Synthetic Derivatives of Abietic Acid with Radical Scavenging Activity

M. Alexandra Esteves,[‡] Nama Narender,[§] Maria J. Marcelo-Curto,[‡] and Bárbara Gigante*,[‡]

INETI, Departamento de Tecnologia de Indústrias Químicas, Estrada do Paço do Lumiar, 22, 1649-038 Lisboa, Portugal

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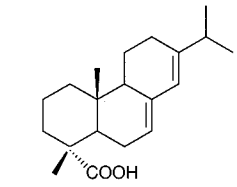
In this work, studies on the arylation of anilines derived from dehydroabietic acid, the main component of disproportionated rosin, are presented. The redox properties of the new diarylamines were investigated by cyclic voltammetry, and their free radical scavenging activity was tested by reduction of the 2,2-diphenyl-1-picrylhydrazyl (DPPH) radical. Three of the diarylamines with lower oxidation potential proved to be as active as isopropyldiphenylamine (IPPD) and superior to *tert*-butylhydroxytoluene (BHT), both commercially available synthetic antioxidants.

Pine rosin constitutes a widely available source of abietic acid, **1**, from which many derivatives have been synthesized.[1,2] Dehydroabietic acid, **2**, the aromatic derivative of **1**, can be obtained from dehydrogenation of **1** or readily isolated from disproportionated rosin,[3] in which it is the main component. Due to the presence of a bulky isopropyl group in the aromatic ring, **2** could be a promising starting material for antioxidants, by the introduction of suitable substituents into the molecule. On the other hand, bearing in mind that the physical behavior (e.g., solubility and volatility) of antioxidants can dominate their behavior under working conditions[4] and that the development of polymer-bound antioxidants could be a solution to antioxidant migration and loss,[5,6] these new abietic acid derivatives, **9**−**23**, due to their high molecular weight and versatile functionality at C-18 could be used as additives in innovative materials possessing improved and competitive qualities.

Herein, we present the results of the synthesis, electrochemical properties, and radical scavenging evaluation of a series of diarylamines, **9**−**23**, obtained by *N*-arylation of rosin anilines.

The synthesis of secondary amines, particularly diarylamines, is important since the reducing properties of these compounds make them suitable as antioxidants or antiozonants, especially as radical scavengers, which react either with O-centered or C-centered radicals.[4,7]

Several methods are available for the direct synthesis of diarylamines, but, in general, they are not straightforward.[8−12] A recent study[11] showed that aryllead triacetates are a class of reagents that mono *N*-arylate amines regiospecifically under copper catalysis, in mild conditions. The yields of diarylamines are high and independent of both the steric hindrance of the diarylamine and the substitution pattern of arylamines containing nonoxidizable substituents. More recently, it has been found that organobismuth reagents (Bi^{III} and Bi^{V}) phenylate aliphatic and aromatic amines, also under copper catalysis, in a mild and high yielding reaction.[12]



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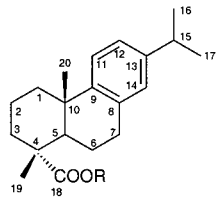
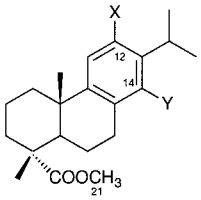
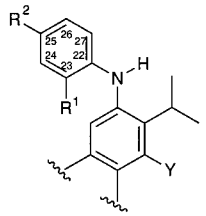


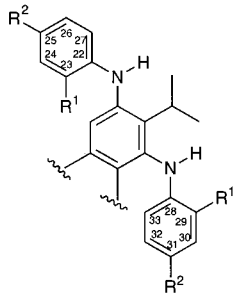
2 R = H
2a R = CH_3



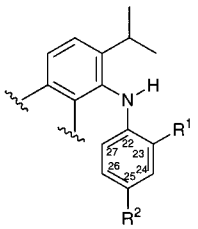
3 X=Y=NH_2
4 X=NH_2, Y=H
5 X=H, Y=NH_2
6 X=NH_2, Y=NO_2



9 R^1=H, R^2=OCH_3, Y=NH_2
11 R^1=H, R^2=OCH_3, Y=H
13 R^1=H, R^2=OCH_3, Y=NO_2
14 R^1=OCH_3, R^2=H, Y=NH_2
16 R^1=OCH_3, R^2=H, Y=H
18 R^1=OCH_3, R^2=H, Y=NO_2
19 R^1=R^2=H, Y=NH_2
21 R^1=R^2=Y=H
23 R^1=R^2=H, Y=NO_2



10 R^1=H, R^2=OCH_3
15 R^1=OCH_3, R^2=H
20 R^1=R^2=H



12 R^1=H, R^2=OCH_3
17 R^1=OCH_3, R^2=H
22 R^1=R^2=H

Results and Discussion

Dehydroabietic acid **2**, used as the starting material, was isolated from dehydrogenated rosin.[3] The anilines **3**, **4**, **5**, and **6**[13] were obtained from the corresponding mono- and dinitro precursors[14] by catalytic hydrogenation with hydrogen under different pressures using Pd/C or Ni/SiO_2 as catalysts. For the regioisomers **4** and **5** a simple, easy, and high-yielding sequential procedure based on the difference of the reaction conditions needed to reduce the nitro groups at C-12 (Pd/C, rt, 100 psi) or at the more constrained C-14 (Pd/C or Ni/SiO_2, 125 °C, and 500 psi) was developed by our group, using a mixture of methyl 12-nitro- and 14-nitrodehydroabietate, as described in the Experimental Section.

* To whom correspondence should be addressed. Fax: +351.217168100. E-mail: barbara.gigante@mail.ineti.pt.
‡ INETI.
§ Present address: IICT, Hyderabad 500007, India.

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Scheme 1

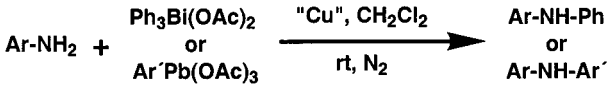

Table 1. *N*-Arylation of Amines **3**−**6**[a] with Aryllead Triacetates **7** and **8** and First Oxidation Potential of Diarylamines **9**−**18**

amine	$ArPb(OAc)_3$ (equiv)	*t* (h)	product (%)[b]	E_p (V)
3	**7** (1.1)	1.5	**9** (70)	0.61
3	**7** (2.2)	4	**10** (41)	0.68
4	**7** (1.1)	1.5	**11** (74)	0.69
5	**7** (1.1)	2	**12** (75)	0.70
6	**7** (1.1)	4	**13** (32)	0.82
3	**8** (1.1)	3	**14** (67)	0.70
3	**8** (2.2)	8	**15** (36)	0.79
4	**8** (1.1)	3	**16** (72)	0.77
5	**8** (1.1)	6	**17** (32)	0.83
6	**8** (1.1)	6	**18** (25)	0.92

[a] All reactions were run at room temperature with Cu(II) acetate (0.1 or 0.2 equiv) as catalyst. [b] Isolated yields, not optimized.

Similar conditions were used for the catalytic hydrogenation of methyl 12,14-dinitrodehydroabietate to yield methyl 12,14-diaminodehydroabietate (**3**) or methyl 12-amino-14-nitrodehydroabietate (**6**).

As resin acids, in general, do not withstand harsh reaction conditions and the aromatic ring of **3**−**6** is hindered by an isopropyl group, the recently reported[11,12] mild *N*-arylation procedures involving aryllead triacetates with an electron-donating substituent in the *para* or *ortho* positions[11] or a pentavalent organobismuth reagent[12] as the aryl donor were chosen (Scheme 1).

