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NEOLIGNANS OF *VIROLA CARINATA* BARK

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Key Word Index—*Virola carinata*; Myristicaceae; bark; neolignans; dihydrocarinatinol; carinatonol; carinatol; NMR.

Abstract—Four neolignans, dehydrodieugenol, its monomethylether, carinatone and carinatin have been isolated from the hexane fraction of the bark of *Virola carinata*. Three new neolignans were separated from the chloroform fraction and examined by spectroscopy and chemical reactions. Their structures were determined as (2*S*, 3*S*)-5-allyl-7-methoxy-3-hydroxymethyl-2-(3′,4′-dimethoxyphenyl)-2,3-dihydrobenzofuran, (2*S*)-1-(3′,4′-dimethoxyphenyl)-2-(3″-allyl-5″-methoxy-6″-hydroxyphenyl)propanone(1)ol(3), (1*S*,2*S*)-1-(3′,4′-dimethoxyphenyl)-2-(3″-allyl-5″-methoxy-6″-hydroxyphenyl)propanol(1) and called dihydrocarinatinol, carinatonol and carinatol, respectively.

INTRODUCTION

In two previous reports [1, 2], four neolignans; dehydrodieugenol, its monomethyl ether, carinatone and carinatin were isolated from the bark of *Virola carinata* (Benth) Warburg. We have now found three more new neolignans in the bark, which were spectroscopically characterized as compounds similar to carinatone and carinatin. Chemical derivation, prepared to confirm the proposed structures was undertaken.

RESULTS AND DISCUSSION

The chloroform extract was chromatographed several times to separate dehydrodieugenol, its monomethyl ether, carinatone (**5**) and three new compounds.

Compound **1**, a resin, $C_{21}H_{24}O_5$ as estimated by high resolution mass spectrometry, gave a negative reaction with ferric chloride–potassium ferricyanide for a phenolic hydroxy group but an IR band at ν3600 cm^{-1} revealed the presence of an alcoholic hydroxy group. Structural assignments of compound **1** were based on spectroscopic comparison with dihydrocarinatin (**3**) which was synthesized from carinatone (**5**) [2]. The significant ^{1}H and ^{13}C NMR spectral similarities showed that an allyl, a methoxy and a 3′, 4′-dimethoxyphenyl group were placed on C-5, C-7 and C-2 of a dihydrobenzofuran ring, respectively. The methylene protons of the hydroxy methyl group appeared at δ 3.94 as a doublet doublet (J = 10.4 and 5.8 Hz), which were coupled with each other and the proton on C-3 at δ 3.61 (doublet triplet, J = 7.2 and 5.8 Hz); a hydroxy proton was not detected. The hydroxymethyl group was also confirmed by ^{13}C NMR (δ 63.93, triplet). Compound **1** was reacted with *p*-toluenesulfonylchloride to give the tosylate (**2**), the methylene protons of the tosyloxymethyl group of which were assigned at δ 4.18 (*dd*, J = 10.0 and 8.2 Hz) and 4.35 (*dd*, J = 10.0 and 4.2 Hz) by ^{1}H NMR. These two protons were coupled with each other and the proton on C-3 at δ 3.73 (*ddd*, J = 8.2, 6.7 and 4.2 Hz). Therefore, compound **1** could possess the hydroxymethyl group instead of the methyl group on C-3 in dihydrocarinatin (**3**). Tosylate (**2**) was treated with $NaBH_3CN$ to give the reduced compound [4], which was identical with dihydrocarinatin (**3**) [2] by means of TLC and IR. The absolute configuration of compound **1** ($[\alpha]_D$ − 12.3°) should be 2*S* and 3*S*, since it afforded dihydrocarinatin (**3**) ($[\alpha]_D$ − 23.2°) [2] in the above reactions without affecting the stereochemical activity. All the spectroscopic data and chemical reactions determined the structure of compound 1 as **1**, (2*S*, 3*S*)-5-allyl-7-methoxy - 3 - hydroxymethyl - 2 - (3′,4′ - dimethoxyphenyl)dihydrobenzofuran. It was named dihydrocarinatinol.

