281. *Polyene Acids. Part VI.* A New* (cis-trans-)*Isomer of Sorbic Acid and its Relation to Hexenolactones.*

By Ulli Eisner, J. A. Elvidge, and R. P. Linstead.

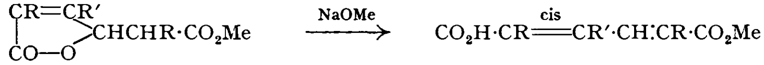
Ring fission of the δ-hexenolactone (II) (racemic parasorbic acid) with methanolic sodium methoxide yields *cis-trans*-sorbic acid, m. p. 35° : its liquid methyl ester is a by-product. The acid has been characterised as the *S*-benzylthiuronium salt, converted into the amide, benzylamide, morpholide, and *iso*butylamide, and reduced to hexanoic acid.

The diene structure of the new acid is shown by the oxidation of its amide to oxalic and oxamic acids, the quantitative hydrogenation of the amide to hexanoamide, the ultra-violet absorption, and the inversion to sorbic acid effected by irradiation or hot alkali. The geometrical configuration follows from the method of preparation and is confirmed by a preparation from 5-hydroxyhex-*cis*-2-enoic acid, obtained from hexenolactone (II) with dilute aqueous alkali and also by semihydrogenation of 5-hydroxyhex-2-ynoic acid.

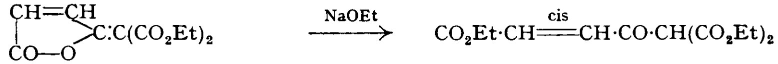
Sorbic acid, m. p. 134·5°, was among the first unsaturated acids known. It was obtained in 1859 by A. W. Hofmann of this College (*Annalen*, 1859, **110**, 129) by the action of alkali or mineral acids on the rowan-berry oil or parasorbic acid. With dilute alkalis, the oily parasorbic acid yielded amorphous salts from which it was regenerated by acid. Doebner (*Ber.*, 1894, **27**, 344) showed that the salts were derived from an unsaturated hydroxy-acid, $C_6H_{10}O_3$, and that parasorbic acid was the corresponding lactone (I) or (II), isomeric with sorbic acid. Sorbic acid was identified as hexa-2 : 4-dienoic acid (Fittig and Barringer, *Annalen*, 1872, **161**, 307; Kachel and Fittig, *ibid.*, 1873, **168**, 276; Doebner, *Ber.*, 1890, **23**, 2372), and much later the lactone was shown to be (+)-hex-2-eno-δ-lactone (Kuhn and Jerchel, *Ber.*, 1943, **76**, 413). The steric configuration of sorbic acid is all-*trans* (see below).

We have demonstrated, in the cases (*a*) and (*b*) shown, that *cis*-unsaturated carboxylic products are formed by the ring-fission of αβ-unsaturated γ-lactones with sodium alkoxides at room temperature. We therefore examined the ring-opening of hex-2-eno-δ-lactone (II) and the isomeric γ-lactone (I) (Δ$^{\alpha}$-homoangelicalactone), in order to determine whether a new (*cis*-)isomer of sorbic acid might be obtained under conditions milder than those applied by Hofmann to parasorbic acid.

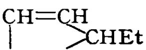
(*a*) [1, 2, 3]



(*b*) [4]



[1] R = R′ = H; *J.*, 1950, 2235. [2] R = H, R′ = Me; *J.*, 1951, 3386.
[3] R = Me, R′ = H; *J.*, 1952, 1026. [4] *J.*, 1951, 1501.



(I)

Synthetic racemic hex-2-eno-δ-lactone was used. Of the methods (i)—(iii) [(i) Haynes and Jones, *J.*, 1946, 503, 954; (ii) Kuhn and Jerchel, *loc. cit.*; (iii) Joly and Amiard, *Bull. Soc. chim.*, 1947, 139] for its preparation, the first was most satisfactory. Method (ii) was simpler but the first stage inconveniently slow. Method (iii) gave mainly sorbic acid, with some lactone which was difficult to isolate. The structure of the product, m. p.

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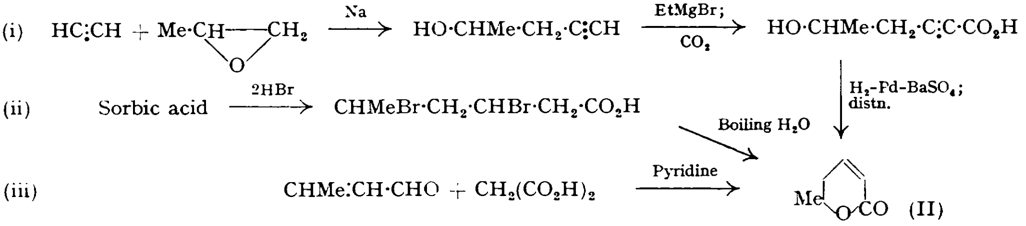
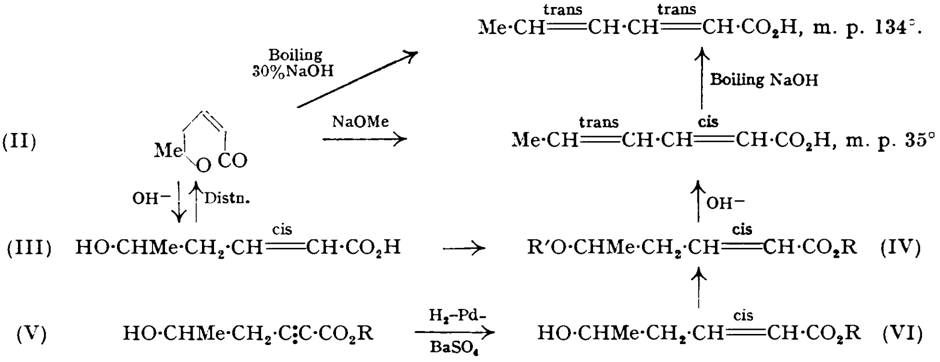
* Part V, *J.*, 1953, 708.

