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(+)-JATROPHOL, (+)-MARMESIN, PROPACIN AND JATROPHIN FROM THE ROOTS OF *JATROPHA CURCAS* (EUPHORBIACEAE)

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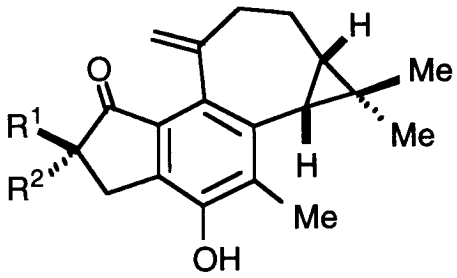
ABSTRACT

*(+)-Jatrophol, 9, (+)-marmesin, **13**, propacin, **15**, and jatrophin, **18**, were isolated from the polar fraction of the crude extract of the root of* Jatropha curcas*; their structures were elucidated by spectroscopic methods and comparison with authentic samples.*

INTRODUCTION

The root of *Jatropha curcas* is a rich source of diterpenes of the daphnane and lathyrane skeletons. Apart from the well known jatropholones A, **1**, and B, **2**,[1-3] we have previously reported the identification of six new compounds, curcusones A-D, 3 - 6,[4] and curculathyranes A, **7**, and B, **8**,[5] which belong to the daphnane and lathyrane groups respectively, from the hexane extract of this plant. Further investigation of the more polar fraction has led to isolation of the titled compounds which constitutes this report.



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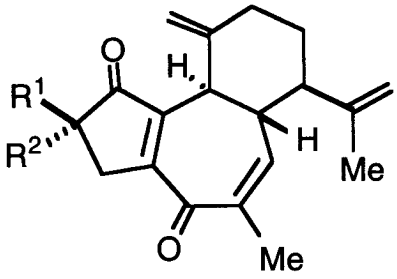
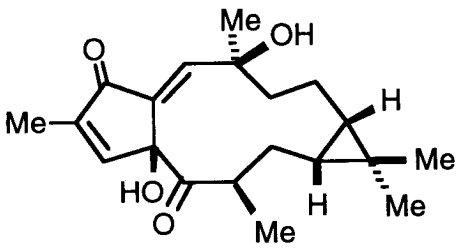
2, $R^1 = Me$; $R^2 = H$



3, $R^1 = Me$; $R^2 = H$
4, $R^1 = H$; $R^2 = Me$
5, $R^1 = Me$; $R^2 = OH$
6, $R^1 = OH$; $R^2 = Me$



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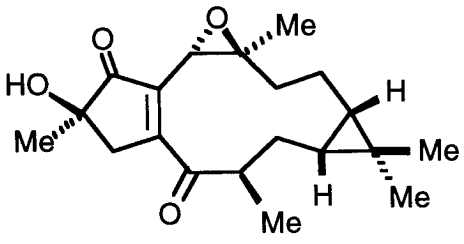

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RESULTS AND DISCUSSION

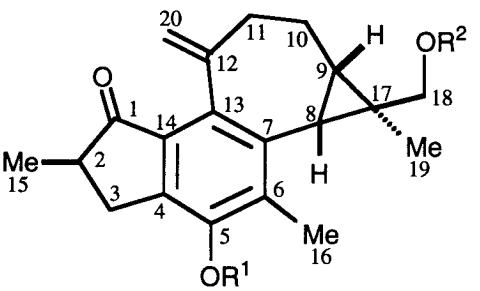
The dried ground roots of *Jatropha curcas* were soaked in hexane at room temperature overnight after which they were filtered off and the process was repeated twice. The combined filtrate was subjected to successive column and preparative layer chromatography to yield jatropholones A and B, curcusones A-D and curculathyranes A and B. The residual material was then subjected to room temperature extraction with methylene chloride to give, after evaporation of the solvent under reduced pressure, a dark brown viscous liquid. Silica gel column chromatography of this material using gradient elution from 40% ethyl acetate in hexane to pure ethyl acetate effected separation into three fractions. Further purification of fraction I by silica gel PLC using 40% ethyl acetate in hexane as the developing solvent gave (+)-jatrophol, **9**, as colourless needles, mp. 195-6° after crystallization from a mixture of methylene chloride-hexane (0.0048% yield from dried roots). PLC separation of fraction II using a mixture of 1% methanol in methylene chloride as eluent yielded (+)-marmesin, **13**, (0.0017%), while similar treatment of fraction III provided propacin, **15**, (0.0035%) and a small amount of jatrophin, **18**, (0.0008%), purified by crystallization from methylene chloride-hexane mixture in every case.

