270. Photochemische Reaktionen

100. Mitteilung[1])

Photochemistry of *N*-Acylimidazoles. V. Photolysis of the *N*-Acylimidazoles of Dehydroabietic Acid and of 13-Deisopropyl-10-epi-dehydroabietic Acid

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(12.IX.78)

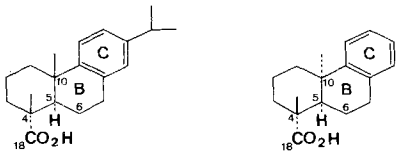
Summary

The irradiation of 1-(dehydroabietoyl)imidazole (**3**) gave no Type II elimination product but yielded instead compounds **6** and **7** by migration of the imidazolylcarbonyl group from C(4') to C(6') of the abietan moiety, probably *via* a cyclobutanol intermediate. Similarly, irradiation of 1-(13'-deisopropyl-10'-epi-dehydroabietoyl)imidazole (**13**) gave only a small amount of Type II fragmentation product **20**, the main products derived from γ-hydrogen abstraction being the cyclobutanol derivatives **16** and **17**.

Results and Discussion. The conformational factors controlling the direction of photochemical Type II reactions (elimination *versus* cyclobutanol formation) have been studied with acylimidazoles derived with simple acyl groups as described in a previous paper [1]. The results suggested the extention of the study to acylimidazoles derived from carboxylic acid groups situated in a more rigid conformational environment as it is found in polycyclic terpenoid systems.

A number of diterpenes show a carboxy group at the 4-position (numbering for diterpenes, see *Scheme 1*). The photoreactions of their *N*-acylimidazoles were of

Scheme 1



1 **2**

[1]) 99. Mitt. s. [1].

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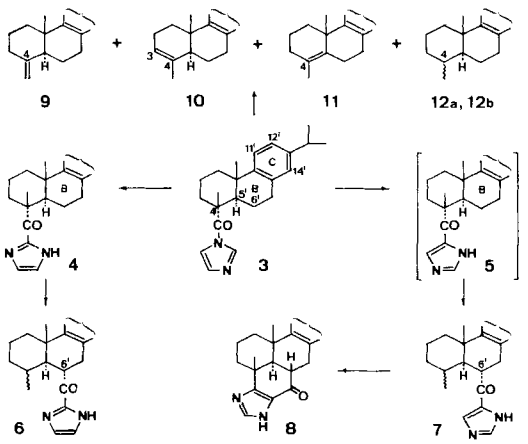
Scheme 2



interest from both the photochemical and from the synthetic point of view, because of the likelihood of hydrogen abstraction from C(6) by the acyl carbonyl group on the one hand, and because of the restricted conformation of the molecule as a whole on the other. Among these compounds dehydroabietic acid (**1**) and 13-deisopropyl-10-epi-dehydroabietic acid (**2**) [2] were chosen, and the photoreactivity of their *N*-acylimidazoles **3** and **13** was studied.

Irradiation of **3** in tetrahydrofuran (THF) with 254-nm-light, followed by chromatographic separation gave the N→C acyl migration product **4** (20%), two different 4′-decarboxy-dehydroabiet-6′-oyl derivatives **6** (4%) and **7** (24%), a compound with a fused pentacyclic ring system **8** (4.5%) and the hydrocarbons **9**–**12** (10%), whereas the expected acyl migration product **5** has not been isolated as yet.

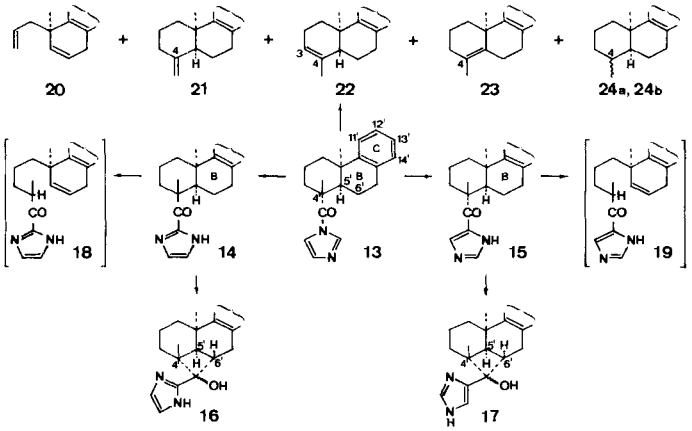
The composition of the hydrocarbon mixture **9**–**12** was determined by a combination of ^{1}H-NMR. spectra and gas chromatographic study of the crude mixture as well as of the isolated products, and their ratio was found to be approximately 45:21:7:25. Product **12** was a mixture of the C(4)-stereoisomers **12a** and **12b**.

Irradiation of **3** with >235-nm-light led to a complex mixture of products; its chromatographic separation gave compounds **6** (7%), **7** (12%), **8** (2.5%) and the hydrocarbon mixture **9**–**12** (17%) whose composition was almost the same as in the previous experiment. In neither irradiation an *A*-ring-seco-compound could be isolated whose formation would be expected from a Type II elimination.

