The Unsensitized Photooxidation of (+)-Limonene, 1,2-Dimethylcyclohexene, and *endo*-Dicyclopentadiene

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The unsensitized photooxidation of (+)-limonene (**1**), 1,2-dimethylcyclohexene (**2**) and *endo*-dicyclopentadiene (**3**) were carried out with Pyrex-filtered light. The singlet-oxygen oxidation was found to occur concurrently with the radical oxidation to the extent of 41% with **1** and 66% with **2**, but not at all with **3**. A reaction path *via* a complex was proposed.

Although sensitized photooxidation has been the subject of a number of recent investigations in connection with the reactivity of singlet oxygen, unsensitized photooxidation has attracted less attention. It has generally been accepted that, in unsensitized photooxidation, the light energy can be assumed to be used for the formation of a radical initiator, and that the reaction proceeds in the same reaction pattern as that of the radical-initiated oxidation.[1] In the present study, we observed that (+)-limonene (**1**), 1,2-dimethylcyclohexene (**2**), and *endo*-dicyclopentadiene (**3**), each possessing only isolated double bonds, suffered oxidation under the influence of the light of a longer wavelength (Pyrex-filtered light) to give results different from those obtained by the radical oxidation; an investigation was then undertaken in order to clarify the relation between the unsensitized photooxidation and the radical oxidation.

Results

(+)-Limonene (**1**), 1,2-dimethylcyclohexene (**2**), and *endo*-dicyclopentadiene (**3**) were oxidized with oxygen in three ways; Ox I—by heating a neat sample at 40—60 °C; Ox II—by irradiation with visible light in the presence of rose bengal (0.5 M in 1 : 1 *t*-butyl alcohol–methanol), and Ox III—by irradiation with Pyrex-filtered light in the absence of any sensitizer (0.5 M in 1 : 1 *t*-butyl alcohol–methanol). The products and product distribution after the reduction ($Na_2S_2O_3$+KI) of the primarily-formed hydroperoxide mixture are summarized in Tables 1—3. The product identification was carried out spectroscopically (see Experimental). The relative retention times on gas chromatography were also compared with those reported[2] in the case of the oxidation products of **1**.

It has been reported[3] that Compounds **10** and **11**, when obtained by the radical oxidation of **1**, are racemic, while both are optically-active when obtained by singlet-oxygen oxidation. In the latter case, Compounds **9** and **12** have also been known to be optically-active. The optical activities obtained in the present study are included in Table 1. It should be noted that the optical activities of **10** and **11**, obtained by Ox III, were reduced compared to those obtained by Ox II, whereas those of **9** and **12** were unchanged irrespective of the oxidation methods (Ox II or Ox III). We inferred from these facts that, in Ox III, some radical oxidation occurs concurrently with the singlet-oxygen oxidation. From the $[\alpha]_D$ values of **10** and **11**, it was estimated that the ratio of both reaction types is 41 : 59 (singlet-oxygen oxidation : radical oxidation). The product distribution also coincided

TABLE 2. YIELDS OF OXIDATION PRODUCTS FROM **2**

	Products				
	13	**14**	**15**	**16**	**17**
Ox I	12	7	39	34	8
Ox II	0	92	8	0	0
Ox III	1	64	22	7	6

TABLE 3. YIELDS OF OXIDATION PRODUCTS FROM **3**

	Products				
	18	**19**	**20**	**21**	**22**
Ox I	8	42	0	18	32
Ox II	0	0	0	0	100
Ox III	15	38	17	0	30

TABLE 1. YIELDS AND OPTICAL ACTIVITIES OF OXIDATION PRODUCTS FROM **1**[a,b]

	Products								
	4	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**
Ox I	14	3	16	14	7	0	26	20	0
							(0)[d]	(0)[c]	
Ox II	0	0	30	7	3	23	8	3	26
						(+92.4)[c]	(−178)[d]	(−71.8)[c]	(+5.71)[c]
Ox III	16	3	22	11	13	10	11	5	10
						(+92.1)	(−32)	(−5.6)	(+7.2)

a) The unparenthesized figures refer to the yield (%), and figures in the parentheses refer to optical activities ($[\alpha]_D$). b) The product distribution in Ox I and Ox II are almost identical with those reported.[2,13] c) Data from Ref. 2. d) As the value in Ref. 2 was that of a mixture, the value from Ref. 14 was indicated.

