLE 1. Chromatography of the Products of the Reaction of Compound (II) on HY

Fraction No.	Solvent, % DE in PE	Yield, g	Notes
1	2	0,005	Mixture of (VI) and (VII) (1:1)
2	"	0,006	Compound (IX)
3	"	0,014	Mixture of (VIII) and (XIII) (1:1)
4	"	0,010	Mixture of (XIII) and (XV) (1.3:1)
5	"	0,007	Compound (XV)
6	50	0,022	Complex mixture
7	100	0,028	Not investigated

TABLE 2. Chromatography of the Products of the Reaction of Compound (II) in an Acid Medium

Fraction No.	Solvent, % DE in PE	Yield, g	Notes
1	2	0,06	Mixture of (VI) and (VII) (1:2)
2	3	0,12	Mixture of (VIII) and (IX) (1:1)
3	10	0,02	Compound (X)
4	100	0,08	Complex mixture, not investigated

the temperature 40°C. The reaction products were eluted with DE. For adsorption chromatography we used silica gels with a grain size of 71-100 μm, and, as solvents, petroleum ether (40-70°C) and DE. Thin-layer chromatography was conducted on Silufol plates. The gas–liquid chromatography of the reaction mixtures and the checking of the individuality of the compounds were carried out on a Chrom-5 instrument under the following recording conditions: glass column (3 mm × 2 m) with the stationary phase SE-30 deposited on Chromaton N-super, column temperature 180°C, carrier gas nitrogen at 30 ml/min.

Reaction of Epimanool (I) on HY. The reaction of 0.3 g of (I) on the zeolite led to a mixture (0.25 mg) which (according to GLC) contained ~15% of the initial epimanool (I) and four reaction products. The product mixture was chromatographed on SiO_2 (100 μm), and PE eluted 180 mg of hydrocarbons (their IR spectrum lacked the absorption bands of functional groups). The total amount of hydrocarbons (180 mg) was chromatographed on SiO_2 (71 μm) with the addition of $AgNO_3$ (20%). The course of separation was monitored by GLC. DE–PE (1:49) eluted 3 mg of a hydrocarbon (IV), identical according to TLC, GLC, and spectral characteristics with an authentic sample of isopimara-8,9-diene. We did not succeed in isolating the other components of the mixture (130 mg) in the pure form.

Production of 13-Hydroxylabda-8(17),14-dien-6-one (II). With stirring, a suspension of 3 g of pyridinium chlorochromate in 50 ml of CH_2Cl_2 was added to a solution of 2.8 g of larixol in 25 ml of CH_2Cl_2, and the reaction mixture was stirred for a day. Then it was chromatographed, and DE–PE (1:4) eluted 1.3 g of compound (II) with $[\alpha]_{594}^{23}$ +76° (c 0.840), n_D^{26} 1.5122. PMR spectrum (200 MHz), ppm: 0.64 (s, CH_3-C_{10}), 0.96 and 1.17 (s, $2CH_3$-C_4), 1.28 (s, CH_3-C_{13}), 2.98 (m, 2H-7), 4.69 (br.s, 1H-17), 4.86 (br.s, 1H-17), 5.07 (dd, J = 11 and 1.5 Hz, 1H-15), 5.20 (dd, J = 17.5 and 1.5 Hz, 1H-15), 5.91 (dd, J = 11 and 17.5 Hz, 1H-14). For the ^{13}C NMR spectrum (200 MHz), see Table 4.

Reaction of 6-Oxolarixol (II) on HY. The reaction products (0.12 g) obtained on the interaction of 0.18 g of compound (II) with the zeolite (consisting of five components according to GLC) were chromatographed on SiO_2 at a ratio of substance to sorbent of 1:40. The results are shown in Table 1.

Reaction of 6-Oxolarixol (II) in a Weak Acid Medium. A mixture of compound (II) (0.34 g) and 20 ml of a mixture of acids (10% of conc. H_2SO_4 and 90% and 99% HCOOH) was kept at room temperature for 5 min. Then 25 ml of a 5% solution of NaOH was added to the reaction mixture, and it was extracted with ether. The ethereal layer was washed with saturated sodium carbonate solution and with water and was dried, and the solvent was distilled off. The mixture of reaction products (0.28 g) contained five components (according to GLC). The results of chromatography are shown in Table 2.