13°, given by route (ii) was proved by Kuhn and Jerchel. Haynes and Jones recorded a boiling point and refractive index similar to those given by Kuhn and Jerchel but no melting point. We have crystallised the lactonic products from the routes (i) and (ii) and confirmed their identity.

The synthetic racemic lactone (II), like the natural (+)-compound, afforded (ordinary) sorbic acid in good yield when treated with boiling 30% sodium hydroxide. Dissolution of the lactone in warm barium or potassium hydroxide, followed by double decomposition with *S*-benzylthiuronium chloride, gave the crystalline thiuronium salt of an unsaturated hydroxy-acid (cf. Doebner, *Ber.*, 1894, **27**, 344), which we have shown to be racemic 5-hydroxyhex-*cis*-2-enoic acid (III). The acid itself was isolated comparatively pure as an oil. It could be titrated with cold 0·05N-alkali, which was without effect upon hexenolactone, it formed a crystalline cinchonidine salt, and with diazomethane it gave the methyl ester, characterised as the 3 : 5-dinitrobenzoate [IV; R = Me, R′ = $CO{\cdot}C_6H_3(NO_2)_2$]. The hydroxy-acid did not lactonise spontaneously, or in boiling ether, but did so on distillation. By semihydrogenation of the acetylenic ester (V; R = Et), Haynes and Jones (*J.*, 1946, **954**) prepared ethyl 5-hydroxyhex-2-enoate (VI; R = Et) which was therefore presumably the racemic *cis*-compound. In boiling hydrochloric acid it afforded racemic hexenolactone (II). We have now prepared the methyl acetylenic ester (V; R = Me) and thence by semi-hydrogenation methyl 5-hydroxyhex-*cis*-2-enoate (VI; R = Me). This gave a 3 : 5-dinitrobenzoate identical with that from the hydroxy-acid (III) produced from hexenolactone and barium hydroxide. The *cis*-structure (III) is therefore certain.

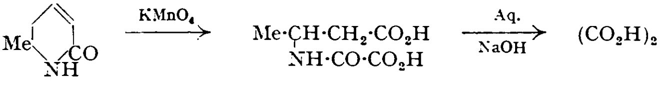




With sodium methoxide in methanol, hexenolactone gave (as expected) an isomeric carboxylic acid, $C_6H_8O_2$, m. p. 35°. A by-product was the corresponding methyl ester, also prepared from the new acid and diazomethane. The new acid was easily soluble in organic liquids, and formed a highly crystalline *S*-benzylthiuronium salt, m. p. 137°. This, however, was unstable on repeated crystallisation, whilst the acid itself quickly resinified : it could however be kept at 0°, under nitrogen. The amide and benzylamide of the acid were stable : the morpholide was an oil and the *iso*butylamide a low-melting solid, both of which soon polymerised. The corresponding amides of sorbic acid were distinct substances, all solids : the sorbic morpholide and *iso*butylamide resinified rapidly.

The unsubstituted amide of the new acid had a melting point (113°) close to that (108°)

of a product with the same formula, prepared at 200° from ammonia and sorbic acid or hexenolactone (Fischer and Schlotterbeck, *Ber.*, 1904, **37**, 2357; Kuhn and Jerchel, *loc. cit.*). However, a mixed melting point, and the ultra-violet light absorption characteristics, indicated that the compounds were not identical. The high-temperature reaction product was shown by Kuhn and Jerchel to be a dihydro-6-methyl-2-pyridone, and they suggested that the double bond was in the 3 : 4-position, as in (VII). This we have proved by oxidising the compound to an acid, $C_6H_9O_5N$, which on hydrolysis gave oxalic acid in good yield. The intermediate acid was evidently β-oxaloamidobutyric acid (VIII).



$$\xrightarrow{KMnO_4} \underset{NH\cdot CO\cdot CO_2H}{Me\cdot CH}\cdot CH_2\cdot CO_2H \xrightarrow[NaOH]{Aq.} (CO_2H)_2$$

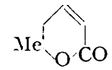
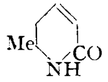
(VII) (VIII)

