chromatography and crystallization since sterols submitted to these processes did not give any ketone. Moreover, it is not possible to explain the formation of 5α-stigmastan-3,6-dione, 5α-stigmast-22-en-3,6-dione and 5α-campestan-3,6-dione by air oxidation of the corresponding sterols since their synthesis would require a reduction step. We conclude, therefore, that steroidal ketones are metabolites produced by enzymatic reactions in the plant.

EXPERIMENTAL

General techniques. Mps: determined on a Kofler hot-stage apparatus, uncorr.; $[\alpha]_D$: $CHCl_3$; ^1H NMR: 60 MHz, $CDCl_3$, TMS as int. standard; MS: 70 eV. GC: He as carrier gas.

Extraction and fractionation of P. dactylifera *stems.* The dried powdered stems (4.1 kg) were extracted exhaustively in a Soxhlet with hexane. This extract was evaporated *in vacuo* and the residue dewaxed by crystallization from hot 95% EtOH (1.5 l.). The dewaxed hexane extract was divided into acidic and neutral (11.35 g) parts by extraction with aq. NaOH. CC of the neutral part over Si gel gave 10 main fractions, with the indicated eluents: Fraction I, 0.16 g, (hexane); II, 0.40 g (hexane–C_6H_6, 7:3); III, 0.021 g (hexane–C_6H_6, 7:3); IV 0.49 g (hexane–C_6H_6, 3:7); V, 0.036 g (hexane–C_6H_6, 1:3); VI, 0.52 (C_6H_6–Et_2O, 9:1). Rechromatography of fraction VI on Si gel with the latter solvent gave fraction VII, 0.085 g VIII, 0.023 g IX, 0.015 g and X, 0.011 g.

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A BENZOPHENONE FROM THE FRUITS OF *CLUSIA ELLIPTICIFOLIA*

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Key Word Index—*Clusia ellipticifolia*; Clusiaceae; vismiaphenone B; isovismiaphenone B; 6-benzoyl-5-hydroxy-2,2,8,8-tetramethyl (2*H*,8*H*)benzo(1,2-*b*:3,4-*b*′)dipyran; friedeline.

Abstract—From the fruits of *Clusia ellipticifolia* collected in Colombia, the following secondary metabolites were isolated: friedeline, vismiaphenone B, isovismiaphenone B and 6-benzoyl-5-hydroxy-2,2,8,8-tetramethyl (2*H*,8*H*)benzo(1,2-*b*:3,4-*b*′)dipyran.

INTRODUCTION

The *Clusia* genus embraces *ca* 200 species [1], 40 of which are known in Colombia and occur in the Amazonian jungle as well as in the Andean regions at *ca* 2000 m. Besides the known friedeline, vismiaphenone B and isovismiaphenone B, we have isolated from the fruits of *C. ellipticifolia* a new benzophenone (**2**), the structure of which was determined by spectroscopic methods.

RESULTS AND DISCUSSION

By conventional procedures, we were able to isolate from the petrol extract of the fruits of *C. ellipticifolia*, three pigments, two of which, vismiaphenone B (**1**) and its isomer isovismiaphenone B, had been previously reported from *Vismia decipiens* [2]. The less polar pigment (**2**) (M^+ 362, R_f, 0.72, Si gel, petrol–EtOAc, 19:1) reacted with ferric chloride on TLC to give a dark green color. It also exhibited an IR band at 1615 cm^{-1} ($\nu_{C=O}$) and gave fragmentation ions with *m/z* 77 and 105, suggesting a benzophenone structure with an unsubstituted ring.

The bathochromic shift of the λ_{max} after aluminium chloride addition and the absence of shift upon addition of sodium acetate revealed a hydroxyl substituent in the second ring *ortho* with respect to the carbonyl group. The presence of this hydroxyl group was confirmed by the presence in the ^1H NMR spectrum of a singlet at δ 12.78 which disappeared upon addition of D_2O. A multiplet at δ 7.59–7.28 (5H) corresponded to a monosubstituted aromatic ring. The lack of other aromatic protons suggested a fully substituted second ring. Doublets at δ 6.74 (1H), 6.56 (1H), 5.52 (1H) and 5.30 (1H) indicated the presence of *cis*-vinylic protons ($J = 10$ Hz) and singlets at δ 1.5 (6H) and 0.99 (6H) the presence of four methyl groups. All of these signals were characteristic of 6,6-dimethyl pyrans. The IR spectrum had bands at 1645 cm^{-1} ($\nu_{C=C}$) and 1385 and 1368 cm^{-1} (gem-methyl groups). All the IR, UV, ^1H NMR and mass data fit the assigned structure, **2** for the new benzophenone. In confirmation of this structure, cyclodehydrogenation of vismiaphenone B(**1**) yielded the benzophenone, **2**, which on reaction with diazomethane gave the dichromene, **3** [2] (Scheme 1).