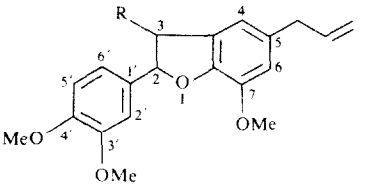
Compound **2**, mp 128–130°, $C_{21}H_{24}O_6$ as estimated by high resolution mass spectrometry, gave a positive phenolic colour reaction with ferrichloride–potassium ferricyanide but a negative colour reaction with Gibbs reagent. These reactions suggested that it was a phenolic compound which had a substituent at a *para*-position to a hydroxy group. Hydroxy groups were shown at ν 3560 cm^{-1} by IR. An aromatic hydroxy proton was assigned at δ 5.90 (singlet) by ^{1}H NMR. An aliphatic hydroxy proton appeared at δ5.17 as a doublet doublet (J = 8.5 and 5.0 Hz) on ^{1}H NMR which was coupled with two protons of a methylene group at δ 3.81 (J = 11.5, 8.3 and 5.0 Hz) and 4.25 (J = 11.5, 8.5 and 6.2 Hz) as a doublet doublet doublet, respectively. Two kinds of hydroxy groups were confirmed by the corresponding acetate after spectroscopic examination. A resinous acetate $C_{25}H_{28}O_8$ by high resolution mass spectrometry showed that it comprised two acetyl groups. An aromatic acetyl group was detected at ν 1760 cm^{-1} by IR and δ 2.43 on ^{1}H NMR. An aliphatic acetyl group appeared at ν 1735 cm^{-1} by IR and δ 1.99 on ^{1}H NMR. A carbonyl

ketone was detected by IR (ν 1670 cm^{-1}) and ^{13}C NMR (δ 199.28). A hydroxy, three methoxy and an allyl group were also identified by ^{1}H and ^{13}C NMR. The mass spectral fragments of compound **2**, $C_{21}H_{22}O_5$ at m/z 354 and $C_{20}H_{22}O_5$ at m/z 342 were determined as the elimination of water from the molecular ion (M^+) followed by the elimination of carbon in due course, respectively. Two fragments, $C_{12}H_{14}O_2$ and $C_9H_9O_3$ were compatible with the proposed constituents by α-cleavage of the ketone of fragment $C_{21}H_{23}O_5$ which was afforded by the loss of a hydroxyl from the M^+. Compound 2 had similar UV absorbance to carinatone. All spectroscopic studies suggested that compound 2 (**4**) was a derivative of propanone(1)ol(3) with dimethoxyphenyl and allyl-methoxy-hydroxyphenyl groups. The ketone group was confirmed by reduction with sodium borohydride giving **6**, a resinous mass. In the propandiol derivative (**6**) a proton on C-1 attached to a hydroxy group which was formed in this reaction was observed at δ 5.12 (J = 8.2 Hz) as a doublet by ^{1}H NMR. One proton on C-2 and two on C-3 appeared at δ 3.49 (multiplet) and 3.70–3.90 (overlapped with three methoxy groups), respectively. These three protons were shifted so closely to each other on ^{1}H NMR that their coupling constants were difficult to determine. The corresponding acetate, a resinous mass $C_{27}H_{32}O_9$ as determined by high resolution mass spectrometry, was composed of one aromatic and two aliphatic acetyl groups, ν 1775 cm^{-1} by IR and δ 2.34 on ^{1}H NMR for the former and ν 1748 and 1743 cm^{-1} and δ 1.92 and 1.94 for the latter. Comparing the original alcohol, the acetate gave better assignments on ^{1}H NMR for four protons; one on C-1, one on C-2 and two on C-3 appeared at δ 6.01 as a doublet (J = 8.2 Hz), 3.72 as a multiplet and 4.01 (J = 11.0 and 6.4 Hz) and 4.28 (J = 11.0 and 5.0 Hz) as a doublet doublet, respectively. **6** was dehydrated with phosphoric acid to give a dihydrobenzofuran derivative, which was identical to **1** by means of TLC and IR. Compound **2**, ($[\alpha]_D$ −171.4°) was laevorotatory, which is the same as carinatone (**5**) [2], therefore, the assymetric carbon at position 2 was determined as the *S*-configuration. Thus, compound 2 was determined to be (2*S*)-1-(3′,4′-dimethoxyphenyl) - 2 - (3″ - allyl - 5″ - methoxy - 6″ - hydroxyphenyl)propanone(1)ol(3), **4**. It was named carinatonol.