The new acid, m. p. 35°, from hexenolactone was undoubtedly a hexa-2 : 4-dienoic acid and therefore a geometrical isomer of sorbic acid. Catalytic reduction afforded hexanoic acid, isolated as the *S*-benzylthiuronium salt; and the amide yielded hexanoamide with an uptake of 2 mols. of hydrogen. This proved the open-chain structure of the amide. Oxidation of the new amide with permanganate gave oxalic and oxamic acids, which proved that the two double bonds were in the αβ- and the γδ-position. Moreover, the new acid and its amides showed ultra-violet light absorption typical of a conjugated diene-acid : the positions of the maxima were close to those for the corresponding (all *trans*-)sorbic derivatives, but the intensities were lower (see Table). The infra-red spectra of the two *iso*butylamides (which have no insecticidal activity) showed the following distinctive bands ($cm.^{-1}$) in Nujol :

cis-trans	1268 (infl.)	1253	1226	1155	997	961	928	834
trans-trans	1261	1156	990	942	867			

The new isomeric acid was rapidly inverted in boiling 30% aqueous sodium hydroxide to sorbic acid but was not inverted by boiling water. In cold alkali, inversion occurred very slowly. Hydrolysis of the amide with boiling alkali was accompanied by inversion and sorbic acid was obtained.

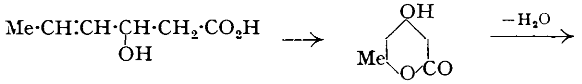
Ultra-violet absorption characteristics in ethanol.

CHMe:CH·CH:CH·COR R	*cis*(αβ)-*trans*(γδ) $\lambda_{max.}$ (Å)	ε	*trans-trans* $\lambda_{max.}$ (Å)	ε		$\lambda_{max.}$ (Å)	ε
OH	2510	16,200	2510 [1]	27,400		2050 [4]	10,700
	2570	17,000	2570	27,400			
	2600	16,200	2630	25,800			
NH_2	2510	22,200	2510	27,200			
	2570	22,200	2570	27,200			
$NH\cdot CH_2Ph$	2500	27,500	2500	32,200		2360	2,600
	2570	29,100	2570	34,600		2470	2,600
	2630	27,500	2620	32,200		2510	2,600
						2560	2,200
$N{<}^{[CH_2]_2}_{[CH_2]_2}{>}O$	2510	15,900	2570	26,800			
	2570	18,100	2650	28,100			
	2640	18,100	—	—			
	2790	10,300	—	—			
$NHBu^i$	2510	23,400	2510 [2]	29,600			
	2570	25,400	2570	31,300			
	2640	20,000	2630	29,600			
OMe	2510	15,700	2580 [3]	31,500			
	2570	17,400	—	—			
	2640	15,700	—	—			

[1] Hauser, Smakula, and Kuhn (*Z. physikal. Chem.*, 1935, **29**, *B*, 371) record $\lambda_{max.}$ 2610 Å, ε = 25,000. [2] Crombie, *Chem. and Ind.*, 1952, 1034. [3] D. G. O'Sullivan, Thesis, London, 1947, p. 77. [4] Haynes and Jones (*J.*, 1946, 954) give ε 10,000 at 2100 Å. Pinder (*J.*, 1952, 2238) records ε 6700 at 2140 Å.

On ultra-violet irradiation in the presence of iodine, the morpholide polymerised a little but was not inverted. The new acid in ether gave no precipitate of relatively insoluble sorbic acid during 16 hours' irradiation but the residue from evaporation of the solvent was substantially sorbic acid (m. p. 118—119°). Irradiation of pure sorbic acid gave a product with a similar low melting point, and this may be due to slight polymerisation or to production of a mixture of geometrical isomers in which sorbic acid predominates.

Configuration.—The long-known form of sorbic acid is undoubtedly *trans-trans*. This follows unambiguously from syntheses (*e.g.*, Doebner, *Ber.*, 1900, **33**, 2140; see von Auwers, *Annalen*, 1923, **432**, 46) and degradation experiments (*e.g.*, Doebner, *Ber.*, 1890, **23**, 2372; Heinänen, *Suomen Kem.*, 1938, *B*, **11**, 2), and is supported by *X*-ray diffraction data (Lonsdale, Robertson, and Woodward, *Proc. Roy. Soc.*, 1941, *A*, **178**, 43). [The formation of hexenolactone (II) as a by-product in the Doebner synthesis of sorbic acid (Joly and Amiard, *loc. cit.*) is probably due to lactonisation of the intermediate β-hydroxy-acid, followed by dehydration :


(II)

and not to intermediate production of *cis*-Δ^α^-unsaturated acid.]

The new hexa-2 : 4-dienoic acid must therefore contain at least one *cis*-arrangement. The method of preparation indicated that it had the *cis*(αβ)-*trans*(γδ)-configuration (see Elvidge, Linstead, and Sims, *J.*, 1951, 3386). However, the acid could not readily be lactonised. With cold 75% sulphuric acid, boiling dilute acids, or on heating alone, only about 6% of neutral material was produced. The acid fractions contained unchanged starting material, polymer, or, on occasion, sorbic acid. The neutral fraction gave a positive Légal test and was therefore lactonic: no ketone was formed by hydrolysis with aqueous alkali, so that hex-2-eno-γ-lactone (I), which would have given 4-ketohexanoic acid, was not present. It seemed therefore that the product might be hex-2-eno-δ-lactone, though attempts to prove this were abortive. Hence other evidence to support the *cis-trans*-configuration of the new sorbic acid was sought.

