ZUSAMMENFASSUNG

Die Struktur von Carpogenin wird bewiesen. Es erwies sich als identisch mit 3α, 14β-Dihydroxy-19-oxo-carden-(20:22)-olid, das teilsynthetisch auf zwei Wegen aus Cannogenin bereitet worden war. Ferner wurde 3α,14β,19-Trihydroxycarden-(20:22)-olid bereitet; es wurde als Carpogenol bezeichnet. Cannogenol wurde erstmals in Kristallen erhalten. Das früher aus den Samen von *Pachycarpus schinzianus* isolierte Genin HPU 28 wurde als Cannogenin identifiziert.

Organisch-chemische Anstalt der Universität Basel

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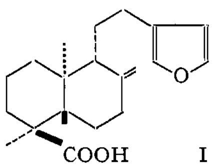
124. Structure and Stereochemistry of Polyalthic Acid, a new Diterpene Acid[1])

by **K. W. Gopinath, T. R. Govindachari, P. C. Parthasarathy** and **N. Viswanathan**

(14. III. 61)

Polyalthia fragrans (Bth.), a large tree belonging to the family *Anonaceae*, is common on the West Coast of India. Extraction of the stem bark of this tree with cold petroleum ether afforded a new crystalline diterpene acid, named polyalthic acid, in a yield of nearly 1 per cent. On the basis of the degradation studies reported in this paper, polyalthic acid has been assigned the structure and stereochemistry depicted in formula (I).



I

Polyalthic acid was purified by chromatography over silicagel, the pure acid melting at 102°. Analyses of the acid as well as the crystalline salts it' forms with cyclohexylamine and diethylamine were in agreement with the formula $C_{20}H_{28}O_3$. The molecular weight of the acid determined by the Rast method was 305 and the equivalent weight by titration 313. Kuhn-Roth determination showed the presence of two C–CH_3 groups and a Zerewitinoff analysis indicated the presence of only one active hydrogen. The presence of three double bonds was established by titration with iodine monochloride as well as by reduction to hexahydropolyalthic acid, characterised as its crystalline diethylamine salt.

Polyalthic acid could not be esterified by the Fischer procedure, but methyl polyalthate, $C_{21}H_{30}O_3$, was obtained by the action of diazomethane. The ester was fairly resistant to alkaline hydrolysis, indicating that the carboxyl group in polyalthic acid is tertiary.

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[1]) Part of this work, dealing with the structure of polyalthic acid, was presented at a meeting of the Swiss Chemical Society held at Fribourg on February 11, 1961. – Veröffentlicht laut besonderem Beschluss des Redaktionskomitees.

Polyalthic acid and methyl polyalthate gave a purple colour in the **Ehrlich** test, suggestive of the presence of a furan ring. Although polyalthic acid did not exhibit an ultraviolet absorption maximum, the end absorption in the 210 mμ region was of a magnitude comparable to those of furan derivatives (Table 1).

Table 1. *Ultraviolet absorption spectra of some substituted furans*

Compound	λ	ε
Marrubiin²)	212	5620
Dihydrocolumbin³)	210	5700
Limonin⁴)	210	6000
Pentaol from obacunone⁴) . .	208	7400
Polyalthic acid	213	6200

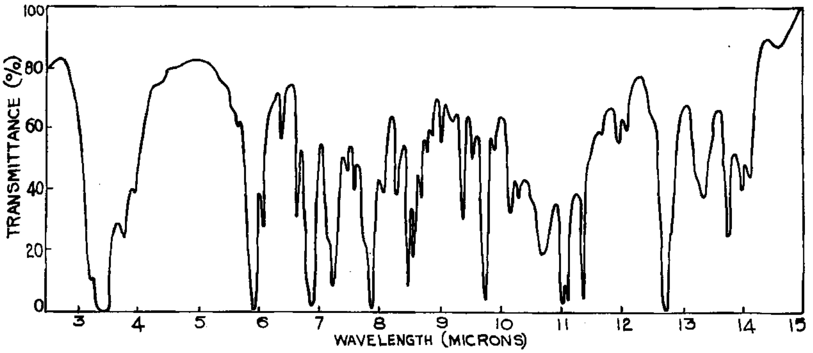

Fig. 1. *IR. Spectrum of polyalthic acid (I) in nujol*

Table 2. *NMR. Spectrum* of polyalthic acid*

τ	Number of protons	Inference
2.69	1 H	α-protons on furan ring⁵)
2.83	1 H	
3.79	1 H	β-proton on furan ring⁵)
5.17	1 H	$>C=CH_2$
5.47	1 H	
8.37	14 H	Cyclic methylene protons
8.9	3 H	$-\overset{\mid}{\underset{\mid}{C}}-CH_3$
9.3	3 H	

* Measured at 60 Mc in $CDCl_3$, with tetramethylsilane as internal indicator, using a Varian Spectrometer.

