Tetrahedron, 1963, Vol. 19, pp. 2051 to 2059. Pergamon Press Ltd. Printed in Northern Ireland

THE STRUCTURES OF FIVE CYCLIC DIKETONES ISOLATED FROM COFFEE

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(*Received* 13 *December* 1962)

Abstract—Five cyclic diketones isolated from coffee oil (four of them isomeric) have been proved to be: (a) 3-methylcyclopentane-1,2-dione; (b) 3,4-dimethylcyclopentane-1,2-dione; (c) 3,5-dimethylcyclopentane-1,2-dione; (d) 3-ethylcyclopentane-1,2-dione; (e) 3-methylcyclohexane-1,2-dione. The structures of these compounds, postulated exclusively on the basis of spectroscopic data (U.V. I.R. and mass spectrometry), were confirmed by synthesis.

THE study of the aroma complex of roasted coffee, which has attracted the attention of chemists for many years,[2] presents some difficulty because the aroma complex is chemically unstable, the concentration of volatiles in roasted coffee is extremely low and, furthermore, only seventeen compounds make up 80% and only thirty compounds make up 90% of the aroma complex, while approximately seventy more compounds constitute the remaining 10% of the mixture.[3]

While the difficulties due to the instability of the flavor complex can be circumvented by employing suitable methods of isolation and separation, the problems encountered in the structural elucidation of compounds which represent only 0·01% or less of the aroma complex can generally be solved only by the use of spectroscopic methods.

It is the purpose of this paper to describe the elucidation of the structures of five chemically related compounds which we have isolated from roasted coffee; this may prove to be of interest to other workers in the flavor field, since it illustrates a general method of attack of flavor problems and emphasizes the importance of the spectroscopic techniques. The structures of these five compounds, three of which had not been previously reported in the literature, were in fact elucidated on quantities of pure materials lower than one milligram; in this range, no degradation work is feasible and structures postulated on the basis of spectroscopic evidence can only be proven by synthesis.

The origin of the samples. (A). The aroma complex was obtained in 0·025% yield (based on the weight of roasted coffee) by stripping the volatile fraction, at room temperature and at a pressure of 0·1–0·2 microns, from the mixture of glycerides secured by extrusion-pressing of whole, roasted coffee beans of a commercial blend. (B). The five compounds of interest (Compounds A–E) were obtained in a pure state, from the aroma complex, by repeated vapor phase chromatography; their retention

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[1] To whom inquiries concerning this paper should be addressed.

[2] For pertinent publications, see: A. Zlatkis and M. Sivetz, *Food Research* **25**, 395 (1960); *J. W. Rhoades, Ibid.* **23**, 254 (1958); T. Reichstein and H. Staudinger, *British Patents* 246.454 and 260.960 and *Perf. and Ess. Oils Record* **46**, 86 (1955); W. R. Johnstone and C. N. Frey, *J. Amer. Chem. Soc.*, **60**, 1624 (1938); S. C. Prescott, R. L. Emerson, R. B. Woodward and A. Heggie, *Food Research* **2**, 165 (1937).

[3] Unpublished data from this Laboratory.

TABLE 1. SOME PHYSICAL PROPERTIES OF COMPOUNDS A–E

Compounds	$R_T{}'^{a}$ (in minutes)	$R_T{}''^{b}$ (in minutes)	λ_{max}^{EtOH}	I.R. Spectrum Fig.
A	37·5	16·3	258	1
B	38·2	16·8	259	2
C	45·3	19·8	259	3
D	58·6	26·9	259	4
E	31·3	20·9	271	5

[a] Ucon polyglycol LB-550-X (Perkin–Elmer Column R). For conditions, see Experimental.
[b] Apiezon J. For conditions, see Experimental.

times on a polar and a non-polar column are indicated in Table 1, together with the pertinent U.V. data[4] (Table 1). The corresponding I.R. spectra are presented in Figs. 1–5.

