Synthesis and Reactions of 2-Arylhydrazinotropones. II.[1] Synthesis of 5-Aryltropolones and B-Ring-Open Colchicine Analogues via Benzidine Type Rearrangement of 2-(2-Arylhydrazino)tropones[2]

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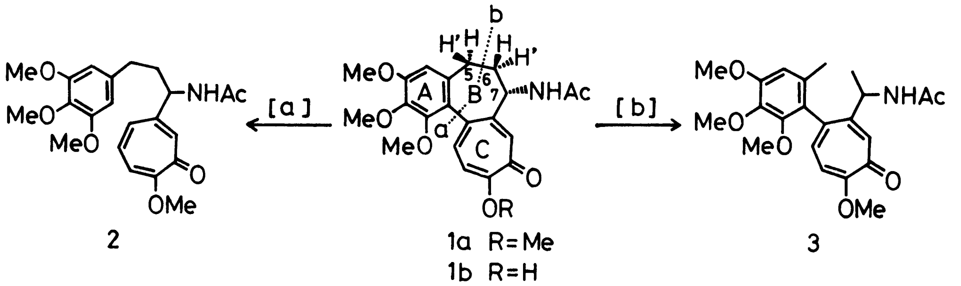
Treatment of a wide variety of 2-(2-arylhydrazino)tropones with ethanolic acid at 50—80°C readily gave the benzidine type rearrangement products, 2-amino-5-(4-aminoaryl)tropones, besides minor amounts of by-products of various type. The main products were conveniently led to the corresponding 5-aryltropolones. Similarly, 2-(2-arylhydrazino)tropones bearing an isopropyl and isopropenyl group at the 4-position afforded 4-substituted 2-amino-5-(4-aminoaryl)tropones as the main products, which were also led to 4-substituted 5-(4-acetamidoaryl)- and 5-(4-methoxyaryl)tropolones. Structural assignments of these products were made on the basis of ^{1}H NMR and other spectral data as well as of chemical transformations to known 5-phenyltropolone and also to 2-acetamido-8-hydroxy-10,10-dimethylcyclohept[*a*]inden-7(10*H*)-one. This synthetic scheme may possibly be utilized for a convenient synthesis of B-ring-open analogues of colchicine.

Colchicine (**1a**), a tricyclic natural troponoid, has attracted considerable attention owing to its marked antimitotic activity.[3] The total synthesis of **1a** has been accomplished so far by more than ten groups.[4] However, as all of these synthetic schemes involve lengthy multisteps and appear to lack general applicability particularly in large scale experiments, exploitation of a general, convenient synthetic method for colchicine analogues has been desired for the study of their structure-activity relationship.[5]

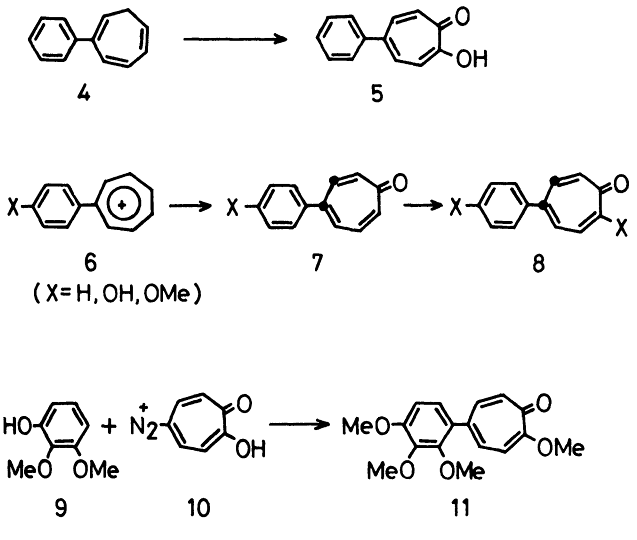
As for antimitotic agents, preparation of two types of the B-ring-open colchicine analogues **2** and **3**, (which can be derived from **1a** by the formal bond-disconnection at [a] and [b], respectively, see Scheme 1), was planned by one of us (T. N.) in order to obtain various information on tublinbinding sites. We have already reported the synthesis of various compounds of type **2**.[6] In the meantime, a synthetic approach for another, potentially useful compounds of type **3**, which are presumed to have a conformation close to that of **1a**, has been made as will be described below.

Although the tropolone nucleus is highly susceptible to various electrophilic substitutions (e.g., nitration, bromination, etc.), it does not undergo the Friedel–Crafts type alkylation and acylation by the usual method.[7,8] The reaction of organolithium or magnesium reagents with tropolones is known to afford C-3 and C-7 substitution products.[9] Thus, as for the preparation of 5-aryltropolones, only a few synthetic methods have been reported so far (see Scheme 2). Namely, 1) the permanganate oxidation of phenyltropilidene (**4**, derived from biphenyl) to give 5-phenyltropolone (**5**) in an extremely low overall yield (0.09%),[10] 2) the two-step conversion (amination and then hydrolysis) of a mixture of 4- and 5-phenyltropones (**7**, derived from phenyltropylium ion



Scheme 1.

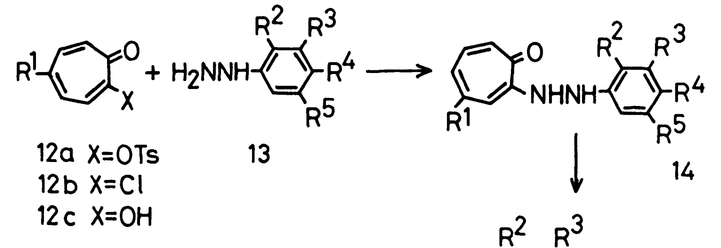
Present addresses: a) Sachigaoka, Asahi-ku, Yokohama-shi 241. b) Yanbian University, Yanji, Jilin, China. c) Koei Chemical Co., Ltd., Osaka 536. d) Fuji Photo Film Co., Ltd., Fujinomiya 418. e) Tosoh Co., Ltd., Shin-Nanyo-shi 746.

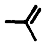


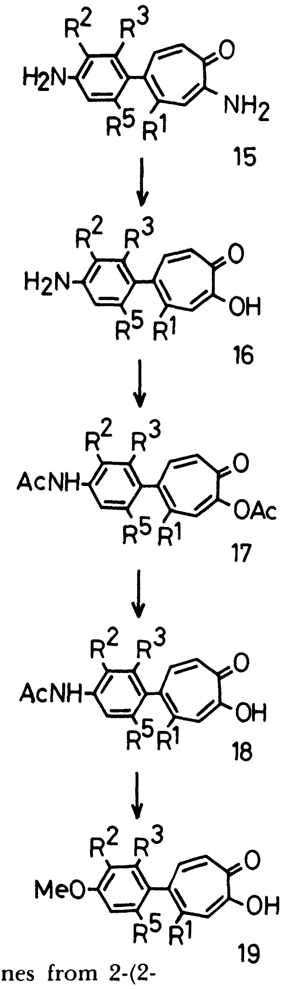
Scheme 2.

6)[11] to give, e.g., 2-methoxy-5-(4-methoxyphenyl)-tropone (**8**, X=OMe),[12] and 3) the thermolysis of 5-diazoniotropolone (**10**) either in benzene alone[7a] or in the presence of 2,3-dimethoxyphenol (**9**) to afford, after methylation, 2-methoxy-5-(2,3,4-trimethoxyphenyl)-tropone (**11**) (which exhibited an appreciable antimitotic activity).[3b,5a] However, all of these procedures have drawbacks either with respect to the low preparative yield or the regioselective control.[13] Thus, virtually no efficient, direct synthetic scheme has been established so far for preparation of 5-aryltropolones and much less tropolones having carbon substituents at both 4- and 5-positions.[13b]

Around 1973, Y. Sugimura[14] of Sankyo Co. (Tokyo) found that the treatment of some of 2-(2-phenylhydrazino)tropones **14** (see Scheme 3) with dilute hydrochloric acid readily afforded major products which he presumed to be derived through a benzidine-type



13-34	R1	R2	R3	R4	R5
a	H	H	H	H	H
b	H	Me	H	H	H
c	H	H	Me	H	H
d	H	H	H	Me	H
e	H	OMe	H	H	H
f	H	H	OMe	H	H
g	H	OMe	OMe	H	H
h	H	OMe	OMe	H	Me
i	H	Cl	H	H	H
j	H	H	Cl	H	H
k	H	NO2	H	H	H
l	H	H	NO2	H	H
m	H	H	H	NO2	H
n	i-Pr	H	H	H	H
o		H	H	H	H
p	"	Me	H	H	H
q	"	H	Me	H	H
r	"	OMe	H	H	H
s	"	H	OMe	H	H
t	"	OMe	OMe	H	H
u	"	OMe	OMe	H	Me



Scheme 3. Synthesis of 5-aryltropolones from 2-(2-arylhydrazino)tropones.

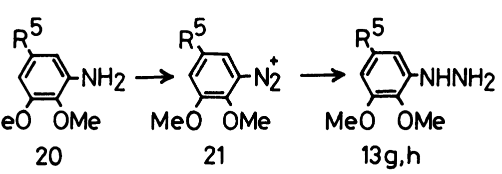
rearrangement. However, before establishing the precise structures of these products, the Sankyo research group had to interrupt this project for various reason and entrusted it to one of us (T. N.), who undertook further investigation in cooperation with the Tohoku Univ. research group. The structures of some of these acid-catalyzed products were then proved[2a] to be 2-amino-5-(4-aminophenyl)tropone (**15a**) and corresponding 5-(4-aminophenyl)tropones. Because of the Tohoku group's concentration on other research projects, the further study on this reaction was later carried out in cooperation with the Okayama and Kumamoto Univ. research groups.

We now wish to describe in this paper our detailed but frequently interrupted studies on this novel benzidine type rearrangement of a wide variety of 2-(2-arylhydrazino)tropones (aryl stands for substituted phenyls or 1-naphthyl hereafter) with or without a carbon-substituent at the 4-position to give 4-substituted (or unsubstituted) 2-amino-5-(4-aminoaryl)-tropones, which can be readily led to various 5-aryltropolones. This method is expected to be applicable to a convenient synthesis of analogues of colchicine (**1a**), such as those of type **3**.

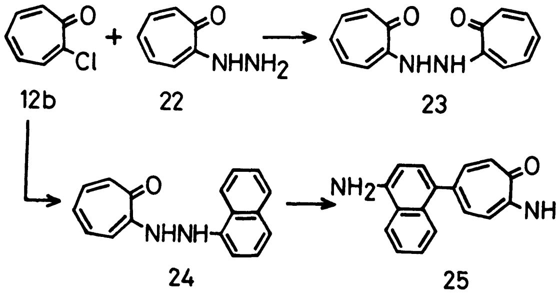
Results and Discussion

Preparation of 2-(2-Arylhydrazino)tropones. We have recently reported[1] a series of 2-(2-phenylhydrazino)tropones **14** available by the condensation of 2-tosyloxytropone (**12a**) with substituted phenylhydrazines **13** (Scheme 3). The preparations of some of the 2-(2-phenylhydrazino)tropones, **14a—d**, **14l**, and **14m**, have also been investigated presently by using another reactive troponoid, 2-chlorotropone (**12b**), but the yields were found to be somewhat less satisfactory for most of these products compared with the case[1] from **12a**. Thus, in order to closely examine the benzidine-type rearrangement of **14** we have prepared a variety of 2-(2-phenylhydrazino)tropones **14a—u** by the reaction of **12a** with **13a—m** (among which **13g** and **13h** were newly prepared from 2,3-dimethoxyanilines **20** via diazonium compounds **21**, see Scheme 4 and the Experimental section).

In addition, for a further examination of the scope of the rearrangement of 2-(2-arylhydrazino)tropone system other than phenyl ring in the moiety, we have also prepared 2,2′-hydrazobis(tropone) (**23**) and 2-[2-(1-naphthyl)hydrazino]tropone (**24**) by the reaction of **12b** with 2-hydrazinotropone (**22**) and 1-naphthylhydrazine, respectively (Scheme 5). Physical data for these new 2-hydrazinotropones are described in the Experimental section and are consistent with their structures.



Scheme 4. Preparation of 2,3-dimethoxyphenylhydrazines. For R^5 of **13g**, **h**, see Scheme 3.

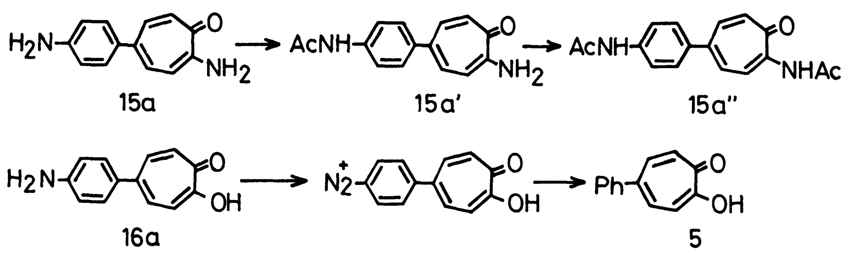


Scheme 5.

