940. *Fermentation Products of Wheat Germ.* (a) *Identification of Methoxy- and 2 : 6-Dimethoxy-*p*-benzoquinone.* (b) *Infra-red Absorption of Some Quinones and 1 : 2-Dicarbonyl Compounds.*

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The compounds isolated by Vuataz (*Helv. Chim. Acta*, 1950, **33**, 433) from wheat germ fermented with baker's yeast have been identified as methoxy-*p*-benzoquinone and 2 : 6-dimethoxy-*p*-benzoquinone. Certain 1 : 2-dicarbonyl derivatives of furan have been prepared which are related to the structure originally put forward for the above compounds. The infra-red absorption spectra of some *p*-benzoquinones, glyoxals, and 1 : 2-diketones have been examined.

(a) The elimination of free glutathione in wheat germ after fermentation with baker's yeast (Hullett and Stern, *Cereal Chem.*, 1941, **18**, 561) was shown by Vuataz (*Helv. Chim. Acta*, 1950, **33**, 433) to be brought about by combination with a specific product (A) of the fermentation; this he isolated and characterised as a dicarbonyl compound, $C_7H_6O_3$, which he formulated as furfurylglyoxal. This was accompanied by a compound (B), which did not combine with glutathione but otherwise resembled the active material; no structure was suggested for this. Compound A has now been identified as methoxy-*p*-benzoquinone and compound B as 2 : 6-dimethoxy-*p*-benzoquinone (cf. Cosgrove, Daniels, Greer, Hutchinson, Moran, and Whitehead, *Nature*, 1952, **169**, 966).

The formula $C_7H_6O_3$ for compound A was confirmed and a methoxyl group detected. Reductive acetylation gave methoxyquinol diacetate. Acetylation under Thiele conditions gave 1 : 4 : 5-triacetoxy-2-methoxybenzene, which had been prepared, but not identified, by Vuataz (*loc. cit.*). These derivatives were identical with authentic specimens (Erdtmann, *Proc. Roy. Soc.*, 1933, *A*, **143**, 177, 191) and prove the nature of A.

Compound B had the formula $C_8H_8O_4$ and contained two methoxyl groups. Reductive acetylation gave 2 : 6-dimethoxyquinol diacetate, so that B was 2 : 6-dimethoxy-*p*-benzoquinone, and this was confirmed by comparison with an authentic specimen.

The light absorption and infra-red spectra of A and B were identical with those of authentic specimens.

Before adequate supplies of compound A became available unsuccessful attempts were made to synthesise furfurylglyoxal. Some isomers incorporating a furan ring and two carbonyl groups were however prepared. Oxidation of 3-2′-furylpropaldehyde with selenium dioxide (Riley, Morley, and Friend, *J.*, 1932, 1875) gave no isolable product, but 1-2′-furylacetone gave a poor yield of 1-2′-furylpropane-1 : 2-dione (but no furfurylglyoxal), this structure being confirmed by identity of the product with that obtained from 2-propionylfuran. An attempt to prepare furfurylglyoxal by hydrolysing and decarboxylating the condensation product of ethyl γγ-diethoxyacetoacetate and ethyl 2-furylacetate (cf. Dakin and Dudley, *J. Biol. Chem.*, 1914, **18**, 29) failed. 5-Methyl-2-furylglyoxal was prepared by Kipnis and Ornfelt's method (*J. Amer. Chem. Soc.*, 1948, **70**, 3948).

(b) *Infra-red Absorption Spectra* [By J. D. S. Goulden].—The table lists the carbonyl stretching frequencies (cm.$^{-1}$) of some of the compounds examined (in chloroform), together

p-Benzoquinone	1676, 1660	Phenylglyoxal	1732, 1704
Methoxy-*p*-benzoquinone	1691, 1657	2-Furylglyoxal	1755, 1686
2 : 6-Dimethoxy-*p*-benzoquinone	1701, 1648	5-Methyl-2-furylglyoxal	1753, 1680

1-2′-Furylpropane-1 : 2-dione	1720, 1662
Furil	1658
Diacetyl	1725

with those of some related compounds. Each of the glyoxal derivatives showed two carbonyl frequencies, the lower frequency bands in each case being of greater intensity than the higher. From the lists of characteristic carbonyl frequencies given by Hartwell, Richards, and Thompson (*J.*, 1948, 1436) and by Cross and Rolfe (*Trans. Faraday Soc.*, 1951, **47**, 354), the higher-frequency band can in each case be assigned to the aldehyde group, and the lower to the keto-group conjugated with the furan or benzene ring. This is supported by the work of Thompson (*Trans. Faraday Soc.*, 1940, **36**, 988) who showed that the carbonyl stretching frequency of glyoxal in the vapour state has a value of 1730 cm.$^{-1}$.

