[1*R*-(1α,4β,5α,7*R)]-7-Bromo-4-isopropyl-1-methylbicyclo[3.1.1]heptan-6-one [(+)-7] and [1*S*-(1α,4β,5α,7*R**)]-7-Bromo-4-isopropyl-1-methylbicyclo[3.1.1]heptan-6-one [(+)-19b].** A solution of 293 mg of a crude **19c–29a** keto ester mixture (from a cyclization of 478 mg (1.5 mmol) and esters **28**) and 1 N potassium hydroxide in 15 mL of methanol and 5 mL of water was refluxed for 2 h. It was poured into 5% sodium hydroxide solution and extracted with ether. The aqueous solution was acidified with 6 N hydrochloric acid and extracted exhaustively with ether. The extract was washed with brine, dried, and evaporated. The residual mixture (247 mg) of acids **19d** and **29b** [IR (CCl_4) (OH) 3100–3400 (m), (C=O) 1787 (s), 1701 (s) cm^{-1}] and 0.05 mL of dimethylformamide were dissolved in 1 mL of dry benzene, and 0.5 mL (5.9 mmol) of oxalyl chloride was added dropwise at 0 °C. The solution was stirred at room temperature for 1 h and then evaporated. A solution of the residue in 5 mL of dry bromotrichloromethane was added dropwise over a 15-min period to a refluxing mixture of 209 mg (1.4 mmol) of sodium 1-oxypyridine-2-thiolate and 13 mg (0.12 mmol) of γ-(dimethylamino)pyridine in 10 mL of dry bromotrichloromethane. Refluxing was continued for 2 h, and the resultant, light orange suspension was filtered through Celite. The filtrate was evaporated, and the residual oil was dissolved in ether. The solution was washed with water and brine, dried, and evaporated. MPLC of the residue and elution with 40:1 petroleum ether–ethyl acetate provided 44 mg (12%) of liquid bromo ketone **7**: $[\alpha]^{23}_D$ +59.9° ($CHCl_3$, c = 0.60); CD_{max} $[\theta]^{21}_{293}$ +3212° ($CHCl_3$, c = 0.10); IR and ^1H NMR spectrally identical with the above sample of racemic ketone **7**.

Anal. Calcd for $C_{11}H_{17}OBr$: C, 53.89; H, 6.99. Found: C, 54.24; H, 7.07.

Further elution afforded 81 mg (22%) of colorless, liquid bromo ketone **19b**: $[\alpha]^{23}_D$ +7.1 ($CHCl_3$, c = 0.70); CD_{max} $[\theta]^{21}_{298}$ +2444 ($CHCl_3$, c = 0.10); IR (CCl_4) (C=O) 1790 (s) cm^{-1}; ^1H NMR δ 0.93, 0.94 (d, 3 each, *i*-Pr methyls), 1.17 (s, 3, 1-Me), 1.5–2.3 (m, 6, methylenes, methines), 3.28 (s, 1, H-5), 4.41 (s, 1, H-7); ^{13}C NMR δ 16.9 (1-Me), 19.6, 19.8 (*i*-Pr methyls), 20.3 (C-3), 32.2 (*i*-Pr CH), 39.2 (C-2), 47.3 (C-4), 52.0 (C-7), 67.1 (C-1), 69.4 (C-5), 212.1 (C=O).

Anal. Calcd for $C_{11}H_{17}OBr$: C, 53.89; H, 6.99 Found: C, 53.99; H, 7.11.

Bromo ketone **19b** semicarbazone: mp 201–202 °C (EtOH).

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Registry No. **1**, 499-75-2; (±)-**2**, 124355-77-7; (±)-**3**, 124439-20-9; (±)-**4**, 124355-78-8; (±)-**5**, 124355-79-9; (±)-**6**, 124355-80-2; **7** (isomer 2), 124379-63-1; (±)-**7**, 124508-22-1; (±)-**8**, 124355-81-3; **9**, 124355-82-4; (±)-**10a**, 124355-83-5; (±)-**10b**, 124355-98-2; (±)-**10c**, 124355-99-3; (±)-**10d**, 124356-00-9; (±)-**10e**, 124439-22-1; (±)-**10f**, 124356-01-0; **11a**, 124379-64-2; **11b**, 124379-66-4; **11c**, 124379-67-5; (±)-**12a**, 124379-65-3; (±)-**12b**, 124379-68-6; **13a**, 2862-86-4; (±)-**13b**, 124356-02-1; (±)-**13c**, 124356-03-2; (±)-**13d**, 124356-04-3; (±)-**13e**, 124356-05-4; (±)-**14a**, 124355-84-6; (±)-**14b**, 124356-06-5; (±)-**14c**, 124356-07-6; (±)-**15**, 124355-85-7; (±)-**16**, 124355-86-8; (±)-**17**, 124355-87-9; **19b**, 124355-88-0; **19b** semicarbazone, 124356-12-3; **19c**, 124356-08-7; **19c** semicarbazone, 124356-17-8; **19d**, 124356-09-8; (±)-**20a**, 124355-89-1; (±)-**21**, 124355-90-4; **22**, 124355-91-5; **23a** (isomer 1), 124355-92-6; **23a** (isomer 2), 124356-18-9; **24a**, 124355-93-7; **24b**, 104857-78-5; **25** (isomer 1), 124355-94-8; **25** (isomer 2), 124439-26-5; **26a**, 124439-21-0; **26b**, 124439-23-2; **26c**, 124356-10-1; **26d**, 124439-24-3; **27**, 124355-95-9; **28**, 124355-96-0; **29a**, 124355-97-1; **29b**, 124356-11-2; i, 22081-48-7; (±)-iia, 124356-13-4; (±)-iib, 124356-14-5; (±)-iic, 124356-15-6; (±)-iid, 124439-25-4; (±)-iiia, 124379-69-7; (±)-iiib, 124379-69-7; (±)-iv, 124356-16-7; ethyl trichloroacetate, 515-84-4; carvomenthone, 5206-83-7; isocarvomenthone, 7065-48-7.