Compound 3, a resinous mass, $C_{21}H_{26}O_5$ as estimated by high resolution mass spectrometry, gave a positive phenol test with ferric chloride–potassium ferricyanide and a negative Gibbs test. The results of colour tests indicated that compound 3 was composed of a phenol which had a substituent at a position *para* to a hydroxy group. TLC and spectroscopic data, especially ^{1}H NMR showed that compound 3 was identical to the major product of two isomers (**7**) which were derived from carinatone (**5**) [2]. Analysis of the AMX$_3$ system by ^{1}H NMR showed similarities to dihydrocarinatin [2] and other dihydrobenzofurans [5] and showed compound 3 to be a 1,2-*trans*-propanol(1) derivative. This was shown by δ 4.75 as a doublet (J = 9.4 Hz) for a proton (A) on C-1 bearing a hydroxy group, δ 3.41 as a doublet quartet (J = 9.4 and 7.0 Hz) for a proton (M) on C-2 bearing a methyl group and δ 1.05 as doublet (J = 7.0 Hz) for methyl protons (C-3) (X_3). The $[\alpha]_D$ value of compound 3 (−10.3°) had the same laevo rotation as dihydrocarinatin which has an all *S* configuration. Compound 3 must therefore be (1*S*, 2*S*) - 1 - (3′, 4′ - dimethoxyphenyl) - 2 - (3″ - allyl - 5″ - methoxy - 6″ - hydroxyphenyl)propanol(1), **7**. It was named carinatol.

EXPERIMENTAL

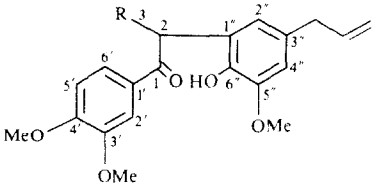
Isolation of compounds. Gradient elution with C_6H_6 and Me_2CO by Si gel CC yielded monomethyl dehydrodieugenol (2% Me_2CO), carinatin [2] (2–5%), a mixture of dehydrodieugenol, compounds 2 and 3 (5–7%) and compound 1



1 R = CH_2OH

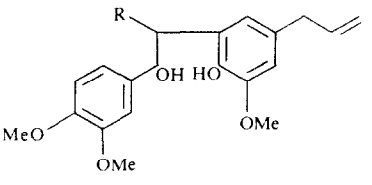
2 R = CH_2O − tosyl

3 R = Me



4 R = CH_2OH

5 R = Me



6 R = CH_2OH

7 R = Me

(10–15%). Further chromatography of the (5–7%) fraction, eluting with 7.5% Me_2CO in C_6H_6 yielded pure dehydrodieugenol and a mixture of dehydrodieugenol and compound 2. Compound 2 was separated in $CHCl_3$–EtOH (97:3) by Si gel CC. Elution with 17% Me_2CO in C_6H_6 gave compound 3 which was purified by prep. TLC using 20% Me_2CO in $CHCl_3$.

Compound 1 (**1**). A resinous mass gave no colour reaction with 1N $FeCl_3$–1N $K_3Fe(CN)_6$, $C_{21}H_{24}O_5$ (found 356.166 for 356.162 by mass spectrometry); $[\alpha]_D^{25} = -12.3°$ in $CHCl_3$; UV $\lambda_{max}^{CHCl_3}$ nm (log ϵ): 286 (3.79), 283 (3.80), 249 (3.83); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3600, 3010, 2945, 2845, 1600, 1520, 1500, 1465, 1265, 1140, 1025, 920. ^1H NMR (200 MHz) ($CDCl_3$): δ 3.34 (2H, *dt*, $J = 7.0$ and 1.2 Hz, CH_2–CH=CH_2), 3.61 (1H, *dt*, $J = 7.2$ and 5.8 Hz, H-3), 3.85 (3H, *s*, OMe), 3.86 (3H, *s*, OMe), 3.88 (3H, *s*, OMe), 3.94 (2H, *dd*, $J = 10.4$ and 5.8 Hz, CH_2OH-3), 5.06 [1H, *ddt*, $J = 10.0$, 2.0 and 1.2 Hz, CH_2–CH=CH_2 (*cis*)], 5.09 [1H, *ddt*, $J = 17.0$, 2.0 and 1.2 Hz, CH_2–CH=CH_2 (*trans*)], 5.58 (1H, *d*, $J = 7.2$ Hz, H-2), 5.97 (1H, *ddt*, $J = 17.0$, 10.0 and 7.0 Hz, CH_2–CH=CH_2), 6.67 (2H, *s*, H-4 and H-6), 6.83 (1H, *d*, $J = 8.5$ Hz, H-5′), 6.95 (1H, *d*, $J = 1.5$ Hz, H-2′), 6.97 (1H, *dd*, $J = 8.5$ and 1.5 Hz, H-6′). ^{13}C NMR (50 MHz) ($CDCl_3$): δ 40.14 (*t*, CH_2–CH=CH_2), 53.82 (*d*, C-3), 55.94 (*q*, OMe × 3), 63.93 (*t*, CH_2OH), 87.85 (*d*, C-2), 109.33 (*d*, C-2′), 110.97 (*d*, C-6), 112.58 (*d*, C-4), 115.74 (*t*, CH_2–CH=CH_2), 116.09 (*d*, C-5′), 118.74 (*d*, C-6′), 127.66 (*s*, C-1′), 133.66 (*s*, C-5), 133.76 (*s*, C-3a), 137.76 (*d*, CH_2–CH=CH_2), 144.30 (*s*, C-7), 146.99 (*s*, C-4′), 148.98 (*s*, C-3′), 149.18 (*s*, C-7a). MS: *m/z* (rel. int.) 356 $[M]^+$ (67.2), 338 (100.0), 326 (8.3).