Similarly, irradiation of 1-(13′-deisopropyl-10′-epi-dehydroabietoyl)imidazole (**13**) in THF with 254-nm-light afforded the N→C acyl migration products **14** (26%) and **15** (17%), and a hydrocarbon mixture **20**–**24** (12%). The composition of the latter was determined in the same way as above and the ratio of **20/21/22/23/24** was found to be approximately 12:31:20:10:24.

Irradiation of **13** with >235-nm-light yielded the cyclobutanol derivatives **16** and **17** in 3 and 11% yield, respectively, and the hydrocarbon mixture **20**–**24** (25%)

Scheme 3

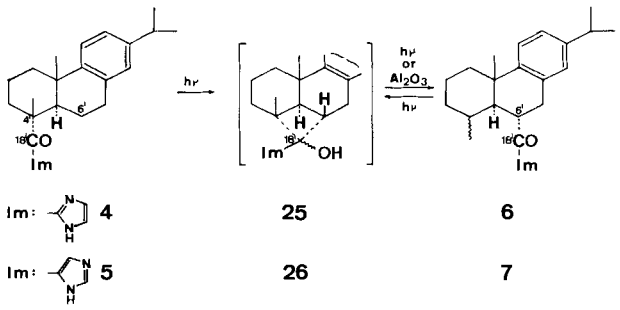


whose composition was almost the same as with 254-nm-light. Again product **24** was found to be a mixture of the C(4)-stereoisomers **24a** and **24b** whose ratio was determined as 1:3 by ^{1}H-NMR. and GLC. data. The low yields of isolated **16** and **17** in this irradiation are mainly due to difficulties in the isolation procedure; the actual yields were probably considerably higher.

Again irradiation of **13** gave very little Type II fragmentation product **20** (up to 3%), cyclobutanol formation appears to be favored. The presence of the expected intermediate Type II elimination products **18** and **19** was inferred spectroscopically in some fractions after column chromatography, but in only very small amount. **18** and **19** could not be obtained in pure form.

The formation of the cyclobutanols **16** and **17** from **13** suggests that the formation of the 4′-decarboxy-dehydroabiet-6′-oyl compounds **6** and **7** in the irradiation of **3** could also proceed *via* the intermediacy of highly strained cyclobutanols such as **25** and **26** *(Scheme 4)*, followed by C(4′)–C(18′) cleavage.

Scheme 4



In fact, the crude irradiation product of **4** in THF gave a spot on TCL. analysis which could conceivably correspond to such a cyclobutanol intermediate. This spot disappeared heaving passed the irradiation mixture through a basic alumina column; it was replaced by the spot of **6** which was isolated in pure form.

As expected from its structure, **8** was found to be derived from **7**. Irradiation of **7** with >280-nm-light in methanol afforded **8** together with a polar compound which was unstable on chromatographic separation and appeared to be mainly reconverted into **7**. Conceivably it could be a cyclobutanol derivative such as **26** *(Scheme 4)*.

8 could be derived from a biradical intermediate having radical sites at C(4') of the terpene moiety and at the 4(5)-position of the imidazole ring the latter being a mesomeric form of the radical generated at the acyl carbon atom.

The hydrocarbons **9–12** and **21–24** are formally decarboxylation products of the corresponding carboxylic acids. They can be derived by a *Norrish* Type I process from the N→C acyl migration products **4** and **5**, and **14** and **15**, respectively, but possibly also through decarbonylation of intermediate acyl radicals.

Structures of products. The structure of all the photoproducts are based essentially on their spectroscopic and analytical data. The imidazole substitution pattern in the acylimidazole derivatives was determined according to previous work [1] [3], and that in the cyclobutanol derivatives was assigned as discussed in the preceding paper [1] in connection with 2- and 4(5)-(7'-hydroxybicyclo[4.2.0]octan-7'-yl)imidazole.

The ^{1}H-NMR. spectra of **6** and **7** indicated the presence of a secondary methyl group in addition to the isopropyl group, and multiplets at 4.56 and 3.88 ppm, respectively, were assigned to the proton on the carbon atom attached to the carbonyl group. The position of this attachement was determined as C(6') *(Scheme 2)* by decoupling the benzylic protons 2 H–C(7') as well as on the basis of the reaction scheme shown in *Scheme 4*. The *α*-configuration of the acyl substituent was inferred on the basis of the observed coupling between H–C(5') and H–C(6') ($J = 11.0$). The proposed mechanism leading to **6** and **7** as well as their thermodynamic stability also lend support to this assumption[3]).

The spectroscopic and analytical data of compound **8** are in accord with the proposed structure. Its molecular formula, $C_{23}H_{28}N_2O$, has two hydrogen atoms less than that of **7**. The NMR. spectra of **8** indicate that both the 4- and 5-position of the imidazole ring are substituted. A one-proton multiplet due to H–C(6') of the dehydroabietic acid moiety appeared at 3.1 ppm; by decoupling it was correlated with a one-proton doublet at 2.14 ppm ($J = 11.5$) the latter being assigned to H–C(5').