Synthesis of 2,3-Dihydro-8-(3-hydroxy-3-methylbut-1-enyl)-7-methoxy-2-phenyl-4*H*-1-benzopyran-4-one: A Novel Structure for Falciformin

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Received May 3, 1989

Synthesis of 2,3-dihydro-8-(3-hydroxy-3-methylbut-1-enyl)-7-methoxy-2-phenyl-4*H*-1-benzopyran-4-one (1) has been achieved in order to verify the proposed structure of falciformin, a new constituent of *Tephrosia falciformis*. The melting point and spectral characteristics of synthetic 1 are not consistent with those reported for the natural sample, thereby showing that the proposed structure is erroneous. Based on the data reported for the natural product, the new structure 2,3-dihydro-5-(1,1-dimethyl-2-hydroxyprop-2-enyl)-6-methoxy-2-phenyl-4*H*-1-benzopyran-4-one (4) is tentatively proposed for falciformin. The mass spectral fragmentation patterns of 1 and 4 are discussed in detail in support of their structures.

2,3-Dihydro-2-phenyl-4*H*-1-benzopyran-4-ones occur abundantly in plants and exhibit different biological activities, e.g. spasmolytic,[1] cytotoxic,[2] antihepatotoxic,[3] and antidiabetic (antigalactosemic cataract).[4] Among acyclic isopentenylated flavonoids, those possessing 3-methyl-

(1) (a) Berger, H.; Holler, H. *Chem. Abstr.* **1958**, *52*, 3267; *Sci. Pharm.* **1957**, *25*, 172. (b) Rossi, G. V.; Packman, E. W.; Goldberg, M. E. *Am. J. Pharm.* **1957**, *129*, 89.

(2) (a) Lasswell, W. L.; Hufford, C. D. *J. Org. Chem.* **1977**, *42*, 1295. (b) Huang, M. T.; Wood, A. W.; Newmark, H. L.; Sayer, J. M.; Yagi, H.; Jerina, D. M.; Conney, A. M. *Carcinogenesis* **1983**, *4*, 1631.

(3) (a) Hahn, G.; Lehmann, H. D.; Kurten, M.; Hebel, H.; Vogel, G. *Chem. Abstr.* **1968**, *69*, 58230; *Arzneim. Forsch.* **1968**, *18*, 698. (b) Machicao, F.; Sonnenbichler, J. *Hoppe-Seyler's Z. Physiol. Chem.* **1977**, *358*, 141. (c) Wagner, H.; Haerhammer, L.; Muenster, R. *Chem. Abstr.* **1968**, *69*, 96396; *Arzneim. Forsch.* **1968**, *18*, 688. (d) Schnabel, R.; Sonnenbichler, J.; Zillig, W. *FEBS Lett.* **1982**, *150*, 400.

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but-2-enyl and 1,1-dimethylprop-2-enyl as substituents are fairly common in nature, but there are very few instances when a 3-hydroxy-3-methylbut-1-enyl alkyl chain is present on the flavonoid skeleton. Falciformin, which is the only example of a 2,3-dihydro-2-phenyl-4*H*-1-benzopyran-4-one having this substituent, has recently been isolated[5] from the pods of *Tephrosia falciformis*. Based on its spectral characteristics alone, it was formulated as 2,3-dihydro-8-(3-hydroxy-3-methylbut-1-enyl)-7-methoxy-2-phenyl-4*H*-1-benzopyran-4-one (1). However it is surprising that the olefinic protons, which are not magnetically equivalent[6] appear as a singlet at δ 6.86. The detailed IR, UV (with shift reagents), and ^{13}C NMR spectral data for the natural compound were not reported. The MS data reported for the natural sample were not explained in terms of the proposed structure 1. The present synthesis shows that the structure previously assigned to falciformin is not correct and suggests a revised structure 4 for it on the basis of the reported spectral data.

Results and Discussion

The base-catalyzed cyclization of 1-[2-hydroxy-4-methoxy-3-(3-methylbut-2-enyl)phenyl]-3-phenylprop-2-enone[8] afforded a single compound in 70% yield, the spectral data of which were compatible with the structure 2,3-dihydro-7-methoxy-8-(3-methylbut-2-enyl)-2-phenyl-4*H*-1-benzopyran-4-one (2). The complete synthesis of flavanone (2) has not been reported thus far.[9] Treatment of 2 with MCPBA in dry chloroform gave the hitherto unknown epoxide 3, the structure of which was fully established from its IR, UV, NMR, and mass spectral data.[11] The base-mediated opening of the epoxide ring in 3 yielded 1, the structure of which is fully established from its various spectral data.