The Benzidine Type Rearrangement of 2-(2-Arylhydrazino)tropones and Reactions of the Rearranged Products. It was then found that the rearrangement was best effected, in most cases, by heating the arylhydrazinotropones **14a—u** at 50—80 °C in a ca. 1:10 mixture of 2 M hydrochloric acid (1 M=1 mol·dm^{-3}) and ethanol for 1—72 h under an inert atmosphere. The reactants were purified by recrystallization and/or silica-gel chromatography to yield 2-amino-5-(4-aminoaryl)tropones **15a—u** and other minor products **29—34** (see later), except for the case of the 2-(*p*-substituted phenylhydrazino)tropones **14d** and **14m**; the latter (**14m**) remained unchanged, while the former (**14d**) gave a mixture of several, air-sensitive products.[15] 2-[2-(1-Naphthyl)hydrazino]-tropone (**24**) similarly underwent the rearrangement to give 2-amino-5-(4-amino-1-naphthyl)tropone (**25**), whereas 2,2′-hydrazobis(tropone) (**23**) remained unchanged under the same acidic conditions (Scheme 5). The diamino compounds **15** stepwisely gave the monoacetyl and diacetyl derivatives as exemplified by treatment of **15a** with acetic anhydride in dichloromethane and in pyridine to give **15a′** and **15a″**, respectively (see Scheme 6).

Alkaline hydrolysis of **15** in ethanolic 2 M KOH under reflux for 10 h afforded 5-(4-aminophenyl)tropolones **16** (Scheme 3). As the 4-substituted 2-amino-5-(4-aminophenyl)tropones **15n—u** and tropolones **16n—u** were in general too air-sensitive to be isolated as pure compounds, they were immediately led to the *N*,*O*-diacetyl derivatives[16] **17n—u** and then 5-(4-acetamidophenyl)tropolones **18n—u** for characterization.

Structures of these newly isolated products **15—18** were established by spectroscopy [UV, IR, ^{1}H NMR, MS, and ^{13}C NMR (for some compounds, particularly **15a—c** and **25** in comparison with the spectra of the corresponding starting materials **14** and **24**)] and elemental analysis; their exact data and the rational assignments for the spectral parameters are described in the Experimental section. Yield of each product of



Scheme 6.

Table 1. Isolated Yields/% of 2-Amino-5-aryltropones **15**, **25**, 5-Aryltropolones **16**, **18**, Acetates **17**, and By-Products **29**—**34**

Starting material	**15**(**17**)[a)]	**29**	Other product[b)]	**16**(**18**)[c)]
14a	78(55)	5		96
14a[d)]	91			
14a[e)]	—		**30** (1.5) **31** (5)	
14b	89			95
14c	87	10		98
14e	48		**32** (19)	87
14f	77	20		90
14g	34			67
14h	35			75
14i	77		**30** (2)	97
14j	79	17	**33** (1)	96
14k[f)]	39		**34** (6)	50
14l[f)]	49	5		71
14l[g)]	33	5	**34** (17)	
14n	(91)			(86)
14o	(72)			(94)
14p	(85)			(100)
14q	(70)			(78)
14r	(48)			(96)
14s	(40)			(72)
14t	(30)			(92)
14u	(33)[h)]			(93)
24			**25** (92)	

a) The value in parentheses is the overall yield of **17** from **14** (via **15** and **16**). b) Yield of each compound is shown in parentheses. c) The value in parentheses is the yield of **18** from **17**. d) Reaction time: 3.5 h. e) Reaction time: 10 min. f, g) The reaction was conducted in 3:2 dioxane–water and in 1-butanol, respectively (see the Experimental section). h) The value is for a mixture (3:2) of **17u** and **17u′**.

the above reactions is listed in Table 1.

The 4-aminophenyl substituent in **15** and **16** was confirmed to be on 5-position by converting a representative product **16a** into known 5-phenyltropolone[10,11] (**5**) upon treatment with nitrous acid, followed by reduction with phosphinic acid (Scheme 6). The unequivocal assignments of the isopropyl and isopropenyl groups of the rearranged products to the 4-position were based on the careful analysis of the 500 (or 200) MHz ^{1}H NMR data of **17** and **18n**—**u**, by taking into account the well-resolved parameters obtained presently for structurally related compounds, such as **1a**, colchiceine (**1b**), and tropolone itself (**12c**) (see Table 2). Characteristic features in the δ and J values for the representative examples of these 4,5-disubstituted tropolones **17** and **18** are summarized in Table 2, and these values have been effectively utilized in precisely determining the positions of substituents for the rest of the polysubstituted tropolones.

The conversion of the 4-acetamido group on the phenyl ring of **18** into 4-methoxyphenyl derivatives is exemplified by the transformations into **19n**, **p**, **q**, **u** upon treatment with ethanolic 1 M HCl under reflux and then with nitrous acid in aq methanol, followed by methylation with dimethyl sulfate in 1 M NaOH (Scheme 3).

Attempts to convert the 4-isopropyl and isopropenyl groups of **18** and **19** into the corresponding acetyl derivatives for the purpose of further manipulation[2b,6] of the functional group to suit more colchicine-like compounds have so far remained unsuccessful (Scheme 7). Namely, the selective ozonolysis of the isopropenyl group of **18o**, **p** was found to cause only profound decomposition in contrast to the successful conversion of 5-isopropenyltropolone to 5-acetyltropolone.[17] In order to obtain

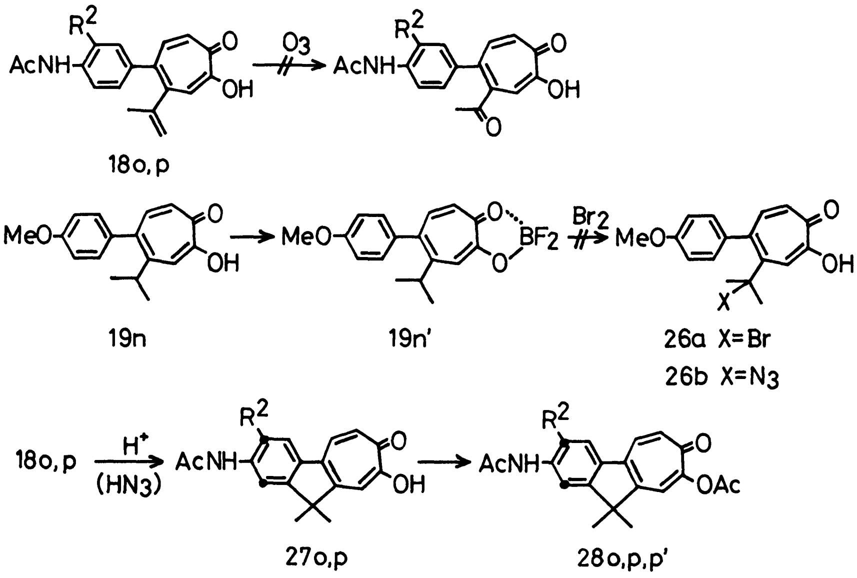
Table 2. ^1H NMR (500 MHz) Parameters for Representative 4-Substituted 5- and 7-Aryltropolones and Their Acetates in $CDCl_3$[a]

Compd	HO-2 (AcO-2)	H-3	Me–C-4 (H_2C=C-4)	H-5	H-6
1a[b,c]	4.00[d]	7.49	e)	—	7.32 $J_{6,7}=10.9$
1b[b,c]	1.8	7.52	f)	—	7.57 $J_{6,7}=12.0$
12c	9.1	7.345 $J_{3,4}=11.3$	7.395 $J_{4,5}=9.3$	7.04 $J_{3,5}=1.3$	7.395 $J_{3,6}=0.8$
18r	1.6	7.43	1.60 (5.06, 5.08)	—	7.42 $J_{5,6}=12.0$
18s[h]	1.6	7.38	1.70[i] (4.85, 4.90[i])	—	7.34 $J_{6,7}=11.5$
17u	(2.38)	7.23	1.71[i] (4.85,[i] 4.87)	—	7.15 $J_{6,7}=12.0$
18u	1.6	7.36	1.74 (4.84, 4.85)	—	7.27 $J_{6,7}=11.6$
17u′	(2.27)	7.48 $J_{3,5}=1.7$	2.17[j] (5.33,[j] 5.46)	7.14 $J_{5,6}=9.8$	7.20
18u′	1.6	7.57 $J_{3,5}=1.7$	2.20[j] (5.34,[j] 5.45)	7.13 $J_{5,6}=10.7$	7.28

Compd	H-7	H-2′ (MeO-2′)	H-3′ (MeO-3′)	AcN-4′ (MeO-4′)	H-5′	H-6′ (Me-6′)
1a[b,c]	6.85	(3.65)	(3.94)	(3.90)	6.53	e)
1b[b,c]	7.33	(3.63)	(3.93)	(3.90)	6.55	f)
12c	7.345					
18r	7.27	6.84 $J_{2',6'}=1.7$	(3.86)	2.23 7.78[g]	8.36 $J_{5',6'}=8.3$	6.92
18s[h]	7.26	(3.73)	7.50 $J_{3',5'}=2.0$	2.20 7.24[g]	6.85 $J_{5',6'}=8.0$	7.03
17u	7.00	(3.66)	(3.83)	2.22 7.76[g]	8.02	(2.06)
18u	7.22	(3.61)	(3.89)	2.22 7.77[g]	8.01	(2.02)
17u′	—	(3.67)	(3.89)	2.22 7.74[g]	8.02	(2.05)
18u′	—	(3.65)	(3.91)	2.23 7.77[g]	8.08	(2.09)

a) Chemical shifts are δ values and coupling constants (J) in Hz (see the Experimental section). The δ value without J indicates either the absence of coupling with other protons or only a small magnitude of J (<ca. 0.5 Hz). b) Although approximate or inadequate data for **1a** (at 270 MHz) and **1b** (at 60 MHz) were reported (Ref. 6f), more accurately resolved, reliable parameters obtained at 500 MHz are shown here. c) The numbering of the A and C rings of **1a** and **1b** corresponds to that of **17** and **18** for the purpose of comparison. d) For MeO-1. e) The proton signals on the B ring (note the numbering of these protons are shown in the formula **1a**): δ=1.86 (1H, brtd, $J_{6,6'}=11.9$, $J_{6',7}=11.8$, $J_{5,6'}=6.6$, $J_{5',6'}\simeq1.3$ Hz, H-6′), 1.98 (3H, s, AcN-7), 2.28 (1H, brsept, $J_{5,6}=12.7$, $J_{6,7}=6.6$, $J_{5',6}=6.5$ Hz, H-6), 2.40 (1H, brtd, $J_{5,5'}=13.7$ Hz, H-5), 2.53 (1H, brdd, H-5′), 4.64 (1H, brdt, $J_{7,NH}=6.7$ Hz, H-7), and 7.02 (1H, brd, HN-7). f) The proton signals on the B ring (note the numbering of these protons are shown in the formula **1b**): δ=1.90 (1H, brsept, $J_{6,6'}=12$, $J_{6',7}=12$, $J_{5,6'}=6.5$, $J_{5',6'}\simeq4$ Hz, H-6′), 2.03 (3H, s, AcN-7), 2.29 (1H, brsept, $J_{5,6}=12$, $J_{6,7}=6.5$, $J_{5',6}=6$ Hz, H-6), 2.34 (1H, brtd, $J_{5,5'}=13$ Hz, H-5), 2.52 (1H, brdt, H-5′), 4.66 (1H, brdt, $J_{7,NH}=6$ Hz, H-7), and 6.21 (1H, brd, HN-7). g) For HN-4′. h) Measured at 200 MHz. i) $J\simeq1.4$ Hz. j) $J\simeq0.8$ Hz.