Sodium borohydride reduction of **8** afforded a secondary alcohol **28** (s. exper. part) whose ^{1}H-NMR. spectrum exhibited a one-proton doublet at 4.39 ppm ($J = 10.0$) demonstrating the presence of a vicinal hydrogen atom. This as well as the fact that **8** was formed by irradiation of **7**, lend further support to the structure suggested.

Hydrocarbons **9–12** were separated into three fractions by silicagel column chromatography. The first contained **12a** and **12b** as a *ca.* 2:1 mixture, the second was found to be pure **11** and the third was obtained as a mixture of **9** and **10** (*ca.* 4.5:1). All spectroscopic properties are given in the exper. part.

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[3]) For the transformation of **6** into 1-methyl-2-(4'-decarboxy-dehydroabiet-6'-oyl)imidazole (**27**) s. exper. part.

Spectral and analytical properties of compound **16** are in agreement with a structure incorporating the hydroxy-imidazolyl-cyclobutane system as discussed in the case of 2-(7′-hydroxybicyclo[4.2.0]oct-7′-yl)imidazole [1]. Further evidence for the cyclobutane ring was obtained by the conversion of **16** to a quaternary salt followed by an alkali-induced fragmentation (*cf.* [1]) to a cyclobutanone derivative (carbonyl band at 1775 cm^{-1}). The nature of substitution at C(6′) of the terpene moiety of **16** was indicated by a one-proton doublet at 1.39 ppm ($J = 10.0$) in its ^{1}H-NMR. spectrum corresponding exclusively to H–C(5′) adjacent to the mono-substituted C(6′). The α-configuration for the substituent at C(6′) is most likely; this is based on the inspection of a molecular model in which an alternative β-configuration seems unfavorable because of the large steric interference between the 4′β-methyl group and the phenyl moiety.

Hydrocarbons **20–24** were separated by gas chromatography; **20**, **24a** and **24b** were each isolated in pure form, while compounds **21–23** were obtainable only as a 3:2:1 mixture in one peak (for the spectroscopic properties s. exper. part). Hydrogenation of the latter mixture over palladium on charcoal led almost exclusively to **24a** (>95% of the product) indicating that **24a** has a 4β-methyl configuration.

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Experimental Part

General. See [4]. Optical rotations $[\alpha]_D^{temp.}$ (% concentration, solvent) were measured in a 0.5 dm tube.

Photolysis of 1-(dehydroabietoyl)imidazole (3). – 1) Two separate THF solutions each containing **3** prepared from 3 g of *dehydroabietic acid* (**1**) and a small excess of *N,N′-carbonyl-diimidazole* (NCD) were irradiated *in situ* (lamp A) for 24 h. The combined mixtures were passed through a column of 200 g of silicagel and elution with hexane/benzene 3:1 gave 220 mg of the hydrocarbon mixture **9–12**. The rest of the products, eluted with chloroform/methanol 4:1, was re-chromatographed on silicagel to give 410 mg of **4**, 70 mg of **6**, 550 mg of **7** and 110 mg of **8** besides 67% of the starting material. **5** could not be obtained in pure form.

2) **3** prepared from 4.5 g of **1** and a small excess of NCD was irradiated *in situ* (lamp B) in THF for 24 h. The mixture was passed through a column of 150 g of silicagel and elution with hexane/benzene 3:1 gave 650 mg of the hydrocarbon mixture **9–12**. The rest of the product, eluted with chloroform/methanol 4:1, was re-chromatographed on silicagel repeatedly affording 110 mg of **6**, 310 mg of **7** and 610 mg of **8**. No starting material was recovered.

2-(Dehydroabietoyl)imidazole (**4**) could not be obtained in crystalline form, $[\alpha]_D^{22°} = +28.6°$ ($c = 1.05$, MeOH). – UV. (MeOH): 277 (16200). – IR. (CCl_4): 3450*m*, 3300*m*, 2960*s*, 2930*s*, 2870*m*, 1650*s*, 1500*m*, 1460*m*, 1450*m*, 1385*s*, 1285*w*, 1118*m*, 1080*m*, 1000*w*, 940*m*, 675*s*. – ^{1}H-NMR. ($CDCl_3$): 7.25–6.80 (*m*, H–C(11′), H–C(12′) and H–C(13′)); 7.13 (br. *s*, H–C(4) and H–C(5)); 3.12 (*d*×*d*, $J_1 = 12$, $J_2 = 2.0$, H–C(5′)); 3.0–1.4 (*m*, 11 H); 1.52 (*s*, H_3C–C(4′)); 1.29 (*s*, H_3C–C(10′)); 1.12 (*d*, $J = 7.0$, $(CH_3)_2CH$). – MS.: 350 (M^+, 21), 335 (11), 328 (11), 268 (10), 253 (26), 239 (34), 197 (18), 149 (18), 119 *(100)*, 78 (74), 59 (36), 43 (61).