The synthetic 1 showed considerable differences in its melting point and spectral data from those reported[5] for the natural sample of falciformin. The synthetic 1 melted at 178–179 °C, whereas the melting point reported for the natural sample[5] is 108 °C. The UV absorption spectrum of synthetic 1 had λ_{max} at 315 and 232 (sh) nm, whereas the reported[5] absorptions for the natural sample are at 260 and 290 nm. Further, the authors[5] reported that the UV absorption maxima for the natural sample did not undergo any change on addition of alkali, but the natural specimen of falciformin, kindly supplied to us by Dr. Khan,[5] was found to undergo a bathochromic shift to 325, 260, and 230 nm on addition of NaOH; it also exhibited significant bathochromic shifts in presence of $AlCl_3$ and NaOMe. However, the UV spectrum of our synthetic 1 did not undergo any change on addition of NaOH, NaOMe, or $AlCl_3$.

The ^1H NMR spectrum of synthetic 1 also showed considerable difference from that of falciformin[5] in the chemical shift values of the alkyl side chain protons. Whereas it was reported that the olefinic protons of falciformin[5] appear as a singlet at δ 6.86, thus being accidentally equivalent, in synthetic 1 they appeared merged at different chemical shift values, δ 4.30–5.55, as a multiplet for H-2 and H-2″ and a multiplet between δ 7.00 and 7.90 for the H-1″, H-5, and B ring protons. Also the natural sample of falciformin exhibited a singlet (6 H) at δ 1.38 for the *gem*-dimethyl group,[5] whereas our synthetic 1 showed these protons as two singlets (3 H each) at δ 1.29 and 1.42. The mass spectral data reported[5] for the natural sample were markedly different from that of our synthetic 1 (Chart I). The base peak was reported for the natural sample at m/z 201, but our synthetic 1 did not show any such fragment; on the other hand, the base peak observed for our synthetic 1 was at m/z 161 and the natural sample had no such fragment. Many other peaks observed in the MS of two samples were different.

(4) (a) Varma, S. D.; Kinoshita, J. H. *Biochem. Pharmacol.* **1976**, *25*, 2505. (b) Varma, S. D.; Kinoshita, J. H. *Biochim. Biophys. Acta* **1974**, *338*, 632. (c) Varma, S. D.; Mikuni, I.; Kinoshita, J. H. *Science* **1975**, *188*, 1215.

(5) Khan, H. A.; Chandrasekharan, I.; Ghanim, A. *Phytochemistry* **1986**, *25*, 767. No degradative evidence was reported for falciformin. Copies of the spectra could not be obtained from the authors; however, a very small amount of the natural sample was sent by them which was barely sufficient to run UV spectrum in presence of shift reagents (NaOH, NaOMe, $AlCl_3$).

(6) We have found, in literature,[7] a few polyphenolic compounds carrying the same C_5 side chain on the heterocyclic nucleus and in all the cases the olefinic protons appear as trans doublets (J = 16–17 Hz). For the natural sample of falciformin also, Khan et al.[5] report the trans double bond from the IR absorption at 970 cm^{-1}, but report a singlet at δ 6.86 in its ^1H NMR spectrum for these protons.

(7) (a) Gray, A. I.; Waigh, R. D.; Waterman, P. G. *J. Chem. Soc., Perkin Trans. 1* **1975**, *488*. (b) Shibata, S.; Noguchi, M. *Phytochemistry* **1977**, *16*, 291. (c) Chan, W. R.; Taylor, D. R.; Willis, C. R. *J. Chem. Soc. C* **1967**, 2540. (d) Kis, Z.; Closse, A.; Sigg, H. P.; Hruban, L.; Snatzke, G. *Helv. Chim. Acta* **1970**, *53*, 1577.

(8) Khanna, R. N.; Khanna, P. L.; Manchanda, V. P.; Seshadri, T. R. *Indian J. Chem.* **1973**, *11*, 1225.

