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ACIDIC COMPOUNDS IN PATCHOULI OIL

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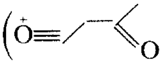
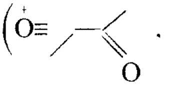
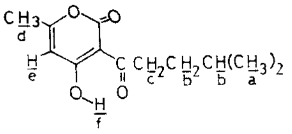
Key Word Index—*Pogostemon cablin*; Labiatae, patchouli oil, 3 - (4 - Methylpentanoyl -)3,4 - dihydro - 6 - methyl - 1,2 - pyran - 2,4 - dione, 3 - (2 - Methylbutyryl -)3,4 - dihydro - 6 - methyl - 1,2 - pyran - 2,4 - dione

Indonesian patchouli oil obtained from *Pogostemon cablin* Benth. by steam distillation gave a yellowish oil on treatment with 1N Na_2CO_3. The yellowish oil was separated by means of column chromatography and the 5% Et_2O-*n*-hexane fraction was examined. The gas chromatogram of this fraction has 2 main peaks at RT 12·4 min. (peak 1) and 7·6 min. (peak 2), the proportions of peak area being 85 and 12% respectively. Recrystallization with absolute ethanol gave needles of **1** (mp 34·5–35·5°), with the same retention time as peak 1. Semicarbazone mp 184·8–185·3° (dec.). On boiling with aq 0·5N NaOH, **1** yielded isoamylmethyl ketone as the main neutral product. IR spectrum of **1**; 3110, 1743, 1723, 1643, 1609, 1565, and 998 cm^{-1}. MS; *m/e* 224 (M^+, 4%), 209 (M^+–Me, 3%), 181(M^+-C_3H_7, 40%), 168(M^+-56, 100%), 153(M^+-71, 81%), 85(, 28%), and 43($\overset{+}{C}_3H_7$, 44%). Elemental analysis of **1** Found; C 64 16%, H 7·25%, N 0·0%, calc. for $C_{12}H_{16}O_4$; C 64·28%, H 7·20%, O 28·54%. NMR ($\delta_{ppm}^{CCl_4}$); (a) 0·96 (*d*, 6H), (b) 1·55 (*m*, 3H), (c) 2·95 (*t*, 2H), (d) 2·23 (*s*, 3H), (e) 5·80 (*s*, 1H), and (f) 16·87 (*s*, 1H). From the above data structure **1** was deduced for this substance. The compound of peak(2) was isolated in the pure state by means of preparative GLC. IR of **2**; 3110, 1743, 1724, 1642, 1608, 1548, 1462, and 998 cm^{-1}. MS; *m/e* 210(M^+, 58%), 168(M^+-56, 15%), 153(M^+–C_4H_9, 100%), 126(M^+–$\overset{+}{O}\equiv C\cdot C_4H_9$, 26%), 85(. 34%), 43($\overset{+}{C}_3H_7$, 29%), and 29($\overset{+}{C}_2H_5$, 10%). NMR ($\delta_{ppm}^{CCl_4}$); (a) 0·93 (*t*, 3H), (b) 1·12 (*d*, 3H), (c) 1·6 (*m*, 2H), (d) 2·25 (*s*, 3H), (e) 3·77 (*m*, 1H), (f) 5·81 (*s*, 1H), and (g) 17·18 (*s*, 1H). The structure assumed for peak(2) from these data is **2**. These two compounds were synthesized by the condensation of corresponding acid chloride with triacetic acid lactone in the presence of H_2SO_4[1]. IR, MS, and NMR of the synthetic specimens were completely in agreement with those of the natural compounds. The formal names for **1** and **2** are 3 - (4 - methylpentanoyl -)3,4 - dihydro - 6 - methyl - 1,2 - pyran - 2,4 - dione and 3 - (2 - methylbutyryl -)3,4 - dihydro - 6 - methyl - 1,2 - pyran - 2,4 - dione respectively. That these structures are in tautomerism with the corresponding enol form, 3 - (4 - methylpentanoyl -)4 - hydroxyl - 6 - methyl - α - pyrone and 3 - (2 - methylbutyryl -)4 - hydroxy - 6 - methyl - α - pyrone is indicated by the NMR spectra.



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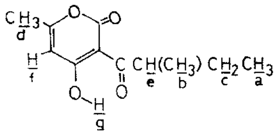

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The presence of two compounds in the original oil was confirmed by the direct GLC of the oil.

