Phytochemistry, Vol. 21, No. 4, pp. 929–931, 1982.
Printed in Great Britain.

0031-9422/82/040929-03$03.00/0

THE NEOLIGNANS (−)-CARINATONE AND CARINATIN FROM *VIROLA CARINATA*

KAZUKO KAWANISHI, YUKIKO UHARA and YOHEI HASHIMOTO

Institute of Pharmacognosy, Kobe Women's College of Pharmacy, Motoyamakita-Machi, Higashinada-Ku, Kobe 658, Japan

(*Received* 14 *November* 1980)

Key Word Index—*Virola carinata*, Myristicaceae; neolignan; (−)-carinatone; carinatin.

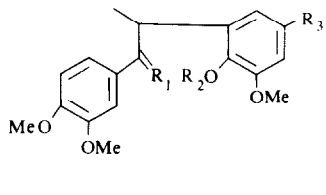
Abstract—From the bark of *Virola carinata* two neolignans have been isolated: (−)-carcinatone, [(2*S*)-1-(3′,4′-dimethoxyphenyl)-2-(3″-allyl-5″-methoxy-6″-hydroxyphenyl)propanone] and carinatin, [5-allyl-7-methoxy-3-methyl-2-(3′,4′-dimethoxyphenyl)benzofuran].

INTRODUCTION

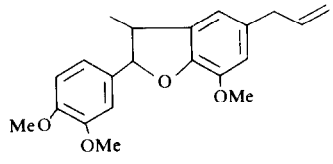
Gottlieb *et al.* [1] have reported that the wood of *Virola carinata* (Benth.) Warburg contains (+)-guaiacin, (−)-galcatin and (−)-*iso*-otobaphenol, whereas we have recently found dehydrodieugenol and monomethyl dehydrodieugenol in the bark [2]. Two neolignans have now been isolated from bark and are the subject of the present paper.

RESULTS AND DISCUSSION

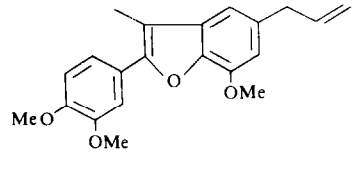
From high resolution mass spectrometry, compound **1** was estimated as $C_{21}H_{24}O_5$. Since it gave a bluish colour with $FeCl_3/K_3Fe(CN)_6$ and no colour with Gibbs reagent, it appeared to be a phenolic compound with a *para* substituent. The presence of the hydroxyl group was identified from IR ν_{max}^{KBr} 3350 cm^{-1} and ^1H NMR δ 5.92 ppm. By IR (ν_{max} 1665 cm^{-1}) and ^{13}C NMR (δ 199.61 ppm) the presence of a carbonyl group was proved. ^1H NMR spectral measurements by decoupling technique supported the assignment of a secondary methyl adjacent to the carbonyl and an allyl group as follows: the former, methyl protons at δ 1.46(*d*, J = 6.8 Hz) and methine proton at δ 5.03(*q*, J = 6.8 Hz) and the latter, CH_2–CH=CH_2 at δ 3.22(*dt*, J = 6.7 and 1.6 Hz), CH_2–C<u>H</u>=CH_2 at δ 5.86(*ddt*, J = 17.0, 9.2 and 6.7 Hz), CH_2–CH=C<u>H</u>$_2$(*cis*) at δ 499(*ddt*, J = 9.2, 2.0 and 1.6) and CH_2–CH=C<u>H</u>$_2$ (*trans*) at δ 4.99(*ddt*, J = 17.0, 2.0 and 1.6 Hz). ^1H NMR [δ 3.85(3 H, *s*) and 3.88 (6 H, *s*)] and ^{13}C NMR [δ 55.93(3 C, *q*)] showed the presence of three methoxyl groups on the aromatic rings. The orientation of protons on two aromatic rings was estimated by spin coupling constants. Two protons on the ring, δ 6.53 and 6.55 (J = 2.0, each) were related to a *meta* orientation for C-2″ and C-4″. Three protons on the other ring δ 6.80(*d*, J = 8.6 Hz), 7.61 (*d*, J = 1.9 Hz) and 7.72 (*dd*, J = 8.6 and 1.9 Hz) were an ABX system for C-5′, C-2′ and C-6′ protons respectively. The above data could be accommodated by structure **1** which was based upon biogenetic considerations [3]. The base ion, $C_9H_9O_3$, is compatible with one of the proposed constitutions by the α-cleavage of the ketone of structure **1**. Acetylation of **1** yielded a monoacetate, **1a**, $C_{23}H_{26}O_6$, IR and ^1H NMR of which revealed an acetyl group at ν_{max} 1760 and 1185 cm^{-1} and acetyl protons at δ 2.35 ppm respectively. By Wolff-Kishner reduction [4], **1** gave a resinous compound, **1b**, $C_{21}H_{28}O_4$, which indicated that an allyl group was hydrogenated as well as the carbonyl ketone. Based on decoupling techniques from ^1H NMR, it was found that the carbonyl group was reduced to methylene, whose protons appeared at δ 2.67 (*dd*, J = 13.5 and 8.7 Hz) and 2.98(*dd*, J = 13.5 and 6.2 Hz). A methyl proton of the secondary methyl