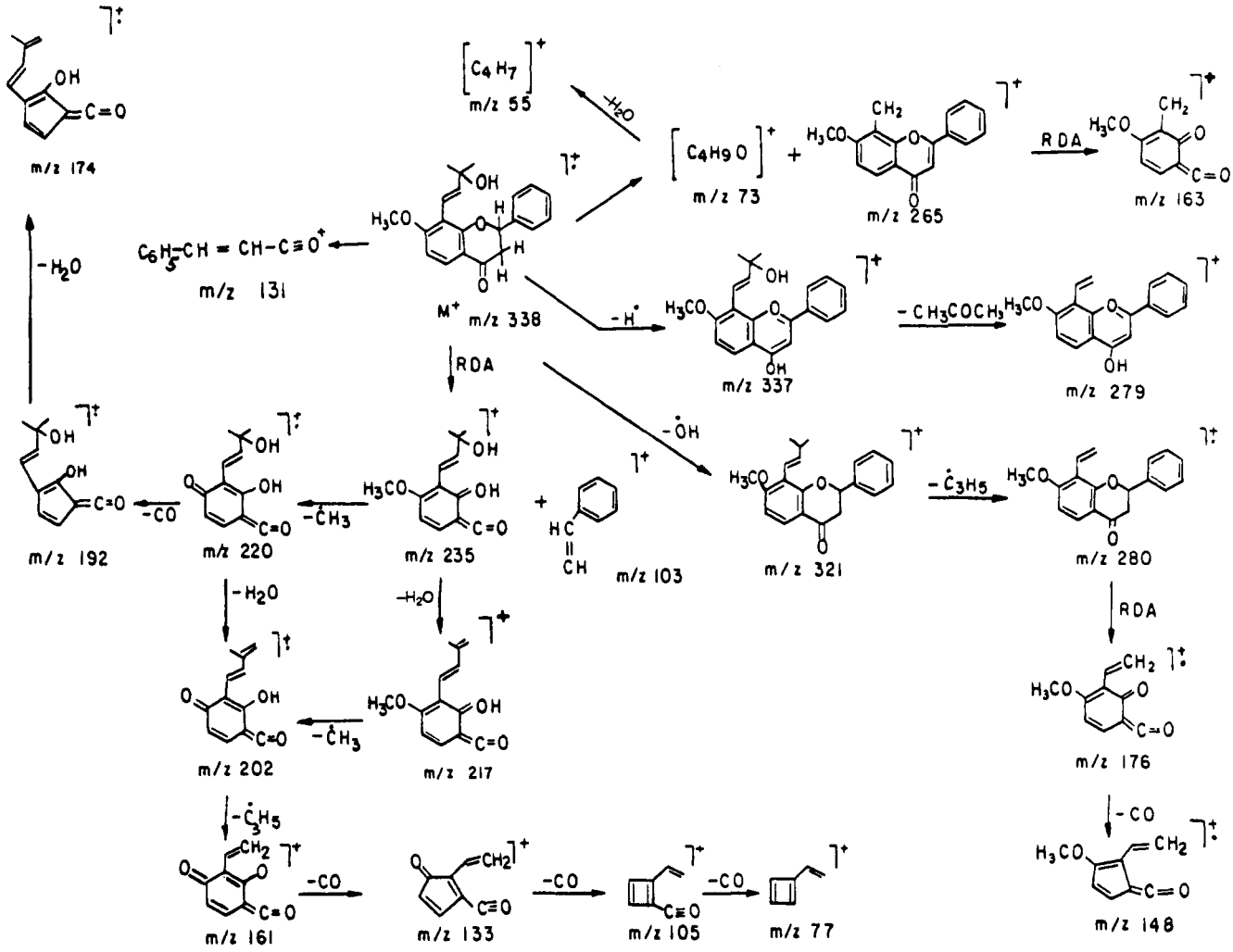
(9) It has, however, been prepared earlier[10] by the cyclization of the corresponding naturally occurring chalcone, derricin, using sodium hydroxide. The melting point, ^1H NMR, and IR data[10] differed slightly from those of our 2. The peaks in the MS of two were observed at the same m/z values. The earlier authors[10] had neither reported the characteristic peaks for the C-2 and C-3 protons in the ^1H NMR spectrum nor the UV spectral absorptions, both of these are characteristic for this class of compounds. The structure of our 2 has been well supported by its UV, NMR, and mass spectral data.

(10) Nascimento, M. C.; Mors, W. B. *Phytochemistry* **1972**, *11*, 3023.

(11) The IR spectrum of 3 exhibited characteristic[12] epoxide band at 1240 cm^{-1} and the ^1H NMR absorption for the C-1″ and C-2″ protons were also in order for similar C_5-epoxy side chain.[12]

(12) (a) Bohlmann, F.; Jakupovic, J. *Phytochemistry* **1979**, *18*, 1367. (b) Austin, P. W.; Seshadri, T. R.; Sood, M. S.; Paul, V. *Tetrahedron* **1968**, *24*, 3247.

Chart I. Mass Spectral Fragmentation of 2,3-Dihydro-8-(3-hydroxy-3-methylbut-1-enyl)-7-methoxy-2-phenyl-4*H*-1-benzoyran-4-one (1)



In view of the marked discrepancies in the data observed for our synthetic 1 and those reported for the natural sample,[5] the proposed structure for falciformin occurring in *T. falciformis* is erroneous and thus needs revision. However, on the basis of the data reported[5] for the natural sample of falciformin, its structure might possibly be 2,3-dihydro-5-(1,1-dimethyl-2-hydroxyprop-2-enyl)-6-methoxy-2-phenyl-4*H*-1-benzopyran-4-one (4). This assignment is fully supported by the IR, UV, ^{1}H NMR, and mass spectral data exhibited by the natural sample.

