Tetrahedron, 1964, Vol. 20, pp. 2951 to 2961. Pergamon Press Ltd. Printed in Northern Ireland

THE VOLATILE CONSTITUENTS OF COFFEE—IV[1]

FURANIC AND PYRROLIC COMPOUNDS

M. A. GIANTURCO,[2] A. S. GIAMMARINO, P. FRIEDEL and
V. FLANAGAN

The Fundamental Research Department of the Coca-Cola Company,
Linden, New Jersey, U.S.A.

(*Received* 10 *July* 1964)

Abstract—The isolation from roasted coffee of twenty-five simple furanic and pyrrolic compounds is reported. All the compounds were identified by spectroscopic methods.

AFTER the pioneering investigation of Reichstein and Staudinger,[3,4] interest in the study of the aromatic constituents of coffee seems to have lain dormant for a number of years. This is certainly not surprising, in view of the prior failure of such eminent chemists to reach a practical solution to the problem.[5]

In recent years, the rapid growth of the soluble-coffee industry and the development of vapor liquid chromatography and of the spectroscopic methods of structural elucidation have favored a revival of interest in this field. Surprisingly, however, the recent investigations have been focused exclusively on the very volatile constituents of the "aroma complex".[6] This choice appears to be somewhat arbitrary, and this approach to have too narrow a base.

With the investigation currently in progress in this laboratory, an attempt is being made to obtain a more complete knowledge of the substances responsible for the aroma of coffee. Figure 1 is a chromatogram of the "aroma complex" presently under investigation. It should be noted that this is a rather simplified representation of the mixture, since hardly any of the peaks of the chromatogram is due to a single component; to the contrary, several of the peaks are themselves due to complex mixtures.[7]

The methods employed for the structural elucidation of a few of the compounds isolated from coffee in this laboratory (in milligram or submilligram amounts) have been illustrated in previous communications, and it is felt that the uncomplicated structures of the majority of these substances do not warrant a detailed description of the work leading to each identification.[1,8,9]

---

[1] Part III of this series, M. A. Gianturco, P. Friedel and A. S. Giammarino, *Tetrahedron* **20**, 1763 (1964).

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

[3] T. Reichstein and H. Staudinger, British Patents 246.454 and 260.960 (1926).

[4] T. Reichstein, *Perfumery and Essential Oils* **46**, 86 (1955).

[5] It may be noted that the early chemical investigations of coffee were probably motivated by the hope, prevalent in war-time Europe, that a satisfactory coffee substitute could be produced from cheap grains.

[6] For a list of pertinent Refs, see: C. Merritt, M. L. Bazinet, J. H. Sullivan and D. H. Robertson, *J. Agr. Food Chem.* **11**, 152 (1963).

[7] Isolation of pure compounds requires chromatography of each of the mixed peaks on one or more different columns. It may be noted that, under the conditions employed, almost all the compounds reported by recent investigators[6] are already eluted at the point indicated, in Fig. 1, by a heavy, vertical line.

[8] M. A. Gianturco, A. S. Giammarino and R. G. Pitcher, *Tetrahedron* **19**, 2051 (1963).

[9] M. A. Gianturco and P. Friedel, *Tetrahedron* **19**, 2039 (1963).

A more concise and orderly presentation of the results will be achieved, instead, by grouping the compounds identified on the basis of some common structural feature and by giving sufficient physical data—for instance, retention times on both a polar and a non-polar column—to enable other investigators to repeat the isolation. Pertinent spectral properties will also be listed. In the case of compounds whose synthesis has not been previously reported, or for which only low-yield synthetic procedures are available, the synthesis adopted in this laboratory will be described.

The present communication, for instance, will deal only with the furanic and pyrrolic compounds so far isolated from the "aroma complex".[10]

Furanic compounds. The aroma and taste of coffee are developed by roasting the green coffee bean, a process that may be considered as a low-temperature pyrolysis. Since sucrose is one of the more drastically degraded constituents of the bean during roasting, it is not surprising that furanic compounds are very numerous in the "aroma complex".[11]

Once obtained in a pure state by repeated vapor liquid chromatography, the furanic compounds could be easily recognized, because their IR spectra show a "pattern", or a group of bands, which is characteristic of the ring and of the substitution type.[12] In this manner, and sometimes with the help of mass spectrometry, the following furanic compounds could be recognized in the "aroma complex": furan, 2-methylfuran, 2,5-dimethylfuran, furfuryl alcohol, furfuryl formate, furfuryl acetate, furfural, 2-acetylfuran, 5-methylfurfural, 5-methyl-2-acetylfuran and N-furfuryl-2-pyrrole.[13] The presence of 2-propylfuran and 2-butylfuran, recently reported from another laboratory, could not be confirmed.[14]

The elucidation of the structures of five other simple, but less common, furanic substances isolated from the "aroma complex"—compounds A–E—is briefly discussed below. Some pertinent physical properties of these compounds are listed in Table 1.

The structure of compound A. A comparison of the IR spectrum of compound A (Fig. 2) with those of 2-acetylfuran (Fig. 3) and of several other furanic compounds revealed the pattern typical of furanic derivatives having an electron-attracting group in the α-position. In agreement with this, the base peak of the mass spectrum of compound A was found to occur—as in the spectrum of the previously isolated

[10] The isolation of the "aroma complex" is described in the Ref. of footnote 8.

