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New Reactions of Isoprenoid Olefins with Aldehydes promoted by Al_2O_3-SiO_2 Catalysts

Nariman F. Salakhutdinov*, Konstantin P. Volcho, Irina V. Il'ina, Dina V. Korchagina, Ludmila E. Tatarova, Vladimir A. Barkhash

Novosibirsk Institute of Organic Chemistry, Novosibirsk 630090, Russia

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Abstract Wide-pored β-zeolite or natural clay askanite-bentonite, when used as catalysts to perform reactions of terpene olefin derivatives with aldehydes, provide unusual transformations yielding new polyheterocyclic compounds.

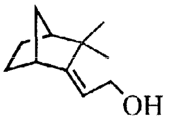
Introduction

This paper deals with a new group of reactions between olefins and aldehydes, where the carbonyl group serves as a structural unit providing heteroatoms for the heterocycle. Curiously enough, olefins and aldehydes rarely use their functional groups in their interactions, although these are highly reactive compounds, which participate in many reactions.[1] The only exception is the Prins reaction, in which a carbonyl compound (most often formaldehyde) adds to an olefin, yielding 1,3-glycols, allyl alcohols, or 1,3-dioxanes (when two formaldehyde molecules participate in the reaction). The "cyclo-Prins" reaction (intramolecular cyclization of ketones) yields a new carbon cycle with a hydroxyl group at the site of branching. The carbonyl group usually acts as an activator; it is not involved in formation of new bonds in the product just as, for example, in the Diels-Alder reaction.

Heterogeneous alumina-silica catalysts often change the activation barriers of transformations. With polyfunctional molecules having flexible conformation such as terpenes and their derivatives these catalysts guide the reaction along unknown routes. One of such routes is the reaction of olefins with aldehydes producing polyheterocyclic compounds.

Results and Discussion

We have already noted the Prins reaction of olefins with formaldehyde. The condensation of a natural olefin such as camphene **1** with formaldehyde in the presence of traditional acid catalysts yields typical products: 8-hydroxymethylcamphene **2** and 1,3-dioxane **3**.[2,3] The camphene skeleton does not change during these transformations.



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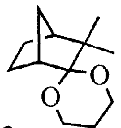

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However, wide-pore β-zeolite used as a catalyst in the same reaction provides unusual products of skeletal rearrangements, such as 10,10-dimethyl-4-oxatricyclo[5.2.1.$0^{1,5}$]decane **4** and 2,6-dimethyl-3-oxatricyclo-[5.2.1.$0^{2,6}$]decane **5** (scheme 1). At the first stage, a protonated aldehyde molecule attacks the olefin double bond in compound **1**. Then the reaction follows one of two routes. The first route is a Wagner-Meerwein rearrangement proceeding with stabilization of the positive charge by bonding with the oxygen atom and yielding ether **4**. The second route is a 1,2-shift of the *exo*-methyl group allowing cation stabilization and producing ether **5**.

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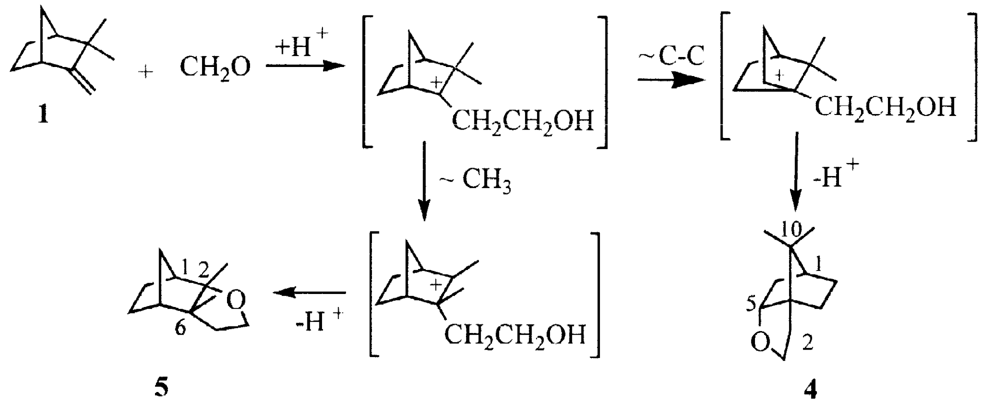
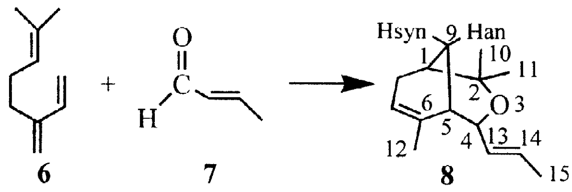
Scheme 1



When the β-zeolite catalyst is used in the reaction of myrcene **6** with dienophilic molecules such as α,β-unsaturated carbonyl compounds, the reaction conditions are milder and more selective, and the reaction gives higher product yields.[4] However, the products are typical for the Diels-Alder reaction.

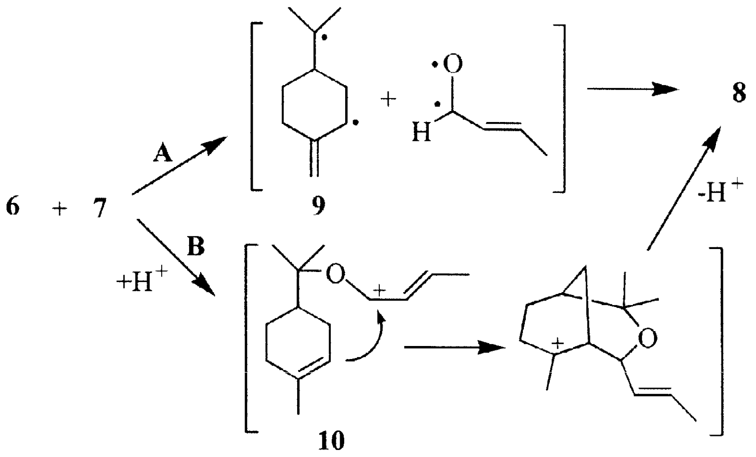
When used as a catalyst in the reaction of triene **6** with crotonaldehyde, askanite-bentonite clay unexpectedly provides 2,2,6-trimethyl-4-(prop-1-enyl)-3-oxabicyclo[3.3.1]non-6-ene **8** (scheme 2). In the course of formation of ether **8**, three π-bonds transform into three σ-bonds, producing two new rings. Therefore, the reaction conforms to the definition of a homo-Diels-Alder reaction. However, this transformation is unusual, because, first, triene **6** enters the reaction with two non-conjugated, but not its conjugated double bonds and, second, α,β-unsaturated aldehyde reacts by the carbonyl group but not by the double bond.

Scheme 2



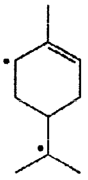
Let us consider the possible mechanisms of these unusual transformations, namely the homolytic (**A**) and the heterolytic (**B**) mechanisms (scheme 3).

Scheme 3



In these cases, reaction presumably proceeds through intermediates **9** and **10**, respectively. In fact, racemic dipentene **11** reacts with aldehyde **7** to give the same bicyclic ether **8** as in the case of myrcene **6**. However, this reaction is not diene synthesis, since diene **11** has no conjugated double bonds, nor the Diels-

Alder homoreaction, since only two double bonds disappear in the latter. Thus the reaction is of particular interest. We have studied the mechanism of bicyclic ether formation using the interaction of diene **11** with aldehydes. If dipentene **11** reacts with aldehyde **7** according to the homolytic mechanism, it can be assumed that the cleavage of the double bond at C-8 is followed by hydride shifts yielding intermediate **12**; the heterolytic mechanism requires no hydride shifts.



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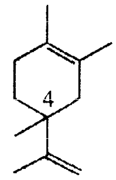

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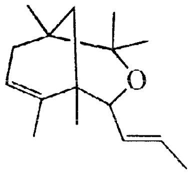

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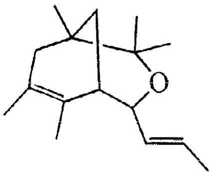

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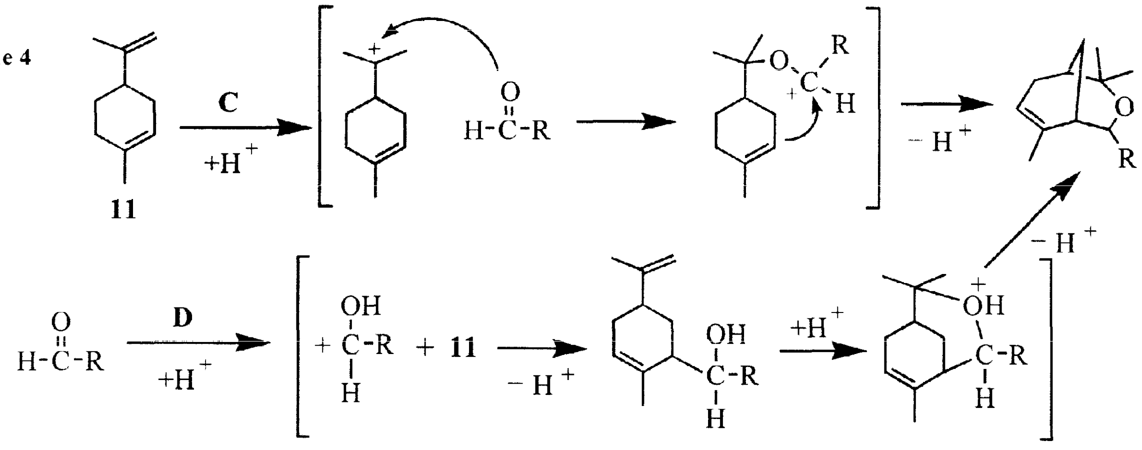
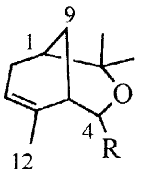
To check both mechanisms, we introduced a model compound, 1,2,4-trimethyl-4-isopropenylcyclohex-1-ene **13** into the reaction with aldehyde **7**. Since compound **13** has a methyl group in position 4, 1,2-hydride shifts cannot occur. Diene **13** interacts with aldehyde **7** over askanite-bentonite clay, yielding ether **14**, whereas in case of the homolytic mechanism, one would expect the formation of isomeric ether **15** with an unaltered carbon skeleton of the moiety derived from the diene. This experiment gives evidence in favor of the heterolytic mechanism, which in turn may follow route **C** or **D** (scheme 4).

Scheme 4



R is $CH{=}CHCH_3$

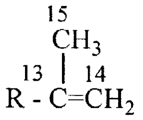
When the reaction proceeds by route **C**, the protonated diene provides an electrophilic attack, while the aldehyde is nucleophilic. In the case of route **D**, the electrophilic protonated aldehyde reacts with the nucleophilic diene. However, we observe no interaction of 1-methylcyclohexene with aldehyde **7** modeling the first step of route **D**. This provides evidence in favor of route **C**.



16 $R - \overset{13}{C}H{=}\overset{14}{C}H_2$

17 $R - \overset{13}{C}H_2\overset{14}{C}H_2\overset{15}{C}H_3$

18 $R - C_6F_5$



19 $R - \overset{13}{C}(\overset{15}{C}H_3){=}\overset{14}{C}H_2$

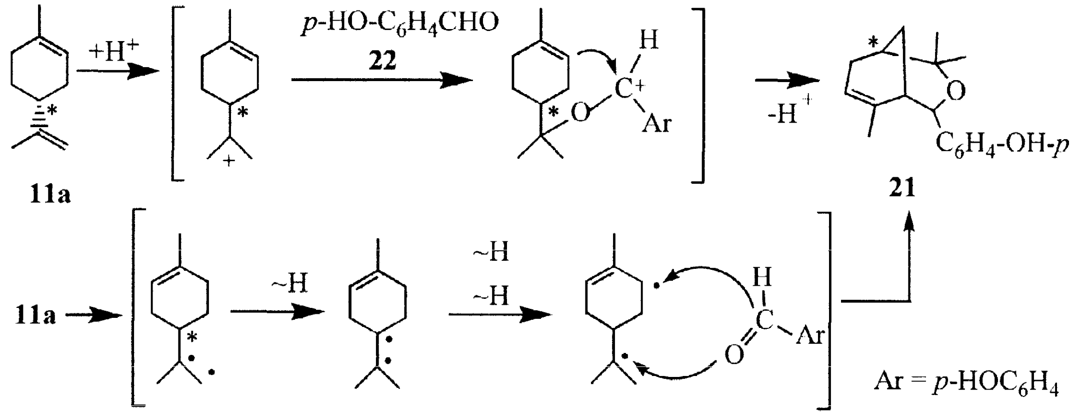
20 $R - C_6H_5$

21 R - *p*- $OH\text{-}C_6H_4$

The proposed mechanism seems to be general in character, since diene **11** interacts with acrolein, butanal, pentafluorobenzaldehyde, α-methylacrolein, benzaldehyde, *p*-hydroxybenzaldehyde to give bicyclic ethers **16-21**, respectively.

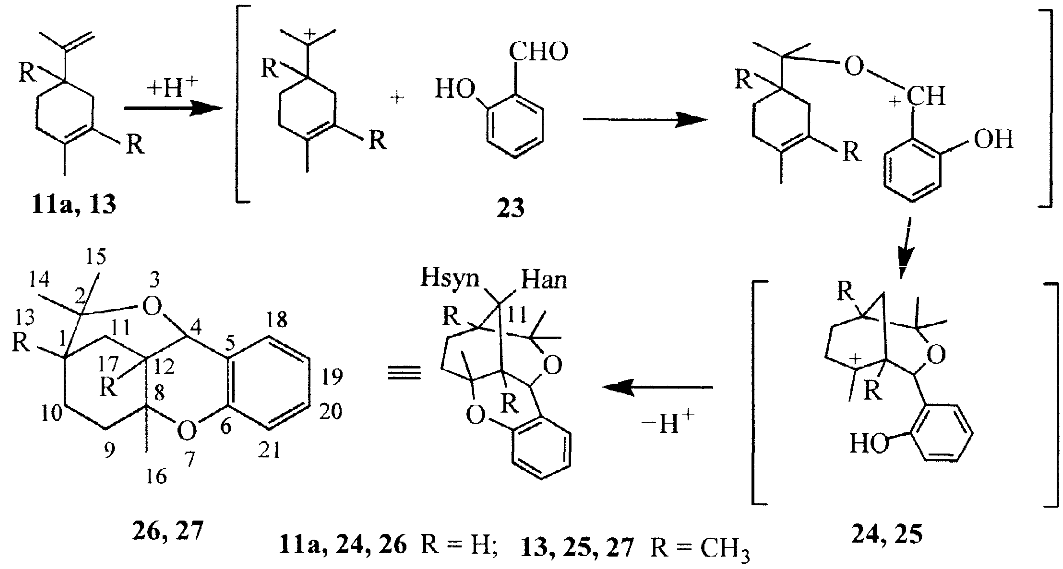
The fact that optically active ether **21** ($[\alpha]^{20}_{580}$= +171.4°, $CHCl_3$) is formed in the reaction of (R)-(+)-limonene **11a** ($[\alpha]^{20}_{580}$= +123°) with *p*-hydroxybenzaldehyde **22** supports the heterolytic mechanism. Scheme 5 shows that the product cannot be optically active if it is formed according to the homolytic mechanism.

Scheme 5



When dienes **11a** and **13** interact with salicylaldehyde **23**, which is an isomer of aldehyde **22**, over the askanite-bentonite clay at room temperature, the reaction does not stop at the stage of bicyclic ether, since the cation centre in intermediates **24** and **25** attacks the hydroxy group to give compounds with a xanthene skeleton linked to a tetrahydropyran ring such as 2,2,8-trimethyl-3,7-dioxa-5,6-benzotricyclo[6.2.2.$0^{4,12}$]dodecane **26** and 1,2,2,8,12-pentamethyl-3,7-dioxa-5,6-benzotricyclo-[6.2.2.$0^{4,12}$]dodecane **27**, respectively (scheme 6).