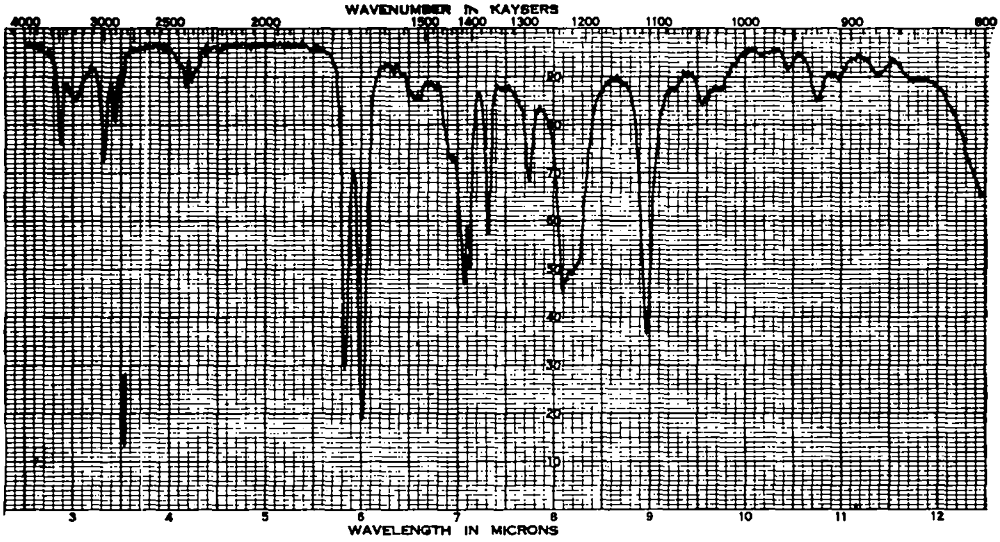

FIG. 1

The structure of compound A. The elucidation of the structure of compound A will be discussed first, since it also provided the key to the structures of compounds B, C and D.

The molecular weight of compound A, determined by mass spectrometry, is 112. Of the various molecular formulas which correspond to such a molecular weight, if one considers only compounds which do not contain any other element but carbon, hydrogen, oxygen and nitrogen,[5] eliminating those formulas which contain less than

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[4] Only wavelengths of maximum absorption could be determined on the natural materials, since the U.V. spectra were measured on samples recovered from the ultramicrocell previously employed for the I.R. determinations.

[5] These formulas are: $C_3H_4N_4O$, $C_4H_4N_2O_2$, $C_4H_8N_4$, $C_5H_4O_3$, $C_5H_8N_2O$, $C_6H_8O_2$, $C_6H_{12}N_2$, $C_7H_{12}O$, C_8H_{16} and C_9H_4 (see Tables in: J. H. Beynon, *Mass Spectrometry and its Applications to Organic Chemistry*, p. 495. Elsevier, New York (1960).