	R_1	R_2	R_3
1	O	H	Allyl
1a	O	COMe	Allyl
1b	H_2	H	*n*—Propyl
1c	OH / H	H	Allyl



2



3

group was observed at δ 1.20(*d*, $J = 7.0$ Hz) and a methine proton at δ 3.39(*m*, $J = 8.7$, 7.0 and 6.2 Hz) which was shown to be adjacent to the new methylene group by decoupling technique. ^{1}H NMR showed that the allyl group was hydrogenated to *n*-propyl, with δ 0.93(3 H, $J = 7.3$ Hz), 1.58(2 H, *m*) and 2.48(2 H, $J = 7.8$ Hz). The molecular ion, 344.196, $C_{21}H_{28}O_4$ (calc. 344.199) and base ion, 193.125, $C_{12}H_{17}O_2$ (calc. 193.125) were calculated to be of propyl grouping rather than allyl by mass spectrometry. It is assumed that a reacting hydrazine generates a di-imide to hydrogenate a carbon–carbon double bond. Compound **1** was reduced with sodium borohydrate to give diastereoisomers of alcohols, **1c**, $C_{21}H_{26}O_5$, of which the major one showed the AMX_3 system on ^{1}H NMR, the methyl protons (X_3) at δ 1.05 (*d*, $J = 7.0$ Hz), the methine proton (M) on the carbon-bearing methyl group at δ 3.41 (*dq*, $J = 9.4$ and 7.0 Hz) and the other methine proton (A) on a carbon bearing a hydroxyl group at δ 4.75(*d*, $J = 9.4$ Hz). Two methine carbons, those bearing a methyl and a hydroxyl group appeared at δ 42.03 and 78.94 respectively on ^{13}C NMR. Compound **1c** was condensed with H_3PO_4 to produce a 2,3-dihydrobenzofuran (**2**) [5], $C_{21}H_{24}O_4$, which had no hydroxyl group detectable by IR. The AMX_3 system was analysed by ^{1}H NMR, (A): δ 5.10(*d*, $J = 9.7$ Hz), (M): 3.45(*dq*, $J = 9.7$ and 6.7 Hz), (X_3): 1.37(*d*, $J = 6.7$ Hz). An aromatic hydroxyl group must be at C-6″ in **1c**, since a dehydration from the 1,4-dihydroxy groups can be regarded as a part of structure **1c**. A *trans*-2,3-dihydrobenzofuran structure was suggested by coupling constants of the proton (A) at C-2 and the methyl protons (X_3) at C-3 by ^{1}H NMR [6]. The 2*S*,3*S* configuration of this compound was confirmed by the similarity of the ORD curve of (−)-melanoxin (2*S*,3*S*), as opposed to the antipodal curve of (+)-obtusafuran (2*R*, 3*R*) [7]. The absolute stereochemistry of **1** ($[\alpha]_D^{25} - 108.7°$) was established to be of the *S* configuration since **2** had an *S* configuration at C-3 and the ORD curve of **1** was similar to *S*-(+)-hydratropic acid [8]. Thus **1** must be (2*S*) - 1 - (3′,4′ - dimethoxyphenyl) - 2 - (3″ - allyl - 5″ - methoxy - 6″ - hydroxyphenyl)propanone; named (−)-carinatone.