The ^{1}H NMR spectrum of falciformin indicated lack of any substitution in the side phenyl ring and the presence of two ortho-coupled aromatic protons in the benzenoid ring. The methoxyl group in falciformin should be at C-6, rather than at C-7,[13] because of the extent of its benzene-induced shift. The alkyl side chain at C-5 can be characterized as 1,1-dimethyl-2-hydroxyprop-2-enyl on the basis of the signals observed in the ^{1}H NMR spectrum of the natural product.[15]

The above structure is also supported by UV spectral absorption maxima—λ_{max} 260 and 290 nm—which shows that the double bond of the C_5 side chain is not in conjugation with the 2,3-dihydro-4*H*-1-benzopyran-4-one ring system. Had the double bond of the side chain been in conjugation with the ring chromophore, as is the case in

(13) The C-6 methoxyl group in flavonoids usually exhibits solvent-induced shift of 0.20–0.28 ppm, while the C-7 methoxyl group undergoes a shift of 0.7–0.8 ppm in the presence of benzene.[14] As falciformin showed[5] a benzene-induced shift for the methoxyl function in its ^{1}H NMR spectrum of 0.23 ppm only, the methoxyl should be at C-6. This is also supported by the formation of stable para quinonoid fragment a at *m/z* 201 (Chart II) as the base peak in the MS of falciformin and other fragments of high intensity [b (16%), c (22%), and d (30%), Chart II].

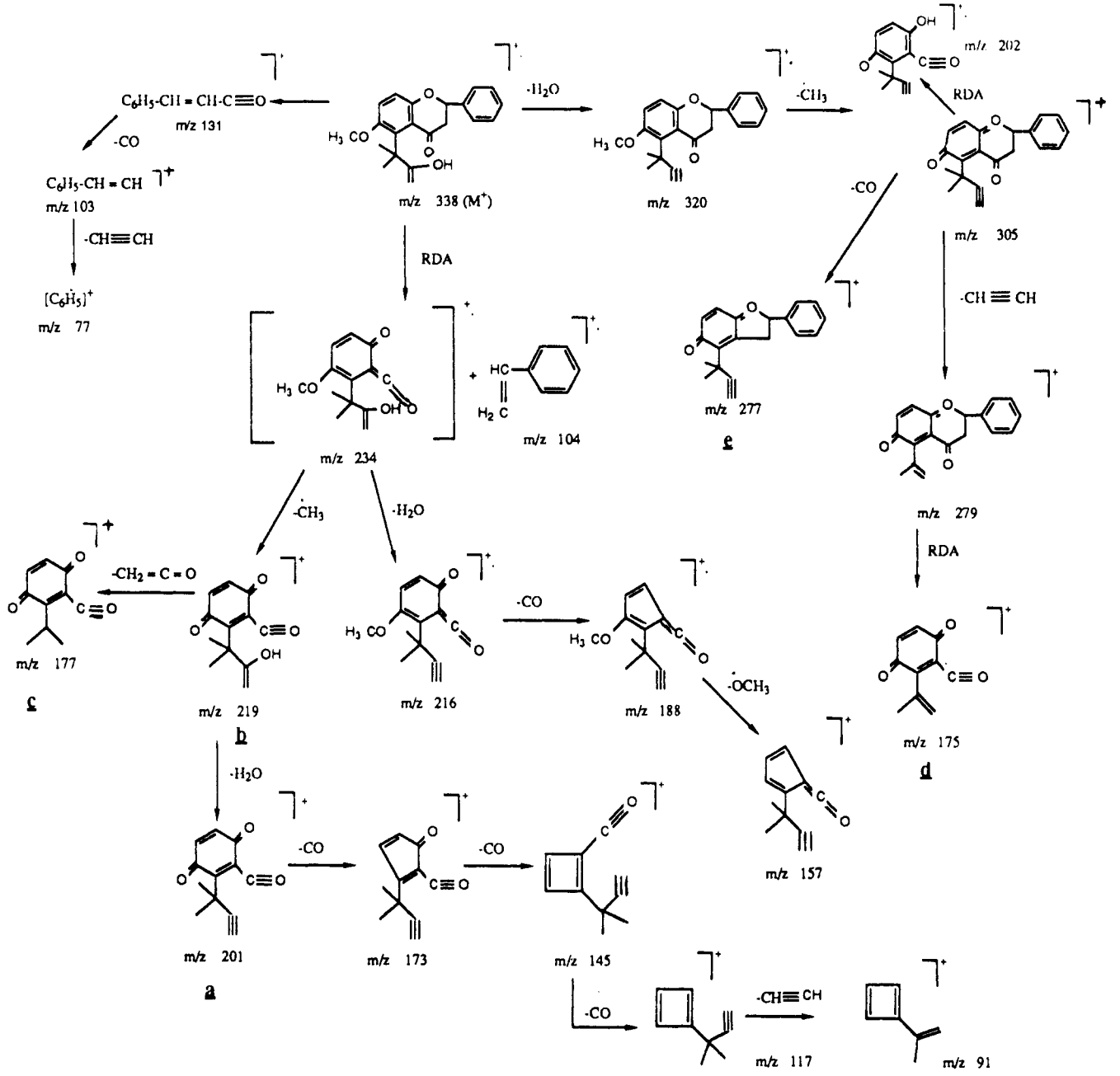
(14) (a) Wilson, R. G.; Bowie, J. H.; Williams, D. H. *Tetrahedron* **1968**, *24*, 1407. (b) Rodriguez, E.; Carman, N. J.; Mabry, T. J. *Phytochemistry* **1972**, *11*, 409.

