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Oxidation of Aromatic Compounds: X.* Oxidative Dehydrotrimerization of (*E*)-1-(3,4-Dimethoxyphenyl)-1-propene in the System CF_3COOH–CH_2Cl_2–PbO_2

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Abstract—Oxidation of isoeugenol methyl ether in the system CF_3COOH–CH_2Cl_2–PbO_2 involves intermediate formation of (*E*)-3,4-$(MeO)_2C_6H_3\overset{+}{C}H-\dot{C}HCH_3$ radical cation whose further transformations follow two main dehydrotrimerization pathways, resulting in formation of two positional and two stereoisomeric products having a tricyclic skeleton.

Numerous model compounds from wood lignin (such as vanillin, piperonal, syringaldehyde, cinnamic acid derivatives, eugenol, isosafrole, etc.) [2], which are products of delignification or other processes of chemical wood processing, are convenient starting materials for the synthesis of new organic structures possessing important biological properties. The present study continues the series of our works on preparative oxidation of aromatic compounds in the system CF_3COOH–CH_2Cl_2–PbO_2. It deals with oxidative transformations of isoeugenol methyl ether (**I**) which is one of the most important model compounds of wood lignin.

Protonation of ether **I** in 100% CF_3COOH at 20°C gives the corresponding carbocation which is converted into indan derivative [3]. Electrochemical addition of pyridine at the double bond of **I** results in formation of a mixture of pyridinium salts [4]. Like derivatives of cynnamic acid [1] and tolan [5, 6], one-electron oxidation of isoeugenol methyl ether (**I**) ($E^{1a}_{p/2} \approx 1.05$ V, relative to a saturated calomel electrode) to radical cation $\mathbf{I}^{+\cdot}$ in the weakly nucleophilic system CF_3COOH–CH_2Cl_2–PbO_2 gives rise to formation of a new C–C bond between the side-chain carbon atoms. This bond is formed as a result of so-called radical attack by radical cation $\mathbf{I}^{+\cdot}$ on initial arylpropene **I** (pathway *a* in Scheme 1). Radical cation adduct **Ia** undergoes one-electron oxidation to dication **Ib** [7, 8]. However, in contrast to derivatives of cinnamic acid and stilbene [9], the overall oxidation process is completed by dehydrotrimerization of the substrate rather than by its dehydrodimerization. By preparative oxidation of ether **I** in the system CF_3COOH–CH_2Cl_2–PbO_2 (0–2°C, 1 h) and subsequent chromatographic separation of the products on silica gel we isolated a mixture of four dehydrotrimers **IIa**, **IIb**, **IIIa**, and **IIIb** in an overall yield of 25–60%. The products are characterized by very similar retention parameters (GLC) and the same molecular weight, M^+ 532 (GC–MS). We succeeded in isolating pure isomer **IIa** (according to the GLC and ^{1}H NMR data) by recrystallization of the product mixture from diethyl ether. Quantitative analysis of the isomer mixture and its preparative separation into individual compounds were effected by HPLC and TLC. The fine stereochemical structure of the isomers was established by ^{1}H NMR spectroscopy.

Scheme 1 shows the mechanisms of formation of compounds **IIa**, **IIb** and **IIIa**, **IIIb**, involving transformations of ambident radical cation $\mathbf{I}^{+\cdot}$ along pathways *a* and *b*, respectively. Pathway *a* includes electrophilic attack by dication **Ib** on the double bond of arylpropene **I** to give new "trimeric" dication **Ic**. Successive deprotonation of the latter [8] and intramolecular cyclization yields final product **IIa** and its diastereoisomer **IIb**. The proposed mechanism of transformation of arylpropene **I** into dication **Ib** is well consistent with the results of detailed electrochemical studies and preparative electrochemical oxidation of structurally related 1,2-bis(4-methoxyphenyl)ethene [9].

* For communication IX, see [1].

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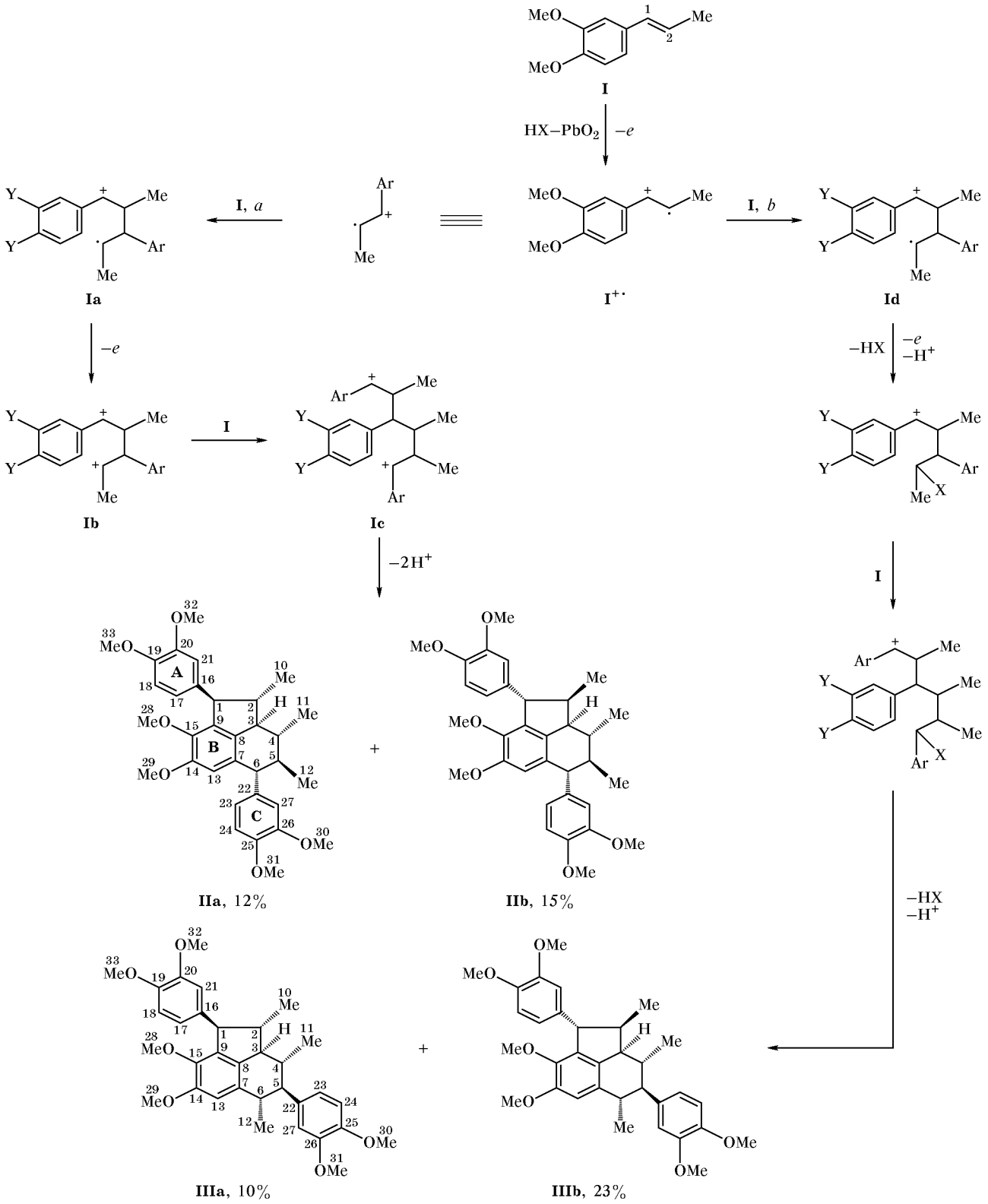
Scheme 1.