[11] The cyclic diketones recently identified in coffee,[8,9] as well as the previously identified maltol[8] (2-methyl-3-hydroxy-γ-pyrone), are also clearly of carbohydratic origin. As expected, these have been found to be accompanied by a large number of compounds of pyrrolic, thiophenic and pyrazinic nature, probably resulting from concomitant thermal decomposition of carbohydrates and proteins. Also present in the "aroma complex" are a few phenolic and pyridinic substances, obviously derived from chlorogenic acid and trigonelline (which are important constituents of the coffee bean), and a large number of simple hydrocarbons, alcohols, mercaptans, sulfides, aldehydes, ketones, hydroxyketones, diketones, acids, esters, lactones and even relatively unreactive anhydrides of low mol. wt.

[12] For the IR characteristics of 2-substituted furanic compounds, see: A. R. Katritzky and J. K. Lagowsky, *J. Chem. Soc.* 657 (1959). For the use of patterns as an aid in the interpretation of the IR spectra of simple substances, see: M. A. Gianturco, *Interpretation of Infrared Spectra* in *Interpretive Spectrometry* (Edited by S. K. Frieman) Reinhold, New York, in press.

[13] For a synthesis of this last compound, more convenient than the one described by Reichstein and previously adopted in this laboratory,[1] see Experimental.

[14] In the original communication (Ref of footnote 6), the compounds were actually reported simply as propyl- and butylfuran. However, the senior author has kindly indicated to us that it was intended to report the tentative identification of the 2-substituted compounds.

FIG. I

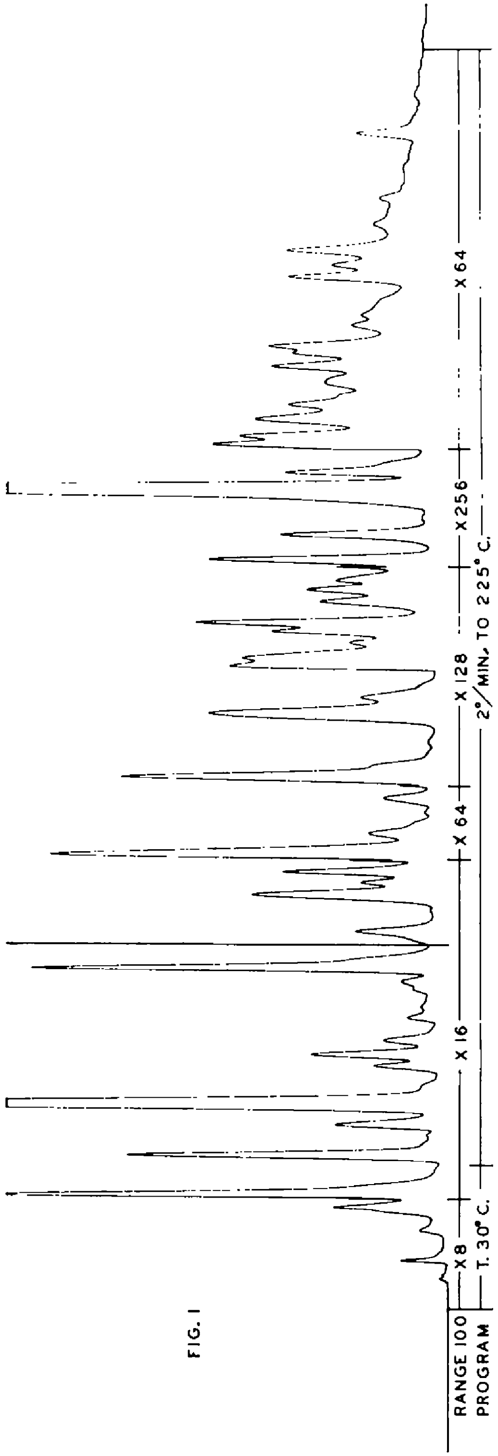


Fig. 1. Chromatogram of "Aroma Complex" of Coffee (for conditions, see Experimental)

TABLE 1. SOME PHYSICAL PROPERTIES OF COMPOUNDS A–E AND RELATED SUBSTANCES

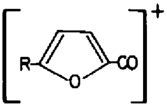
	Mass Spectrometry					
Compound	Base peak	Mol wt	$\lambda_{CO}^{CHCl_3}$ (μ)	$\lambda_{max}^{EtOH\,a}$ (mμ)	R_T[b] (min)	Color
A	95	138	5·80 + 5·98	280	25·8	yellow
B	95	152	5·79 + 6·00	284	49·1	yellow
2-Acetylfuran	95	110	– 5·93	268	9·7	none
C	109	152	5·82 + 6·02	296	53·6	yellow
5-Methyl-2-acetylfuran	109	124	– 5·97	282	21·0	none
D	81	128	– –	–	17·4	none
E	91	148	– –	–	29·5	none

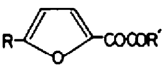
[a] The paucity of the material available did not permit the determination of the extinction coefficients of λ_{max}^{EtOH} of compounds A–E.

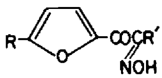
[b] Silicone rubber column at 100°. For conditions, see Experimental.

2-acetylfuran—at m/e = 95. This peak corresponds to ion Ia, or its equivalent, and is common to the mass spectra of many furoyl compounds.[15]

The mol. wt. (138, mass spectrometry), the presence of intense bands at 5·80 and 5·98 microns in the IR spectrum, the value of λ_{max}^{EtOH} and the vividly yellow color of the material led to the conclusion that compound A should have structure IIa. This was confirmed by synthesis.