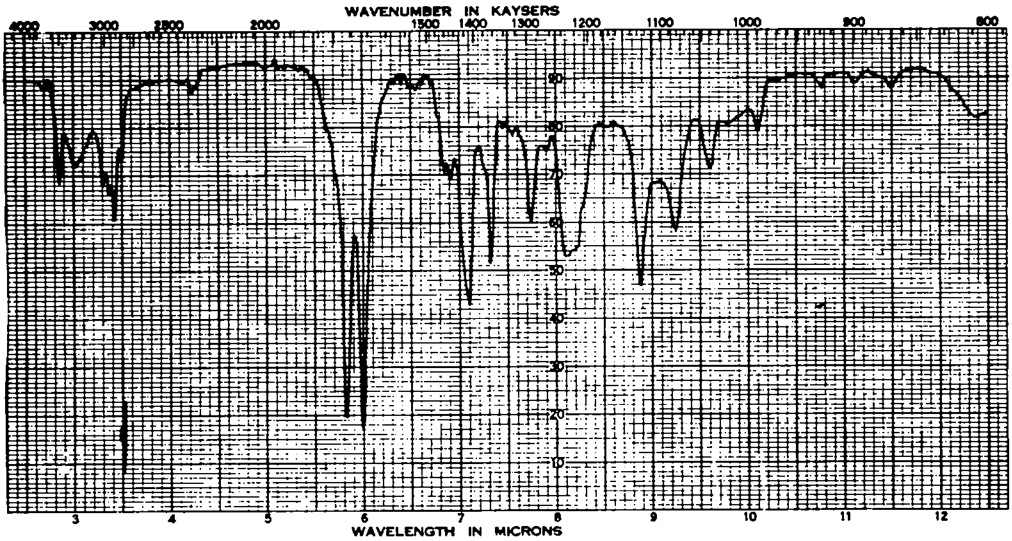


Fig. 2

two oxygen atoms (the I.R. spectrum of compound A suggested the presence of a carbonyl and an hydroxyl group) and taking into account the isotope abundances, we decided to tentatively accept $C_6H_8O_2$ as the molecular formula of compound A.

To a formula $C_6H_8O_2$ must correspond three points of unsaturation which, in view of the presence of one carbonyl and one hydroxyl group in the molecule, could be accommodated by: (a) one $>C{=}O$, one $>C{=}C<$, one ring; (b) one $>C{=}O$,