EXPERIMENTAL

Analytical methods For column chromatography Kieselgel-G was used with *n*-hexane, 5%-Et_2O–*n*-hexane, 10%-Et_2O–*n*-hexane, 50%-Et_2O–*n*-hexane and Et_2O as eluting solvents. For analytical and preparative GLC, Shimadzu GC-4AP was used with OV-1 as the stationary phase at 180°. NMR spectra were obtained using TMS as the internal standard. IR spectra were obtained in liquid film.

Triacetic acid lactone. A soln of dehydroacetic acid (20 g) in 90% H_2SO_4 (100 g) was heated in an oil bath at 140° for 1 min, the reaction mixture was poured on crushed ice immediately Resulting crystals were filtered and recrystallized from diluted ethanol. MP 187° Yield 6·9 g.

4-*Methylpentanoyl chloride.* 4-Methylpentanoic acid (23·2 g) was added dropwise into $SOCl_2$ (28·6 g) under refluxing during the course of 30 min and the reaction mixture was refluxed for 1 hr. It was distilled directly and the fraction of bp 119–131° was collected. Yield 17·4 g.

2-*Methylbutyryl chloride.* DL-2-Methylbutyric acid (16·7 g) was treated by the same way as above bp 106–119°C. Yield 14·8 g

3 - (4 - *Methylpentanoyl* -)3,4 - *dihydro* - 6 - *methyl* - 1,2 - *pyran* - 2,4 - *dione.* Triacetic acid lactone (3·1 g) was added to 4-methylpentanoyl chloride (9 7 g) previously mixed with 0·5 ml of H_2SO_4 and cooled with ice H_2O below 10°. The mixture was gradually heated and kept at 85–90° for 30 min. After generation of HCl gas ceased the reaction mixture was poured onto crushed ice The resulting oil was extracted with *n*-hexane, washed with H_2O, dried and evaporated. The oil obtained was purified by means of column chromatography using Kieselgel-G and then alumina. Yield 0·65 g

3 - (2 - *Methylbutyryl* -)3,4 - *dihydro* - 6 - *methyl* - 1,2 - *pyran* - 2,4 - *dione* DL 2-Methylbutyryl chloride was treated in the same way as above. Yield 0·2 g.

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A NEW DITERPENOID ACETATE FROM *SIDERITIS REVERCHONII*[*]

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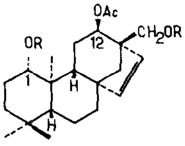
Key Word Index—*Sideritis reverchonii*; Labiatae; *ent* - 15 - beyerene, *ent* - 16*S* - atis - 13 - ene and *ent* - 8,5 - *friedo*pimar - 5 - ene derivatives.

Plant. Sideritis reverchonii Wk. *Source.* Reduced areas in the S. of the Iberian Peninsula (Cerro de San Antón, near Málaga). *Previous work.* None. *Present work.* From the aerial parts of the species quoted above have been isolated eight diterpenoids previously described: *ent* - 8, 5 - *friedo*pimar - 5 - ene - 15*S*,16 - diol (lagascol) [1], *ent* - 8,5 - *friedo*pimar - 5 - ene - 11β,15*S*,16 - triol (lagascatriol)[2], *ent* - 15 - beyerene - 12α,17 - diol (tobarrol)[1], *ent* - 15 - beyerene - 7α,17 - diol (benuol)[1], *ent* - 15 - beyerene - 1β,12α,17 - triol (jativatriol)[3], *ent* - 15 - beyerene - 7α,12α,17 - triol (conchitriol)[3], *ent* - 16*R* - atis - 13 - ene - 16,17 - diol (serradiol)[1] and *ent* - 16*R* - atis - 13 - ene - 1β,16,17 - triol (sideritol)[4], plus a new compound **1** ($C_{22}H_{34}O_4$), which when subjected to the action of Ac_2O in pyridine solution affords **2**, identical (physical and spectroscopic data) with the triacetate of jativatriol. The NMR spectrum of **1** shows a narrow multiplet at δ 5·18 assigned to the equatorial proton geminal to the C-12 acetoxyl function[3].



1 R = H
2 R = Ac

The new diterpenoid (**1**) is thus 12-acetyl jativatriol (*ent* - 12α - acetoxy - 15 - beyerene - 1β,17 - diol).

EXPERIMENTAL

For general details on extraction and separation of diterpenes from *Sideritis*, see part 17[1] of this series; for most experimental details, see part 13[3]. The previously described compounds have been characterized by their physical and spectrospcopic (IR and NMR) data and by

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[*] Part 26 in the series' Studies on diterpenes from *Sideritis* genus'. For part 25 see von Carstenn-Lichterfelde, C , Rodríguez, B and Valverde, S. (1975) *Experientia* **31**, 757.