fairly well with the calculated values based on this ratio.*

It is evident from the results in Table 2 that, in the case of **2** also, the singlet-oxygen oxidation and the radical oxidation occur concurrently in Ox III, the ratio in the present case being 66: 34.** This ratio became larger as the reaction was carried out with a more dilute solution in the case of **2**, while it was almost independent of the concentration in the case of **1** (Tables 4 and 5).

TABLE 4. THE RATIO OF SINGLET-OXYGEN PARTICIPATION AS A FUNCTION OF CONCENTRATION IN CASE OF **1** (after 20 hr)

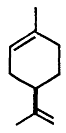
Concentration (M)	0.25	0.5	0.1	1.5	Neat
Percent of singlet-oxygen participation	39	41	40	35	26

TABLE 5. THE RATIO OF SINGLET-OXYGEN PARTICIPATION AS A FUNCTION OF CONCENTRATION IN CASE OF **2** (after 5 hr)

Concentration (M)	0.19[a]	0.22	0.5	Neat[b]
Percent of singlet-oxygen participation	90	77	66	35

a) After 20 hr. b) Unfiltered or Pyrex-filtered light.

Contrary to the results obtained with the Ox-III oxidations of **1** and **2**, where singlet-oxygen oxidation constituted a considerable part of the reaction, only radical oxidation was observed in the Ox-III oxidation of **3** (Table 3). This conclusion was derived from the observation that the same product distribution as obtained by Ox III was obtained when Ox I and irradiation in the absence of oxygen were applied consecutively to **2**. Obviously, Ox III is essentially the same as the radical oxidation (Ox I) and the apparent differences in product distributions (with **18**, **20**, and **21**) in Ox I and Ox III may be assumed to arise from a secondary phototransformation of the primary products. This reasoning was supported by the facts that **21** afforded **20** on irradiation with Pyrex-filtered light[6] and that the hydroperoxide **23**, which is a presumable intermediate in the Ox-I oxidation of **3**, and which is actually obtained in an almost pure state by the singlet-oxygen oxidation of **3**, afforded **18**, in addition to **20**, under the irradiation.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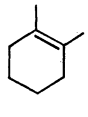
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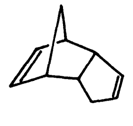
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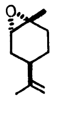
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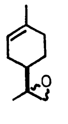
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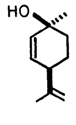
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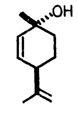
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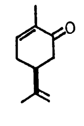
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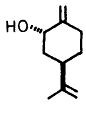
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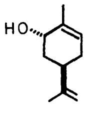
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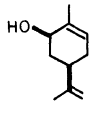
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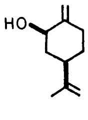
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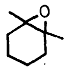
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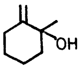
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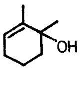
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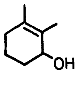
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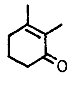
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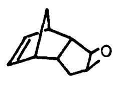
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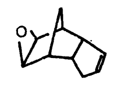
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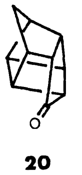
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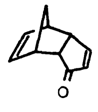
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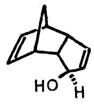
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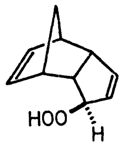
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Discussion

It was amusing that olefins which should not absorb the working light underwent photoreaction, and that the participation of singlet-oxygen oxidation was observed only in cases of **1** and **2**. Chien[7] has studied the mechanism of the initiation of the photooxidation of hydrocarbons in the wavelength region where there are no allowed transitions. He postulated, mainly on the basis of the kinetic data, two processes, the charge-transfer excitation and the oxygen-perturbed S–T ex-

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* The unsensitized photooxidation of **1** has been reported by Schenck and his co-workers,[2] where a product distribution almost identical with that in the radical oxidation is obtained. This result contradictory to ours is conceivable since, under their reaction conditions (irradiation for 43 hr at 50 °C in a quartz vessel), the radical reaction would necessarily become more important than the inherent photochemical reaction of the olefin.