(15) Two singlets at δ 1.38 (6 H) and 6.86 (2 H) for the *gem*-dimethyl and vinylic protons, respectively. The structure 4 explains better the magnetic equivalence of these groups (protons). Normally the compounds having a vinylic hydroxyl group are not stable, but structure 4 is probably stabilized by the intramolecular hydrogen bonding between the carbonyl oxygen and the enolic hydroxyl group. The model of 4 shows that it could be a stable structure. Moreover, there are examples of naturally occurring compounds possessing a 1,1-dimethylallyl functionality.[16] There are also compounds occurring in nature containing chelated enolic hydroxy functions.[17] The alternative structure 5 for falciformin does not explain the mass spectral fragmentation, the shifts in the UV spectrum on addition of $AlCl_3$, NaOH, and NaOMe, and the magnetic equivalence of the *gem*-dimethyl group in the ^{1}H NMR spectrum of the natural sample as reported by Khan et al.[5] The structure 5 is also ruled out on biogenetic considerations, as to the best of our knowledge no naturally occurring compound having this type of C_5 side chain is known. Similarly, another alternate 6 is ruled out because falciformin exhibited strong $(M - OH)^+$ and $(M - H_2O)^+$ fragments at 321 (22) and 320 (52), respectively, which can be explained for the enolic structure 4, and not for the phenolic structure 6.

(16) (a) Steck, W.; Bailey, B. K.; Skyluk, J. P.; Gamborg, O. L. *Phytochemistry* **1971**, *10*, 191. (b) Reisch, J.; Szendrei, K.; Minker, E.; Novak, I. *Tetrahedron Lett.* **1968**, 4305. (c) *Ibid.* **1970**, 4395. (d) Reyes, R. E.; Gonzalez, A. G. *Phytochemistry* **1970**, *9*, 833.

(17) (a) De Keukeleire, D.; Verzele, M. *Tetrahedron* **1970**, *26*, 385. (b) Stout, G. H.; Krahn, M. M.; Breck, G. D. *Tetrahedron Lett.* **1968**, 3285.

Chart II. Mass Spectral Fragmentation of 2,3-Dihydro-5-(1,1-dimethyl-2-hydroxyprop-2-enyl)-6-methoxy-2-phenyl-4*H*-1-benzopyran-4-one (4)



structure 1, λ_{max} values for falciformin should have been observed at higher wavelengths; the synthetic 1 had λ_{max} at 315 and 232 (sh) nm. Also the bathochromic shifts undergone by the UV spectrum of the natural sample with alkali and $AlCl_3$ are explained by structure 4 as there is an enolic, chelated hydroxyl function. Further support for the chelated carbonyl function in falciformin is provided by its IR absorption[5] at 1650 cm^{-1}; normally, the carbonyl frequency in chromanones is around 1680 cm^{-1}. Further evidence in support of our proposed structure 4 is provided by the expected mass spectral fragmentation pathways (cf. Chart II),[18] which explain all the peaks reported for the natural sample of falciformin. The MS[5] shows the M^+ peak at m/z 338 and the base peak at m/z 201; other significant fragments are at m/z 321 ($M^+ - OH$), 320 ($M^+ - H_2O$), 219 (A ring fragment $- CH_3)^+$, 216 (A ring fragment $- H_2O)^+$, and 104 (B ring fragment)$^+$. The earlier authors[5] did not explain the mass spectral data of falciformin with respect to their proposed structure 1. The distinctive difference in the MS of our synthetic 1 and natural falciformin[5] was the cleavage of the alkyl side chain, whereas synthetic compound showed fragments (Chart I) with cleavage of the side chain, the natural compound (Chart II), had the side chain intact in most of the fragments because of the relative stability of the acetylenic function (in MS of 4) over the 1,3-diene system (in MS of 1) obtained by the elimination of a water molecule

(18) The base peak at m/z 201 is due to the formation of stable para quinonoid fragment a, which is feasible only in case the OMe function is at C-6 in falciformin. Also, the peak at m/z 267 (9)[5] is probably misprint; it should be at m/z 277 and is due to the formation of stable fragment e as shown in Chart II. Such fragments are characteristic of flavonoids carrying a C-6 methoxy function.[19]

(19) (a) Dreyer, D. L. *J. Org. Chem.* **1968**, *33*, 3574. (b) *Ibid.* **1968**, *33*, 3577. (c) Parmar, V. S.; Jain, R.; Simonsen, R.; Boll, P. M. *Tetrahedron* **1987**, *43*, 4247.

from the respective molecular ion and "A ring fragments" of the two compounds; the mode of cleavage of the carbon framework of the C_5 side chain in **1** and **4** is also different. In light of the above observations, we propose structure **4**, 2,3-dihydro-5-(1,1-dimethyl-2-hydroxyprop-2-enyl)-6-methoxy-2-phenyl-4*H*-1-benzopyran-4-one, for falciformin. To the best of our knowledge, this compound is not known in the literature and represents a novel structure among naturally occurring prenylated flavonoids.