Scheme 6

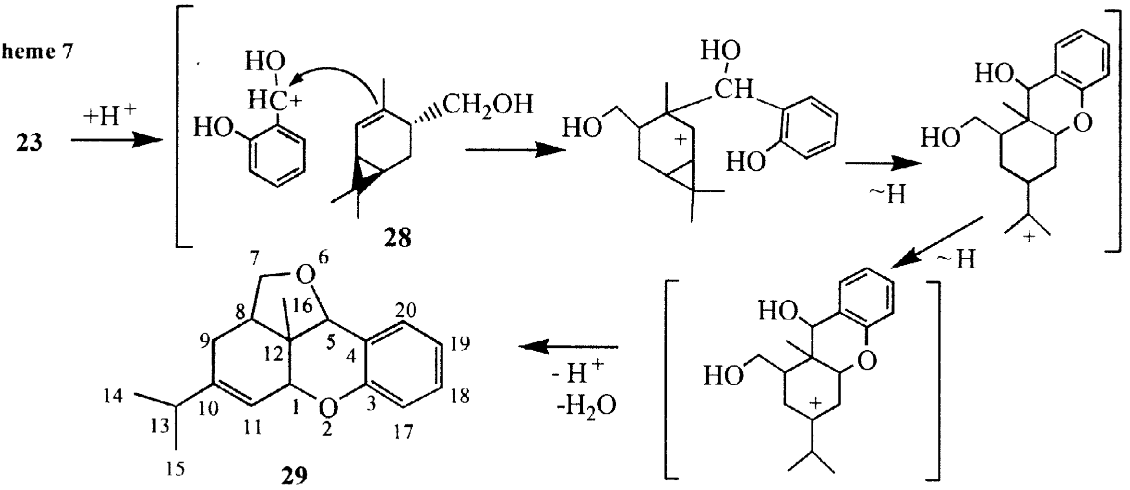


Expanding our studies, we have introduced the menthane and carane derivatives of monoterpene containing an alcohol group into the reaction with aldehyde **23**. When *trans*-4-hydroxymethyl-2-carene (valterol) **28** interacts with aldehyde **23** over the askanite-bentonite clay at room temperature, the forming product has a xanthene skeleton linked to the tetrahydrofuran ring as in 12-methyl-10-isopropyl-2,6-dioxa-3,4-

benzotricyclo[6.3.1.$0^{5,12}$]dodec-10-ene **29**, but not to the tetrahydropyran ring as in **26** and **27** (scheme 7). The following mechanism is most likely. Protonated aldehyde **23** attacks the double bond of hydroxyolefin **28**, producing the α-cyclopropylcarbinyl ion, which is then transformed to compound **29** via heterocyclization.

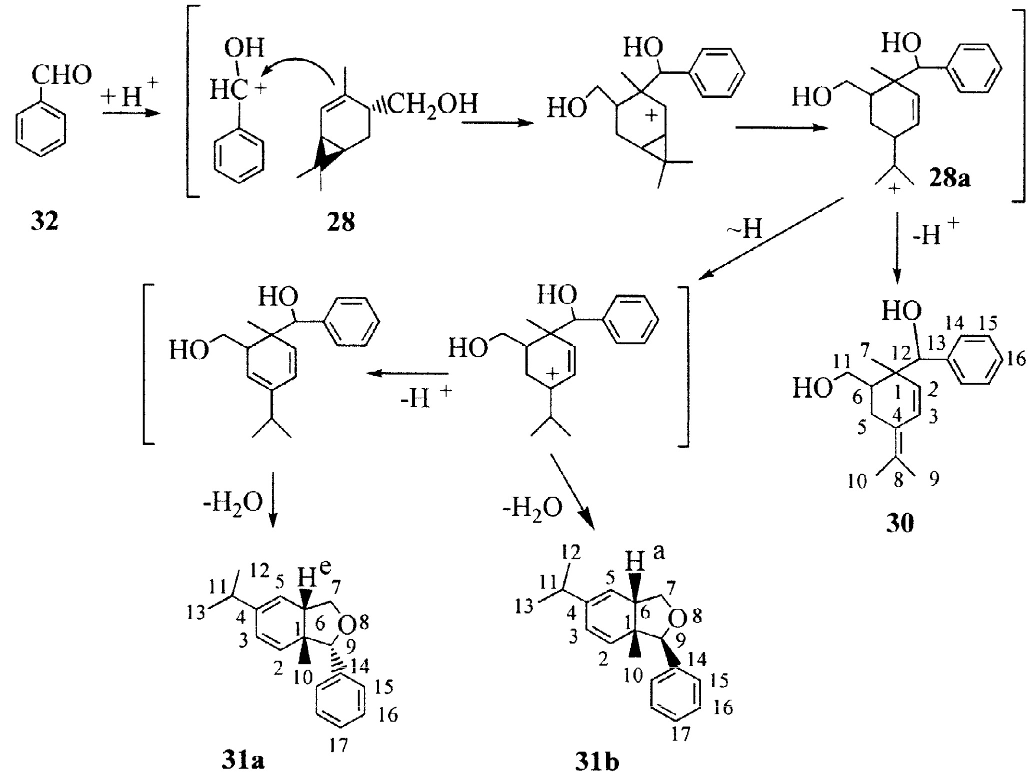
Formation of products **30** and **31a** in the reaction of hydroxyolefin **28** with benzaldehyde **32** also agrees well with the suggested mechanism (scheme 8). In this case, the attack of the double bond of hydroxyolefin **28** by protonated aldehyde **32**, yielding 6-hydroxymethyl-1-(α-hydroxybenzyl)-p-mentha-2,4(8)-diene **30**, is of prime importance.

Scheme 7



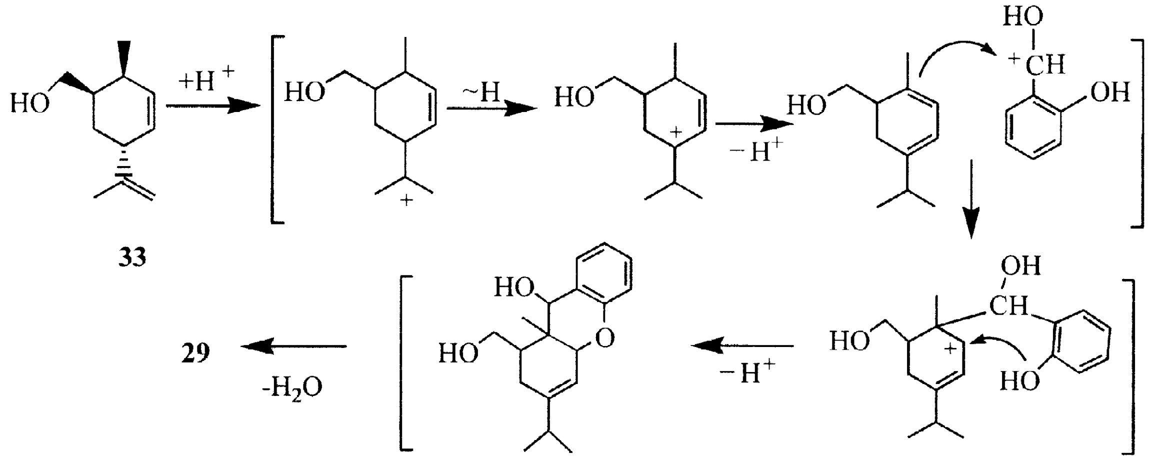
The products of intramolecular cyclization of intermediate **28a**, 4-isopropyl-1β-methyl-9α-phenyl-8-oxabicyclo[4.3.0]nona-2,4-diene **31a** and 4-isopropyl-1β-methyl-9β-phenyl-8-oxabicyclo[4.3.0]nona-2,4-diene **31b**, are formed in less amounts.

Scheme 8



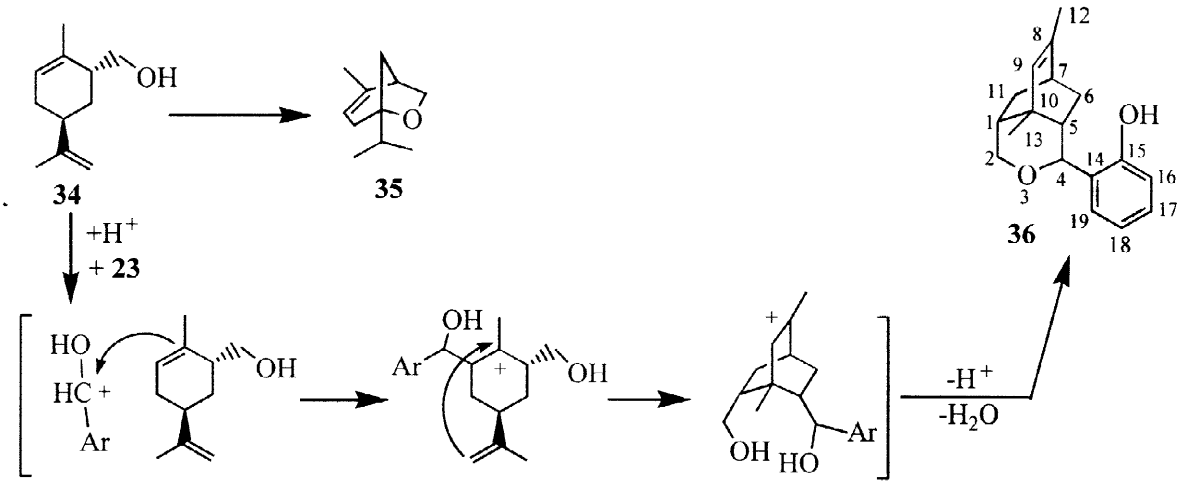
We also consider a scheme starting with the protonation of the cyclopropane ring of hydroxyolefin **28** as an alternative mechanism for the formation of **29**. In this case we take into account that 6-hydroxymethylisolimonene **33** interacts with aldehyde **23** to yield compound **29**, since it is impossible for a protonated aldehyde to attack hydroxyolefin **33** at the first carbon atom without its preliminary isomerization (scheme 9).

Scheme 9



As 6-hydroxymethyllimonene **34**, which is an isomer of **33**, interacts with aldehyde **23** on the clay, a completely different product forms (scheme 10).

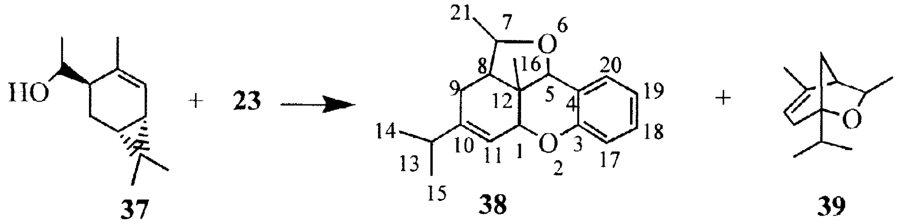
Scheme 10



While 4-methyl-1-isopropyl-7-oxabicyclo[3.2.1]oct-3-ene **35** anticipated as a product of an intramolecular reaction of compound **34**, 8,10-dimethyl-4-(2-hydroxyphenyl)-3-oxatricyclo[5.3.1.$0^{5,10}$]undec-8-ene **36** seems to be a very unusual product. We failed to find any example in the literature confirming that the bicyclo[2.2.2]octane skeleton forms from compounds possessing the *p*-menthadiene skeleton. Therefore, we suggest scheme for the formation of **36** involving only tertiary carbocations leading to closing of the bicyclo[2.2.2]octane and tetrahydropyran rings. Note that, although **34** has the skeleton of p-mentha-1,8-diene, it reacts with aldehyde **23** in an absolutely different manner from diene **11a**.

The reaction of *trans*-4-(1-hydroxyethyl)-2-carene **37** with aldehyde **23** produces 7,12-dimethyl-10-isopropyl-2,6-dioxa-3,4-benzotricyclo[6.3.1.0^{5,12}]dodec-10-ene **38**, which is a homologue of **29**, and also 4,6-dimethyl-1-isopropyl-7-oxabicyclo[3.2.1]oct-3-ene **39** [5] (scheme 11).

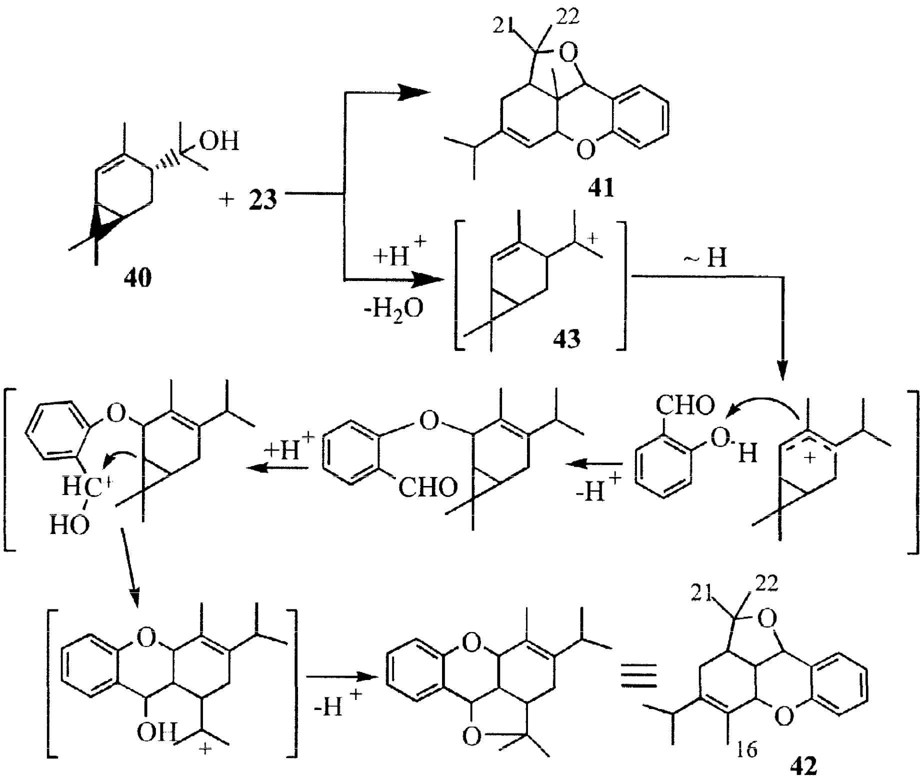
Scheme 11



When an additional methyl group is introduced into the hydroxyethyl fragment of compound **37**, the reactivity of *trans*-4-(1-methyl-1-hydroxyethyl)-2-carene **40** with aldehyde **23** changes dramatically. In addition to 7,7,12-trimethyl-10-isopropyl-2,6-dioxa-3,4-benzotricyclo[6.3.1.0^{5,12}]dodec-10-ene **41**, most likely formed similarly to **29**, the reaction mixture contains 7,7,11-trimethyl-10-isopropyl-2,6-dioxa-3,4-benzotricyclo[6.3.1.0^{5,12}]dodec-10-ene **42**; the ratio of **41**: **42** is 1.5:1 according to GLC. The different arrangement of methyl groups in product **42** requires a different mechanism of interaction, as shown in scheme 12.

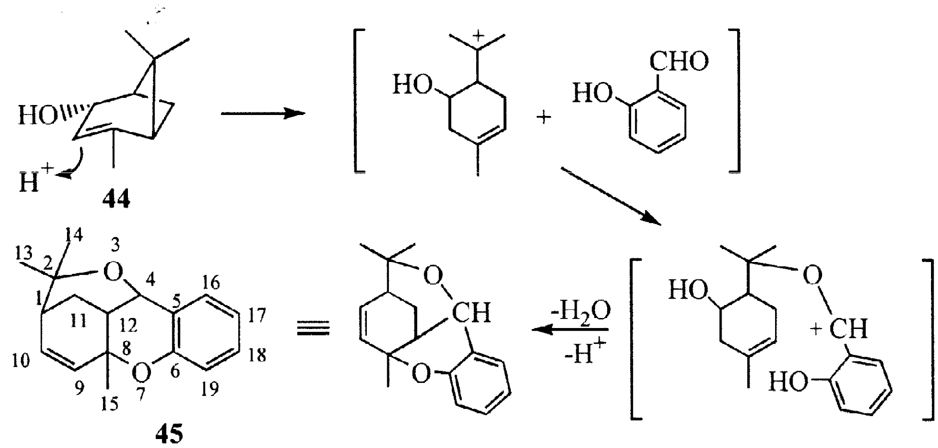
Tertiary cation **43** is relatively stable, which ensures all transformations. With **28** and **37** the protonation of the alcohol group followed by dehydration would yield unstable primary and secondary cations, respectively. In this case, realization of scheme 12 is hardly probable.