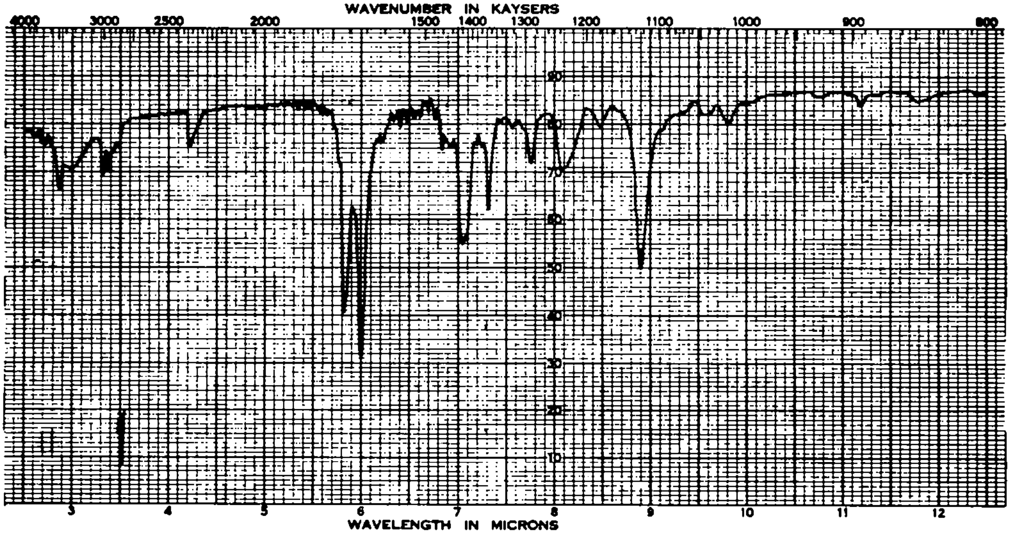


Fig. 3

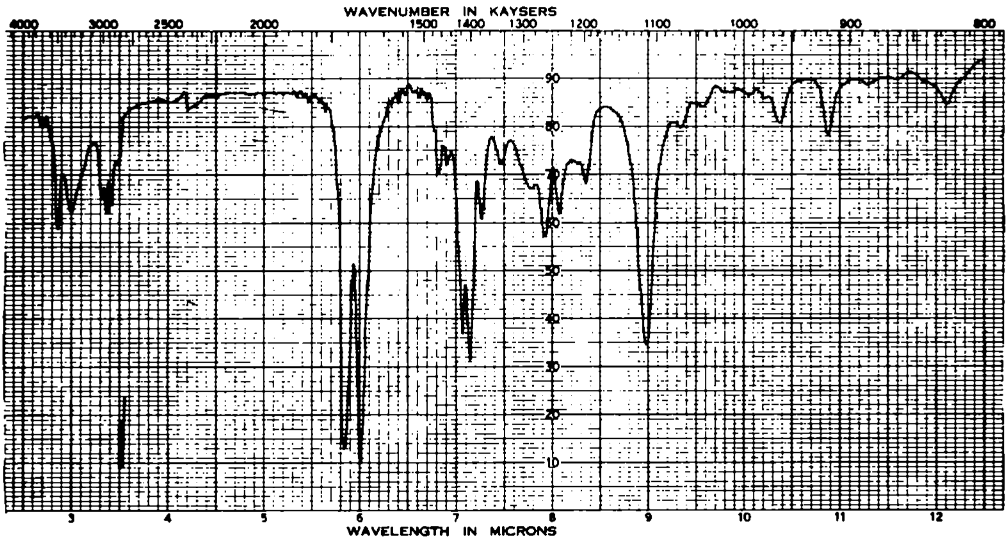


FIG. 4

two $>C{=}C<$; (c) one $>C{=}O$, two rings; (d) one $>C{=}O$, one $-C{\equiv}C-$. Types (c) and (d), however, could be eliminated solely on the basis of the U.V. data ($\lambda_{\max}^{\mathrm{EtOH}}$ of compound A = 258 mμ). Thus, only types (a) and (b) remained to be considered.

Of the various structures which could correspond to a compound of molecular formula $C_6H_8O_2$ and containing one carbonyl, one carbon–carbon double bond and