The molecular formula, $C_{20}H_{24}O_3$, for (+)-jatrophol, **9**, was deduced from its mass spectrum (*m/e* 312, M+) and elemental analysis (found: C, 76.63; H, 7.91 %). Although the spectroscopic data of **9** was closely related to that of jatropholone B, **2**, its mass spectrum differed from **2** by an additional 16 mass units, inferring the presence of an extra hydroxy group. The ^{1}H NMR spectrum of **9** was very similar to that of **2** except for the absence of one of the high field methyl signals at δ 1.26 and the presence of a two-proton methylene singlet at δ 3.46 which suggested that one of the methyl groups on the cyclopropane ring in the jatropholone B skeleton was hydroxylated.

The conclusion that the extra hydroxy group in **9** was situated at *C-18* (see numbering in structure **9**), and not the alternative *C-19*, was reached *via* the following rationalization: the two methyl groups on the cyclopropane ring in jatropholone B resonated at δ 0.86 and 1.26, of which the higher field absorption was assigned to the *Me-19* due to the shielding effect of the aromatic nucleus at close proximity. In the nmr spectrum of 9 the methyl absorption at δ 0.86 was present but, as already mentioned, the resonance at δ 1.26 was replaced by the methylene absorption at δ 3.46, hence hydroxylation must be at *C-18*.

The stereochemistry of the stereochemically labiled *C-2* in **9** was proposed upon comparison of its nmr spectrum to that of jatropholone B, **2**. It should be noted that the physical properties of the epimeric jatropholones A and B, **1** and **2**, are very similar[1-3] and that their stereochemical relationship at *C-2* was demonstrated by the conversion of either compound to a mixture of both upon treatment with mild base.[1]

Various derivatives: monomethyl ether, **10**, mono- and diacetates, **11** and **12** respectively, prepared from **9** according to standard methods, all exhibited physical properties in agreement with the proposed structures.

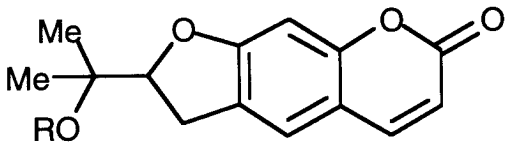


9, $R^1 = R^2 = H$
10, $R^1 = Me$; $R^2 = H$
11, $R^1 = COMe$; $R^2 = H$
12, $R^1 = R^2 = COMe$

Compound **13** was obtained as colourless needles, mp. 185-6° from a methylene chloride-hexane mixture. Elemental analysis (found: C, 68.28; H, 5.74 %) and its mass spectrum (*m/e* 246, M+) gave the molecular formula as $C_{14}H_{14}O_4$. The IR spectrum displayed strong absorptions at 3560, 1720, 1620 cm^{-1} indicating the presence of a hydroxy group and possibly a coumarin nucleus. The ^{1}H NMR spectrum exhibited signals corresponding to the

hydroxy group at δ 2.90 as a broad singlet (disappeared with D_2O). Two low-field doublets at δ 6.13 and 7.63 (J = 10 Hz in both cases) were attributed to the two olefinic protons of the coumarin moiety. Two aromatic protons appeared as two singlets at δ 6.63 and 7.23 and a one-proton triplet at δ 4.73 (J = 9 Hz) was assigned to the methine proton coupled to the adjacent methylene group which itself appeared as a doublet (J = 9 Hz) at δ 3.20. Two uncoupled methyl groups resonated as two singlets at δ 1.23 and 1.30.

Comparison of the above data together with those of its acetate derivative (Ac_2O-pyridine) to the published data of (+)-marmesin, **13**, and its acetate, **14**,[6,7] revealed that they were identical in all respects. Marmesin was originally isolated from the indigenous Indian plant, *Aegle marmelos* Correa,[6] and later from the Hawiian shrub *Pelea barbigera*,[7] both of the Rutaceae family.