Compound 2 (**4**). Colourless crystals, mp 128–130°, bluish-green colour with 1N $FeCl_3$–1N $K_3Fe(CN)_6$ and no colour with Gibbs reagent. $C_{21}H_{24}O_6$ (found 372.156 for 372.157); $[\alpha]_D^{25} - 171.4°$ in $CHCl_3$; UV $\lambda_{max}^{CHCl_3}$ nm (log ϵ): 308 (4.06), 281 (4.18), 242 (4.11); IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3560, 3020, 2945, 2850, 1670, 1640, 1595, 1585, 1520, 1500, 1465, 1420, 1020, 920, 850. ^1H NMR ($CDCl_3$): δ 2.49 (1H, *dd*, $J = 8.3$ and 6.2 Hz, H-2), 3.20 (2H, *dt*, $J = 6.8$ and 1.4 Hz, CH_2–CH=CH_2), 3.81 (1H, *ddd*, $J = 11.5$, 8.3 and 5.0 Hz, H-3), 3.86 (3H, *s*, OMe), 3.88 (6H, *s*, OMe), 4.25 (1H, *ddd*, $J = 11.5$, 8.5 and 6.2 Hz, H-3), 4.99 [1H, *ddt*, $J = 9.8$, 2.0 and 1.4 Hz, CH_2–CH=CH_2 (*cis*)], 4.99 [1H, *ddt*, $J = 16.8$, 2.0 and 1.4 Hz, CH_2–CH=CH_2 (*trans*)], 5.17 (1H, *dd*, $J = 8.5$ and 5.0 Hz, CH_2OH-2), 5.83 (1H, *ddt*, $J = 16.8$, 9.8 and 6.8 Hz, CH_2–CH=CH_2), 5.90 (1H, *s*, OH), 6.49 (1H, *d*, $J = 1.9$ Hz, H-2″ or H-4″), 6.57 (1H, *d*, $J = 1.9$ Hz, H-4″ or H-2″), 6.81 (1H, *d*, $J = 8.6$ Hz, H-5′), 7.61 (1H, *d*, $J = 1.9$ Hz, H-2′), 7.69 (1H, *dd*, $J = 8.6$ and 1.9 Hz, H-6′). ^{13}C NMR ($CDCl_3$): δ 39.82 (*t*, CH_2–CH=CH_2), 48.24 (*d*, CH–C=O), 55.82 (*q*, OMe), 55.94 (*q*, OMe × 2), 63.90 (*t*, CH_2OH), 110.09 (*d*, C-2′), 110.11 (*d*, C-4″), 110.88 (*d*, C-2″), 115.74 (*t*, CH_2–CH=CH_2), 120.41 (*d*, C-5′), 122.22 (*s*, C-1′), 123.53 (*d*, C-6′), 129.30 (*s*, C-3″), 131.86 (*s*, C-1″), 137.35 (*d*, CH_2–CH=CH_2), 140.88 (*s*, C-5″), 146.66 (*s*, C-4′), 148.67 (*s*, C-3′), 153.25 (*s*, C-6″), 199.28 (*s*, C=O). MS *m/z* 372 $[M]^+$ (6.8), 354 (2.1), 342 (9.7), 190 (19.8), 165 (100).