Funke and Karrer (*Helv. Chim. Acta*, 1949, **32**, 1016) had converted methyl sorbate into *trans-trans*-muconaldehydic ester, and we found that oxidation of the latter with silver oxide (cf. Wendler, Slater, Trenner, and Tishler, *J. Amer. Chem. Soc.*, 1951, **73**, 719) gave methyl hydrogen *trans-trans*-muconate in 18% yield. However, an attempt similarly to convert the methyl *cis-trans*-sorbate into a muconate failed at the first stage, ω-bromination with *N*-bromosuccinimide being accompanied by inversion.

We next examined elimination of the elements of water from the *cis*-hydroxy-acid (III). By treatment of the ethyl ester toluene-*p*-sulphonate (IV; R = Et, R′ = p-$C_6H_4Me{\cdot}SO_2$), or, better, the methanesulphonyl derivative of the methyl ester with cold aqueous alkali (cf. Linstead, Owen, and Webb, *J.*, 1953, 1211) the new isomeric sorbic acid was obtained. The *cis*-configuration about the αβ-double bond was thus directly shown, and additional good evidence provided for the *trans*-configuration about the γδ-double bond (see Elvidge, Linstead, and Sims, *loc. cit.*).

Bruylants and Rowies (*Bull. Soc. chim. Belg.*, 1951, **59**, 244) recently claimed the preparation of *cis-trans*-sorbic nitrile, and amide (m. p. 103°), in small yield *via* the condensation of cyanoacetic acid with crotonaldehyde, but no proof of configuration was given.

The action of sodium methoxide on the unsaturated γ-lactone (I) is very different from that on the δ-lactone. No *cis-trans*-sorbic acid was found—the product was almost entirely ketonic and some 4-ketohexanoic acid was isolated as the 2 : 4-dinitrophenylhydrazone. The lactone (I) is known to rearrange readily to the Δ^{β}-isomer (Lukeš, *Coll. Czech. Chem. Comm.*, 1929, **1**, 461). Presumably this occurs first, under the influence of the alkoxide, so that ring-opening to the enolate ion of the corresponding β-keto-ester follows. The esters of lævulic acids are very easily hydrolysed and the isolation of 4-ketohexanoic acid was presumably a result of the particular method of working. More complex ketonic material was present in the reaction mixture, presumably derived by alkoxide-induced self-condensation of the 4-keto-ester, but was not identified. The reaction of the lower homologue, Δ^{α}-angelicalactone, with sodium alkoxide is similarly complicated (Eskola, Udd, Leppänen, and Stjernvall, *Suomen Kem.*, 1947, *B*, **20**, 13) and apparently yields bimolecular condensation products of *cyclo*pentane-1 : 3-dione.

EXPERIMENTAL

Hex-2-eno-δ-lactone (II) (*Racemic δ-Methyl-Δ^{α}-pentenolide*).—*Method* (i). This (Haynes and Jones, *loc. cit.*) gave a lactone of m. p. 12·8—13·5°, b. p. 102·5—103°/12 mm., n_D^{18} 1·4710 (Found: C, 64·4; H, 7·3. Calc. for $C_6H_8O_2$: C, 64·3; H, 7·2%).

Method (ii). Hydrobromic acid (400 c.c.; *d* 1·45) was treated with dry hydrogen bromide until 170 g. had been absorbed. Finely powdered sorbic acid (87 g.) was added, and the mixture agitated and treated further with hydrogen bromide at intervals during 7 weeks, after which 2 : 5-dibromohexanoic acid (92 g.), m. p. 45—52°, was collected. According to Kuhn and Jerchel's method (*loc. cit.*), this acid (30 g.) and water (350 c.c.) were heated under reflux for 2—3 hours. Extraction with ether and distillation gave the following fractions at 13 mm.: (*a*) b. p. 106—107°, n_D^{23} 1·4700; (*b*) 108—109°, n_D^{23} 1·4700; (*c*) 109—112°, n_D^{23} 1·4710; (*d*) 112—116°, n_D^{23} 1·4721. When cooled to 0° and seeded with the solid lactone from method (i), fractions (*a*), (*b*), and (*c*) solidified. The solid had m. p. 11·5° undepressed by the preceding preparation.

Reaction with boiling sodium hydroxide. The lactone (II) (106 mg.) was treated with boiling 30% sodium hydroxide (4 c.c.) for 50 min. The solution was cooled, acidified, and chilled in ice, and the *trans-trans*-sorbic acid collected (69·5 mg., 65%). Crystallised from water it had m. p. 128—130°, undepressed by authentic material.

Reaction with barium hydroxide. The lactone (II) (1 g.) and saturated barium hydroxide solution (27 c.c.) were heated on the steam-bath for 2·5 hours. The cooled solution was treated with carbon dioxide, and the filtrate concentrated under reduced pressure to 15 c.c. *S*-Benzylthiuronium chloride (3 g.) in water was added. *S-Benzylthiuronium 5-hydroxyhex*-cis-2-*enoate* (1·55 g.) formed needles, m. p. 116—117°, from ethyl acetate (Found: C, 56·4; H, 6·9; N, 9·3. $C_{14}H_{20}O_3N_2S$ requires C, 56·7; H, 6·8; N, 9·45%).