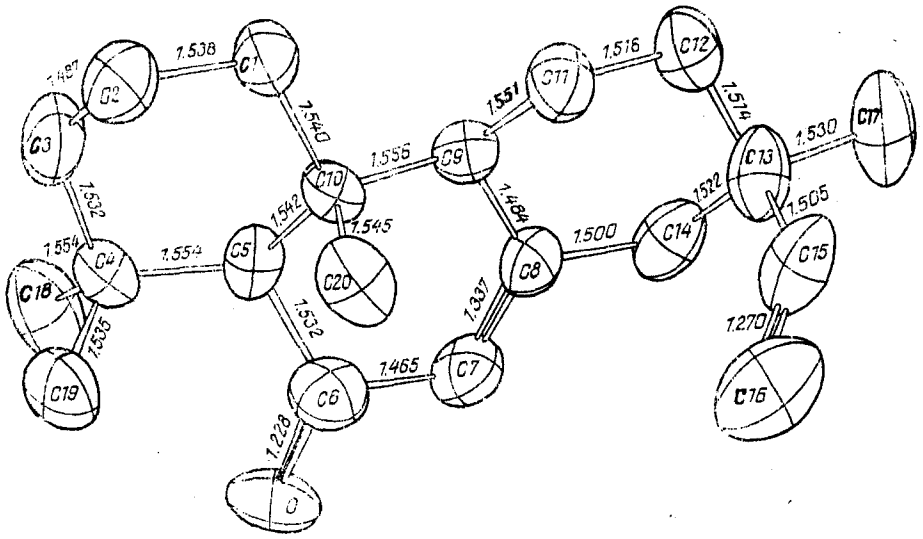


Fig. 1. Crystal structure and relative configuration of pimara-7,8-dien-6-one (VIII).

Pimara-7,8-dien-6-one (VIII). The rechromatography of the 2nd fraction (0.09 g) on SiO_2 (100 μm) impregnated with 20% of $AgNO_3$, using DE in PE (6%) yielded 0.035 g of compound (VIII) and 0.045 g of compound (IX). Compound (VIII) had mp 76-78°C (acetonitrile) and $[\alpha]_{594}^{25}$ −30° (c 0.267). IR spectrum, $\nu_{max}^{CCl_4}$, cm^{-1}: 870, 920 (C=C), 1680 (C=O). PMR spectrum (200 MHz), ppm: 0.85, 1.01, 1.09, 1.18 (3H each, s, tertiary methyl groups), 4.89 (dd, J = 17.5 and 1 Hz, 1H-15), 4.99 (dd, J = 11 and 1 Hz, 1H-15), 5.58 (dd, J = 11 and 17.5 Hz, 1H-14), 5.71 (m, 1H-7). For the ^{13}C NMR spectrum, see Table 4. Empirical formula $C_{20}H_{30}O$ (found, m/z 286.2318; calculated 286.2297. Mass spectrum, m/z (%): 286(60) − M^+, 271(27) − $(M - 15)^+$, 215(10), 203(100), 162(80), 147(95), 134(70), 109(18), 105(25), 91(0), 81(28), 67(22), 55(35), 41(48).

X-Ray Structural Analysis of Compound (VIII) was done on a Syntex $P2_1$ diffractometer using Cu radiation with a graphite monochromator. The crystals of (I) were rhombic, with a = 7.5439(6), b = 11.137(1), c = 21.078(3) Å, space group $P2_12_12_1$, Z = 4, d_{calc} = 1.07 g/cm^3. The intensities of 1420 independent reflections were measured by the $2\theta/\omega$ scanning method in the interval $2\theta < 116°$. In the calculation we used 1072 of the observed reflections without allowance for absorption, μ = 4.9 cm^{-1}. The structure was interpreted by the direct method using the SHELX 86 program.

The structure of the molecule and the relative configurations of the asymmetric centers and also the bond lengths are shown in Fig. 1. Rings A and C of the molecule have the chair form, while ring B is a distorted half-chair [29]. The enone system is conjugated − the torsional angle O=C6−C7=C8 is 173.0°, and the length of the C6−C7 bond, 1.465(9) Å, agrees with the mean length of 1.464 Å for this fragment [30].