$C_{23}H_{30}N_2O$ (350.49) Calc. C 78.81 H 8.63 N 7.99% Found C 78.59 H 8.68 N 7.81%

2-(4′-Decarboxy-dehydroabiet-6′-oyl)imidazole (**6**) could not be obtained in crystalline form, $[\alpha]_D^{22°} = +124.8°$ ($c = 1.25$, MeOH). – UV. (MeOH): 277 (17100). – IR. (CCl_4): 3440*w*, 3260*s*, 2960*s*, 2920*s*, 2865*m*, 1660*s*, 1500*w*, 1415*s*, 1310*w*, 1160*m*, 1115*m*, 1080*m*, 1030*m*, 930*m*. – ^{1}H-NMR. ($CDCl_3$): 7.30 and 7.21 (2 br. *s*, H–C(4) and H–C(5)); 7.26–6.82 (*m*, H–C(11′), H–C(12′) and H–C(14′)); 4.56 (*m*, H–C(6′)); 3.40–2.60 (*m*, 2 H–C(7′) and $(CH_3)_2CH$); 2.50–1.40 (*m*, 8 H); 1.31 (*s*, H_3C–C(10′)); 1.20

(*d*, J=7.0, $(CH_3)_2CH$); 0.96 (*d*, J=7.0, H_3C–C(4′)). – MS.: 350 (M^+, 23), 335 (10), 322 (61), 307 (11), 279 (4), 257 (4), 239 (7), 225 (4), 213 (7), 197 (9), 183 (9), 155 (11), 141 (20), 109 (20), 96 (72), 78 (59), 68 *(100)*, 50 (22), 43 (24).

$C_{23}H_{30}N_2O$ (350.49) Calc. C 78.81 H 8.63 N 7.99% Found C 78.62 H 8.49 N 8.10%

160 mg of crude **6** were dissolved in dry THF and treated with a small excess of sodium hydride. When reaction ceased an excess of methyl iodide was added. Repeated chromatography of the product afforded 110 mg of *1-methyl-2-(4′-decarboxy-dehydroabiet-6′-oyl)imidazole* (**27**) as a gum. – UV. (MeOH): 274 (17400). – IR. (CCl_4): 2960*s*, 2930*s*, 2870*m*, 1673*s*, 1500*w*, 1465*m*, 1410*s*, 1288*w*, 1154*w*, 1000*w*, 915*w*. – ^{1}H-NMR. ($CDCl_3$): 7.16 and 7.03 (2*s*, H–C(4) and H–C(5)); 7.30–6.74 (*m*, H–C(11′), H–C(12′) and H–C(14′)); 4.59 (*m*, H–C(6′)); 4.00 (*s*, CH_3N); 3.4–2.5 (*m*, 2 H–C(7′) and $(CH_3)_2CH$); 2.45–1.34 (*m*, *ca.* 8 H); 1.28 (*s*, H_3C–C(10′)); 1.18 (*d*, J=7.0, $(CH_3)_2CH$); 0.97 (*d*, J=7.0, H_3C–C(4′)). – MS.: 364 (M^+, 18), 349 (9), 336 (64), 321 (18), 293 (2), 265 (4), 239 (2), 197 (4), 183 (5), 167 (6), 155 (6), 141 (12), 110 (28), 96 (10), 82 *(100)*, 55 (4).

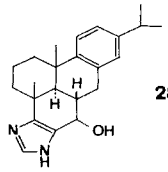
4(5)-(4′-Decarboxy-dehydroabiet-6′-oyl)imidazole (**7**), m.p. 230–232° (from acetone), $[\alpha]_D^{22°} = +120°$ (c=1.36, MeOH). – UV. (MeOH): 270 (17100). – IR. ($CHCl_3$): 3430*m*, 3240*w*, 2960*s*, 2925*s*, 2860*m*, 1655*s*, 1555*m*, 1500*w*, 1385*m*, 1345*m*, 1130*m*, 1095*m*, 980*w*. – ^{1}H-NMR. ($CDCl_3$): 7.87 (*s*, H–C(2) and H–C(4 or 5)); 7.46–6.75 (*m*, H–C(11′), H–C(12′) and H–C(14′)); 3.88 (*m*, H–C(6′)); 3.20–3.00 (*m*, 2 H–C(7′)); 2.84 (*sept.*, J=7, $(CH_3)_2CH$); 2.50–2.00 (*m*, 2 H); 2.00–1.40 (*m*, 6 H); 1.28 (*s*, H_3C–C(10′)); 1.18 (*d*, J=7.0, $(CH_3)_2CH$); 0.97 (*d*, J=7.0, H_3C–C(4′)). – MS.: 350 (M^+, 100), 335 (75), 322 (5), 317 (9), 307 (12), 293 (4), 279 (5), 267 (4), 255 (9), 239 (16), 225 (11), 197 (25), 183 (14), 173 (16), 155 (12), 95 (67), 69 (18), 55 (19), 43 (19).