4-(1-azido-1-methylethyl) derivatives (e.g., **26b**) to effect the Schmidt-type reaction[17,18] (to give the corresponding 4-acetyl compounds), preparation of the bromo derivative **26a** was first sought by converting **19n** to the difluoroborane complex **19n′** and then by treatment with bromine under a tungsten light. However, **19n′** did not give **26a** but remained unchanged, most likely owing to the steric congestion around the 4-isopropyl side chain. On the other hand, the treatment of **18o, p** with sodium azide-concd sulfuric acid in chloroform resulted in, instead of the anticipated rearrangement to yield the acetyl derivatives,[17] a surprisingly facile ring closure to give indenotropolones (cyclohept[*a*]inden-7(10*H*)-one derivatives) **27o, p** (Scheme 7), which were led to acetates[16] **28o—p′** for characterization (see the Experimental section). The intramolecular cyclization was confirmed to readily proceed in the absence of sodium azide at room temperature, further supporting the neighboring positions of the aryl and isopropenyl

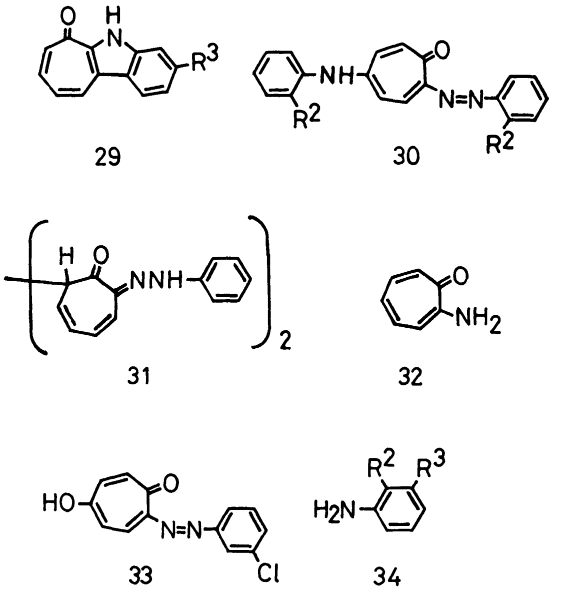


Scheme 7. Attempted preparations of 4-acetyl-5-aryltropolones. For R^2 of **18**, **27**, and **28o**, **p**, see Scheme 3.

groups on the tropolone ring in **18o**—**u**.

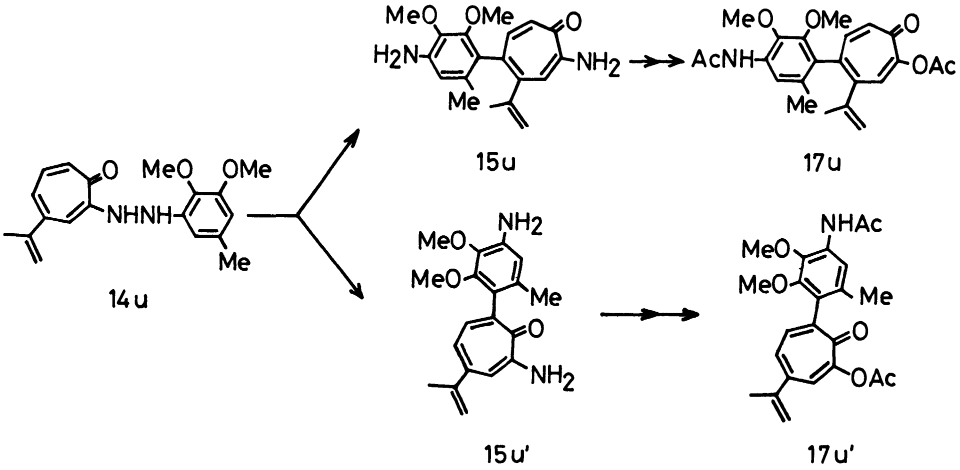
It is noteworthy that the rearrangement reactions of **14** resulted in the formation of minor amounts of by-products of various types. These were intensively studied in detail for the reactions of 2-(2-phenylhydrazino)tropones **14a**—**m**, and the following compounds were isolated (see Scheme 8):[15] a) The 3,*o*-type rearrangement products, indolotropones (6*H*-cyclohept[*b*]indol-6-one derivatives) **29**; b) the 5-semidine type rearrangement products, 5-anilino-2-arylazotropones **30**; c) the oxidative dimeric compound, 6,6′-bis(phenylhydrazono)-1,1′-[bi-2,4-cycloheptadien-1-yl]-7,7′-dione (**31**);[1] d) miscellaneous products, 2-aminotropone (**32**),[18] 2-arylazo-5-hydroxytropone (**33**), and *o*-[20] and *m*-nitroanilines[21] (**34**) (see Table 1 for yield of each compound).

Moreover, by a careful, chromatographic separation (after the alkaline hydrolysis and acetylation) of the reaction products of 2-[2-(2,3-dimethoxy-5-methylphenyl)hydrazino]-4-isopropenyltropone (**14u**), we isolated, besides the major 5,*p*-rearranged product **17u**, a minor amount of a by-product, whose structure was proved to be the 7,*p*-rearranged compound **17u′** by MS and ^{1}H NMR spectroscopy (see Scheme 9 and Table 2). It is noted that the signals due to 4-isopropenyl group in **17u′** were appreciably shifted to the downfield (ca. 0.5 ppm) from the corresponding signals of **17u** and appeared at δ 2.3 and 5.3—5.4 that coincide with the δ values of 4-isopropenyl group of β-dolabrin acetate,[22] thus supporting the assignment of the phenyl ring of **17u′** at the 7-position. This in turn shows the formation of a minor proportion of the corresponding 2-aminotropone **15u′** (Scheme 9) by the rearrangement of **14u**. Both **15u** and **15u′**, however, quickly turned into a dark tar during the attempted purification.



Scheme 8. Minor products of the rearrangement reaction. For R^2 and R^3 of **29**, **30**, and **34**, see Scheme 3.

Other remarks that would closely relate to the aspect of the reaction mechanism are as follows: 1) The presence of electron-donating substituents on the phenyl ring in **14** tends to accelerate the rearrangement, whereas that of an electron-withdrawing group markedly suppresses the reaction. 2) The rearrangement of **14o** proceeds much more smoothly than **14n**, suggesting that the presence of an electron-withdrawing group on the tropone ring of **14** appears to accelerate the reaction. 3) When substituent(s) is present at 3- (and 5-) position of the phenyl ring of **14**



Scheme 9. The 5,*p*- and 7,*p*-rearrangement of **14u**.

and becomes bulkier, the yield of the product **15** tends to decrease and the amount of by-products increases.[15]

Closer studies on the rearrangement products using more variety of 2-arylhydrazinotropones of type **14**, particularly in connection with precursors bearing suitable substituents (e.g., R^1=CH(Me)NHAc and R^5=Me), are in progress.[15] Nevertheless, these findings in the present rearrangement are believed to be of value from the viewpoint of the development of the fundamental chemistry of troponoids,[7] and also to give important suggestions on further clarification of the reaction mechanism of benzidine rearrangement in general, which is still considered to contain certain ambiguity in many respects.[23] Moreover, present work demonstrates an effective way for preparation of a wide range of 5-aryltropolones having carbon-substituents at 4-position that are otherwise hardly available, and this methodology is expected to be useful in the development of a new, convenient route to colchicine analogues.

Experimental

Melting points were determined with a Thomas Hover MR or Yanagimoto MP-S3 instrument and are uncorrected. All reactions were monitored by TLC (Merck silica gel 60F, 0.25 mm) with an appropriate solvent system (mostly with MeOH-$CHCl_3$, $CHCl_3$-AcOEt, and/or AcOEt–hexane). Preparative TLC and column chromatography were performed with Merck Kiesel Gel 60G and Wako C-200 silica gel, respectively. Yields of products **15**—**18** and **29**—**34** are given in Table 1. The UV spectra were recorded in MeOH with a Hitachi EPS-3T spectrophotometer. The IR spectra were taken as KBr disk (unless otherwise stated) with a Shimadzu IR-27G, Hitachi 215, or JASCO A-102 spectrometer. The ^{1}H NMR spectra were measured in $CDCl_3$ (unless otherwise stated) with a Hitachi R24, R24B, or R-600 (60 MHz), Varian HA-100 (100 MHz), JEOL-FX200 (200 MHz) or Varian VXR-500 instrument (500 MHz, the SC-NMR Lab., Okayama Univ.) at 27 °C. Chemical shifts are recorded as δ values relative to tetramethylsilane as the internal standard measured at 60 MHz (unless otherwise stated). The assignments of all signals were made by employing a first-order analysis with the aid of decoupling technique and the parameters were confirmed by a computer-assisted simulation analysis. ^{13}C NMR spectra were recorded with a JEOL FX-100 (25 MHz) in DMSO-d_6. Mass spectra were taken on a Hitachi M-52 low-resolution or JEOL JMX-HX100 (with a JEOL JMA-DA5000 mass data system) high-resolution instrument and are given in terms of m/z (rel intensity) compared with the base peak.

Preparation of 2,3-Dimethoxy- (13g) and 2,3-Dimethoxy-5-methylphenylhydrazine (13h).[24] 2,3-Dimethoxyaniline[25] (15.9 g) was added dropwise to an ice-cooled 6 M HCl (40 cm^3), and then a solution of sodium nitrite (7.4 g) in water (20 cm^3) was added at 0—5 °C over a period of 30 min. Stirring was continued for 30 min at this temp. A solution of tin(II) chloride (110.6 g) in concd HCl (120 cm^3) was added at 0—5 °C over a period of 2 h. The mixture was stirred for 1 h at this temp and poured into an ice-cooled solution of NaOH (125.4 g) in water (314 cm^3). Black precipitates were filtered off and the filtrate was extracted with benzene. The combined organic layers were dried (Na_2SO_4) and concentrated in vacuo. The residue was distilled to give **13g** as pale yellow crystals (12.3 g, 75% yield): bp 122—124 °C/2 Torr (1 Torr=133.322 Pa), mp 78—82 °C; IR (neat) 3350 cm^{-1} (NH); ^{1}H NMR δ=3.72, 3.78 (3H each, 2s, MeO-2,3), 3.07—4.37 (3H, brm, $NHNH_2$), and 6.20—7.11 (3H, m, ArH*), *Aromatic H.

Anal. ($C_8H_{12}N_2O_2$) C, H, N.

Similar procedures starting with 2,3-dimethoxy-5-methylaniline[26] (20.9 g) afforded **13h** as a yellow viscous oil (16.1 g, 71%): bp 133—134 °C/3 Torr; IR (neat) 3400—3300 cm^{-1}; ^{1}H NMR δ=2.23 (3H, s, Me-5), 3.74, 3.80 (3H each, 2s, MeO-2,3), and 6.07—6.73 (2H, m, ArH).

Anal. ($C_9H_{14}N_2O_2$) C, H, N.

General Procedure for the Preparation of 2-(2-Arylhydrazino)tropones 14a—d, 14k, 14m, 23, and 24 from 2-Chlorotropone (12b). To a mixture of arylhydrazine **13** (1.2 mmol) and triethylamine (1.2 mmol, or 2.2 mmol when the arylhydrazine hydrochloride was used) in methanol (1 cm^3) was added **12b** (1.0 mmol) in methanol (2 cm^3) under nitrogen at room temp, and then the mixture was gently refluxed for 1.5—20 h; when the starting materials were not soluble enough in MeOH alone, a certain amount of tetrahydrofuran (THF) was added as a co-solvent.

When the starting material **12b** almost disappeared (by TLC), the solvent was evaporated in vacuo. The residue was diluted with cold brine and extracted with $CHCl_3$ or CH_2Cl_2 (AcOEt or THF, if necessary). The combined organic layers were dried (Na_2SO_4) and evaporated in vacuo. The residue (when it was a solid) was recrystallized from an appropriate solvent (see below) to give the corresponding product; the filtrate was concentrated in vacuo and the residue was chromatographed in a column of silica gel, giving an additional amount of the product.

2-(2-Phenylhydrazino)tropone[27,28] **(14a).** Yellow prisms (48% yield from **12b** and **13a**, cf. Ref. 1, 66% yield using **12a**); mp 168 °C (from benzene, lit,[27] mp 168 °C); UV $\lambda_{\max}$ 246 ($\log \varepsilon$ 4.52), 335 (4.04), and 400 nm (4.05); IR 3270 (NH) and 1598 cm^{-1} (C=O); ^{1}H NMR (100 MHz, DMSO-d_6) δ=6.6—7.4 (10H, m, ArH), 8.1 (1H, brm, NH-1′), and 9.0 (1H, brm, NH-2); ^{13}C NMR δ=109.3 (C-3), 112.3 (C-2′, 6′), 119.4 (C-4′), 123.3 (C-5), 129.3 (C-3′, 5′), 130.3 (C-7), 136.4 (C-4), 137.1 (C-6), 147.1 (C-1′), 156.2 (C-2), and 176.2 (C-1); MS m/z 212 (M$^+$; 78.5), 105 (4), 93 (100), and 77 (17).