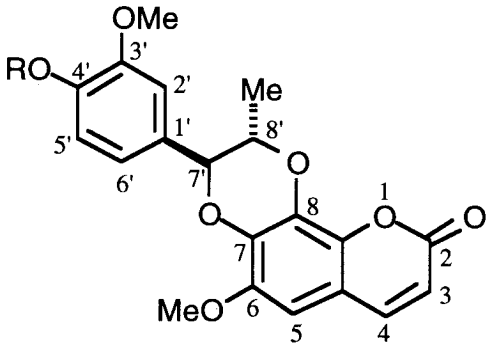


13, R = H
14, R = COMe

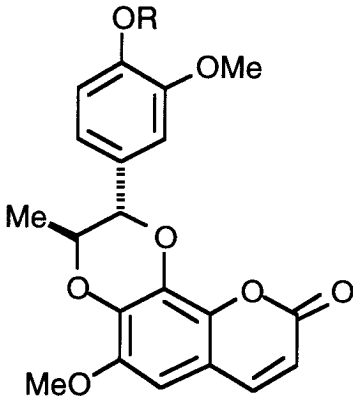
Compound **15** was crystallized from a mixture of methylene chloride-hexane as colourless plates, mp. 225-6°. Elemental analysis (found: C, 64.62; H, 4.94 %) and its mass spectrum (*m/e* 370, M^+) established the molecular formula of $C_{20}H_{18}O_7$. The IR absorptions at 3400 (broad), 1700 and 1620 cm^{-1} indicated the presence of hydroxy and coumarin groups similar to those observed in marmesin, **13**. The ^1H NMR spectrum of **15** displayed two sets of doublets at δ 6.30 and 7.90 (both with J = 9 Hz) corresponding to the coumarin olefinic protons. Four aromatic protons appeared as a singlet at δ 7.03 (1H) and a broad singlet at δ 6.86 (3H). Two methine protons resonated at δ 4.06 and 4.53 as a multiplet and a doublet (J = 8 Hz) respectively. A singlet at δ 3.80 (6H) was assigned to two methoxy groups and a doublet integrating for three protons at δ 1.20 (J = 8 Hz) to a methyl group. Finally, a phenolic hydroxy group (confirmed by the formation of methylether and acetate **16** and **17** respectively) showed a broad singlet at δ 9.23 (disappeared with D_2O)

The above data indicated that compound **15** contained a coumarin moiety, two methoxy and one phenolic hydroxy groups. These accounted for five of the seven oxygen atoms present in the molecule. The remaining two oxygen atoms were concluded to be part of the dioxide linkage of the coumarino-lignan skeleton from the characteristic cleavage pattern in its mass spectrum: a retro Diels-Alder reaction on the dioxane moiety in **15** gave rise to the prominent peaks observed at *m/e* 208, 206, and 164 (100 %). The base peak at *m/e* 164 also indicated that the hydroxy group in **15** was located on ring D (at position 4', since a lower field shift of proton 5' in the NMR spectrum of the acetate derivative, **17**, was observed) as shown. Finally, the *trans*- relationship of the aryl and methyl groups in **15** was deduced from the coupling constant of 8 Hz between *H-7'* - *H-8'* as well as from biosynthetic considerations.

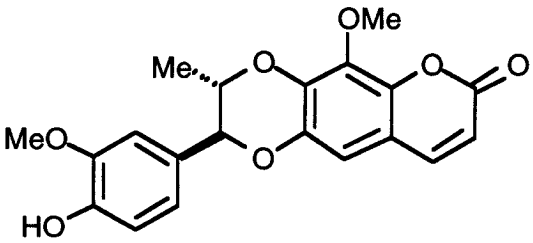
In fact, four possible structures, **15**, **18**, **20** and **21** could accommodate the above described data, but, however, the linear structures, **20** and **21**, were subsequently ruled out by the NOE experiments on the acetate derivative, **17**. As shown in the enlarged figure of **17**, irradiation of the lone aromatic absorption at δ 6.52 caused enhancements of both methoxy (δ 3.86) and olefinic proton (δ 7.61) absorptions. Irradiation of the methoxy protons at δ 3.86 effected only the aromatic but not the olefinic proton, while similar treatment at δ 7.61 caused the enhancement of the peak at δ 6.52. These results suggested that the aromatic proton (δ 6.52) was situated between the methoxy group and the olefinic proton of the coumarin moiety.



15, R = H
16, R = Me
17, R = COMe



18, R = H
19, R = COMe



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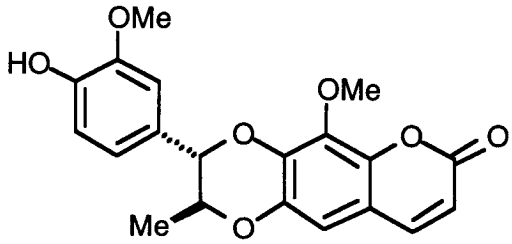