Scheme 12



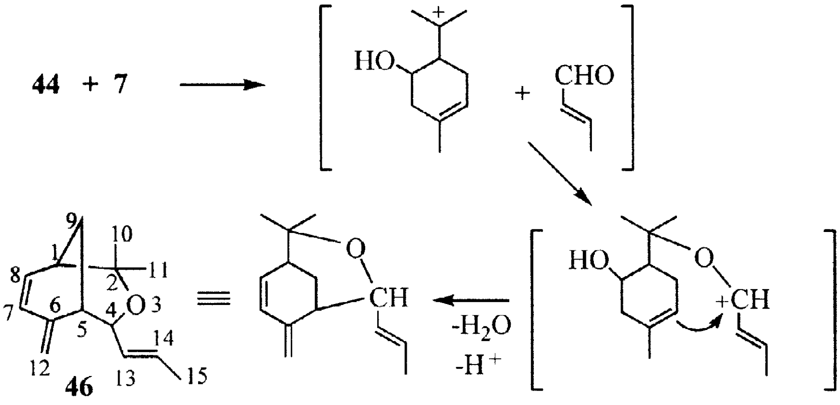
When a hydroxyolefin possessing a pinane skeleton such as *trans*-verbenol **44** reacts with aldehyde **23**, we observe compounds with a xanthene skeleton linked to a tetrahydropyran ring such as 2,2,8-trimethyl-3,7-dioxa-5,6-benzotricyclo[6.2.2.0^{2,12}]dodec-9-ene **45** as in the case of dienes **11a** and **13** (scheme 13). In this case the cation originating from hydroxyolefin **44** acts as an electrophilic species, but first undergoes skeleton rearrangements.

Scheme 13



With aldehyde **7** hydroxyolefin **44** forms a bicyclic compound with three double bonds such as 2,2-dimethyl-4-propenyl-6-methylene-3-oxabicyclo[3.3.1]non-7-ene **46**. Here again **44** most likely acts as a precursor of an electrophilic species (scheme 14).

Scheme 14

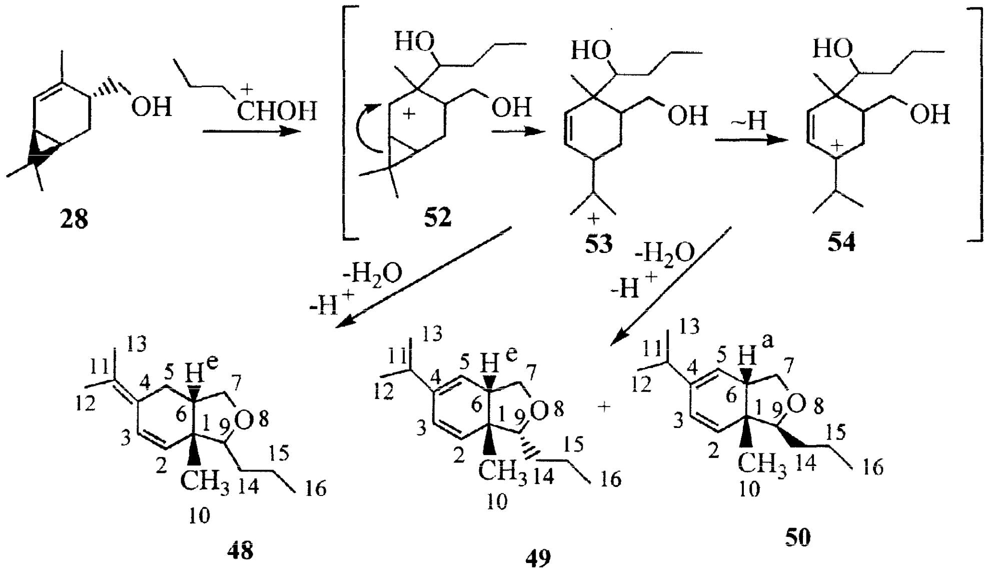


Therefore, the reaction route leading to different heterocyclic systems depends not only on the presence or absence of hydroxy groups in the substrates (hydroxyolefins **28** and **44** *vs* dienes **11a** and **13**) but also on the substrate structure.

The unusual reaction of hydroxyolefin **28** with aromatic aldehyde **23**, yielding a rather complex compound **29** (a potential analogue of anti-AIDS preparations[6]) from relatively simple reagents under mild conditions, prompted us to study the interactions of hydroxyolefin **28** with aliphatic aldehydes.

When **28** reacts with butyraldehyde **47** over the askanite-bentonite clay, it affords the following compounds: 1-methyl-4-isopropylidene-9-propyl-8-oxabicyclo[4.3.0]non-2-ene **48**, 1-methyl-4-isopropyl-9-propyl-8-oxabicyclo[4.3.0]nona-2,4-dienes **49** and **50**, and compound **51**. According to NMR and mass-spectrometry, the latter corresponds to the addition of two molecules of aldehyde **47**. A possible mechanism of formation of **48-50** is the following. Protonated aldehyde **47** attacks the double bond of hydroxyolefin **28** yielding a relatively stable α-cyclopropylcarbinyl ion **52**. The cyclopropane ring opening produces homoallyl ion **53**, which converts to a more stable ion **54** after the 1,2-shift of the hydrogen atom. After the cyclization of the latter two ions followed by the loss of a proton and water, bicyclic ethers **48-50** form (scheme 15).

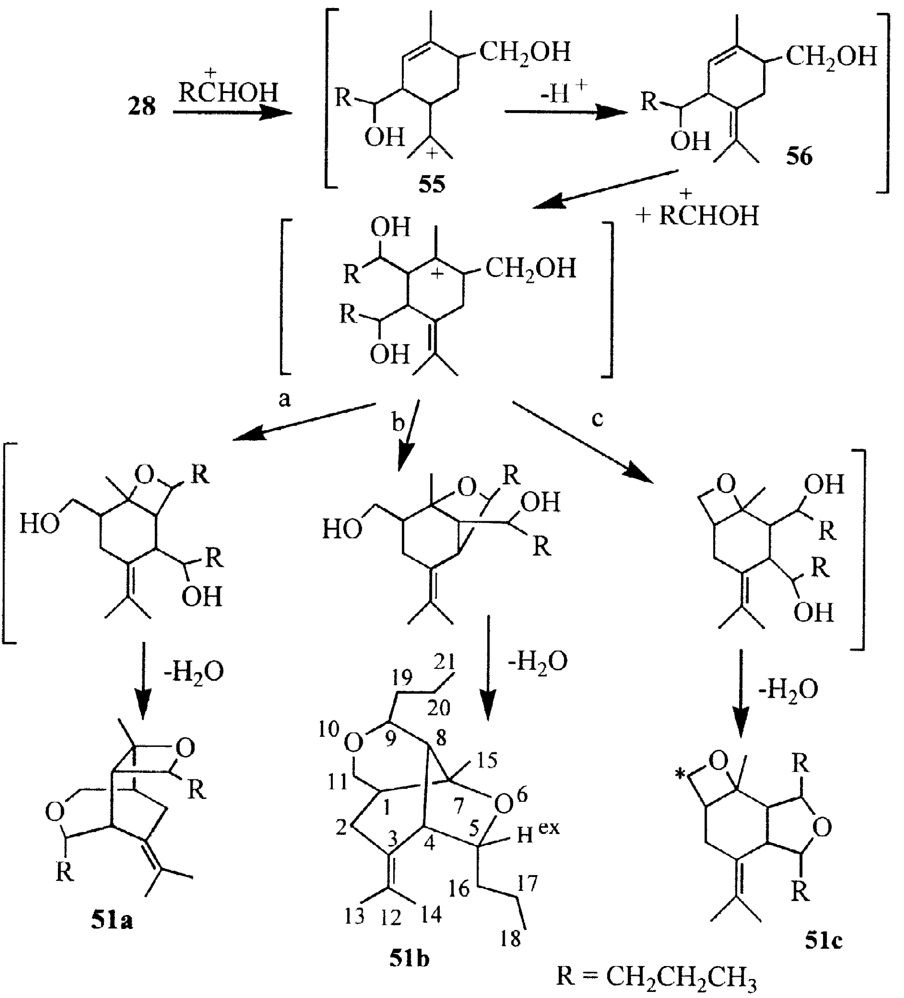
Scheme 15



Compound **51** may have one of three structures **51a-c**. Scheme 16 shows a possible mechanism of their formation. The protonated aldehyde attacks the hydroxyolefin on the cyclopropane ring producing carbocation **55**, which turns to *p*-menthadiol **56** after proton elimination. The second aldehyde molecule attacks compound **56** at the secondary but not at the tertiary carbon atom in the *endo*cyclic double bond, as in the previous case. Intramolecular cyclization then may occur by one of three different routes, which yield cyclic ethers **51a-c** after elimination of water.

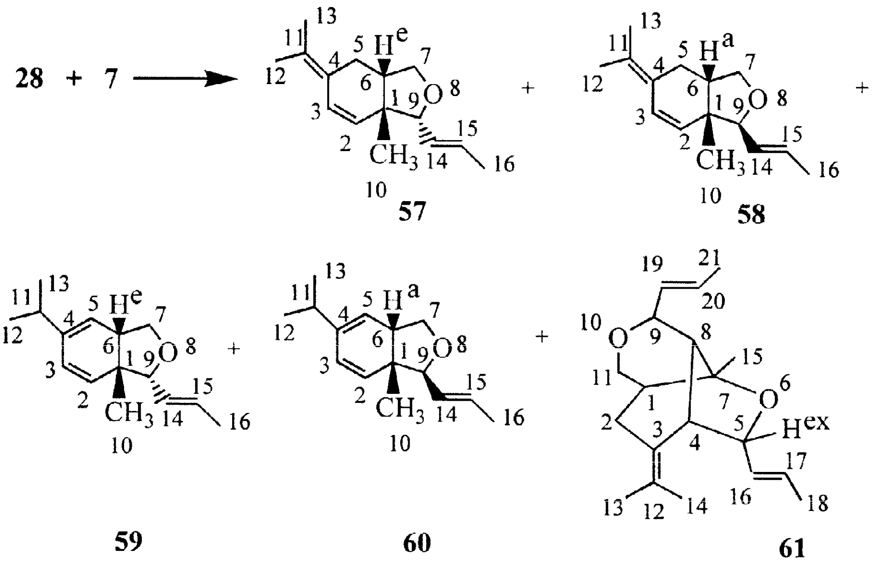
Formation of **51c** is unlikely, since, according to[7], the geminal constant of spin-spin coupling of protons at carbon linked to oxygen in the four-atom ring (carbon atom in structure **51** is marked by an asterisk) is equal to 6-7 Hz. In our case, J_{H-H}= 11.5 Hz, which corresponds to larger rings. The choice between structures **51a** and **51b** is made based on the Raman spectrum, which show an intense band at 833 cm^{-1}. However, it was shown elsewhere [8] that the spectrum of compound **51a** with a trimethyleneoxide ring should exhibit a band at 1028 cm^{-1} reflecting the symmetric stretching vibrations of the ring. Another stretching frequency, 813 cm^{-1} characterizes the tetrahydropyran ring and agrees well with the frequency obtained in our work. Moreover, the intensity of the band increases when the ring of the cyclic ethers becomes larger.[8] An intense band at 833 cm^{-1} therefore is evidence in favor of structure **51b,** namely 7-methyl-3-isopropylidene-5,9-dipropyl-6,10-dioxatricyclo[5.4.0.$0^{4,8}$]undecane. This conclusion is supported by the spin-spin coupling constant $^1J_{C-H}$ obtained from the NMR spectrum of compound **51**. For carbon atoms in the α-position with respect to oxygen in the rings we have found the following $^1J_{C-H}$: 144.1 Hz for the carbon atom at 81.63 ppm, 137.3 Hz for the carbon atom at 74.38 ppm, and 141.5 Hz for the carbon atom at 71.47 ppm. These values are typical for the α-carbon atoms of the five- and six - but not four-membered rings. In the latter case we should expect $^1J_{C-H}$ about 149.5 Hz.[9] Note that varying the reaction conditions for compounds **28** and **47** can radically change the reaction route to produce either **51** (preliminary deposition of aldehyde **47** on the catalyst) or **48** (simultaneous deposition of the reagents and lowering the reaction temperature to 0 °C).

Scheme 16



When hydroxyolefin **28** reacts with crotonaldehyde **7**, which possesses the same skeleton as aldehyde **47** but an additional double bond, a set of products is obtained. Among the products are bicyclic compounds such as 1-methyl-4-isopropylidene-9-(1-propenyl)-8-oxabicyclo[4.3.0]non-2-enes **57**, **58** and 1-methyl-4-isopropyl-9-(1-propenyl)-8-oxabicyclo[4.3.0]nona-2,4-dienes **59** and **60** as well as tricyclic compound **61**, namely, 7-methyl-3-isopropylidene-5,9-di(1-propenyl)-6,10-dioxatricyclo[5.4.0.0^{4,8}]undecane (scheme 17).

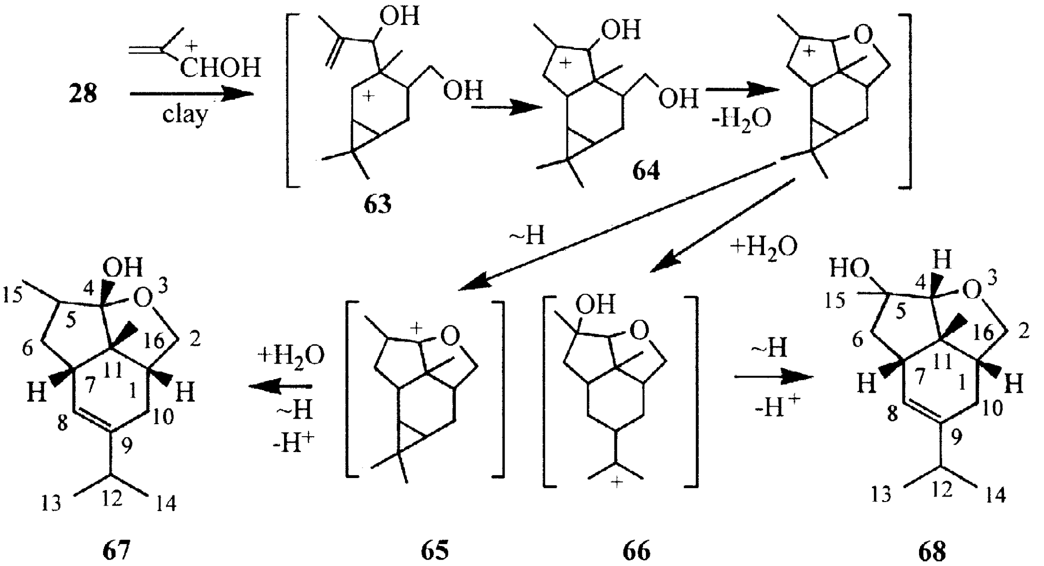
Scheme 17



If liquid catalysts such as CF_3CO_2H or $BF_3{\cdot}Et_2O$ are used instead of clay as catalysts in the reaction of hydroxyolefin **28** with aldehyde **7**, we observe only substituted tetrahydrofurans. There are no products resulting from the additon of two aldehyde molecules to compound **28**. Hydroxyolefin **28** does not react with aldehyde **7** when the reaction occurs over β-zeolite.

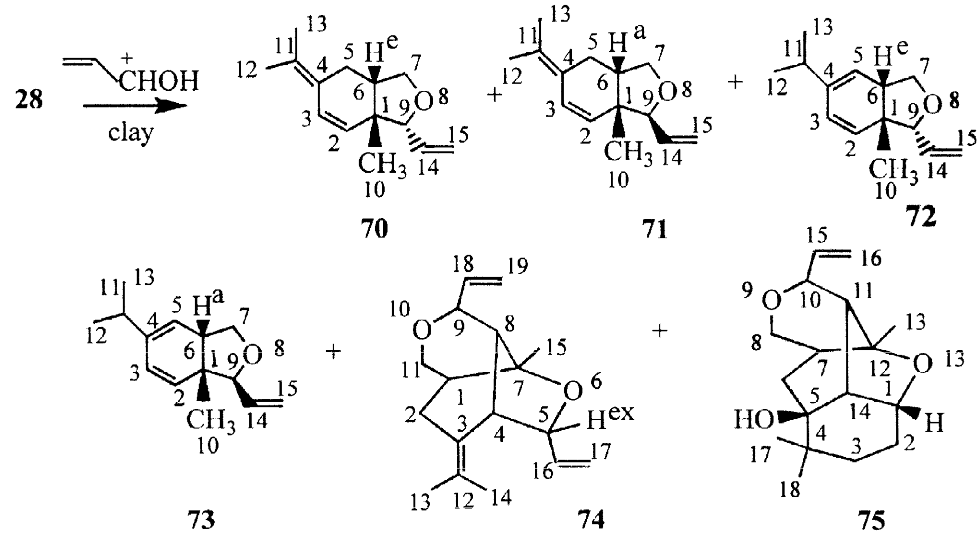
When **28** interacts with the isomer of **7**, α-methylacrolein **62**, the reaction follows a different route (scheme 18).