2-[2-(*o*-Tolyl)hydrazino]tropone (14b): Yellow prisms (40% yield from **12b** and **13b** hydrochloride, cf. Ref. 1, 82% yield using **12a**); mp 90—91 °C (from benzene); UV $\lambda_{\max}$ 246 ($\log \varepsilon$ 4.25), 335 (3.78), and 400 nm (3.76); IR 3270, 3250 (NH), and 1590 cm^{-1} (C=O); ^{1}H NMR (100 MHz, DMSO-d_6) δ=2.26 (3H, s, Me-2′), 6.4—7.5 (9H, m, ArH), 7.59 (1H, brs, NH-1′), and 8.98 (1H, brs, NH-2); ^{13}C NMR δ=17.4 (Me-2′), 109.2 (C-3), 110.7 (C-6′), 119.5 (C-4′), 122.3 (C-2′), 123.1 (C-5), 126.7 (C-3′), 129.9 (C-5′), 130.3 (C-7), 136.4 (C-4,6), 145.2 (C-1′), 156.7 (C-2), and 176.0 (C-1); MS m/z 226 (M$^+$; 100), 107 (95), and 106 (80).

Anal. ($C_{14}H_{14}N_2O$) C, H, N.

2-[2-(*m*-Tolyl)hydrazino]tropone (14c): Yellow prisms (57% yield from **12b** and **13c** hydrochloride, cf. Ref. 1, 72% yield using **12a**); mp 148 °C (from benzene); UV $\lambda_{\max}$ 246 ($\log \varepsilon$ 4.37), 358 (4.05), and 400 nm (3.91); IR 3300, 3240 (NH), 1600, and 1590 cm^{-1} (C=O); ^{1}H NMR (100 MHz, DMSO-d_6) δ=2.18 (3H, s, Me-3′), 6.48 (1H, brd, $J_{4',5'}$=8 Hz, H-4′), 6.52 (1H, brs, H-2′), 6.56 (1H, brd, $J_{3,4}$=10 Hz, H-3), 6.6—7.1 (1H, m, H-5), 6.67 (1H, brd, $J_{5',6'}$=8 Hz, H-6′), 6.87 (1H, brt, H-5′), 7.00 (1H, brd, $J_{6,7}$=11.5 Hz, H-7), 7.24 (1H, brt, $J_{4,5}$=10.0, $J_{4,6}$=1.5 Hz, H-4), 7.28 (1H, ddd, $J_{5,6}$=9.5 Hz, H-6), 8.0 (1H, brs, NH-1′), and 9.0 (1H, brs NH-2); ^{13}C NMR δ=21.1 (Me-3′), 109.2 (C-3), 109.8 (C-2′), 112.8 (C-6′), 120.0 (C-4′), 123.2 (C-5), 129.0 (C-5′), 130.0 (C-7), 136.3 (C-4,6), 138.1 (C-3′), 147.6 (C-1′), 156.1 (C-2), and 176.0 (C-1); MS m/z 226 (M$^+$; 73.4) and 106 (100).

Anal. ($C_{14}H_{14}N_2O$) C, H, N.

2-[2-(*p*-Tolyl)hydrazino]tropone (14d): Yellow needles (53% yield from **12b** and **13d** hydrochloride, cf. Ref. 1, 63% yield using **12a**); mp 162—164 °C (from benzene); UV $\lambda_{\max}$ 245 ($\log \varepsilon$ 4.60), 335 (4.12), and 402 nm (4.10); IR 3260 (NH) and 1600 cm^{-1} (C=O); ^{1}H NMR (100 MHz, DMSO-d_6) δ=2.30 (3H, s, Me-4′), 5.7 (1H, brm, NH-1′), 6.6—7.4 (9H, m, ArH), and 8.3 (1H, brm, NH-2); MS m/z 226 (M$^+$; 100), 107 (80), and 106 (91).

Anal. ($C_{14}H_{14}N_2O$) C, H, N.

2-[2-(*m*-Nitrophenyl)hydrazino]tropone (14k): Yellow prisms (53% yield from **12b** and **13k**, cf. Ref. 1, 62% yield using **12a**); mp 188—190 °C (from $CHCl_3$–benzene); UV $\lambda_{\max}$ 246 ($\log \varepsilon$ 4.75), 335 (4.25), and 398 nm (4.28); IR 3260 (NH) and 1600 cm^{-1} (C=O); ^{1}H NMR (100 MHz, DMSO-d_6) δ=6.6—7.7 (9H, m, ArH), 8.7 (1H, brs, NH-1′), and 9.3 (1H, brs, NH-2); MS m/z 257 (M$^+$; 100), 138 (13), and 121 (7).

Anal. ($C_{13}H_{11}N_3O_3$) C, H, N.

2-[2-(*p*-Nitrophenyl)hydrazino]tropone (14m): Yellow prisms (53% yield from **12b** and **13m**, cf. Ref. 1, 51% yield using **12a**); mp 185 °C decomp (from benzene); UV $\lambda_{\max}$ 243 ($\log \varepsilon$ 4.26), 340 (4.01), and 398 nm (4.09); IR 3300, 3200 (NH), and 1600 cm^{-1} (C=O); ^{1}H NMR (100 MHz, DMSO-d_6) δ=6.75 (2H, brd, J=9 Hz, H-2′,6′), 6.755 (1H, brd, $J_{3,4}$=10 Hz, H-3), 6.76 (1H, brdd, $J_{4,5}$=10, $J_{5,6}$=9 Hz, H-5), 7.03 (1H, brd, $J_{6,7}$=11.5 Hz, H-7), 7.26 (1H, brt, H-4), 7.34 (1H, brdd, H-6), 8.08 (2H, brd, J=9 Hz, H-3′,5′), 9.31 (1H, brs, NH-1′), and 9.4 (1H, brs, NH-2); MS m/z 257 (M$^+$; 100) and 138 (5).

Anal. ($C_{13}H_{11}N_3O_3$) C, H, N.

2,2′-Hydrazobis(tropone) (23): Pale yellow crystals (70% yield from **12b** and **22**); mp 190 °C (from $CHCl_3$–benzene); UV $\lambda_{\max}$ 245 ($\log \varepsilon$ 4.58), 336 (4.16), and 404 nm (4.27); IR 3300 (NH), 1610, and 1590 cm^{-1} (C=O); ^{1}H NMR (100 MHz, DMSO-d_6) δ=6.60 (2H, brd, $J_{3,4}$=9.5 Hz, H-3), 6.77 (2H, brdd, $J_{4,5}$=10.0, $J_{5,6}$=8.5 Hz, H-5), 7.06 (2H, brd, $J_{6,7}$=11.5 Hz, H-7), 7.24 (2H, brdd, H-4), 7.36 (2H, ddd, $J_{4,6}$=1.5 Hz, H-6), and 9.36 (2H, brs, NH-2); MS m/z 240 (M$^+$; 100), 121 (21), and 105 (4).

Anal. ($C_{14}H_{12}N_2O_2$) C, H, N.

2-[2-(1-Naphthyl)hydrazino]tropone (24): Yellow prisms (15% yield from **12b** and 1-naphthylhydrazine); mp 150 °C (from $CHCl_3$–benzene); IR 3300, 3200 (NH), and 1597 cm^{-1} (C=O); ^{1}H NMR (100 MHz, DMSO-d_6) δ=6.55 (1H, dd, J=7, 2.5 Hz, H-2′), 6.65—7.6 (9H, m, ArH), 7.86 (1H, brdd, J=6.5, 3 Hz, H-5′), 8.28 (1H, brdd, J=6.5, 3 Hz, H-8′), 8.70 (1H, m, NH-1′), and 9.25 (1H, brs, NH-2); ^{13}C NMR δ=104.9 (C-2′), 109.1 (C-3), 119.2, 121.5, 122.2 (C-8′a), 123.2 (C-5), 124.6, 126.0, 126.4, 128.1, 130.1 (C-7), 133.9 (C-4′a), 136.6 (C-4), 136.8 (C-6), 142.5 (C-1′), 156.0 (C-2), and 176.1 (C-1); MS m/z 262 (M$^+$; 100), 143 (46), 142 (21), and 105 (27).

Anal. ($C_{17}H_{14}N_2O$) C, H, N.

General Procedure for the Benzidine-Type Rearrangement of 2-(2-Arylhydrazino)tropones 14, 23, and 24. A. Procedure for 14a—f,i,j,m, 23, and 24: A mixture of **14** (or **23** or **24**) (1 mmol) and 2 M HCl (6.3 cm^3, 12.5 mmol) in ethanol (50 cm^3) was heated at 50—80 °C for 1 h (for **14a—f**, **24**), or refluxed for 5—6 h (for **14m**, **23**) or 12 h (for **14i,j**) under nitrogen. The mixture was neutralized with cold 2 M NaOH solution and extracted with ethyl acetate. The extract was washed with water and then with brine. The organic layer was dried (Na_2SO_4) and concentrated. When crystals were separated, they were collected and recrystallized. The filtrate was concentrated and chromatographed on preparative TLC plates (with chloroform, ethyl acetate, or diethyl ether). When no crystals appeared on evaporation of the AcOEt extract, the residue was directly chromatographed.

B. Procedure for 14g,h: A mixture of **14** (0.2 mmol) and 2 M HCl (1.3 cm^3) in ethanol (10 cm^3) was refluxed for 2 h under nitrogen. The reaction mixture was similarly worked up.

C. Procedure for 14k,l: A mixture of **14** (1 mmol) and 2 M HCl (6.3 cm^3) in 3:2 dioxane–water (50 cm^3) was refluxed for 72 h under nitrogen. The reaction mixture was similarly worked up.

D. Procedure for 14l: A mixture of **14l** (1 mmol) and

2 M HCl (6.3 cm^3) in 1-butanol (50 cm^3) was refluxed for 72 h under nitrogen. The reaction mixture was similarly worked up.

E. Procedure for 14n—u: A mixture of a 4-substituted 2-(2-arylhydrazino)tropone **14** (50 mg), ethanol (10 cm^3), and 2 M HCl (2.5 cm^3) was refluxed under nitrogen for 1—3.5 h. When the starting material **14** almost disappeared (by TLC), the mixture was concentrated at 40—50 °C under reduced pressure. When crystals separated, they were filtered off and washed with benzene to give crude **15** (as hydrochloride). This was stirred with cold, saturated aq $NaHCO_3$ under nitrogen and extracted with ethyl acetate, giving unstable **15** after recrystallization. If the hydrochloride of **15** did not precipitate, the reaction mixture was taken to pH 8 with cold 2 M KOH and the solvent was concentrated in vacuo. The residue was extracted with CH_2Cl_2 or AcOEt. The combined organic layers were dried (Na_2SO_4) and evaporated in vacuo to give crude **15n—u**. As these products were not stable enough to be purified, they were immediately subjected to the next step (see later).

2-Amino-5-(4-aminophenyl)tropone (15a): Yellow prisms; mp 203—204 °C (from $CHCl_3$-benzene); UV λ_{max} 240 (log ε 4.44), 375 (4.28), and 402sh nm (4.20); IR 3450, 3300 (NH), and 1610 cm^{-1} (C=O); ^{1}H NMR (100 MHz, DMSO-d_6) δ=5.2 (2H, brs, H_2N-4′), 6.7 (2H, brd, J=8.5 Hz, H-3′,5′), 7.3 (2H, brd, J=8.5 Hz, H-2′,6′), 7.5 (2H, m, H_2N-2), and 6.9—7.8 (4H, m, H-3,4,6,7); ^{13}C NMR δ=113.0 (C-3), 114.5 (C-3′,5′), 127.9 (C-2′,6′), 129.3 (C-7), 129.9 (C-1′), 133.9 (C-4), 136.0 (C-5,6), 148.2 (C-4′), 156.7 (C-2), and 174.6 (C-1); MS m/z 212 (M$^+$; 75.6) and 184 (100).

Anal. ($C_{13}H_{12}N_2O$) C, H, N.

Compound **15a** (50 mg, 0.24 mmol) was treated with acetic anhydride (0.22 cm^3) in 3:5 dichloromethane–benzene (8 cm^3) at 40 °C for 3 h under nitrogen to give 2-amino-5-(4-acetamidophenyl)tropone (**15a′**, 60 mg, 100% yield): Yellow crystals; mp>300 °C; IR 3425, 3250 (NH), 1680 (amide), and 1605 cm^{-1} (C=O); ^{1}H NMR (DMSO-d_6) δ=2.20 (3H, s, AcN), 7.02 (2H, brd, J=9 Hz, H-3′,5′), 7.0—7.8 (8H, m, ArH, H_2N-2), and 10.1 (1H, brm, NH-4′); MS m/z 254 (M$^+$; 100), 212 (5), and 182 (97).

Treatment of **15a′** (21 mg) with Ac_2O-pyridine at 20 °C for 2 h under nitrogen gave 2-acetamido-5-(4-acetamidophenyl)tropone (**15a″**, 24 mg, 97%): Yellow crystals; mp>300 °C; IR 3350, 3250 (NH), 1701, 1678 (amide) and 1600 cm^{-1} (C=O); ^{1}H NMR (DMSO-d_6) δ=2.10 (3H, s, AcN-4′), 2.20 (3H, s, AcN-2), 6.9—8.0 (8H, m, ArH), 9.1, and 9.2 (1H each, brm, 2NH); MS m/z 296 (M$^+$; 80.0), 253 (100), 223 (27), and 184 (57).