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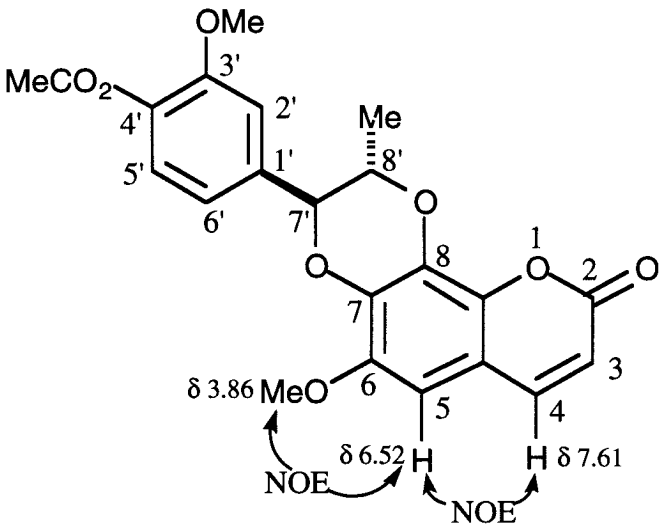

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Structures **15** and **18** were originally proposed as alternative candidates for propacin, a coumarino-lignan isolated from *Protium opacum* (Burseraceae).[8] Subsequent synthetic work by the Italian group[9] led to the availability of both compounds and the isolated propacin was shown to be **15** by comparison of natural with synthetic samples. Later, the identification of **18** from *Jatropha glandulifera* (Euphorbiaceae) was reported,[2] hence both **15** and **18** are naturally occurring coumarino-lignans. Upon comparison of our compound from *Jatropha curcas* to the standard sample of propacin (by Dr. Blasko and Professor Cordell of the University of Illinois, U.S.A.), it was found that they were identical in all respects and therefore the structure of compound **15** was confirmed.

Having firmly established the structure **15**, identification of compound **18** (obtained as colourless plates, mp. 242° from a mixture of methylene chloride-hexane), was straightforward. The isomeric nature of compound **18** and propacin was immediately apparent from their mass spectral patterns which were almost identical, and the elemental analysis of **18** which also established the same molecular formula of $C_{20}H_{18}O_7$. Further inspection of the IR, UV and especially the NMR spectra of **18** revealed that they were identical to those reported earlier.[2]

Recently there appeared a report on the isolation of jatropholones A and B, **1** and **2**, jatrophol, **9**, and compound **18** (named "jatrophin") from the roots of *Jatropha curcas*.[10] Interestingly, however, no regio- and stereochemical structures of **9** were put forward and the molecular structure was tentatively presented as a "two dimensional" skeleton. Also there was no mention of isolation of marmesin, **13**, or of the major coumarino-lignan component, propacin **15**. This report thus extends the scope of the study of chemical

constituents from the roots of *Jatropha curcas*, from which altogether nine diterpenes; one furanocoumarin and two coumarino-lignans have been isolated. These compounds are: jatropholones A and B, **1** and **2**, curcusones A-D, **3 - 6**, and curculathyranes A and B, **7** and **8**, from the non-polar extract,[4,5] and jatrophol, **9**, marmesin, **13**, propacin, **15**, and jatrophin, **18**, from the more polar methylene chloride extract.[11]

EXPERIMENTAL

^{1}H NMR spectra were recorded either on a Varian EM-360 or a Bruker 400 MHz spectrophotometer. ^{13}C NMR, mass spectra and elemental analyses were performed by the Scientific and Technological Research Equipment Center, Chulalongkorn University. Optical rotations were performed by the Department of Medical Science, Ministry of Public Health, Thailand. Ultraviolet spectra were measured on a Beckman or a Shimadzu UV-Visible spectrophotometer, and infrared spectra were determined on a Jasco A-302 Infrared spectrophotometer. Melting points were determined on an electrothermal melting point apparatus and were uncorrected. Merck's Kieselgel 60 (particle size 0.063 - 0.200 mm) and Kieselgel 60 PF_{254} were used for the column and preparative layer chromatography respectively.

Dried ground roots of *Jatropha curcas* (3.2 kg), collected from Mae Hong Sorn province in northern Thailand, were soaked in hexane (10 L) at room temperature overnight and the extract was filtered. The process was repeated twice and the combined filtrate was subjected to column and preparative layer chromatography to yield jatropholone A, **1**, (862 mg, 0.0269 %), jatropholone B, **2**, (539 mg, 0.0168 %), curcusone A, **3**, (240 mg, 0.0075 %), curcusone B, **4**, (344 mg, 0.0107 %), curcusone C, **5**, (20 mg, 0.0006 %), curcusone D, **6**, (80 mg, 0.0025 %), curculathyrane A, **7**, (166 mg, 0.0052 %), curculathyrane B, **8**, (19 mg, 0.0006 %).