Scheme 18



The methyl substituent in the α-position of aldehyde **62** and thus of intermediate **63** favors the interaction of the cation centre with the terminal double bond but not the opening of the cyclopropane ring as with intermediate **52**. Tricyclic intermediate **64** undergoes heterocyclization, protonation, various shifts of hydrogen, and stabilization of cations **65** and **66**, when an external nucleophilic species adds and deprotonation occurs, yielding 5,11-dimethyl-9-isopropyl-4-hydroxy-3-oxatricyclo[5.3.1.0^{4,11}]undec-8-ene **67** and 5,11-dimethyl-9-isopropyl-5-hydroxy-3-oxatricyclo[5.3.1.0^{4,11}]undec-8-ene **68**, respectively.

Scheme 19



In going from aldehyde **62** to its homologue acrolein **69**, a different reaction occurs. We have isolated a tetracyclic compound, 4,4,12-trimethyl-10-vinyl-5-hydroxy-9,13-dioxatetracyclo[9.2.1.$0^{7,12}$.$0^{5,14}$]tetradecane **75**, in addition to two diastereoisomers 1-methyl-4-isopropylidene-9-vinyl-8-oxabicyclo[4.3.0]non-2-enes **70** and **71**, 1-methyl-4-isopropyl-9-vinyl-8-oxabicyclo[4.3.0]nona-2,4-dienes **72** and **73**, and the product of addition of two aldehyde molecules 7-methyl-3-isopropylidene-5,9-divinyl-6,10-dioxatricyclo[5.4.0.$0^{4,8}$]-undecane **74** (scheme 19).

^1H and ^{13}C NMR spectra were used to elucidate the structure of all compounds obtained. The spatial arrangement of phenyl and methyl groups in compounds **31a,b** was determined as follows. The 0.4 ppm shift of the signal of the methyl group at C-1 upfield for **31b** relative to **31a** shows the screening effect of the phenyl group. Therefore, the methyl and phenyl groups at the neighboring C-1 and C-9 atoms in **31b** are *cis*-located. With a *trans*-arrangement (according to the Dreiding models), the benzene ring screens the hydrogen atom at C-2 and H-3 to a lesser extent, since H-2 and H-3 in the spectrum of isomer **31a** are diamagnetically shifted by 0.61 and 0.21 ppm, respectively, compared to those in isomer **31b**.

Cis-fusion of six- and five-membered rings is known to provide less strain than *trans*-fusion.[10] Earlier we have supported this conclusion for **31a,b**.[11] Therefore, we believe that **48-50, 57-60, 70-73** have *cis*-fusion between the six- and five-membered rings.

The equatorial position of H-6 in **48, 49, 57, 59, 70, 72** follows from the values of the long-range spin-spin coupling constants $^4J_{6e,2}$, which are 1.2-1.5 Hz. The values agree well with the literature data [12], showing that the couplings for the 1,3-diequatorial protons $^4J_{e,e}$ in the six-membered ring are equal to 1-2 Hz, unlike $^4J_{a,a}$ and $^4J_{a,e}$, which are less than 1 Hz. In compounds **50, 58, 60, 71, 73** there is no interaction between H-6 and H-2. Thus, H-6 occupies an axial position. The axial position of H-6 in **58** and **71** is confirmed by $^3J_{6a,5a}$, which equals 8 Hz. In compounds **48, 57, 70** the vicinal constant $^3J_{5a,6}$ is 4.5 Hz and $^3J_{5e,6}$ is 3-3.5 Hz; these values are typical for $^3J_{a,e}$ and $^3J_{e,e}$, respectively. Therefore, H-6 is equatorial in these compounds. The value of the W-coupling $J_{6e,2}$ confirms the *cis*-fusion of rings in these compounds. With *trans*-fusion, H-6 cannot occupy the equatorial position according to the Dreiding model and we would have failed to record the W-coupling.

It is difficalt to determine the configuration of substitutents at C-9 in **48, 57, 70** and **58, 71** as well as in **49, 59, 72** and **50, 60,73**. Nevertheless, comparing the chemical shifts of the carbon atoms C-1, C-2 and C-9 in the ^{13}C NMR spectra of **49** and **50**, **59** and **60**, **72** and **73** with those of compounds **31a** and **31b**, we assume that substituents at C-1 and C-9 are in the *trans*-position in **49**, **59** and **72**, and in the *cis*-position in **50**, **60** and **73**.

A similar comparison of the chemical shifts of C-2 and C-9 for **57** and **58** and for **70** and **71** (for C-1, the difference between chemical shifts is less than 1 ppm) suggests the *trans*-position of substituents in **57** and **70** and the *cis*-position in **58** and **71**. In compounds **49**, **57**, **59**, **70** and **72**, in which H-6 is equatorial, the substituent at C-9 is in the *trans*-position with respect to the 1-CH_3 group, while in compounds **50, 58, 60, 71** and **73** with an axial H-6, the substituent at C-9 is in the *cis*-position with respect to 1-CH_3 group. Analysis of the Dreiding model shows that in the latter case there is steric hindrance to the *trans*-position of the substituents at C-1 and C-9.

In compounds **51**, **61**, and **74**, H-5 is in the *exo*-position, as follows from the values of vicinal constants $^3J_{5,4}$, which are 3.5-4 Hz. For *endo*-H-5, this value should be less than 1 Hz.[13] The equatorial position of H-1 in the same compounds follows from the constants for the H-2a, H-2e and two protons at C-11 (see Experimental). This conclusion is confirmed by the fact that, according to the Dreiding model, H-1 cannot be axial.

The Dreiding model and the constants for two H-10 show that in **67** and **68** H-1 is equatorial and is in the *cis*-position with respect to the methyl group at C-11, H-7, and the OH group at C-4 in **67** or H-4 in **68**.

In **75**, H-1 is in the *exo*-position, since $^3J_{1,14}$ is equal to 3 Hz, and is in the *cis*-position relative to the OH group at C-5 and the methyl group at C-12.

Conclusions

Alumina-silica catalysts used in the reactions of terpene olefins and their derivatives with aromatic and aliphatic aldehydes direct these processes along previously unknown routes. Thus, complex heteropolycyclic compounds with earlier unknown skeletons form under mild reaction conditions from relatively simple reagents. The reactions do not proceed without catalysts or in the presence of acetic acid. For these reactions, it is hardly possible to apply the widely known assumptions and regulations typical for homogeneous reactions such as homology, isomerism and vinylogy distribution, etc. Indeed, similar homologues such as acrolein and α-methylacrolein, vinylogues such as formaldehyde and acrolein, and isomers such as α-methylacrolein and crotonaldehyde undergo different transformations.

At present, we have no reliable data of the adsorption of even relatively simple organic substrates on the catalyst surface; it is dificalt to predict a priori the reactivities of complex polyfunctional compounds like terpenoids under the reaction conditions. The currently available experimental data allow only several empirical conclusions about the reactivity of terpenoids. However, further accumulation of data will certainly make it possible to summarize and classify the data obtained and thus to predict the reactivities of various substrates.

Experimental

^{1}H and ^{13}C NMR spectra were recorded using a Bruker AM-400 spectrometer in $CDCl_3$. Chloroform was used as internal standard (δ_H 7.24, δ_C 76.90 ppm). ^{1}H NMR spectra were analyzed with double resonance ^{1}H-^{1}H. Signals in ^{13}C NMR spectra were assigned with selective and off-resonance proton irradiation using differential spectra modulated with long-range spin-spin interaction ^{13}C-^{1}H (LRJMD). LRJMD experiment conditions were optimized for constant $J_{C\text{-}H}$ equal to 5 Hz. ^{13}C NMR spectra are given in the Tables.

Raman spectra were recorded using a Coderg PH-1 spectrometer with helium-neon laser in CCl_4.

All chemicals and solvents were obtained from commercial sources and were used after purification by column chromatografy (SiO_2) or distillation. Reagents and products were analyzed with GLC with a flame-ionization detector, column temperature 60-250 °C, and helium the carrier gas. Chromatograph model 3700 was equipped with a glass capillary column 17000x25 mm, phase VS-30. Products were separated over SiO_2 (40-100 μ), gave one peak in GLC and correct NMR spectra.

Elemental composition was determined by high resolution mass spectrometry using Finnigan 8200. Specific rotation was determined with Polamat A spectrometer in $CHCl_3$.

Askanite-bentonite clay was obtained by acidic activation of bentonite clays from the Askansk deposit. The catalyst was calcined for 3 h at 120 °C just before use. β-Zeolite was obtained as described [14], SiO_2/Al_2O_3 ~40, d ~ 8 Å, it was calcined for 2 h at 500 °C before use.

These compounds were prepared using literature procedures: **13**[15]; **28**[16]; **33**[17]; **34**[18]; **40**[20].

The reaction of camphene **1** *with with paraform on zeolite β.* 1 g of camphene, 0.5 g of paraform, 2 g of zeolite and 12 ml of anhydrous toluene were heated for 12 h at 100 °C. Then, after purification on a column with Al_2O_3, 0.868 g (yield 71%) of a mixture containing compounds **4** and **5** were obtained, their ratio being 1.3:1 (GLC). Chromatography on the SiO_2 column (eluent containing from 1 to 10% of diethyl ether in pentane) produced 0.196 g (16%) of **4** and 0.143 g (12%) of **5**. **Compound 4: ^{1}H NMR**, δ: 0.82 s, 1.01 s ($C^{11}H_3$, $C^{12}H_3$), 1.13 m (H^{8en}, H^{9en})1.55 dd (H^{6en}, $J_{6en,6ex}$ 13, $J_{6en,5en}$ 7.5), 1.66 dd ($2H^2$, J 7, 7), 1.70 – 1.82 m (H^{8ex}, H^{9ex}, H^7), 1.98 dddd (H^{6ex}, J 13, $J_{6ex,5en}$ 3.5, $J_{6ex,7}$ 3, $J_{6ex,8ex}$ 3), 3.65 dd (H^{5en}, J 7.5, 3.5), 3.90 dt and 4.03 dt ($2H^3$, J 8, 7). **Compound 5: ^{1}H NMR**, δ: 1.04 s ($C^{11}H_3$), 1.12 s ($C^{12}H_3$),1.28 dddd (H^{9ex}, $J_{9,9}$ 12.5, $J_{9ex,8ex}$ 12.5, $J_{9ex,1}$ 4, $J_{9ex,8en}$ 4), 1.33 ddd (H^{10an}, $J_{10,10}$ 10, $J_{10an,1}$=$J_{10an,7}$=1.5), 1.41 dddd (H^{8ex}, $J_{8,8}$ 12.5, 12.5, $J_{8ex,7}$ 4, $J_{8ex,9en}$ 4), 1.51 ddd (H^5, $J_{5,5'}$ 13, $J_{5,4}$ 8.5, $J_{5,4'}$ 8.5), 2.04 ddd ($H^{5'}$, J 13, $J_{5',4}$ 7, $J_{5',4'}$ 4.5), 1.62 dddd (H^{8en}, J 12.5, 4, $J_{8en,9en}$ 8.5, $J_{8en,10syn}$ 2.5), 1.75 dm (H^{10syn}, J 10), 1.77 m (H^{9en}), 1.83 dm (H^7, J 4), 1.98 dm (H^1, J 4), 3.81 ddd ($H^{4'}$, $J_{4,4'}$ 8.5, J 8.5, 7), 3.90 ddd (H^4, J 8.5, 8.5, 4.5).

The reaction of dipentene **11** *with aldehydes on askanite-bentonite clay. A. With crotonaldehyde.* 0.074 g of diene **11** and 0.06 g of crotonaldehyde in 1.5 ml of CH_2Cl_2 were added to 0.65 g of clay suspended in 1.5 ml of CH_2Cl_2 and mixed for 2 hours at 20 °C. Cromatography on the SiO_2 column (eluent contained from 0 to

4% of diethyl ether in pentane) produced 0.31 g (33%) of ether **8**. **Compound 8:** m/e for $C_{14}H_{22}O$: calc. 206.1671, obs. 206.1670. **^{1}H NMR**, δ: 1.18 s, 1.27 s ($C^{10}H_3$, $C^{11}H_3$), 1.42 ddd (H^1, $J_{1,8ex}$ 6, $J_{1,9syn}$=$J_{1,9an}$ 3), 1.58 ddd (H^{9syn}, $J_{9syn,9an}$ 12, 3, $J_{9syn,5}$ 3), 1.61 ddd ($C^{15}H_3$, $J_{15,14}$ 6.5, $J_{15,13}$ 1.5, $J_{15,4}$ 1), 1.64 m ($C^{12}H_3$), 1.89 m (H^5), 2.01 dddd (H^{8ex}, $J_{8ex,8en}$ 18, 6, $J_{8ex,5}$ 3, $J_{8ex,7}$ 1), 2.12 dddd (H^{9an}, J 12, 3, $J_{9an,5}$ 3, $J_{9an,8en}$ 1), 2.28 br.d (H^{8en}, J 18), 4.17 br.d (H^4, $J_{4,13}$ 7), 5.37 ddq (H^{13}, $J_{13,14}$ 15.5, J 7, 1.5), 5.45 m (H^7), 5.59 dqd (H^{14}, J 15.5, 6.5, $J_{14,4}$ 1).

B. With acrolein. 0.52 g of diene **11** and 0.53 g of acrolein dissolved in 15 ml of CH_2Cl_2 were added to 6.87 g of clay suspended in 15 ml of CH_2Cl_2, and boiled for 4 h. Then 0.64 g of the product was subjected to chromatography on SiO_2 (eluent contained 0.5% diethyl ether in pentane) to evolve 0.040 g of ether **16**. **Compound 16:** m/e for $C_{13}H_{20}O$: calc. 192.1514, obs. 192.1522. **^{1}H NMR**, δ: 1.23 s, 1.30 s ($C^{10}H_3$, $C^{11}H_3$), 1.47 ddd (H^1, $J_{1,8ex}$ 6.5, $J_{1,9syn}$ 3, $J_{1,9an}$ 3), 1.64 ddd (H^{9syn}, $J_{9syn,9an}$ 12.5, $J_{9syn,1}$ 3, $J_{9syn,5}$ 3), 1.66 m ($C^{12}H_3$), 1.98 ddd (H^5, J 3, $J_{5,9an}$ 3, $J_{5,4}$ 2), 2.04 dddq (H^{8ex}, $J_{8ex,8en}$ 18, J 6.5, $J_{8ex,7}$ 3, $J_{8ex,12}$ 2.5), 2.17 dddd (H^{9an}, J 12.5, 3, 3, $J_{9an,8en}$ 1), 2.32 dm (H^{8en}, J 18), 4.24 dddd (H^4, $J_{4,13}$ 6, J 2, $J_{4,14\text{-}trans}$ 2, $J_{4,14\text{-}cis}$ 2), 5.02 ddd ($H^{14\text{-}cis}$, $J_{14\text{-}cis,13}$ 10.5, $J_{14,14}$, J 2), 5.21 ddd ($H^{14\text{-}trans}$, $J_{14\text{-}trans,13}$ 17, J 2, 2), 5.49 m (H^7), 5.78 ddd (H^{13}, J 17, 10.5, 6).

C. With butyraldehyde. 0.52 g of diene **11** and 0.52 g of butyraldehyde in 10 ml of CH_2Cl_2 were added to 5.64 g of clay suspended in 15 ml of CH_2Cl_2, then the mixture was boiled for 5 h. The reaction mixture was separated on SiO_2 (eluent - pentane) to evolve 0.49 g of ether **17**. **Compound 17:** m/e for $C_{14}H_{24}O$: calc. 208.1827, obs. 208.1825. **^{1}H NMR**, δ: 0.87 t ($C^{15}H_3$, J 7), 1.18 s, 1.26 s ($C^{10}H_3$, $C^{11}H_3$), 1.46 ddd (H^1, $J_{1,8ex}$ 6, $J_{1,9an}$ 3.5, $J_{1,9syn}$ 3), 1.60 ddd (H^{9syn}, $J_{9,9}$ 12, $J_{9syn,5}$ 3.5, J 3), 1.71 m($C^{12}H_3$), 1.88 ddd (H^5, J 3.5, $J_{5,9an}$ 3, $J_{5,4}$ 2), 2.03 dddq (H^{8ex}, $J_{8,8}$ 19, J 6, $J_{8ex,7}$ 3, $J_{8ex,12}$ 2.5), 2.10 dddd (H^{9an}, J 12, 3.5, 3, $J_{9an,8en}$ 1), 2.31 dm (H^{8en}, J 19), 3.65 ddd (H^4, $J_{4,13}$ 8, $J_{4,13'}$ 5, J 2), 5.49 m (H^7), 1.46-1.27 m (2 CH_2).