$C_{23}H_{30}N_2O$ (350.49) Calc. C 78.81 H 8.63 N 7.99% Found C 78.67 H 8.58 N 7.94%

4(5)-(4′-Decarboxy-dehydroabiet-6′-oyl)-5(4),4′-didehydro-imidazole (**8**), m.p. 288–290° (from acetone), $[\alpha]_D^{22°} = +28°$ (c=1.0, MeOH). – UV. (MeOH): 265 (17600). – IR. ($CHCl_3$): 3440*m*, 3200*m*, 2960*s*, 2935*s*, 2875*m*, 1650*s*, 1560*w*, 1500*w*, 1380*s*, 1315*w*, 1085*w*, 830*w*. – ^{1}H-NMR. ($CDCl_3$): 7.90 (*s*, H–C(2)); 7.32–6.90 (*m*, H–C(11′), H–C(12′) and H–C(14′)); 3.45–3.00 (*m*, 3 H); 2.82 (*sept.*, J=7.0, $(CH_3)_2CH$); 2.55–1.50 (*m*, 7 H); 1.40 (*s*, H_3C–C(4′)); 1.33 (*s*, H_3C–C(10′)); 1.21 (*d*, J=7.0, $(CH_3)_2CH$). – ^{13}C-NMR. ($CDCl_3$): 192.3 *(s)*; 165.4 *(s)*; 146.3 *(s)*; 145.9 *(s)*; 140.8 *(d)*; 133.0 *(s)*; 126.8 *(d)*; 124.4 (*s* and *d)*; 123.8 *(d)*; 51.8 *(d)*; 40.1 *(d)*; 38.7 *(t)*; 37.4 *(s)*; 36.8 *(s)*; 35.2 *(t)*; 33.5 *(d)*; 29.3 *(t)*; 24.0 (3 *qa*); 22.1 *(qa)*; 18.5 *(t)*. – MS.: 348 (M^+, 90), 333 *(100)*, 318 (3), 305 (11), 291 (17), 275 (3), 247 (2), 213 (5), 161 (23), 159 (19), 133 (5), 117 (4), 95 (4), 43 (6).

$C_{23}H_{28}N_2O$ (348.47) Calc. C 79.27 H 8.10 N 8.04% Found C 79.06 H 8.16 N 8.03%

To 30 mg of **8** in 3 ml of methanol were added 50 mg of sodium borohydride. The mixture was stirred at room temp. for 30 min. Work-up and TLC. separation afforded the reduction product **28** (23 mg), m.p. 215–218° (dec.; from acetone). – IR. ($CHCl_3$): 3600*w*, 3460*m*, 3500–2400 br., 2990*w*, 2960*s*, 2930*s*, 2860*m*, 1600*w*, 1490*w*, 1470–1400 *m* br., 1380*m*, 1085*m*, 1050*m*, 1030*m*, 990*w*, 960*w*, 830*w*. – ^{1}H-NMR. ($CDCl_3$): 7.23 (*s*, H–C(2)); 7.20–6.80 (*m*, H–C(11′), H–C(12′) and H–C(14′)); 4.39 (br. *d*, J=10.0, H–C(18′)); 3.25–2.60 (*m*, 3 H); 2.40–1.40 (*m*, 10 H); 1.47 (*s*, H_3C–C(4′)); 1.22 (*s*, H_3C–C(10′)); 1.19 (*d*, J=7.0, $(CH_3)_2CH$). – MS.: 350 (M^+, 0), 332 (43), 317 *(100)*, 301 (16), 275 (25), 258 (6), 231 (5), 197 (5), 183 (4), 157 (3), 151 (5), 145 (8), 131 (6), 97 (4), 83 (5), 71 (6), 69 (6), 57 (8), 55 (7), 43 (10).



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Hydrocarbon mixture **9**–**12**, liquid. – IR. (CCl_4): 3460*s*, 3430*s*, 3365*s*, 1650*w*, 1610*w*, 1500*m*, 1460*m*, 1440*m*, 1370*m*, 1173*w*, 1080*w*, 1067*w*, 885*m*. – ^{1}H-NMR. ($CDCl_3$): 5.47 (*m*, 0.07 H, H–C(3) of **10**); 4.87 and 4.62 (2 br. *s*, 0.45 H, H_2C=C(4) of **9**); 1.37 (*s*, 0.63 H, H_3C–C(10) of **11**); 1.67 (*s*, 0.63 H, H_3C–C(4) of **11**); 1.04–0.89 (*m*, 0.75 H, H_3C–C(4) of **12a** and **12b**). – MS.: 254 (21), 239 *(100)*, 226 (2), 224 (2), 197 (30), 169 (6), 167 (4), 165 (5), 159 (6), 155 (9), 143 (5), 141 (10), 117 (7), 115 (5), 112 (7), 91 (8).

The mixture **9–12** was chromatographed on silicagel and eluted with hexane yielding first a mixture of **12a** and **12b**, then **11** and finally a mixture of **9** and **10**. *Mixture* **9/10**, liquid. – IR. (CCl_4): 3080*w*, 3060*w*, 2965*s*, 2940*s*, 2880*m*, 2850*m*, 1650*m*, 1615*w*, 1500*m*, 1460*m*, 1440*m*, 1375*m*, 1070*w*, 890*s*, 865*w*. – ^{1}H-NMR. ($CDCl_3$): 7.38–6.90 (*m*, H–C(11), H–C(12) and H–C(14)); 5.47 (*m*, 0.13 H, H–C(3) of **10**); 4.87 and 4.62 (2 br. *s*, 1.7 H, H_2C=C(4) of **9**); 3.0–1.3 (*m*, *ca.* 11 H); 1.23 (*d*, J=6.0, $(CH_3)_2CH$ of **9** and **10**); 1.04 (*s*, 0.4 H, H_3C–C(10) of **10**); 1.00 (*s*, 2.6 H, H_3C–C(10) of **9**). – MS.: 254 (M^+, 42), 239 *(100)*, 225 (2), 223 (2), 211 (9), 197 (85), 169 (14), 141 (18), 129 (14), 117 (11), 115 (11), 91 (11), 43 (12).