Compound **3**, $C_{21}H_{22}O_4$, determined by high resolution mass spectrometry, contained a furan group from the IR (880 cm^{-1}). Compound **3** has three methoxyl groups and an allyl group, from NMR studies. The substitution of these groups on the rings was determined as being the same as in **1** from the coupling constants in ^{1}H NMR. The methyl group at δ 2.42 (3 H, *s*) on ^{1}H NMR could be located on the unsaturated carbon. From spectral data and biogenetic considerations, structure **3** is proposed for this neolignan. The dihydrobenzofuran (**2**) was dehydrogenated to a benzofuran with Pd–C in decalin [6]. The furan ring was also directly synthesized from **1** by dehydration with stannous chloride in acetic and hydrochloric acids [9]. Thus the 4-keto butyl alcohol, grouping of **1** might be enolated in acid solution to butadien-1,4-dialcohol from which the elimination of water would be facilitated The synthetic products were identical with the natural one by mmp, IR and TLC respectively. Thus **3** is identified as 5 - allyl - 7 - methoxy - 3 - methyl - 2 - (3′,4′ - dimethoxyphenyl)benzofuran. It is named carinatin.

EXPERIMENTAL

Isolation of **1**. Eluted fraction (2.64 g) with gradient solvents of C_6H_6 and $CHCl_3$ (0–100%), to which were added $CHCl_3$ and MeOH (0–100%) on a Si gel column, were re-chromatographed on Si gel (100 g) with gradient solvents of C_6H_6 and MeOH (0–100%). Elution of 10% MeOH in C_6H_6 gave a mixture (three spots on TLC), (2.5 g) which was chromatographed on another column with C_6H_6 and Me_2CO. Compound **1** (1.0 g) was eluted with 5% Me_2CO in C_6H_6, mp 103° (recrystallized from C_6H_6 and petrol). $C_{21}H_{24}O_5$ (found 356.161 for 356.162 by MS); $[\alpha]_D^{25} = -108.7°$ in $CHCl_3$; UV $\lambda_{max}^{CHCl_3}$ nm (log ϵ): 304(4.093), 277(4.021), 243(3.944); ^{1}H NMR (200 MHz)($CDCl_3$) δ 1.46 (3 H, *d*, $J = 6.8$, Hz, H-3), 3.22 (2 H, *dt*, $J = 6.7$ and 1.6 Hz, CH_2–CH=CH_2), 3.85(3 H, *s*, OMe), 3.88(6 H, *s*, OMe), 4.99[1 H, *ddt*, $J = 17.0$, 2.0 and 1.6 Hz, CH_2–CH=CH_2 (*trans*)], 4.99[1 H, *ddt*, $J = 9.2$, 2.0 and 1.6 Hz, CH_2–CH=CH_2(*cis*)], 5.03 (1 H, *q*, $J = 6.8$ Hz, H-2), 5.86(1 H, *ddt*, $J = 17.0$, 9.2 and 6.7 Hz, CH_2–CH=CH_2), 5.92(1 H, *s*, OH), 6.53(1 H, *d*, $J = 2.0$ Hz, H-2″ or H-4″), 6.55(1 H, *d*, $J = 2.0$ Hz, H-4″ or H-2″), 6.80 (1 H, *d* = 8.6 Hz, H-5′), 7.61(1 H, *d*, $J = 1.9$ Hz, H-2′), 7.72 (1 H, *dd*, $J = 8.6$ and 1.9 Hz, H-6′); ^{13}C NMR (50 MHz)($CDCl_3$) δ 17.89 (*q*, C-3), 39.80(*d*, C-2), 39.98(*t*, CH_2–CH=CH_2), 55.93(*q*, OMe × 3), 109.50 (*d*, C-2′), 110.21(*d*, C-4″), 111.22(*d*, C-2″), 115.62(*t*, CH_2–CH=CH_2), 120.04(*d*, C-5′), 123.25(*d*, C-6′), 127.58(*s*, C-1′), 129.69(*s*, C-3″), 131.91(*s*, C-1″), 137.64(*d*, CH_2–CH=CH_2), 140.44(*s*, C-5″), 146.61(*s*, C-4′), 148.82(*s*, C-3′), 153.03(*s*, C-6″), 199.61(*s*, C-1): MS *m*/*z*: 356[M]$^+$ (22.3%), 191(2.2), 165(100); ORD [dioxane; *c* 0.00055 (600–230 nm)] $[\phi]_{600} - 65$, $[\phi]_{400} - 647$, $[\phi]_{350} - 1553$, $[\phi]_{320} - 2654$, $[\phi]_{310} - 3236$, $[\phi]_{304} - 2719$, $[\phi]_{285} - 129$, $[\phi]_{276}$ 0, $[\phi]_{266} + 6214$, $[\phi]_{260} + 12\,233$, $[\phi]_{251} + 15\,534$, $[\phi]_{244} + 10\,227$, $[\phi]_{236} + 8673$.