I


II


III

a: R = H
b: R = CH_3

a: R = H; R′ = CH_3
b: R = H; R′ = C_2H_5
c: R = R′ = CH_3

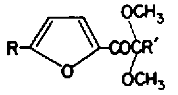
1-(2′-Furyl)-propane-1,2-dione (IIa) has been previously obtained by selenium dioxide oxidation of 1-(2′-furyl)-propan-2-one (17% yield) or of 1-(2′-furyl)- propan-1-one (4% yield).[16] In this laboratory, the compound was prepared in 60% overall yield by acid catalyzed hydrolysis (or by transoximation) of 1-(2′-furyl)-2-oximino-propan-1-one (IIIa), which in turn was obtained by nitrosation of 1-(2′-furyl)-propan-1-one. It may be noted that the nitrosation reaction (butyl nitrite in MeOH-HCl) yielded, as a major by-product (VPC), a substance to which is assigned, on the basis of analytical and spectral data, structure IVa. The data include the elemental analysis ($C_9H_{12}O_4$), the IR spectrum ($\lambda_{C=O}^{CHCl_3}$ at 5·91 μ, strong ketal absorption between 9·0 and 9·7 μ), the UV spectrum (λ_{max}^{EtOH} 277 mμ) and the mass spectrum. The latter showed the presence of intense peaks at m/e = 89 and m/e = 95 (fragmentation between the carbonyl and the aliphatic carbon conjuncted to it), in addition to diagnostically important peaks at m/e = 153 (elimination of —OCH_3) and 169 (elimination of —CH_3). To a minor by-product of the nitrosation reaction (not analyzed) is

---

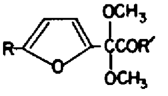
[15] F. W. McLafferty, *Mass Spectral Correlations.* American Chemical Society, Washington (1963).

[16] D. J. Cosgrove, D. G. H. Daniels, J. K. Whitehead and J. D. S. Gouldon, *J. Chem. Soc.* 4821 (1952).

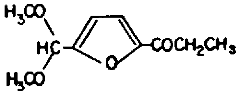
tentatively assigned structure Va, on the basis of the spectral data (see experimental). Compound IVa is formed in excellent yield—together with very small amounts of Va—when dry hydrochloric acid is bubbled for a few minutes through a methanolic solution of IIa maintained at −30°.



IV



V



VI

a: R = H; R′ = CH_3
b: R = H; R = C_2H_5
c: R = R′ = CH_3

The structure of compound B. The principal difference between the IR spectrum of this substance and that of compound A (IIa) was found to be in the aliphatic C—H stretching and bending regions. In particular, in place of the intense band at 7·33 microns present in the spectrum of IIa (methyl group adjacent to a carbonyl), only relatively weak absorption was observed in this region of the IR spectrum of compound B.

This observation, coupled with the mass spectral and UV data of Table 1, led to the postulation of structure IIb for compound B. The previously unknown 1-(2′ furyl)-butane-1,2-dione (IIb) was synthesized by a procedure essentially analogous to that employed for IIa; the synthetic material was found to be identical with B isolated from coffee (IR, UV, R_T's on a polar and non-polar column).

Also in this case, the main product of the nitrosation reaction (IIIb) leading to IIb was accompanied by two ketals, to which are attributed structures IVb and Vb respectively. Interestingly, when dry hydrochloric acid was bubbled for a few minutes through a methanolic solution of IIb maintained at −30°, IVb and Vb were formed in a ratio of approximately 3:7 (VPC). When IIa was treated in the same manner, IVa was by far the predominant product (see above and Experimental).

The structure of compound C. The main clue to the structure of this compound was obtained from its mass spectrum. This yielded the mol wt (152) and showed a very intense base peak at m/e = 109, corresponding to ion Ib or its equivalent. This peak had already been noted in the mass spectrum of 5-methyl-2-acetylfuran and is probably common to the spectra of compounds containing a methyl-substituted furoyl unit. This information, coupled with the IR, UV and chromatographic data of Table I, led to the synthesis of the previously unknown 1-[(5′-methyl)-2′-furyl]-propane-1,2-dione (IIc), which proved to be identical with compound C (IR, UV, R_T's on a polar and non-polar column). The synthesis of IIc was analogous to those of IIa and IIb. To the main by-product of the nitrosation reaction leading to IIc via IIIc is assigned structure IVc, on the basis of analytical and spectral data (Experimental). To a minor by-product (not analyzed) could not be assigned structure Vc; instead, the chromatographic and spectral data suggest for it structure VI. The spectral data include: (a) $\lambda_{C=O}^{CHCl_3}$ at 5·93 microns;[17] (b) acetal absorption hypsochromically shifted—like the ketal absorption of Va and Vb—with respect to that

---

[17] The carbonyl stretching absorptions of Va and Vb occur at 5·73 microns.