The aryllead species used in this work, *p*-methoxyphenyllead **7** and *o*-methoxyphenyllead **8** triacetates, were prepared by plumbylation[11,15] and tin−lead exchange,[11,16] respectively, and were used to arylate **3**−**6**, yielding the *p*- and *o*-methoxyphenylamines **9**−**18** (Table 1).

From Table 1, it can be seen that the diarylamines **9**−**18** were obtained in moderate to good yields. For the same arylamine substrate, the coupling reactions were faster and more efficient with *p*-methoxyphenyllead triacetate (**6**) than with its *ortho*-substituted analogue **8**. Moderate yields, not increased by temperature, were obtained in the diarylation of the nitroamine **6** to **13** (32%) and **18** (25%), due to the presence of the electron-withdrawing nitro group in *meta* position (C-14). For the arylation of both amino groups at C-12 and C-14 in **3**, 2-fold higher quantities of aryllead triacetates (2.2 equiv) and catalyst (0.2 equiv) and longer reaction times were used (Table 1). Despite this, the yields were moderate for **10** (41%) and **15** (36%), mainly due to incomplete conversion of the amino group at C-14 and the presence of unidentified colored products, possibly stemming from oxidation−reduction reactions involving a Cu(III) intermediate.[11] The same was observed for reactions yielding **13** and **18**.

Phenylation of the arylamines **3**−**6** to diarylamines **19**−**23** was performed following a recent procedure[12,17] with triphenylbismuth diacetate in the presence of copper(II) pivalate as the catalyst. A typical reaction required a mixture of 1 equiv of the starting arylamine in the presence of a small excess of the Bi(V) derivative (1.1 equiv) and of Cu(II) pivalate (0.1 equiv) in dichloromethane at room temperature. As shown in Table 2, excellent yields in short reaction times (5 min) were obtained.

The 2-fold higher amounts of reagent and catalyst were also used whenever two amino groups were present in the molecule, such as in the case of methyl 12,14-diaminodehydroabietate (**3**). The reactions were so fast that no significant differences were observed due to amine basicity or steric hindrance factors. Although *N*-arylation of amines could, in principle, also be performed with triarylbismuth diacetates, the use of these reagents is limited by difficulties in their preparation.[12]

Table 2. *N*-Phenylation of Amines **3**−**6**[a] with $Ph_3Bi(OAc)_2$ and First Oxidation Potential of Diarylamines **19**−**23**

amine	*t* (min)	product (%)[b]	E_p (V)
3	5	**19** (85)	0.71
3	60	**20** (83)	0.99
4	5	**21** (91)	0.85
5	5	**22** (92)	1.00
6	5	**23** (90)	1.07

[a] All reactions were run at room temperature with $Ph_3Bi(OAc)_2$ (1.1 or 2.2 equiv) and Cu(II) pivalate (0.1 or 0.2 equiv) as catalyst. [b] Isolated yields, not optimized.

All the new diarylamines **9**−**23** were isolated and characterized by FTIR, NMR, and MS spectrometry, as well as elemental analysis, as indicated in the Experimental Section.

Since one of the properties of a compound determining its ability to act as antioxidant is a low oxidation potential,[18−22] **9**−**23** were examined by cyclic voltammetry. Furthermore, their free radical scavenging activity was evaluated using the 1,1-diphenyl-2-picrylhydrazyl (DPPH) radical. The results were compared to those obtained with the commercial antioxidants isopropyldiphenylamine (IPPD) and *tert*-butylhydroxytoluene (BHT).

From the measured first oxidation potentials (E_p) (Tables 1 and 2) it was observed that the diarylamines with a *p*-methoxy substituent in the aryl moiety (**9**−**13**) have a first oxidation potential lower than their analogues with an *o*-methoxy (**14**−**18**) or no substituent (**19**−**23**). This lowering effect, higher when the methoxy substituent is *para* rather than *ortho*, is due to the electron-releasing character of that group, which inductively delocalizes the charge in the radical cation resulting from oxidation, thus improving its stability and shifting the first oxidation potential cathodically.[18,19,22]

Such effect is imparted when an electron-releasing primary amino group is present at C-14 (**9**, **14**, and **19**). On the contrary, a strong destabilizing effect is observed when an electron-withdrawing nitro group is at C-14, as seen with **13**, **18**, and **23** having the highest oxidation potentials.

The radical scavenging properties of compounds **9**−**23** were evaluated against the 2,2-diphenyl-1-picrylhydrazyl (DPPH) radical by a spectrophotometric assay.[23,24] The results, expressed as the percentage of DPPH radical reduced, were compared with those obtained under similar conditions for IPPD and BHT (Figure 1).

Three groups of compounds were observed in terms of radical scavenging behavior: a group that includes the most active compounds, **9**−**11**, with **9** being even superior to IPPD; another including compounds **12**−**14** and **19**, which exhibits moderate activity, with **13** and **14** as active as BHT; and a third group, **15**−**18**, **20**−**23**, with marginal radical scavenging activity.

It was not possible to establish a straightforward relationship between the oxidation potential and the radical scavenging activity, but it is interesting to point out that the three compounds (**9**, **10**, and **11**) that exhibited the highest radical scavenging activity and the lowest oxidation potential have a *p*-methoxyphenyl moiety. The enhanced antioxidant activity of **9** over **10** and **11** is probably related with the presence of the primary amino group at C-14;

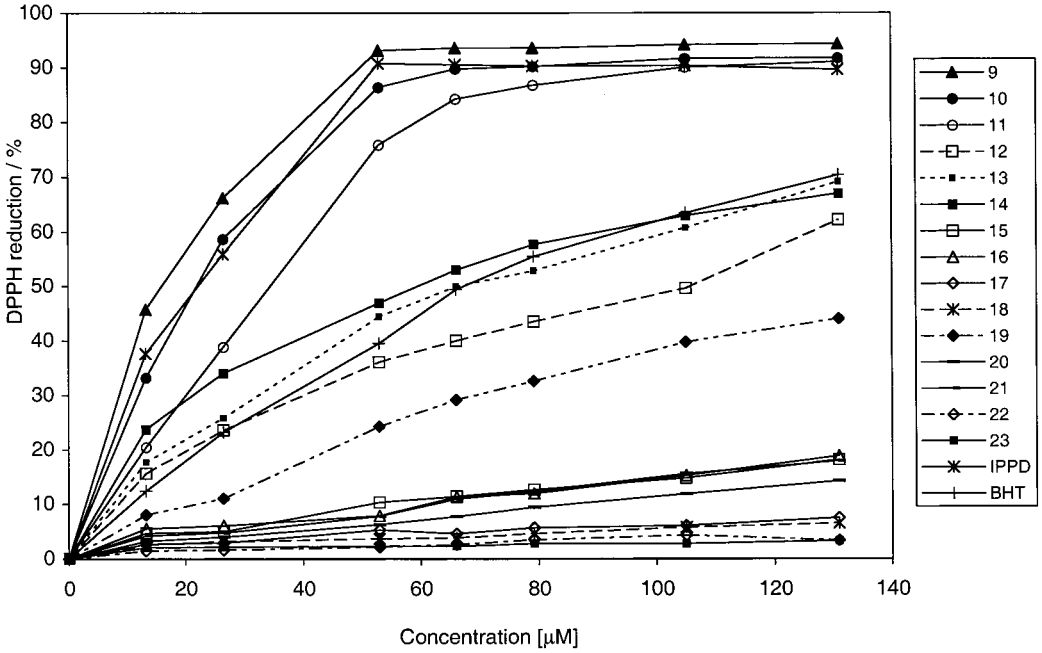

Figure 1. Scavenging activity of compounds **9**−**23** toward the DPPH radical, compared to those of IPPD and BHT.

furthermore, among all the other compounds, only those with a primary amino group, **14** and **19**, had significant activity.