2-Amino-5-(4-amino-3-methylphenyl)tropone (15b): Yellow prisms; mp 204 °C (from benzene); UV λ_{max} 244 (log ε 4.56) and 382 nm (4.40); IR 3450, 3325 (NH), 1610, and 1600 cm^{-1} (C=O); ^{1}H NMR (100 MHz, DMSO-d_6) δ=2.14 (3H, s, Me-3′), 4.0 (2H, m, H_2N-4′), 6.70 (1H, brd, J=8.5 Hz, H-5′), 6.9—7.3 (4H, m, H-3,7,2′,6′), 7.32 (2H, brm, H_2N-2), and 7.49 (2H, brdd, J=12, 2 Hz, H-4,6); ^{13}C NMR δ=17.3 (Me-3′), 112.1 (C-3), 114.0 (C-5′), 121.1 (C-3′), 124.3 (C-2′), 128.1 (C-6′), 128.7 (C-7), 130.0 (C-1′), 133.2 (C-4), 135.7 (C-5,6), 145.4 (C-4′), 155.6 (C-2), and 174.2 (C-1); MS m/z 226 (M$^+$; 100) and 198 (75).

Anal. ($C_{14}H_{14}N_2O$) C, H, N.

2-Amino-5-(4-amino-2-methylphenyl)tropone (15c): Yellow prisms; mp 153—155 °C (from benzene); UV λ_{max} 249 (log ε 4.51), 362 (4.15), and 410 nm (4.02); IR 3400—3100 (NH) and 1605 cm^{-1} (C=O); ^{1}H NMR (100 MHz, DMSO-d_6) δ=2.08 (3H, s, Me-2′), 4.99 (2H, brs, H_2N-4′), 6.42 (1H, brd, $J_{5',6'}$=8 Hz, H-5′), 6.46 (1H, brs, H-3′), 6.84 (1H, brd, H-6′), 7.3 (2H, brm, H_2N-2), and 6.9—7.4 (4H, m, H-3,4,6,7); ^{13}C NMR δ=19.8 (Me-2′), 111.3 (C-3,3′), 115.6 (C-5′), 128.0 (C-6′), 129.3 (C-7), 131.3 (C-1′), 134.8 (C-2′), 136.1 (C-5), 136.7 (C-4), 138.4 (C-6), 147.2 (C-4′), 156.7 (C-2), and 174.4 (C-1); MS m/z 226 (M$^+$; 76.6) and 198 (100).

Anal. ($C_{14}H_{14}N_2O$) C, H, N.

2-Amino-5-(4-amino-3-methoxyphenyl)tropone (15e): Yellow prisms; mp 185 °C (from benzene); UV λ_{max} 244 (log ε 3.92) and 387 nm (3.78); IR 3395, 3270 (NH), and 1615 cm^{-1} (C=O); ^{1}H NMR (DMSO-d_6) δ=3.87 (3H, s, MeO-3′), 4.85 (2H, brm, H_2N-4′), 6.5—7.8 (7H, m, ArH), and 7.35 (2H, brm, H_2N-2); MS m/z 242 (M$^+$; 100), 214 (43), 199 (24), 172 (13), and 171 (59).

Found: m/z 242.1063. Calcd for $C_{14}H_{14}N_2O_2$: M, 242.1056.

2-Amino-5-(4-amino-2-methoxyphenyl)tropone (15f): Yellow prisms; mp 185—187 °C (from benzene); UV λ_{max} 245 (log ε 4.64) and 380 nm (4.41); IR 3400, 3245 (NH), and 1605 cm^{-1} (C=O); ^{1}H NMR (DMSO-d_6) δ=3.70 (3H, s, MeO-2′), 5.2 (2H, brm, H_2N-4′), 7.25 (2H, brm, H_2N-2), 7.25—7.45 (7H, m, ArH); MS m/z 242 (M$^+$; 100), 214 (67), and 199 (13).

Anal. ($C_{14}H_{14}N_2O_2$) C, H, N.

2-Amino-5-(4-amino-2,3-dimethoxyphenyl)tropone (15g): Yellow prisms; mp 166—167 °C (from benzene); IR ($CHCl_3$) 3400, 3355 (NH), and 1610 cm^{-1} (C=O); ^{1}H NMR δ=3.66 (3H, s, MeO-2′), 3.92 (3H, s, MeO-3′), 6.09 (2H, brm, H_2N-4′), 6.55 (1H, d, $J_{5',6'}$=9Hz, H-5′), 6.89 (1H, d, H-6′), 6.96 (1H, d, $J_{6,7}$=11 Hz, H-7), 7.15—7.65 (3H, m, ArH), and 7.35 (2H, brm, H_2N-2); MS m/z 272 (M$^+$; 100), 244 (63), and 229 (6).

Found: m/z 272.1176. Calcd for $C_{15}H_{16}N_2O_3$: M, 272.1161.

2-Amino-5-(4-amino-2,3-dimethoxy-6-methylphenyl)tropone (15h): Yellow prisms; mp 120—122 °C (from benzene); IR ($CHCl_3$) 3380, 3350 (NH), and 1610 cm^{-1} (C=O); ^{1}H NMR δ=2.00 (3H, s, Me-6′), 3.59 (3H, s, MeO-2′), 3.85 (3H, s, MeO-3′), 6.30 (2H, brm, H_2N-4′), 6.42 (1H, s, H-5′), 6.95—7.2 (4H, m, ArH), and 7.35 (2H, brm, H_2N-2); MS m/z 286 (M$^+$; 100), 271 (8), 254 (45), and 243 (11).

Found: m/z 286.1321. Calcd for $C_{16}H_{18}N_2O_3$: M, 286.1317.

2-Amino-5-(4-amino-3-chlorophenyl)tropone (15i): Yellow prisms; mp 230 °C decomp (from ethanol), UV λ_{max} 245 (log ε 4.49) and 378 nm (4.37); IR 3330, 3205 (NH), and 1610 cm^{-1} (C=O); ^{1}H NMR (DMSO-d_6) δ=5.35 (2H, brm, H_2N-4′), 6.90 (1H, brd, $J_{5',6'}$=8.5 Hz, H-6′), 7.0—7.7 (6H, m, ArH), and 7.45 (2H, brm, H_2N-2); MS m/z 248 (M+2; 31), 246 (M$^+$; 92), 220 (34), 218 (100), 182 (13), 154 (11), 109 (19), and 91 (25).

Found: m/z 246.0560. Calcd for $C_{13}H_{11}N_2OCl$: M, 246.0560.

2-Amino-5-(4-amino-2-chlorophenyl)tropone (15j): Yellow prisms; mp 161—162 °C (from chloroform); UV λ_{max} 248 (log ε 4.11) and 363 nm (3.86); IR 3345 (NH) and 1605 cm^{-1} (C=O); ^{1}H NMR (DMSO-d_6) δ=5.45 (2H, brm, H_2N-4′), 6.4—7.7 (7H, m, ArH), and 7.45 (2H, brm, H_2N-2); MS m/z 248 (M+2; 33), 246 (M$^+$; 99), 220 (34), 218 (100), 182 (17), 154 (11), and 109 (18).

Found: m/z 246.0537. Calcd for $C_{13}H_{11}N_2OCl$: M, 246.0560.

2-Amino-5-(4-amino-3-nitrophenyl)tropone (15k): Yellow prisms; mp 253—254 °C (from ethyl acetate); UV λ_{max} 247 ($\log \varepsilon$ 4.54) and 372 nm (4.49); IR 3445, 3290 (NH), and 1635 cm^{-1} (C=O); ^{1}H NMR (DMSO-d_6) δ=5.60 (2H, brm, H$_2$N-4′), 6.8—7.5 (5H, m, H-3,4,6,7,5′), 7.52 (2H, brm, H$_2$N-2), 7.70 (1H, dd, $J_{5',6'}$=8, $J_{2',6'}$=2 Hz, H-6′), and 8.14 (1H, d, H-2′); MS m/z 257 (M$^+$; 100), 229 (36), and 183 (41).

Found: m/z 257.0799. Calcd for $C_{13}H_{11}N_3O_3$: M, 257.0800.

2-Amino-5-(4-amino-2-nitrophenyl)tropone (15l): Yellow prisms; mp 246—247 °C (from ethyl acetate); UV λ_{max} 250 ($\log \varepsilon$ 4.45), 358 (4.20), and 409 nm (4.07); IR 3420, 3280 (NH), and 1620 cm^{-1} (C=O), ^{1}H NMR (DMSO-d_6) δ=5.85 (2H, brm, H$_2$N-4′), 6.6—7.3 (7H, m, ArH), and 7.65 (2 H, brm, H$_2$N-2); MS m/z 257 (M$^+$; 100), 240 (11), 212 (18), 201 (22), 197 (33), 185 (20), 184 (36), 183 (28), 182 (45), 169 (43), and 154 (31).

Found: m/z 257.0805. Calcd for $C_{13}H_{11}N_3O_3$: M, 257.0800.

2-Amino-5-(4-amino-1-naphthyl)tropone (25): Yellow prisms; mp 173 °C (from benzene); IR 3350 (NH) and 1603 cm^{-1} (C=O); ^{1}H NMR (100 MHz, DMSO-d_6) δ=4.4 (2H, brs, H$_2$N-4′), 5.8 (2H, brs, H$_2$N-2), 6.74 (1H, d, $J_{2',3'}$=8 Hz, H-3′), 6.98 (1H, d, $J_{3,4}$=12 Hz, H-3), 7.19 (1H, d, H-2′), 6.9—7.5 (4H, m, H-4,6,6′,7′), 7.67 (1H, brdd, $J_{5',6'}$=7, $J_{5',7'}$=3Hz, H-5′), and 8.13 (1H, brdd, $J_{7',8'}$=6.5, $J_{6',8'}$=3 Hz, H-8′); ^{13}C NMR δ=112.1 (C-3), 122.9 (C-4′a), 124.0, 125.3, 126.0, 128.0 (C-2′), 129.0 (C-7), 132.0 (C-1′), 135.8 (C-5), 138.0 (C-4), 139.7 (C-6), 144.6 (C-8′a), 157.7 (C-4′), 159.5 (C-2), and 175.2 (C-1); MS m/z 262 (M$^+$; 72.2), 234 (100), and 217 (54).

Anal. ($C_{17}H_{14}N_2O$) C, H, N.

6*H*-Cyclohept[*b*]indol-6-one (29a):[29] Yellow prisms; mp 267 °C (from benzene, lit,[29] 245—246 °C).

3-Methyl-6*H*-cyclohept[*b*]indol-6-one (29c): Yellow prisms; mp 226 °C (from benzene); UV λ_{max} 229 ($\log \varepsilon$ 4.49), 282 (4.44), 312 (4.38), 326 (4.33), 394 (4.86), and 410 nm (3.99); IR 3200 (NH) and 1605 cm^{-1}; ^{1}H NMR (DMSO-d_6) δ=2.45 (3H, s, Me-3), 6.9—7.8 (5H, m, ArH), 8.00 (1H, d, $J_{1,2}$=8 Hz, H-1), 8.16 (1H, d, $J_{9,10}$=10 Hz, H-10), and 12.3 (1H, brm, HN-5); MS m/z 209 (M$^+$; 100), 181 (92), 180 (78), and 152 (16).

Found: m/z 209.0833. Calcd for $C_{14}H_{11}NO$: M, 209.0841.

3-Methoxy-6*H*-cyclohept[*b*]indol-6-one (29f): Yellow prisms; mp 251—252 °C (from benzene); UV λ_{max} 228 ($\log \varepsilon$ 4.42), 281 (4.23), 317 (4.46), 390 (3.75), 410 nm (3.85); IR 3180 (NH) and 1625 cm^{-1} (C=O); ^{1}H NMR (DMSO-d_6) δ=3.82 (3H, s, MeO-3), 6.7—7.7 (5H, m, ArH), 8.18 (1H, d, $J_{1,2}$=9 Hz, H-1), 8.30 (1H, d, $J_{9,10}$=11 Hz, H-10), and 12.4 (1H, brm, HN-5).

Anal. ($C_{14}H_{11}NO_2$) C, H, N.