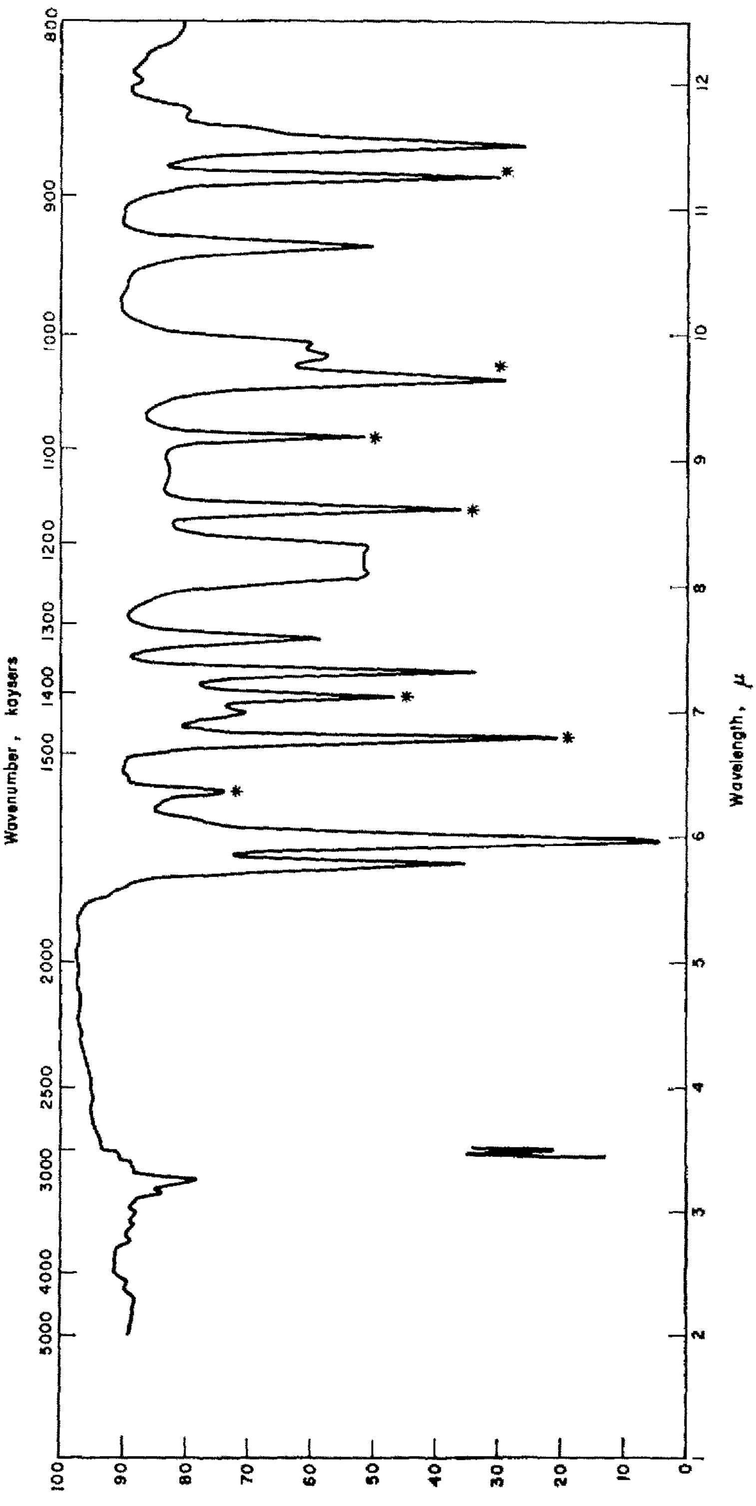


FIG. 2. IR Spectrum ($CHCl_3$) of Compound A

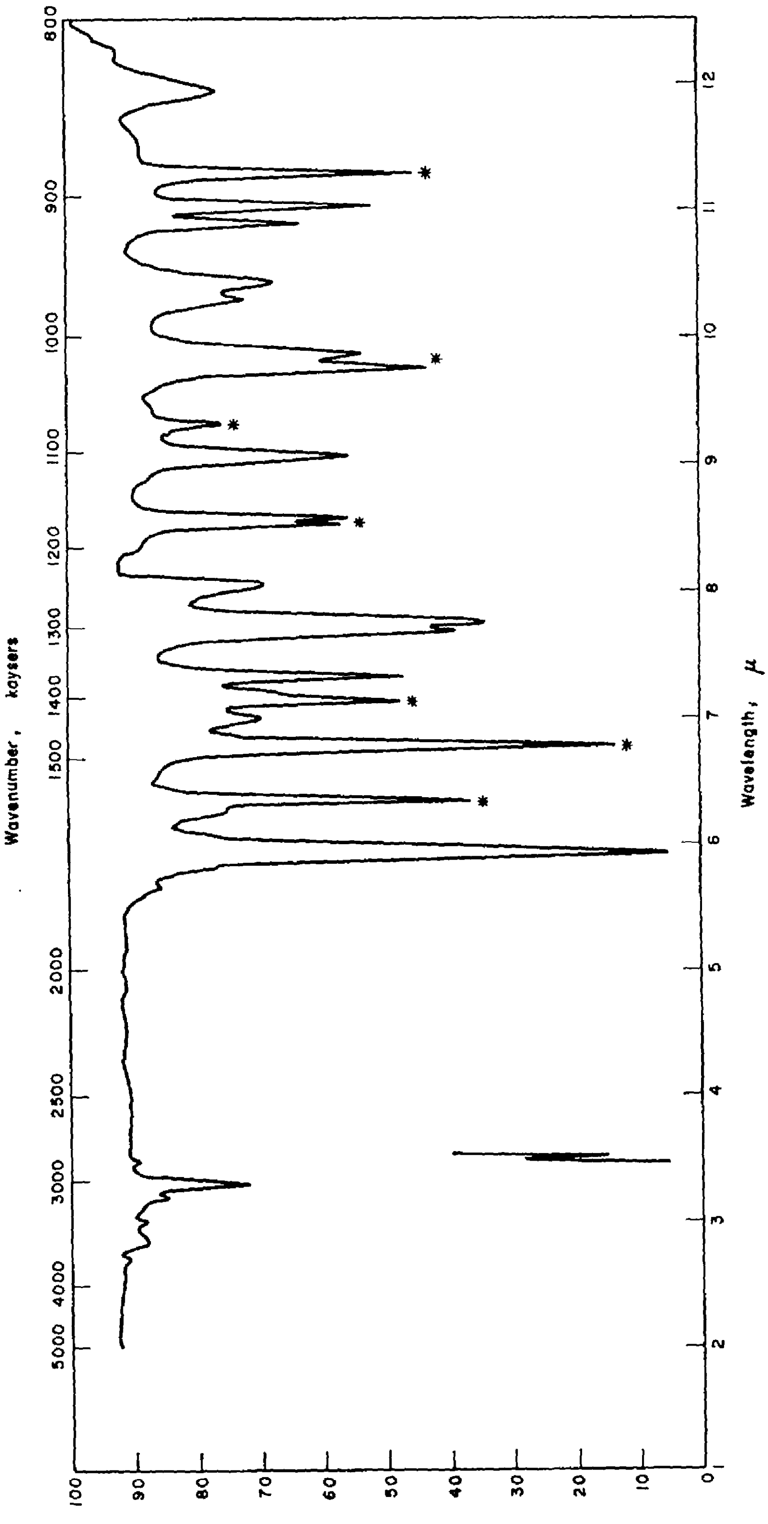
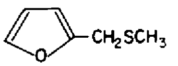