X = CF_3COO, Y = MeO, Ar = 3,4-$(MeO)_2C_6H_3$.

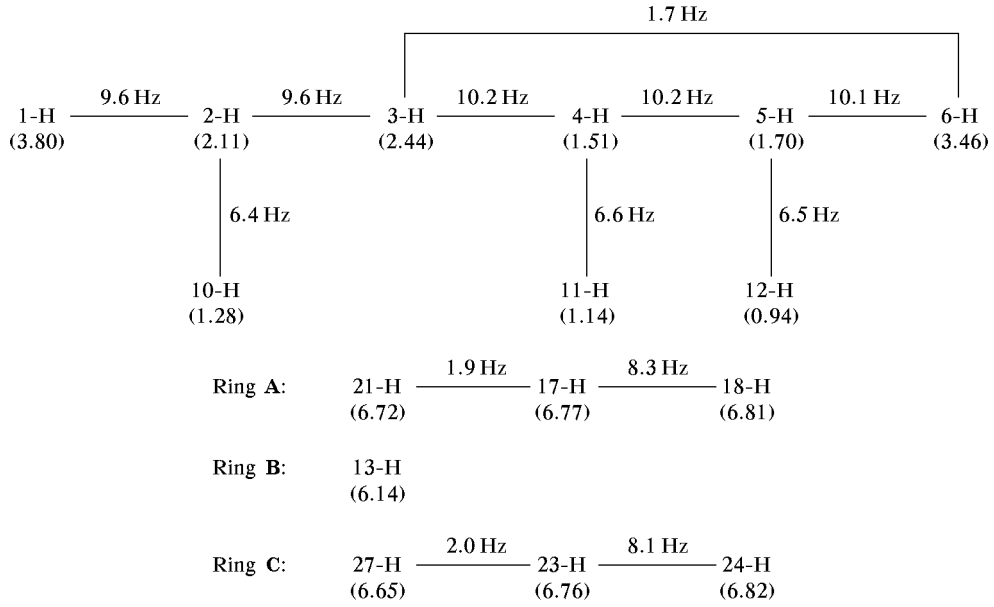


Fig. 1. Scheme of proton–proton couplings in the tricyclic skeleton and aromatic rings **A**, **B**, and **C** in molecule **IIa** (the proton chemical shifts δ, ppm, are given in parentheses).

After one-electron oxidation, the key stae of pathway *b* is electrophilic attack on initial arylpropene **I** by ambident radical cation $\mathbf{I}^{+\cdot}$. As in the synthesis of substituted indan, the formation of C–C bond in dimeric radical-cation adduct **Id** occurs in the cross-coupling mode, i.e., with participation of side-chain C^1 and $C^{2'}$ atoms. Finally, a new type of isomeric dehydrotrimers (**IIIa** and **IIIb**) is obtained with alternating methyl and aryl substituents in the cyclohexane fragments. It is seen (Scheme 1) that all four isomers **IIa**, **IIb**, **IIIa**, and **IIIb** are characterized by the same stereochemical structure of the cyclohexane fragments.

An analogous transformation pattern was observed for isosafrole. However, the methylenedioxy fragment therein is sensitive to oxidation, and the reaction is accompanied by decomposition processes. By preparative oxidation of isosafrole we obtained a product with M^+ 484; on the basis of the ^{1}H NMR data [10], it was assigned a structure corresponding to isomer **IIa**.

The isolated products, dehydrotrimers **IIa**, **IIb**, **IIIa**, and **IIIb**, are amorphous substances, so that we failed to obtain single crystals suitable for X-ray analysis. In order to determine their fine structure, we performed a complex NMR study, including various ^{1}H and ^{13}C NMR techniques: double homonuclear resonance, two-dimensional homo- and heteronuclear correlation spectroscopy (COSY), COLOC experiment, and NOE. The numbering of carbon atoms in structural isomers **IIa**/**IIb** and **IIIa**/**IIIb** is shown in Scheme 1. The spectral data are partially illustrated by Figs. 1–7. The detailed examination was performed with (1*R**,2*R**,2a*R**,3*R**,4*R**,5*R**)-1,5-bis-(3,4-dimethoxyphenyl)-2,3,4-trimethyl-7,8-dimethoxy-1,2,2a,3,4,5-hexahydroacenaphthylene (**IIa**) [8, 11] as an example.

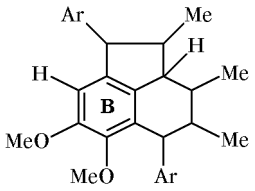
Three well resolved doublets at δ 0.94, 1.14, and 1.28 ppm in the ^{1}H NMR spectrum of **IIa** [9] belong to protons of the C^{10}–C^{12} methyl groups, and six singlets at δ 3.21, 3.55, 3.83, 3.83, 3.85, and 3.87 ppm correspond to protons of the C^{28}–C^{33} methoxy groups. The other signals in the region 0.9–3.9 ppm were assigned on the basis of the two-dimensional ^{1}H–^{1}H COSY spectrum.* Analysis of ^{1}H signals on successive selective saturation of the doublets at δ 0.94, 1.14, and 1.28 ppm (10-H–12-H) revealed particular spin–spin coupling constants for weakly coupled protons whose signals appeared as nonoverlapping multiplets. For example, the ^{1}H–^{1}H COSY spectrum showed that the 1-H doublet at δ 3.80 ppm and the 2-H signal at δ 2.11 ppm belong to a single spin system with J = 9.6 Hz. The 2-H proton in turn is coupled with the $C^{10}H_3$ methyl protons (δ 1.28 ppm, J = 6.4 Hz) and 3-H (δ 2.44 ppm). By selective suppresion of the 10-H doublet we succeeded in determining the third coupling constant between 2-H and 3-H (J = 9.6 Hz). Figure 1 illustrates the results of analysis of the aliphatic region of the ^{1}H and ^{1}H–^{1}H

* The detailed spectral data are available from the authors.