5-Hydroxyhex-cis-2-*enoic Acid* (III).—Hex-2-eno-δ-lactone (II) (1 g.) and N-potassium hydroxide (10 c.c.) were heated on the steam-bath for 5 min. The solution was cooled in ice, acidified with 2N-sulphuric acid (5 c.c.) and extracted 5 times with ether, the temperature being kept at 0°. The ethereal extracts were washed twice with water, dried ($MgSO_4$), and evaporated under reduced pressure (at room temp.), 5-hydroxyhex-*cis*-2-enoic acid (1·01 g.) being left as an oil (Found, by titration with 0·05N-NaOH: equiv., 155. Calc. for $C_6H_{10}O_3$: equiv., 130. Therefore, purity = 84%). Hexenolactone did not react with 0·05N-sodium hydroxide under similar conditions.

The acid (0·168 g.) in ether was treated with a solution of cinchonidine (0·3 g.) in acetone. After several days, crystals of the cinchonidine *salt* separated as needles, which after several crystallisations from acetone had m. p. 133·5—134·5° (Found: N, 6·6. $C_{25}H_{32}O_4N_2$ requires N, 6·6%).

Methyl 5-Hydroxyhex-cis-2-*enoate* (VI; R = Me).—(*a*) 5-Hydroxyhex-*cis*-2-enoic acid (from hexenolactone, above) in ether was treated with ethereal diazomethane, the solvent evaporated under reduced pressure, and the methyl 5-hydroxyhex-*cis*-2-enoate distilled; it had b. p. 62—64°/0·5 mm., n_D^{23} 1·4592, and was characterised as the 3 : 5-*dinitrobenzoate*, which crystallised from methanol as pale yellow prisms, m. p. 86—87° (Found: N, 8·3. $C_{14}H_{14}O_8N_2$ requires N, 8·3%).

(*b*) 5-Hydroxyhex-2-ynoic acid (Haynes and Jones, *J.*, 1946, 503) was heated overnight under reflux with methanol (10 vols.) containing 1% of sulphuric acid, and the neutral product distilled to yield *methyl 5-hydroxyhex-2-ynoate*, b. p. 83°/0·12 mm., n_D^{22} 1·4680 (Found: C, 58·6; H, 7·1. $C_7H_{10}O_3$ requires C, 59·15; H, 7·1%). A portion (740 mg.) in methyl acetate (40 c.c.) was semihydrogenated (allowed hydrogen uptake: 120 c.c. at 766 mm./23°) over 2% palladium–strontium carbonate. The derived 3 : 5-dinitrobenzoate had m. p. 85—87° alone and when mixed with the previous preparation.

cis-trans-*Sorbic Acid*.—(*a*) Hexenolactone (II) (3·2 g., 1 mol.) was kept with a solution of sodium (0·66 g., 1 mol.) in methanol (100 c.c.) for 30 min. The solvent was distilled off under reduced pressure, the residue dissolved in water, and the solution washed with ether and acidified with hydrochloric acid. The solution was extracted 3 times with ether, the ethereal extracts were washed with water, dried ($MgSO_4$), and evaporated. The residual oil (2·49 g., 78%) crystallised slowly at 0°, and was recrystallised from pentane (by cooling to —70°), affording needles of cis-trans-*sorbic acid*, m. p. 32—35° (Found: C, 64·4, H, 7·4%; equiv., 112. $C_6H_8O_2$ requires C, 64·3; H, 7·2%; equiv., 112). The acid distilled unchanged under reduced pressure and had b. p. 121—125°/16 mm. It polymerised during 2—3 hours at room temperature, but much more slowly at 0°, to a clear brittle resin.

The S-*benzylthiuronium* salt, prepared in water, crystallised from ethyl acetate (rapidly, to avoid decomposition) as needles, m. p. 137° (Found : N, 9·9. $C_{14}H_{18}O_2N_2S$ requires N, 10·1%).

(*b*) Hexenolactone (II) (5·6 g.) was treated with methanolic sodium methoxide (from 1·15 g. of sodium). The acidic fraction afforded *cis-trans*-sorbic acid (4·0 g., 71%). From the neutral fraction, methyl *cis-trans*-sorbate (see below) was obtained which after two distillations had b. p. 80°/21 mm., n_D^{21} 1·4944. Light absorption in ethanol: max. at 2510, 2570 Å; ε = 18,300, 21,800.

Derivatives of cis-trans-*Sorbic Acid.*—*cis-trans*-Sorbic acid and diazomethane in ether gave, after two distillations of the product, *methyl* cis-trans-*sorbate*, b. p. 60°/11 mm., n_D^{22} 1·4948 (Found : C, 66·0; H, 8·0. $C_7H_{10}O_2$ requires C, 66·6; H, 8·0%).