Isolation of **3**. Eluents of 1% Me_2CO in C_6H_6 from a Si gel column (80 mg) gave crystals, mp 88–91° (ex. EtOH). $C_{21}H_{22}O_4$ (found 338.148 for 338.152 by MS); UV $\lambda_{max}^{CHCl_3}$ nm (log ϵ): 307(4.428), 244(4.100): ^{1}H NMR ($CDCl_3$) δ 2.42(3 H, *s*, Me × 3), 3.48(2 H, *dt*, $J = 6.7$ and 1.6 Hz, CH_2–CH=CH_2), 3.93(3 H, *s*, OMe), 3.97(3 H, *s*, OMe), 4.02(3 H, *s*, OMe), 5.09 [1 H, *ddt*, $J = 10.8$, 2.0 and 1.6 Hz, CH_2–CH=CH_2(*cis*)], 5.12 [1 H, *ddt*, $J = 17.0$, 2.0 and 1.6 Hz, CH_2–CH=CH_2(*trans*)], 6.05(1 H, *ddt*, $J = 17.0$, 10.8 and 6.7 Hz, CH_2–CH=CH_2), 6.63(1H, *d*, $J = 1.4$ Hz, H-6), 6.93(1 H, *d*, $J = 1.4$ Hz, H-4), 6.94(1 H, *d*, $J = 9.0$ Hz, H-5′), 7.33(1 H, *dd*, $J = 9.0$ and 2.2, H-6′) 7.33(1 H, *d*, $J = 2.2$ Hz, H-2′); ^{13}C NMR ($CDCl_3$) δ 9.64(*q*, Me × 3), 40.64(*t*, CH_2–CH=CH_2), 55.93(*q*, OMe), 56.04(*q*, OMe), 56.10(*q*, OMe), 107.57(*d*, C-2′), 110.05 (*d*, C-6), 110.25(*s*, C-3), 111.01(*d*, C-4), 111.10(*d*, C-5′), 115.58(*t*, CH_2–CH=CH_2), 119.89(*d*, C-6′), 124.29(*s*, C-3a), 133.03(*s*, C-1′), 135.16(*s*, C-5), 138.01(*d*, CH_2–CH=CH_2), 141.48(*s*, C-7), 144.71(*s*, C-4′), 148.94(*s*, C-2 and C-3′), 151.24(*s*, C-7a); MS *m*/*z*: 338[M]$^+$ (100), 323(9.8), 254 (6.0).

Derivatives of **1**. The acetate was a resin (**1a**), $C_{23}H_{26}O_6$ (found 398.170 for 398.173); ^{1}H NMR ($CDCl_3$) δ 1.43(3 H, *d*, $J = 6.9$ Hz, H-3), 2.35(3 H, *s*, OCOMe), 3.27(2 H, *dt*, $J = 6.7$ and 1.6 Hz, CH_2–CH=CH_2), 3.79(3 H, *s*, OMe), 3.88(3 H, *s*, OMe), 3.89(3 H, *s*, OMe), 4.64 (1 H, *q*, $J = 6.6$ Hz, H-2), 5.01 [1 H, *ddt*, $J = 17.9$, 2.0 and 1.6 Hz, CH_2–CH=CH_2(*trans*)], 5.02[1 H, *ddt*, $J = 9.3$, 2.0 and 1.6 Hz, CH_2–CH=CH_2(*cis*)], 5.87 (1 H, *ddt*, $J = 17.9$, 9.3 and 6.7 Hz, CH_2–CH=CH_2), 6.57(1 H, *d*, $J = 1.7$ Hz, H-2″ or H-4″), 6.63(1 H, *d*, $J = 1.7$ Hz, H-4″ or H-2″), 6.79(1 H, *d*, $J = 8.2$ Hz, H-5′), 7.52(1 H, $J = 2.0$ Hz, H-2′), 7.55(1 H, *dd*, $J = 8.2$ and 2.0 Hz, H-6′); MS *m*/*z*: 398 [M]$^+$ (9.6), 356(6.7), 338(4.5), 165(100). Wolff–Kishner reduction of **1** gave a resinous product, $C_{21}H_{28}O_4$ (found 344.196 for 344.199); UV $\lambda_{max}^{CHCl_3}$ nm (log ϵ): 282(3.663), 243(3.625); ^{1}H NMR ($CDCl_3$) δ 0.93(3 H, *t*, $J =$