COSY spectra. These data were obtained by joint examination of the 3-H (δ 2.44 ppm) and 6-H signals (δ 3.46 ppm) which give a cross-peak in the ^1H–^1H COSY spectrum (Fig. 1). We thus determined the corresponding coupling constant, J = 1.7 Hz. We also estimated couplings between 4-H (δ 1.51 ppm) and protons of the $C^{11}H_3$ group (δ 1.14 ppm, J = 6.6 Hz), as well as between the $C^{12}H_3$ protons (δ 0.94 ppm) and 5-H (δ 1.70 ppm, J = 6.5 Hz). In addition, the 3-H proton (δ 2.44 ppm) was found to be coupled with 4-H (δ 1.51 ppm, J = 10.2 Hz), 4-H with 5-H (δ 1.70 ppm, J = 10.2 Hz), and 5-H with 6-H (δ 3.46 ppm, J = 10.1 Hz).

In order to assign signals belonging to aromatic protons in rings **A**, **B**, and **C** (see Scheme 1) we performed a series of additional homonuclear double resonance experiments which allowed us to establish a scheme of couplings between the corresponding protons and estimate particular coupling constants for nonoverlapping multiplets (Fig. 1). The procedure included monitoring of variations of multiplet signals on successive saturation of the multiplets centered at δ 6.65, 6.72, 6.81, and 6.82 ppm. For exampe, suppression of the 27-H signal (δ 6.65 ppm) induces change of the multiplicity of the 23-H signal located at δ 6.76 ppm, which unambiguously indicates that these protons form a single spin system with a coupling constant of 2.0 Hz. Likewise, assignments were made for the other nonoverlapping aromatic multiplets in the ^1H NMR spectrum.

Structure **IIa$_1$** with another substitution pattern in aromatic ring **B** could be an alternative to trimer **IIa**. In order to make a detailed assignment of the ^{13}C NMR carbon signals and thus choose unambiguously between structures **IIa** and **IIa$_1$**, we have recorded two-dimensional ^{13}C–^1H COSY and ^{13}C–^1H COLOC spectra (Figs. 2, 3).



IIa$_1$

Ar = 3,4-$(MeO)_2C_6H_3$.

Analysis of the spectra showed that the quaternary C^{16} atom with δ 136.96 ppm in the ^{13}C–^1H COLOC spectrum (Fig. 3) gives cross-peaks with the 1-H and

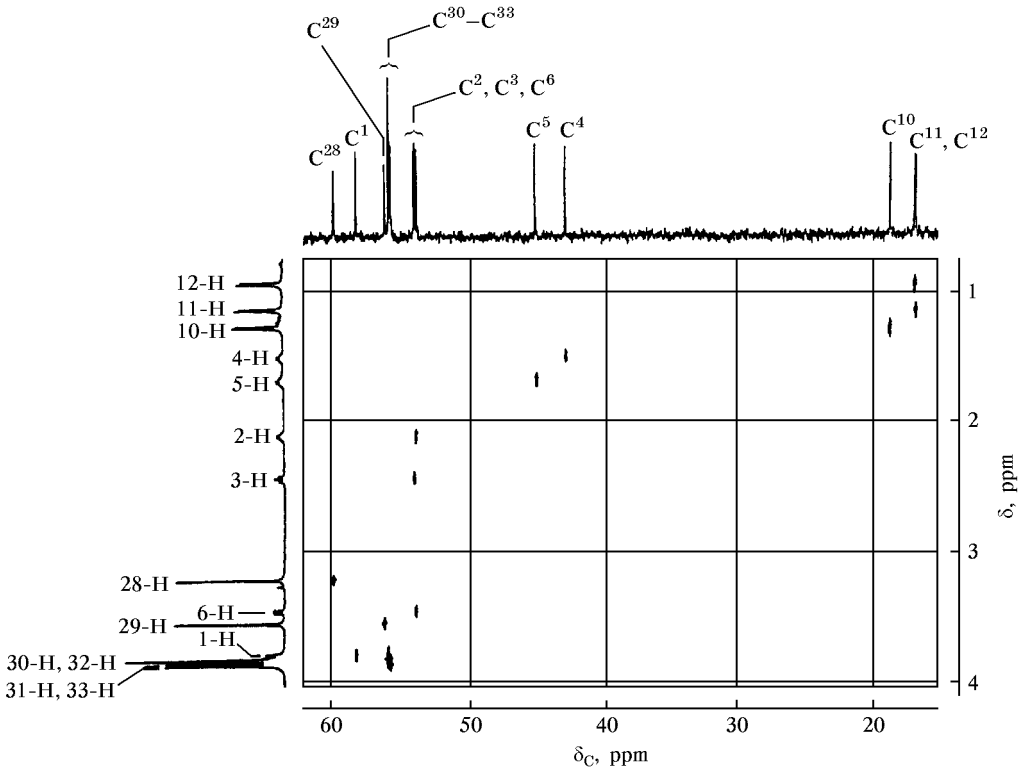


Fig. 2. A fragment of the ^{13}C–^1H COSY spectrum of compound **IIa**.