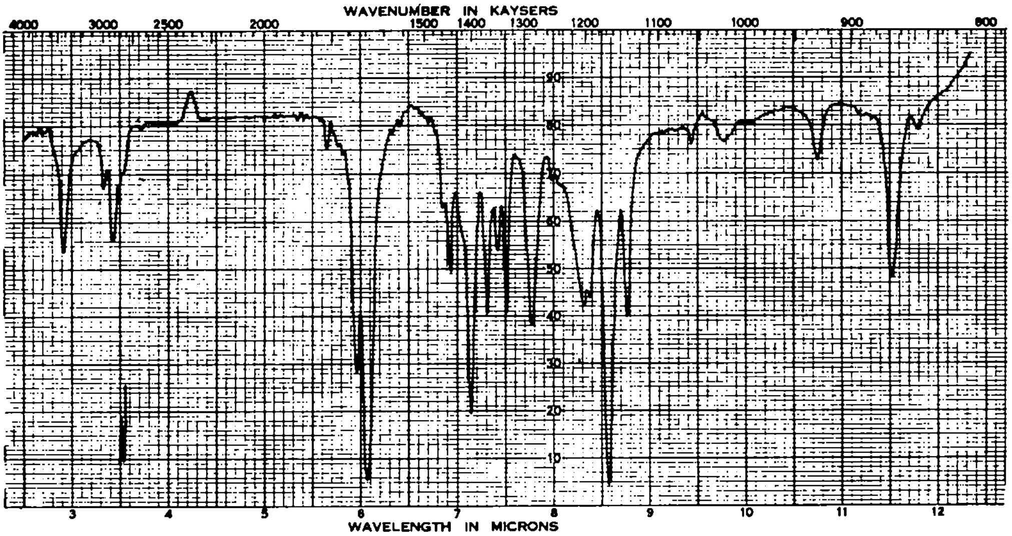


FIG. 5

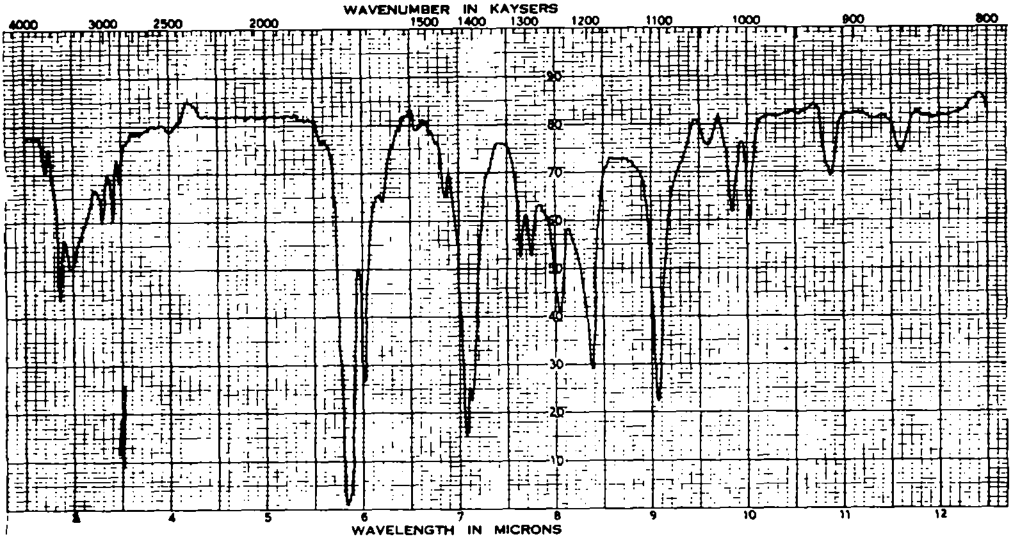


FIG. 6

one ring (type (a), above), we considered as likely possibilities the following cyclic diketones (I–IV), which are either known to be or can be expected to be strongly enolized. In fact, microtests with ferric chloride and with indicators (and the bathochromic shifts observed when the ethanolic solutions on which the U.V. spectra were determined were made alkaline) confirmed the hypothesis that compound A and the related compounds B, C and D are enols of considerable acidity.

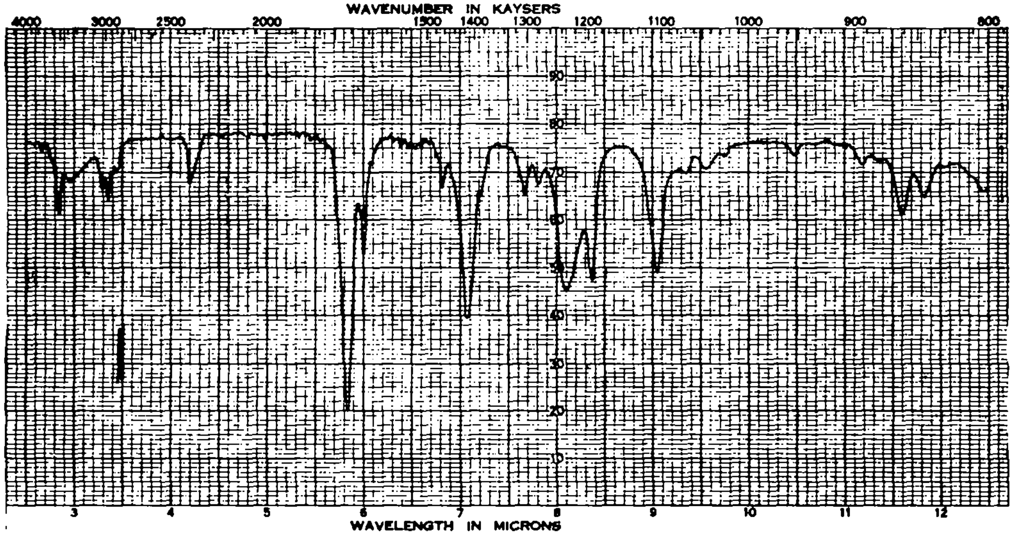
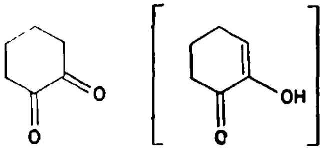
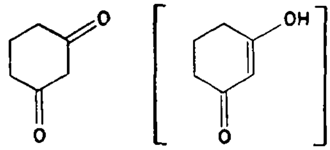