In conclusion, anilines can be obtained from rosin and further used as chemical precursors in N-substitution reactions to afford new and more valuable compounds, such as diarylamines. By choice of appropriate substituents, derivatives can be obtained that exhibit potentially useful properties.

Experimental Section

General Experimental Procedures. FTIR spectra were recorded on Perkin-Elmer 1725 and UV−vis spectra on Hitachi 150-20 spectrophotometers. Fourier transform (FT) NMR spectra were run on a General Electric QE-300 spectrometer with resonance frequence of 300.65 for ^{1}H and 75.6 MHz for ^{13}C, using an appropriate solvent as designated. The chemical shifts are reported in δ (ppm, TMS) and coupling constants in Hz. EI mass spectra were determined on a Kratos MS 25RF instrument at 70 eV. Microanalyses were performed on a Carlo Erba 1106R microanalyzer. GC analyses were performed in a Hewlett-Packard 5890 gas chromatograph, equipped with a flame ionization detector and a HP 3396A integrator, with He as the carrier gas and using a BP-1 column SGE (15 m × 0.32 mm × 0.25 μm); a temperature program (240 °C for 2 min, 240−280 °C at 10 °C/min, 280 °C for 10 min) was used in most of the work (split ratio of 100:1). Si gel for TLC refers to Merck Si gel GF254 and for flash chromatography (FC) to Merck Si gel 60, 230−400 mesh. Organic extracts were dried over anhydrous sodium sulfate.

The electrochemical instrumention for CV consisted of an EG&G Princeton Applied Research Potentiostat Model 273A, connected to the data acquisition software (EG&G PAR Electrochemical Analysis Model 273 version 3.0). A three-electrode system with a platinum counter electrode, a platinum working electrode, and a potassium chloride saturated calomel reference electrode (SCE) was used. A 10^{-1} M solution of tetrabutylammonium hexafluorophosphate in acetonitrile was used as the supporting electrolyte. The tetrabutylammonium hexafluorophosphate (98%) was purified by recrystalization from ethanol and dried under vacuum prior to use. Acetonitrile p.a. grade was distilled twice, first over CaH_2 and then over P_2O_5, under nitrogen. The solutions used in the cyclic voltammetry assays were 5 mM diarylamine in 0.1 M supporting electrolyte. Solutions were degassed and kept under argon throughout each experiment. Measurements were conducted at 25 ± 0.1 °C using a sweep rate of 50 mV/s.

Radical scavenging evaluation was performed in spectrophotometric assays by the addition of 5−50 μL solutions of each diarylamine **9**−**23** (8×10^{-3} M) in methanol to a 1 cm path length quartz/glass cell containing 3 mL of a freshly prepared solution of DPPH in methanol (8×10^{-5} M). The absorbance was measured at 517 nm, 30 min after addition of the diarylamine, and the percentage of reduction was calculated.

Dehydroabietic acid (**2**),[3] its methyl ester **2a**,[13] and the nitro derivatives,[14] 4-methoxyphenyllead triacetate (**7**),[15] 2-methoxyphenyllead triacetate (**8**),[16] diacetate triphenylbismuth,[12] and copper pivalate,[17] were prepared according to the literature. Tetrabutylammonium hexafluorophosphate (98%) and 2,2-diphenyl-1-pycrilhydrazil (DPPH, 95%) were purchased from Aldrich. All other reagents were from Merck and were of the highest quality available. Solvents for the reactions were reagent grade and were dried and distilled prior to use following standard procedures. The solvents for extraction and chromatography were of technical grade, freshly distilled before use.

Stepwise Synthesis and Isolation of Methyl 12-Aminodehydroabietate (4) and Methyl 14-Aminodehydroabietate (5) from the Mixture of Methyl 12-Nitro- and Methyl 14-Nitrodehydroabietate. (A) A solution of a mixture of methyl 12-nitro- and methyl 14-nitrodehydroabietate (55:45) (5.20 g, 14.5 mmol) in ethanol (180 mL) was hydrogenated (H_2, 100 psi) in the presence of Pd/C 5% (0.42 g) for 3 h at room temperature. After filtration, the filtrate was evaporated under reduced pressure to afford a yellow gum, which was dried under vacuum (4.53 g).

(B) The yellow gum (4.53 g) was dissolved in dry diethyl ether (100 mL) and acidified with gaseous hydrochloric acid to precipitate the methyl 12-aminodehydroabietate hydrochloride, which after filtration yielded white crystals from methanol/diethyl ether (2.48 g, η = 85%). The solution of the hydrochloride salt (2.48 g) in H_2O was neutralized with NaOH (10%) at 0 °C. After extraction with dichloromethane and drying, the solvent was evaporated and the residue recrystallized from Et_2O/petroleum ether yielded methyl 12-aminodehydroabietate (**3**) as white crystals: mp 137−137.5 °C (137−137.5 °C).[13]

(C) The filtrate of B was treated with NaOH (10%) at 0 °C and extracted with dichloromethane to yield, after evaporation of the solvent and recrystalization from methanol, methyl 14-

nitrodehydroabietate (2.10 g, 90%) as light yellow crystals: mp 192−194 °C (193−194 °C).[13,14]

(D) Methyl 14-nitrodehydroabietate (2.00 g, 5.6 mmol) in ethanol (60 mL) was hydrogenated (H_2, 500 psi) in the presence of Ni/SiO_2 (0.16 g) at 125 °C for 4 h. The mixture was filtered and the solvent evaporated under reduced pressure to yield, after drying under vacuum and recrystalization from petroleum ether, methyl 14-aminodehydroabietate (**5**, 1.57 g, 85%) as white crystals: mp 99−100 °C (100.5−102 °C).[13]

Synthesis of 4- and 2-Methoxyphenyldiarylamines Derived from Methyl Dehydroabietate (2a). General Procedure. To a solution of amines **3**−**6** (3.04 mmol) and copper diacetate (0.30 or 0.60 mmol) in dry dichloromethane (20 mL) was added 4-methoxyphenyllead triacetate (**7**) or 2-methoxyphenyllead triacetate (**8**) (3.34 or 6.68 mmol). The mixture was stirred at room temperature, under N_2, until the complete consumption of the amine (TLC) or, in the cases where conversion was not complete, until no further reaction evolution was observed. The reaction mixture was filtered through Celite, concentrated under reduced pressure, and purified by FC (Et_2O/petroleum ether, 1:2 to 1:1).