7.3 Hz, $CH_2CH_2CH_3$), 1.20(3 H, *d*, *J* = 7.0 Hz, H-3), 1.58 (2 H, *m*, CH_2–CH_2–Me), 2.48(2 H, *t*, *J* = 7.8 Hz, CH_2–CH_2–Me), 2.67(1 H, *dd*, *J* = 13.5 and 8.7 Hz, H-1), 2.98(1 H, *dd*, *J* = 13.5 and 6.2 Hz, H-1), 3.39(1 H, *m*, *J* = 8.7, 7.0 and 6.2 Hz, H-2), 3.80(3 H, *s*, OMe), 3.84(3 H, *s*, OMe), 3.86(1 H, *s*, OMe), 5.56(1 H, *s*, OH), 6.55(1 H, *d*, *J* = 2.0 Hz, H-2″ or H-4″), 6.59(1 H, *d*, *J* = 2.0 Hz, H-4″ or H-2″), 6.64(1 H, *d*, *J* = 1.6 Hz, H-2′), 6.70(1 H, *dd*, *J* = 1.6 and 8.0 Hz, H-6′), 7.28(1 H, *d*, *J* = 8.0 Hz, H-5′); MS *m*/*z*: 344 $[M]^+$ (27.6), 193(100). $NaBH_4$ reduction of **1** gave a mixture of major and minor alcohol products, **1b** inseparable by TLC, $C_{21}H_{26}O_5$ (found 358.177 for 358.178), ^1H NMR ($CDCl_3$) (major one) δ 1.05 (3 H, *d*, *J* = 7.0 Hz, H-3), 3.32 (2 H, *dt*, *J* = 7.0 and 1.6 Hz, CH_2–CH=CH_2), 3.41(1 H, *dq*, *J* = 9.4 and 7.0 Hz, H-2), 3.87(3 H, *s*, OMe), 3.88 (3 H, *s*, OMe), 3.89 (3 H, *s*, OMe), 4.75(1 H, *d*, *J* = 9.4 Hz, H-1), 5.07[1 H, *ddt*, *J* = 10.4, 2.0 and 1.6 Hz, CH_2–CH=CH_2(*cis*)], 5.08 [(1 H, *ddt*, *J* = 17.0, 2.0 and 1.6 Hz, CH_2–CH=CH_2(*trans*)], 5.95(1 H, *ddt*, *J* = 17.0, 10.4 and 7.0 Hz, CH_2–CH=CH_2), 6.00(1H, *s*, OH), 6.62(1 H, *d*, *J* = 1.8 Hz, H-2″ or H-4″), 6.64(1 H, *d*, *J* = 1.8 Hz, H-4″ or H-2″), 6.84(1 H, *d*, *J* = 8.6 Hz, H-5′), 6.93 (1 H, *dd*, *J* = 8.6 and 2.0 Hz, H-6′), 6.93(1 H, *d*, *J* = 2.0, H-2′), ^{13}C NMR ($CDCl_3$) (major one) δ 17.07 (*q*, C-3), 40.11 (*t*, CH_2–CH=CH_2), 42.03(*d*, C-2), 55.84(*q*, OMe × 3), 78.94(*d*, C-1), 109.44(*d*, C-2′), 109.73(*d*, C-4″), 110.69(*d*, C-2″), 115.58(*t*, CH_2–CH=CH_2), 119.49(*d*, C-5′), 120.45(*d*, C-6′), 129.04(*s*, C-1′), 131.58 (*s*, C-3″), 135.68(*s*, C-1″), 137.78(*d*, CH_2–CH=CH_2), 142.12 (*s*, C-5″), 146.75 (*s*, C-4′), 148.50(*s*, C-3′), 148.91(*s*, C-6″); MS *m*/*z*: 358 $[M]^+$ (6.5), 340(46.2), 192(100), 167(90.7). Dehydration with H_3PO_4 of **1b** gave a resinous product **2** which was purified by CC with C_6H_6 and MeOH. $C_{21}H_{24}O_4$ (found 340.169 for 340.168), UV $\lambda_{max}^{CHCl_3}$ nm (log ϵ): 286(3.859), 282(3.866), 246(4.083); ^1H NMR ($CDCl_3$) δ 1.37(3 H, *d*, *J* = 6.7 Hz, Me × 3), 3.35(2 H, *dt*, *J* = 6.8 and 1.9 Hz, CH_2–CH=CH_2), 3.45(1 H, *dq*, *J* = 9.7 and 6.7 Hz, H-3), 3.87(3 H, *s*, OMe), 3.88(6 H, *s*, OMe), 5.05[1 H, *ddt*, *J* = 17.0, 2.0 and 1.6 Hz, CH_2–CH=CH_2(*trans*)], 5.10(1 H, *d*, *J* = 9.7 Hz, H-2), 5.10[1 H, *ddt*, *J* = 10.2, 2.0 and 1.6 Hz, CH_2–CH=CH_2(*cis*)], 5.98(1 H, *ddt*, *J* = 17.0, 10.2 and 6.8 Hz, CH_2–CH=CH_2), 6.60(1 H, *d*, *J* = 2.0 Hz, H-2″ or H-4″), 6.62(1 H, *d*, *J* = 2.0 Hz, H-4″ or H-2″), 6.83(1 H, *d*, *J* = 8.0 Hz, H-5′), 6.96(1 H, *dd*, *J* = 8.0 and 2.0 Hz, H-6′), 6.99(1 H, *d*, *J* = 2.0 Hz, H-2′), ^{13}C NMR ($CDCl_3$) δ 17.48 (*q*, Me × 3), 40.20(*t*, CH_2–CH=CH_2), 45.75(*d*, C-3), 55.91(*q*, OMe × 3), 93.58(*d*, C-2), 109.55(*d*, C-2′), 110.81(*d*, C-6), 111.90(*d*, C-4), 115.55(*t*, CH_2–CH=CH_2), 115.61 (*d*, C-5′), 119.23(*d*, C-6′), 132.76(*s*, C-1′), 133.16(*s*, C-5), 133.53(*s*, C-3a and C-7), 137.88(*d*, CH_2–CH=CH_2), 144.04(*s*, C-4′), 149.13(*s*, C-3′ and C-7a); MS *m*/*z*: 340 $[M]^+$ (100); ORD [dioxane; *c* 0.0008 (600–241 nm) and 0.0004(241–222 nm)][ϕ]$_{600}$ − 43, [ϕ]$_{400}$ − 43, [ϕ]$_{250}$ − 595, [ϕ]$_{241}$ − 1063, [ϕ]$_{238.2}$ 0, [ϕ]$_{233.6}$ + 1190, [ϕ]$_{228}$ + 2465, [ϕ]$_{225}$ + 1742, [ϕ]$_{222}$ + 1318.