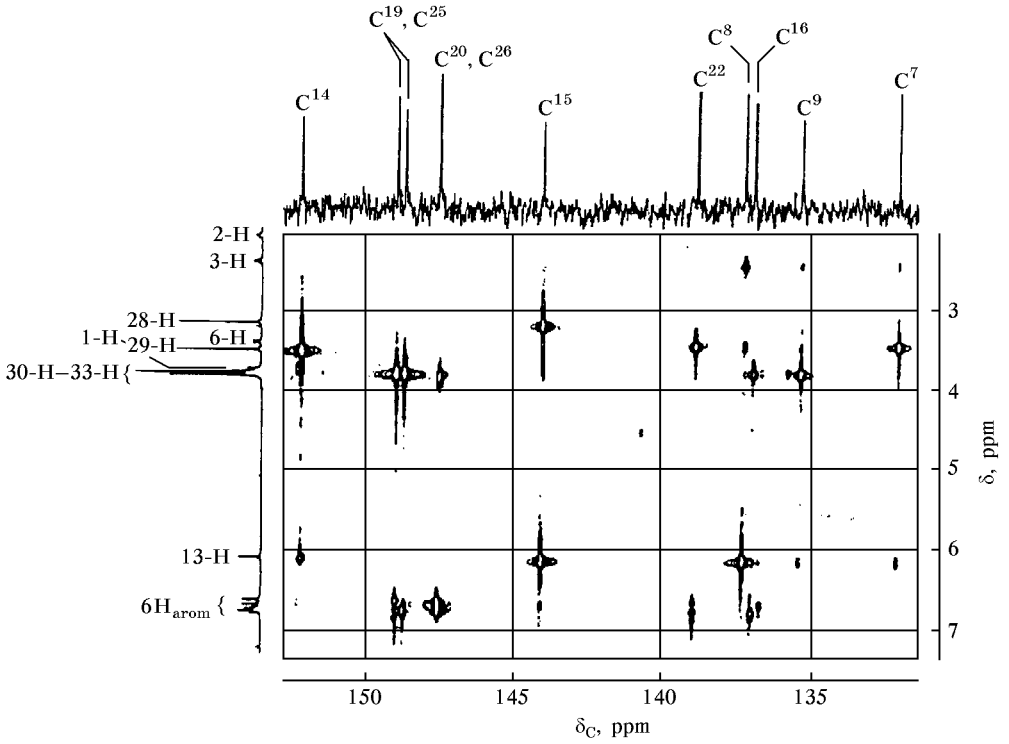


Fig. 3. A fragment of the $^{13}C–^{1}H$ COLOC spectrum of compound **IIa**.

18-H protons at δ 3.80 and 6.81 ppm. These data indicate that aromatic ring **A** is linked to the five-membered ring through the $C^{16}–C^{1}$ bond (δ_C 136.96 and 58.26 ppm, respectively). Taking into account alternation of $^{13}C–^{1}H$ spin–spin coupling constants in the aromatic region of the spectrum, the 18-H proton (δ 6.81 ppm) attached to C^{18} (δ_C 111.00 ppm) is located in the *meta* position with respect to the bond linking the rings.

The $^{13}C–^{1}H$ COSY spectrum of compound **IIa** (Fig. 2) revealed a long-term coupling between 1-H (δ 3.80 ppm) and the C^{21} and C^{17} carbon atoms in ring **A** (δ_C 111.99 and 120.63 ppm, respectively), as well as with the 21-H and 17-H protons attached thereto (δ = 6.72 and 6.77 ppm, respectively), which suggests that each carbon atom, C^{21} and C^{17} is located *ortho* with respect to the carbon atom linked to the five-membered ring. Likewise, we established that ring **C** is linked to the six-membered ring through the $C^{22}–C^{6}$ bond (δ_C 138.84 and 53.95 ppm, respectively) and assigned the ^{13}C and ^{1}H signals from the corresponding molecular fragment.

It was most difficult to choose between alternative structures **IIa** and **IIa$_1$**. On the basis of the existence of appreciable couplings between C^{7} (δ_C 131.91 ppm) and 6-H and 13-H (δ 3.46 and 6.14 ppm, respectively) and the presence of a cross-peak arising from C^{6} (δ_C 53.95 ppm) and 13-H (δ 6.14 ppm) the following conclusions were drawn: (1) The C^{7} atom of aromatic ring **B** simultaneously belongs to the six-membered ring; (2) The 13-H proton in ring **B** (attached to C^{13}, δ_C 111.60 ppm) is located nearer to the six-membered ring than to the five-membered one; (3) The couplings of C^{8} (δ_C 137.24 ppm) with 3-H, 6-H, 1-H, and 13-H (δ 2.44, 3.46, 3.80, and 6.14 ppm, respectively) indicate that the C^{8} atom belongs to ring **B** and is located in the site of junction of the five- and six-membered rings. These conclusions determined unambiguous choice in favor of structure **IIa**. The positions of methoxy groups in the aromatic rings of molecule **IIa** were established on the basis of the $^{13}C–^{1}H$ COLOC spectrum (Fig. 3). Joint analysis of the $^{13}C–^{1}H$ and $^{13}C–^{1}H$ COSY spectra allowed us to assign the corresponding ^{1}H and ^{13}C signals (Fig. 4).

In a similar way, we analyzed the NMR spectra of the three other isomeric trimers (compounds **IIb**, **IIIa**, and **IIIb**; Figs. 5–7). Some specific spectral features of these isomers should be noted. The spectra of **IIb**, as well as of **IIIb**, revealed no coupling between 1-H (δ 4.11 ppm) and 2-H (δ 2.60 ppm); however, their vicinal arrangement follows from detailed examination of the $^{13}C–^{1}H$ COSY and $^{13}C–^{1}H$ COLOC

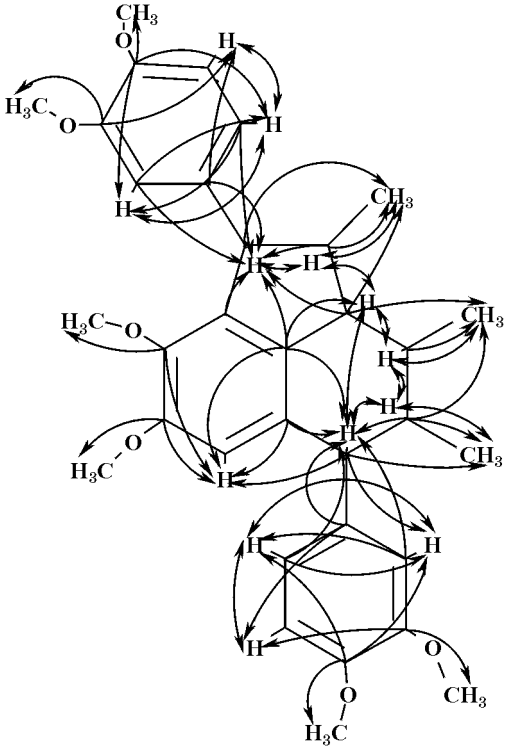


Fig. 4. Scheme of $^{1}H–^{1}H$ (↔) and $^{13}C–^{1}H$ (→) couplings in molecule **IIa**, derived from the $^{1}H–^{1}H$ COSY and $^{13}C–^{1}H$ COLOC spectra.