** The Ox-I and Ox-II oxidations of **2** have been reported by Foote.[4] Although results identical with ours have been obtained in case of Ox II, no description of **13** and **17** has appeared in the case of Ox I, in contrast to our results. This might be due to their over-reducing of the primary products by using $NaBH_4$ as a reducing reagent. Farmer and Sutton[5] have obtained a 1: 1 mixture of two hydroperoxides which are presumable precursors of **15** and **16** by the unsensitized photooxidation of **2**, and claimed an identity in mechanism between unsensitized photooxidation and radical oxidation. We traced the reaction under their reaction conditions (at 35 °C with a neat sample in a quartz vessel) and obtained **14** (38.6%) and **15** (32.8%) as the main products after the reduction of the hydroperoxide intermediates. The ratio of **16** was quite low (6%); it might be suspected that they were led to an erroneous conclusion as to the structure of the product deluded by the isomerization during the chemical-identification process of the products.

citation, as the most probable primary processes for this type of photooxidation. The possible formation of singlet oxygen has been suggested, but as a process of minor importance in the cases he studied.

We considered that singlet oxygen might be produced through a) sensitization by some impurities present in the reactants, b) sensitization by the primarily-formed radical oxidation products, and c) charge-transfer excitation.

The UV spectrum of **1** (1 cm path length, neat) showed a fine structure in the 250—270 nm region which was ascribable to some aromatics. The fine structure could not be removed by ordinary purification methods (distillation, column chromatography on alumina). *p*-Cymene, whose UV spectrum was very similar to the fine structure observed with the limonene sample, is the most probable candidate for the aromatic impurity. We, therefore, carried out the Ox-III oxidation of **1** in the presence of varying amounts of *p*-cymene, but the reaction pattern was unchanged in the *p*-cymene concentration region of 0—3.5 mg/8 ml. Thus, the Path a could be ruled out. As for the Path b, we considered that the most probable radical oxidation product which could sensitize the singlet-oxygen formation was carvone (**8**, $\lambda_{\max}$ 315 nm (ε 47)); therefore, Ox III with varying amounts of **8** was carried out. The results are shown in Fig. 1. Evidently **8** acted as a sensitizer for the singlet-oxygen formation, but the following consideration revealed that this sensitization is not responsible for the total of the singlet-oxygen participation observed in Ox III. The amounts of **8** present in the reaction mixture obtained by the Ox-III oxidation of **1** with (3 mg) and without the initial addition of **8** are indicated by Lines I and II respectively in Fig. 2. The amount of **8** corresponding to the A area must be responsible for the extra singlet-oxygen participation of 0.7% (=2.6—1.9%; see arrows in Fig. 1), effected by the initial addition of **8**. The singlet-oxygen participation induced solely by the primarily-formed **8**, whose amount corresponds to the B area, should thus amount to 0.6% (=0.7%×(area B/areaA)), which corresponds to only one-third of the total singlet-oxygen oxidation observed in the Ox-III oxidation of **1**. A similar treatment was undertaken for the Ox-III oxidation of **2** by assuming **17** ($\lambda_{\max}$ 305 nm(ε 60)) as the possible sensitizer. From the results shown in Figs. 3 and 4, it was calculated that only one-third of the singlet-oxygen participation was ascribable to the sensitization by **17**. Further support that a mechanism other than unsaturated ketone sensitization for the singlet-oxygen formation was probably operating was obtained from the following observation. If the carvone sensitization were the sole path for the singlet-oxygen formation in the Ox III oxidation of **1**, then:

$$\{\mathrm{d}[\text{singlet-oxygen products}]/\mathrm{d}t\}_{t=0} = 0$$
$$\text{and } \{\mathrm{d}[\text{radical products}]/\mathrm{d}t\}_{t=0} > 0.$$