Isopimara-7,8-dien-6-one (IX). The compound (IX) obtained on chromatography (see above) had mp 79-82°C (acetonitrile) and $[\alpha]_{594}^{24}$ −16° (c 0.565). IR spectrum, $\nu_{max}^{CCl_4}$, cm^{-1}: 870, 920 (C=C), 1680 (C=O). PMR spectrum (200 MHz), ppm: 0.88, 0.95, 1.09, 1.20 (3H each, s, tertiary methyl groups), 4.91 (dd, J = 11 and 1 Hz, 1H-15), 4.95 (dd, J = 17.5 and 1 Hz, 1H-15), 5.70 (m, 1H-7), 5.80 (dd, J = 17.5 and 11 Hz, 1H-14). For the ^{13}C NMR spectrum, see Table 4. Empirical formula $C_{20}H_{30}O$ (found, m/z 286.2296; calculated 286.2297). Mass spectrum, m/z (%): 286(55) − M^+, 271(100) − $(M - 15)^+$, 253(12), 243(10), 229(10), 215(20), 203(62), 201(65), 173(10), 161(20), 147(50), 134(15), 119(20), 105(20), 95(15), 91(22), 81(22), 69(35), 57(30), 44(100).

Fraction 1 (Table 2), consisting of a mixture of compounds (VI) and (VII), could not be separated into its individual components by rechromatography.

Pimara-8,9-dien-6-one (VI). Gaseous HCl was passed through a solution of 0.027 g of compound (VIII) in chloroform for 30 min, and the solvent was evaporated. According to GLC, the reaction product consisted of two components. By chromatography, 7 mg of compound (VI) and 10 mg of the initial compound (VIII) were isolated. Compound (VI) consisted of a viscous colorless oil. PMR spectrum (400 MHz), ppm: 0.90 (3H), 0.99 (6H), 1.25 (3H) − s, ter-

tiary methyl groups, 2,39 (s, 1H-5), 2.59 (br.s, 1H-7), 2.73 (br.s, 1H-7), 4.87 (dd, J = 11 and 1.5 Hz, 1H-15), 4.87 (dd, J = 17.5 and 1.5 Hz, 1H-15), 5.78 (dd, J = 11 and 17.5 Hz, 1H-14). For the ^{13}C NMR spectrum (400 MHz), see Table 4.

Isopimara-8,9-dien-6-one (VII). In a similar way to compound (VIII), 0.035 g of compound (IX) was isomerized with gaseous HCl for 1.5 h. According to GLC, the reaction product consisted of two components. Chromatography led to the isolation of 11 mg of the initial compound (IX) and 11 mg of compound (VII) – a colorless oil. PMR spectrum (200 MHz), ppm: 0.91, 0.966, 0.974, 1.24 (3H each, tertiary methyl groups), 2.37 (s, 1H-5), 2.61 (br.s, 1H-9), 2.73 (br.s, 1H-7), 4.89 (dd, J = 17.5 and 1.5 Hz, 1H-15), 4.93 (dd, J = 11 and 1.5 Hz, 1H-15), 5.78 (dd, J = 11 and 17.5 Hz, 1H-14).

6-Oxo-α-hibanol Formate (X). Compound (X) (fraction 3, Table 2), consisted of a viscous yellow oil, $[\alpha]_{594}^{24}$ –2° (c 1.130). IR spectrum, $\nu_{max}^{CCl_4}$, cm^{-1}: 910, 1180, 1715, 1720. PMR spectrum (200 MHz), ppm: 0.88, 1.20, 1.22 (3H each), 0.89 (6H) (s, tertiary methyl groups), 4.50 (br.s, 1H-14), 8.29 (d, J = 1 Hz, 1H-15). For the ^{13}C NMR spectrum, see Table 4. Empirical formula $C_{21}H_{32}O_3$ (found m/z 332.2366; calculated 332.2351). Mass spectrum, m/z (%): 332(100) – M^+, 271(25), 258(12), 249(27), 203(10), 151(25), 121(15), 109(20), 95(17), 91(12), 81(15), 69(42), 59(12), 55(28), 43(30).