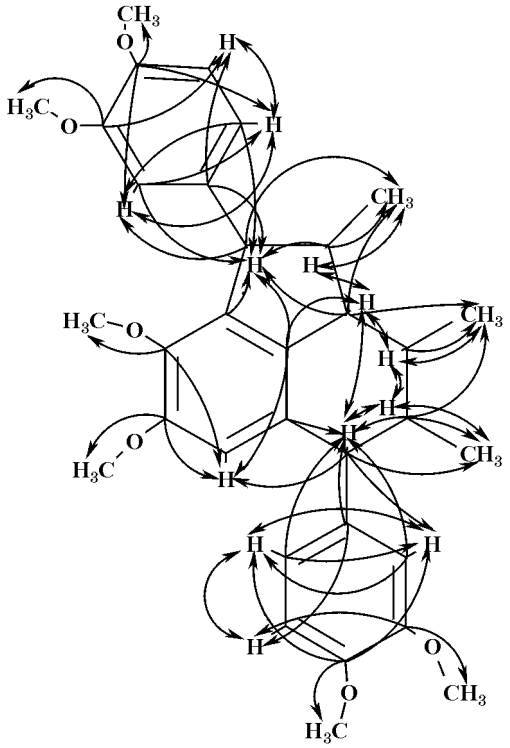


Fig. 5. Scheme of $^{1}H–^{1}H$ (↔) and $^{13}C–^{1}H$ (→) couplings in molecule **IIb**, derived from the $^{1}H–^{1}H$ COSY and $^{13}C–^{1}H$ COLOC spectra.

spectra. We estimated precise coupling constants for the 1-H–6-H protons from the ^{1}H NMR spectra of compounds **IIa** and **IIb**, which were recorded with decoupling from the methyl group protons, and analyzed the Karplus dependences of *J* versus dihedral angles between the vicinal C−H bonds. Unlike trimer **IIa**, the 5-H signal of **IIIa** is displaced downfield, while the 6-H signal is displaced upfield. This pattern is explained by change of the position of aromatic ring **C** in going from structure **IIa** to **IIIa**; it is consistent with the observed downfield shift of the 13-H signal in going from **IIa** to **IIIa**. The 13-H proton in **IIa** (δ 6.14 ppm) falls into the shielding area of aromatic ring **C**.

The fine stereochemical structures of all four isomers **IIa**, **IIb**, **IIIa**, and **IIIb** were determined by comparative analysis of their most favorable conformers, which was performed by the molecular mechanics procedure using Alchemie 2, Chem3D, and Hyperchem 97 software (on the basis of vicinal proton coupling constants) [12]. The results (see Scheme 1) are consistent with the experimental NOE data [13].

Thus, our study of oxidative transformations of isoeugenol methyl ether allowed us to estimate the direction and selectivity of concurrent reactions of its ambident radical cation, which lead to formation of new carbon–carbon bonds [14, 15].

EXPERIMENTAL

The ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AM-500 spectrometer at 500 MHz for ^{1}H and 125.76 MHz for ^{13}C. Chloroform-*d* was used as solvent and internal reference (δ 7.25 ppm, residual protons; δ_C 77.0 ppm). The IR spectra were obtained on a Specord 75IR spectrometer from solutions in chloroform. The mass spectra were run on an MKh-1321 instrument, and GC–MS data were obtained on a Hewlett–Packard HP-5995 mass spectrometer (energy of ionizing electrons 70 eV, separator temperature 240°C, ion source temperature 250°C) using an Ultra-2 quartz capillary column, 25 000 × 0.32 mm (95% of methylsilicone and 5% of phenylmethylsilicone, film thickness 0.53 μm).

HPLC analysis of the reaction mixtures and preparative separation of diastereoisomeric products were performed on a Beckman Gold System instrument equipped with a Model 168 UV detector. A Hypersil

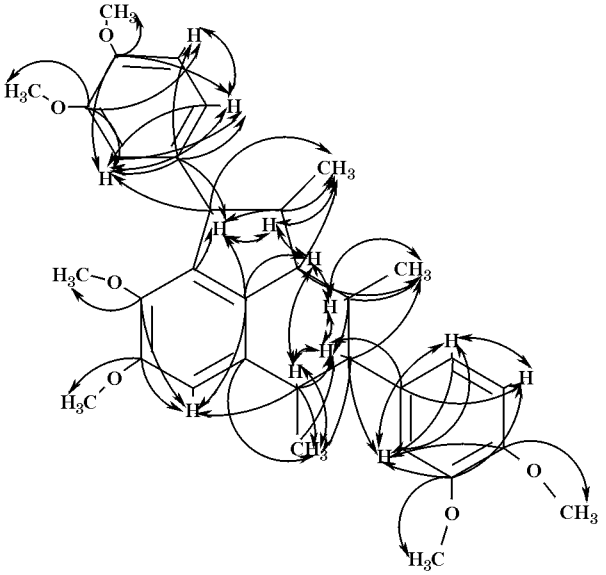


Fig. 6. Scheme of ^{1}H–^{1}H (↔) and ^{13}C–^{1}H (→) couplings in molecule **IIIa**, derived from the ^{1}H–^{1}H COSY and ^{13}C–^{1}H COLOC spectra.

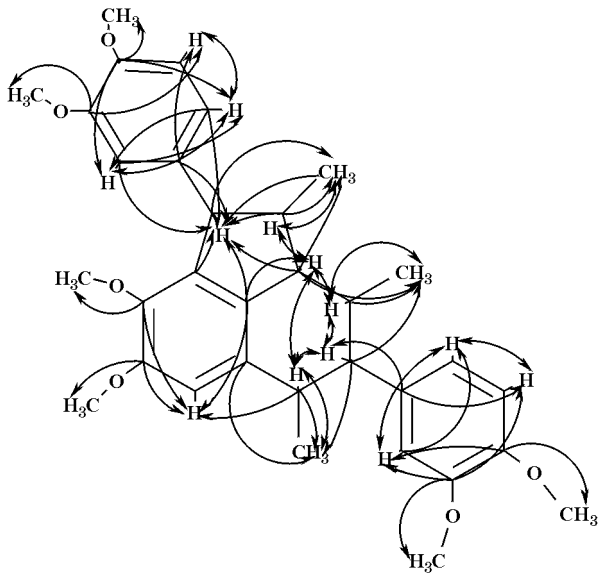


Fig. 7. Scheme of ^{1}H–^{1}H (↔) and ^{13}C–^{1}H (→) couplings in molecule **IIIb**, derived from the ^{1}H–^{1}H COSY and ^{13}C–^{1}H COLOC spectra.