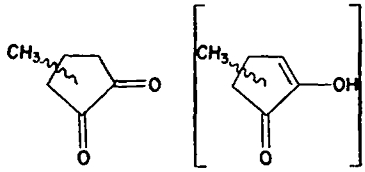
FIG. 7



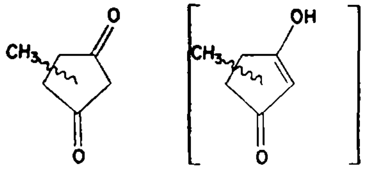
I



II



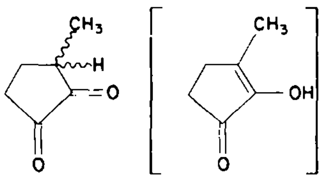
III



IV

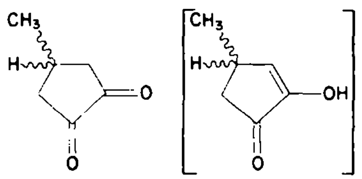
Structures of the types I, II and IV, as well as other 5-membered cyclic structures with an exocyclic carbonyl, which by necessity would have to be formylic, could be rejected on spectroscopic grounds (position of maximal absorption in the U.V. or position, shape and intensity of the I.R. bands corresponding to stretching vibrations of the hydroxyl and carbonyl groups and of the carbon–carbon double bond of the enolic forms, lack of the typical I.R. bands due to stretching of the C–H bond of the formyl group, etc.).

These considerations left the choice of structures V and VI, corresponding to structure III above, for compound A, provided that it actually contained one >C=O, one —OH, one ring and one >C=C< (type (a) above).



V

3-Methylcyclopentane-1,2-dione or
3-Methylcyclopent-2-en-2-ol-1-one
(Identical with compound A)



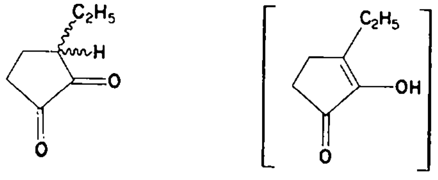
VI

4-Methylcyclopentane-1,2-dione or
4-Methylcyclopent-2-en-2-ol-1-one

Consequently, both compounds V and VI were obtained. A comparison (I.R. and U.V. spectra and R_T's on a polar and a non-polar column) of the natural and synthetic materials proved that compound A has the structure V.

The structures of compounds B, C *and* D. A comparison of the I.R. and U.V. spectra of compounds A, B, C and D (Figs. 1–4 and Table 1) with each other and with those of synthetic cyclopentane-1,2-dione and 4-methylcyclopentane-1,2-dione (Figs. 6 and 7 and Experimental part) clearly showed that: (a) A, B, C and D must be structurally very similar; (b) B, C and D must have one, and only one, alkyl substituent in position 3, since the wavelength of maximum absorption in the U.V. lies close to 258 mμ for A, B, C and D, but at 251 and 252 mμ, respectively, for cyclopentane-1,2-dione and for 4-methylcyclopentane-1,2-dione.

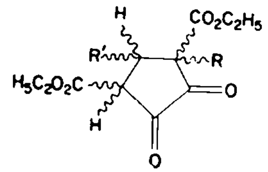
With this information at hand, we synthesized 3-ethylcyclopentane-1,2-dione (3-ethylcyclopent-2-en-2-ol-1-one, VII), a compound not previously reported in the chemical literature and which proved to be identical (I.R., U.V., R_T's on a polar and non-polar column) with compound D.



VII

3-Ethylcyclopentane-1,2-dione or
3-Ethylcyclopent-2-en-2-ol-1-one
(Identical with compound D)

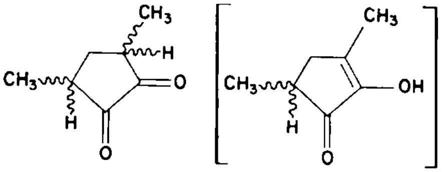
The synthesis of compound VII was accomplished by alkylation of 3,5-dicarbethoxycyclopentane-1,2-dione (VIIIa) followed by hydrolysis and decarboxylation of the resulting 3,5-dicarbethoxy-3-ethylcyclopentane-1,2-dione (VIIIb).