D. With pentafluorobenzaldehyde. 0.62 g of diene **11** and 0.49 g of pentafluorobenzaldehyde dissolved in 10 ml of CH_2Cl_2 were added to 5.15 g of clay suspended in 13 ml of CH_2Cl_2, and then were kept for 3 h in 20 °C. After two-step chromatography on SiO_2 and on SiO_2/20%$AgNO_3$ (eluent - 0.5% diethyl ether in pentane) 0.041 g of ether **18** were evolved. **Compound 18:** m/e for $C_{17}H_{17}F_5O$: calc. 332.1199, obs. 332.1188. **^{1}H NMR**, δ: 1.25 m ($C^{12}H_3$), 1.29 s, 1.37 s ($C^{10}H_3$ and $C^{11}H_3$), 1.57 ddd (H^1, $J_{1,8ex}$ 6.5, $J_{1,9syn}$ 3, $J_{1,9an}$ 3), 1.71 ddd (H^{9syn}, $J_{9syn,9an}$ 12.5, $J_{9syn,5}$ 3, J 3), 2.10 dm (H^{8ex}, $J_{8ex,8en}$ 18.5), 2.13 m (H^5), 2.29 dddd (H^{9an}, J 12.5, 3, $J_{9an,5}$ 3, $J_{9an,8en}$ 1), 2.42 dm (H^{8en}, J 18.5), 5.19 d (H^4, $J_{4,5}$ 2), 5.55 m (H^7).

E. With α-methylacrolein. 0.68 g of diene **11** and 0.69 g of α-methylacrolein in 10 ml of CH_2Cl_2 were added to 6.87 g clay suspended in 15 ml of CH_2Cl_2, and were boiled for 4 hours. After treatment 1.108 g of reaction mixture obtained were exposed to chromatography on SiO_2 (eluent - 5% diethyl ether in pentane) to evolve 0.051 g of ether **19**. **Compound 19:** m/e for $C_{14}H_{22}O$: calc. 206.1671, obs. 206.1667. **^{1}H NMR**, δ: 1.23 s, 1.29 s ($C^{10}H_3$, $C^{11}H_3$), 1.48 m (H^1), 1.58 m ($C^{12}H_3$), 1.66 m (H^{9syn}), 1.74 m ($C^{15}H_3$), 2.02 dm (H^{8ex}, $J_{8ex,8en}$ 18), 2.15 dddd (H^{9an}, $J_{9an,9syn}$ 12, $J_{9an,1}$ 3, $J_{9an,5}$ 3, $J_{9an,8en}$ 1), 2.17 m (H^5), 2.30 dm (H^{8en}, J 18), 4.05 m (H^4), 4.75 m and 5.00 m ($2H^{14}$),), 5.44 m (H^7).

F. With benzaldehyde. 0.51 g of diene **11** and 0.53 g of benzaldehyde in 10 ml of CH_2Cl_2 were added to 5.15 g of clay suspended in 13 ml of CH_2Cl_2, and were kept for 3 h at 20 °C. After treatment and chromatography on SiO_2 (eluent - 1% diethyl ether in pentane) 0.331 g of ether **20** were obtained. **Compound 20:** m/e for $C_{17}H_{22}O$: calc. 242.1671, obs. 242.1675. **^{1}H NMR**, δ: 0.96 m ($C^{12}H_3$), 1.43 s, 1.47 s ($C^{10}H_3$, $C^{11}H_3$),1.62 ddd (H^1, $J_{1,8ex}$ 6.5, $J_{1,9syn}$ 3, $J_{1,9an}$ 3), 1.81 ddd (H^{9syn}, $J_{9,9}$ 12, $J_{9syn,5}$ 3, J 3), 2.17 dddq (H^{8ex}, $J_{8ex,8en}$ 18.5, J 6.5, $J_{8ex,7}$ 3, $J_{8ex,12}$ 2.5), 2.28 ddd (H^5, J 3, $J_{5,9an}$ 3, $J_{5,4}$ 2), 2.42 dddd (H^{9an}, J 12, 3, 3, $J_{9an,8en}$ 1), 2.49 dm (H^{8en}, J 18.5), 4.96 d (H^4, J 2), 5.52 m (H^7), 7.25 t (H^{16}, $J_{16,15}$ 7.5), 7.34 d ($2H^{15}$, J 7.5), 7.41 t ($2H^{14}$, $J_{14,15}$ 7.5).

G. With p-hydroxybenzaldehyde. 0.4 g of diene **11** and 0.180 g of aldehyde dissolved in 10 ml of CH_2Cl_2 were added to 2 g of clay suspended in 10 ml of CH_2Cl_2, and were mixed for 2 h at room temperature. Then the catalyst was filtered off and the solvent was distilled off. Thus obtained reaction mixture was exposed to chromatography on 25 g of SiO_2 (eluent - from 5 to 20% of diethyl ether in pentane) to obtain 0.147 g (yield 39%) of compound **21**.. **Compound 21:** M.p.141-142 °C, m/e for $C_{17}H_{22}O_2$: calc. 258.16197, obs. 258.16170. ^{1}**H NMR**, δ: 0.90 ddd ($C^{12}H_3$, $J_{12,7}=J_{12,8ex}=2.5$, $J_{12,8en}$ 2), 1.31 s, 1.37 s ($C^{10}H_3$, $C^{11}H_3$), 1.53 dddd (H^1, $J_{1,8ex}$ 6.5, $J_{1,9syn}=J_{1,9an}=3$, $J_{1,8en}\sim1$), 1.69 ddd (H^{9syn}, $J_{9,9}$ 12.5, $J_{9syn,1}=J_{9syn,5}=3$), 2.06 dddq (H^{8ex}, $J_{8ex,8en}$ 18.5, J 6.5, $J_{8ex,7}$ 3, J 2.5), 2.11 ddd (H^5, J 3, $J_{5,9an}$ 3, $J_{5,4}$ 2.5), 2.31 dddd (H^{9an}, J 12.5, 3, 3, $J_{9an,8en}$ 1.5), 2.38 dm (H^{8en}, J 18.5), 4.81 d (H^4, J 2.5), 5.43 m (H^7), 6.69 d ($2H^{15}$, J 8), 7.14 d ($2H^{14}$, J 8).

The reaction of 1,2,4-trimethyl-4-isopropenylcyclohex-1-ene with salicylaldehyde. 0.1 g of diene and 0.3 g of aldehyde in 7 ml of CH_2Cl_2 were added to 3 g of clay suspended in 10 ml of CH_2Cl_2, and were mixed at room temperature for 5 h 40 min. After treatment and two separations on SiO_2 (eluent - from 1 to 3% diethyl ether in pentane) and on neutral Al_2O_3 (eluent - 5% diethyl ether in pentane) 0.131 g (yield 75%) of compound **26** were obtained. **Compound 26:** m/e for $C_{19}H_{26}O_2$: calc. 286.19327, obs. 286.19393. ^{1}**H NMR**, δ: 1.23 s, 1.43 s ($C^{14}H_3$, $C^{15}H_3$), 1.40 dddd (H^1, $J_{1,10a}$ 4, $J_{1,10e}=J_{1,11syn}=J_{1,11an}=3$), 1.53 d ($C^{16}H_3$, $J_{16,9a}$ 1), 1.55 m (H^{10a}, H^{9e}), 1.82 br.ddd (H^{12}, $J_{12,4}=J_{12,11syn}=J_{12,11an}=3$), 1.87 ddd ($H^{11syn}$, $J_{11syn,11an}$ 13.5, J 3, 3), 2.08 ddddd (H^{10e}, $J_{10e,10a}$ 13.5, $J_{10e,9a}$ 5, $J_{10e,1}=J_{10e,9e}=J_{10e,11an}=3$), 2.32 dddd ($H^{11an}$, J 13.5, 3, 3, 3), 2.64 br.ddd (H^{9a}, $J_{9a,9e}=J_{9a,10a}=13.5$, J 5), 4.62 d ($H^4$, J 3), 6.81 d ($H^{21}$, J 8), 6.85 td ($H^{19}$, J 7.5, 1), 7.17 dd ($H^{18}$, J 7.5, 1.5), 7.18 ddd (H^{20}, $J_{20,21}$ 8, $J_{20,19}$ 7.5, $J_{20,18}$ 1.5).

The reaction of limonene ***11a*** *with salicylaldehyde.* 0.4 g of diene **11a** and 0.190 g of aldehyde in 10 ml of CH_2Cl_2 were added to 2 g of clay suspended in 10 ml of CH_2Cl_2, and were mixed for 9 h at room temperature. After reaction mixture treatment and chromatography first on 25 g of SiO_2 (eluent - 5% diethyl ether in pentane) and then on neutral Al_2O_3 (from 1 to 4% of diethyl ether in pentane) 78 mg (yield 28%) of compound **27** were obtained.**Compound 27:** M.p. 59 °C, m/e for $C_{17}H_{22}O_2$: calc. 258.16197 , obs. 258.16220, $[\alpha]^{20}_{580}$ + 10.7° (c. 0.94, $CHCl_3$). ^{1}**H NMR**, δ: 0.76 s and 0.80 s ($C^{13}H_3$, $C^{17}H_3$), 1.15 s and 1.34 s ($C^{14}H_3$, $C^{15}H_3$), 1.25 ddd (H^{10a}, $J_{10a,10e}=J_{10a,9a}=14$, $J_{10a,9e}$ 5), 1.40 d (H^{11syn}, $J_{11syn,11an}$ 14), 1.42 d ($C^{16}H_3$, $J_{16,9a}$ 1), 1.48 ddd (H^{9e}, $J_{9e,9a}$ 12.5, $J_{9e,10a}$ 5, $J_{9e,10e}$ 2), 1.80 dd (H^{11an}, J 14, $J_{11an,10e}$ 3.5), 1.98 dddd (H^{10e}, J 14, $J_{10e,9a}$ 5, J 3.5, 2), 2.77 dddd (H^{9a}, J 14, 12.5, 5, 1), 4.15 s (H^4), 6.78 d (H^{21}, J 8), 6.85 td (H^{19}, J 7.5, 1), 7.16 d (H^{18}, J 7.5), 7.17 ddd (H^{20}, J 8, 7.5, 1.5).

The reaction of trans-6-hydroxymethyllimonene ***34*** *with salicylaldehyde.* 30 mg of compound **34** and 30 mg of aldehyde in 1 ml of CH_2Cl_2 were added to 200 mg of clay suspended in 1 ml of CH_2Cl_2 and mixed for 3 h at room temperature. After treatment reaction mixture was separated on 20 g of neutral alumina (eluent - 2-20% diethyl ether in hexane) to evolve 8 mg of initial hydroxyolefin **34,** 7 mg of ether **35** (yield 32%), and 12 mg of compound **36** (yield 34%). ^{1}H and ^{13}C NMR spectra of **compound 35** coincide with those given in [5]. **Compound 36:** m/e for $C_{18}H_{22}O_2$: calc. 270.16197, obs. 270.16220. νOH 3360 cm^{-1} (CCl_4). ^{1}**H NMR**, δ: 1.31 dm (H^{1ex}, $J_{1ex,11ex}$ 11), 1.33 s ($C^{13}H_3$), 1.35 dddd (H^{6ex}, $J_{6ex,6en}$ 12.5, $J_{6ex,5ex}$ 11, $J_{6ex,7}=J_{6ex,11ex}=3$), 1.56 ddd (H^{11en}, $J_{11en,11ex}$ 12.5, $J_{11en,1ex}$ 3.5, $J_{11en,7}$ 3), 1.60 ddd (H^{6en}, J 12.5, $J_{6en,5ex}$ 3.5, $J_{6en,7}$ 3), 1.65 dddd (H^{11ex}, J 12.5, 11, 3, $J_{11ex,7}$ 3), 1.69 dddd (H^{5ex}, J 11, 3.5, $J_{5ex,1ex}$ 2, $J_{5ex,4}$ 1.5), 1.77 d ($C^{12}H_3$, $J_{12,9}$ 1.5), 2.24 m (H^7), 3.78 dd (H^2, $J_{2,2'}$ 11.5, $J_{2,1ex}$ 2), 3.99 dd ($H^{2'}$, J 11.5, $J_{2',1ex}$ 2), 5.05 d (H^4, J 1.5), 5.54 dq (H^9, $J_{9,7}$ 2, J 1.5), 6.76 td (H^{18}, J 8, 1.5), 6.82 dd (H^{16}, H^{19}, J 8, 1.5), 7.10 td (H^{17}, J 8, 1.5), 8.89 s (OH).

The reaction of trans-4-(1-hydroxyethyl)-2-carene ***37*** *with salicylaldehyde.* 180 mg of compound **37** and 400 mg of aldehyde in 8 ml of CH_2Cl_2 were added to 2 g of clay suspended in 10 ml of CH_2Cl_2 and mixed for 30 min at room temperature. After treatment reaction mixture was separated on 40 g of neutral Al_2O_3 (eluent - 2-4% diethyl ether in pentane) to evolve 58 mg of compound **38** (yield 20.4%) and 42 mg of compound **39** (yield 23%). **Compound 38:** m/e for $C_{19}H_{24}O_2$: calc. 284.17762, obs. 284.17722, $[\alpha]^{20}_{580}$ - 24.9° (c. 3.1, $CHCl_3$). ^{1}**H NMR**, δ: 1.02 d and 1.03 d ($C^{14}H_3$, $C^{15}H_3$, J 7), 1.18 s ($C^{16}H_3$), 1.23 d ($C^{21}H_3$, J 6.5), 1.98 dd (H^9, $J_{9,9'}$ 15, $J_{9,8}$ 6), 2.11 ddd (H^8, $J_{8,9'}$ 8, $J_{8,7}$ 6, J 6), 2.29 m ($H^{9'}$), 2.30 septet (H^{13}, J 7), 4.13 d (H^1, $J_{1,11}$ 5), 4.25 qd (H^7, J 6.5, 6), 4.36 s (H^5), 5.64 ddd (H^{11}, J 5, $J_{11,13}=J_{11,9'}=1.5$), 6.94 dd (H^{17}, J 8, 1), 6.96 td (H^{19}, J 7.5, 1), 7.21 ddd (H^{18}, $J_{18,17}$ 8, $J_{18,19}$ 7.5, $J_{18,20}$ 1.5), 7.31 dd (H^{20}, J 7.5, 1.5). **Compound 39:** $[\alpha]^{20}_{580}$ +16.4° (c. 0.98, $CHCl_3$). ^{1}H and ^{13}C NMR spectra of **39** coincide with those given in [5].

The reaction of trans-4-(1-methyl-1-hydroxyethyl)-2-carene ***40*** *with salicylaldehyde.* 49.7 mg of **40** and 100 mg of aldehyde in 3 ml of CH_2Cl_2 were added to 0.3 g of clay suspended in 3 ml of CH_2Cl_2, mixed at room temperature for 10 min. After treatment reaction mixture was separated on 20 g of SiO_2 (eluent - 1-4% diethyl ether in pentane) to evolve 8 mg of **41**, 9 mg of **42** and 14 mg of mixed **41** and **42**, ratio **41**:**42** = 1.6:1

(summed yield 41%). **Compound 41:** m/e for $C_{20}H_{26}O_2$: calc. 298.19397, obs. 298.19220. ^{1}**H NMR**, δ: 1.09 d ($C^{14}H_3$, $C^{15}H_3$, J 7), 1.11 s ($C^{16}H_3$), 1.13 s and 1.32 s ($C^{21}H_3$, $C^{22}H_3$), 2.11-2.23 m(H^8, 2H^9), 2.35 septet (H^{13}, J 7), 3.85 br.d (H^1, $J_{1,11}$ 5), 4.59 s (H^5), 5.71 dm (H^{11}, J 5, $J_{11,13}$ and $J_{11,9}$ 1-1.5), 6.94 dd (H^{17}, J 8, 1), 6.96 td (H^{19}, J 7.5, 1), 7.23 ddd (H^{18}, $J_{18,17}$ 8, $J_{18,19}$ 7.5, $J_{18,20}$ 1.5), 7.28 dd (H^{20}, J 7.5, 1.5). **Compound 42:** m/e for $C_{20}H_{26}O_2$: calc. 298.19397, obs. 298.19280. ^{1}**H NMR**, δ: 0.89 d and 0.94 d ($C^{14}H_3$, $C^{15}H_3$, J 7), 1.21 s and 1.31 s ($C^{21}H_3$, $C^{22}H_3$), 1.83 d ($C^{16}H_3$, $J_{16,9}$ 2), 1.93 ddq (H^9, $J_{9,9'}$ 15, $J_{9,8}$ 10, $J_{9,16}$ 2), 2.03 dd ($H^{9'}$, J 15, $J_{9',8}$ 6), 2.15 ddd (H^8, J 10, 6, $J_{8,12}$ 9), 2.88 septet (H^{13}, J 7),), 3.09 ddd (H^{12}, J 9, $J_{12,5}$ 9, $J_{12,1}$ 7), 4.32 d (H^1, J 7), 5.02 d (H^5, J 9), 6.89 dd (H^{17}, J 8, 1), 6.95 td (H^{19}, J 7.5, 1), 7.16 ddd (H^{18}, $J_{18,17}$ 8, $J_{18,19}$ 7.5, $J_{18,20}$ 1.5), 7.29 dd (H^{20}, J 7.5, 1.5).