ODS (250 × 4.6 mm) column packed with a Sigma–Aldrich stationary phase (5 μm) was used for the analytical purpose; eluent acetonitrile–water, 70 : 30, flow rate 1 ml/min; working wavelengths 220 and 280 nm; sample volume 20 μl. Preparative separations were effected with the aid of a Partisil ODS-3 column (250 × 9.6 mm) packed with a Whatman stationary phase (10 μm); eluent acetonitrile–water, 70 : 30, flow rate 3 ml/min; working wavelength 280 nm, sample volume 100 μl.

The purity of the initial compounds and reaction products was checked by HPLC and TLC (Silufol UV-254 plates). The reaction mixtures were preliminarily separated by column chromatography on silica gel (40–100 μm, Chemapol) using gradient elution with hexane–ether mixtures (gradually going to pure ether).

The yields of oxidation products **IIa**, **IIb**, **IIIa**, and **IIIb** strongly depended on the reaction conditions; they were estimated from the weights of fractions obtained after separation by column chromatography and subsequent separation by TLC. For comparison, Scheme 1 gives the results of HPLC analysis of isomeric composition of the reaction mixture before preliminary separation.

Oxidation of isoeugenol methyl ether (I) in the system CF_3COOH–CH_2Cl_2–PbO_2. A solution of 0.6 ml (8.2 mmol) of CF_3COOH in 3.1 ml of CH_2Cl_2 was cooled to 0–5°C, and 0.5 ml (3 mmol) of compound **I** was added under vigorous stirring. Lead(IV) oxide, 0.4 g (1.65 mmol), was then added, and the resulting suspension was stirred for 1 h at 0–2°C. When the reaction was complete, the mixture was poured into 100 ml of diethyl ether. The ether solution was washed with water, a saturated aqueous solution of sodium hydrogen carbonate, and water again, dried over Na_2SO_4, and evaporated. The residue was subjected to column chromatography on silica gel to obtain 0.373 g (60%) of a mixture of products **IIa**, **IIb**, **IIIa**, and **IIIb**.

(1*R,2*R**,2a*R**,3*R**,4*R**,5*R**)-1,5-Bis(3,4-dimethoxyphenyl)-7,8-dimethoxy-2,3,4-trimethyl-1,2,2a,3,4,5-hexahydroacenaphthylene (IIa)** was isolated by recrystallization from diethyl ether of a honey-like mixture of four isomeric trimers, which solidified on storage. After additioal washing with acetone, the yield of **IIa** was 0.065 g (10%). mp 167–168°C. IR spectrum, ν, cm^{-1}: 610, 645, 715, 720, 755, 770, 850, 980, 1025, 1210 s, 1250, 1260, 1275, 1350, 1380, 1420, 1475, 1490, 1515, 1600, 1615, 2850, 2890, 2950, 2975, 3015. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.94 d (3H, $C^{12}H_3$, *J* = 6.5 Hz), 1.14 d (3H, $C^{11}H_3$, *J* = 6.6 Hz), 1.28 d (3H, $C^{10}H_3$, *J* = 6.4 Hz), 1.51 d.d.q (1H, 4-H, *J* = 10.2, 10.2, 6.6 Hz), 1.70 d.d.q (1H, 5-H, *J* = 10.2, 10.1, 6.5 Hz), 2.11 d.d.q (1H, 2-H, *J* = 9.6, 9.6, 6.4 Hz), 2.44 d.d.d (1H, 3-H, *J* = 10.2, 9.6, 1.7 Hz), 3.21 s (3H, $OC^{28}H_3$), 3.46 d.d (1H, 6-H, *J* = 10.1, 1.7 Hz), 3.55 s (3H, $OC^{29}H_3$), 3.80 d (1H, 1-H, *J* = 9.6 Hz), 3.83 s (6H, $OC^{31}H_3$, $OC^{32}H_3$), 3.85 s (3H, $OC^{30}H_3$), 3.87 s (3H,

$OC^{33}H_3$), 6.14 s (1H, 13-H), 6.65 d (1H, 27-H, J = 2.0 Hz), 6.72 d (1H, 21-H, J = 1.9 Hz), 6.76 d.d (1H, 23-H, J = 8.1, 2.0 Hz), 6.77 d.d (1H, 17-H, J = 8.3, 1.9 Hz), 6.81 d (1H, 18-H, J = 8.3 Hz), 6.82 d (1H, 24-H, J = 8.1 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 16.85 q ($C^{11}H_3$, J = 124.4 Hz), 16.93 q ($C^{12}H_3$, J = 124.8 Hz), 18.73 q ($C^{10}H_3$, J = 124.6 Hz), 43.13 d (C^4, J = 124.7 Hz), 45.30 d (C^5, J = 125.4 Hz), 53.95 d (C^6, $J \approx$ 125 Hz), 54.06 d (C^2, $J \approx$ 125 Hz), 54.16 d (C^3, $J \approx$ 125 Hz), 55.84 q ($OC^{33}H_3$, J = 143.8 Hz), 55.89 q ($OC^{30}H_3$, J = 143.8 Hz), 55.99 q ($OC^{31}H_3$, $OC^{32}H_3$, J = 144.0 Hz), 56.27 q ($OC^{29}H_3$, J = 143.7 Hz), 58.26 d (C^1, J = 127.5 Hz), 59.77 q ($OC^{28}H_3$, J = 143.8 Hz), 111.00 d (C^{18}, J = 157.2 Hz), 111.03 d (C^{24}, J = 157.5 Hz), 111.60 d (C^{13}, J = 155.2 Hz), 111.99 d.d.d (C^{21}, J = 154.6, ~6, ~6 Hz), 112.37 d.d.d (C^{27}, J 154.6, ~7, ~7 Hz), 120.63 d.d.d (C^{17}, J = 151.1, ~7, ~7 Hz), 121.83 d.d.d (C^{23}, J = 152.0, ~7, ~7 Hz), 131.91 d (C^7, J = 6.9 Hz), 135.34 d (C^9, J = 6.5 Hz), 136.96 s (C^{16}), 137.24 s (C^8), 138.84 s (C^{22}), 144.01 s (C^{15}), 147.52 s ($2C^{19,25}$), 148.69 s (C^{20}), 148.95 s (C^{26}), 152.24 s (C^{14}). Mass spectrum, m/z (I_{rel}, %): 534 (6) $[M+2]^+$, 533 (39) $[M+1]^+$, 532 (100) M^+. Found, %: C 74.82; H 7.37. $C_{33}H_{40}O_6$. Calculated, %: C 74.41; H 7.57. M 532.