VIII

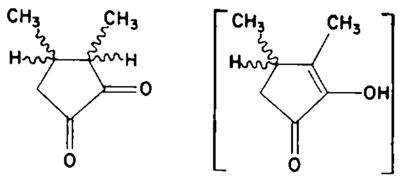
(a) $R = R' = H$
(b) $R = C_2H_5$; $R' = H$
(c) $R = H$; $R' = CH_3$
(d) $R = R' = CH_3$

The structures of compound A and D having thus been established, it could be deduced, on the basis of the R_T's on a non-polar column (Table 1), that B and C could likely be isomers of compound D ($C_7H_{10}O_2$), a supposition which was proven to be correct by determinations of molecular weights by mass spectrometry (m.w. 126). Therefore, we concluded that B and C should be 3,4- and 3,5-dimethylcyclopentane-1,-2-dione.[6] These compounds, not previously reported in the chemical literature, were synthesized: the synthetic 3,5-dimethylcyclopentane-1,2-dione (IX) proved to be identical with compound B and the synthetic 3,4-dimethylcyclopentane-1,2-dione (X) was identical with compound C (I.R., U.V., R_T's on a polar and a non-polar column).



IX

3,5-Dimethylcyclopentane-1,2-dione or
3,5-Dimethylcyclopent-2-en-2-ol-1-one
(Identical with compound B)



X

3,4-Dimethylcyclopentane-1,2-dione or
3,4-Dimethylcyclopent-2-en-2-ol-1-one
(Identical with compound C)

3,4-Dimethylcyclopentane-1,2-dione (X) was synthesized by alkylation of 3,5-dicarbethoxy-4-methylcyclopentane-1,2-dione (VIIIc) followed by hydrolysis and decarboxylation of the resulting 3,5-dicarbethoxy-3,4-dimethylcyclopentane-1,2-dione

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[6] The possibility of B and/or C having two methyl groups on the same carbon atom (3,3- or 4,4-dimethylcyclopentane-1,2-dione) was rejected on spectroscopic grounds, since both the 3,3- and the 4,4-dimethyl-compounds would be expected to absorb in the U.V. at the same wavelength as cyclopentane-1,2-dione or 4-methylcyclopentane-1,2-dione (251–252 mμ).

(VIIId). The synthesis of 3,5-dimethylcyclopentane-1,2-dione (IX) was, instead, accomplished by direct alkylation of the methyl ether of the commercially available 3-methylcyclopent-2-en-2-ol-1-one, followed by cleavage of the ether function.

The structure of compound E. Compound E, the fifth cyclic diketone isolated from coffee in the course of our investigation, proved to be (mass spectrometry) an isomer of Compounds B, C and D ($C_7H_{10}O_2$). A comparison of its I.R. and U.V. spectra with those of A, B, C and D and of the commercially available cyclohexane-1,2-dione suggested that compound E could be a methylcyclohexane-1,2-dione. Furthermore, a comparison of the λ_{max}^{EtoH} (U.V.) of cyclohexane-1,2-dione (265 mμ) and of compound E (271 mμ) strongly suggested that the methyl group in the latter should occupy position 3. These suppositions were proven to be correct by a comparison of Compound E (I.R., U.V., R_T's on a polar and non-polar column) and synthetic 3-methylcyclohexane-1,2-dione (XI).

XI

3-Methylcyclohexane-1,2-dione or
3-Methylcyclohex-2-en-2-ol-1-one
(Identical with compound E)

EXPERIMENTAL

All vapor phase chromatography was carried out in 6′ × 0·25″ stainless steel columns packed with: (a) R_T' Ucon polyglycol LB-550-X (Perkin–Elmer column R) at 150° with a flow rate of 100 ml helium per min; (b) R_T'' 20% of Apiezon J on 40–80 mesh Firebrick at 125° with a flow rate of 130 ml helium per min. Retention times are expressed in min.