The reaction of trans-verbenol **44** *with salicylaldehyde.* 0.3 g of verbenol **44** and 0.5 g of aldehyde in 15 ml of CH_2Cl_2 were added to 3 g of clay suspended in 10 ml of CH_2Cl_2, and mixed for 30 min at room temperature. After treatment reaction mixture was separated on 30 g of SiO_2 (eluent - 0-10% diethyl ether in hexane) to evolve 80 mg of compound **45** (yield 12%). **Compound 45:** m/e for $C_{17}H_{20}O_2$: calc. 256.14632, obs. 256.14477, $[\alpha]^{20}_{580}$ -26.7° (c. 3, $CHCl_3$). ^{1}**H NMR**, δ: 1.16 s, 1.51 s ($C^{13}H_3$, $C^{14}H_3$), 1.53 s ($C^{15}H_3$), 1.91 ddd (H^{12}, $J_{12,11an}$ 4, $J_{12,11syn}$ 3, $J_{12,4}$ 3), 1.96 ddd (H^1, $J_{1,11syn}$ 3.5, $J_{1,10}$ 3, $J_{1,11an}$ 3), 2.12 ddd (H^{11syn}, $J_{11,11}$ 13, J 3.5, 3), 2.35 dddd (H^{11an}, J 13, 4, 3, $J_{11an,10}$ 0.5), 4.67 d (H^4, J 3), 5.87 dd (H^{10}, J 3, 0.5), 5.89 br.s (H^9), 6.82 dd (H^{19}, J 8, 1), 6.84 ddd (H^{17}, $J_{17,16}$ 7.5, $J_{17,18}$ 7.5, $J_{17,19}$ 1), 7.13 dd (H^{16}, J 7.5, 2), 7.19 ddd (H^{18}, $J_{18,19}$ 8, J 7.5, $J_{18,16}$ 2).

The reaction of trans-verbenol **44** *with crotonoaldehyde.* 0.3 g of verbenol **44** and 0.6 g of aldehyde in 10 ml of CH_2Cl_2 were added to 2.5 g of clay suspended in 10 ml of CH_2Cl_2, and mixed for 25 min at room temperature. After treatment reaction mixture was separated on 25 g of SiO_2 (eluent - 0-5% diethyl ether in hexane) to evolve 0.105 g of compound **46** (yield 26%). **Compound 46:** $[\alpha]^{20}_{580}$ -85.7° (c. 14, $CHCl_3$). ^{1}**H NMR**, δ: 1.09 s, 1.32 s ($C^{10}H_3$, $C^{11}H_3$), 1.65 dd ($C^{15}H_3$, $J_{15,14}$ 6.5, $J_{15,13}$ 1.5), 1.78 ddd (H^{9syn}, $J_{9,9}$ 12.5, $J_{9syn,1}$ 3, $J_{9syn,5}$ 3), 1.92 dddd (H^1, $J_{1,8}$ 6.5, $J_{1,9an}$ 3, J 3, $J_{1,5}$ 1), 2.12 dddd (H^{9an}, J 12.5, 3, $J_{9an,8}$ 1.5), 2.19 dddd (H^5, J 3, 3, 1, $J_{5,4}$ 2.5), 4.13 dd (H^4, $J_{4,13}$ 7, J 2.5), 4.57 dd (H^{12}, $J_{12,12'}$ 2, $J_{12,8}$ 2), 4.91 ($H^{12'}$, J 2), 5.36 ddq (H^{14}, J 15.5, 6.5, $J_{14,4}$ 1), 5.84 dddd (H^8, $J_{8,7}$ 9.5, J 6.5, 2, 1.5), 6.17 (H^7, J 9.5).

The reaction of trans-4-hydroxymethyl-2-carene **28**(valterol) *with aldehydes. A. With salicylaldehyde.* 3 g of clay in 13 ml of CH_2Cl_2 were added to 279 mg of compound **28** and 600 mg of aldehyde dissolved in 12 ml of CH_2Cl_2, and were mixed for 30 min at room temperature. After treatment reaction mixture was separated on 50 g of neutral Al_2O_3 (eluent - from 0 to 3% of diethyl ether in pentane) to evolve 282 mg of compound **29** (yield 62%). **Compound 29:** m/e for $C_{18}H_{22}O_1$: calc. 270.16197 , obs. 270.16220, $[\alpha]^{20}_{580}$ -15.7° (c. 1.14, $CHCl_3$). ^{1}**H NMR**, δ: 1.042 d and 1.044 d ($C^{14}H_3$, $C^{15}H_3$, J 7), 1.13 s ($C^{16}H_3$), 2.14 dd (H^9, $J_{9,9'}$ 17, $J_{9,8}$ 3), 2.23 dddd ($H^{9'}$, J 17, $J_{9',8}$ 6.5, $J_{9',11}$ 2, $J_{9',1}$ 1.5), 2.30 septet (H^{13}, J 7), 2.45 dddd (H^8, $J_{8,7}$ 9, $J_{8,7'}$ 8, J 6.5, 3), 3.66 dd (H^7, J 9, $J_{7,7'}$ 8), 3.97 dd ($H^{7'}$, J 8, 8), 3.98 br.d (H^1, $J_{1,11}$ 4.5), 4.50 s (H^5), 5.64 br.d (H^{11}, J 4.5), 6.95 d (H^{17}, J 8), 6.97 td (H^{19}, J 7.5, 1), 7.23 ddd (H^{18}, $J_{18,17}$ 8, $J_{18,19}$ 7.5, $J_{18,20}$ 1.5), 7.27 dd (H^{20}, J 7.5, 1.5).

B. With benzaldehyde. 3 g of clay suspended in 10 ml of CH_2Cl_2 were added to 300 mg of **28** and 600 mg of aldehyde dissolved in 12 ml of CH_2Cl_2, and were mixed for 50 min at room temperature. After treatment reaction mixture was separated on 30 g of SiO_2 (eluent - from 0 to 3% diethyl ether in pentane) to obtain 169 mg of compound **30** (yield 34%) and 153 mg of mixture. The latter was step-wise separated on SiO_2 and neutral Al_2O_3 (same eluent) to evolve 38 mg of compound **31a** (yield 8.3%) and 27 mg of compound **31b** (yield 6%). **Compound 30:** $[\alpha]^{20}_{580}$ + 65.5° (c. 0.73, $CHCl_3$), νOH 3450 cm^{-1} (CCl_4). ^{1}**H NMR**, δ: 1.11 s (C^7H_3), 1.74 br.s and 1.77 d (C^9H_3 and $C^{10}H_3$, J 2), 2.28 br.d (H^5, J 16), 2.49 ddddd (H^6, $J_{6,11}$ 9.5, $J_{6,11'}$ 9, $J_{6,5}$ 4.5, $J_{6,5'}$ 3, $J_{6,2}$ 2), 2.54 dd ($H^{5'}$, J 16, 3), 3.65 dd (H^{11}, J 9.5, $J_{11,11'}$ 8), 4.02 dd ($H^{11'}$, J 9, 8), 4.62 s (H^{12}), 4.73 br.d (H^2, $J_{2,3}$ 10.5), 6.38 d (H^3, J 10.5), 7.24-7.35 m (C_6H_5). **Compound 31a:** $[\alpha]^{20}_{580}$ + 20.9° (c. 1.34, $CHCl_3$). ^{1}**H NMR**, δ: 0.988 d and 0.991 d ($C^{12}H_3$, $C^{13}H_3$, J 7), 1.02 s ($C^{10}H_3$), 2.26 br.septet (H^{11}, J 7), 2.73 dddd (H^6, $J_{6,7}$ 9.5, $J_{6,7'}$ 8, $J_{6,5}$ 6, $J_{6,2}$ 1), 3.74 dd (H^7, J 9.5, $J_{7,7'}$ 8), 4.22 dd ($H^{7'}$, J 8, 8), 4.73 s (H^9), 4.92 br.d (H^2, $J_{2,3}$ 10), 5.42 dddd (H^5, J 6, $J_{5,3}$ 1.5, $J_{5,2}$=$J_{5,11}$=1), 5.70 dd (H^3, J 10, 1.5), 7.26 br.t (H^{17}, J 8), 7.28 br.d (2H^{15}, J 8), 7.32 td (2H^{16}, J 8, 1.5). **Compound 31b:** $[\alpha]^{20}_{580}$ + 20° (c. 1.14, $CHCl_3$). ^{1}**H NMR**, δ: 0.61 s ($C^{10}H_3$), 1.05 d ($C^{12}H_3$, $C^{13}H_3$, J 7), 2.32 septet dd (H^{11}, J 7, $J_{11,6}$ 1.5, $J_{11,5}$ 1), 2.81 ddddd (H^6, $J_{6,7}$ 8, $J_{6,7'}$ 5.5,

$J_{6,5}$ 4, $J_{6,11}$ 1.5, $J_{6,2}$ 1), 3.79 dd ($H^{7'}$, $J_{7,7'}$ 8, J 5.5), 4.45 dd (H^{7}, J 8, 8), 4.71 s (H^{9}), 5.30 dddd (H^{5}, J 4, $J_{5,3}$ 1.5, $J_{5,2}=J_{5,11}=1$), 5.53 br.d (H^{2}, J 10), 5.91 dd (H^{3}, J 10, 1.5), 7.21-7.37 m (C_6H_5).

C. With butyraldehyde. 1 g of the latter was added to 3 g of clay suspended in 10 ml of CH_2Cl_2. Then 400 mg of valterol **28** in 15 ml CH_2Cl_2 were added drop by drop to the suspension for 10 min, and mixed for 30 min at room temperature. After catalyst filtering-off reaction mixture was separated on 30 g of SiO_2 (eluent 0-7% of diethyl ether in hexane) to evolve 120 mg of **48** (yield 22.6%), 50 mg of compound **49** (yield 9.4%), 49 mg of compound **50** (yield 9.2%), 360 mg of compound **51b** (yield 51.2%). **Compound 48:** m/e for $C_{15}H_{24}O$: calc. 220.18310, obs. 220.18289 , $[\alpha]^{20}_{580}$ +8.8° (c. 6.3, $CHCl_3$). **^{1}H NMR**, δ: 0.92 t ($C^{16}H_3$, J 7), 1.03 s ($C^{10}H_3$), 1.33 m and 1.55 m ($2H^{15}$), 1.38-1.51 m ($2H^{14}$), 1.70 br.s ($C^{13}H_3$), 1.75 d ($C^{12}H_3$, $J_{12,5a}$ 2), 2.21 ddqq (H^{5a}, $J_{5,5}$ 15.5, $J_{5a,6e}$ 4.5, J 2, $J_{5a,13}$ 1), 2.26 ddddd (H^{6e}, $J_{6e,7'}$ 9, $J_{6e,7}$ 8.5, J 4.5, $J_{6e,5e}$ 3.5, $J_{6e,2}$ 1.5), 2.44 ddd (H^{5e}, J 15.5, 3.5, $J_{5e,3}$ 1), 3.40 dd (H^{7}, J 8.5, $J_{7,7'}$ 8), 3.44 dd (H^{9}, $J_{9,14}$ 9, $J_{9,14'}$ 3), 3.82 dd ($H^{7'}$, J 9, 8), 5.37 ddm (H^{2}, $J_{2,3}$ 10, J 1.5), 6.47 ddm (H^{3}, J 10, 1). **Compound 49:** m/e for $C_{15}H_{24}O$: calc. 220.18270, obs. 220.18289 , $[\alpha]^{20}_{580}$ -67.8° (c. 6.5, $CHCl_3$). **^{1}H NMR**, δ: 0.92 s ($C^{10}H_3$), 0.93 t ($C^{16}H_3$, J 7), 0.981 d and 0.984 d ($C^{12}H_3$ and $C^{13}H_3$, J 7), 1.33 m and 1.57 m ($2H^{15}$), 1.43 m (H^{14}), 1.50 m ($H^{14'}$), 2.25 septet dd (H^{11}, J 7, $J_{11,5}$ 1.5, $J_{11,6e}$ 1), 2.53 ddddd (H^{6e}, $J_{6e,7}$ 9, $J_{6e,7'}$ 8.5, $J_{6e,5}$ 6, $J_{6e,2}$ 1.2, J 1), 3.48 dd (H^{7}, J 9, $J_{7,7'}$ 8), 3.55 dd (H^{9}, $J_{9,14}$ 9.5, $J_{9,14'}$ 3), 4.01 dd ($H^{7'}$, J 8.5, 8), 5.35 dddd (H^{5}, J 6, 1.5, $J_{5,3}$ 1.5, $J_{5,2}$ 1), 5.54 ddd (H^{2}, $J_{2,3}$ 10, J 1.2, 1), 5.83 dd (H^{3}, J 10, 1.5). **Compound 50:** m/e for $C_{15}H_{24}O$: calc. 220.18270, obs. 220.18332 , $[\alpha]^{20}_{580}$ +10.6° (c. 6.2, $CHCl_3$). **^{1}H NMR**, δ: 0.89 s ($C^{10}H_3$), 0.91 t ($C^{16}H_3$, J 7), 0.99 d ($C^{12}H_3$ and $C^{13}H_3$, J 7), 1.24 - 1.57 m ($2H^{14}$, $2H^{15}$), 2.24 septet dd (H^{11}, J 7, $J_{11,5}$ 1.5, $J_{11,6a}$ 1.5), 2.62 dddd (H^{6a}, $J_{6a,7'}$ 8, $J_{6a,7}$ 6, $J_{6a,5}$ 4, J 1.5), 3.47 dd (H^{9}, $J_{9,14}$ 9, $J_{9,14'}$ 3), 3.50 dd (H^{7}, $J_{7,7'}$ 8, J 6), 4.20 dd ($H^{7'}$, J 8, 8), 5.19 dddd (H^{5}, J 4, 1.5, $J_{5,3}$ 1.5, $J_{5,2}$ 1), 5.46 dd (H^{2}, $J_{2,3}$ 10, J 1), 5.76 dd (H^{3}, J 10, 1.5). **Compound 51b:** m/e for $C_{19}H_{32}O$: calc. 292.24022, obs. 292.24049, $[\alpha]^{20}_{580}$ +71.3° (c. 7.5, $CHCl_3$). **^{1}H NMR**, δ: 0.87 t and 0.90 t ($C^{18}H_3$, $C^{21}H_3$, J 7), 1.13-1.57 m (4 CH_2), 1.38 s ($C^{15}H_3$), 1.63 ddddd (H^{1e}, $J_{1e,2a}$ 5.5, $J_{1e,11'}$ 2.5, $J_{1e,8}$ 2, $J_{1e,11}$ 1.5, $J_{1e,2e}$ 1.5), 1.64 d and 1.66 d ($C^{13}H_3$, $C^{14}H_3$, J 2.5 and J 1.5), 1.76 ddd (H^{8}, $J_{8,4}$ 4, $J_{8,9}$ 3, J 2), 2.36 ddm (H^{2a}, $J_{2a,2e}$ 16, J 5.5), 2.41 br.d (H^{2e}, J 16), 3.09 dd (H^{4}, J 4, $J_{4,5}$ 3.5), 3.50 ddd (H^{9}, $J_{9,19}$ 8, $J_{9,19'}$ 5, J 3), 3.57 ddd (H^{11}, $J_{11,11'}$ 11.5, J 1.5, $J_{11,2}$ 1), 3.72 dd ($H^{11'}$, J 11.5, 2.5), 3.94 ddd (H^{5ex}, $J_{5ex,16}$ 7, $J_{5ex,16'}$ 6, J 3.5).