Maclurin [3], bronianone [3], xanthochymol [4, 5], isoxanthochymol [5], vismiaphenones A and B and isovismiaphenone B [2], clusianone [6], garcinol, isogarcinol and camboginol [7] and kolanone [8] have already been reported in the Guttiferae. 6-Benzoyl-5-hydroxy-2,2,8,8-tetramethyl(2*H*,8*H*)benzo(1,2-*b*:3,4-*b*′) dipyran is a new benzophenone derived from ploroglucinol. Its presence may be of interest in biogenetic and taxonomic studies.

EXPERIMENTAL

Plant material. The fruits of *Clusia ellipticifolia* Cuatr., were collected in August 1981, near Bogotá (municipio de San Antonio del Tequendama) and identified by Dr. R. Jaramillo (Instituto de Ciencias Naturales de la Universidad Nacional de Colombia). A voucher sample, (229396) is deposited at the National Herbarium.

Extraction and separation. The fruits (200 g) were extracted with petrol in a Soxhlet apparatus. The extract was concd to dryness to give a gummy product (3 g). The crude extract (2.5 g) was chromatographed on Si and the column was eluted with petrol to give a mixture of triglycerides (180 mg). Further elution with petrol containing increasing amounts of EtOAc produced the successive separation of friedeline (16 mg), benzophenone, **2** (330 mg), isovismiaphenone B (140 mg), vismiaphenone B (830 mg) and unidentified substances.

Friedeline. Identified by comparison with an authentic sample (mp, TLC, IR).

Vismiaphenone B and isovismiaphenone B. Oil and yellow microcrystals respectively, were identified by ^1H NMR UV and IR spectroscopy and by comparison with the ^1H NMR spectrum of an authentic sample kindly provided by Dr. F. Delle Monache, Centro Chimica dei Recettori (CNR), Rome. Isovismiaphenone mp 126–128°.

6-*Benzoyl*-5-*hydroxy*-2,2,8,8-*tetramethyl*(2H,8H)*benzo*(1,2-b:3,4-b′)*dipyran.* Orange crystals, mp 146–148° uncorr. (petrol). UV λ_{max}^{MeOH} nm: 250 sh, 265 sh, 275, 290 sh, 335 sh; $\lambda_{max}^{MeOH+AlCl_3}$ nm: 267, 278, 300 sh, 360; $\lambda_{max}^{MeOH+AlCl_3+HCl}$ nm: 267, 277, 301 sh, 356; $\lambda_{max}^{MeOH+NaOAc}$ nm: 249 sh, 264 sh, 275, 290 sh, 334 sh; IR $\nu_{max}^{CHCl_3}$ cm^{-1}: 3060, 2930, 2860, 1645, 1610 sh, 1595, 1648, 1450, 1430, 1385, 1368, 1310, 1280, 1140; IR ν_{max}^{film} cm^{-1}: 3200–2400 broad and complex band; ^1H NMR (60 MHz, $CDCl_3$): δ 12.78 (1H, *s*), 7.59–7.28 (5H, *m*), 6.74 (1H, *d*, $J = 10$ Hz), 6.56 (1H, *d*, $J = 10$ Hz), 5.52 (1H, *d*, $J = 10$ Hz), 5.30 (1H, *d*, $J = 10$ Hz), 1.5 (6H, *s*), 0.99 (6H, *s*); EIMS (70 eV) *m/z* (rel. int.): 362 $[M]^+$ (16), 347 $[M-15]^+$ (100), 319 (3), 269 (4), 127 (11), 105 $[C_6H_5-C\equiv O]^+$ (20), 77 $[C_6H_5]^+$ (22), m*: 332.5 (362–347), m*: 208.5 (347–269).

Methylation with CH_2N_2 yielded dichromene, **3**, after chromatographic separation. ^1H NMR ($CDCl_3$): similar to that previously reported [2].

Cyclodehydrogenation of vismiaphenone B. Vismiaphenone B (72 mg) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ 45 mg) in C_6H_6 were refluxed for 1 hr. After filtration to remove DDQ-H_2, evaporation and chromatographic separation (Si, C_6H_6), 15 mg benzophenone, **2**, was obtained and identified by comparison with an authentic sample (mp, TLC, ^1H NMR).