The physical properties of the synthetic samples were determined on materials purified by preparative gas chromatography; their purity was checked by analytical chromatography.

The I.R. spectra were determined in $CHCl_3$ solutions on a Beckman I.R. 4 spectrophotometer, employing a beam condenser and an ultra-micro cell (path length: 0·115 mm). Slit program: 0·55 mm at 10 μ; gain: 3%; period: 2; scanning speed: 1 μ/min.

M.p's., uncorrected, were determined on a Kofler melting point apparatus. B.p.'s are also uncorrected.

Materials

Cyclopentane-1,2-*dione* was prepared by the method of Hesse[7] and purified by V.P.C.; m.p. 50–52° (Lit.[7] 56°); λ_{max}^{EtOH} 251 mμ; log ε = 3·94; R_T': 25·2; R_T'': 8·5.

4-*Methylcyclopentane*-1,2-*dione* was prepared by the method of Hesse[8] and purified by V.P.C.; m.p. 60–62°. (In the Lit.,[8] it is reported that this compound boils at 96–97°/17 mm and solidifies on cooling.); λ_{max}^{EtOH} 252 mμ; log ε = 3·90; R_T': 27·8; R_T'': 9·7.

3-*Methylcyclopentane*-1,2-*dione*. The sample employed, of commercial origin,[9] was found to be pure by V.P.C.; m.p. 102–104° (Lit.[8] 106°); λ_{max}^{EtOH} 258 mμ; log ε = 4·05; R_T': 37·5; R_T'': 16·3.

3-*Methylcyclohexane*-1,2-*dione* was prepared by the method of Wallach[10] and purified by V.P.C.; m.p. 60–62° (Lit.[10] 62–63°); λ_{max}^{EtOH} 271 mμ; log ε = 3·99; R_T': 31·3; R_T'': 20·9.

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[7] G. Hesse and E. Bücking, *Liebigs Ann.* **563**, 31 (1949).

[8] G. Hesse and K. Böckmann, *Liebigs Ann.* **563**, 37 (1949).

[9] K & K Laboratories, Inc., Jamaica, N.Y., New York.

[10] Wallach, *Liebigs Ann.* **414**, 314 (1916–17) ; **437**, 180 (1924).

The synthesis of 3,4-dimethylcyclopentane-1,2-dione, 3,5-dimethylcyclopentane-1,2-dione and 3-ethylcyclopentane-1,2-dione will be described in detail in a forthcoming publication, together with a discussion of the I.R. and mass spectra of all the cyclopentane-1,2-diones and cyclohexane-1,2-diones prepared in the course of this work. However, the pertinent physical properties for these compounds are as follows:

3,4-*Dimethylcyclopentane*-1,2-*dione*. m.p. 71–72°: $\lambda_{\max}^{\mathrm{EtOH}}$ 259 mμ; $\log \varepsilon = 4{\cdot}06$; $R_T' = 45{\cdot}3$; $R_T'' = 19{\cdot}8$.

3,5-*Dimethylcyclopentane*-1,2-*dione*. m.p. 91–92°; $\lambda_{\max}^{\mathrm{EtOH}}$ 259 mμ; $\log \varepsilon = 4{\cdot}07$; $R_T' = 38{\cdot}2$; $R_T'' = 16{\cdot}8$.

3-*Ethylcyclopentane*-1,2-*dione*. b.p. 65–68/1 mm (solidifies on cooling to C.A. 20°); $\lambda_{\max}^{\mathrm{EtOH}}$ 259 mμ; $\log \varepsilon = 4{\cdot}04$; $R_T' = 58{\cdot}6$; $R_T'' = 26{\cdot}9$.

Acknowledgements—We wish to extend our thanks to Mr. Paul Friedel of this Laboratory for the synthetic work and to Dr. S. K. Freeman and Mr. H. A. Bandarovich of International Flavors and Fragrances, Union Beach Research Laboratory, Union Beach, N.J., for the mass spectra.