D. With crotonoaldehyde. 0.17 g of valterol **28** and 0.3 g of aldehyde in 10 ml of CH_2Cl_2 were added to 2.5 g of clay suspended in 10 ml of CH_2Cl_2, and mixed for 30 min at room temperature. After treatment reaction mixture was separated on 25 g of SiO_2 (eluent - 0-30% diethyl ether in hexane) to evolve 0.027 g of compound **57** (yield 12.1%), 0.04 g of compound **58** (yield 17.9%), 0.017 g of compound **59** (yield 7.6%), 0.008 g of compound **60** (yield 3.6%) and 0.046 g of compound **61** (yield 15.6%). **Compound 57:** m/e for $C_{15}H_{22}O$: calc. 218.16706, obs. 218.16619 , $[\alpha]^{20}_{580}$ +55.9° (c. 6.3, $CHCl_3$). **^{1}H NMR**, δ: 1.00 s ($C^{10}H_3$), 1.71 br.s ($C^{13}H_3$), 1.72 dd ($C^{16}H_3$, $J_{16,15}$ 6.5, $J_{16,14}$ 1.5), 1.76 d ($C^{12}H_3$, $J_{12,5a}$ 2), 2.22 ddqq (H^{5a}, $J_{5,5}$ 15, $J_{5a,6e}$ 4.5, J 2, $J_{5a,13}$ 1), 2.29 ddddd (H^{6e}, $J_{6e,7'}$ 9, $J_{6e,7}$ 8.5, $J_{6e,5a}$ 4.5, $J_{6e,5e}$ 3, $J_{6e,2}$ 1.5), 2.45 ddd (H^{5e}, J 15, 3, $J_{5e,3}$ 1), 3.45 dd (H^{7}, J 8.5, $J_{7,7'}$ 8), 3.85 dd ($H^{7'}$, J 9, 8), 3.86 d (H^{9}, $J_{9,14}$ 8), 5.33 br.dd (H^{2}, $J_{2,3}$ 10, J 1.5), 5.47 ddq (H^{14}, $J_{14,15}$ 15, J 8, 1.5), 5.71 dqd (H^{15}, J 15, 6.5, $J_{15,9}$ 1), 6.46 br.dd (H^{3}, J 10, 1). **Compound 58:** m/e for $C_{15}H_{22}O$: calc. 218.16706, obs. 218.16619 , $[\alpha]^{20}_{580}$ +19.6° (c. 4.5, $CHCl_3$). **^{1}H NMR**, δ: 0.97 s ($C^{10}H_3$), 1.70 dd ($C^{16}H_3$, $J_{16,15}$ 6.5, $J_{16,14}$ 1.5), 1.73 br.s and 1.77 br.s ($C^{12}H_3$, $C^{13}H_3$),), 2.12 dddd (H^{6a}, $J_{6a,5a}$ 8, $J_{6a,7'}$ 7.5, $J_{6a,7}$ 5.5, $J_{6a,5e}$ 5), 2.27 br.dd (H^{5a}, $J_{5,5}$ 15, J 8) 2.39 br.dd (H^{5e}, J 15, 5), 3.50 dd (H^{7}, $J_{7,7'}$ 8, J 5.5), 4.06 dd ($H^{7'}$, J 8, 7.5), 4.07 dd (H^{9}, $J_{9,14}$ 7.5, $J_{9,15}$ 1), 5.32 d (H^{2}, $J_{2,3}$ 10), 5.45 ddq (H^{14}, $J_{14,15}$ 15, J 7.5, 1.5), 5.64 dqd (H^{15}, J 15, 6.5, 1), 6.41 d (H^{3}, J 10). **Compound 59:** m/e for $C_{15}H_{22}O$: calc. 218.16706, obs. 218.16600 , $[\alpha]^{20}_{580}$ +36.9° (c. 3.0, $CHCl_3$). **^{1}H NMR**, δ: 0.91 s ($C^{10}H_3$), 0.992 d and 0.995 d ($C^{12}H_3$, $C^{13}H_3$, J 7), 1.73 dd ($C^{16}H_3$, $J_{16,15}$ 6.5, $J_{16,14}$ 1.5), 2.26 septet dd (H^{11}, J 7, $J_{11,5}$ 1.5, $J_{11,6e}$ 1), 2.55 ddddd (H^{6e}, $J_{6e,7}$ 9, $J_{6e,7'}$ 8.5, $J_{6e,5}$ 6, $J_{6e,2}$ 1.2, J 1), 3.52 dd (H^{7}, J 9, $J_{7,7'}$ 8), 3.98 br.d (H^{9}, $J_{9,14}$ 8), 4.06 dd ($H^{7'}$, J 8.5, 8), 5.38 dddd (H^{5}, J 6, 1.5, $J_{5,3}$ 1.5, $J_{5,2}$ 1), 5.47 ddq (H^{14}, $J_{14,15}$ 15, J 8, 1.5), 5.52 ddd (H^{2}, $J_{2,3}$ 10, J 1.2, 1), 5.70 dqd (H^{15}, J 15, 6.5, $J_{15,9}$ 1), 5.83 dd (H^{3}, J 10, 1.5). **Compound 60:** m/e for $C_{15}H_{22}O$: calc. 218.16706, obs. 218.16600 , $[\alpha]^{20}_{580}$ +29° (c. 6.6, $CHCl_3$). **^{1}H NMR**, δ: 0.89 s ($C^{14}H_3$), 1.00 d ($C^{12}H_3$, $C^{13}H_3$, J 7), 1.71 dd ($C^{16}H_3$, $J_{16,15}$ 6.5, $J_{16,14}$ 1.5), 2.26 septet dd (H^{11}, J 7, $J_{11,5}$ 1.5, $J_{11,6a}$ 1), 2.66 dddd (H^{6a}, $J_{6a,7'}$ 8, $J_{6a,7}$ 6, $J_{6a,5}$ 4, J 1), 3.56 dd (H^{7}, $J_{7,7'}$ 8, J 6), 3.92 d (H^{9}, $J_{9,14}$ 8), 4.24 dd ($H^{7'}$, J 8, 8), 5.22 dddd (H^{5}, J 4, 1.5, $J_{5,3}$ 1.5, $J_{5,2}$ 1), 5.44 dd (H^{2}, $J_{2,3}$ 10, J 1), 5.46 ddq (H^{14}, $J_{14,15}$ 15, J 8, 1.5), 5.66 dqd (H^{15}, J 15, 6.5, 1), 5.79 dd (H^{3}, J 10, 1.5). **Compound 61:** m/e for $C_{19}H_{28}O$: calc. 292.24022, obs. 292.24049 , $[\alpha]^{20}_{580}$ +118.6° (c. 9.5, $CHCl_3$). **^{1}H NMR**, δ: 1.41 s ($C^{15}H_3$), 1.60 d (J 2) and 1.67 m ($C^{13}H_3$ and $C^{14}H_3$), 1.64 dd ($C^{18}H_3$, $J_{18,17}$ 6.5, $J_{18,16}$ 1.5), 1.66 m (H^{1e}), 1.68 dd ($C^{21}H_3$, $J_{21,20}$ 6.5, $J_{21,19}$ 1.5), 1.83 ddd (H^{8}, $J_{8,4}$ 4, $J_{8,9}$ 3, $J_{8,1e}$ 1.5), 2.40 ddqqm (H^{2a}, $J_{2a,2e}$ 15, $J_{2a,1}$ 6, J 2, 1.5), 2.47 br.d (H^{2e}, J 15), 3.20 dd (H^{4}, J 4, $J_{4,5}$ 3.5), 3.62 ddd (H^{11}, $J_{11,11'}$ 11.5, $J_{11,1e}$=$J_{11,2a}$=1.5), 3.77 dd ($H^{11'}$, J 11.5, $J_{11',1e}$ 2.5), 4.00 dd (H^{9}, $J_{9,19}$ 7, J 3), 4.34 dd (H^{5}, $J_{5,16}$ 8, J 3.5), 5.32 ddq (H^{16}, $J_{16,17}$ 15, J 8, 1.5), 5.44 ddq (H^{19}, $J_{19,20}$ 15, J 7, 1.5), 5.66 dqd (H^{20}, J 15, 6.5, $J_{20,9}$ 1), 5.71 dqd (H^{17}, J 15, 6.5, $J_{17,4}$ 1).

E. With α-methylacrolein. 0.3 g of the α-methylacrolein in 12 ml CH_2Cl_2 was added drop by drop to 3 g of clay and 0.3 g valterol **28** suspended in 8 ml of CH_2Cl_2 and mixed for 30 min at room temperature. After catalyst filtering-off reaction mixture was separated on 20 g of neutral Al_2O_3 (eluent 0-50% of diethyl ether in hexane) to evolve 64 mg of compound **67** (yield 3.7%) and 64 mg of compound **68** (yield 15%). **Compound 67:** m/e for $C_{15}H_{24}O_2$: calc. 236.17762, obs. 236.17860 , $[\alpha]^{20}_{580}$ +30° (c. 2.2, $CHCl_3$), (ν_{max} cm^{-1}, CCl_4): 3610, 3420. **^{1}H NMR**, δ: 0.83 ddd (H^{6}, $J_{6,5}$ 13, $J_{6,6'}$ 12, $J_{6,7}$ 11), 0.948 d and 0.951 d ($C^{13}H_3$, $C^{14}H_3$, J 7), 1.00 d ($C^{15}H_3$, J 6.5), 1.04 s ($C^{16}H_3$), 1.81 ddd ($H^{6'}$, J 12, $J_{6',5}$ 6.5, $J_{6',7}$ 2), 1.81 dd (H^{10a}, $J_{10a,10e}$ 17, $J_{10a,1e}$ 2.5), 1.95 ddq (H^{5}, J 13, 6.5, 6.5), 2.06 m (H^{7}), 2.11 dddd (H^{10e}, J 17, $J_{10e,1}$ 5.5, $J_{10e,8}$ 2.5, $J_{10e,7}$ 2.5), 2.15 br.septet (H^{12}, J 7), 2.25 br.s (OH), 2.29 dddd (H^{1e}, $J_{1e,2}$ 11, $J_{1e,2'}$ 8, J 5.5, 2.5), 3.24 dd (H^{2}, J 11, $J_{2,2'}$ 8), 3.96 dd ($H^{2'}$, J 8, 8), 5.33 ddd (H^{8} $J_{8,7}$ 3.5, J 2.5, $J_{8,12}$ 1). **Compound 68:** m/e for $C_{15}H_{24}O_2$: calc. 236.17762, obs. 236.17671 , $[\alpha]^{20}_{580}$ +31.8° (c. 3.2, $CHCl_3$). **^{1}H NMR**, δ: 0.93 d ($C^{13}H_3$, $C^{14}H_3$, J 7), 1.25 s and 1.28 s ($C^{15}H_3$, $C^{16}H_3$), 1.26 dd (H^{6}, $J_{6,6'}$ 13, $J_{6,7a}$ 12), 1.80 dd (H^{10a}, $J_{10a,10e}$ 17, $J_{10a,1e}$ 2.5), 1.91 ddd ($H^{6'}$, J 13, $J_{6',7a}$ 7.5, $J_{6',4}$ 2), 2.10 dddd (H^{10e}, J 17, $J_{10e,1e}$ 5.5, $J_{10e,8}$ 2.5, $J_{10e,7a}$ 2.5), 2.13 septet (H^{12}, J 7), 2.21 dddd (H^{1e}, $J_{1e,2}$ 11, $J_{1e,2'}$ 8, J 5.5, 2.5), 2.44 dddd (H^{7a}, J 12, 7.5, 2.5, $J_{7a,8}$ 4), 3.29 dd (H^{2}, J 11, $J_{2,2'}$ 8), 3.61 d (H^{4}, J 2), 3.79 dd ($H^{2'}$, J 8, 8), 5.31 dd (H^{8}, J 4, 2.5), 9.04 br.s (OH).

F. With acrolein. 300 mg of valterol **28** and 300 mg of aldehyde in 10 ml of CH_2Cl_2 were added to 2.5 g of clay suspended in 10 ml of CH_2Cl_2, and mixed for 30 min at room temperature. After treatment reaction mixture was separated on 25 g of SiO_2 (eluent - 0-10% diethyl ether in hexane) to evolve 108 mg of compound **70** (yield 21.8%), 11.5 mg of compound **71** (yield 3.1%), 10 mg of compound **72** (yield 2.9%), 16 mg of compound **73** (yield 4.3%), 43 mg of compound **74** (yield 9.1%) and 37 mg of compound **75** (yield 7.8%). **Compound 70:** m/e for $C_{14}H_{20}O$: calc. 204.15141, obs. 204.15118 , $[\alpha]^{20}_{580}$ +21.1° (c. 6.6, $CHCl_3$). **^{1}H NMR**, δ: 1.04 s ($C^{10}H_3$), 1.71 br.s ($C^{13}H_3$), 1.76 d ($C^{12}H_3$, $J_{12,5a}$ 2), 2.23 ddqq (H^{5a}, $J_{5,5}$ 15.5, $J_{5a,6e}$ 4.5, J 2, $J_{5a,13}$ 1), 2.31 ddddd (H^{6e}, $J_{6e,7}$ 9, $J_{6e,7'}$ 9, J 4.5, $J_{6e,5e}$ 3, $J_{6e,2}$ 1.5), 2.46 ddd (H^{5e}, J 15.5, 3, $J_{5e,3}$ 1), 3.48 dd (H^{7}, J 9, $J_{7,7'}$ 8), 3.89 dd ($H^{7'}$, J 9, 8), 3.92 ddd (H^{9}, $J_{9,14}$ 7, $J_{9,15cis}$ 1.2, $J_{9,15trans}$ 1.2), 5.21 ddd (H^{15cis}, $J_{15cis,14}$ 10.5, $J_{15,15}$ 2, J 1.2), 5.26 ddd ($H^{15trans}$, $J_{15trans,14}$ 17, J 2, 1.2), 5.30 br.d (H^{2}, $H_{2,3}$ 10), 5.82 ddd (H^{14}, J 17, 10.5, 7), 6.46 br.d (H^{3}, J 10). **Compound 71:** m/e for $C_{14}H_{20}O$: calc. 204.15141, obs. 204.15138 , $[\alpha]^{20}_{580}$ +47.1° (c. 7.0, $CHCl_3$). **^{1}H NMR**, δ: 0.97 s ($C^{10}H_3$), 1.73 br.s and 1.77 br.s ($C^{12}H_3$, $C^{13}H_3$), 2.13 dddd (H^{6a}, $J_{6a,5a}$ 8, $J_{6a,7'}$ 7, $J_{6a,7}$ 5.5, $J_{6a,5e}$ 5), 2.28 ddqq (H^{5a}, $J_{5a,5e}$ 15.5, J 8, $J_{5a,12}$=$J_{5a,13}$=l), 2.39 ddqq (H^{5e}, J 15.5, 5, $J_{5e,12}$ 1, $J_{5e,13}$ 1), 3.54 dd (H^{7}, $J_{7,7'}$ 8, J 5.5), 4.09 dd ($H^{7'}$, J 8, 7), 4.14 ddd (H^{9}, $J_{9,14}$ 7, $J_{9,15cis}$ 1.2, $J_{9,15trans}$ 1.2), 5.15 ddd (H^{15cis}, $J_{15cis,14}$ 10.5, $J_{15,15}$ 2, J 1.2), 5.22 ddd ($H^{15trans}$, $J_{15trans,14}$ 17, J 2, 1.2), 5.35 br.d (H^{2}, $J_{2,3}$ 10), 5.81 ddd (H^{14}, J 17, 10.5, 7), 6.43 d (H^{3}, J 10). **Compound 72:** m/e for $C_{14}H_{20}O$: calc. 204.15141, obs. 204.15120 , $[\alpha]^{20}_{580}$ -8.2° (c. 6.1, $CHCl_3$). **^{1}H NMR**, δ: 0.95 s ($C^{10}H_3$), 0.993 d and 0.998 d ($C^{12}H_3$, $C^{13}H_3$, J 7), 2.26 septet dd (H^{11}, J 7, $J_{11,5}$ 1.5, $J_{11,6e}$ 1), 2.58 ddddd (H^{6e}, $J_{6e,7}$ 9.5, $J_{6e,7'}$ 9, $J_{6e,5}$ 6, $J_{6e,2}$ 1.2, J 1), 3.56 dd (H^{7}, J 9.5, $J_{7,7'}$ 8), 4.04 ddd (H^{9}, $J_{9,14}$ 7, $J_{9,15cis}$ 1.2, $J_{9,15trans}$ 1.2), 4.10 dd ($H^{7'}$, J 9, 8), 5.22 ddd (H^{15cis}, $J_{15cis,14}$ 10.5, $J_{15cis,15trans}$ 2, J 1.2), 5.26 ddd ($H^{15trans}$, $J_{15trans,14}$ 17, J 2, 1.2), 5.39 dddd (H^{5}, J 6, 1.5, $J_{5,3}$ 1.5, $J_{5,2}$ 1), 5.51 ddd (H^{2}, $J_{2,3}$ 10, J 1.2, 1), 5.84 dd (H^{3}, J 10, 1.5), 5.84 ddd (H^{14}, J 17, 10.5, 7). **Compound 73:** m/e for $C_{14}H_{20}O$: calc. 204.15141, obs. 204.15120, $[\alpha]^{20}_{580}$ +12.3° (c. 9.8, $CHCl_3$). Raman spectrum (ν_{max} cm^{-1}, CCl_4): 827. **^{1}H NMR**, δ: 0.90 s ($C^{10}H_3$), 1.00 d ($C^{12}H_3$, $C^{13}H_3$, J 7), 2.27 septet dd (H^{11}, J 7, $J_{11,5}$ 1.5, $J_{11,6a}$ 1), 2.68 dddd (H^{6a}, $J_{6a,7'}$ 8, $J_{6a,7}$ 6, $J_{6a,5}$ 4, J 1), 3.61 dd (H^{7}, $J_{7,7'}$ 8, J 6), 4.00 ddd (H^{9}, $J_{9,14}$ 7, $J_{9,15cis}$ 1.2, $J_{9,15trans}$ 1.2), 4.28 dd ($H^{7'}$, J 8, 8), 5.17 ddd (H^{15cis}, $J_{15cis,14}$ 10.5, $J_{15cis,15trans}$ 2, J 1.2), 5.23 ddd ($H^{15trans}$, $J_{15trans,14}$ 17, J 2, 1.2), 5.24 dddd (H^{5}, J 4, 1.5, $J_{5,3}$ 1.5, $J_{5,2}$ 1), 5.47 dd (H^{2}, $J_{2,3}$ 10, J 1), 5.81 ddd (H^{14}, J 17, 10.5, 7), 5.82 dd (H^{3}, J 10, 1.5). **Compound 74:** m/e for $C_{17}H_{24}O_2$: calc. 260.17762, obs. 260.17737, $[\alpha]^{20}_{580}$ +53.3° (c. 26.2, $CHCl_3$). **^{1}H NMR**, δ: 1.45 s