Hydrocarbon **11**, liquid. – IR. (CCl_4): 2970*s*, 2940*s*, 2880*s*, 2840*m*, 1615*w*, 1500*m*, 1460*m*, 1435*m*, 1420*m*, 1370*m*, 1230*w*, 1180*w*, 1050*w*, 890*w*. – ^{1}H-NMR. ($CDCl_3$): 7.35–6.90 (*m*, H–C(11), H–C(12) and H–C(14)); 3.0–1.4 (*m*, 11 H); 1.66 (*s*, H_3C–C(4)); 1.36 (*s*, H_3C–C(10)); 1.21 (*d*, J=7.0, $(CH_3)_2CH$). – MS. 254 (M^+, 3), 239 *(100)*, 223 (3), 211 (3), 195 (7), 181 (3), 165 (6), 155 (6), 141 (7), 129 (3), 112 (4), 91 (3), 43 (5).

Mixture **12a/12b**, liquid. – IR. (CCl_4): 2960*s*, 2930*s*, 2875*s*, 1615*w*, 1500*m*, 1460*m*, 1380*m*, 1070*w*, 890*w*. – ^{1}H-NMR. ($CDCl_3$): 7.34–6.90 (*m*, H–C(11), H–C(12) and H–C(14)); 3.0–1.3 (*m*, 13 H); 1.31 (*d*, J=7.0, $(CH_3)_2CH$); 1.16 and 1.09 (2*s*, each *ca.* 1.5 H, H_3C–C(10)); 1.00 and 0.93 (2*d*, J=7.0, each *ca.* 1.5 H, H_3C–C(4)). – MS.: 256 (M^+, 26), 241 *(100)*, 199 (8), 185 (31), 159 (86), 143 (15), 129 (14), 117 (18), 91 (7), 43 (13).

Photolysis of 1-(13′-deisopropyl-10′-epi-dehydroabietoyl)imidazole (13). – 1) **13** prepared from 2.58 g of the acid **2** and a small excess of NCD was irradiated *in situ* (lamp A) in THF for 18 h. The mixture was passed through a column of 100 g of silicagel. Elution with hexane/benzene 3:1 gave 77 mg of a hydrocarbon mixture **20–24**. The rest of the products, eluted with chloroform/methanol 4:1, was re-chromatographed on silicagel repeatedly to give 310 mg of **14** and 200 mg of **15** besides 61% of starting acid.

2) **13** prepared from 5.16 g of **2** as above was irradiated (lamp B) in THF for 20 h. The mixture was passed through a column of 200 g of silicagel and elution with hexane/benzene 3:1 gave 1.1 g of a hydrocarbon mixture **20–24**. The rest of the products, eluted with chloroform/methanol 4:1, was re-chromatographed on silicagel giving 180 mg of **16** and 650 mg of **17**. No starting material was recovered.

2-(13′-Deisopropyl-10′-epi-dehydroabietoyl)imidazole (**14**), m.p. 116–118° (from acetone/hexane). – UV. (MeOH): 279 (9700). – IR. ($CHCl_3$): 3450*s*, 3300*w*, 2940*s*, 2880*m*, 1655*s*, 1490*w*, 1460*m*, 1448*m*, 1405*m*, 1385*s*, 1280*w*, 1118*w*, 1085*s*, 1005*m*, 937*s*, 852*w*, 650*w*. – ^{1}H-NMR. ($CDCl_3$): 7.30–6.80 (*m*, H–C(11′), H–C(12′), H–C(13′), H–C(14′), H–C(4) and H–C(5)); 3.41 (*d*×*d*, J_1=12, J_2=3, H–C(5′)); 3.10–2.84 (*m*, 2 H); 2.44–1.15 (*m*, 8 H); 1.39 (*s*, H_3C–C(4′)); 1.03 (*s*, H_3C(10′)). – MS.: 308 (M^+, *100*), 293 (79), 280 (43), 265 (75), 252 (6), 197 (43), 166 (57), 149 (36), 138 (40), 131 (51), 115 (23), 96 (68), 68 (87), 43 (30), 41 (40).