3-Chloro-6*H*-cyclohept[*b*]indol-6-one (29j): Yellow prisms; mp 191—192 °C (from benzene); UV λ_{max} 233 ($\log \varepsilon$ 4.42), 272 (4.37), 280 (4.38), 314 (4.36), 386 (3.84), and 404 nm (3.96); IR 3175 (NH) and 1615 cm^{-1} (C=O); ^{1}H NMR (DMSO-d_6) δ=6.9—7.8 (5H, m, ArH), 8.32 (1H, brd, $J_{9,10}$=11 Hz, H-10), 8.35 (1H, d, $J_{1,2}$=8 Hz, H-1), and 12.4 (1H, brm, HN-5); MS m/z 231 (M+2; 25), 229 (M$^+$; 79), 203 (34), 201 (100), and 166 (45).

Found: m/z 229.0246. Calcd for $C_{13}H_8NOCl$: M, 229.0295.

3-Nitro-6*H*-cyclohept[*b*]indol-6-one (29l): Yellow crystals; mp>300 °C (from benzene-methanol); UV λ_{max} 249 ($\log \varepsilon$ 4.29), 310 (4.39), 336 (4.17), 404 (3.81), and 420 nm (3.90); IR 3180 (NH) and 1620 cm^{-1} (C=O); ^{1}H NMR (DMSO-d_6) δ=7.0—8.65 (7H, m, ArH) and 12.9 (1H, brm, HN-5); MS m/z 240 (M$^+$; 100), 212 (43), 166 (73), and 139 (55).

Found: m/z 240.0537. Calcd for $C_{13}H_8N_2O_3$: M, 240.0535.

5-Anilino-2-phenylazotropone (30a): Dark red needles; mp 183—184 °C (from benzene); UV λ_{max} 235 ($\log \varepsilon$ 4.38), 320 (4.25), and 495 nm (4.31); IR (CHCl$_3$) 3000 (NH) and 1590 cm^{-1} (C=O); ^{1}H NMR δ=6.6—7.0 [1H, m, H-4″ (PhN-5)], 7.1—7.6 (10H, m, ArH), 7.66 (1H, d, $J_{3,4}$=10 Hz H-3), 7.8—8.05 [2H, m, H-2′,6′ (PhN=N-2)], and 9.3 (1H, brm, NH-5); ^{13}C NMR δ=111.3 (C-3), 122.4, 123.5, 124.6, 125.9, 126.6, 129.1, 129.9 (C-4), 131.3 (C-7), 137.6, 138.0, 151.3 (C-1″), 152.9 (C-1′), 155.7 (C-2), and 172.0 (C-1); MS m/z 301 (M$^+$; 16), 272 (9), 196 (41), 181 (26), 167 (87), 115 (8), and 77 (100).

Anal. ($C_{19}H_{15}N_3O$) C, H, N.

5-(2-Chloroanilino)-2-(2-chlorophenylazo)tropone (30i): Dark red prisms; mp 176 °C (from benzene-hexane); UV λ_{max} 266 ($\log \varepsilon$ 4.33), 272 (4.36), and 490 nm (4.54); IR (CHCl$_3$) 3010 (NH) and 1620 cm^{-1} (C=O); ^{1}H NMR δ=6.3—8.0 (12H, m, ArH) and 9.56 (1H, brm, NH).

Anal. ($C_{19}H_{13}N_3OCl_2$) C, H, N.

2-(3-Chlorophenylazo)-5-hydroxytropone (33): Dark red microcrystals; mp 117 °C decomp (from benzene); UV λ_{max} 299 ($\log \varepsilon$ 3.92) and 502 nm (3.87); IR (CHCl$_3$) 3260 (OH) and 1590 cm^{-1} (C=O); ^{1}H NMR δ=6.6—8.2 (8H, m, ArH) and 9.4 (1H, brm, OH); MS m/z 262 (M+2; 24), 260 (M$^+$; 74), 232 (8), 141 (10), 139 (33), 121 (100), and 111 (95).

Found: m/z 260.0356. Calcd for $C_{13}H_9N_2O_2Cl$: M, 260.0353.

General Procedure for Hydrolysis of 2-Amino-5-(4-aminoaryl)tropones 15. Compound **15** (0.5 mmol) was dissolved in ethanol (8 cm^3) and 6 M KOH (3.5 cm^3); if necessary, some THF was added as a co-solvent. The mixture was refluxed under nitrogen for 3—12 h, brought to pH 7 with 2 M HCl, and then concentrated in vacuo. When **16** separated as crystals, they were filtered off and washed with cold water (and then with a little benzene). The filtrate was extracted with AcOEt or CH$_2$Cl$_2$. The combined organic layers were dried (Na$_2$SO$_4$) and evaporated in vacuo to give additional **16**. The products **16n—u** were not stable enough for purification and therefore immediately acetylated (see later).

5-(4-Aminophenyl)tropolone (16a): Yellow prisms; mp 185—186 °C (from benzene-methanol); UV λ_{max} 238 ($\log \varepsilon$ 4.55), 256 (4.50), and 390 nm (4.38); IR 3440, 3360 (NH), 3150 (OH), and 1620 cm^{-1} (C=O); ^{1}H NMR δ=5.1 (3H, brm, H$_2$N-4′, HO-2), 6.70 (2H, brd, J=8.5 Hz, H-3′,5′), 7.1—7.2 (4H, m, ArH), and 7.25 (2H, brd, J=8.5 Hz, H-2′,6′); MS m/z 213 (M$^+$; 100) and 185 (98).

Anal. ($C_{13}H_{11}NO_2$) C, H, N.

Treatment of **16a** (54 mg) with cold nitrous acid, followed by reduction with phosphinic acid, gave 5-phenyltropolone (**5**)[10,11] as pale yellow plates (15 mg, 30% overall yield); mp 126 °C (lit,[10] 125—126 °C).

5-(4-Amino-3-methylphenyl)tropolone (16b): Yellow prisms; mp 157—158 °C (from benzene-methanol); UV λ_{max} 238 ($\log \varepsilon$ 4.50), 256 (4.44), and 393 nm (4.30); IR 3440, 3370 (NH), 3240 (OH), and 1615 cm^{-1} (C=O); ^{1}H NMR δ=2.20 (3H, s, Me-3′), 5.2 (3H, brm, H$_2$N-4′, HO-2), 6.69 (1H, brd, $J_{5',6'}$=9 Hz, H-5′), and 6.9—7.2 (6H, m, ArH).

Anal. ($C_{14}H_{13}NO_2$) C, H, N.

5-(4-Amino-2-methylphenyl)tropolone (16c): Yellow prisms; mp 115—117 °C (from benzene–methanol); UV λ_{max} 240sh ($\log \varepsilon$ 4.52), 251 (4.55), 358 (4.18), and 390sh nm (4.15); IR 3430 (NH), 3170 (OH), and 1615 cm^{-1} (C=O); ^{1}H NMR δ=2.15 (3H, s, Me-2′), 5.4 (3H, brm, H_2N-4′, HO-2), 6.50 (1H, brd, $J_{3',5'}$=2.5 Hz, H-3′), 6.51 (1H, brdd, $J_{5',6'}$=8.5 Hz, H-5′), 7.00 (1H, brd, H-6′), and 7.2—7.6 (4H, brs, ArH).

Anal. ($C_{14}H_{13}NO_2$) C, H, N.

5-(4-Amino-3-methoxyphenyl)tropolone (16e): Yellow prisms; mp 155—157 °C (from benzene–methanol); UV λ_{max} 238 ($\log \varepsilon$ 4.61), 257 (4.50), and 398 nm (4.37); IR 3460, 3320 (NH), 3200 (OH), and 1620 cm^{-1} (C=O); ^{1}H NMR δ=3.90 (3H, s, MeO-3′), 5.60 (3H, brm, H_2N-4′, HO-2), 6.67 (1H, brd, $J_{5',6'}$=8.5 Hz, H-5′), 6.84 (1H, brs, H-2′), and 7.1—7.8 (5H, brs, ArH).

Anal. ($C_{14}H_{13}NO_3$) C, H, N.

5-(4-Amino-2-methoxyphenyl)tropolone (16f): Yellow prisms; mp 167—169 °C (from benzene–methanol); UV λ_{max} 237 ($\log \varepsilon$ 4.58), 256 (4.55), and 397 nm (4.30); IR 3470, 3380 (NH), 3200 (OH), and 1610 cm^{-1} (C=O); ^{1}H NMR δ=3.76 (3H, s, MeO-2′), 5.05 (3H, brm, H_2N-4′, HO-2), 6.15—6.45 (2H, m, H-3′,5′), 7.05 (1H, brd, $J_{5',6'}$=8 Hz, H-6′), and 7.2—7.65 (4H, m, ArH).

Anal. ($C_{14}H_{13}NO_3$) C, H, N.

5-(4-Amino-2,3-dimethoxyphenyl)tropolone (16g): Yellow prisms; mp 110—111 °C (from benzene); IR 3465, 3350 (NH), 3200 (OH), and 1605 cm^{-1} (C=O); ^{1}H NMR δ=3.69 (3H, s, MeO-2′), 3.84 (3H, s, MeO-3′), 5.45 (3H, brm, H_2N-4′, HO-2), 6.72 (1H, d, $J_{5',6'}$=8.5 Hz, H-5′), 7.0—7.65 (4H, m, ArH), and 7.03 (1H, d, H-6′).

Anal. ($C_{15}H_{15}NO_4$) C, H, N.

5-(4-Amino-2,3-dimethoxy-6-methylphenyl)tropolone (16h): Yellow prisms; mp 98—100 °C (from benzene); IR 3470, 3360 (NH), 3200 (OH), and 1610 cm^{-1} (C=O); ^{1}H NMR δ=2.06 (3H, s, Me-6′), 3.72 (3H, s, MeO-2′), 3.86 (3H, s, MeO-3′), 5.20 (3H, brm, H_2N-4′, HO-2), 6.72 (1H, s, H-5′), and 7.05—7.7 (4H, m, ArH).

Anal. ($C_{16}H_{17}NO_4$) C, H, N.

5-(4-Amino-3-chlorophenyl)tropolone (16i): Yellow prisms; mp 136—138 °C (from benzene–methanol); UV λ_{max} 238 ($\log \varepsilon$ 4.49), 256 (4.42), and 376 nm (4.32); IR 3450, 3350 (NH), 3200 (OH), and 1620 cm^{-1} (C=O); ^{1}H NMR δ=5.60 (3H, brm, H_2N-4′, HO-2), 6.76 (1H, brd, $J_{5',6'}$=8.5 Hz, H-5′), and 7.0—7.6 (6H, m, ArH).

Anal. ($C_{13}H_{10}NO_2Cl$) C, H, N.

5-(4-Amino-2-chlorophenyl)tropolone (16j): Yellow prisms; mp 161—163 °C (from benzene–methanol); UV λ_{max} 240sh ($\log \varepsilon$ 4.58), 256 (4.61), 355 (4.30), 358 (4.30), and 390sh nm (4.23); IR 3460, 3370 (NH), 3240 (OH), and 1605 cm^{-1} (C=O); ^{1}H NMR (DMSO-d_6) δ=5.10 (3H, brm, H_2N-4′, HO-2), 6.60 (2H, m, H-3′,5′), and 7.1—7.2 (5H, m, ArH).

Anal. ($C_{13}H_{10}NO_2Cl$) C, H, N.

5-(4-Amino-3-nitrophenyl)tropolone (16k): Yellow prisms; mp 272—275 °C (from chloroform–ethyl acetate); UV λ_{max} 241sh ($\log \varepsilon$ 4.49), 256 (4.52), 367 (4.41), and 390sh nm (4.36); IR 3480 (NH), 3180 (OH), and 1620 cm^{-1} (C=O); ^{1}H NMR (DMSO-d_6) δ=5.10 (3H, brm, H_2N-4′, HO-2) and 7.1—7.8 (7H, m, ArH).

Anal. ($C_{13}H_{10}N_2O_4$) C, H, N.

5-(4-Amino-2-nitrophenyl)tropolone (16l): Yellow prisms; mp 250—253 °C (from chloroform–ethyl acetate); UV λ_{max} 352 ($\log \varepsilon$ 4.58), 356 (4.31), 360 (4.32), and 394sh nm (4.25); IR 3480, 3380 (NH), 3180 (OH), and 1620 cm^{-1} (C=O); ^{1}H NMR (DMSO-d_6) δ=5.05 (3H, brm, H_2N-4′, HO-2) and 7.0—7.9 (7H, m, ArH).

Anal. ($C_{13}H_{10}N_2O_4$) C, H, N.

Acetylation of 5-(4-Aminoaryl)tropolones 16 to 5-(4-Acetamidoaryl)tropolone Acetates 17. A mixture of **16** (50 mg), pyridine (2.5 cm^3), and acetic anhydride (0.16 cm^3) was stirred overnight at 20 °C under argon. The volatile material was evaporated in vacuo and the residue was purified in a column of silica gel to give **17**. The complete characterization of **17n—t** was made as the corresponding tropolones **18n—t** after hydrolysis (see later).