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[2] W. Cocker, B. E. Cross, S. R. Duff, J. T. Edward & T. F. Holley, J. chem. Soc. *1953*, 2540.

[3] D. H. R. Barton & D. Elad, J. chem. Soc. *1956*, 2085.

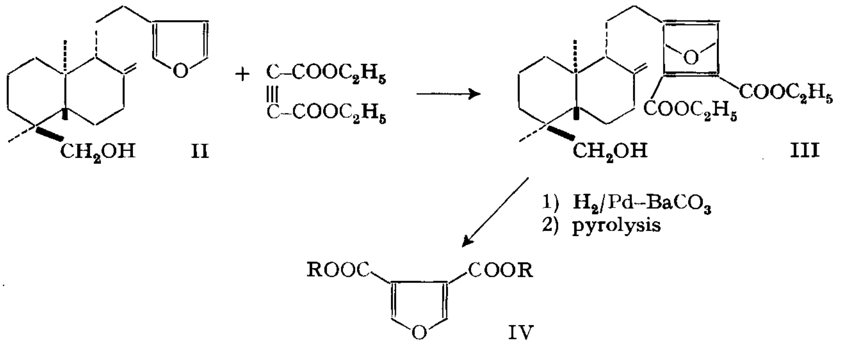
[4] T. Kubota & T. Tokoroyama, Chemistry & Ind. *1957*, 1298.

[5] E. J. Corey, G. Slomp, Sukh Dev, S. Tobinaga & R. Glazier, J. Amer. chem. Soc. *80*, 1204 (1958).

The infrared absorption spectrum (nujol) of polyalthic acid (Fig. 1) had bands at 6·7 and 11·4 μ, supporting the presence of a furan ring in the compound. Other characteristic bands were at 3·25, 6·1 and 11·2 μ (exocyclic methylene), and 5·9 μ (carboxyl).

The NMR. spectrum of polyalthic acid again indicated the presence in the molecule of a β-substituted furan ring. Positions of the principal peaks are recorded in Table 2. The difference of 25 c.p.s. between the two C–CH_3 peaks could be due to the presence of a carboxyl group on one of the methyl-bearing carbon atoms.

The presence of a β-monosubstituted furan ring in polyalthic acid, indicated by the colour reaction, UV., IR. and NMR. spectra, was confirmed chemically by the application of the ALDER-RICKERT degradation[6]) to polyalthyl alcohol (II), obtained by the lithium aluminium hydride reduction of methyl polyalthate. The alcohol was allowed to react with diethyl acetylenedicarboxylate to afford an amorphous adduct III in which the infrared bands of the furan ring were absent. Catalytic reduction of the adduct in ethyl acetate with Pd-$BaCO_3$ followed by pyrolysis of the product yielded diethyl furan-3,4-dicarboxylate (IVa), which on alkaline hydrolysis gave furan-3,4-dicarboxylic acid (IVb), identical (m.p., mixed m.p. and IR.) with an authentic specimen.



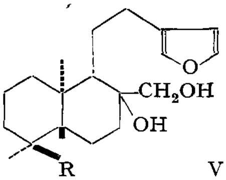
II

III

IV

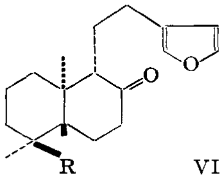
a: R = C_2H_5 b: R = H

Ozonolysis of polyalthic acid as well as of its methyl ester produced formaldehyde in good yield. The ring containing the exocyclic methylene group was shown to be six-membered by the following sequence of reactions: Hydroxylation of polyalthic acid with osmium tetroxide gave a crystalline diol Va, $C_{20}H_{30}O_5$, having IR. peaks (nujol) at 2·9 μ (OH), 5·9 μ (COOH), 6·7 and 11·4 μ (furan). Cleavage of this diol



V

a: R = COOH
b: R = CH_2OH



VI

a: R = COOH
b: R = $COOCH_3$
c: R = CH_2OH

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[6]) K. ALDER & H. F. RICKERT, Ber. deutsch. chem. Ges. *70*, 1354 (1937).

with sodium metaperiodate gave the keto-acid VIa. This was methylated to the keto-ester VIb, which showed only a single peak at 5·85 μ in the carbonyl region, due to poor resolution. Repetition of the above sequence with polyalthyl alcohol gave the triol Vb, cleavage of which yielded the keto-alcohol VIc, exhibiting an infrared peak at 5·85 μ, which can be ascribed to a six-membered ketone.