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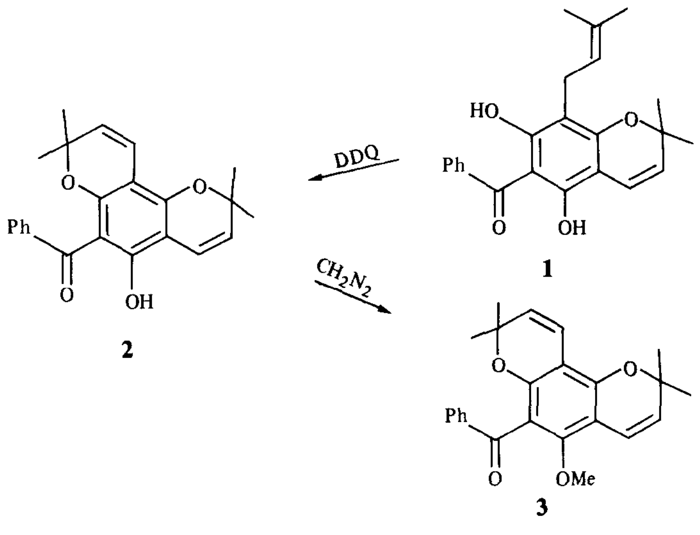

Scheme 1.

was measured by Dr. Benjamin Rodríguez, Consejo Superior de Investigaciones Científicas Madrid, Spain.

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5-METHOXY-2,2,8-TRIMETHYL-10-SENECIOYL-2*H*,6*H*-BENZO(1,2-b; 5,4-b')DIPYRAN-6-ONE FROM *SPATHELIA WRIGHTII*

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Key Word Index—*Spathelia wrightii*; Rutaceae; pyranochromone; 5-methoxy-2,2,8-trimethyl-10-senecioyl-2*H*,6*H*-benzo (1,2-b; 5,4-b')dipyran-6-one.

Abstract—From leaflets of *Spathelia wrightii* a new pyranochromone has been isolated, the spectroscopic properties of which are in accordance with the structure 5-methoxy-2,2,8-trimethyl-10-senecioyl-2*H*,6*H*-benzo(1,2-b; 5,4-b')dipyran-6-one (**1**).

From dried leaflets of *Spathelia wrightii* a pyranochromone was isolated in 2.9% yield. High resolution mass spectrometry revealed the elemental composition $C_{21}H_{22}O_5$. The structure was mainly deduced from NMR spectral information. The ^1H NMR signals (Table 1) were assigned and partial structures recognized by comparison with chemical shift data and coupling constants of compounds containing the 2,2-dimethylchromene [1–3] and 2-methylchromone ring systems [4] or the senecioyl side chain [5]. In deuterochloroform the signals of the C-14 and C-18 methyl groups coincide. Their membership to two spin systems was detected by decoupling experiments. The observed NOE values (Fig. 1) are only in agreement with one (**1**) of the 12 possible arrangements of the substituents at the benzene ring. In the NOE experiments, difficulties arose from the superimposition of the signals of H-14 and H-18 in deuterochloroform and the neighbourhood of the signals of H-14 and H-19 in deuterobenzene, respectively. Irradiation on the signal at $\delta 2.18$ in deuterobenzene showed that the C-18 methyl group does not produce a NOE. Therefore, the following measurements were carried out in deuterochloroform considering that signal enhancement by irradiation on the signal at $\delta 2.24$ has to be attributed exclusively to the C-14 methyl group. The ^{13}C NMR spectrum (Table 2), including the ^{13}C–^1H long-range coupling constants (Table 3), is in agreement with structure **1**. Signals were assigned by comparison with reported data for furochromones [6], mulberrochromene [7] and isobutenyl phenyl ketone [8] as well as by determination of the ^{13}C–^1H long-range coupling constants via selective decoupling experiments.

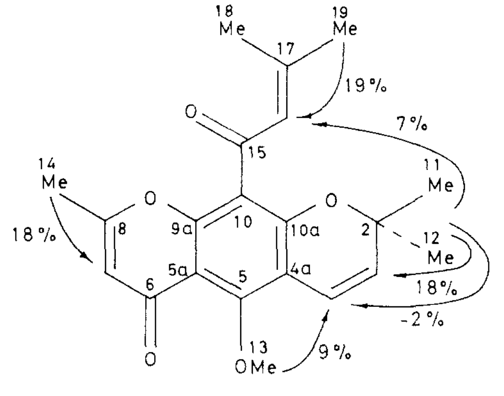

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Fig. 1. NOE values for 5-methoxy-2,2,8-trimethyl-10-senecioyl-2*H*,6*H*-benzo(1,2-b;5,4-b')dipyran-6-one (**1**).