Dehydrogenation of **2**. Pd–C (10% 3 mg) was added to **2** (51 mg) in 5 ml decalin and the mixture refluxed for 24 hr. The product was chromatographed on Si gel in *n*-hexane and C_6H_6, crystallized and confirmed to be identical with **3** by means of mmp, IR and TLC.

Condensation of **1**. A mixture of 0.2 ml HOAc, and 0.2 ml. conc HCl was heated to boiling, into which $SnCl_2$ (110 mg) and **1** (30 mg) in HOAc (0.1 ml) were added. After cooling the solution was diluted with 0.4 ml H_2O, extracted with $CHCl_3$, purified by TLC, crystallized from EtOH and identified as **3** by means of mmp, IR and TLC.

Acknowledgements—The authors thank Dr. William A. Rodorigues of the Instituto Nacional de Pesquisas de Amazonas, Manaus, Brazil for furnishing the identified plant. They are also grateful to Professor Shigeru Kuwata and Dr. Takashi Yamada of Konan University (Kobe) and Drs. Makiko Sugiura and Kayoko Saiki of our College for measurements of ORD, NMR and MS spectra.

REFERENCES

1. Gottlieb, O. R., Maia, J. G. S. and Ribeiro, M. N. S. (1976) *Phytochemistry* **15**, 773.
2. Kawanishi, K. and Hashimoto, Y. (1981) *Phytochemistry* **20**, 1166.
3. Gottlieb, O. R. (1978) *Fortschr. Chem. Org. Naturst.* **35**, 1.
4. Minlon, H. (1946) *J. Am. Chem. Soc.* **68**, 2487.
5. Colonge, J. and Clerc, G. (1955) *Bull. Soc. Chim. Fr.* 834.
6. Donnelly, B. J., Donnelly, D. M. X., O'Sullivan, A. M. and Prendergast J. P. (1969) *Tetrahedron* **25**, 4409.
7. Lima, O. A., Gottlieb, O. R. and Magalhães, M. T. (1972) *Phytochemistry* **11**, 2031.
8. Sjöberg, B. (1960) *Acta. Chem. Scand.* **14**, 273.
9. Lutz, R. E. and McGinn, E. C. (1942) *J. Am. Chem. Soc.* **64**, 2585.