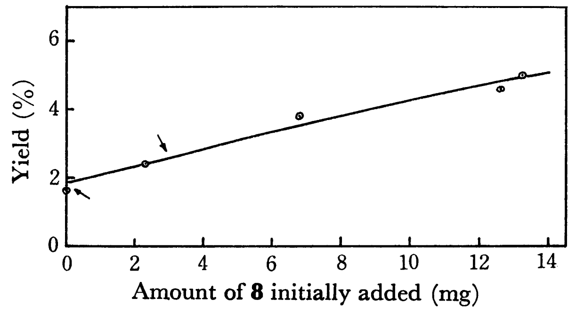

Fig. 1. Total yield of products from singlet-oxygen oxidation after 20 hr *vs.* amount of initially added **8** (mg in 8 ml of 0.5 M solution of **1** in 1 : 1 *t*-butyl alcohol–methanol).

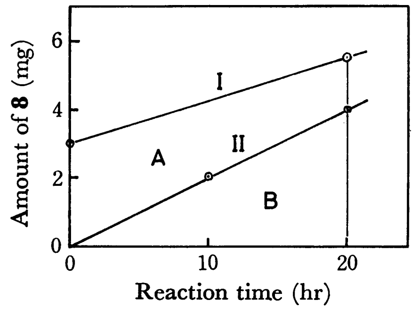

Fig. 2. Amount of **8** present in the reaction mixture as a function of time. (8 ml of 0.5 M solution of **1** in 1 : 1 *t*-butyl alcohol–methanol).
I: With initial addition of 3 mg of **8**. II: Without initial addition.

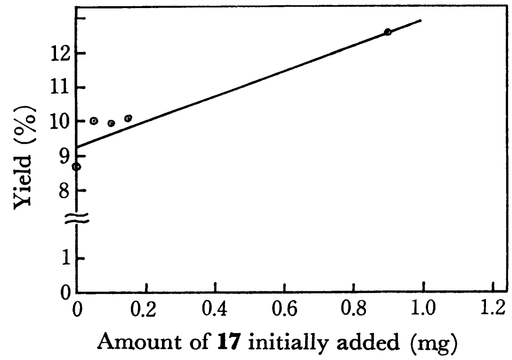

Fig. 3. Total yield of products from singlet-oxygen oxidation after 5 hr *vs.* amount of initially added **17** (mg in 2 ml of 0.5 M solution of **2** in 1 : 1 *t*-butyl alcohol–methanol).

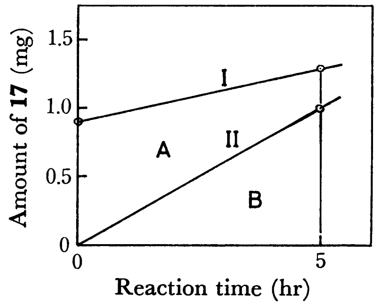

Fig. 4. Amount of **17** present in the reaction mixture as a function of time. (2 ml of 0.5 M solution of **2** in 1 : 1 *t*-butyl alcohol–methanol). I: With initial addition of 9 mg of **17**. II: Without initial addition.

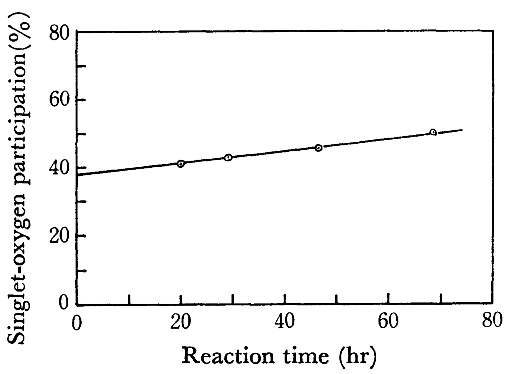

Fig. 5. Percent of singlet-oxygen participation as a function of time.