The residual material was further extracted with methylene chloride and the extract was concentrated under reduced pressure to give a brown viscous liquid which was chromatographed on a silica gel column using gradient elution from 40% ethyl acetate in hexane to pure ethyl acetate as to obtain three major fractions, I - III. Further purification of fraction I by silica gel preparative layer chromatography using 40% ethyl acetate in hexane as eluent provided jatrophol, **9**, (152 mg, 0.0048 %). PLC separation of fraction II using a mixture of 1% methanol in methylene chloride as eluent yielded marmesin, **13**, (56 mg, 0.0017 %). Similar treatment of fraction III afforded propacin, **15**, (112 mg, 0.0035 %) and jatrophin, **18**, (26 mg, 0.0008 %).

JATROPHOL, 9

Colourless needles; mp. 195-196° (from a mixture of methylene chloride-hexane) (lit.[10] mp. 190-2°); $[\alpha]_D^{25}$ +96.6° (*c* 0.705 in DMSO); ν_{max} (Nujol), 3400 (broad), 1690 cm^{-1}; λ_{max}(EtOH), 224 (log E 6.1276), 272 (log E 5.7494), 320 (log E 5.2462) nm; *m/e* (relative intensity), 312 (M^+, 100), 297 (11), 281 (43), 253 (34), 240 (37), 225 (35); 1H NMR (d in DMSO-d_6), 0.86 (s, 3H, Me), 0.92-1.16 (m, 2H, -CH-CH-), 1.22 (d, J = 7 Hz, 3H, Me), 1.69 (m, 2H, -CH_2-), 2.26 (s, 3H, Me), 2.36-2.60 (m, 4H, 2 x -CH_2-), 3.08-3.35 (m,

^{1}H, -CO-CH-), 3.46 (s, 2H, -CH2-OH), 4.56 (broad s, 1H, =CH), 4.66 (s, 1H, -OH, disappeared with D_2O), 5.13 (broad s, 1H, =CH), 8.83 (s, 1H, -OH, disappeared with D_2O); ^{13}C NMR (δ in DMSO-d_6), 11.9 (q), 13.3 (q), 16.9 (t), 20.9 (t), 22.0 (d), 25.4 (d), 24.7 (s), 30.7 (q), 33.5 (t), 41.9 (d), 70.5 (t), 114.5 (t), 131.1 (s), 132.3 (s), 132.8 (s), 135.7 (s), 138.0 (s), 145.5 (s), 151.3 (s), 207.6 (s). Analysis; Calcd. for $C_{20}H_{24}O_3$: C, 76.89; H, 7.74. Found: C, 76.63; H, 7.91 %.

5-METHOXYJATROPHOL, 10

Methylation of jatrophol employing the standard procedure (Me_2SO_4-anhydrous K_2CO_3-acetone/reflux) followed by purification of the crude product by preparative layer chromatography (silica gel, 10% ethyl acetate in hexane as eluent) yielded 5-METHOXYJATROPHOL (72 %) as colourless needles; mp. 129-130° (from hexane); ν_{max} (Nujol), 3450, 1710 cm^{-1}; *m/e* (relative intensity), 326 (M^+, 100), 311 (14), 295 (39), 267 (30), 253 (38); ^{1}H NMR (δ in $CDCl_3$), 0.83-1.16 (m, 2H, -CH-CH-), 0.93 (s, 3H, Me), 1.30 (d, J = 7 Hz, 3H, Me), 1.53-2.00 (m, 2H, -CH_2-), 2.26 (s, 1H, -OH, disappeared with D_2O), 2.30 (s, 3H, Me), 2.43-2.90 (m, 4H, 2 x -CH_2-), 3.10-3.40 (m, 1H, -CO-CH-), 3.60 (s, 2H, -CH_2OH), 3.86 (s, 3H, -OMe), 4.66 (broad s, 1H, =CH), 5.23 (broad s, 1H, =CH). Analysis; Calcd. for $C_{21}H_{26}O_3$: C, 77.27; H, 8.03. Found: C, 77.23; H, 8.08 %.

Acetylation of jatrophol

Acetylation of jatrophol with acetic anhydride-pyridine at room temperature for 2 hours afforded, after separation by PLC (silica gel, 1% methanol in methylene chloride as eluent), 5-ACETYLJATROPHOL, **11**, (63 %) and 5,18-DIACETYLJATROPHOL, **12**, (18 %). When the reaction was left stirring at room temperature for 24 hours the fully acetylated compound **12** was obtained in 88 % yield.