Rasmussen, Tunnicliff, and Brattain (*J. Amer. Chem. Soc.*, 1949, **71**, 1068) have shown that little or no interaction takes place across the –CO·CO– bond of 1 : 2-diketones and this has been confirmed by unpublished work of the authors. It was therefore expected that the two carbonyl frequencies of 1-2′-furylpropane-1 : 2-dione would be very close to those of furil and diacetyl. The infra-red spectrum of 1-2′-furylpropane-1 : 2-dione shows these expected frequencies and thus confirms the identity of the compound.

The electron-insulating effect of a methylene group in furfurylglyoxal should considerably reduce the conjugation of the keto-group with the furan ring. By comparison with the results of Hartwell, Richards, and Thompson (*loc. cit.*), its two carbonyl frequencies should be in the region of 1730 cm.$^{-1}$. Substance A had an infra-red absorption spectrum identical with that of methoxy-*p*-benzoquinone, both carbonyl frequencies being less than 1700 cm.$^{-1}$.

EXPERIMENTAL

M. p.s are uncorrected. Microanalyses are by Drs. Weiler and Strauss, Oxford.

Identification of Compound A.—Compound A, isolated from fresh defatted wheat germ (Vuataz, *loc. cit.*), formed yellow needles or light brown plates, m. p. 143—144°, from ethyl acetate–light petroleum (b. p. 60—80°; 1 : 4) [Found: C, 61·0; H, 4·3; OMe, 22·8%; *M* (Barger's method), 140. Calc. for $C_6H_3O_2$·OMe: C, 60·9; H, 4·35; OMe, 22·5%; *M*, 138]. The m. p. was not depressed by admixture with authentic methoxy-*p*-benzoquinone (Erdtmann, *loc. cit.*). Light absorption of both compounds in chloroform: Max. at 2540 and 3600 Å; ε = 15,800 and 1560 respectively.

Reductive acetylation gave colourless needles which, when recrystallised from methanol, had m. p. alone and mixed with authentic methoxyquinol diacetate, 94—95° (Found: C, 58·7; H, 5·5. Calc. for $C_{11}H_{12}O_5$: C, 58·9; H, 5·4%).

Acetylation under Thiele conditions gave colourless needles which, when recrystallised from aqueous acetic acid, had m. p. alone and mixed with authentic 1 : 4 : 5-triacetoxy-2-methoxybenzene, 141—142° (Found: C, 55·4; H, 4·9. Calc. for $C_{13}H_{14}O_7$: C, 55·3; H, 5·0%).

Identification of Compound B.—Compound B was isolated from the fermentation mixture as yellow needles from ethyl acetate, m. p. 259—260° [Vuataz, *loc. cit.*, gives m. p. 244—245° (decomp.)] [Found: C, 57·2; H, 4·7; OMe, 36·0. Calc. for $C_6H_2O_2(OMe)_2$: C, 57·1; H, 4·8; OMe, 36·9%]. The m. p. was not depressed with an authentic specimen of 2 : 6-dimethoxy-*p*-benzoquinone (Baker, *J.*, 1941, 665). Light absorption of natural and synthetic specimens in chloroform: Max. at 2880 Å; ε = 16,600 (Braude, *J.*, 1945, 490, gives max. at 2880 and 3320 Å; ε = 15,400 and 1670 respectively for a specimen having m. p. 236°).

Reductive acetylation gave colourless needles. Recrystallised from light petroleum (b. p. 80—100°) they had m. p., alone and mixed with authentic 2 : 6-dimethoxyquinol diacetate, 127—128° (Erdtmann, *loc. cit.*, gives 133° for a specimen crystallised from acetic acid, 128° when recrystallised from water; Hofmann, *Ber.*, 1878, **11**, 333, and Hesse, *Annalen*, 1893, **276**, 332, give 128° for material recrystallised from water) (Found: C, 57·1; H, 5·8. Calc. for $C_{12}H_{14}O_6$: C, 56·7; H, 5·5%).