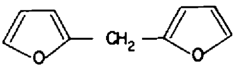
FIG. 3. IR Spectrum ($CHCl_3$) of 2-acetylfuran

of IVa, b, c; (c) λ_{max}^{EtOH} 290 mμ. Moreover, a peak at m/e = 75, corresponding to ion $[CH(OCH_3)_2]\oplus$, overshadows any other peak in the mass spectrum of the substance. As expected IVc—but not VI—was formed in good yield by bubbling dry hydrochloric acid through a methanolic solution of IIc at −30°.[18]

The structure of compound D. The IR spectrum of this substance indicated the presence of a 2-alkyl substituted furan system. The mass spectrum gave the mol wt (128) and the high relative intensity of the M + 2 peak suggested the presence of sulfur in the molecule.[19] These data led to the molecular formula C_6H_8OS and to structure VII for compound D. The previously unreported methyl 2-furfuryl sulfide (VII), obtained from the commercially available 2-furfuryl mercaptan, proved to be identical with compound D (IR, R_T's on a polar and non-polar column).



VII



VIII

The structure of compound E. The IR spectrum of this substance again indicated the presence of a 2-alkyl substituted furan system in the molecule and the mass spectrum gave the mol wt (148). At this point, consideration of the relative intensity of the isotopic peak at M + 1 suggested the molecular formula $C_9H_8O_2$ (six points of unsaturation). With these data, the structure of the previously known 2,2'-difurylmethane (VIII) seemed to be the most probable for compound E.[20] This postulation was proven to be correct by a direct comparison of the synthetic material with the substance isolated from coffee (IR, mass spectrum and R_T's on a polar and a non-polar column).

Pyrrolic compounds. In addition to pyrrole and N-methylpyrrole, whose presence in coffee has been reported by Reichstein and Staudinger,[3] seven pyrrolic compounds have been isolated from the "aroma complex" in the course of this investigation. Some physical properties of these substances, compounds F–L, are indicated in Table 2.

TABLE 2. SOME PHYSICAL PROPERTIES OF COMPOUNDS F–L

Compound	$\lambda_{C=O}^{CCl_4}$ (μ)	$\lambda_{N-H\ (free)}^{CCl_4}$ (μ)	λ_{max}^{EtOH} (mμ)	Mass Spectrometry		R_T*
				C=O Function	Mol wt	
F	6·00	2·89	288	Formyl	95	21·5
G	6·05	2·89	285	Keto	109	32·8
H	6·05	2·89	285	Keto	123	53·7
I	5·94	—	287	Formyl	109	17·4
J	5·98	—	286	Keto	123	28·5
K	6·03	2·89	297	Formyl	109	56·8
L	5·98	—	296	Formyl	123	45·2

* Silicone rubber column at 100°. For conditions, see Experimental.

---

[18] Clearly, the formation of VI in the reaction leading to IIc must depend upon prior nitrosation of the activated ring —CH_3 group of 1-[(5'-methyl)-2'-furyl]-propan-1-one.

[19] The contribution of the S^{34} isotope to the mass spectrum often permits the facile detection of sulfur in a molecule. In this instance, the odour of the compound had permitted us to anticipate this conclusion.

[20] For some brief comments on the mass spectrum of 2,2'-difurylmethane, see: K. Biemann, *Mass Spectrometry*, p. 139. McGraw-Hill, New York (1963).

On the basis of these data, the following structures were postulated, and later confirmed by comparison with synthetic samples. Compound F: 2-pyrrolaldehyde; compound G: 2-acetylpyrrole; compound H: 2-propionylpyrrole; compound I: N-methyl-2-pyrrolaldehyde; compound J: N-methyl-2-acetylpyrrole; compound K: 5-methyl-2-pyrrolaldehyde; compound L: N-methyl-5-methyl-2-pyrrolaldehyde.[21] The mass spectra of compounds F–L conform to the type to be expected of pyrrolic compounds having a carbonyl group conjuncted to the ring[23] and, since a forthcoming publication on the subject has been announced,[24] no useful purpose would be served by elaborating on this matter. It will only be pointed out that the principal fragmentation mode of these compounds consists in the expulsion of the alkyl group (or the hydrogen atom) conjuncted to the carbonyl, followed by loss of a molecule of carbon monoxide. The stepwise nature of this process is clearly indicated by the occurrence of conspicuous metastable peaks at the appropriate m/e values.