The relative locations of the exocyclic methylene group and the β-monosubstituted furan ring were established as follows: Ozonolysis of polyalthic acid in acetic acid followed by oxidation of the derived α-keto-acid with alkaline hydrogen peroxide gave the keto-dicarboxylic acid VII (IR. spectrum, Fig. 2). Reduction of this acid with sodium borohydride afforded the lactone acid VIIIa, which was converted to the lactone ester VIIIb by diazomethane. The lactone acid VIIIa had infrared bands (KBr) at 5·78 μ (δ-lactone) and 5·9 μ (COOH), and the lactone ester VIIIb showed peaks (KBr) at 5·74 μ (δ-lactone) and 5·81 μ ($COOCH_3$) (Figs. 3 and 4).

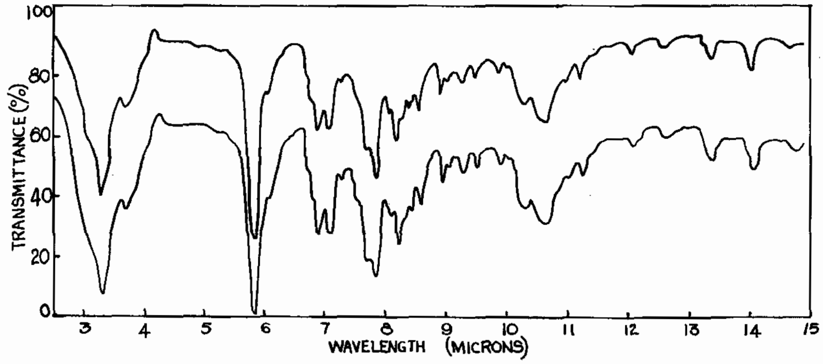


Fig. 2. *IR. Spectra of the keto-dicarboxylic acids VII and X in KBr*
Top: Acid X from neoabietic acid.
Bottom (20% lower): Acid VII from polyalthic acid.

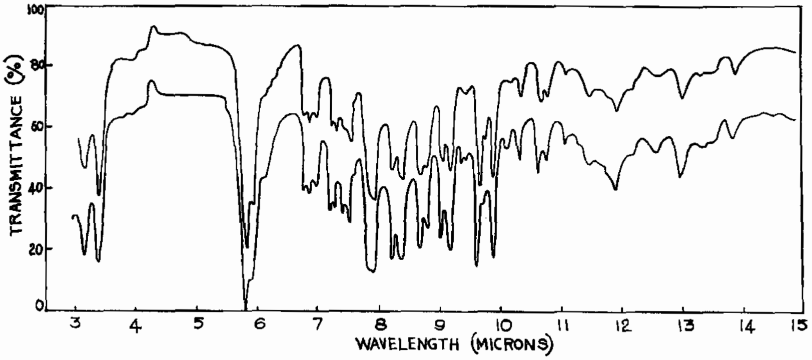
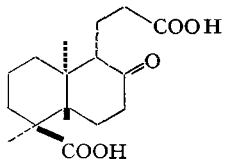
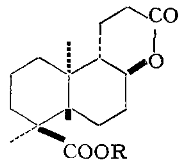


Fig. 3. *IR. Spectra of the lactone acids VIIIa and XIa in KBr*
Top: Lactone acid XIa from neoabietic acid.
Bottom (20% lower): Lactone acid VIIIa from polyalthic acid.

The nature of the carbon skeleton of polyalthic acid was shown by selenium dehydrogenation, which gave as the major product 1,2,5-trimethylnaphthalene, identified by comparison with an authentic specimen (m.p., mixed m.p. and IR. spectra of the trinitrobenzene adducts and UV. spectra of the hydrocarbons). A phenanthrene derivative, in all probability 1,7-dimethylphenanthrene, was also obtained in the dehydrogenation. Other bicyclic diterpenes with suitably oriented unsaturated side chains, such as manoyl oxide[7]) and agathenedicarboxylic acid[8]), have been known to yield phenanthrene derivatives on dehydrogenation with selenium.