(1*S,2*S**,2a*R**,3*R**,4*R**,5*R**)-1,5-Bis(3,4-dimethoxyphenyl)-7,8-dimethoxy-2,3,4-trimethyl-1,2,2a,3,4,5-hexahydroacenaphthylene (IIb).** The ether mother liquor containing a mixture of the three other trimers (see above) was evaporated on a rotary evaporator, and the residue was recrystallized from cooled acetone. The product was additionally purified by HPLC. Yield 0.08 g (13%). mp 66–68°C. IR spectrum, ν, cm^{-1}: 570, 645, 710, 730, 775, 810, 850, 915, 965, 990, 1030, 1215–1285 s, 1300, 1355, 1380, 1420, 1475, 1495, 1515, 1600, 1615, 2850, 2890, 2950, 2975, 3015. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.90 d (3H, $C^{12}H_3$, J = 6.5 Hz), 0.95 d (3H, $C^{10}H_3$, J = 7.0 Hz), 0.96 d (3H, $C^{11}H_3$, J = 6.3 Hz), 1.42 d.d.q (1H, 4-H, J = 10.8, 10.8, 6.3 Hz), 1.65 d.d.q (1H, 5-H, J = 10.8, 10.2, 6.5 Hz), 2.60 d.q (1H, 2-H, J = 7.0, 6.0 Hz), 2.95 d.d.d (1H, 3-H, J = 10.8, 6.0, 2.0 Hz), 3.39 d.d (1H, 6-H, J = 10.2, 2.0 Hz), 3.57 s (3H, $OC^{28}H_3$), 3.62 s (3H, $OC^{29}H_3$), 3.84 s (3H, $OC^{31}H_3$), 3.85 s (6H, $OC^{30}H_3$, $OC^{32}H_3$), 3.89 s (3H, $OC^{33}H_3$), 4.11 s (1H, 1-H), 6.16 s (1H, 13-H), 6.63 d.d (1H, 17-H, J = 8.3, 2.0 Hz), 6.67 d (1H, 27-H, J = 2.0 Hz), 6.75 d.d (1H, 23-H, J = 8.2, 2.0 Hz), 6.75 d (1H, 18-H, J = 8.3 Hz), 6.78 d (1H, 21-H, J = 2.0 Hz), 6.82 d (1H, 24-H, J = 8.2 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 15.87 q ($C^{10}H_3$, J = 123.9 Hz), 16.69 q ($C^{12}H_3$, J = 123.8 Hz), 16.80 q ($C^{11}H_3$, J = 123.8 Hz), 36.25 d (C^4, J = 125.5 Hz), 45.02 d (C^5, J = 123.8 Hz), 47.20 d (C^2, J = 133.9 Hz), 48.47 d (C^3, J = 125.5 Hz), 53.48 d (C^6, J = 124.8 Hz), 55.76 d (C^1, $J \approx$ 125 Hz), 55.82 q ($OC^{30}H_3$, J = 144.1 Hz), 55.84 q ($OC^{31}H_3$, $OC^{33}H_3$, J = 144.1 Hz), 55.90 q ($OC^{32}H_3$, J = 144.1 Hz), 56.03 q ($OC^{29}H_3$, J = 144.1 Hz), 60.39 q ($OC^{28}H_3$, J = 144.1 Hz), 110.96 d (C^{18}, J = 157.7 Hz), 111.02 d (C^{24}, J = 157.7 Hz), 111.40 d (C^{13}, J = 154.3 Hz), 111.48 d (C^{21}, J = 154.2 Hz), 112.53 d (C^{27}, J = 156.3 Hz), 119.06 d (C^{17}, J = 159.4 Hz), 121.66 d (C^{23}, J = 159.3 Hz), 133,55 d (C^7, J = 5.6 Hz), 134.61 s (C^9), 135.54 s (C^8), 136.69 s (C^{16}), 138.69 s (C^{22}), 144.85 s (C^{15}), 147.38 s (C^{25}), 147.46 s (C^{19}), 148.77 s (C^{20}, C^{26}), 151.87 s (C^{14}). Mass spectrum, m/z (I_{rel}, %): 533 (28) $[M+1]^+$, 532 (91) M^+. Found, %: C 74.65; H 7.41. $C_{33}H_{40}O_6$. Calculated, %: C 74.41; H 7.57. M 532.

After separation of isomers **IIa** and **IIb**, the acetone mother liquor was evaporated on a rotary evaporator under reduced pressure.

(1*R,2*R**,2a*R**,3*R**,4*R**,5*S**)-1,4-Bis(3,4-dimethocyphenyl)-7,8-dimethoxy-2,3,5-trimethyl-1,2,2a,3,4,5-hexahydroacenaphthylene (IIIa) and (1*S**,2*S**,2a*R**,3*R**,4*R**,5*S**)-1,4-bis(3,4-dimethoxyphenyl)-7,8-dimethoxy-2,3,5-trimethyl-1,2,2a,3,4,5-hexahydroacenaphthylene (IIIb)** were separated by repeated chromatography using 20 analytical Silufol UV-254 plates and subsequent additional purification by HPLC. Yield of **IIIa** 0.05 g (8%), mp 138–140°C. IR spectrum, ν, cm^{-1}: 610, 650, 705, 725, 750, 770, 850, 975, 1025, 1210 s, 1255, 1300, 1335, 1350, 1380, 1420, 1460, 1480, 1510, 1600, 1615, 2845, 2885, 2950, 2975, 3015. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.78 d (3H, $C^{11}H_3$, J = 6.5 Hz), 1.20 d (3H, $C^{12}H_3$, J = 6.9 Hz), 1.23 d (3H, $C^{10}H_3$, J = 6.5 Hz), 1.85 d.d.q (1H, 4-H, J = 10.8, 10.8, 6.5 Hz), 2.11 d.d.q (1H, 2-H, J = 9.6, 9.6, 6.5 Hz), 2.24 d.d (1H, 5-H, J = 10.8, 9.6 Hz), 2.37 d.d.d (1H, 3-H, J = 10.8, 9.6, 1.3 Hz), 2.97 d.q.d (1H, 6-H, J = 9.6, 6.9, 1.3 Hz), 3.26 s (3H, $OC^{28}H_3$), 3.79 d (1H, 1-H, J = 9.6 Hz), 3.79 s (3H, $OC^{29}H_3$), 3.85 s (3H, $OC^{32}H_3$), 3.86 s (3H, $OC^{33}H_3$), 3.87 s (3H, $OC^{30}H_3$), 3.88 s (3H, $OC^{31}H_3$), 6.68 s (1H, 13-H), 6.71 d (1H, 27-H, J = 1.9 Hz), 6.74 d.d (1H, 23-H, J = 8.1, 1.9 Hz), 6.75 d (1H, 21-H, J = 1.9 Hz), 6.79 d.d (1H, 17-H, J = 8.1, 1.9 Hz), 6.81 d (1H, 18-H, J = 8.1 Hz), 6.83 d (1H, 24-H, J = 8.1 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ, ppm: 17.88 q ($C^{11}H_3$, J = 125.5 Hz), 18.52 q ($C^{10}H_3$, J = 127.2 Hz), 20.57 q ($C^{12}H_3$, J = 127.2 Hz), 40.59 d (C^6, J = 127.2 Hz), 41.85 d (C^4, J = 127.2 Hz), 54.04 d (C^2, J = 128.9 Hz), 54.47 d