$C_{20}H_{24}N_2O$ (308.41) Calc. C 77.88 H 7.84 N 9.08% Found C 77.49 H 7.65 N 9.15%

4(5)-(13′-Deisopropyl-10′-epi-dehydroabietoyl)imidazole (**15**), m.p. 124–126° (from acetone/hexane), $[\alpha]_D^{22°} = -80°$ (c=1.0, MeOH). – UV. (MeOH): 260 (9600). – IR. (CCl_4): 3440*m*, 3280*m*, 2930*s*, 1650*s*, 1540*w*, 1490*w*, 1463*m*, 1407*w*, 1380*w*, 1333*s*, 1140*s*, 1090*m*, 945*w*, 910*w*. – ^{1}H-NMR. ($CDCl_3$): 7.52 and 7.50 (2*s*, H–C(2) and H–C(4 or 5)); 7.30–6.96 (*m*, H–C(11′), H–C(12′), H–C(13′) and H–C(14′)); 3.08–2.70 (*m*, 3 H); 2.40–1.30 (*m*, 8 H); 1.26 (*s*, H_3C–C(4′)); 1.10 (*s*, H_3C–C(10′)). – MS.: 308 (M^+, 54), 293 (24), 275 (4), 265 (4), 213 (4), 197 (17), 183 (4), 166 (26), 143 (43), 131 *(100)*, 119 (28), 117 (28), 95 (30), 69 (20), 55 (20), 43 (20).

$C_{20}H_{24}N_2O$ (308.41) Calc. C 77.88 H 7.84 N 9.08% Found C 77.58 H 7.57 N 8.94%

2-[(4′-Decarboxy-13′-deisopropyl-10′-epi-abiet-4′,6′-diyl)hydroxymethyl]imidazole (**16**), m.p. 213–214° (from ethyl acetate). – UV. (MeOH): 259 (717), 266 (876), 274 (865). – IR. ($CHCl_3$): 3580*w*, 2965*m*, 3500–2400 br., 2960*s*, 2920*s*, 2860*m*, 1490*m*, 1445*m*, 1375*m*, 1075*m*, 1040*m*, 1020*m*, 930*w*. – ^{1}H-NMR. ($CDCl_3$): 7.50–6.90 (*m*, H–C(11′), H–C(12′), H–C(13′), H–C(14′)); 7.11 (*s*, H–C(4) and H–C(5)); 2.90–1.60 (*m*, *ca.* 9 H); 1.39 (*d*, J=10, H–C(5′)); 1.26 (*s*, H_3C–C(4′)); 1.08 (*s*, H_3C–C(10′)). – MS.: 308 (M^+, 89), 290 (21), 275 (26), 185 (34), 149 (40), 123 *(100)*, 98 (38), 82 (30), 69 (47), 43 (23). – ^{13}C-NMR. (MeOH): 150.5 *(s)*; 149.0 *(s)*; 137.6 *(s)*; 129.1 *(d)*; 129.0 *(d)*; 127.2 *(d)*; 125.4 *(d)*; 122.0 (2*d*); 80.1 *(s)*; 49.8 *(s)*; 47.1 *(d)*; 44.6 *(t)*; 41.8 *(d)*; 36.0 *(qa)*; 35.9 *(s)*; 31.0 *(t)*; 27.2 *(t)*; 24.2 *(t)*; 16.1 *(qa)*. – MS.: 308 (M^+, 89), 290 (21), 275 (26), 185 (34), 149 (40), 123 *(100)*, 98 (38), 82 (30), 69 (47), 42 (23).

$C_{20}H_{24}N_2O$ (308.41) Calc. C 77.88 H 7.84 N 9.08% Found C 77.66 H 7.88 N 8.97%

4(5)-[(4'-Decarboxy-13'-deisopropyl-10'-epi-abiet-4',6'-diyl)hydroxymethyl]imidazole (**17**), m.p. 191–192° (from acetone), $[\alpha]_D^{22°} = -69.2°$ ($c = 1.30$, MeOH). – UV. (MeOH): 259 (721), 266 (880), 274 (865). – IR. ($CHCl_3$): 3580*w*, 3460*m*, 3500–2400 br., 2960*s*, 2930*s*, 2865*m*, 1490*m*, 1447*m*, 1370*m*, 1070*m*, 1010*m*, 975*m*, 930*w*, 910*w*, 830*w*. – ^{1}H-NMR. (CD_3OD): 7.74 (br. *s*, H–C(2)); 7.01 (*s*, H–C(4 or 5)); 7.44–6.90 (*m*, H–C(11'), H–C(12'), H–C(13') and H–C(14')); 3.0–1.5 (*m*, 9 H); 1.41 (*d*, $J = 10$, H–C(5')); 1.32 (*s*, H_3C–C(4')); 0.94 (*s*, H_3C–C(10')). – ^{13}C-NMR. (CD_3OD): 150.6 *(s);* 137.6 *(s);* 137.0 *(s);* 135.9 *(d);* 129.1 *(d);* 129.0 *(d);* 127.2 *(d);* 125.4 *(d);* 121.0 *(d);* 80.6 *(s);* 49.9 *(s);* 47.9 *(d);* 44.9 *(t);* 41.9 *(d);* 36.1 *(s);* 36.0 *(qa);* 31.0 *(t);* 27.2 *(t);* 24.4 *(t);* 16.4 *(qa).* – MS.: 308 (M^+, 25), 290 (40), 275 (30), 185 (34), 147 (26), 123 (74), 95 (28), 43 *(100).*