VII



VIII

a: R = H
b: R = CH_3

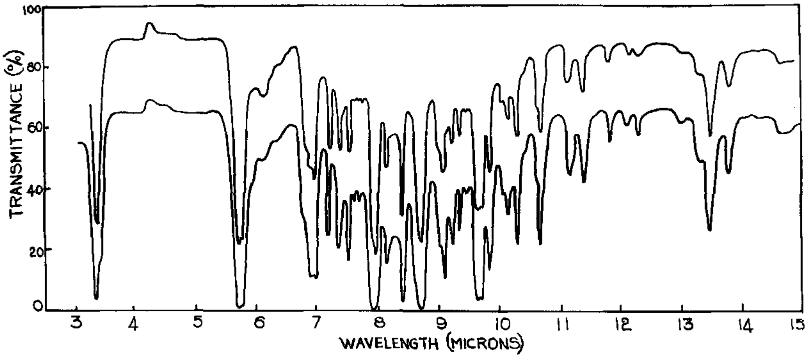


Fig. 4. *IR. Spectra of the lactone esters VIIIb and XIb in KBr*
Top: Lactone ester XIb from neoabietic acid.
Bottom (20% lower): Lactone ester VIIIb from polyalthic acid.

Dehydrogenation of the lactone acid VIIIa with selenium gave 1-ethyl-5-methylnaphthalene, identified by comparison with an authentic specimen.

The ester number of methyl polyalthate was determined under standard conditions. A comparison with other esters of diterpenoid acids (Table 3) indicates an equatorial conformation for the ester function.

Table 3. *Ester hydrolysis in 0.5N ethanolic potassium hydroxide*

Ester	Time (h)	Ester number
Methyl podocarpate[9])	2	0
Methyl vouacapenate[10])	$4^{1}/_{2}$	2.2
Methyl abietate[10])	$2^{1}/_{2}$	73
Methyl vinhaticoate[10])	$2^{1}/_{4}$	109
Methyl polyalthate	5	67

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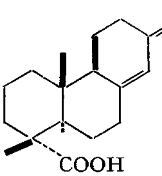
[7]) J. R. Hosking & C. W. Brandt, Ber. deutsch. chem. Ges. *68*, 37 (1935).

[8]) L. Ruzicka & J. R. Hosking, Helv. *13*, 1402 (1930).

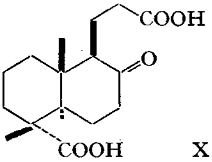
[9]) W. P. Campbell & D. Todd, J. Amer. chem. Soc. *64*, 928 (1942).

[10]) F. E. King, D. H. Godson & T. J. King, J. chem. Soc. *1955*, 1117.

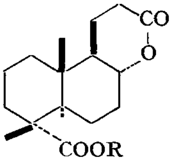
On the basis of the evidence discussed above the gross structure depicted in I for polyalthic acid may be taken as proved. Confirmation of the correctness of this structure as well as proof for the stereochemistry indicated in formula I was provided by a correlation with neoabietic acid (IX) of established structure and configuration[11]). Drastic ozonolysis of neoabietic acid followed by oxidation with alkaline hydrogen peroxide yielded the keto-dicarboxylic acid X. This acid melted at 212° as did the acid VII obtained from polyalthic acid. The infrared spectra (KBr) (Fig. 2) as well as the X-ray powder patterns of the two acids were identical. The specific rotations measured at the sodium line were approximately of the same magnitude, but opposite in sign. The two acids must therefore have an antipodal relationship. Since the absolute configuration of neoabietic acid has been proved to be as shown in IX, the absolute configuration depicted for polyalthic acid in formula I may be taken as proved. Further confirmation of this antipodal relationship between the two keto-dicarboxylic acids was obtained by comparison of the compounds VIIIa and VIIIb from polyalthic acid with the lactone acid XIa and the methyl ester XIb derived from the keto-dicarboxylic acid X from neoabietic acid. The two pairs of compounds had identical melting points and infrared spectra (Figs. 3 and 4), but the specific rotations were approximately equal in magnitude but opposite in sign.



IX



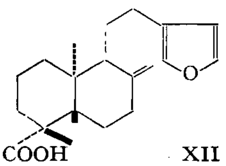
X



XI

a: R = H b: R = CH_3

Hence polyalthic acid possesses the "wrong" configuration with respect to steroids like iresin[12]), farnesiferol A[13]), eperuic acid[14]), cafestol[15]) and andrographolide[16]).



XII

It is interesting to note that daniellic acid[17]) isolated from the African copal tree, *Daniellia oliveri*, has been shown to have the structure and stereochemistry shown in XII, differing from polyalthic acid only in having an axially oriented carboxyl group.

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[11]) C. Djerassi, R. Riniker & B. Riniker, J. Amer. chem. Soc. *78*, 6362 (1956).

[12]) C. Djerassi & S. Burstein, J. Amer. chem. Soc. *80*, 2593 (1958); M. G. Rossmann & W. N. Lipscomb, *ibid.* *80*, 2592 (1958).

[13]) L. Caglioti, H. Naef, D. Arigoni & O. Jeger, Helv. *41*, 2278 (1958).