Compound 3 (**7**). Identical to the major isomer formed from carinatone (**5**) with $NaBH_4$ [2].

Tosylate (**2**). **1** (20 mg) in 0.1 ml C_6H_5N into which *p*-toluenesulfonylchloride was added was stirred below 10°, for 30 min followed by 3 hr stirring below 20°. The reaction mixture was acidified with 1 ml 3.5% HCl and extracted with $CHCl_3$, dried (Na_2SO_4), concd to dryness *in vacuo* and purified by prep. TLC to obtain a resinous mass. ^1H NMR ($CDCl_3$): δ 2.45 (3H, *s*, Me of tosyl), 3.30 (2H, *dt*, $J = 6.7$ and 1.2 Hz, CH_2–CH=CH_2), 3.73 (1H, *ddd*, $J = 8.2$, 6.7 and 4.2 Hz, H-3), 3.83 (3H, *s*, OMe), 3.86 (6H, *s*, OMe × 2), 4.18 (1H, *dd*, $J = 10.0$ and 8.2 Hz, CH_2–O–tosyl-3), 4.35 (1H, *dd*, $J = 10.0$ and 4.2 Hz, CH_2–O–tosyl-3), 5.07 [1H, *ddt*, $J = 9.5$, 2.0 and 1.2 Hz, CH_2–CH=CH_2 (*cis*)], 5.08 [1H, *ddt*, $J = 17.6$, 2.0 and 1.2 Hz, CH_2–CH=CH_2 (*trans*)], 5.43 (1H, *d*, $J = 6.7$ Hz, H-2), 5.94 (1H, *ddt*, $J = 17.6$, 9.5 and 6.7 Hz, CH_2–CH=CH_2), 6.54 (1H, *d*, $J = 1.4$ Hz, H-4 or H-6), 6.65 (1H, *d*, $J = 1.4$ Hz, H-6 or H-4), 6.81 (1H, *d*, $J = 9.0$ Hz, H-5′), 6.88 (1H, *d*, $J = 2.0$ Hz, H-2′), 6.88 (1H, *dd*, $J = 9.0$ and 2.0 Hz, H-6′), 7.34 (2H, *d*, $J = 7.4$ Hz, aromatic H of tosyl), 7.77 (2H, *d*, $J = 7.4$ Hz, aromatic H of tosyl). MS: *m/z* 510 $[M]^+$ (26.7), 338 (100), 323 (27.0), 149 (46.5).

Reduction of tosylate (**2**). **2** (15 mg) in 1 ml hexamethylphosphoramide was stirred with $NaBH_3CN$ (3 mg) at 80° for 10 hr, then diluted with H_2O and extracted with $CHCl_3$. After evapn, drying and purification by prep. TLC the product was confirmed to be dihydrocarinatin (**3**) by means of TLC, IR and mass spectrometry.

Acetate of **4**. Prepared in the usual way, colourless crystals, mp 125–126°, IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3020, 2940, 2845, 1760, 1735, 1670, 1635, 1590, 1580, 1510, 1490, 1460, 1415, 1015, 915, 840. ^1H NMR ($CDCl_3$): δ 1.99 (3H, *s*, OAc), 2.43 (3H, *s*, OAc), 3.27 (2H, *dt*, $J = 6.8$ and 1.6 Hz, CH_2–CH=CH_2), 3.80 (3H, *s*, OMe), 3.89 (3H, *s*, OMe), 3.90 (3H, *s*, OMe), 4.31 (1H, *dd*, $J = 11.0$ and 6.0 Hz, H-3), 4.69 (1H, *dd*, $J = 11.0$ and 8.5 Hz, H-3′), 5.02 [1H, *ddt*, $J = 16.4$, 2.0 and 1.6 Hz, CH_2–CH=CH_2 (*trans*)], 5.04 [1H, *ddt*, $J = 11.2$, 2.0 and 1.6 Hz, CH_2–CH=CH_2 (*cis*)], 5.06 (1H, *dt*, $J = 8.5$ and 6.0 Hz, H-2), 5.87 (1H, *ddt*, $J = 16.4$, 11.2 and 6.8 Hz, CH_2–CH=CH_2), 6.60 (1H, *d*, $J = 2.0$ Hz, H-2″ or H-4″), 6.70 (1H, *d*, $J = 2.0$ Hz, H-4″ or H-2″), 6.84 (1H, *d*, $J = 8.7$ Hz, H-5′), 7.56 (1H, *d*, $J = 2.0$ Hz, H-2′), 7.60 (1H, *dd*, $J = 8.7$ and 2.0 Hz, H-6′), MS: *m/z* 456 $[M]^+$ (0.9), 396 (25.1), 354 (27.1), 165 (100), 151 (70.5).