5-ACETYLJATROPHOL, 11

Colourless needles, mp. 166-167° (from hexane); ν_{max} ($CHCl_3$), 3450, 1710 cm^{-1}; *m/e* (relative intensity), 354 (M^+, 100), 323 (24), 294 (32), 281 (55); ^{1}H NMR (δ in $CDCl_3$), 0.70-1.00 (m, 2H, -CH-CH-), 0.90 (s, 3H, Me), 1.23 (d, J = 7 Hz, 3H, Me), 1.53-1.96 (m, 2H, -CH_2-), 1.86 (s, 1H, -OH, disappeared with D_2O), 2.16 (s, 3H, -CO-Me), 2.33 (s, 3H, Me), 2.43-2.83 (m, 4H, 2 x -CH_2-), 3.13-3.42 (m, 1H, -CO-CH-), 3.53 (s, 2H, -CH_2OH), 4.70 (broad s, 1H, =CH), 5.21 (broad s, 1H, =CH). Analysis; Calcd. for $C_{22}H_{26}O_4$: C, 74.55; H, 7.39. Found: C, 74.49; H, 7.36 %.

5,18-DIACETYLJATROPHOL, 12

Colourless semi-solid; ν_{max} ($CHCl_3$), 1750, 1720, 1700 cm^{-1}; *m/e* (relative intensity), 396 (M^+, 100), 354 (11), 336 (27), 294 (93); ^{1}H NMR (δ in $CDCl_3$), 0.80-1.10 (m, 2H, -CH-CH-), 0.90 (s, 3H, Me), 1.23 (d, J = 7 Hz, 3H, Me), 1.60-1.96 (m, 2H, -CH_2-), 2.03 (s, 3H, -CO-Me), 2.16 (s, 3H, -CO-Me), 2.30 (s, 3H, Me), 2.43-2.90 (m, 4H, 2 x -CH_2), 2.96-3.43 (m, 1H, -CO-CH-), 3.83 and 4.10 (AB system, J = 11 Hz, 2H, -C-CH_2-O-CO-), 4.63 (broad s, 1H, =CH), 5.16 (broad s, 1H, =CH). Analysis; Calcd. for $C_{24}H_{28}O_5$: C, 72.71; H, 7.12. Found: C, 72.88; H, 7.09 %.

(+)-MARMESIN, 13

Colourless needles, mp. 185-186° (from methylene chloride-hexane) (lit.[6] mp. 189.5° from H_2O, lit.[7] mp. 164-170° from EtOH); [a] 25, D +27° (*c* 0.660 in $CHCl_3$); ν_{max} ($CHCl_3$), 3560, 1720, 1620 cm^{-1}; λ_{max} (EtOH), 224 (log E 4.1618), 334 (log E 3.9591) nm; *m/e* (relative intensity), 246 (M+, 61), 213 (24), 188 (87), 187 (100), 175 (16), 160 (29), 59 (43); ^1H NMR (δ in $CDCl_3$ + DMSO-d_6), 1.23 (s, 3H, Me), 1.30 (s, 3H, Me), 2.90 (broad s, 1H, -OH, disappeared with D_2O), 3.20 (d, J = 9 Hz, 2H, -CH_2-), 4.73 (t, J = 9 Hz, 1H, -O-CH-), 6.13 (d, J = 10 Hz, 1H, -CO-CH=), 6.63 (s, 1H, Ar-H), 7.23 (s, 1H, Ar-H), 7.63 (d, J = 10 Hz, 1H, =CH-). Analysis; Calcd. for $C_{14}H_{14}O_4$: C, 68.28; H, 5.73. Found: C, 68.28; H, 5.74 %.

MARMESIN ACETATE, 14

Acetylation (acetic anhydride-pyridine/ 90°/ 12 hr.) of (+)-marmesin yielded, after purification of the crude product by PLC (silica gel, 30% ethyl acetate in hexane) followed by crystallization from a mixture of methylene chloride-hexane, MARMESIN ACETATE (66 %) as colourless needles, mp. 125-6° (lit.[6] mp. 130° from H_2O); ν_{max} ($CHCl_3$), 1740, 1720, 1620 cm^{-1}; *m/e* (relative intensity), 288 (M^+, 13), 228 (31), 213 (100), 187 (20), 185 (5), 175 (12); ^1H NMR (δ in $CDCl_3$), 1.50 (s, 3H, Me), 1.56 (s, 3H, Me), 1.93 (s, 3H, -CO-Me), 3.20 (d, J = 8 Hz, 2H, -CH_2-), 5.10 (t, J = 8 Hz, 1H, -O-CH-), 6.16 (d, J = 10 Hz, 1H, -CO-CH=), 6.73 (s, 1H, Ar-H), 7.20 (s, 1H, Ar-H), 7.56 (d, J = 10 Hz, =CH-). Analysis; Calcd. for $C_{16}H_{16}O_5$: C, 66.66; H, 5.59. Found: C, 66.46; H, 5.59 %.