Experimental Section

All melting points were determined on the H_2SO_4 bath and are uncorrected. Silica gel (BDH, 10–40 μm) was used for TLC, and silica gel (BDH, 60–120 mesh) was used for column chromatography. UV spectra were recorded on a Beckman DU-2 spectrophotometer, IR spectra on a Shimadzu Model 435 spectrophotometer; the NMR spectra were recorded on a Perkin-Elmer R-32 (90 MHz) or on a JEOL JNM FX-200 FT (200 MHz) NMR spectrometer with TMS as the internal standard and mass spectra were recorded on a Varian Mat 331 A instrument.

2,3-Dihydro-7-methoxy-8-(3-methylbut-2-enyl)-2-phenyl-4*H*-1-benzopyran-4-one (2). To a solution of 1-[2-hydroxy-4-methoxy-3-(3-methylbut-2-enyl)phenyl]-3-phenylprop-2-enone[8] (0.36 g in 24 mL of alcohol) was added a solution of sodium acetate (0.24 g in 7 mL of water), the mixture was refluxed for 6 h, and it was diluted with water (50 mL) and extracted with chloroform (5 × 20 mL); removal of the solvent from the organic layer yielded the crude product. It was purified by preparative TLC (petroleum ether–benzene, 7:3) and crystallized from chloroform/petroleum ether as colorless needles (0.25 g): mp 104–5 °C; $R_f^{25°}$ 0.60 (C_6H_6–$CH_3CO_2C_2H_5$, 9:1); gave a yellowish-red color with concentrated H_2SO_4; UV (MeOH) 310 (sh), 284, 235 (sh) nm; IR (Nujol) 1680, 1590, 1570, 1498, 1330, 1310, 1265, 1218, 1170, 1105, 1080, 900, 840, 700 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.60 (s, 6 H, 2 CH_3), 2.80–3.10 (m, 2 H, 2 H-3), 3.35 (d, J = 7 Hz, 2 H, 2 H-1″), 3.90 (s, 3 H, OCH_3), 5.18 (t, J = 7 Hz, 1 H, H-2″), 5.45 (q, 1 H, H-2), 6.66 (d, J = 9 Hz, 1 H, H-6), 7.35–7.55 (m, 5 H, B ring protons), 7.85 (d, J = 9 Hz, 1 H, H-5); ^{13}C NMR ($CDCl_3$) δ 17.64 (C-5″), 22.07 (C-4″), 25.67 (C-1″), 44.32 (C-3), 55.76 (OCH_3), 79.27 (C-2), 105.0 (C-4a), 115.22 (C-8), 118.0 (C-6), 122.0 (C-5), 125.82 (C-3′, C-5′), 126.18 (C-3″), 128.20 (C-2″), 128.76 (C-2′, C-6′), 131.9 (C-4′), 139.5 (C-1′), 160.01 (C-8a), 163.19 (C-7), 191.26 (C-4); mass spectrum m/z (%) 323 $(M + 1)^+$ (27), 322 (M^+) (100), 321 $(M - 1)^+$ (60), 307 $(M^+ - CH_3)$ (14), 279 (40), 267 (32), 217 (27), 218 (A ring fragment)$^+$ (51), 203 (37), 190 (48), 175 (55), 163 (91), 131 $(C_6H_5CH{=}CHCO)^+$ (30), 104 (B ring fragment)$^+$ (23), 103 (18), 91 (27.3), 77 $(C_6H_5)^+$ (18), 55 $(C_4H_7)^+$ (9), 28 (39).

2,3-Dihydro-8-(2,3-epoxy-3-methylbutyl)-7-methoxy-2-phenyl-4*H*-1-benzopyran-4-one (3). To a stirred solution of **2** (0.26 g in 10 mL of dry chloroform) was added a solution of *m*-chloroperbenzoic acid (0.38 g in 30 mL of dry chloroform) dropwise during 0.5 h, with temperature being maintained between 0 and 5 °C, and the mixture was stirred at 25 °C for 24 h. The chloroform layer was thoroughly washed with aqueous sodium bicarbonate (1%) and dried over anhydrous sodium sulfate; evaporation of the organic layer yielded a light yellowish-brown oil from which **3** was obtained as a pale yellow oil (0.25 g; $R_f^{25°}$ 0.44, C_6H_6–EtOAc, 9:1) by passing through a short column. It gave a yellowish-brown color with concentrated H_2SO_4: UV (MeOH) 235 (sh), 282, 317 (sh) nm; IR (Nujol) 1672, 1592, 1372, 1265, 1240, and 1100 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.25 (s, 6 H, 2 CH_3), 2.50–3.30 (m, 4 H, 2 H-1″ and 2 H-3), 3.80–4.05 (m, 4 H, OCH_3 and H-2″), 5.20–5.85 (m, 1 H, H-2), 6.60 (d, J = 9 Hz, H-6), 7.35 (bs, 5 H, B ring protons), 7.85 (d, J = 9 Hz, H-5); ^{13}C NMR ($CDCl_3$) δ 18.81 (C-5″), 22.55 (C-4″), 24.46 (C-1″), 44.50 (C-3), 56.0 (OCH_3), 59.50 (C-3″), 63.26 (C-2″), 79.50 (C-2), 105.0 (C-4a), 126.0 (C-8), 127.5 (C-6), 128.40 (C-5), 129.97 (C-3′, C-5′), 133.65 (C-2′, C-6′), 134.56 (C-4′), 138.70 (C-1′), 163.5 (C-8a), 170.46 (C-7), 191.41 (C-4); mass spectrum m/z (%) 339 $(M + 1)^+$ (8.5), 338 (M^+) (33.8), 323 (2), 295 (24.05), 280 (11.05), 267 (27.3), 234 (4), 193 (31.2), 192 (18.2), 191 (86.45), 177 (23.4), 176 (82.55), 175 (44.2), 164 (24.05), 163 (100), 161 (11.7), 156 (37.05), 148 (45.15), 141 (11.7), 139 (35.75), 133 (37.05), 131 (20.15), 120 (12.35), 111 (20.8), 105 (31.2), 104 (25.35), 103 (18.85), 92 (11.05), 91 (11.05), 78 (80.27), 77 $(C_6H_5)^+$ (33.15), 75 (15.6), 73 (61.1), 71 (6), 65 (7.8), 59 (8.45), 51 (13.65), 50 (11.7). Anal. Calcd for $C_{21}H_{22}O_4$: C, 74.56; H, 6.51. Found: C, 74.01; H, 6.91.