[14]) C. Djerassi & D. Marshall, Tetrahedron *1*, 247 (1958).

[15]) C. Djerassi, M. Cais & L. A. Mitscher, J. Amer. chem. Soc. *80*, 247 (1958).

[16]) M. P. Cava & B. Weinstein, Chemistry & Ind. *1959*, 851.

[17]) G. Ourisson, personal communication (Tetrahedron, in press).

Experimental

All melting points are uncorrected. Ultraviolet absorption spectra were measured with a BECKMAN Model DU Spectrophotometer in 95% ethanol. Infrared spectra were taken using a PERKIN-ELMER Infracord Spectrophotometer. Petroleum ether refers to the fraction b. p. 40–60°.

Isolation of polyalthic acid: 10 kg of the powdered stem bark were percolated twice in the cold with petroleum ether for three days. The combined extracts were concentrated to about 500 ml and left in the ice chest for ten days. The almost colourless solid (80–100 g) that separated out was washed with ice-cold petroleum ether and purified by chromatography over silicagel in benzene solution. From 10 g of the crude product were obtained 7 g of polyalthic acid. Crystallisation from petroleum ether containing a small amount of benzene gave colourless, heavy prisms, m. p. 102°, $[\alpha]_D^{28} = -46°$ ($c = 5$ in ethanol). The acid gave a purple colour in the EHRLICH test. IR. spectrum see Fig. 1.

$C_{20}H_{28}O_3$ Calc. C 76.0 H 8.9 1 act. H 0.32 2 (C)-CH_3 9.49% M. W. 316 $|^{=}$ 3
Found „ 76.4 „ 9.0 1 „ „ 0.24 2 „ „ 8.09% „ „ 305[18]) $|^{=}$ 3.03[20])
„ 76.3 „ 9.1 „ „ 311, 313[19])

The *cyclohexylamine salt* of polyalthic acid, prepared in hot ethyl acetate solution, crystallised from acetone in needles and had m. p. 186–190° (dec.), $[\alpha]_D^{28} = -25.07°$ ($c = 3.45$ in chloroform).

$C_{26}H_{41}O_3N$ (415) Calc. C 75.2 H 9.9% Found C 74.8 H 10.3%

The *diethylamine salt* of polyalthic acid, prepared in hot acetone, crystallised from acetone in needles, m. p. 139–141°, $[\alpha]_D^{28} = -31.8°$ ($c = 4.34$ in chloroform).

$C_{24}H_{39}O_3N$ (389) Calc. C 74.0 H 10.0% Found C 73.5 H 9.8%

Methyl polyalthate: A solution of 10 g of polyalthic acid in 20 ml of methanol was treated with ethereal diazomethane obtained from 20 g of nitrosomethylurea. After 24 h the solvents were evaporated and the residue distilled *in vacuo* to yield 10 g of methyl polyalthate, b. p. 188°/1 mm, $n_D^{25} = 1.520$, $[\alpha]_D^{28} = -37.86°$ ($c = 7.0$ in ethanol).

$C_{21}H_{30}O_3$ (330) Calc. C 76.4 H 9.1% Found C 76.5, 76.6 H 9.5, 9.3%

With 0.5N ethanolic potassium hydroxide, methyl polyalthate had ester numbers of 31.5 (2 h reflux period), 42.1 (3 h) and 67.0 (5 h).

Catalytic reduction of polyalthic acid: A solution of 2 g of polyalthic acid in 25 ml of glacial acetic acid was shaken with hydrogen at 50 lbs/in² in presence of 400 mg of ADAMS' catalyst. After 3 h the catalyst was filtered off and the solvent evaporated *in vacuo*. The product was extracted with ether, the ether extract washed with water, dried over $MgSO_4$, and the solvent removed to yield hexahydropolyalthic acid as a viscous oil. The *diethylamine salt* of the acid crystallised from acetone in slender needles, m. p. 142–148° (dec.).

$C_{24}H_{45}O_3N$ (395) Calc. C 72.9 H 11.4% Found C 72.6 H 11.3%

1.8 g of the reduced acid were treated with ethereal diazomethane from 8 g of nitrosomethylurea to yield, after evaporation of the solvent and distillation *in vacuo*, 1.5 g of *methyl hexahydropolyalthate* as a colourless oil, b. p. 155–160°/0.3 mm.

$C_{21}H_{36}O_3$ (336) Calc. C 75.0 H 10.7% Found C 75.0 H 10.9%

The reduced acid as well as the ester gave negative EHRLICH test for furans.