$C_{20}H_{24}N_2O$ (308.41) Calc. C 77.88 H 7.84 N 9.08% Found C 77.62 H 7.92 N 8.97%

Hydrocarbon mixture **20–24**, liquid. – IR. (CCl_4): 3070*w*, 3010*w*, 2940*s*, 2865*s*, 1645*w*, 1490*m*, 1445*m*, 1377*m*, 1080*w*, 1037*w*, 910*w*, 892*m*. – ^{1}H-NMR. (CCl_4): 7.4–6.9 (*m*, H–C(11), H–C(12), H–C(13) and H–C(14)); 6.00–5.60 (*m*, 1.54 H, olefinic H); 3.35 (*m*, 0.24 H, 2 H–C(7) of **20**); 0.97 (*d*, $J = 7.0$, 0.54 H, H_3C–C(4) of **24b**); 0.93 (*d*, $J = 6$, 0.18 H, H_3C–C(4) of **24a**). – MS.: 214 (15), 212 *(100),* 199 (31), 197 (66), 183 (12), 171 (15), 169 (20), 157 (19), 155 (46), 143 (75), 141 (58), 129 (49), 117 (54).

The GLC. of the crude mixture of **20–24** (15% SE-52 on *Chromosorb* W, 220°) showed 4 peaks with an area ratio of *ca.* 2:1:10:3 in order of their retention time, the first (5.5 min), the second (14 min), the third (16.4 min) and 4th peak (18.6 min) corresponding to **20**, **24a**, **21/22/23**, and **24b**, respectively. Each peak was collected separately. *Hydrocarbon* **20**, liquid. – IR. (CCl_4): 3070*s*, 3010*s*, 2960*s*, 2920*s*, 1643*m*, 1490*s*, 1450*s*, 1370*m*, 1035*w*, 992*s*, 913*s*. – ^{1}H-NMR. ($CDCl_3$): 7.40–6.95 (*m*, H–C(11), H–C(12), H–C(13) and H–C(14)); 5.95–5.30 (*m*, 3 H, olefinic H); 4.98–4.65 (*m*, 2 H, H_2C=C); 3.30 (*m*, 2 H–C(7)); 2.70–2.00 (*m*, 2 H); 1.33 (*s*, CH_3). – MS.: 184 (< 1), 143 *(100),* 128 (61), 115 (19).

Mixture **21/22/23**, liquid. – IR. (CCl_4): 3065*m*, 3010*m*, 2930*s*, 2865*m*, 2840*m*, 1648*m*, 1490*m*, 1448*m*, 1377*m*, 1350*w*, 1080*w*, 1035*w*, 890*m*. – ^{1}H-NMR. ($CDCl_3$): 7.30–6.80 (*m*, H–C(11), H–C(12), H–C(13) and H–C(14)); 5.38 (*m*, 0.32 H, H–C(3) of **22**); 4.70 (br. *s*, 1.04 H, H_2C=C(4) of **21**); 1.29, 1.26 and 1.18 (3*s*, 1.6 H, 1.0 H and 0.5 H, H_3C=C(10)). – MS.: 212 *(100),* 197 (48), 183 (10), 169 (18), 155 (42), 141 (47), 129 (36), 117 (34), 91 (19).

The mixture **21/22/23** was hydrogenated in THF over 10% Pd/C to give a liquid, almost pure single product identified as *hydrocarbon* **24a** after purification by GLC. – IR. (CCl_4): 3060*w*, 3020*w*, 2910*s*, 1490*m*, 1460*m*, 1447*m*, 1375*m*, 1285*w*, 1050*w*, 1020*w*, 960*w*, 940*w*. – ^{1}H-NMR. (CCl_4): 7.25–6.90 (*m*, H–C(11), H–C(12), H–C(13) and H–C(14)); 3.0–1.0 (*m*, 12 H); 1.18 (*s*, H_3C–C(10)); 0.93 (*d*, $J = 6.0$, H_3C–C(4)). – MS.: 214 (M^+, 29), 199 (94), 171 (12), 143 (41), 129 (29), 117 *(100),* 91 (12).

$C_{16}H_{22}$ (214.34) Calc. C 89.65 H 10.35% Found C 89.54 H 10.11%

Hydrocarbon **24b**, liquid. – IR. (CCl_4): 3060*w*, 3010*w*, 2920*s*, 2860*s*, 1490*m*, 1460*m*, 1445*m*, 1380*m*, 1292*w*, 1040*w*, 943*w*, 890*w*. – ^{1}H-NMR. (CCl_4): 7.30–6.80 (*m*, H–C(11), H–C(12), H–C(13) and H–C(14)); 3.0–1.0 (*m*, 12 H); 1.39 (*s*, H_3C–C(10)); 0.97 (*d*, $J = 7.0$, H_3C–C(4)). – MS.: 214 (M^+, 44), 199 (79), 171 (47), 155 (18), 143 (61), 129 (50), 117 *(100),* 91 (19).

$C_{16}H_{22}$ (214.34) Calc. C 89.65 H 10.35% Found C 89.38 H 10.05%

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