Methyl 12-(4-Methoxyphenyl)amino-14-aminodehydroabietate (9). 4-Methoxyphenyllead triacetate (**7**, 1.64 g, 3.34 mmol) and methyl 12,14-diaminodehydroabietate (**3**, 1.05 g, 3.04 mmol) gave **9** (0.96 g, 70%) as white needles (Et_2O/petroleum ether, 1:1): mp 155−156 °C; FTIR (KBr) ν_{max} 3402 (N−H), 1724 (C═O) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.18 (3H, s, H-20), 1.25 (3H, s, H-19), 1.32 (3H, d, J = 7 Hz, H-16 or H-17), 1.33 (3H, d, J = 7 Hz, H-16 or H-17), 1.49−1.52 (1H, m, H-1a), 1.58−1.65 (1H, m, H-6a), 1.69−1.84 (4H, m, H-2 and H-3), 1.89−2.01 (1H, m, H-6e), 2.20 (1H, brd, J = 13 Hz, H-1e), 2.32 (1H, brd, J = 12 Hz, H-5), 2.5−2.7 (2H, m, H-7), 3.54 (1H, sept, J = 7 Hz, H-15), 3.66 (3H, s, H-21), 3.75 (3H, s, OCH_3-25), 6.58 (1H, s, H-11), 6.69 (2H, brd, J = 9 Hz, H-23 and H-27), 6.77 (2H, brd, J = 9 Hz, H-24 and H-26); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 38.4 (C-1), 18.7 (C-2), 36.9 (C-3), 47.8 (C-4), 44.5 (C-5), 21.6 (C-6), 25.5 (C-7), 116.3 (C-8), 148.7 (C-9), 37.2 (C-10), 111.3 (C-11), 139.8 (C-12), 123.0 (C-13), 142.9 (C-14), 26.0 (C-15), 20.6 (C-16), 20.7 (C-17), 178.9 (C-18), 16.6 (C-19), 24.8 (C-20), 51.6 (C-21), 141.2 (C-22), 117.4 (C-23) and (C-27), 115.1 (C-24) and (C-26), 154.6 (C-25), 55.9 (OCH_3-25); EIMS m/z 450 [M^+] (100), 435 (7), 391 (4); *anal.* C 74.54%, H 8.71%, N 6.08%, calcd for $C_{28}H_{38}N_2O_3$, C 74.63%, H 8.50%, N 6.22%.

Methyl 12,14-Bis[(4-methoxyphenyl)amino]dehydroabietate (10). 4-Methoxyphenyllead triacetate (**7**, 3.28 g, 6.68 mmol) and methyl 12,14-diaminodehydroabietate (**3**, 1.05 g, 3.04 mmol) gave **9** (0.69 g, 41%) as an amorphous pink solid: FTIR (KBr) ν_{max} 3405 (N−H), 1723 (C═O) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.17 (3H, s, H-20), 1.21 (3H, d, J = 5 Hz, H-16 or H-17), 1.22 (3H, d, J = 2 Hz, H-16 or H-17), 1.24 (3H, s, H-19), 1.58−1.71 (7H, *m*, H-1a, H-2, H-3, H-6), 2.12 (2H, brt, J = 9 Hz, H-1e and H-5), 2.5−2.8 (2H, m, H-7), 3.44−3.58 (1H, m, H-15), 3.62 (3H, s, H-21), 3.74 (3H, s, OCH_3-31), 3.78 (3H, *s*, OCH_3-25), 6.44 (2H, brd, J = 9 Hz, H-29 and H-33), 6.74 (2H, brd, J = 8 Hz, H-30 and H-32), 6.82 (4H, s, H-23, H-24, H-26 and H-27), 7.03 (1H, s, H-11); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 37.8 (C-1), 18.4 (C-2), 36.4 (C-3), 47.4 (C-4), 44.3 (C-5), 21.3 (C-6), 26.0 (C-7), 127.9 (C-8), 148.8 (C-9), 37.0 (C-10), 116.7 (C-11), 138.3 (C-12), 134.9 (C-13), 140.5 (C-14), 26.5 (C-15), 21.3 (C-16), 21.3 (C-17), 178.9 (C-18), 16.3 (C-19), 24.9 (C-20), 51.8 (C-21), 139.2 (C-22), 118.0 (C-23 and C-27), 114.6 (C-24, C-26, C-30 and C-32), 153.0 (C-25), 55.5 (OCH_3-25 and OCH_3-31), 141.2 (C-28), 114.2 (C-29 and C-33), 152.0 (C-31); EIMS m/z 556 [M^+] (100), 497 (5), 359 (7); *anal.* C 75.56%, H 8.01%, N 4.95%, calcd for $C_{35}H_{44}N_2O_4$, C 75.50%, H 7.97%, N 5.03%.

Methyl 12-(4-Methoxyphenyl)aminodehydroabietate (11). 4-Methoxyphenyllead triacetate (**7**, 1.64 g, 3.34 mmol) and methyl 12-aminodehydroabietate (**4**, 1.00 g, 3.04 mmol) gave **11** (0.98 g, 74%) as an amorphous white solid: FTIR (KBr) ν_{max} 3393 (N−H), 1719 (C═O) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.19 (3H, s, H-20), 1.21 (3H, d, J = 7 Hz, H-16 or H-17), 1.23 (3H, d, J = 7 Hz, H-16 or H-17), 1.27 (3H, s, H-19), 1.33−1.44 (2H, m, H-1a and H-6a), 1.54−1.84 (5H, m, H-2, H-3 and H-6e), 2.15 (1H, brd, J = 13 Hz, H-1e), 2.25 (1H, dd, J = 13 Hz, 1.8, H-5), 2.86 (2H, t, J = 4 Hz, H-7), 3.05 (1H, sept, J = 7 Hz, H-15), 3.68 (3H, s, H-21), 3.79 (3H, s, OCH_3-25), 5.20 (1H, brs, N*H*-12), 6.83 (4H, s, H-23, H-24, H-26 and H-27), 6.93 (1H, s, H-11), 7.03 (1H, s, 14-H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 37.9 (C-1), 18.5 (C-2), 36.6 (C-3), 47.7 (C-4), 44.9 (C-5), 21.8 (C-6), 29.5 (C-7), 128.9 (C-8), 147.6 (C-9), 37.0 (C-10), 116.5 (C-11), 138.5 (C-12), 136.9 (C-13), 126.3 (C-14), 27.2 (C-15), 22.9 (C-16), 23.1 (C-17), 179.1 (C-18), 16.4 (C-19), 25.0 (C-20), 51.9 (C-21), 139.2 (C-22), 118.3 (C-23 and C-27), 114.7 (C-24 and C-26), 153.5 (C-25), 55.6 (OCH_3-25); EIMS m/z 435 [M^+] (100), 238 (7), 59 (84); *anal.* C 77.07%, H 8.70%, N 2.98%, calcd for $C_{28}H_{37}NO_3$, C 77.20%, H 8.56%, N 3.22%.