2,3-Dihydro-8-(3-hydroxy-3-methylbut-1-enyl)-7-methoxy-2-phenyl-4*H*-1-benzopyran-4-one (1). In a dry 250-mL three-necked round-bottomed flask fitted with an effective reflux condenser, a dropping funnel, a rubber septum, a magnetic stirring bar, and a nitrogen inlet tube to maintain constant flow of dry nitrogen gas were placed dry diethyl amine (0.15 mL) and dry ether (15 mL). The flask was immersed in ice bath maintained at 0–5 °C, and *n*-butyllithium in hexane (1.4 M, 1 mL) was added carefully through the rubber septum by means of a syringe. After stirring for 10 min, a solution of **3** (0.3 g) in dry ether (7 mL) was added dropwise over a period of 30 min, and the mixture was stirred at 50 °C for 1 h, and the ether layer was washed successively with dilute hydrochloric acid (4 × 20 mL) followed by water (3 × 10 mL). The ether layer was then dried over anhydrous sodium sulfate, the solvent was removed, the resulting yellow-brown gummy solid was then purified by preparative TLC (C_6H_6–$CH_3CO_2C_2H_5$, 9:1), and the band having $R_f^{25°}$ 0.23 yielded **1**. It crystallized from petroleum ether–chloroform as colorless needles (0.2 g): mp 178–79 °C; gave a yellow color with concentrated H_2SO_4; UV (MeOH) 315, 232 (sh); +$AlCl_3$ 316, 228 (sh); +NaOMe 308; +NaOH 312, 226 (sh) nm; IR (Nujol) 3450, 1670, 1610, 1560, 1440, 1370, 1330, 1268, 1230, 1200, 1110, 1080, 975, and 760 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.29 and 1.42 (2 s, 6 H, 2 CH_3), 1.75 (bs, 1 H, OH), 2.80–3.55 (m, 2 H, 2 H-3), 3.85 (s, 3 H, OCH_3), 4.30–5.55 (m, 2 H, H-2, H-2″), 6.32 (d, J = 9 Hz, 1 H, H-6), 7.00–7.90 (m, 7 H, H-1″, H-5 and B ring protons); ^{13}C NMR ($CDCl_3$) δ 26.48 (C-5″), 27.50 (C-4″), 49.20 (C-3), 55.52 (OCH_3), 71.52 (C-2), 91.21 (C-3″), 104.12 (C-4a), 125.80 (C-8), 128.17 (C-3′, C-5′), 128.67 (C-2″), 129.0 (C-2′, C-6′), 129.04 (C-1″), 130.01 (C-6), 131.67 (C-5), 142.50 (C-4′), 144.30 (C-1′), 160.50 (C-8a), 163.05 (C-7), 192.25 (C-4); mass spectrum m/z (%) 339 (17), 338 (18), 337 (46), 323 (4), 321 (5), 280 (68), 279 (34), 265 (30), 235 (39), 220 (7), 217 (12), 202 (16), 192 (19), 176 (24), 175 (29), 174 (20), 163 (15), 161 (100), 148 (18), 133 (19), 131 (34), 105 (18), 103 (26), 77 (20), 73 (45), 58 (24), 55 (14), 41 (14), 28 (13), 18 (17), 15 (4). Anal. Calcd for $C_{21}H_{22}O_4$: C, 74.56; H, 6.51. Found: C, 73.92; H, 6.98.

UV data of a natural sample of falciformin:[5] UV (MeOH) 260 and 290 nm; no shift with alkali; shifts with other reagents not reported.

UV data as recorded by us of a natural specimen of falciformin:[5] UV (MeOH) 230, 258, 290 nm; +$AlCl_3$ 218, 260 (sh), 282, 312 (sh), 358; +NaOH 230, 260, 325 nm; +NaOMe 254 (sh), 274, 290, 322, 400 nm.

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