PROPACIN, 15

Colourless plates, mp. 225-6° (from methylene chloride-hexane) (lit.[8] mp. 226-8° from $CHCl_3$-MeOH, lit.[9] mp. 225-7°); $[\alpha]_D^{25}$ +1.6° (*c* 0.255 in DMSO); ν_{max} ($CHCl_3$), 3400 (broad), 1700, 1620 cm^{-1}; λ_{max} (EtOH), 208 (log E 3.7143), 232 (log E 4.0814), 326 (log E 4.3784) nm; *m/e* (relative intensity), 370 (M^+, 31), 208 (2), 206 (5), 164 (100), 149 (13); ^1H NMR (δ in DMSO-d_6), 1.20 (d, J = 8 Hz, 3H, Me), 3.80 (s, 6H, 2 x -OMe), 4.06 (m, 1H, -O-CH-Me), 4.53 (d, J = 8 Hz, 1H, -O-CH-Ar), 6.30 (d, J = 9 Hz, 1H, -CO-CH=), 6.86 (broad s, 3H, Ar-H), 7.03 (s, 1H, Ar-H), 7.90 (d, J = 9 Hz, 1H, =CH-), 9.23 (broad s, 1H, -OH, disappeared with D_2O); Analysis; Calcd. for $C_{20}H_{18}O_7$: C, 64.86; H, 4.90. Found: C, 64.62; H, 4.94 %.

PROPACIN METHYLETHER, 16

Methylation of propacin according to the method described above (Me_2SO_4-K_2CO_3-acetone/reflux) followed by purification by PLC (silica gel, methylene chloride as eluent) and crystallization from a mixture of methylene chloride-hexane afforded PROPACIN METHYLETHER (56 %) as colourless plates, mp. 181-2°; ν_{max} (Nujol), 1710 cm^{-1}; *m/e* (relative intensity), 384 (M^+, 29), 178 (100), 164 (2), 163 (22); ^1H NMR (δ in $CDCl_3$), 1.29 (d, J = 8 Hz, 3H, Me), 3.88 (s, 3H, -OMe), 3.90 (s, 6H, 2 x -OMe), 4.23 (m, 1H, -O-CH-

Me), 4.68 (d, J = 8 Hz, 1H, -O-CH-Ar), 6.31 (d, J = 9 Hz, 1H, -CO-CH=), 6.52 (s, 1H, Ar-H), 6.88-6.92 (m, 3H, Ar-H), 7.61 (d, J = 9 Hz, 1H, =CH-); ^{13}C NMR (δ in $CDCl_3$), 17.1 (q), 56.0 (q), 56.1 (q), 56.3 (q), 74.3 (d), 81.3 (d), 100.2 (d), 105.7 (s), 110.7 (d), 111.5 (d), 114.1 (d), 120.6 (d), 128.4 (s), 135.1 (s), 138.2 (s), 140.0 (s), 143.7 (d), 145.9 (s), 149.5 (s), 150.2 (s), 167.7 (s). Analysis; Calcd. for $C_{21}H_{20}O_7$: C, 65.62; H, 5.24. Found: C, 65.41; H, 5.37 %.