To a solution of the acid (2·2 g.) in pentane at 0°, oxalyl chloride (2·2 c.c.) and pyridine (1 drop) were added. After 2·5 hours at room temperature and 1 hour at 35—40°, the solution was evaporated under reduced pressure. Dry ether was distilled from the residue, which was then dissolved in benzene and treated at 0° with gaseous ammonia. The solution was filtered, and the solid repeatedly extracted with boiling ethyl acetate. Evaporation of the combined extracts and filtrate afforded cis-trans-*sorbamide* (1·47 g.) which after several crystallisations from ethyl acetate–light petroleum (b. p. 60—80°) and sublimation at 100°/20 mm. had m. p. 113—114° (Found : N, 12·5. C_6H_9ON requires N, 12·6%).

cis-trans-Sorbic acid (0·55 g.) was converted into its acid chloride as above and the ethereal solution treated with benzylamine (1·1 g.) in ether (10 c.c.) at 0°. After 1 hour, the solution was washed successively with water, 2N-sulphuric acid, aqueous sodium hydrogen carbonate, and water, and dried ($MgSO_4$), and the ether distilled off. N-*Benzyl*-cis-trans-*sorbamide* (0·88 g.) crystallised from light petroleum (b. p. 40—60°) as needles, m. p. 82—83° (Found : N, 7·2. $C_{13}H_{15}ON$ requires N, 7·0%).

The *morpholide*, prepared similarly, was an oil, b. p. *ca.* 115°/0·5 mm., n_D^{23} 1·5451 (Found : N, 7·6. $C_{10}H_{15}O_2N$ requires N, 7·7%).

The iso*butylamide* was obtained as an oil which after two distillations at 90°/0·1 mm. solidified and had m. p. 33—35° (Found : N, 8·1. $C_{10}H_{17}ON$ requires N, 8·4%).

Derivatives of trans-trans-*Sorbic Acid.*—The S-*benzylthiuronium* salt crystallised from methanol–ether as laths, m. p. 169—170° (Found: C, 60·4; H, 6·6. $C_{14}H_{18}O_2N_2S$ requires C, 60·4; H, 6·5%).

The amide prepared from the acid *via* the acid chloride had m. p. 168—169° after crystallisation from water or ethyl acetate. Doebner and Wolff (*Ber.*, 1901, **34**, 2221) give m. p. 168°.

The *benzylamide* crystallised from benzene in needles, m. p. 130·5—131·5° (Found : N, 7·1. $C_{13}H_{15}ON$ requires N, 7·0%).

The *morpholide* crystallised from light petroleum (b. p. 60—80°) in silky needles, m. p. 75—76° (Found : N, 7·6. $C_{10}H_{15}O_2N$ requires N, 7·7%). It polymerised rapidly at room temperature, more slowly at 0°.

2 : 3-*Dihydro-2-methyl-6-pyridone* (VII).—The lactam (Fischer and Schlotterbeck, *loc. cit.*), after several crystallisations from ethyl acetate–light petroleum (b. p. 60—80°) and sublimation at 100°/20 mm., had m. p. 105·5—106°. A mixture with *cis-trans*-sorbamide had m. p. 75—80°.

Oxidation of the Lactam.—The lactam (0·55 g.) in water (40 c.c.) was treated with potassium permanganate (2·1 g., 4O) in water (150 c.c.) at 0° (stirring), the solution was decolorised (Na_2SO_3), boiled, and filtered, and the filtrate extracted continuously with ether, to yield N-(1-*carboxy-2-propyl*)*oxamic acid* (VIII) (0·75 g.), which crystallised from ethyl acetate–light petroleum (b. p. 60—80°) as needles, m. p. 156—157° (decomp.) (Found : N, 7·5. $C_6H_9O_5N$ requires N, 8·0%). The acid (0·33 g.) and 10% aqueous sodium hydroxide were boiled under reflux for 2 hours, and the solution was acidified and filtered. The filtrate was heated to boiling, treated with aqueous calcium chloride (0·5 g.), and neutralised with 2N-ammonia. The precipitated calcium oxalate (0·223 g., 80%) was treated with hydrochloric acid and continuously extracted with ether, affording oxalic acid, m. p. 185° (decomp., with softening at 95—100°) undepressed by an authentic specimen.

Hydrogenation of cis-trans-*Sorbic Acid.*—The acid (7 mg.) in ethanol in the presence of Adams's catalyst absorbed 1·55 mols. of hydrogen. The filtered solution was neutralised with dilute aqueous sodium hydroxide, concentrated to small volume under reduced pressure, and treated with *S*-benzylthiuronium chloride (20 mg.) in water. The precipitated solid had m. p. 146—147°, undepressed in admixture with S-*benzylthiuronium hexanoate*, which crystallised from ethanol in laths, m. p. 149·5—150° (Found : N, 9·8. $C_{14}H_{22}O_2N_2S$ requires N, 9·9%).

Hydrogenation of cis-trans-*Sorbamide.*—The amide (448 mg.) in ethanol (10 c.c.) was hydrogenated in the presence of Adams's catalyst (30 mg.) (uptake of hydrogen : 210 c.c. at 21°/772 mm. Calc. for 2 mols. : 192 c.c.). Evaporation of the filtered solution under reduced pressure and crystallisation of the residue from water afforded hexanoamide, m. p. 98—99° undepressed by authentic material.