1-2′-*Furylpropane*-1 : 2-*dione*.—(a) *From* 1-2′-*furylacetone*. 1-2′-Furylacetone was prepared in 33% yield by hydrolysing and decarboxylating the product formed by condensing ethyl α-chloropropionate (Frankland and Garner, *J.*, 1914, **105**, 1101) and furfuraldehyde (Darzens, *Compt. rend.*, 1906, **142**, 214). The ketone (15 g.) was added to a solution of selenium dioxide (13·6 g.) in dioxan (75 c.c.) and water (2·5 c.c.) at 50°. The mixture was refluxed and stirred for 4 hours. Next morning the selenium was filtered off with suction on a pad of paper pulp and the solvent removed *in vacuo* from the filtrate. The tarry residue was chromatographed in chloroform on activated alumina. The impurities were strongly adsorbed and a yellow band was eluted with chloroform. The oil recovered from the eluate and distilled *in vacuo* gave 1-2′-*furylpropane*-1 : 2-*dione*, b. p. 94—95°/16 mm., yellow plates [from ethyl acetate–light petroleum (b. p. 60—80°, 1 : 2)], m. p. 64—65° (2·9 g.) (Found: C, 60·6; H, 4·15. $C_7H_6O_3$

requires C, 60·9; H, 4·35%). Light absorption in ethanol: Max. at 2820 Å; ε = 8270. The 2 : 4-*dinitrophenylhydrazone* formed dark red needles (from aqueous acetic acid), m. p. 208—209° (Found: C, 48·6; H, 3·2; N, 17·3. $C_{13}H_{10}O_6N_4$ requires C, 49·0; H, 3·1; N, 17·5%).

(b) *From 2-propionylfuran.* Furan (46 g.) was acylated at 10—15° with propionic anhydride (102 g.) and hydriodic acid (1·2 c.c.; *d* 1·70) (Hartough and Kosak, *J. Amer. Chem. Soc.*, 1946, **68**, 2639). 2-Propionylfuran, obtained in 43% yield (b. p. 78—80°/17 mm.) (Gilman and Calloway, *J. Amer. Chem. Soc.*, 1933, **55**, 4197), was oxidised with selenium dioxide as described above. Refluxing was continued for 5½ hours but the reaction was not complete. After removal of the selenium and unchanged starting material under reduced pressure, 1·4 g. of 1-2′-furylpropane-1 : 2-dione distilled. Recrystallised from ethyl acetate–light petroleum (b. p. 60—80°; 1 : 2), it had m. p. 60—61° alone and mixed with sample obtained from 1-2′-furylacetone (Found: C, 60·7; H, 4·6%).

5-*Methyl-2-furylglyoxal.* 2-Methylfuran (Kizhner, *J. Gen. Chem. U.S.S.R.*, 1931, **1**, 1212) was acetylated at 0—10° by use of hydriodic acid (*d* 1·70). 2-Acetyl-5-methylfuran was oxidised with selenium dioxide as above. 5-Methyl-2-furylglyoxal (9% yield) distilled as a yellow oil, b. p. 109—110°/20 mm. Its *semicarbazone*, m. p. 213—215°, formed colourless rosettes from *iso*amyl alcohol (Found: C, 49·5; H, 4·7; N, 21·3. $C_8H_9O_3N_3$ requires C, 49·2; H, 4·65; N, 21·5%).

2-Furylglyoxal (Kipnis and Ornfelt, *loc. cit.*), b. p. 65—66°/4 mm., phenylglyoxal (Riley and Gray, *Org. Synth.*, 1943, Coll. Vol. II, 509), b. p. 190°/150 mm., and diacetyl (B.D.H.), b. p. 88°, were freshly distilled before examination of their spectra. Furil (Hartman and Dickey, *J. Amer. Chem. Soc.*, 1933, **55**, 1228), recrystallised from methanol, had m. p. 162—163°.

The infra-red spectra were examined in a 1·1-mm. cell with a Grubb Parsons S.3. Spectrometer and a rock-salt prism and a.c. thermocouple detector.

The light absorption measurements were made in a Unicam S.P. 500 Quartz Spectrophotometer employing 1·0-mm. cells.

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