6-Oxo-α-hibanol (XVII). A solution of 0.032 g of the keto formate (X) in 2 ml of absolute ethanol was treated with 20 mg of KOH, and the mixture was heated until dissolution had taken place. It was left overnight at room temperature and was then boiled for 10 min. The solvent was distilled off, water was added, extraction was performed with ether, and the ethereal layer was dried. The reaction products (0.03 g) were chromatographed on SiO_2, and DE–PE (1:4) eluted 0.01 g of compound (XVII) with mp 165-168°C (methanol–water) and $[\alpha]_{594}^{25}$ –2° (c 0.771). IR spectrum, $\nu_{max}^{CCl_4}$, cm^{-1}: 1710 (C=O), 3640 (OH). PMR spectrum (400 MHz), ppm: 0.89 (6H), 0.93, 1.21 (3H each, s, tertiary methyl groups), 2.11 (s, 2H-7), 2.72 (d, J = 13.5 Hz, 1H-14), 2.96 (br.s, OH). For the ^{13}C NMR spectrum, see Table 4. Empirical formula $C_{20}H_{32}O_2$ (found, m/z 304.2407; calculated 304.2402). Mass spectrum, m/z (%): 304(100) – M^+, 289(12), 271(10), 261(12), 201(62), 203(10), 151(32), 121(20), 109(27), 95(15), 81(15), 69(12), 55(17), 43(13), 41(18).

Production of Compound (III). A solution of 1 g of compound (II) in DE was deposited on Al_2O_3 with the addition of boric acid (5%), and the mixture was allowed to stand until the initial compound had disappeared (2 days; monitoring by TLC). Then the sorbent was filtered off and the solvent was distilled off. This gave 0.9 g of compound (III) with $[\alpha]_{594}^{23}$ +144° (c 1.008) and n_D^{26} 1.5122. PMR spectrum (200 MHz), ppm: 0.82 (3H, s, CH_3-C_{10}), 1.10 and 1.13 (3H each, s, $2CH_3$-C_4), 1.30 (3H, s, CH_3-C_{13}), 1.89 3H, br.s, CH_3-CH_8), 5.09 (dd, J = 10.5 and 1 Hz, 1H-15), 5.18 (dd, J = 17.5 and 1 Hz, 1H-15), 5.72 (m, 1H-7), 5.91 (dd, J = 10.5 and 17.5 Hz, 1H-14). For the ^{13}C NMR spectrum, see Table 4.

Reaction of 13-Hydroxylabda-7,14-dien-6-one (III) on Zeolite HY. The reaction product (0.19 g) obtained from the interaction of compound (III) (0.26 g) with the zeolite was chromatographed on SiO_2 (100 μm) with the addition of 20% of $AgNO_3$. The results of chromatography are shown in Table 3.

Fraction 1 (Table 3) consisted of a mixture of compounds (XI) and (XII) in a ratio of 1:4. IR spectrum, $\nu_{max}^{CCl_4}$, cm^{-1}: 1120, 1380, 1680. UV spectrum, λ_{max}, nm: 240 (ε 16070). PMR spectrum (200 MHz), ppm: 5.2-5.6, m; 5.75, br.s; 5.8, br.s; 6.10, d, J = 8 Hz; 6.5, d, J = 8 Hz. A comparison of the total PMR spectra of compounds (XI) and (XII) with those of trans- and cis-neoabienols [21] showed their identity in the weak-field region (5-6.5 ppm).

cis-Labda-7,12,14,trien-6-one (XIII). Fraction 2 (Table 3) was treated with hexane (5 ml), whereupon compound (XIII) remained in the residue and compound (XIV) passed into the mother solution (monitoring by GLC). The residue was recrystallized from methanol, giving compound (XIII) with mp 148-151°C and $[\alpha]_{594}^{22}$ +51° (c 0.588). IR spectrum, $\nu_{max}^{CCl_4}$, cm^{-1}: 920 ($HC=CH_2$), 1640, 3100 (C=C), 1680 (C=O). UV spectrum, λ_{max}, nm: (ε 24000). PMR spectrum (200 MHz), ppm: 0.86, 1.11, 1.15, 1.80, 1.83 (3H each, s, tertiary methyl groups), 5.12 (dd, J = 11 and 1 Hz, 1H-15), 5.22 (dd, J = 17.5 and 1 Hz, 1H-15), 5.36 (m, 1H-12), 5.75 (br.s, 1H-7), 6.74 (dd, J = 11, 17.5, and 1 Hz, 1H-14). For the ^{13}C NMR spectrum (200 MHz), see Table 4.