Oxidation of cis-trans-*Sorbamide.*—The amide (810 mg.) in water (50 c.c.) was treated with a solution of potassium permanganate (6·32 g.; 8O) in water (200 c.c.) at 0° with stirring. The solution was filtered, decolorised with sodium sulphite, boiled to coagulate manganese dioxide, and filtered. The filtrate was acidified with acetic acid, heated to boiling, and treated with a hot solution of calcium chloride (0·8 g.) in water. After addition of 2N-ammonia, the mixture was allowed to cool, and the precipitated calcium oxalate collected (filtrate *A*), washed, and dried (yield, 384 mg.). Addition of aqueous hydrochloric acid to the salt, followed by continuous ether-extraction, afforded oxalic acid (156 mg.), which after crystallisation from ethyl acetate–light petroleum (b. p. 60—80°), had m. p. 100° with resolidification and then m. p. 183—184° (decomp.), undepressed by an authentic specimen. The filtrate *A* from the calcium oxalate was continuously extracted with ether for 20 hours. Evaporation of the ether afforded oxamic acid (203 mg.) which after one crystallisation from water had m. p. 202—204° (decomp.).

Inversion Experiments with cis-trans-*Sorbic Acid and its Derivatives.*—(a) *Boiling water. cis-trans*-Sorbic acid (24 mg.) and water (2·5 c.c.) were heated under reflux for 20 min. Evaporation of the solution in a desiccator afforded crystals of unchanged starting material, identified by m. p. and conversion into the *S*-benzylthiuronium salt.

(b) *Sodium hydroxide.* (i) The acid (0·2 g.) was boiled in 30% sodium hydroxide solution (7·5 c.c.) under reflux for 1·3 hours, cooled, acidified, chilled in ice, and filtered. The *trans-trans*-sorbic acid (yield, quantitative) was crystallised from water (charcoal), and then had m. p. 131—132° undepressed by authentic material. (ii) The *cis-trans*-acid (0·1 g.) in 30% sodium hydroxide solution (4 c.c.) was kept for 7 weeks in the dark at room temperature. The solution was acidified at 0° and the precipitated acid (50 mg.) recrystallised from water; it then had m. p. 123—126° undepressed by *trans-trans*-sorbic acid. (iii) *cis-trans*-Sorbamide (34 mg.) and 30% sodium hydroxide solution (2 c.c.) were heated under reflux for 1 hour. Acidification of the cooled solution precipitated an acid with m. p. 127—129°, undepressed by *trans-trans*-sorbic acid.

(c) *Irradiation. cis-trans*-Sorbic acid (21 mg.) in dry ether (1 c.c.) containing a trace of iodine was irradiated with ultra-violet light from a Hanovia lamp for 16 hours. The solution was evaporated under reduced pressure, and the residual solid acid (m. p. 100—105°) recrystallised twice from carbon tetrachloride. It then had m. p. 118—119°, and m. p. 122—124° when mixed with *trans-trans*-sorbic acid.

(d) Irradiation of the *cis-trans*-morpholide under similar conditions effected no appreciable change [Found, for recovered material: $n_D^{22·5}$ 1·5452; light adsorption in ethanol, max. at 2510, 2580, 2640 Å (ε = 15,400, 17,000, 17,000)].

Irradiation of *trans-trans*-sorbic acid under similar conditions yielded material with m. p. 114—118°, raised to 117—120° after one crystallisation from carbon tetrachloride.

Lactonisation Attempts.—(*a*) *cis-trans*-Sorbic acid (1 g.) and water (10 c.c.) containing hydrochloric acid (3 drops) were heated under reflux for 12 hours. The cooled solution was made alkaline (Na_2CO_3) and extracted with ether. Evaporation of the extract afforded an oil (50 mg.) which gave a positive Légal test. From the alkaline aqueous phase, by acidification and ether-extraction, unchanged starting material (0·6 g.) was recovered, identified as the *S*-benzylthiuronium salt.

(*b*) *cis-trans*-Sorbic acid (1 g.) was heated at 154° for 2·5 hours and the product shaken with 2N-sodium carbonate and ether. From the aqueous phase unchanged starting material (0·55 g.) was recovered, identified as above. Evaporation of the ether afforded an oil (0·1 g.) which gave a positive Légal test, but no precipitate was obtained with aqueous 2 : 4-dinitrophenylhydrazine hydrochloride after alkaline hydrolysis of a portion. Derivation of a salt of (III) from the oil was not achieved.

Oxidation of trans-trans-*Muconaldehydic Methyl Ester.*—The ester aldehyde (Funke and Karrer, *loc. cit.*) (115 mg.; purified by sublimation at 100°/20 mm.) in methanol (5 c.c.) was shaken for 2 days with an alkaline suspension of silver oxide, made by treating silver nitrate (0·5 g.) in water (5 c.c.) with potassium hydroxide (175 mg.) in 95% methanol (7·5 c.c.). The mixture was filtered, and the residue washed with water (100 c.c.) and the filtrate with ether. The aqueous layer was acidified (HCl), and methyl hydrogen *trans-trans*-muconate (18·5 mg.), m. p. 161—162°, isolated with ether.