Therefore, the plots of

$$d[\text{singlet-oxygen products}]/dt/d[\text{radical products}]/dt \approx [\text{singlet-oxygen products}]/[\text{radical products}]$$

should extrapolate to zero at zero time. Such a plot is shown in Fig. 5, which does not intercept zero, in contrast to the above assumption. As another scheme for the singlet-oxygen formation, we considered a route *via* a C–T complex (Path c). When the UV spectra were measured with neat samples of **1**, **2**, and **3** which had been bubbled with 1 atom of oxygen for 5 min prior to the measurement, the end absorption moved to a wavelength longer by about 10 nm as compared with those of the oxygen-free samples. The original spectra were restored when the samples were bubbled with nitrogen. It might be reasonable, therefore, to assume that a C–T excitation is the primary step in Ox III, and that singlet oxygen would be formed by Reaction (1). With these arguments, we should consider why no singlet-oxygen participation was observed with **3**, in contrast to the observations with **1** and **2**.

$$\text{Olefin} + {}^3\text{O}_2 \xrightarrow{h\nu} (\text{Olefin–O}_2)^* \longrightarrow \text{Olefin} + {}^1\text{O}_2\ (\Delta \text{ or } \textstyle\sum) \qquad (1)$$

One is inclined to believe that only Path b is operative here, since this path would clearly explain the absence of singlet-oxygen participation in the case of **3** because of the photo-instability of the unsaturated ketone **21**, a potential sensitizer. However, we still persist in Path c for the following reason. Previous work[4] has shown that the reaction of singlet oxygen is quite sensitive to the electron density in the double bond of the olefin, and that the reactivity towards singlet oxygen increases with the number of alkyl groups attached to the double-bond carbon. Therefore, **1** and **2**, which have tri- and tetra-alkyl-substituted olefins respectively, would react with singlet oxygen more rapidly than **3**, disubstituted olefin. The situation is also clearly demonstrated by the fact that, with **1**, only trisubstituted olefin is attacked by singlet oxygen. If the rate of the reaction between singlet oxygen and **3** is fairly slow, the competing reactions of triplet species or $\sum^1\text{O}_2$, which are other products of Reaction (1) and possible initiators for the radical reaction, would become important and only radical-oxidation products would result. The dependence of the ratio of the singlet-oxygen participation on the concentration in the case of **2** (Table 5) would be another support for the involvement of the complex, since it is conceivable that the chain reaction would be easily terminated in a dilute solution, while the reaction through a complex would proceed as effectively in a dilute solution as in the more concentrated solution. However, the absence of a definite concentration dependence in the case of **1** can not be clearly interpreted.

In conclusion, we are inclined to favor the idea that the participation of charge-transfer excitation in the unsensitized photooxidation of olefin induces a competing singlet-oxygen oxidation and radical oxidation, but it remains uncertain, at this stage of the investigation, to what degree Path b is involved, particularly there is uncertainty as to the analyses of **8** or **17**; the possibility that compounds other than **8** or **17** could also serve as sensitizers for singlet-oxygen formation was also taken into account.

Experimental

The IR spectra were obtained in neat form with liquid samples and in KBr pellet form with solid samples. The NMR spectra were measured on a JEOL MH 60 (60 MHz) spectrometer with a CCl_4 solution; the chemical shifts are represented in δ values relative to the internal TMS standard. The mass spectra were measured on a Hitachi RMS-4 mass spectrometer.

Starting Materials. **1**: A commercial sample was passed through an alumina column. $[\alpha]_D^{26.5} = +112.6°$. Lit:[3] $[\alpha]_D^{20} = +122.4°$. **2**: A material prepared by the dehydration of 1,2-dimethylcyclohexanol[8] was purified by preparative gas chromatography. The sample could not be freed from 2,3-dimethylcyclohexene (5—7%), as revealed by the NMR spectrum. **3**: A commercial sample was fractionated through a packed column 80 cm in length.

General Methods of Oxidation. *Ox. I*: The sample was kept at 40—60 °C for 5—10 hr while oxygen was bubbled through. *Ox. II*: A 0.5M solution of the sample in *t*-butyl alcohol–methanol (1: 1) containing a small amount of rose bengal was irradiated at 18—20 °C with a tungsten lamp (200 W) for 10—20 hr, while oxygen was bubbled through. *Ox. III*: A 0.5M solution of the sample in *t*-butanol-methanol (1: 1) was irradiated at 18—20 °C with Pyrex-filtered light for 5—20 hr while oxygen was bubbled through.