(C^3, J = 128.9 Hz), 55.87 q ($OC^{30}H_3$, $C^{31}H_3$, $C^{33}H_3$, J = 144.1 Hz), 56.01 q ($OC^{32}H_3$, J = 144.1 Hz), 56.41 q ($OC^{29}H_3$, J = 144.1 Hz), 58.26 d (C^1, J = 128.9 Hz), 58.61 d (C^5, J = 120.4 Hz), 59.91 q ($OC^{28}H_3$, J = 144.1 Hz), 109.67 d (C^{13}, J = 154.3 Hz), 110.95 d (C^{18}, C^{24}, J = 157.8 Hz), 111.01 d (C^{27}, J = 157.7 Hz), 111.90 d (C^{21}, J = 154.3 Hz), 120.60 d (C^{17}, J = 159.4 Hz), 120.98 d (C^{23}, J = 157.7 Hz), 132.98 s (C^7), 135.83 d (C^9, J = 5.3 Hz), 136.66 s (C^8, C^{16}), 137.45 s (C^{22}), 143.96 s (C^{15}), 147.37 s (C^{25}), 147.51 s (C^{19}), 148.64 s (C^{20}), 149.05 s (C^{26}), 152.38 s (C^{14}). Mass spectrum, *m*/*z* (I_{rel}, %): 533 (28) $[M+1]^+$, 532 (79) M^+. Found, %: C 74.39; H 7.33. $C_{33}H_{40}O_6$. Calculated, %: C 74.41; H 7.57. *M* 532.

Yield of **IIIb** 0.11 g (18%). mp 93–95°C. IR spectrum, ν, cm^{-1}: 600, 610, 720, 750, 790, 800, 850, 980, 1025, 1190, 1210 s, 1250, 1260, 1300, 1325, 1350, 1375, 1415, 1465, 1490, 1510, 1600, 1615, 2850, 2890, 2950, 2975, 3015. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.60 d (3H, $C^{11}H_3$, J = 6.4 Hz), 0.97 d (3H, $C^{10}H_3$, J = 7.1 Hz), 1.18 d (3H, $C^{12}H_3$, J = 6.8 Hz), 1.75 d.d.q (1H, 4-H, J = 10.8, 10.8, 6.4 Hz), 2.21 d.d (1H, 5-H, J = 10.8, 10.2 Hz), 2.58 d.q (1H, 2-H, J = 7.1, 6.6 Hz), 2.90 d.d.d (1H, 3-H, J = 10.8, 6.6, 1.7 Hz), 2.92 d.q.d (1H, 6-H, J = 10.2, 6.8, 1.7 Hz), 3.59 s (3H, $OC^{28}H_3$), 3.83 s (3H, $OC^{33}H_3$), 3.85 s (6H, $OC^{29}H_3$, $OC^{32}H_3$), 3.86 s (3H, $OC^{30}H_3$), 3.87 s (3H, $OC^{31}H_3$), 4.11 s (1H, 1-H), 6.59 d.d (1H, 17-H, J = 8.3, 2.1 Hz), 6.69 d (1H, 27-H, J = 2.0 Hz), 6.71 d.d (1H, 23-H, J = 8.2, 2.0 Hz), 6.72 s (1H, 13-H), 6.73 d (1H, 18-H, J = 8.2 Hz), 6.77 d (1H, 21-H, J = 2.1 Hz), 6.81 d (1H, 24-H, J = 8.2 Hz). ^{13}C NMR spectrum ($CDCl_3$), δ_C, ppm: 15.99 q ($C^{10}H_3$, J = 125.5 Hz), 17.61 q ($C^{11}H_3$, J = 125.5 Hz), 20.12 q ($C^{12}H_3$, J = 127.2 Hz), 35.37 d (C^4, J = 123.8 Hz), 40.05 d (C^6, J = 122.1 Hz), 47.10 d (C^2, J = 133.9 Hz), 49.16 d (C^3, J = 123.8 Hz), 55.83 q ($OC^{31}H_3$, $OC^{33}H_3$, J = 144.1 Hz), 55.87 q ($OC^{32}H_3$, J = 144.1 Hz), 55.93 q ($OC^{30}H_3$, J = 144.1 Hz), 55.96 d (C^1, $J \approx$ 123 Hz), 56.18 q ($OC^{29}H_3$, J = 144.1 Hz), 58.13 d (C^5, J = 128.9 Hz), 60.47 q ($OC^{28}H_3$, J = 144.1 Hz), 109.69 d (C^{13}, J = 154.5 Hz), 110.99 d (C^{18}, C^{24}, J = 159.4 Hz), 111.54 d (C^{21}, C27, J = 156.0 Hz), 119.04 d (C^{17}, C^{23}, J = 159.4 Hz), 134.51 s (C^7), 135.04 s (C^8), 135.21 s (C^9), 136.63 s (C^{16}), 137.15 s (C^{22}), 144,81 s (C^{15}), 147.37 s (C^{25}), 147.41 s (C^{19}), 148.83 s (C^{20}), 148.98 s (C^{26}), 151.97 s (C^{14}). Mass spectrum, *m*/*z* (I_{rel}, %): 533 (59) $[M+1]^+$, 532 (64) M^+. Found, %: C 74.77; H 7.54. $C_{33}H_{40}O_6$. Calculated, %: C 74.41; H 7.57. *M* 532.

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