Ozonolysis. – Isolation of formaldehyde: A solution of 1 g of polyalthic acid in 25 ml of chloroform was treated at 0° with a stream of ozonised oxygen (3% ozone) during a period of 2 h. The solvent was evaporated at 30° *in vacuo* and the residue distilled with steam after the addition of 50 mg of zinc dust. The distillate, when treated with dimedon, afforded 300 mg of formaldehyde methone, m. p. 189°, alone or when admixed with an authentic sample.

Ozonolysis of methyl polyalthate under similar conditions also gave formaldehyde (identified as the dimedon derivative) in good yield.

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[18]) By the RAST method.

[19]) Equivalent weight by potentiometric titration.

[20]) By iodine value estimation.

Diol Va from polyalthic acid: A mixture of 220 mg of polyalthic acid and 270 mg of osmium tetroxide in 10 ml of dry purified dioxan was left at room temperature for 24 h. The resulting complex was decomposed with hydrogen sulphide and the black precipitate filtered off. Evaporation of the filtrate *in vacuo*, followed by crystallisation of the residue from benzene, gave 130 mg of the diol as needles, m. p. 180°, $[\alpha]_D^{28} = -9.85°$ ($c = 8.2$ in methanol).

$C_{20}H_{30}O_5$ (350) Calc. C 68.6 H 8.6% Found C 68.4 H 8.2%

Keto-ester VIb from the above diol: 130 mg of the above diol in 15 ml of methanol were treated with 10 ml of 0.1 M sodium metaperiodate and left overnight at room temperature. Dilution with water and extraction with ether gave an oily product which was filtered through a column of silicagel in benzene. The amorphous keto-acid was methylated with diazomethane and the product sublimed *in vacuo* (bath temperature 180°/0.05 mm) to yield the keto-ester. The latter gave a positive Zimmermann test ($-CO-CH_2-$).

Polyalthyl alcohol (II): A solution of 3 g of methyl polyalthate in 50 ml of dry ether was added dropwise with stirring to a suspension of 2 g of lithium aluminium hydride in 40 ml of dry ether. The mixture was stirred at room temperature for 3 h and left overnight. The complex was decomposed with water, the ether layer dried over Na_2SO_4 and the solvent removed to yield polyalthyl alcohol as a colourless oil, b. p. 174–175°/0.2 mm, $n_D^{25} = 1.536$, $[\alpha]_D^{28} = -52.18°$ ($c = 4.12$ in chloroform).

$C_{20}H_{30}O_2$ (302) Calc. C 79.5 H 9.9% Found C 79.3 H 10.0%

Triol Vb from polyalthyl alcohol: A mixture of 100 mg polyalthyl alcohol and 150 mg osmium tetroxide in 10 ml of dry dioxan was allowed to stand at room temperature for 48 h. The product was decomposed with hydrogen sulphide and worked up as usual to give 80 mg of the triol as an oil.

Keto-alcohol VIc from the above triol: 80 mg of the above triol in 20 ml of methanol were treated with 10 ml of 0.1 M sodium metaperiodate and left overnight. Extraction with ether gave the keto-alcohol as an oil. This gave positive Zimmermann and Ehrlich tests ($-CO-CH_2-$ and furan rings, respectively).

Alder-Rickert *degradation of polyalthyl alcohol:* A mixture of 900 mg of polyalthyl alcohol and 600 mg of diethyl acetylenedicarboxylate was heated at 100° for 15 h. The glassy adduct was dissolved in 30 ml of dry ethyl acetate and reduced at a hydrogen pressure of 25 lbs/in^2, using 200 mg of 5% Pd-$BaCO_3$, during a period of 2 h. The catalyst was filtered off, the solvent evaporated and the gummy residue distilled *in vacuo* after a little preliminary heating. The fraction b. p. 100–120°/0.5 mm was collected and hydrolysed with 25 ml of 10% methanolic potassium hydroxide to yield furan-3,4-dicarboxylic acid as needles from ethyl acetate, m. p. 212°, undepressed on admixture with an authentic sample of the acid made by a similar sequence of reactions, starting from furan itself. The IR. spectra (KBr) of the two samples were identical.

Keto-dicarboxylic acid VII from polyalthic acid

a) *Ozonolysis of polyalthic acid:* A solution of 5 g of polyalthic acid in 30 ml of acetic acid was treated with ozonised oxygen (3% ozone) at 10° during a period of 7 h. The solvent was evaporated *in vacuo*, the residue dissolved by warming in 50 ml of 10% aqueous sodium hydroxide and treated dropwise with excess 30% hydrogen peroxide at 10°. After stirring for 1 h the alkaline solution was left overnight at room temperature. Acidification followed by extraction with ether gave 4.5 g of a crude acidic material which was directly methylated with ethereal diazomethane (from 15 g of nitrosomethylurea). The product was distilled *in vacuo* to yield two fractions: Fraction I: b. p. 160–180°/0.4 mm, mobile oil; 2.5 g. Fraction II: b. p. 180–220°/0.4 mm, viscous gum; 1 g.