Methyl 14-(4-Methoxyphenyl)aminodehydroabietate (12). 4-Methoxyphenyllead triacetate (**7**, 1.64 g, 3.34 mmol) and methyl 14-aminodehydroabietate (**5**, 1.00 g, 3.04 mmol) gave **12** (0.99 g, 75%) as white needles from ethanol: mp 155−157 °C; FTIR (KBr) ν_{max} 3391 (N−H), 1723 (C═O) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.11 (3H, d, J = 7 Hz, H-16 or H-17), 1.14 (3H, d, J = 7 Hz, H-16 or H-17), 1.22 (3H, s, H-20), 1.25 (3H, s, H-19), 1.30−1.39 (1H, m, H-6a), 1.48−1.56 (1H, m, H-1a), 1.62−1.80 (5H, m, H-2, H-3 and H-6e), 2.16 (1H, dd, J = 12, 1.5 Hz, H-5), 2.32 (1H, brd, J = 12 Hz, H-1e), 2.6−2.8 (2H, m, H-7), 3.13 (1H, sept, J = 7 Hz, H-15), 3.62 (3H, s, H-21), 3.73 (3H, s, OCH_3-25), 4.85 (1H, brs, N*H*-14), 6.42 (2H, brd, J = 9 Hz, H-23 and H-27), 6.73 (2H, brd, J = 9 Hz, H-24 and H-26), 7.15 (1H, d, J = 8 Hz, H-12), 7.19 (1H, d, J = 8 Hz, H-11); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 38.1 (C-1), 18.6 (C-2), 36.5 (C-3), 47.6 (C-4), 44.4 (C-5), 21.4 (C-6), 26.3 (C-7), 133.1 (C-8), 148.3 (C-9), 37.1 (C-10), 122.3 (C-11), 123.4 (C-12), 143.5 (C-13), 136.7 (C-14), 27.7 (C-15), 23.4 (C-16), 24.0 (C-17), 179.1 (C-18), 16.5 (C-19), 25.2 (C-20), 51.9 (C-21), 141.2 (C-22), 114.2 (C-23 and C-27), 114.7 (C-24 and C-26), 152.2 (C-25), 55.7 (OCH_3-25); EIMS m/z 435 [M^+] (100), 420 (6), 252 (6); *anal.* C 77.16%, H 8.66%, N 2.91%, calcd for $C_{28}H_{37}NO_3$, C 77.20%, H 8.56%, N 3.22%.

Methyl 12-(4-Methoxyphenyl)amino-14-nitrodehydroabietate (13). 4-Methoxyphenyllead triacetate (**7**, 1.64 g, 3.34 mmol) and methyl 12-amino-14-nitrodehydroabietate (**6**, 1.14 g, 3.04 mmol) gave **13** (0.47 g, 32%) as yellow crystals (Et_2O/hexane, 1:1): mp 118−120 °C; FTIR (KBr) ν_{max} 3448 (N−H), 1725 (C═O) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.15 (3H, s, H-20), 1.20 (3H, s, H-19), 1.34 (3H, d, J = 7 Hz, H-16 or H-17), 1.35 (3H, d, J = 7 Hz, H-16 or H-17), 1.39−1.44 (2H, m, H-1a and H-6a), 1.60−1.83 (5H, m, H-2, H-3, and H-6e), 2.03 (1H, brd, J = 13 Hz, H-1e), 2.18 (1H, dd, J = 13, 1.8 Hz, H-5), 2.6−2.8 (2H, m, H-7), 2.96 (1H, sept, J = 7 Hz, H-15), 3.66 (3H, s, H-21), 3.80 (3H, *s*, OCH_3-25), 5.27 (1H, brs, N*H*-12), 6.86 (2H, s, H-23 and H-27), 6.87 (2H, s, H-24 and H-26), 7.09 (1H, s, H-11); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 37.7 (C-1), 18.3 (C-2), 36.3 (C-3), 47.4 (C-4), 44.0 (C-5), 20.7 (C-6), 24.1 (C-7), 118.3 (C-8), 149.4 (C-9), 37.3 (C-10), 117.6 (C-11), 141.5 (C-12), 124.8 (C-13), 152.3 (C-14), 28.2 (C-15), 20.7 (C-16), 20.7 (C-17), 178.6 (C-18), 16.4 (C-19), 24.8 (C-20), 52.0 (C-21), 137.0 (C-22), 114.8 (C-23 and C-27), 120.2 (C-24 and C-26), 154.7 (C-25), 55.5 (OCH_3-25); EIMS m/z 480 [M^+] (100), 450 (7), 435 (4); *anal.* C 69.79%, H 7.71%, N 5.73%, calcd for $C_{28}H_{36}N_2O_5$, C 69.98%, H 7.55%, N 5.83%.

Methyl 12-(2-Methoxyphenyl)amino-14-aminodehydroabietate (14). 2-Methoxyphenyllead triacetate (**8**, 1.64 g, 3.34 mmol) and methyl 12,14-diaminodehydroabietate (**3**, 1.05 g, 3.04 mmol) gave **14** (0.92 g, 67%) as a white amorphous solid: FTIR (KBr) ν_{max} 3402 (N−H), 1724 (C═O) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.20 (3H, s, H-20), 1.26 (3H, s, H-19), 1.31 (3H, d, J = 7 Hz, H-16 or H-17), 1.32 (3H, d, J = 7 Hz, H-16 or H-17), 1.38−1.45 (1H, m, H-1a), 1.49−1.56 (1H, m, H-6a), 1.60−1.75 (4H, m, H-2 and H-3), 1.78−1.93 (1H, m, H-6e), 2.15 (1H, brd, J = 13 Hz, H-1e), 2.24 (1H, brd, J = 12 Hz, H-5), 2.4−2.6 (2H, m, H-7), 3.42 (1H, sept, J = 7 Hz, H-15), 3.66 (3H, s, H-21), 3.91 (3H, s, OCH_3-23), 5.76 (1H, s, N*H*-12), 6.62 (1H, d, J = 7 Hz, H-27), 6.68 (1H, t, J = 7 Hz, H-25), 6.68 (1H, s, H-11), 6.76 (1H, t, J = 7 Hz, H-26), 6.84 (1H, d, J = 8 Hz, H-24); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 38.0 (C-1), 18.5 (C-2), 36.5 (C-3), 47.6 (C-4), 44.0 (C-5), 21.4 (C-6), 25.5 (C-7), 117.0 (C-8), 148.5 (C-9), 36.9 (C-10), 113.0 (C-11), 137.1 (C-12), 124.3

(C-13), 142.8 (C-14), 25.9 (C-15), 20.5 (C-16), 20.7 (C-17), 179.1 (C-18), 16.5 (C-19), 24.9 (C-20), 51.9 (C-21), 137.7 (C-22), 146.6 (C-23), 109.8 (C-24), 117.0 (C-25), 121.0 (C-26), 112.0 (C-27), 55.6 (O*C*H$_3$-23); EIMS *m/z* 450 [M$^+$] (100), 435 (5), 389 (4); *anal.* C 74.75%, H 8.71%, N 6.27%, calcd for $C_{28}H_{38}N_2O_3$, C 74.63%, H 8.50%, N 6.22%.