Reduction of **4**. **4** (52 mg) in MeOH was reacted with $NaBH_4$ (50 mg) in MeOH and allowed to stand overnight. The reaction product was concd to dryness *in vacuo*, H_2O added and extracted with $CHCl_3$. It was purified by prep. TLC to give **6** as a resinous mass, IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3550, 3010, 2945, 2840, 1605, 1520, 1470, 1265, 1140, 1025, 920. ^1H NMR ($CDCl_3$): δ 3.29 (2H, *dt*, $J = 6.7$ and 1.2 Hz, CH_2–CH=CH_2), 3.49 (1H, *m*, H-2), 3.70–3.90 (2H, overlapped with OMe), 3.82 (3H, *s*, OMe), 3.86 (3H, *s*, OMe), 3.88 (3H, *s*, OMe), 5.05 [1H, *ddt*, $J = 9.8$, 2.0 and 1.2 Hz, CH_2–CH=CH_2 (*cis*)], 5.06 [1H, *ddt*, $J = 17.6$, 2.0 and 1.2 Hz, CH_2–CH=CH_2 (*trans*)], 5.12 (1H, *d*, $J = 8.2$ Hz, CH–OH), 5.91 (1H, *ddt*, $J = 17.6$, 9.8 and 6.7 Hz, CH_2–CH=CH_2), 6.22 (1H, *s*, phenolic OH), 6.58 (1H, *d*, $J = 2.0$ Hz, H-2″ or H-4″), 6.64 (1H, *d*, $J = 2.0$ Hz, H-4″ or H-2″), 6.82 (1H, *d*, $J = 8.0$ Hz, H-6′), 6.86 (1H, *d*, $J = 2.0$ Hz, H-2′), 6.92 (1H, *dd*, $J = 8.0$ and 2.0 Hz, H-5′).

Acetate of **6**. Prepared in the usual way, resinous mass, IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3020, 2950, 2850, 1775, 1748, 1743, 1600, 1520, 1470, 1380, 1245, 1143, 1030. ^1H NMR ($CDCl_3$): δ 1.92 (3H, *s*, alcoholic OAc), 1.94 (3H, *s*, alcoholic OAc), 2.34 (3H, *s*, phenolic OAc), 3.32 (2H, *dt*, $J = 6.8$ and 1.2 Hz, CH_2–CH=CH_2), 3.72 (1H, overlapped, H-2), 3.78 (3H, *s*, OMe), 3.80 (3H, *s*, OMe), 3.86 (3H, *s*, OMe), 4.01 (1H, *dd*, $J = 11.0$ and 6.4 Hz, CH_2OAc), 4.28 (1H, *dd*, $J = 11.0$ and 5.0 Hz, CH_2OAc), 5.06 [1H, *ddt*, $J = 15.5$, 2.0 and 1.2 Hz, CH_2–CH=CH_2 (*trans*)], 5.07 (1H, *ddt*, $J = 11.4$, 2.0 and 1.2 Hz, CH_2–CH=CH_2 (*cis*)], 5.91 (1H, *ddt*, $J = 15.5$, 11.4 and 6.8 Hz, CH_2–CH=CH_2), 6.01 (1H, *d*, $J = 8.2$ Hz, CH–OAc), 6.63 (1H, *d*, $J = 1.8$ Hz, H-2″ or H-4″), 6.67 (1H, *d*, $J = 1.8$ Hz, H-4″ or H-2″), 6.70 (1H, *d*, $J = 1.8$ Hz, H-2′), 6.81 (1H, *d*, $J = 8.0$ Hz, H-6′), 6.86 (1H, *dd*, $J = 8.0$ and 1.8 Hz, H-5′). MS: *m/z* 500 $[M]^+$ (12.8), 338 (29.0), 209 (40.6), 190 (21.6), 167 (100).

Dehydration of **6**. **6** (40 mg) was refluxed in 16 ml 20%

H_3PO_4 for 5 hr, extracted with $CHCl_3$, dried (Na_2SO_4), concd *in vacuo* and then purified by prep. TLC. The product was identified as dihydrocarinatinol **7** by means of TLC, IR and mass spectrometry.

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