Fraction I, which gave a positive Zimmermann test, was refluxed with 40 ml of 12% methanolic potassium hydroxide at 140° for 5 h. The methanol was distilled off, the residue diluted with water and extracted with ether to remove traces of non-acidic material. The aqueous solution was acidified and extracted with ether. The solvent was removed and the residue triturated with dry ether to yield 800 mg of the keto-dicarboxylic acid, crystallising from ethyl acetate in needles, m. p. 211–212° (dec.), $[\alpha]_D^{28} = +11.6°$ ($c = 4.05$ in methanol). IR. spectrum see Fig. 2.

$C_{16}H_{24}O_5$ Calc. C 64.9 H 8.1% equiv. wt. (for dibasic acid) 148
(296) Found ,, 64.6 ,, 8.0% ,, ,, ,, ,, ,, 152

b) *Ozonolysis of methyl polyalthate:* 5 g of methyl polyalthate in 50 ml of chloroform were ozonised at 0° for 8 h. The reaction product was worked up as before to yield 1.1 g of the keto-dicarboxylic acid, m. p., and mixed m. p. with the above acid, 211–212° (dec.).

Lactone acid VIIIa from polyalthic acid: A solution of 2 g of the keto-dicarboxylic acid in 30 ml of methanol was treated with 1 g of sodium borohydride and left overnight at room temperature. Acidification afforded 1.5 g of the lactone acid, crystallising from ethyl acetate in prisms, m.p. 237–238°, $[\alpha]_D^{28} = +64.4°$ ($c = 3.57$ in methanol). IR. spectrum see Fig. 3.

$C_{16}H_{24}O_4$ (280) Calc. C 68.6 H 8.6% Found C 68.0 H 8.2%

Lactone ester VIIIb from polyalthic acid: 500 mg of the foregoing lactone acid were methylated with ethereal diazomethane (from 3 g of nitrosomethylurea). Evaporation of the solvent followed by chromatography in benzene over alumina gave 400 mg of the lactone ester, crystallising from ethyl acetate as cubes, m.p. 170°, $[\alpha]_D^{28} = +88.3°$ ($c = 0.9$ in methanol). IR. spectrum see Fig. 4.

$C_{17}H_{26}O_4$ (294) Calc. C 69.4 H 8.8% Found C 69.4, 69,3 H 8.8, 9.1%

Dehydrogenation of polyalthic acid: An intimate mixture of 2 g of polyalthic acid and 4 g of selenium was heated at 310–320° in a sealed tube for 60 h. The products from six such batches were combined and extracted continuously with petroleum ether in a Soxhlet for 6 h. The solvent was evaporated and the residue chromatographed over a column of alumina ground with enough silver oxide to remove selenium. The eluate was evaporated, the residue distilled *in vacuo* and the following fractions collected: Fraction I: b.p. 80–130°/0.2 mm; 2.5 g. Fraction II: b.p. 130–150°/0.2 mm; 2.5 g. Fraction III: b.p. 150–170°/0.2 mm; 1 g.

Treatment of fraction I with *sym*-trinitrobenzene gave 15 mg of an orange-yellow adduct, which after four crystallisations from methanol melted at 158–159°, alone or when mixed with an authentic specimen of the trinitrobenzene adduct of 1,2,5-trimethylnaphthalene. The infrared spectra (KBr) of the two samples were identical. The naphthalene, regenerated from the adduct by passage through a column of alumina, had λ_{max} 230, 287 and 325 mμ (log ε 4.87, 3.77 and 3.01) and λ_{min} 249 and 320 mμ (log ε 3.3 and 2.75).

Fraction II yielded 5 mg of a yellow trinitrobenzene adduct, which was crystallised thrice from methanol to yield needles, m.p. 158–160°. The regenerated hydrocarbon had UV. maxima at 260, 280, 302, 330 and 345 mμ.

Fraction III gave 10 mg of a sparingly soluble, deep red trinitrobenzene adduct. Repeated crystallisations from ethanol afforded red needles, m.p. 216–218° (dec.). The regenerated hydrocarbon had UV. maxima at 245, 270, 280, 330, 345 and 380 mμ.