5-(4-Acetamidophenyl)tropolone Acetate (17a): Yellow prisms; mp 215 °C (from benzene); UV λ_{max} 247 ($\log \varepsilon$ 4.07) and 354 nm (4.02); IR 3320—3200 (NH), 1755, 1695 (amide), and 1590 cm^{-1} (C=O); ^{1}H NMR (DMSO-d_6) δ=2.10 (3H, s, AcN-4′), 2.30 (3H, s, AcO-2), 7.1—8.0 (8H, m, ArH), and 10.0 (1H, brm, NH); MS m/z 297 (M$^+$; 24.0), 254 (100), 226 (13), 212 (11), and 184 (65).

Anal. ($C_{17}H_{15}NO_4$) C, H, N.

5-(4-Acetamidophenyl)-4-isopropyltropolone Acetate (17n): Yellow oil; ^{1}H NMR δ=1.01 (6H, d, J=7 Hz, Me_2C-4), 2.09 (3H, s, AcN-4′), 2.40 (3H, s, AcO-2), 2.75 (1H, sept, HC-4), 7.1—7.8 (7H, m, ArH), and 10.1 (1H, brs, NH).

5-(4-Acetamidophenyl)-4-isopropenyltropolone Acetate (17o): Yellow oil; ^{1}H NMR δ=1.56 (3H, brs, MeC-4), 2.18 (3H, s, AcN-4′), 2.36 (3H, s, AcO-2), 5.06 (2H, brs, H_2C=C-4), 7.1—7.8 (7H, m, ArH), and 8.43 (1H, brm, NH).

5-(4-Acetamido-3-methylphenyl)-4-isopropenyltropolone Acetate (17p): Yellow syrup; ^{1}H NMR δ=1.58 (3H, brs, MeC-4), 2.20 (3H, s, AcN-4′), 2.28 (3H, brs, Me-3′), 2.35 (3H, s, AcO-2), 5.05 (2H, brs, H_2C=C-4), and 7.1—8.0 (7H, m, ArH, NH).

5-(4-Acetamido-2-methylphenyl)-4-isopropenyltropolone Acetate (17q): Yellow syrup; ^{1}H NMR δ=1.59 (3H, brs, MeC-4), 2.16 (6H, brs, AcN-4′, Me-2′), 2.36 (3H, s, AcO-2), 4.92 (2H, brs, H_2C=C-4), and 7.05—7.85 (7H, m, ArH, NH).

5-(4-Acetamido-3-methoxyphenyl-4-isopropenyltropolone Acetate (17r): Yellow oil; ^{1}H NMR δ=1.59 (3H, brs, MeC-4), 2.23 (3H, s, AcN-4′), 2.37 (3H, s, AcO-2), 3.88 (3H, s, MeO-3′), 5.07 (2H, brs, H_2C=C-4), 6.2—7.57 (6H, m, ArH), and 7.82 (1H, m, NH).

5-(4-Acetamido-2-methoxyphenyl)-4-isopropenyltropolone Acetate (17s): Yellow oil; ^{1}H NMR δ=1.65 (3H, brs, MeC-4), 2.18 (3H, s, AcN-4′), 2.37 (3H, s, AcO-2), 3.78 (3H, s, MeO-2′), 4.90 (2H, brs, H_2C=C-4), and 6.95—8.1 (7H, m, ArH, NH).

5-(4-Acetamido-2,3-dimethoxyphenyl)-4-isopropenyltropolone Acetate (17t): Yellow oil; ^{1}H NMR δ=1.70 (3H, brs, MeC-4), 2.22 (3H, s, AcN-4′), 2.37 (3H, s, AcO-2), 3.73 (3H, s, MeO-2′), 3.89 (3H, s, MeO-3′), 4.92 (2H, brs, H_2C=C-4), 6.92 (1H, d, $J_{5',6'}$=8.5 Hz, H-6′), 7.12 (1H, d, $J_{6,7}$=11.0 Hz, H-7), 7.18 (1H, s, H-3), 7.39 (1H, d, H-6), 7.9 (1H, brm, NH), and 8.18 (1H, brd, H-5′).

5- and 7-(4-Acetamido-2,3-dimethoxy-6-methylphenyl)-4-isopropenyltropolone Acetates (17u,u′): A mixture (3:2 by ^{1}H NMR) of **17u** and **17u′** (respectively) was obtained as a yellow oil, which was rechromatographed in a prepacked silica-gel column (Merck Lobar, Size A) with 1:3 AcOEt–hexane to give only small proportions of pure **17u** and **17u′** (besides mostly overlapping fractions).

17u: Colorless prisms; mp 161.5—163 °C (from AcOEt-hexane); ^{1}H NMR (500 MHz), see Table 2; MS *m/z* 412 (M+1; 10.8) 411 (M^+; 40.7), 370 (26), 369 (100), 354 (22), 338 (15), 327 (13), 326 (16), 312 (44), 296 (44), 284 (15), 268 (21), 253 (16), and 252 (15).

Found: *m/z* 411.1666. Calcd for $C_{23}H_{25}NO_6$: M, 411.1682.

17u′: A pale yellow syrup; ^{1}H NMR (500 MHz), see Table 2; MS *m/z* 411 (M^+; 10.3), 381 (11), 380 (40), 369 (14), 354 (15), 340 (28), 339 (27), 338 (100), and 281 (10).

Found: *m/z* 411.1640. Calcd for $C_{23}H_{25}NO_6$: M, 411.1682.

Hydrolysis of 5-(4-Acetamidoaryl)tropolone Acetates 17 to 5-(4-Acetamidoaryl)tropolones 18. Compound **17** (50 mg) was treated with 1:1 1 M KOH–ethanol (4 cm^3) at 20 °C overnight. The solvent was evaporated in vacuo. The residue was diluted with cold water, taken to pH 4 with dil HCl, and extracted with CH_2Cl_2. The combined organic layers were dried (Na_2SO_4) and evaporated in vacuo. The residue was chromatographed in a column of silica gel to provide **18**.

5-(4-Acetamidophenyl)-4-isopropyltropolone (18n): Yellow needles; mp 250 °C decomp (from AcOEt); IR 3300 (OH, NH), 1675 (amide), and 1600 cm^{-1} (C=O); ^{1}H NMR δ=1.09 (6H, d, J=7 Hz, Me_2C-4), 2.09 (2H, s, AcN-4), 2.85 (1H, sept, HC-4), 7.1—7.8 (8H, m, ArH, OH), and 10.1 (1H, brs, NH); MS *m/z* 297 (M^+; 70.2), 282 (100), 254 (61), and 240 (15).

Found: *m/z* 297.1342. Calcd for $C_{18}H_{19}NO_3$: M, 297.1365.

5-(4-Acetamidophenyl)-4-isopropenyltropolone (18o): A pale yellow crystalline powder: mp 119—121 °C (from AcOEt–hexane); ^{1}H NMR δ=1.62 (3H, brd, J=1.5 Hz, MeC-4), 2.22 (3H, s, AcN-4′), 5.03, 5.06 (1H each, both brs, H_2C=C-4), 5.5 (1H, brm, HO-2), 7.25 (1H, d, $J_{6,7}$=11.5 Hz H-7), 7.26 (2H, brd, $J_{2',3'}=J_{5',6'}$=8 Hz, H-2′,6′), 7.39 (1H, d, H-6), 7.44 (1H, s, H-3), 7.49 (2H, brd, H-3′,5′), and 7.8 (1H, brm, NH); MS *m/z* 295 (M^+; 81.2), 280 (100), 252 (41), 238 (18), 210 (73), and 195 (31).

Found: *m/z* 295.1205. Calcd for $C_{18}H_{17}NO_3$: M, 295.1208.

5-(4-Acetamido-3-methylphenyl)-4-isopropenyltropolone (18p): Yellow prisms; mp 172—174 °C (from AcOEt–benzene, cf. Ref. 2b, mp 85 °C decomp[30]); ^{1}H NMR (500 MHz) δ=1.60 (3H, s, MeC-4), 2.23 (3H, brs, AcN-4′), 2.27 (3H, brs, Me-3′), 5.01, 5.05 (1H each, both brs, H_2C=C-4), 7.03 (1H, brm, NH), 7.13 (1H, brd, $J_{2',6'}$=1.7 Hz, H-2′), 7.15 (1H, brdd, $J_{5',6'}$= 8.3 Hz, H-6′), 7.26 (1H, d, $J_{6,7}$=11.6 Hz, H-7), 7.38 (1H, d, H-6), 7.42 (1H, s, H-3), and 7.87 (1H, brd, H-5′); MS *m/z* 309 (M^+; 97.8), 294 (100), 266 (26), 252 (31), 238 (20), 224 (66), and 209 (46).

Found: *m/z* 309.1353. Calcd for $C_{19}H_{19}NO_3$: M, 309.1365.

5-(4-Acetamido-2-methylphenyl)-4-isopropenyltropolone (18q): Yellow prisms; mp 177—179 °C (from AcOEt–benzene); ^{1}H NMR (500 MHz) δ=1.63 (3H, brs, MeC-4), 2.12 (3H, brs, Me-2′), 2.19 (3H, brs, AcN-4′), 4.90 [1H, brs, (*E*)-HC=C-4], 4.94 [1H, brquint, J=1.3 Hz, (*Z*)-HC=C-4], 7.03 (1H, brd, $J_{5',6'}$=8.3 Hz, H-6′), 7.20 (1H, brm, NH), 7.23 (1H, d, $J_{6,7}$=11.7 Hz, H-7), 7.25 (1H, d, H-6), 7.31 (1H, brdd, $J_{3',5'}$=1.9 Hz, H-5′), 7.39 (1H, s, H-3), and 7.42 (1H, brd, H-3′); MS *m/z* 309 (M^+; 36.6), 294 (40), 266 (21), 250 (21), 224 (64), 222 (100), and 209 (40).

Found: *m/z* 309.1336. Calcd for $C_{19}H_{19}NO_3$: M, 309.1365.

5-(4-Acetamido-3-methoxyphenyl)-4-isopropenyltropolone (18r): Pale yellow needles; mp 169—171 °C (from AcOEt–hexane); ^{1}H NMR (500 MHz), see Table 2; MS *m/z* 325 (M^+; 100), 310 (20), 282 (82), 268 (94), 254 (52), 240 (66), 223 (28), 209 (24), 197 (15), and 195 (16).

Found: *m/z* 325.1296. Calcd for $C_{19}H_{19}NO_4$: M, 325.1314.

5-(4-Acetamido-2-methoxyphenyl)-4-isopropenyltropolone (18s): Pale yellow needles; mp 108—110 °C (from light petroleum); ^{1}H NMR (200 MHz), see Table 2; MS *m/z* 325 (M^+; 100), 310 (12), 282 (76), 268 (91), 254 (42), and 240 (53).

Found: *m/z* 325.1332. Calcd for $C_{19}H_{19}NO_4$: M, 325.1314.

5-(4-Acetamido-2,3-dimethoxyphenyl)-4-isopropenyltropolone (18t): Pale amber fine prisms: mp 159—159.5 °C (from AcOEt–cyclohexane); ^{1}H NMR (200 MHz) δ=1.73 (3H, brs, MeC-4), 2.22 (3H, s, AcN-4′), 3.63 (3H, s, MeO-2′), 3.88 (3H, s, MeO-3′), 4.83, 4.92 (1H each, both brs, H_2C=C-4), 6.85 (1H, d, $J_{5',6'}$=8.3 Hz, H-6′), 7.22 (1H, d, $J_{6,7}$=11.5 Hz, H-7), 7.33 (1H, s, H-3), 7.34 (1H, d, H-6), 7.79 (1H, brs, NH), and 8.06 (1H, brd, H-5′); MS *m/z* 355 (M^+; 16), 324 (19), 312 (11), 298 (12), and 43 (100).

Found: *m/z* 355.1435. Calcd for $C_{20}H_{21}NO_5$: M, 355.1420.

5- and 7-(4-Acetamido-2,3-dimethoxy-6-methylphenyl)-4-isopropenyltropolones (18u,u′): Pale yellow needles (a 3:2 mixture of **18u** and **18u′**, respectively, which were not separable even repeating chromatography); mp[§] 75 °C (from AcOEt–hexane).

18u: ^{1}H NMR[§] (500 MHz) see Table 1; MS[§] *m/z* 369 (M^+; 51), 338 (85), 326 (100), and 312 (31).

Found: *m/z* 369.1555. Calcd for $C_{21}H_{23}NO_5$: M, 369.1576.

18u′: ^{1}H NMR[§] (500 MHz) see Table 2.