The oxidized mixture obtained by each oxidation method was stirred vigorously with a solution containing KI (3 g) and $Na_2S_2O_3 \cdot 5H_2O$ (4.5 g) in 10 ml of water for 40 hr. The organic material was extracted with ether, and the solvent was evaporated *in vacuo*. The residue was analyzed on a gas chromatograph, *p*-cymene being used as the internal reference. Although calibration curves were not obtained with all the oxidation products, we assumed that the relative sensitivities for the gas chromatographic detection did not deviate very much from each other; a calibration curve was obtained only with **10** in the case of **1** and with **14** in the case of **2**. Each product was obtained in a pure state by preparative gas chromatography.

*Product Identification.**** **4**: IR; Identical with the reported datum.[9] NMR; δ 1.27 (3H, s), 1.72 (3H, s), 2.93 (1H, dist. t), 4.75 (2H, s). **5**: IR; 1680, 842, and 795 cm^{-1}. NMR; δ 1.20 (3H, s), 1.63 (3H, s), 2.45 (2H, ABq) and 5.35 (1H, b. s). **6**: IR; Identical with the reported value.[2] NMR; δ 1.21 (3H, s), 1.71 (3H, s), 3.69 (1H, b.s, OH), 4.78

*** Abreviations: dist.: distorted, b: broad.

(2H, s), and 5.62 (2H, s). **7**: IR; Identical with the reported value.2) NMR; δ 1.23 (3H, s), 1.72 (3H, s), 3.60 (1H, b.s, OH), 4.6—4.8 (2H, m), and 5.5—5.65 (2H, m). **8**: IR; 3075, 1675, 895, and 800 cm^{-1}. NMR; δ 1.80 (6H, s), 2.45 (5H, b.s), 4.83 (2H, s), and 6.75 (1H, dist. t). **9**: IR; Identical with the reported value.2) NMR; δ 1.70 (3H, s), 4.25 (1H, dist. t), 3.50 (1H, b.s), and 4.69 (4H, b.s). **10**: IR; 3330, 1644, 1055, 889, and 810 cm^{-1}. NMR; δ 1.75 (6H, s), 3.65 (1H, s, OH), 3.89 (1H, dist. t), 4.68 (2H, s), and 5.45 (1H, b.s). **11**: IR; 3330, 1645, 1038, 889, and 810 cm^{-1}. NMR; δ 1.73 (3H, s), 1.74 (3H, s), 4.10 (1H, b.s, OH), 4.71 (2H, s), and 5.45 (1H, b.s). **12**: IR; Identical with the reported value.2) NMR; δ 1.72 (3H, s), 3.80 (1H, b.s, OH), 4.70 (3H, s), and 4.96 (1H, s). **13**: IR; No characteristic band. NMR; δ 1.21 (6H, s), and 1.2—1.8 (m). **14**: IR; 3380, 1640, and 890 cm^{-1}. NMR; δ 1.23 (3H, s), 1.50 (6H, b.s), 1.9—2.4 (2H, b.d), 3.27 (1H, s, OH), 4.40 (1H, b.s), and 4.64 (1H, d). **15**: IR; 3380 cm^{-1}. NMR; δ 1.16 (3H, s), 1.62 (b.s), 2.64 (1H, s, OH), and 5.13 (1H, b.s). **16**: IR; 3380, and 1640 cm^{-1}. NMR; δ 1.66 (s), 1.73 (s), 1.6—2.0 (m), 2.30 (1H, s, OH), and 3.85 (1H, b.s). **17**: IR; 1660 cm^{-1}. NMR; 1.74 (3H, s), 1.95 (3H, s), and 2.2—2.4 (m). **18**10): MS; *m/e* 148, 117, 91, and 66. IR; 1573, and 832 cm^{-1}, NMR; δ 1.42 (2H, dist. q, for endomethylene) and 5.98 (2H, d). **19**10): MS; *m/e* 148, 117, 91, 82, and 66. IR; 1616, and 844 cm^{-1}. NMR; δ 1.10 (2H, ABq, endomethylene with an anisotropic effect by the epoxy ring) and 5.75 (2H, m). **20**6), **21**11), and **22**12): Identical with those of the authentic samples.

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