Dehydrogenation of the lactone acid VIIIa: 800 mg of the lactone acid were mixed with 1 g of powdered selenium and the mixture heated in a sealed tube at 300–320° for 40 h. The reaction product was worked up as above to yield 25 mg of a pale yellow trinitrobenzene adduct, crystallising from methanol as slender needles, m.p. 126–127°, undepressed on admixture with an authentic sample of the trinitrobenzene adduct of 1-ethyl-5-methyl-naphthalene. The infrared spectra (KBr) of the two specimens were identical. The hydrocarbon, regenerated from the adduct, had λ_{max} 225, 275, 285, 300 and 320 mμ (log ε 4.71, 3.75, 3.82, 3.67 and 2.63).

Keto-dicarboxylic acid X from neoabietic acid: A solution of 500 mg of neoabietic acid in 25 ml of dry methylene chloride was treated with ozonised oxygen (3% ozone) at −70° during a period of 2 h. The solvent was evaporated *in vacuo*, the residue dissolved by warming in 10 ml of 10% aqueous sodium hydroxide and treated with 3 ml of 30% hydrogen peroxide at 10°. After leaving overnight, the alkaline solution was acidified and extracted repeatedly with ether. The ether extract was washed with water, dried over $MgSO_4$ and the solvent distilled off. Chromatography of the residue in benzene-ethanol (100:1) over silicagel gave 50 mg of the keto-diacid, crystallising from ethyl acetate in needles, m. p. 212° (dec.), $[\alpha]_D^{28} = -16.5°$ ($c = 2.2$ in methanol). IR. spectrum see Fig. 2.

$C_{16}H_{24}O_5$ (296) Calc. C 64.9 H 8.1% Found C 65.0 H 7.7%

Lactone acid XIa from neoabietic acid: 40 mg of the foregoing keto-dicarboxylic acid in 5 ml of methanol were treated with 50 mg of sodium borohydride and left overnight at room temperature. The mixture was acidified with 1 N hydrochloric acid and extracted with ether. Evaporation of the solvent and crystallisation of the residue from ethyl acetate gave 30 mg of the lactone acid in prisms, m.p. 238–239°, $[\alpha]_D^{28} = -68.4°$ ($c = 0.48$ in methanol). IR. spectrum see Fig. 3.

Lactone ester XIb from neoabietic acid: 20 mg of the above acid were methylated with diazomethane (from 1 g of nitrosomethylurea) to yield 15 mg of the lactone ester, crystallising from ethyl acetate in cubes, m. p. 170°, $[\alpha]_D^{28} = -80.6°$ ($c = 0.92$ in methanol). IR. spectrum see Fig. 4.

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SUMMARY

Polyalthic acid, a new diterpene acid isolated from *Polyalthia fragrans* (BTH.), has been shown, by degradation and correlation with neoabietic acid, to have the structure and stereochemistry depicted in formula I.

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125. Die Kristallstruktur des wasserfreien Chrom(II)-chlorides

von **H. R. Oswald**

(17. IV. 61)

1. Einleitung. – Die wasserfreien Dichloride einer Reihe zweiwertiger Metalle (Mg, Ni, Co, Fe, Mn u. a.) kristallisieren in hexagonalen Schichtengittern (*C*19-Typ), wobei das Metallatom oktaedrisch koordiniert ist. Dagegen kristallisieren sämtliche drei Modifikationen des wasserfreien $ZnCl_2$ in anderen Gittertypen mit tetraedrischer Viererkoordination (OSWALD & JAGGI[1]). $CuCl_2$ besitzt ein monoklines Gitter mit Ketten von planaren $CuCl_4$-Gruppen, die so angeordnet sind, dass das Kupferatom seine bevorzugte, deformiert-oktaedrische (4 + 2)-Koordination erhält (WELLS[2]). Wir haben vermutet, dass das sehr hygroskopische, leicht oxydierbare $CrCl_2$ ähnlich kristallisiert wie $CuCl_2$, da nach den Ergebnissen der Kristallfeldtheorie das Cr^{2+}-Ion mit der Elektronenkonfiguration $3d^4$ ähnliche Eigenschaften haben sollte wie das Cu^{2+}-Ion mit $3d^9$. Diese Vermutung wird gestützt durch die Tatsache, dass beide Verbindungen nadelig kristallisieren.

2. Die Strukturbestimmung von $CrCl_2$

$CrCl_2$ wurde aus metallischem Cr und trockenem, O_2-freiem HCl-Gas bei 1200° im Quarzrohr in Form einer weissen, asbestartigen, nadelig kristallisierten Masse erhalten (Fischer[3]). Es wurde ausschliesslich unter reinstem Stickstoff und über P_2O_5 (Trockenbox) weiter verarbeitet.

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