EXPERIMENTAL[25]

Vapor-liquid chromatography was carried out in an all-glass system. The support for the stationary phase was, in all cases, 60–80 mesh HMDS-treated Chromosorb W. The flow rate, with the exception of the chromatogram of Fig. 1, was 70 ml He/min. The other pertinent VPC conditions were as follows: (a) [$R_T{}^a$]: 4m × 0·25″ 15% dega packed column, programmed in the following manner: 14 min isothermal at 60°, followed by programming at a rate of 15°/min up to 100° and by subsequent programming at 1·5°/min; (b) [$R_T{}^b$]: 2 m × 0·25″ 15% silicone rubber SE 30 packed column, operated at 100°; (c) [$R_T{}^c$]: idem, operated at 150°. Retention times ($R_T{}^a$, $R_T{}^b$, $R_T{}^c$ above) are expressed in min.

The analytical chromatogram of Fig. 1 was obtained under the following conditions: 4 m × 3 mm ID 5% Triton 305 packed column; flow: 30 ml He/min; programming: as indicated in Fig. 1; mode of injection: on column; mode of detection: flame ionization; sample size: 2 μl. The instrument employed was an F & M model 810, equipped with a dual column system.

The IR spectra were determined on a Beckman IR4 spectrophotometer, employing a beam condenser and an ultramicrocell (path length: 0.115 mm).

The mass spectra were determined on a CEC 21–103C instrument.

Materials. The following compounds were either commercially available or were prepared by standard methods described in the literature.[26] All compounds were purified by VPC before comparison of their spectral properties with those of substances isolated from coffee. The numbers in parenthesis following the name of each compound correspond to $R_T{}^a$ and $R_T{}^b$, respectively (see above).

Furan (4·5, 0·6); 2-methylfuran (6·5, 1·4); 2,5-dimethylfuran (10·5, 2·7); furfural (39·3, 6·0); furfuryl acetate (41·4, 15·3); 2-acetylfuran (42·6, 9·7); furfuryl formate (43·8, 9·7); 5-methylfurfural (46·7, 13·4); furfuryl alcohol (47·9, 6·8); 5-methyl-2-acetylfuran (49·5, 21·0).

N-Methylpyrrole (24·6, 3·5); pyrrole (39·0, 3·5); N-methylpyrrol-2-aldehyde (50·6, 17·4); N-methyl-2-acetylpyrrole (53·5, 28·5); N-methyl-5-methylpyrrol-2-aldehyde (61·2, 45·2); 2-acetylpyrrole

---

[21] The considerable differences observed between the $\surd_s$ (C═O) values of the N-substituted carbonyl pyrroles and those of the corresponding unsubstituted compounds (Table 2) can be attributed to the fact that the latter form dimers in solution.[22]

[22] P. Mirone and V. Lorenzelli, *Ann. Chim., Rome* **49,** 59 (1959).

[23] H. Budzikiewicz, C. Djerassi and D. Williams, *Intrepretation of Mass Spectra of Organic Compounds.* Holden–Day, San Francisco (1964).

[24] Ref. of footnote 23, p. 243.

[25] Analyses by Mr. Josef Nemeth of the Department of Chemistry and Chemical Engineering of the University of Illinois, Urbana, Illinois.

[26] For leading references on furanic compounds, [a] A. P. Dunlop and F. N. Peters, *The Furans,* Reinhold Publishing Co., New York (1953); [b] *Syntheses of Heterocyclic Compounds* (Edited by A. L. Mndzhoian) Vols. 1-4. Consultants Bureau, New York (1960). For a recent review on the chemistry of pyrrolic compounds, E. Bottazzi and L. I. Krimen, *Chem. Revs.* **63,** 511 (1963).

(67·8,32·8); pyrrol-2-aldehyde (69·0, 21·5); 2-propionylpyrrole (70·7, 53·7); 5-methylpyrrol-2-aldehyde (75·5, 56·8).

1-(2'-*Furyl*)-2-*oximinopropan*-1-*one* (IIIa). A solution of 11·3 g (0·11 mole) freshly distilled butyl nitrite in 80 ml methanol was added dropwise over a period of 4 hr to 12·4 g (0·10 mole) 1-(2'-furyl)-propan-1-one in 200 ml methanol containing 44 ml conc. HCl. After stirring overnight at room temp, the solution was cooled in ice, neutralized with 2N NaOH and freed of methanol by distillation through a short column (red. press.). The pH was adjusted to 4–5, the precipitate was filtered off, washed with water and dried. The yield of crude IIIa, m.p. 108·5–110°, was 13 g (85%). This material was completely suitable for the preparation of IIa. A sample, washed free of IIa with hexane and crystallized from H_2O, had m.p. 114–115°. (Found: C, 54·82; H, 4·55; N, 8·98. $C_7H_7NO_3$ requires: C, 54·90; H, 4·58; N, 9·15%).

