$=CHCH_2]^+$ (100).

$$[\alpha]^{\lambda}_{24^\circ} = \frac{589 \quad 578 \quad 546 \quad 436\,\text{nm}}{+45 \quad +48 \quad +55 \quad +95} \ (CHCl_3;\ c\ 0.97).$$

Acknowledgement—We wish to thank Professor F. Ehrendorfer, Institute for Botany, University of Vienna, for providing the plant material.

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Phytochemistry, Vol. 22, No. 9, pp. 2087–2088, 1983.
Printed in Great Britain.

0031-9422/83 \$3.00+0.00
Pergamon Press Ltd.

CONSTITUENTS OF A HEXANE EXTRACT OF *PHOENIX DACTYLIFERA*

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(*Revised received* 18 *January* 1983)

Key Word Index—*Phoenix dactylifera*; Palmae; steroids; ketones; hydroxyketones; diketones.

Abstract—In addition to known compounds, two new steroid diones, 5α-stigmast-22-en-3,6-dione and 5α-campestan-3,6-dione, were isolated from stems of *Phoenix dactylifera*.

Phoenix dactylifera L. was collected at Parque Municipal of Elche (Alicante) and authenticated by Professor Mansanet, Department of Botany, University of Valencia. Previous work on this plant includes the chromatographic detection of flavonoids [1–3] and waxes [4] in a general taxonomic study of Palmae. The chemical constituents of the pollen [5] and palm-dates [6] have also been studied.

The neutral fraction from a dewaxed hexane extract of the stems of *P. dactylifera* was separated into six main fractions (I–VI) by CC. Fractions I, II and IV were mixtures of hydrocarbons (C_{26}–C_{31}), esters (alcohols: lupeol, β-sitosterol, stigmasterol and campesterol; fatty acids: 10, 12:1, 16, 18:1 and 18:2) and triglycerides (16, 18:2), respectively. Fractions III and V were lupyl acetate and lupeol. On analytical TLC, fraction VI was separated into a major component and four minor ones. The major component was separated by crystallization and was identified as a mixture of β-sitosterol, stigmasterol and campesterol.

Careful CC of the mother liquors of crystallization of fraction VI allowed the isolation of the four minor components (fractions VII–X) which were further purified by prep. TLC and recrystallization. The components of these preparations were identified by spectroscopy and by comparative GC, fraction VII: 3% SE-30, 300°, with natural authentic sample [7]; fraction VIII: 3% OV-17, 300° with natural [8] and synthetic [9] specimens; fractions IX and X: 3% OV-17, 300° (IX) and 3% OV-17, 310° (X) with synthetic specimens [10, 11]. Fraction VII was a mixture of stigmast-4-en-3-one [412 $[M]^+$ (86.2%)], stigmasta-4-22-dien-3-one [410 $[M]^+$ (7.9%)] and campest-4-en-3-one [398 $[M]^+$ (5.8)]; mp 86–87° (ether–methanol); $[\alpha]^{25}_D$ +77.5°; IR ν_{max} cm^{-1}: 1670 (C=O), 1610 (C=C), 860 (C=C–H); ^{1}H NMR ($CDCl_3$): δ5.75 (*br s*, –CO–CH=C), 2.2–2.4 (*m*, $-CH_2-CO-$); UV λ^{EtOH}_{max} 241 nm (log ε 4.15). Fraction VIII was a mixture of 5α-stigmastan-3,6-dione [428 $[M]^+$ (74.7%)], 5α-stigmast-22-en-3,6-dione [426 $[M]^+$ (12.9%)] and 5α-campestan-3,6-dione [414 $[M]^+$ (12.3%)]; mp 196–197° (chloroform–methanol); IR ν_{max} cm^{-1}: 1710 and 1720 (C=O); ^{1}H NMR ($CDCl_3$): δ2.1–2.6 (*m*, $3CH_2CO + 1CHCO$). 5α-Stigmastan-3,6 was known to occur naturally [8, 12–14]. However, this is the first report of the natural occurrence of the latter two diones. Fraction IX was a mixture of stigmast-4-en-3,6-dione [426 $[M]^+$ (92.6%)], stigmasta-4,22-dien-3,6-dione [424 $[M]^+$ (3.0%)] and compest-4-en-3,6-dione [412 $[M]^+$ (4.4%)]; mp 162–163° (methanol); IR ν_{max} cm^{-1}: 1680 (conjugated C=O), 1605 (C=C), 865 (=C–H); UV λ^{EtOH}_{max} 251 nm (log ε 4.01). Fraction X was a mixture of 6β-hydroxystigmast-4-en-3-one [428 $[M]^+$ (77.4%)], 6β-hydroxystigmasta-4,22-dien-3-one [426 $[M]^+$ (10.2%)], and 6β-hydroxycampest-4-en-3-one [414 $[M]^+$ (12.4%)]; mp 208–210° (ether); IR ν_{max} cm^{-1}: 3500 (O–H), 1695 (conjugated C=O), 1615 (C=C), 880 (=C–H); UV λ^{EtOH}_{max} 238 nm (log ε 4.12).

The isolation of steroid ketones, hydroxyketones and diketones from *P. dactylifera* is not unexpected [7, 8, 12, 13]; certainly they are not artifacts produced by air oxidation of sterols during the process of extraction, 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.; $[\alpha]_D$: $CHCl_3$; ^{1}H 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.

Acknowledgements—We are grateful to Dr. D. J. Slatkin, Department of Pharmacognosy, University of Pittsburg, and Dr. W. H. Hui, Department of Chemistry, University of Hong Kong, for gifts of authentic samples.

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Phytochemistry, Vol. 22, No. 9, pp. 2088–2090, 1983.
Printed in Great Britain.
0031–9422/83 $3.00 + 0.00

A BENZOPHENONE FROM THE FRUITS OF *CLUSIA ELLIPTICIFOLIA*

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(*Revised received* 13 *December* 1982)

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