Methyl 12,14-Bis[(2-methoxyphenyl)amino]dehydroabietate (15). 2-Methoxyphenyllead triacetate (**8**, 3.28 g, 6.68 mmol) and methyl 12,14-diaminodehydroabietate (**3**, 1.05 g, 3.04 mmol) gave **15** (0.61 g, 36%) as white crystals (EtOH/hexane, 1:1): mp 182−183 °C; FTIR (KBr) ν_{max} 3401 (N−H), 1725 (C═O) cm^{-1}; ^{1}H NMR (CDCl$_3$, 300 MHz) δ 1.21 (3H, s, H-20), 1.22 (6H, d, J = 8 Hz, H-16 and H-17), 1.23 (3H, s, H-19), 1.34−1.37 (1H, m, H-6a), 1.46−1.55 (1H, m, H-1a), 1.60−1.78 (5H, m, H-2, H-3, and H-6e), 2.10 (1H, brd, J = 10 Hz, H-5), 2.13 (1H, brd, J = 10 Hz, H-1e), 2.6−2.8 (2H, m, H-7), 3.50 (1H, sept, J = 7 Hz, H-15), 3.63 (3H, s, H-21), 3.92 (3H, s, OC*H*$_3$-23), 3.93 (3H, s, OC*H*$_3$-29), 5.54 (1H, s, N*H*-14), 6.02 (1H, *s*, N*H*-12), 6.17 (1H, dd, J = 8, 1.2 Hz, H-33), 6.64−6.76 (3H, m, H-25, H-31, and H-32), 6.80−6.89 (4H, m, H-24, H-26, H-27, and H-30), 7.23 (1H, s, H-11); ^{13}C NMR (CDCl$_3$, 75 MHz) δ 38.4 (C-1), 18.7 (C-2), 36.9 (C-3), 47.8 (C-4), 44.9 (C-5), 21.6 (C-6), 25.9 (C-7), 130.3 (C-8), 149.1 (C-9), 37.5 (C-10), 120.0 (C-11), 138.4 (C-12), 139.0 (C-13), 136.8 (C-14), 27.1 (C-15), 21.6 (C-16), 21.6 (C-17), 178.8 (C-18), 16.6 (C-19), 25.0 (C-20), 51.6 (C-21), 138.1 (C-22), 147.9 (C-23), 110.9 (C-24), 117.8 (C-25), 121.4 (C-26), 112.6 (C-27), 137.6 (C-28), 146.8 (C-29), 110.6 (C-30), 116.9 (C-31), 121.6 (C-32), 111.3 (C-33), 56.0 (O*C*H$_3$-23) and (O*C*H$_3$-29); EIMS *m/z* 556 [M$^+$] (100), 497 (7), 359 (8); *anal.* C 75.41%, H 8.19%, N 4.95%, calcd for $C_{35}H_{44}N_2O_4$, C 75.50%, H 7.97%, N 5.03%.

Methyl 12-(2-Methoxyphenyl)aminodehydroabietate (16). 2-Methoxyphenyllead triacetate (**8**, 1.64 g, 3.34 mmol) and methyl 12-aminodehydroabietate (**4**, 1.00 g, 3.04 mmol) gave **16** (0.95 g, 72%) as an amorphous white solid: FTIR (KBr) ν_{max} 3428 (N−H), 1728 (C═O) cm^{-1}; ^{1}H NMR (CDCl$_3$, 300 MHz) δ 1.14 (6H, t, J = 7 Hz, H-16 and H-17), 1.16 (3H, s, H-20), 1.22 (3H, s, H-19), 1.33−1.44 (2H, m, H-1a and H-6a), 1.54−1.84 (5H, m, H-2, H-3 and H-6e), 2.14 (1H, brd, J = 13 Hz, H-1e), 2.21 (1H, dd, J = 12, 2.1 Hz, H-5), 2.84 (2H, q, J = 4 Hz, H-7), 3.04 (1H, sept, J = 7 Hz, H-15), 3.62 (3H, s, H-21), 3.86 (3H, s, OC*H*$_3$-23), 5.78 (1H, brs, N*H*-12), 6.66 (1H, t, J = 2 Hz, H-25), 6.69 (1H, d, J = 5 Hz, H-27), 6.70 (1H, t, J = 5 Hz, H-26), 6.80 (1H, brd, J = 9 Hz, H-24), 6.91 (1H, s, H-14), 7.12 (1H, s, H-11); ^{13}C NMR (CDCl$_3$, 75 MHz) δ 38.2 (C-1), 18.6 (C-2), 36.9 (C-3), 47.8 (C-4), 45.2 (C-5), 21.9 (C-6), 29.7 (C-7), 130.8 (C-8), 147.8 (C-9), 37.2 (C-10), 120.2 (C-11), 136.9 (C-12), 140.1 (C-13), 126.6 (C-14), 27.7 (C-15), 23.2 (C-16), 23.3 (C-17), 178.9 (C-18), 16.6 (C-19), 25.0 (C-20), 51.7 (C-21), 136.8 (C-22), 147.5 (C-23), 110.6 (C-24), 117.8 (C-25), 121.3 (C-26), 112.7 (C-27), 55.8 (O*C*H$_3$-23); EIMS *m/z* 435 [M$^+$] (100), 406 (3), 360 (6); *anal.* C 77.18%, H 8.79%, N 3.20%, calcd for $C_{28}H_{37}NO_3$, C 77.20%, H 8.56%, N 3.22%.

Methyl 14-(2-Methoxyphenyl)aminodehydroabietate (17). 2-Methoxyphenyllead triacetate (**8**, 1.64 g, 3.34 mmol) and methyl 14-aminodehydroabietate (**5**, 1.00 g, 3.04 mmol) gave **17** (0.42 g, 32%) as an amorphous white solid: FTIR (KBr) ν_{max} 3428 (N−H), 1728 (C═O) cm^{-1}; ^{1}H NMR (CDCl$_3$, 300 MHz) δ 1.11 (3H, d, J = 7 Hz, H-16 or H-17), 1.14 (3H, d, J = 7 Hz, H-16 or H-17), 1.22 (3H, s, H-20), 1.24 (3H, s, H-19), 1.32−1.39 (1H, m, H-6a), 1.52−1.57 (1H, m, H-1a), 1.64−1.80 (5H, m, H-2, H-3, and H-6e), 2.17 (1H, brd, J = 12 Hz, H-5), 2.33 (1H, brd, J = 12 Hz, H-1e), 2.6−2.8 (2H, m, H-7), 3.12 (1H, sept, J = 7 Hz, H-15), 3.62 (1H, s, H-21), 3.94 (3H, s, OC*H*$_3$-23), 5.52 (1H, brs, N*H*-14), 6.10 (1H, dd, J = 7, 2 Hz, H-27), 6.69 (2H, dq, J = 8, 2 Hz, H-25 and H-26), 6.84 (1H, dd, J = 8, 2 Hz, H-24), 7.17 (1H, d, J = 8 Hz, H-12), 7.21 (1H, d, J = 8 Hz, H-11); ^{13}C NMR (CDCl$_3$, 75 MHz) δ 38.1 (C-1), 18.6 (C-2), 36.5 (C-3), 47.6 (C-4), 44.4 (C-5), 21.3 (C-6), 26.0 (C-7), 133.6 (C-8), 148.3 (C-9), 37.1 (C-10), 122.6 (C-11), 123.4 (C-12), 144.2 (C-13), 135.9 (C-14), 27.7 (C-15), 25.2 (C-16), 25.2 (C-17), 179.1 (C-18), 16.5 (C-19), 25.2 (C-20), 51.9 (C-21), 136.9 (C-22), 146.4 (C-23), 109.7 (C-24), 116.5 (C-25), 121.5 (C-26), 110.5 (C-27), 55.6 (O*C*H$_3$-23); EIMS *m/z* 435 [M$^+$] (100), 420 (3), 360 (4), 147 (8); *anal.* C 77.31%, H 8.75%, N 2.98%, calcd for $C_{28}H_{37}NO_3$, C 77.20%, H 8.56%, N 3.22%.