($C^{15}H_3$), 1.58 d ($C^{14}H_3$, $J_{14,2a}$ 2.5), 1.65 d ($C^{13}H_3$, $J_{13,2a}$ 1.5), 1.70 ddddd (H^{1e}, $J_{1e,2a}$ 6.5, $J_{1e,11'}$ 2.5, $J_{1e,8}$ 2, $J_{1e,11}$ 1.5, $J_{1e,2e}$ 1), 1.91 ddd (H^8, $J_{8,4}$ 4, $J_{8,9}$ 3, J 2), 2.39 ddqqd (H^{2a}, $J_{2a,2e}$ 16, J 6.5, 2.5, 1.5, $J_{2a,11}$ 1.5), 2.46 br.d (H^{2e}, J 16), 3.26 ddd (H^4, $J_{4,5ex}$ 4, J 4, $J_{4,2e}$ 1), 3.65 ddd (H^{11}, $J_{11,11'}$ 11.5, J 1.5, 1.5), 3.81 dd ($H^{11'}$, J 11.5, 2.5), 4.08 dddd (H^9, $J_{9,18}$ 6.5, J 3, $J_{9,19\mathit{cis}}$ 1.2, $J_{9,19\mathit{trans}}$ 1.2), 4.41 dddd (H^{5ex}, $J_{5ex,16}$ 7, J 4, $J_{5ex,17\mathit{cis}}$ 1.2, $J_{5ex,17\mathit{trans}}$ 1.2), 5.10 ddd ($H^{17\mathit{cis}}$, $J_{17\mathit{cis},16}$ 10.5, $J_{17\mathit{cis},17\mathit{trans}}$ 2, J 1.2), 5.13 ddd ($H^{19\mathit{cis}}$, $J_{19\mathit{cis},18}$ 10.5, $J_{19\mathit{cis},19\mathit{trans}}$ 2, J 1.2), 5.17 ddd ($H^{19\mathit{trans}}$, $J_{19\mathit{trans},18}$ 17, J 2, 1.2), 5.25 ddd ($H^{17\mathit{trans}}$, $J_{17\mathit{trans},16}$ 17, J 2, 1.2), 5.68 ddd (H^{16}, J 17, 10.5, 7), 5.79 ddd (H^{18}, J 17, 10.5, 7). **Compound 75:** m/e for $C_{17}H_{26}O_3$: calc. 278.18818, obs. 278.18830, $[\alpha]^{20}{}_{580}$ +37.5° (c. 12.1, $CHCl_3$). ν OH 3480 cm^{-1} (CCl_4). **^{1}H NMR**, δ: 0.93 s, 1.00 s ($C^{17}H_3$, $C^{18}H_3$), 1.40 ddd (H^{6e}, $J_{6c,6a}$ 15, $J_{6e,7e}$ 1, $J_{6e,14}$ l), 1.41 s ($C^{19}H_3$), 1.63-1.87 m ($2H^2$, $2H^3$), 1.70 br.d (H^{7e}, $J_{7e,6a}$ 8), 1.81 ddm (H^{11}, $J_{11,14}$ 4, $J_{11,10}$ 3), 2.35 ddd (H^{14}, J 4, $J_{14,1ex}$ 3, J 1), 2.65 ddd (H^{6a}, J 15, 8, $J_{6a,8}$ 1.5), 3.65 ddd (H^8, $J_{8,8'}$ 11.5, $J_{8,7e}$ 1.5, J 1.5), 3.83 dd ($H^{8'}$, J 11.5, $J_{8',7e}$ 2.5), 4.02 m (H^{1ex}), 4.11 dddd (H^{10}, $J_{10,15}$ 6.5, J 3, $2J_{10,16}$ 1.5), 4.72 s (OH), 5.21 ddd ($H^{16\mathit{cis}}$, $J_{16\mathit{cis},15}$ 10.5, $J_{16,16}$ 1.5, J 1.5), 5.30 ddd ($H^{16\mathit{trans}}$, $J_{16\mathit{trans},15}$ 17, J 1.5, 1.5), 6.09 ddd (H^{15}, J 17, 10.5, 6.5).

Table 1. **^{13}C NMR Data for Compounds 4, 5, 8, 16-21** (chemical shifts are given in ppm)*

C_i	4	5	8	16	17	18	19	20	21
1	57.50 s	50.34 d	33.74 d	33.91 d	34.20 d	33.68 d	34.12 d	33.77 d	33.86 d
2	25.15 t	91.37 s	74.73 s	75.04 s	74.61 s	76.05 s	75.00 s	75.04 s	75.33 s
3	71.14 t	-	-	-	-	-	-	-	-
4	-	68.78 t	74.24 d	74.63 d	73.22 d	69.71 d	74.92 d	73.98 d	73.88 d
5	89.76 d	37.06 t	39.98 d	39.98 d	38.25 d	39.58 d	37.34 d	41.35 d	41.45 d
6	36.92 t	50.77 s	133.20 s	133.22 s	133.44 s	131.45 s	133.44 s	132.91 s	133.14 s
7	46.51 d	48.55 d	123.22 d	123.41 d	123.54 d	124.68 d	122.76 d	123.06 d	123.09 d
8	27.21 t	24.42 t	27.45 t	27.58 t	28.40 t	27.42 t	27.55 t	27.50 t	27.55 t
9	28.66 t	22.55 t	27.71 t	27.95 t	27.74 t	27.87 t	28.23 t	28.14 t	28.05 t
10	45.77 s	39.79 t	28.41^a q	28.48^a q	28.57^a q	28.34^a q	28.49^a q	28.47^a q	28.51^a q
11	20.40^a q	22.66 q	23.79^a q	23.90^a q	23.86^a q	23.29^a q	23.87^a q	23.76^a q	23.82^a q
12	20.32^a q	24.82 q	24.82 q	24.95 q	25.10 q	23.65 q	24.38 q	23.86 q	24.05 q
13			132.42 d	139.47 d	36.86 t		144.79 s	142.69 s	134.91 s
14			124.97 d	113.94 t	19.43 t		109.51 t	125.46d	126.76 d
15			17.45 q		13.84 q		20.17 q	127.58 d	114.66 d
16								126.31 d	154.20 s

Table 2. **^{13}C NMR Data for Compounds 26, 27, 29, 30, 31a,b, 36, 38, 41**
(chemical shifts are given in ppm)*

C$_i$	**26**	**27**	**29**	**30**	**31a**	**31b**	**36**	**38**	**41**
1	34.51 d	35.03^a s	78.12 d	45.19 s	46.66 s	45.18 s	36.14 d	79.56 d	78.23 d
2	74.58 s	77.67 s	-	127.64 d	129.72 d	132.38 d	67.82 t	-	-
3	-	-	156.37 s	125.57 d	124.06 d	123.60 d	-	155.91 s	157.04 s
4	66.43 d	73.06 d	126.66 s	123.73 s	126.05 s	125.75 s	77.74 d	125.16 s	127.12 s
5	121.97 s	121.20 s	83.10 d	23.45 t	115.04 d	119.27 d	41.67d	82.02 d	81.17 d
6	153.09 s	152.67 s	-	44.27 d	45.76 d	46.35 d	28.98 t	-	-
7	-	-	73.03 t	22.46 q	74.29 t	74.14 t	35.04 d	76.74 d	83.39 s
8	77.37 s	79.52 s	44.46 d	129.66 s	-	-	145.67 s	51.13 d	52.98 d
9	32.05 t	34.22 t	24.49 t	20.59 q	91.63 d	88.27 d	131.44 d	24.86 t	24.21 t
10	25.86 t	34.62 t	146.52 s	19.74 q	22.11 q	22.62 q	34.54 s	151.95 s	148.12 s
11	26.36 t	41.11 t	116.88 d	69.93 t	32.83 d	33.01 d	32.49 t	117.91 d	116.98 d
12	36.47 d	34.35^a s	46.27 s	90.12 d	21.39 q	21.34 q	19.49 q	48.42 s	47.51 s
13	-	21.02^b q	34.64 d	138.55 s	21.31 q	21.24 q	20.82 q	34.61 d	35.01 d
14	28.18 q	24.24 q	20.82 q	126.85^a d	139.74 s	139.31 s	124.49 s	20.76^a q	21.08^a q
15	24.05 q	25.43 q	20.65 q	127.56^a d	126.63^a d	126.14^a d	156.66 s	20.32^a q	20.78^a q
16	26.55 q	22.36 q	23.76 q	127.22 d	127.75^a d	127.67^a d	117.08 d	26.68 q	26.35 q
17	-	21.25^b q	117.41 d		127.26 d	127.03 d	128.19 d	117.76 d	117.62 d
18	130.32^a d	131.05^c d	129.52^a d				119.22 d	129.96^{b}d	129.49 d
19	119.55 d	119.73 d	121.85 d				126.20 d	121.84 d	121.98 d
20	129.44^a d	129.23^c d	129.36^a d					129.33^{b}d	129.85 d
21	116.72 d	116.48 d						15.40 q	23.77 q
22									30.65 q

Table 3. **^{13}C NMR Data for Compounds 42, 45, 46, 48-50, 51b, 57**
(chemical shifts are given in ppm)*

C$_i$	**42**	**45**	**46**	**48**	**49**	**50**	**51b**	**57**
1	78.63 d	36.91 d	37.50 d	43.62 s	44.73 s	43.55 s	42.31 d	44.73 s
2	-	73.22 s	73.68 s	127.64 d	129.41 d	132.19 d	31.69 t	127.83 d
3	156.54 s	-	-	126.28 d	124.58 d	123.13 d	127.30 s	126.00 d
4	127.25 s	66.72 d	74.82 d	129.51 s	140.13 s	138.57 s	43.28 d	129.58 s
5	72.68 d	122.01 s	41.16 d	23.73 t	116.20 d	118.94 d	81.63 d	23.66 t
6	-	153.67 s	142.06 s	44.33 d	45.89 d	46.69 d	-	44.01 d
7	83.41 s	-	131.41 d	69.42 t	73.64 t	73.75 t	78.77 s	69.78 t
8	47.92 d	76.18 s	130.86 d	-	-	-	51.05 d	-
9	22.35 t	134.66 d	28.18 t	88.21 d	89.54 d	86.62 d	74.38 d	89.51 d
10	143.20 s	128.87 d	28.60^a q	22.67 q	22.93 q	21.87 q	-	22.21 q
11	123.61 s	26.04 t	22.99^a q	123.99 s	32.83 d	32.96 d	71.47 t	123.86 s
12	43.75 d	36.41 d	114.00 t	20.49^a q	21.34^a q	21.28^a q	121.62 s	20.51^a q
13	29.43 d	28.27^{a}q	131.86 d	19.73^a q	21.27^a q	21.18^a q	20.30^a q	19.72^a q
14	20.00^a q	22.83^a q	126.30 d	32.50 t	33.52 t	32.41 t	20.02^a q	127.85 d
15	19.85^a q	29.64 q	17.67 q	20.53 t	20.41 t	20.41 t	22.45 q	129.43 d
16	16.76 q	129.73 d		14.16 q	14.14 q	14.17 q	32.27 t	17.84 q
17	117.88 d	119.35 d		-	-	-	19.63^c t	-
18	128.77 d	129.57 d		-	-	-	14.26^b q	-
19	121.99 d	116.62 d		-	-	-	36.48 t	-
20	128.64 d			-	-	-	19.13^c t	-
21	23.46 q			-	-	-	14.09^b q	-
22	28.03 q							

Table 4. **^{13}C NMR Data for Compounds 58- 61, 67, 68**
(chemical shifts are given in ppm)*

C_i	**58**	**59**	**60**	**61**	**67**	**68**
1	45.01 s	45.88 s	44.60 s	41.78 d	41.34 d	44.11d
2	131.53 d	129.74 d	132.44 d	31.44 t	71.84 t	72.16 t
3	124.91 d	124.43 d	123.22 d	127.05 s	-	-
4	128.75 s	140.61 s	139.05 s	45.47 d	115.19 s	97.63 d
5	26.59 t	115.94 d	118.58 d	82.11d	40.32 d	80.59 s
6	43.63 d	45.47 d	46.11 d	-	37.76 t	46.80 t
7	71.61 t	74.01 t	74.05 t	79.09 s	41.97 d	42.52 d
8	-	-	-	51.93 d	120.62 d	119.42 d
9	87.27 d	90.90 d	88.09 d	75.63 d	137.46 s	137.87 s
10	21.48 q	22.32 q	22.25 q	-	22.62 t	22.07 t
11	125.08 s	32.86 d	32.99 d	71.46 t	48.39 s	48.72 s
12	20.57[a] q	21.38[a] q	21.29[a] q	121.79 s	34.90 d	34.78 d
13	19.73[a] q	21.31[a] q	21.25[a] q	20.31[a] q	21.15[a] q	21.13[a] q
14	128.37[b] d	128.71 d	127.98 d	19.92[a] q	20.80[a] q	20.79[a] q
15	128.55[b] d	129.25 d	129.08 d	22.34 q	11.37 q	23.47 q
16	17.77 q	17.81 q	17.79 q	130.05 d	23.61 q	26.46 q
17	-	-	-	127.84 d	-	-
18	-	-	-	17.77 q	-	-
19	-	-	-	130.37 d	-	-
20	-	-	-	127.61 d	-	-
21	-	-	-	17.81 q	-	-

Table 5. **^{13}C NMR Data for Compounds 70-75** (chemical shifts are given in ppm)*

C_i	**70**	**71**	**72**	**73**	**74**	**75**
1	44.94 s	45.10 s	46.08 s	44.74 s	41.79 d	78.10 d
2	127.45 d	131.22 d	129.45 d	132.19 d	31.41 t	24.07 t
3	126.08 d	125.09 d	124.58 d	123.57 d	126.67 s	37.50 t
4	129.71 s	128.94 s	140.66 s	139.18 s	45.52 d	37.80 s
5	23.58 t	26.42 t	115.80 d	118.62 d	82.24 d	70.99 s
6	44.01 d	43.45 d	45.46 d	46.00 d	-	33.18 t
7	70.02 t	71.84 t	74.23 t	74.27 t	79.54 s	41.28 d
8	-	-	-	-	51.75 d	71.14 t
9	89.59 d	87.33 d	91.00 d	88.11 d	75.83 d	-
10	22.19 q	21.44 q	22.22 q	22.09 q	-	76.08 d
11	123.73 s	124.96 s	32.86 d	32.98 d	71.51 t	50.90 d
12	20.50^a q	20.57^a q	21.37^a q	21.30^a q	122.04 s	77.62 s
13	19.71^a q	19.73^a q	21.29^a q	21.25^a q	20.27 q	-
14	135.27 d	135.76 d	136.03 d	135.41 d	19.97 q	45.29 d
15	117.11 t	116.26 t	117.02 t	116.66 t	22.32 q	136.39 d
16	-	-	-	-	135.23 d	116.95 t
17	-	-	-	-	115.59 t	23.57^a q
18	-	-	-	-	137.39 d	20.42^a q
19	-	-	-	-	117.20 t	22.10 q

* The values of the chemical shifts denoted with the same letter may be exchanged within the row.

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