The acidic solution from which IIIa had been obtained was made alkaline (conc. NaOH) and extracted with ether. Work up of the ether solution yielded 1·4 g of an oil of the following approximate composition (VPC)[27]: 1-(2'-furyl)-propan-1-one, 20·5%; 1-(2'-furyl)-2,2-dimethoxypropan-1-one, IVa, 78%; 1-(2'-furyl)-1,1-dimethoxypropan-2-one, Va, 1·5%. Compound IVa, obtained pure by VPC, had the following characteristics: R_T^c 12·2; $\lambda_{CO}^{CHCl_3}$ 5·93μ; ketal absorption; between 8·5 and 9·7μ, with the strongest band at 9·5μ; λ_{max}^{EtOH} 277 mμ; mass spectrum: prominent peaks at m/e 89, 95, 153, 169. Compound Va, obtained in very minute amounts (VPC), had: R_T^c 6·6; $\lambda_{CO}^{CHCl_3}$ 5·73 μ; ketal absorption: between 8·6 and 9·3 μ, with the strongest band at 9·0 μ. The most prominent peak in its mass spectrum was at m/e 141 (fission of the bond between the carbonyl and the ketal carbon).

1-(2'-*Furyl*)-2,2-*dimethoxypropan*-1-*one* (IVa). A fine stream of dry HCl was passed through 1 g IIa (see below) in 20 ml methanol at −30°, until the solution had lost almost completely its original yellow color (2–3 min). The mixture was poured over ice-cold 20% NaOH, saturated with NaCl and ether extracted. Since VPC indicated that the organic layer contained, besides IVa, small amounts of IIa and Va, the ether solution was repeatedly washed with small amounts of 40% $NaHSO_3$ before drying and removal of the solvent. Distillation yielded 0·88 g (66% yield) chromatographically pure IVa, $b_{1\cdot2}$ 96°, n_D^{23} 1·4970, identical (IR, R_T^c) with the sample obtained in the preparation of IIIa (Found: C, 58·46; H, 6·57. $C_9H_{12}O_4$ requires: C, 58·69; H, 6·57%).

1-(2'-*Furyl*)-*propane*-1,2-*dione* (IIa). (a) This compound was obtained, by direct steam distillation, from a solution of IIIa in 10% H_2SO_4. Saturation of the distillate with NaCl, ether extraction, drying and removal of the solvent yielded IIa in 70% yield. After crystallization from pet. ether, IIa had m.p. 58–58·5° (lit.[16] 60–61°; 64–65°), λ_{max}^{EtOH} 280 mμ, lg ε 3·9213 (lit.[16] 282, 3·9175); R_T^a 58·8; R_T^b 25·8. (Found: C, 60·59; H, 4·47. Calc. for $C_7H_6O_3$: C, 60·87; H, 4·38%). (b) The same product (IIa) was obtained in 75% yield when 1·4 g IIIa, 11 ml H_2O, 3·8 ml 37% HCl and 7 ml formalin was stirred at room temp. The heterogenous mixture became gradually homogenous and IIa began crystallizing from it after 45'. After a total reaction time of 2 hr, filtration, washing with H_2O and drying yielded essentially pure IIa.

1-(2'-*Furyl*)-2-*oximinobutan*-1-*one* (IIIb). With the exception of the isolation procedure, the preparation of IIIb from 1-(2'-furyl)-butan-1-one was completely analogous to that of IIIa from 1-(2'-furyl)-propan-1-one. Thus, the reaction mixture, after overnight stirring at room temp, was neutralized with 2N NaOH, freed of the bulk of the methanol (red. press.), saturated with NaCl and ether extracted. The material contained in the ether was separated in an alkali-soluble and an alkali-insoluble fraction by shaking with 10% NaOH and backwashing with ether. Acidification of the alkaline solution yielded IIIb (7·6 g, 45% yield, m.p. 75–77°). Washing with hexane and crystallization from H_2O yielded pure material, m.p. 78°. (Found: C, 57·42; H, 5·61; N, 8·24.$C_8H_9NO_3$ requires: C, 57·48; H, 5·43; N, 8·38%).

The alkali-insoluble fraction contained in the ether amounted to 4 g; VPC indicated the following composition:[27] 1-(2'-furyl)-butan-1-one, 50%; 1-(2'-furyl)-2,2-dimethoxybutan-1-one, IVb, 48%; 1-(2'-furyl)-1,1-dimethoxybutan-2-one, Vb, 1·5%; 1-(2'-furyl)-butane-1,2-dione, IIb, 0·5%. A pure sample of IVb was obtained by VPC; R_T^c 16·7; $\lambda_{CO}^{CHCl_3}$ 5·93 μ; ketal absorption: between 8·6 and 9·54 μ, with the strongest band at 9·48 μ; λ_{max}^{EtOH} 277 mμ; mass spectrum: most prominent peaks at m/e = 95 and m/e = 103 (fission between the carbonyl and the ketal carbon). A pure sample of Vb was also obtained by VPC; R_T^c 9·9; $\lambda_{CO}^{CHCl_3}$ 5·74 μ; ketal absorption: between 8·5 and 9·5 μ, with the strongest band at 9·06 μ.

---

[27] The per cent areas in the chromatogram were taken to indicate per cent composition.

1-(2′-*Furyl*)-2,2-*dimethoxybutan*-1-*one* (IVb) *and* 1-(2′ *furyl*)-1,1-*dimethoxybutan*-2-*one* (Vb). A 5% solution of IIb in methanol, cooled to −30°, was treated with dry HCl, as in the preparation of IVa from IIa. However, this mixture is much more prone to decomposition and the reaction must be quenched (NaOH) when the color of the solution is still distinctly yellow. Ether extraction of the alkaline solution, followed by preparative VPC, yielded IVb and Vb in a ratio of approximately 3:7. The following analytical data were obtained: IVb ($R_T{}^c$ 16·7), (Found: C, 60·22; H, 7·20. $C_{10}H_{14}O_4$ requires: C, 60·59; H, 7·12); Vb ($R_T{}^c$ 9·9), (Found: C, 60·42; H, 7·39. $C_{10}H_{14}O_4$ requires: C, 60·59; H, 7·12). For spectral properties of IVb and Vb see preparation of IIIb above.