Methyl 12-(2-Methoxyphenyl)amino-14-nitrodehydroabietate (18). 2-Methoxyphenyllead triacetate (**8**, 1.64 g, 3.34 mmol) and methyl 12-amino-14-nitrodehydroabietate (**6**, 1.14 g, 3.04 mmol) gave **18** (0.36 g, 25%) as an amorphous yellow solid: FTIR (KBr) ν_{max} 3452 (N−H), 1728 (C═O) cm^{-1}; ^{1}H NMR (CDCl$_3$, 300 MHz) δ 1.20 (3H, s, H-20), 1.25 (3H, s, H-19), 1.32 (6H, t, J = 7 Hz, H-16 and H-17), 1.40−1.47 (2H, m, H-1a and H-6a), 1.67−1.88 (5H, m, H-2, H-3, and H-6e), 2.14 (1H, brd, J = 13 Hz, H-1e), 2.21 (1H, dd, J = 12, 2.1 Hz, H-5), 2.6−2.8 (2H, m, H-7), 2.94 (1H, sept, J = 7 Hz, H-15), 3.67 (3H, s, H-21), 3.93 (3H, s, OC*H*$_3$-23), 5.98 (1H, brs, N*H*-12), 6.78−6.85 (3H, m, H-25, H-26, and H-27), 6.90 (1H, dd, J = 7, 2 Hz, H-24), 7.36 (1H, s, H-11); ^{13}C NMR (CDCl$_3$, 75 MHz) δ 37.8 (C-1), 18.4 (C-2), 36.4 (C-3), 47.4 (C-4), 44.0 (C-5), 20.7 (C-6), 24.3 (C-7), 120.3 (C-8), 149.4 (C-9), 37.4 (C-10), 121.2 (C-11), 139.3 (C-12), 128.1 (C-13), 153.0 (C-14), 28.5 (C-15), 20.8 (C-16), 20.9 (C-17), 178.7 (C-18), 16.4 (C-19), 24.8 (C-20), 52.1 (C-21), 134.3 (C-22), 147.5 (C-23), 110.3 (C-24), 119.0 (C-25), 121.0 (C-26), 112.7 (C-27), 55.7 (O*C*H$_3$-23); EIMS *m/z* 480 [M$^+$] (100), 446 (7), 339 (4); *anal.* C 69.76%, H 7.74%, N 5.70%, calcd for $C_{28}H_{36}N_2O_5$, C 69.98%, H 7.55%, N 5.83%.

Synthesis of Phenyldiarylamines Derived from Methyl Dehydroabietate (2a). General Procedure. Diacetate triphenylbismuth (3.34 or 6.68 mmol) was added with stirring to a solution of methyl dehydroabietate amine **3**−**6** (3.04 mmol) and copper pivalate (0.30 or 0.60 mmol) in dry dichloromethane (20 mL). After the appropriate time shown in Table 1, the reaction mixture was poured into a solution of 3 N hydrochloric acid (20 mL), neutralized with a 10% sodium bicarbonate solution, and extracted twice with ethyl acetate. The organic extracts were dried over anhydrous sodium sulfate, and the solvent was removed by evaporation under vacuum. The residue obtained was purified by FC (Et$_2$O/petroleum ether, 1:1).

Methyl 12-(Phenyl)amino-14-aminodehydroabietate (19). Diacetate triphenylbismuth (1.86 g, 3.34 mmol) and methyl 12,14-diaminodehydroabietate (**3**, 1.05 g, 3.04 mmol) gave **19** (1.09 g, 85%) as white crystals (Et$_2$O/hexane, 1:9): mp 150−152 °C; FTIR (KBr) ν_{max} 3370 (N−H), 1718 (C═O)) cm^{-1}; ^{1}H NMR (CDCl$_3$, 300 MHz) δ 1.20 (3H, s, H-20), 1.26 (3H, s, H-19), 1.32 (3H, d, J = 7 Hz, H-16 or H-17), 1.33 (3H, d, J = 7 Hz, H-16 or H-17), 1.40−1.47 (1H, m, H-1a), 1.49−1.56 (1H, m, H-6a), 1.60−1.75 (4H, m, H-2 and H-3), 1.81−1.93 (1H, m, H-6e), 2.14 (1H, brd, J = 12 Hz, H-1e), 2.23 (1H, dd, J = 12, 1.8 Hz, H-5), 2.5−2.6 (2H, m, H-7), 3.46 (1H, sept, J = 8 Hz, H-15), 3.67 (3H, s, H-21), 5.21 (1H, brs, N*H*-12), 6.66 (1H, s, H-11), 6.68 (2H, d, J = 8 Hz, H-23 and H-27), 6.74 (1H, t, J = 7 Hz, H-25), 7.16 (2H, t, J = 7 Hz, H-24 and H-26); ^{13}C NMR (CDCl$_3$, 75 MHz) δ 38.0 (C-1), 18.5 (C-2), 36.5 (C-3), 47.6 (C-4), 44.1 (C-5), 21.3 (C-6), 25.5 (C-7), 111.2 (C-8) 148.6 (C-9), 36.9 (C-10), 112.9 (C-11), 137.8 (C-12), 124.2 (C-13), 142.9 (C-14), 25.9 (C-15), 20.5 (C-16), 20.6 (C-17), 179.1 (C-18), 16.5 (C-19), 24.9 (C-20), 51.9 (C-21), 147.4 (C-22), 114.4 (C-23 and C-27), 129.1 (C-24) and (C-26), 117.9 (C-25); EIMS *m/z* 420 [M$^+$] (100), 405 (9), 345 (5), 223(13); *anal.* C 77.26%, H 8.76%, N 6.88%, calcd for $C_{27}H_{36}N_2O_2$, C 77.10%, H 8.63%, N 6.66%.

Methyl 12,14-Bis(phenylamino)dehydroabietate (20). Diacetate triphenylbismuth (3.72 g, 6.68 mmol) and methyl 12,14-diaminodehydroabietate (**3**, 1.05 g, 3.04 mmol) gave **20** (1.25 g, 83%) as an amorphous solid: FTIR (KBr) ν_{max} 3381 (N−H), 1719 (C═O) cm^{-1}; ^{1}H NMR (CDCl$_3$, 300 MHz) δ 1.20 (6H, t, J = 4 Hz, H-16 and H-17), 1.21 (3H, s, H-20), 1.23 (3H, s, H-19), 1.34−1.38 (1H, m, H-6a), 1.41−1.51 (1H, m, H-1a), 1.61−1.76 (5H, m, H-2, H-3, and H-6e), 2.16 (1H, brd, J = 13 Hz, H-1e), 2.18 (1H, dd, J = 6, 2.4 Hz, 5-H), 2.6−2.8 (2H, m, H-7), 3.53 (1H, sept, J = 7 Hz, H-15), 3.62 (3H, s, H-21), 5.02 (1H, brs, N*H*-14), 5.40 (1H, brs, N*H*-12), 6.48 (2H, d, J = 8 Hz, H-29 and H-33), 6.71 (1H, t, J = 7 Hz, H-31), 6.77 (1H, t, J = 7 Hz, H-25), 6.79 (2H, d, J = 8 Hz, H-23 and H-27), 7.15 (2H, t, J = 8 Hz, 30-H and H-32), 7.18 (1H, s, H-11), 7.21 (2H, t, J = 8 Hz, H-24 and H-26); ^{13}C NMR (CDCl$_3$, 75 MHz) δ 38.2 (C-1), 18.6 (C-2), 36.8 (C-3), 47.7 (C-4), 44.7 (C-5), 21.5 (C-6), 26.3 (C-7), 139.3 (C-8), 149.3 (C-9), 37.4 (C-10), 120.1 (C-11),

137.9 (C-12), 139.3 (C-13), 137.9 (C-14), 27.1 (C-15), 21.6 (C-16), 21.7 (C-17), 178.8 (C-18), 16.5 (C-19), 25.0 (C-20), 51.7 (C-21), 147.4 (C-22), 115.3 (C-23 and C-27), 129.3 (C-24 and C-26), 118.9 (C-25), 146.6 (C-28), 113.3 (C-29 and C-33), 129.3 (C-30 and C-32), 117.9 (C-31); EIMS *m/z* 496 [M^+] (100), 299 (7), 136 (12), 77 (14); *anal*. C 79.78%, H 8.31%, N 5.42%, calcd for $C_{33}H_{40}N_2O_2$, C 79.80%, H 8.12%, N 5.64%.