PROPACIN ACETATE, 17

Acetylation (Ac_2O-pyridine/room temperature/ 24 hours) of propacin gave, after crystallization from methanol, PROPACIN ACETATE (83 %) as colourless plates, mp. 205-206° (lit.[8] mp. 202-5° from C_6H_6 lit.[9] mp. 200-1° from C_6H_6); ν_{max} (Nujol), 1740, 1730, 1620 cm^{-1}; *m/e* (relative intensity), 412 (M^+, 20), 370 (18), 208 (2), 206, (6), 164 (100); ^{1}H NMR (d in $CDCl_3$, 400 MHz), 1.33 (d, J = 6.4 Hz, 3H, Me), 2.32 (s, 3H, -CO-Me), 3.86 (s, 3H, -OMe), 3.89 (s, 3H, -OMe), 4.22 (dq, J = 7.8, 6.4 Hz, 1 H, -O-CH-Me), 4.72 (d, J = 7.8 Hz, 1H, -O-CH-Ar), 6.31 (d, J = 9.6 Hz, 1H, -CO-CH=), 6.52 (s, 1H, Ar-H), 6.95 (d, J = 2 Hz, 1H, Ar-H), 6.97 (dd, J = 2, 8.6 Hz, 1H, Ar-H), 7.08 (d, J = 8.6 Hz, 1H, Ar-H), 7.61 (d, J = 9.6 Hz, 1H, =CH-); ^{13}C NMR (δ in $CDCl_3$), 16.2 (q), 19.7 (q), 55.3 (q), 55.6 (q), 73.4 (d), 80.2 (d), 99.6 (d), 110.8 (s), 111.0 (d), 113.3 (d), 119.4 (d), 122.4 (d), 128.1 (s), 130.7 (s), 133.9 (s), 139.6 (s), 135.8 (s), 142.8 (d), 145.1 (s), 150.8 (s), 159.8 (s), 167.7 (s). Analysis; Calcd. for $C_{22}H_{20}O_8$: C, 64.08; H, 4.89. Found: C, 64.16; H, 5.07 %.

JATROPHIN, 18

Colourless plates, mp. 242° (from methylene chloride-hexane) (lit.[2] mp. 245-8° from EtOAc-petrol, lit.[10] mp. 242-4°); ν_{max} ($CHCl_3$), 3400, 1705, 1620 cm-1; λ_{max} (EtOH), 208 (log E 3.5225), 235 (log E 3.9920), 326 (log E 4.2870) nm; *m/e* (relative intensity), 370 (M^+, 40), 208 (4), 206 (2), 164 (100), 149 (15); ^{1}H NMR (δ in DMSO-d_6), 1.20 (d, J = 7.5 Hz, 3H, Me), 3.78 (s, 6H, 2 x -OMe), 4.25 (m, 1H, -O-CH-Me), 4.70 (d, J = 7.5 Hz, 1H, -O-CH-Ar), 6.27 (d, J = 9 Hz, 1H, -CO-CH=), 6.81(s, 1H, Ar-H), 6.90 (broad s, 3H, Ar-H), 7.90 (d, J = 9 Hz, 1H, =CH-), 9.10 (broad s, 1H, -OH, disappeared with D_2O); Analysis; Calcd. for $C_{20}H_{18}O_7$: C, 64.86; H, 4.90. Found: C, 64.93; H, 4.77 %.

JATROPHIN ACETATE, 19

Acetylation (Ac_2O-pyridine/room temperature/ 24 hours) of jatrophin gave, after crystallization from methanol, JATROPHIN ACETATE (86 %) as colourless plates, mp. 186° (lit.[2] mp. 185-6° from MeOH); ν_{max} (Nujol), 1720, 1610 cm^{-1}; *m/e* (relative intensity), 412 (M^+, 26), 370 (16), 208 (5), 206 (10), 164 (100); ^{1}H NMR (δ in $CDCl_3$), 1.28 (d, J = 6.8 Hz, 3H, Me), 2.30 (s, 3H, -CO-Me), 3.86 (s, 6H, 2 x -OMe), 4.21 (dq, J = 7.5, 6.8 Hz, 1H, -O-CH-Me), 4.70 (d, J = 7.5 Hz, 1H, -O-CH-Ar), 6.20 (d, J = 9 Hz, 1H, -CO-CH=), 6.45 (s, 1H, Ar-H), 6.92 (broad s, 3H, Ar-H), 7.51 (d, J = 9 Hz, 1H, =CH). Analysis; Calcd. for $C_{22}H_{20}O_8$: C, 64.08; H, 4.89. Found: C, 64.11, H, 4.97 %.

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11. The structure drawings do not imply their absolute stereochemistries.

บทคัดย่อ

การศึกษาเพิ่มเติมเกี่ยวกับส่วนประกอบทางเคมีของรากสบู่ดำ (*Jatropha curcas*) แยกได้ (+)-Jatrophol, **9**, (+)-marmesin, **13**, propacin, **15**, และ jatrophin, **18** จากส่วนที่สกัดด้วยตัวทำละลายโพล่าร์ สูตรโครงสร้างรวมทั้งสเตอริโอเคมิสตรี้ของสารที่แยกได้นี้หาได้โดยกรรมวิธีทางสเปคโตรสโคปี รวมไปถึงการเปรียบเทียบกับสารมาตรฐานในบางกรณี