ω-Bromination of Methyl cis-trans-*Sorbate.*—The ester (12·53 g.), carbon tetrachloride (1 c.c.). and *N*-bromosuccinimide (5·85 g., 0·33 mol.) were heated at 120—130° for 30 min. (cf.

Heilbron, Jones, and O'Sullivan, *J.*, 1946, 866). Milder conditions were ineffective. Fractionation of the liquid product gave (i) methyl *trans-trans*-sorbate (8·7 g.), b. p. 60—63°/10 mm., $n_{\rm D}^{18}$ 1·5012—1·5027, characterised by conversion into the benzylamide, and (ii) crude methyl ω-bromo-*trans-trans*-sorbate (0·83 g.), b. p. 73—77°/0·1 mm., $n_{\rm D}^{18}$ 1·5263, and 0·36 g., b. p. 77—83°/0·1 mm., $n_{\rm D}^{18}$ 1·5321. Fraction (ii) (100 mg.), potassium phthalimide (100 mg.), and dry methanol (2 c.c.) were heated under reflux for 2 hours (cf. Karrer and Schwyzer, *Helv. Chim. Acta*, 1946, **29**, 1191). On cooling of the solution to 0°, methyl ω-phthalimido-*trans-trans*-sorbate (28 mg.) crystallised, having m. p. 150—152° undepressed by a specimen prepared from authentic methyl ω-bromo-*trans-trans*-sorbate, b. p. 80°/0·5 mm., $n_{\rm D}^{21}$ 1·5409.

Dehydration of 5-*Hydroxyhex*-cis-2-*enoic Acid: Formation of* cis-trans-*Sorbic Acid*.—(*a*) Ethyl 5-hydroxyhex-*cis*-2-enoate (Haynes and Jones, *J.*, 1946, 954) (3 g.) in pyridine (5 c.c.) was added at 0° to a pyridine solution (5 c.c.) of toluene-*p*-sulphonyl chloride (3·6 g.). The mixture was kept at 0—2° overnight, and ice-water then added. The solution was extracted 4 times with chloroform, and the extract washed with dilute sulphuric acid, aqueous sodium hydrogen carbonate, and water, dried ($MgSO_4$), and evaporated. The crude oily toluenesulphonyl derivative was stirred with N-potassium hydroxide (50 c.c.) for 6 days, and the oily acidic fraction (1·21 g.) subsequently isolated with ether. The pentane-soluble fraction was dissolved in water, and the solution neutralised with dilute aqueous sodium hydroxide. The derived *S*-benzylthiuronium salt had m. p. 139—140°, undepressed in admixture with the salt of *cis-trans*-sorbic acid obtained above.

(*b*) Methyl 5-hydroxyhex-*cis*-2-enoate (3·43 g.) in dried pyridine (3 c.c.) was treated at 0° with methanesulphonyl chloride (2 c.c.) in pyridine (3 c.c.), and the crude derivative stirred with N-potassium hydroxide (90 c.c.) overnight. Isolation as before with ether and extraction with pentane afforded an oil (0·62 g., 23%) which slowly crystallised. Recrystallisation from pentane (at −70°) afforded *cis-trans*-sorbic acid, m. p. 28—31°. The *S*-benzylthiuronium salt had m. p. and mixed m. p. 140—141°.

Action of Sodium Methoxide.—Δ^{α}-Homoangelicalactone (I) (racemic γ-ethyl-Δ^{α}-butenolide), prepared according to Kuhn and Jerchel (*loc. cit.*), had b. p. 99—100°/19 mm., $n_{\rm D}^{22}$ 1·4561. The lactone (I) (3·69 g.) was dissolved in ice-cold methanolic sodium methoxide (100 c.c.; from 0·76 g. of sodium), the solvent at once removed under reduced pressure (without heating), and the residue dissolved in water. The solution was acidified, extracted with ether several times, and the ether back-extracted with 2N-sodium carbonate. Isolation from the acidified aqueous phase with ether afforded an oil (2·6 g.), which was extracted with pentane: at −70° the extract remained clear and did not deposit *cis-trans*-sorbic acid. The pentane-insoluble fraction (0·65 g.), in acetic acid (25 c.c.) with 2 : 4-dinitrophenylhydrazine, gave a dinitrophenylhydrazone (0·24 g.) and filtrate *B*. After crystallisation from ethyl acetate, the derivative had m. p. 186° alone and when mixed with 4-(2 : 4-*dinitrophenylhydrazono*)*hexanoic acid*, which formed needles, m. p. 187—189°, from benzene or ethyl acetate (Found: N, 18·1. $C_{12}H_{14}O_6N_4$ requires N, 18·0%). Authentic 4-ketohexanoic acid was prepared in 26% yield from diethylcadmium and succinic anhydride (cf. de Benneville, *J. Org. Chem.*, 1941, **6**, 462).

By concentration of the filtrate *B*, a second *derivative* (0·66 g.) was separated, which after crystallisation from ethyl acetate had m. p. 193° (Found: C, 41·35; H, 3·6; N, 21·8, 22·9%). The m. p. was depressed to 160° by the above dinitrophenylhydrazone.

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