1-(2′-*Furyl*)-*butane*-1,2-*dione* (IIb). This product was obtained by steam distilling it from a solution of IIIb in 10% H_2SO_4; saturation with NaCl, ether extraction, drying and removal of the solvent gave IIb in 64% yield; b_6 95–96°; n_D^{22} 1·5172; λ_{max}^{EtOH} 284 mμ; lg ε 3·9444; $R_T{}^a$ 63·5; $R_T{}^b$ 49·1. (Found: C, 62·87; H, 5·37. $C_8H_8O_3$ requires C, 63·15; H, 5·30%).

1-[(5′-*Methyl*)-2′-*furyl*]-2-*oximinopropan*-1-*one* (IIIc). The preparation of this compound by nitrosation of 1-[(5′-methyl)-2′-furyl]-propan-1-one was completely analogous to the preparation of IIIb. The main product (IIIc) was isolated as an alkali-soluble fraction in 81% yield; m.p. 106–107° from H_2O. (Found: C, 57·32; H, 5·65; N, 8·28. $C_8H_9NO_3$ requires: C, 57·48; H, 5·43; N, 8·38%).

Work up of the alkali-insoluble material yielded an oil consisting (VPC) of 92% IVc and 8% of a compound to which is tentatively assigned structure VI. The available physical data for the two substances are as follows. For IVc: $R_T{}^c$ 20·9; $\lambda_{CO}^{CHCl_3}$ 5·95 μ; ketal absorption: between 8·4 and 9·7 μ, with the strongest band at 9·70 μ; λ_{max}^{EtOH} 288·5; mass spectrum: most prominent peaks at m/e = 89 and m/e = 109 (fission between the carbonyl and the ketal carbon). For VI: $R_T{}^c$: 17·6; $\lambda_{CO}^{CHCl_3}$ 5·93 μ; ketal absorption: between 8·8 and 9·7 μ, with the strongest band at 9·35 μ; λ_{max}^{EtOH} 290 mμ; mass spectrum: most prominent peak at m/e = 75 $[CH(OCH_3)_2]^{\oplus}$.

1-[(5′-*Methyl*)-2′-*furyl*]-2,2-*dimethoxypropan*-1-*one* (IVc). This compound was prepared from IIc, by a method completely analogous to that described above for IVa. The yield of distilled product pure by VPC, was 70%; b_1 105–106°; n_D^{23} 1·5028; $R_T{}^c$ 20·9. (Found: C,60·32; H, 7·15. $C_{10}H_{14}O_4$ requires: C, 60·59; H, 7·12%). This product was identical (IR, $R_T{}^c$) to the analogous sample obtained in the preparation of IIIc (see above).

1-[(5′-*Methyl*)-2′-*furyl*]-*propane*-1,2-*dione* (IIc). This compound was steam distilled directly from a solution of IIIc in 10% H_2SO_4; saturation with NaCl, ether extraction, drying and removal of the solvent gave IIc in 58% yield; b_6 96°; n_D^{23} 1·5320; λ_{max}^{EtOH} 296 mμ; lg ε 3·9785; $R_T{}^a$ 64·6; $R_T{}^b$ 53·6. (Found: C, 62·94; H, 5·29. $C_8H_8O_3$ requires: C, 63·15; H, 5·30%).

2-*Furfuryl methyl sulfide* (VII). This compound was prepared from 2-furfuryl mercaptan and dimethyl sulphate in essentially quantitative yield; b_{28} 62–63°; $n_D^{22.5}$ 1·5210; $R_T{}^a$ 41·2; $R_T{}^b$ 17·4. (Found: C, 56·11; H, 6·16; S, 24·75. C_6H_8OS requires: C, 56·22; H, 6·29; S, 25·01%).

2,2′-*Difurylmethane* (VIII). This compound was prepared by a procedure described in the literature;[28] b_{13} 75°; n_D^{22} 1·5038; $R_T{}^a$ 47·8; $R_T{}^b$ 29·5. (Found: C, 72·83; H, 5·60. Calc. for $C_9H_8O_2$: C, 72·96; H, 5·44%).

N-*Furfuryl-2-pyrrole*. This compound was previously synthesized in this laboratory[1] by dry distillation of saccaric acid and furfuryl amine, according to the procedure of Reichstein.[29] A more convenient preparation is as follows: a solution of equimolecular amounts of furfuryl amine and 2,5-dimethoxytetrahydrofuran[30] in glacial acetic acid is refluxed for 30′, made alkaline (2N NaOH) and submitted to steam distillation. Ether extraction of the distillate, drying and removal of the solvent gives essentially pure N-furfuryl-2-pyrrole in approximately 70% yield; b_1 77–79°; n_D^{21} 1·5317; $R_T{}^a$ 61·3; $R_T{}^b$ 53·2.

[28] W. H. Brown and H. Sawatzky, *Canad. J. Chem.* **34,** 1147 (1956).

[29] T. Reichstein, *Helv. Chim. Acta* **13,** 349 (1930).

[30] Available from Aldrich Chemical Co., Inc., Milwaukee, Wisconsin, U.S.A.