TABLE 3. Chromatography of the Products of the Reaction of Compound (III) on HY

Fraction No.	Solvent, % DE in PE	Yield, g	Notes
1	4	0,015	Mixture of (XI) and (XII) (1:4)
2	"	0,065	Mixture of (XIII) and (XIV) (1:1)
3	5	0,01	Mixture of (XIII), (XIV), and (XV)
4	"	0,045	Compound (XV)
5	100	0,05	Resin

TABLE 4. Chemical Shifts (ppm) and Multiplicities of the Signals in the ^{13}C NMR Spectra of Compounds (II, III, VI, VIII, IX, X, XIII, XIV, XV, XVI, and XVII)

C atoms	II	III	VI	VIII	IX	X
1	38,84 t	38,70 t	41,11 t	39,03 t	39,07 t	39,41 t
2	18,19[a] t	18,08 t	18,48 t	18,15 t	18,14 t	17,95 t
3	41,09 t	43,12 t	42,55 t	43,02 t	42,96 t	42,37 t
4	32,50 s	32,15 s	32,17 s	32,05 s	32,02 s	32,39 s
5	57,36 d	56,60 d	61,87 d	52,63 d	52,25 d	47,75 t
6	207,83 s	199,98 s	210,30 s	200,20 s	200,20 s	210,96 s
7	55,71 t	128,38 d	47,40 t	126,67 d	127,47 d	53,08 t
8	143,41 t	158,66 s	122,67 s	158,84 s	157,88 s	49,83 s
9	66,38 d	63,60 d	138,05 s	63,24 d	63,07 d	65,69 d
10	41,42 s	43,33 s	34,72 s	40,30 s	40,03 s	39,81 s
11	18,58 t	21,27 t	20,90 t	20,44 t	19,84 t	19,50 t
12	42,73 s	44,60 t	33,76[b] t	37,08 t	35,31 t	28,93[a] t
13	73,25 s	73,19 s	29,59[a] s	37,69 s	37,05 s	43,00 s
14	145,06 d	144,68 d	36,56[b] t	44,34 t	45,42 t	82,58 d
15	111,68 t	112,02 t	147,95 d	144,97 d	148,79 d	31,99[a] t
16	27,75 q	27,71 t	110,06 t	113,92 t	110,09 t	29,56[a] t
17	109,92 t	21,90 q	23,96 q	30,13 q	21,91[a] q	24,21 q
18	32,70 q	33,34 q	32,54 q	33,63 q	33,62 q	32,66 q
19	21,51 q	21,39[a] q	21,67 q	21,69 q	21,77[a] q	21,78 q
20	15,70 q	14,54 q	20,29 q	15,12 q	15,08 q	16,44 q
21						160,74 d

(continuation of Table 4)

C atoms	XIII	XIV	XV	XVI	XVII
1	39,22 t	38,65 t	39,32 t	40,15 t	39,41 t
2	18,20 t	18,09 t	15,53 t	17,86 t	18,02 t
3	43,03 t	43,09 t	43,09 t	42,94 t	42,47 t
4	32,21 s	32,19 s	32,24 s	32,42 s	32,03 s
5	56,70 d	55,99 d	56,62 d	60,17 d	46,58 d
6	199,99 s	200,01 s	199,82 s	199,04 s	212,37 s
7	128,65 d	128,54 d	128,75 d	128,61 d	53,74 t
8	158,34 s	158,36 s	157,99 s	154,06 s	50,38 s
9	63,39 d	63,52 d	63,45 d	62,99 d	65,63 d
10	43,03 s	43,05 s	43,09 s	42,67 s	39,72 s
11	24,99 t	25,91 d	25,93 t	143,58 d	19,46 t
12	131,43[a] d	33,71 d	133,56[a] d	135,45 d	29,05[a] t
13	131,86 s	145,92 s	133,70 s	197,19 s	43,17 s
14	133,30[a] d	138,51 d	141,07[a] d	27,38 q	82,85 d
15	114,25 t	116,34 t	110,85 t	—	32,12[a] t
16	19,73 q	113,34 t	11,90 q	—	31,49[a] t
17	22,52 q	22,01 q	22,24 q	22,65 q	24,62 q
18	33,43 q	33,36 q	33,44 q	33,42 q	32,67 q
19	21,51 q	21,41 q	21,53 q	21,53 q	21,62 q
20	14,87 q	14,57 q	14,88 q	15,90 q	16,55 q

[a,b] May change places within a given compound.