Methyl 12-(Phenyl)aminodehydroabietate (21). Diacetate triphenylbismuth (1.86 g, 3.34 mmol) and methyl 12-aminodehydroabietate (**4**, 1.00 g, 3.04 mmol) gave **21** (1.12 g, 91%) as an amorphous white solid: FTIR (KBr) ν_{max} 3387 (N−H), 1727 (C═O) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.16 (3H, s, H-20), 1.19 (3H, d, J = 4 Hz, H-16 or H-17), 1.20 (3H, d, J = 3 Hz, H-16 or H-17), 1.26 (3H, s, H-19), 1.39−1.49 (2H, m, H-1a and H-6a), 1.61−1.83 (5H, m, H-2, H-3, and H-6e), 2.16 (1H, brd, J = 12 Hz, H-1e), 2.24 (1H, dd, J = 12 Hz, 1.8, 5-H), 2.89 (2H, m, H-7), 3.07 (1H, sept, J = 7 Hz, H-15), 3.67 (3H, s, H-21), 5.31 (1H, brs, N*H*-12), 6.77 (2H, d, J = 8 Hz, H-23 and H-27), 6.80 (1H, t, J = 6 Hz, H-25), 6.95 (1H, s, 14-H)), 7.13 (1H, s, H-11), 7.19 (2H, t, J = 8 Hz, H-24 and H-26); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 37.8 (C-1), 18.4 (C-2), 36.5 (C-3), 47.6 (C-4), 44.8 (C-5), 21.7 (C-6), 29.6 (C-7), 136.6 (C-8), 147.7 (C-9), 37.0 (C-10), 119.7 (C-11), 136.6 (C-12), 139.4 (C-13), 126.4 (C-14), 27.3 (C-15), 23.1 (C-16), 23.3 (C-17), 179.1 (C-18), 16.4 (C-19), 25.0 (C-20), 51.9 (C-21), 146.4 (C-22), 114.8 (C-23 and C-27), 129.2 (C-24 and C-26), 118.6 (C-25); EIMS *m/z* 405 [M^+] (100), 330 (22), 208 (12); *anal.* C 79.79%, H 8.88%, N 3.29%, calcd for $C_{27}H_{35}NO_2$, C 79.96%, H 8.70%, N 3.45%.

Methyl 14-(Phenyl)aminodehydroabietate (22). Diacetate triphenylbismuth (1.86 g, 3.34 mmol) and methyl 14-aminodehydroabietate (**5**, 1.00 g, 3.04 mmol) gave **22** (1.13 g, 92%) as white crystals (Et_2O/hexane, 1:9): mp 165−167 °C; FTIR (KBr) ν_{max} 3387 (N−H), 1727 (C═O) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.11 (3H, d, J = 7 Hz, H-16 or H-17), 1.14 (3H, d, J = 7 Hz, H-16 or H-17), 1.22 (3H, s, H-20), 1.25 (3H, s, H-19), 1.35 (1H, 2d, J = 8 Hz, H-6a), 1.48−1.56 (1H, m, H-1a), 1.64−1.79 (5H, m, H-2, H-3, and H-6e), 2.17 (1H, dd, J = 13 Hz, 1.8, 5-H), 2.33 (1H, brd, J = 12 Hz, H-1e), 2.6−2.8 (2H, m, H-7), 3.17 (1H, sept, J = 7 Hz, H-15), 3.62 (3H, s, H-21), 5.02 (1H, brs, N*H*-14), 6.46 (2H, d, J = 8 Hz, H-23 and H-27), 6.70 (1H, t, J = 7 Hz, H-25), 7.12 (2H, t, J = 8 Hz, H-24 and H-26), 7.21 (2H, d, J = 8 Hz, H-11 and H-12); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 38.1 (C-1), 18.6 (C-2), 36.5 (C-3), 47.5 (C-4), 44.4 (C-5), 21.3 (C-6), 26.3 (C-7), 133.7 (C-8), 148.4 (C-9), 37.1 (C-10), 122.8 (C-11), 123.4 (C-12), 144.1 (C-13), 135.7 (C-14), 27.7 (C-15), 23.3 (C-16), 24.0 (C-17), 179.0 (C-18), 16.4 (C-19), 25.2 (C-20), 51.9 (C-21), 147.2 (C-22), 112.8 (C-23 and C-27), 129.2 (C-24 and C-26), 117.6 (C-25); EIMS *m/z* 405 [M^+] (100), 390 (21), 330 (20), 208 (11); *anal.* C 79.75%, H 8.74%, N 3.23%, calcd for $C_{27}H_{35}NO_2$, C 79.96%, H 8.70%, N 3.45%.

Methyl 12-(Phenyl)amino-14-nitrodehydroabietate (23). Diacetate triphenylbismuth (1.86 g, 3.34 mmol) and methyl 12-amino-14-nitrodehydroabietate (**6**, 1.14 g, 3.04 mmol) gave **23** (1.23 g, 90%) as yellow crystals (Et_2O/petroleum ether, 1:9): mp 180−181 °C; FTIR (KBr) ν_{max} 3376 (N−H), 1719 (C═O) cm^{-1}; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.18 (3H, s, H-20), 1.25 (3H, s, H-19), 1.31 (3H, d, J = 4 Hz, H-16 or H-17), 1.33 (3H, d, J = 4 Hz, H-16 or H-17), 1.40−1.47 (2H, m, H-1a and H-6a), 1.62−1.85 (5H, m, H-2, H-3, and H-6e), 2.11 (1H, brd, J = 13 Hz, H-1e), 2.20 (1H, dd, J = 12, 1.2 Hz, 5-H), 2.6−2.8 (2H, m, H-7), 2.96 (1H, sept, J = 7 Hz, H-15), 3.67 (3H, s, H-21), 5.35 (1H, brs, N*H*-12), 6.82 (2H, d, J = 8 Hz, H-23 and H-27), 6.88 (1H, t, J = 7 Hz, H-25), 7.25 (2H, t, J = 8 Hz, H-24 and H-26), 7.28 (1H, s, H-11); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 37.8 (C-1), 18.4 (C-2), 36.4 (C-3), 47.4 (C-4), 44.1 (C-5), 20.6 (C-6), 24.2 (C-7), 120.7 (C-8), 149.7 (C-9), 37.4 (C-10), 121.3 (C-11), 139.7 (C-12), 128.0 (C-13), 152.5 (C-14), 28.4 (C-15), 20.9 (C-16 and C-17), 178.4 (C-18), 16.4 (C-19), 24.7 (C-20), 51.9 (C-21), 144.8 (C-22), 116.3 (C-23 and C-27), 129.4 (C-24 and C-26), 120.2 (C-25); EIMS *m/z* 450 [M^+] (100), 433 (13), 405 (5), 375 (7); *anal*. C 71.93%, H 7.86%, N 5.92%, calcd for $C_{27}H_{34}N_2O_4$, C 71.97%, H 7.61%, N 6.22%.

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