General Procedure for the Preparation of 4-Substituted 5-(4-methoxyaryl)tropolones 19. A mixture of 5-(4-acetamidoaryl)-tropolone **18** (50 mg), ethanol (6 cm^3), and 2 M HCl (3 cm^3) was refluxed under argon for 12—36 h. The solvent was evaporated in vacuo. The residue was diluted with water (1 cm^3), EtOH (0.5 cm^3), and 2 M HCl (0.16 cm^3) at 0 °C, to which was slowly added, at 0 °C, sodium nitrite (1.2 equiv mol) dissolved in water (0.4 cm^3). The mixture was stirred at 5 °C for 2 h, diluted with water (50 cm^3), and then refluxed for 2 h under argon. The solvent was evaporated in vacuo. The residue was diluted with cold water and extracted with CH_2Cl_2. The combined organic layers were dried (Na_2SO_4) and evaporated in vacuo. The residue was suspended in cold water (1.5 cm^3) and 1 M NaOH (0.5 cm^3), and dimethyl sulfate (0.036 cm^3) was added. The mixture was stirred under argon at 5 °C for 30 min and then 70 °C for 1 h. After cooling, it was extracted with AcOEt and then with CH_2Cl_2. The combined organic layers were dried (Na_2SO_4) and evaporated in vacuo. The residue was chromatographed in a column of silica gel with benzene to provide **19**.

4-Isopropyl-5-(4-methoxyphenyl)tropolone (19n): Colorless needles (42% yield from **18n**); mp 114—115 °C (from

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[§] For specimen consisting of a ca. 3:2 mixture of **u** and **u′** form, because their separation could not be achieved.

benzene–cyclohexane); ^{1}H NMR δ=1.19 (6H, d, J=7.0 Hz, Me$_2$C-4), 3.01 (1H, brsept, J=7.0 Hz, HC-4), 3.89 (3H, s, MeO-4′), 6.93 (2H, brd, J=8.5 Hz, H-3′,5′), 7.11 (2H, brd, J=8.5 Hz, H-2′,6′), 7.19 (1H, d, $J_{6,7}$=12.0 Hz, H-7), 7.38 (1H, d, H-6), 7.43 (1H, s, H-3), and 7.45 (1H, brm, OH); MS *m/z* 270 (M$^+$; 100), 242 (36), 227 (43), 212 (11), and 196 (11).

Found: *m/z* 270.1224. Calcd for C$_{17}$H$_{18}$O$_3$: M, 270.1256.

4-Isopropyl-5-(4-methoxyphenyl)tropolone Difluoroborane Complex (19n′). Treatment of **19n** with an equivalent amount of boron trifluoride etherate in benzene–ether at 5 °C for 1 h, followed by purification using column chromatograhy on silica gel gave **19n′**: Colorless fine prisms (90% yield); mp 214—215 °C (from benzene–cyclohexane); ^{1}H NMR δ=1.20 (6H, d, J=7.0 Hz, Me$_2$C-4), 3.20 (1H, sept, J=7 Hz, HC-4), 3.88 (3H, s, MeO-4′), 7.01 (2H, brd, $J_{2',3'}$=$J_{5',6'}$=8.5 Hz, H-3′,5′), 7.18 (2H, brd, H-2′,6′), 7.62 (1H, d, $J_{6,7}$=11 Hz, H-6), 7.90 (1H, s, H-3), and 7.99 (1H, d, H-7); MS *m/z* 318 (M$^+$; 100), 290 (12), 275 (45), and 260 (11).

Found: *m/z* 318.1215. Calcd for C$_{17}$H$_{17}$O$_3$BF$_2$: M, 318.1239.

4-Isopropenyl-5-(4-methoxy-3-methylphenyl)tropolone (19p): Yellow needles (51% yield from **18p**); mp 146—147 °C (from ether–light petroleum); ^{1}H NMR δ=1.60 (3H, s, MeC-4), 2.22 (3H, s, Me-3′), 2.6 (1H, brm, OH), 3.86 (3H, s, MeO-4′), 5.04 (2H, brs, H$_2$C=C-4), 6.78 (1H, brd, $J_{5',6'}$=8.5 Hz, H-5′), 7.04 (1H, brs, H-2′), 7.06 (1H, brd, H-6′), 7.23 (1H, d, $J_{6,7}$=12.0 Hz, H-7), 7.40 (1H, d, H-6), and 7.42 (1H, s, H-3); MS *m/z* 282 (M$^+$; 100), 267 (80), 239 (71), 224 (51), 208 (22), and 181 (20).

Found: *m/z* 282.1198. Calcd for C$_{18}$H$_{18}$O$_3$: M, 282.1256.

4-Isopropenyl-5-(4-methoxy-2-methylphenyl)tropolone (19q): Pale yellow needles (40% yield from **18q**); mp 131—132 °C (from light petroleum); ^{1}H NMR δ=1.64 (3H, brs, MeC-4), 2.12 (3H, s, Me-2′), 3.85 (3H, s, MeO-4′), 4.93 (2H, m, H$_2$C=C-4), 6.71 (1H, brd, $J_{5',6'}$=8.5 Hz, H-5′), 6.77 (1H, brs, H-3′), 6.98 (1H, brd, H-6′), 7.20 (1H, d, $J_{6,7}$=12.0 Hz, H-7), 7.30 (1H, d, H-6), and 7.40 (1H, s, H-3); MS *m/z* 282 (M$^+$; 100), 267 (79), 239 (53), 224 (25), and 208 (9).

Found: *m/z* 282.1250. Calcd for C$_{18}$H$_{18}$O$_3$: M, 282.1256.

4-Isopropenyl-5- and 7-(2,3,4-trimethoxy-6-methylphenyl)tropolone (19u,u′): A mixture (3:2) of **19u** and **19u′** (respectively) was obtained as a yellow syrup (49% yield from **18u,u′**), which was chromatographically inseparable.

19u: ^{1}H NMR§ (500 M Hz) δ=1.25 (brs, HO-2), 1.74 (3H, brs, MeC-4), 2.00 (3H, brs, Me-6′), 3.69 (3H, s, MeO-2′), 3.87, 3.878 (3H each, 2s, MeO-3′,4′), 4.88 (2H, brs, H$_2$C=C-4), 6.50 (1H, brs, H-5′), 7.22 (1H, d, $J_{6,7}$=11.7 Hz, H-7), 7.27 (1H, d, H-6), and 7.38 (1H, s, H-3); MS§ *m/z* 342 (M$^+$; 88), 327 (27), 312 (100), 311 (73), 292 (72), 281 (99), 268 (64), 253 (82), and 238 (81).

Found:§ *m/z* 342.1428. Calcd for C$_{20}$H$_{22}$O$_5$: M, 342.1463.

19u′: ^{1}H NMR§ (500 MHz) δ=1.25 (brs, HO-2), 2.04 (3H, brs, Me-6′), 2.20 (3H, brs, MeC-4), 3.69 (3H, s, MeO-2′), 3.88, 3.89 (3H each, 2s, MeO-3′,4′), 5.32, 5.45 (2H, 2brs, H$_2$C=C-4), 6.62 (1H, s, H-5′), 7.12 (1H, dd, $J_{5,6}$=10.7, $J_{3,5}$=1.7 Hz, H-5), 7.31 (1H, d, H-6), and 7.57 (1H, d, H-3).

2-Acetamido-8-hydroxy-10,10-dimethylcyclohept[*a*]inden-7(10*H*)-one (27o) and Its Acetate (28o). To a solution of **18o** (10 mg) in CHCl$_3$ (1 cm^3) was successively added concd sulfuric acid (0.5 cm^3) and sodium azide (3 mg) at 5 °C. The mixture was heated under argon at 70 °C for 2 h. The solvent was evaporated in vacuo. The residue was diluted with cold water, taken to pH 3 with NaHCO$_3$, and extracted with CH$_2$Cl$_2$. The combined organic layers were dried (Na$_2$SO$_4$) and evaporated in vacuo to give **27o** as a pale amber crystalline powder (6 mg, 60%): mp 295—300 °C decomp (from EtOH–AcOEt–benzene); ^{1}H NMR δ=1.50 (6H, s, Me$_2$C-10), 2.20 (3H, s, AcN-2), 7.36 (1H, brd, $J_{3,4}$=8.5 Hz, H-4), 7.42 (1H, d, $J_{5,6}$=11.5 Hz, H-6), 7.51 (1H, s, H-9), 7.62 (1H, brd, H-3), 7.63 (1H, d, H-5), and 7.72 (1H, brs, H-1); MS *m/z* 295 (M$^+$; 100), 280 (6), 267 (8), 253 (17), 225 (26), 210 (22), and 182 (8).

Found: *m/z* 295.1174. Calcd for C$_{18}$H$_{17}$NO$_3$: M, 295.1208.

The above reaction was effected in the absence of sodium azide at 20 °C within 5 h.

27o (6.0 mg) was dissolved in pyridine (1 cm^3) and acetic anhydride (0.5 cm^3), and the mixture was stirred overnight at 20 °C under argon. The volatile material was evaporated in vacuo and the residue was purified in a column of silica gel with AcOEt–hexane as an eluant, giving **28o** as amber prisms (5.1 mg, 74% yield): ^{1}H NMR (500 MHz) δ=1.47 (6H, brs, Me$_2$C-10), 2.22 (3H, s, AcN-2), 2.38 (3H, s, AcO-8), 7.32 (1H, d, $J_{5,6}$=10.6 Hz, H-6), 7.38 (1H, brs, H-9), 7.38 (1H, brd, $J_{3,4}$=8.4 Hz, H-4), 7.43 (1H, brm, NH), 7.46 (1H, brd, H-5), 7.62 (1H, brd, H-3), and 7.78 (1H, brs, H-1); MS *m/z* 337 (M$^+$; 11), 296 (90), 295 (100), 280 (21), 267 (29), 253 (53), 238 (14), 225 (63), 224 (27), 210 (48), 181 (30), 180 (21), and 43 (22).

Found: *m/z* 337.1285. Calcd for C$_{20}$H$_{19}$NO$_4$: M, 337.1314.

2-Acetamido-8-hydroxy-1,10,10- (and 3,10,10)-trimethylcyclohept[*a*]inden-7(10*H*)-one (27p) and Their Acetates (28p,p′). The similar treatment of **18p** (10 mg) as those for **27o** and **28o** gave the products as isomeric mixtures with regard to the 1- and 3-methyl group.

27p: A yellow powder (5 mg, 50% yield); ^{1}H NMR δ=1.49, 1.60* (6H, s, Me$_2$C-10), 2.21 (3H, brs, AcN-2), 2.35, 2.40* (3H, brs, Me-1,3), 6.9—8.2 (ca. 7H, m, ArH, NH, OH);* signals presumably due to the minor 1-methyl isomer (ca. 30%) in the chromatographically inseparable mixture; MS *m/z* 309 (M$^+$; 100), 294 (10), 268 (15), 267 (18), 239 (13), and 225 (10).

28p (3,10,10-trimethyl isomer): Yellow fine prisms (40% yield from **27p**) after separation from the minor product **28p′** (see below) by silica-gel column chromatography with 1:1 AcOET–hexane; mp 233—235 °C (from AcOEt); ^{1}H NMR δ=1.47 (6H, s, Me$_2$C-10), 2.22 (3H, brs, AcN-2), 2.35 (3H, brs, Me-3), 2.37 (3H, s, AcO-8), 7.30 (1H, d, $J_{5,6}$=11.0 Hz, H-6), 7.35 (1H, brs, H-9), 7.36 (1H, brs, H-4), 7.43 (1H, brd, H-5), 7.50 (1H, brs, H-1), and 8.05 (1H, brm, NH); MS *m/z* 351 (M$^+$; 5.2), 309 (100), 297 (10), 294 (9), 268 (13), 267 (15), 265 (11), 239 (17), 225 (16), 209 (10), and 43 (60).

Found: *m/z* 351.1452. Calcd for C$_{21}$H$_{21}$NO$_4$: M, 351.1471.

28p′ (1,10,10-trimethyl isomer): A yellow solid (25% yield from **27p** after the chromatographic purification); ^{1}H NMR δ=1.59 (6H, s, Me$_2$C-10), 2.21 (3H, brs, AcN-2), 2.38 (3H, s, AcO-8), 2.42 (3H, brs, Me-1), 7.32 (1H, d, $J_{5,6}$=11 Hz, H-6), 7.39 (1H, brs, H-9), 7.47 (1H, brd, $J_{3,4}$=8.5 Hz, H-4), 7.55 (1H, brd, H-5), 7.62 (1H, brd, H-3), and 7.95 (1H, brm, NH); MS *m/z* 351 (M$^+$; 3.3), 309 (100), 297 (18), 267 (18), 239 (15), 225 (11), 209 (10), and 43 (45).

Found: *m/z* 351.1445. Calcd for C$_{21}$H$_{21}$NO$_4$: M, 351.1471.

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