Labda-7,13,14-trien-6-one (XIV). After the separation of compound (XIII), the mother solution was evaporated, giving compound (XIV) as a semicrystalline mass (its purity was checked by GLC). IR spectrum, $\nu_{max}^{CCl_4}$, cm^{-1}: 910 ($HC=CH_2$), 1600, 1630 (C=C), 1680 (C=O). UV spectrum, λ_{max}, nm: 230 (ε 21050). PMR spectrum (200 MHz), ppm: 0.81, 1.11, 1.13, 1.93 (3H each, s, tertiary methyl groups), 5.00 (br.s, 1H-16), 5.05 (br.s, 1H-16), 5.08 (d, J = 10.5 Hz, 1H-15), 5.22 (d, J = 17.5 Hz, 1H-15), 5.74 (br.s, 1H-7), 6.36 (dd, J = 10.5 and 17.5 Hz, 1H-14). For the ^{13}C NMR spectrum (200 MHz), see Table 4.

trans-Labda-7,12,4-trien-6-one (XV). Fraction 4 (Table 3) was recrystallized from DE, giving compound (XV) with mp 142.5-144°C and $[\alpha]_{594}^{8}$ +33° (c 0.84). IR spectrum, $\nu_{max}^{CCl_4}$, cm^{-1}: 910 ($HC{=}CH_2$), 1610, 1640, 3100 (C=C), 1680 (C=O). UV spectrum, λ_{max}, nm: 238 (ε 21000). PMR spectrum (200 MHz), ppm: 0.87, 1.11, 1.15, 1.75, 1.82 (3H each, s, tertiary methyl groups), 4.93 (d, J = 11 Hz, 1H-15), 5.08 (d, J = 17.5 Hz, 1H-15), 5.47 (m, 1H-12), 5.75 (br.s, 1H-7), 6.34 (dd, J = 11 and 17.5 Hz, 1H-14). For the ^{13}C NMR spectrum (200 MHz), see Table 4.

Reaction of Compound (III) in an Acid Medium. The ketone (III) (0.34 g) was kept in 15 ml of the mixture of acids (see above) at room temperature for 15 min. The reaction mixture was worked up in a similar way to that for the ketone (II). According to TLC, the product (0.28 g) was a very complex mixture. It was chromatographed on SiO_2, and elution with 2% of DE in PE yielded 0.03 g of a mixture of compounds (XI) and (XII). The remaining fractions consisted of mixtures of polymeric products (M^+ 572, 614).

15,16-Bisnorlabda-7,11-diene-6,13-dione (XVI). When the mixture of compounds (XI) and (XII) was rechromatographed on SiO_2 impregnated with $AgNO_3$, DE–PE (1:5) eluted 5 mg of the white crystalline product (XVI), with mp 141-143°C (hexane with the addition of DE) and $[\alpha]_{594}^{24}$ +79° (c 0.252). IR spectrum, $\nu_{max}^{CCl_4}$, cm^{-1}: 1680 (C=O). UV spectrum, λ_{max}, nm: 240 (ε 25200). PMR spectrum (200 MHz), ppm: 0.97 (3H, s, CH_3-C_{10}), 1.12 and 1.16 (3H each, s, $2CH_3$-C_4), 1.73 (3H, br.s, CH_3-C_8), 2.28 (3H, s, CH_3-C_{13}), 2.97 (d, J = 11 Hz, 1H-9), 5.87 (m, 1H-7), 6.20 (d, J = 16 Hz, 1H-12), 6.63 (dd, J = 11 and 16 Hz, 1H-11). For the ^{13}C NMR spectrum (200 MHz), see Table 4. Empirical formula $C_{18}H_{26}O_2$ (found, m/z 274.1956; calculated, 274.1933). Mass spectrum, m/z (%): 274(17) – M^+, 259(21) – $(M-15)^+$, 232(10), 191(15), 161(10), 150(20), 135(10), 122(15), 108(55), 91(10), 77(10), 69(12), 55(12), 43(100).

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